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Structural Control of Conjugation in Functionalized Polythiophenes

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ABSTRACT: A comparative analysis of the electrochemical and optical properties of 3-substituted poly(thiophenes) has been carried out on four polymer structures, poly(3-methylthiophene) (PMT), poly(3-isoamylthiophene) (PiAT), poly(3-nonylthiophene) (PNT), and poly(3-(3,6-dioxyheptyl)thiophene) (PDHT). The spectroelectrochemical properties of these polymers have been investigated by cyclic voltammetry (CV), derivative cyclic voltammetric absorptometry (DCVA), and spectroelectrochemistry. CV shows that the symmetry of the anodic and cathodic waves increases from PMT to PDHT; furthermore in this latter case, a second redox system appears in the CV. The DCVA responses of the polymers indicate that the oxidation potential decreases in the order PiAT > PMT > PNT > PDHT whereas the increasing symmetry of the curves suggests an increasing electrochemical reversibility. UV-visible absorption spectra have been recorded in situ at various applied potentials. In the undoped state, the absorption maximum of the polymers shifts bathochromically from PiAT to PDHT and the absorption spectrum of PDHT exhibits several defined structures resembling those previously observed at low temperature on poly(3-alkylthiophenes). Upon electrochemical doping, the spectroscopic behavior of PiAT, PNT, and PDHT differs from that of PMT by a more intense absorption at $\simeq$1.5 eV at the intermediate doping level and by a more pronounced narrowing of the band gap with the appearance of metallic-like behavior at high applied potential. These effects that are particularly evident in PDHT are interpreted by an extension of the effective mean conjugation length resulting from the stabilization of more planar conformations.

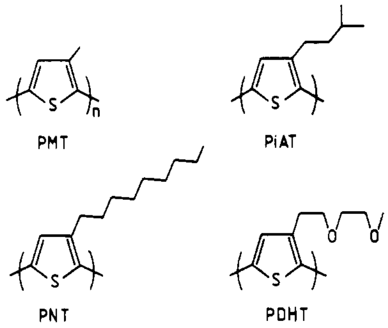
Introduction

Electrogenerated conducting poly(thiophenes) have recently attracted increasing attention owing to the unique electronic and electrochemical properties of their conjugated π system.[1] Although their conduction mechanism is still subject to controversies,[2] these materials are extensively investigated in view of their potential technological applications in the fields of energy storage,[3] molecular electronic devices,[4] and modified electrodes.[5]

As already shown, the transition between the doped and the undoped states results in important modifications of the visible absorption spectrum of the polymer. On the basis of these electrooptical properties, the use of poly(thiophenes) films as active element in smart windows and electrochromic display devices has been considered by several groups.[6]

It has been shown previously that the structure of the starting monomer controls to a large extent the electronic and spectroelectrochemical properties of the resulting polymer. Thus the 3,4-disubstitution of poly(thiophene) by alkyl groups induces large steric interactions that result in an important torsion angle between thiophene monomer units in the polymer chain. This departure from planarity results in a 200-250 nm hypsochromic shift of the absorption maximum compared to that of the unsubstituted polymer.[7] In the case of linear poly(3-alkylthiophenes), we have previously shown that the length of the alkyl chain exerts an important effect on the structure and properties of the polymer, leading to an increase of the mean conjugation length and electrochemical reversibility. This effect being maximum for an alkyl chain length of seven to nine carbons. On the other hand, in polymers 3-substituted by branched alkyl chains, the distance between the secondary carbon atom and the thiophene ring determines the amplitude of the torsion angle between adjacent thiophene monomers in the polymer chain and hence the electrical and spectroelectrochemical properties of the resulting polymer.[8]

Chart I



As a further step in the analysis of the structure-property relationships in functionalized poly(thiophenes), we describe here the electrosynthesis and spectroelectrochemical properties of a new electrogenerated conducting polymer poly(3-(3,6-dioxyheptyl)thiophene) (PDHT). In order to emphasize the effects of the structural factors on the electrochemical and spectroscopic properties of poly(thiophenes), the spectroelectrochemical properties of PDHT have been compared to those of three poly(3-alkylthiophenes); e.g. PMT, selected as a reference compound owing to its high conductivity,[9] PNT, which has been shown to be the most conjugated polymer among linear poly(3-alkylthiophenes),[8] and PiAT, in which the steric hindrance to conjugation originating from the branched substituent has been reduced by the insertion of a spacer of adequate chain length $(CH_2)_2$.

