In Situ Conductivity of a Polythiophene from a Branched Alkoxy-Substituted Tetrathiophene. Enhancement of Conductivity by Conjugated Cross-Linking of Polymer Chains

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Anodic coupling of 2,3,5-tris(4-pentoxy-2-thienyl)thiophene (an α,α-coupled terthiophene thiophene branched at the central thiophene ring) produces a polyconjugated polymer with a linear structure segmented by the thiophene branches. The conductivity (15 S cm^{-1}), confined in a narrow potential window (0.3 V) by charge localization in tetrathiophene sequences, is strongly enhanced by occasional cross-linking in comparison with that of the polymer methyl-capped at the thiophene branches (0.02 S cm^{-1}).

Introduction

The production of polyconjugated polymers has mainly been concentrated on obtaining linear structures that could allow long conjugated sequences and hence high conductivity. In any case fast charge transport requires also easy interchain hopping so that connection between polymer chains is a crucial point for conductivity. As a part of our continuing study of the mediated intrachain charge hopping in conducting polymers,[1] we have addressed the action of conjugated links between polymer chains. To this end we considered nonlinear monomers that could give branched polymeric structures, choosing an α,α-coupled terthiophene thiophene branched at the central thiophene ring, namely, 2,3,5-tris(2-thienyl)-thiophene. Furthermore, to increase its reactivity to coupling and therefore obtain a long-chain polymer, we used substitution with alkoxy groups at the external 4 positions which make highly reactive the adjacent 5 positions.[2]

This paper reports the electrochemical polymerization of 2,3,5-tris(4-pentoxy-2-thienyl)thiophene (branched tetrathiophene, BT_4) and its methyl-capped homologue 2,5-bis(4-pentoxy-2-thienyl)-3-(4-pentoxy-5-methyl-2-thienyl)-thiophene ($MeBT_4$, Scheme 1), the characterization of the resulting polymers, and their in situ conductivity behavior. Comparison is made with the corresponding characteristics of the polymer from the parent nonbranched terthiophene 4,4′-dipentoxy-2,2′:5′,2′-terthiophene (ET_3, Scheme 1). The analogous nonsubstituted branched monomers have been previously produced and electrochemically coupled to polymer.[3,4] For the sake of completeness we also report the recent production of a branched polythiophene from 3′,3′-bis(terthiophene).[5]

Experimental Section

Chemicals and Reagents. Acetonitrile (AN) was reagent grade (Uvasol, Merck) with a water content <0.01%. The supporting electrolyte tetraethylammonium perchlorate (Et_4NClO_4) was previously dried under vacuum at 70 °C. The syntheses of 4,4′-dipentoxy-2,2′:5′,2′-terthiophene (ET_3) and of the relevant polymer were reported previously.[6] The other monomers were synthesized as described below. 5-Iodo-4-pentoxythiophene and 3-pentoxythiophen-5-boronic acid were prepared as previously reported.[6] 2,3,5-Triiodothiophene was prepared following the procedure reported in the literature.[7]

All reactions involving air- and water-sensitive materials were performed in dried glassware under argon. Air- and water-sensitive solutions were transferred with double-ended needles, and solvents were dried on potassium benzophenone-ketyl.

2-Iodo-5-methyl-4-pentoxythiophene. The compound was prepared from 5-iodo-4-pentoxythiophene in ethyl ether by reaction with LDA (lithium diisopropylamine) and quenching with MeI at −78 °C. The title compound was isolated in 80% yield and 100% purity because of an almost 100% metal−halogen exchange.[8]

^1H NMR ($CDCl_3$) δ (ppm) 6.90 (s, H_3); 3.90 (t, OCH_2); 2.24 (s, CH_3); 1.70 (m, CH_2); 1.39 (m, CH_2); 0.92 (t, CH_3). ^{13}C NMR ($CDCl_3$) δ (ppm) 153.16 (C_4); 127.64 (C_3H); 123.32 (C_5); 72.25 (OCH_2); 66.89 (C_2); 29.32, 28.07, 22.39 (CH_2); 13.97, 10.80 (CH_3).

2,3,5-Tris(4-pentoxy-2-thienyl)thiophene (BT_4). The compound was prepared by the Suzuki cross-coupling reaction[9]

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(1) Zotti, G.; Zecchin, S.; Schiavon, G.; Berlin, A.; Pagani, G.; Canavesi, A. *Chem. Mater.* **1995,** *7*, 2309.

