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Redox Active p-Nitrophenyl Units bond to Electrodeposited Conducting Polythiophene Films

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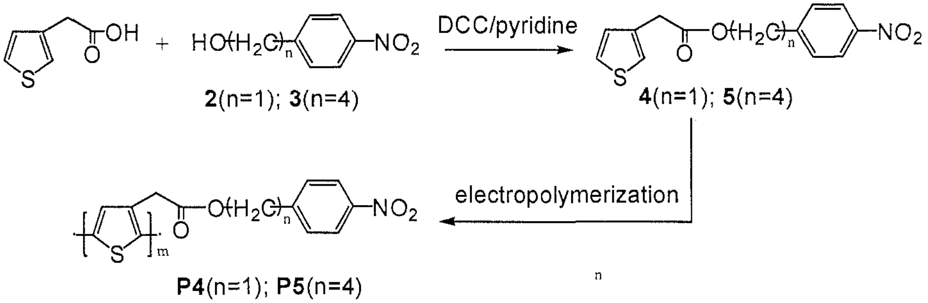
Summary

Two new thiophene derivatives bearing redox active p-nitrophenyl units were synthesized and electropolymerized to conducting polymers. It is found that not only the structure of monomer, but also the employed polymerization conditions have considerable effect on the electroactivity of the bonded redox groups of resulting polymer films. Depending on used conditions such as polymerization time, the polymerization of the same monomer could result in a polymer with well-defined redox transition of the nitrophenyl group or a polymer, in which the redox group is completely electrochemical inaccessible. Using designed experiments, we explained this phenomenon. These investigations provide further knowledge about the behaviors of redox group attached to electrode surface.

Introduction

Functionalization of the β-position of the thiophene system or the N-position of the pyrrole ring system followed by electropolymerization provides an effective method for the modification of electrode surfaces, and can result in the combination of specific properties of attached functional groups with those of conjugated π-electron systems[1-5]. In this connection, the insertion of redox active units into electrodeposited conducting polymer films for catalytic purposes has drawn particular interest in recent years[6-14]. The main reasons come from the following two respects. Firstly, it is believed that, in comparison with a non-conducting polymer backbone, conducting polymers should be a suitable matrix to improve the electronic accessibility of the redox sites and the activity of catalytic groups could thereby be controlled electrochemically. Secondly, the direct formation of fast adhesive functionalized conducting polymer films on electrode surfaces by electropolymerization of the corresponding monomers represents a convenient approach for practical applications.

The p-nitrophenyl group is a redox active unit, which is of special interest for materials science and electrochemistry due to its electrocatalytic properties[15], nonlinear optical characteristics[16], biological activity[17] as well as the reducibility of nitro group to amino group by both chemical and electrochemical approach[18]. The incorporation of such functional group into conjugated π-electron systems such as polypyrrole[19], polyazulene[20] and polythiophene[21-24] has been reported. Here, with the emphasis on the influence of polymer film thickness on the electroactivity of the pendant redox units, we report two new eletrogenerated conducting polythiophene derivatives bearing p-nitrophenyl groups (see Scheme).



Experimental

Monomer synthesis

The monomers **4** and **5** were synthesized according to Scheme1. The general procedure for these syntheses is as follows: 1.42g (10 mmol) thiophene-3-acetic acid, 4ml pyridine and 10 mmol of the corresponding alcohol were dissolved in 50 ml CH_2Cl_2. Under electromagnetic stirring this solution was cooled in an ice bath for 20 min and then 2.27g (11 mmol) DCC were added. The reaction mixture was kept at room temperature for further 20 h. After separation of the formed precipitate the filtrate was washed in turn with 4% HCl, 8% $NaHCO_3$ and water, and dried over $MgSO_4$. After the removal of solvent under reduced pressure, the product was collected and purified by silicagel column chromatography using an appropriate hexane/ethyl acetate mixture as eluent.

