Synthesis, polymerization and characterization of substituted dithieno[3,4-b:3',4'-d]thiophenes

Seiji Inaoka and David M. Collard*

School Of Chemistry and Biochemistry and the Polymer Education and Research Center, Georgia Institute of Technology, Atlanta, GA 30332–0400, USA

Chemical or electrochemical oxidation of substituted dithieno[3,4-b:3',4'-d]thiophenes provides polymers with defined regiochemical structures. These materials have lower bandgaps (0.7–0.9 eV) than the unsubstituted fused heteroarene. Potential cycling of the 1,3-dimethyl substituted polymer film shows repetitive p- and n-dopability. The chemically-prepared dioctyl analog is soluble in common solvents such as chloroform, dichloromethane and THF. However, overoxidation of the polymers at an electrode surface presents a limitation to the polymerization of substituted analogs of the parent fused heteroarene.

Introduction

Low-bandgap, n-doped conjugated polymers are of interest for their potential use in a variety of electrooptical devices such as electrochemical capacitors,[1] batteries, electrochromic devices, and polymer light-emitting diodes.[2] A common method employed to prepare polymers with low bandgaps is to incorporate fused arenes as repeat units in polymers with conjugated backbones. These fused arenes impart quinoid character to the polymer, and lower the bandgap relative to a simple polyheterocycle.[3–6] For example, polyisothianaphthalene, PITN (derived from benzo[c]thiophene,[5,7–9] has a lower bandgap (*ca.* 1 eV)[10] than polythiophene (*ca.* 2 eV). Whereas polythiophene and its alkylated derivatives are stable upon oxidation (*i.e.*, p-doping) but unstable to reduction (n-doping),[11] PITN undergoes reversible p- and n-doping. The effect of increasing the extent of electron delocalization by fusion of more conjugated rings (*e.g.*, naphtho[2,3-c]thiophene[12]) or sulfur-containing rings has been shown by calculation[13] and by polymerization of other arene-fused thiophenes, including: thieno[3,2-b]thiophene,[14] dithieno[3,2-b:2',3'-d]thiophene,[15] dithieno[1,2-c:3,4-c']benzene,[16] dithieno[2,1-b:3,4-b']benzene,[16] dithieno[3,4-b:3',4'-d]thiophene SEQ compounds **1**,[17] dithieno[3,4-b:3',2'-d]thiophene[18] and dithieno[3,4-b:2',3'-d]thiophene.[18]
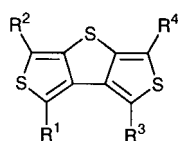
1, R¹=R²=R³=R⁴=H
2, R¹=CH₃, R²=R³=R⁴=H
3, R¹=R²=CH₃, R³=R⁴=H
4, R¹=R²=*n*-C₈H₁₇, R³=R⁴=H

Despite good electronic and optical properties, polymers derived from these monomers are insoluble and are therefore difficult to process. In addition, these monomers possess a number of nonequivalent sites through which polymerization could take place. For example, monomer **1** possesses two pairs of equivalent α-thienyl positions available for polymerization.[19] Accordingly, four different repeat units could be incorporated into the polymer chain (*i.e.*, 1,3-diyl, 1,5-diyl, 1,7-diyl and 3,5-diyl), Fig. 1. In addition, there is the added feature of orientation of each repeat unit in a sequence (that is, the possibility of 1,3-, 1,1- and 3,3- couplings in a polymer consisting of thienyl units linked exclusively through the 1- and 3- positions, *i.e.*, head-to-tail, head-to-head and tail-to-tail couplings). X-Ray analysis[20] and theoretical calculations[21] suggest that the polymer prepared by oxidation of **1** consists primarily of 1,3-diyl units. The backbone with 1,3-diyl repeat units is best suited to retain planarity. A polymer consisting of 1,7-diyl linkages would require twisting of repeat units out of planarity, thereby resulting in a decrease in the conjugation length of the polymer. However, the monomer might undergo further reactions at the remaining α-positions to form trivalent or tetravalent crosslinking units. Although the infrared spectrum of poly**1** indicates the presence of thiophene α-C–H bonds,[22] the structure of this polymer is relatively poorly defined.

The conjugation of dithieno[3,4-b:3',4'-d]thiophene, **1**, decreases the oxidation potential (*ca.* +1.0 V *versus* SCE) relative to thiophene (+2.1 V). The resulting polymer has a low bandgap (1.1 eV)[22] and it is stable to repeated p- and n-doping.[23] p-Doped (*i.e.*, oxidized) poly**1** is transparent and the neutral polymer is opaque. This combination of properties led us to investigate the synthesis of poly(dithieno[3,4-b:3',4'-d]thiophene)s with defined microstructures by substitution of the parent fused heterocycle at selected sites with methyl groups (*i.e.*, monomers **2** and **3**). We have also prepared a soluble derivative by substitution of the parent heterocycle with flexible octyl substituents (*i.e.*, monomer **4**).

Results and discussion

Synthesis

Dithieno[3,4-b:3',4'-d]thiophene **1** and substituted analogs were prepared by copper-mediated ring closure of dibromodithienyl sulfide **7** according to the method of Jong and Janssen.[24] 3,4-Dibromothiophene **6** was prepared by bromination of thiophene with Br₂ in CHCl₃ at reflux[25] followed by treatment of the isolated tetrabromothiophene with zinc dust in acetic acid to selectively dehalogenate the α-thienyl positions.[25] Lithiation of **6** with *n*-butyllithium at −78 °C gave 3-bromo-4-lithiothiophene, which is stable at low temperature, but which undergoes a 'halogen dance' at higher temperatures.[26] Treatment of 3-bromo-4-lithiothiophene with bis(phenylsulfonyl) sulfide gave 4,4'-dibromo-3,3'-dithienyl sulfide, **7**. Dilithiation of **7** with *n*-butyllithium and ring closure catalyzed by copper(II) chloride gave dithieno[3,4-b:3',4'-d]thiophene **1**, Scheme 1.