(2) Heinze, J.; Dietrich, M. *Dechema Monograph.* **1990,** *114*, 125. Dietrich, M.; Heinze, J. *Synth. Met.* **1991,** *41−43*, 503.

(3) Visy, C.; Lukkari, J.; Kankare, J. *Macromolecules* **1993**, *26*, 3295.

(4) Visy, C.; Lukkari, J.; Kankare, J. *Macromolecules* **1994**, *27*, 3322.

(5) Tanaka, S.; Kumei, M. *J. Chem. Soc., Chem. Commun.* **1995**, 815.

(6) Zotti, G.; Gallazzi, M. C. Zerbi, G.; Meille, S. V. *Synth. Met.* **1995,** *73*, 217.

(7) Gronowitz, S.; Vilks, V. *Ark. Kemi,* **1963,** *21*, 191.

(8) Gallazzi, M. C.; et al., to be published.

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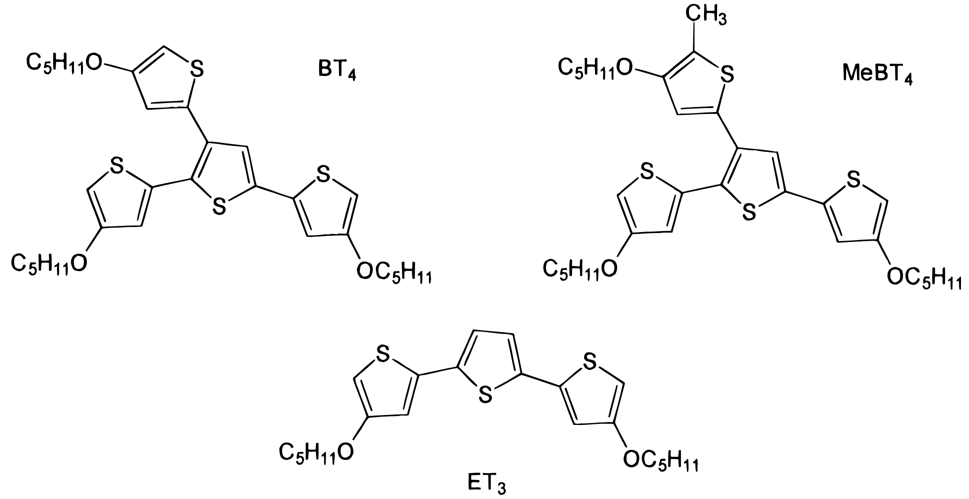
Scheme 1



as follows. A mixture of 2,3,5-triiodothiophene (8.46 g, 18.3 mmol), Pd(Ph$_3$P)$_4$ (0.64 g), and 1,2 DME (75 mL) was stirred under argon for 10 min. Then 3-pentoxythiophen-5-boronic acid (14.4 g, 67 mmol) and a water solution of 2 M NaHCO$_3$ (73 mL) were added simultaneously, and the mixture was refluxed overnight. The product was purified by flash chromatography on silica gel with 80:20 hexane−chloroform. Two fractions were collected. The second fraction consists of the title compound which was recrystallized from pentane as a yellow solid (60% yield).

^{1}H NMR (CDCl$_3$) aromatic region δ (ppm) 7.14 (s); 6.87 (d, J = 1.7 Hz); 6.84 (d, J = 1.75 Hz); 6.80 (d, J = 1.65 Hz); 6.23 (d, J = 1.7 Hz); 6.20 (d, J = 1.63 Hz); 6.15 (d, J = 1.66 Hz). ^{13}C NMR (CDCl$_3$) δ (ppm) 157.65; 157.23; 136; 135.5; 134.8; 133; 132.5; 130.05; 125.7; 119.93; 119.2; 116.41; 98.84; 97.7; 96.77; 70.1; 28.9; 28.16; 22.42; 13.99.

The first fraction consists of the product of partial substitution 3′-iodo-4,4′-dipentoxy-2,2′:5′,2′-terthiophene, which was isolated and recrystallized from pentane (30% yield).

^{1}H NMR (CDCl$_3$) aromatic region, δ (ppm) 7.13 (d, J = 1.59 Hz); 7.12 (s); 6.84 (d, J = 1.64 Hz); 6.28 (d, J = 1.7 Hz); 6.17 (d, J = 1.68 Hz).

