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Thiophene:Alkylthiophene Copolymers from Substituted Dialkyloligothiophenes

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Oxidation of a series of dioctyloligothiophenes, in which the terminal thiophene rings are substituted at the 3-position, affords mixtures of soluble oligomers and polymers consisting of substituted and unsubstituted thiophene-2,5-diyl repeat units. Polymers derived from these oligomers have conjugation lengths approaching that of 100% head-to-tail PATs and have high electrical conductivities (~40 S cm^{-1}). Electrochemical oxidation of low concentrations of oligomers, by cycling to a potential just positive of the onset of oxidation, affords films of the corresponding dimers that are insoluble in acetonitrile but that can be spectroscopically characterized in chlorinated solvents. These dimers are intermediates in the formation of the corresponding polymers. Electrochemical oxidation at high monomer concentrations or at potentials far positive of the oxidation potential affords films containing monomer, dimer, and polymer. Chemical oxidation of dialkylated terthiophene and quarterthiophene affords dimeric and polymeric materials that are useful for comparisons to intermediates formed during electrochemical polymerization. The oligomers and polymers were characterized by NMR, infrared, and visible spectroscopy, cyclic voltammetry, and X-ray diffraction.

Introduction

Substituted polythiophenes have been the subject of intense interest because of their high electrical conductivity, thermal and chemical stability, amenability to chemical modification, and reversible redox properties.[1] Although polythiophene itself is intractable, alkyl-substituted polythiophenes are soluble in common organic solvents and melt at relatively low temperatures.[2] Other physical properties which have attracted recent interest include solvatochromism,[3] thermochromism,[4] and luminescence.[5] Oligothiophenes have also been investigated as suitable materials for electronic devices.[6]

Polythiophenes are conveniently prepared by chemical and electrochemical oxidative routes, or by organometallic arene coupling. Oxidative routes afford the doped (i.e., conductive) form of polymer directly, but these materials suffer from a high density of defects in bond connectivity (i.e., coupling through the β-positions of the thiophene ring).[7] The desire to prepare polymers with tunable electronic and optical properties has recently been addressed by controlling the microstructure of poly(3-alkylthiophene)s (PATs). Since 3-alkylthiophenes possess neither a symmetry axis nor an inversion center, coupling at the 2- and 5-positions leads to both head-to-head and head-to-tail couplings (Scheme 1). Even though head-to-tail coupling is sterically favored, 10–20% head-to-tail couplings may occur during oxidative polymerization.[8,9] Elegant new synthetic approaches, in which the 2- and 5-positions of 3-alkylthiophene are differentiated, allow for the preparation of regioregular head-to-tail PATs.[10,11] The enhanced electronic and optical properties of regioregular PATs

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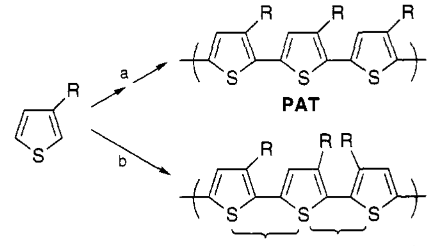
Scheme 1



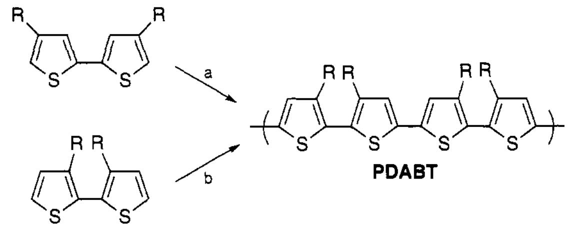
[a] References 10 and 11. [b] References 8 and 9.

are ascribed to the absence of steric interactions between alkyl substituents on neighboring thiophene repeat units. Such interactions cause a twisting around the backbone, thereby disrupting conjugation.

The formation of copolymers is a common approach to materials with tailored properties. The properties of copolymers are determined by the structure, ratio, and sequence of the repeat units derived from the comonomers. Copolymerization of thiophenes has been performed by oxidative[12] and organometallic[13] routes to prepare polymers with random regiochemistry and sequence. Preparation of copolymers with defined repeat unit structure, regiochemistry, sequence, and molecular weight is important in order to further investigate and exploit the wide range of desirable properties of polythiophenes.

Copolymerization of oligothiophenes is particularly attractive because the oligomers themselves have tunable properties that affect the behavior of the resulting polymers. The use of oligothiophenes as building blocks for polythiophene was originally suggested in order to decrease the oxidation potential of the monomer relative to thiophene (anodic peak potential, E_{pa}, versus SCE: thiophene, +2.0 V; bithiophene, +1.3 V; terthiophene, +1.1 V)[14] and thereby decrease the extent of overoxidation of the polymeric product. However, overoxidation of the polymer formed at the high positive potentials required for thiophene oxidation affords materials with higher conductivities than materials deposited by oxidation of oligothiophenes under more mild conditions.[15] Use of oligomers as starting materials should also decrease the density of defects in connectivity by virtue of their predetermined 2,5-substitution. However, detailed analysis of polymerization intermediates and resulting polymers is difficult owing to the insolubility of the oligothiophenes produced.

Scheme 2



[a] Reference 16. [b] References 17 and 18.

The regiochemistry of alkylthiophene incorporation into polymers can also be controlled by using symmetrically disubstituted bithiophenes as monomers. Polymerization of symmetrically substituted 4,4′-dialkyl-2,2′-bithiophenes[16,17] or 3,3′-dialkyl-2,2′-bithiophenes[18] (i.e., **2**) affords poly(3,4′-dialkyl-2,2′-bithiophene-2,5′-diyl)s (PDABTs) in which the alkylthiophene repeat units are arranged with alternating (i.e., strictly head-to-head) regiochemistry (Scheme 2). 3,3′-Disubstitution of 2,2′-bithiophene impedes coplanarity of the aromatic rings, as demonstrated by the hypsochromic shift in λ_{max} and high oxidation potentials for **2** relative to unsubstituted 2,2′-bithiophene.[19] The regiochemical arrangement of substituents has a strong influence on the conjugation length of polythiophenes. The electronic spectra of solid films of PDABTs have a peak at 390 nm, whereas regiorandom PATs absorb at approximately 490 nm. Regioregular PATs give rise to a sharp absorption at 520 nm.[10] The enhanced conjugation of regioregular PATs leads to a lower oxidation potential (+0.80 V for octyl, +0.65 V for dodecyl), and sharp voltammetric waves, relative to regiorandom polymers (+0.85 V for octyl, 0.72 V for dodecyl)[10] and PDABTs (+0.96 V).[16] However, the voltammetric wave for oxidation of PDABT is sharper than expected for a surface-confined redox-active species, which has been interpreted as arising from initial retardation of oxidation (owing to steric repulsion between substituents on adjacent repeat units) followed by an abrupt change in polymer structure, after which the oxidation is accelerated.[16]

Other alkyl-substituted oligothiophenes have been used as building blocks for the synthesis of sequence-specific copolymers. Roncali et al. reported that elec-

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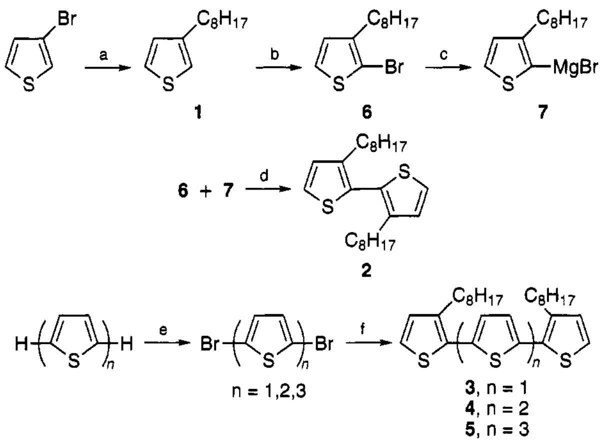
Scheme 3



[a] $C_8H_{17}MgBr$, $NiCl_2(dppp)$. [b] Br_2, CCl_4, −15 °C. [c] Mg, $BrCH_2CH_2Br$, THF, sonication. [d] $NiCl_2(dppp)$, Et_2O, Δ. [e] Br_2, $CHCl_3$, **7**, $NiCl_2(dppp)$, Et_2O. [f] room temperature.

trochemical oxidation of 3′-alkyl-2,2′:5′,2″-terthiophenes results in the formation of more extensively conjugated polymers than those prepared from unsubstituted terthiophene.[20] Although these monomers lead to sequence-specific copolymers, they lack 2-fold symmetry, thereby resulting in regiorandom placement of the alkyl substituent. Kantizidis et al. reported that the symmetrically substituted monomer 3′,4′-dibutyl-2,2′:5′,2″-terthiophene[21] is subject to ferric chloride oxidative polymerization to afford a soluble high molecular weight polymer. However, the resulting polymer, when doped with iodine, is only moderately conductive (10 S cm^{-1}). Preliminary studies of oligomers and polymers derived from other oligothiophenes have also appeared: 3,3″-dialkyl-2,2′:5′,2″-terthiophene,[22] 3,3‴-dialkyl-2,2′:5′,2″:5″,2‴-quaterthiophene,[23] 4-(4-octylphenyl)-2,2′-bithiophene,[24] 3-octyl-4′-methyl-2,2′-bithiophene,[9,25] dialkylsexithiophenes,[26] and longer polyalkylated oligothiophenes.[27]