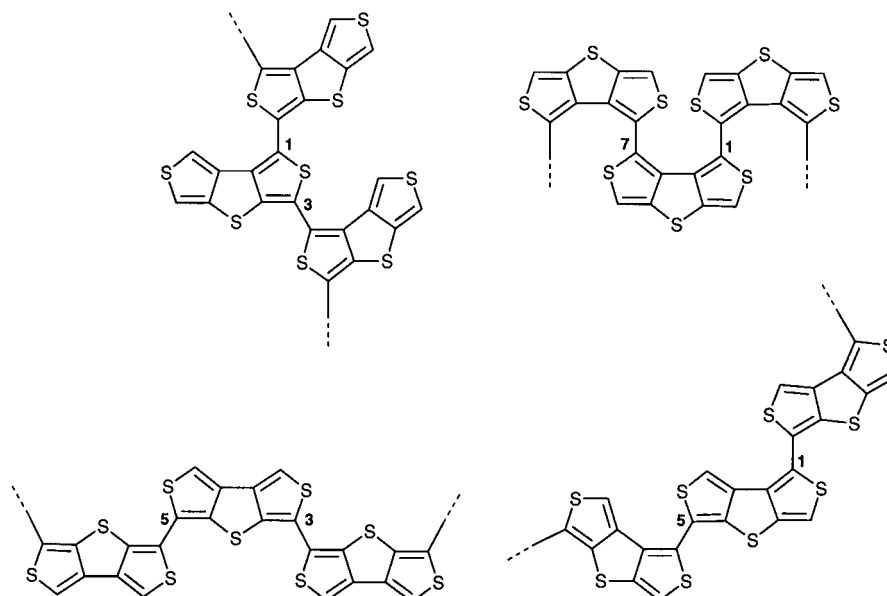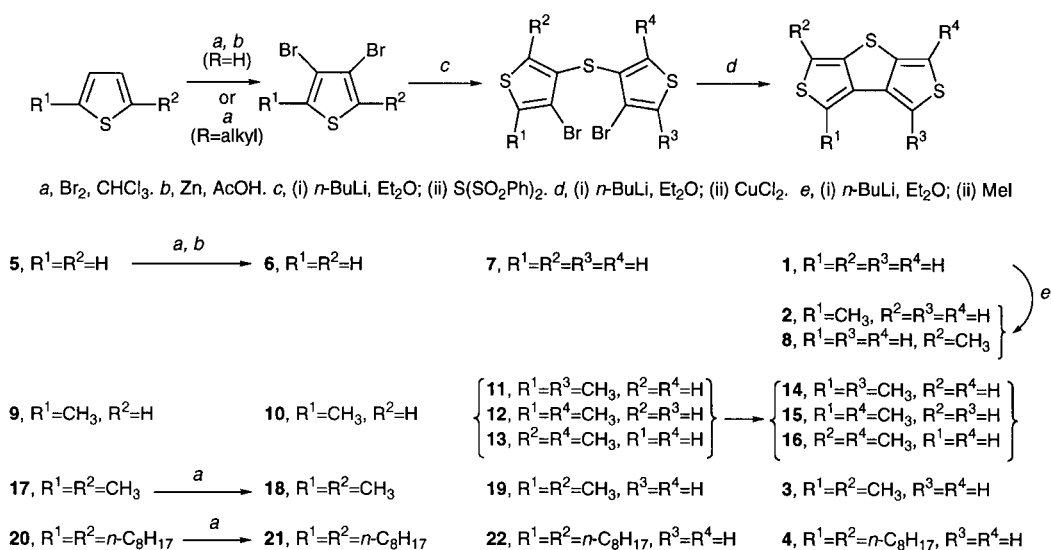Treatment of **1** with bromine resulted in a black insoluble solid. Bromination (Br₂, CHCl₃) of **1** with NBS in DMF[27]

Fig. 1 Regioregular (head-to-tail) triads of 1,3-, 1,7-, 3,5- and 1,5 poly(thieno[3,4-b:3′,4′-d]thiophenediyl), poly**1**.

gave two isomers of bromodithieno[3,4-b:3′,4′-d]thiophene. The major isomer (mp 88–93 °C (dec.), ^{1}H NMR (CDCl$_3$) δ 7.08 (d, 1H, J = 2.6 Hz), 7.38 (s, 1H), 7.47 (d, 1H, J = 2.6 Hz)) could be isolated from the mixture by recrystallization from hexane. Attempts to alkylate this isomer (with undetermined regiochemistry) with alkylmagnesium bromides in the presence of NiCl$_2$(dppp)[28] failed to produce the corresponding alkyldithieno[3,4-b:3′,4′-d]thiophenes. This is in accord with the observation that although a wide variety of bromoarenes are subject to alkylation under these conditions, 2-bromothiophene is relatively unreactive to Kumada coupling to alkyl Grignard reagents.[29] However, a methyl substituted dithieno[3,4-b:3′,4′-d]thiophene, **2**, was available by lithiation of **1** at −78 °C followed by reaction with methyl iodide.[30] This procedure gave a crude mixture of both isomers of methyldithieno[3,4-b:3′,4′-d]thiophene, **2** and **8**, Scheme 1. Recrystallization from hexanes gave pure 1-methyl isomer, **2**. This major component gives a ^{1}H NMR spectrum with peaks at δ 7.03, 7.24 and 7.43 ppm. ^{1}H NMR of the crude mixture has additional peaks at δ 6.76, 7.02 and 7.39 ppm corresponding to the other regioisomer, **8**. The structure of **2** was confirmed by X-ray crystallography.

A mixture of 1,5-, 3,5- and 1,7-dimethyl-substituted

dithieno[3,4-b:3′,4′-d]thiophenes (**14**, **15**, **16**) was synthesized starting from 2-methylthiophene, **9**. Bromination of **9** followed by selective debromination with zinc dust in acetic acid gave 3,4-dibromo-2-methylthiophene **10**. Lithiation of **10** followed by treatment with bis(phenylsulfonyl) sulfide gave a mixture of three isomers (2,2′-, 2,5′-, 5,5′-) of 4,4′-dibromodimethyl-3,3′-dithienyl sulfide (**11**, **12**, **13**), which were inseparable. Dilithiation of the mixture, followed by copper-mediated ring closure, gave a mixture of 1,5-, 3,5-, and 1,7-dimethyldithieno[3,4-b:3′,4′-d]thiophene. This mixture was also inseparable and this route was abandoned.

