

Electroactive films of interpolymer complexes of polyaniline with polyamidulosulfonic acids: advantageous features in some possible applications

Alexander A. Nekrasov · Oxana L. Gribkova ·
Victor F. Ivanov · Anatoly V. Vannikov

Received: 4 December 2009 / Revised: 16 March 2010 / Accepted: 21 March 2010 / Published online: 23 April 2010
© Springer-Verlag 2010

Abstract With the purpose of determining prospects of possible applications of interpolymer complexes of polyaniline (PANI) with poly(amidosulfonic acid)s, we have performed a comparative study of polyaniline films prepared by electrochemical polymerization of aniline in the presence of the polyacids distinguished by different rigidities of the polymer backbone: (1) poly(2-acrylamido-2-methyl-1-propanosulfonic acid) (flexible backbone); (2) poly-*p,p'*-(2,2'-disulfoacid)-diphenylen-iso-phthalamid (semi-rigid backbone); (3) poly-*p,p'*-(2,2'-disulfoacid)-diphelylen-tere-phthalamid (rigid backbone); and (4) a copolymer of the latter two acids with monomer feed ratio 1:1 (co-PASA). Spectroelectrochemical studies in the UV–vis–NIR range showed that PANI complexes with rigid-chain polyacids far more effectively modulate absorbance in the Vis–NIR range and can be considered as promising candidates for “smart windows” development. Due to the presence of bulky unmovable polyacid anion, PANI interpolymer complexes (particularly those with the semi-rigid-chain polyacids) possess much wider pH range of electroactivity than common PANI, which is of great importance for biosensor applications. The interpolymer complexes with flexible-chain and semi-rigid-chain polyacids exhibit good optical response to ammonia vapors at conditions of high humidity, which make them promising materials for the development of ammonia optical sensors.

Keywords Polyaniline · Electrochemical polymerization · Template-guided polymerization · Electrochromic devices · NIR absorbance modulation · pH-dependent electroactivity · Ammonia gas sensors

Introduction

Main advantages of using sulfonic polyacids for aniline matrix polymerization are the following: (1) fast polymerization due to the preliminary association of aniline monomer to the sulfonic groups of the polyacid [1, 2]; (2) low content of by-products in the final polymer due to preferential head-to-tail coupling of these associated monomers; (2) improved film forming and mechanical properties of the resulting polymer and good adherence to different substrates; (3) possibility to modify the structure of the polymer with the purpose of changing its optical and electrical properties; (4) improved morphology and structural uniformity of the films; and (5) improved resource characteristics of the films in various applications.

Recently, numerous papers were published devoted to investigations of electrochromic phenomena in polyaniline [3–6], ammonia sensing properties [7–10], and development of potentiometric and amperometric biosensors [11–13] on the basis of this conducting polymer. Among the most important characteristics of polyaniline, as long as the sensor and biosensor applications are concerned, is pH dependence of electroactivity. In this respect, polyaniline films doped with polymeric and low molecular sulfonic acids possess unique properties, allowing one to expand their application areas.

In this work, we present a comparative study of operation characteristics in the above mentioned applications of polyaniline films prepared by electrochemical

A. A. Nekrasov (✉) · O. L. Gribkova · V. F. Ivanov ·
A. V. Vannikov
A.N. Frumkin Institute of Physical Chemistry
and Electrochemistry RAS,
Leninskii prospect 31,
Moscow 119991, Russia
e-mail: secp@elchem.ac.ru

polymerization of aniline in the presence of the following four poly(amidosulfonic acids): (1) poly(2-acrylamido-2-methyl-1-propanosulfonic acid) (PAMPSA, flexible backbone); (2) poly-*p,p'*-(2,2'-disulfoacid)-diphenyl-iso-phthalamid (i-PASA, semi-rigid backbone); (3) poly-*p,p'*-(2,2'-disulfoacid)-diphenyl-*ter*-phthalamid (t-PASA, rigid backbone); and (4) a copolymer of the latter two acids with monomer feed ratio 1:1 (co-PASA). Structures of the monomer units of the studied polyacids are presented in Fig. 1. Common PANI films electrochemically deposited in the presence of inorganic acid (HCl) were used for a comparison.

