

Electrochemical and spectroscopic properties of poly-4,4'-dialkoxy-2,2'-bipyrroles

Gabriela Broncová · Sergey Anikin · Ulrich Lange · Pavel Matějka · Martin Krondak · Vladimír Král · Vladimír M. Mirsky

Received: 6 January 2009 / Revised: 23 July 2009 / Accepted: 29 July 2009 / Published online: 19 August 2009
© Springer-Verlag 2009

Abstract The structure and the electrochemical and spectral properties of two conductive electrochemically polymerized substituted bipyrroles 4,4'-methoxy-2,2'-bipyrrole and 4,4'-butoxy-2,2'-bipyrrole were studied and compared. The polymers were characterized by cyclic voltammetry, FT-Raman spectroscopy, scanning electron microscopy, and in situ conductivity measurements at different pH and redox state.

Keywords Conducting polymer · Polydialkoxybipyrroles · Raman spectroscopy · Cyclic voltammetry · Conductivity

Introduction

Conducting polymers, such as polypyrrole, polyaniline, and polythiophene, are multifunctional materials, which are

used in numerous applications in different branches of science [1–6]. Their multifunctional properties can be controlled by the substitution of the monomer molecule. One of the polymers most commonly used in conductivity sensors is polypyrrole due to its simple polymerization, stability, and good electrical conductivity. Polypyrrole exhibits a wide range of conductivity, which depends on the preparation conditions (monomer concentration, doping anions used, solvent, etc. [2, 7]) and, most importantly, on substitutions on the monomer [8, 9]. Polypyrrole conductivity can be altered by the selection of an appropriate substituent moiety, e.g., a film of poly(3,4-dimethoxypyrrole) prepared by electrochemical polymerization is more conductive than an unsubstituted polypyrrole [10]. Additionally, substitution of the monomer allows one to tune the pH and potential dependence of polypyrrole's conductivity.

The resistance of electrode–polymer systems can be measured using a 2-point technique. In this case, the measured resistance includes the resistance of the film and of the contacts [11, 12]. In contrast, a 4-point technique allows one to determine the bulk resistance of the polymer [7, 11, 13]. To obtain information about the contacts, the consecutive application of 2- and 4-point techniques was published by Partridge et al. [13]. Mirsky et al. suggested simultaneous measurement of two- and four-point resistances [4], which was then further developed in [14].

The increasing number of conducting polymer applications is accelerating the search for new polymers, which can be directly deposited on the required surface and show similar or even better properties than the most commonly used polypyrrole. In this paper, we report the electrochemical [cyclic voltammetry (CV) and 4-point conductivity technique] and spectroscopic [FT-Raman spectroscopy and scanning electron microscopy (SEM)] characterization of two polymers prepared from 4,4'-methoxy-2,2'-bipyrrole and

G. Broncová (✉) · P. Matějka · M. Krondak · V. Král
Department of Analytical Chemistry,
Institute of Chemical Technology Prague,
Technická 5,
166 28 Prague, Czech Republic
e-mail: Gabriela.Broncova@vscht.cz

S. Anikin
Institute of Organic Chemistry, University of Regensburg,
93040 Regensburg, Germany

U. Lange · V. M. Mirsky
Institute of Analytical Chemistry, Chemo- and Biosensors,
University of Regensburg,
93040 Regensburg, Germany

V. M. Mirsky
BCV-Nanobiotechnology Department,
Lausitz University of Applied Sciences,
01968 Seiftenberg, Germany

4,4'-buthoxy-2,2'-bipyrrole. The chemical synthesis of these substituted bipyrroles was described by Merz et al. [15]. We described earlier the first applications of these polymers [5].

Experimental

Materials and methods

Both 4,4'-methoxy-2,2'-bipyrrole (MBPyr) and 4,4'-buthoxy-2,2'-bipyrrole (BBPyr) were synthesized using a previously described procedure [15]. Bu_4NPF_6 (electrochemical grade) was obtained from Fluka. Acetonitrile (HPLC quality) and the rest of the standard chemicals [CH_3COOH (glacial), NaCl , NaOH , HCl , Na_2HPO_4 , TRIS; all analytical grade] were purchased from Merck. All solutions were prepared with Millipore water.

The gold and platinum electrodes on silicon supports were provided by R. Bosch GmbH (Germany). Electropolymerization of the dialkoxybipyrroles was performed with a potentiostat/galvanostat Autolab PGSTAT-12 (Eco-Chemie, The Netherlands). A three-electrode cell consisted of a Pt or Au working electrode, an Ag wire reference electrode, and a Pt wire as the counter electrode. The polymer films were prepared by cyclic voltammetry between -1.1 and 0.8 V at a scan rate of 100 mV/s. All films were prepared in acetonitrile solution containing 0.1 M Bu_4NPF_6 and 1% Millipore water. All films were prepared under an argon atmosphere.

The structure of the bipyrrole films was studied with a JSM 6400 scanning electron microscope (JEOL, Japan). FT-Raman spectra were obtained using an Equinox 55/S Fourier-transform near-infrared spectrometer equipped with an FRA 106/S FT-Raman module (Bruker, Germany) and

$1,064$ nm Nd-YAG laser (Coherent, USA). The laser power exerted for excitation was 50 mW. One thousand twenty-four interferograms were accumulated to obtain a single spectrum with 2 cm^{-1} resolution.

Conductivity measurements were performed with an electrometer unit (Keithley 617) and a source monitor unit (Keithley 2400) against a saturated Ag/AgCl reference electrode. A detailed description of the apparatus and the conductivity measurement principle has been described in [4, 5].

All solutions (acetate, phosphate, and TRIS) for conductivity and CV measurements were prepared from the appropriate 5 -mmol/L concentrated salts and 100 -mmol/L NaCl . pH values were measured with a WTW 526/538 pH Meter (WTW, Germany).

Results and discussion

Electropolymerization of dialkoxybipyrroles by cyclic voltammetry

Preparation of the poly(4,4'-dimethoxy-2,2'-bipyrrole), abbreviated as poly(MBPyr), was described previously by [15], whereas the preparation of the electropolymer from 4,4'-dibutoxy-2,2'-bipyrrole (poly(BBPyr)) is presented by authors in [5]. The polymerization conditions for this derivative were investigated, and it was found that a solution of 0.1 M Bu_4NPF_6 in acetonitrile gave the best results. Films were prepared on a gold and/or platinum interdigitated pattern on a silicon support (abbreviated as Au–Si or Pt–Si electrodes). The method used was cyclic voltammetry between -1.1 and 0.8 V vs. an Ag wire (Fig. 1).