We have investigated the synthesis and oxidative polymerization of a series of oligothiophenes **1**−**5** (Scheme 3) in which both terminal rings are substituted in the 3-position. Octyl substituents are incorporated at the 3-position of the terminal rings to provide solubility and to sterically hinder coupling at β-positions without obstructing polymerization at the free α-positions. Oxidative polymerization affords copolymers consisting of thiophene-2,5-diyl and 3-alkylthiophene-2,5-diyl repeat units. The repeat unit sequence and relative regiochemistry of the resulting polymer is ensured by the symmetry of the substituted oligothiophenes used as monomers. The solubility characteristics of oligomers of **1**−**5** allow for the isolation and identification of oligomers formed during electrochemical polymerization. Oxidation of **3** and **4** affords highly conjugated polymers in which the alkyl substituents facilitate solubility without presenting hindrance to a planar backbone. We present the synthesis, oxidative polymerization and electrochemical characterization of **1**−**5**. Resulting oligomers and polymers were separated and identified spectroscopically. The electrochemical characterization, separation of oligomers, and comparison of oligomers to intermediates in the polymerization pathway are discussed in relation to reports of similiar monomers reported recently.[20,21]

Experimental Section

General Procedures. Thiophene, 3-bromothiophene, 2,5-dibromothiophene, 1-bromooctane, 1,2-dibromoethane, 2,2′-bithiophene, lithium perchlorate, and bis(diphenylphosphino)-1,3-propanenickel(II) chloride, $NiCl_2(dppp)$, were purchased from Aldrich and used as received. Ferric chloride (Aldrich) was dried under vacuum at 100 °C for 4 h and stored under dry nitrogen. Chloroform was washed with water, dried over phosphorous pentoxide, and distilled under dry nitrogen. Diethyl ether was dried over sodium benzophenone ketyl and distilled under dry nitrogen immediatly prior to use. Flash column chromatography was performed on silica gel (40 μm, Baker).

^{1}H NMR spectra were obtained on a Varian Gemini-300 spectrometer operating at 300 MHz. All samples were dissolved in $CDCl_3$ and referenced against internal tetramethylsilane (TMS). Infrared and ultraviolet−visible spectra were obtained on a Nicolet 520 FT-IR and a Perkin-Elmer Lambda 19 spectrometer, respectively. Mass spectra were collected on a VG Analytical II-250J instrument using electron bombardment ionization.

Films of polymer were deposited on glass discs by spin-coating a chloroform solution (ca. 40 μL, 1 mg/mL) at 2000 rpm using a Specialty Coating Systems P-6000 spin coater. Film thicknesses were measured by surface profilometry (Tencor Alpha-step 100). Spin-coated polymer films were doped by iodine vapor for 24 h, and conductivity measurements were made with a four-point probe.[28]

Electrochemical experiments were performed on a BAS 100B electrochemical analyzer in a three-electrode single-compartment cell equipped with a 2.0 mm^2 platinum disk working electrode, a platinum wire counter electrode, and a saturated calomel reference electrode (SCE). Acetonitrile was distilled from calcium hydride under dry nitrogen immediately prior to use.

3-Octylthiophene (1). Octylmagnesium bromide was prepared in anhydrous ether and treated with 3-bromothiophene according to the method of Kumada[29] to afford 3-octylthiophene (86%) as a colorless liquid: bp 127 °C/5 mmHg. ^{1}H NMR δ 0.88 (t, 3H, J = 7 Hz, $-CH_3$), 1.2−1.4 (m, 10H), 1.63 (p, 2H, J = 8 Hz, β-CH_2), 2.62 (t, 2H, J = 8 Hz, α-CH_2), 6.92 (dd, 1H, J = 3, 1 Hz, H-2), 6.94 (dd, 1H, J = 5, 1 Hz, H-4), 7.24 (dd, 1H, J = 5, 3 Hz, H-5). IR (neat) 3105, 3052, 2933, 2855, 1466, 1407, 1242, 1084, 861, 841, 782, 729, 690, 643 cm^{-1}. UV ($CHCl_3$) λ_{max} 232 nm, ϵ_{max} 1.08 × 10^4.

2-Bromo-3-octylthiophene. A solution of Br_2 (4.90 g, 30.7 mmol) in CCl_4 (16 mL) was added slowly to a solution of 3-octylthiophene (6.01 g, 30.7 mmol) in CCl_4 (16 mL) at −20 °C and stirred for 2 h. The CCl_4 solution was washed with water (3 × 50 mL) and dried over $MgSO_4$, and the CCl_4 was removed to give 6.58 g of light brown crude product which was distilled at 95 °C/5 mmHg to afford 2-bromo-3-octylthiophene (5.72 g, 68%) as a colorless liquid. ^{1}H NMR δ 0.88 (t, 3H, J =

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7 Hz, $-CH_3$), 1.2–1.3 (m, 10H), 1.57 (p, 2H, J = 8 Hz, β-CH_2), 2.56 (t, 2H, J = 8 Hz, α-CH_2), 6.80 (d, 1H, J = 6 Hz, H-4), 7.19 (d, 1H, J = 6 Hz, H-5). IR (neat) 3118, 3059, 2934, 2854, 1743, 1539, 1466, 1407, 1374, 1229, 1091, 999, 880, 828, 716, 644, 584 cm^{-1}.

2-(3-Octylthienyl)magnesium Bromide. A solution of 2-bromo-3-octylthiophene (1.00 g, 3.64 mmol) and 1,2-dibromoethane (0.683 g, 3.64 mmol) in anhydrous ether (10 mL) was added to a suspension of magnesium turnings (0.176 g, 7.24 mmol) in anhydrous ether (10 mL) under N_2 and sonicated until complete disappearance of the magnesium. The resulting Grignard reagent was used immediately in subsequent coupling reactions.

5,5′-Dibromo-2,2′-bithiophene. A solution of Br_2 (3.84 g, 24.1 mmol) in chloroform (20 mL) was added slowly to a solution of 2,2′-bithiophene (2.00 g, 12.0 mmol) in chloroform (30 mL) at room temperature and stirred for 2 h. The solution was washed with water (3 × 50 mL) and dried over $MgSO_4$, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (petroleum ether) to give 5,5′-dibromo-2,2′-bithiophene as a yellow solid (3.20 g, 82%), mp: 145–6 °C (lit. mp:[30] 142 °C). ^{1}H NMR δ 6.85 (d, 2H, J = 4 Hz, H-3), 6.96 (d, 2H, J = 4 Hz, H-4). IR (KBr) 3102, 3074, 3046, 1509, 1431, 1207, 1074, 983, 870, 800 cm^{-1}.

5,5″-Dibromo-2,2′:5′,2″-terthiophene. 2,2′:5′,2″-Terthiophene (2.29 g, 9.23 mmol) was treated with Br_2 (2.96 g, 18.5 mmol) to afford 5,5″-dibromo-2,2′:5′,2″-terthiophene as a yellow solid (3.20 g, 85%), mp: 153–4 °C (lit. mp:[30] 154 °C). ^{1}H NMR δ 6.92 (d, 2H, J = 4 Hz, H-3), 6.98 (d, 2H, J = 4 Hz, H-4), 7.00 (s, 2H, H-3′). IR (KBr) 3088, 1509, 1432, 1256, 1228, 1193, 1067, 975, 849, 800, 695, 660, 526, 456 cm^{-1}.

3,3′-Dioctyl-2,2′-bithiophene (2). A solution of 2-(3-octylthienyl)magnesium bromide prepared from 2-bromo-3-octylthiophene (1.00 g, 3.64 mmol) was added slowly to a mixture of 2-bromo-3-octylthiophene (900 mg, 3.28 mmol) and $NiCl_2$(dppp) (59.0 mg, 10.2 μmol) in anhydrous ether (15 mL). The mixture was heated to reflux for 18 h and poured into a mixture of crushed ice and 2 M HCl (25 mL). The organic layer was separated, and the aqueous layer was extracted with ether (3 × 25 mL). The combined organic layers were dried over magnesium sulfate, the solvent was removed under reduced pressure and the residue was purified by flash chromatography (petroleum ether) to afford 3,3′-dioctyl-2,2′-bithiophene (0.70 g, 35%) as a colorless liquid. ^{1}H NMR δ 0.87 (t, 6H, J = 7 Hz, $-CH_3$), 1.2–1.3 (m, 20H), 1.55 (p, 4H, J = 8 Hz, β-CH_2), 2.49 (t, 4H, J = 8 Hz, α-CH_2), 6.97 (d, 2H, J = 5 Hz, H-4), 7.28 (d, 2H, J = 5 Hz, H-5). IR (neat) 3109, 3067, 2961, 2919, 2856, 1761, 1521, 1474, 1409, 1368, 1242, 108, 884, 842, 770, 721, 695, 660 cm^{-1}. UV ($CHCl_3$) λ_{max} 247 nm, ϵ_{max} 4.60 × 10^4.

3,3″-Dioctyl-2,2′:5,2″-terthiophene (3). A solution of 2-(3-octylthienyl)magnesium bromide prepared from of 2-bromo-3-octylthiophene (1.00 g, 3.84 mmol) was added slowly to a mixture of 2,5-dibromothiophene (0.290 g, 1.21 mmol) and $NiCl_2$(dppp) (59.0 mg, 10.2 mmol) in anhydrous ether (15 mL). The mixture was heated to reflux for 18 h and poured into a mixture of crushed ice and 2 M HCl (25 mL). The organic layer was separated and the aqueous layer was extracted with ether (3 × 25 mL). The combined organic extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography (petroleum ether) to afford **3** (434 mg, 75%) as a yellow liquid. ^{1}H NMR δ 0.87 (t, 6H, J = 7 Hz, $-CH_3$), 1.2–1.4 (m, 20H), 1.65 (p, 4H, J = 8 Hz, β-CH_2), 2.78 (t, 4H, J = 8 Hz, α-CH_2), 6.95 (d, 2H, J = 5 Hz, H-4), 7.06 (s, 2H, H-3′), 7.18 (d, 2H, J = 5 Hz, H-5). IR (neat) 3105, 3065, 2967, 2934, 2861, 1756, 1657, 1565, 1512, 1473, 1374, 1242, 1202, 1091, 1058, 848, 802, 729, 663 cm^{-1}. UV ($CHCl_3$) λ_{max} 338 nm, ϵ_{max} 4.59 × 10^4.