3-thiophene acetic acid-4-nitrobenzyl ester (**4**), colorless crystals 2.49g (90%), m.p. 57-58 °C. ^1H n.m.r. ($CDCl_3$, ppm): 8.16 (d, 2H), 7.40 (d, 2H), 7.28 (m, 1H), 7.16 (d, 1H), 7.04 (d, 1H), 5.20 (s, 2H), 3.72 (s, 2H). ^{13}C n.m.r. ($CDCl_3$, ppm): 170.5, 147.6, 142.9, 132.9, 128.3, 125.9, 123.7, 123.1, 64.9, 35.6. Anal. calcd for $C_{13}H_{11}O_4NS$ (277.2): C 56.32; H 3.97; S 11.55. Found: C 56.57; H 4.22; S 11.24.

3-thiophene acetic acid-4-(4-Nitrophenyl)butyl ester (**5**), yellow oil 2.68g (84%), ^1H n.m.r. ($CDCl_3$, ppm): 8.12 (d, 2H), 7.28 (m, 3H), 7.08 (d, 1H), 7.02 (d, 1H), 4.10 (t, 2H), 3.64 (s, 2H), 2.72 (t, 2H), 1.68 (m, 4H). ^{13}C n.m.r. ($CDCl_3$, ppm): 171.1, 149.8, 146.3, 133.5, 129.1, 128.4, 125.7, 122.8. Anal. calcd for $C_{16}H_{17}O_4NS$ (319.2): C 60.20; H 5.33; S 10.04. Found: C 60.42; H 5.40; S 10.51.

Electrochemistry

The determination of the oxidation potentials of the monomer **4** and **5** as well as their electropolymerization were carried out with a HEKA PG 28 potentiostat in a one-compartment three-electrode cell. The anode was a platinum disk electrode (16 mm^2) polished with 0.05 μm diamond paste and then sonicated in distilled water before use. The counter electrode was a Pt wire. An Ag/AgCl electrode was chosen as reference electrode. Before each electrochemical experiment the reaction medium was purged with argon for 10 min at room temperature.

Results and discussion

The DCC-method is a widely used one-pot esterification method, which allows the conversion of a carboxylic acid at ambient temperature and under essentially neutral conditions into an ester in high yield[25]. Using this method, the new thiophene derivatives **4** and **5** bearing redox active p-nitrophenyl units were synthesized, which are characterized with different long spacers between the thiophene ring and the nitrophenyl moiety. The yields of these syntheses are 90% and 84% for the monomer 4 and 5, respectively.

The electrochemical characterization of the synthesized monomers **4** and **5** was carried out in a three-electrode cell described in Experimental, in which a low concentration (10^{-3} M) of the corresponding monomer in acetonitrile containing 0.1 M TBAP as supporting electrolyte salt was used in order to prevent the occurrence of polymerization. Fig. 1 shows the cyclic voltammograms of the two monomers in the potential range from –1.4 to +2.2 V (vs. Ag/AgCl). As expected, in addition to the typical irreversible oxidation of the thiophene ring subunit at positive potentials, the presence of the additional one-electron reversible redox couple of $R\text{-}NO_2/R\text{-}NO_2^{\bullet-}$ [19] in the negative potential range was observed. The reversible redox transition of the nitro moiety in **4** occurs at the potentials E_p^{red}= -0.82 V and E_p^{oxd}= -0.74 V (E^o= -0.78 V), which are a little more positive than those (E_p^{red}= -0.90 V, E_p^{oxd}= -0.82 V, E^o= -0.86 V) of the nitro group in **5**. Probably, due to the short spacer in **4** the carbonyl group still exerts an electron-withdrawing effect on the nitrophenyl system and hence, makes the nitro group easily to be reduced and subsequently to be reoxidized. These observed redox potentials of the monomers **4** and **5** are comparable to those of p-nitrotoluence[15] and poly(p-nitrostyrene)[26].

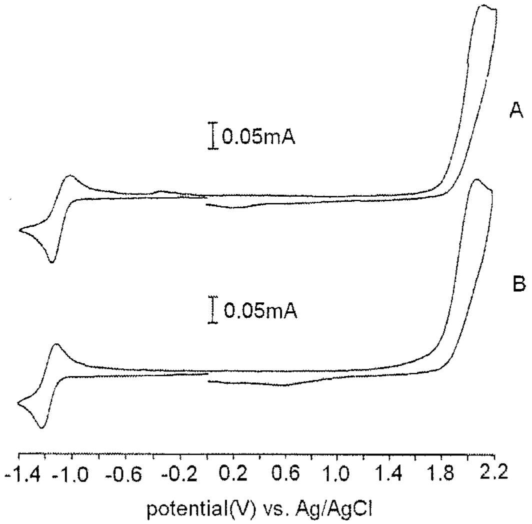


Figure 1. Cyclic voltammograms of monomer **4** (A) and **5** (B) recorded in a 10^{-3} M acetonitrile solution containing 0.1 M TPAB as supporting electrolyte salt at a scan rate of 100 mV/s.

