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Chemosensitive properties of poly-4,4'-dialkoxy-2,2'-bipyrrroles

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Abstract Chemosensitive properties of 4,4'-dimethoxy-2,2'-bipyrrrole and 4,4'-dibutoxy-2,2'-bipyrrrole were investigated. These new conductive polymers were polymerized by cyclic voltammetry on the platinum and gold interdigitated electrodes designed for 2- and 4-point measurement of lateral conductivity. Thus, obtained polymers demonstrated high sensitivity to HCl in the parts per million concentration range. Kinetics of the gaseous HCl influence on the ratios of conductivities measured by 2- and 4-point techniques was analyzed. Some response of the polymers conductance towards NH₃, NO and oxygen was also observed, but with much lower sensitivity than towards HCl. In aqueous solutions, the polymer conductivity was pH dependent; in comparison with 4,4'-dibutoxy-2,2'-bipyrrrole, the conductivity range of the methoxy derivative was shifted to acidic range for about two pH units. A possibility to use the pH dependence for the development of enzymatic biosensors with pH transducing was demonstrated.

Keywords Conductive polymer · Sensor · Conductivity · HCl · Alkoxybipyrrroles · Alkoxybipyrrroles

Introduction

Changes of physical properties of conductive polymers on exposure to different chemical species make them attractive for the applications in chemical sensors. The most

studied conducting polymer is polyaniline [1], which displays sensitivity to pH [2–6], ammonia [7–10], various alcohol vapours [11–13], NO_x [9, 14–16], H₂S [14], SO₂ [14], CO [14], CH₄ [14], CO₂ [16–19], dimethyl methylphosphonate [9], hydrogen halides [20], hydrogen cyanide [20], halogens [20], monochloroacetic acid [20], chloroform [21], water vapour [13, 22] and H₂ [23, 24]. Another thoroughly investigated conducting polymer is polypyrrol, which is sensitive towards pH [5, 25–28], hydrogen halides, hydrogen cyanide, 1,3,5-trichloromethylbenzene, methylbenzyl bromide, bromobenzyl cyanide, cyanogen [29, 30] chloride and cyanogen bromide.

Conductive polymers often provide very high sensitivity, while a selectivity of their response is usually relatively poor; the latter fact was illustrated above by the large amount of chemical compounds influencing electrical properties of conductive polymers. However, a combination of a large number of conductive polymers with different chemosensitive properties in an array allows one to form highly selective artificial nose or tongue. This is the reason for a strong interest to new conductive polymers. Recently, new types of bipyrrroles were synthesized [31]. Here we describe chemosensitive properties of this new class of conductive polymers.

Experimental

4,4'-dimethoxy-2,2'-bipyrrrole (MBPyr) and 4,4'-dibutoxy-2,2'-bipyrrrole (BBPyr) were synthesized according to the procedure described previously [31] (Fig. 2). They were polymerized from acetonitrile (Fluka, HPLC grade) solution with 1% of water (Millipore) and with 0.1 M of tetrabutylammonium hexafluorophosphate (Bu₄NPF₆, Fluka, electrochemical grade). The platinum and gold electrodes on silicon support were prepared by photolithography (Fig. 1). Electropolymerization of both bipyrrroles were performed with a potentiostat/galvanostat Autolab PGSTAT-12 (Eco-Chemie, The Netherlands) controlled by vendor software. A three-electrode cell comprising a working Pt electrode, a reference electrode (Ag wire) and a Pt wire as the counter electrode were used. Electropolymerized films were prepared by cyclic voltammetry with potential sweep (50 cycles) between –1.1 and 0.8 V with 100 mV/s scan rate