The analysis of the electrochemical and spectroscopic properties of these polymers by cyclic voltammetry, deriv-

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ative cyclic voltammetric absorptometry, and in situ UV-visible absorption spectroscopy shows that the nature of the substituent at the 3-position controls to a large extent the structure and properties of the resulting polymer. Thus when compared to PMT and PiAT, PNT and particularly PDHT exhibit a higher electrochemical reversibility associated to a more extended conjugation.

Experimental Section

Reagents and Solvents. The synthesis of the monomers has been already described.[10] The solvents nitrobenzene and acetonitrile were purified according to the previously described procedures.[11] The electrolytes tetrabutylammonium hexafluorophosphate and lithium perchlorate (Fluka purum) were used without further purification.

Electrochemistry. For electrochemical characterization, the polymers were synthesized in a three-electrode cell from a reaction medium involving 2×10^{-1} mol L^{-1} monomer and 2×10^{-2} mol L^{-1} Bu_4NPF_6 in nitrobenzene. The solutions were degassed by argon bubbling prior to electropolymerization that was performed under an argon atmosphere. The polymers were grown on platinum disk electrodes ($S = 7 \times 10^{-2}$ cm^2) under galvanostatic conditions, using a deposition charge of 100 mC cm^{-2} and current densities of 2–5 mA cm^{-2}. A platinum wire was used as a counter electrode and a saturated calomel electrode (SCE) as a reference. After polymerization the films were rinsed with acetone, dried, and transferred in another cell containing 10^{-1} mol L^{-1} $LiClO_4$ in dry acetonitrile. Electrochemical synthesis and cyclic voltammetry were performed by using a PAR 173 potentiostat/galvanostat equipped with a PAR 175 universal programmer and a PAR 179 plug-in digital coulometer.

Spectroelectrochemistry. Films for in situ UV-visible absorption spectroscopy and derivative cyclic voltammetric absorptometry (DCVA) were prepared from the same reaction medium on indium–tin oxide (ITO) electrodes (2 × 1 cm). After the synthesis, the films were rinsed with acetone, dried, and electrochemically undoped in 10^{-1} mol L^{-1} $LiClO_4$ in dry acetonitrile. Absorption spectra were recorded on a Cary 219 spectrometer. Spectroelectrochemical experiments were performed in a 1 × 1 cm quartz cuvette that was inserted in the spectrometer by means of micropositioners. A Pt wire was used as a counter electrode, and an Ag wire served as a quasi-reference. DCVA responses have been obtained by derivatization of the absorbance variation at the absorption maximum of the undoped polymers, when the films are submitted to a potential sweep at low scan rate (5 mV s^{-1}). Electroreflexion[12] was performed on polymer films deposited on a 0.7 cm^2 Pt disk by using the above-described conditions. The anode was then placed in a cell equipped with a quartz window and containing 10^{-1} mol L^{-1} $LiClO_4$ in dry acetonitrile. A platinum ring was used as a counter electrode and an Ag wire as a reference. The analyzing source was a 5-mW He–Ne laser (λ_{em} = 632.8 nm), and the variation of the intensity of the reflected light was monitored by an Hamamatsu G1118 GaAsP photodiode connected to a recorder.

Results and Discussion

Cyclic Voltammetry. The comparison of the cyclic voltammograms of the four polymers, recorded in 10^{-1} mol L^{-1} $LiClO_4$ in dry acetonitrile (Figure 1), shows that the symmetry of the curves expressed by the ratio of the anodic and cathodic peak currents (I_{pa}/I_{pc}) increases markedly for the polymers containing large substituents. Furthermore, as appears in Figure 1d, the introduction of ether groups in the alkyl substituent induces strong modifications of the electrochemical behavior of the polymer. Thus the cyclic voltammogram of PDHT differs markedly from those of the alkyl-substituted polymers by showing two distinct successive components: a first pair of voltammetric waves at ca. 0.4 and a main redox system at 0.8 V/SCE. The amount of charge reversibly exchanged during redox cycles indicates that the doping levels range between 22 and 25%. In PDHT, the charge exchanged when activating only the first system corresponds to about one-third of the full redox charge. The potential of the anodic current peak (E_{pa}) occurs at 0.54, 0.85, 0.94, and 0.80 V/SCE for respectively PMT, PiAT, PNT, and PDHT, suggesting a corresponding sequence of the oxidation potentials. However, a direct correlation of these data with the respective oxidation potentials of the polymers is not straightforward due to the occurrence of important charging capacitive currents. As shown already, this phenomenon renders very delicate the interpretation of the cyclic voltammetric data and their correlation with the molecular structure and properties of the polymers.[8]