1,3-Dialkyl-substituted dithieno[3,4-b:3′,4′-d]thiophenes **3** and **4** were available by ring closure of 2,5-dialkyl-4,4′-dibromo-3,3′-dithienyl sulfides **19** and **22**. 2,5-Dimethylthiophene, **17**, is commercially available, while 2,5-dioctylthiophene **20** was prepared by successive Friedel–Crafts acylation of thiophene[31] followed by Wolff–Kishner reduction[32] or by dilithiation of thiophene followed by treatment with 1-bromooctane and TMEDA.[33] These 2,5-dialkylthiophenes were treated with Br$_2$ to give 2,5-dialkyl-3,4-dibromothiophene, **18** or **21**. A mixture of 2,5-dialkyl-3,4-dibromothiophene, **18** or **21**, and *ca.* 4 equivalents of 3,4-dibromothiophene was treated with *n*-butyllithium, followed

a, Br$_2$, CHCl$_3$. *b*, Zn, AcOH. *c*, (i) *n*-BuLi, Et$_2$O; (ii) S(SO$_2$Ph)$_2$. *d*, (i) *n*-BuLi, Et$_2$O; (ii) CuCl$_2$. *e*, (i) *n*-BuLi, Et$_2$O; (ii) MeI

5, R^1=R^2=H $\xrightarrow{a, b}$ **6**, R^1=R^2=H

7, R^1=R^2=R^3=R^4=H

1, R^1=R^2=R^3=R^4=H

2, R^1=CH$_3$, R^2=R^3=R^4=H

8, R^1=R^3=R^4=H, R^2=CH$_3$

9, R^1=CH$_3$, R^2=H

10, R^1=CH$_3$, R^2=H

11, R^1=R^3=CH$_3$, R^2=R^4=H
12, R^1=R^4=CH$_3$, R^2=R^3=H
13, R^2=R^4=CH$_3$, R^1=R^4=H

14, R^1=R^3=CH$_3$, R^2=R^4=H
15, R^1=R^4=CH$_3$, R^2=R^3=H
16, R^2=R^4=CH$_3$, R^1=R^4=H

17, R^1=R^2=CH$_3$ $\xrightarrow{a}$ **18**, R^1=R^2=CH$_3$

19, R^1=R^2=CH$_3$, R^3=R^4=H

3, R^1=R^2=CH$_3$, R^3=R^4=H

20, R^1=R^2=*n*-C$_8$H$_{17}$ $\xrightarrow{a}$ **21**, R^1=R^2=*n*-C$_8$H$_{17}$

22, R^1=R^2=*n*-C$_8$H$_{17}$, R^3=R^4=H

4, R^1=R^2=*n*-C$_8$H$_{17}$, R^3=R^4=H

Scheme 1

by treatment with bis(phenylsulfonyl) sulfide, to give the corresponding 2,5′-dialkyl-4,4′-dibromo-3,3′-dithienyl sulfide (**19** or **22**), 2,2′,5,5′-tetraalkyl-4,4′-dibromo-3,3′-dithienyl sulfide, and **1**, all of which were separable by careful column chromatography. Dilithiation of **19** or **22**, followed by copper-mediated ring closure, gave 1,3-dialkyldithieno[3,4-*b*:3′,4′-*d*]thiophenes, **3** and **4**, respectively.

Electrooxidative polymerization

Polymerizations were carried out by cyclic voltammetry of solutions of monomers in dry acetonitrile (100 mM LiClO$_4$) on gold or ITO electrodes, Fig. 2. Cyclic voltammograms of **1** show an onset for monomer oxidation at approximately +1.0 V (*versus* SCE) whereas methyl (**2**) and dimethyl (**3**) analogs have slightly lower oxidation potentials (*ca.* +900 mV), consistent with the inductive electron donating effects of alkyl substituents. Repeated potential cycling of a solution of **1** between 0 and +1.02 V results in the deposition of a polymer film on the electrode surface, and the appearance of a broad reversible redox wave in the cyclic voltammogram at approximately +700 mV. Cyclic voltammetry of **2** over this potential range deposited a polymer film on the electrode. However, the growth of a reversible polymer redox wave was not observed. Cyclic voltammetry of **3** over the same potential range deposits a polymer film on the electrode and results in the slow growth of a reversible redox wave at *ca.* +600 mV. Continuous cycling to the same limiting positive potential, or
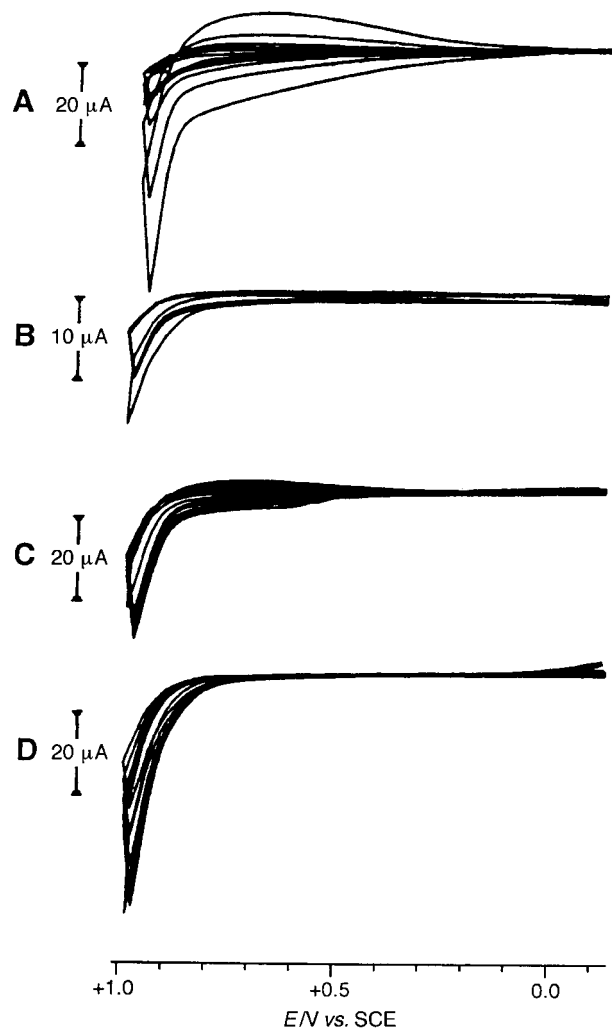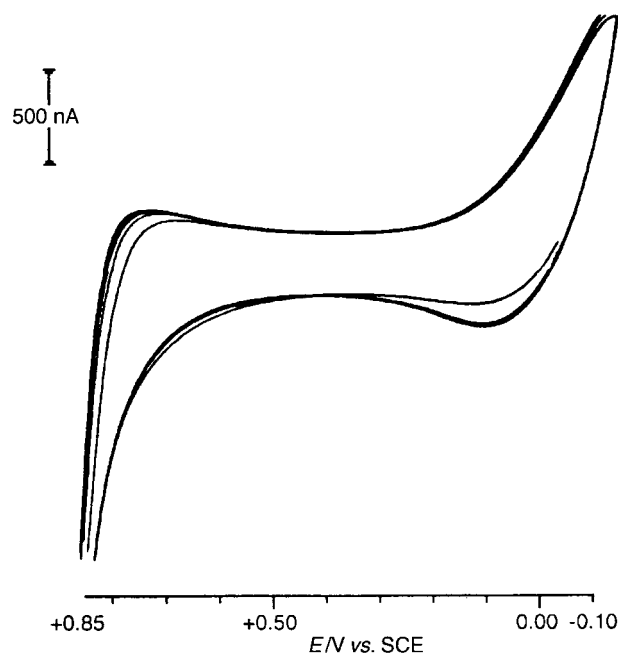

