Repeat Unit Symmetry Effects on the Physical and Electronic Properties of Processable, Electrically Conducting, Substituted Poly(1,4-bis(2-thienyl)phenylenes)

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ABSTRACT: The effect of repeat unit symmetry on the physical and electronic properties of a series of conjugated polymers composed of 2,5-disubstituted 1,4-bis(2-thienyl)phenylene repeat units, symmetrically and asymmetrically substituted with methoxy, heptoxy, dodecyloxy, hexadecyloxy, eicosinoxy, and hexyl groups has been studied. The polymers were prepared via an oxidative polymerization using ferric chloride and isolated after dedoping with ammonium hydroxide. The neutral polymers, soluble in common organic solvents including chloroform, methylene chloride, and tetrahydrofuran, are predominantly linked at the 5 and 5′ positions of the thiophene rings to yield fully conjugated main chains that are stable to 360 °C under nitrogen. Molecular weight analyses indicate weight-average degrees of polymerization (X_w) of ca. 10–20, and, thus, a substantial fraction of chains in each sample contains 30–50 aromatic rings. Differential scanning calorimetry studies revealed that melt transitions, indicative of molecular ordering, are present in the symmetrically substituted polymers. The order found in these polymers was confirmed by X-ray diffraction and was found to persist at elevated temperatures, yielding birefringent melts, suggestive of liquid crystalline order. The asymmetrically substituted polymers were found to be amorphous. Upon oxidation of the insulating polymers, bipolaronic charge carriers were formed with the oxidized polymers exhibiting electrical conductivities up to 4 Ω^{-1} cm^{-1}.

Introduction

The introduction of substituent groups onto conjugated polymers has been utilized to a great extent in controlling their resulting physical and electronic properties. As a result of the incorporation of different side groups, processability (by way of solution or melt processing) and electronic tunability (in terms of conducting and optical properties) have resulted.[1-3]

Polythiophene, synthesized with linkages through the 2 and 5 positions, has a symmetric repeat unit and is a highly crystalline polymer.[4] Due to the rigidity of the backbone, and strong interchain interactive forces, polythiophene is completely insoluble and infusible. Its substituted derivatives, on the other hand, have attracted significant attention because of their resulting solution and melt processability when flexible alkyl groups are introduced onto the thiophene ring.[5] Although desirable qualities are exhibited by these polymers, the substituent incorporated removes the symmetry of the thiophene repeat unit. This asymmetry leads to configurational head-to-head and tail-to-tail defects, causing deleterious effects on the crystallinity of the resulting polymer. Approximately 20% of the linkages along the polymer backbone are head-to-head as determined by NMR spectroscopy.[6,7]

X-ray diffraction studies by Winokur and co-workers[8] revealed that, during oxidative doping, a change in size of the unit cell volume ensues that requires a cooperative motion of the alkyl chains, the polymeric backbones, and the dopant ions. With the presence of the these defects, this cooperative motion is hampered, thus, resulting in a decrease in the electrical conductivity of the polymer after redox doping.

The use of 3,3′-dialkyl-2,2′-bithiophene monomers resulted in a more ordered polymer composed exclusively of alternating head-to-head and tail-to-tail linkages.[7] Molecular order induced in these polymers resulted in higher electrical conductivities. Another method of synthesizing symmetric polythiophenes has been carried out by the introduction of substituents at both the 3 and 4 positions of the thiophene ring. Steric interactions between the side groups, however, decreased conjugation, and inferior electrical conductivities resulted.[9]

Comparable to polythiophene, poly(*p*-phenylene) (PPP) has a highly symmetric repeat unit and has been found to be highly crystalline, completely insoluble, and infusible.[10] Soluble PPP's have been synthesized by the incorporation of alkyl chains at the 2 and 5 positions of the phenylene ring.[11] The addition of these substituents does not affect the symmetry of the repeat unit; however, due to steric interactions, adjacent rings are essentially orthogonal to one another.[12] This destroys conjugation along the polymer chains, and relatively large electronic band gaps are obtained from these polymers.[11] Aside from this steric interaction, another problem encountered in the preparation of PPP is that the phenylene monomer needs to be activated by introducing reactive sites for polymerization. This has been accomplished by the palladium-catalyzed coupling of boronic acid derivatives and PPP's with number-average degrees of polymerization of up to 100 have been prepared.[11b] No redox or electrical properties were reported for these polymers.

In this respect, with the broad range of symmetric and asymmetric substitution possibilities on phenylene rings coupled with the synthetic flexibility in polymerizing thiophenes, interest in polymers containing both phenylene and thiophene moieities along the conjugated backbone has developed. Various systems that have been studied include the preparation of completely alternating phenylene–thiophene copolymers,[13] the random copolymerization of 1,4-dibromobenzene and 2,5-dibromothiophene,[14] and the utilization of 1,4-bis(2-thienyl)ben-

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zene monomers to yield polymers with alternating bithiophene and phenylene[15,16] or alternating thiophene and phenylene[17] repeat units.

Recently, we reported the preparation and characterization of polymers from 1,4-bis(2-thienyl)benzenes with the incorporation of methyl and methoxy substituents on the phenylene unit.[16] In this study, we elucidated substituent effects by both theoretical and experimental evaluation of electronic properties, redox behavior, and electrical conductivities. This study revealed that the incorporation of alkoxy substituents on the phenylene unit resulted in polymers with electronic band gaps, and conductivities after doping, comparable to poly(3-alkylthiophenes).

In extending this work, we have symmetrically and asymmetrically incorporated long-chain substituents, including heptoxy, dodecyloxy, hexadecyloxy, eicosinoxy, and hexyl groups, onto the phenylene moiety of a series of 2,5-disubstituted 1,4-bis(2-thienyl)benzenes and examined the effect of the length of the side chain, as well as the symmetry of the repeat unit, on the physical and electrical properties of the resulting polymers. The polymerization was carried out by a ferric chloride oxidative route with a subsequent dedoping with ammonium hydroxide. These polymers, analogous to substituted polythiophenes, are soluble in common organic solvents with the predominant formation of linkages at the 5 and 5′ positions of the terminal thiophene rings. A differential scanning calorimetry study carried out on these polymers revealed that symmetric inclusion of substituents within the polymer repeat unit results in molecular ordering as evidenced by the observation of melt transitions. This order, which was found only in the symmetrically substituted polymers, was confirmed by X-ray diffraction. Interestingly, symmetrically substituted polymers with long alkoxy substituents also exhibited multiple endothermic transitions and birefringence in the melt suggestive of liquid crystalline behavior. Upon solution oxidation of the initially insulating polymers, bipolaronic charge carriers were formed with the doped polymers exhibiting electrical conductivities up to 4 Ω^{-1} cm^{-1}.

Results and Discussion

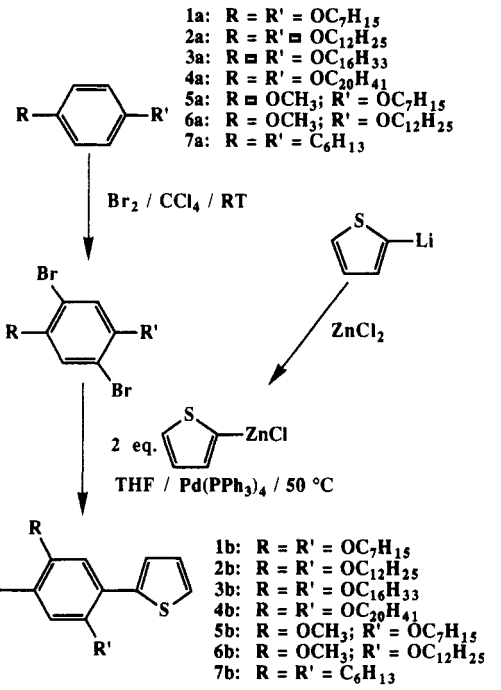
Monomer Synthesis. The approach taken in the synthesis of a series of 2,5-disubstituted 1,4-bis(2-thienyl)-benzene monomers is outlined in Scheme I.

Long-chain alkoxy substituents were introduced onto the benzene ring through the use of the Williamson ether synthesis[18] from hydroquinone for symmetric disubstitution and 4-methoxyphenol for asymmetric substitution. The hexyl substituents were incorporated using a Grignard coupling reaction.[19]

The derivatives with long alkoxy side groups were successfully halogenated with elemental bromine in CCl_4 to selectively brominate the 2 and 5 positions. No catalysts were necessary because of the activation of these sites as a result of the electron-donating effect of the alkoxy substituents. The products were all purified by recrystallization to yield compounds in excess of 80%. These reactions were also carried out in CH_2Cl_2 and $CHCl_3$ to give the same desired products, but reactions in CCl_4 gave the best isolated yields. 1,4-Dihexylbenzene was brominated with elemental bromine with a small amount of iodine used as a catalyzing oxidizing agent.[19] The structure and purity of these benzene derivatives were confirmed by ^{1}H and ^{13}C NMR spectroscopies, as listed in the Experimental Section.

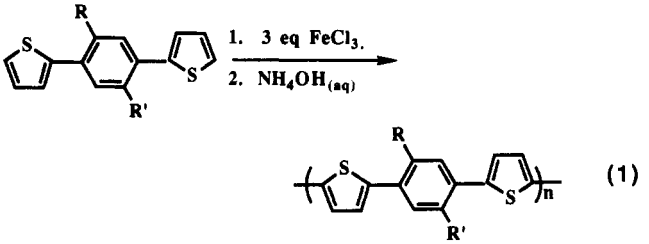
The thiophene moiety was incorporated onto the phenylene unit by the reaction of organometallic 2-thienyl

Scheme I



intermediates. The use of 2-thienylzinc chloride with a palladium(0) catalyst in the formation of 2-thienylbenzenes and 2-furanylbenzenes has been reported by Pelter et al.[17] 2-Thienylzinc chloride was prepared by lithiation of thiophene and a subsequent transmetallation reaction of 2-thienyllithium with anhydrous zinc chloride. This reagent was treated with the 2,5-disubstituted 1,4-dibromobenzene derivatives in the presence of palladium(0) tetrakis(triphenylphosphine) as catalyst at 50 °C under inert conditions. The 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 spectroscopies, listed in Tables I–III, and elemental analyses, found in the Experimental Section.

