

New Low-Gap Polymers from 3,4-Ethylenedioxythiophene-Bis-Substituted Electron-Poor Thiophenes. The Roles of Thiophene, Donor–Acceptor Alternation, and Copolymerization in Intrinsic Conductivity

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New low-gap thiophene-based regular copolymers are produced by anodic coupling of 3,4-ethylenedioxythiophene-2,5-substituted thieno[3,4-*b*]pyrazine (TP), cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene-4-one (CO), and 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]dithiophene (CN). The copolymers are characterized by cyclic voltammetry, FTIR reflection–absorption and UV–vis spectroscopy, electrochemical quartz crystal microbalance analysis, and in situ p- and n-conductivity measurement. The copolymers show low optical gaps (measured at the maximum absorption) and electrochemical gaps (measured from redox potentials) in the range 0.8–1.3 eV. The CN-based polymer displays the lowest reported electrochemical gap (0.8 V). Random copolymers of CO and 3,4-ethylenedioxythiophene (EDT) have also been produced and compared with the relevant regular copolymer. Copolymerization of CO with increasing amounts of EDT decreases the gap. From an analysis of redox potential as a function of EDT fraction, it is found that the gap is limited by the redox potentials of the individual homopolymers. Localization of n-doping carriers in the polythiophene chains is progressively increased by donor–acceptor alternation and then by copolymerization till the expected intrinsic conductivity is made completely p-type.

1. Introduction

The production of low-gap conducting polymers has been particularly rich in the recent past with the main purpose of producing polymers with high intrinsic conductivity.¹ An increased interest in low-gap polymers has recently been found for applications in infrared electrochromic displays.²

It is noteworthy that most of these polymers are thiophene-based.¹ Low-gap polymers were initially those in which the quinoid character was stabilized, such as in polyisothianaphthene.³ We will name these polymers *quinoid-type* low-gap polymers. A later class was formed by those in which the presence of π -electron acceptor

substituents stabilizes a nonaromatic form, such as in the poly(cyclopentadithiophene)s.^{4,5} These polymers will be named *non-aromatic-type* low-gap polymers. The latest contribution has come from polythiophenes which regularly alternate thiophene rings substituted with electron donor (D) and acceptor (A) moieties. The resulting alternation of electron-rich and -poor units in the polyconjugated backbone causes the reduction of the gap.⁶ These polymers will be called *DA-type* low-gap polymers.

Before proceeding, we need to give a clarification since in our opinion too many polymers have been claimed to be low-gap. In fact, the band gap, either optical, i.e., the energy at the maximum of absorption, E_g (and not the ill-defined onset of absorption), or electrochemical, i.e., the difference of oxidation and reduction redox poten-

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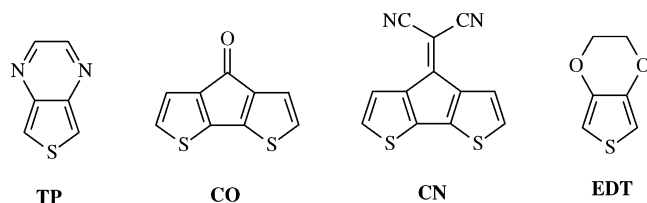
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Chart 1



tials, ΔE° (and not of the ill-defined onsets of oxidation or reduction), may be so high that the assumed categorization as low-gap polymers should in those cases be rejected. Among several such examples we mention the polymer from $\Delta^{4,4'}$ -dicyclopenta[2,1-*b*:3,4-*b'*]dithiophene (electrochemical E° -based gap, 1.7 eV, vs an onset-based gap, <0.8 eV)⁷ and 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene, which displays an optical onset-based gap of 1.2 eV but an absorption maximum at 2.2 eV.⁸

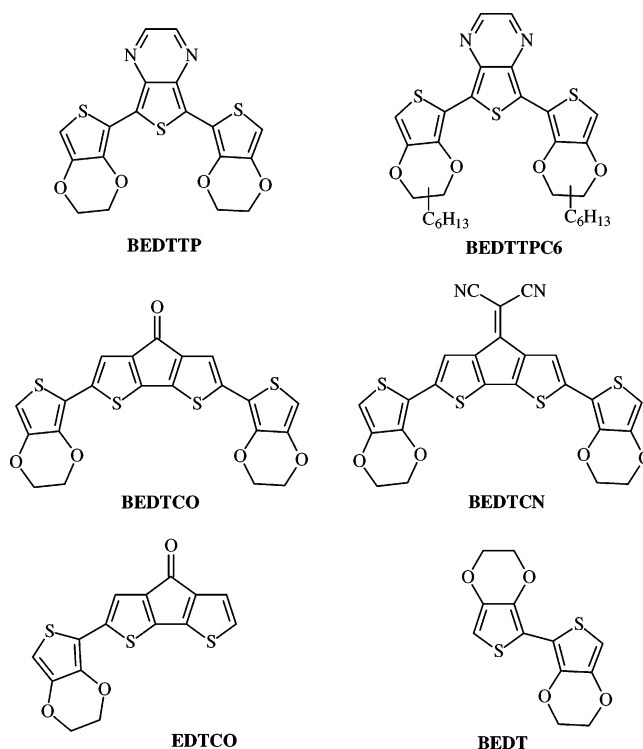
Following therefore the firm theoretically based approach of considering the maximum of absorption,⁹ we have selected as representative low-gap homopolymers those constituted by the monomeric units thieno[3,4-*b*]pyrazine (TP), cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (CO), and 4-dicyanomethylene-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (CN) shown in Chart 1.

The polymer produced from 2,3-dihexyl-TP shows a maximum absorption at 1.35 eV.¹⁰ This is a marked decrease of the gap from that of regioregular polyalkylthiophenes (2.2 eV).¹¹ This polymer belongs to the quinoid-type family of low-gap polymers.

The cyclopentadithiophene unit has been modified with a carbonyl moiety at the 4-position (CO).⁴ Polymerization of CO has produced a non-aromatic-type polymer with maximum absorption at 1.7 eV.⁴ Since poly(cyclopentadithiophene)s display their maximum absorption at 2.1 eV,¹² poly(CO) is a low-gap polymer though the gap lowering is relatively modest. CN has lowered the gap further in the relevant non-aromatic-type polymer since the maximum absorption is at 1.3 eV.⁵ For this polymer a detailed in situ conductivity investigation has been performed for both p- and n-doping.¹³ Moreover, both CO and CN dimers have been recently produced as models for the low-gap polymers and their redox and optical properties given.¹⁴

The quinoid and the DA approaches to low-gap polymers have also been combined using 3,4-ethylenedioxythiophene (EDT) (see Chart 1) as a D comonomer. EDT, an electron-rich thiophene in which the thiophene ring is protected from degradation at the 3 and 4 positions, and 2,3-dihexyl-TP have been α -linked, and the resulting monomer has been electropolymerized to

Chart 2



a copolymer with maximum absorption at 0.87 eV,¹⁵ which is the lowest energy gap value so far reported.

