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Novel, Highly Conducting, and Soluble Polymers from Anodic Coupling of Alkyl-Substituted Cyclopentadithiophene Monomers

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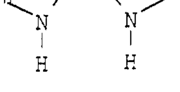
ABSTRACT: A series of 4-*n*-alkyl- and 4,4-di-*n*-alkyl-substituted cyclopentadithiophenes (C_nCPDT and $(C_n)_2$CPDT, n = 1, 3, 4, 6, 8, and 16) were synthesized and polymerized by anodic coupling in 0.1 M TEAP + AN. Electrochemistry, IR and electronic spectroscopies, elemental analysis, and in situ conductivity indicate that the polymers are oxidized to the conductive state (0.5 anion per monomeric unit) in two steps and in a single step for poly[C_nCPDT] and poly[$(C_n)_2$CPDT], respectively. The polymers are highly conductive (80–300 S/cm for poly[C_nCPDT] and 2–40 S/cm for poly[$(C_n)_2$CPDT]) and soluble in $CHCl_3$ (degree of polymerization = 10–40 for poly[C_{16}CPDT] and for poly[$(C_4)_2$CPDT]). Absorption maxima, in the range 545–605 nm, are anomalously red shifted to 640 and 680 nm for poly[$(C_8)_2$CPDT] and poly[$(C_{16})_2$CPDT].

Introduction

The redox potentials of conducting polymers are an important property for application purposes of these materials. Neutral polypyrrole, because of its low oxidation potential, is an oxygen-sensitive material. We proposed[1] that the availability of pyrrole-based monomers capable of originating polymers endowed with increased redox potentials would be highly beneficial for producing environmentally stable materials. Conversely, oxidized polythiophene is a relatively strong oxidant and can be easily dedoped by several environmental agents. It would, therefore, be desirable to have available thiophene-based polymers with decreased redox potential. For this purpose, we proposed[1] a careful tailoring of the monomer structure by inserting between two "external" polymerogenic five-membered heterocycles a central ring which had to be relatively electron-withdrawing in the case of pyrrole-based monomers and electron-donating in the case of thiophene-based monomers. Thus, we were able to obtain pyrrole-based polymers characterized by good conductivity starting from pyrrolo[3,2-*g*]indole (1) and dipyrrolo[1,2-*a*:2′,1′-*c*]pyrazine (2).[2] Furthermore, we were able to target the dithieno[3,2-*b*:2′,3′-*d*]pyrrole (3) as a candidate responding to the above requisite for a thiophene-based monomer. The results were successful,[3] both on the side of conductivity and on the side of redox potential.



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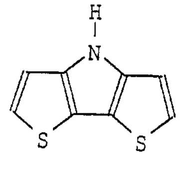

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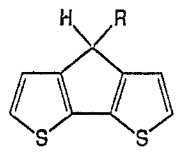
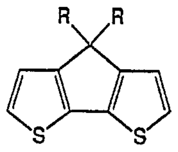
The tricyclic compounds 1–3 possess further profitable structural items. First, the two external polymerogenic heterocyclic units are linked through the α,α'-positions, thus mimicking, as dimers, the correct structure of the final polymer. Second, the central ring locks the two external rings in a planar conformation, thus favoring conjugation along the polymeric unsaturated chain. We have discussed[1] how dramatically the conductivity of pyrrole-based polymers can be affected by the torsional angle between the heterocyclic moieties constituting the backbone. Third, monomers 1–3 can, in principle, be functionalized by conveniently designed residues capable of providing special properties to the final polymers. Compound 3, for instance, can be easily alkylated at the nitrogen atom, and the corresponding polymer becomes partially soluble. Such a functionalization is remote from the sites that couple during oxidative polymerization and, therefore, does not interfere with the conformation of the backbone.

With the purpose of producing polyconjugated polymers which would both take advantage of the above-mentioned conditions and be highly soluble, we considered the carbocyclic analogue of compound 3, 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene (4),[4-6] with alkyl (C_nCPDT) and dialkyl ($(C_n)_2$CPDT) substitution at the bridging methylene group. This paper deals with the synthesis of these monomers, their electropolymerization, and the characterization of the resulting polymers.