The electropolymerization of the monomers **4** and **5** was performed by potentiodynamic technique in a 0.2 M solution of the corresponding monomer in acetonitrile containing 0.1 M TBAP as supporting electrolyte salt. The switching potential range from 0.0 to +2.0 V (vs. Ag/AgCl) was used for both monomers during the polymerization processes. The thickness of the resulting polymers (amount of polymer formation) was controlled by the number of potential sweeping cycles or was monitored by the amount of charge passed during polymerization. Fig. 2A and Fig. 2B display the potentiodynamic polymerization of the monomers **4** and **5**. As shown in Fig. 2A-B, with the potential scanning, the successive growth of a redox wave at potentials lower than the oxidation potential of the corresponding monomer appears, indicating that a redox active polymer was formed on the working electrodes.

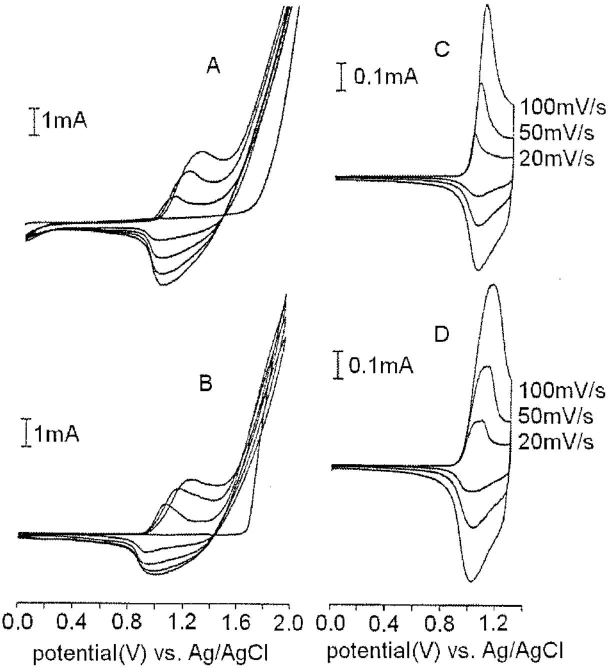


Figure 2. Potentiodynamic polymerization of monomer **4** (A) and **5** (B) (0.2 M) in 0.1 M TBAP acetonitrile solution at a scan rate of 100 mV/s as well as the cyclic voltammograms of the resulting polymer **P4** (C) and **P5** (D) in a monomer-free electrolyte solution at different scan rates.

The resulting new polymers **P4** and **P5** (P refers to polymer) were electrochemically characterized in a monomer-free electrolyte solution. The characterization was firstly limited in the positive potential range (see Fig. 2C-2D). It is clearly seen that under different sweeping rates (20, 50 and 100 $mV.s^{-1}$) both polymers exhibit the typical redox behavior of conjugated polythiophene[3-4]. During the doping – dedoping (oxidation-reduction) process, both polymers also show the characteristic electrochromism of conjugated polymers. When switched from the neutral form to the doped (oxidized) state, the color of the polymer layers changes from brown to dark blue. In addition, the cathodic and anodic peak currents change linearly with scans rates, revealing that the redox active species are anchored to the electrode surface and the redox reactions are not limited by diffusion[3-4].

The redox transitions of the pendant p-nitrophenyl groups in polymers (**P4** and **P5**) were observed, when the potential range was extended to the negative range. As an illustrative example, Fig. 3A displays the cyclic voltammogram (CV) of polymer P5 in a board potential range (-1.6 V to +1.6 V vs. Ag/AgCl). It is visible that besides the conjugated π-electron (polymer) system the pendant nitrophenyl units exhibit a well-defined reversible redox transition of R-NO_2/R-$NO_2^{\bullet-}$ (E_p^{red}= -1.4 V, E_p^{oxd}= -0.92 V, E^o= -1.16 V). As expected, during the reduction of the nitrophenyl groups a characteristic dark brown color of the polymer layers was observed in all cases. The transitions occur at potentials comparable to those of the corresponding monomer. However, due to the kinetic limitation of the charge transport in polymer films[27], the peak separation of the redox couple R-NO_2/R-$NO_2^{\bullet-}$ is clearly larger than that of the monomers (see Fig.1 and Fig. 3A).

