An Electrochemically Prepared Small-Bandgap Poly(biheteroarylidenemethine): Poly{bi[(3,4-ethylenedioxy)thienylene]methine}

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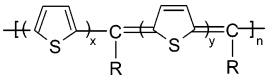
ABSTRACT: The electrochemical polymerization of bis(2-thienyl)methanes carrying substituents either on the methylene carbon or on the thiophene rings is reported. Poly(dithienylenemethylene)s are formed which undergo in-situ dehydrogenation to poly(dithienylenemethine)s. Bis(3,4-ethylenedioxythienyl)-methane gave a very low-gap material (0.4 V onset-based bandgap). This value is much lower than those previously reported for chemically prepared materials having the same conjugated backbone but carrying different substituents. The unsubstituted bis(2-thienyl)methane gives a similar low-gap polymer as well, but overoxidation and probably misjunction defects are present. No polymer was formed in the case of 2,2′-bis(2-thienyl)propane, for which the possibility of producing a conjugated polymer is precluded by the lack of at least one hydrogen atom on the carbon bridging the thiophene units. Full electrochemical and optical characterization data for the polymers are reported, and the polymerization and p- and n-doping processes are discussed.

Introduction

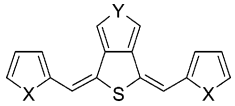
The basic design of polyconjugated heterocyclic materials has been traditionally developed along lines which involve the direct conjunction of the α and α′ positions of five-membered heteroarenes having different levels and typologies of substitution. Alternatively, systems endowed with conjugative properties are inserted between heterocyclic units (either identical or different), with variable intercalation periods. In 1986, Jenekhe first devised a strategy for the design of new heterocyclic electroactive materials, which was founded on the consideration that conjugation can be maintained by interposing a methine group between pairs of heterocyclic units, according to the general structure reported in Scheme 1 for thiophene-based polymers.[1] These materials would constitute, in theory, a class of small-bandgap conducting polymers, since quinoid moieties are incorporated in the conjugated backbone.

A rather ample series of compounds with different block sizes was chemically prepared through a synthetic scheme involving nonconjugated poly(thienylenemethylene)s as precursors which were dehydrogenated with bromine to the corresponding poly(thienylenemethine)s. Wudl carefully reexamined the experimental work, giving evidence that these materials were actually *doped* since containing bromine bonded covalently and ionically.[2] DDQ dehydrogenation of poly(thienylenemethylene)s gave poly(heteroarylenemethine)s which were fully characterized chemically, spectroscopically, and electrochemically.[3] Some of these conjugated materials were found to have a bandgap as small as 1.14 eV and intrinsic conductivities of about 10^{-3}−10^{-1} S/cm. More recently, Hanack tried an electrochemical approach to this kind of material by anodic oxidation of a series of bis(heteroaryl)arenemethylidenes having the general structure reported in Scheme 2.[4] Detailed spectroelectrochemical investigations demonstrated that regioregular α−α-linked oligomeric materials were obtained, with a rather high 1.8−2.1 eV bandgap. Short chain lengths were attributable to the stability of the monomeric radical cations formed in the first electrochemical oxidation step, due in turn to the extended π-electron system of these compounds. Additional effects leading to higher bandgaps and a bad film quality were related to the high anodic potentials required to effect the oligomerization process.

Scheme 1. General Structure of Poly(thienylenemethine)s



Scheme 2. Hanack's Bis(heteroaryl)arenemethylidenes



X = S, NCH_3

Y = S, CH=CH

We considered that monomeric units capable of generating such polymers through an oxidative process could also possess the basic structure of the bis(2-thienyl)methane (**1a**) bearing at least one oxidatively removable hydrogen atom on the carbon atom bridging the heterocyclic units.

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These monomers are simple and accessible, but the strategy of their electroxidative polymerization to obtaining poly[(bithienylene)methine]s had been probably discarded on the basis of the consideration that a forecasted breakdown was the high value of their electrochemical oxidative potential. Exploring this strategy was the aim of the present work.

