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$\Delta^{4,4'}$-Dicyclopenta[2,1-*b*:3,4-*b*′]dithiophene. A Conjugated Bridging Unit for Low Band Gap Conducting Polymers

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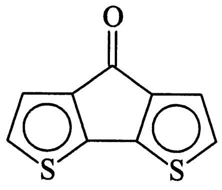
$\Delta^{4,4'}$-Dicyclopenta[2,1-*b*:3,4-*b*′]dithiophene has been prepared from cyclopenta[2,1-*b*:3,4-*b*′]bithiophen-4-one and its electrochemical and spectroscopic properties have been characterized. Its low HOMO−LUMO gap and facile electrochemical polymerization make it an attractive building block for low band gap conducting polymers. Films of poly-($\Delta^{4,4'}$-dicyclopenta[2,1-*b*:3,4-*b*′]dithiophene) on electrodes have been characterized by cyclic voltammetry, electronic absorption spectroscopy, IR spectroscopy, and in situ conductivity measurements. The spectroscopic and electrochemical results confirm the formation of a polymeric material with long conjugation length and low band gap (ca. 0.5 eV). The intrinsic conductivity is consistent with this band gap.

Introduction

Among conducting polymers, polythiophene is particularly attractive because of its high conductivity and good environmental stability in both its p-doped and undoped states.[1−3] Furthermore, its structural versatility has made possible the development of numerous thiophene-based polymers with various desired properties, such as high stability,[4] superior conductivity,[3] processability,[5] solubility,[6−8] and low band gap.[9,10] To achieve polythiophene of high quality, in addition to the careful optimization of electrosynthesis conditions from the thiophene monomer,[11−14] oligomers, particularly 2,2′-bithiophene and 2,2′:5′,2″-terthiophene, have been employed as precursors.[15−18] Owing to the lower oxidation potentials and exclusive α−α′ linkages in these precursors, polybithiophene and polyterthiophene are expected to be closer to the ideal polythiophene structure than materials prepared from thiophene itself.[15] Substantial work on comparative studies of the electrochemical and spectroscopic properties of polymers synthesized from thiophene, bithiophene, and terthiophene has been reported.[1,15]

Conducting polymers prepared from bithiophene precursors with electron-withdrawing groups at an sp^2-carbon bridging the β and β' positions form an interesting branch of conducting polymers with reduced band gaps (E_g < 1.5 eV).[10,19] For example, cyclopenta[2,1-*b*:3,4-*b*′]bithiophen-4-one (**1**) produces a polymer with a band gap of ca. 1.2 eV[20] and poly(4-dicyanomethylene-cyclopenta[2,1-*b*:3,4,*b*′]bithiophene) (**2**) has one of the



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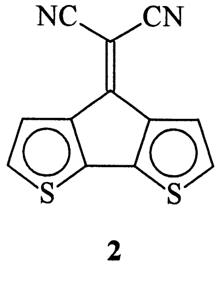

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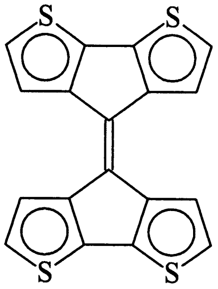
lowest band gaps (ca. 0.8 eV)[21] reported to date for a thiophene-based system.

The linking of two bridged bithiophene moieties by a double bond, as in $\Delta^{4,4'}$-dicyclopenta[2,1-*b*:3,4-*b'*]-dithiophene (structure **3**),[22,23] represents an intriguing extension of this group of polythiophenes. We report here that **3** can be electrochemically polymerized to produce low band gap materials with substantial conductivity. Films of poly-**3** on electrodes have been characterized by cyclic voltammetry, infrared spectroscopy, electronic absorption spectroscopy, and in situ conductivity measurements.



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The attraction of **3** over other cyclopentadithiophenes that have been reported is that its four thiophene rings allow it to cross-link conjugated systems in a well-defined way, with conjugation in two dimensions. It may therefore be an attractive building block for molecular electronic systems in which it can act as a four-way electronic junction.