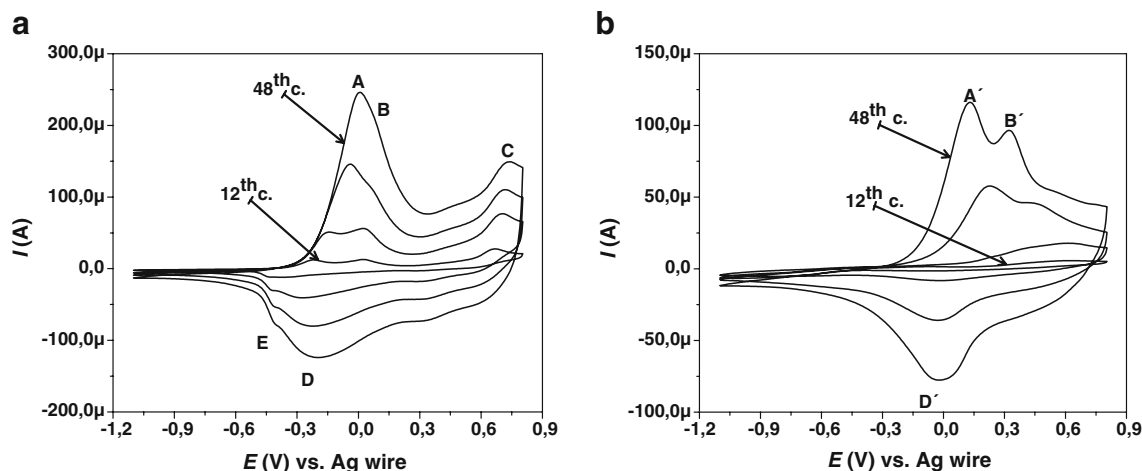


Fig. 1 Cyclic voltammograms of electropolymerization of 0.002 mol/L dialkoxybipyrrole at Au–Si electrodes at 100 mV/s during 50 cycles from acetonitrile with 0.1 mol/L Bu_4NPF_6 as supporting electrolyte and 1%

water content over a potential range from -1.1 to 0.8 V: **a** poly(MBPyr) and **b** poly(BBPyr)

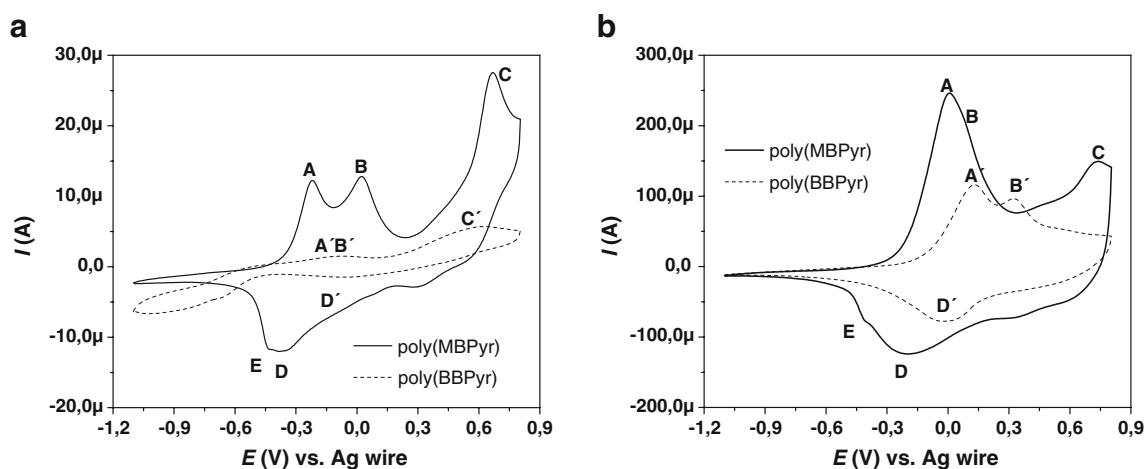


Fig. 2 Comparison of cyclic voltammograms of polymerization of dialkoxybipyrrole layers in 12th cycle (a) and 48th cycle (b) of preparation

Polymerization was performed in the presence of a small amount of water (1%), which accelerates the polymerization process and improves the mechanical properties of the film [16]. The polymer surface was observed to grow rapidly during each cycle. The reason for the high reactivity is the high-spin density at the outer α position of the bipyrrole system.

Three separated peaks A, B, and C were observed in the anodic area of the voltammogram at potentials -220 , 20 , and 670 mV for poly(MBPyr) in the first cycles (Fig. 2a), whereas, in last cycles, peaks A and B are merged (Fig. 2b). In contrast, peaks A' and B' in the voltammogram of poly(BBPyr) were merged for the first cycles (Fig. 2a) but well separated in the last cycles (Fig. 2b).

Potentiodynamic conditions used during the preparation of polypyrrole influence the shape of cyclic voltammogram. The number of oxidation waves depends on both applied potential and choice of supporting electrolyte. The two peaks in Fig. 2 are referred in literature [16]. The different pyrrole structure results from different chain lengths of the oligomers formed during polymerization process. This was reported by Heinze et al. for the polymerization of unsubstituted pyrrole in acetonitrile containing various amounts of acid [16, 17]. The structure of PPy is very complex, and many structural forms and/or intermediates can be observed. Additional oxidation wave belongs to still unknown structural form of polypyrrole [16]. For poly

(MBPyr, the form with the higher oxidation potential dominates in the later cycles, whereas for poly(BBPyr), one form dominates at the beginning of polymerization, and, during later cycles, both peaks are present and shifted to higher potential. The same oxidation peaks were also reported for alkylated PPy [18].

The shapes of the cathodic parts of the records are also different for the first polymerization cycles. Two peaks (D, E) were observed at potentials -370 and -430 mV for poly(MBPyr), and only one broad peak D' was observed for the butoxy derivative (Fig. 2a). The cathodic part of the voltammograms did not change during polymerization; only peak D changed its maxima from -370 to -200 mV for poly(MBPyr). The values of potentials for the peaks mentioned are summarized in Table 1 for the 12th and 48th cycles.

In comparison with poly(MBPyr), the potentials of the redox peaks of poly(BBPyr) are shifted towards more positive values. Furthermore, the current was significantly lower for poly(BBPyr) during the initial cycles of polymerization (Fig. 2). A faster increase in the peak area for poly(BBPyr) starts after the 20th cycle, but the peak height did not reach the value for poly(MBPyr). It is clear that the length of the substituent affects the polymerization process [19].

