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Spectroelectrochemical and potentiometric studies of functionalised electroactive polymers

Ján Tarábek[a], Peter Rapta[a,b], Evelyn Jähne[c], Dirk Ferse[c], Hans-Jürgen Adler[c], Michel Maumy[d], Lothar Dunsch[a,*]

[a] *Leibniz-Institut für Festkörper- und Werkstoffforschung, Abteilung Elektrochemie und leitfähige Polymere,*
Helmholtzstrasse 20, D-01069 Dresden, Germany
[b] *Slovak University of Technology, Faculty of Chemical and Food Technology, Department of Physical Chemistry,*
Radlinského 9, SK-81237 Bratislava, Slovak Republic
[c] *Technische Universität Dresden, Insitut für Makromolekulare Chemie und Textilchemie, Mommsenstrasse 4, D-01069 Dresden, Germany*
[d] *Laboratoire de Recherche Organique, ESPCI, 10 rue de Vauquelin, F-75231 Paris, France*

Abstract

The design and characterisation of new electroactive polymers carrying functional (receptor) groups for ion recognition in the main or the side chain of the polymer are presented. For this purpose, thiophene polymer with an acetophenone group, 6-hydroxy-2-(2-(3-thienyl)-ethoxy)-acetophenone (3-AcpT), as well as salen-based polymers such as poly[(6,6′-bis-(*o*-methoxyphenyl)-2,2′-bipyridine)Ni(II)] and poly[(*N*,*N*′-bis-(salicylidene)-ethylendiamine)Cu(II)] were studied. As spectroelectrochemical methods in situ ESR, ESR/UV–vis–NIR and FTIR spectroelectrochemistry were applied to follow both the paramagnetic and the diamagnetic species formed in redox reactions. Quantitative spectroelectrochemical analysis supports the preferable formation of ESR-silent (dicationic) chain segments upon oxidation in investigated polymer and copolymer structures, where the bipolarons and two interacting polarons in singlet state should be considered. The presented contribution besides the spectroelectrochemical characterisation discusses the potentiometric and voltammetric responses of salen-based polymers and copolymers in detection of Ni^{2+}-ions.

Keywords: Conducting polymers; Electrochemical polymerisation; Sensorics; Ion-selective electrodes; Potentiometry; Spectroelectrochemistry

1. Introduction

Conducting polymers (CPs)-based chemical sensors are preferred sensor structures as CPs exhibit sensitivity to minor perturbations because of their collective redox properties [1]. Their use in all-solid-state ion-selective electrodes (ISE), where no inner solution is required (Fig. 1), results in an asymmetric electrode configuration (Fig. 1c) which has several advantages as compared to the classical symmetric configuration (Fig. 1a): mechanical stability (the electrode can be applied in arbitrary positions) and ion-selective microelectrodes with such configuration can be easily prepared as compared to symmetric configuration. Mentioned electrode construction is important in on-line analysis [1]. The main problem of such electrode configuration is the potential instability on electrode substrate/membrane interface [2]. Therefore, an interlayer is required, consisting of electroactive polymers. The coupling of electronic and ionic charge transport processes in such polymers serves as an ion-to-electron transducer, thus stabilising the substrate/membrane interface [3]. Due to this feature, conducting polymers unlike the classical liquid polymer membrane electrode can be applied without any plasticizer which ensures sufficient mobility of membrane components and ions [4]. The receptor (ionophore) groups can be introduced into the polymer phase as counter ions in the doping process [5], as a component of a mixture including the conducting polymer [6] or fixed in the main or side chains of the polymer. The last mentioned version (Fig. 1c) is presented for salen and acetophenone (Fig. 2)

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* Corresponding author. Tel.: +49 351 465 9660; fax: +49 351 465 9745.
E-mail address: l.dunsch@ifw-dresden.de (L. Dunsch).

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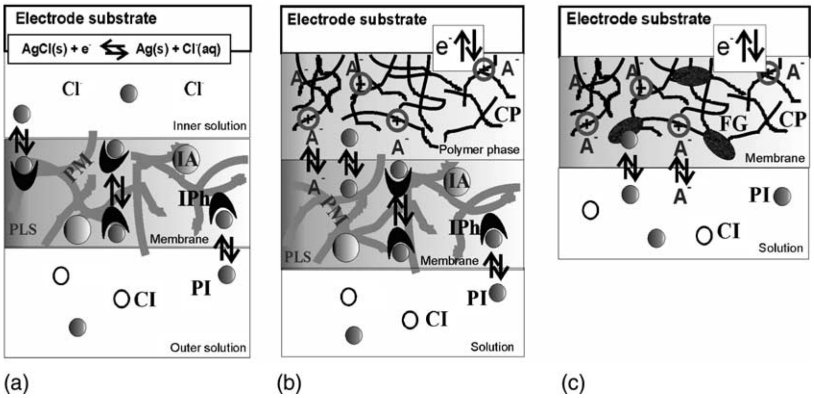

Fig. 1. Schematic diagrams of ion-selective membrane electrodes: (a) symmetrical configuration, (b) asymmetrical solid state configuration with a conducting polymer as second layer, (c) asymmetrical configuration with the functionalised conducting polymer working both as conductor and ion-selective membrane (MI: measured primary ion, CI: counter ion, IPh: ionophore, PM: polymer matrix, PLS: plasticizer, IA: ionic additives, CP: conducting polymer, A$^-$: counter ion by the doping, FG: functional group).