Experimental Section

Chemicals and Electrodes. Nitrobenzene (Aldrich, 99.93+ AnalaR grade), acetonitrile (Aldrich, 99.93+% Biotech grade), Bu_4NPF_6 (Fluka, electrochemical grade), and other chemicals were used as received. Working electrodes were either Pt disks (5.2×10^{-3} cm^2 or 1.2×10^{-4} cm^2) sealed in glass or indium/tin oxide coated glass (10 Ω/square, Donnelly Corp.).

Synthesis of 3. A solution of cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene-4-one[24] (202 mg, 1.04 mmol) and Lawesson's reagent (1.30 g, 3.12 mmol) in dry benzene was refluxed for 12 h under a nitrogen atmosphere. The reaction mixture was cooled and the solvent was then removed by rotary evaporation affording a solid, which was purified by column chromatography (silica gel, hexane:dichloromethane 9:1) to give a dark brown solid (40 mg, 0.11 mmol, 22%). mp 237−240 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.52 (d, $J = 5.0$ Hz, 4H), 7.10 (d, $J = 5.0$ Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.7, 140.9, 125.2, 124.4, 121.4. MS m/z (%) 352 (M^+, 100), 320 (7), 307 (13), 176 (14). HRMS: calculated for $C_{18}H_8S_4$, 351.95089; found, 351.94977.

Polymerization of 3. Films of poly-**3** were formed on electrodes by the anodic electrochemical polymerization of **3** (ca. 2−5 mM) in nitrobenzene containing 0.01 M Bu_4NPF_6. Typically, films were formed by cycling the potential between 0 and +1.5 V at 100 mV s^{-1}. All polymerizations and electrochemical experiments were carried out at ambient temperature (22 ± 2 °C). Polymer films were rinsed with acetone and dried in air before further experiments.

Electrospray mass spectroscopy of one sample that had been dissolved in a 1:3 mixture of *N*-methylpyrrolidone and DMF at 70 °C and then diluted with acetonitrile showed peaks at $m/z = 2466$ ($n = 7$), 2114, and 1516, as well as peaks at 1058 and 706, corresponding to the trimer and dimer, respectively. This indicates that a polymeric material is formed during the anodic deposition of films of **3**.

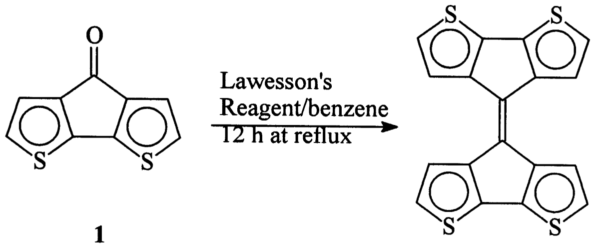
Polymer Film Thickness. The thickness of a film of poly-**3** deposited on a 0.0127-cm diameter Pt wire was estimated by scanning electron microscopy from the increase in diameter. This provided a relationship of 1.6 μm cm^2 C^{-1} between film thickness and voltammetric charge that was used to estimate the thicknesses of all other films.

Conductivity Measurements. A thin film of poly-**3** deposited on a Pt disk electrode was coated with gold by vacuum deposition, and dual working electrode experiments were performed with a Pine Instruments RDE4 bi-potentiostat in a four-electrode cell containing acetonitrile + 0.01 M Bu_4NPF_6.[25] In one type of experiment, the potentials of both the underlying Pt electrode and the gold film were slowly scanned (10 mV s^{-1}) relative to the reference electrode, with a 10-mV potential difference maintained between them. The resistance of the polymer film at each potential during the scan was calculated from the current by applying Ohm's law. In a second type of experiment, the potential of the gold film was held at 0 V vs SSCE while the potential of the underlying Pt disk was scanned. The resistance at each potential was calculated from the current (i) using $R = s/i$, where s is the slope of a plot of log(i) vs E.[26] Conductivity vs potential plots obtained by these two methods agreed well at high doping levels (-0.7 V < E < 0.4 V) but diverged in the intermediate potential range where the current in the first type of experiment (fixed $\Delta E = 10$ mV) became too small to measure accurately. The higher potential differences across the film in the second type of experiment (and thus higher currents) allowed us to extend the measurements to lower conductivities.

