Chem. Mater. **1997,** *9,* 2945−2950

Electrochemical Polymerization of Mixed Alkyl−Alkoxybithiophenes and -terthiophenes. Substitution-Driven Polymerization from Thiophene Hexamers to Long-Chain Polymers

G. Zotti*

Istituto di Polarografia ed Elettrochimica Preparativa, Consiglio Nazionale delle Ricerche,
c.o Stati Uniti 4, 35020 Padova, Italy

R. A. Marin and M. C. Gallazzi

Dipartimento di Chimica Industriale e Ingegneria Chimica, Politecnico di Milano,
p.zza L. da Vinci 32, 20133 Milano, Italy

Received May 5, 1997. Revised Manuscript Received July 7, 1997[⊗]

Anodic coupling of mixed alkyl−alkoxy bithiophenes and terthiophenes to polymers has been performed in acetonitrile. The polymers have been characterized by cyclic voltammetry (CV), UV−vis, FTIR, and MALDI spectroscopies and in situ conductivity. Long-chain highly conducting polymers or sexithiophenes are produced by CV deposition depending on the substitution pattern. Unusual symmetry (nonhysteresis) of CV responses for the sexithiophene films is attributed to solvent swelling.

Introduction

Solubility is a property of primary importance for the application of polythiophenes both as conducting polymers and in electronic and optical devices. Solubility has been achieved by introducing alkyl substituents in the thiophene unit and polymers with good electrical and optical properties have been obtained. For such properties the regiochemistry of substitution is very relevant,[1] and both the conductivity and the optical properties can be enhanced increasing the regioselectivity of the polymerization process. As far as the stability of the doped state is concerned, it can be achieved by releasing the alkyl crowding along the chain[2] or by introducing alkoxy groups.[3] Polymers containing alkoxy groups in regiochemically defined positions have been obtained through the polymerization of suitably substituted oligomers. Very high or low molecular weight polymers have been obtained depending on the substitution pattern of the starting oligomers, but only low molecular weight polymers resulted to be soluble.[3] Polymers bearing both alkyl and alkoxy substituents on the same chain attracted our interest for two reasons. The first is the possibility of increasing the solubility. The other is that the presence of substituents with modulated electron-releasing properties and different steric requirements might provide materials with interesting chromic behavior and preferential sites for charge carrier recombination useful for LED applications.

A possible strategy for producing alkyl−alkoxythiophene copolymers having a regiochemically defined substitution pattern was the polymerization of suitably designed oligomers. The regiochemistry of the substitution was carefully planned in view of the polymerization reaction. In the monomer design, for what concerns the group location, positions that might give rise to vicinal substitution (head-to-head) in the polymer had to be avoided for steric reasons in the case of alkyl groups. On the contrary steric hindrance due to vicinal alkoxy groups is almost irrelevant[4] whereas a higher reactivity in the polymerization is expected when the alkoxy groups are α-positioned respect to the coupling position.[5]

Following these directives we have synthesized some selected bithiophene and terthiophene monomers bearing both alkyl and alkoxy groups. The monomers, 3-octyl-4′-pentoxybithiophene (OPBT), 3′-octyl-4,4″-dipentoxyterthiophene (ODPTT), and 3′-pentoxy-3,3″-dioctylterthiophene (PDOTT), are shown in Scheme 1. In the bithiophene we have placed an alkyl group at the internal β-position of one thiophene ring and an alkoxy group at the external β-position of the other ring. In one terthiophene, PDOTT, the terminal thiophene rings were substituted by alkyl groups at the internal β-positions while in the other, ODPTT, by alkoxy groups at the external β-positions. The dialkylated terthiophene 3,3″-dihexylterthiophene (DHTT) was also investigated for comparison.

Leclerc et al.[6] have previously oxidatively coupled bithiophenes in which each thiophene ring was substituted by an alkyl or alkoxy group but the selected substitution pattern was 3,3′ or 4,4′, i.e., such as to place the substituents in the inner or outer positions of the

---

* Correspondence should be addressed to gzotti@pdadr1.pd.cnr.it.

[⊗] Abstract published in *Advance ACS Abstracts*, October 15, 1997.

(1) Gallazzi, M. C.; Castellani, L.; Zerbi G.; Sozzani, P. *Synth. Met.* **1991**, *41*, 495.

(2) Gallazzi, M. C.; Castellani, L.; Marin, R. A.; Zerbi, G. *J. Polym. Sci. A, Polym. Chem.* **1993**, *31*, 3339.