Interestingly, we found that the redox activity of the pendant nitrophenyl groups depends strongly on the thickness of the formed polymer films. In Fig. 3 the evolution of the redox activity of the pendant nitrophenyl groups with film thickness is displayed. As shown in Fig. 3A, the pendant nitrophenyl groups in thin films (prepared by one cycle) exhibit a well-defined, symmetric redox characteristic. However, with increasing film thickness the symmetry of redox waves disappears firstly (see Fig. 3B-3C) and, finally, the electrochemical accessibility of the nitrophenyl groups are fully lost (see Fig. 3D).

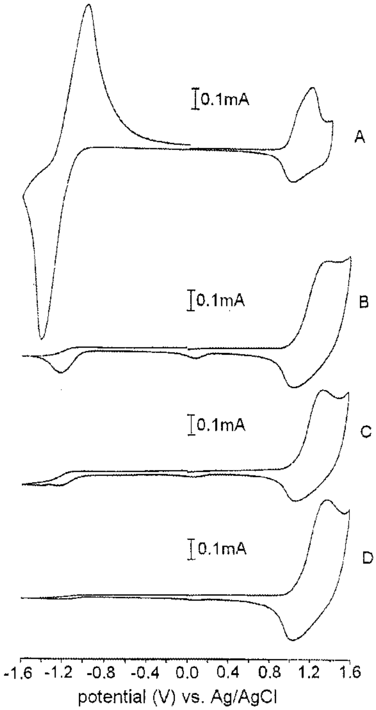


Figure 3. Cyclic voltammograms of polymer **P5** in a monomer-free electrolyte solution at a scan rate of 100 mV/s: A: polymer prepared by one cycle; B: polymer prepared by two cycles; C: polymer prepared by three cycles; D: polymer prepared by four cycles.

FTIR-spectroscopy studies confirm that in all cases the nitrophenyl groups were correctly incorporated into the synthesized polymer films, which show two characteristic adsorptions of nitro groups at 1550 and 1350 cm^{-1}. All mechanistic studies showed that the length of the conjugated chain does not depend on the number of potentiodynamic cycles applied during electropolymerization[3], indicating that the progress of electropolymerization does not cause the decrease of the electrical conductivity of the resulting film. Therefore, the most likely reason for the above-described observation is the considerable influence of the thickness of the film on the rate of electron transport, not the resistivity (conductivity) effects. In fact, the evolution of the peak-potential difference supports this interpretation. In Fig. 3A, the potential difference between oxidation and reduction peak of the synthesized polymer is 0.23V. However, with forthcoming increased thickness of the polymer films the potential difference changes from +0.23 V to +0.38 V (see Fig. 3A-3D). This result clearly indicates that upon increasing thickness the electron transport in films becomes more and more difficult.

As with polymer **P5**, similar results were also observed in the case of polymer **P4**. However, it is found that the length of the spacer between the thiophene ring and the nitrophenyl moiety has some influence on the redox behavior of the nitrophenyl group. In contrast to the well-defined, symmetric redox wave (I_p^{oxd}/I_p^{red} =1)[28] of nitrophenyl groups in polymer **P5** (see Fig. 3A), the redox wave of the nitrophenyl groups attached onto polymer **P4** exhibit only a symmetry of 0.3 (I_p^{oxd}/I_p^{red}). The reason may be that, due to the short spacer between the thiophene ring and the nitrophenyl moieties in polymer **P4**, the formation of a extended conjugated polymer backbones is hindered by bulky nitrophenyl groups and, as consequence, polymer **P4** possesses a lower conductivity than polymer **P5**.