Polymerization. Oxidative polymerization using ferric chloride has been utilized previously in preparing high molecular weight poly(3-alkylthiophenes),[6,20] as shown in reaction 1. While most polymerizations were carried out



(1)

1c: R = R' = OC_7H_{15}
2c: R = R' = $OC_{12}H_{25}$
3c: R = R' = $OC_{16}H_{33}$
4c: R = R' = $OC_{20}H_{41}$
5c: R = OC_7H_{15}; R' = OCH_3
6c: R = $OC_{12}H_{25}$; R' = OCH_3
7c: R = R' = C_6H_{13}

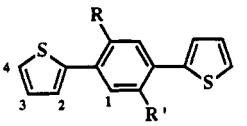
at room temperature, polymers **3c** and **4c** were prepared at 60 °C, which was required for complete dissolution of the monomer. These two polymers remained in solution during synthesis, while all of the other polymers precipitated out of solution in the form of dark blue powders. Partially oxidized polymers were isolated by precipitation into methanol, washed with chloroform, ether, methanol, and water, and then fully dedoped by compensation with aqueous ammonium hydroxide.

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

	arom C–H str			aliphatic C–H str				ring str: phenyl		ring str: thiophene			CH_3 deformn	arom OOP bends: phenyl		arom OOP bends: thiophene		
cmpd	α	β	ϕ															
1b	3101	3067	3001	2954	2935	2865	2853	1573	1534	1493	1470	1434	1389	882	809	989		852
1c		3064	2994	2946	2926	2863	2854	1602	1528	1486	1467	1454	1390		845		786	
2b	3105	3074	3005	2957	2916	2863	2848	1582	1534	1491	1468	1432	1390	894	819	975		852
2c		3066	2996	2954	2921	2862	2851	1603	1532	1485	1466	1436	1387		848		790	
3b	3107	3076		2916		2852			1538	1492	1469	1432	1387		801	992		852
3c		3064		2922		2846		1603	1532	1484	1464	1407	1388		846		788	
4b	3105	3076		2917		2849			1535	1492	1470	1435	1392		801	996		851
4c		3066		2919		2850		1602	1531	1485	1466	1415	1385		848		786	
5b	3089	3066	3003	2941	2921	2864	2851	1588	1532	1489	1458	1427	1393	898	821	991		855
5c		3065	2991	2949	2928	2864	2853	1603	1529	1488	1460	1434	1398		847		789	
6b	3092	3066	2990	2941	2923	2863	2850	1580	1534	1490	1464	1428	1394	898	818	991		847
6c		3066	2992	2950	2923	2865	2851	1604	1530	1486	1461	1435	1396		849		788	
7b	3100	3070	3006	2948	2915	2863	2852	1600	1534	1491	1467	1434	1385	893	833	965		847
7c		3067	3008	2951	2924	2868	2853	1602	1534	1487	1460	1436	1376	901	843		803	
PT[a]		3063								1491	1453	1441					788	
P3HT[b]		3055		2959	2930	2858	2850			1512	1458	1439					825	

[a] PT = polythiophene. [b] P3HT = poly(3-hexylthiophene).

Table II
^1H NMR Chemical Shifts and Assignments for Monomers and Neutral Polymers (ppm)



cmpd	H-1	H-2	H-3	H-4	H-R
1b	7.25 (s)	7.33 (d)	7.09 (t)	7.53 (d)	4.07 (t), 1.89 (q), 1.26 (m), 0.88 (t)
1c		7.0–7.5			4.1, 1.3–2.2, 0.9
2b	7.25 (s)	7.33 (d)	7.08 (t)	7.53 (d)	4.07 (t), 1.89 (q), 1.26 (m), 0.88 (t)
2c		7.0–7.5			4.1, 1.3–2.2, 0.9
3b	7.24 (s)	7.33 (d)	7.06 (t)	7.54 (d)	4.08 (t), 1.24 (m), 0.9 (m)
3c		7.0–7.6			7.1, 1.2–2.0, 0.9
4b	7.25 (s)	7.32 (d)	7.09 (t)	7.55 (d)	4.06 (t), 1.88–0.85 (m)
4c		7.5–7.2			4.06, 1.94–0.88
5b	7.23 (s), 7.26 (s)	7.33 (d)	7.09 (t)	7.54 (d), 7.51 (d)	4.09 (t), 3.93 (s), 1.90 (q), 1.32 (m), 0.89 (t)
5c		7.0–7.8			4.1, 3.9, 1.3–2.2, 0.9
6b	7.23 (s), 7.25 (s)	7.33 (d)	7.09 (t)	7.53 (d), 7.52 (d)	4.08 (t), 3.93 (s), 1.89 (q), 1.26 (m), 0.88 (t)
6c		7.0–7.8			4.1, 3.9, 1.2–2.2, 0.9
7b	7.28 (s)	7.33 (d)	7.09 (t)	7.04 (d)	2.69 (t), 1.54 (q), 1.29 (m), 0.84 (t)
7c		6.8–7.6			2.7, 1.2–2.0, 0.8

As the partially oxidized polymers were washed with methanol and water, a color change due to partial dedoping was observed. A more drastic color change was observed for **7c** in contrast to the alkoxy-substituted polymers which can be attributed to the difference in the oxidation potentials of these conjugated polymers as discussed previously for the methyl and methoxy substituted poly(1,4-bis(2-thienyl)phenylenes).[16]

All of the above polymerizations were carried out for 20 h. The effect of polymerization time on the resulting polymer's molecular weight and band gap was used to optimize the polymerization conditions using **2c** as an example. In addition, elevated polymerization temperatures were examined in the preparation of polymers **2c′** and **2c″**, which also precipitated out of solution during polymerization. The results from these experiments will be discussed with the polymer physical properties.

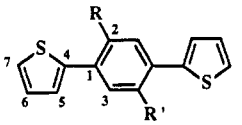
Neutral Polymer Structure. The structure and purity of all neutral polymers were analyzed using FT-IR, ^1H NMR, and ^{13}C NMR spectroscopies and elemental analyses. The relevant results of these studies are listed in Tables I–III.

The FT-IR results agree closely with results for the corresponding short-chain alkyl and alkoxy substituted poly(1,4-bis(2-thienyl)phenylenes) reported previously.[16] These findings illustrate the stability of the monomer under the polymerization conditions, as well as the retention of symmetry of the repeat unit after polymerization. This latter phenomenon suggests the formation of predominantly linear, α- and α'-linked, chains during polymerization.

The C–H stretching vibrations for monomer (**2b**) and polymer (**2c**) are compared in Figure 1. Note the disappearance of the vibration associated with the thiophene α-C–H stretch in the polymer while the vibrations attributed to the thiophene β-C–H, and the phenylene C–H stretches remain. This is in contrast to the dimethoxy substituted polymer reported previously[16] which exhibited residual α-C–H absorbances and suggests that higher molecular weights have been attained for the polymer substituted with longer dodecyloxy side chains. This is not surprising as the dodecyloxy side groups enhance the solubility and the polymer can grow to longer chain lengths prior to precipitation. Comparable results were observed for all other polymers.

In an attempt to improve molecular weights further by increasing polymer solubility, polymerizations were carried out at elevated temperatures of 60 °C (in chloroform) and 130 °C (in 1,1,2,2-tetrachloroethane) to yield polymers **2c′** and **2c″**, respectively. Identical FT-IR spectra were obtained from these polymers, which indicated the structural integrity of the repeat unit under these more rigorous

Table III
^{13}C NMR Chemical Shifts and Assignments for Monomers and Neutral Polymers (ppm)



cmpd	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-R
1b	122.99	149.24	112.88	139.28	125.14	125.62	126.69	69.69, 31.73, 29.38, 29.03, 26.15, 22.58, 14.06
1c	122	149	112	137	125	126	138	69.8, 32.8, 29.5, 29.1, 26.3, 22.7, 14.1
2b	122.94	149.12	112.78	139.29	125.13	125.63	126.69	69.70, 31.92, 29.66, 29.40, 26.21, 22.69, 14.12
2c	122	149	121	137	125	126	138	69.8, 31.9, 29.7, 29.4, 26.3, 22.7, 14.1
3b	122.87	149.15	112.69	139.23	125.08	125.84	126.67	69.68, 31.94, 29.70, 29.41, 26.22, 22.72, 14.16
3c	125	149	112	138	126	125	137	69.9, 31.9, 29.7, 26.3, 22.6, 14.0
4b	122.87	149.22	112.85	139.28	126.65	125.59	125.1	69.75, 31.94, 29.71, 29.42, 26.24, 26.72, 14.13
4c	122	149	112	138	126	125	137	69.9, 31.9, 29.7, 26.4, 22.7, 14.0
5b	123.00	149.37	112.10	139.13	125.17	125.62	126.69	69.70, 56.40, 31.72, 29.38, 29.03, 26.15, 22.57, 14.05
	122.91	149.79	113.01	139.17	125.39	125.68	126.85	
5c	122	149	112	137	125	126	138	69.8, 56.5, 31.8, 29.4, 29.1, 26.3, 22.6
6b	122.90	149.37	112.07	139.15	125.17	125.63	126.72	69.71, 56.42, 31.92, 29.66, 29.39, 26.21, 22.69, 14.13
	123.00	149.79	112.99	139.20	125.42	125.72	126.88	
6c	122	149	112	137	125	126	139	69.7, 56.4, 31.9, 29.6, 26.2, 22.7, 14.1
7b	142.73	133.48	132.21	138.57	125.17	126.36	126.99	33.07, 31.57, 31.49, 29.25, 22.55, 14.05
7c	143	134	133	132	126	125	139	33.1, 31.5, 29.2, 22.5, 14.0

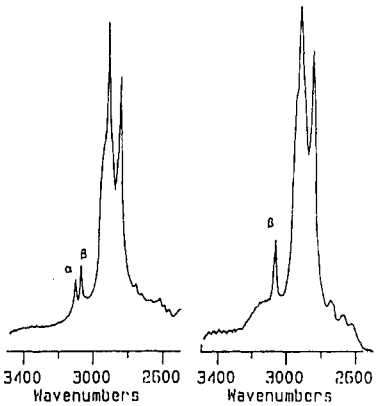


Figure 1. Aromatic C–H stretches of 1,4-bis(2-thienyl)-2,5-didodecyloxybenzene, (**2b**, left) and poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene), (**2c**, right).

polymerization conditions.

