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Poly(3-arylthiophenes): Syntheses of Monomers and Spectroscopic and Electrochemical Characterization of the Corresponding Polymers

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Several arylthiophene derivatives were synthesized using the Kumada cross-coupling reaction and electropolymerized at a platinum electrode with the aim of investigating the effect of the number of thiophene unit and substitution pattern of the monomers on the spectroscopic and charge storage properties of the resulting polymers. The electrochemical oxidation of these monomers showed a decrease of the anodic peak potential as the number of thiophene units is increased: 1.2−1.4, 1.0, and 0.75 V for the mono-, bi-, and terthiophene, respectively. The polymers having one phenyl ring per thiophene unit displayed a larger band gap with the exception of poly-3-phenyl-thiophene, which showed a much smaller band gap. The lower band gap for the later can be explained by the higher reactivity of the cation radical (as evidenced by a high oxidation potential) which led to a highly conjugated polymer. The cyclic voltammograms of the same polythiophene derivatives is characterized by a significant charge unbalance between the doping and undoping charge and most showed a limited cycle lifetime. On the other hand, poly-3-phenyl thiophene, poly-3′-(1-naphthyl)-2,2′:5′,2″-terthiophene are the more stable and also show a relatively good balance between doping and undoping charge for both the *p*- and *n*-doping redox processes. The highest voltammetric charge density evaluated by considering the weight of monomer unit was recorded for poly-3-phenyl thiophene despite the fact that some poly terthiophene derivatives have a lower phenyl ring/thiophene unit ratio.

Introduction

Conducting polymers have been the subject of numerous studies in the past two decades.[1] The interest in these materials stems from potential applications in electrochromic devices, light-emitting diodes, lightweight batteries, and electrochemical supercapacitors. Polythiophene and its derivatives[2−26] make up an interesting class of these materials since their band gaps can be tailored by changing the chemical structure of the monomer or oligomer. In addition, the effect on the physical properties of varying the 3- or 4-substituent

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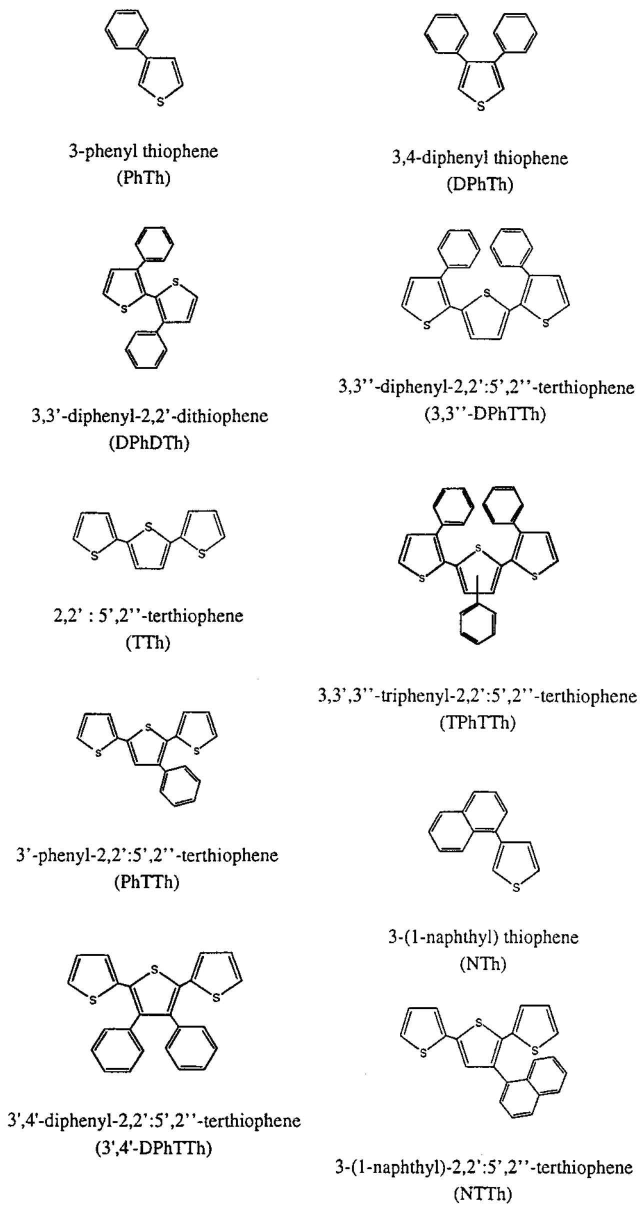
has been studied by several groups. For instance, polythiophene derivatives bearing substituents such as alkyl chains and alkoxy groups have been prepared and it was shown that the redox potential, the extent of conjugation, and the conductivity of the polymer strongly depend on the nature of the substituents.[2−17] Moreover, the addition of alkyl chains has been shown to increase the solubility of the polymer and impart processability to the resulting polymer.[3] Thiophene derivatives with ionizable groups such as sulfonate and amine were used to generate self-doped polymers[3,25] which could be used to control ionic transport during redox cycling in the *p*- and *n*-doped states.[14d] Polythiophenes with recognition sites such as crown ether have shown selectivity for alkali-metal cations and could be used for chemical sensing.[3,6,13,26]

We are particularly interested in polythiophenes bearing a phenyl ring[14,15b] since the resulting polymers show both *n*- and *p*-doping, a property which is important if these compounds are to be used in electrochemical supercapacitors and other energy conversion systems such as lightweight batteries. In a supercapacitor based on an *n*- and *p*-doped polymer,[15−17] the negative polymeric electrode can be cycled in the *n*-doped potential range whereas the positive electrode can be cycled in the *p*-doped domain. On the other hand, the electropolymerization of polythiophene requires a very high positive potential ($>$1.5 V vs Ag/Ag$^+$) which leads to some overoxidation of the resulting polymer. An approach proposed to minimize this phenomena was to use bi- and terthiophene as precursor for the polymer since they exhibit lower potential for the formation of the radical cation.[4−7,8c]

The side chain density of substituents on the oligomers can also strongly influence the properties of the polymer. In this work, the side chain density was modified with the aims of (i) minimizing the steric effects and evaluating the effect of substitution on the spectroscopic properties and (ii) increasing the specific charge capacity of the polymer by decreasing the number of phenyl group per thiophene unit. To the end, a set of arylthiophene derivatives (see Scheme 1) was synthesized and used to generate the corresponding polymers by electrochemical deposition. The effect of the number and nature (phenyl vs 1-naphthyl) of substituents on the electrochemical and spectroscopic properties of these polymers was also systematically investigated.

Scheme 1. Structure of thiophene monomers and oligomers investigated in this study.



Experimental Section

Chemicals. Bromine, 3-bromothiophene, bromobenzene, 1-bromonaphthalene, 3,4-dibromothiophene, *N*-bromosuccinimide (NBS), and dichloro[1,3-bis(diphenylphosphinopropane)]-Ni^{II} [NiCl$_2$(DPPP)] were obtained from Aldrich Chemical Co. and were used without further purification. 3-Phenylthiophene **1**,[27] 3,4-diphenylthiophene **13**,[28] 2-bromo-3-phenylthiophene **2,**[29] and 3-(1-naphthyl)thiophene **10**[17a] were prepared as previously reported. THF and diethyl ether were dried over sodium benzophenone ketyl anion radical and distilled under a dry nitrogen atmosphere immediately prior use. All reactions involving organometallic reagents were carried out under nitrogen.