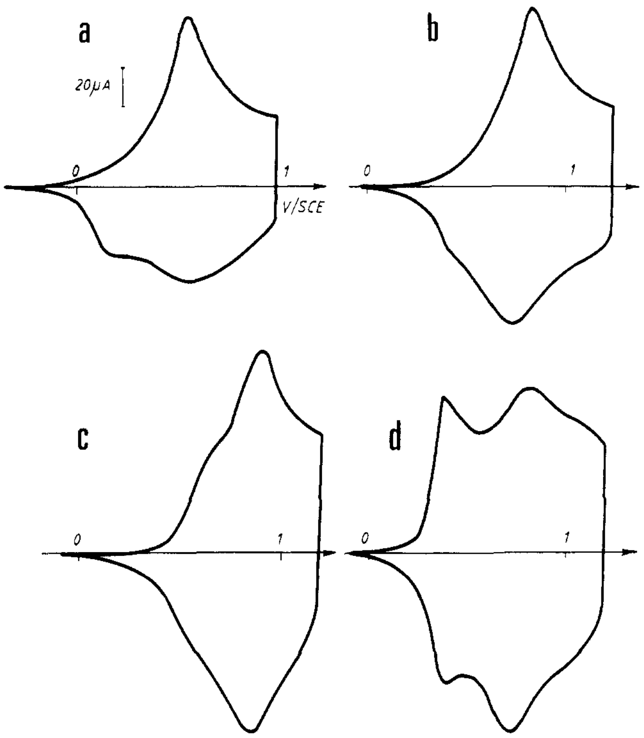

Figure 1. Cyclic voltammograms recorded in 10^{-1} mol L^{-1} $LiClO_4/CH_3CN$ (deposition charge = 100 mC cm^{-2} on Pt; scan rate = 50 mV s^{-1}): (a) PMT, (b) PiAT, (c) PNT, (d) PDHT.

Previous works on electrogenerated poly(pyrrole) have shown that in its oxidized form, this polymer acts as a porous metal electrode with a high surface to volume ratio and a large double-layer capacitance.[13] More recently, both theoretical and experimental studies have demonstrated that the capacitive charge represents a significant part of the overall amount of charge stored in the polymer film during its oxidation.[14] According to these works, this capacitive charging current is at the origin of the current plateaus observed after the anodic peak in the cyclic voltammograms. However, this interpretation has been contested by Heinze et al., who have explained these current plateaus by a distribution of redox states with increasingly higher energies, thus considering that the whole current is Faradaic.[15] A further comparison of the voltammograms in Figure 1 shows that the ratio of the intensity of the current plateau to that of the main anodic peak is much larger in PiAT, PNT, and PDHT compared to PMT. If one adopts the hypothesis of capacitive currents, this would suggest that the relative contribution of the capacitive charging current is larger in polymers bearing large substituents.

Derivative Voltammetric Absorptometry. A more precise description of the purely Faradaic component

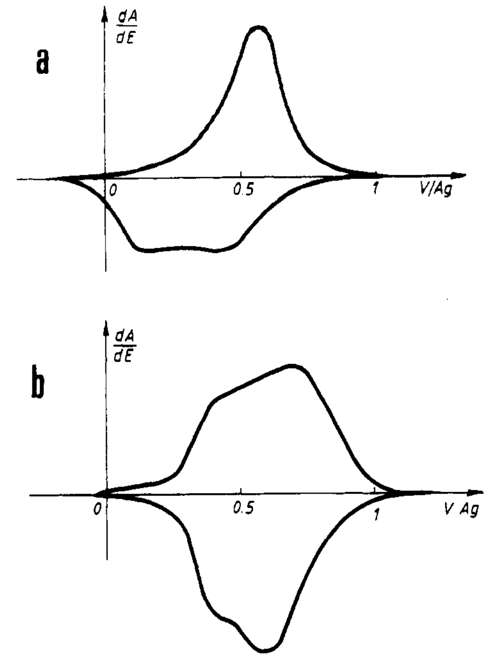

Figure 2. DCVA responses recorded in 10^{-1} mol L^{-1} $LiClO_4/CH_3CN$ (deposition charge = 50 mC cm^{-2} on ITO; scan rate = 5 mV s^{-1}): (a) PMT, (b) PiAT.

involved in the electrochemical doping/undoping process of the polymers can be provided by the use of derivative cyclic voltammetric absorptometry (DCVA). It has been shown already that the presentation of the absorbance of the film vs applied potential in a derivative format leads to a response that is morphologically identical with a cyclic voltammogram but presents the advantage to be insensitive to non-Faradaic charge-consuming processes.[16]