^1H NMR chemical shifts and assignments for the polymers are shown in Table II. A comparison, between monomer **2b** and polymer **2c** is shown in Figure 2 as an example. The retention of all of the resonances assigned to the aliphatic protons and most of the aromatic protons verify the monomers are stable under the polymerization conditions used. The significantly lower intensity at 7.50 ppm in the polymer, relative to the monomer, is caused by proton elimination from the 5 and 5′ monomer positions during polymerization, as expected. The loss of peak splitting in all of the resonances resulted from the different carbon environments along the polymeric chain. Quantitation of molecular weight, using the ratio of the integrated aromatic peak versus the isolated aliphatic resonances at about 4.0 ppm ($-CH_2O-$ for all the alkoxy substituted polymers), was carried out and will be discussed later.

The random polymerization of asymmetric monomers leads to both head-to-head and head-to-tail linkages, and thus the polymer formed is aregic and contains configurational isomers, as shown in Figure 3. Symmetric monomers, on the other hand, contain only head-to-tail linkages, are isoregic, and only contain conformational isomers. It is interesting to note that the introduction of asymmetry as in the cases of **5c** and **6c** does not complicate the ^1H NMR spectra. This results from the electronic similarity of the alkoxy substituents (methoxy versus hep-

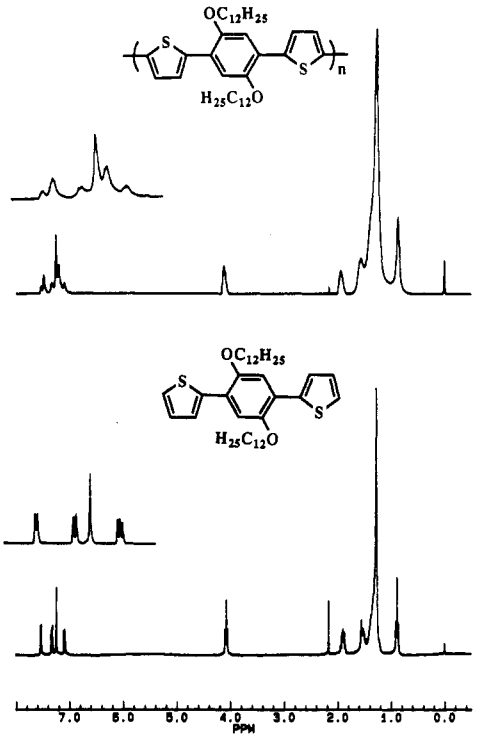


Figure 2. ^1H NMR spectra of 1,4-bis(2-thienyl)-2,5-didodecyloxybenzene, (**2b**) and poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene) (**2c**).

toxy or dodecyloxy groups) and is suggestive of the absence of interactions of the side chains with the polymer backbone.

^{13}C NMR spectra were obtained at 50 °C in CCl_4 as the elevated temperatures enhanced polymer solubility. The chemical shifts obtained and their assignments are listed in Table III. The spectra support the fact that a predominantly linear, α- and α'-linked, polymer is formed. The observed simplicity of the spectra is again attributed to the symmetric nature of the repeat units; that is, limited overlapping resonances were observed. A comparison between a symmetrically substituted polymer, **2c**, and an asymmetrically substituted polymer, **6c**, is shown in Figure 4. The asymmetric polymers (**5c** and **6c**) exhibited a splitting of the peak at ca. 150 ppm due to the differences in the substituent groups.

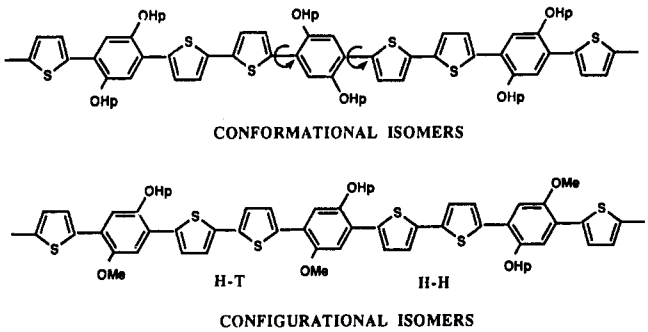


Figure 3. Conformational and configuration isomers formed for the symmetrically and asymmetrically substituted poly(1,4-bis(2-thienyl)phenylenes).

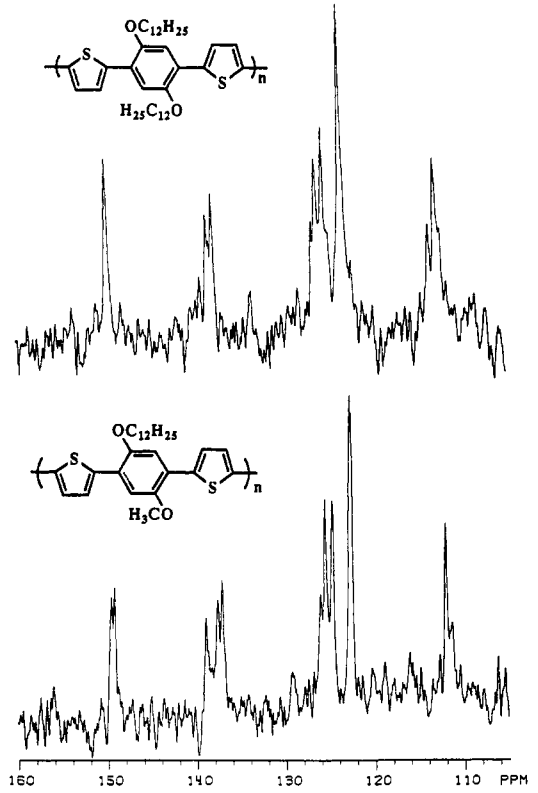


Figure 4. Aromatic regions of the ^{13}C NMR spectra for poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene) (**2c**) and poly(1,4-bis(2-thienyl)-2-didodecyloxy-5-methoxyphenylene) (**4c**).

The elemental compositions of the polymers support the structures depicted for each polymer with the results listed in the Experimental Section.

Physical Properties of the Neutral Polymers. As observed for poly(3-alkylthiophenes),[5,20] the incorporation of long alkyl and alkoxy substituents onto the conjugated 1,4-bis(2-thienyl)phenylene polymer backbone imparts both solubility and fusibility. All the polymers studied here were soluble in common organic solvents, such as, chloroform, carbon tetrachloride, tetrahydrofuran, dichloromethane, toluene, and 1,1,2,2-tetrachloroethane. This is in contrast to the methyl and methoxy substituted poly(1,4-bis(2-thienyl)phenylenes) which are completely insoluble and infusible.[16] Solubility of the alkoxy substituted polymers increased as the side chain was lengthened and solubility was highest in hot toluene or tetrachloroethane. Effects of long-chain substitution on various rigid-rod polymers has been discussed previously, including work on polyesters, polyamides, and poly(*p*-phenylenes).[21] During the oxidative polymerization, the short chain alkoxy substituted polymers, **1c**, **2c**, **5c**, and **6c**, precipitated in the reaction medium while polymers **3c** and **4c**, containing the longer hexadecyloxy and eicosinoxy side groups, remained soluble. The hexyl substituted polymer **7c** behaved similarly to **3c** and **4c**, even though a relatively short chain was incorporated. This is attributed to a lower extent of conjugation and higher flexibility of this polymer, as discussed previously for the methyl and methoxy substituted polymers through theoretically derived results.[16]

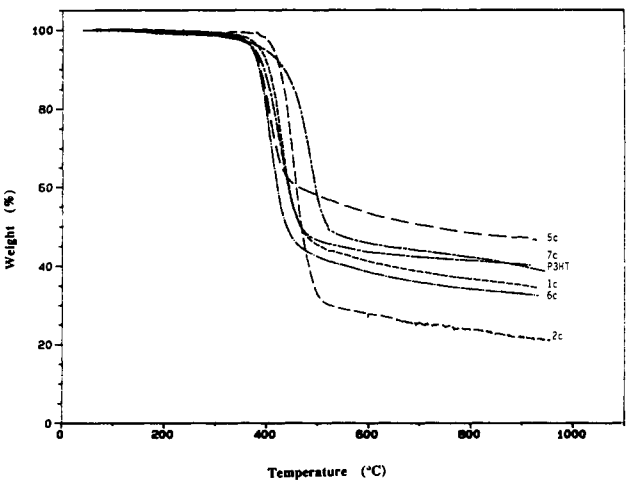


Figure 5. TGA scans for poly(1,4-bis(2-thienyl)phenylenes) carried out under nitrogen atmosphere.

The polymers were purified by reprecipitation after dedoping with ammonium hydroxide (see Experimental Section) and subsequently dissolved in hot toluene. Brittle yet free-standing films were cast from these solutions. Redox doping and electrical conductivity measurements, to be discussed later, were carried out on annealed films. The mechanical properties of the polymer films improved after initial annealing of solution-cast films at 200 °C for 4 h.