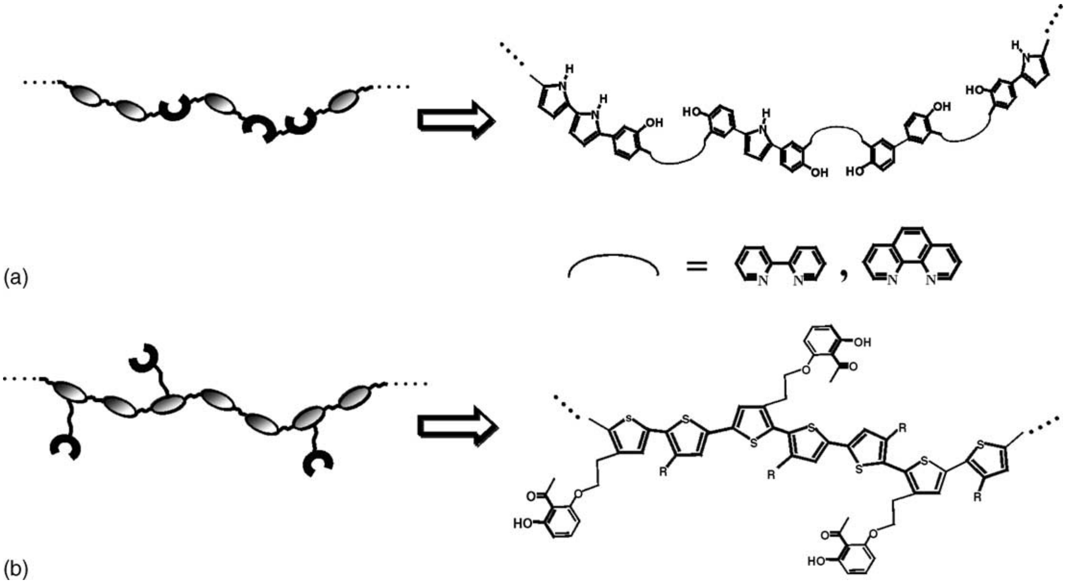

Fig. 2. Functional conducting polymers with the receptor group in the (a) main chain (pyrrole/salen-copolymer) and (b) in the side chain (thiophene-copolymer with the acetophenone-functional group).

groups, respectively. They are known for their selective interaction with divalent ions [7,8] and can be simply introduced into the polymer chain.

To follow the redox processes in polymers for electrochemical sensorics, spectroelectrochemical methods have to be applied [9,10] due to complementary nature of the molecular structural and electrochemical informations. Here, we use the triple simultaneous in situ ESR/UV–vis–NIR spectroelectrochemistry for direct detection of paramagnetic (by ESR spectroscopy) as well as both paramagnetic and diamagnetic species (by UV–vis–NIR spectroscopy) formed during an electrochemical process. Furthermore, we used FTIR–ATR spectroelectrochemistry to study the structural changes in the polymer during the redox process.

The spectroelectrochemical analysis of conducting polymers and copolymers involves the application of different charge-carrier models: segments of a polymer- or copolymer-chain are transferred into paramagnetic *polarons* (where the spin-density is delocalised over several monomer units) and diamagnetic *diionic centres* (the electron density is also delocalised over several monomer units) [11]. The oligomeric structures of different chain length [11,12] as well as polymers such as polyaniline [13] and polypyrrole [14] have different diionic centres: bipolarons, dimeric structures (π- or σ-dimer) and two interacting polarons on a single chain in singlet state [11]. In this contribution, the complex spectroelectrochemical study on poly(Cu-salen) and copolymer 3-methylthiophene (3-MT) with 6-hydroxy-

2-(2-(3-thienyl)-ethoxy)-acetophenone (3-AcpT) as well as poly(3-methylthiophene) is performed to clarify the nature of the diamagnetic dicationic structures in the polymer and copolymer structures.

The main scope of this contribution is the spectroelectrochemical study of presented structures in order to find out the mechanism which describes the redox behaviour of investigated polymers and copolymers. However, we also present here the possible direction of their analytical application (as mentioned above), which can be followed in the future. Application of the electrochemically synthesised Ni-bpsalen and its copolymer with pyrrole (Py) without any other additional membrane as sensitive layers for the potentiometric and voltammetric detection of Ni^{2+} is presented. The application of the 3-methylthiophene/6-hydroxy-2-(2-(3-thienyl)-ethoxy)-acetophenone copolymer in this contribution is not discussed. It serves as a model system for describing the polymer charge-transfer processes on functionalised conducting polymers in the side chain with functional receptor groups for divalent heavy metal ions.

2. Experimental

2.1. Chemicals

The functionalised thiophene monomer 6-hydroxy-2-(2-(3-thienyl)-ethoxy)-acetophenone was synthesised by reaction of 2-(thiophen-3-yl ethyl)bromide with 2,6-dihydroxyacetophenone [15]. Cu-salen and Ni-bpsalen were synthesised as described elsewhere [16,17]. Acetonitrile (ACN, puriss.; absolute; $w(H_2O) \leq 0.001\%$), 3-methylthiophene (purum, ≥98.0%, GC) purchased from Fluka and ferrocene (p.a., ≥98.0%) purchased from Merck were used as received. Pyrrole of a purity of >98% (GC) purchased from Merck was doubly distilled and stored in the cold. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) and tetraethylammonium perchlorate (TEAP) of puriss. quality (Fluka) were dried under reduced pressure at 70 °C for 24 h and stored in a glove box. For potentiometry, following chemicals were used as received: ethylenedioxythiophene (EDOT) was purchased from Bayer (purity > 98%, GC); sodium polystyrenesulfonate (NaPSS, $M_w \approx 70{,}000$) from Aldrich; polyvinylchloride (PVC, $M_w \approx 75{,}000$) from Fluka; tetrahydrofuran (THF) purris. from Fluka; tetrakis-(4-chlorphenyl)-borate (KTClPB) (purity ≥ 99%, GC) from Fluka and 2-nitrophenyl-octylether (NPOE) with a purity of ≥99% (GC) from Fluka.