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

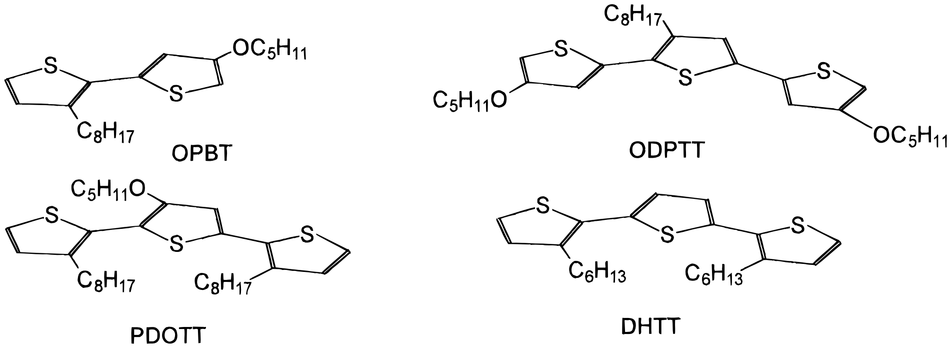
(4) Meille, S. V.; Farina, A.; Bezziccheri, F.; Gallazzi, M. C. *Adv. Mater.* **1994**, *6*, 848.

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

(6) Faid, K.; Cloutier, R.; Leclerc, M. *Macromolecules* **1993**, *26*, 2501.

S0897-4756(97)00295-0 CCC: $14.00

Scheme 1. Formulas for Monomers



bithiophene. Copolymers with mixed alkyl−alkoxy substituents have also been reported.[7,8]

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 monomers 3-octyl-4′-pentoxy-2,2′-bithiophene (OPBT), 3′-octyl-4,4″-dipentoxy-2,2′:5′,2″-terthiophene (ODPTT), and 3′-pentoxy-3,3″-dioctyl-2,2′:5′,2″-terthiophene (PDOTT) were prepared as follows and purified by flash chromatography with hexane/$CHCl_3$ (70/30) as eluent. The monomer 3,3″-dihexylterthiophene (DHTT) was prepared according to the literature.[1,2]

3-Octyl-4′-pentoxy-2,2′-bithiophene (OPBT). The compound was prepared by coupling 3-octyl-2-iodothiophene and 4-pentoxythiophene-2-boronic acid in the presence of tetrakis(triphenylphosphine)palladium(0) [$Pd(PPh_3)_4$] and sodium bicarbonate in dimethoxyethane.[9] 3-Octyl-2-iodothiophene was prepared from 3-octylthiophene[10] with I_2 and HgO as reported for 3-pentoxy-2-iodothiophene.[3] 4-Pentoxythiophene-2-boronic acid was prepared as reported.[3] The product is a yellow oil (60% yield).

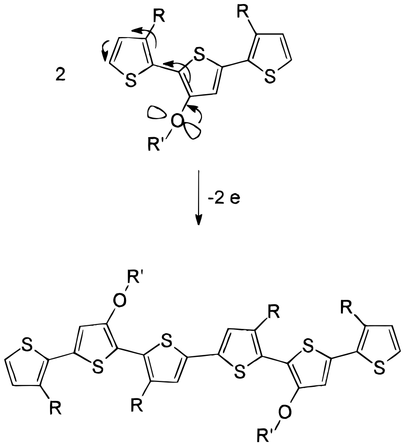
^1H NMR ($CDCl_3$, aromatic region, δ, ppm) 7.16 (d, $J = 5.1$, H_5), 6.91 (d, $J = 5.2$, H_4), 6.79 (d, $J = 1.7$, $H_{3'}$), 6.20 (d, $J = 1.7$, $H_{5'}$). ^{13}C NMR (*$CDCl_3$*, aromatic region) 157.49 ($C_{4'}$), 139.83 (C_3), 135.11 ($C_{2'}$), 130.87 (C_2), 130.06 (C_4), 123.85 (C_5), 118.28 ($C_{3'}$), 97.07 ($C_{5'}$). UV−vis ($CHCl_3$) $\lambda_{max} = 308$ nm.

3′-Octyl-4,4″-dipentoxy-2,2′:5′,2″-terthiophene (ODPTT). The compound was prepared by coupling 4-pentoxythiophene-2-boronic acid[3] and 2,5-dibromo-3-octylthiophene[11] in dimethoxyethane/1 M sodium bicarbonate using tetrakis(triphenylphosphine)palladium(0) as catalyst.[9] The product is obtained as a yellow oil (64% yield).

^1H NMR ($CDCl_3$, aromatic region, δ, ppm) 6.98 (s, $H_{4'}$) 6.84 (d, $J = 1.58$, $H_{3''}$), 6.81 (d, $J = 1.57$, H_3), 6.21 (d, $J = 1.49$, $H_{5''}$), 6.12 (d,$J = 1.49$, H_5). ^{13}C NMR ($CDCl_3$, aromatic region) 157.7, 157.5, 140.47, 135.6, 135.47, 134.6, 130.0, 126.34, 118.14, 116.0, 97.2, 96.3. UV−vis (*$CHCl_3$*) $\lambda_{max} = 357$ nm.

