



the suspension was stirred 2 days at ambient temperature under argon atmosphere. The resulting blue solution was then precipitated with methanol, and the obtained dark blue material was washed copiously with methanol and water and extracted with methanol in a Soxhlet extractor for 24 h. This process leads to the undoping of the polymer which turns red. The resulting material was subsequently dried under vacuum and dissolved in  $\text{CHCl}_3$  under stirring, and the solution was filtrated.

Electropolymerization were carried out in galvanostatic conditions ( $6 \text{ mA cm}^{-2}$ ), at ambient temperature in a single-compartment cell containing 0.1 M monomer and 0.02 M  $\text{Bu}_4\text{NPF}_6$  in nitrobenzene. The applied electrical conditions have been optimized with regard to the electrochemically measured doping level and to the maximum bathochromic shift of the absorption maximum.<sup>23</sup> Solutions were degassed by 15 min of argon bubbling prior to electrodeposition which was performed under an argon atmosphere. Films were grown on indium-tin oxide coated glass electrodes (ITO) using an ITO plate as counter electrode. Thin films for electrochemical and optical characterization were prepared on  $2 \times 1\text{-cm}$  ITO electrodes using a deposition charge of  $60 \text{ mC cm}^{-2}$ . After deposition, the films were electrochemically undoped at  $-0.2 \text{ V/SCE}$  until the residual cathodic current reached a constant value, rinsed with acetone, and dried with an argon flow. Larger scale electrosyntheses were performed in the same conditions using an ITO electrode of  $4\text{-cm}^2$  area. A deposition charge of 60 C yielded 58 mg of doped polymer corresponding to a faradaic yield of 94% (assuming a doping level of 25%, which is the value generally observed on PDHT).<sup>7a,19,21</sup> The polymer (polyE) was then extracted with methanol, dried, and dissolved in chloroform as described above for polyC.

$^1\text{H}$  NMR spectra were obtained on a 300-MHz Bruker instrument using saturated  $\text{CDCl}_3$  polymers solutions. Electrochemical and spectroscopic characterizations of the soluble polymers were carried out on films cast on ITO electrodes from saturated chloroform solutions. Cyclic voltammetry was performed in a three-electrode cell containing 0.1 M  $\text{LiClO}_4$  in dry acetonitrile. Solvents and electrolytes were purified as already reported.<sup>9a</sup> A Pt wire served as counter electrode and a saturated calomel electrode (SCE) as reference. Electrochemistry was performed with a PAR 173 potentiostat-galvanostat equipped with a PAR 175 universal waveform programmer and a PAR 179 plug-in digital coulometer. Electronic absorption spectra were recorded on a Cary 3032 spectrometer.

## Results and Discussion

**Structural Characterization.** The method of preparation exerts a considerable effect on the solubility of PDHT. Thus polyC is soluble in  $\text{CHCl}_3$  up to 50% of the as-synthesized polymer, with a maximum concentration of 36 g/L. Conversely, polyE contains 80% of insoluble material and the maximum solubility ( $\approx 3 \text{ g/L}$ ) is inferior by more than 1 order of magnitude to that of polyC. These large differences suggest that both the soluble and the insoluble fractions of polyE have higher molecular weights than their polyC counterparts.

Although soluble poly(alkylthiophenes) (PATs) have been extensively investigated,<sup>1,12,13</sup> quantitative results concerning solubility are very scarce and furthermore, the few available data show noticeable discrepancy. Thus, a polymer concentration of 1 g/L has been used in various analyses of the optical properties of solutions or solution-cast films of chemically or electrochemically prepared poly-(3-hexylthiophene) (PHT).<sup>24,25</sup> This concentration seems to roughly represent the maximum solubility of PHT as shown by the maximum solubility of 0.8 g/L reported for chemically synthesized PHT.<sup>16</sup> However, a solubility of 200 g/L has been claimed for the same polymer prepared in the same conditions.<sup>13</sup>