Additionally, the influence of a protective argon atmosphere on the polymerization of poly(MBPyr) was tested.

Table 1 The values of peak potentials in 12th and 48th cycle of dialkoxybipyrrole polymerization

		poly(MBPyr)					poly(BBPyr)			
12th cycle	Peak	A	B	C	D	E	A'B'	C'	D'	
	Potential (mV)	-220	20	670	-370	-430	-75	620	-65	
48th cycle	Peak	A	B	C	D	E	A'	B'	C'	D'
	Potential (mV)	0	75	730	-200	-410	130	325	^a	-10

^a The peak was not observed

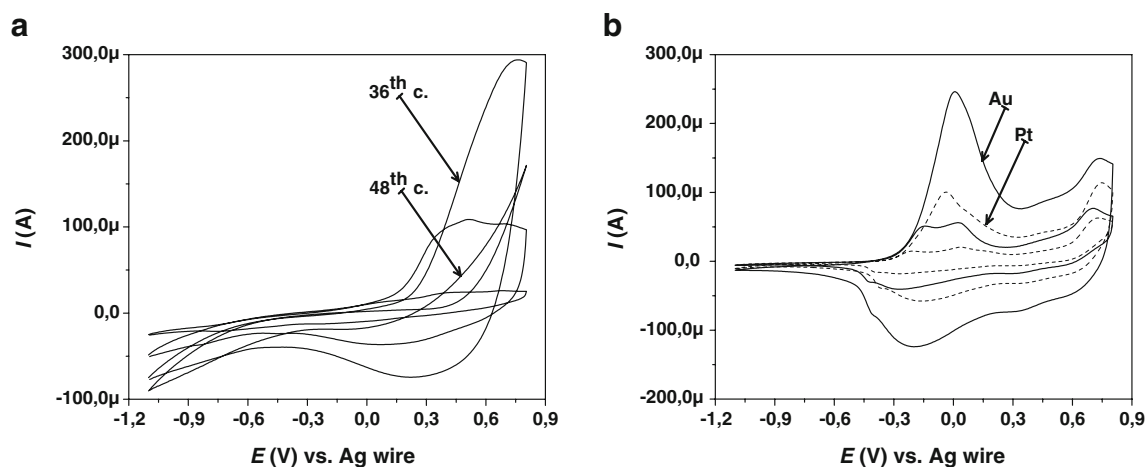


Fig. 3 Comparison of polymerization of poly(MBPyr) on Au–Si and Pt–Si electrodes under air (a) and argon atmosphere (b)

The polymerization in the presence of air was slower, and the current significantly decreased during the final cycles (Fig. 3a). All subsequent experiments were performed with electrodes prepared under argon because the polymers prepared in the presence of oxygen exhibited no electrochemical activity and were not electrically conductive. Polymerization on the gold and platinum surfaces was similar (Fig. 3b); only the peak current was higher for the polymerization on the gold than on platinum. The supporting electrode material is one of the factors which affect polymerization.

The characterization of poly(dialkoxybipyrrole) layers by FT-Raman spectroscopy and scanning electron microscopy

FT-Raman spectroscopy

Polymers prepared by cyclic voltammetry [unsubstituted polypyrrole, poly(MBPyr), and poly(BBPyr)] on Au–Si and Pt–Si supports were characterized using Raman spectroscopy. Unsubstituted polypyrrole deposited on the Au–Si substrate (Fig. 4a) provides a spectrum similar to the spectra described in the literature [20–22].

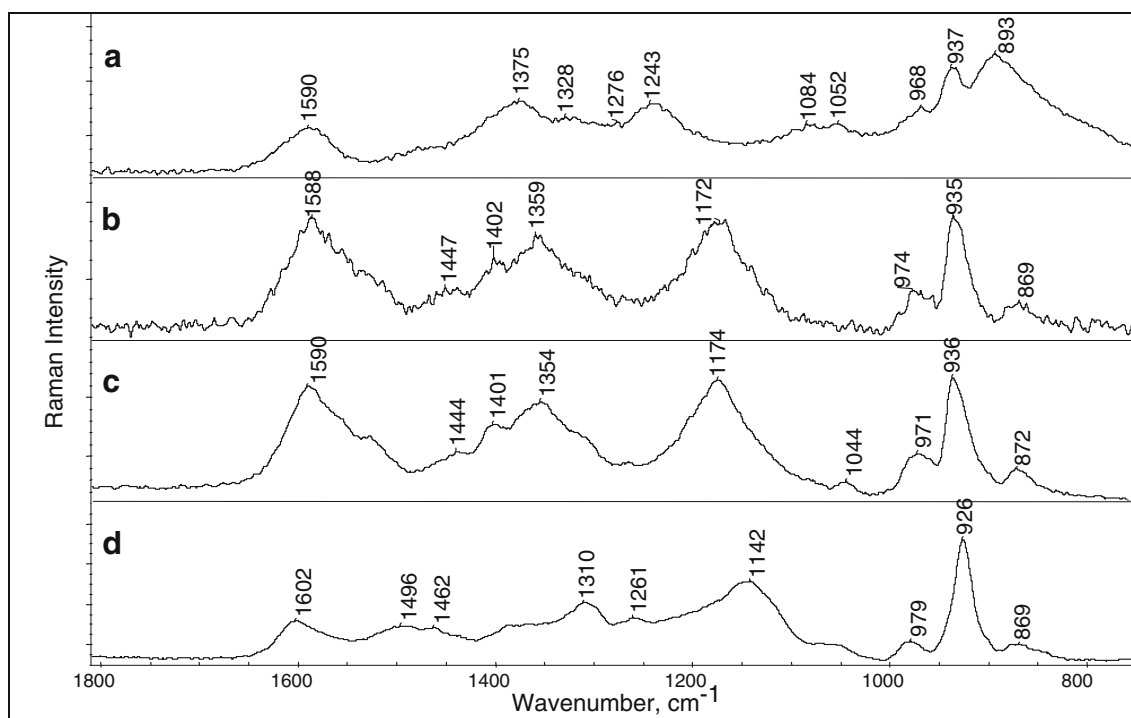


Fig. 4 FT-Raman spectra of polymer layers prepared by CV in acetonitrile with 0.1 mol/L Bu_4NPF_6 and 1% water on Au–Si or Pt–Si supports: a polypyrrole on Au–Si, b poly(MBPyr) on Pt–Si, c poly(MBPyr) on Au–Si, and (d) poly(BBPyr) on Au–Si