3′-Pentoxy-3,3″-dioctyl-2,2′:5′,2″-terthiophene (PDOTT). The compound was prepared by coupling the Grignard reagent of 3-octyl-2-iodothiophene and 2,5-dibromo-3-pentoxythiophene with $NiCl_2dppp$ as catalyst in ethyl ether at 40 °C for 3 h.[12] 2,5-Dibromo-3-pentoxythiophene was prepared from 3-pentoxythiophene and NBS in DMF.[13] The product is a yellow oil (77% yield).

Scheme 2. Anodic Coupling of PDOTT



^1H NMR ($CDCl_3$, aromatic region, δ, ppm) 7.24 (d, $J = 5.2$, H_5), 7.17 (d, $J = 5.2$, $H_{5''}$), 6.93 (d, $J = 5.2$, $H_{4''}$, H_4), 6.90 (s, $H_{4'}$). ^{13}C NMR ($CDCl_3$, aromatic region) 153.43, 140.78, 133.6, 131.17, 130.7, 129.44, 127.1, 124.9, 124.1, 116.3. UV−vis ($CHCl_3$) $\lambda_{max} = 336$ nm.

3,3′′,4′′′,3′′′′′-Tetrahexyl-4′,3′′′′-dipentoxy-2,2′:5′,2′′:5′′2′′′ :5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene. The compound was produced by anodic coupling of PDOTT (see results and Scheme 2). Coupling resulted to have occurred at the 5 position with a regioselectivity of more than 90%.

^1H NMR (*$CDCl_3$*, aromatic region, δ, ppm) 7.18 (d, $J = 5.1$, H_5, 2H), 7.00 (s, $H_{4''}$, 2H), 6.95 (d, $J = 5.2$, H_4, 2H), 6.92 (s, $H_{3'}$, 2H). ^{13}C NMR ($CDCl_3$, aromatic region, δ, ppm) 114.50, 124.18 (CH), 125.73 (CH), 125.98 (CH), 128.74, 130.68 (CH), 131.20, 136.31, 140.27 (2C), 141.28, 153.65. UV−vis (*$CHCl_3$*) $\lambda_{max} = 420$ nm.

Apparatus and Procedure. Experiments were performed at room temperature under nitrogen in three-electrode cells. The counter electrode 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. 20 Ω/square resistance, from Balzers, Liechtenstein) was used. A platinum sheet (15 cm^2) was used in preparative electrolyses.

Electronic spectra were taken with a Perkin-Elmer Lambda 15 spectrometer, and IR spectra on a Perkin-Elmer 2000 FTIR spectrometer. Matrix-assisted laser desorption ionization (MALDI) mass spectra were taken on a Reflex TOF spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as matrix.

The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.[14] The relevant working electrode was a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with interband spacing of 6

---

(7) Roux, C.; Leclerc, M. *Chem. Mater.* **1994**, *6*, 620.

(8) Hanna, R. ; Leclerc, M. *Chem. Mater.* **1996**, *8*, 1512.

(9) Gronowitz, S. : Peters, D. *Heterocycles* **1990**, *30*, 645.

(10) Van Pham, C.; Mark Jr., H. B.; Zimmer, H. *Synth. Commun.* **1986**, *16*, 689.

(11) Delabouglise, D.; Hmyene, M.; Horowitz, G.; Yassar, A.; Garnier, F. *Adv. Mater.* **1992**, *4*, 107.

(12) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.

(13) Mitchell, R. H.; Lai, Y. H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733.

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

Table 1. Peak Potential E_p for Monomers, Redox Potential $E°$, Maximum Absorption as Film λ (in $CHCl_3$ Solution in Brackets) and in Situ Conductivity σ for Polymers

monomer	$E_p{}^a$/V^b	$E°$/V^b	λ/nm	σ/S cm^{-1}
OPBT	0.80	0.03/0.37	485(464)	
ODPTT	0.54	−0.25/0.10	600,670sh(530)	120
PDOTT	0.48	0.14/0.37	460(420)	
DHTT	0.65	0.20/0.60	530	110

[a] At a scan rate of 0.1 V s^{-1} and 10^{-3} M monomer concentration. [b] Versus Ag/Ag$^+$ reference electrode.