2.2. Electrochemical experiments

All described electrochemical experiments were done in a glove box (oxygen and water content below 1 ppm) in a standard one-compartment electrochemical cell containing platinum wire-loop as a counter electrode, double junction Ag-wire/Ag^+ (0.01 M $AgNO_3$ in ACN)/0.1 M $TBAPF_6$ (TEAP) in ACN as a reference electrode and platinum mesh (0.2 cm^2, 1024 meshes/cm^2) contacted with platinum wire sealed in soft glass as working electrode. The reference electrode was calibrated by the ferrocene/ferrocenium (Fc/Fc^+) redox couple. The polymerisation of 3-MT was done potentiostatically at 1.5 V versus Fc/Fc^+ and the copolymerisation of 3-MT with 3-AcpT was performed potentiodynamically between −0.3 V and 1.5 V versus Fc/Fc^+. The poly(Cu-salen) was synthesised potentiodynamically between −0.40 V and 0.65 V versus Fc/Fc^+. For all experiments, the EG&G PAR 273A potentiostat/galvanostat and the standard software package M270 were used.

2.3. Spectroelectrochemical measurements

In situ ESR/UV–vis–NIR spectroelectrochemical experiments were performed in the flat ESR cell filled with 0.1 M $TBAPF_6$/ACN. As a working electrode, the laminated ITO or Pt-μ-mesh (1024 meshes/cm^2, active surface 0.1 cm^2) was used. Polymers and copolymers were prepared onto laminated electrodes (for the detailed preparation of laminated electrodes, see [13,14]). As a counter electrode platinum wire and as a quasi-reference electrode Ag-wire was used. The cell was filled and tightly closed in the glove box while the experiments were done in the optical ESR cavity (ER 4104OR, Bruker, Germany) outside the box. ESR spectra were recorded by the ELEXSYS E-500 X-band CW spectrometer (Bruker, Germany). UV–vis–NIR spectra were taken by TIDAS (J & M, Germany) spectrometer. Both the ESR spectrometer and the UV–vis–NIR spectrometer were linked to a HEKA potentiostat PG 285. Triggering was performed by the software package PotPulse 8.53 (HEKA Electronic, Germany). The absolute number of ESR-active species formed during the cyclovoltammetric scan was determined by the Mn–ESR standard calibrated against the ESR strong pitch [13,14].

Quantitative in situ ESR spectroelectrochemistry of poly(Cu-salen) was done in a cell located in double ESR cavity ER 4105DR (Bruker, Germany), which contained in the second cavity the strong pitch sample. The in situ UV–vis spectroelectrochemical experiments were carried out inside the TE_{102} optical cavity ER 4104OR (Bruker). Optical spectra were taken by an INSTASPEC II (UV–vis, LOT Oriel, Germany) spectrometer. ESR spectra were recorded by the EMX X-band CW spectrometer (Bruker). Simulations of the ESR spectra were performed by the WINEPR SimFonia 1.25 software. Both the ESR spectrometer and the UV–vis spectrometer were linked to HEKA potentiostat PG 390. Triggering was performed by the software package PotPulse 8.53 (HEKA Electronic, Germany).

ESR spectra of poly(Cu-salen) on Pt-μ-mesh-electrode (1024 meshes/cm^2) in different redox states at 77 K were recorded ex situ after applying a certain potential step, controlled by the potentiostat HEKA PG 284, for 30 s and immediately inserting of the ESR cell into liquid nitrogen. The electrode connections to the potentiostat were removed after cooling. A standard ESR cell was used with an Ag-wire as quasi-reference electrode and a Pt-μ-mesh as counter electrode.

In situ FTIR–ATR spectroelectrochemical experiments were carried out in a special spectroelectrochemical cell already described elsewhere [18]. An IFS 66v spectrometer (Bruker, Germany) equipped with a fast MCT detector (600–7000 cm^{-1}) with the resolution of 2 cm^{-1} was used. ITO electrode covered by the polymer film and positioned between the ZnSe–ATR crystal and the cell body was used as a working electrode. The potentiostat HEKA PG 284 was applied for controlling the potential sequence at the electrode system.

In all spectroelectrochemical measurements, the silver-wire quasi-reference electrode was calibrated against $\mathrm{Fc/Fc^+}$ redox system. Its potential −0.13 V versus SCE (saturated calomel electrode) was stable and was estimated by the $\mathrm{Fc/Fc^+}$ redox-system (derived from $E_{1/2}$ ($\mathrm{Fc/Fc^+}$) = 0.25 V versus Ag quasi-reference electrode and $E_{1/2}$ ($\mathrm{Fc/Fc^+}$) = 0.38 V versus SCE [19]).