Corresponding bands were observed in the spectra of all the polymers [polypyrrole (Fig. 4a), poly(MBPyr; Fig. 4c), and poly(BBPyr; Fig. 4d)]. These bands were in the ranges 1,605 to 1,585, 980 to 965, and 940 to 925 cm^{-1} [20–22]. The band between 1,605 and 1,585 cm^{-1} is assigned to the valence vibration of the ring with a significant contribution from the vibrations of double bonds (C=C). The wave number of this band is dependent on the dopant and solvent used in the polymerization of the film [20]. For polypyrrole and poly(MBPyr), its maximum is at 1,590 cm^{-1} ; for poly(BBPyr), the band is shifted 12 cm^{-1} higher, i.e., to 1,602 cm^{-1} . The bands at 968 cm^{-1} for polypyrrole, 971 cm^{-1} for poly(MBPyr), and 979 cm^{-1} for poly(BBPyr) are assigned to a deformation vibration of the ring. The third most intensive band in all three spectra is probably related to a deformational mode of the pyrrole ring [21, 23], although Liu et al. [20] assign this band to the vibration of the doping anion (ClO_4^-).

Other parts of the spectra differed according to the measured polymer. Valence ring vibrations with a major contribution from single C–C bonds are displayed as a band at 1,375 cm^{-1} for polypyrrole. For alkoxybipyrroles, this band was shifted down to 1,354 cm^{-1} for the methoxy and to 1,310 cm^{-1} for the butoxy derivatives. A new band,

assigned to a C–O bond, occurred at poly(MBPyr) spectra at 1,174 cm^{-1} . The same band in butoxy derivative spectra was shifted by 32 to 1,142 cm^{-1} . The new broad band between 1,450 and 1,550 cm^{-1} in poly(BBPyr) spectra is merged from two single bands at 1,496 and 1,462 cm^{-1} , which are assigned to vibrations of the ring and polymeric chain. The second is significantly affected by pyrrole ring substituents, and the same vibration occurs at 1,444 cm^{-1} with poly(MBPyr). Aside from ring vibration, this band is also the result of the vibration of $-\text{O}-\text{CH}_2-$ or $-\text{O}-\text{CH}_3$ groups.

Spectra measured on both Au–Si (Fig. 4c) and Pt–Si (Fig. 4b) surfaces correspond to each other in terms of the wave numbers of the bands ($\pm 1-3 \text{ cm}^{-1}$) and relative intensity of bands. The higher overall intensity of the peaks for the gold surface is a result of surface-enhanced Raman scattering and also results in a better signal-to-noise ratio.

Scanning electron microscopy

The surface morphology of the two poly(dialkoxybipyrroles) films was investigated by SEM. The surface of both polymers differs and depends on the bipyrrole molecule substituents (Fig. 5). Poly(MBPyr) exhibits a finer and more regular structure (Fig. 5a, b). This polymer compactly

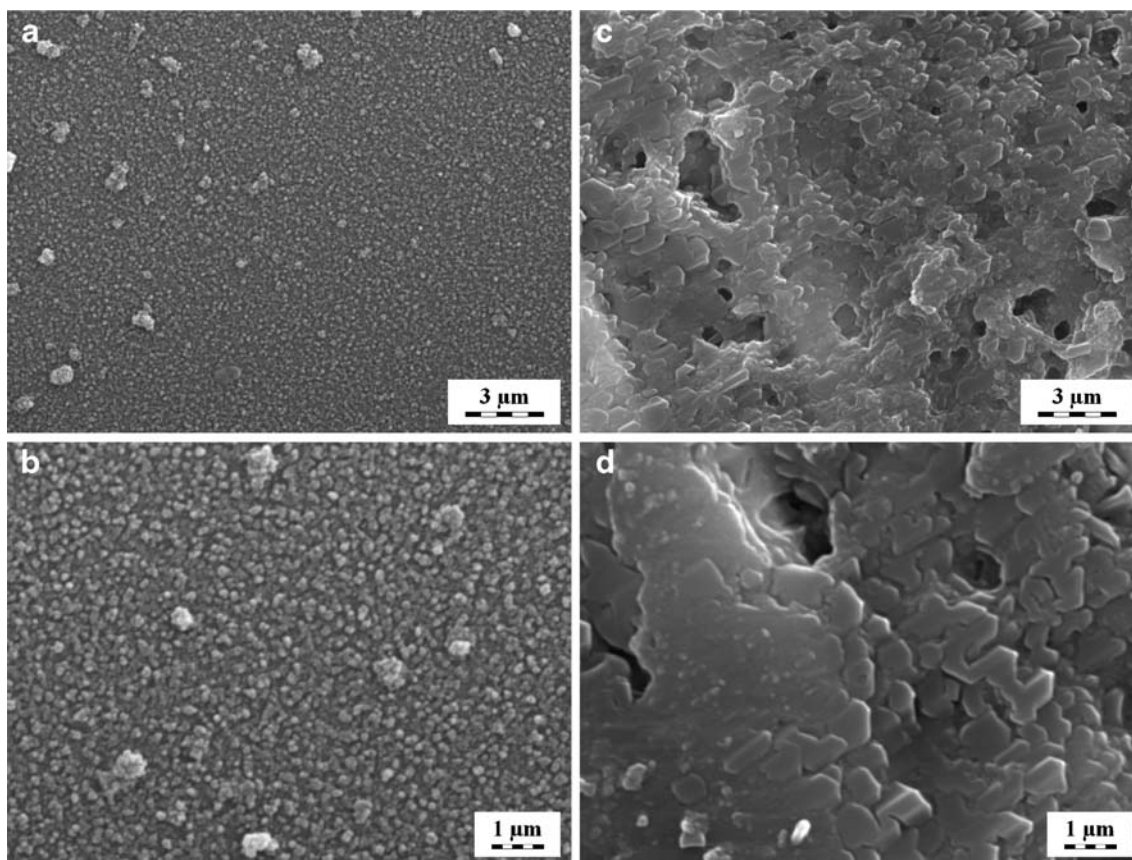


Fig. 5 SEM micrographs of poly(dialkoxybipyrroles): **a, b** poly(MBPyr) and **c, d** poly(BBPyr)

covers the surface, and lateral polymerization was more intensive than for poly(BBPy). In contrast, the polymer of poly(BBPy) grows more intensively in vertical direction resulting in a bulky structure (Fig. 5c, d).