Procedures. *2-(3-Phenylthienyl)magnesium Bromide,* **3**. A solution of freshly distilled **2** (1.00 g, 4,18 mmol) and 1,2-dibromoethane (0.683 g, 3.64 mmol) in anhydrous ether (10 mL) was added to a suspension of magnesium turnings (0.177 g, 7.38 mmol) in anhydrous ether (10 mL) under N$_2$. The reaction mixture was gently heated under reflux for 1 h or until most of the magnesium had disappeared. The resulting Grignard reagent (~0.21 M) was used immediately in subsequent coupling reactions.

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*3,3′-Diphenyldithiophene, **4***. A solution of **3**, freshly prepared from 2-bromo-3-phenylthiophene (2.06 g, 8.62 mmol), was added via cannula to a mixture of 2-bromo-3-phenylthiophene (1.69 g, 7.07 mmol) and $NiCl_2$(dppp) (27 mg, 0.05 mmol) in anhydrous ether (10 mL). The mixture was heated under reflux for 3 h, and the $NiCl_2$(dppp) (9 mg, 0.017 mmol) was added at intervals of 30 min during the first 2 h of reflux. The mixture was carefully hydrolyzed with H_2O (30 mL), and the organic layer was separated. The aqueous layer was extracted with ether (3 × 30 mL), and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude residue was separated on silica gel (chromatotron, 2 × 4 mm, petroleum ether) to afford 0.836 mg (37%) of ′**4** as a colorless crystalline solid. Mp: 125 °C. IR (cm^{-1}): 3031, 3044, 1602, 1487, 1069, 872, 763. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.36 (d, $J = 5.3$ Hz, 2H, H-5, 5′), 7.17−7.12 (m, 6H, Ph-H), 7.10 (d, $J = 5.3$ Hz, 2H, H-4, 4′), 7.07−7.02 (m, 2H, Ph-H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 141.13, 135.89, 130.00, 129.31, 128.33, 127.98, 126.55, 125.94. MS (FAB) *m/z* (rel int): 319 ($M^+ + 1$, 34), 318 (M^+, 85). Anal. Calcd for $C_{20}H_{14}S_2$: C, 75.43; H, 4.43; S, 20.13. Found: C, 75.11; H, 4.40; S, 19.79.

*3,3″-Diphenyl-2,2′:5′,2″-terthiophene, **6***. A solution of **3**, freshly prepared from 2-bromo-3-phenylthiophene (2.51 g, 10.5 mmol), was transferred via cannula to a mixture of 2,5-dibromothiophene (1.10 g, 4.54 mmol) and $NiCl_2$(dppp) (27 mg, 0.05 mmol) in anhydrous ether (10 mL). The mixture was refluxed for 3 h, and $NiCl_2$(dppp) (9 mg, 0.017 mmol) was added at intervals of 30 min during the first 2 h of reflux. The mixture was carefully hydrolyzed with H_2O (30 mL), and the organic layer was separated. The aqueous layer was extracted with ether (3 × 30 mL). The combined organic layers were dried over $MgSO_4$, and then the solvent was removed under reduced pressure. Finally, the desired product was separated from the crude residue using silica gel (chromatotron, 2 × 4 mm, petroleum ether) to afford 0.69 mg (38%) of ″″″**6**, a light green powder. Mp: 139−140 °C. IR (cm^{-1}): 3097, 3023, 2903, 1650, 1485, 869, 818, 754. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.34−7.30 (m, 10H, Ph-H), 7.23 (d, $J = 5.2$ Hz, 2H, H-4, 4″), 7.03 (d, $J = 5.2$ Hz, 2H, H-5, 5″), 6.78 (s, 2H, H-3′, 4′). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 139.02, 136.10, 131.36, 130.59, 129.20, 128.96, 128.39, 127.38, 126.55, 124.00. MS (FAB) *m/z* (rel int): 401(M^+, 40), 400 (M^+, 68). Anal. Calcd for $C_{24}H_{16}S_3$: C, 71.90; H, 4.02; S, 24.02. Found: C, 71.93; H, 3.98; S, 24.03.

*2,5-Dibromo-3-phenylthiophene, **7.*** A solution of Br_2 (1.52 g, 9.50 mmol) in chloroform (10 mL) was added slowly to a solution of **1** (0.760 g, 4.75 mmol) in chloroform (15 mL) at 0 °C. The solution was allowed to warm to room temperature and was stirred for 2 h. The reaction mixture was washed with water (3 × 25 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude product was purified using silica gel (chromatotron, 2 × 4 mm, petroleum ether) to afford 1.17 g (78%) of **7**, a yellow oil. Bp: 145 °C (1 mm Hg). IR (cm^{-1}): 3078, 3051, 2848, 1697, 1646, 1490, 984, 828, 754, 694. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.52−7.47 (m, 2H, Ph-H), 7.46−7.39 (m, 2H, Ph-H), 7.39−7.33 (m, 1H, Ph-H), 7.02 (s, 1H, H-4). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 142.25, 134.25, 131.91, 128.74, 128.68, 128.27, 111.44, 107.92. Anal. Calcd for $C_{10}H_6SBr_2$: C, 37.76; H, 1.90; S, 10.08. Found: C, 37.75; H, 1.89; S, 10.12. GC-MS (70 eV) *m/z* (rel int): 320 ($M^+ + 2$, $^{81}Br_2$, 3), 318 (M^+, ^{79}Br, ^{81}Br, 7), 316 ($M^+ - 2$, $^{79}Br_2$, 4), 158 (100), 114 (27), 79 (29).

*3,3′,3″-Triphenyl-2,2′:5′,2″-terthiophene, **8** (TPhTTh)*. A solution of **3**, freshly prepared from 2-bromo-3-phenylthiophene (3.00 g, 12.5 mmol), was transferred via cannula to a mixture of **7** (1.49 g, 4.68 mmol) and $NiCl_2$(dppp) (200 mg, 0.37 mmol) in anhydrous ether (30 mL). The mixture was refluxed for 1 h, and $NiCl_2$(dppp) (25 mg, 0.05 mmol) was added at intervals of 30 min during the subsequent 2 h of reflux. The mixture was carefully hydrolyzed with H_2O (30 mL), and the organic layer was separated. The aqueous layer was extracted with ether (4 × 30 mL). The combined organic layers was dried over $MgSO_4$, and then the solvent was removed under reduced pressure. Finally, the desired product was separated from the crude residue using silica gel (chromatotron, 2 × 4 mm, petroleum ether) to afford 0.290 mg (13%) of ″″″″**8** a light green powder. Mp: 54−55 °C. IR (cm^{-1}): 3088, 3023, 3014, 2922, 1651, 1591, 1476, 1067,1016, 874, 809, 731. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.42−7.38 (m, 2H), 7.37−7.24 (m, 5H), 7.14−7.11 (m, 3H), 7.09−7.05 (m, 4H), 7.03−6.98 (m, 3H), 6.97 (s, 1H, H-4′), 6.94−6.90 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 141.27, 141.18, 139.33, 136.20, 136.02, 135.80, 135.55, 130.61, 129.61, 129.56, 129.29, 128.54, 128.49, 128.42, 128.31, 128.20, 127.97, 127.95, 127.54, 126.62, 126.59, 125.97, 124.97, 124.20. MS (FAB) *m/z* (rel int): 477 ($M^+ + 1$, 48), 476 (M^+, 100). Anal. Calcd for $C_{30}H_{20}S_3$: C, 75.59; H, 4.23; S, 20.18. Found: C, 75.41; H, 4.11; S, 20.20.