3,3‴-Dioctyl-2,2′:5′,2″:5″,2‴-quaterthiophene (4). 5,5′-Dibromobithiophene was treated with 2-(3-octylthienyl)magnesium bromide (according to the method outlined above for the preparation of **3**) to afford **4** (530 mg, 79%) as a yellow liquid. ^{1}H NMR δ 0.87 (t, 6H, J = 7 Hz, $-CH_3$), 1.3–1.4 (m, 20H), 1.64 (p, 4H, J = 8 Hz, β-CH_2), 2.78 (t, 4H, 8 Hz, α-CH_2), 6.94 (d, 2H, J = 5 Hz, H-4), 7.02 (d, 2H, J = 4 Hz), 7.13 (d, 2H, J = 4 Hz), 7.18 (d, 2H, J = 5 Hz, H-5). IR (neat) 3105, 3072, 2967, 2927, 2861, 1749, 1552, 1512, 1473, 1420, 1381, 1308, 1229, 1098, 1058, 927, 880, 841, 802, 729, 696, 657 cm^{-1}. UV ($CHCl_3$) λ_{max} 377 nm, ϵ_{max} 6.65 × 10^4. MS (EI) 554.2 (M^+).

3,3⁗-Dioctyl-2,2′:5′,2″:5″,2‴-5‴,2⁗-quinquethiophene (5). The title compound was prepared according to the general method described for the synthesis of **3**. The crude product was purified by flash column chromatography. Futher purification was achieved by HPLC using a Waters μPorasil 25 × 200 mm column packed with 10 μm silica gel (hexane) to afford **5** (0.120 g, 12%) as a yellow liquid. ^{1}H NMR δ 0.85 (t, 6H, J = 7 Hz, $-CH_3$), 1.1–1.3 (m, 20H), 1.38 (p, 4H, J = 8 Hz, β-CH_2), 2.25 (t, 4H, 8 Hz, α-CH_2), 6.85 (s, 2H, H-3″), 6.89 (d, 2H, J = 5 Hz), 6.91 (d, 2H, J = 5 Hz, H-4), 7.16 (d, 2H, J = 5 Hz, H-5), 7.27 (d, 2H, J = 5 Hz). IR (neat) 3105, 3072, 2967, 2921, 2855, 1736, 1604, 1558, 1506, 1466, 1407, 1374, 1269, 1230, 1038, 894, 841, 795, 723, 644 cm^{-1}. UV ($CHCl_3$) λ_{max} 367 nm. MS (EI) 636.3 (M^+).

Chemical Oxidation of 3. A suspension of dry $FeCl_3$ (137 mg, 0.845 mmol) in $CHCl_3$ (30 mL) was stirred for 15 min. A solution of **3** (100 mg, 0.212 mmol) in chloroform (20 mL) was added dropwise over 15 min, and the resulting blue suspension was stirred overnight. The mixture was poured into methanol (1 L), and the resulting precipitate was filtered and continuously extracted with petroleum ether and chloroform, respectively, in a Soxhlet extractor for 24 h each in order to separate the residual oxidant, oligomers, and polymer. The petroleum ether fraction was stirred for 18 h with 5% aqueous hydrazine. The organic layer was separated, and the solvent was removed under reduced pressure. The orange residue was purified by flash chromatography (petroleum ether) to afford 3,3″,3‴,3′′′′′,3-tetraoctyl-2,2′:5′,2″:5″,5‴:2‴,2⁗:5⁗,2′′′′′-sexithiophene, **(3)₂** (30 mg, 15%), as a yellow liquid. ^{1}H NMR δ 0.87 (t, 12H, J = 7 Hz, $-CH_3$), 1.2–1.4 (m, 40H), 1.66 (p, 8H, J = 8 Hz, β-CH_2), 2.77 (t, 4H, J = 8 Hz, α-CH_2), 2.79 (t, 4H, J = 8 Hz, α-CH_2), 6.95 (d, 2H, J = 5 Hz, H-4), 7.01 (s, 2H, H-4″), 7.07 (d, 2H, J = 4 Hz), 7.08 (d, 2H, J = 4 Hz), 7.19 (d, 2H, J = 5 Hz, H-5). IR (neat) 3118, 3072, 2979, 2927, 2854, 1736, 1643, 1558, 1466, 1387, 1256, 1098, 1025, 880, 814, 729, 670 cm^{-1}. UV ($CHCl_3$) λ_{max} 404 nm.

The chloroform soluble fraction was treated with 5% aqueous hydrazine and purified by flash chromatography (10% petroleum ether:chloroform) to afford poly(4,3″-dioctyl-5,2′:5′,2″-terthiophene-2,5″-diyl), poly**3**, as a red solid (10 mg, 10%). ^{1}H NMR δ 0.8–1.0 (m, 6H, $-CH_3$), 1.2–1.4 (m, 20H), 1.6–1.7 (m, 4H, β-CH_2), 2.7–2.9 (m, 4H, α-CH_2), 7.02 (s, 2H, H-4), 7.09 (s, 2H, H-3′). IR (neat) 3065, 2960, 2921, 2848, 1736, 1506, 1466, 1374, 1281, 1190, 1078, 821, 781, 729, 670 cm^{-1}. UV ($CHCl_3$) λ_{max} 517 nm.

To increase the yield of polymer and simplify the purification of products, the oxidation of **3** (250 mg) was repeated at 50 °C for 48 h. The mixture was washed with 5% aqueous hydrazine, and the solvent was removed under reduced pressure. The resulting red solid was purified by flash chromatography (petroleum ether) that was systematically diluted with chloroform until all the material had eluted from the column. The only isolated products were **(3)₂** (38 mg, 15%) and poly**3** (212 mg, 85%).

Chemical Oxidation of 4. A suspension of $FeCl_3$ (117 mg, 0.721 mmol) and **4** (100 mg, 0.180 mmol) in $CHCl_3$ (50 mL) was stirred for 24 h and worked up in the same manner described in the previous section for the chemical oxidation of **3**. The petroleum ether soluble fraction afforded 3,3‴,3⁗,3′′′′′′′-tetraoctyl-2,2′:5′,2″:5″,2‴:5‴,5⁗:2⁗, 2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,2′′′′′′′-octithiophene, **(4)₂**, (30 mg, 15%). ^{1}H NMR δ 0.8–1.0 (m, 12H, $-CH_3$), 1.2–1.5 (m, 40H), 1.6–1.8 (m, 8H, β-CH_2), 2.76 (t, 4H, J = 8Hz, α-CH_2), 2.79 (t, 4H, J = 8Hz, α-CH_2), 6.95 (d, 2H, J = 5 Hz, H-4), 7.01 (s, 2H, H-4‴), 7.03 (d, 2H, J = 4 Hz), 7.05 (d, 2H, J = 4 Hz), 7.14 (d, 4H, J = 4 Hz), 7.19 (d, 2H, J = 5Hz, H-5). IR (neat) 3118, 3072, 2967, 2934, 2861, 1743, 1670, 1624, 1564, 1512, 1473, 1381, 1242, 1210, 1058, 887, 841, 795, 729, 696, 663 cm^{-1}. UV ($CHCl_3$) λ_{max} 438 nm.

The chloroform soluble fraction was washed with 5% hydrazine and purified with flash chromatography (petroleum

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[30] Pham, C. V.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark, H. B.; Zimmer, H. *Phosporus, Sulfur, Silicon* **1989**, *46*, 157.

ether:chloroform) to afford 3,3‴,3⁗,3′′′′′′′,3′′′′′′′′,3′′′′′′′′′′′-hexaoctyl-2,2′:5′,2″:5″,2‴:5‴,5⁗:2⁗,2′′′′′:5′′′′′,2′′′′′′:5′′′′′′,5′′′′′′′:2′′′′′′′,2′′′′′′′′:5′′′′′′′′,2′′′′′′′′′:5′′′′ ′′′′′,2′′′′′′′′′′′-duodecithiophene, **(4)**$_3$, as a red film (3 mg, 1%). ^{1}H NMR δ 0.81−0.98 (m, 12H, $-CH_3$), 1.0−1.5 (m, 40H), 1.6−1.8 (m, 8H, β-CH_2), 2.7−2.9 (m, 8H, α-CH_2), 6.95 (d, 2H, J = 5 Hz, H-4), 7.0−7.2 (m, 16H), 7.21 (d, 2H, J = 5 Hz, H-5). IR (neat) 3072, 2968, 2877, 1733, 1586, 1480, 1432, 1390, 1319, 1291, 1242, 1165, 1074, 1032, 947, 891, 757, 716, 653, 568 cm^{-1}. UV ($CHCl_3$) λ_{max} 440 nm.

To prepare polymer and to simplify the purification of the oxidation products of **4**, the reaction was repeated at 50 °C; the crude product was treated with aqueous hydrazine and chromatographed directly. The only isolated products were **(4)**$_2$ (183 mg, 73% yield) and poly**4** (25 mg, 10% yield). ^{1}H NMR δ 0.86−0.89 (m, 6H, $-CH_3$), 1.20−1.50 (m, 20H), 1.60−1.80 (m, 4H, β-CH_2), 2.74−2.90 (m, 4H, α-CH_2), 7.01 (s, 2H, H-4), 7.05 (d, 2H, J = 3 Hz), 7.14 (d, 2H, J = 3 Hz). IR (neat) 3067, 2968, 2919, 2849, 1747, 1649, 1502, 1453, 1425, 1375, 1200, 1066, 828, 793, 765, 723, 681 cm^{-1}. UV ($CHCl_3$) λ_{max} 463 nm.