The polymer's thermal stabilities were determined using thermogravimetric analyses (TGA) under either nitrogen or air. Figure 5 shows the thermograms for the neutral polymers, and all exhibited an onset of degradation greater than 360 °C under nitrogen with no weight loss at lower temperatures. This is comparable by the corresponding polythiophenes and previously reported 1,4-bis(2-thienyl)-phenylene polymers with methyl and methoxy substituents.[16] The weight loss accounted for at this transition can be attributed to the cleavage of the side chain for all the polymers. A thermogram of poly(3-hexylthiophene) is included for comparison. When air was used as the TGA carrier gas, stability to 300 °C was observed with very little char residue (ca. 1.0%) remaining indicative of the efficient removal of inorganic salts after workup.

Molecular weight approximations were obtained using gel permeation chromatography (GPC), against polystyrene standards, as well as NMR integration. A summary of the molecular weights as a function of substitution is listed in Table IV. In the GPC studies, the polymers were not completely solubilized by the THF. In that the soluble fraction represents ca. 75% of the entire sample, the values reported here represent a low estimate.

Primary molecular weight analysis by ^1H NMR integration was carried out by determining the integration ratio of the entire aromatic region versus the isolated aliphatic peak (attributable to the $-CH_2O-$) at 4.2 ppm. Integration errors greatly affect the outcome of these analyses, and, thus, the error is ca. ±10%. A number-average degree of polymerization of about 6 repeat units (18 aromatic rings) was obtained for all the alkoxy

Table IV
Molecular Weight Analyses of the Polymers

polymer	solubility[a] (mg/mL)	molecular weight analysis		
		GPC-UV, M_w	M_w/M_n	NMR, M_n
1c	7.8	4700	1.95	2400 (6)
2c	8.1	5500	1.69	3600 (6)
2c′		5400	1.42	
2c″		19000	3.93	
3c	13.0	9900	1.87	
4c	13.0	9900	1.71	
5c	8.0	5900	2.93	2000 (6)
6c	8.6	6700	2.40	2400 (6)
7c	16.0	8600	2.46	na

[a] In chloroform.

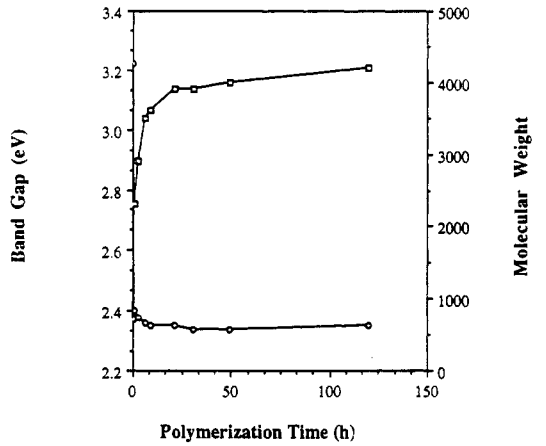


Figure 6. Relationship between polymerization time, GPC number-average molecular weights (□) and electronic band gaps (○) for poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene) (**2c**).

substituted polymers when analyzed by this method. This comparison was not possible for **7c** since the α-methylene protons are not completely resolved from the remaining aliphatic protons in the NMR spectra. Application of the GPC-determined polydispersities, with values ranging between 1.5 and 3.0, to the number-average molecular weights (M_n) determined by NMR yield weight-average degrees of polymerization (X_w) of 9–18 repeat units. Thus, a significant fraction of the chains present in a sample contain a relatively high chain length composed of 30–50 aromatic rings.

In an attempt to improve these molecular weights, a study of the effect of polymerization time was carried out. The GPC-determined M_w's and UV–vis transition edge energies (measured as the onset of absorption for all the polymers $\pi-\pi^*$ transition) are shown in Figure 6 as a function of polymerization time at room temperature. These results reveal that, after a polymerization time of 9 h, an insignificant increase in molecular weight, or further decrease in band gap, resulted. The reaction time used for the preparation of all of the polymers studied was more than sufficient to obtain an optimum molecular weight.

Motivated by the fact that the polymer solubility improved at elevated temperatures, 1,4-bis(2-thienyl)-2,5-didodecyloxybenzene (**2b**) was polymerized at 60 °C in chloroform (**2c′**) and 130 °C in 1,1,2,2-tetrachloroethane (**2c″**). Again, the polymers precipitated during synthesis, which was the likely limiting factor in achieving longer chain lengths. While little effect on M_w was observed at 60 °C, a substantial increase to 19 000 was observed at 130 °C. At the same time, a considerable broadening of the molecular weight distribution was observed. It is likely that the slightly improved solubility at 130 °C allows polymerization to a higher degree.

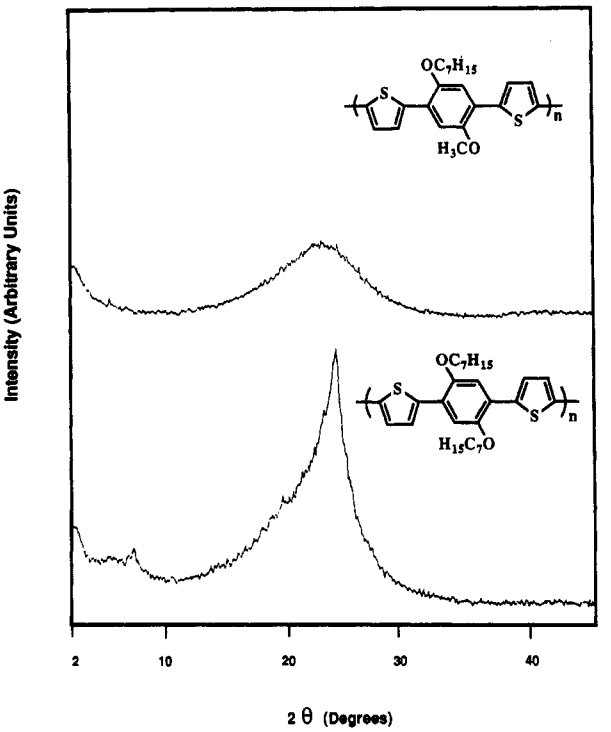


Figure 7. X-ray diffraction patterns for poly(1,4-bis(2-thienyl)-2,5-diheptoxyphenylene) (**1c**) and poly(1,4-bis(2-thienyl)-2-heptoxy-5-methoxyphenylene) (**5c**).

Long-Range Order. Of major interest in these polymers is the effect of symmetric and asymmetric substitution on the repeat unit and thus, the regiospecificity of the polymer structure on the physical and electronic properties. Monomers which contain equivalent 2,5-dialkoxy substituents on the phenylene ring (**1b**, **2b**, **3b**, and **4b**) can only undergo head-to-tail type couplings and the polymer is isoregic. When the 2,5 substituents are different (**5b** and **6b**), on the other hand, coupling is expected to occur relatively randomly and a polymer with an aregic structure is formed.

X-ray diffraction was carried out on samples that had been annealed at 200 °C for 4 h, as shown in Figures 7–9. As expected, the symmetric polymers, **1c**, **2c**, and **3c** yielded distinct diffraction peaks that indicate a high degree of molecular order. The asymmetric polymers **5c** and **6c** exhibited broad amorphous scattering with no discernable order. A listing of the peaks and their relative intensities is shown in Table V.

The crystalline polymers **1c**, **2c** and **3c** exhibit sharp diffraction patterns due to molecular spacings on the order of 0.3–0.4 nm which can be assigned to coplanar stacking of the aromatic chains. In addition, these polymers all exhibit distinct diffraction peaks at low angles, which are due to interlayer spacings of 1.244, 1.295, and 2.035 nm, respectively. This long-range order suggests strong interactions between alkoxy substituents on adjacent stacks, and the structures of these polymers may be similar to the model developed for poly(3-alkylthiophenes) by Winokur et al.[8] Using an integral breadth of 0.68° for polymer **2c** (Table V) leads to an average crystalline size of 1.31 nm.[22] This represents an average domain size through the thickness dimension of the film. The lower intensity and breadth of the low-angle peaks for polymers **1c** and **3c** preclude this analysis.

Order in these polymers was also studied by differential scanning calorimetry (DSC). Figure 10 shows exemplary DSC scans of the symmetric didodecyloxy substituted polymer **2c** and the asymmetric methoxydodecyloxy

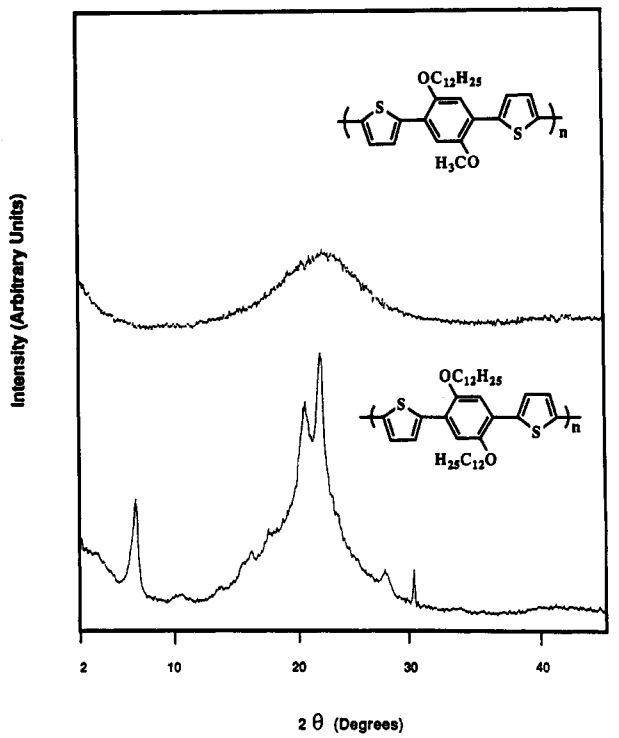


Figure 8. X-ray diffraction patterns for poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene) (**2c**) and poly(1,4-bis(2-thienyl)-2-dodecyloxy-5-methoxyphenylene) (**6c**).