Figures 2 and 3 represent the DCVA responses of the four polymers synthesized on ITO. These curves show that the symmetry of the anodic and cathodic waves increases from PMT to PDHT, in agreement with the increasing electrochemical reversibility suggested by the cyclic voltammograms. The comparison of these curves with their corresponding voltammograms shows that for PMT the shapes of both curves are rather similar while, account being taken for the different reference electrodes, the anodic peak occurs approximately at the same potential (Figure 2a). In contrast, in the case of the polymers bearing large substituents, the responses obtained with the two techniques present striking differences. The electrochemical behavior indicated by DCVA appears more complex than suggested by cyclic voltammetry, and several successive components are observed in the DCVA responses of these polymers. In the case of PiAT, the main anodic wave occurs at 0.7 V/Ag, while a broad shoulder is observed at 0.4 V (Figure 2b). The comparison of this curve with that of PNT shows that two anodic components are observed at the same potentials but their relative intensities are inverted (Figure 3a). The DCVA response of PDHT differs strongly from the previous ones by a further increase of the relative intensity of the 0.5 V wave and by the appearance of an intense first redox system at 0.1 V/Ag (Figure 3b). The potential of the main anodic peak decreases according to the sequence PiAT > PMT > PNT > PDHT, which indicates a corresponding decrease of the oxidation potential and suggests an extension of the mean conjugation length. These results are in agreement with previous results on poly(3-alkylthiophenes)[8] and indicate that the introduction of

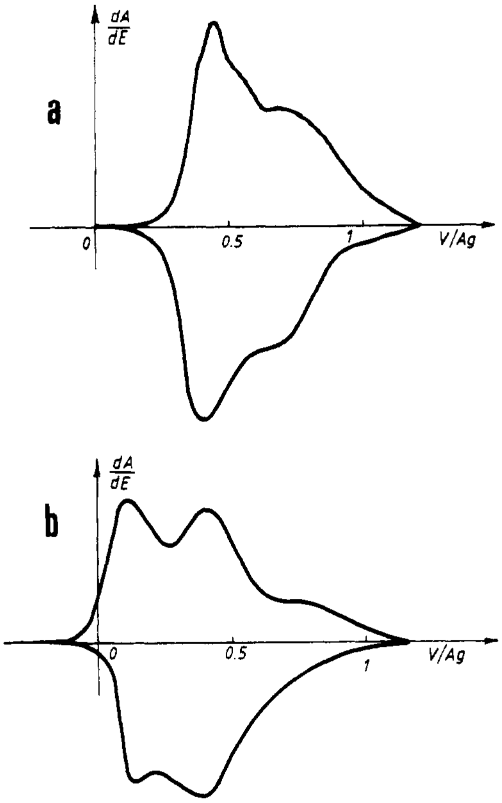

Figure 3. DCVA responses recorded in 10^{-1} mol L^{-1} $LiClO_4/CH_3CN$ (deposition charge = 50 mC cm^{-2} on ITO; scan rate = 5 mV s^{-1}): (a) PNT, (b) PDHT.

linear alkyl and oxyalkyl substituents leads to an increased symmetry of the anodic and cathodic processes that suggests a higher degree of electrochemical reversibility.

Spectroelectrochemistry. In order to investigate in more details the effects of substitution on the mean conjugation length in poly(thiophenes), the spectroelectrochemical properties of the four polymers in the undoped and the doped states have been analyzed. Figure 4 shows the in situ absorption spectra of the polymers recorded at various applied potentials. The spectra of the undoped PMT, PiAT, and PNT are rather similar in shape and differ essentially by the position of the absorption maximum at 520, 510, and 535 nm, respectively. These results can be related to the values of the oxidation potentials indicated by DCVA and confirm the increase of the mean conjugation length associated with long alkyl and oxyalkyl substituents. As could be expected from the electrochemical data, the absorption spectrum of PDHT differs markedly from those of the alkyl-substituted polymers. The absorption maximum occurs at 552 nm which represents a 57-nm bathochromic shift compared to its alkyl homologue poly(3-heptylthiophene).[8] Furthermore, in contrast to the broad absorption band observed with the alkyl-substituted polymers, the spectrum of neutral PDHT exhibits several well-resolved structures: an absorption maximum at 552 nm, a new band at 600 nm, and a shoulder at 510 nm.