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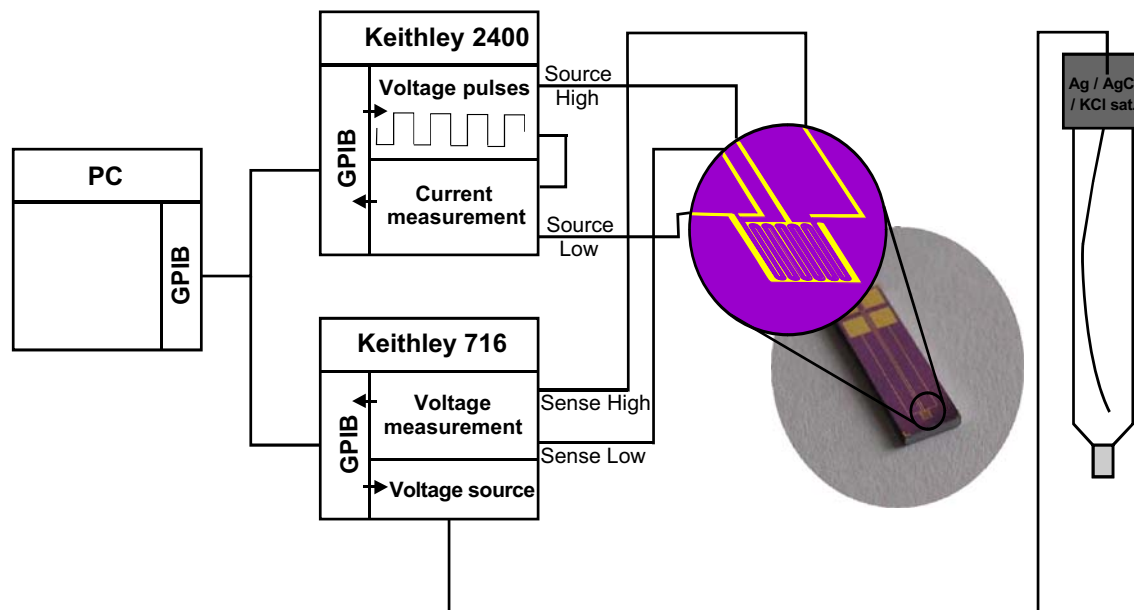


Fig. 1 Set-up for simultaneous 2- and 4-point conductivity measurements

under argon atmosphere. The resulting polymer films were checked by optical microscopy.

Electrolytes for investigation of pH dependence were prepared from solution of 100 mM NaCl and 5 mM buffer (sodium acetate for pH 2, 3, 4, phosphate for pH 5, 6, 7 and TRIS for pH 8, 9 and 10), adjusted by HCl or NaOH. All chemicals were from Merck in analytical grade purity.

The conductance/resistance measurements were made using apparatus described previously [32]. The Keithley 2400 (Keithley, USA) was used as the source unit generating voltage pulses (typically ± 50 mV of 1 s duration) and measuring electrical current through the electrodes. The voltage related to the 4-point conductivity measurement was measured by high-impedance voltmeter Keithley 617 or Keithley 2000 (Keithley, USA). For characterization of potential dependence of the resistance of polymer layers, the auxiliary voltage source of Keithley 617 was used to control potential of the electrode with polymeric layer against reference electrode (saturated Ag/AgCl electrode 6.0726.100 by Metrohm, Switzerland). Both devices were controlled by in-lab written software through GPIB interface. The control routines were written in the Agilent-VEE 6.01 programming environment (Agilent, USA).

Mixing of gases was controlled by metal-sealed mass flow controllers 1479A by MKS (USA). The valves were

controlled by in-lab software written in LabView 6.1 (National Instruments, USA). Argon, nitrogen, synthetic air, ammonia in nitrogen (400 mg/m^3), HCl in nitrogen (200 ppm) and NO in nitrogen (400 mg/m^3) were from Linde (Germany).