*3′-Phenyl-2,2′:5′,2″-terthiophene, **9** (TPhTTh)*. A solution of 2-(thienyl)magnesium bromide, freshly prepared from 2-bromothiophene (3.00 g, 18.4 mmol) and magnesium turnings (0.55 g, 23 mmol) in diethyl ether (30 mL), was added via cannula to a mixture of **7** (2.13 g, 6.70 mmol) and $NiCl_2$(dppp) (50 mg, 0.09 mmol) in anhydrous ether (40 mL). The mixture was heated under reflux for 3 h, during which time the $NiCl_2$(dppp) (27 mg, 0.05 mmol) was added at intervals of 30 min during the first 2 h of reflux. The mixture was carefully hydrolyzed with H_2O (50 mL), and the organic layer was separated. The aqueous layer was extracted with ether (3 × 50 mL). The combined organic layers was dried over $MgSO_4$, the solvent was removed under reduced pressure, and the crude residue was purified over silica gel (chromatotron, 3 × 4 mm, petroleum ether) to afford 1.34 mg (62%) of ″″**9**, a yellow powder. Mp: 77−78 °C. IR (cm^{-1}): 3070, 3026, 2930, 1650, 1484, 1038, 820. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.41−7.34 (m, 5H, Ph-H), 7.24 (dd, $J = 5.1$, 1.1 Hz, 1H), 7.21 (dd, $J = 3.6$, 1.1 Hz, 1H), 7.18 (dd, $J = 5.1$, 1.2 Hz, 1H), 7.15 (s, 1H, H-4′), 7.04 (dd, $J = 5.1$, 3.6 Hz, 1H), 6.99 (dd, $J = 3.6$, 1.2 Hz, 1H), 6.98 (dd, $J = 5.1$, 3.6 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 139.43, 136.75, 135.96, 135.58, 135.37, 130.34, 129.22, 128.38, 127.85, 127.55, 127.12, 126.92, 126.38, 125.69, 124.61, 123.82. MS (FAB) *m/z* (rel int): 325 ($M^+ + 1$, 38) and 324 (M^+, 100). Anal. Calcd for $C_{18}H_{12}S_3$: C, 66.63; H, 3.73; S, 29.64. Found: C, 66.49; H, 3.68; S, 29.69.

*2,5-Dibromo-3-(1-naphthyl)thiophene, **11***. To a solution of **10** (6.36 g, 30.2 mmol) in 140 mL of a 50:50 (v/v) of chloroform−acetic acid at 23 °C was added all at once NBS (11.25 g, 63 mmol). The solution was stirred for 5 min and then was gently refluxed for 40 min. The reaction mixture was allowed to cool to room temperature and then diluted with 200 mL of H_2O; the chloroform layer was separated, and the aqueous phase was extracted with $CHCl_3$ (2 × 200 mL). The extracts were first combined in one organic phase which was washed once with a 200 mL portion of KOH (1 M), H_2O, $NaHCO_3$ (5%), H_2O, and brine and dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was purified by chromatography using silica gel (chromatotron, 10 × 4 mm, petroleum ether) to afford 10.1 g (91% yield) of **11** as a thick oil which slowly crystallized on standing, providing a white solid. Mp: 51−52 °C. IR (cm^{-1}): 3041, 1499, 1416, 965, 828, 795, 768. ^1H NMR (300 MHz, $CDCl_3$, ppm): 7.92 (d, $J = 7.4$ Hz, 2H), 7.21 (d, $J = 8.2$, 1.4 Hz, 1H), 7.58−7.50 (m, 3H), 7.45−7.43 (dd, $J = 7.0$, 1.4 Hz, 1H), 7.04 (s, 1H, H-4). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 141.46, 133.65, 132.76, 131.97, 131.46, 128.86, 128.42, 127.86, 126.49, 126.09, 125.53, 125.17, 111.01, 110.48. GC-MS (70 eV) *m/z* (rel int): 370 ($M^+ + 2$, $^{81}Br_2$, 2), 368 (M^+, ^{79}Br, ^{81}Br, 4), 366 ($M^+ - 2$, $^{79}Br_2$, 2), 210 (5), 208 (100), 163 (13), 104 (10). Anal. Calcd for $C_{14}H_8SBr_2$: C, 45.68; H, 2.19; S, 8.71. Found: C, 45.68; H, 2.18; S, 8.68.

*3′-(1-Naphthyl)-2,2′:5′,2″-terthiophene, **12***. A freshly prepared solution of 2-(thienyl)-magnesium bromide (10 mL, 1.2 M, 12 mmol) in diethyl ether, was transferred via cannula to a mixture of 2,5-dibromo-3-(1-naphthyl)thiophene (1.50 g, 4.07 mmol) and $NiCl_2$(dppp) (217 mg, 0.40 mmol) in anhydrous ether (30 mL). The mixture was heated under reflux for 4 h and was subsequently allowed to cool to room temperature. The dark reaction mixture was hydrolyzed with aqueous HCl (1%, 50 mL), and the organic layer was separated. The aqueous layer was then extracted with ethyl acetate (4 × 50 mL), and the combined organic layers was dried over $MgSO_4$. The solvent was removed under reduced pressure, and the crude

Table 1. Electrochemical and UV/vis Data for Aryl-Substituted Thiophenes Monomers and Oligomers and the Corresponding Polymers

monomer (concn, mM)	E_{pa}[a] (V)	E_{gal}[b] (V)	λ max[c] (nm)	E_{pp}[d] (V)	E_{pn}[e] (V)	λ max/E_{gUV}[f] (nm/eV)	E_{gCV}[g] (eV)
PhTh(10)	1.38	1.04	250	0.66	−1.96	488/1.9	2.0
DPhTh(12.6)	1.28	1.12	290	0.77	−2.28	498/2.1	2.3
DPhDTh(6.3)	1.00	0.96	305	0.75	−2.05	412/2.4	2.4
TPhTTh(10)	0.78	0.64	340	0.73	−2.13	444/2.2	2.4
3,3″-DPhTTh(12.6)	0.72	0.63	350	0.59	−2.02	464/2.2	2.3
PhTTh(10)	0.74	0.64	350	0.56	−1.98	480/2.1	2.2
3′,4′-DPhTTh(10)	0.77	0.69	354	0.56	−2.06	504/1.9	2.1
TTh(12.5)	0.79	0.56	360	0.79	−2.14	460/1.9	2.6
NTh(10)	1.18	1.01	295	0.68	−2.02	446/2.4	2.3
NTTh(10)	0.75	0.65	350	0.54	−1.95	500/2.0	2.3