The evolution of the spectroscopic characteristics of the four polymers shows that the structure of the substituent controls to a large extent the polymer structure and the mean conjugation length. Several examples have shown that the introduction of strong electron-donating alkoxy groups significantly reduces the band gap of poly(thiophene) or poly(thienylene vinylene).[17] Since in the case of the four polymers analyzed here, the electronic effects of the various substituents on the electronic den-

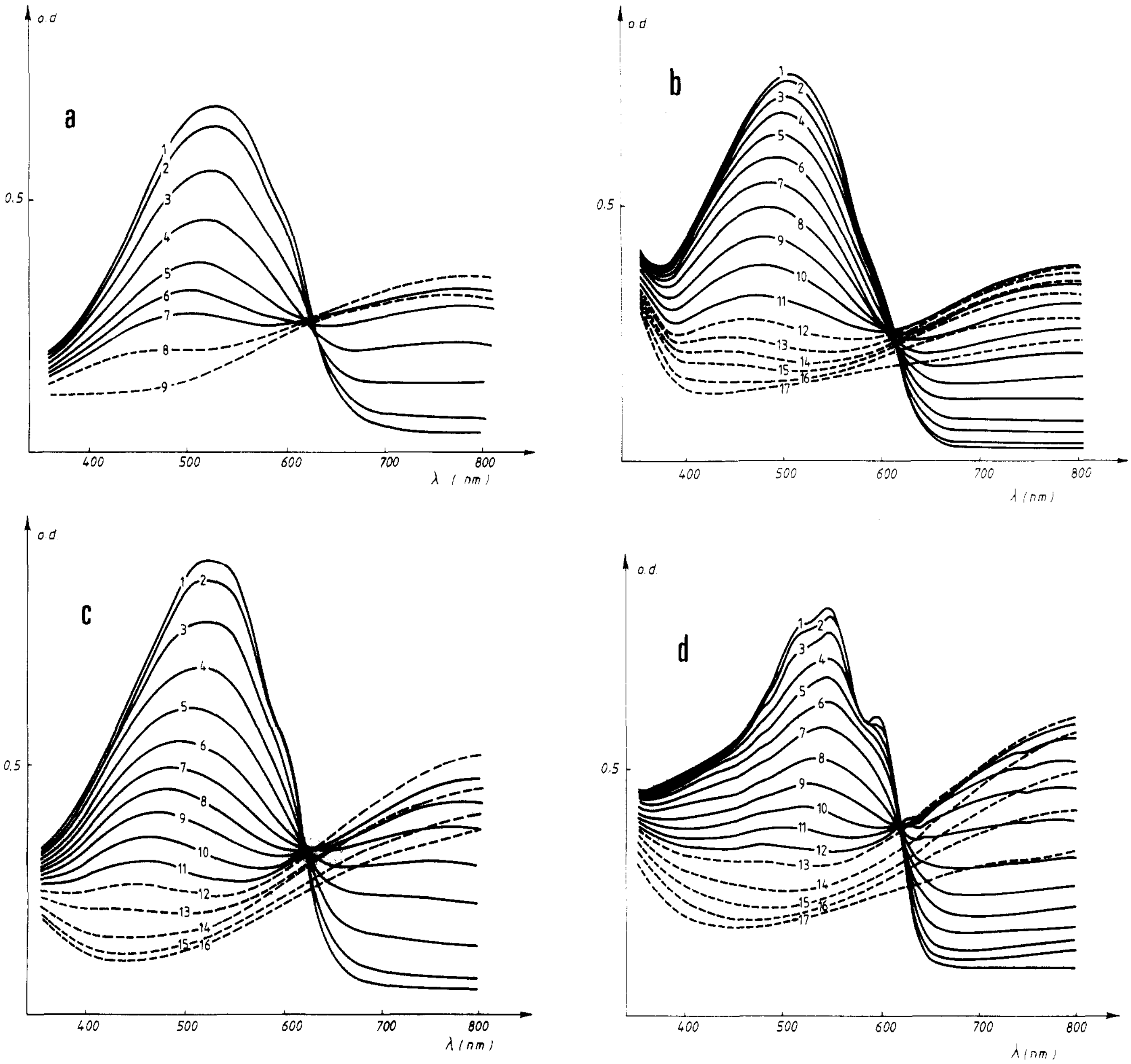

Figure 4. Absorption spectra of the polymers recorded in situ at various applied potentials (electrolytic medium, 10^{-1} mol L^{-1} $LiClO_4/CH_3CN$). (a) PMT (deposition charge = 40 mC cm^{-2} on ITO): (1) −0.2 V/Ag; (2) 0.3; (3) 0.4; (4) 0.45; (5) 0.5; (6) 0.55; (7) 0.6; (8) 0.7; (9) 1.1. (b) PiAT (50 mC cm^{-2} on ITO): (1) −0.2; (2) 0.3; (3) 0.4; (5) 0.45; (6) 0.5; (7) 0.55; (8) 0.6; (9) 0.65; (10) 0.7; (11) 0.75; (12) 0.8; (13) 0.85; (14) 0.9; (15) 0.95; (16) 1.05; (17) 1.1. (c) PNT (50 mC cm^{-2} on ITO): (1) −0.2; (2) 0.35; (3) 0.4; (4) 0.45; (5) 0.5; (6) 0.55; (7) 0.6; (8) 0.65; (9) 0.7; (10) 0.75; (11) 0.8; (12) 0.85; (13) 0.9; (14) 1; (15) 1.05; (16) 1.1. (d) PDHT (50 mC cm^{-2} on ITO): (1) −0.2; (2) 0.1; (3) 0.15; (4) 0.2; (5) 0.25; (6) 0.3; (7) 0.35; (8) 0.4; (9) 0.45; (10) 0.5; (11) 0.55; (12) 0.6; (13) 0.65; (14) 0.75; (15) 0.85; (16) 0.95; (17) 1.1.

sity of the aromatic ring are approximately equivalent to that of an alkyl substituent (as confirmed by the similarity of the oxidation potential of the monomers (1.80 V/SCE), the steady bathochromic shift of the absorption maximum observed from PiAT to PDHT must have another origin.

Absorption bands corresponding to the low-energy peaks of the PDHT spectrum have been observed in recent studies of the thermochromic and solvatochromic effects in poly(3-alkylthiophenes).[18] New absorption bands at 2.01 and 2.24 eV associated with thermochromic behavior were observed both on polymer solutions and on thin solid films cast from solutions of poly(3-hexylthiophene) (PHT). Solvatochromism leading to similar changes of the optical spectrum was observed upon addition of a poor solvent such as methanol to chloroform PHT solutions. Rughooputh et al. have attributed the two new absorption peaks occurring at 2.04 and 2.21 eV to a vibronic structure with 0–0 transition at 2.04 eV and a vibronic side band at 2.21 eV.