R = CH_3; C_1CPDT
R = n-C_3H_7; C_3CPDT
R = n-C_4H_9; C_4CPDT
R = n-C_6H_{13}; C_6CPDT
R = n-C_8H_{17}; C_8CPDT
R = n-$C_{16}H_{33}$; C_{16}CPDT



R = CH_3; $(C_1)_2$CPDT
R = n-C_3H_7; $(C_3)_2$CPDT
R = n-C_4H_9; $(C_4)_2$CPDT
R = n-C_6H_{13}; $(C_6)_2$CPDT
R = n-C_8H_{17}; $(C_8)_2$CPDT
R = n-$C_{16}H_{33}$; $(C_{16})_2$CPDT

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Experimental Section

Chemicals and Reagents. All melting points are uncorrected. All reactions of air- and water-sensitive materials were performed in flame-dried glassware under nitrogen. Air- and water-sensitive solutions were transferred with double-ended needles. The solvents used in the reactions were dried by conventional methods and freshly distilled under nitrogen. Acetonitrile (AN) was distilled twice over P_2O_5 and once over CaH_2. The supporting electrolyte, tetraethylammonium perchlorate (TEAP), was previously dried under vacuum at 70 °C. 4*H*-Cyclopenta[2,1-*b*:3,4-*b*′]dithiophene[4,5] was obtained according to a preparative modification;[6] all other chemicals were reagent grade and used as received.

Procedure for the Preparation of C_1CPDT and $(C_1)_2$CPDT. $(C_1)_2$CPDT. *n*-BuLi (1.6 N) in *n*-hexane (0.69 mL, 1.1 mmol) was added dropwise to a stirred solution of CPDT (178 mg, 1.0 mmol) in THF (18 mL), keeping the temperature at 0 °C. After 1.5 h of stirring at room temperature, MeI (156 mg, 1.1 mmol) was added at 0 °C, and the resulting solution was kept stirring at room temperature for 2 h. After the temperature was lowered again to 0 °C, 1.6 N *n*-BuLi in *n*-hexane (0.63 mL, 1.0 mmol) was added dropwise, and the reaction mixture was stirred at room temperature for 1.5 h. MeI (142 mg, 1.0 mmol) was added at 0 °C and the solution kept stirring overnight at room temperature. Flash chromatography of the residue (silica gel, petroleum ether) followed by washing with isopropyl alcohol afforded the title compound (70.1 mg, 34% yield), mp 180 °C. Anal. Calcd for $C_{11}H_{10}S_2$: C, 64.56%; H, 4.88%. Found: C, 64.26%; H, 4.57%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.58 (6 H, s *Me*), 7.00–7.18 (4 H, AB system, $J^{A,B}$ = 5.54 Hz, thiophene protons).

C_1CPDT. This compound was prepared following the same procedure described above for $(C_1)_2$CPDT until the addition of the first amount of MeI. Stirring was continued overnight; the reaction mixture was poured into NaCl-saturated water and extracted with Et_2O. The organic phase was washed with water and dried (Na_2SO_4) and the solvent evaporated. Flash chromatography of the residue (silica gel, petroleum ether) afforded C_1CPDT impure of $(C_1)_2$CPDT. Pure C_1CPDT was obtained by treatment of the mixture with isopropyl alcohol, filtration of the insoluble portion (mostly $(C_1)_2$CPDT), and evaporation of the solvent (72 mg, 38% yield). Anal. Calcd for $C_{10}H_8S_2$: C, 62.46%; H, 4.19%. Found: C, 62.67%; H, 4.34%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.20 (3 H, d, J = 8.50 Hz, *Me*), 3.68 (1 H, q, J = 8.50 Hz, H^4), 7.07–7.18 (4 H, AB system, $J^{A,B}$ = 4.89 Hz, thiophene protons).

