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Electrochemical materials science: tailoring intrinsically conducting polymers. The example: substituted thiophenes

Received: 27 March 2005 / Revised: 9 May 2005 / Accepted: 27 May 2005 / Published online: 2 August 2005
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Abstract A series of 3-(*p*-X-phenyl) thiophene monomers (X = -H, -CH₃, -OCH₃, -COCH₃, -COOC₂H₅, -NO₂) was electrochemically polymerized to furnish polymer films that could be reversibly reduced and oxidized (*n*- and *p*-doped). The oxidation potentials of the monomers and formal potentials of the *n*- and *p*-doping processes of polymers were correlated with resonance and inductive effects of the substituents on the phenyl ring as well as the semiempirically calculated heat of formation of the monomer radical cations.

Introduction

Conducting polymers have attracted much attention because of their potential use in rechargeable batteries [1], electrochromic display devices [2] and supercapacitors [3–5]. Polyheterocycles have become important in these areas due to their facile electrochemical polymerization and doping. Polythiophenes exhibit promising properties both in their conducting and neutral states [6]. Although *p*-type doping has been well investigated, *n*-type doping studies are comparatively rare due to the poor stability of the polymers at extremely negative potentials.

On the other hand, only a limited number of conducting polymers can be electrochemically *n*-doped [7, 8], usually at fairly negative potentials, and for this reason electrochemists have concentrated more on *p*-dopable conducting polymers, such as polypyrrole [9–13] and polyaniline [14, 15] where aqueous solutions can be used.

Sato et al. [16] have found that poly-3-phenylthiophene is highly *p*-dopable and also suggested its

application in a *p*-*n* junction diode. The high *p*-doping activity of poly-3-phenylthiophene was explained in terms of a favorable conjugation effect between the phenyl rings and the polythiophene backbone [17]. On the other hand, Onoda et al. [18] studied the *n*-doping properties of poly-3-phenylthiophene films and found a high degree of electrochemical reversibility. However, this group concluded that rather than being in conjugation with the polythiophene backbone, the phenyl rings were perpendicular to it and the interchain charge transport processes limited the observed electronic properties.

Guerrero et al. [19] studied the relationship between the redox properties of a series of para-substituted 3-phenylthiophene monomers and obtained polymers with Hammett substituent constants and found that there is a good relation between the redox properties and Hammett constants.

Sato et al. [17] and Guerrero et al. [19] further demonstrated that the oxidation potential of poly-3-phenylthiophene increased when an electron-withdrawing substituent was placed on the phenyl ring and the electron-donating groups produced a stable anion-doped material. Thus, the oxidation potential decreased.

We have investigated the role of various para substituents (-H, -CH₃, -OCH₃, -COOC₂H₅, -COCH₃, -NO₂) on oxidation of the monomer and on *p*- and *n*-doping processes of 3-phenylthiophene. Redox properties of the monomers and polymers obtained by cyclic voltammetry were correlated with Hammett substituent constants and semiempirically calculated heat of formation of monomer radical cations obtained with Gaussian98 software.

Experimental section

Chemicals

Tetraethylammoniumtetrafluoroborate (TEATFB) (ACROS, 99%) was recrystallized thrice from methanol

Presented at the 4th Baltic Conference on Electrochemistry, Greifswald, March 13–16, 2005

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and dried under vacuum at 140 °C for 24 h. Acetonitrile (Merck, anhydrous, < 10 ppm H₂O) was used without further purification.

Synthesis and electrochemical measurements

3-phenylthiophenes derivatives (**1–6**, see Fig. 1) were synthesized by cross coupling reactions according to Suzuki's method with tetrakis(triphenylphosphine) palladium(0), Pd(PPh₃)₄, as catalyst [20]. ¹H, ¹³C NMR and GC mass spectroscopy have confirmed their high purity.

Anodic electropolymerization was used to prepare polymers by applying constant electrode potential (oxidation potential) for 2–4 min. After each polymerization process the film was washed with acetonitrile to remove any traces of oligomers.

All electrochemical experiments were carried out at room temperature with nitrogen-purged solutions. A three-compartment cell containing a Pt disc (diameter = 1 mm) electrode (99.99%, Schiefer, Hamburg) embedded in glass was used as working electrode. The platinum disk electrode was polished with diamond polishing paste down to 0.3 μm and then to 0.05 μm with aqueous alumina slurry. A platinum sheet counter electrode, and a non-aqueous Ag/AgCl reference electrode filled with the supporting electrolyte solution were used. The reference electrode potential was verified frequently with respect to an aqueous saturated calomel electrode because the employed non-aqueous reference electrode system is prone to potential drift [21]. A custom built potentiostat interfaced with a standard PC via an ADDA-converter card operating with custom developed software was used to record cyclic voltammograms (CVs).

Semiempirical calculations were carried out on a personal computer using the program GAUSSIAN98W [22] with the method AM1 [23].