2.4. Potentiometry

In all experiments, the triple distilled, deionised water with resistivity of 18 MΩ cm was used. The poly(Ni-bpsalen) and its copolymer with pyrrole were electrochemically synthesised onto glassy-carbon electrodes according to already described pre-pulse procedure [20]. After washing with ACN and water, electrodes were used without conditioning. For potentiometric measurement at Ni-bpsalen, glassy-carbon electrodes were at first electrochemically (galvanostatically, 0.014 mA for 700 s) covered with poly(ethylenedioxythiopnene) (PEDOT). The polymer was synthesised from 0.01 M EDOT/0.1 M NaPSS aqueous solution. After polymerisation, the modified electrodes were rinsed with water and conditioned over night in 0.01 M $\mathrm{Ni(NO_3)_2}$ solution. All membrane components, Ni-bpsalen, PVC, NPOE and KTClPB, were with the following composition dissolved in THF: 0.4 wt.%; 33.6 wt.%; 61.0 wt.% and 5.0 wt.%, respectively. This composition was for salen-ionophor found to reach the best sensitivity and selectivity [8]. Prepared solution was afterwards applied on the top of the PEDOT-covered glassy-carbon electrode and THF was left to evaporate as previously described [21]. Finally, the electrode was rinsed with water. Measurements were done at (26 ± 2) °C with home-made multi-channel millivolt-meter connected to a computer for data acquisition. As reference electrode, commercially available Ag/AgCl/3 M KCl electrode (Metrohm) was used. Concentration changes during the measurement of calibration curves were provided by automatic diluting system purchased from Metrohm. 0.01 M $\mathrm{Ni(NO_3)_2}$ solution served as stock solution by the dilution. In order to suppress the influence of $\mathrm{O_2}$ on the potentiometric response [22] of mentioned electroactive polymers or copolymers, solutions were bubbled with inert gas ($\mathrm{N_2}$ or Ar). Selectivity coefficient was determined by separate solution method [23] where the activity coefficients were calculated according to extended Debye–Hückel method [24]. Solution of interfering ions was prepared from the corresponding nitrate ($\mathrm{Cd^{2+}}$, $\mathrm{Zn^{2+}}$), $\mathrm{O_2{}^{2-}}$ ($\mathrm{Mn^{2+}}$) and $\mathrm{Cl^-}$ ($\mathrm{Na^+}$) salts.

3. Results and discussion

3.1. Spectroelectrochemistry on poly(Cu-salen)

The variation of the metal-ion centres in polysalens was done in order to describe the poly(salen) redox processes in general for their potential application in electrochemical sensorics [9] and catalysis [25]. The study of poly(Cu(II)-salen) revealed similar FTIR and UV–vis features as in the case of poly(Ni(II)-salens) [26], but differences in the ESR behaviour. During the cyclovoltammetry, only a reversible quenching of broad ESR-line (Fig. 3) characterised by *g*-values, $g_\perp = 2.075$ and $g_\parallel = 2.127$ of the Cu(II)-centres during the cyclovoltammetric experiment was observed at room temperature as well as during the ex situ ESR-spectroelectrochemical experiment at 77 K. Quantitative analysis showed a decrease in the number of ESR-active centres from 9×10^{13} to 5×10^{12} and again increase to 8.5×10^{13}. Since the salen ligand cannot stabilise the Cu(III) state [27], the quenching of the broad ESR-line of poly(Cu(II)-salen) during the oxidation can be explained by the preferable formation of ESR silent species where an antiparallel spin-coupling between the unpaired electrons of the copper-ion and unpaired electrons on bisphenol moieties takes place as shown in Fig. 4. The copper ions are engaged in the chelate cycles, but the complete chelate cycles are not depicted for the simplicity in the

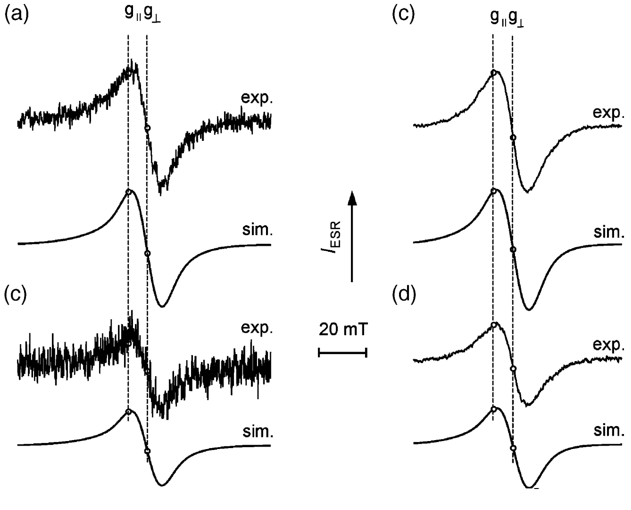

Fig. 3. Experimental (exp.) and simulated (sim.) ESR spectra of the reduced poly(Cu-salen): (a) accumulation of 10 ESR spectra and (b) the first ESR spectrum of the polymer taken at the beginning of the in situ spectroelectrochemical experiment (room temperature); (c) accumulation of 5 ESR spectra and (d) the first ESR spectrum of the polymer taken at the beginning of the ex situ spectroelectrochemical experiment (77 K).