2,5-Bis(4-pentoxy-2-thienyl)-3-(4-pentoxy-5-methyl-2-thienyl)thiophene (MeBT$_4$). The compound was synthesized by coupling the Grignard reagent of 2-iodo-5-methyl-4-pentoxythiophene (0.507 g, 1.63 mmol) and 3′-iodo-4,4′-dipentoxy-2,2′:5′,2′-terthiophene (0.710 g, 1.3 mmol), with NiCl$_2$dppp (8 mg) as catalyst in ethyl ether at 40 °C for 3 h.[9] MeBT$_4$ is a brown-yellow oil (61% yield).

^{1}H NMR (CDCl$_3$) aromatic region, δ (ppm) 7.1 (s); 6.85 (d, J = 1.7 Hz); 6.83 (d, J = 1.79 Hz); 6.78 (s); 6.21 (d, J = 1.6 Hz); 6.15 (d, J = 1.54 Hz). ^{13}C NMR (CDCl$_3$) δ (ppm) 157.64; 157.22; 152.43; 135.87; 134.78; 133.33; 132.78; 130.41; 129.99; 125.63; 119.74; 117.76; 116.34; 98.58; 96.7; 71.95; 70.12; 53.4; 29.31; 28.9; 28.16; 22.4; 13.9; 10.7.

Apparatus and Procedure. Experiments were performed at room temperature under nitrogen in three electrode cells. The counterelectrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in AN (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. 80% transmittance, ca. 20 Ω/square resistance, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm^2) was used in reflection−absorption IR spectroscopy and preparative electrolyses.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer; IR spectra in reflection−absorption on a Perkin-Elmer 2000 FTIR spectrometer; ESR spectra were taken on an X-band ER 100D Bruker spectrometer following the procedure previously described.[10]

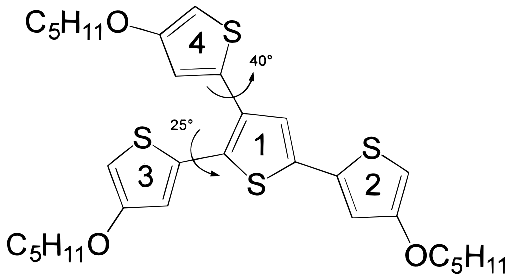


Figure 1. Ring numbering and conformation of BT$_4$.

The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.[11] The relevant working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with interband spacing of 6 μm, typically polymer-coated with the passage of 20 mC, which ensured the attainment of limiting resistance conditions. The resulting film was thick enough (some micrometers) to make the conductivity thickness independent.[12] Poly(3-methylthiophene) (60 S cm^{-1} [13]) was used as conductivity standard.

Results and Discussion

Electrochemical Polymerization of BT$_4$. The cyclic voltammogram CV of BT$_4$ in AN + 0.1 M Et$_4$NClO$_4$ displays a single irreversible oxidation peak at 0.60 V (at a scan rate of 0.1 V s^{-1}). This potential and the maximum absorption in CHCl$_3$ (360 nm) are close to that of the non-thienyl-substituted terthiophene ET$_3$,[6] which indicates roughly that a terthiophene chain is involved in oxidation as well as in the electronic optical transition. Molecular modeling shows that thiophene ring 4 (Figure 1), which is tilted by ca. 40° from the plane of ring 1 (rings 1 and 2 are almost coplanar), causes the neighboring ring 3 to twist by ca. 25° from ring 1. Therefore we may consider the molecule as a linear terthiophene with a terminal thiophene ring slightly distorted from coplanarity with the two other rings by the fourth branching thiophene ring.

The monomer polymerizes easily with potential cycling. In monomer-free solution the redox response of

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(9) Jayasuriya, N.; Kagan, J. *Heterocycles* **1986,** *24*, 2901.

(10) Zotti, G.; Schiavon, G. *Synth. Met.* **1989,** *31*, 347.

(11) Schiavon, G.; Sitran, S.; Zotti, G. *Synth. Met.* **1989,** *32*, 209.

(12) Yassar, A.; Roncali, J.; Garnier, F. *Macromolecules* **1989**, *22*, 804.