Fig. 3 Cyclic voltammogram of thin film of electrochemically-deposited poly**3** in monomer-free electrolyte solution (0.1 M LiClO$_4$ in acetonitrile, 100 mV s^{-1}).

proceeding to higher potentials, results in the gradual loss of electroactivity.

Thin films of electrochemically deposited polymers of 3 were electrochemically cycled in the absence of redox-active monomer to determine onsets for oxidation and reduction, Fig. 3. Poly**3** shows an oxidation peak (p-doping) with the onset at +750 mV, and a reduction peak (n-doping) with the onset at +50 mV, giving a bandgap of 0.7 eV, which is lower than that of poly**1** (1.1 eV). A possible explanation for this observation is that **3** is polymerized through the unsubstituted α-positions of the monomer to afford a polymer consisting of exclusively 1,3-diyl units whereas the polymer derived from electro-oxidative polymerization of **1** contains other linkages.

Electrochemical polymerization of **4** on a bare gold, platinum or ITO electrode formed an oily liquid on the electrode surface. In order to promote polymerization, we modified an ITO electrode with a monolayer of chlorodimethyl{11-[3′-(2,2′:5′:2″-terthienyl)]undecyl}silane. The oxidation potential of this surface species (E_{onset} +650 mV) is lower than that of the dithieno[3,4-*b*:3′,4′-*d*]thiophene derivatives (E_{onset} +900 mV) and we have demonstrated a catalytic effect for polymerization of monomers on such modified surfaces.[34] Electrochemical polymerization of **3** and **4** on ITO-modified electrodes gave polymers, suggesting that the surface terthienyl group promotes polymerization of dithienothiophenes.

UV–VIS spectra of neutral poly**3** and poly**4** are shown in Fig. 4. Poly**3** has absorptions at 500 and 950 nm, and an onset at about 1350 nm. This onset gives a bandgap of the polymer film of 0.9 eV, similar to the bandgap derived from redox switching. The absorbance at 500 nm suggests that a large fraction of the polymer is electronically inactive, presumably as a result of overoxidation.

Poly**4** has absorptions at 550 and 1100 nm, and a threshold at about 1750 nm. This threshold gives a bandgap of the polymer film as *ca.* 0.7 eV. Again, the absorbance at 550 nm suggests the formation of electronically inactive species by overoxidation. Electrochemical oxidation or reduction of the film of poly**3** did not show significant spectral change. This result implies that most of the material deposited on the electrode has lost electroactivity presumably due to the overoxidation.
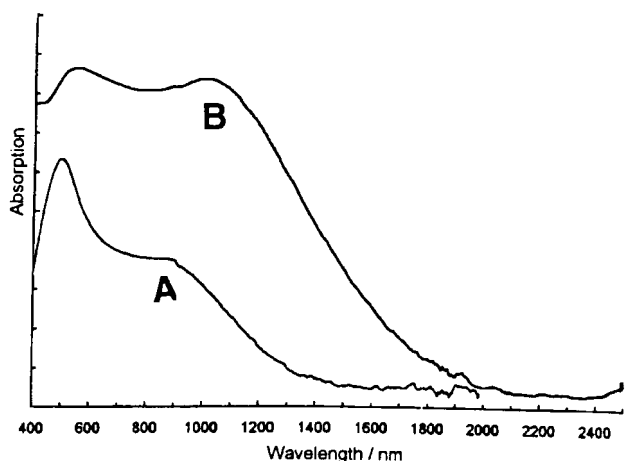

Fig. 2 Electrochemical polymerization of monomers **1–4**: cyclic voltammograms of monomers (50 mM) in dry acetonitrile (100 mM LiClO$_4$) on gold electrodes ($V = 100$ mV s^{-1}). A, **1**; B, **2**; C, **3**; and D, **4**.

Fig. 4 UV–VIS spectra of neutral (*i.e.*, undoped) films of electro-chemically-deposited poly**3** and poly**4**: A, poly**3**; B, poly**4**.

Chemical polymerization

Chemical oxidation of **1**, **3** and **4** with anhydrous $FeCl_3$ (4 eq.) in $CHCl_3$ gave the corresponding polymers which were precipitated in methanol, and dedoped by stirring with 5% aqueous hydrazine. Chemically polymerized poly**4** is soluble in chloroform, while poly**1** and poly**3** are insoluble. Gel permeation chromatography of poly**4** gave a molecular weight (relative to polystyrene standards) as $M_n = 1200$, which implies an average degree of polymerization of only three. However, both ^{1}H NMR and IR spectra of poly**4** suggest the disappearance of aromatic C–H bonds, which are the end groups of the polymer. This observation suggests that the molecular weight of poly**4** is actually much higher than that determined by GPC. We assume that this discrepancy arises from the use of polystyrene as a calibration standard, which adopts dramatically different hydrodynamic volumes than does poly**4**.