General Procedure for the Preparation of C_nCPDT and $(C_n)_2$CPDT (n = 3, 4, 6, 8, 16). *n*-BuLi (1.6 N) in *n*-hexane (0.69 mL, 1.1 mmol) was added dropwise to a stirred solution of CPDT (178 mg, 1.0 mmol) in THF (10 mL) maintained at 0 °C. Stirring was continued for 1.5 h at room temperature, and after the solution was cooled to 0 °C, the proper *n*-alkyl halide (1.1 mmol) was added. After 2 h of stirring at room temperature, 1.6 N *n*-BuLi in *n*-hexane (0.31 mL, 0.5 mmol) was added at 0 °C, stirring was continued for 1.5 h at room temperature, and then *n*-alkyl halide (0.5 mmol) was added at 0 °C. The reaction mixture was stirred overnight at room temperature, poured into NaCl-saturated water, and extracted with Et_2O. The organic phase was dried (Na_2SO_4) and the solvent evaporated. Flash chromatography (silica gel, petroleum ether) of the residue afforded, in order of elution, $(C_n)_2$CPDT and C_nCPDT. Yields based on starting CPDT and analytical data of the obtained compounds are reported as follows. The ^{1}H NMR spectra of C_{16}CPDT and $(C_{16})_2$CPDT are reported as an example.

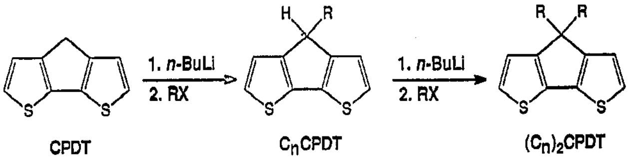
C_3CPDT. Alkylating agent, *n*-propyl bromide; 31% yield, oil. Anal. Calcd for $C_{12}H_{12}S_2$: C, 65.41%; H, 5.49%. Found: C, 66.12%; H, 5.31%.

$(C_3)_2$CPDT. Alkylating agent, *n*-propyl bromide; 40% yield, mp 66–67 °C. Anal. Calcd for $C_{15}H_{18}S_2$: C, 68.65%; H, 6.91%. Found: C, 69.23%; H, 6.88%.

C_4CPDT. Alkylating agent, *n*-butyl iodide; 45% yield, oil. Anal. Calcd for $C_{13}H_{14}S_2$: C, 66.62%; H, 6.02%. Found: C, 66.45%; H, 5.88%.

$(C_4)_2$CPDT. Alkylating agent, *n*-butyl iodide; 35% yield, low melting point solid. Anal. Calcd for $C_{17}H_{22}S_2$: C, 70.19%; H, 7.59%. Found: C, 70.29%; H, 7.63%.

Scheme 1



C_6CPDT. Alkylating agent, *n*-hexyl bromide; 32% yield, oil. Anal. Calcd for $C_{15}H_{18}S_2$: C, 68.65%; H, 6.91%. Found: C, 58.47%; H, 7.02%.

$(C_6)_2$CPDT. Alkylating agent, *n*-hexyl bromide; 45% yield, oil. Anal. Calcd for $C_{21}H_{30}S_2$: C, 72.77%; H, 8.72%. Found: C, 72.92%; H, 8.63%.

C_8CPDT. Alkylating agent, *n*-octyl bromide; 45% yield, oil. Anal. Calcd for $C_{17}H_{22}S_2$: C, 70.19%; H, 7.59%. Found: C, 70.21%; H, 7.52%.

$(C_8)_2$CPDT. Alkylating agent, *n*-octyl bromide; 47% yield, oil. Anal. Calcd for $C_{25}H_{38}S_2$: C, 74.56%; H, 9.51%. Found: C, 74.73%; H, 9.68%.

C_{16}CPDT. Alkylating agent, hexadecyl bromide; 45% yield, mp 57–58 °C. Anal. Calcd for $C_{25}H_{38}S_2$: C, 74.56%; H, 9.51%. Found: C, 74.30%; H, 9.63%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (3 H, t, *Me*), 1.25 (26 H, m, CH_2), 1.50 (4 H, m, CPDTCH_2CH_2), 1.75 (4 H, m, CPDTCH_2), 3.60 (1 H, t, H^4), 7.05–7.14 (4 H, AB system, $J^{A,B}$ = 4.89 Hz, thiophene protons).