Results and discussion

Sensitivity to gaseous HCl

Initial conductivity of the methoxy derivative is about 20–30 times higher than that of the butoxy derivative (Figs. 3 and 4). Probably, additional methylene groups of non-conductive butoxy groups increase the distance between

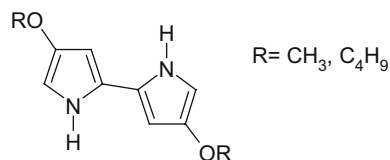


Fig. 2 The structure of bipyrrol monomers. *R* represents $-\text{CH}_3$ group for the methoxy derivative and $-(\text{CH}_2)_3\text{CH}_3$ group for the butoxy derivative

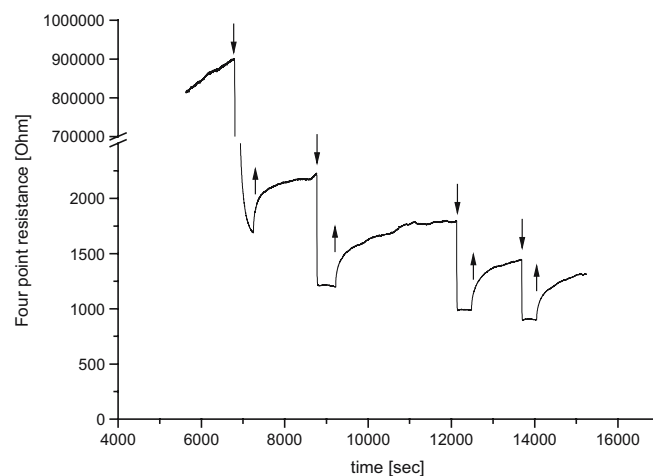


Fig. 3 Response of freshly synthesized polydibutoxybipyrrole film towards 200 ppm gaseous HCl in nitrogen. Desorption was performed in pure nitrogen

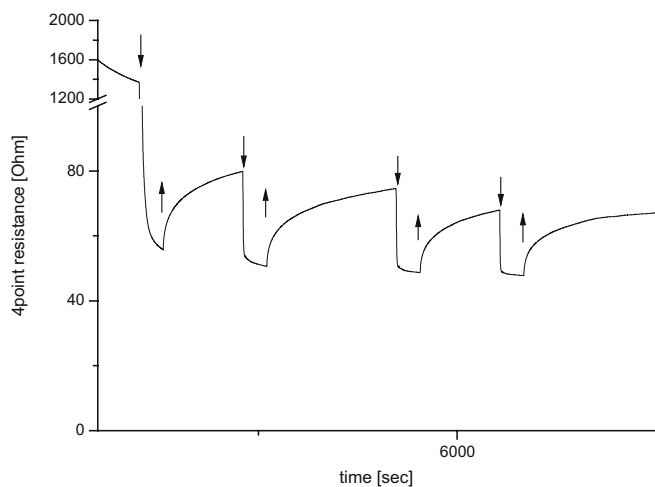


Fig. 4 Response of freshly synthesized polydimethoxybipyrrole film towards 200 ppm gaseous HCl in nitrogen. Desorption was performed in pure nitrogen

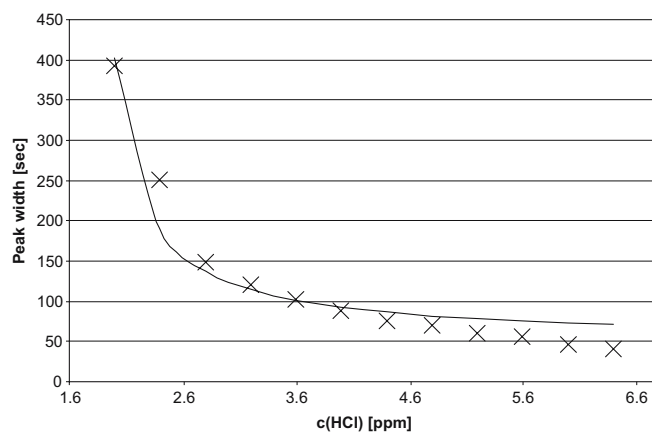


Fig. 6 Concentration dependence of R_2/R_4 peak width at 70°C. The peaks were induced by additions of different concentrations of gaseous HCl