Results and Discussion

Synthesis. Synthetic routes to dioctyl-substituted oligothiophenes (dimer to pentamer) are shown in Scheme 3. 3-Bromothiophene was coupled with 1-octylmagnesium bromide in the presence of catalytic $NiCl_2$(dppp) according to the method of Kumada[29] to afford 3-octylthiophene (**1**) in 86% yield. Bromine (1 equiv) was slowly added to **1** at −15 °C to afford 2-bromo-3-octylthiophene, **6** (68%). 2-(3-Octylthienyl)magnesium bromide, **7**, was prepared by entrainment of **6** with 1 equiv of dibromoethane and 2 equiv of magnesium in ether with sonication. Although the Grignard reagent could be prepared directly (1 equiv of magnesium) in tetrahydrofuran, the subsequent nickel-catalyzed coupling reaction as carried out by Zimmer et al.[19b] proceeded to afford low yields of oligothiophenes. Preparation of the magnesium reagent in ether was necessary in order to facilitate effective coupling to the appropriate dibromothiophene. Attempts to prepare the Grignard reagent in ether (by addition of iodine or application of heat or sonication) failed to afford the organometallic reagent and necessitated the entrainment procedure. Treatment of 2-(3-octylthienyl)magnesium bromide with 2-bromo-3-octylthiophene and catalytic $NiCl_2$(dppp) gave the dimer **2** (35%). 2,5-Dibromothiophene was coupled with 2 equiv of the Grignard reagent to afford the dioctyltrimer **3** (75%). **7** (2 equiv) was similarly coupled with 5,5′-dibromo-2,2′-bithiophene and 5,5″-dibromo-2,2′:5′,2″-terthiophene to afford the dioctyltetramer **4** (75%) and the dioctyl pentamer **5** (11%), respectively. The yield of **5** was low because the coupling did not proceed to high conversion and the mixture of products was difficult to separate. Preparative HPLC was used to separate **5** from the monocoupled product and 3-octylquarterthiophene.

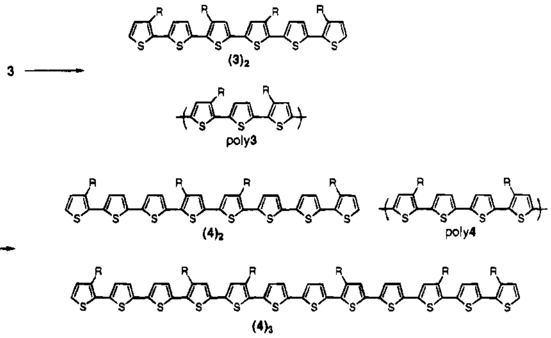
Chemical Oxidation of Dioctyloligothiophenes. Oligomers **2**−**4** were oxidized using 4 equiv of ferric chloride in chloroform solution at room temperature[31] to afford mixtures of the corresponding oligomers and polymer (Scheme 4). The dimer **2** was converted to the polymer in high conversion. However, trimer **3** afforded a mixture of **(3)**$_2$ (15%), poly**3** (10%), and unreacted starting material. Tetramer **4** resisted polymerization to afford unreacted starting material, the dimer **(4)**$_2$ (15%), and trimer **(4)**$_3$ (1%). Elevating the temperature to 50 °C for the oxidation of **3** and **4** afforded higher yields of oligomers and polymers: **(3)**$_2$ (15%), poly**3** (85%), **(4)**$_2$ (73%), and poly(**4**) (10%), respectively. Products from chemical oxidation were separated and purified by careful column chromatography. Structural assignments of oligomers derived from **3** and **4** were made primarily through ^{1}H NMR spectroscopy.

Table 1. UV/Vis Data for Alkyl-Substituted Oligothiophenes

compound	no. of rings	λ_{max},^{a}/nm	$\epsilon/10^4$ M L^{-1} cm^{-1}
1	1	232 (226)	1.08
2	2	247 (305)	4.60
3	3	338 (360)	4.59
4	4	377 (391)	6.65
5	5	367 (416)	7.00
(3)$_2$	6	404 (438)	5.76
(4)$_2$	8	438 (440)	25.1
(4)$_3$	12	440	
poly**1**		440 [484]^b	
poly**2**		390 [390]^b	
poly**3**		437 [517]^b	
poly**4**		463 [514]^b	

[a] Obtained in chloroform solution. Numbers in parentheses are the values reported for the unsubstituted oligothiophenes in chloroform.[14f,30] [b] Numbers in brackets are λ_{max} of thin films spin-coated from chloroform.

Scheme 4



The hydrogens in the α- and β-positions (i.e., 5- and 4-positions, respectively) of terminal 3-octylthiophene-2-yl units of all of the oligothiophenes studied give a distinctive pair of doublets (J = 5.4 Hz) at ca. δ 7.0 and ca. δ 7.2 ppm and peaks appropriate for the internal unsubstituted thiophene-2,5-diyl units. In addition, the dimers of **3** and **4** (i.e., **(3)**$_2$ and **(4)**$_2$), give rise to a singlet for the internal alkyl-substituted thiophene-2,5-diyl unit, and one or two pairs of doublets (J = 4 Hz) for the β-hydrogens of unsubstituted thiophene-2,5-diyl units, respectively. The absence of the pair of doublets corresponding to terminal 3-octylthiophene-2,5-diyl units in the spectra of poly**3** and poly**4** indicates the formation of high molecular weight materials.

Ultraviolet−Visible Spectral Characterization of Alkyloligothiophenes and Polymers. The electronic spectral data for the alkyl-substituted oligothiophenes and polymers are summarized in Table 1. The absorption maxima (λ_{max}) of unsubstituted oligothiophenes increases with the number of rings. Values of λ_{max} for the dialkyloligothiophene series **1**−**5**, the corresponding unsubstituted oligothiophenes, and selected other substituted oligothiophenes are plotted in Figure 1A. Although the inductive donation of alkyl substituents causes a small bathochromic shift in the electronic absorption of **1** relative to thiophene, the alkyl substitution of **2**−**5** causes a hypsochromic shift relative

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(31) Hotta, S.; Soga, M.; Sonoda, N. *Synth. Met.* **1986**, *26*, 267. Yoshino, K.; Nakajima, S.; Sugimoto, R. *Jpn. J. Appl. Phys.* **1987**, *26*, 1038.

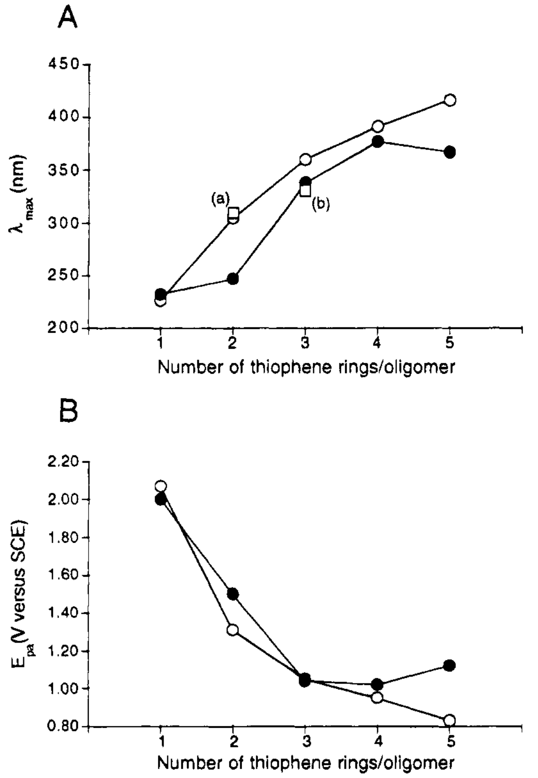

Figure 1. Electronic spectra and oxidation potentials of dioctyloligothiophenes **1**–**5** (●) and comparison unsubstituted (○)[14f] and other substituted oligothiophenes (□). (A) Plot of absorption maximum (λ_{max}) versus number of thiophene rings. (B) Plot of oxidation potential (E_{pa}) versus number of thiophene rings. Literature data: unsubsituted oligothiophenes;[14f,29] (a) 4,4′-dihexyl-2,2′-bithiophene;[16] (b) 3′,4′-dibutyl-2,2′:5′,2″-terthiophene;[21] 3′-octyl-2,2′:5′,2″-terthiophene.[20]

to the corresponding unsubstituted oligothiophenes (Figure 1).[32] The low absorption maximum (274 nm) of **2** relative to 2,2′-bithiophene is explained by severe twisting of the conjugated backbone owing to steric repulsion between the alkyl groups. The inductive donation of the alkyl groups of 4,4′-dioctyl-2,2′-bithiophene (λ_{max} = 310 nm)[16b] causes a bathochromic shift without giving rise to twisting steric interactions. As the number of thiophene rings separating the alkyl-substituted terminal rings of the series **1**–**5** increases the steric interaction between substituents decreases; the oligomers become electronically similiar to their unsubstituted derivatives and the λ_{max} values in the two series merge.

The solution absorption maximum of the tetraalkyloctithiophene, **(4)$_2$** (438 nm), is similiar to that of electrochemically synthesized poly(3-alkylthiophene)s (430–440 nm). The similarity of the absorption for **(4)$_2$** and PATs indicates that the regiorandom poly(3-alkylthiophene)s contain relatively short conjugated segments. Although the high degree of alkyl substitution of PATs (i.e., one substituent per ring) provides electron density to the thiophene backbone, head-to-head couplings cause a twisting steric effect.