Also CN has been mixed with EDT by anodic coupling of the monomers to non-aromatic-DA-type copolymers with the purpose of producing a progressive modulation of the gap.¹⁶ A theoretical investigation of these monomers and of their homo- and copolymers has faced the problem of the decrease of conductivity in gap lowering through the donor-acceptor approach.¹⁷

In fact, a regular copolymer of these comonomers has not been reported yet. We have therefore addressed the role of the EDT moiety in decreasing the band gap of DA-type low-gap polythiophenes, investigating the result of capping with EDT both ends of TP, CO, and CN. In this approach, which bypasses the occurrence of random copolymerization, EDT is the D component and the others (TP, CO, and CN) are the A components. To this purpose we performed the synthesis of 2,5-bis-EDT-substituted TP (BEDTTP), CO (BEDTCO), and CN (BEDTCN) (BEDT = 3,4:3',4'-bis(ethylenedioxy)-2,2'-bithiophene) shown in Chart 2, their polymerization by anodic coupling, the electrochemical and optical characterization of the resulting polymers, and the investigation of their in situ p- and n-conductivities. The CO-based polymers have been taken as a typical case, and to this end we performed also a detailed electrochemical and optical analysis of (i) copolymerization of CO with EDT, (ii) polymerization of the asymmetric monomer EDTCO, and (iii) its copolymerization with BEDT (Chart 2), comparing the results with those from the regular BEDTCO polymer. Finally, the DA approach to low-gap polymers and the use of copolymers have been discussed.

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2. Experimental Section

Chemicals and Reagents. Melting points were measured on a melting point apparatus and are uncorrected. All reactions of air- and water-sensitive materials were performed under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles.

Anhydrous solvents used in the reactions were obtained from reagent grade solvents (Fluka) as follows: THF was distilled from sodium/benzophenone, toluene was stored over calcium hydride, refluxed, and distilled. DMF was stored over 4 Å molecular sieves, followed by distillation under reduced pressure. Acetonitrile was reagent grade (Uvasol, Merck) with a water content of <0.01%. The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C. All other chemicals were reagent grade and used as received.

The following compounds were prepared according to literature procedures: TP,¹⁸ 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene,¹⁹ CO,¹⁹ 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene,²⁰ 2-hexyl-2,3-dihydrothieno[3,4-*b*][1,4]-dioxin,²¹ and BEDT.²²

Poly(dithienylvinylene) films were electrodeposited as previously reported.²³ Regioregular head-to-tail-coupled poly(3-octylthiophene) has been produced chemically according to McCullough¹¹ and film cast from a 1% CHCl_3 solution.

¹H and ¹³C NMR spectra were recorded on a Bruker FT 500 (500 MHz for ¹H) and on a Bruker FT 300 (300 MHz for ¹H); chemical shift values are given in parts per million.

5,7-Dibromothieno[3,4-*b*]pyrazine. *N*-Bromosuccinimide (320 mg, 1.80 mmol) was added portionwise to a solution of TP (121 mg, 0.89 mmol) in DMF (20 mL). After 4 h of stirring, the solvent was evaporated at reduced pressure, water was added, and the resulting mixture was extracted with ether. The organic phase was washed with water and dried (Na_2SO_4) and the solvent evaporated to give the title compound as a yellow solid which was used without any further purification for the next step. ¹H NMR (CDCl_3): δ 8.49 (s).

5,7-Bis[3,4-(ethylenedioxy)thien-2-yl]thieno[3,4-*b*]pyrazine (BEDTTP). A mixture of 5,7-dibromo-thieno[3,4-*b*]pyrazine (177 mg, 0.60 mmol), 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (756 mg, 1.75 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (100 mg, 0.14 mmol), and DMF (20 mL) was heated at 90–100 °C for 4 h. The solvent was evaporated and the residue purified by flash chromatography (silica gel, CH_2Cl_2) to give the title compound as a blue solid (143 mg, 57% yield). Mp: >200 °C. Anal. Calcd for $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_3$: C, 51.93; H, 2.88; N, 6.72. Found: C, 51.79; H, 2.82; N, 6.65. ¹H NMR (CDCl_3): δ 4.32 (m, 4H), 4.49 (m, 4H), 6.45 (s, 2H), 8.51 (s, 2H). ¹³C (CDCl_3): δ 65.07, 65.88, 101.43, 128.02, 135.72, 138.73, 141.75, 143.39, 154.61. MS: *m/e* 416 (M^+).

2(3)-Hexyl-5-(tributylstannyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin. BuLi (1.6 M in hexane, 3.19 mL) was added dropwise to a solution of 2-hexyl-2,3-dihydrothieno[3,4-*b*][1,4]-dioxin (1.00 g, 4.42 mmol) in THF (75 mL), keeping the temperature at –78 °C. After the solution was stirred for 0.5 h and warmed to –40 °C, tributylstannyl chloride (1.93 g, 5.93 mmol) was added and the resulting mixture warmed to room temperature and stirred for 8 h. The solvent was evaporated and the residue dissolved in hexane and filtered. The solvent was removed under vacuum to afford the title compound as an oil which was used without any further purification for the next step. ¹H NMR (CDCl_3): δ 0.89 (m, 12H), 1.32 (m, 28H), 3.80 (m, 1H), 4.07 (m, 2H), 6.53 (s, 1H).

5,7-Bis[2(3)-hexyl-2,3-dihydrothieno[3,4-*b*][1,4]dioxin-5-yl]thieno[3,4-*b*]pyrazine (BEDTTPC6). This compound was prepared following the same procedure described for BEDTTP, using 2(3)-hexyl-5-(tributylstannyl)-2,3-dihydrothieno[3,4-*b*][1,4]dioxin and 5,7-dibromothieno[3,4-*b*]pyrazine as reagents. The residue was purified by flash chromatography (silica gel; petroleum ether/ CH_2Cl_2 , 6:4) to give the title compound as a blue solid (51% yield). Mp: >200 °C. Anal. Calcd for $\text{C}_{30}\text{H}_{36}\text{N}_2\text{O}_4\text{S}_3$: C, 61.65; H, 6.16; N, 4.79. Found: C, 61.57; H, 6.12; N, 4.71. ¹H NMR (CDCl_3): δ 0.91 (m, 6H), 1.55 (m, 20H) 4.21 (m, 6H), 6.42 (s, 2H), 8.49 (s, 2H). MS: *m/e* 584 (M^+).

2,6-Dibromo-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene. *N*-Bromosuccinimide (1.48 g, 8.34 mmol) was added portionwise to a solution of 4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (0.98 g, 4.14 mmol) in DMF (20 mL). After 5 h of stirring, water was added and the resulting mixture extracted with ether. The organic phase was washed with water and dried (Na_2SO_4) and the solvent evaporated to give the title compound as a brown solid which was used without any further purification for the next step. ¹H NMR (CDCl_3): δ 4.25 (s, 4H), 6.95 (s, 2H).