Results and discussion

Electrochemical polymerization and cyclic voltammetry

Acetonitrile was chosen as a solvent because of its high dielectric constant, [24] low viscosity (0.3 cP = 0.3 mPa s), wide potential window (−2.8 to +3.3 V vs. SCE), and low nucleophilicity [25–27]

Monovalent polarizable cations such as quaternary alkyl ammonium salts are known to be effective counter

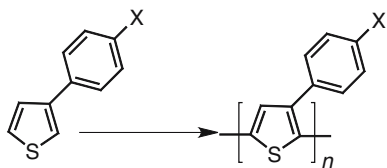


Fig. 1 Investigated of 3-phenylthiophenes

ions for reversible *n*-doping processes so we used TEA-TFB Et₄NBF₄. This electrolyte was chosen rather than TBATFB Bu₄NBF₄ because the Et₄N⁺ cation can easily penetrate into the film due to its smaller size [28]. Alkali metal salts are not suitable electrolyte materials for our purpose because *n*-doping of polythiophene appears to be inhibited by the large solvation shell which accompanies them in acetonitrile solution, [29, 30] although *n*-doping of poly-3-phenyl benzene in LiClO₄ electrolyte in acetonitrile has been reported [31]. Even trace amounts of alkali metal cations present in the electrolyte have been shown to impede severely the ability to *n*-dope polythiophene [29]. The *n*-dopability was better at higher electrolyte concentrations.

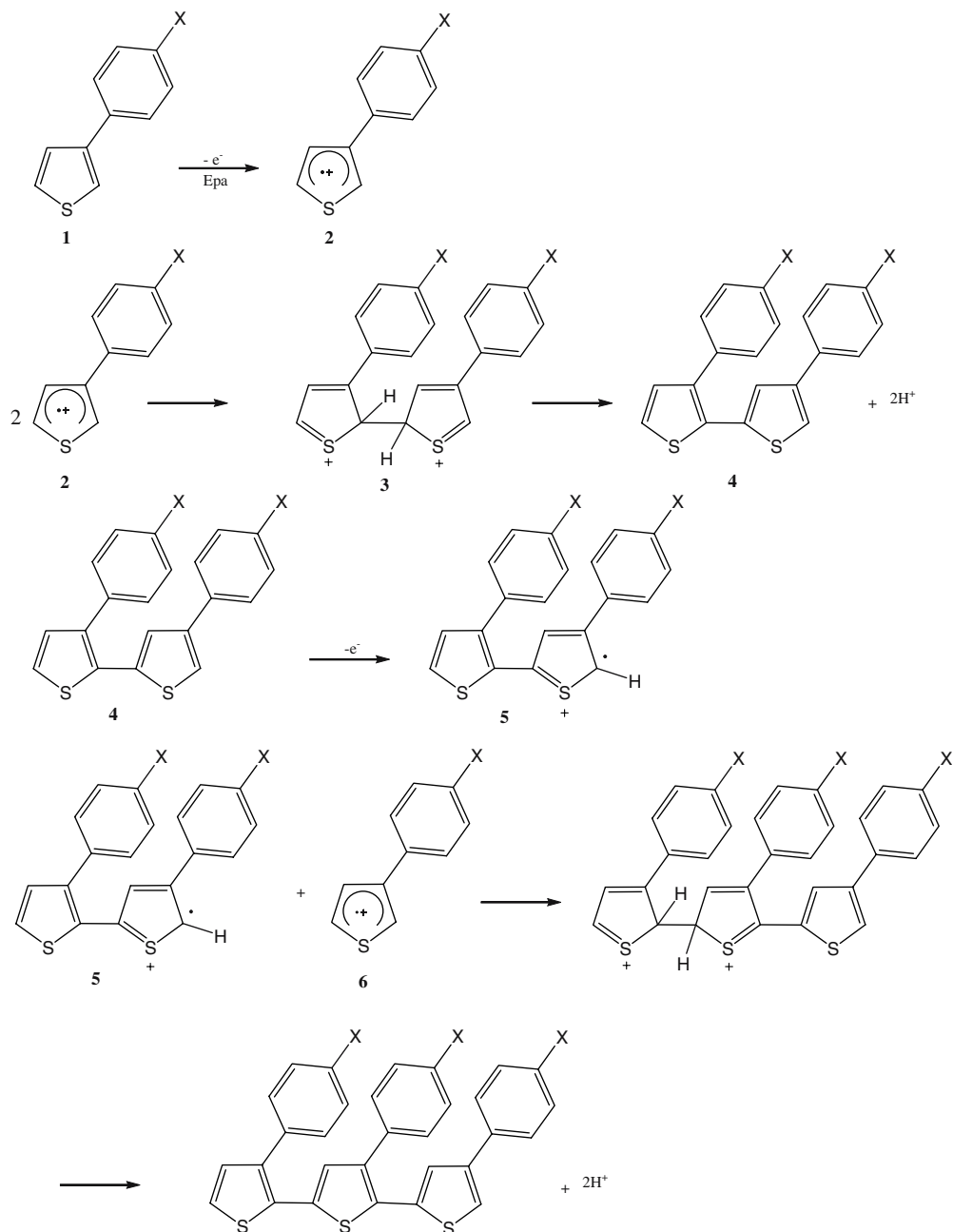
Electropolymerization was chosen because it presents several distinct advantages such as absence of catalyst, direct grafting of the doped conducting polymer onto the electrode surface (which is of particular interest for electrochemical applications), easy control of the film thickness by the deposition charge, and possibility to perform a first in situ characterization of the growing process of the polymer by electrochemical and/or spectroscopic techniques [32].