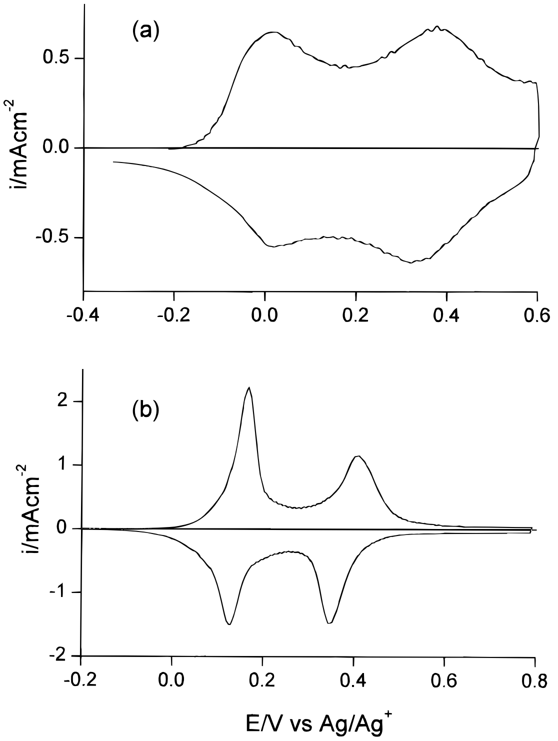


Figure 1. Cyclic voltammogram for (a) poly(OPBT) and (b) poly(PDOTT) in AN + 0.1 M Et_4NClO_4. Scan rate 0.1 V s^{-1}; reversible charge 3.3 mC cm^{-2}.

μm, typically polymer-coated with the passage of 20 mC, which ensured the attainment of limiting resistance conditions. Poly(3-methylthiophene) (60 S cm^{-1} [15]) was used as conductivity standard.

Results and Discussion

Electrodeposition and Cyclovoltammetric Analysis of the Polymers. The cyclic voltammogram CV of the compounds in AN + 0.1 M Et_4NClO_4 displays a single irreversible oxidation peak at potentials given in Table 1. Polymerization occurs with potential cycling over the oxidation peak.

In monomer-free solution the redox response of the poly(OPBT) deposit (Figure 1a) appears as a clearly defined couple of processes involving the same charge ($E°_1 = 0.03$ V; $E°_2 = 0.37$ V). The charge yield (ratio of reversible charge to deposition charge for the neutral state of the polymer) is variable due to dissolution of the oxidized species but may be as high as 30%. It must be remarked that potentiostatic deposition, performed at the peak potential, leads in the long run to a degraded CV response of the deposits attributable to overoxidation.

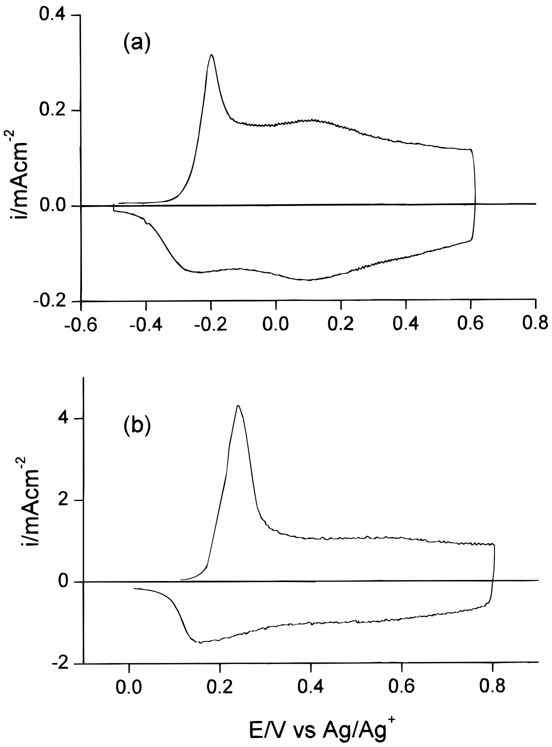


Figure 2. Cyclic voltammogram for (a) poly(ODPTT) and (b) poly(DHTT) in AN + 0.1 M Et_4NClO_4. Scan rate 0.1 V s^{-1}; reversible charge (a) 1.0 mC cm^{-2}; (b) 8.0 mC cm^{-2}.

The behavior of PDOTT is similar since the CV of the polymer deposit shows a couple of cycles with the same charge ($E°_1 = 0.14$ V; $E°_2 = 0.37$ V; Figure 1b). The deposit tends also in this case to dissolve in the oxidized form so that the charge yield is difficult to evaluate, but it may attain values of ca. 40%. Once more overoxidation occurs in prolonged potentiostatic deposition.

In the case of ODPTT polymerization occurs without giving sign of oligomer dissolution. In monomer-free solution the redox response of the polymer film appears as a broad capacitive process starting at $E°_1 = -0.25$ V with a further round feature at $E°_2 = 0.1$ V (Figure 2a). The ratio of the reversible charge (measured at 0.6 V) to the charge used for deposition (measured at the neutral state of the polymer) is ca. 50% from which, taking into account that dissolution does not occur during deposition, a value of 33% (one charge per three thiophene rings) is evaluated for the doping level of the oxidized polymer. No appreciable degradation is observed in the course of potentiostatic polymerization, which constitutes a further difference from the other polymers.

The electrochemical parameters are summarized in Table 1 along with the spectral and conductivity data, which are reported and discussed in the following section.