[18a] This interpretation has been contested by Inganäs et al. on the basis of the different temperature dependence of these absorption peaks. These authors have interpreted the occurrence of these low-temperature absorption features in terms of conformational changes involving rotations around single bonds and leading to more planar conformations and hence longer effective mean conjugation lengths.[18b]

In the case of PDHT, the fact that the spectrum of the undoped polymer in the dry state is identical with that recorded in situ, when the polymer chains are surrounded by solvent molecules, appears merely consistent with the second interpretation. In this context, the occurrence of low-energy absorption peaks at 2.05 and 2.21 eV in the spectrum of PDHT could correspond to stabilized conformations resulting from the interactions between oxyalkyl chains and leading to longer effective mean conjugation lengths.

Although further work is still required to elucidate the mechanism by which ether groups can contribute to stabilize such more conjugated conformations, it can already be stated that at least two aspects will have to be considered: (i) a single chain mechanism, in which the stabilized conformations result from the interactions between oxyalkyl chains grafted on adjacent monomers and (ii) the matrix effect of the polyether chains when considered as a solvent for the poly(thiophene) backbone. In this latter case, the observed conformations could originate from the modification of the hydrophilic/lipophilic balance due to the attachment of hydrophilic ether groups onto the hydrophobic poly(thiophene) backbone.

The evolution of the absorption spectrum of poly(thiophene) derivatives upon electrochemical doping has been investigated by several groups.[19] As the doping proceeds, the intensity of the interband absorption decreases continuously and its absorption maximum shifts hypsochromically. Concurrently, two new absorption features appear in the subgap region at $\simeq$0.5 and 1.5 eV. These absorption bands have been attributed to electronic transitions between the valence band and two bipolaron levels symmetric with respect to the gap center.[19a] At the highest doping level, the spectrum presents the characteristics of the free-carrier absorption of the metallic state.