Scheme 1 shows the proposed mechanism for the electropolymerization of 3-phenylthiophene derivatives in analogy to the already known coupling reactions of aromatic compounds [32–34]. The first electrochemical step is the oxidation of the monomer (1) to its radical cation (2). Since the electron transfer reaction is much faster than the diffusion of the monomer from the bulk solution, it follows that a high concentration of radicals is continuously maintained near the electrode surface. The second step involves the coupling of two radicals (2) to produce a dihydrodimer (3) dication that leads to a dimer (4) after the loss of two protons and rearomatization. This rearomatization constitutes the driving force of the chemical step. Due to the applied potential the dimer (4), which is more easily oxidized than the monomer, is present in its radical form (5) and undergoes further coupling with a monomeric radical (6). Electropolymerization proceeds then through successive electrochemical and chemical steps according to a general E(EC)_n scheme, until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface.

The oxidation potentials of the monomers were measured by cyclic voltammetry at 100 mV/s in acetonitrile (first cycle) containing 0.2 M Et₄NBF₄ and low monomer concentration (0.05 M) in order to prevent polymerization. Figure 2 shows the CVs of the monomers (1–6) during the polymerization. Soluble oligomers were observed to stray away from the electrode with subsequent coloration of the monomers solution, and the resulting polymer films were very thin especially the ones with electron donating substituents.

The possibility to undergo electropolymerization does not depend on the nature of the substituent on the phenyl ring. The monomers with electron withdrawing groups like COCH₃ (σ_p = 0.36) or NO₂ (σ_p = 0.80) as

Scheme 1 Mechanism of electropolymerization of 3-phenylthiophene derivatives



well as with donor groups like CH_3 ($\sigma_p = -0.18$) or OCH_3 ($\sigma_p = -0.15$) were electrooxidized yielding stable electroactive polymers. The electropolymerization of the monomers with electron withdrawing (**4**, **5**, **6**) substituents proceeds with low current efficiency and requires higher anodic potentials, while those with electron donating groups (**1**, **2**, **3**) show lower oxidation potential. The corresponding radicals are stabilized and formation of soluble short chain oligomers is more favorable [35]. Alternatively these radicals can thus diffuse away from the electrode surface to form soluble oligomers in solution.

Cyclic voltammograms of polymers recorded at a scan rate of 100 mV/s are shown in Fig. 3 for the studied

polymer films. Formal potentials for both *p*- and *n*-doping processes were estimated by averaging the anodic and cathodic peak potentials of each process.

Changes in the molecular structure of a monomer affect the voltammetric response of the monomer and the polymer film in various ways. The effect of substitution on the redox properties of the monomers and polymers stem from interplay of steric and electronic (resonance/inductive) factors. The latter can be estimated from Hammett σ constants [36]. For the 3-arylthiophenes studied here, the substituents in the para position makes σ_p (which is the sum of inductive (σ_I) and resonance (σ_R) contributions) the most appropriate. It is important to note that these effects do not always