Conductivity

Conductivity was measured using a four-point probe. Pressed pellets were made from poly**1**, poly**3**. The I_2-doped pellets have conductivities of 0.15 and 0.20 S cm^{-1}, respectively. A thin film of poly**4** film was cast from $CHCl_3$ solution and doped to give a conductivity of 5.1 S cm^{-1}. The higher conductivity of poly**4** compared to the other two polymers is probably due to the difference in the physical form of the samples.

Conclusions

A series of selectively substituted dithieno[3,4-*b*:3′,4′-*d*]thi-ophenes were synthesized. Chemical or electrochemical oxidation gives the corresponding polymers with defined regiochemical structures. The chemically prepared dioctyl analog is soluble in common solvents such as chloroform, dichloromethane and THF. However, overoxidation of the polymers at an electrode surface presents a serious limitation to the polymerization of substituted analogs. Thin films of 1,3-dimethyl and 1,3-dioctyl analogs were prepared by electro-chemical polymerization. Bandgaps for the films are 0.9 and 0.7 eV, respectively, lower than that of the unsubstituted polymer. Potential cycling of the 1,3-dimethyl substituted polymer film shows repetitive p- and n-dopability.

Experimental

Reagents

Thiophene, 2-methylthiophene, 2,5-dimethylthiophene, *n*-butyllithium (2.5 M solution in hexanes), sodium sulfinate, sulfur dichloride, octanoyl chloride, iron(III) chloride, and

chloroform-*d* ($CDCl_3$) were obtained from the Aldrich Chemical Co. (Milwaukee, WI) and used as received. Aluminum chloride, ethylene bromide, acetic acid, bromine, zinc dust, iron powder, sodium hydroxide, methanol, chloro-form and hydrochloric acid were obtained from Fisher Scientific (Fair Lawn, NJ) and used as received. Acetone and hexane were obtained from Chemcentral-Atlanta (Doraville, GA) and were purified by distillation under normal pressure. Tetrahydrofuran (THF) and diethyl ether were obtained from Fisher Scientific and were purified by distillation over sodium or potassium benzophenone ketyl. Dimethyl sulfoxide (DMSO, Fisher) was purified by distillation under reduced pressure and was stored over 4 Å molecular sieves. Copper(II) chloride (Fisher) was recrystallized from methanol, and dried in an oven at 150 °C.

Instrumentation

^{1}H and ^{13}C NMR analyses were carried out on a Varian Gemini 300 spectrometer at 300 and 75 MHz, respectively. IR analysis was carried out on a Nicolet 520 FT-IR spectrometer. Melting points were measured on a Mel-temp II melting point analyzer.

Cyclic voltammograms were recorded on a Bioanalytical Systems BAS-100 Electrochemical Analyzer with a saturated calomel electrode (SCE) and platinum wire or gold counter electrode in anhydrous propylene carbonate (Aldrich) contain-ing 0.1 M $LiClO_4$. Cyclic voltammograms were determined at 100 mV s^{-1} and were integrated graphically.

UV–VIS spectra were recorded on a Perkin Elmer Lambda 19 UV–vis–NIR spectrometer. Solid films were prepared by electrochemical oxidation of monomer solution in acetonitrile using an ITO glass working electrode.

The resistivity of the doped polymer film was recorded on a Phillips PM2534 System Multimeter with an Alessi 54 four-point probe. Film thickness was recorded on a Tencor Alpha-Step 100 profilometer.

3,4-Dibromothiophene, 6

Thiophene was treated with 4 equiv. of Br_2 in $CHCl_3$ to afford tetrabromothiophene (63%) as an off-white crystalline solid according to the method of Gronowitz,[26] mp 114–116 °C (lit.[26] 115.5–116 °C). IR (KBr) 1280, 730 cm^{-1}. Treatment of tetrabromothiophene with zinc in acetic acid according to the method of Gronowitz gave 3,4-dibromothiophene[25] (67%) as a colorless liquid: bp 99–103 °C/13 mmHg (lit.[25] 96.5–99 °C/11 mmHg). ^{1}H NMR ($CDCl_3$) δ 7.31 (s, thienyl C3,C4). IR (KBr) 3100, 1480, 1390, 1320, 1110, 920, 850, 780, 690 cm^{-1}.

Bis(phenylsulfonyl) sulfide

SCl_2 (7.8 g, 75 mmol) was added dropwise to the dispersion of sodium benzenesulfonate (25 g, 0.16 mol) in toluene (400 mL). The mixture was stirred at room temperature for 2 h, the mixture was filtered and the solvent was removed under reduced pressure. The solid material was recrystallized from toluene to afford bis(phenylsulfonyl) sulfide (19.2 g, 81%) as a white crystalline solid, mp 125–130 °C. ^{1}H NMR ($CDCl_3$) δ 7.60 (dd, 2H, *J* = 7 Hz, 7.5 Hz), 7.72 (t, 1H, *J* = 7 Hz), 7.87 (d, 1H, *J* = 7.5 Hz), 8.02 (d, 1H, *J* = 7.5 Hz). IR (KBr) 3060, 1453, 1334, 1150, 1071, 755, 716, 683 cm^{-1}.

4,4′-Dibromo-3,3′-dithienyl sulfide, 7

A solution of 4-bromo-3-thienyllithium in anhydrous ether was prepared by addition of a 1.6 M solution of *n*-BuLi in ether (60 mL, 96 mmol) to a stirred solution of **6** in Et_2O (100 mL) at −70 °C. Bis(phenylsulfonyl) sulfide (15.3 g, 48.0 mmol) was added to the mixture in small portions over 30 min. The mixture was stirred at −70 °C for 2 h, warmed

to 0 °C, and H_2O (10 mL) was added. The solution was filtered. The organic phase was separated and the aqueous solution was washed with Et_2O (120 mL). The combined organic portions were washed with H_2O (3 × 50 mL), dried over $MgSO_4$, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel, petroleum ether) to yield **7** (7.31 g, 43%) as a yellow liquid. ^{1}H NMR ($CDCl_3$) δ 7.18 (d, 2H, $J = 3.5$ Hz, thienyl C2), 7.36 (d, 2H, $J = 3.5$ Hz, thienyl C5). IR (KBr) 3070, 1440, 1310, 930, 870, 800, 790 cm^{−1}.