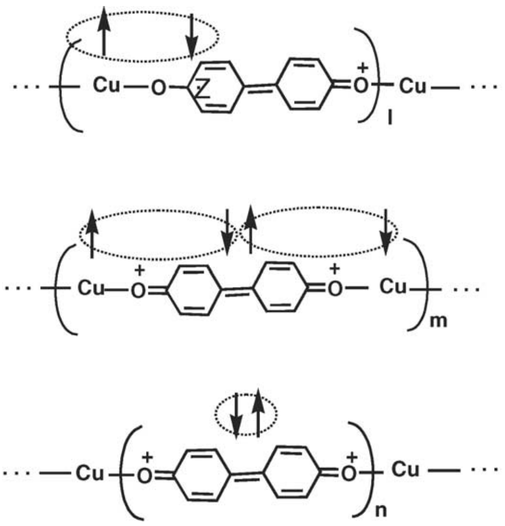

Fig. 4. Schematic diagram of the antiparallel spin–spin coupling in the polymer chain in the oxidised poly(Cu-salen). Indexes *l*, *m*, *n* represent the different number of polymer segments where the antiparallel spin–spin coupling takes place.

figure. FTIR–ATR measurements (here not shown) demonstrated that the $-CH_2-N{=}CH-$ moiety is not involved in the electrochemical charge-transfer process and therefore, Fig. 4 shows schematically the main chain of the polymer, where the charge-transfer process takes place.

3.2. Spectroelectrochemistry on the copolymer of 3-methylthiophene with 6-hydroxy-2-(2-(3-thienyl)-ethoxy)-acetophenone

The electrochemical synthesis of new thiophene-based conducting polymers with functional (receptor) groups for ion-recognition in the side chain of the polymer is often impossible because thiophenes substituted in 3-position particularly with larger functional groups can hinder the polymerisation sterically. For that reason, these monomers have to be electro-copolymerised using monomers with similar oxidation potentials as the functionalised monomer. We used 6-hydroxy-2-(2-(3-thienyl)-ethoxy)-acetophenone as a monomer with a functional group. Its electrochemical oxidation does not lead polymer film formation on electrode surfaces. Only oligomer formation was detected. As 3-methylthiophene has a similar oxidation potential like the functionalised monomer, electro-copolymerisation was successfully done. The copolymer formation was shown by MALDI–TOF mass spectrometry. The redox processes of this conducting copolymer were studied in detail by triple in situ ESR/UV–vis–NIR-cyclovoltammetry (Fig. 5) to get more details on the type of charge carriers like polarons, bipolarons or dimers. The analysis of paramagnetic and diamagnetic species formed during the electrochemical doping of polymer and copolymer gives new insights in the state of charged species. The changes in the number of paramag-

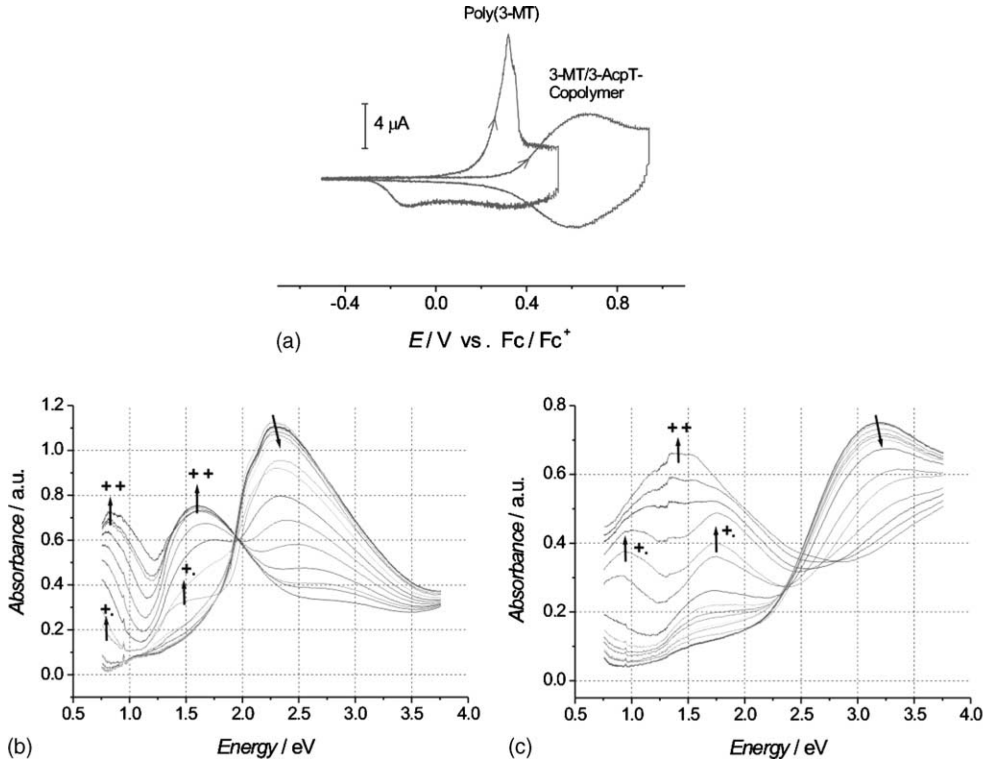

Fig. 5. ESR/UV–vis–NIR spectroelectrochemistry of poly(3-methylthiophene) and 3-MT/3-AcpT copolymer on ITO electrodes, UV–vis–NIR spectra recorded in 0.1 M $TBAPF_6$/CAN at 0.005 V/s: (a) cyclic voltammograms, (b) UV–vis–NIR spectra for poly(3-methylthiophene), and (c) UV–vis–NIR spectra for copolymer.