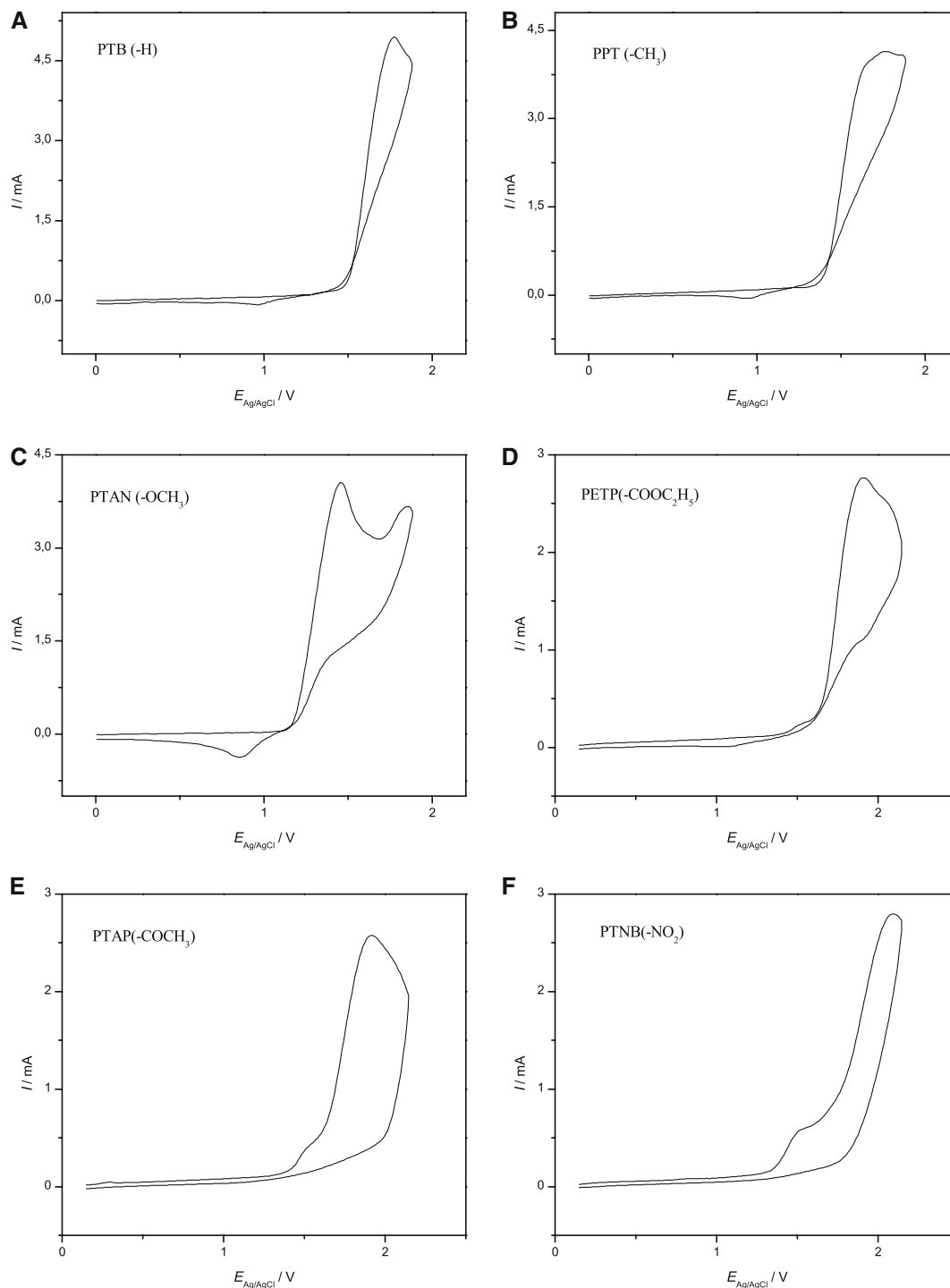


Fig. 2 Cyclic voltammograms of monomers (first cycle) recorded in acetonitrile containing 0.2 M Et₄NBF₄ and 0.05 M monomers: **a** PTB, **b** PPT, **c** PTAN, **d** PETB, **e** PTAP and **f** PTNB, at a scan rate of 100 mV/s. See Table 1 for the acronyms of polymers

work in the same direction. [28, 37–41]. Table 1 lists the σ_i , σ_r , and σ_p constants, the oxidation potentials of the monomers, the formal redox potentials for their respective polymers and the heat of formation for the monomers. Figures 4, 5 and 6 show the respective cor-

relations with σ_p for the monomers and polymers. These trends are as expected with the potentials shifting cathodically (more negative direction) for electron donating substituents ($\sigma_p < 0$) and anodically (more positive potentials) for electron withdrawing groups ($\sigma_p > 0$). These new results are in agreement with published results [19, 28, 37–41]

Increasing the upper positive and decreasing the lower negative potential is limited by destruction of the polymers film. It has been observed that the size of the