Spectral Characterization and Conductivity of the Polymers. Both poly(OPBT) and poly(PDOTT) deposits are very soluble in $CHCl_3$, suggesting a low degree of polymerization. The UV−vis spectrum of poly(OPBT) film shows a strong and narrow band at 485 nm (Figure 3a) which shifts hypsochromically to 464 nm in $CHCl_3$ solution. This latter value, compared with those of alkyl-substituted thiophene oligomers, is close to that of the tetradecyl-substituted thiophene dodecam-

---

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

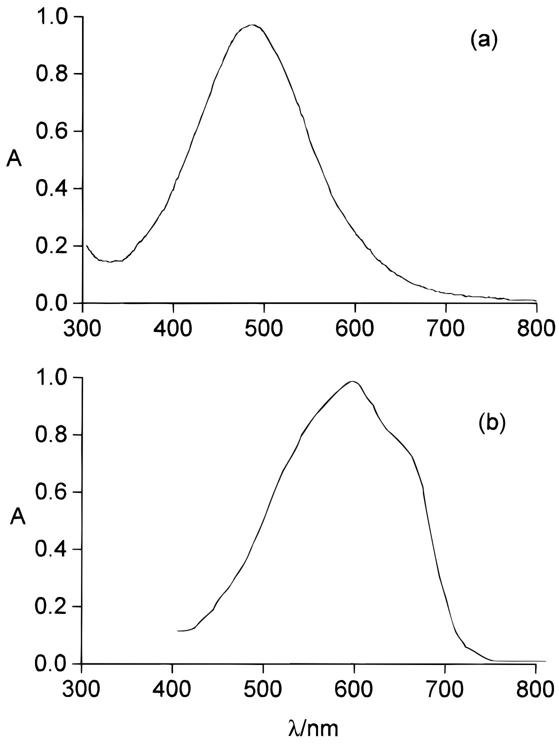


Figure 3. UV−vis spectra of (a) poly(OPBT) and (b) poly(ODPTT) on ITO.

er T_{12} (465 nm)[16] and a little higher than that of a T_{12} with two hexyl groups over three thiophene rings, reported to display a maximum absorption at 448 nm.[17] This comparison confirms that the polymer chain length is low but the exact determination of the degree of polymerization was made with mass analysis of the deposits dissolved in $CHCl_3$. The MALDI spectrum (Figure 4a) has shown a strong peak at 1089 *m/z*, due to the $[M + H]^+$ ion of T_6, with a minor one (some 2−5%) at 1451 *m/z* due to the corresponding ion of T_8. It is therefore clear that the polymer material is in fact constituted by a thiophene hexamer and that the UV−vis absorption maximum is bathochromically shifted from the expected region. As a matter of fact the alkoxy group causes a lowering of the optical gap in polythiophenes in comparison with the alkyl group.[3]

The poly(PDOTT) film displays similar spectral characteristics. In $CHCl_3$ solution it shows a strong band at 420 nm. This value is close to that of the didodecyl-substituted T_6 (423 nm in the same solvent[18]). The suggestion that the product is the T_6 oligomer was in this case confirmed by MALDI, which shows a single peak at 1115 *m/z* ($[M + H]^+$ ion, Figure 4b). The dominance of the alkyl substituents in the monomer accounts for the absence of bathochromic effects from the alkoxy substituent in this case.

In situ conductivity of these hexameric deposits was not obtained because deposition to high thickness was not possible without degradation. In any case a low conductivity, in the range 10^{-2}−10^{-1} S cm^{-1}, is expected from data of doped T_6's in the literature.[19−21]

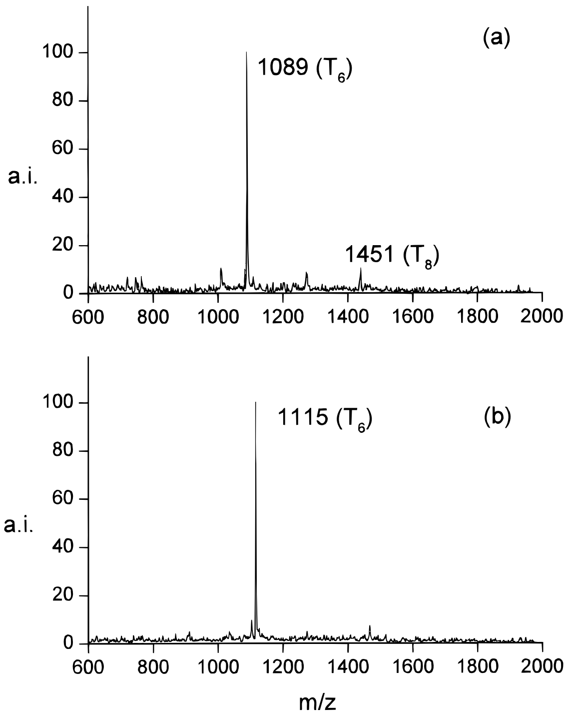


Figure 4. MS Maldi spectrum for (a) poly(OPBT) and (b) poly(PDOTT).