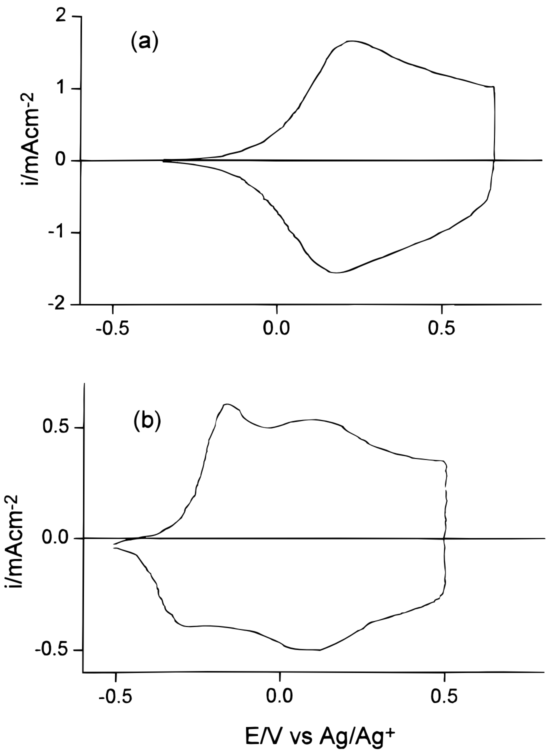

Figure 2. Cyclic voltammetry for (a) poly(BT$_4$) and (b) poly(ET$_3$) in AN + 0.1 M Et$_4$NClO$_4$. Scan rate: 0.1 V s^{-1}; reversible charge: (a) 8.3 mC cm^{-2}; (b) 2.7 mC cm^{-2}.

the polymer deposit (Figure 2a) appears as a single cycle (E_0 = 0.20 V) without the splitting attributable to spin dimerization of radical cations (polarons)[14] which was previously observed in poly(ET$_3$) (Figure 2b).[6] It appears that ring 4, besides twisting the adjacent rings, causes also an increased spacing between polymer chains therefore preventing the π-dimerization of the radical cations. The same twisting of the chain, which reduces its conjugation, is responsible for the positive shift of E_0 of poly(BT$_4$) in comparison with that of poly(ET$_3$) clearly evident in Figure 2.

The ratio of the reversible charge, measured at the potential limit of stability (0.8 V) over the deposition charge, the latter measured at the neutral state, is 50%, which result conforms to the stoichiometry of 2 electrons/monomer for coupling, given that 0.25 electron/thiophene ring are used for doping.[13,15] This conclusion requires that the polymer is deposited without losses in solution and has a relatively high degree of polymerization, which was actually found by electrolytic experiments.

Bulk electrolysis requires 3.0 electrons/monomer, in agreement with the CV response, and yields a dark deposit in a colorless solution, i.e., without formation of dissolved oligomeric forms. This confirms both that the polymer is produced without losses and that low oligomers are not formed so that the polymer chains are relatively long. The bulk neutral polymer, which was obtained in 100% yield as a dark-red product by reduction with hydrazine, is insoluble in CHCl$_3$, which further supports a high degree of polymerization.

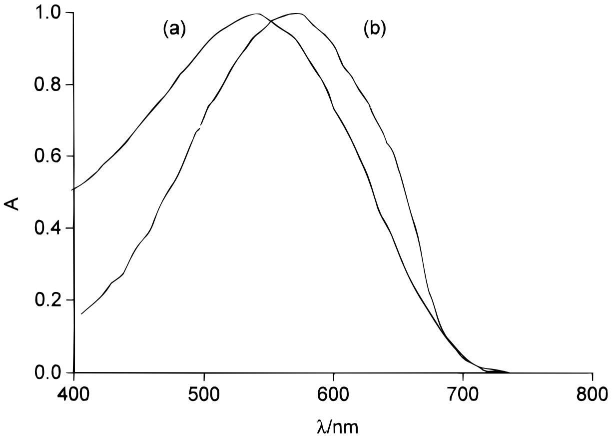

Figure 3. UV–vis spectra of (a) poly(BT$_4$) and (b) poly(ET$_3$).

All these data indicate that the polymer results from coupling of two of the three positions available in the monomer for coupling, displaying a linear sequence of thiophene rings instead of a cross-linked network, though the data cannot rule out occasional cross-linkings.

Spectroscopic Characterization of Poly(BT$_4$). The UV–vis spectrum of the neutral poly(BT$_4$) film shows a strong band at 540 nm (Figure 3a). This value is lower than that for poly(ET$_3$) (560 nm,[6] Figure 3b), which is in line with the segmentation of conjugation operated by the side ring, but the difference is not marked as expected by the slight torsion of the plane of the thiophene rings.