Characterization of poly(dialkoxybipyrrole) layers prepared on gold silicon electrodes by cyclic voltammetry

Poly(dialkoxybipyrrole) films prepared on the Au–Si support were characterized by cyclic voltammetry in the potential range -0.6 to 0.8 V (against an Ag/AgCl electrode). The Pt–Si support limits the potential range to -0.2 to 0.8 V in acidic solutions because of the low charge transfer overpotential of hydrogen on the platinum. Therefore, only the gold electrodes were used for the cyclic voltammetry characterization. The electrochemical activity of both polymers was examined in aqueous solutions with pH 2, 4, 5, and 7 (Fig. 6a, b). Both poly(dialkoxybipyrroles) show a higher electrochemical activity in acidic solution (pH 2). An increase in pH resulted in a decrease in the current of the redox peaks and thus, to a decrease in the electrochemical activity of the films.

Poly(MBPy) not only shows electrochemical activity at pH 2 but also provides a similar response at pH 4. The potentials of the redox peaks are shifted towards more negative values for less acidic solutions. The current is reduced at pH 5, but the peaks are still noticeable, and at pH 7, the films show almost no electrochemical activity (Fig. 6a). The butoxy derivative loses its electrochemical activity faster with increasing pH: the redox peaks already disappear at pH 4 (Fig. 6b). Figure 6c demonstrates the higher redox activity of the methoxy derivative film compared with that of the butoxy derivative.

Influence of pH and electrode potential on the conductivity of poly(dialkoxybipyrrole) layers and measurement of conductivity of poly(dialkoxybipyrroles) by 4-point technique

The dependence of polymer conductivity on pH

The simultaneous 2- and 4-point technique was used to measure pH influence on conductivity of both polydialkoxybipyrroles and unsubstituted polypyrrole. The measurements were performed at a potential of 0.0 V against a saturated Ag/AgCl electrode at pH from 2 to 10. The same buffers as for voltammetric measurement were used (acetate buffer for pH from 2 to 4, phosphate buffer for pH range from 5 to 7, and TRIS for pH range between 8 and 10). Measurement started at low pH. For all three polymers, an increase of pH led to decrease of their conductivity (Fig. 7).

There are two plateaus on the conductivity plot versus pH for poly(MBPy); Fig. 7a). The first is in the acidic range

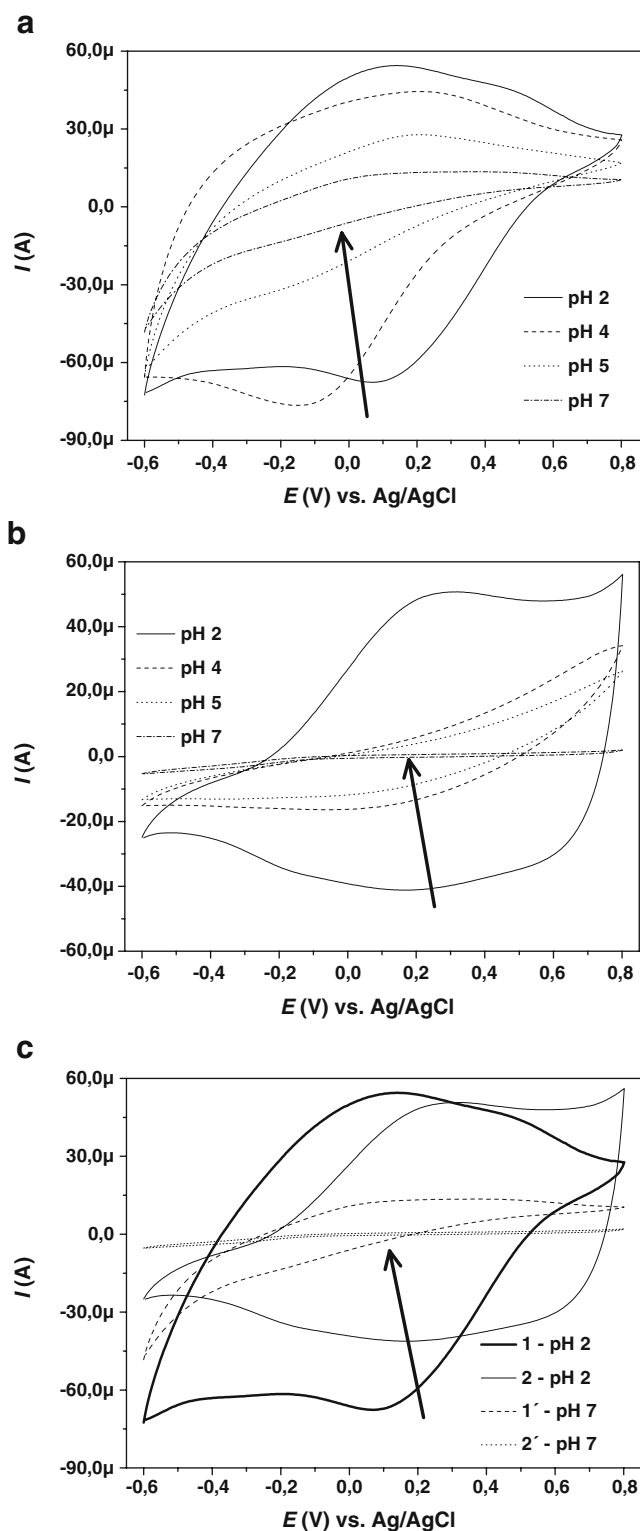


Fig. 6 Characterization of polymers by cyclic voltammetry with scan rate 100 mV/s in aqueous solution at pH 2, 4, 5, and 7: **a** poly (MBPy), **b** poly(BBPy), and **c** comparison of the behavior of poly (dialkoxybipyrroles) at pH 2 and 7. Arrows denote the increase in pH together with a decrease in the electrochemical activity