Dithieno[3,4-*b*:3′,4′-*d*]thiophene, 1

A 2.5 M solution of *n*-BuLi in hexanes (19.6 mL, 49.5 mmol) was added to the solution of **7** (8.8 g, 24.7 mmol) in ether (25 mL) in an externally cooled dropping funnel at −70 °C and the mixture was stirred for 45 min. The solution was then added to a vigorously stirred suspension of $CuCl_2$ (2.96 g, 22.0 mmol) in Et_2O (150 mL) at −50 °C. The mixture was stirred at −50 °C for 1 h and then at room temperature overnight. H_2O (25 mL) was added and the gray precipitate was filtered. The ether layer was separated, washed with 2 M HCl (3 × 80 mL) and H_2O (3 × 80 mL), and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude mixture was purified in portions by column chromatography (silica gel, petroleum ether). Recrystallization from petroleum ether gave **1** (0.96 g, 23%) as a colorless crystalline solid, mp 84–85 °C (lit.[24] 87–87.5 °C). ^{1}H NMR ($CDCl_3$) δ 7.04 (d, 2H, $J = 2.6$ Hz, C3,C5), 7.48 (d, 2H, $J = 2.6$ Hz, C1,C7). IR (KBr) 3080, 1460, 1310, 910, 750, 680 cm^{−1}.

1-Methyldithieno[3,4-*b*:3′,4′-*d*]thiophene, 2

A 2.5 M solution of *n*-BuLi in ether (1.02 mL, 2.55 mmol) was added to the solution of **1** (0.500 g, 2.55 mmol) in THF (8 mL) at −78 °C under N_2. The mixture was stirred for 45 min, and a solution of methyl iodide (0.39 g, 2.8 mmol) in THF (2 mL) was added dropwise. The solution was stirred for another 2 h and poured into H_2O (100 mL). The mixture was extracted with CH_2Cl_2 (3 × 40 mL) and the combined extracts were washed with H_2O (3 × 40 mL) and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (silica gel; hexanes) to give a crude mixture. Recrystallization from hexanes gave **2** (100 mg, 18%) as a light yellow crystalline solid. ^{1}H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 7.03 (d, 1H, $J = 2.6$ Hz, C5), 7.243 (s, 1H, C1), 7.429 (d, 1H, $J = 2.6$ Hz, C7). IR (neat) 3100 (thiophene C–H str.), 2920, 2840, 1500, 1450, 1420, 1200, 1050, 850, 800, 740, 700 cm^{−1} (thiophene out-of-plane). Analysis for $C_9H_6S_3$, Calcd: C, 51.44; H, 2.88; S, 45.68. Found: C, 51.40; H, 2.96; S, 45.42%.

3,4-Dibromo-2-methylthiophene, 10

A solution of Br_2 (244 g, 1.53 mol) in $CHCl_3$ (50 mL) was added dropwise to the solution of 2-methylthiophene, **9** (50 g, 0.51 mol) in $CHCl_3$ (50 mL) containing iron powder as a catalyst (60 mg, 1.1 mmol) in a 500 mL round bottomed flask. The crude mixture was dissolved in hexanes and the solution was passed through a column of silica gel to remove colored material. The solvent was removed under reduced pressure and the residue was recrystallized from hexanes to give 2,3,4-tribromo-5-methylthiophene as a light yellow crystalline solid (21.6 g, 13%), mp 76–79 °C. ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H, CH_3). IR (neat) 2910, 2860, 1450, 1280, 1140, 820 cm^{−1}.

A 2.5 M solution of *n*-BuLi in hexanes (25.5 mL, 63.0 mmol) was added dropwise to the solution of 2,3,4-tribromo-5-methylthiophene (21 g, 63 mmol) in Et_2O (150 mL) at −78 °C. The mixture was stirred at −78 °C for 45 min and MeOH (50 mL) and H_2O (150 mL) were added. The mixture was

extracted with diethyl ether (4 × 70 mL) and the combined extracts were washed with water (3 × 80 mL) and dried over magnesium sulfate. The solvent was removed at reduced pressure and the residue was passed through a column of silica gel to remove colored material. The solvent was removed under reduced pressure to give **10** (10.2 g, 64%) as a yellow liquid. ^{1}H NMR ($CDCl_3$) δ 2.46 (s, 3H, CH_3), 7.16 (s, 1H, thienyl C5). IR (neat) 3130, 2940, 2860, 1500, 1450, 1310, 1140, 1000, 880, 820 cm^{−1}.

2-Octanoylthiophene

$AlCl_3$ (107 g, 0.8 mol) was added in portions to the solution of octanoyl chloride (65 g, 0.40 mol) and thiophene (34 g, 0.40 mol) in benzene (200 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h, warmed to room temperature and stirred overnight. Aqueous HCl (3%, 100 mL) was added and the organic layer was washed with water (4 × 250 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield 2-octanoylthiophene (85 g, 100%) as a yellow liquid. ^{1}H NMR ($CDCl_3$) δ 0.90 (t, 3H, $J = 7$ Hz, C8 CH_3), 1.2–1.5 (m, 8H), 1.75 (p, 2H, $J = 7$ Hz, C3 CH_2), 2.89 (t, 2H, $J = 7$ Hz, C2 CH_2), 7.13 (dd, 1H, $J = 5.1$ Hz, 3.6 Hz, thienyl C4), 7.62 (dd, 1H, $J = 5.1$ Hz, 1.5 Hz, thienyl C5), 7.71 (dd, 1H, $J = 3.6$ Hz, 1.5 Hz, thienyl C3). IR (neat) 2955, 2927, 2855, 1664, 1416, 1235, 721 cm^{−1}.