Results and Discussion

Monomer Synthesis. Compound **3** was obtained in 22% yield by treating cyclopenta[2,1-*b*:3,4-*b'*]-dithiophene-4-one (**1**) with 3 equiv of Lawesson's reagent under a nitrogen atmosphere (12 h reflux in benzene) (Scheme 1). Our original intention here was to prepare cyclopenta[2,1-*b*:3,4-*b'*]dithiophene-4-thioketone, which has been predicted to form a low band gap polymer with good n-type conductivity.[27] However, this compound was not detected in the reaction mixture. The formation of **3** was expected since a similar dimer is obtained from fluorenone, in addition to the thioketone.[28]

Scheme 1



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Electrochemistry of the Monomer and Electrochemical Polymerization. Figure 1 shows cyclic vol-

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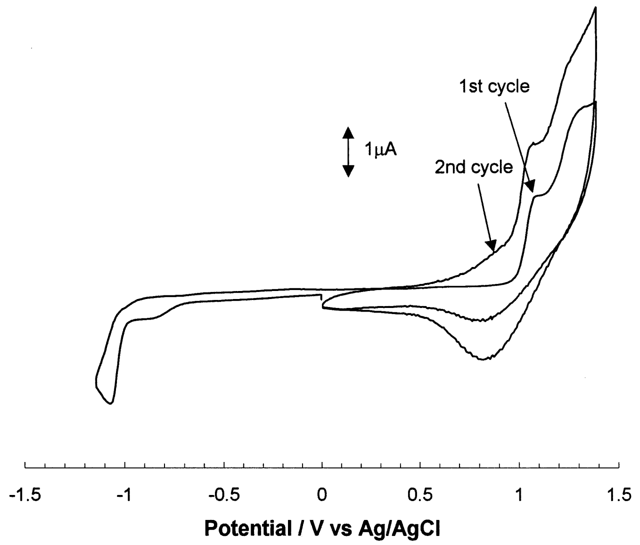

Figure 1. Cyclic voltammograms (100 mV s^{-1}) of **3** (<1 mM) in acetonitrile containing 0.01 M Bu_4NPF_6.

tammograms for the reduction and oxidation (first two cycles) of **3** at a Pt electrode. The cathodic cycle was performed first to avoid contamination of the electrode surface by the polymer formed during anodic cycling.

Reduction of **3** occurs at a peak potential of ca. −1.1 V and is preceded by a small pre-peak at ca. −0.9 V. During the first anodic cycle, oxidation waves are observed at peak potentials of +1.12 and +1.37 V. In the reverse scan, there is a reduction wave at ca. +0.80 V that can be attributed to the undoping (reduction) of polymeric material deposited on the electrode during the forward scan (see below). In the second cycle, both the oxidation and reduction currents are increased compared to the first cycle, and a new anodic wave appears at a lower potential (ca. +0.9 V). These observations are typical of conducting polymer formation on the electrode surface.[29]

Compared to bithiophene, which exhibits a formal potential for oxidation of ca. +1.3 V vs SCE,[15] **3** is significantly more easily oxidized ($E°' \sim 1.16$ V vs SCE). Thus, the bridging group at the 3−3′ positions of the bithiophene unit in **3** is seen to increase the energy level of the HOMO. This is in contrast to the effects of the ketone and dicyanoethene bridging groups of **1** and **2**, which have little influence on the HOMO energy of bithiophene.[21] The electron-withdrawing effects of these groups may offset any increase in the HOMO energy that would be caused by the bridging group, although it is more likely that the increase in HOMO energy in **3** is due to its delocalization over the two linked bithiophene units. Indeed, the two oxidation waves observed for **3** in Figure 1 indicate that the two bithiophene units are oxidized sequentially and that there are strong electronic interactions between them.

The formal potential for reduction of **3** (ca. −1.1 V) is much less negative than for bithiophene (−2.2 V vs SCE) and between the values of −1.2 and −0.8 V for **1** and **2**, respectively.[21] Thus, the substantial lowering of the LUMO energy produced by the sp^2-bridging group is observed even in the absence of an electron-withdrawing substituent.