Previous works have shown that poly(3-octylthiophene) and poly(3-tetradecylthiophene), prepared in electrosynthesis conditions optimized according to the procedure

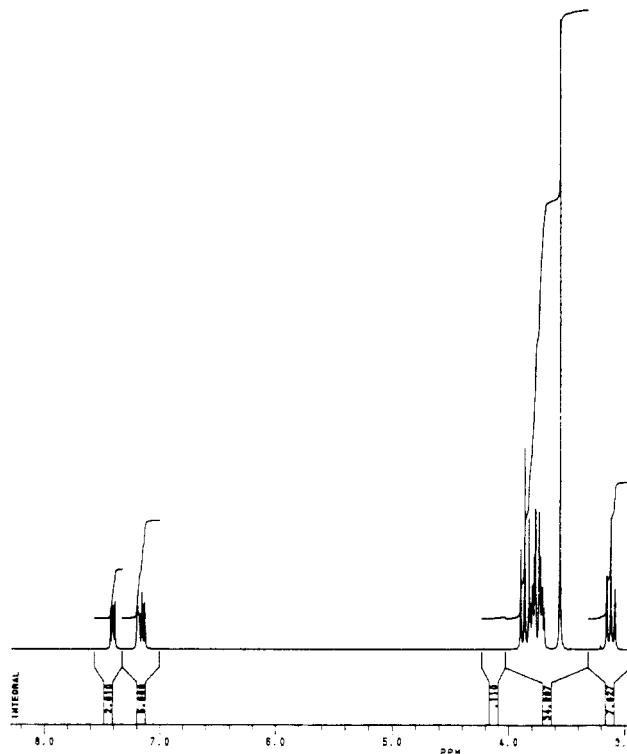


Figure 1.  $^1\text{H}$  NMR spectrum of DHT.

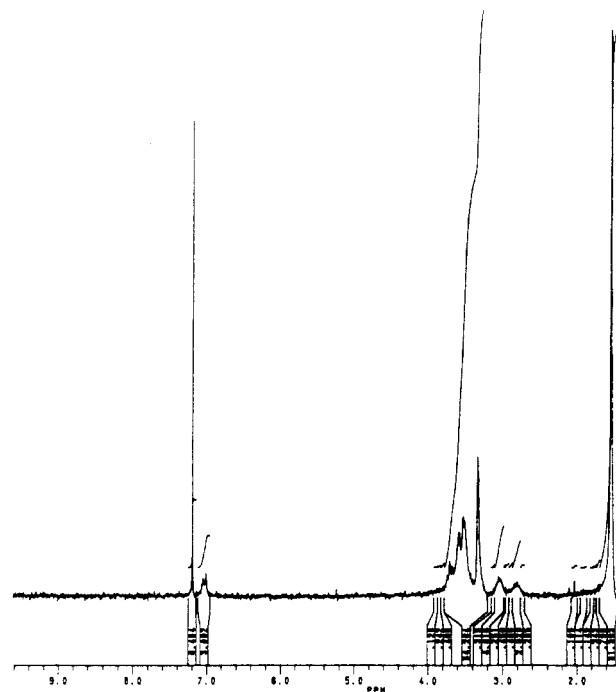


Figure 2.  $^1\text{H}$  NMR spectrum of polyC in saturated  $\text{CDCl}_3$  solution.

used here, contain respectively 3 and 10% of soluble fractions.<sup>23</sup> More recent works have confirmed the partial solubility of PATs and their strong dependence on electrosynthesis conditions.<sup>15,26,27</sup> Thus the fact that polyE contains 20% of soluble fraction suggests that, compared to an alkyl chain of equivalent length, the diether side chain increases the solubility of the substituted PT. On the other hand, these results also show that electropolymerization leads to a polymer containing a lower proportion of less soluble material than the chemical synthesis.