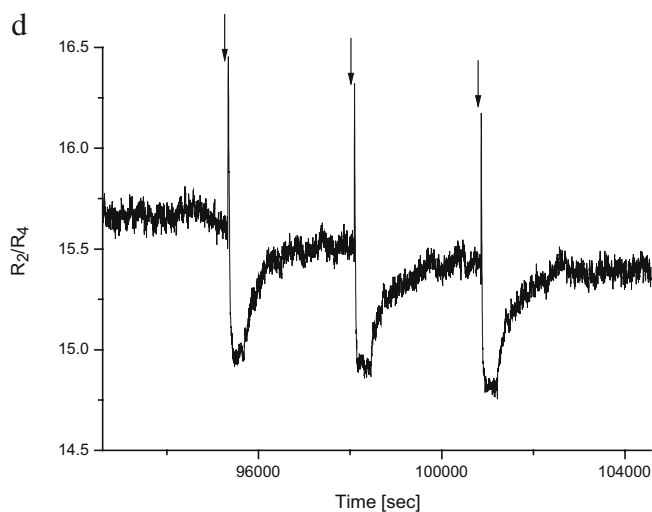
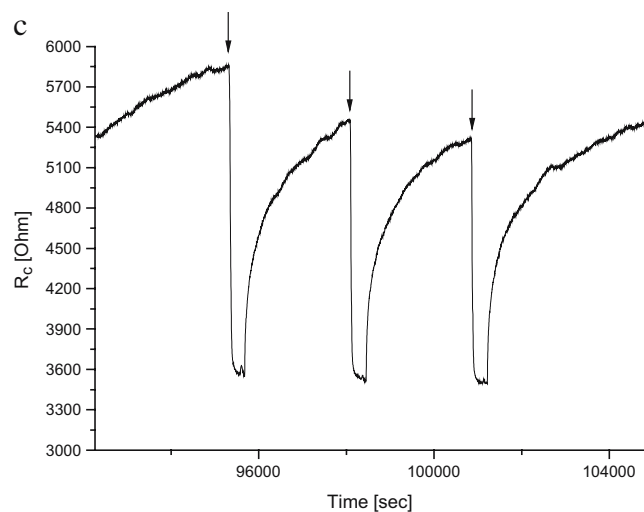
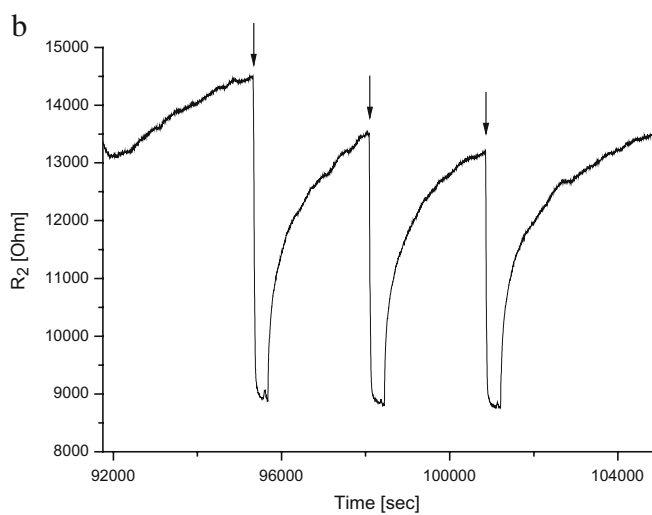
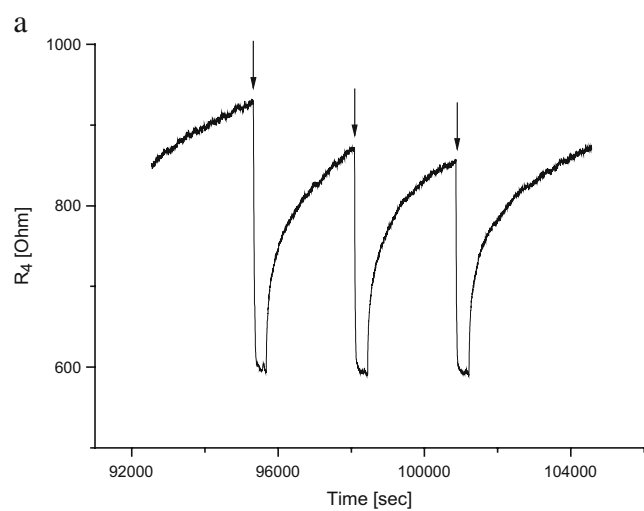