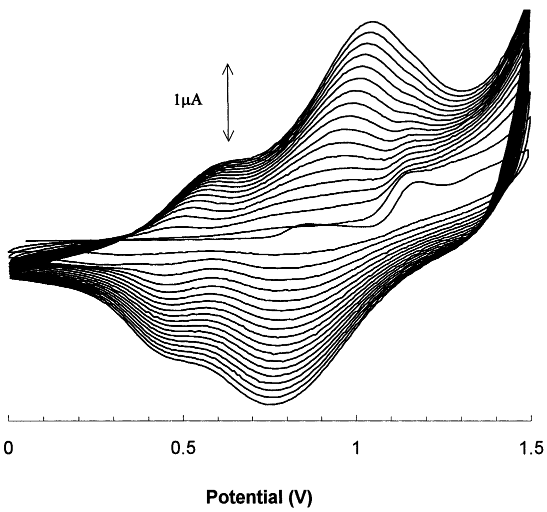

Figure 2. Cyclic voltammograms (100 mV s^{-1}) recorded during the formation of a poly-**3** film on a Pt electrode under potential cycling conditions from 5 mM **3** in nitrobenzene containing 0.01 M Bu_4NPF_6. Currents increased during cycling.

From the difference in the peak potentials for oxidation and reduction of **3**, its electrochemical HOMO−LUMO gap can be estimated to be ca. 2.2 eV. Both the HOMO and LUMO shifts of **3** relative to bithiophene lead to a reduction in the HOMO−LUMO gap and make **3** one of the lowest HOMO−LUMO gap precursors for conducting polymers reported to date.

Poly-**3** films were prepared for further characterization by the potential cycling method, as illustrated in Figure 2 (see Experimental Section for details). Since **3** is not very soluble in acetonitrile (solubility <1 mM), its electrochemical polymerization was performed in nitrobenzene. Continuous potential cycling between 0 and +1.5 V results in a steady increase in the polymer waves at ca. +0.55 and +0.9 V. Following such experiments, a brown film is observed coating the electrode.

Constant potential and constant current polymerization were also tried, but both failed to produce sustained growth of good quality films. At constant potential, the polymer growth rate decayed rapidly with time, while at constant current the potential rapidly rose to values that caused oxidative degradation of the film.

Electronic Absorption Spectroscopy. UV−vis absorption spectroscopy of **3** (Figure 3, curve A) was carried out in acetonitrile. **3** exhibits a strong $\pi-\pi^*$ absorption with a maximum at 380 nm (3.26 eV) and an onset of ca. 440 nm (2.8 eV). These values indicate that the HOMO−LUMO gap for **3** is ca. 0.8 eV lower than that of bithiophene ($\lambda_{max} = 302$ nm (4.1 eV)[30]). This is somewhat lower than the difference of 1.3 eV (2.2 eV for **3** and 3.5 eV for bithiophene) estimated by cyclic voltammetry.

Also shown in Figure 3 (curve B) is an electronic absorption spectrum of a poly-**3** film that had been electrochemically deposited on an indium/tin oxide coated glass slide and then held at 0 V for 2 min to ensure that it was in the undoped state. From the onset

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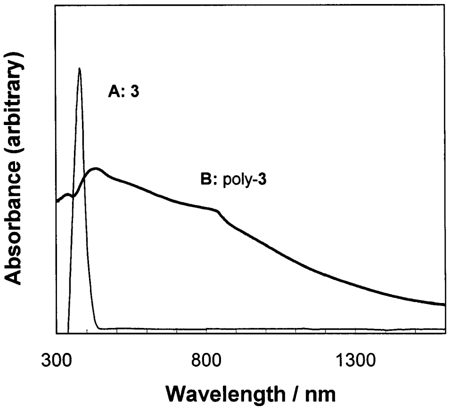

Figure 3. Electronic absorption spectra of **3** in acetonitrile and a poly-**3** film on an indium/tin oxide electrode.

of absorption of >1600 nm, a band gap of <0.8 eV is obtained. This band gap is much lower than that of polythiophene (2.2 eV)[10] and comparable to that of poly-**2**, making poly-**3** one of the lowest band gap conducting polymers reported to date.