The IR spectrum, which for the rest is similar to that of the monomer, shows that the band at 700 cm^{-1}, attributable to a CH out-of-plane deformation at the terminal thiophene rings, if referred to that at 2940 cm^{-1}, due to CH stretching at the alkyl chains, has lost intensity in comparison with the monomer, whereas the corresponding band at 800 cm^{-1}, due to the inner rings, has increased. These results are those expected from the coupling reaction. From the intensity ratio A_{700}/A_{2940}, which has decreased by a factor of ca. 3 in respect with the monomer, it appears that roughly two couplings are produced per each monomer.

Electrosynthesis and Characterization of Poly(MeBT$_4$). All the above-reported electrochemical and spectroscopic data indicate that the thiophene branches are not involved in coupling. Therefore capping of ring 4 at the 5 position (e.g., by methylation) would give the same results. This suggestion has been checked in our case by the analysis of the polymer from the methyl-capped monomer MeBT$_4$. This monomer is oxidized at the same potential of BT$_4$ and the CV of the polymer is displayed at the same redox potential of poly(BT$_4$). Moreover the UV–vis spectrum of the polymer shows the maximum absorption at the same wavelength, and the neutral polymer is insoluble in CHCl$_3$. All these results show unequivocally that polymers from BT$_4$ and MeBT$_4$ have the same structure.

The trend in the IR spectroscopy observed for poly(BT$_4$) is reproduced also in poly(MeBT$_4$) with the difference that the intensity ratio A_{700}/A_{2940} decreases much more (ca. 6–8 times). In fact in an infinite polymer the band at 700 cm^{-1} was expected to disappear completely so that the residual signal indicates some oligomeric character. On these bases and given the similarity of this polymer with poly(BT$_4$), we may argue

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(13) Tourillon, G.; Garnier, F. *J. Phys. Chem.* **1983,** 87, 2289.

(14) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993,** *5,* 620.

(15) Kaneto, K.; Yoshino, K.; Inuishi, Y. *Jpn. J. Appl. Phys.* **1982,** *21,* L567.

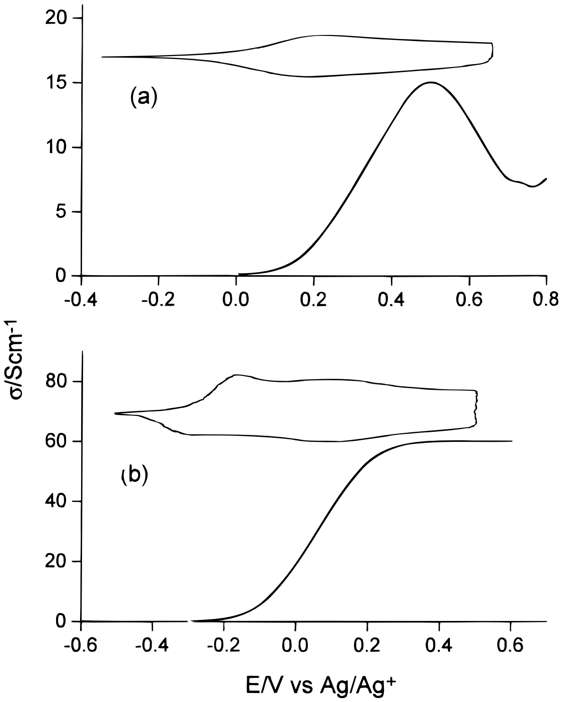

Figure 4. In situ conductivity vs potential of (a) poly(BT_4) and (b) poly(ET_3) in AN + 0.1 M Et_4NClO_4. Upper: CV for comparison.

that the decrease of the band at 700 cm^{-1} for the latter allows that some branching has in fact occurred during its formation. Unfortunately a quantitative assessment of branching does not appear viable.

In Situ Conductivity and ESR. The in situ conductivity of poly(BT_4) as a function of the potential is a bell-shaped curve with a maximum conductivity of 15 S cm^{-1}, which decreases to 50% at the maximum allowed oxidation level at 0.8 V (Figure 4a). Poly(MeBT$_4$) shows the same picture, the only difference being the much lower value of the maximum conductivity (0.02 Scm^{-1}). In contrast, the in situ conductivity of the linear poly(ET_3) (Figure 4b) displays the regular sigmoidal shape with a limiting conductivity of 60 S cm^{-1} [6] at the same doping level of poly(BT_4).