The phenomenon that redox active units incorporated into conjugated π-electron systems cannot be electrochemically accessible is not a new one. Bäuerle et al. reported the synthesis of a quinone-functionalized poly(3-alkylthiophene)[9]. Although the quinone functions were unchanged associated in the resulting polymer, all attempts to electrochemically addressing the pendant redox active units under different conditions failed. Salmon et al. described electrogenerated polypyrrole bearing a p-nitrophenyl group[19]. To electrochemically detect the pendant nitrophenyl groups, however, several cyclic potential sweeps were required for synthesized films. The so-called "break-in" phenomenon occurring usually in nonconducting polymer matrices[29] was observed in this conjugated polymer system. It is remarkable that in conducting polymers the above-described blocking phenomenon was only reported in the cases of redox active groups of the receptor type (i.e. redox transitions occurring in the negative potential range). In the cases of conducting polymers bearing redox active groups of the donor type such as TTF and ferrocene the similar phenomenon has not been described so far.

To demonstrate the different sensibility of these two types (donor and acceptor type) of redox systems toward the thickness of conducting polymer films and at the same time to support the explanation that the kinetic limitation of the charge transport in the synthesized polymers is responsible for our observed results, we designed the following experiments. The Pt-electrodes modified by electrogenerated poly(3-methylthiophene) with different thickness were prepared. Using these electrodes as well as a pristine (bar) Pt-electrode, we probed the electrochemical behavior of ferrocene (10^{-3} M) and p-nitrotoluene (10^{-3} M) mixture, which simultaneously exist in the used electrolyte solution. Fig. 4 displays the observed results.

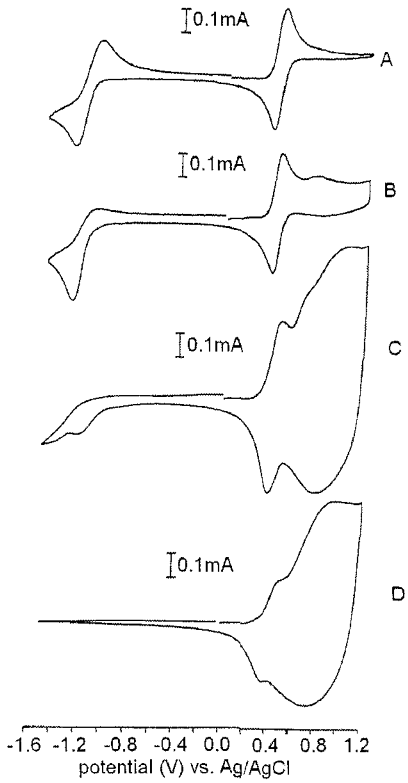


Figure 4. Cyclic voltammograms of ferrocene (10^{-3} M) and p-nitrotoluene (10^{-3} M) dissolved in an acetonitrile solution containing 0.1 M TBAP. Different working electrodes were used: A: pristine (bar) Pt-electrode; B: Pt-electrode with poly(3-methylthiophene) prepared by one cycle; C: Pt-electrode with poly(3-methylthiophene) prepared by five cycles; D: Pt-electrode with poly(3-methylthiophene) prepared by ten cycles.

As expected, ferrocene and p-nitrotoluene exhibit independently a well-defined redox transition at their expected redox potentials by using a pristine (bar) Pt-electrode (see Fig. 4A). After the electrodeposition of polymer films [poly(3-methylthiophene)] on Pt-electrode surfaces with different film thickness, however, both redox active compounds show full different electrochemical evolution. In the case of ferrocene (donor type), the well-defined redox transition of ferrocene was observed in all cases (see the positive potential range in Fig. 4A-4D). Although the charge transfer of ferrocene in a thick polymer film shows no problem (see Fig. 4D), the peak-potential becomes continually broad . The redox activity of p-nitrotoluene exhibits, however, a strong dependence of the polymer thickness (see the negative potential range in Fig. 4A-D). With increased film thickness, the symmetry of the redox wave firstly disappears and finally, the redox group cannot be detected.

Since the conductivity of the polymer is low during both the oxidation of ferrocene and the reduction of nitrobenzene, the different rate constants of electron transfer should be responsible for observed electrochemical behavior. This observed influence of the film thickness on the electroactivity of p-nitrophenyl groups is identical with the observation with polymers **P4** and **P5**. Although some differences between these two systems (system1: nitrophenyl groups incorporated into polymer films; system 2: nitrotoluene in electrolyte solution) exist, the designed experiment strongly supports our explanation. These results clearly indicate that, in order to obtain a conjugated polymer with active redox groups, especially redox groups with lower electron transfer rate constant, it is necessary that the polymer film should not only process good electrical conductivity, but also be very thin.