$(C_{16})_2$CPDT. Alkylating agent, hexadecyl bromide; 35% yield, mp 43–44 °C. Anal. Calcd for $C_{41}H_{70}S_2$: C, 74.56; H, 9.51%. Found: C, 74.30; H, 9.63%. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.85 (6 H, t, *Me*), 1.15 (56 H, m, CH_2), 1.80 (4 H, m, CPDTCH_2), 6.91–7.12 (4 H, AB system, $J^{A,B}$ = 4.90 Hz, thiophene protons).

Apparatus and Procedure. Experiments were performed at 25 °C under nitrogen in three electrode cells in AN + 0.1 M TEAP. The counterelectrode was platinum; the reference electrode was silver/0.1 M silver perchlorate in acetonitrile (0.34 V vs. SCE). The voltammetric apparatus (AMEL) 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 glassy carbon disk electrode (0.2 cm^2). For electronic spectroscopy, a 0.8–2.5-cm indium–tin–oxide (ITO) sheet (ca. 80% transmittance, ca. 300 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; IR spectra were taken on a Perkin-Elmer 682 spectrometer.

The apparatus and procedures used in the in situ conductivity experiments were previously described in detail.[7] The conductivity of the polymers from poly[C_{16}CPDT] and poly[$(C_{16})_2$CPDT] could not be obtained due to the low solubility of the monomers which prevented us from obtaining deposits thick enough for the measurements.

Results and Discussion

Synthesis of the Substrates. The synthetic access to the 4-*n*-alkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes, C_nCPDT, and to the 4,4-di-*n*-alkyl-4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophenes, $(C_n)_2$CPDT, is reported in Scheme 1. The mono- and dialkyl derivatives, with the exception of the methyl derivatives C_1CPDT and $(C_1)_2$CPDT, were obtained in a one-pot reaction of 4*H*-cyclopenta[2,1-*b*:3,4-*b*′]dithiophene, CPDT, first with an equimolar amount of *n*-BuLi followed by an equimolar amount of alkylating agent and second with a half molar amount of *n*-BuLi and alkylating agent. The products of mono- and dialkylation were separated by flash chromatography. C_1CPDT and $(C_1)_2$CPDT were obtained in two separate steps because their separation by flash chromatography was not possible.

Electrochemical Synthesis and Characterization of the Polymers. The cyclic voltammogram (CV) of the monomers in AN + 0.1 M TEAP displays a single oxidation

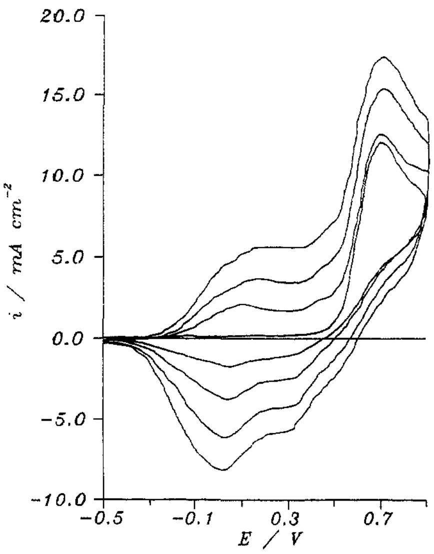


Figure 1. Repetitive cyclic voltammogram for 2×10^{-2} M C_8-CPDT in CH_3CN + 0.1 M TEAP. Scan rate: 0.1 V/s.

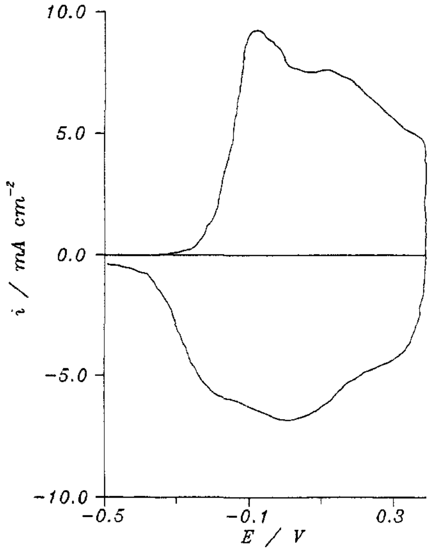


Figure 2. Anodic cyclic voltammogram for poly[C_8CPDT] in CH_3CN + 0.1 M TEAP. Scan rate: 0.1 V/s. Reversible charge: 50 mC/cm^2.

peak at 0.65 V (at 0.1 V/s). With continuous cycling of the potential, a redox cycle, due to the growing polymer, develops (Figure 1).