The very low onset of absorption of poly-**3** indicates that it is a highly conjugated material. On the basis of both experimental and theoretical studies of polythiophenes and other conjugated polymers, it is known that there is a linear correlation between the position of the electronic absorption band and the inverse of the conjugation length of the polymer.[31] The slope of $\pi-\pi^*$ energy gaps vs $1/n$ (where n is the number of rings in the conjugated chain) is similar for thiophene (3.9 eV) and pyrrole (3.7 eV). We can reasonably use these values (in this case the thiophene value) to estimate conjugation lengths in new materials. From the onset of the absorbance of poly-**3** (<0.8 eV from Figure 3, curve B) and the onset of absorption of **3** (2.8 eV from Figure 3, curve A, $n_3 = 2$), the conjugation length ($n_{\mathrm{pol}} = 3.9/(3.9/n_3 + \Delta E_{\mathrm{pol}} - \Delta E_3)$) is found to be infinite. In other words, the decrease in band gap in going from **3** to poly-**3** is within experimental error of the decrease observed on going from bithiophene to polythiophene of effectively infinite conjugation length. In practical terms, this means that it can reasonably be concluded that n_{pol} for poly-**3** is >20.

If, on the other hand, the peak absorbances from Figure 3 are used in this calculation (3.26 eV for **3** and 3.02 eV for poly-**3**), the conjugation length appears to be only 2.3 (1.1 repeat units of **3**). This indicates that a wide range of conjugation lengths are present in the film, and this is consistent with the way in which **3** would be expected to polymerize (Figure 4). Thus, extended polymerization at the 5-positions of rings A and B (defined as the more extensively coupled bithiophene segment of each monomer unit) would be expected to produce highly conjugated chains, while growth of side chains at rings C and/or D would be expected to be sterically restricted, producing shorter conjugated chains. The prominence of the peak at 410 nm in the spectrum of poly-**3** (Figure 4) suggests that the polymer is primarily linear and that most of the pendent segments (rings C and D) are monomeric (i.e., $R_C = R_D = H$).

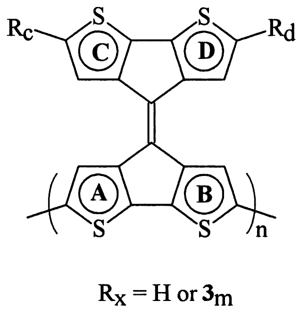

Figure 4. Expected structure of poly-**3**.

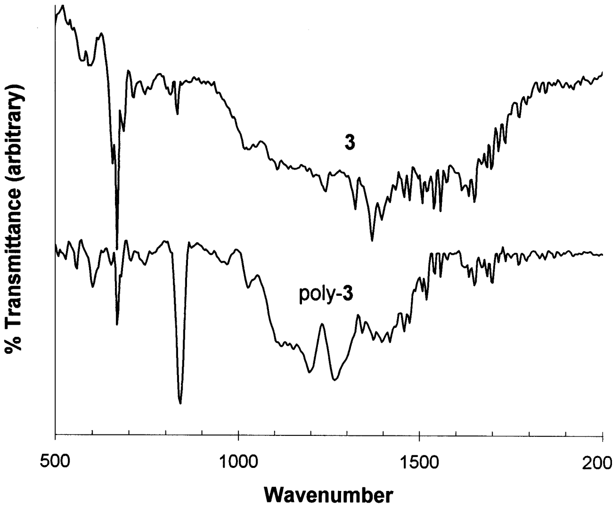

Figure 5. IR spectra (KBr disks) of **3** and poly-**3**.

The electronic absorption spectrum of poly-**3** provides very strong evidence that electrochemical oxidation of **3** does indeed produce a highly conjugated polymer on the electrode surface. It can be inferred from the spectrum that the monomer unit remains intact in the polymer, that the linkages are predominantly at the 5-positions, and that the polymer is not highly defective. If any of these conclusions were not true, it would be impossible to reasonably explain the strong absorbance of poly-**3** extending to wavelengths above 1500 nm.