Fig. 5 Response of the sensor towards repeated exposure to gaseous HCl. **(a)** 4-point resistance, **(b)** 2-point resistance, **(c)** calculated contact resistance and **(d)** R_2/R_4 ratio. Here and in other

figures, the symbols \uparrow and \downarrow indicate correspondingly the beginning and the end of the exposure to an analyte

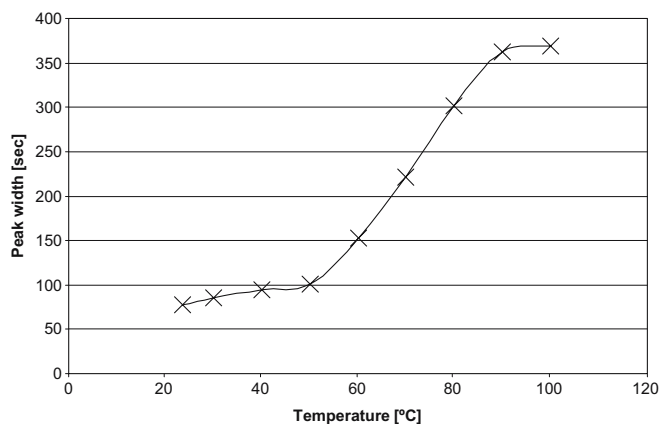


Fig. 7 Temperature dependence of R_2/R_4 peak width. The peaks were induced by additions of 2 ppm of gaseous HCl

conductive backbones of adjacent polymer chains thus decreasing charge transfer between polymer molecules.

The same trend is observed in the reaction with HCl. The conductivity of both films is decreased, but the difference still remains. During the first exposure to HCl, the resistance falls down rapidly. After the saturation of binding places inside the film, the new base line was established, and response towards HCl became lower but reversible. The resistive response depends on the gas concentration according to the Langmuir adsorption isotherm with binding constant of about 1.5 ppm HCl. The upper detection limit is about 3 ppm.

Temperature influence on the response kinetics was measured in the temperature range between 25 and 100°C. The kinetics was determined as a slope of conductivity changes at every 20 or 40 s of HCl adsorption and desorption. In contrast to our earlier results with other polymers, where Arrhenius-type behavior was observed, both polydimethoxybipyrrole and polydibutoxybipyrrole displayed no temperature dependence. This result suggests that the response kinetics is limited not by the binding of HCl with corresponding binding sites but by its diffusion in the polymer layer.

To test this suggestion, quantitative comparison of kinetics measured by 2- and 4-point techniques (R_2 and R_4 correspondingly) was performed. The following idea was explored. In general, one can imagine influence of HCl on bulk polymer resistance, on resistance of polymer/metal contacts or on both these resistance. HCl influence on R_4 indicates that HCl really modifies bulk polymer resistance. If contact resistance (R_c) is much less than resistance of bulk polymer, R_2 is proportional to R_4 : $R_2 = \alpha R_4$, where α is a geometrical factor (for the present electrode geometry $\alpha \approx 3$). For polydimethoxybipyrrole and polydibutoxybipyrrole, the ratio of R_2/R_4 is about 15, this indicates the contribution of the contact resistance R_c into the measured R_2 resistance. Based on the geometrical consideration, the value of R_c can be estimated as $R_2 - 3R_4$. This value was being calculated from experimental data for R_2 and R_4 and is shown on Fig. 5c. It is to note that R_c is effected by HCl. Therefore, HCl modifies both bulk polymer resistance and resistance of a polymer/metal contact. However, HCl can reach contacts only after diffusion through the whole thickness of the polymer layer. If this diffusion is slower than the binding of HCl to the polymer, one can expect some time delay between R_2 and R_4 response to HCl addition. This leads to the peak of the ratio R_2/R_4 (Fig. 5d). According to this model, parameters of this peak (height, width) are determined by different physicochemical processes (binding to bulk polymer, diffusion through bulk polymer, binding to polymer/metal interface) and therefore can be dependent on HCl concentration and temperature. Such dependencies are shown on the Figs. 6 and 7. The concentration dependence in Fig. 6 can be used for the analytical applications.