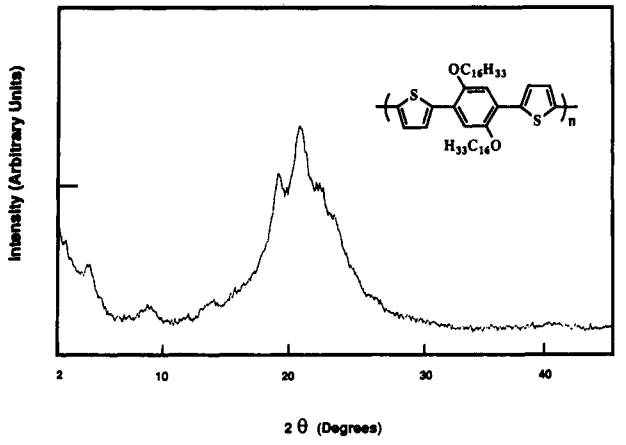


Figure 9. X-ray diffraction pattern for poly(1,4-bis(2-thienyl)-2,5-dihexadecyloxyphenylene) (**3c**).

substituted polymer, **6c**. A compilation of the DSC transitions observed for all of the polymers is given in Table VI.

All the symmetrically substituted alkoxy polymers, **1c**, **2c**, **3c** and **4c**, exhibited three endothermic transitions whereas the asymmetrically substituted polymers, **5c** and **6c**, only exhibited two. The lowest temperature transition, T_1, present in all of the polymers, was assigned to side-chain crystallization. A similar transition has been observed for the dialkyl substituted PPP's.[11b] The size of this transition increased as the length of the side chain was increased while the temperature of the transition decreased.

The two high-temperature transitions, T_2 and T_3, are attributed to the polymer backbone. T_2, for the symmetrically alkoxy substituted polymers is, tentatively assigned to a phase transition to a liquid crystalline state. Birefringence under crossed polarized light in optical microscopy was observed to persist up to T_3 in polymer **3c**, suggestive of liquid crystalline behavior. T_3 is assigned

Table V
Summary of X-ray Diffraction Results for the Symmetrically Substituted Polymers[a]

polymer	2θ peak maximum/deg	d spacings/nm	integral breadth/deg
1c	7.1 (br, w)	1.244	
	23.58 (s, st)	0.377	3.98
2c	6.82 (very s, st)	1.295	0.68
	20.6 (s, st)	0.431	
	21.82 (very s, st)	0.407	
	27.16 (br, w)	0.328	
	29.48 (very s, w)	0.303	0.18
3c	4.34 (w)	2.034	
	9.08 (br, w)	0.973	
	19.22 (sh, st)	0.461	
	20.92 (st)	0.424	
	22.4 (sh, w)	0.396	

[a] Abbreviations: st, strong; m, medium; w, weak; s, sharp; br, broad; sh, shoulder.

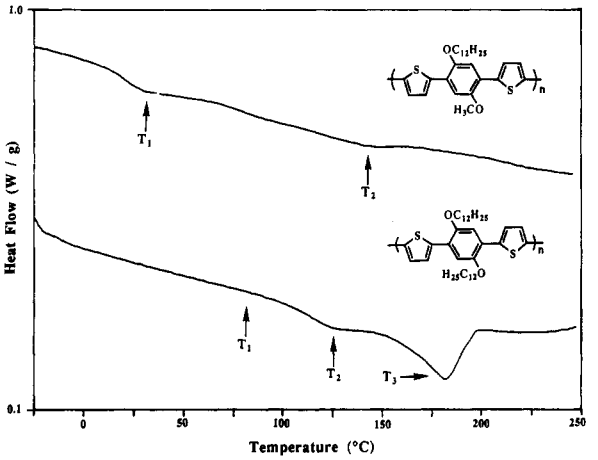


Figure 10. DSC scans for symmetric poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene) (**2c**) and asymmetric poly(1,4-bis-(2-thienyl)-2-dodecyloxy-5-methoxyphenylene) (**6c**).

Table VI
DSC Transitions for the Neutral Polymers (°C)

polymer	T_1	T_2	T_3
1c	79	150	205
2c	90	117	158
3c	51	122	165
4c	69	133	149
5c	44	103	
6c	21	132	
7c		22	

to a phase change to an isotropic melt. Temperatures beyond T_3 exhibited completely dark optical micrographs under crossed polarizers.

T_2 from the DSC results of the asymmetrically substituted polymers is assigned to a glass transition. There was no discernable birefringence when this polymer was analyzed by polarized light microscopy. This result, coupled with the X-ray diffraction results, leads us to believe that asymmetric substitution enforces the amorphous nature of the polymer.

On the basis of these results, the polymers that are isoregic, with symmetric inclusion of alkoxy substituents, are all semicrystalline. When asymmetry is introduced into the repeat unit, the polymer formed is aregic and amorphous. The dihexyl substituted polymer **7c** only exhibited a glass transition which is attributed to the flexible, nonplanar polymer backbone; thus, the polymer is amorphous.

Band Gap and Polymer Oxidation. An onset of the π–π^* transition, in solution, of 2.4 eV was observed for all

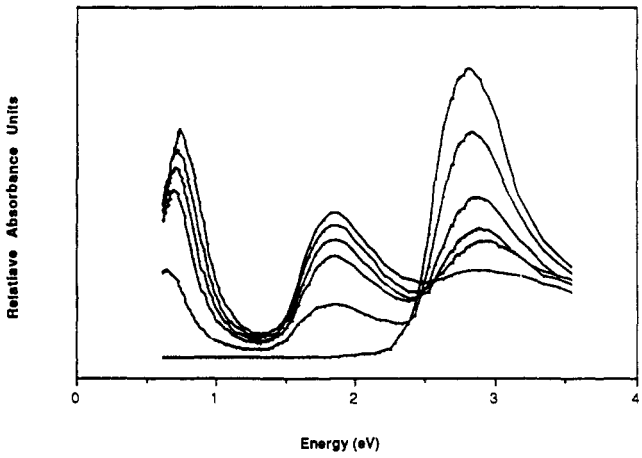


Figure 11. Solution doping of poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene (**2c**) with $NOPF_6$ in chloroform with doping levels of 0.00, 0.25, 0.50, 0.75, 1.00, and 2.00.

of the symmetric and asymmetric alkoxy substituted polymers and 3.0 eV for the dihexyl substituted polymer. The effects of the alkyl and alkoxy substituents on the electronic band gap in poly(1,4-bis(2-thienyl)phenylenes)[16] discussed previously are verified here.

A hypsochromic (blue) shift was observed for the transitions reported here relative to the methyl and methoxy substituted poly(1,4-bis(2-thienyl)phenylenes) since the values for the latter polymers were obtained on solid films where the polymer chains tend to be locked in the preferred conformation.[23] No difference was observed in the transition energies for the symmetric and asymmetric alkoxy substituted polymers because of the electronic similarity of the alkoxy substituents with respect to the polymer backbone. This is also indicative of the absence of steric interactions from the longer side groups, which might force the aromatic rings further from planarity.

Polymer solutions in chloroform were titrated with an acetonitrile solution of nitrosonium hexafluorophosphate, $NOPF_6$, to prepare varying levels of oxidized polymer. Upon incremental addition of oxidizing agent, the reduction of the intensity of the interband transition in the neutral polymer was accompanied by the emergence of two new midgap absorptions at 0.8 and 1.75 eV. This phenomenon is consistent with the formation of bipolaronic charge carriers.[24] A set of sample spectra obtained from the solution doping experiment performed on **2c** is shown in Figure 11. All of the other alkoxy substituted polymers **1c**, **3c**, **4c**, **5c** and **6c**, exhibited identical results. When **7c** was oxidized accordingly, very minute changes were observed in the spectra even when excess oxidant was added. this is attributed to the difficulty in forming the necessary planar backbone in polymer **7c**. The large twist angle, together with the high barriers to rotation, inhibits the planarity of the polymer backbone, and, thus, oxidation to the conductive form is quite difficult.

Electrical Conductivities. All of the neutral polymers prepared here exhibited conductivities less than or equal to 10^{-7} Ω^{-1} cm^{-1}. Upon oxidation with $NOPF_6$, elevated conductivities, up to 4 Ω^{-1} cm^{-1} for the alkoxy substituted polymers and 10^{-6} Ω^{-1} cm^{-1} for the hexyl substituted polymer, were observed. Analogous to the methyl substituted polymer, the presence of the alkyl substituent does not permit extended conjugation lengths or doping and little conductivity increase is observed.[16] A summary of the conductivity results is listed in Table VII.

Nitrosonium salt was used to oxidize the polymers since we have previously observed higher electrical conductivities using this dopant than with iodine. This phenomenon

Table VII
Electrical Conductivities for the Neutral and Oxidized Polymers

polymer	neutral form/ (Ω^{-1} cm^{-1})	oxidized form (Ω^{-1} cm^{-1})	
		pressed pellet	cast film
1c	$\leq 10^{-9}$	1	2
2c	$\leq 10^{-8}$	4	2
3c	$\leq 10^{-7}$ [a]		3
4c	$\leq 10^{-7}$ [a]		1
5c	$\leq 10^{-8}$	2×10^{-1}	
6c	$\leq 10^{-8}$	2×10^{-1}	
7c	$\leq 10^{-9}$	3×10^{-8}	

[a] Measurements carried out on cast film.

is consistent with the oxidation characteristics of poly(*p*-phenylene) and poly(*p*-phenylenevinylene) where oxidants stronger than iodine are necessary in obtaining high electrical conductivities.[25] Conductivity measurements were carried out on both pressed pellets and cast film samples.

In order to improve the molecular order and material properties, solution-cast polymer films were annealed prior to oxidation. It was found that annealing not only improves the molecular order but also enhances the polymer's mechanical strength in that annealed films retained their material integrity after doping, whereas the unannealed samples easily cracked upon oxidation. Similar conductivities, however, were obtained for both oxidized annealed and unannealed samples.