2,6-Dibromo-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one. Concentrated hydrochloric acid (6 mL) was added dropwise to a solution of 2,6-dibromo-4,4-ethylenedioxy-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophene (1.27 g, 3.22 mmol) in THF (10 mL). After 1 h of stirring, the reaction mixture was extracted with CH_2Cl_2 , the organic phase washed with water and dried (Na_2SO_4), and the solvent evaporated. Flash chromatography of the residue (silica gel; CH_2Cl_2 /petroleum ether, 8:2) afforded the title compound as a violet solid (1.70 g, 75% yield). Mp: 190–192 °C. Anal. Calcd for $\text{C}_9\text{H}_2\text{Br}_2\text{OS}_2$: C, 30.89; H, 0.57. Found: C, 30.77; H, 0.61. ¹H NMR (CDCl_3): δ 6.99 (s). ¹³C (CDCl_3): δ 113.95, 139.49, 148.63, 180.45.

2,6-Bis[3,4-(ethylenedioxy)thien-2-yl]-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (BEDTCO). A mixture of 2,6-dibromo-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (103 mg, 0.29 mmol), 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (424 mg, 0.93 mmol), $\text{Pd}(\text{PPh}_3)_4$ (11 mg, 0.01 mmol), and toluene (10 mL) was refluxed for 5 h. After cooling, the solid precipitated was filtered and washed several times with petroleum ether to give the title compound as a green solid (91 mg, 63% yield). Mp: >300 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{12}\text{O}_5\text{S}_4$: C, 53.39; H, 2.54. Found: C, 53.25; H, 2.39. ¹H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 4.24 (m, 4H), 4.34 (m, 4H), 6.25 (s, 2H), 7.05 (s, 2H). ¹³C ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 64.36, 64.91, 97.35, 116.66, 137.73, 137.98, 141.59, 141.80, 146.73, 146.86. MS: *m/e* 416 (M^+).

2-[3,4-(Ethylenedioxy)thien-2-yl]-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (EDTCO). A mixture of 2,6-dibromo-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-one (101 mg, 0.29 mmol), 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (419 mg, 0.92 mmol), $\text{PdCl}_2(\text{PPh}_3)_2$ (25 mg, 0.04 mmol), and DMF (10 mL) was heated at 90–100 °C for 8 h. The solvent was evaporated and the residue washed several times with petroleum ether and purified by flash chromatography (silica gel, CH_2Cl_2 /petrol ether 9:1) to give, in elution order, the title compound as a solid (16 mg) and BEDTCO (39 mg, 30% yield). The following are data for EDTCO. Anal. Calcd for $\text{C}_{15}\text{H}_8\text{O}_3\text{S}_3$: C, 53.89; H, 2.39. Found: C, 53.76; H, 2.35. ¹H NMR (CDCl_3): δ 4.25 (m, 2H), 4.33 (m, 2H), 6.23 (s, 1H), 6.97–7.00 (AB system, 2H), 7.09 (s, 1H). MS: *m/e* 334 (M^+).

2,6-Bis[3,4-(ethylenedioxy)thien-2-yl]-4*H*-cyclopenta[2,1-*b*:3,4-*b'*]dithiophen-4-ylidenemalononitrile (BEDTCN). A mixture of BEDTCO (17 mg, 0.04 mmol), malononitrile (8 mg, 0.13 mmol), one drop of piperidine, and THF (5 mL) was refluxed for 14 h. After cooling, petroleum ether was added and the solid filtered and washed with petroleum ether to give the title compound as a dark solid (11 mg, 59% yield). Mp: >300 °C. Anal. Calcd for $\text{C}_{24}\text{H}_{12}\text{N}_2\text{O}_4\text{S}_4$: C, 55.38; H, 2.31; N, 5.38. Found: C, 55.29; H, 2.25; N, 5.32. ¹H NMR ($\text{C}_2\text{D}_2\text{Cl}_4$): δ 4.27 (m, 4H) 4.37 (m, 4H), 6.31 (s, 2H), 7.47 (s, 2H). MS: *m/e* 520 (M^+).

Electrochemical Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three electrode cells. The counter electrode was platinum; the

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Scheme 1

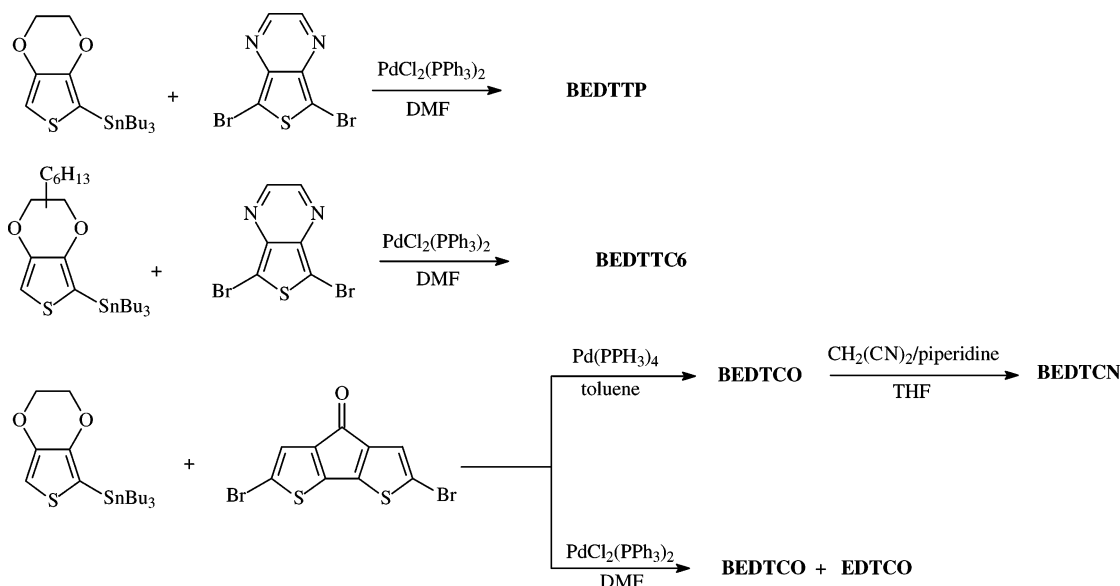


Table 1. Oxidation and Reduction Peak Potentials E_p and Maximum Absorption λ_m for Monomers and Oxidation and Reduction Redox Potentials E° , Electrochemical Gap ΔE° , Maximum Absorption λ_p , and Optical Gap E_g for Polymers

monomer	E_p/V	E° ^b /V	$\Delta E^\circ/V$	λ_m^a/nm	λ_p/nm	E_g/eV
BEDTTP	0.20, -1.62	-0.40, -1.70	1.30	355, 583	490, 950	1.30
BEDTPC6	0.21, -1.63	-0.50, -1.70	1.20	355, 589	480, 940	1.30
EDTCO	0.51, -1.50	-0.10, -1.60	1.50	345, 558	445, 750	1.65
BEDTCO	0.42, -1.45	-0.35, -1.60	1.25	380, 612	500, 800	1.55
BEDTCN	0.53, -0.95	-0.30, -1.10, -1.55	0.80	360, 820	545, 1300	0.95
TPC6	1.35, -2.01 ⁴³	0.1, -1.5 ⁴⁴	1.60 ⁴⁴	307 ⁴⁴	915 ¹⁰	1.35
CO	0.98, -1.54	0.45, -1.50	1.95	472 ¹⁴	740	1.70
CN	1.08, -1.03 ¹⁴	0.50, -1.05 ⁵	1.55	576 ¹⁴	950	1.30