Results and Discussion

As expected, we found that bis(2-thienyl)methane (**1a**), prepared according to the literature,[5] displayed on oxidation peak potential $E_p = 1.40$ V a quite high value in comparison to that ($E_p < 0.9$ V) exhibited by thiophene-based monomers able to produce materials reasonably devoid of misjunction and overoxidation defects. We found that the polymerization of **1a** occurred when working in concentrated (typically 0.05 M) acetonitrile solution in the presence of 0.1 M Bu_4NClO_4, either by potential cycling over the oxidation peak, or in a potentiostatic oxidation at 1.3 V. The CV of thin films (storing reversible charges Q_r lower than 2 mC cm^{-2}) of poly(**1a**) in monomer-free solution displayed reversible oxidation and reduction processes at $E° = -0.1$ and -1.1 V, respectively, pointing to an energy gap as low as 1 eV, while in the case of relatively thick films (typically $Q_r = 5$ mC cm^{-2}) the CV displayed the oxidation process characterized by a very strong separation (ca. 0.5 V) of anodic and cathodic peak potentials, suggesting that some degradative process had occurred. Poly(**1a**) was found insoluble in the common organic solvents. The UV−vis spectrum of the undoped film showed a long tail with a shoulder at 400 nm, while the blue oxidized form showed absorption maxima at 490 and 620 nm. Structurally significant data were drawn from the FTIR spectrum of oxidized poly(**1a**), which was characterized by a strong band at 1670 cm^{-1} and by a very strong one at 1410 cm^{-1}, the former due to carbonyl functions resulting from overoxidation and the latter attributable to skeleton vibrational modes. A marked decrease of the C−H deformation band at 700 cm^{-1} present in the monomer and the appearance of a strong one at 810 cm^{-1} were in agreement with an oxidative coupling at the α-positions. Very strong were found also the perchlorate bands. The spectrum of undoped poly(**1a**) was dominated by the C−H bending band at 805 cm^{-1} and by the above-mentioned bands shifted to 1620 and 1430 cm^{-1}. Very similar findings were obtained in the case of known 1,1′-bis(2-thienyl)ethane (**1b**), prepared according to the literature,[6] which gave a material, in which the presence of overoxidation defects were still evident.

Interestingly, no polymer was formed on the electrode surface in the case of 2,2′-bis(2-thienyl)propane (**1c**), as expected when considering that the possibility of producing a conjugated polymer from (**1c**) was precluded by the lack of at least one hydrogen atom on the carbon bridging the thiophene units. Monomer **1c** was prepared by lithiation of **1b** at the methylenic carbon, followed by quenching of the anion with iodomethane.

Even though the electrical properties of the polymeric materials obtained from **1a** and **1b** were modest when compared to those exhibited by many popular polyheterocyclic materials, we found these results encouraging, since they suggested that high-quality poly[(bi[thienylene)methine]s were really accessible through this route, provided that electron-richer monomers would be employed.

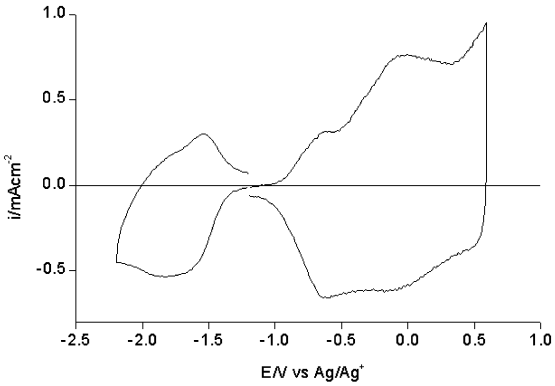
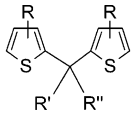


Figure 1. Cyclic voltammogram for oxidation and reduction of poly(**1d**) in acetonitrile solution in the presence of 0.1 M Bu_4NClO_4. Scan rate: 0.1 V s^{-1}.