[a] Peak potential of the anodic wave for the monomer or oligomer vs Ag/Ag$^+$. [b] Steady-state potential during the galvanostatic electropolymerization vs Ag/Ag$^+$. Current density = 0.64 mA/cm^2 (TPhTTh, current density = 6.4 mA/cm^2 and working electrode consisted of carbon paper). [c] Absorption maximum for a $CHCl_3$ solution of the monomer, $c = 0.1$ mM and path length = 1 cm. [d] Average of the anodic and cathodic potential peaks for *p*-doping vs Ag/Ag$^+$. [e] Average of the anodic and cathodic potential peaks for *n*-doping vs Ag/Ag$^+$. [f] Absorption maximum (λ max) and band gap taken from onset of the $\pi-\pi^*$ transition (E_{gUV}). [g] Electrochemical band gap taken as the difference between the formal potential for onset of *n*- and *p*-doping.

residue was separated using silica gel (chromatotron, 3 × 4 mm, petroleum ether) to afford 839 mg (55%) of 3′-(1-naphthyl)-2,2′:5′,2″-terthiophene, **12**, a yellow powder. Mp: 73−74 °C. IR (cm^{-1}): 3106, 3051, 1503, 1039, 818 and 690. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.82−7.78 (m, 2H, Ar−H), 7.66 (d, J = 8.2 Hz, 1H, Ar−H), 7.43−7.34 (m, 3H, Ar−H), 7.28 (ddd, J = 8.2, 6.8, 1.4 Hz, 1H, Ar−H), 7.12 (dd, J = 3.6, 1.1 Hz, 1H, H-3 or 3″), 7.10 (dd, J = 5.2, 1.1 Hz, 1H-5 or 5″), 7.03 (s, 1H, H-4′), 6.92 (dd, J = 5.1, 3.6 Hz, 1H, H-4 or 4′), 6.82 (dd, J = 5.2, 1.1 Hz, 1H, H-5″ or 5), 6.77 (dd, J = 3.7, 1.1 Hz, 1H, H-3″ or 3), 6.65 (dd, J = 5.1, 3.7 Hz, 1H, H-4″ or 4). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 137.07, 136.88, 135.81, 134.61, 134.02, 133.73, 132.65, 132.44, 128.48, 128.21, 127.99 (2C), 127.92, 126.79, 126.35, 126.02, 125.75, 125.50, 125.35, 125.22, 124.64, 123.87. MS (FAB) *m/z* (rel int): 375 (M$^+$ + 1, 45), 374 (M$^+$, 100). Anal. Calcd for $C_{22}H_{14}S_3$: C, 70.55; H, 3.77; S, 25.68. Found: C, 70.49; H, 3.74; S, 25.58.

2,5-Dibromo-3,4-diphenylthiophene, ***14***. 3,4-Diphenylthiophene (1.03 g, 4.36 mmol) was reacted with NBS (1.55 g, 8.72 mmol) in 40 mL of a 50:50 (v/v) solution of chloroform−acetic acid. The mixture was stirred for 5 min, refluxed for 45 min, and worked up as described above for compound **11**, to give, after chromatography, 1.63 g (95% yield) of **14**, as a pale yellow solid. Mp: 144 °C. IR (cm^{-1}): 3060, 3032, 1508, 1480, 1324, 1025, 988, 763, 690. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.23−7.20 (m, 6H, 2 × m, *p*-Ph-H), 7.06−7.05 (m, 4H, 2 × *o*-Ph-H). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 142.41, 134.64, 130.35, 128.15, 127.88, 109.76. GC-MS (70 eV) *m/z* (rel int): 370 (M$^+$, $^{81}Br_2$, 4), 368 (M$^+$, ^{79}Br, ^{81}Br, 6), 366 (M$^+$, $^{79}Br_2$, 4), 208 (100), 163 (40), 104 (35). Anal. Calcd for $C_{16}H_{10}SBr_2$: C, 48.76; H, 2.56; S, 8.13. Found: C, 48.67; H, 2.53; S, 8.13.

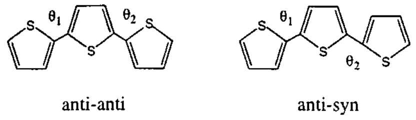
3′,4′-diphenyl-2,2′:5,2′-terthiophene, ***15*** ***(3′,4′-DPhTTh)***. 2-(Thienyl)magnesium bromide (3.1 mL, 1.1 M, 4 eq) in diethyl ether was added to a mixture of 2,5-dibromo-3,4-diphenylthiophene (0.335 g, 0.84 mmol) and $NiCl_2$(dppp) (120 mg, 0.23 mmol) in anhydrous ether (20 mL). The mixture was stirred for 15 min, refluxed for 3 h, and worked up as described above for compound **12**, to give, after chromatography, 128 mg (38% yield) of **15**, as a pale yellow crystalline solid. Mp: 155−156 °C. IR (cm^{-1}): 3069, 3013, 2866, 1696, 1646, 1558, 1540, 1490, 1223, 814, 841, 772, 694. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 7.19−7.17 (m, 6H, Ph-H), 7.10−7.06 (m, 6H, Ph-H + H-5, 5″), 6.95 (dd, J = 3.7, 1.1 Hz, 2H, H-3, 3″), 6.87 (dd, J = 5.0, 3.7 Hz, 2H, H-4, 4″). ^{13}C NMR (75.4 MHz, $CDCl_3$, ppm): 140.19, 136.30, 136.09, 131.32, 130.93, 128.27, 127.56, 127.09, 126.09, 125.78. MS (FAB) *m/z* (rel int): 401 (M$^+$ + 1, 12), 400 (M$^+$, 33), 89 (91), 77(100), 51 (70). Anal. Calcd for $C_{24}H_{16}S_3$: C, 71.90; H, 4.02; S, 24.02. Found: C, 72.12; H, 3.99; S, 24.06.