Figures 1–3 show the  $^1\text{H}$  NMR spectra of the monomer, polyC, and polyE, respectively. The 7.4 ppm peak in the spectrum of DHT is assigned to the aromatic proton in

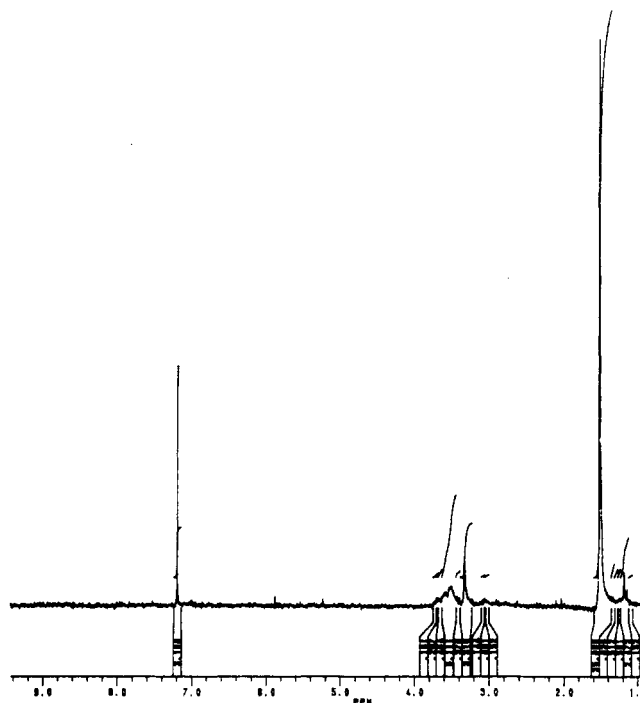


Figure 3.  $^1\text{H}$  NMR spectrum of polyE in saturated  $\text{CDCl}_3$  solution.

the  $\beta$ -position, and that at 7.15 ppm, to the aromatic proton in the  $\alpha$ -position. Peaks at 3.8, 3.55, and 3.1 ppm are assigned to the hydrogens of the  $\beta$ - $\omega$  methylene groups, methoxy group, and  $\alpha$ -methylene group, respectively. Peaks at 3.75–3.45, 3.3, and 3.05–2.82 ppm in the spectrum of polyC confirm the presence of the diether side chain in the polymer. On the other hand, the presence of the 7.03 ppm doublet, which corresponds to aromatic protons in the  $\alpha$ -positions of the thiophene ring, indicates that polyC contains a significant amount of irregular  $\alpha$ - $\beta'$  or  $\beta$ - $\beta'$  linkages. For both polymers, the peak corresponding to the aromatic protons in the  $\beta$ -position was not observed, presumably because of the presence of traces of  $\text{CHCl}_3$  in  $\text{CDCl}_3$  which led to a peak at 7.2 ppm, whose relative intensity was considerably enhanced by the low polymer concentrations. Previous works on 3-substituted PTs have attributed the splitting of the aryl methylene peak to the occurrence of both HT and HH linkages, the low-field peak being assigned to HT coupling.<sup>6c,15,16,28,29</sup> On the basis of this attribution, the relative integration of the peaks of the aryl methylene protons ( $\delta = 3.05$  and 2.82 ppm) leads to an estimated HH content of ca. 40% for polyC. In spite of the limited resolution due to the poor solubility of polyE, the spectrum of this polymer presents several differences with the previous one. The absence of the 7.03 ppm peak suggests that polyE does not contain  $\alpha$ - $\beta'$  or  $\beta$ - $\beta'$  irregular linkages. Furthermore, the fact that only the 3.05 peak of the  $\alpha$ -methylene protons is observed seems to indicate that the structure of polyE involves essentially HT configurations.