netic centres (Fig. 6) led us to conclude that the UV–vis–NIR absorption maxima of reduced (3.20 eV) and polaronic segments (1.76 eV and 0.92 eV) for copolymer are shifted to higher energies as compared to poly(3-methylthiophene) (reduced segment: 2.30 eV, polarons: 1.47 eV). The comparison is presented in Fig. 5. A dramatic increase of intensity in the range of 0.77–1.03 eV for poly(3-methylthiophene) in early stages of electrochemical doping is caused by a second polaronic absorption band with the maximum at lower energies. Comparing the changes in the number of polarons with the transferred charge, one can see more than 10-tuple difference. This points to a thermodynamically preferred formation of dicationic segments. It is characteristic for longer (>6 monomer units in the chain) extended conjugated π-systems including oligomers as well as polymers [11,28]. For short chain oligomers, it was shown that their mono-charged forms are stabilised by dimerisation [29,30]. Slight extension of π-conjugation (≈4–8 monomer units in chain) causes the formation of stable mono-charged structures which can be converted at higher doping levels into stable diions [29,31].

The electronic structure of oligomers with 6–12 monomer units in the chain can be described as a quasi-band structure and therefore, they were taken as model systems for the description of charge-carriers in conducting polymers [32]. Janssen and coworkers found that extension to about 10 monomer units in the oligomer chain causes a significant change in UV–vis–NIR spectra of dicationic segments: instead of one bipolaronic band, occurring between two polaronic ones, a two-band absorption appears with similar intensity of bands [11]. Based on quantum-chemical calculation, this absorption was explained by the formation of two interacting polarons in one chain. As a similar feature was observed (Fig. 5) in our case for poly(3-methylthiophene), the two absorption bands point to the formation of two polarons on a single chain in the singlet state [11,33]. Contrary to this, the copolymer forms bipolarons as shown by one broad absorption band between the two polaronic ones [11]. While the potential dependence of the number of polarons for poly(3-methylthiophene) is similar to that of other conducting polymers such as polyaniline [13] and polypyrrole [14], the potential dependence of polarons for copolymer differs substantially (Fig. 6). Maxima appear around switching potential as observed for lower molecular structures [34]. Taking into account the shift of the absorption maxima to lower en-

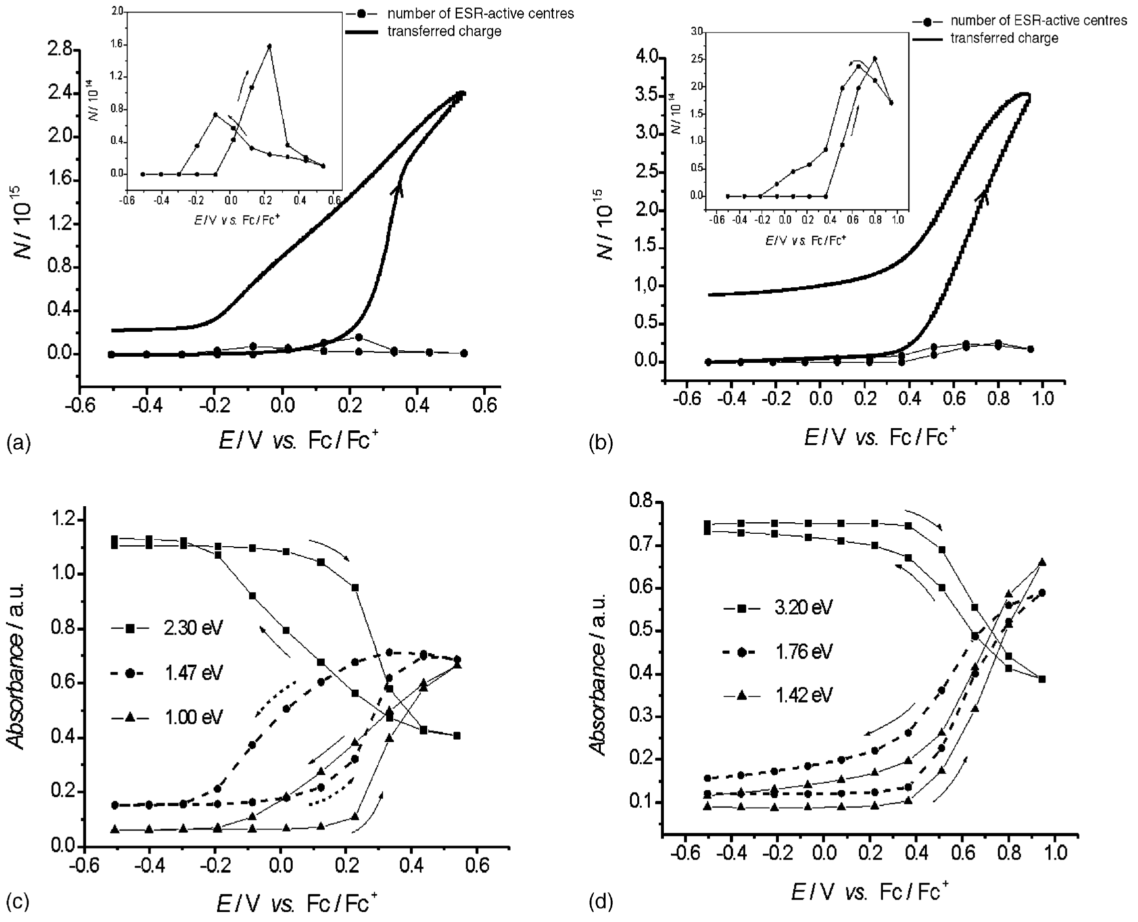

Fig. 6. Potential dependence of the paramagnetic centres and of transferred charge evaluated (a) for poly(3-MT) and (b) 3-MT/3-AcpT-copolymer, (c) potential dependence of absorption at certain energies (in eV) for poly(3-MT) and (d) potential dependence of absorption at certain energies for the copolymer (experimental conditions as in Fig. 5).