Procedure. The working electrodes consisted of a platinum disk (diameter = 1 mm) sealed inside a glass tube or epoxy, carbon paper, and tin oxide-coated glass. The platinum disk electrode was polished with diamond polishing paste to a level of 1 μm and then to 0.05 μm with an aqueous alumina slurry (Techmet, Canada). A platinum wire was affixed to the carbon paper electrode (0.5 cm × 1 cm and 0.010 in. thick from 0.010 in. thick Spectracorp.) with silver epoxy (Dynaloy, Inc.) and dried at 60 °C. The resulting electrode was completed by covering the dried silver epoxy with insulating epoxy (The Dexter Corporation). Prior to any measurements, the carbon paper electrodes were washed in methanol in an ultrasonic bath for 1−2 min and dried at 50 °C. A transparent tin oxide-coated glass electrode was used for the spectroscopic measurements of the polymer. The transparent electrode was cleaned by soaking in a 1 M HNO_3 solution for 1 min. Platinum gauze and an Ag/Ag$^+$ (0.1 M tetrabutylammonium perchlorate + 10 mM $AgNO_3$) electrode were used as the counter and reference electrodes, respectively. All potentials were reported versus the Ag/Ag$^+$ reference electrode. Electrochemical measurements were performed in a one-compartment cell using a three-electrode configuration which was placed inside a drybox filled with nitrogen. The electropolymerization was performed galvanostatically at an appropriate current density on platinum, tin oxide, or carbon paper electrodes from an acetonitrile solution of the monomer containing 1 M Et_4NBF_4 (see Table 1). The oxidation potential of the monomers were evaluated by cyclic voltammetry with a platinum electrode in the same solutions at a scan rate of 100 mV/s. Following polymerization, the electrodes were rinsed with acetonitrile and characterized by cyclic voltammetry.

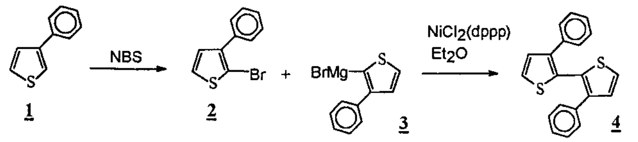
Equipment. ^{1}H NMR spectra were recorded using a Varian 300 MHz spectrometer. Chemical shifts are reported in parts per million (δ), and the signals have been designated as follows: s (singlet), d (doublet), t (triplet), and m (multiplet). Melting points were determined with a Fisher-Johns melting point apparatus and are uncorrected. Mass spectra were obtained using a VG Auto-SpecQ FAB$^+$ Magnet BpI or a GC-MS (GCD plus gas chromatography−electron ionization detector, HPG 1800A GCD system) equipped with a 5% cross-linked Ph Me silicone HP 19091 J-433 column. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR instrument. Separations were carried out on silica gel (7749 Merck) using circular chromatography (chromatotron, model 7924, Harrison Research). Cyclic voltammetry was performed using either a potentiostat/galvanostat model M273 (EG&G Princeton Applied Research) or an electrochemical interface SI1287 (Solartron Instruments) connected to a PC, and the electrochemical protocols were controlled with a model M263A (EG&G) and with DC Corrware (Scribner Associates, version 2.1b) software, respectively. Elemental analyses were carried out at the Chemistry Department of the Université de Montréal on a Fisons Instrument SPA, model EA1108, and all were within 0.4% of theoretical values. The UV−visible spectra of the monomers dissolved in $CHCl_3$ and the polymers grown onto tin oxide electrode were measured with an Hewlett-Packard model 8452A spectrophotometer.

Molecular Modeling. The geometry of thiophenes depends strongly on whether a monomer, a dimer, or a trimer is being considered. In the case of a dimer or a trimer, one or two axes

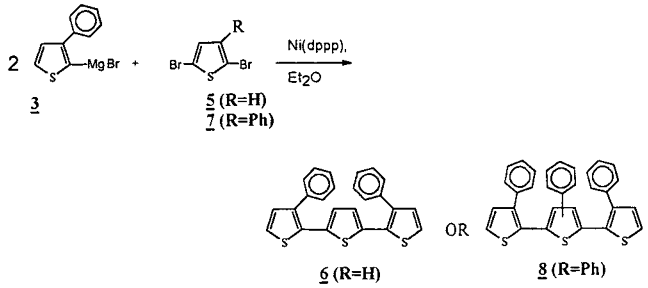
Scheme 2. Planar anti–anti and anti–syn geometries of terthiophene.



Scheme 3



Scheme 4



of rotation can be found, respectively, a fact which should be taken into consideration when determining the most stable geometry. If the torsional angle, Θ, between the two rings is 0°, the configuration is called syn whereas an anti configuration is obtained if the torsional angle is 180°; i.e., if the thiophene moieties are antiparallel. Planar anti–anti and anti–syn geometries are provided as representative examples for a trimer in Scheme 2. The minima energy geometries were calculated using UNIX Spartan software (Spartan, ver. 3.1.3 GL). The model UHF/AM1 was used. The planar syn–syn and syn geometries were assigned as the initial conformation in calculations involving the trimers and the dimers, respectively. The geometry was then determined for torsional angles from 0 to 180°, in increments of 30°. The most stable geometry was then calculated for each conformation.

Results and Discussion

Synthesis of the Monomers and Oligomers. Thiophene oligomers **1** and **3** were prepared via a sequence of Kumada-type[28] coupling reactions (i.e., a nickel-catalyzed Grignard-Wurtz cross-coupling reaction involving an arylbromide and a Grignard reagent). **4** was prepared by coupling **3** with **2**, as shown in Scheme 3.**6** was prepared by coupling 2 equiv of **3** with 1 equiv of **5** (Scheme 4). Similarly, when 1 equiv of **7** is used instead of **5**, **8** was obtained. **7** was synthesized via the addition of 2 equiv of bromine to **1** (Scheme 4).

9 was prepared from 2 equiv of 2-thienylmagnesium bromide and 1 equiv of **7** (Scheme 5). Similarly, the use of **11**, instead of **7**, gave the corresponding 3-(1-naphthyl)-2,2′:5′,2″-terthiophene (NTTh), **12**. **11** was synthesized via the addition of 2 equiv of *N*-bromosuccinimide to **10**.[17a]

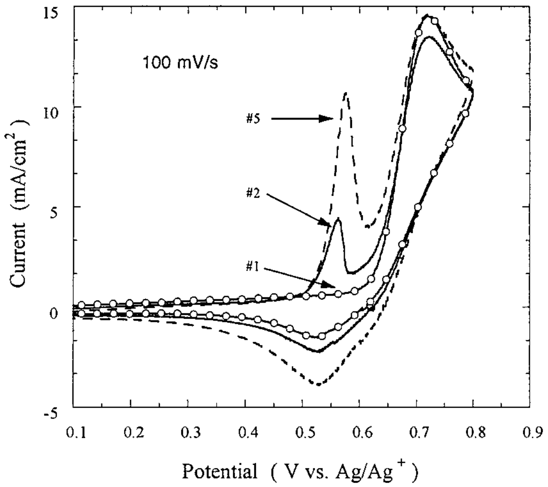
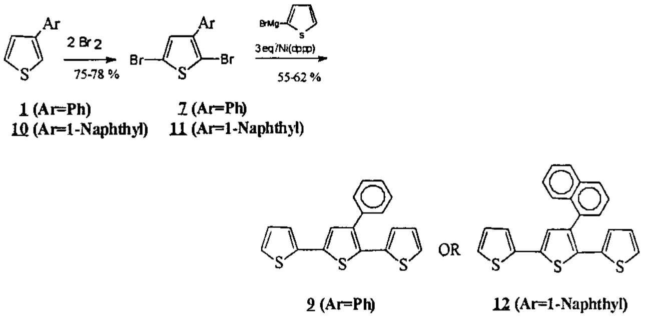
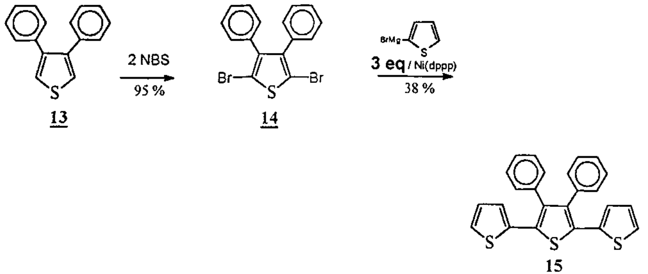


Figure 1. First (#1) cyclic voltammogram and cycles #2 and #5 during the electrochemical polymerization of ″″″3,3″-DPhTTh at a platinum electrode from 12.6 mM 3,3″-DPhTTh in 1 M Et_4NBF_4/acetonitrile at a scan rate of 100 mV/s.