From the CV of the polymer film in monomer-free solution, one obtains the reversible charge. Its ratio to the charge for deposition, measured at the neutral state, is ca. 25% for poly[C_nCPDT]'s, a value that indicates for the oxidized polymer a dopant anion content of 0.5 anion per monomeric unit. For poly[$(C_n)_2$CPDT]'s, the figure is much lower (ca. 7%), which is attributable to the appreciable solubility of the oxidized oligomers evidenced by coloring of the solution during deposition. The cyclic voltammogram of the poly[C_nCPDT]'s displays two oxidation redox processes (Figure 2), which is the feature of poly(bithiophene) in the backward (reductive) scan,[8] though in our case the twin peak is clearly shown both in the forward (oxidative) and in the backward (reductive) half-cycles. In marked contrast, poly[$(C_n)_2$CPDT]'s display a single neat redox process (Figure 3). As the splitting of the system is attributed to π-dimerization of the oligomeric segments of the polymer,[9] we believe that the absence of splitting is due to a strong decrease of the π-interaction by the bulky and symmetrical alkyl substituents.[10]

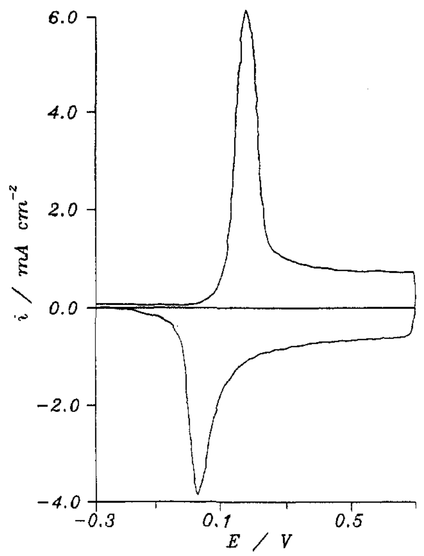


Figure 3. Anodic cyclic voltammogram for poly[$(C_8)_2$CPDT] in CH_3CN + 0.1 M TEAP. Scan rate: 0.1 V/s. Reversible charge: 8.5 mC/cm^2.

Table 1. Redox Potentials for Poly[C_nCPDT]

monomer	E^0_1/V	E^0_2/V	$E^{0\,a}$/V
C_1CPDT	0.02	0.29	0.15
C_3CPDT	-0.25	0.02	-0.11
C_4CPDT	-0.25	0.04	-0.10
C_6CPDT	-0.2	0.07	-0.06
C_8CPDT	-0.15	0.08_5	-0.03
C_{16}CPDT	-0.06	0.12	0.03

[a] $E^0 = (E^0_1 + E^0_2)/2$.

Table 2. Redox Potentials for Poly[$(C_n)_2$CPDT]

monomer	E^0/V
$(C_1)_2$CPDT	-0.05
$(C_3)_2$CPDT	0.0
$(C_4)_2$CPDT	0.02_5
$(C_6)_2$CPDT	0.07
$(C_8)_2$CPDT	0.12_5
$(C_{16})_2$CPDT	0.17

The redox potentials, E^0, taken as the average of the oxidation and reduction peak potentials, are given in Tables 1 and 2. E^0 values for poly[C_nCPDT]'s fall in a narrow range (0.2 V) around 0.0 V, i.e., close to the extrapolated value for polythiophene (0.07 V vs. F_c/F_c^+, corresponding to ca. 0.1 V vs. Ag/Ag$^+$ [11]), which suggests a high degree of polymerization. Moreover, they are not correlated with the number of carbon atoms in the alkyl chain (n).

For the poly[$(C_n)_2$CPDT]'s, the E^0 values, though in the same range, increase steadily with n, which is explained by a decreased Coulombic interaction between the polycationic chain and the anion as the spacing alkyl group becomes larger.