Since the ability of oxidant to penetrate the annealed, and more highly crystalline, cast films may be hampered, a study of doping times was carried out. Doping times of 10, 30, 60, and 120 min and 24 h were all used, and it was found that after 30 min of exposure to $NOPF_6$ solution, saturation doping had occurred and the maximum conductivity was observed.

It is known that the introduction of long chains onto the polythiophene backbone decreases the resulting electrical conductivity of the oxidized form.[26] In these substituted poly(1,4-bis(2-thienyl)phenylenes), on the other hand, comparable electrical conductivities are exhibited by the polymers independent of the length of the side chain, as evident in Table VII. When symmetry effects are analyzed, conductivity differences are observed. All the symmetric alkoxy polymers exhibited electrical conductivities between 1 and 4 Ω^{-1} cm^{-1}. When asymmetry is introduced, this conductivity falls 1 order of magnitude to ca. 10^{-1} Ω^{-1} cm^{-1}. We attribute this to the amorphous nature of these polymers. When long alkyl chains are incorporated, as in the case of polymer **7c**, order is not a factor since large energy barriers are present for planarity to be achieved. The low conductivity demonstrated by **7c** is analogous to that of the dimethyl substituted polymer reported previously,[16] where conformations dictate nonplanarity of the polymer chain and the polymer redox dopes with difficulty.

Conclusions

A series of symmetrically and asymmetrically substituted polymers from 2,5-disubstituted 1,4-bis(2-thienyl)-benzenes, with long alkyl and alkoxy substituents, have been prepared by oxidative polymerization with ferric chloride. Neutral polymers were isolated after dedoping with ammonium hydroxide. The structures of the polymers are consistent with linkages predominantly at the 5 and 5′ carbons of the terminal thiophenes. These polymers are soluble in common organic solvents and are melt processable. The incorporation of the long substituents have introduced flexibility, as well as order, to the systems, as evidenced by the presence of multiple endothermic

transitions in DSC, birefringence in optical microscopy, and distinct peaks in X-ray diffraction. All the polymers are stable up to 360 °C under nitrogen with the cleavage of the side chain proceeding at this point.

Upon oxidation of the insulating form of the polymers with $NOPF_6$, highly conductive materials, with conductivities on the order of 10^0 Ω^{-1} cm^{-1} for the alkoxy substituted polymers, were obtained. Solution doping experiments performed on these polymers indicate that, upon oxidation, two new midgap absorptions are formed, due to bipolaronic charge carriers. The differences in the physical and electronic properties of the polymers studied were attributed to the steric effects in polymer **7c** and the regiospecificity in the alkoxy substituted polymers.

Experimental Section

Reagents and Starting Materials. Etherial solvents, THF and ether, used in the monomer preparations were dried by refluxing with sodium benzophenone ketyl. Chloroform was dried by refluxing over phosphorus pentoxide. The reagents, hydroquinone, 4-methoxyphenol, 1-bromoheptane, 1-bromododecane, 1-bromohexadecane, 1-bromoeicosane, bromine, 2-thienyllithium (1.0 M in THF), *n*-butyllithium (2.5 M in hexanes), tetrakis(triphenylphosphine)palladium(0) catalyst, and ferric chloride were all obtained from Aldrich Chemicals and used without further purification. Concentrated ammonium hydroxide was used as received from Baxter Scientific. 1,4-Dihexylbenzene and 1,4-dibromo-2,5-dihexylbenzene were prepared according to literature preparations.[19] Melting points were determined and corrected using a Meltemp capillary apparatus.

1,4-Diheptoxybenzene (1a). A solution of KOH (0.401 mol) in 100 mL of ethanol was slowly added to a stirred solution of hydroquinone (0.182 mmol) in 150 mL of ethanol. The reaction was stirred at room temperature for 1 h. A solution of 1-bromoheptane (0.477 mol) in 25 mL of ethanol was added dropwise. The reaction was stirred at 50 °C for 24 h. The reaction was quenched by pouring the mixture into water. The product was isolated by extraction into methylene chloride. Solvent evaporation followed by recrystallization of the product from hot methanol resulted in white platelet crystals [mp = 53–54 °C (lit.[18] mp = 57–58 °C), 76%].

1,4-Didodecyloxybenzene (2a). Compound **2a** was prepared according to the procedure described for **1a** utilizing hydroquinone (0.091 mol), KOH (0.199 mol), and 1-bromododecane (0.208 mol). Recrystallization from hot ethanol gave a white solid [mp = 70–72 °C (lit.[27] mp = 74 °C), 77%].

1,4-Dihexadecyloxybenzene (3a). Compound **3a** was prepared according to the procedure described for **1a** utilizing hydroquinone (0.045 mol), KOH (0.100 mol), and 1-bromohexadecane (0.091 mol) in an ethanol–ether (1:1) mixture. Recrystallization from chloroform gave a white solid [mp = 86–87 °C (lit.[27] mp = 85 °C), 63%].

1,4-Dieicosinoxybenzene (4a). Compound **4a** was prepared according to the procedure described for **1a** utilizing hydroquinone (0.024 mol), KOH (0.050 mol), and 1-bromoeicosane (0.052 mol) in tetrahydrofuran. Recrystallization from chloroform gave a white solid [mp = 97–98 °C, 30%]. Anal. Calcd for $C_{46}H_{86}O_2$: C, 82.38; H, 12.83. Found: C, 82.40; H, 12.93. ^1H NMR (ppm): 6.82 (s), 3.89 (t), 1.56 (q), 1.25 (m), 0.87 (t). ^{13}C NMR (ppm): 153.30, 115.51, 68.79, 31.95, 29.70, 29.48, 26.11, 22.70, 14.10.

1-Heptoxy-4-methoxybenzene[28] (5a). Compound **5a** was prepared according to the procedure described for **1a** utilizing 4-methoxyphenol (0.081 mol), KOH (0.087 mol), and 1-bromoheptane (0.088 mol). Recrystallization from ethanol resulted in white platelet crystals (mp = 39–40 °C, 76%). Anal. Calcd for $C_{14}H_{22}O_2$: C, 75.62; H, 9.99. Found: C, 75.75; H, 10.08. ^1H NMR (ppm): 6.82 (s), 3.89 (t), 3.46 (s) 1.75 (q), 1.34 (m), 0.89 (t). ^{13}C NMR (ppm): 153.60, 153.25, 115.39, 114.56, 68.63, 55.67, 31.74, 29.35, 29.03, 25.96, 22.55, 14.02.

1-Dodecyloxy-4-methoxybenzene (6a). Compound **6a** was prepared according to the procedure described for **1a** utilizing 4-methoxyphenol (0.081 mol), KOH (0.089 mol), and 1-bromododecane (0.104 mol). Recrystallization from ethanol resulted in a white solid (mp = 52–54 °C, 97%). Anal. Calcd for $C_{19}H_{32}O_2$: C, 78.01; H, 11.05. Found: C, 78.05; H, 10.09. ^1H NMR (ppm): 6.83 (s), 3.89 (t), 3.76 (s), 1.75 (q), 1.26 (m), 0.89 (t). ^{13}C NMR (ppm): 153.61, 153.285, 115.40, 114.56, 68.65, 55.71, 31.90, 29.60, 29.38, 26.05, 22.69, 14.11.

1,4-Dibromo-2,5-diheptoxybenzene. A solution of bromine (0.094 mol) in 50 mL of carbon tetrachloride was slowly added to a solution of **1a** (0.038 mol) in 100 mL of carbon tetrachloride. The mixture was allowed to stir for 20 h at room temperature. The reaction was quenched by washing with aqueous KOH. After water washes, the solvent was removed. The solid product obtained was recrystallized from ethanol to produce a white clumped solid (mp = 59–60 °C, 88%). Anal. Calcd for $C_{20}H_{32}O_2Br_2$: C, 51.80; H, 6.97. Found: C, 51.57; H, 6.90. ^1H NMR (ppm): 7.08 (s), 3.94 (t), 1.80 (q), 1.45 (m), 0.89 (t). ^{13}C NMR (ppm): 150.07, 118.47, 111.12, 70.30, 31.74, 29.10, 28.96, 25.88, 22.56, 14.06.

1,4-Dibromo-2,5-didodecyloxybenzene. 1,4-Dibromo-2,5-didodecyloxybenzene was prepared according to the procedure described for 1,4-dibromo-2,5-diheptoxybenzene using **2a** (0.023 mol) and bromine (0.058 mol). After recrystallization from ethanol–benzene (3:1), a white fluffy solid resulted (mp = 77–79 °C, 92%). Anal. Calcd for $C_{30}H_{52}O_2Br_2$: C, 59.59; H, 8.69. Found: C, 58.92; H, 8.72. ^1H NMR (ppm): 7.08 (s), 3.93 (t), 1.80 (q), 1.25 (m), 0.88 (t). ^{13}C NMR (ppm): 150.05, 118.44, 111.10, 70.28, 31.91, 29.53, 29.30, 29.09, 25.91, 22.58, 14.11.

1,4-Dibromo-2,5-dihexadecyloxybenzene. 1,4-Dibromo-2,5-dihexadecyloxybenzene was prepared according to the procedure described for 1,4-dibromo-2,5-diheptoxybenzene using **3a** (0.028 mol) and bromine (0.010 mol). After recrystallization from chloroform, a white fluffy solid resulted (mp = 88–89 °C, 84%). Anal. Calcd for $C_{38}H_{68}O_2Br_2$: C, 63.68; H, 9.49. Found: C, 63.38; H, 9.84. ^1H NMR (ppm): 7.05 (s), 3.91 (t), 1.80 (q), 1.23 (m), 0.89 (t). ^{13}C NMR (ppm): 149.99, 118.36, 111.04, 70.26, 31.92, 29.68, 29.36, 29.09, 25.91, 22.70, 14.14.