^a In CHCl₃. ^b $E^\circ = (E_{p,ox} + E_{p,red})/2$.

reference electrode was 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 either platinum (0.003 cm²) or glassy carbon (0.2 cm²) minidisk electrodes. For electronic spectroscopy an 0.8 × 2.5 cm indium-tin oxide (ITO) sheet (ca. 80% transmittance, ca. 20 Ω sq⁻¹ resistance, from Balzers, Liechtenstein) was used.

FTIR spectra of the polymer films were taken in reflection-absorption mode on a Perkin-Elmer 2000 FTIR spectrometer; electronic spectra were obtained on a Perkin-Elmer Lambda 9 UV-vis-near-IR spectrometer.

Electrochemical quartz crystal microbalance (EQCM) analysis was performed with a platinum-coated AT-cut quartz electrode (0.2 cm²), resonating at 9 MHz, onto which the polymers were deposited. The oscillator circuit was homemade, and the frequency counter was an Agilent model 53131A. Measurements were performed either ex situ (to correlate polymer dry mass and redox charge) or in situ (to correlate polymer mass changes with potential or redox charge).

The apparatus and procedures used for the in situ dc conductivity experiments were previously described in detail.^{24,25} The electrode for conductivity measurements was typically a two-band platinum electrode (0.3 cm × 0.01 cm for each band) with an interband spacing of 20 μm. In the case of conductivities lower than 10⁻² S cm⁻¹, the electrode was a microband array platinum electrode (5 μm bandwidth, 100 nm thick) with an 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, and k the cell constant.

3. Results and Discussion

Synthesis of the Monomers. The synthetic access to the monomers prepared for the first time in the context of this work is depicted in Scheme 1. BEDTTP, BEDTPC6, and BEDTCO were obtained by Stille coupling reaction of the proper 2-(tributylstannyl)EDT with 5,7-dibromo-TP and 2,6-dibromo-CO, catalyzed by PdCl₂(PPh₃)₂ or Pd(PPh₃)₄. In the case of 2,6-dibromo-CO, if the reaction is carried out in DMF with PdCl₂(PPh₃)₂ as catalyst, together with the desired product, some EDTCO is obtained in low yield. This compound is presumably the result of a monocoupling reaction followed by a metal-halogen exchange and hydrolysis. BEDTCO is obtained in higher yield if the reaction is carried out in toluene with Pd(PPh₃)₄. BEDTCN is finally obtained by Knoevenagel condensation of BEDTCO with malononitrile in the presence of piperidine.

Polymer Electrosynthesis and Electrochemistry. The redox properties of the investigated monomers and polymers are summarized in Table 1. Redox potentials E° of polymers are given as the average of forward and backward CV peak potentials: $E^\circ = (E_{p,ox} + E_{p,red})/2$. The table also reports the data of the homopolymers for comparison. All the produced polymers are insoluble in the commonly used solvents.

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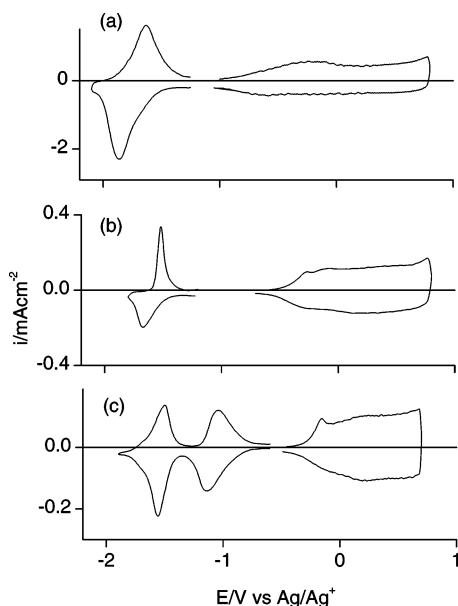


Figure 1. Cyclic voltammetry of (a) poly(BEDTTP), (b) poly(BEDTCO), and (c) poly(BEDTCN) in acetonitrile + 0.1 M Bu_4NClO_4 . Scan rate: 0.1 V s^{-1} . Reversible charge: (a) 7, (b) 1.3, and (c) 0.8 mC cm^{-2} .

BEDTTP. The EDT-disubstituted TP-based monomer BEDTTP is oxidized at $E_p = 0.20 \text{ V}$, i.e., with a large negative shift compared with the thiophene-disubstituted TP ($E_p = 0.63 \text{ V}^{26}$), due to the electron-donor EDT moieties. Film formation occurs easily potentiostatically at the peak potential.

The polymer film is reversibly oxidized and reduced (Figure 1a). The monomer is similarly reduced reversibly in a one-electron step at a potential very close to that of the polymer. On the contrary, the oxidation process of the polymer is 0.6 V more negative than that of the monomer. This indicates that the reduction charge is much more localized than the oxidation charge.

Comparison with poly(TPC6) (Table 1) shows that the EDT units lower the electrochemical gap, but only a moderate DA effect is observed in this case on the band gap. The dihexyl-substituted monomer BEDTTPC6 behaves similarly to BEDTTP.

CO and EDTCO. The electrochemical properties of monomer CO and of its polymer were reported previously.⁴ Polymer film formation occurs potentiostatically at the peak potential from a 10^{-2} M solution of the monomer.

The poly(CO) film is reversibly oxidized at $E^o = 0.45 \text{ V}^4$ and reversibly reduced at $E^o = -1.50 \text{ V}$. The monomer is reversibly reduced in a one-electron step at a potential very close to that of the polymer. On the contrary, the oxidation process of the polymer is ca. 0.5 V more negative than that of the monomer. Also in this case the reduction charge is much more localized than the oxidation charge.

The EDT-monosubstituted monomer EDTCO (ca. 10^{-3} M standard solution in acetonitrile) is oxidized with easy film formation. The polymer film is reversibly oxidized and reduced, and the resulting electrochemical gap (ΔE^o

$= 1.50 \text{ V}$) is decreased markedly from that of poly(CO) (1.95 V) by alternation with EDT.