Poly[$(C_n)_2$CPDT]'s are reversibly reduced at ca. -2.3 V (Figure 4), while for the poly[C_nCPDT]'s, potential cycling progressively reduces the response, which is due to scavenging of acidic cyclopentadienic protons by the produced polyanion, as observed in the case of polyfluorene.[12]

In agreement with CV data, exhaustive oxidation of the monosubstituted monomers requires ca. 2.5 electrons per molecule. Conversely, the electrolysis charge for the disubstituted monomers is lower (ca. 2 electrons per molecule) due to the fact that dissolution and bulk precipitation prevents complete oxidation. The polymers were obtained in the neutral state by reducing the oxidized

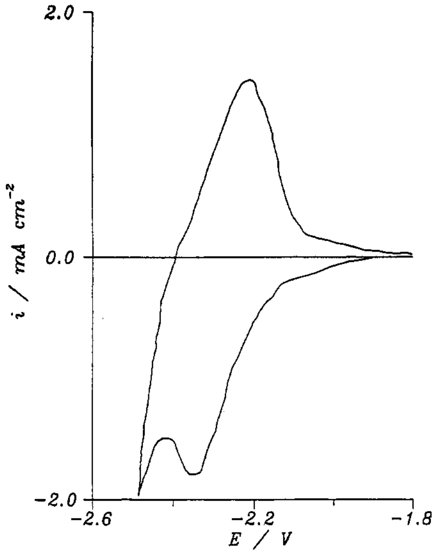


Figure 4. Cathodic cyclic voltammogram for poly[$(C_8)_2$CPDT] in CH_3CN + 0.1 M TEAP. Scan rate: 0.1 V/s. Reversible charge: 3 mC/cm^2.

Table 3. Intensity Ratio (*R*) of IR Bands (See Text) and Relevant Degree of Polymerization (n_p)

monomer	R	n_p
C_1CPDT	0.30	10
C_3CPDT	0.255	12
C_4CPDT	0.19	15
C_6CPDT	0.2	14
C_8CPDT	0.1	30
C_{16}CPDT	0.04	70
$(C_1)_2$CPDT	0.3	10
$(C_3)_2$CPDT	0.24	12
$(C_4)_2$CPDT	0.3	10
$(C_6)_2$CPDT	0.28	10
$(C_8)_2$CPDT	0.07	40

deposits at the electrode and completing the dedoping process with hydrazine, followed by washing with AN and drying.

Polymer Solubility and Degree of Polymerization. The neutral polymers are soluble in $CHCl_3$ when the alkyl chain is sufficiently long and are more soluble if the monomers are disubstituted. Thus, the poly[$(C_n)_2$CPDT]'s are soluble for $n \geq 4$, while the poly[C_nCPDT]'s are soluble only for $n = 16$.

Poly[$(C_8)_2$CPDT] is very soluble (32 g/L). Since most of the polymers are insoluble or slightly soluble in any case, their degree of polymerization was determined by IR analysis following the method by Furukawa et al.[13] All the polymers show in the CH out-of-plane deformation zone a strong band at 810–825 cm^{-1}, due to backbone rings (B band), and a band in the range 650–680 cm^{-1}, due to the terminal rings (T band). The degree of polymerization (n_p) may be obtained from the intensity ratio $R = A_T/A_B$ and by using the relationship $n_p = (2.7/R) + 1$ (obtained from CPDT and poly[$(C_8)_2$CPDT] in CS_2 solution). The results are given in Table 3. From this table, we see that the polymer chains are made up of 20–150 thiophene rings; i.e., they are considerably long considering polythiophene (n_p = 10–35[13]). Also, it appears that n_p increases as n increases, a result that conforms to poly(3-alkoxythiophenes) for which n_p ranges from 5 to 8 with n = 1–3 to 10–50 and with n = 10–14.[14] Since the solubility of the oxidized oligomers increases as n increases, this result is strong support to the model of polymer growth based on the precipitation of oligomers when conditions of critical solubility are attained.[15]