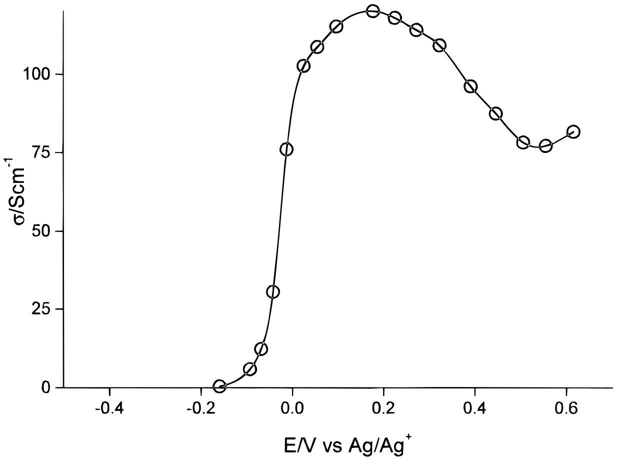


Figure 5. In situ conductivity of poly(ODPTT) in AN + 0.1 M Et_4NClO_4.

Different from the previous polymers, the poly(ODPTT) deposit is a smooth regular film which is only partially soluble in $CHCl_3$. It shows a strong band at 600 nm with a shoulder at 660 nm (Figure 3b). This value, compared with those of the polymers from dipentoxy-substituted terthiophenes,[3] suggests an average approximate length of 30 thiophene rings.

The in situ conductivity (Figure 5) gives a maximum value of 120 S cm^{-1} for the oxidized polymer (at ca. 20% doping), i.e., a relatively high value, compatible with a long-conjugated poly(alkylthiophene). FTIR of neutral poly(ODPTT) shows the band pattern of the monomer with main differences in the δ_{CH} region. Here only two bands at 797 and 729 cm^{-1}, with intensity ratio 2:1, are displayed, which are due to the hydrogen atoms in the

---

(16) Yassar, A.; Delabouglise, D.; Hmyene, M.; Nessak, B.; Horowitz, G.; Garnier, F. *Adv. Mater.* **1992**, *4*, 490.

(17) Sato, M.; Hiroi, M. *Synth. Met.* **1995**, *71*, 2085.

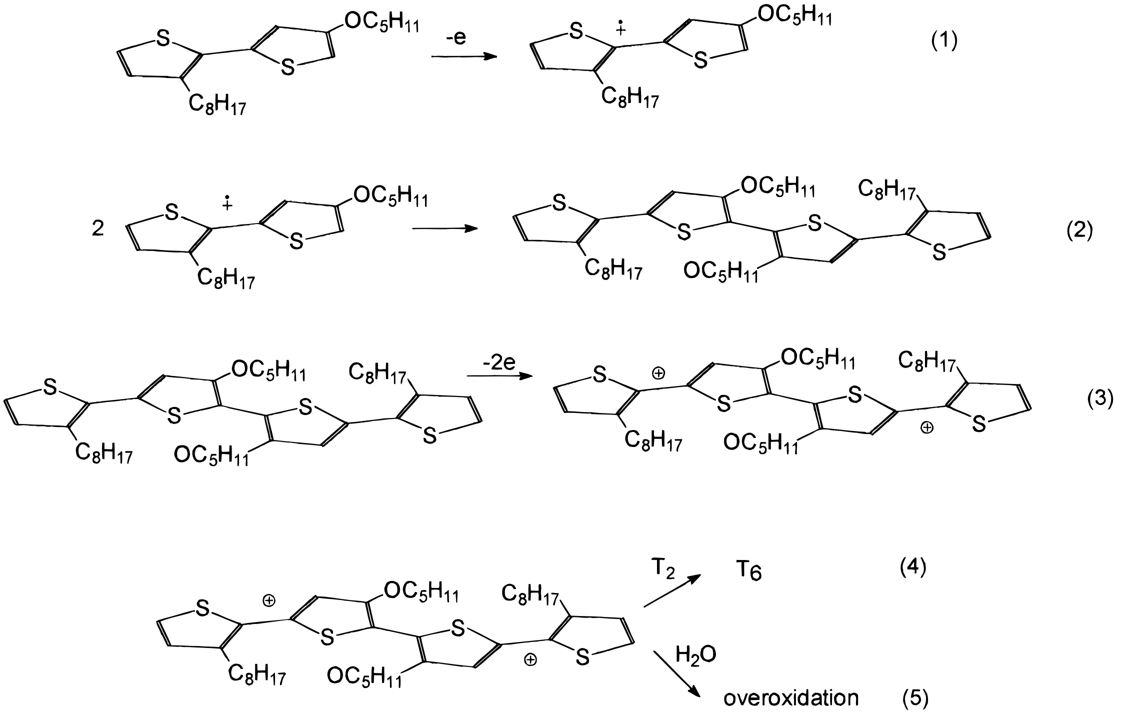
(18) Havinga, E. E.; Rotte, I.; Meijer, E. W.; Hoeve, W. T.; Wynberg, H. *Synth. Met.* **1991**, *43*, 473.