The electronic spectra of spin-coated films of poly(dioctyloligothiophene)s show narrow absorption peaks in the range 390–514 nm, which are plotted in Figure 2A along with values for unsubstituted poly(oligothiophene)s and other selected substituted poly(oligothiophene)s.

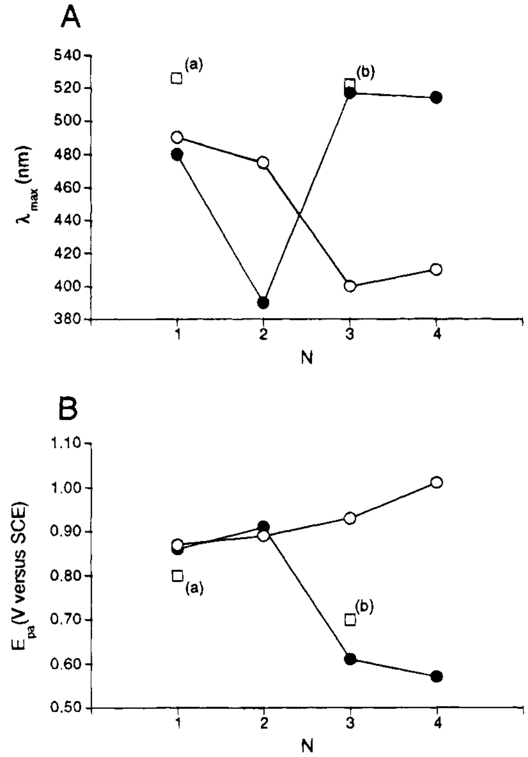

Figure 2. Electronic spectra maxima and oxidation potentials of polymers prepared dioctyloligothiophenes **1**–**4** and comparison to polymers derived from unsubstituted[14f] and other substituted oligothiophenes. (A) Plot of absorption maximum (λ_{max}) of chemically prepared polymers spin-coated on glass versus number of thiophene rings in starting oligomer, *N*. (B) Plot of oxidation potential (E_{pa}) of electrochemically prepared polymer versus number of thiophene rings in starting oligomer, *N*. Literature data: unsubstituted poly(oligothiophene)s;[14f,29] (a) regioregular poly(3-octylthiophene);[10] (b) poly(3′,4′-dibutyl-2,2′:5′,2″-terthiophene);[21] poly(3′-octyl-2,2′:5′,2″-terthiophene).[20]

The wavelength of the $\pi-\pi^*$ transition for poly**2**, in which the octylthiophene-2,5-diyl units are oriented head-to-head (390 nm), is much lower than that of regioregular head-to-tail polyoctylthiophene (520 nm).[10b] This low absorption maximum indicates a short conjugation length of the polymer owing to nonplanarity of the thiophene backbone. The values of λ_{max} for poly**3** and poly**4** (517 and 514 nm, respectively) indicate an increase in the conjugation length of the polymer backbone as a result of the unsubstituted thiophene units inserted in the repeat unit, which reduce steric interactions between octyl groups. The conjugation lengths in these polymers are similiar to those for 100% head-to-tail polyalkylthiophene.[10b] In particular, the spectrum of poly**3**, resembles the spectrum of head-to-tail poly(3-octylthiophene) with significant shoulders at 550 and 600 nm which indicate the presence of additional long-range ordered structures.

Infrared Spectroscopy. The principal infrared-active vibration bands observed in all of the oligomers studied are similiar. A single peak at approximately 3060 cm^{-1} is due to C_β–H stretching vibrations, while the C_α–H stretching mode is observed at approximately 3100 cm^{-1}. The ratio of the intensities of the C_α–H stretch to the C_β–H stretch decreases throughout the series **2**–**5** as the relative number of β-hydrogens increases relative to the number of α-hydrogens. The C_α–H stretching peak is absent from the spectrum for the polymers, indicating a relatively high molecular weight, and a high degree of α–α coupling (Figure 3). All of the poly(dioctyloligothiophene)s give infrared

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[32] Nakayama, J.; Konishi, T.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1988**, *27*, 1731.

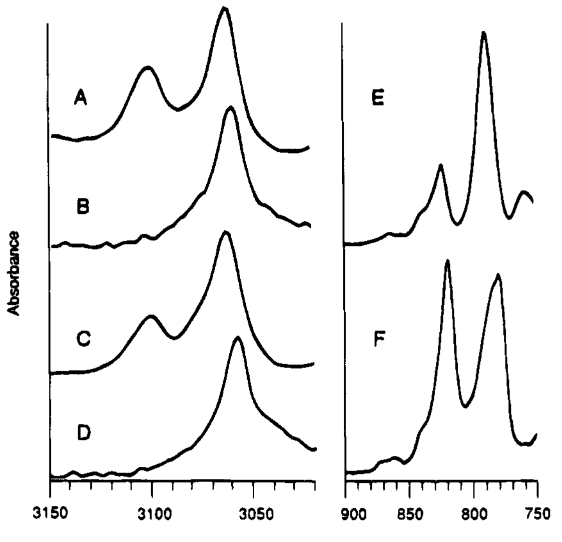

Figure 3. Infrared spectra of **3**, poly**3**, **4**, and poly**4**. C_α–H (ca. 3100 cm^{-1}) and C_β–H (ca. 3060 cm^{-1}) stretch: (A) **3**; (B) poly**3**; (C) **4**; (D) poly**4**. C–H out-of-plane vibrations for substituted (ca. 825 cm^{-1}) and unsubstitued (ca. 785 cm^{-1}) thiophene 2,5-diyl units in polymers: (E) poly**3**; (F) poly**4**.

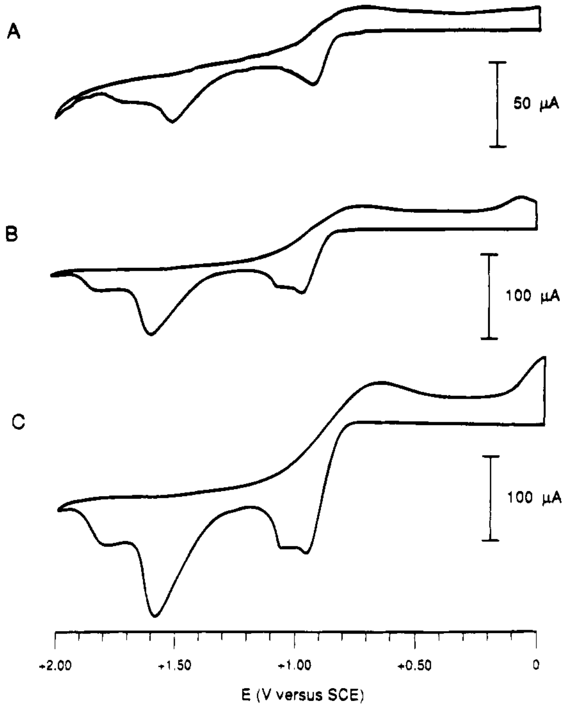

Figure 4. Cyclic voltammograms for **3** in acetonitrile (0.1 M $LiClO_4$) recorded at a scan rate of 100 mV s^{-1}: (A) 1 mM; (B) 5 mM; (C) 10 mM.

spectra characteristic of 2,5-coupled alkyl-substituted polythiophenes. Minor differences are observed in the band positions depending on the ratio of octyl groups to thiophene rings.

The absorption bands between 850 and 670 cm^{-1} are due to the ring C_β–H out-of-plane bending vibrations,[33] and the appearance of this region of the spectrum is sensitive to the thiophene ring substitution pattern. Strong sharp absorptions at 821–828 cm^{-1} are characteristic of trisubstituted thiophenes, and in the present case are indicative of alkyl-substituted thiophenes coupled through the 2- and 5-positions.[34] Bands at 781–793 cm^{-1} are assigned to unsubstituted thiophene-2,5-diyl out-of-plane C_β–H stretch. As the length of the oligomer increases from **1** to **4**, the relative intensity of the peak at ca. 785 cm^{-1} increases relative to that at 825 cm^{-1} in the corresponding polymer. Bands at 722–729 cm^{-1} (assigned to the methylene group C–H out-of-plane bending[35]) and 1375 cm^{-1} (methyl deformation) occur with similiar intensities in the spectra of all of the monomers, oligomers, and polymers.

The region of the spectra corresponding to the thiophene ring stretching mode indicates some differences between polymers obtained from dioctyloligothiophenes and 3-alkylthiophenes. The spectra of poly**2**–**4** show only two bands at 1452–1466 and 1501–1505 cm^{-1}, which are assigned to the C=C symmetric and antisymmetric stretching modes, respectively. For poly(3-alkylthiophene)s (PATs) three bands are observed in the same region.[13c,33] The presence of an inversion center in the repeat unit causes three bands to collapse to two. Similiar features have been reported for poly(3′,4′-dibutyl-2,2′:5,2″-terthiophene),[21] 4,4′-dialkyl-2,2′-bithiophene,[16] and poly(3,3′-dihexyl-2,2′-bithiophene),[18] which also contain inversion centers.

Determination of Oxidation Potentials. Due to the availability of unsubstituted α-positions, the radical cations resulting from the electrooxidation of **2**–**5** are free to chemically couple. This irreversible process renders the determination of the redox potentials difficult. However, the use of low substrate concentration and high scan rates allows the observation of successive oxidation processes associated with the formation of two cationic species, the radical cation and the dication of the substrate. The cyclic voltammograms of 1 mM solutions of **1**–**5** in acetonitrile (0.1 M $LiClO_4$) indicate oxidation waves with peaks (E_{pa}) at +2.00, +1.50, +1.04, +1.02, and +1.12 V, respectively (all potentials are referenced to SCE). The oxidation potential of unsubstituted oligothiophenes decreases with the number of rings (Figure 1B). An alkyl substituent on the thiophene decreases the oxidation potential through inductive electron donation which stabilizes the radical cation. The dioctylbithiophene **2** possesses a higher oxidation potential than 2,2′-bithiophene by virtue of steric interaction between substituents on adjacent rings, which decreases conjugation through p-orbital overlap. Whereas the oxidation potential continues to decrease upon extending the length of unsubstituted oligomers, we observe a leveling off and a slight increase as the dialkylated oligomer length increases. We cannot, at present, provide a satisfactory explanation as to the cause of this trend.