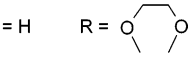
Scheme 3. Bis(2-thienyl)methane Monomers



1a R = R' = R" = H

1b R = R' = H R" = Me

1c R = H R' = R" = Me

1d R' = R" = H R = 

We planned introducing efficient electron-releasing substituents on the heterocyclic moieties, and we chose to use the substitution typology present in the 3,4-ethylenedioxythiophene (EDOT), one of the electron-richest thiophene monomers available ($E_p = 1.04$ V),[7] and the substrate designed for testing was the bis[2-(3,4-ethylenedioxy)thienyl]methane (**1d**) (Scheme 3). Great advantages of this design were related to the fact that the α regioselectivity of the polymerization was assured, and no sites where left available where overoxidation processes could occur.

The synthesis of **1d** was achieved by reaction of the lithium anion of commercially available EDOT with diiodomethane. Overall yields are modest (30%), but the synthesis is simple and straightforward.

The voltammogram of **1d** in acetonitrile in the presence of 0.1 M Bu_4NClO_4 displayed an irreversible oxidation peak at $E_p = 1.02$ V, i.e., at a much lower potential than unsubstituted bis(2-thienyl)methanes **1a**−**c**. Polymerization occurred easily even if diluted solutions ($(2-5) \times 10^{-3}$ M) were employed, and rather thick films of poly(**1d**) (up to some micrometers) could be deposited. EQCM analysis showed that the electrochemical deposition occurred with a linear increase in mass in relationship with the deposition charge. The CV of the polymeric film in monomer-free solution displayed a twin reversible oxidation process with $E° = -0.6$ and 0.0 V (Figure 1). The CV was found stable up to a switching potential of 0.8 V. The polymer can also be n-doped, with partial reversibility, at $E° = -1.60$ V (Figure 1). The charge involved in the reduction process is roughly the 50% of that used in the oxidative cycle. The $E°$ values of poly(**1d**) are negatively shifted (by 0.5 V) from those of poly(**1a**), in agreement with the electron-richer character of 3,4-ethylenedioxythiophene in comparison with thiophene.

From these data it can be inferred that poly(**1d**) is a low-gap polymer, with an electrochemical energy gap

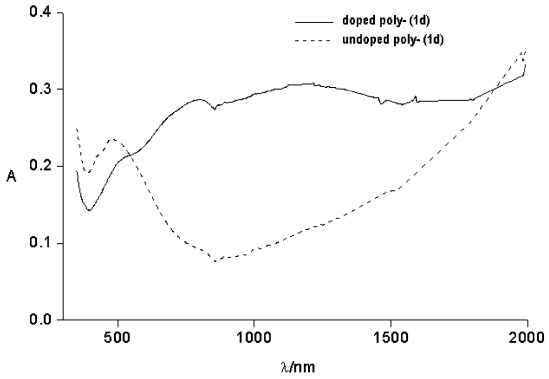


Figure 2. UV−vis−NIR spectrum of undoped (- - -) and oxidized (—) poly(**1d**) on ITO.

$\Delta E°$ of 1.0 eV (based on the $E°$ values). The CV onsets are found at −0.95 V (oxidation) and −1.35 V (reduction), with an onset-based gap of 0.4 eV. This value is much lower than the lowest onset-based gap values (1.3 eV) exhibited by Jenekhe's PBTPQ series of polymers, alternating α,α′-bithiophene, and phenyl-substituted methine moieties.[3] This outstanding difference might be attributed to a severe distortion of the conjugated chain from planarity produced in PBTQs by steric interactions due to the aryl rings located on the methinic carbons.

Poly(**1d**) was found insoluble in the common organic solvents.