(19) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Adv. Mater.* **1993**, *5*, 551.

(20) Hoeve, W.; Wynberg, H.; Havinga, E. E.; Meijer, E. W.; *J. Am. Chem. Soc.* **1991**, *113*, 5887.

(21) Fichou, D.; Horowitz, G.; Xu, B.; Garnier, F. *Synth. Met.* **1990**, *39*, 243.

Scheme 3. Anodic Coupling of OPBT



alkoxy- and alkyl-substituted thiophene rings, respectively. The absence of other bands in this region, assignable to hydrogen atoms at the terminal thiophene rings, is a clear confirmation of the relatively high degree of polymerization of the polymer.

Coupling Processes. The results given above clearly indicate that among the selected compounds only the trimer with the external alkoxy groups ODPTT produces a long-chain polymer, which is due to the high reactivity to coupling of the relevant terminal α-positions.[5]

At the opposite, in the case of the trimer with terminal alkyl groups PDOTT the reactivity appears to be low, which, coupled with the low solubility of the oligomers, produces a neat precipitation of the T_6. The low reactivity was unexpected since alkyl groups do not in general create obstacles to the production of long-chain polythiophenes. In any case we have checked this expectation analyzing the electrochemical oxidation of 3,3′′-dialkylterthiophene DHTT and the characteristics of the resulting polymer. DHTT is anodically coupled to polymer at 0.65 V and the CV cycle of the polymer shows the oxidation process at $E°_1 = 0.2$ V with a round feature at $E°_2 = 0.6$ V (Figure 2b), an overall picture common to the long-chain polymers such as poly(ODPTT) (Figure 2a). In agreement with this suggestion the polymer displays a maximum absorption at 530 nm, compatible with a highly conjugated (long-chain) poly(alkylthiophene),[27] and the in situ conductivity is high and comparable to that of poly(ODPTT) (110 S cm^{-1}).

It is therefore clear that the lower reactivity of the radical cation of PDOTT is due to the presence of the inner alkoxy substituent. We suggest that the unpaired electron in the radical cation is mainly localized at the internal thiophene ring therefore producing a marked decrease of the reactivity to coupling. The external α-positions display some localization of the unpaired electron with a density that is in any case expected to be different at the two terminal thiophene rings. Therefore the dimer produced from PDOTT was expected to be regiospecific (one isomer). This has been shown by NMR analysis of a bulk sample of the dimer (see Experimental Section) which has indicated that the product was essentially one regioisomer and presumably the sexithiophene derived from coupling at the α-position closest to the alkoxy group (Scheme 2). In fact electrophilic substitution reactions on PDOTT have given 100% of the 5-substituted product.[23]

Using the above-described reasoning on the localization of the unpaired electron, we may explain the production of the T_6 from OPBT. We suggest that coupling occurs according to the following pathway (Scheme 3). The radical cation of the dimer T_2 (eq 1) couples to tetramer T_4 (eq 2) at the T_4 is oxidized to dication T_4^{2+} [3,24] (eq 3); T_4^{2+} reacts with T_2 diffusing from the bulk to give the radical $T_4^{•+}$ and $T_2^{•+}$, which subsequently couple to T_6 (eq 4). If T_2 diffusion is scarce, as in prolonged potentiostatic and stationary conditions, T_4^{2+} undergoes competitive attack by water (eq 5) giving overoxidized materials. To conclude, in the case of OPBT the high reactivity of the alkoxy-terminated ring is rapidly quenched after the dimerization, and further couplings involve the radical cation of a thiophene tetramer, much less reactive because of the confinement of the unpaired electron in the internal dialkoxybithiophene moiety.

Shape of the CV Responses. In this section we will discuss the characteristics of the CV responses for the

---

(22) Roncali, J.; Garreau, R.; Yassar, A.; Marque, P.; Garnier, F.; Lemaire, M. *J. Phys. Chem.* **1987**, *91*, 6706.

(23) Gallazzi, M. C., private communication.

(24) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 430.

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

(26) Meerholtz, K.; Heinze, J. *Electrochim. Acta* **1996**, *41*, 1839.

(27) Yu, Y.; Gunic, E.; Zinger, B.; Miller, L. L. *J. Am. Chem. Soc.* **1996**, *118*, 1013.