Figure 4 shows the absorption spectra of PMT, PiAT, PNT, and PDHT at various applied potentials. The comparison of the evolution of these spectra upon electrochemical doping shows that up to a potential of ca. 0.7 V/Ag the same general behavior is observed with all the polymers, namely, a decrease of the interband absorption and a simultaneous increase of the absorbance at 800 nm (1.5 eV) which corresponds to the upper bipolaron level.[19a] Increasing the applied potential and hence the doping level produces a decrease of the intensity of the $\pi \rightarrow \pi^*$ transition, an hypsochromic shift of its absorption maximum, and an increase of the intensity of the 800-nm band. Up to an applied potential of 0.7 V/Ag, these absorbance variations occur around on isosbestic point at 620 nm, indicating that only two phases coexist. The application of even more anodic potentials produces a further bleaching of the interband absorption and the departure from the isosbestic point while the absorbance decreases in the whole spectral range analyzed (350–800 nm) as shown by the spectra in dashed line in Figure 4. At the highest applied potential (1.1 V/Ag) the spectroscopic characteristics of the four polymers appear consistent with the appearance of a quasi-metallic behavior. This evolution of the spectroscopic properties of the four polymers upon doping appears in good agreement with previous works on PT[19a] and PMT[19b] but contrasts to the recent results of Hotta et al. on PMT, in which a residual interband absorption was still apparent even at the highest doping level.[19c] This evolution of the absorption spectra differs also markedly from the spectroscopic behavior of the soluble fractions of PATs, on which the characteristics of the metallic absorption have not been observed.[19d]

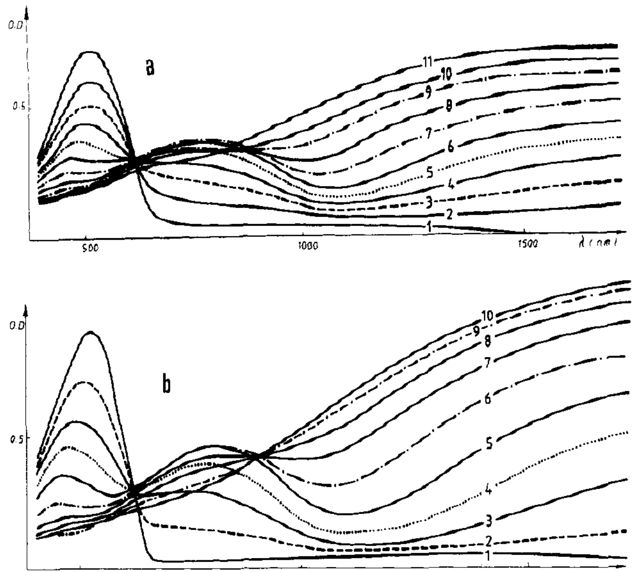

Figure 5. In situ absorption spectra recorded in 10^{-1} mol L^{-1} $LiClO_4/CH_3CN$ at various applied potentials (vs Ag). (a) PMT (40 mC cm^{-2} on ITO): (1) −0.2; (2) 0.2; (3) 0.4; (4) 0.5; (5) 0.55; (6) 0.6; (7) 0.7; (8) 0.8; (9) 0.9; (10) 1; (11) 1.1. (b) PNT (50 mC cm^{-2} on ITO): (1) −0.2; (2) 0.4; (3) 0.5; (4) 0.6; (5) 0.7; (6) 0.8; (7) 0.9; (8) 1; (9) 1.05; (10) 1.1.

A closer examination of the absorption spectra of the various polymers upon electrochemical doping shows that the spectroscopic behavior of the polymers bearing large substituents, PiAT, PNT, and particularly PDHT, differs from that of PMT on two points. At an applied potential of ca. 0.7 V/Ag the absorbance at 800 nm with respect to the intensity of the $\pi \rightarrow \pi^*$ transition at −0.2 V/Ag increases from PMT to PDHT. Furthermore, the decrease of the absorbance in the whole spectral range between 0.7 and 1.1 V/Ag becomes more pronounced. A more precise illustration of this point is given by the comparison of the absorption spectra of PMT and PNT that had been recorded up to 2 μm in a previous set of experiments (Figure 5). These spectra show that the increased contrast observed in the 600–800 nm between 0.7 and 1.1 V/Ag on PNT is associated to (i) a bathochromic shift from 790 to 810 nm of the absorption maximum of the bipolaron band, (ii) an increase of the intensity of this band relative to that of the $\pi \rightarrow \pi^*$ transition at −0.2 V, and (iii) a more pronounced decrease of the absorbance in the visible region associated to an increase of the absorbance beyond 1500 nm. These spectra show also that the transition from the bipolaron state to the quasi-metallic behavior occurs around an isosbestic point that shifts bathochromically from 860 nm for PMT to 900 nm for PNT. In summary, these results show that the extension of the mean conjugation length indicated by the bathochromic shift of the absorption maximum of the $\pi \rightarrow \pi^*$ transition of PNT and PDHT compared to PMT is correlated to a shift toward lower energy of the highest energy bipolaron band and to a sharper transition from the upper bipolaron level to the metallic state. These changes of the spectroscopic behavior induced by the substitution of the poly(thiophene) backbone result in an enhanced optical contrast in the 600–800 nm region between the intermediately and the heavily doped forms of the polymer and consequently to a reduced contrast between the undoped and the heavily doped forms.