Sensitivity to NH_3 , O_2 and NO

Sensitivity to the acidic gas HCl allowed us to expect an opposite effect on exposure to basic gases [7–10]. It was demonstrated in investigation of ammonia effects on the conductivity of bipyrroles: an exposure to ammonia leads

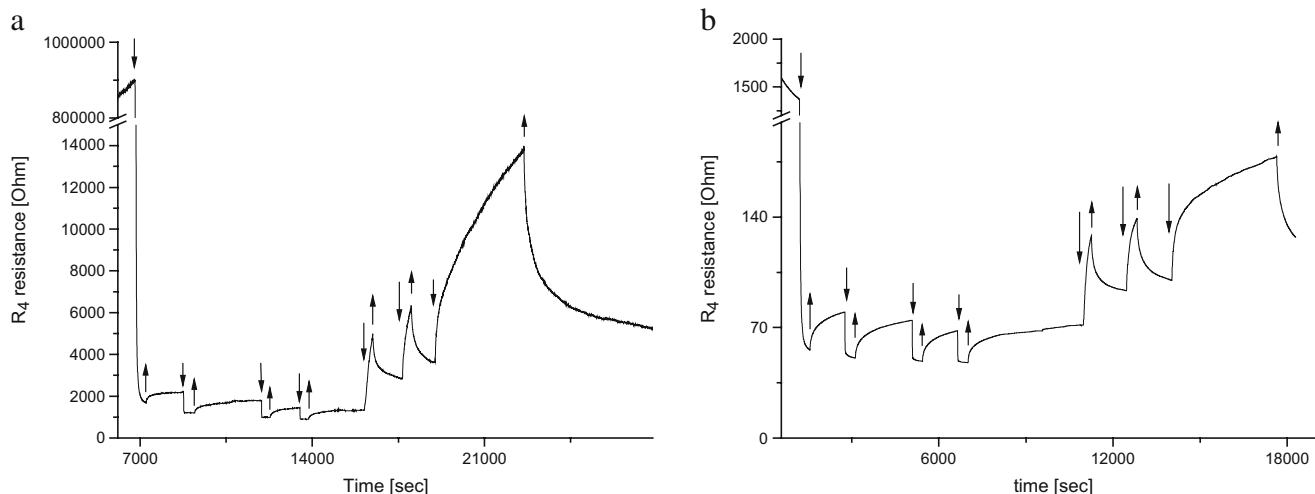


Fig. 8 Response of polymerized dibutoxy (a) and dimethoxy (b) derivative on exposure to HCl and NH_3