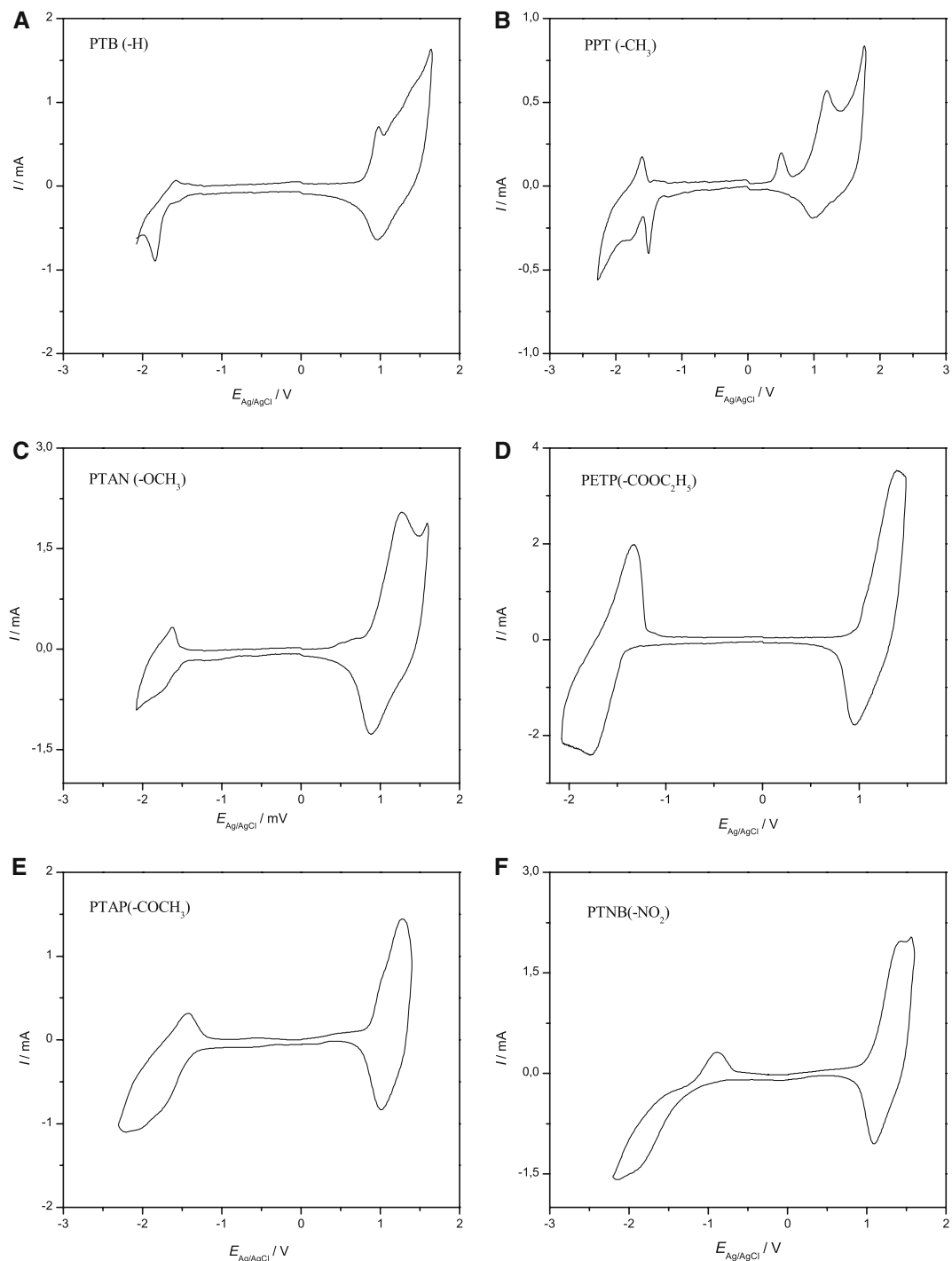


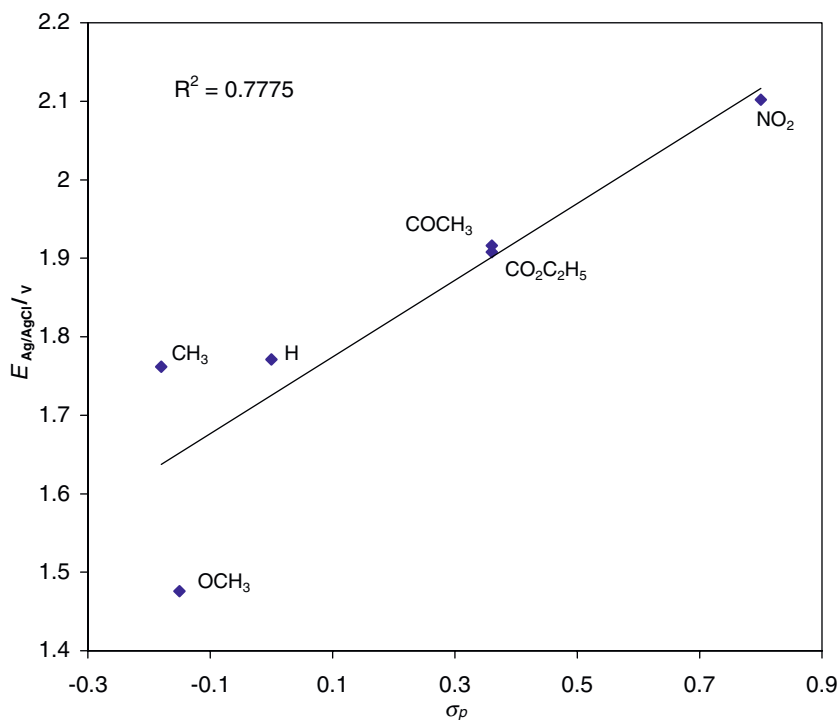
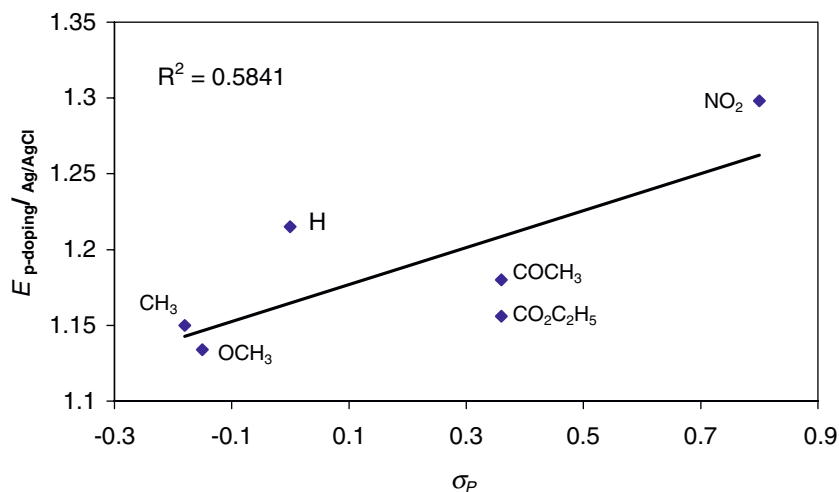
Fig. 3 Cyclic voltammograms of polymer films coated on Pt electrode immersed in 0.2 M Et_4NBF_4 acetonitrile solution: **a** PTB, **b** PPT, **c** PTAN, **d** PETB, **e** PTAP, **f** PTNB, at scan rate of 100 mV/s. See Table 1 for the acronyms of polymers