**Cyclic Voltammetry.** Figure 4 compares the CVs of a directly electrogenerated PDHT film with those of solution-cast polyC and polyE films. The CV of electrogenerated PDHT exhibits a first anodic shoulder at 0.25 V followed by two anodic waves peaking at respectively 0.50 and 0.87 V/SCE that constitute the characteristic cyclic voltammetric signature of PDHT.<sup>7a,18,19,21</sup> The CV of polyE presents strong similarities with that of PDHT; however several noticeable differences appear, namely, a slight but significant positive shift of the anodic peak potential, a decrease of the resolution of the second wave, and a marked

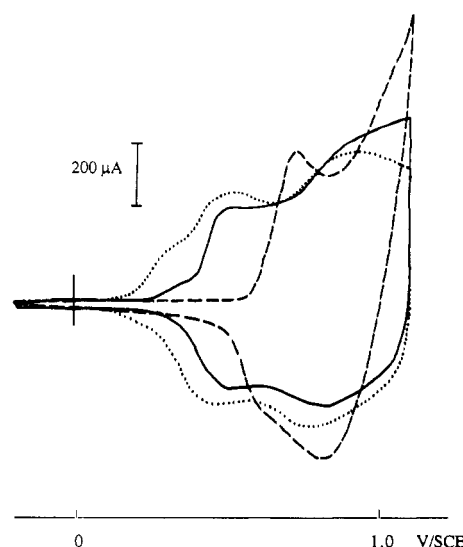
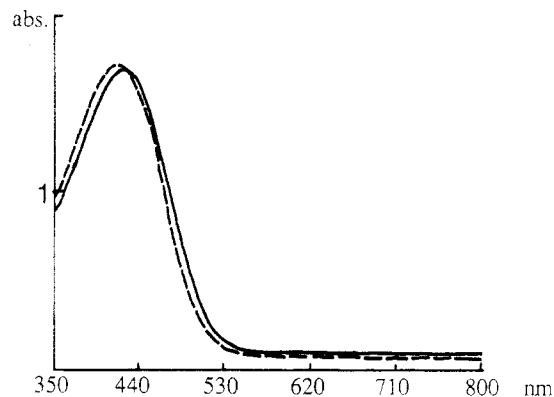


Figure 4. Cyclic voltammograms of polymers in 0.1 M  $\text{LiClO}_4/\text{CH}_3\text{CN}$ , (scan rate  $10 \text{ mV s}^{-1}$ , electrode area  $2 \text{ cm}^2$ ): (dotted line) electrodeposited PDHT film (deposition charge  $60 \text{ mC cm}^{-2}$ ); (dashed line) polyC cast on ITO from  $\text{CHCl}_3$  solution; (solid line) polyE cast on ITO from  $\text{CHCl}_3$  solution.

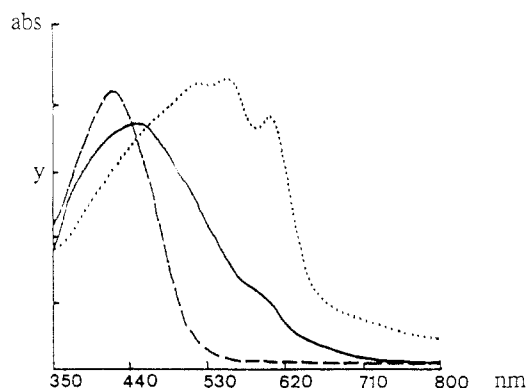
decrease of the relative intensity of the first wave. The CV of polyC differs strongly from the previous ones and exhibits only one redox system with an anodic peak at 0.72 V. Furthermore, the CV appears highly dissymmetrical and the ratio of the anodic to the cathodic current peaks ( $I_{pa}/I_{pc}$ ), which is close to unity for PDHT, increases up to 1.75. These results show that the method of synthesis exerts a considerable effect on the electrochemical behavior of the soluble polymers and that only electropolymerization leads to a soluble material with electrochemical properties close to those of electrodeposited PDHT.