Table 4. Polymer Conductivities (σ) and Maximum Absorptions as Film (λ_f) and in $CHCl_3$ Solution (λ_s)

monomer	σ/S cm^{-1}	λ_f/nm	$\lambda_s{}^a$/nm
C_1CPDT	80	545	(i)
C_3CPDT	80	580	(i)
C_4CPDT	80	580	(i)
C_6CPDT	200	600	(i)
C_8CPDT	300	590	560(ss)
C_{16}CPDT		600	605(s)
$(C_1)_2$CPDT	40	550	560(ss)
$(C_3)_2$CPDT	20	540	585(ss)
$(C_4)_2$CPDT	30	570	590(s)
$(C_6)_2$CPDT	7	590	610(s)
$(C_8)_2$CPDT	2	640	550(s)
$(C_{16})_2$CPDT		680	566(s)

[a] i = insoluble; ss = slightly soluble; s = soluble in $CHCl_3$.

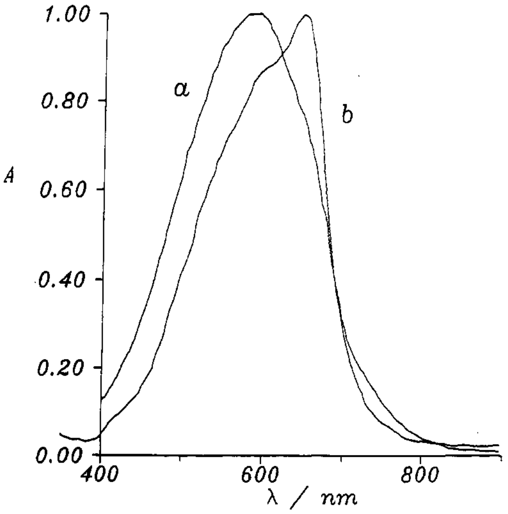


Figure 5. UV–Vis spectrum for (a) poly[C_8CPDT] and (b) poly[$(C_8)_2$CPDT].

UV-Vis Spectroscopy of the Polymers. From the spectral data, summarized in Table 4, we see that the maximum absorption of the neutral polymer films, with the only exceptions being poly[$(C_8)_2$CPDT] and poly[$(C_{16})_2$CPDT], falls in the range 545–600 nm, i.e., close to the extrapolated value for infinite polythiophene (ca. 540 nm[11]), in agreement with the CV results and with the measured degree of polymerization. The red shift (up to 60 nm) may be to a large extent attributed to the electronic effect of coplanarization in the monomers, which shifts the maximum absorption from 302 nm in bithiophene to 316–320 nm in $CHCl_3$ solution. Conversely, the red shifts of poly[$(C_8)_2$CPDT] and poly[$(C_{16})_2$CPDT] are more pronounced (100–140 nm). In addition, while the other polymers (in the solid state and in solution) and the monomers (in solution) show a maximum with a shoulder (Figure 5a), the spectra of poly[$(C_8)_2$CPDT] and poly[$(C_{16})_2$CPDT] in the solid state display an invertion of the intensity ratio (Figure 5b). The difference may be due to different contributions of the vibronic components of the band and reflect a higher ordering in the solid state for poly[$(C_n)_2$CPDT]'s with long alkyl chains. This suggestion is supported by the spectroelectrochemistry of poly[$(C_8)_2$CPDT] in which the first stages of oxidation cause a more marked decrease of the low-energy band. It is likely that the insertion of oxidative defects (polarons) disrupts the order.

Apart from poly[$(C_8)_2$CPDT] and poly[$(C_{16})_2$CPDT], solvatochromic changes from the solid state to solution are scarce. Also, thermochromic changes (from 25 to 200 °C) are negligible. In addition, it has been observed that poly[$(C_8)_2$CPDT] does not show any solvatochromic

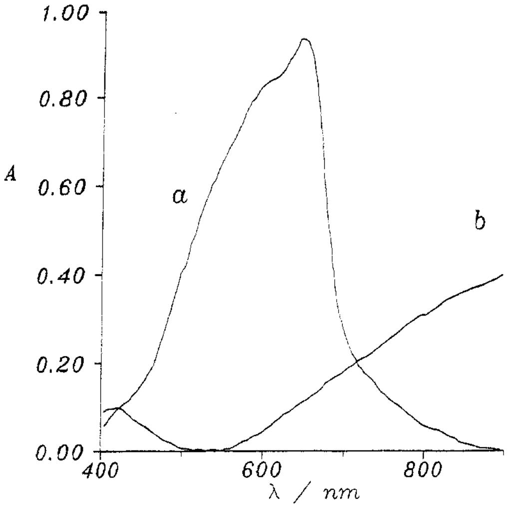


Figure 6. Spectroelectrochemistry for poly[$(C_8)_2$CPDT]: (a) neutral; (b) oxidized.