BEDTCO. The EDT-disubstituted monomer CO, scarcely soluble in acetonitrile, has been investigated in $\text{CH}_2\text{Cl}_2 + 0.1 \text{ M Bu}_4\text{NClO}_4$, where it is oxidized with polymerization.

The polymer film is reversibly oxidized and reduced (Figure 1b). The monomer is reversibly reduced at $E^o = -1.45 \text{ V}$, i.e., with a moderate shift compared with the polymer. Making a comparison with poly(CO) and poly(EDTCO), it is clear that the electrochemical gap has been strongly decreased further (from 1.95 to 1.50 V and finally to 1.25 V).

The extent of the reduction process depends on the film thickness. Whereas the reversible oxidation charge Q_{ox} increases linearly with the deposition charge Q_d up to a thickness of several micrometers (on the basis of redox stoichiometry and assuming a density of 1 g cm^{-3}), the reversible reduction charge Q_r behaves similarly up to $Q_d = \text{ca. } 10 \text{ mC cm}^{-2}$, and then Q_r decreases to very low levels at film thicknesses higher than 100 nm .

BEDTCN. BEDTCN is scarcely soluble in ordinary solvents. In hot tetrachloroethane, where a ca. $5 \times 10^{-4} \text{ M}$ solution may be prepared, and with added $0.1 \text{ M Bu}_4\text{NClO}_4$, the monomer is polymerized anyway.

The polymer film is reversibly oxidized in a single process and reversibly reduced in two isoelectronic steps (Figure 1c). The first reversible reduction of the monomer, obtained in tetrachloroethane (for solubility reasons) on a glassy carbon electrode, shows also in this case only a moderate shift in the polymer. From the redox potentials of the polymer a very low electrochemical gap (0.8 eV) is evaluated, i.e., the minimum value ever recorded. Comparison with poly(CN) shows that the electrochemical gap has also been in this case strongly decreased (almost halved) by alternation with bis-EDT units.

As in the case of poly(BEDTCO) and with similar limits, the extent of the reduction is limited by the film thickness. The result is accounted for by a slow electron transport in a redox-type conduction among localized states.²⁷ This has precluded the possibility of measuring for these polymers the conductivity of the n-doped form (see below).

EQCM Analysis. The stoichiometry of p- and n-doping and the relevant changes of composition were investigated by EQCM analysis. We have previously found that the reversible oxidation of polythiophenes involves roughly the same amount of charge independently from the monomer type. Thus, 1.0 electron for the cyclopentadithiophene²⁸ and 0.6 electron for the EDT²⁹ moieties were measured at 0.8 V so that a value of 0.5 electron per thiophene ring may be taken as a good approximate value for the repeat units used in this investigation.

Poly(BEDTTP) has been chosen as a typical example of the polymers investigated here. EQCM correlation of dry mass in the undoped state and reversible charge (measured at the maximum allowed oxidation, namely,

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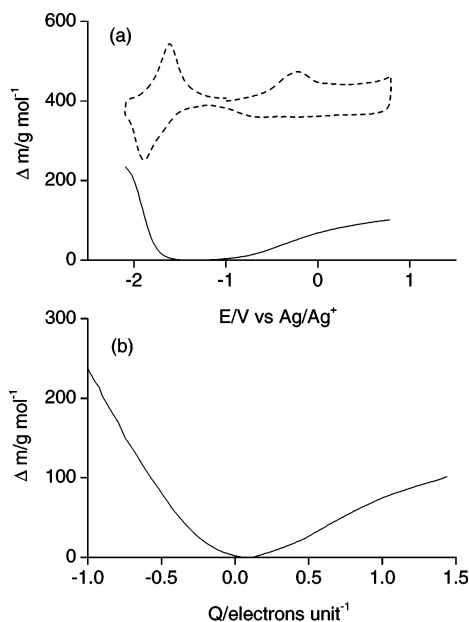


Figure 2. In situ EQCM analysis vs (a) potential and (b) charge for poly(BEDTTP) in acetonitrile + 0.1 M Bu₄NClO₄. Scan from oxidation to reduction. Dashed curve: cyclic voltammogram for comparison.

that obtained at 0.8 V) indicates that 1.5 electrons per monomeric unit (0.5 electron per thiophene ring) are exchanged during an oxidation CV cycle. The stoichiometric rule above is therefore once more confirmed.

In each of the reductive processes the exchanged charge corresponds to 1.0 electron per monomeric unit.

The mass changes during the redox processes are shown in Figure 2. The mass increases almost linearly with charge with a slope corresponding to the uptake of the perchlorate anion during oxidation and of the tetrabutylammonium cation during reduction.

UV–Vis Spectroscopy. The electronic spectra of monomers and undoped polymers (Figures 3 and 4) show two absorption maxima, attributable to transitions from the thiophene-based valence band to its antibonding counterpart (for the high-energy transition) and to the substituent-localized and narrow conduction band (for the low-energy transition).¹⁷

The undoped poly(BEDTTP) film displays a maximum absorption in the near-IR region at 950 nm (Figure 3a), which indicates a very low optical gap (1.3 eV).

The low-energy maximum absorption of poly(BEDTCO) in the undoped state (Figure 3b) is at 800 nm (1.55 eV), whereas the undoped polymer film from EDTCO displays its maximum at 750 nm. Thus, a significantly higher optical gap is measured for poly(EDTCO), in agreement with the electrochemical gap.

In the undoped form poly(BEDTCN) displays its low-energy maximum absorption at 1300 nm (Figure 3c). The optical gap (0.95 eV) is one of the lowest ever reported.

The oxidized form of all these polymers is a light blue color with an extended plateau in the near-IR.

A comparison between the optical and the electrochemical gaps (see Table 1) evidences a substantial agreement between the two sets of data, thus providing further support to the validity of considering standard

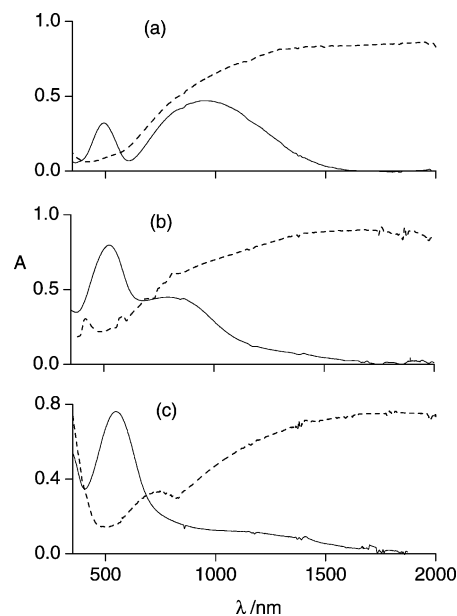


Figure 3. Spectroelectrochemistry of (a) poly(BEDTTP), (b) poly(BEDTCO), and (c) poly(BEDTCN) on ITO in acetonitrile + 0.1 M Bu₄NClO₄: (—) undoped and (---) p-doped forms.