Previous works have shown that a good correlation is generally observed between the oxidation potential and the optical bandgap of simple thiophene derivatives.<sup>9,31,32</sup> However, the interpretation of the CVs of PTs containing large substituents is rendered considerably more complex by side chains interactions which significantly affect the electrochemical behavior of the conjugated PT backbone.<sup>8,18,23,33</sup> This problem becomes particularly evident in the case of PDHT for which it has been shown that the specific electrochemical behavior observed in the presence of  $\text{Li}^+$ , i.e. negative shift of the peaks potentials, intensification of the first redox system, and increase of electroactivity, is related to a synergic combination of several mechanisms resulting from the complexation of  $\text{Li}^+$  by the oligo(oxyethylene) side chains.<sup>7a,18–21</sup> With these provisions in mind, the differences observed in the oxidation potential of the three polymers indicate that effective conjugation is more extended in polyE than in polyC and that both soluble polymers are less conjugated than electrodeposited PDHT. This conclusion appears consistent with the structural disorder indicated by the NMR data of polyC.

**UV-Visible Absorption Spectroscopy.** Figure 5 shows the electronic absorption spectra of the chloroform solutions of polyC and polyE. These spectra are rather similar and show a single absorption band with  $\lambda_{\text{max}}$  at 418 and 424 nm for polyC and polyE, respectively. These maxima appear slightly hypsochromically shifted compared to those of PAT solutions which are generally observed around 435–440 nm.<sup>16,23,34,35</sup> The absorption maximum of polyC is consistent with the limited extent of conjugation indicated by  $^1\text{H}$  NMR and electrochemical data. However, the difference between the maxima of



**Figure 5.** Electronic absorption spectra of polyC (dashed line) and polyE (solid line) in chloroform.



**Figure 6.** Electronic absorption spectra of neutral PDHT films: (dotted line) electrodeposited film (deposition charge  $60 \text{ mC cm}^{-2}$ ,  $\gamma = 1.0$ ); (dashed line) polyC cast on ITO from  $\text{CHCl}_3$  solution ( $\gamma = 0.7$ ); (solid line) polyE cast on ITO from  $\text{CHCl}_3$  solution ( $\gamma = 0.2$ ).

polyC and polyE appears rather limited in regard to what could be expected from the difference in their oxidation potentials. This small difference of  $\lambda_{\text{max}}$  could originate from the coil structure adopted by the neutral polymer chains in solution.<sup>34,35</sup> This coil conformation could level down the differences in the effective mean conjugation length existing in the rodlike structure adopted by the polymer chains in the solid state. This hypothesis is supported by the absorption spectra of solution-cast films of polyC and polyE (Figure 6) which show that, in the solid state, the absorption maximum of polyC is observed at 435 nm whereas that of polyE occurs at 445 nm. These results confirm, in agreement with NMR and electrochemical data, that polyE is more conjugated than polyC and that both soluble polymers are considerably less conjugated than electrodeposited PDHT ( $\lambda_{\text{max}} = 556 \text{ nm}$ ).<sup>20,21</sup> The spectrum of polyE exhibits weak shoulders around 530 and 610 nm, reminiscent of the characteristic fine structure (FS) observed in the spectrum of electro-generated PDHT.<sup>7a,18,20,21</sup> Previous works on PATs have shown that this vibrational FS is inherent to the conjugated PT backbone and more or less enhanced by side chains interactions.<sup>8,23,24,34,35</sup> In the case of PDHT, optoelectrochemical experiments have suggested that the resolution of FS depends on the extent and rigidity of the conjugated  $\pi$  system.<sup>20,21</sup> In this context, the progressive hypsochromic shift of  $\lambda_{\text{max}}$  and loss of FS observed from PDHT to polyC could reflect a decrease of the relative fraction of the most conjugated and most rigid segments contained in the longest insoluble chains. In the case of polyC this shortening of the mean conjugation length is further enhanced by  $\alpha$ - $\beta'$  linkages that disrupt the conjugation along the chain and also by the important proportion of