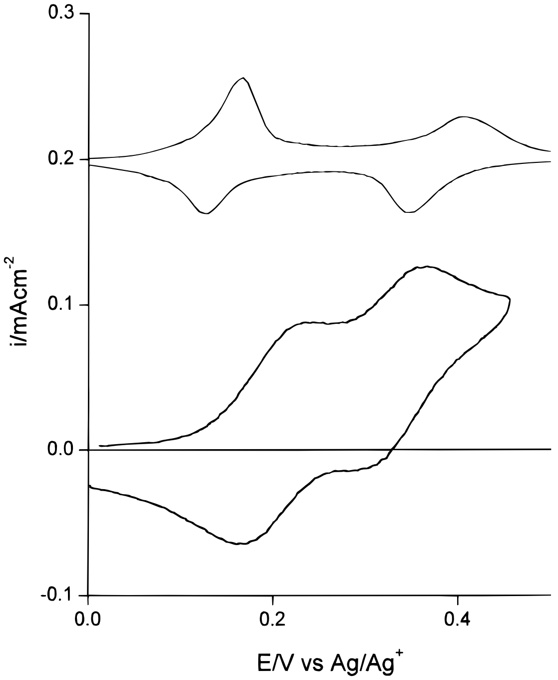


Figure 6. Cyclic voltammogram for PDOTT dimer 5 × 10^{-4} M in CH_2Cl_2 + 0.1 M Et_4NClO_4. Scan rate 0.1 V s^{-1}. Upper: CV of the film in AN + 0.1 M Et_4NClO_4 for comparison.

investigated polymers, which in our opinion give new contributions to the understanding of the electrochemistry of polythiophenes.

Clear differences are observed in the CVs of the hexamers in comparison with the long-chain polymers. The former show two clear isoelectronic processes with a low level of capacitive current at the anodic limit, particularly for the pure hexamer from PDOTT. As recently shown for T_6 films,[25] each process involves the exchange of one electron with production of the cation radical and dication. This result has been recently questioned[26] so that we have confirmed our indication also with the actual compounds. This has been done in two ways, namely, (i) relating the reversible charges and the absorbance of $CHCl_3$ solutions of the deposits and (ii) by CV analysis of the compound in solution. For the first method the extinction coefficient of the PDOTT dimer in $CHCl_3$ was evaluated and applied to deposits for which the reversible charge was measured prior to their dissolution in the same solvent. The relationship indicates the exchange of 2.0 ± 0.2 electrons in the overall redox cycle.

For the second method, the PDOTT dimer dissolved in CH_2Cl_2 solution displays two reversible oxidation processes (Figure 6) at $E° = 0.2$ and 0.33 V with peak heights and anodic–cathodic peak separation (ΔE_p = 60 mV) corresponding to the passage of one electron each by comparison with a TTF sample. It must be observed that the redox potential values are constant in the range 10^{-4}–10^{-3} M, showing that the radical cation, which in this medium does not undergo π-dimerization,[27] is stabilized by 0.13 V, as for similar hexamers,[28] whereas in the solid state it appears to benefit an extra stabilization of 0.1 V due to π-dimerization.[25,29] The low capacitive currents, mainly attributable to some higher oligomers, are strongly increased in the CV of the long-chain polymers. In the latter further oxidation processes appear only as round features almost buried in the capacitive plateau.

The CVs of the T_6 deposits are exceptionally clean and symmetric, without the hysteretic features encountered with polythiophenes in general and in particular with thiophene oligomers such as the tetradecylsubstituted T_{12}[16] and T_6 itself.[25] An easier movement of the electrolyte within the material, favored by the affinity with the alkoxy substituent, is the suggested cause of the phenomenon, as recently found in ether-substituted polypyrroles.[30] Solvent swelling of polythiophenes is essential to its electroactivity as recently confirmed in self-doped polymers.[31] This result, which assigns to electrolyte permeation the control of the hysteresis phenomenon, appears to rule out definitely explanations based on isomerization or conformational changes during doping.[32]

Conclusions

The results of this investigation on alkyl–alkoxy-substituted thiophene oligomers have evidenced the relevance of the oligomer design to the products of the polymerization reaction. Depending on the substitution pattern, long-chain polymers or well-defined high-purity hexamers can be obtained. The main role in determining the reaction path is played by the location of the alkoxy group so that in fact the results are the outcome of a subtle balance of factors related to such regiochemistry.

Furthermore the unusually symmetrical CV response of the mixed alkyl–alkoxy-substituted thiophene hexamers as film has evidenced that the hysteretic distortion commonly found in polythiophenes as well as in many electroactive polymers is in fact due to scarce electrolyte permeation into the solid films.

Acknowledgment. The authors would like to thank Mr. R. Salmaso and Mr. S. Sitran of the CNR for their technical assistance.

CM970295O

---

(28) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.

(29) Hapiot, P.; Audebert, P.; Monnier, K.; Pernaut, J. M.; Garcia, P. *Chem. Mater.* **1994**, *6*, 1549.

(30) Delabouglise, D.; Garnier, F. *Adv. Mater.* **1990**, *2*, 91.

(31) Tatsuma, T.; Hioki, Y.; Oyama, N. *J. Electroanal. Chem.* **1995**, *396*, 371.

(32) Heinze, J.; Storzbach, M.; Mortensen, J. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 960.