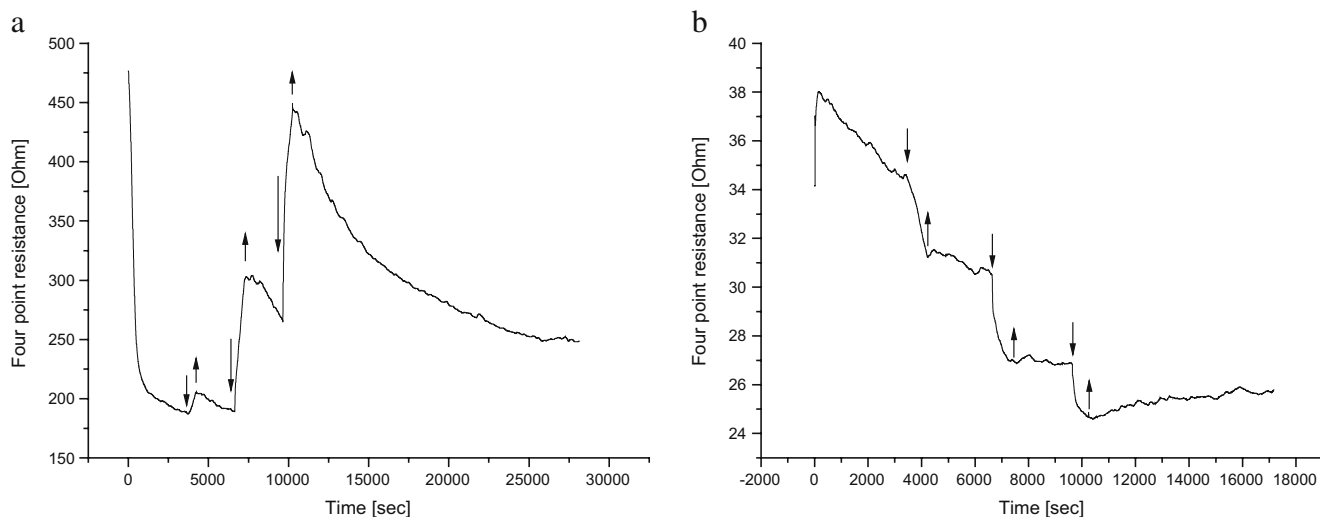


Fig. 9 Resistance response of dibutoxy (a) and dimethoxy (b) bipyrrroles on exposure to NO at 120°C. The analyte concentrations for subsequent additions of gas were 3.3, 33 and 330 ppm of NO

to the increase of resistance of sensors, which were treated by HCl before (Fig. 8). The kinetics is slower than that of HCl response. The magnitude of the first response to HCl is larger than that of the reversible responses to HCl, but still several orders lower than the irreversible response to HCl during the first polymer exposure to this gas. The response to ammonia is not completely reversible: subsequent cycles of adsorption/desorption result in a shift of the base line.

An exposure of polymers to oxidizing and reducing gases was investigated. An exposure to oxygen results in small effects with very slow kinetics: only about 3% decrease of the polymer resistance was induced by replacement of nitrogen atmosphere by artificial air (20% oxygen in nitrogen). The effect was not changed by temperature increasing from 22 to 110°C. The response is reversible but very slow, typical response time is about

30 min. Small and poor reversible effects were observed on exposure to reductive gas—NO. The reversibility was better for poly(bipyrrole) polymer and was improved by increasing of temperature till 120°C (Fig. 9).

pH sensitivity and applications as pH transducers

Protonation of pyrrol nitrogen of polypyrroles leads to strong increase of the polymer conductivity [33]. The same effect is observed for bipyrrroles (Fig. 10). Methoxy derivative is protonated at more alkalic pH value than butoxy derivative, appeared pK are 3.9 and 6.1 correspondingly. This pK shift is probably caused by higher dielectrical constant of the butoxypolypyrrole. This fact can be used for design of pH-dependent conductive poly-