The FTIR spectrum of oxidized poly(**1d**) was characterized by four strong bands between 1490 and 1360 cm^{-1}, present also in the monomer, attributable to skeleton vibrational modes, and an additional strong and large band at 1100 cm^{-1}, resulting from the superimposition of the band due to perchlorate anion (accompanied by a band at 620 cm^{-1}) and EDOT's bands (1180 and 1070 cm^{-1} in the monomer). As expected, the α-aromatic CH stretching band at 3100 cm^{-1} was absent. No significant bands in the 1700−1600 cm^{-1} region were observed, indicating that overoxidation processes did not occur.

The UV−vis−NIR spectrum (Figure 2) of the oxidized blue polymer film showed a strong absorption extending into the infrared region with a broad maximum at 1200 nm, while the undoped, brownish-gray, air-sensitive form was characterized by a broad absorption with maximum at ca. 500 nm covering the whole range, confirming that poly(**1d**) is a very small-gap material.

The positive charge stored in the polymer at 0.8 V, determined by EQCM in acetonitrile solution in the presence of 0.1 M Bu_4NClO_4, corresponded to one electron per repeating unit. Also, the reversible oxidation process occurred with a linear relationship between mass and charge increase; the slope corresponded to 75 g mol^{-1} (uptake of about one perchlorate anion per electron).

The evaluation of conductivity was performed in situ with the microband electrode. A redox-like conduction, with a peak of 1×10^{-3} S cm^{-1} at around 0.0 V, corresponding to the second redox potential of the oxidation scan, was found (Figure 3a). The relationship between conductivity and charge showed a bell-shaped relationship with the maximum at 0.75 electrons per repeating unit (Figure 3b). The low value of the maximum conductivity was in line with those measured for I_2-doped poly(thienylenemethine)s (10^{-1}−10^{-3} S cm^{-1}),[3]

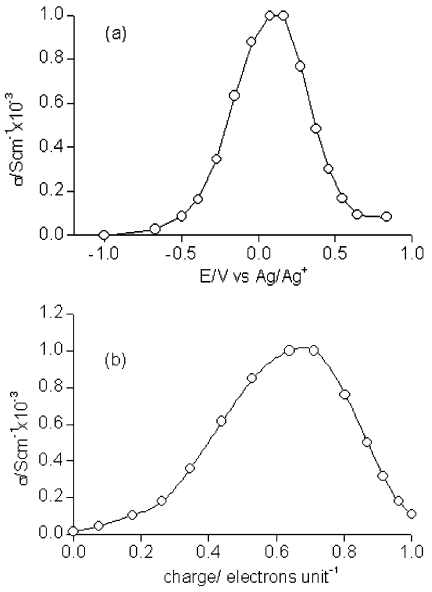


Figure 3. In-situ conductivity (a) vs potential and (b) vs charge of poly(**1d**) in acetonitrile solution in the presence of 0.1 M Bu_4NClO_4.

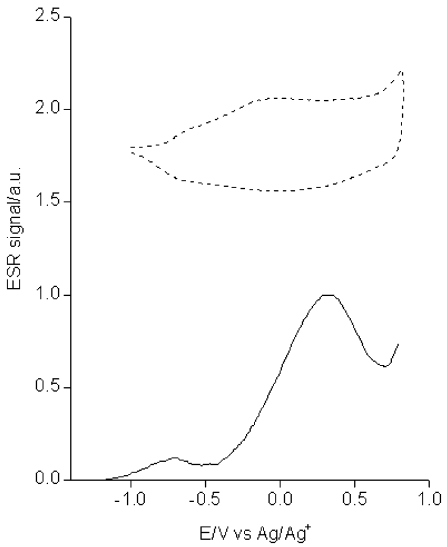
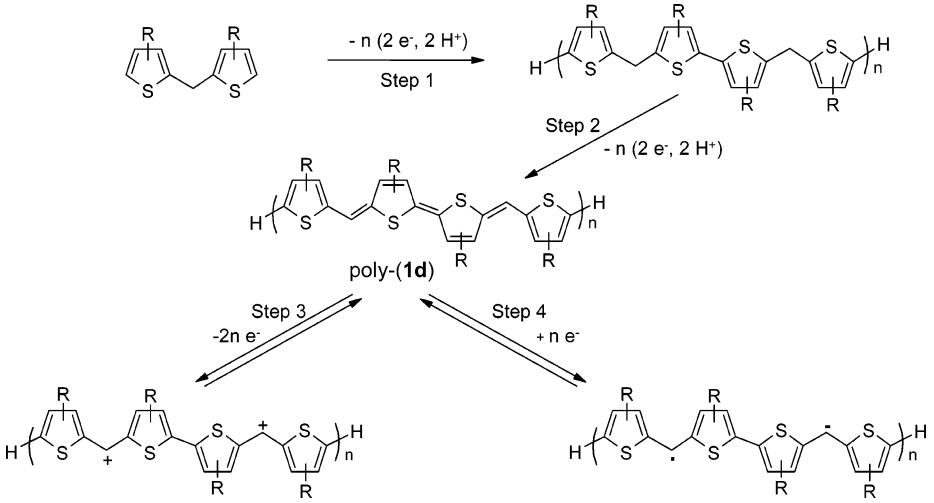