Electrooxidation of Dioctylterthiophene (3). Single-scan voltammograms of **3** at concentrations of 1, 5, and 10 mM in acetonitrile are shown in Figure 4A–C. Cyclic voltammograms of dilute solutions (i.e., 1 mM, Figure 4A) exhibit an anodic peak (E_{pa1}) at +0.97 V followed by a broad wave at +1.60 V (E_{pa2}). Although neither of these waves is reversible, E_{pa1} is assigned to the oxidation of **3** to the radical cation $\mathbf{3}^{\bullet+}$. The second oxidation wave (E_{pa2}) is ascribed to the formation of the terthienyl dication based on comparison to data reported

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(33) Horak, M.; Hyams, I. J.; Lippincott, E. R. *Spectrosc. Acta* **1966**, *22*, 1355.

(34) Hotta, S.; Rughooputh, S. D. D. V.; Heeger, A. J.; Wudl, F. *Macromolecules* **1987**, *20*, 212.

(35) Winokur, M. J.; Spiegel, D.; Kim, Y.; Hotta, S.; Heeger, A. J. *Synth. Met.* **1989**, *28*, C419.

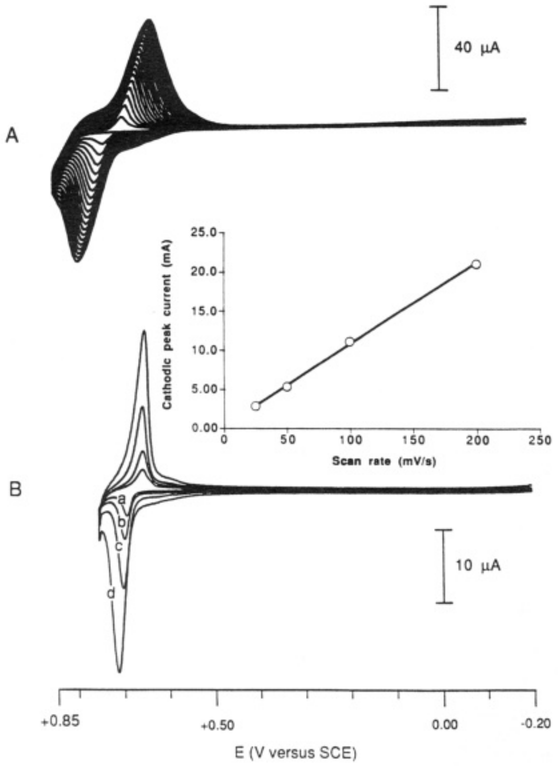

Figure 5. Electrodeposition of **(3)$_2$** by cyclic volyammetry (acetonitrile/0.1 M $LiClO_4$): (A) −0.20 to +0.85 V of 1 mM **3**, 100 mV s^{-1}. (B) Cyclic voltammogram of film prepared in part A in monomer-free acetonitrile (0.1 M $LiClO_4$) at various potential sweep rates: (a) 25, (b) 50, (c) 100, (d) 200 mV s^{-1}. Inset: plot of cathodic peak current (i_{pc}) versus potential sweep rate (ν).

for end-substituted oligothiophenes which are incapable of coupling owing to the lack of free α-positions.[36] The values of E_{pa1} and E_{pa2} for **3** are similiar to those reported for unsubstituted terthiophene and 3′-substituted terthiophenes,[20] with a small anodic shift in E_{pa1} attributed to the $+I$ effect of the alkyl substituents.

A single-sweep cyclic voltammogram of a 5 mM solution of **3** is shown in Figure 4B. Increasing the concentration of **3** improves the sharpness of the waves at E_{pa1} and E_{pa2} and a new wave emerges at +1.05 V (E_{pa3}). The height of the peak at E_{pa3} increases further upon increasing the concentration of **3** to 10 mM (Figure 4C). The dependence of the intensity of E_{pa3} on concentration indicates an aggregation process. Recent electrochemical studies of terthiophene and median ring-substituted terthiophenes suggest that E_{pa3} corresponds to the oxidation of the π-dimer radical cation $\mathbf{3}{\cdot}\mathbf{3}^{\bullet+}$ to afford 2 equiv of radical cation $\mathbf{3}^{\bullet+}$. Roncali reports the monosubstituted 3′-octylterthiophene has an E_{pa3} of +1.32 V. The shift to lower oxidation potential for **3** is consistent with the inductive donation by the second alkyl substituent, although different intermolecular steric interactions might also induce changes in the structure of the π-dimer radical cation. A wave at approximately +1.90 V is ascribed to the degradation of products by overoxidation.[20]

Electrochemical Synthesis of Tetraoctylhexathiophene, (3)$_2$. A multisweep cyclic voltammogram recorded for 1 mM **3** in acetonitrile is shown in Figure 5A. The cyclic voltammogram shows an anodic onset in the potential region corresponding to the formation of the radical cation (E_{onset} = +0.77 V). Repetitive cycling up to a positive switching potential of +0.85 V results in the deposition of a material with a lower oxidation potential (+0.72 V), and a cathodic peak corresponding to reduction (+0.69 V, Figure 5A). The difference in potentials between the anodic and cathodic peaks (ΔE) increases upon continued cycling as the film becomes thicker and ion diffusion becomes rate limiting. When a thin film of the material (deposited in three cycles under the same conditions as in Figure 5A) is rinsed with acetonitrile and placed in monomer-free electrolyte, the cyclic voltammogram shows the presence of a surface-confined reversible redox couple (Figure 5B). The peak current (i_{pc}) is proportional to the potential scan rate (ν, Figure 5 inset). The difference between the peak potentials (ΔE) is small and the width of the peak at half-height (ΔE) is only 30 mV. The sharpness of this peak and the small difference in peak potentials strongly suggest the oxidation of a single species with a defined conjugation length. Generally the reduction peaks in substituted poly(thiophene)s are much broader than the oxidation peaks. This is not the case for the material deposited by cycling the potential to +0.85 V; the anodic and cathodic waves are both narrow and of comparable width. Thus the insulator to metal transition is abrupt in both the oxidation and reduction part of the cycle. It has previously been suggested that the oxidative doping of PDABT is retarded due to the structural rearrangement of the backbone to adopt the planar form, at which point oxidation is accelerated.[16] In the present case a related phenomenon also occurs upon reduction, as shown by the sharp cathodic wave. The material deposited under these conditions is soluble in petroleum ether. Comparison to materials isolated from chemical oxidation of **3** by thin-layer chromatography (TLC) indicates that the electrochemically deposited material is not poly**3** but the dimer **(3)$_2$**. Potentiostatic electrolysis of 5 mM **3** at +0.85 mV affords a chloroform-soluble film which ^{1}H NMR shows to contain only trapped **3** and the dimer **(3)$_2$**. The dimer **(3)$_2$** is also formed by electrooxidation of **3** from more concentrated solutions, but the clean deposition of **(3)$_2$** is observed only if *dilute* solutions of **3** are cycled *just positive* of the onset for oxidation.

Electropolymerization of Dioctylterthiophene (3). When a concentrated (22.5 mM) solution of **3** is cycled to a positive switching potential of +0.85 V, new reversible redox-active species are deposited (Figure 6). The reversible wave corresponding to redox switching of **(3)$_2$** is still observed (+0.76 V). After several scans the voltammogram shows the emergence of two new reversible oxidation waves at lower potentials. The potential of the first reversible wave, +0.62 V (anodic) and +0.51 V (cathodic), corresponds to the values obtained from the cyclic voltammetry of chemically prepared poly**3**. The cyclic voltammogram of authentic chemically prepared poly**3**, cast by evaporation of a dilute chloroform solution on the electrode is shown in Figure 6C. Continued potential cycling of a concentrated solution of **3** leads to increased film thickness and a positive shift in the anodic peak potentials. TLC analysis of the resulting film shows three spots whose R_f values correspond to authentic samples of **3**, **(3)$_2$**, and poly**3**. A reversible redox wave at intermediate potentials (E_{pa} = 0.70 V) might indicate the presence of **(3)$_3$**,

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[36] Guay, J.; Kassai, P.; Diaz, A.; Wu, R.; Tour, J. M. *Chem. Mater.* **1992**, *4*, 1097.