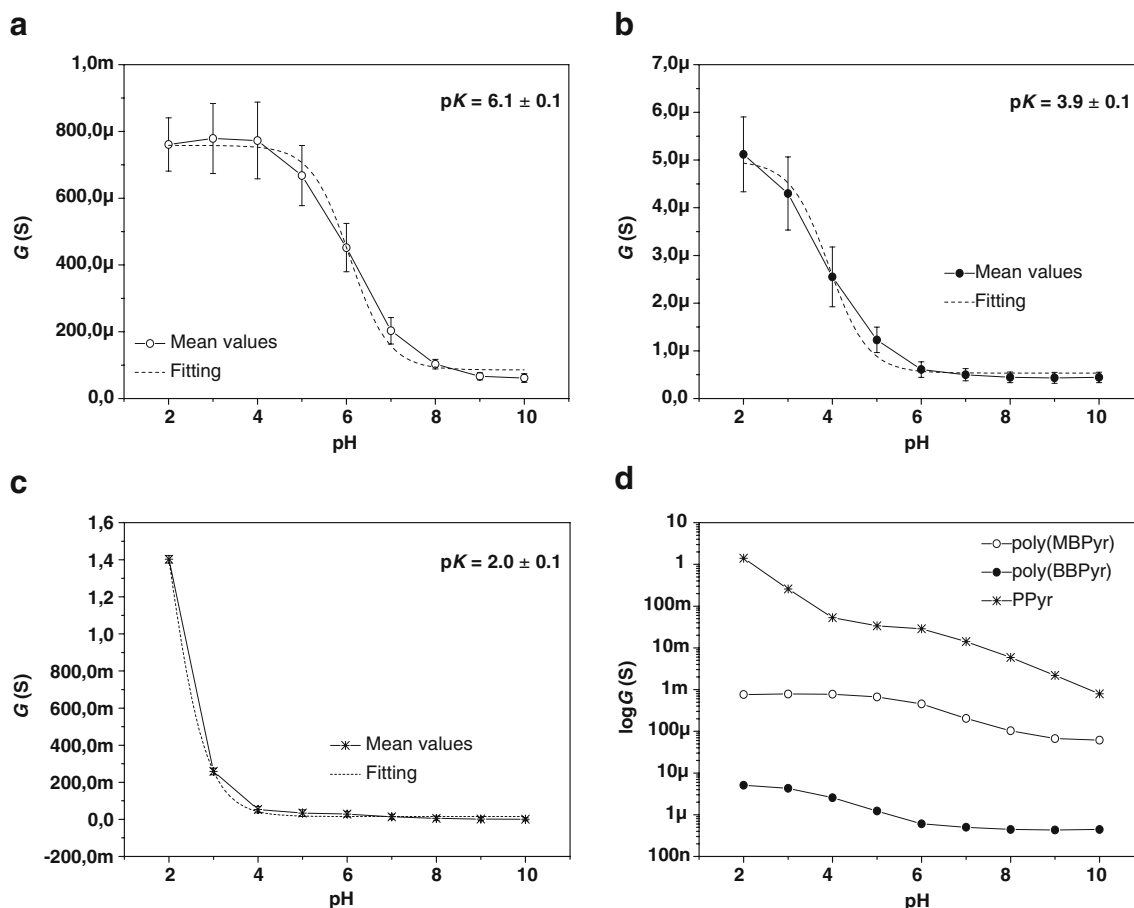


Fig. 7 Dependencies of polymer conductivity on pH with error abscissas of repeated measurement for five electrodes and regress fitting (dashed line) with calculated pK for: **a** poly(MBPyr), **b** poly

(BBPyr), and **c** polypyrrole. For comparison, conductivity/pH plots of all three polymers were also constructed with a logarithmic y axis (**d**)

between pH 2 and 4, and the second is in the basic range of pH 8 to 10. The polymer is most conductive in acidic pH with conductivity between 750 and $780 \mu\text{S}$. This value is nearly ten times higher than the conductivity of a deprotonated film under basic conditions, which was between 60 and $100 \mu\text{S}$.

Poly(BBPyr) (Fig. 7b) is also most conductive at pH 2, but its conductivity falls steeply with increasing pH, and the second long plateau of the deprotonated film is shifted to lower pHs. An origin of the first plateau observed with poly (MBPyr) is not perfectly clear. It could result either from the neutral form of the pyrrole nitrogen (NH) or from its protonated form (NH₂⁺). Poly(BBPyr) is completely deprotonated at pH > 6. At 0 V, the deprotonated poly (BBPyr) film is poorly conductive with a conductivity of $0.5 \mu\text{S}$. Polypyrrole shows a long plateau in the pH from 4. At lower pH, it is probably protonated with excess of mobile charge carriers [2, 24], which enhances its conductivity, whereas, at pH > 6, a complete deprotonation of the nitrogen occurs (Fig. 7c, d). This simultaneous 2- and 4-point technique measures a total conductivity and does

not distinguish between electron and ion conductivity. The protonation of polypyrrole occurs in acid medium, and if there are enough of intercalated dopant ions in polymer framework, then conductivity of polypyrrole can increase [2, 24]. As a result, the amount of doping anion included in polymeric matrix and acidity of solution control polymer matrix protonation [24].

As expected, the protonated form of both dialkoxy-pyrroles is more conductive than the deprotonated one. Teh et al. [25] reported that the higher conductivity at low pH is caused by an increase in p -doping of the polymer. Moreover, when the nitrogen atom in the pyrrole ring binds a hydrogen cation, then its positive charge is then delocalized across the aromatic system, which results in a conductivity change [26]. The increased positive charge is compensated by higher amount of counter ions, which then participate on increase of ionic conductivity [24]. The results from conductivity measurements are in good agreement with previous results from cyclic voltammetry because both polymers are most electrochemically active and most conductive at pH 2. The methoxy derivative has

the same activity and conductivity at pH 4 in contrast to the butoxy derivative, which has a significantly reduced electrochemical activity and conductivity at pH 4.

At 0 V, the conductivity of the methoxy derivative is about two orders of magnitude higher than that of the butoxy derivative and about three orders of magnitude lower than polypyrrole (at pH 2). The reason for this is the different oxidation state of the polymers at 0 V. Furthermore, the decrease in the charge transfer rate caused by the longer alkyl chain results in the significant decrease of conductivity of poly(BBPyr). A similar behavior was observed by Masuda et al. [27], who tested poly(3-methylpyrrole) and poly(3-octylpyrrole) and proved that the conductivity of the polymer decreases with elongation of the substituent. The logarithm of the dissociation constant of poly(MBPyr) is 6.1. Therefore, this film stays protonated up to a higher pH than poly(BBPyr), which has a pK of 3.9. Polypyrrole's first pK is 2.0, whereas the second pK is around 9. The values of the pK of the polymeric film were calculated from the dependence of their conductivity on pH. This plot was then fitted with the sigmoid function (1):

$$G = \left(G^{\max} + G^{\min} \cdot \left(10^{(pH-pK_a)} \right) \right) / \left(10^{(pH-pK_a)} + 1 \right) \quad (1)$$

In this equation, G^{\max} is the maximum value of the polymer conductivity measured at the lowest pH (in this case, pH 2), whereas G^{\min} is the minimal conductivity of polymer measured at the highest pH (in this case, pH 10).