The shape of the relationship of conductivity with potential would suggest a mixed-valence conduction, as previously observed in polypyrrole as a contribution to the bipolaron conduction.[16] This would correspond to an equal concentration of polarons and bipolarons at the maximum conductivity, which was checked by in situ ESR measurements.

Oxidation of the polymer produces an ESR signal with an intensity which initially corresponds to 1 spin/extracted electron, attains a maximum of 0.7 spin/electron, and then decreases to 0. The maximum is located at a potential close the E_0 value of the polymer (Figure 5). From a comparison of the spin concentration and the conductivity as a function of the doping level (Figure 6) it is clear that at the maximum conductivity the spin concentration is practically null. This result rules out that the maximum of the conductivity is due to a mechanism involving polarons and bipolarons.

After this, the most reasonable explanation is that the conductivity is displayed in a potential window of rather limited width (ca. 0.3 V at half-height) which would indicate that a strong narrowing of the valence band has occurred (in, e.g., poly(3-methylthiophene) the conductivity window is ca. 1.1 V wide[17]). The origin of this electronic localization may be found in the expected structure of the polymer chain. Given the monomer structure, coupling is not expected to occur in a random fashion but to follow the route depicted in Figure 7 in which the coupling sites are starred. The coplanarity of rings 1 and 2, which creates a bithiophene moiety within the monomer, suggests that the radical cation is thereby localized so that the initial coupling would involve the 5 position of ring 2. Oxidation of the resulting dimeric species, containing a coplanar tetrathiophene (T_4) segment, will produce a radical cation localized at the less distorted terminal rings 3. Thus polymerization will at the end produce a polymer chain containing alternating T_4 and T_2 sequences with the side-linked thiophenes acting as the bending sites.

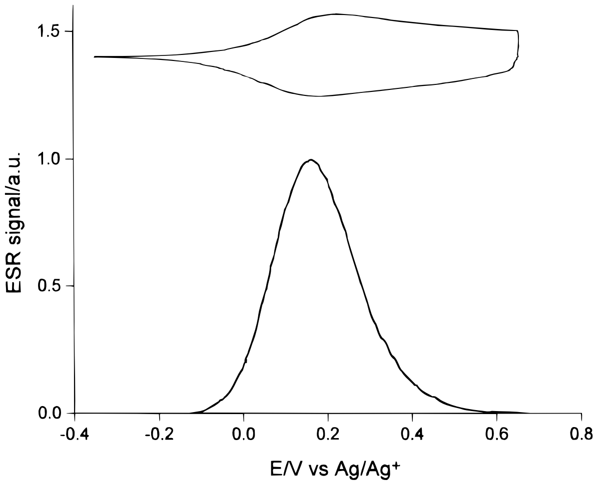

Figure 5. ESR signal vs potential of poly(BT_4) in AN + 0.1 M Et_4NClO_4. Upper: CV for comparidson.

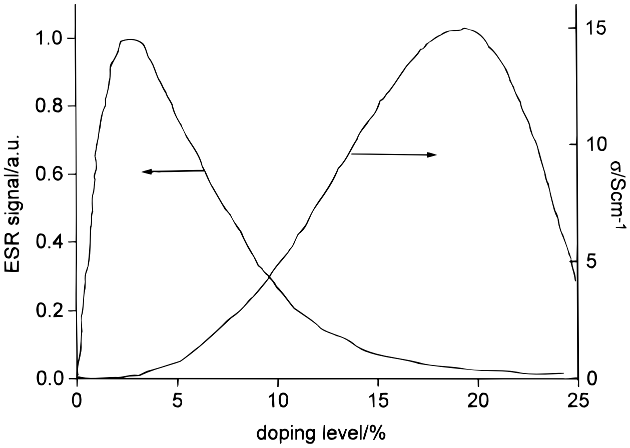

Figure 6. ESR signal and in situ conductivity vs doping level of poly(BT_4) in AN + 0.1 M Et_4NClO_4.

The structure constituted by alternating T_4 and T_2 moieties is oxidized at the T_4 sections. This gives at first conductivity to the material but at the maximum charge level, corresponding to two positive charges per T_4 sequence, alternation of charged (dication) T_4 and neutral T_2 segments creates a new insulating (in our case less conducting) state.

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(16) Zotti, G.; Schiavon, G. *Chem. Mater.* **1991,** *3,* 62.