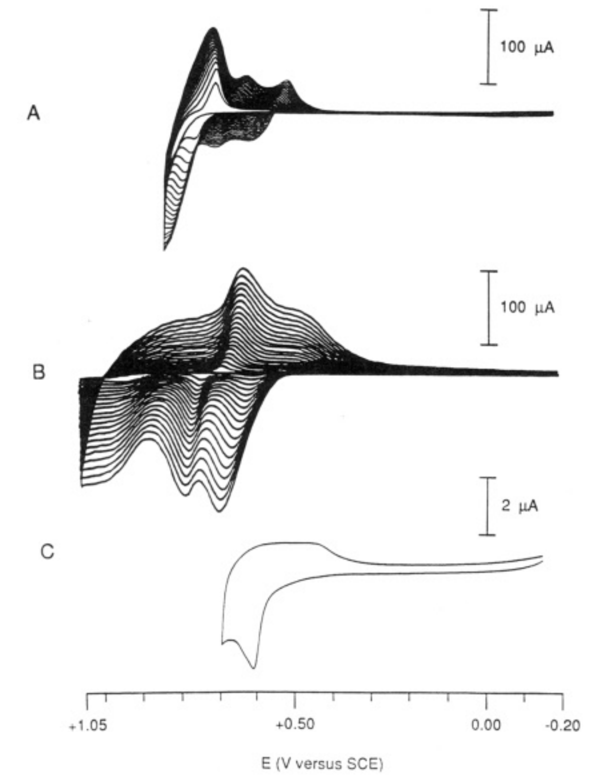

Figure 6. Electrochemical polymerization of **3**. (A) Cyclic voltammogram (−0.20 to +0.85 V) of concentrated (22.5 mM) solution of **3** in acetonitrile (0.1 M $LiClO_4$), 100 mV s^{-1}. (B) Cyclic voltammogram of a film of chemically prepared poly**3** recorded in monomer-free acetonitrile (0.1 M $LiClO_4$) solution at a scan rate of 50 mV s^{-1}; the polymer film was cast on the electrode by evaporation of a chloroform solution. (C) Cyclic voltammogram of **3** (2.25 mM) in acetonitrile (0.1 M $LiClO_4$) to high potential (−0.20 to +1.05 V), 300 mV s^{-1}.

although chemical synthesis did not afford this oligomer, and this wave is absent in the cyclic voltammograms of materials deposited under different electrochemical conditions.

A cyclic voltammogram obtained by successive potential cycling of 1 mM **3** in acetonitrile to a higher positive switching potential (+1.05 V) is shown in Figure 6B. Increasing the positive switching potential increases the rate of deposition and dramatically changes the appearance of the voltammogram compared to that observed when the positive switching potential is limited to lower values. In addition to the irreversible oxidation of **3**, and the reversible oxidation of $\mathbf{3_2}$, an anodic peak ascribed to the oxidation of poly**3** emerges along with a broad cathodic shoulder corresponding to its reduction. The shape and redox potentials of this new feature are similar to those of the chemically synthesized polymer (Figure 6C). No peak corresponding to intermediate oligomers (i.e., $\mathbf{(3)_3}$) is observed.

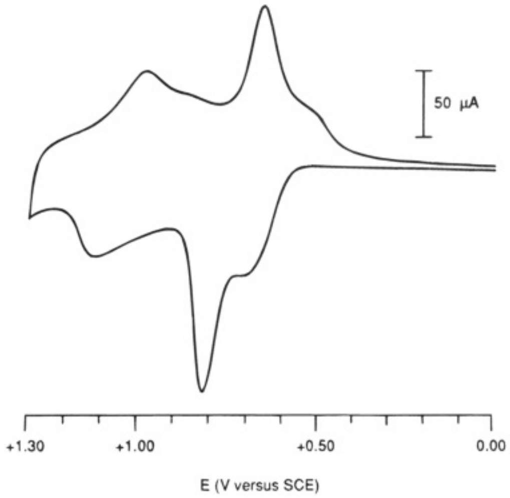

Figure 7. Cyclic voltammogram of electrochemically deposited poly**3** containing trapped **3** and $\mathbf{(3)_2}$ measured by a single potential scan between (0.00 to +1.30 V) in monomer-free acetonitrile (0.1 M $LiClO_4$), 180 mV s^{-1}.

Transfer of $\mathbf{(3)_2}$/poly**3** films to monomer-free electrolyte solution affords the cyclic voltammogram shown in Figure 7. Waves corresponding to reversible redox switching of the polymer and dimer are still present. The well-defined reversible wave with E_{pa} at +1.12 V is assigned to monomer oxidation. Previous work has shown that electropolymerization of terthiophene and substituted oligothiophenes results in the trapping of significant amounts of monomer in the deposited film.[14,20,37] The apparent reversible oxidation of the trapped dioctylterthienyl is striking in contrast with the irreversible waves observed in homogeneous solutions at a bare platinum electrode (Figure 4). This contradiction can be explained by immobilization of **3** in a matrix of poly**3**, which limits the rate of coupling of $\mathbf{3}^{\bullet+}$. However, repetitive cycling to +1.30 V results in the disappearance of this wave along with an increase in the size of the $\mathbf{(3)_2}$ and poly**3** waves, which is consistent with homocoupling of the trapped monomer or coupling of $\mathbf{3}^{\bullet+}$ to higher oligomers.

When a freshly deposited $\mathbf{(3)_2}$/poly**3** film is transferred to monomer-free solution, the waves corresponding to monomer, $\mathbf{(3)_2}$, and poly**3** are apparent (Figure 8A). After the electrode is washed in a vigorous stream of acetonitrile, a new cyclic voltammogram shows a decrease in the height of the peak ascribed to $\mathbf{(3)_2}$ oxidation (Figure 8B). The dimer is more soluble than the polymer. The slight increase in polymer oxidation current may be explained by further coupling of the trapped **3** into the polymer. After several minutes of vigorous washing in acetonitrile the cyclic voltammogram shows one reversible oxidation wave which corresponds to poly**3** (Figure 8C). There is no evidence for **3** or $\mathbf{(3)_2}$ trapped in the film. The polymer film is robust enough to be vigorously washed in acetonitrile, but it is freely soluble in chloroform.

Potentiostatic electrolysis of a saturated solution of **3** (approximately 50 mM) at +1.05 V affords a thick red film on the electrode which dissolves in chloroform. TLC and NMR analysis indicate that **3**, $\mathbf{(3)_2}$, and poly**3** are present in approximately equal concentrations.

Electrochemical Oxidation of Dioctylquaterthiophene (4). A cyclic voltammogram recorded for 1 mM **4** in acetonitrile (0.1 M $LiClO_4$) shows an onset of oxidation at +0.73 V corresponding to the formation of the radical cation (Figure 9A). Repetitive cycling to a positive switching potential of +0.775 V produces a sharp reversible wave at +0.68 V. Since the anodic potential is limited to the first oxidation potential of **4**, this supports the proposal that electrodeposition occurs via the radical cation state. The deposited material is soluble in petroleum ether. The sharpness of the cyclic voltammetric waves ($\Delta E_{fwhm} = 30$ mV), and the small difference in peak potentials ($\Delta E_p = 30$ mV) strongly suggests the oxidation of a single species with a defined

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(37) Zotti, G.; Schiavon, G. *Synth. Met.* **1987**, *18*, 139.

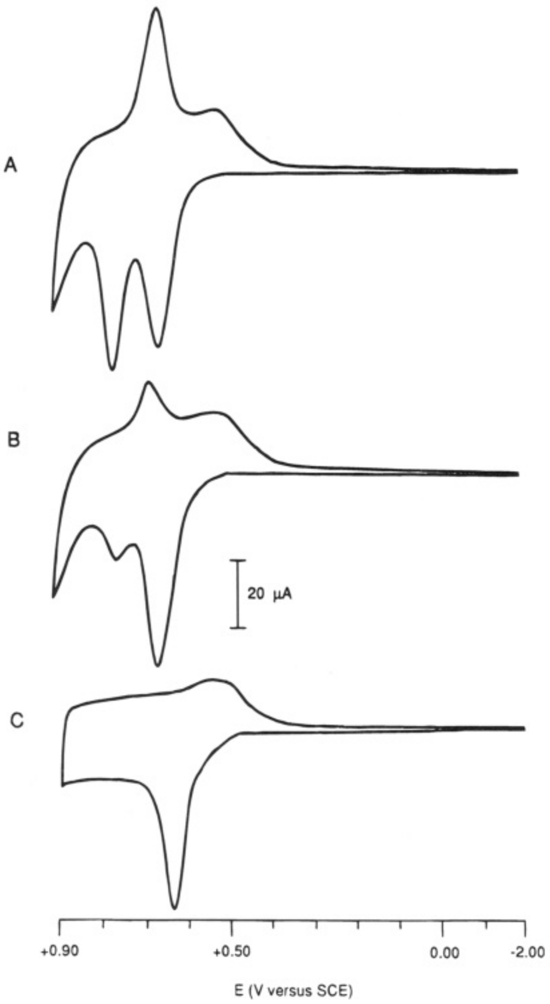

Figure 8. Cyclic voltammograms of electrochemically deposited poly**3** measured in monomer-free acetonitrile (0.1 M $LiClO_4$), 50 mV s^{-1} after (A) no rinsing, (B) mild rinsing, and (C) vigorous rinsing with acetonitrile.

conjugation length. Comparison to authentic materials by thin layer chromatography (TLC) indicates that the deposited material is the dimer **(4)**$_2$ rather than poly**4**. Cyclic voltammograms of a thin film of electrochemically deposited **(4)**$_2$ using scan rates (ν) between 25 and 200 mV s^{-1} indicate that the anodic peak current (i_{pa}) scales linearly with the potential scan rate (ν) as expected for an electroactive surface-confined species (not shown).

Cyclic voltammetry at higher concentrations of **4** (i.e., 5 mM, Figure 9B) shows a 10-fold increase in the rate of deposition on the electrode. The peaks corresponding to **(4)**$_2$ oxidation and reduction occur initially at +0.68 and +0.65 V, respectively, with the peak separation increasing as the film thickness increases. A cyclic voltammogram of chemically synthesized **(4)**$_2$ deposited on the electrode from chloroform solution shows the same redox potentials and peak shape as the electrochemically deposited material from the electrooxidation of **4** (Figure 9C).