HH couplings which generate distortions in the conjugated backbone by means of steric substituent interactions.<sup>16,17,36</sup> These two types of conjugation defects probably contribute to the higher solubility of polyC by decreasing both the rigidity of the polymer chains and the interchain attractive interactions. Differences in the molecular weights of the two polymers can also significantly affect the solubility; however, reliable data are difficult to obtain since the polystyrene standards generally used for this purpose have been shown to lead to an overestimation of at least 1 order of magnitude of the molecular weight of PATs.<sup>26</sup>

The structure and properties of PATs prepared by both chemical and electrochemical routes have been analyzed by several groups.<sup>15-17,30</sup> Consistent results have been reported showing that the molecular weight, solubility, and ratio of HH to HT coupling ( $\approx 15$ –20%) were roughly independent of the method of preparation.<sup>15-17</sup> In this context, the results obtained with PDHT appear rather astonishing since the chemical and the electrochemical syntheses produce in this case quite different materials. Thus compared to PATs, the chemical polymerization leads to a deterioration of the stereo- and regioregularity of the polymer, whereas in contrast, electropolymerization leads to a less soluble polymer with no apparent structural disorder. This unexpected result must be discussed in relation with the particular chemical structure of DHT and the specificities of the chemical and electrochemical polymerizations. The main difference between alkylthiophenes and DHT concerns the presence of the embryonic poly(ethylene oxide) side chain. As previously shown, these side substituents confer to PDHT the ability to complex  $\text{Li}^+$  and others metallic cations.<sup>7,20,21,37</sup> Thus, a possible explanation of the poor selectivity of the oxidative polymerization of DHT in the presence of  $\text{FeCl}_3$  could involve the complexation of  $\text{FeCl}_3$  by the oligo-(oxyethylene) side chains. The adoption by the side chains of the optimal geometry for efficient complexation could contribute to an orientation of the thiophene rings favoring the occurrence of irregular couplings during polymerization. This hypothesis is supported by recent results which have shown that poly(ethylene oxide) forms coordination complexes with  $\text{FeCl}_3$ .<sup>38</sup> On the other hand, the orientation of monomer units could also account for the considerably better stereo- and regioselectivity of the electrochemical polymerization of DHT compared to that of alkylthiophenes. As a matter of fact, it seems reasonable to assume that the dipolar moment of DHT is significantly higher than that of 3-alkylthiophenes. Consequently, DHT molecules have probably a higher propensity to orient under the intense electric field of the electrode-solution interface than alkylthiophenes. This preferential orientation leads to a higher regioselectivity of the electrochemical polymerization. Furthermore and contrary to PATs,<sup>19</sup> PDHT exhibits a highly hydrophilic character afforded by the hydrophilic polyether side chain attached to the hydrophobic thiophene ring. This dissymmetry between the hydrophilic and lipophilic parts of the molecule can contribute also to the orientation of monomer units during electropolymerization.

## Conclusion

A comparative analysis of the structure and properties of the soluble fractions of chemically and electrochemically synthesized PDHT has been carried out. Although compared to an alkyl chain of equivalent length, the polyether side chain increases the solubility of the PT backbone, both types of polymers are only partially soluble and solution-cast films show electrochemical and optical

properties significantly inferior to those of insoluble electrodeposited films. Furthermore, and contrary to the case of PATs, electrochemical and chemical syntheses lead to polymers showing considerable differences in solubility, structure and electrochemical and optical properties. Although the chemical route leads to the most soluble polymer, this polymer exhibits a limited extent of conjugation due to the poor regio- and stereoselectivity of the chemical polymerization of DHT in the presence of  $\text{FeCl}_3$ . Conversely, the fact that the electrochemical polymerization of DHT is more stereo- and regioselective than in the case of 3-alkylthiophenes suggests a better propension of DHT to orient under an electric field due to the dissymmetry introduced in the monomer molecule by the diether side chains. These results indicate that an efficient chemical synthesis of conjugated polymers containing oligo(oxyethylene) side chains should resort to other strategies such as Grignard coupling or the use of oxidants that cannot be complexed by polyether chains.

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