substituents does not have a significant effect. Moreover, steric factors do not significantly affect the oxidation potentials of the monomers. The overall diminished substituent effect in the polymers suggests a decreased conjugation between the substituted phenyl rings and the polythiophene backbone. Figures 5 and 6 also show

that the difference between the *p*- and *n*-doping formal potentials of the polymers is essentially unchanged upon substitution. This is expected since the symmetries of the frontier orbitals of 3-arylthiophenes are such that the substituents can interact with both energy levels, shifting them downward (or upward) to comparable extents, thus the ΔE_{gap} remains essentially the same [19, 32, 42]. The very weak correlation between σ_p values and the *p*-doping in this series of polymers suggests that a different mechanism is responsible for the stabilization of the π -system in the case of excess positive charge. The sulfur

Table 1 σ_i , σ_r , σ_p , oxidation potentials, formal potentials of *p*- and *n*-doping and heat of formation of the monomers in gas phase and solution

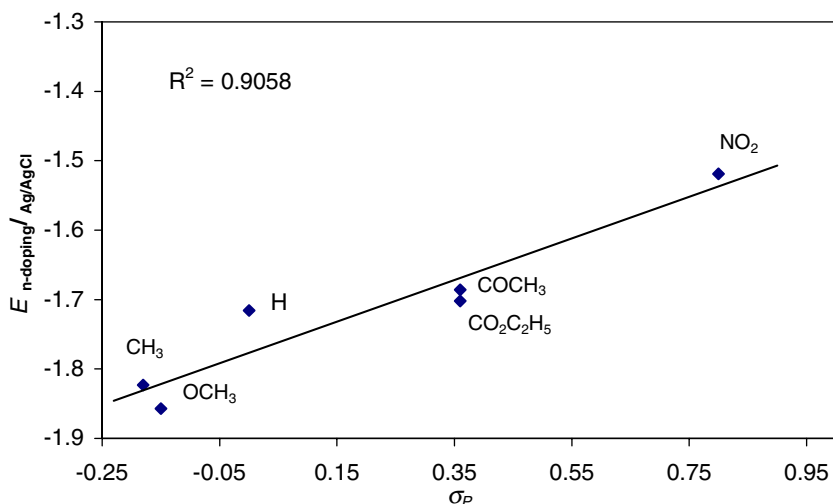
Monomers	Acronym for polymer	Hammett values ³⁴			$E_{ox, Ag/AgCl}/V$	$\Delta H_f / \text{kcal/mol}$ in gas phase	$\Delta H_f / \text{kcal/mol}$ in CH_3CN	Polymer	
		σ_i	σ_r	σ_p				$E_{n\text{-doping}}/V$	$E_{p\text{-doping}}/V$
-H	PTB	0	0	0	1.771	185.94	140.17	-1.716	1.215
-CH ₃	PPT	-0.05	-0.13	-0.18	1.762	182.88	139.09	-1.823	1.150
-OCH ₃	PTAN	0.27	-0.42	-0.15	1.476	178.57	140.22	-1.857	1.134
-CO ₂ C ₂ H ₅	PETB	0.20	0.16	0.36	1.908	184.96	148.70	-1.702	1.156
-COCH ₃	PTAP	0.20	0.16	0.36	1.916	190.93	143.13	-1.686	1.180
-NO ₂	PTNB	0.65	0.15	0.80	2.102	200.59	144.60	-1.519	1.298