IR Spectroscopy. Figure 5 shows IR spectra of **3** and poly-**3.** The spectra are broadly similar, indicating that the polymer has similar structural features to the monomer. However, there are significant differences that are consistent with the expected mode ($\alpha-\alpha'$) of polymerization.[32] The new band at 1195 $\mathrm{cm^{-1}}$ can be assigned to inter-ring C−C bonds between monomer units and is consistent with coupling at the α-positions. The common band at 667 $\mathrm{cm^{-1}}$ is probably the "out-of-plane" mode of the $C_\alpha-H$ bonds.[32] Its decrease in relative intensity with polymerization is again consistent with $\alpha-\alpha'$ coupling. The new intense band at 840 $\mathrm{cm^{-1}}$ in the polymer is due to the dopant ion, PF_6^-.

The absence of any strong bands in the1700−1800-$\mathrm{cm^{-1}}$ region for the polymer indicates that there has not been significant overoxidation during its synthesis. Overoxidation would lead to nucleophilic attack of water at the β-positions of the thiophene rings and the creation of carbonyl defects.[33]

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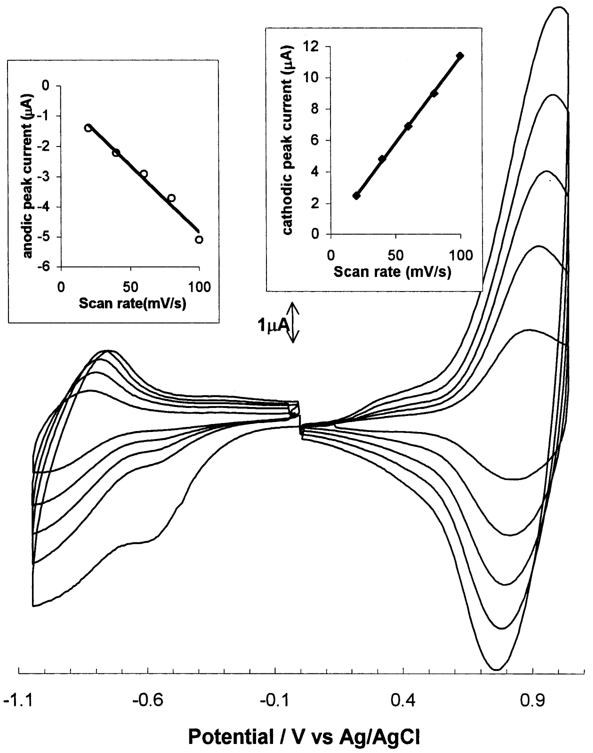

Figure 6. Cyclic voltammograms (10−100 mV s^{-1}) of a poly-**3** coated Pt electrode in acetonitrile containing 0.01 mol dm^{-3} Bu_4NPF_6.

Electrochemistry of Poly-3 Films. Cyclic voltammograms of a poly-**3** coated Pt electrode at various sweep rates in monomer-free acetonitrile containing 0.01 M Bu_4NPF_6 are shown in Figure 6. p-Doping of the polymer film is observed as a reversible wave in the 0 to +1.10 V region, while n-doping appears as a broader and less reversible wave in the 0 to −1.1 V region. Peak currents for both waves increase approximately linearly with increasing potential sweep rate (see insets in Figure 6), indicating that they correspond to rapid surface processes.