Scheme 5



Scheme 6



The synthesis of **15** involved the dibromation of **13** with 2 equiv of NBS which provided the thiophene derivative **14**. An excess of 2-thienylmagnesium bromide was subsequently coupled to **14** to yield **15** (Scheme 6).**Cyclic Voltammetry of the Oligomers.** Figure 1 shows cyclic voltammogram for 12.6 mM 3,3″-diphenyl-2,2′:5′,2″-terthiophene (3,3″-DPhTTh) in 0.1 M Et_4NBF_4/acetonitrile. The onset of the anodic current was observed at about 0.6 V and corresponds to the formation of the radical cation. Further cycling to more positive potentials yielded an anodic peak at 0.72 V. On the return scan, a cathodic wave was found at 0.53 V which is related to the reduction of the polymer generated during the forward scan. This was confirmed by consecutive cyclic voltammograms recorded for the same solution as shown in Figure 1. This figure also displays an anodic wave at 0.57 V. Both of these anodic and the cathodic waves grew upon continuous cycling which indicated that the polymer film had become thicker. Cyclic voltammograms were also recorded for other thiophene monomers and oligomers, and the peak potentials of the anodic wave corresponding to the first cycle are presented in Table 1. The electrochemical oxidation of these monomers and oligomers was also followed galvanostatically at a current density of 0.64 mA/cm^2 (6.4 mA/cm^2 for TPhTTh). The steady-state electrode potential recorded after about 300 s were also included in Table 1. The electrode potentials were recorded for the duration of galvanostatic deposition so as to determine whether the polymer may have degraded during this process. As anticipated, we observed slightly smaller potential values for the oligomers using this method than those corresponding to the anodic peak on the cyclic voltammogram of the polymer thus obtained. The potential values for these terthiophene monomers were more negative than the potential limit for overoxidation of the corresponding polymer. The trends found for both the anodic peak and steady-state potentials (see Table 1) were similar, and the data for the former will be used in the following discussion.

The oxidation potentials for the 3-arylthiophene monomers were the highest (1.2−1.38 V) of the compounds investigated. The bithiophene derivative, DPhDTh, showed an anodic peak at a lower potential (1.0 V), whereas a value in the range of 0.75 V was observed for the terthiophenes. As expected, the oxidation potential decreased with increasing number of thiophene units as was previously reported for unsubstituted[4] as well as substituted thiophenes.[5−7] The position of the anodic peak is also strongly influenced by the electron-withdrawing or -donating ability of the substituent at the 3-position of the thiophene ring. The oxidation potential of poly(3-phenylthiophene) (PhTh; $E_{pa} = 1.38$ V) was lower than thiophene ($E_{pa} = 1.76$ V)[8a] because the radical cation of the former is stabilized by resonance with the phenyl group. The addition of a second phenyl group at the 4-position enhanced this effect and led to an even lower oxidation potential (1.28 V). The 3-(1-naphthyl) derivative displayed an even lower oxidation potential $E_{pa} = 1.18$ V since stabilization by resonance is stronger for a 1-naphthyl group. The oxidation potential for DPhDTh was similar to that of the unsubstituted bithiophene.[8b,18,19] In this case, the resonance effect of the phenyl groups is counterbalanced by steric effects which tend to increase the oxidation potential. Surprisingly, the effect of the addition of one, two, or three phenyl groups on a terthiophene unit and even two phenyl groups on the middle thiophene unit of a terthiophene had limited effect on the value of the anodic peak potential. These results indicate that conjugation involving the terthiophene backbone is not significantly influenced by the electronic effects associated with the substitution with phenyl groups.[12b] This was confirmed with UV−visible spectroscopy data as will be discussed later.

All of the oligomers investigated in this study undergo oxidative polymerization. It is interesting to note that even the thiophene bearing two phenyl groups (DPhTh) can yield a polymer by electrochemical oxidation. This is in agreement with a previous study for a 3,4-diphenylpyrrole which also polymerize despite the presence of the two phenyl groups on the pyrrole monomer.[30] However, in a recent study, the electropolymerization of a bulky bis(salicylidene) thiophene derivative failed, whereas the same substituent on a terthiophene unit afforded an electroactive polymer.[31]

Molecular Modeling. Calculations revealed that DPhDTh lies in an anti[32] conformation and that the angle between the two thiophene rings, θ, is 153°. This conformation is close to that previously found for bithiophene: anti with $\theta = 147.9°$.[32] However, a syn conformation with $\theta = 42.2°$ should also be possible for bithiophene. This conformation is precluded in the case of diphenyl dithiophene as there are phenyl substituents present. Such a conformation would require that both phenyl rings be placed on the same side of the thiophene ring. Recent studies of terthiophene have shown that the lowest energy minimum may be found for the anti−anti ($\theta_1 = \theta_2 = 148°$) conformation but that other minima could also be found for the syn−anti ($\theta_1 = 44°$ and $\theta_2 = 149°$) and the syn−syn ($\theta_1 = \theta_2 = 44°$) conformers.[33] The results of studies of symmetrically substituted terthiophenes have concluded that these structures are the most stable conformations although the torsional angles varied according to the nature of the substituents.[36] In the case of the PhTTh derivatives, the number of phenyl substituents were varied, and the computations clearly indicated that the stability of the conformers was influenced by the number of phenyl rings. The lowest minima for PhTTh and NTTh was close to that reported earlier for terthiophene, which would suggest that the steric hindrance of the aryl group in these oligomers is negligible. This is consistent with the fact that the redox potential for radical cation formation is not influenced by steric effects but rather by resonance (vide supra). On the other hand, as anticipated, the conformations of 3,3″-DPhTTh ($\theta_1 = 86°$ and $\theta_2 = 173°$) and TPhTTh ($\theta_1 = 39°$ and $\theta_2 = 137°$) differed significantly from that found for TTh due to the steric hindrance of the phenyl rings.