Figure 4. In-situ ESR vs potential of poly(**1d**) in acetonitrile solution in the presence of 0.1 M Bu_4NClO_4.

which in turn is much lower than that found in the case of poly(thienylene)s. A redox-type conduction mechanism or charge localization might be possible explanations for this behavior. As for the low conductivity of poly(**1d**) (despite the small bandgap) in comparison to that exhibited by the parent polyheterocycles, the main problem is related to the narrow bandwidth of these materials. Special applications not requiring high-conductivity properties should be envisaged.

ESR measurements performed in situ during the oxidative scan gave two signals in rough correspondence with the two redox potentials (Figure 4). The more intense signal, with $g = 2.0035$, quite similar that found in the case of PEDOT, occurs at the second redox process, and it is low (0.04 spins per electron). That occurring at the first redox potential is about 10 times lower. The signals seem to be connected to the production of free spins during the processes of spin generation and dimerization, with a strong magnetic coupling reducing spin concentration.

Scheme 4. General Scheme of the Electrochemical Polymerization of Bis(2-thienyl)methanes and p- and n-Doping of the Polymers



Scheme 4 may account for the results reported above. After the usual α-coupling (step 1), a second two-electron oxidation process involves the two methylene groups of each dimeric subunit (step 2), with release of protons from the benzhydrilic carbons, made more acidic by the oxidation process. The resulting conjugated backbone, characterized by a sequence of aromatic and quinoid segments alternating regularly, is 2-fold degenerate in the ground state and is predicted to display a low gap, as found (1.2 eV vs 2.1 eV described for PT).[1,8−10] It can undergo either a two-electron reversible oxidation processes (step 3) or a one-electron reversible reduction reaction (step 4). Positively and negatively doped polymers are represented in Scheme 3 only by structures characterized by aromatic thiophene rings and by charge defects localized on benzhydrilic-type carbons, which are the most suitable sites to host charges, even though electronic delocalization is ample and many alternative mesomeric structures are imaginable. This situation could be in agreement with the charge localization hypothesis put forward before.

Conclusions

The advantages of the route reported in this paper for acceding to poly(thienylenemethines) are the accessibility of the starting monomer **1d**, the electrooptical properties exhibited by the resulting polymer, related to its low gap, and the possibility that this strategy offers from a synthetic point of view of preparing new materials carrying specific functions on the methinic carbon. In particular, it opens interesting perspectives to the preparation of functionalized polymers containing the EDOT moiety, which does not have free sites for introducing substituents.

Experimental Section

Materials and Reagents. The solvents used in the reactions were dried by conventional methods and freshly distilled under nitrogen. Acetonitrile was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte Bu_4NClO_4 was previously dried under vacuum at 70 °C. All other chemicals were reagent grade and used as received. Bis(2-thienyl)methane (**1a**)[5] and 1,1′-bis(2-thienyl)ethane (**1b**)[6] were already known in the literature and were prepared according to the reported procedures. 2,2′-Bis(2-thienyl)propane (**1c**) and bis[2-(3,4-ethylenedioxy)thienyl]methane (**1d**) were prepared according to the procedures described below.