(17) Ofer, D.; Crooks, R. M.; Wrighton, M. S. *J. Am. Chem. Soc.* **1990**, *112*, 7869.

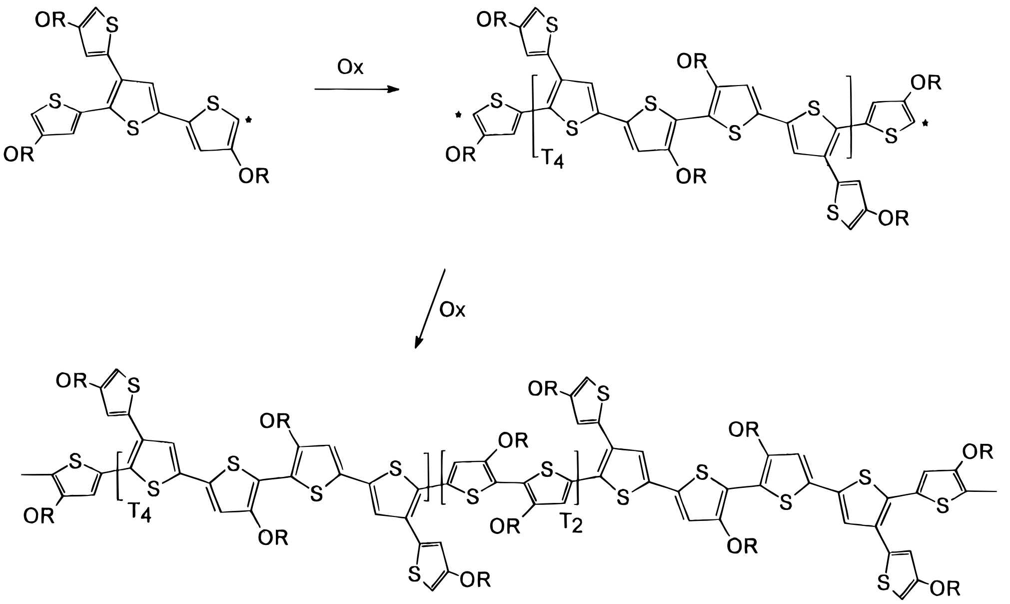

Figure 7. Scheme for anodic coupling of the branched tetramers.

The discussion above may account for the unusually narrow potential window of conductivity in the branched polymers but we must point out that the result most interesting to the purpose of this investigation comes from a comparison among their maximum conductivities and that of the parent nonbranched polymer. The much lower (more than 3 orders of magnitude) conductivity of the methyl-capped polymer in comparison with that of the nonbranched polymer is the result of the high interchain distance due to chain twisting induced by the side rings and mostly by their steric hindrance. Comparing the branched polymers, we may observe that the methyl group does increase the branch bulkiness, but the latter is clearly dominated by the long-chain alkoxy substituent. Therefore the steric change does not appear to be significant enough to explain the 1000 times lower conductivity of the methyl-capped polymer. The higher conductivity of the uncapped polymer is better explained by the occasional occurrence of cross-coupling which launches conjugated bridges across the polymer chains.

Conclusions

Anodic coupling of linear terthiophenes, bearing thienyl substituents able to couple further, results not in a fully cross-linked network but in a linear structure, originating from the monomeric linear terthiophene, with the occasional occurrence of bridges across the chains. The side substituent decreases the conductivity of the polymer, due to the increased spacing between the chains, but conjugated bridges created between the chains act as electrical shorts with a significant increase of conductivity.

Branches in the polyconjugated polymers segment the conjugated sequence therefore causing the appearance of a narrow potential window of conductivity. The resulting insulator−conductor−semiconductor switching properties are analogous with those displayed by polyconjugated polymers containing alternating acceptor and donor moieties.[18] Such properties make these materials interesting for possible applications in organic electronic devices. Moreover the envisaged alternation of different conjugated sequences and the consequent bandgap modulation may increase the efficiency of organic light emitting diodes based on these materials.[19,20]

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(18) Zotti, G.; Pagani, G., to be published.

(19) Meyers, F.; Heeger, J.; Bredas, J. L. *J. Chem. Phys.* **1992**, *97*, 2750.

(20) Burn, P. L.; Holmes, A. B.; Kraft, A.; Bradley, D. D. C.; Brown, A. R.; Friend, R. H.; Gymer, R. W. *Nature* **1992**, *356*, 47.