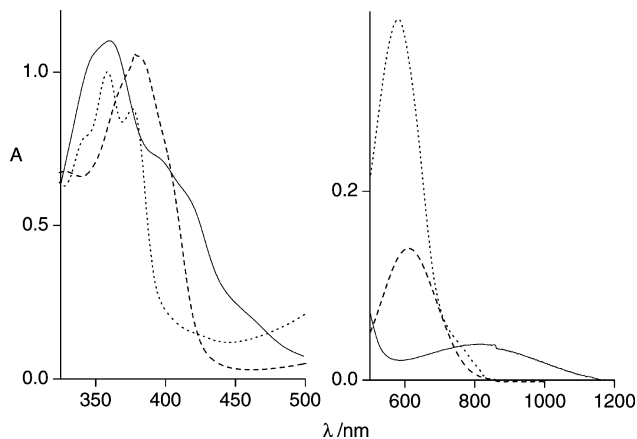


Figure 4. UV–vis–near-IR spectra of (dotted line) BEDTTP in CHCl₃, (dashed line) BEDTCO in CH₂Cl₂, and (solid line) BEDTCN in tetrachloroethane.

redox potentials and absorption maxima for a correct evaluation of energy gaps.

The absorbance at the low-energy band of these polymers (Figure 3) and of their monomers (Figure 4) progressively decreases in the series BEDTTP > BEDTCO > BEDTCN. The band intensity decreases both in comparison with that of the high-energy band and in absolute terms (BEDTTP, $\epsilon = 6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in CHCl₃; BEDTCO, $\epsilon = 1.7 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in CHCl₃; BEDTCN, $\epsilon = 1.0 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$ in tetrachloroethane). The progressive decrease of the transition moment, which is probably associated with the increased localization of the transition, is of high importance for applications.

In Situ Conductivity. The results of in situ conductivity measurements for the polymers investigated here and their homopolymers for comparison are summarized in Table 2.

The polymer from BEDTTP becomes conductive at oxidation (Figure 5a) with a plateau of conductivity 0.5 S cm⁻¹ and at reduction at the first reduction step

Table 2. p- and n-Conductivities σ for Polymers

monomer	$\sigma_p/\text{S cm}^{-1}$	$\sigma_n/\text{S cm}^{-1}$
BEDTTP	0.5	0.01
BEDTTPC6	15	0.03
BEDTCO	0.3	
BEDTCN	> 10	
TPC6 ¹⁰	0.04	
CO	15	0.01
CN ¹³	0.6	0.005

(Figure 5b) with a redox-type conductivity (centered at the redox potential)²⁷ of $10^{-2} \text{ S cm}^{-1}$.

Similarly, poly(BEDTTPC6) becomes p-conductive with a plateau of 15 S cm^{-1} and n-conductive with a peak of 0.03 S cm^{-1} . The p-conductivity is much increased, compared with BEDTTP, possibly due to ordering by the alkyl chain, as observed in alkyl-substituted poly(EDT).³⁰ On the contrary, the n-conductivity is only moderately increased.

The maximum conductivity of oxidized poly(BEDTCO) is 0.3 S cm^{-1} , i.e., practically the same as that of poly(BEDTTP). The undoped polymer form could not be reduced completely (see above), thus preventing the n-conductivity from being measured. This behavior suggests that the carbonyl group hinders charge transport. In fact, in the parent poly(CO) we found that the 15 S cm^{-1} p-conductivity drops to $10^{-2} \text{ S cm}^{-1}$ in n-doping, with a p/n-conductivity ratio of 1500.

Poly(BEDTCN) becomes conductive at oxidation, but the maximum coverage of the electrode gap was incomplete (due to loose mechanical properties of the polymer) so that only a lower limit of conductivity ($> 10 \text{ S cm}^{-1}$) could be determined. Due to difficult charge transport the n-conductivity could not be measured. In fact, the 0.6 S cm^{-1} p-conductivity of poly(CN) drops to $5 \times 10^{-3} \text{ S cm}^{-1}$ in n-doping,¹³ and in our case the drop is expectedly even more severe.

It results that n-conductivity decreases strongly going from the homo- to the copolymers so that it is not even measured in the latter. This fact must be ascribed to the increased hopping distance among redox centers in the copolymer produced by the insertion of the bis-EDT subunits.

CO-co-EDT and BEDTCO-co-BEDT Polymerization. For the production of real copolymers (and not of blends) in the copolymerization via anodic coupling it is required that the oxidation potentials of the concurrent monomers are close (within 0.1 V) so that their radical cations are produced at the same time. In our case CO (0.98 V) and EDT (1.04 V) fulfill this requirement as well as the couple BEDTCO (0.42 V) and BEDT (0.51 V²²). This opens up the possibility of a comparison between the random copolymers from the two copolymerization mixtures and the regular copolymer described above.

Copolymerization may be followed by FTIR spectroscopy as well as by integration of the redox charges of the polymers. The FTIR reflection-absorption spectrum of the undoped poly(CO-co-EDT) film shows the strong bands of the ethylenedioxy moieties (C–O–C stretching mode) at 1070 cm^{-1} ³¹ and of the carbonyl moiety (C=O

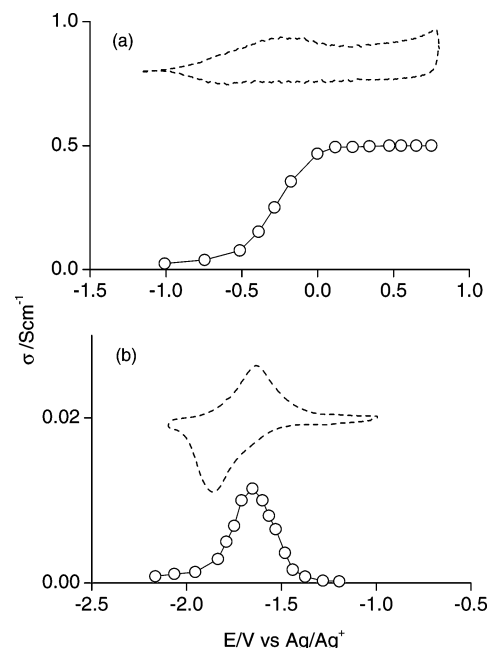


Figure 5. In situ (a) p- and (b) n-conductivity of poly(BEDTTP) in acetonitrile + 0.1 M Bu_4NClO_4 . Dashed curves: cyclic voltammograms for comparison.

stretching mode) at 1700 cm^{-1} . The bands are of the same intensity in the BEDTCO monomer (two EDT moieties and one CO moiety), which makes the evaluation of the copolymer composition straightforward.