Ultraviolet−Visible Spectroscopy of the Oligomers. The electronic spectral data of the $\pi-\pi^*$ transition of the 3-aryl-substituted oligothiophenes have been summarized in Table 1. The electronic spectra (Figure 1, Supporting Information) were obtained for a 0.1 mM solution in chloroform for each of the monomers and oligomers investigated in this study. The absorption maximum (λ_{max}) was the lowest for the monomers and increased with the number of monomer thiophene units. A similar trend has been reported in the literature for substituted[8] and unsubstituted thiophenes[5] although the magnitude of the variation in λ_{max} differed for both the substituted and unsubstituted units. The resonance effect of the phenyl and the 1-naphthyl groups was evidenced by a redshift of λ_{max} from 226 nm[8] for the unsubstituted thiophene to 250, 290, and 295 nm for the 3-phenyl-, 3,4′-diphenyl-, and 3-(1-naphthyl)-substituted thiophenes, respectively. In the case of 3,3′-DPhDTh, its λ_{max}, 305 nm, was identical to that of bithiophene[8,20] and is in line with our electrochemical data (vide supra). The resonance effect of the phenyl groups would seem to be counterbalanced by the steric effect. For the terthiophene derivative, the effect of a third phenyl group was confirmed by the observation that the absorption maximum of TPhTTh was slightly blueshifted with respect to that observed for TTh ($\lambda_{max} = 360$ nm).[9,20,21] It should be noted that the absorption

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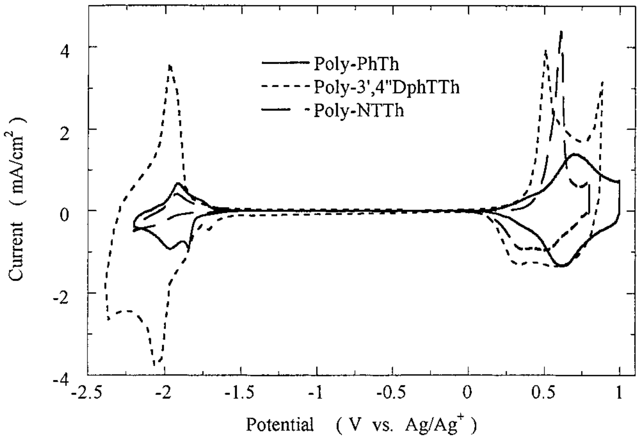

Figure 2. Cyclic voltammogram for poly-PhTh (—), ″″″3′-4′-DPhTTh (- - -) and, ″″poly-NTTh (- – -) in 1 M Et_4NBF_4/ acetonitrile a scan rate of 100 mV/s.

maxima for substituted TTh is in the range 340−360 nm.[5,9]

Ultraviolet−Visible Spectroscopy of the Polymers. The UV−visible spectra (Figure 2, Supporting Information) of as-prepared polymer films following electrochemical reduction at 0 V exhibited well-resolved and structured bands (except poly-NTh) with an absorption maximum for the $\pi-\pi^*$ transition ranging from 412 to 504 nm. Table 1 gives λ_{max} for various polythiophenes as well as their band gap as evaluated from spectroscopic and electrochemical data. The electronic spectra of these polymers were very sensitive to the nature of any 3-substituents owing to both steric and electronic effects.[2] The onset of the $\pi-\pi^*$ transition band was taken as the "spectroscopic" band gap, E_{gUV}. The data in Table 1 show that the smallest band gaps were observed for un- and monosubstituted polyterthiophene, poly-PhTh, poly DPhTh, and poly-3,4′-DPhTTh. On the other hand, poly-NTh, poly-3,3″-DPhTTh, poly-TPhTTh, and poly-DPhDTh displayed the largest band gaps of the various polythiophenes investigated in this study.

The band gap of electronically conducting polymers is influenced by (i) the reactivity of the radical cation being generated, (ii) the steric hindrance of the substituents of the thiophene ring monomer, and (iii) the steric hindrance of the substituents on the oligomers following coupling of cation radicals. The effect of the reactivity of the cation radicals is evidenced with poly-PhTh (E_{gUV} = 1.9 eV) and poly-TPhTTh (E_{gUV} = 2.2 eV). A quick look at their monomers suggest that the electrochemically generated polymers should be identical because the polymers only consist of repeating PhTh units. Moreover, the monomer with the highest reactivity (PhTh) gives rise to the polymer with the lowest band gap because coupling of the corresponding cation radicals is more favorable and leads to the generation of polymer with longer chains. Steric effects are clearly demonstrated by the large band gap found for poly-NTh (E_{gUV} = 2.4 eV) and poly-DPhTh (E_{gUV} = 2.1 eV) in comparison with that of poly-PhTh (E_{gUV} = 1.9 eV). The bulkiness of the 1-naphthyl and the 3- and 4-phenyl (on one thiophene unit) substituents yielded less conjugated polymers. Finally, the third factor, which involves the phenyl/thiophene ring ratio, is demonstrated by the study of various polyterthiophene derivatives. Thus, polymers with the highest ratio, poly-TPhTh and poly-3,3″-DPhTTh, are characterized by a larger band gap than those having only one phenyl unit per three thiophene rings: poly-3′,4′-DPhTTh, poly-NTTH, and poly-PhTTH.

Presumably, the reactivity of the cation radical influences strongly the length of the polymer chains, but the effective conjugation length, which governs the position of the absorption maxima of the polymers, is mostly influenced by structural factors (e.g., steric hindrance of the substituents; factors ii and iii). On the other hand, it is worth mentioning that correlation of band gap values with the nature, number of substituents, and number of thiophene units should be made with caution. It was reported earlier that conjugation depended strongly on the applied electrical conditions.[10a] For example, the absorption maximum for poly(3-decylthiophene) was increased from 426 to 502 nm by increasing the current density during growth from 0.5 to 10 mA/cm^2. Thus, different growth conditions could contribute to some extent to the variation in the observed λ_{max}. Nonetheless, we feel the trends in the data of Table 1 can be satisfactorily explained by the three factors mentioned above.

Electrochemistry of the Polymers. *Redox Potential.* Figure 2 shows cyclic voltammograms for the *n*- and *p*-doping for poly-PhTh, poly-3,4′DPhTTh, and poly-NTTh. Tables 1 and 2 report the relevant voltammetric data extracted from such cyclic voltammograms of all polymers investigated. The cyclic voltammograms of the polymers (Supporting Information, Figure 3) have some common features. First, each polythiophene displayed *p*-doping at 0.5−0.8 V and *n*-doping at −2.0 to −2.2 V, respectively. Second, the cyclic voltammograms of each polymer (except poly-NTTh) exhibited prepeaks before the main *p*- and *n*-doping waves. These prepeaks have been observed and investigated previously[11a,15,22,34] and will not be discussed further here. It should be noted that poly-NTTh did not show *n*-doping during the first cycle[17a] but that redox waves appeared after about 15 continuous cycles. The same phenomenon seems to be common for *n*-doping as was previously reported and may be attributed to the slow uptake of countercations by the reduced polymer.[23,24] The potential corresponding to *p*-doping provided information about the electronic properties of the polymer. For instance, the potential for *p*-doping usually decreases to less positive values when the extent of conjugation is increased. Polymers resulting from the electropolymerization of oligomers having one or two unsubstituted thiophene units (PhTTh, NTTh, 3,3″-DPHTTh, and 3,4″-DPhTTh) showed *p*- and *n*-doping waves in the same range (0.55 and −2 V, respectively) and were located at the lowest absolute potential value of the polythiophenes investigated. Monosubstituted polythiophene showed *p*-doping at slightly more positive potential (0.65 V), whereas the formal potential for both *p*- and *n*-doping for the fully substituted bi- and terthiophene were shifted to higher absolute values (0.75 and −2.1 V, respectively). The higher values for the poly bi- and poly terthiophene relative to those of the polythiophene reflect the lower reactivity of the later cation radical which leads to less extended conjugation for the polymer. Finally, poly-