2-Octylthiophene

2-Octanoylthiophene (85 g, 0.4 mol) and an 85% solution of hydrazine hydrate (45 mL, 0.79 mol) were added to a solution of NaOH (60 g) in diethylene glycol (700 mL) in a 1 L three-neck flask. The stirred mixture was heated at reflux for 1 h and a condenser was attached for distillation. The aqueous distillate was separated at frequent intervals from the organic layer and returned to the flask. The operation was discontinued when the distillate no longer contained an organic layer (approximately 3 h). The combined organic layers were washed with H_2O (4 × 125 mL) and dried over $MgSO_4$ and the solvent was removed under reduced pressure to afford 2-octylthiophene (44.3 g, 56%) as a light yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, $J = 7$ Hz, C8 CH_3), 1.27 (m, 10H), 1.67 (p, 2H, $J = 7$ Hz, C2 CH_2), 2.82 (t, 2H, $J = 7$ Hz, C1 CH_2), 6.76 (dd, 1H, $J = 1.5$ Hz, 3.3 Hz, thienyl C3), 6.92 (dd, 1 H, $J = 3.3$ Hz, 5.1 Hz, thienyl C4), 7.10 (dd, 1H, $J = 1.5$ Hz, 5.1 Hz, thienyl C5). IR (neat) 3050, 2955, 2920, 2854, 1465, 1440, 850, 819 cm^{−1}.

2-Octanoyl-5-octylthiophene

$AlCl_3$ (46.7 g, 0.35 mol) was added in portions to a solution of octanoyl chloride (37 g, 0.22 mol) and 2-octylthiophene (44 g, 0.22 mol) in benzene (200 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h, warmed to room temperature and stirred overnight. Water (200 mL) was added and the organic layer was washed with aqueous HCl (1.5%, 3 × 150 mL) and water (2 × 100 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield 2-octanoyl-5-octylthiophene (74 g, 100%) as a yellow oil. ^{1}H NMR ($CDCl_3$) δ 0.88 (t, 6H, $J = 7$ Hz, C8, C8′ CH_3), 1.2–1.4 (m, 18H), 1.71 (m, 4H, C3 and C2′ CH_2), 2.89 (t, 4H, $J = 7$ Hz, C2 and C1′ CH_2), 6.80 (d, 1H, $J = 3.5$ Hz, thienyl C4), 7.53 (d, 1H, $J = 3.5$ Hz, thienyl C3). IR (neat) 3050, 2950, 2930, 2840, 1650, 1450, 1220, 800 cm^{−1}.

2,5-Dioctylthiophene, 20

(A) Wolff–Kishner reduction of 2-octanoyl-5-octylthiophene. 2-Octanoyl-5-octylthiophene (74 g, 0.23 mol) and an 85% solution of hydrazine hydrate (25 mL, 0.43 mol) were added to a solution of NaOH (35 g) in diethylene glycol (400 mL) in a 1 L three-neck flask. The stirred mixture was heated at reflux

for 3 h. The mixture was extracted with toluene (3×100 mL). The extracts were washed with 5% HCl (2×250 mL) and water (2×500 mL) and dried over MgSO$_4$. The solvent was removed under reduced pressure and the residue was distilled under reduced pressure to afford **20** (31 g, 44%) as light yellow oil, bp 140–150 °C/0.8 mmHg. ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 6H, $J = 7$ Hz, C8 and C8′ CH$_3$), 1.27 (m, 20H), 1.64 (p, 4H, $J = 7$ Hz, C2 and C2′ CH$_2$), 2.73 (t, 4H, $J = 7$ Hz, C1 and C1′ CH$_2$), 6.55 (s, 2H, thienyl C–H). IR (neat) 3060, 2960, 2920, 2840, 1490, 1390, 810, 740 cm^{-1}.

(B) Dialkylation of thiophene. A 2.5 M solution of *n*-BuLi in hexanes (90.0 mL, 225 mmol) was added dropwise to a solution of thiophene (8.41 g, 100 mmol) and TMEDA (26.2 g, 225 mmol) in hexanes (200 mL). The mixture was heated at reflux, stirred for 4 h and 1-bromooctane (38.6 g, 200 mmol) was added. The mixture was stirred at reflux for 20 h and poured into a saturated solution of NaHCO$_3$ (500 mL). The organic layer was separated, washed with a saturated solution of NaHCO$_3$ (2×500 mL) and H$_2$O (2×250 mL), dried over MgSO$_4$, and the solvent and other impurities were removed under reduced pressure. The residue was purified by flash column chromatography (silica gel; hexanes) to give **19** (25.6 g, 83%) as a light yellow liquid.

3,4-Dibromo-2,5-dimethylthiophene, 18

A solution of Br$_2$ (37.3 g, 235 mmol) in CHCl$_3$ (30 mL) was added dropwise to a solution of 2,5-dimethylthiophene, **17** (25.0 g, 223 mmol) in CHCl$_3$ (30 mL) at 0 °C. The mixture was stirred for 4 h and saturated aqueous NaHCO$_3$ was added (100 mL). The organic layer was separated, and the aqueous layer was extracted with CHCl$_3$ (100 mL). The combined extracts were dried over MgSO$_4$ and solvent was removed under reduced pressure to give a crude product. This crude product was distilled under reduced pressure to afford 3-bromo-2,5-dimethylthiophene (20 g) and **18** (10 g, 15%), bp 70–75 °C/2.5 mmHg, mp 38–40 °C. ^{1}H NMR (CDCl$_3$) δ 2.40 (s, 6H, CH$_3$). IR (neat) 2950, 2910, 2820, 1500, 1340, 1250, 1120, 1000, 820 cm^{-1}.

3,4-Dibromo-2,5-dioctylthiophene, 21

Compound **20** (3.1 g) was treated with Br$_2$ (2 equiv.) according to the method described for the synthesis of **18**. The product was purified by flash column chromatography (silica gel; hexanes) to afford **21** as a colorless liquid (44% yield). ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 6H, $J = 7$ Hz, C8 and C8′ CH$_3$), 1.2–1.4 (m, 20H), 1.62 (p, 4H, $J = 7$ Hz, C2 and C2′ CH$_2$), 2.77 (t, 4H, $J = 7$ Hz, C1 and C1′ CH$_2$). IR (neat), 2920, 2860, 1460, 1340, 1250, 1120, 1000, 820 cm^{-1}.