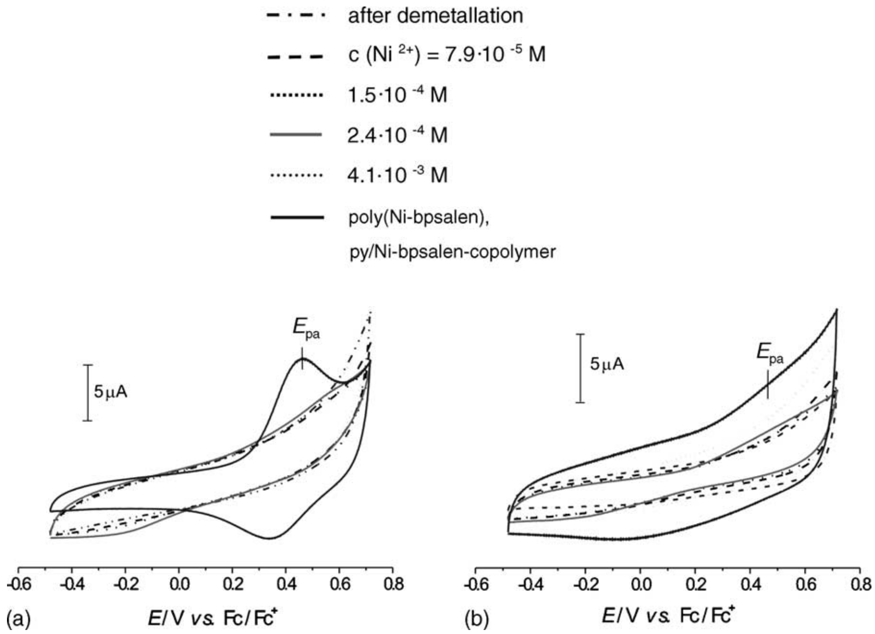

Fig. 7. Cyclic voltammetry of Ni^{2+}-remetallised (a) poly(Ni-bpsalen and (b) pyrrole/Ni-bpsalen-copolymer in 0.1 M $TBABF_4$/ACN for different Ni^{2+} concentrations (scan rate, 50 mV s^{-1}).

ergies compared with poly(3-methylthiophene), the different spectral responses can be explained by a shorter chain-length in the copolymer as in the case of poly(3-methylthiophene). This is probably caused by the fact that the copolymerisation was done with the small molar amount of 3-methylthiophene ($x_{3\text{-MT}} = 0.3$). It has been clearly demonstrated that here the copolymerisation changes in the case of thiophenes the electronic states of the polymer chain completely. This has to be taken into account for the application of functionalised polythiophenes.

3.3. Voltammetric detection of Ni^{2+}

Demetallisation of (Ni-bpsalen) results in an ionophor functionalised polymer (which is electrochemically inactive) in main chain which can be used for detection of divalent heavy-metal ions (such as Ni^{2+} and Cu^{2+}) [17]. It was shown that demetallised poly(Ni-bpsalen) remetallised with Ni^{2+} and Cu^{2+} exhibits the highest electroactivity among the other metal ions such as Co^{2+}, Mn^{2+}, Zn^{2+} (80–90% of electroactivity of the original poly(Ni-bpsalen)) [17]. This is possible only with a higher concentration of heavy-metal ions, owing to the rigid structure of the salen polymer. As salen polymers are not sufficiently conductive in their oxidised state for electrochemical sensor applications [16], we copolymerised the Ni-bpsalen with pyrrole to diminish the rigidity and also to enhance the conductivity of the polymeric structure. Both the polymer and copolymer were at first demetallised and afterwards immersed into the solutions with increasing concentration of nickel ions. As shown in Fig. 7, with increasing concentration of nickel ions, the polymer remains electrochemically inactive, while the copolymer shows an increase of voltammetric current around the oxidation potentials of pyrrole and salen oligomeric centres even at lower concentrations (≈0.0001 M). It indicates that the copolymer as a sensitive layer has enhanced the sensoric response.