As far as the CV redox charge is concerned, a comparison of the reduction charge of the carbonyl moiety (one electron per CO moiety) and of the oxidation charge of the thiophene rings at 0.8 V (with the electron stoichiometry of 0.5 electron per thiophene ring; see above) allows an alternative evaluation of the copolymer composition.

For CO-co-EDT copolymerization the experimental results from both FTIR and CV indicate that potentiostatic oxidation of the monomeric mixture in acetonitrile (typically $3 \times 10^{-3} \text{ M}$ in CO and 5×10^{-4} to $4 \times 10^{-3} \text{ M}$ in EDT) at 1.0 V produces a copolymer with 6 times more EDT content than indicated by the monomeric ratio in the solution. The composition was not particularly dependent on the used potential. Detailed analysis of the oxidative redox cycle (Figure 6) shows that while the reduction process occurs at a fixed potential the oxidation process shifts cathodically as the EDT content increases, pointing to the limit of the homopolymer (-0.6 V ^{30,32}). From this result we may conclude that the “vanishingly small” onset-based gap claimed previously¹⁶ is not in fact achievable by this route since the gap is dictated by the redox values of the individual homopolymers only.

In agreement with these results, the UV-vis-near-IR spectra of the CO-EDT copolymers above (Figure 7) show that the low-energy band shifts bathochromically and weakens as the EDT content increases.

The electrochemical and optical shifts are definitive proof that we deal with a real copolymer. Similarly, the copolymerization of 3-butyl- and 3,4-dibutylthiophene has given polymers with a progressive shift of electro-

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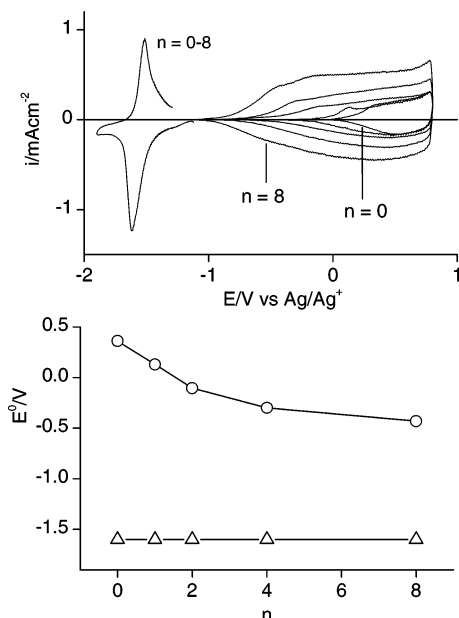


Figure 6. (Top) Cyclic voltammograms of poly(CO-co-EDT n) as a function of n (0, 1, 2, 4, 8) in acetonitrile + 0.1 M Bu₄NClO₄. (Bottom) E^0_{ox} (circles) and E^0_{red} (triangles) vs n . Scan rate: 0.1 V s⁻¹.

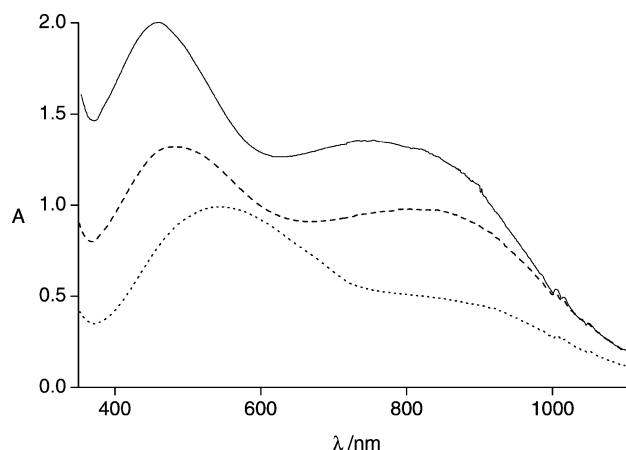


Figure 7. UV-vis-near-IR spectra of poly(CO-co-EDT n) as a function of monomer ratio n . $n = 1$ (solid line), 2 (dashed line), and 4 (dotted line).

chemical (oxidative redox potential) and optical (energy gap) properties with the monomer molar fraction.^{33,34}

The increase of the EDT component clearly decreases the relative contribution of both the reduction charge and the low-energy absorption (see Figures 6 and 7), which clearly poses serious limits to the application of the copolymerization approach for the production of low-gap polymers.

For BEDTCO-co-BEDT polymerization the CV results indicate that potentiostatic oxidation of the monomeric mixture in CH₂Cl₂ (typically 5×10^{-4} M in BEDTCO and 5×10^{-4} to 2×10^{-3} M in BEDT) at 0.6 V produces a copolymer with the same EDT molar fraction as that in the solution. This is due to a practical equalization of the reactivities of the radical cations due to the fact that both monomers are EDT-ended. The potential shift

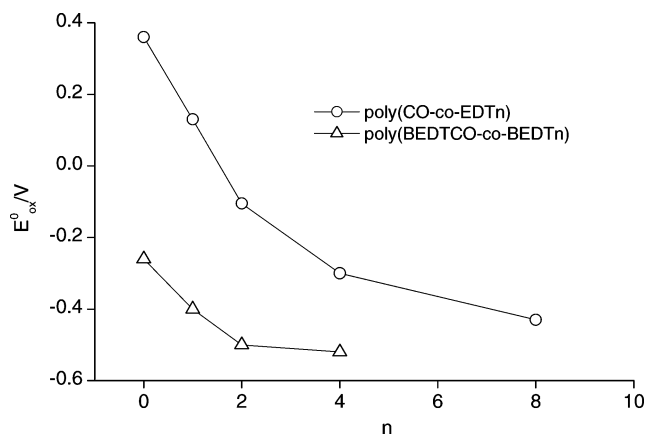


Figure 8. Oxidation redox potential E^0_{ox} of (○) poly(CO-co-EDT n) and (△) poly(BEDTCO-co-BEDT n) vs n .

occurs also in this case (Figure 8) though clearly from a more negative starting value and with a slower progression.

A comparison of copolymers of the same composition but produced by either route does not evidence significant electrochemical differences, which is a final confirmation of the efficient copolymerization in the considered cases.

Charge Localization in the Investigated Polymers. The subunits of the investigated regular copolymers are BEDT as electron donor and TP, CO, or CN as electron acceptor moieties. The oxidation process might to a first approximation be assumed to involve the BEDT moiety alone. Yet the charge is situated on the CH backbone of this dimeric moiety and is conjugated with the CH backbone of the acceptor. Thus, it results that, contrary to a first thought, the positive charge is in fact delocalized over the whole CH backbone of the polymer chain. As a consequence the oxidation potential of the BEDT molecule (0.51 V²²), which is roughly the same (0.5 V) in the CO- and CN-based monomers, is strongly shifted to the negative direction (by ca. 0.7 V) in the polymers.