Fig. 4 Plot of the oxidation potential of the monomers against σ_p values**Fig. 5** Plot of oxidation potential of the polymers (*p*-doping) against σ_p values

atom in the thiophene ring is known to stabilize the structure of the π -conjugated polythiophene, but participates only to a very limited extent in the delocaliza-

tion of the electrons of the π -system [37, 42, 43]. Therefore, upon the oxidation of the π -system the electron rich sulfur atom stabilizes the oxidized state by

Fig. 6 Plot of reduction potential of the polymers (n -doping) against σ_p values



electron donation. If the acquired excess positive charge is delocalized over the sulfur atom and the coupling between phenyl derivatives and the sulfur is weak then the p -doping potentials are expected to be approximately constant and independent of the σ_p values. Similarly, if the sulfur orbitals are weakly coupled to the polymeric π -system, the electron withdrawing character of the phenyl substituents will dominate the main contribution to the stabilization of the excess charge in the n -doped state.

In Figs. 7 and 8 inductive as well as resonance effects are correlated with oxidation potentials. From these figures it is obvious that the resonance effect dominates the inductive effect [44, 45]. Thus, the resonance effect plays a more important role to obtain good correlations between oxidation potentials of the monomers and Hammett constants (Fig. 4).

Zuman [46] pioneered a classic method for determining how the oxidation (or reduction) potential of an organic substance is affected by electron-withdrawing or electron-supplying groups by studying the correlation between the reduction potentials and Hammett con-

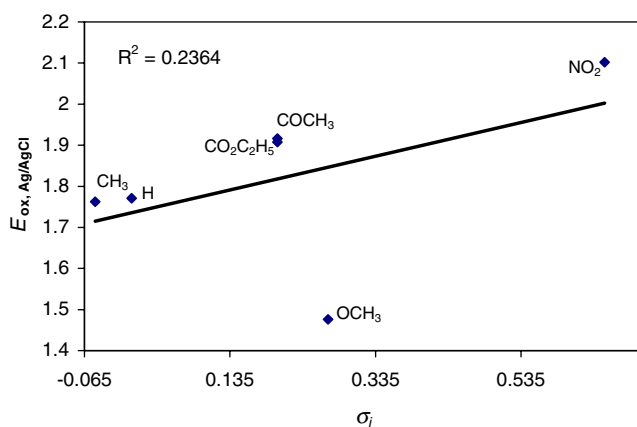


Fig. 7 Plot of the oxidation potential of the monomers against σ_i values

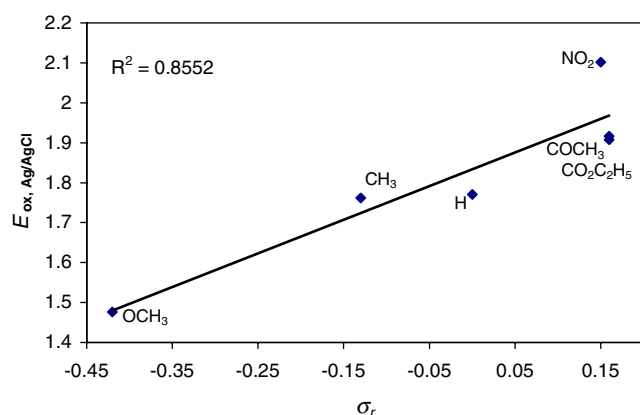


Fig. 8 Plot of the oxidation potential of the monomers against σ_r values

stants. This procedure has a number of limitations: (a) compounds containing certain substituents, such as amino or carbonyl group, which are capable of interaction with the electroactive group via resonance, fall far from the correlation line, (b) the method is limited to substituted aromatics; it cannot be used to estimate the reduction (or oxidation) potentials of any other type of compounds such as conjugated polyenes, heterocyclic substances and polycyclic benzenoid and non-benzenoid aromatic hydrocarbons (PAH). Thus, we used a semi-empirical method to calculate the heat of formation for the monomers in gas phase as well as in liquid phase (acetonitrile) (1–6) (see Table 1). Figures 9 and 10 show the correlation between the oxidation potentials and the heat of formation of these monomers in gas and liquid phases, respectively. It has been observed that with included solvent effect the correlation shows a smaller value of R^2 , which means that the correlation between the oxidation potentials and heat of formation is not as good as in the gas phase.