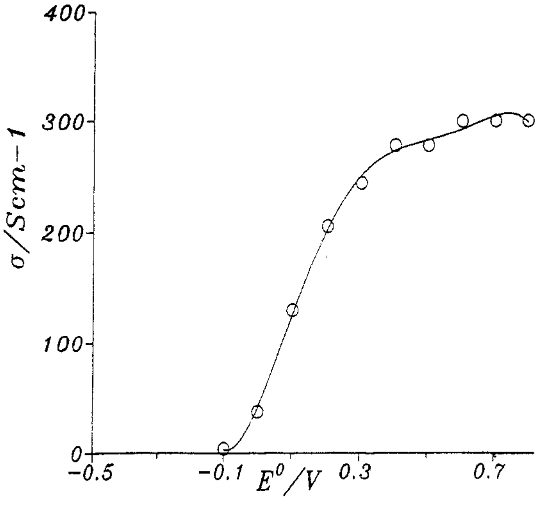


Figure 7. In situ conductivity for poly[C_8CPDT].

transition from 100% $CHCl_3$ to 99% MeOH + 1% $CHCl_3$. The fact that solvatochromic and thermochromic effects are minor or absent is due to the location of the alkyl substituents at the 4 position interlocking the thiophene rings of the monomer in a planar disposition. Therefore, the polymers are well-stabilized in a rod conformation with good coplanarity of the thiophene rings.

Conductivity of the Polymers. Following the general behavior of conducting polymers, spectroelectrochemistry shows that oxidation turns the color from deep violet (maximum at 550–600 nm) to light blue (maximum > 900 nm) (Figure 6), and in situ conductivity indicates that at the same time the polymer becomes conductive (Figure 7).

The oxidized polymers, for which elemental analysis indicates the presence of the counteranion in ca. 0.5 ratio to the monomeric unit, in agreement with the electrochemical data and previous results,[3] are highly conductive (see Table 4). In particular, the conductivities of the poly[C_nCPDT]'s (25–300 S/cm) are in line with that of the most conductive polythiophenes,[16] and the values within the series are not correlated either with the alkyl chain length or with the redox potentials. All these facts point to the attainment of limiting conditions of conductivity by interchain hopping without a regular intervention of the alkyl groups.

Poly[$(C_n)_2$CPDT]'s are on the average 10 times less conductive (2–40 S/cm), which may be explained by the more pronounced spacing effect of the disubstitution. In addition, along the series, there is a decrease of conductivity as n is increased, which parallels the correlation of n with the redox potentials. A similar effect was previously found in polypyrroles 3,4-ring-fused with alkyl chains of increased length.[17] This behavior indicates once more charge transport by interchain hopping, but in this case the chains are regularly separated by the alkyl moieties.

Conclusion

The coplanarity of the thiophene rings imposed by the bridging methylene group and the alkyl substitution at the bridging point far from the coupling sites has produced soluble polythiophenes with extended conjugation and high conductivity. The high coplanarity of the polythiophene backbone is so stabilized by the location of the alkyl substituents that it is not perturbed by thermal or solvation changes and eases intrachain conduction to such an extent that control of conduction is operated by interchain hopping only.

In the polymers from monosubstituted monomers, the possible random distribution of the substituents in the space might result in less ordered materials in which the polymer chains are in any case closely spaced as indicated by the display of high conductivity and π-dimerization. On the contrary, disubstitution, which gives symmetry to the monomeric unit, produces materials in which chains are regularly spaced by the substituent moieties, as indicated by the correlation of conductivity and redox potentials with the alkyl chain length.

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