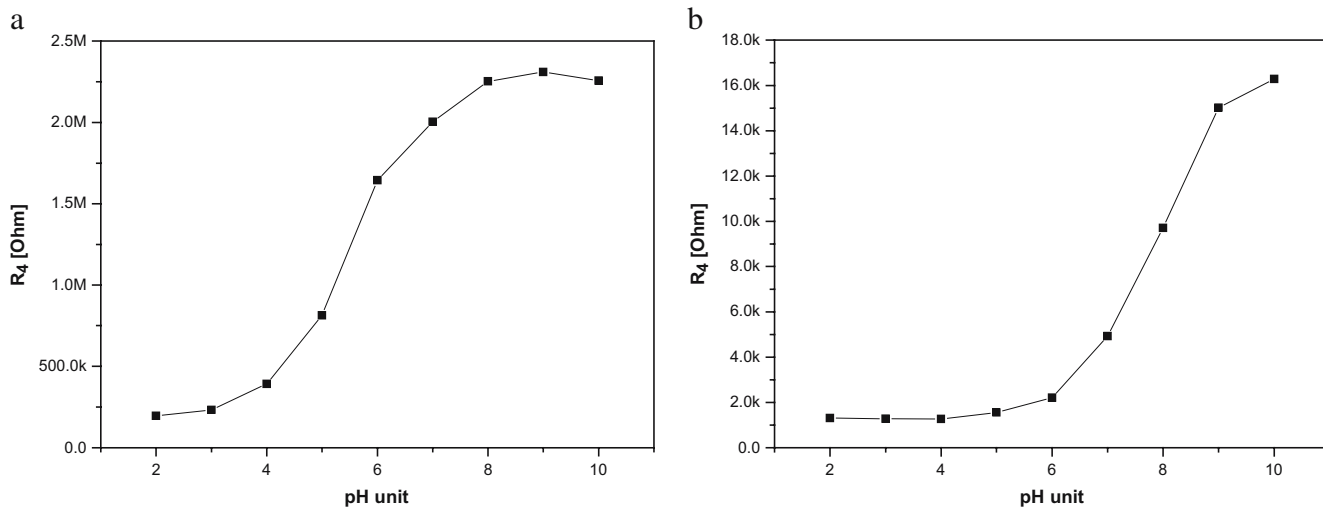


Fig. 10 Dependence of the conductivity of dibutoxy (a) and dimethoxy (b) bipyrrroles on pH at electrode potential of 0 mV vs Ag/AgCl_{sat}

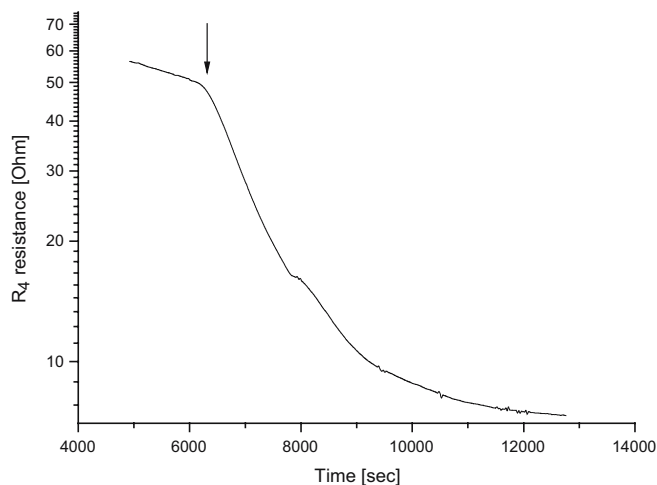


Fig. 11 Resistance response of the biosensor with immobilized glucose oxidase and pH transducer based on poly-4,4'-dialkoxy-bipyrroles. The *arrow* indicates addition of 10 mM glucose

mers with desired pK : one can expect even higher pK shift to the acidic direction for more hydrophobic bipyrrole derivatives.

pH sensitivity of poly-4,4'-dialkoxy-bipyrroles allows one to use these materials not only as conductive pH sensors but also as conductive pH transducers for enzymatic biosensors. This application was demonstrated by fabrication of simple biosensor for determination of glucose. For this aim, 5 mg of D-glucose oxidase (Aldrich, 1,200 units/mg) was put between dialysis membrane and polymer coated inter-digital electrode. Addition of D-glucose into the solution with this biosensor resulted in formation of acidic products and in expected increase of the polymer conductance (Fig. 11).

Conclusion

We have described sensitive properties of the new materials—electropolymerized poly-4,4'-dimethoxybipyrrole and poly-4,4'-dibutoxybipyrrole. These conductive polymers demonstrated high sensitivity to acidic (hydrogen chloride) and basic (ammonia) gases, but relatively low sensitivity to oxidative and reducing gases. Electrical conductivity of the new polymers is pH dependent, and the range of pH sensitivity is different for dimethoxy and dibutoxy derivatives. We have demonstrated a possible application of these materials as conductive pH transducers in an enzymatic biosensor. However, the most important analytical result is that these materials are chemosensitive but are different from known conductive polymers. It allows us to suggest an application of these polymers as element of sensor arrays (artificial noses or artificial tongues) with impedometric signal transducing.

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