2,2′-Bis(2-thienyl)propane (**1c**). A 1.6 N solution of butyllithium (0.25 mL) was added to a solution of **1a** (0.060 g) in dry THF (1 mL) and DMSO (1 mL) at −10 °C, under stirring, in a nitrogen atmosphere. Iodomethane was added (0.047 g), and the mixture was maintained at 0 °C for 1 h; then the procedure of the addition of butyllithium (0.25 mL) and iodomethane (0.047 g) was repeated. After the usual workup the crude product was purified by column chromatography (silica gel; hexane) to give **1c** as a colorless oil (53%). ^{1}H NMR (δ, $CDCl_3$): 1.9 (6 H, s, 2 CH_3), 6.9 (2 β and 2 β' H, m), 7.2 (2 α H, dd).

Bis[2-(3,4-ethylenedioxy)thienyl]methane (**1d**). A 1.6 N solution of butyllithium (13.2 mL) was added to a solution of EDOT (3.0 g) in dry THF (10 mL) at −50 °C, under stirring, in a nitrogen atmosphere. Diiodomethane was added (0.85 mL) at −20 °C after 30 min. The mixture was left to react at 0 °C for 3 h. After the usual workup the crude product was purified by column chromatography (silica gel; 1:1-dichloromethane: hexane) to give **1d** as a cream-colored solid with mp 109 °C (i-PrOH) (27%).^{1}H NMR (δ, $CDCl_3$): 4.0 (2 H, s, CH_2), 4.16−4.21 (8 H, m, 2 OCH_2-CH_2O), 6.15 (2 α H, s). MS (EI): 296 *m*/*z*.

Electrochemical Apparatus and Methods. Experiments were performed at room temperature in three electrode cells under nitrogen. The counter electrode was platinum; the reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. The working electrode for cyclic voltammetry was a platinum minidisk electrode (0.003 cm^2). For electronic spectroscopy a 0.8 × 2.5 cm indium−tin oxide (ITO) sheet (ca. 20 ohm/square resistance, from Balzers, Liechtenstein) was used.

Electronic spectra were taken with a Perkin-Elmer Lambda 9 spectrometer, and IR spectra were taken on a Perkin-Elmer 2000 FTIR spectrometer. ESR spectra were taken on a Bruker ER 100D following the procedure previously described.[11] Absolute spin calibration was performed with VOSO4.5 H2O crystals, and *g*-value calibration was performed with thin films of DPPH ($g = 2.0036$).[12]

The apparatus and procedures used for the in-situ conductivity experiments were previously described in detail.[12] The electrode for conductivity measurements was a microband array platinum electrode (5 μm bandwidth, 100 nm thick) with interband spacing of 5 μm. The deposit was thick enough to ensure minimum resistance, under which condition the conductivity σ is given by $\sigma = k/(R - R_0)$, where R is the measured resistance, R_0 the lead resistance (100 ohm), and k the cell constant (0.2 cm^{-1}).

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a gold-coated AT-cut quartz electrode (0.2 cm^2), resonating at 9 MHz, onto which the polymers were deposited (typically 10−20 $\mu g\ cm^{-2}$). The oscillator circuit was homemade,[13] and the frequency counter was a Hewlett-Packard model 5316B. Calibration of the quartz crystal microbalance was performed with silver deposition from a 10^{-2} M solution of $AgNO_3$ in acetonitrile + 0.1 M Bu_4NClO_4. Data were collected by a microcomputer with homemade analyzing software by which frequency changes $\Delta\nu$ were monitored as mass changes Δm.

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Supporting Information Available: Cyclic voltammogram of poly(**1a**) and poly(**1d**); EQCM mass change of poly(**1d**) vs potential and vs charge. This material is available free of charge via the Internet at http://pubs.acs.org.

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