The chosen function sufficiently fits the measured data (Fig. 7a–c). Small differences between measured data and model values could be due to other minor factors affecting conductivity (e.g., surface electrostatic forces). Furthermore, the pH seems to influence the redox behavior and, therefore, the oxidation state of the polymers (compare CV data and Fig. 7). The influence of these factors was neglected in this simple model.

The comparison of the conductivities of the polymers prepared on the Pt–Si and Au–Si supports showed that the conductivity of the film on the gold electrode was slightly higher than the films prepared on the platinum, as was expected from polymerization data.

The repeated response of poly(dialkoxybipyrroles) toward pH change was tested by subsequent measurement in solutions with pH 4, 5, and 6. The conductivity decreases during the cycling of pH (Fig. 8). For Poly(MBPyr), this decrease is low and most significant at pH 6, in contrast to poly(BBPyr) for which the decrease is much higher and more obvious at pH 4. A probable explanation is the higher stability of poly(MBPyr) compared with poly(BBPyr). A similar trend was observed for alkyl-substituted polypyrrole [27].

Conductivity dependencies of poly(dialkoxybipyrroles) on applied potential

An electrical conductivity of conducting polymers depends not only on their protonation but also on redox state, which can be changed by variation of electrode potential. Therefore, the influence of electrode potential at different pH was studied. The conductivity was first measured at 0.0 V against saturated silver/silver chloride electrode, following a potential change from -0.6 V to $+0.6$ V in steps of 0.1 V in acetate buffer with pH 2. Figure 9a demonstrates that the conductivity of the methoxy derivative film is reduced tenfold (from 840 to 70 μ S) after the first change in potential from 0 to -0.6 V. This change was not so strong for the butoxy derivative, but the conductivity changed by about 30% from 6 to 4 μ S.

The following increase in applied potential results in a conductivity increase. The conductivity maximum of 431 μ S was observed at $+0.3$ V; the next increase in potential led to a sharp decrease in conductivity. This maximum with a conductivity of 307 μ S was shifted to $+0.5$ V for poly(BBPyr). Surprisingly, the conductivity of

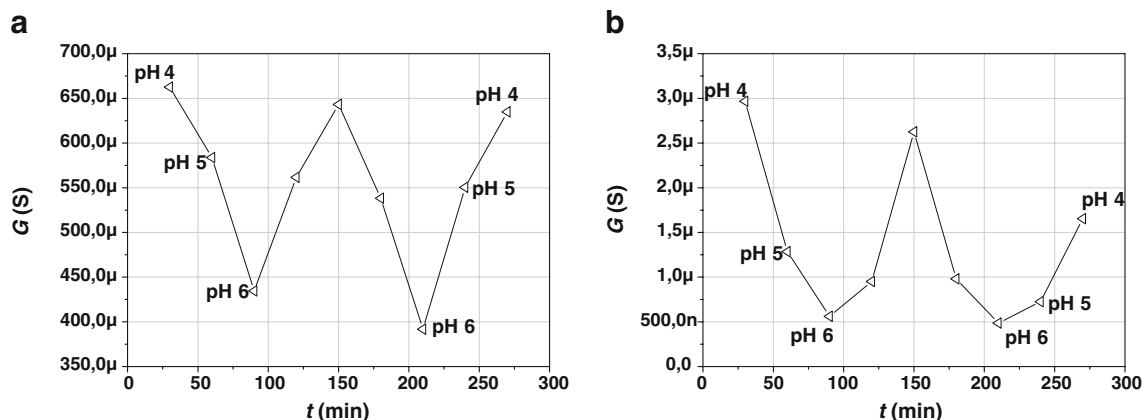


Fig. 8 Changes in polymer conductivity over time in aqueous solution at pH 4, 5, and 6: **a** poly(MBPyr) and **b** poly(BBPyr)

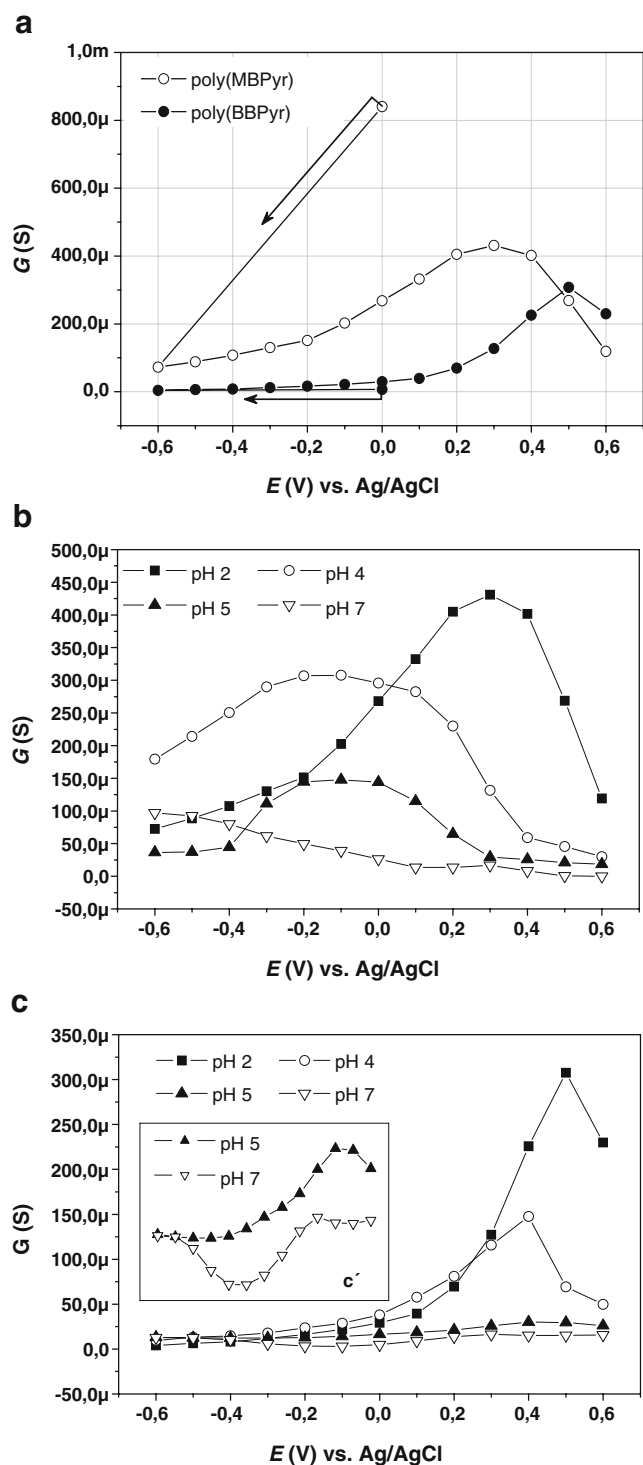


Fig. 9 Comparison of conductivity dependencies of both poly(dialkoxybipyrroles) on applied potential (vs. Ag/AgCl) in solution at pH 2 (a), where the arrows denote the first change in potential from 0.0 to -0.6 V; then the potential was changed in 0.1 V steps to positive potential values. The conductivity dependencies of poly(MBPyr) (b) and poly(BBPyr) (c) on applied potential (vs. Ag/AgCl) in solutions at pH 2, 4, 5, and 7; c' marks the dependence of poly(BBPyr) at pH 5 and 7