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Table 2. Electrochemical Data for the Polythiophenes

polymer^{a}	$Q_{n+}{}^{b}$ (mC/cm$^{2)}$	$Q_{n-}{}^{c}$ (mC/cm^{2})	$Q_{p+}{}^{d}$ (mC/cm^{2})	$Q_{p-}{}^{e}$ (mC/cm^{2})	ratio^{f} p^{+}/n^{-}	lifetime^{g} # cycle
(Poly)						
PhTh	2.4	3.3	8.3	6.7	2.5	150
DPhTh	3.4	18.5	25.7	11.6	1.4	12
DPhDTh	4.4	11.0	11.9	5.5	1.1	40
TPhTTh	2.4	7.4	5.9	2.1	0.8	50
3,3″-DPhTTh	11.3	24.5	27.5	15.4	1.1	35
PhTTh	1.1	3.2	7.5	4.6	2.3	250
3′,4′-DPhTTh	8.8	15.5	15.3	8.6	1.0	80
TTh	42	107	104	35	0.97	20
NTh	2.5	9.9	9.2	2.7	0.9	45
NTTh	1.6	2.1	6.8	5.7	3.2	200

^{a} Deposited charge = 200 mC/cm^{2}. ^{b} Charge of the anodic wave for *n*-undoping. ^{c} Charge of the cathodic wave for *n*-doping. ^{d} Charge of the anodic wave for *p*-doping. ^{e} Charge of the cathodic wave for *p*-undoping. ^{g} Decrease of the *p*-doping charge to 60% of the initial value upon cycling over the whole potential window of the cyclic voltammogram. ^{f} Ratio of the *p*-doping ($Q_{p+}{}^{d}$) and *n*-doping ($Q_{n-}{}^{c}$) charges; $Q_{p+}{}^{d}/Q_{n-}{}^{c}$.

DPhTh showed the furthest shift due to the presence of two phenyl rings on one thiophene which cause much steric hindrance and the least extended conjugation of the polymers investigated.

The band gap may also be determined electrochemically by the potential difference between the onset of the *p*- and *n*-doping redox waves. This provided an estimate of the HOMO−LUMO gap. In polythiophene, the HOMO (π level) is confined to the carbon atoms, whereas the LUMO (π^* level) is related to both the sulfur and carbon atoms.[35] Table 1 shows that the band gaps determined electrochemically were consistent with the UV−visible data. The differences between the sets of band gap values may be attributed to the fact that the *n*- and *p*-doping values are affected by various parameters including polymer film thickness and electrolyte used for cycling.[2] Interestingly, a plot of the *p*- and *n*-doping formal potentials (with the values placed in increasing order; see Figure 4 in Supporting Information) showed a slightly higher slope for the *p*-doping process suggesting that the HOMO was more affected than the LUMO for the polymers that showed an increase in their band gap.[35] Consequently, the steric and electronic effects seemed to have a stronger influence on the LUMO than on the HOMO.

Electrochemistry of the Polymers. *Voltammetric Charge.* The voltammetric charges for *p*-doping (Q_{p+}), *p*-undoping (Q_{p-}), *n*-doping (Q_{n+}), and *n*-undoping (Q_{n-}) were obtained by integration of the appropriate redox wave and are listed in Table 2 for polymers grown to a total charge of 200 mC/cm^{2}. Several observations can be made. First, a significant charge unbalance is noticed between the doping and undoping charges for both the *p*- and *n*-doping processes for some polymers. This could suggest that irreversible degradation is occurring. Indeed, the lifetime cycle (Table 2) of polymers showing the larger charge unbalance is poor. A noticeable exception is poly-PhTTh which showed the highest stability among the polymer investigated. In this case, the charge unbalance is attributed to the presence of short chain length oligomers in the deposited film which might undergo postpolymerization during the early cycles of the cyclic voltammetry experiments.[5] Second, the *p*-/*n*-doping ratio (ratio $^{p+}/_{n-}$ of Table 2) is close to 1 for most of the polymers except for the more stable for which $^{p+}/_{n-}$ ratios of 2−3 were obtained. This can be also clearly seen in Figure 2 for poly-PhTh and poly-NTTh. This result is unexpected and at the present time we do not have any clear explanation for this behavior. Third, no definitive trend can be established between the voltammetric charge and the number of thiophene units of the precursor. This contrasts with the results reported for polythiophene, polybithiophene, and polyterthiophene, which indicated that the voltammetric charge increased with the size of the thiophene unit.[5] If the polymerization efficiency does not change, a much higher voltammetric charge is expected for the terthiophene since two electrons are required to generate three thiophene units of the polymer, whereas only one thiophene unit is obtained with a monothiophene. Thus, it is clear that the polymerization efficiency of poly-PhTTh is smaller than of poly-PhTh since poly-PhTTh gave slightly lower voltammetric charges.

For an application of these polymer materials as active electrode material in either capacitors or batteries, it is important to maximize the energy density or the amount of charge that can be stored per weight of polymer. For example, for the same mass of poly-PhTh and poly-PhTTh and assuming a similar doping level, the later should show an increase of 50% of its voltammetric charge per unit weight of monomer unit due to the smaller number of phenyl groups per thiophene unit. However, the data of Table 2 seem to demonstrate that, contrary to the expectation, poly-PhTh which has the highest number of phenyl rings per thiophene unit has the highest voltammetric charge density (among the polymers showing the longer lifetime). This demonstrates the importance of highly reactive cation radicals which are required for the generation of polymers with longer polymer chains and effective conjugation length. Nonetheless, it is clear that a systematic study involving higher polymer loading and careful weighing of the deposited polymers is needed since the deposition efficiency is lower than 100%. This is evidenced by the formation of highly colored oligomers during the electropolymerization of these polymers which can be explained by a decrease of the coupling probability for a terthiophene derivative cation radical to that of a monomer cation radical.

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Supporting Information Available: UV-vis spectra of various thiophene and polythiophene derivatives; cyclic voltammograms for poly(PhTh), poly(DPhTh), poly(DPhDTh), poly(TTh), poly(PhTTh), poly(3,4′,-PhTTh), poly(3,3″,-PhTTh), poly(TPhTTh), poly(NTh), poly(NTTh); a plot of the *p*- and *n*-doping formal potentials (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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