The formal potentials for the main p-doping and n-doping processes, from Figure 6, are ca. +0.9 and −0.9 V, respectively. The difference of $\Delta E_{\text{pol}} \sim 1.8$ eV corresponds to a conjugation length ($n_{\text{pol}} = 3.9/(3.9/n_3 + \Delta E_{\text{pol}} - \Delta E_3)$ with $\Delta E_3 \sim 2.2$ eV) of ca. 2.5, which is consistent with the value obtained from the peak in the electronic absorption spectrum. The onsets of p-doing and n-doping are ca. +0.2 and −0.3 V, respectively, corresponding to a band gap of ca. 0.5 eV and a conjugation length of ca. 16, which is consistent with the result from the onset of electronic absorption. Given the difficulty of accurately determining onset potentials and wavelengths, the agreement with the optical band gap (<0.8 eV) is good. Thus, both the optical and electrochemical results indicate that poly-**3** consists of reasonably long conjugated chains, with shorter side chains. There are also likely to be some cross-links, but their existence (or not) cannot be established from the optical and electrochemical data.

In Situ Conductivity Measurements. In situ conductivity measurements were made by a dual-electrode sandwich technique in which a porous gold film evaporated over a polymer film on a Pt electrode acts as a second electronic contact.[25] Figure 7 shows cyclic voltammetry of a film used in one such experiment, together with a plot of conductivity vs potential obtained from dual-electrode voltammetry. The range of the initial voltammogram was restricted to avoid possible degradation of the film before the conductivity measurements.

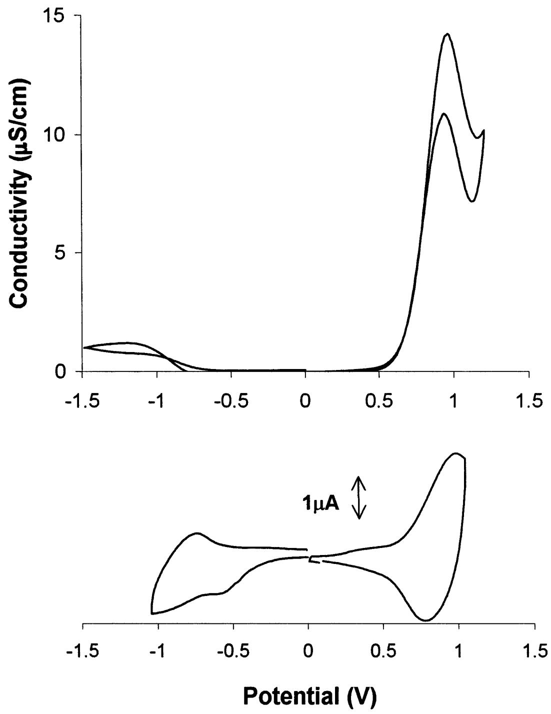

Figure 7. Cyclic voltammograms (100 mV s^{-1}) and in situ conductivity as a function of potential (in acetonitrile containing 0.01 mol dm^{-3} Bu_4NPF_6) for a poly-**3** film sandwiched between a Pt disk electrode and a porous gold film. Conductivity data were obtained with a fixed 10 mV potential difference between the Pt and Au contacts to the film.

In Figure 7, the p-type conductivity of the polymer rises to a maximum of ca. 1.4×10^{-5} S cm^{-1} at +0.98 V. On the reverse scan, the conductivity peak occurs at approximately the same potential, but is 25% lower, indicating some instability of the film at high potential. The n-type conductivity, observed in the negative scan, is ca. 10 times smaller than the p-type conductivity, peaking at 1.2×10^{-6} S cm^{-1} at ca. −1.1 V. This is consistent with the high p-type/n-type conductivity ratios observed for poly(3-methylthiophene)[34] and poly-**2**.[35]

The conductivity of poly-**3** is much lower than those observed for polylthiophene and poly-**2**, which have reported maximum p-type conductivities of 0.1 and 0.6 S cm^{-1},[35,36] respectively. Since the doping levels of all three polymers are similar, the mobility of charge carriers must be very low in poly-**3**. This may be due to a greater rigidity in the polymer, due to cross-linking, which would inhibit interchain electron hopping. It may also be due to a larger average interchain distance caused by the larger size of the monomer unit and inefficient packing of the branched polymer chains.