poly(MBPyr) at the maximum was only half of the original conductivity measured at the initial 0.0 V (840 μ S); for poly(BBPyr), the conductivity increased by a factor of 100.

Varying the pH shifts the potential of conductivity maximum, but the general trend remains the same for both polymers (Fig. 9b, c). For pH 4 and 5, the maximum is shifted to -0.1 V for poly(MBPyr) and to +0.4 V for poly(BBPyr). Similar effects were also observed for other conducting polymers [9].

A different trend was observed at pH 7. The conductivity decreases with increasing potential up to 0.1 V for poly(MBPyr) and to -0.1 V for poly(BBPyr) and then increases with a maximum at +0.3 V for both polymers. The subsequent increase in potential did not influence film conductivity.

This increase or decrease in the conductivity of both polymers corresponds with the results from the cyclic voltammetry measurements. Both polymers have a higher conductivity in most acidic solutions where the anodic current was also highest (Fig. 6). The maximum anodic current for poly(MBPyr) was between +0.1 and 0.3 V in most acidic solutions, and the conductivity of this film was maximal with an applied potential of +0.3 V. For poly(BBPyr), the anodic peak was between 0.2 and 0.5 V, and the maximum conductivity was reached at an applied potential of 0.5 V. For poly(MPyr), in the low potential region, the conductivity at pH 4 was significantly higher than that at pH 2, which is again in agreement with CV data: the anodic current was higher at pH 4 than at pH 2. The conductivity of both polymers was affected by the applied potential at pH 7, but the total conductivity and electrochemical activity were very low.

In general, the conductivity of poly(dialkoxybipyrroles) is strongly affected by pH and applied potential, similar to other conducting polymers such as polyaniline [6], polypyrrole [26], and poly-N-alkylpyrroles [9].

Conclusion

Poly(4,4'-methoxy-2,2'-bipyrrole) prepared by cyclic voltammetry exhibits a higher electrochemical activity than the butoxy derivative. This activity varies with the length of the substituted bipyrrole skeleton. It was observed that films generated on a gold surface in an argon atmosphere are more conductive than polymers prepared on a platinum surface and/or without a protective argon atmosphere. The conductivity of poly(dialkoxybipyrroles) changes significantly with the pH of the measured solution and the applied potential, which changes the redox state of polymer. Both polymers reached their maximum conductivity at a potential between 0.3 and 0.5 V (when partially oxidized). The polymers were less conductive at high positive potential

and at high negative potential. The methoxybipyrrole is a promising material for future sensor applications due to its compact structure, conductive stability, and relatively high conductivity in acidic solution (pH 2–5).

Acknowledgement Financial support from the Ministry of Education of the Czech Republic Grant No. MSM 6046137307 is gratefully acknowledged. The authors are grateful to Professors A. Merz, O. S. Wolfbeis, and K. Volka for fruitful discussions.

References

1. Trojanowicz M (2003) *Mikrochim Acta* 143:75
2. Maksymiuk K (2006) *Electroanalysis* 18:1537
3. Fang Q, Chetwynd DG, Covington JA, Toh C-S, Gardner JW (2002) *Sens Actuators B* 84:66
4. Hao Q, Kulikov V, Mirsky VM (2003) *Sens Actuators B* 94:352
5. Krondak M, Broncova G, Anikin S, Merz A, Mirsky VM (2006) *J Solid State Electrochem* 10:185
6. Lange U, Roznyatovskaya V, Mirsky VM (2008) *Anal Chim Acta* 614:1
7. Hung S-L, Wen T-C, Gopalan A (2002) *Mater Lett* 55:165
8. Chen Y, Imrie CT, Cooper JM, Glidle A, Morris DG, Ryder KS (1998) *Polym Int* 47:43
9. Zotti G, Zecchin S, Schiavon G, Vercelli B (2003) *Chem Mater* 15:4642
10. Gassner F, Graf S, Merz A (1997) *Synth Met* 87:75
11. Timofeeva ON, Lubentsov BZ, Sudakova EZ, Chernyshov DN, Khidekel ML (1991) *Synth Metals* 40:111
12. Agbor NE, Petty MC, Monkman AP (1995) *Sens Actuators B* 28:173
13. Partridge AC, Harris P, Andrews MK (1996) *Analyst* 121:1349
14. Lange U, Mirsky VM (2008) *J Electroanal Chem* 622:246
15. Merz A, Anikin S, Lieser B, Heinze J, John H (2003) *Chem A Eur J* 9:449
16. Zhou M, Pagels M, Geschke B, Heinze J (2002) *J Phys Chem B* 106:10065
17. Zhou M, Heinze J (1999) *J Phys Chem B* 103:8443
18. Costantini N, Cagnolati R, Nucci L, Pergola F, Ruggeri G (1998) *Synth Met* 92:139
19. Cross MG, Walton D, Morse NJ, Mortimer RJ, Rosseinsky DR, Simmonds DJ (1985) *J Electroanal Chem* 189:389
20. Liu Y-C, Hwang B-J (2000) *Synth Met* 113:203
21. Crowey K, Cassidy J (2003) *J Electroanal Chem* 547:75
22. Jenden ChM, Davidson RG, Turner TG (1993) *Polymer* 34:1649
23. Mikat J (2001) *Synth Met* 119:649
24. Michalska A, Maksymiuk K (2003) *Mikrochim Acta* 143:163
25. Teh K-S, Lin L (2005) *J Micromechanics Microengineering* 15:2019
26. Inganäs O, Erlandsson R, Nylander C, Lundström I (1984) *J Phys Chem Solids* 45:432
27. Masuda H, Kaeriyama K (1991) *J Mater Sci* 26:5637