Although ΔG is more directly related to the oxidation potential of the electrode than ΔH , the correlation of the

Fig. 9 Plot of oxidation potentials of the monomers against heat of formation in gas Phase

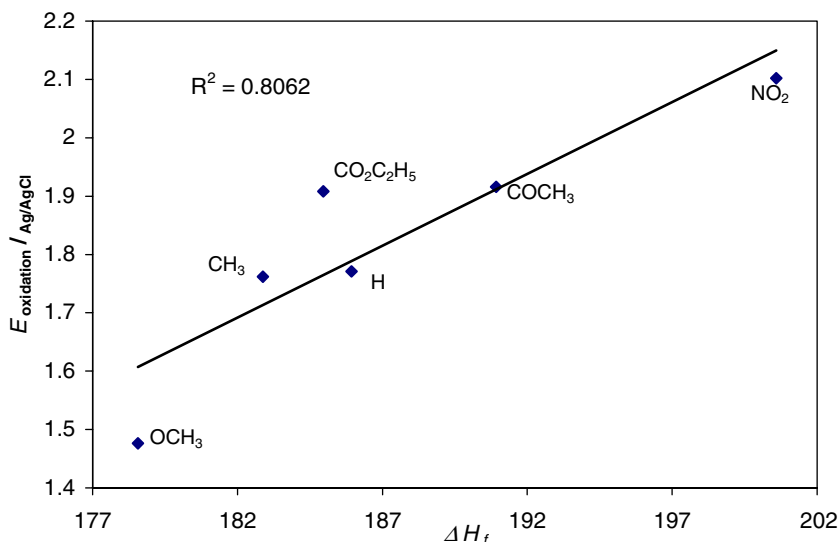
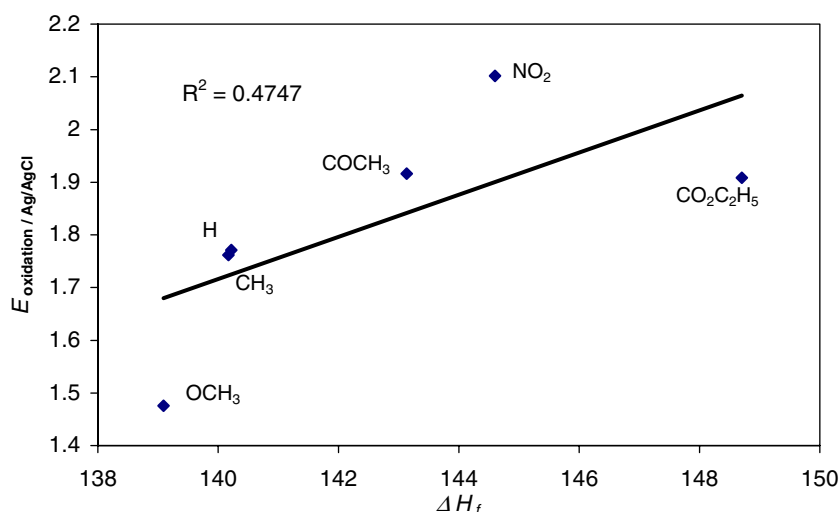


Fig. 10 Plot of oxidation potentials of the monomers against heat of formation in acetonitrile



oxidation potentials of the monomers (1–6) was based on ΔH values only. Calculation of ΔS and subsequently of ΔG is basically possible. The obtained values of both entities show considerable uncertainty. Ab initio molecular orbital (MO) methods provide total energies as the sum of electronic and nuclear–nuclear repulsion energies for molecules; isolated in vacuum, without vibration at 0 K. From the 0 K potential surface and using the harmonic oscillator approximation, they can calculate the vibrational frequencies, ν_i , of the normal modes of vibration. Using these, they can calculate vibrational, rotational and translational contributions to the thermodynamic quantities that arise from heating the system from 0 to T K. However, at 298.15 K, due to higher number of degrees of freedom the degree of uncertainty is larger and therefore this calculated values of ΔG have too large uncertainty.

In some cases a prepeak was observed for both n - and p -doping processes. Prepeaks for polythiophene have been previously explained suggesting a charge-trapping

mechanism [19, 29] that was initially discovered by Murray et al. [35, 47] at bilayer films of redox polymers. The prepeak appears before the peak for the n -doping process and corresponds to the release of most of the p -doped charge that had been trapped in the film while in its neutral state. Similarly, the prepeak appears before the peak for p -doping process. It corresponds to the release of most of the n -doped charge that had been trapped in the film while in its neutral state. The size of the prepeaks depends on the current density for growth, and the condition of the film.

Conclusion

Six monomers/polymers (PTB, PPT, PTAN, PETB, PTAP and PTNB) have been synthesized. Their redox properties have been characterized using cyclic voltammetry. Using the Hammett model, the σ value for each monomer as well as n - and p -doping for each polymer

was found to be related to the electropolymerization potential. The semiempirical calculation gives a good correlation between the heat of formation and oxidation potentials of the monomers.

Acknowledgments Financial support from the funds of the Chemische Industrie and the Deutsche Forschungsgemeinschaft (Graduiertenkolleg GRK 829/1) is gratefully acknowledged. We are grateful to K. Banert for helpful discussions and support in synthesis of the monomers. Finally we thank H.-J. Schäfer for helpful discussions.

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