References

1 Deronzier, A., Moutet, J. C., *Acc. Chem. Res.*, 1989, 22, 249.
2 Heinze, J., *Topics in Current Chemistry*, Springer-Verlag Berlin Heidelberg, 1990, 1.
3 Roncali, J., *Chem. Rev.*, 1997, 97, 173.
4 Schopf, G., Koßmehl, G., *Adv. Polym. Sci.*, 1996, 129, 1.
5 Audebert, P., Bidan, G., Lapkowski, M., *J. Chem. Soc., Chem. Commun.*, 1986, 887.
6 Mirrazaei, R., Parker, D., Munro, H. S., *Synth. Met.*, 1989, 30, 265.
7 Grimshow, J., Perera, S. D., *J. Electroanal. Chem.*, 1990, 278, 278.
8 Bäuerle, P., Gaudl, K. U., Götz, G., *Springer Ser. Solid State Sci.*, 1992, 384, 107.
9 Bäuerle, P., Götz, G., Hiller, M., Scheib. S., Fisher, T., et al., *Synth. Met.*, 1993, 61, 71.
10 Thobie-Gautier, G., Gorgues, A., Jubault, M., Roncali, J., *Macromolecules*, 1993, 26, 4094.
11 Zhu, S. S., Swager, T. M., *Adv. Mater.*, 1996, 8, 497.
12 Kingsborough, R. P., Swager, T. M., *Adv. Mater.*, 1998, 10, 1100.
13 Huchet, L., Akoudad, S., Roncali, J., *Adv. Mater.*, 1998, 10, 541.
14 Van de Mark, M. R., Miller, L. L., *J. Am. Chem. Soc.*, 1978, 100, 3223.
15 Kim, Y. W., Jin, J., Jin, M. Y., Choi, K. Y., Kim, J. J., Zyung, T., *Polymer*, 1997, 38, 2269.
16 Alvarez-Lueje, A., Pessoa, H., Nunez-Vergara, L. J., Squella, J. A., *Bioelectrochemistry and Bioenergtics*, 1998, 46, 21.
17 Kokkinidis, G., Papoutsis, A., Papanastasiou, G., *J. Electroanal. Chem.*, 1993, 359, 253.
18 Velazquez Rosenthal, M., Skotheim, T. A., Melo, A., Florit, M. I., Salmon, M., *J. Electroanal. Chem.*, 1985, 185, 297.
19 Schuhmann, W., Huber, J., Mirlach, A., Daub, J., *Adv. Mater.*, 1993, 5, 124.
20 Lemaire, M., Garreau, R., Delabouglise, D., Roncali, J., Youssoufi, H. K., Garnier, F., *New J. Chem.*, 1990, 14, 359.
22 Greenwals, Y., Wie, X., Jeglinski, S., Poplawski, J., Ehrenfreund, E., Speiser, S., Vardeny, Z. V., *Synth. Met.*, 1995, 69, 321.
23 Zotti, G., Berlin, A., Pagani, G., Schiavon, G., Zecchin, S., *Adv. Mater.*, 1995, 7, 48.
24 Li, G., Koßmehl, G., Welzel, H. P., Plieth, W., Zhu, H., *Macromol. Chem. Phys.*, 1998, 199, 2737.
25 Hassner, A., Alexanian, V., *Tetrahedron Letters*, 1978, 46, 4475.
26 Salmon, M., Diaz, A., Goitia, J., Miller, J. S., Eds., "*Chemically Modified Surface in Catalysis and Electrocatalytsis*", ACS, Washington 1982, vol. 65.
27 Bäuerle, P., Hiller, M., Scheib, S., Solkolowski, M., Umbach, E., *Adv. Mater.*, 1996, 8, 219.
28 I_p^{red}: peak current of reduction wave of nitrophenyl groups in polymer P4 and P5; I_p^{oxd}: peak current of oxidation wave of nitrophenyl groups in polymer P4 and P5.
29 Kaufman, F. B., Schroeder, A. H., Engler, E. M., Kramer, S. R., Chambers, J. Q., *J. Am. Chem. Soc.*, 1980, 102, 483.