3.4. Potentiometric detection of Ni^{2+}

The functionalised poly(Ni-bpsalen) was directly applied onto an electrode substrate as a selective membrane without any additional ion-selective membrane. Since the ISE are conditioned prior to measurement, the sensitive polymer layer should also be conditioned. This pre-treatment means for polysalen electrodes demetallisation in order to get polyligand structure for detection and the remetallisation as for conditioning. Therefore, to make the pre-treatment easier, we have directly applied the poly(Ni-bpsalen). Fig. 8 shows the potentiometric responses of the salen polymer in $Ni(NO_3)_2$ solution. As can be seen, the electrode exhibits a slight anionic response, due to the incorporation of small counter ions, which compensate the positive charge on the polymer and copolymer chain [21]. The application of sodium dodecylsulfate adsorbed on the membrane surface [35] enhances the cationic response against nickel ions. Although the response (slope from linear regression: 12 ± 1 mV/log a (Ni^{2+}) for polysalen) deviates from the ideal behaviour as electroactive polymers exhibit always a mixed potentiometric cation–anionic response [4,36], the response can be enhanced by adding the ionic additives which block the counter ion exchange. It was shown by Bobacka et al. that the total polymerisation charge in the electrochemical synthesis of conducting polymer membranes can influence the potentiometric slope. The higher the polymerisation

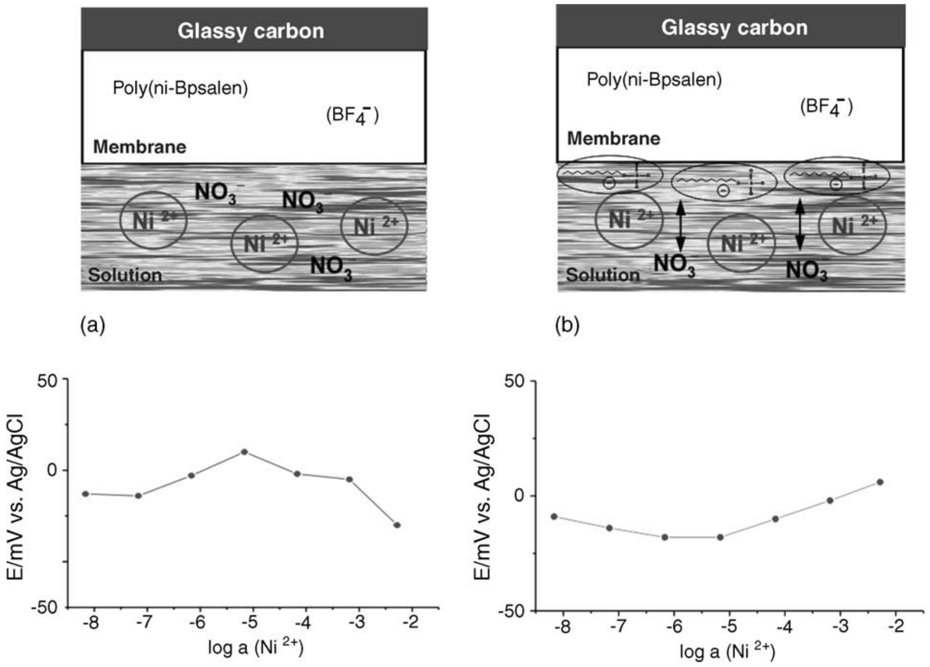

Fig. 8. Schematic diagrams of the ion-selective electrodes with the experimental potentiometric response for poly(Ni-bpsalen) taken in $Ni(NO_3)_2$ solution (a) in the absence or (b) with 0.01 M natrium-1-dodecansulfonate as back electrolyte.

charge, the higher is the slope of potentiometric response [4,21,37]. This is valid only up to a certain polymerisation charge (thickness) for which the maximal slope is reached. On further increasing of the polymerisation charge, the slope remains constant [37]. In our case, the polymerisation charge for the poly(Ni-bpsalen)-membrane synthesis was only ≈2 mC and therefore, the lower value of the potentiometric slope could also be caused by the small polymerisation charge. This effect should be the subject of further investigation. Similarly to the sub-Nerstian response of polypyrrole/Cl^- membrane [36], the selectivity coefficient in our case was also calculated for the brief overview by separate solution method. A substantial improvement was found for the new electrode, poly(Ni-bpsalen): $\log K(Ni^{2+}, Cd^{2+}) = -1.10$; $\log K(Ni^{2+}, Mn^{2+}) = -0.54$; $\log K(Ni^{2+}, Zn^{2+}) = -1.52$; $\log K(Ni^{2+}, Na^{+}) = -0.10$ in comparison to the electrode with an ion-selective membrane where the Ni-bpsalen monomer was used as ionophore: $\log K(Ni^{2+}, Cd^{2+}) = -0.22$; $\log K(Ni^{2+}, Mn^{2+}) = 0.49$; $\log K(Ni^{2+}, Zn^{2+}) = -0.07$; $\log K(Ni^{2+}, Na^{+}) = 2.34$. These results showed that poly(Ni-bpsalen) can be applied as selective membrane for the potentiometric detection of Ni^{2+} ions even without conditioning.

4. Conclusions

In the case of poly(Cu-salen), it was shown that the quenching of the intensity of ESR signal is caused by the antiparallel spin-coupling of unpaired electrons on copper ion and unpaired electrons on the ligand moieties. The triple ESR/UV–vis–NIR spectroelectrochemical analysis of redox processes of poly(3-methylthiophene) and its copolymer with acetophenone functionalised thiophene-monomer points to the different nature of dicationic diamagnetic structures: bipolaronic and two polarons on single chain in singlet state, respectively. It was shown that voltammetric and potentiometric detection of nickel ions by applying only the copolymer or polymer electrodes without any additional membranes is possible. The important result was the observation of the improvement of sensor responses; however, this area should be the subject of further detailed studies. The electrochemical polymerisation and copolymerisation onto electrode surfaces show a very convenient and easy way how to prepare such electrodes, which can be directly applied in electrochemical sensorics.

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