1,4-Dibromo-2,5-dieicosinoxybenzene. 1,4-Dibromo-2,5-dieicosinoxybenzene was prepared according to the procedure described for 1,4-dibromo-2,5-diheptoxybenzene using **4a** (0.015 mol) and bromine (0.050 mol). After recrstyallization from chloroform, a white fluffy solid resulted (mp = 92–93 °C, 77%). Anal. Calcd for $C_{46}H_{84}O_2Br_2$: C, 66.66; H, 10.14. Found: C, 66.18; H, 10.37. ^1H NMR (ppm): 7.08 (s), 3.94 (t), 1.80 (q), 1.49 (m), 0.87 (t). ^{13}C NMR (ppm): 150.06, 118.47, 111.12, 70.32, 31.93, 29.70, 29.36, 29.09, 25.94, 22.70, 14.13.

1,4-Dibromo-2-heptoxy-5-methoxybenzene. 1,4-Dibromo-2-heptoxy-5-methoxybenzene was prepared according to the procedure described for 1,4-dibromo-2,5-diheptoxybenzene using **5a** (0.059 mol) and bromine (0.149 mol). This preparation resulted in a thick orange oil which was not further purified (90%). Anal. Calcd for $C_{14}H_{20}O_2Br_2$: C, 44.23; H, 5.31. Found: C, 43.99; H, 5.15. ^1H NMR (ppm): 7.01 (s), 3.90 (t), 3.81 (s), 1.78 (q), 1.42 (m), 0.88 (t). ^{13}C NMR (ppm): 150.44, 150.11, 118.37, 116.89, 111.16, 110.53, 69.96, 56.63, 31.87, 29.26, 29.10, 26.05, 22.70, 14.25.

1,4-Dibromo-2-dodecyloxy-5-methoxybenzene. 1,4-Dibromo-2-dodecyloxy-5-methoxybenzene was prepared according to the procedure described for 1,4-dibromo-2,5-diheptoxybenzene using **6a** (0.035 mol) and bromine (0.087 mol). After precipitation in methanol, a white fluffy solid resulted (mp = 56–58 °C, 76%). Anal. Calcd for $C_{19}H_{30}O_2Br_2$: C, 50.67; H, 6.73. Found: C, 50.72; H, 6.87. ^1H NMR (ppm): 7.09 (s), 3.95 (t), 3.84 (s), 1.80 (q), 1.25 (m), 0.88 (t). ^{13}C NMR (ppm): 150.41, 150.14, 118.57, 116.95, 111.22, 110.35, 70.32, 56.97, 31.90, 29.55, 29.53, 29.30, 29.09, 25.90, 22.58, 14.11.

1,4-Bis(2-thienyl)-2,5-diheptoxybenzene (1b). A solution of 2-thienyllithium (0.044 mol) in THF was added dropwise into a solution of anhydrous zinc chloride (0.042 mol) in THF at room temperature. The mixture was allowed to stir for 1 h. The resulting 2-thienylzinc chloride was then slowly added to a solution of 1,4-dibromo-2,5-diheptoxybenzene (0.011 mol) with $Pd(PPh_3)_4$ (60 mg) in THF. The reaction was heated to 50 °C and stirred at this temperature for about 72 h. The reaction was cooled and quenched by pouring the reaction mixture into a 1.5 M HCl solution. The ether layer was neutralized by washing with water. The ether solution was then dried over calcium chloride, and the solvent was evaporated. The preparation resulted in a yellow granular product upon recrystallization in

an ethanol–benzene (3:1) mixture (mp = 77–78 °C, 89%). Anal. Calcd for $C_{28}H_{38}O_2S_2$: C, 71.45; H, 8.54. Found: C, 71.36; H, 8.23.

1,4-Bis(2-thienyl)-2,5-didodecyloxybenzene (2b). Compound **2b** was prepared according to the procedure described for **1b** utilizing 2-thienyllithium (0.040 mol), zinc chloride (0.041 mol), 1,4-dibromo-2,5-didodecyloxybenzene (0.010 mol), and $Pd(PPh_3)_4$ (60 mg), resulting in a yellowish fluffy solid upon recrystallization in an ethanol–benzene (3:1) mixture (mp = 77–78 °C, 92%). Anal. Calcd for $C_{38}H_{58}O_2S_2$: C, 74.68; H, 9.58. Found: C, 74.50; H, 9.39.

1,4-Bis(2-thienyl)-2,5-dihexadecyloxybenzene (3b). Compound **3b** was prepared according to the procedure described for **1b** utilizing 2-thienyllithium (0.083 mol), zinc chloride (0.087 mol), 1,4-dibromo-2,5-dihexadecyloxybenzene (0.022 mol), and $Pd(PPh_3)_4$ (60 mg), resulting in a yellowish fluffy solid upon recrystallization in chloroform (mp = 86–87 °C, 70%). Anal. Calcd for $C_{46}H_{74}O_2S_2$: C, 76.45; H, 10.24; S, 8.90. Found: C, 76.36; H, 10.90; S, 8.97.

1,4-Bis(2-thienyl)-2,5-dieicosinoxybenzene (4b). Compound **4b** was prepared according to the procedure described for **1b** utilizing 2-thienyllithium (0.048 mol), zinc chloride (0.047 mol), 1,4-dibromo-2,5-dieicosinoxybenzene (0.012 mol), and $Pd(PPh_3)_4$ (60 mg), resulting in a yellowish fluffy solid upon recrystallization in chloroform (mp = 98–99 °C, 85%). Anal. Calcd for $C_{54}H_{88}O_2S_2$: C, 77.88; H, 10.50; S, 7.71. Found: C, 77.35; H, 11.62; S, 7.62.

1,4-Bis(2-thienyl)-2-heptoxy-5-methoxybenzene (5b). Compound **5b** was prepared according to the procedure described for **1b** utilizing 2-thienyllithium (0.053 mol), zinc chloride (0.052 mol), 1,4-dibromo-2-heptoxy-5-methoxybenzene (0.013 mol), and $Pd(PPh_3)_4$ (60 mg), resulting in a yellow solid product upon recrystallization in an ethanol–benzene (3:1) mixture (mp = 55–56 °C, 67%). Anal. Calcd for $C_{22}H_{26}O_2S_2$: C, 68.34; H, 6.79; S, 16.59. Found: C, 68.34; H, 6.62; S, 16.57.

1,4-Bis(2-thienyl)-2-dodecyloxy-5-methoxybenzene (6b). Compound **6b** was prepared according to the procedure described for **1b** utilizing 2-thienyllithium (0.045 mol), zinc chloride (0.049 mol), 1,4-dibromo-2-dodecyloxy-5-methoxybenzene (0.011 mol), and $Pd(PPh_3)_4$ (60 mg), resulting in a yellow fluffy solid upon recrystallization in an ethanol–benzene (3:1) mixture (mp = 57–58 °C, 89%). Anal. Calcd for $C_{27}H_{36}O_2S_2$: C, 70.99; H, 7.96; S, 14.04. Found: C, 71.23; H, 8.10; S, 14.29.

1,4-Bis(2-thienyl)-2,5-dihexylbenzene (7b). Compound **7b** was prepared according to the procedure described for **1b** utilizing 2-thienyllithium (0.045 mol), zinc chloride (0.046 mol), 1,4-dibromo-2,5-dihexylbenzene (0.015 mol), and $Pd(PPh_3)_4$ (60 mg), resulting in an off-white solid product upon recrystallization in an ethanol–benzene (3:1) mixture (mp = 59–61 °C, 88%). Anal. Calcd for $C_{26}H_{34}S_2$: C, 72.85; H, 9.47; S, 17.68. Found: C, 72.80; H, 9.03; S, 17.87.

Poly(1,4-bis(2-thienyl)-2,5-diheptoxyphenylene) (1c). A solution of compound **1b** (0.002 mol) in 20 mL of chloroform was added to a stirred solution of ferric chloride (0.008 mol) in 100 mL of chloroform. The mixture was stirred for 20 h at room temperature with a slow dynamic flow of N_2. The blue-black solution was precipitated from 300 mL of methanol. The blue-black residue was collected by filtration and washed with successive portions of methanol and water. The blue-black powder was dedoped by stirring in 30 mL of concentrated NH_4OH for 18 h. The resulting brick red material was isolated by filtration and washed thoroughly with methanol and water. The powder was dried in a vacuum desiccator overnight. Final purification was effected by reprecipiting $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{28}H_{38}O_2S_2$: C, 71.43; H, 8.15. Found: C, 70.59; H, 7.71.

Poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene) (2c). Compound **2b** (0.0016 mol) was polymerized according to the procedure described for **1c** utilizing ferric chloride (0.0058 mol). A blue-black residue was collected prior to compensation with NH_4OH. After the sample was dedoped, a red-orange powder was collected and dried in a vacuum desiccator overnight. Final purification was effected by reprecipitating $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{38}H_{56}O_2S_2$: C, 74.93; H, 9.29. Found: C, 75.44; H, 9.31.

Study of Polymerization Time versus Molecular Weight on 2c. Compound **2b** (1.67 mmol) was polymerized according to the procedure described for **1c** utilizing ferric chloride (7.56 mmol). About 10-mL aliquots were taken at specific times (1, 3, 6, 9, 21, 30, 49, and 120 h), and the polymerization was quenched by precipitating into MeOH. The powders were collected by filtration. The partially oxidized polymers were completely dedoped by compensation with concentrated NH_4OH(aq) for 45 min. The red-orange powders were isolated by filtration and successively washed with MeOH and water and finally dried in a vacuum desiccator overnight. Final purification was effected by reprecipitating $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. The molecular weights were determined for each sample by GPC analysis.

Poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene (2c'). Compound **2b** (0.0016 mol) was polymerized according to the procedure described for **1c** utilizing ferric chloride (0.0058 mol) while being heated to 60 °C. A blue-black residue was collected prior to compensation with NH_2OH. After the sample was dedoped, a red-orange powder was collected and dried in a vacuum oven at 70 °C overnight. Final purification was effected by reprecipitating $CHCl_2$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{38}H_{56}O_2S_2$: C, 74.93; H, 9.29; S, 10.53. Found: C, 73.61; H, 9.22; S, 10.21.