The reduction process involves highly localized sites, namely, the pyrazine ring and the carbonyl or the dicyanomethylene moieties. For this reason the redox potential of the acceptor moiety in the monomer (see, e.g., BEDTCO) is in practice the same as that of the isolated acceptor molecule (see, e.g., CO) and is only slightly (0.1 V at most) shifted to the negative direction in the polymer.

A further difference between the oxidation and the reduction processes is their half-height width W , which is high for the oxidation (1.2 V at least, capacitive plateau) and quite narrow (ca 0.2 V, redox bell) for the reduction process (Figure 1).

From the reduction redox potentials (CN > CO > TP) and the extent of electrochemical reduction, from the intensity of the low-energy bands and the n -doping conductivity values, it results that localization is stronger in CO and CN than in TP. It is suggested that in TP the charge is distributed over the pyrazine-fused thiophene ring rather than localized on the pyrazine ring alone, and this allows a comparatively higher mobility.

Charge Localization and Conductivity in Polythiophenes. Gap lowering by the donor-acceptor ap-

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proach is in general accompanied in fact by band narrowing, which means that charge localization leads to a decreased level of conductivity.¹⁷ Moreover, DA alternation also decreases dramatically the gap lowering with the increase of the degree of polymerization.¹⁷ This outcome may be a positive result since low DP oligomers are in practice as conducting as long-chain polymers, but it is in any case a limitation of the DA approach.

The conductivity of polyconjugated polymers in general is expected to be symmetrical for p- and n-doping. In fact, polyacetylene, which may be p- and n-doped with Lewis acids and alkali metals, respectively,³⁵ displays similar conductivities in the two types of doping. Yet in polythiophenes a strong decrease of conductivity from p- to n-doping is the general rule. Polythiophene electrochemically n-doped with tetrabutylammonium ion displays a conductivity of ca. $5 \times 10^{-2} \text{ S cm}^{-1}$ vs 15 S cm^{-1} for the tetrafluoroborate p-doped material; i.e., the n-conductivity is ca. 300 times lower.³⁶ In poly(3-methylthiophene)³⁷ conductivity of the n-doped form is ca. 100 times lower than that of the p-doped form. Also the conductivity of the p- and n-doped forms of poly(dithienylvinylene)²³ are in a 300 ratio. All the polymers investigated here follow this rule.

Also the shape of the cyclic voltammograms in polythiophenes shows large potential windows (capacitive current plateaus) for oxidation and narrow redox-like peaks for reduction, in agreement with wide and narrow bands, respectively. Chemically prepared regioregular poly(3-octylthiophene)¹¹ and anodically coupled poly(dithienylvinylene), which is appreciably defect free due to the low oxidation potential of the monomer,²³ show a p-doping cyclic voltammogram 0.6–0.8 V wide but a narrow (ca 0.1 V) n-doping cyclic voltammogram (Figure 9). Since no DA alternation is present in these polymers, the reason for the asymmetrical CV behavior must be ascribed to the thiophene component itself in every case.

Localization of charge in polythiophenes may in principle be traced to the different localization of the LUMO (on the sulfur atoms) and of the HOMO (on the polyacetylene CH backbone) orbitals. Quantomechanical calculations on the isolated polyconjugated polymer chain³⁸ have in fact shown that whereas the valence band is constituted exclusively by carbon $2p_z$ orbitals, p_z orbitals of the heteroatoms take part in the conduction band, and this is reflected, e.g., in the different ESR g values, 2.0045 for anions³⁹ and 2.0025 for cation radicals.⁴⁰ Bandwidths of valence and conduction bands are in any case comparable.³⁸ It is therefore suggested that the reason for the different charge localization in the bulk material lies on an intermolecular (rather than intramolecular) basis, i.e., that π -interaction is weaker among orbitals constituting a partially filled conduction band than among those forming a partially empty valence band. In agreement with this suggestion

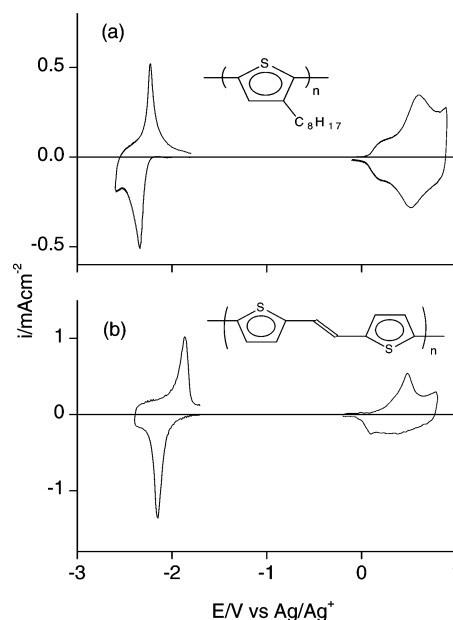


Figure 9. Cyclic voltammograms of (a) poly(3-octylthiophene) and (b) poly(dithienylvinylene) in acetonitrile + 0.1 M Bu_4NClO_4 . Scan rate: 0.1 V s^{-1} .

thiophene radical anions do not show any tendency to π -dimerize,⁴¹ different from radical cations.⁴²

As a conclusion charge localization is in fact already present in non-DA-type polythiophenes. It is then enhanced in DA-type polymers and is finally brought to higher limits in copolymers.

4. Conclusions

Anodic coupling of monomers constituted by two 3,4-ethylenedioxythiophene units α -linked to thienopyrazine, cyclopentadithiophen-4-one, and 4-dicyanomethylenecyclopentadithiophene has produced new low-gap thiophene-based polymers. The regular copolymers thus produced show optical gaps (measured at the maximum absorption) in the range 0.95–1.30 eV and electrochemical gaps (measured from redox potentials) in almost the same range (0.80–1.30 V). Alternation of electron donor bis-3,4-ethylenedioxythiophene subunits is so effective in gap lowering that the dicyano monomer has produced a regular copolymer with the lowest reported electrochemical gap (0.8 V).

Copolymerization of acceptor monomers with increasing amounts of 3,4-ethylenedioxythiophene as donor comonomer does decrease the gap but at the expense of optical and electrochemical densities. From an analysis of the redox potential as a function of comonomer fraction, it results that the gap is limited by the redox potentials of the individual homopolymers only, as reasonably expected. Thus, a vanishingly small gap is not achievable by this route.

Finally, it must be stressed that the DA copolymerization approach to gap lowering dealt with in this paper

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brings about negative effects on the expected intrinsic conductivity entirely limited to the n-type component. Negative charges produced in n-doping are localized in the polythiophene chains already without DA moieties, and addition of DA alternation localizes the n-type conductivity carriers further. An even lower n-conductivity is produced in copolymers by a higher content of 3,4-ethylenedioxythiophene units due to increased electron hopping distances. The final result is that in

these polymers the intrinsic conductivity is completely p-type.

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