4,4′-Dibromo-2,5-dimethyl-3,3′-dithienyl sulfide, 19

A 2.5 M solution of *n*-BuLi in hexanes (43.0 mL, 108 mmol) was added dropwise to a solution of **18** (5.6 g, 21 mmol) and bis(phenylsulfonyl) sulfide (20 g, 83 mmol) in Et$_2$O (100 mL) at −78 °C. The mixture was stirred for 45 min and **6** (16.4 g, 5.20 mmol) was added in small portions. The mixture was stirred at −78 °C for 2 h, ethanol was added, and the mixture was warmed to room temperature. The mixture was washed with H$_2$O (3×100 mL), dried over MgSO$_4$ and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel; hexanes) to give **7** (4.6 g) and **19** (2.9 g, 35% based on **18**) as a light yellow liquid. ^{1}H NMR (CDCl$_3$) δ 2.40 (s, 3H, CH$_3$–thienyl C2), 2.54 (s, 3H, CH$_3$–thienyl C5), 6.49 (d, 1H, thienyl C2′), 7.289 (d, 1H, thienyl C5′). IR (neat) 3105, 2916, 2850, 1520, 1480, 1320, 1140, 1030, 922, 851, 778 cm^{-1}.

4,4′-Dibromo-2,5-dioctyl-3,3′-dithienyl sulfide, 22

A mixture of **21** (5 g, 10.7 mmol) and **6** (10.4 g, 43.0 mmol) was treated with *n*-BuLi followed by **7** (8.40 g, 26.9 mmol) according to the procedure described above for the preparation of **19**. The product was purified by flash column chromatography (silica gel; hexanes) to give **1** (3.6 g) and **22** (2.3 g, 37.5% based on **21**) as a light yellow liquid. ^{1}H NMR (CDCl$_3$) δ 0.87 (t, 6H, $J = 7$ Hz, C8), 1.2–1.4 (m, 20H), 1.5–1.7 (m, 4H, C2), 2.78 (t, 2H, $J = 7$ Hz, C1–thienyl C2), 2.94 (t, 2H, $J = 7$ Hz, C1–thienyl C5), 6.40 (d, 1H, thienyl C2), 7.28 (d, 1H, thienyl C5). IR (neat) 3105, 2960, 2920, 2840, 1520, 1380, 1140, 1030, 922, 851, 778 cm^{-1}.

1,3-Dimethyldithieno[3,4-*b*:3′,4′-*d*]thiophene, 3

A 2.5 M solution of *n*-BuLi in hexanes (6.0 mL, 15 mmol) was added dropwise to the solution of **19** (2.87 g, 7.48 mmol) in Et$_2$O (15 mL) in an externally-cooled dropping funnel at −78 °C, and stirred for 45 min. The mixture was added to a vigorously stirred suspension of CuCl$_2$ (2.7 g, 20 mmol) in Et$_2$O (50 mL) at −50 °C. The mixture was stirred for 2 h, and MeOH (20 mL) and H$_2$O (20 mL) was added. The mixture was extracted with hexanes (4×50 mL) and combined extracts were washed with H$_2$O (4×50 mL), dried over MgSO$_4$, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (silica gel; hexanes) followed by recrystallization from hexanes to give **3** (0.30 g, 16%) as a light yellow crystalline solid. ^{1}H NMR (CDCl$_3$) δ 2.37 (s, 3H, CH$_3$–C3), 2.63 (s, 3H, CH$_3$–C1), 7.00 (d, 1H, $J = 2.6$ Hz, C5), 7.33 (d, 1H, $J = 2.6$ Hz, C7). IR (neat) 3130, 2920, 2850, 1500, 1450, 1360, 1140, 850, 780 cm^{-1}. Analysis for C$_{10}$H$_8$S$_3$, Calcd: C, 53.58; H, 3.60; S, 42.82. Found: C, 53.47; H, 3.64; S, 42.53%.

1,3-Dioctyldithieno[3,4-*b*:3′,4′-*d*]thiophene, 4

Compound **22** (0.34 g, 0.59 mmol) was treated with *n*-BuLi and CuCl$_2$ according to the procedure given above for the preparation of **3**. The product was purified by flash column chromatography (silica gel; hexanes) to give **4** (103 mg, 40%) as a light yellow liquid. ^{1}H NMR (CDCl$_3$) δ 0.88 (t, 6H, $J = 7$ Hz, C8), 1.2–1.45 (m, 20H), 1.72 (p, 4H, $J = 7$ Hz, C2), 2.71 (t, 2H, $J = 7$ Hz, C1), 2.99 (t, 2H, $J = 7$ Hz, C1′), 6.99 (d, 1H, $J = 2.6$ Hz, C5), 7.30 (d, 1H, $J = 2.6$ Hz, C7). IR (neat) 3130, 2960, 2920, 2850, 1500, 1450, 1360, 1140, 850, 780 cm^{-1}. Analysis for C$_{24}$H$_{36}$S$_3$, Calcd: C, 68.54; H, 8.63; S, 22.83. Found: C, 68.46; H, 8.57; S, 22.68%.

Chemical polymerization of 1,3-dioctyldithieno[3,4-*b*:3′,4′-*d*]thiophene

A dispersion of anhydrous FeCl$_3$ (0.15 g, 0.95 mmol) in dry CHCl$_3$ (15 mL) was added to a solution of **4** (0.10 g, 0.24 mmol) in CHCl$_3$ (12 mL) and the mixture was stirred for 1 d. MeOH (20 mL) was added to the mixture and a dark purple solid precipitated. The precipitate was extracted in a Soxhlet extractor with MeOH for 1 d, followed by extraction with acetone for 1 d and with CHCl$_3$ for 1 d. Flash column chromatography (silica gel; hexanes–CH$_2$Cl$_2$) of the fraction extracted with CHCl$_3$ gave 15 mg of a red solid, and by changing the eluent to CH$_2$Cl$_2$, a further 25 mg was recovered. ^{1}H NMR (CDCl$_3$) δ 2.88 (broad, 2H), 2.62 (broad, 2H), 1.6 (broad, 4H), 1.5–1.1 (broad, 22H), 0.8 (broad, 6H). IR (neat) 2950, 2920, 2850, 1700, 1470 1280, 1220, 1180 cm^{-1}.

Acknowledgement

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