Poly(1,4-bis(2-thienyl)-2,5-didodecyloxyphenylene) (2c''). Compound **2b** (0.0017 mol) was polymerized according to the procedure described for **1c** using 1,1,2,2-tetrachloroethane as solvent with ferric chloride (0.0060 mol) while being heated to 130 °C. A blue-black residue was collected prior to compensation with NH_4OH. After the sample was dedoped, a brick-red powder was collected and dried in a vacuum desiccator overnight. Final purification was effected by reprecipitating $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{38}H_{56}O_2S_2$: C, 74.93; H, 9.29; S, 10.53. Found: C, 69.76; H, 8.15; S, 9.71.

Poly(1,4-bis(2-thienyl)-2,5-dihexadecyloxyphenylene) (3c). Compound **3b** (0.0010 mol) was polymerized at 60 °C according to the procedure described for **1c** utilizing ferric chloride (0.004 mol). A blue-black residue was collected prior to compensation with NH_4OH. After the sample was dedoped, a red-orange powder was collected and dried in a vacuum desiccator overnight. Final purification was effected by reprecipitating $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{46}H_{72}O_2S_2$: C, 76.66; H, 10.00; S, 8.88. Found: C, 73.59; H, 9.71; S, 8.46.

Poly(1,4-bis(2-thienyl)-2,5-dieicosinoxyphenylene) (4c). Compound **4b** (0.0010 mol) was polymerized at 60 °C according to the procedure described for **1c** utilizing ferric chloride (0.0040 mol). A blue-black residue was collected prior to compensation with NH_4OH. After the sample was dedoped, a red-orange powder was collected and dried in a vacuum desiccator overnight. Final purification was effected by reprecipitating $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{54}H_{88}O_2S_2$: C, 78.07; H, 10.36; S, 7.71. Found: C, 74.60; H, 10.29; S, 7.25.

Poly(1,4-bis(2-thienyl)-2-heptoxy-5-methoxyphenylene) (5c). Compound **5b** (0.0026 mol) was polymerized according to the procedure described for **1c** utilizing ferric chloride (0.0093 mol). A blue-black residue was collected prior to compensation with NH_4OH. After the sample was dedoped, a brick red powder was collected and dried in a vacuum desiccator overnight. Final purification was effected by reprecipitating $CHCl_2$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{22}H_{26}O_2S_2$: C, 68.34; H, 6.79. Found: C, 68.36; H, 6.28.

Poly(1,4-bis(2-thienyl)-2-dodecyloxy-5-methoxyphenylene) (6c). Compound **6b** (0.0022 mol) was polymerized according to the procedure described for **1c** utilizing ferric chloride (0.0111 mol). A blue-black residue was collected prior to compensation with NH_4OH. After the sample was dedoped, a brick red powder was collected and dried in a vacuum desiccator overnight. Final purification was effected by reprecipitating $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{27}H_{34}O_2S_2$: C, 71.31; H, 7.55. Found: C, 70.89; H, 7.79.

Poly(1,4-bis(2-thienyl)-2,5-dihexylphenylene) (7c). Compound **7b** (0.0010 mol) was polymerized according to the procedure described for **1c** utilizing ferric chloride (0.0105 mol).

Workup was carried out by evaporating half of the reaction solvent and precipitating in 300 mL of methanol. A green powder was isolated that was dedoped with NH_4OH to yield a yellow material which was thoroughly washed with methanol and water. The powder was dried under dynamic vacuum overnight. Final purification was effected by reprecipitating $CHCl_3$ solutions into CH_3OH, filtering, and vacuum drying. Anal. Calcd for $C_{26}H_{32}S_2$: C, 76.40; H, 7.91. Found: C, 76.43; H, 7.72.

Structural Identification of Monomers and Polymers. Infrared 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 monomers with the polymers.

^1H NMR spectra for all the monomers and polymers were obtained as solutions in deuterated chloroform and recorded on Bruker 300 MSL FT-NMR or Nicolet 200 FT-NMR spectrometers. Solution ^{13}C NMR spectra, using TMS as internal reference for both the monomers and polymers, were obtained using a Bruker 300 MSL FT-NMR or a Nicolet 200 FT-NMR using the $CDCl_3$ triplet at 77 ppm as an approximate internal reference.

Elemental analyses were obtained on a Perkin-Elmer 2400 CHN analyzer or by Robertson Laboratory, Inc., Madison, NJ.

Thermal Analysis. The thermal stability of the polymers was studied by thermogravimetric analysis (TGA) on a Du Pont 951 instrument. The temperature program included an equilibration temperature at 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 unless otherwise stated. In order to evaluate if any inorganic residue was still present in the materials isolated, the TGA scans were performed under an air purge.

Differential scanning calorimetry (DSC) scans were run on a Du Pont 951 instrument using a temperature program that included an equilibration temperature at 250 °C and then the sample was cooled at 10 °C/min to −50 °C. The samples were kept at this temperature for 1 min and then heated to 250 °C at 10 °C/min. All samples were run under a blanket of nitrogen.

Molecular Weight. Relative molecular weights were determined by gel permeation chromatography (GPC) against polystyrene standards using a Waters 840 system and tetrahydrofuran as the eluting solvent. Ultrastyragel columns (Waters), with porosities of 10 000, 5000, and 1000 Å in series, were used.

An absolute molecular weight analysis was carried out using the ^1H NMR spectra integration of the aromatic region (Ar–*H*), corresponding to four protons in the monomer and three times the number of repeat units plus the two end group protons in a long polymer chain, and the isolated methylene (–OC*H*$_2$–), corresponding to two protons for both monomers and twice the number of repeat units for the polymer. A ratio indicative of the polymer chain length is obtained.

X-ray Diffraction. Polymer films for X-ray diffraction studies were prepared by melting polymer powders at 200 °C for 4 h and then slowly cooling the melt (1 °C/min) to room temperature. X-ray diffraction studies were performed using a Rigaku D/MAX-11TB system with a θ/θ goniometer and a graphite monochromator. The power level was 50 kV/20 mA with Cu Kα radiation (λ = 1.5418 Å). The sample was kept stationary while scattering angles from 2° to 45° were scanned in the reflection mode. The scanning rate was 10°/min, and the data was summed over 10 scans. The data were smoothed and analyzed for d spacings and integral breadths. All of the polymer samples used in X-ray diffraction experiments were annealed.

Optical Microscopy. Optical microscopy was carried out on a Leitz–Wetzlar polarizing microscope equipped with a heating stage which was calibrated with a naphthalene standard. The polymers were heated at a rate of 4–5 °C/min. The polymer samples were solution cast on glass slides, annealed at 200 °C for 4 h, and slowly cooled to room temperature (1 °C/min).

Oxidative Doping of Polymers. Solution doping experiments were carried out on the soluble polymers as dilute solutions (>1 mM) in chloroform. Nitrosyl hexafluorophosphate ($NOPF_6$) was used as received from Strem Chemicals and dissolved in acetonitrile (20 mM). Oxidized polymer solutions were prepared by adding appropriate amounts of $NOPF_6$ and the spectra of the incremently doped solutions obtained on a Varian 2300 spectrophotometer (scans ranged from 200 to 2000 nm).

Oxidation of the conjugated polymers by $NOPF_6$ for conductivity measurements was carried out as a solution in chloroform. In all cases, 4 equiv of the oxidizing agent was utilized to ensure the complete extent of polymer oxidation. The reaction was allowed to proceed for 30 min, and the solid oxidized polymer was isolated by vacuum filtration and finally washed with chloroform. The solids, as dark blue-black powders, were dried in a vacuum desiccator overnight. Polymer films were cast from hot polymer solutions (20 mg/mL) in toluene. Polymer films with thicknesses of about 1–5 μm were annealed at 200 °C for 4 h and then slowly cooled to room temperature (1 °C/min). Polymer oxidation was carried out under N_2 atmosphere by soaking the films in $NOPF_6$ solutions in acetonitrile. The films were then washed with acetonitrile and dried under vacuum.

Conductivity Measurements. Measurements were made using a Keithley 610C electrometer or a Keithley 197 autoranging microvolt digital multimeter. Samples were prepared as pressed pellets, pressed between two wires in a capillary tube or solution cast on a glass slide. The Van der Pauw technique[29] was used to determine the conductivity for the pressed pellets, the two-probe method was employed for the capillary samples and the four-probe method for the cast films.

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References and Notes

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Registry No. **1a**, 65128-45-2; **1b**, 135020-69-8; **1c** (homopolymer), 135020-70-1; **2a**, 3230-09-9; **2b**, 135021-02-2; **2c** (homopolymer), 135021-03-3; **3a**, 137436-24-9; **3b**, 135859-76-6; **3c** (homopolymer), 135859-77-7; **4a**, 137436-25-0; **4b**, 137436-26-1; **4c** (homopolymer), 137436-35-2; **5a**, 20743-97-9; **5b**, 135020-67-6; **5c** (homopolymer), 135020-68-7; **6a**, 137436-27-2; **6b**, 135020-71-2; **6c** (homopolymer), 135020-72-3; **7b**, 137436-28-3; **7c** (homopolymer), 137436-36-3; $NOPF_6$, 16921-91-8; 1,4-dibromo-2,5-dihexylbenzene, 117635-21-9; 1,4-dibromo-2,5-diheptoxybenzene, 137436-29-4; 1,4-dibromo-2,5-didodecyloxybenzene, 137436-30-7; 1,4-dibromo-2,5-dihexadecyloxybenzene, 137436-31-8; 1,4-dibromo-2,5-dieicosinoxybenzene, 137436-32-9; 1,4-dibromo-2-heptoxy-5-methoxybenzene, 137436-33-0; 1,4-dibromo-2-dodecyloxy-5-methoxybenzene, 137436-34-1; 2-thienylzinc chloride, 81745-84-8.