Log plots of conductivity vs potential, obtained from an experiment in which the potential of the gold contact

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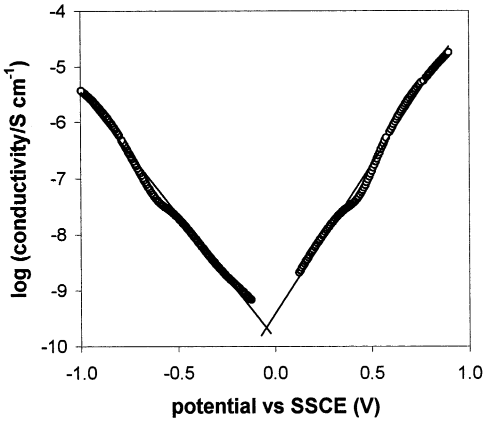

Figure 8. Log plot of in situ conductivity as a function of potential (in acetonitrile containing 0.01 mol dm^{-3} Bu_4NPF_6) for a poly-**3** film sandwiched between a Pt disk electrode and a porous gold film. The gold film was maintained at 0 V vs SSCE in this experiment.

was maintained at 0 V (vs SSCE) while the potential of the Pt disk was scanned (from 0 to +0.9 V and then from 0 to −1.0 V), are shown in Figure 8 (the somewhat higher conductivities observed in this experiment relative to those in Figure 7 are within the normal range of variation seen for electrochemically prepared films). The approximately exponential increases in conductivity as the polymer is p-doped (i.e., as the potential is increased from ca. −0.05 V) or n-doped (decreasing potential) are typical of conjugated polymers.[35,37,38] The intercepts of lines through these two regions of the log plot in Figure 8 give an approximate measure of the polymer's intrinsic conductivity.[35] The value of 2×10^{-10} S cm^{-1} is similar to the intercept (1.0×10^{-9} S cm^{-1}) obtained for poly-**2**,[35] a similar polymer with a similar band gap (0.8 eV). In that case the intercept method used here (because we could not obtain accurate conductivity values in the potential range of ca. ± 0.1 V) underestimates the intrinsic conductivity by about an order of magnitude, and so the intrinsic conductivity of poly-**3** is probably closer to 10^{-9} S cm^{-1}.

The band gap (E_g) of poly-**3** was estimated from the conductivity data using the equation for thermal excitation of a semiconductor, $C_{p,\text{intrinsic}} \sim 4.2 \times 10^{-5}$ exp($-E_g/2kT$).[39] This method has been shown to be accurate for poly-**2**[35] and copolymers of **2** with 3,4-ethylenedioxythiophene.[40] The concentration of thermally excited p-type charge carriers, $C_{p,\text{intrinsic}}$, was estimated to be ca. 10^{-8} mol cm^{-3} from the ratio of the intrinsic conductivity ($\sigma_{\text{intrinsic}} \sim 2 \times 10^{-10}$ S^{-1} cm^{-1}) to the maximum p-type conductivity ($\sigma_{p,\max} = 1.8 \times 10^{-5}$ S cm^{-1}) and an estimated maximum p-doping level ($C_{p,\max}$) of ca. 10^{-3} mol cm^{-3} (i.e., $C_{p,\text{intrinsic}} \sim \sigma_{\text{intrinsic}}C_{p,\max}/\sigma_{p,\max}$).[35] This analysis yields a band gap of ca. 0.4 eV, which is consistent (within experimental error) with the electrochemical (0.5 eV) and optical (<0.8 eV) band gaps.

Conclusions

The conjugated bridge between the bithiophene units in structure **3** causes a substantial lowing of the HOMO−LUMO gap relative to bithiophene and significant decreases relative to other bridged bithiophenes, such as **1** and **2**. This in turn leads to a lowering of the band gap of the conjugated polymer formed by electrochemical polymerization. The band gap of poly-**3** is ca. 0.5 eV, while the band gaps of polybithiophene, poly-**1**, and poly-**2** are ca. 2.2, 1.2, and 0.8 eV, respectively. Unfortunately, the lower band gap of poly-**3** does not translate into a higher intrinsic conductivity, relative to poly-**2**, because the mobility of charge carriers is lower. Nevertheless, the very low HOMO−LUMO gap of **3** together with its four linkable thiophene terminals may make it a useful component for cross-linking low band gap systems and of value as a building block for molecular electronic systems.

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