Further evidence of this phenomenon can be obtained by analyzing the time-resolved electroreflection transients of PDHT at 632.8 nm (Figure 6). As appears in Figure 6b, when the polymer is switched between 0 and 0.7 V/Ag, (which corresponds to the activation of the first redox system of the CV curve in Figure 1d and to the maximum intensity of the bipolaron band at 1.5 eV),

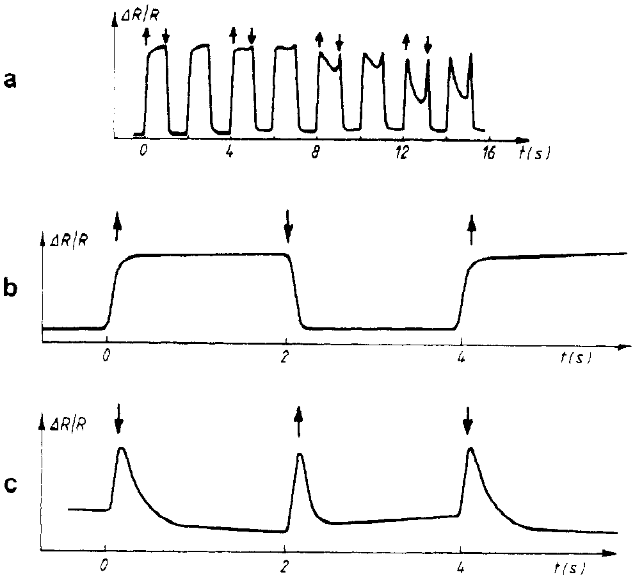

Figure 6. Electroreflection responses of PDHT at 632.8 nm (deposition charge = 50 mC cm^{-2} on Pt) (↑, anodic potential on; ↓, anodic potential off): (a) between −0.2 and +0.7, +0.8, +0.9, and +1 V/Ag; (b) between −0.2 and +0.7 V/Ag; (c) between −0.2 and 1.1 V/Ag.

two stable optical states are observed, similarly to what is observed on PMT.[20] In contrast, the decrease of absorbance observed in the 600–800 nm region when applying potentials higher than 0.7 V/Ag (Figure 4d) results in a strong modification of the electroreflection response. The maximum contrast is observed only transitory and the response evolves steadily toward only one stable optical state when the film is switched between 0 and 1.1 V/Ag (Figure 6c). These results confirm that the optoelectronic properties of poly(thiophene) can be widely tuned by the appropriate substitution of the polymer backbone.

Conclusion

In summary, the spectroelectrochemical properties of four substituted poly(thiophenes) have been analyzed. Both cyclic voltammetry and DCVA show that the polymers bearing long linear alkyl and oxyalkyl substituents exhibit a lower oxidation potential and a higher degree of electrochemical reversibility. In situ spectroelectrochemical experiments carried out at various applied potentials have shown that the mean conjugation length is significantly larger in PNT and particularly PDHT. This extension of the mean conjugation length is associated to a bathochromic shift of both the $\pi \rightarrow \pi^*$ and the highest energy bipolaron bands, which leads to a more pronounced narrowing of the band gap upon doping and to a more marked transition to the quasi-metallic state at high doping levels. In the case of alkyl substituents, this effect has been interpreted by an improvement of the long-range order induced by lipophilic interactions between alkyl chains whereas the unusual absorption features of PDHT suggest that the ether groups contribute to stabilize more planar conformations corresponding to more extended effective mean conjugation lengths. Although a detailed understanding of the role played by the ether groups on the structure and properties of PDHT still requires further work, these results can already have interesting implications in the field of modified electrodes and molecular electronics and show that the control of the structure and spectroelectrochemical properties of functionalized poly(thiophenes) can be achieved by adequate modification of the molecular structure of the monomer.

Registry No. PMT (homopolymer), 84928-92-7; PiAT (homopolymer), 110851-70-2; PNT (homopolymer), 110851-64-4; PDHT (homopolymer), 120245-40-1.

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