The cyclic voltammogram of a film of **(4)**$_2$ deposited by cycling to 0.78 V (i.e., Figure 9B) and transferred into monomer-free electrolyte is shown in Figure 10A. The film still contains unreacted monomer which undergoes partially reversible oxidation at $E_{pa} = +0.75$ V. All of the trapped monomer is consumed upon one excursion to +1.0 V to afford a new redox-active species ($E_{pa} = +0.55$ V), with a concomitant decrease in the area of the peak corresponding to redox switching of **(4)**$_2$. This new peak corresponds to the redox potential of chemically prepared poly**4**. This assignment was made by comparison to the cyclic voltammetry of chemically prepared poly**4** which is shown in Figure 10. Accordingly, **(4)**$_2$ is formed excusively at low potentials. Only upon excursion to high positive potentials is the polymer formed.

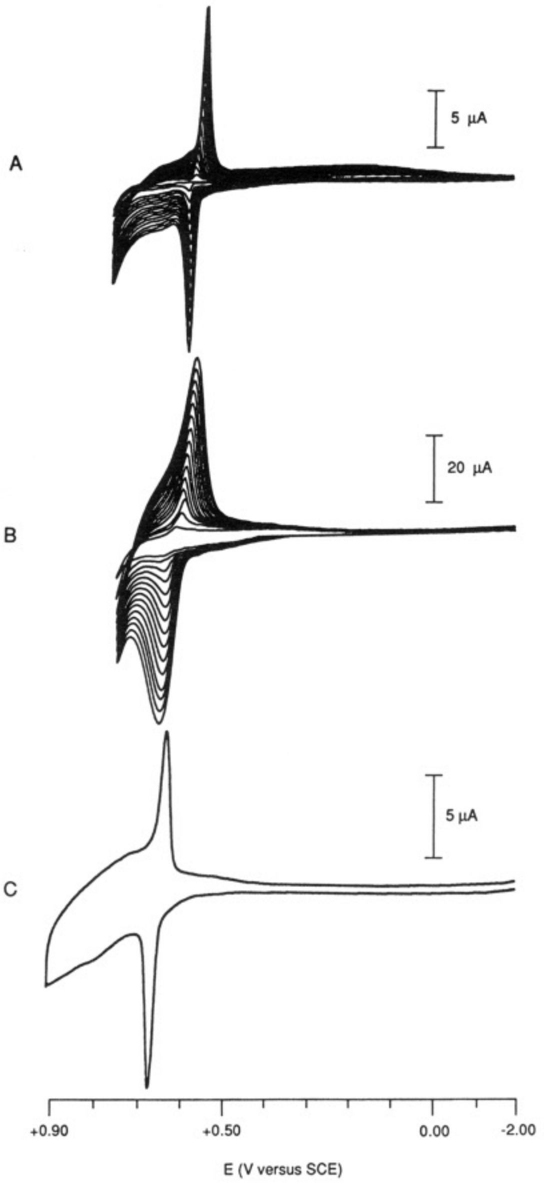

Figure 9. (A) Electrodeposition of **(4)**$_2$ by cyclic voltammetry (0.00 to +0.78 V) in acetonitrile (0.1 M $LiClO_4$), at 20 mV s^{-1}. (B) A subsequent scan, 0.00 and +0.80 V, at 20 mV s^{-1}. (C) Cyclic voltamogram of chemically prepared **(4)**$_2$ deposited on the electrode by evaporation of a chloroform solution, 50 mV s^{-1}.

Polymer Oxidation Potentials. The oxidation potentials (E_{pa}) of electrochemically deposited films of poly**1**−**4** agree with those of chemically prepared polymers and are plotted in Figure 2B along with values for unsubstituted poly(oligothiophenes). Although the polymerization of thiophene requires application of high potentials relative to that required for polymerization of unsubstituted oligothiophenes[1] (Figure 1B), the resulting polymer possesses a lower oxidation potential than poly(oligothiophene)s. It has been suggested that the longer unsubstituted oligothiophenes are more susceptible to coupling through β-positions, which leads to higher polymer redox potentials and higher energy

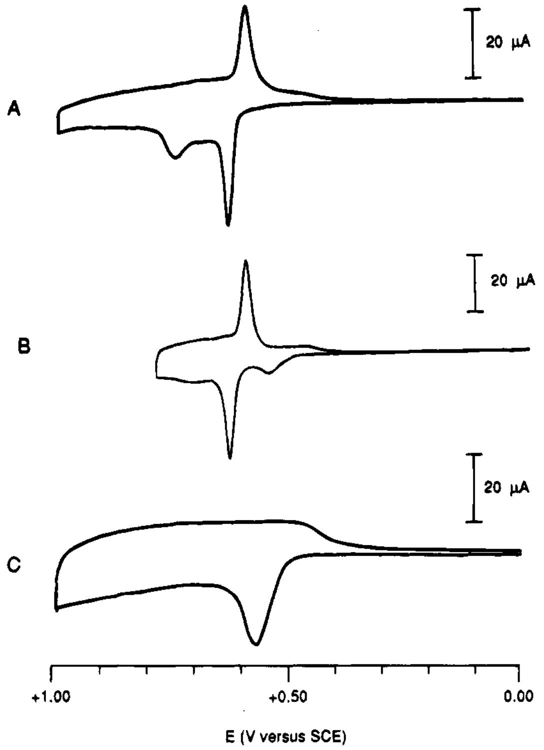

Figure 10. Cyclic voltammograms for $(4)_2$ and poly4. (A) Film of $(4)_2$ recorded in monomer-free electrolyte solution to a positive switching potential of 1.0 V. (B) After treatment shown in Figure 10A. (C) Poly4 measured in monomer-free acetonitrile (0.1 M $LiClO_4$), 100 mV s^{-1} (the polymer film was cast from a chloroform solution of chemically prepared poly4).

Table 2. Electrochemical Data for Alkyl Substituted Oligothiophenes[a]

compound	E_{pa}/ V(vs SCE)	E_{ca}/ V(vs SCE)	ΔE_p/ mV	$\Delta E_{a,fwhm}$/ mV
(3)$_2$	0.72	0.69	30	30
(3)$_3$	0.70	0.67	30	
(4)$_2$	0.68	0.65	30	29
poly**3**	0.67	0.50	170	64
poly**4**	0.57	0.52	100	73

[a] Recorded for thin films on the electrode surface in 0.1 M $LiClO_4$/MeCN, 100 mV s^{-1}.

electronic transitions (Figure 2A). In addition, the unsubstituted poymers are all insoluble, which makes detailed characterization difficult. The oxidation potential of poly**2** is only slightly higher than that for regiorandom PATs or poly(bithiophene). This is consistant with a sterically induced decrease in the backbone planarity and is in accord with the short-wavelength electronic absorptions. Poly**3** and poly**4** possess particularly low oxidation potentials compared to unsubstituted poly(oligothiophene)s and PATs (Table 2). This is surprising given the decreased electronic contribution by alkyl groups on the backbones of these less-substituted polymers (i.e., the density of alkyl substituents on poly**3** and poly**4** is lower than that of PATs), but it is in accord with a planar, highly conjugated polythiophene backbone. Thus, polymers with high electronic absorptions and low oxidation potentials, similar to those for regioregular head-to-tail PATs, can be produced by choosing a monomer in which head-to-head linakages are avoided (e.g., **3** and **4**).

X-ray Scattering. Preliminary studies by X-ray scattering show that neutral poly**3** and poly**4** are polycrystalline. Three low-angle reflections observed are consistent with repeat distances of 16.67 and 22.36 Å for poly**3** and poly**4**, respectively. The narrow widths of these X-ray features indicate highly ordered domains of polymer.

Polymer Conductivities. Electrical conductivity measurements were made on thin films of polymer using a four-probe at room temperature. Polymer films were spin-coated from chloroform solution and doped with iodine vapor for 24 h. Poly**3** and poly**4** have conductivities of 45 and 33 S cm^{-1}, respectively. The electronic spectra and redox behavior of these polymers clearly indicate that these polymers have long conjugation lengths. In addition, the electronic spectrum of poly**3** shows well-defined shoulders at higher wavelengths which are consistent with the presence of domains of higher conjugation that are not present in poly**4**, which may explain the difference in conductivity. Both polymers are more conductive than regiorandom poly(3-octylthiophene) (~1 S cm^{-1})[10] and PDABT (2–4 S cm^{-1})[16] prepared by the same method, but not as conductive as head-to-tail poly(3-octylthiophene), 200 S cm^{-1}.[10]

Conclusions. Oxidation of a series of symmetrically substituted dialkyloligothiophenes affords soluble oligomers and polymers with defined regiochemistry. The side chains impart solubility to the growing polymer chains, thereby allowing for chain extension without early precipitation of low molecular weight oligomers in chemical oxidations. The appearance of various voltammetric peaks upon oxidation of thiophenes has previously been assigned to oligomers (dimers and trimers), often without strong supporting evidence which is difficult to obtain owing to the insolubility of the deposited material. Cyclic voltammetry of materials deposited by electrochemical oxidation of **3** and **4** clearly indicate the formation of intermediates (longer oligomers) in the polymerization pathway. Owing to their solubility, these can be identified spectroscopically by comparison to materials prepared by chemical oxidation. Under mild electrochemical conditions (low concentration, low potential) in a poor solvent (acetonitrile), the oligomers are deposited exclusively.

Oxidation of symmetrical dialkyloligothiophenes affords thiophene:3-alkylthiophene copolymers of defined sequence and regiochemistry which lack head-to-head alkylthiophene linkages. Poly(dialkyloligothiophene)s derived from the symmetrical oligomers **3** and **4** are highly conjugated, with low-energy $\pi-\pi^*$ electronic transitions and particularly low reversible redox potentials. The steric interactions between substitutents which cause a twisting of the poly(3-alkylthiophene) backbone are relieved by incorporating unsubstituted thiophene-2,5-diyl units. Accordingly, the copolymer can adopt a highly conjugated planar conformation. The properties of polythiophenes are thereby tailored by variation of both the placement and density of alkyl substituents along the backbone.

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