Recently [14], we have investigated peculiarities of the electrochemical synthesis of polyaniline in the presence of PAMPSA, i-PASA, and t-PASA and performed electrochemical, spectroelectrochemical, and morphological characterization of the films obtained. It was shown that the rigidity of polymer matrix backbone plays an important role in the course of the synthesis and significantly influences the electronic structure of the resulting interpolymer complexes. On the basis of comparison of electrochemical and spectroelectrochemical properties of the obtained interpolymer films and conventional PANI, it was supposed that flexible-chain polyacid can adapt its structure to the rigid conjugated macromolecule of emeraldine form of PANI, while in the interpolymer complex with rigid-chain polyacid PANI, in its turn, has to adjust its conformation to match the structure of polyacid. This results in the hindrances in forming quinoid fragments of PANI, which manifest themselves in the distortions of spectroelectrochemical properties of PANI in such complexes.

On the basis of experiments published in [14, 15], we have made suppositions concerning the structures of interpolymer complexes of PANI with flexible-chain, semi-rigid-chain, and rigid-chain polyacids. In full conformity with [16] for the complexes of PANI with flexible-chain polyacids

(PAMPSA), we propose a double-strand structure. For other objects discussed in this paper, our quantum chemical calculations (semi-empirical PM3-method) showed that semi-rigid-chain i-PASA has a slightly bent backbone. Therefore, it can somehow adapt its structure to the structure of polyaniline. In contrast to this, t-PASA is absolutely straight and rigid. Therefore, the distance between sulfonic groups is much longer in this case. Comparing the distances between the sulfonic groups with the typical distances between amine moieties in PANI (also obtained from the results of molecular modeling), we may suppose that a shorter distance between sulfonic groups allows i-PASA to form with polyaniline both double-strand and brush-type interpolymer complexes, as shown in Fig. 2.

On the contrary, t-PASA seems to be capable of forming only brush-type complexes. Therefore, in this case, standard polyaniline fragments are attached as side chains to the polyacid macromolecules. We believe that a mixed structure similar to that observed in the case of semi-rigid-chain i-PASA can be applied for the interpolymer complex of PANI with the co-polymer, co-PASA, because conformation of this polyacid in solution is close to i-PASA [17].

Judging from the differences in the structure, one can reasonably expect that these interpolymer complexes may possess significantly different functional characteristics in the above discussed possible applications. In this work, our goal was rather to screen briefly the operation characteristics of these promising, in our opinion, materials than to reveal the mechanisms responsible for the observed differences in their behavior.

Experimental

Potentiostatic electrochemical deposition of the films of interpolymer complexes of PANI with PAMPSA (commer-

Fig. 1 Structures of the monomer units of the polyacids studied in the paper

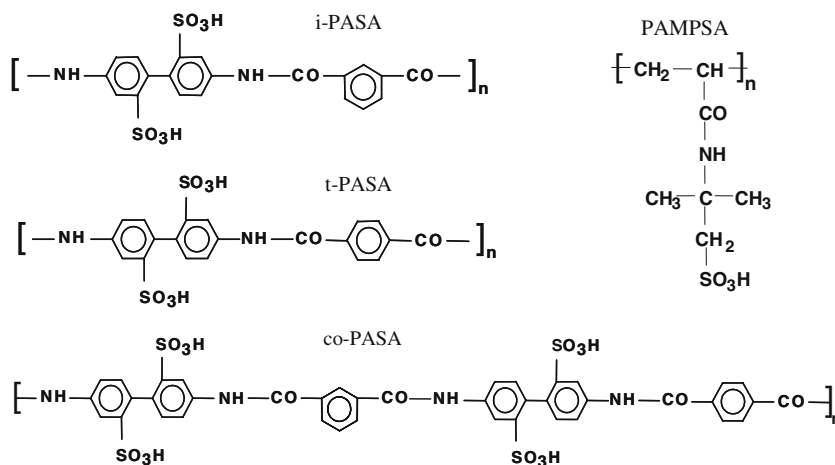
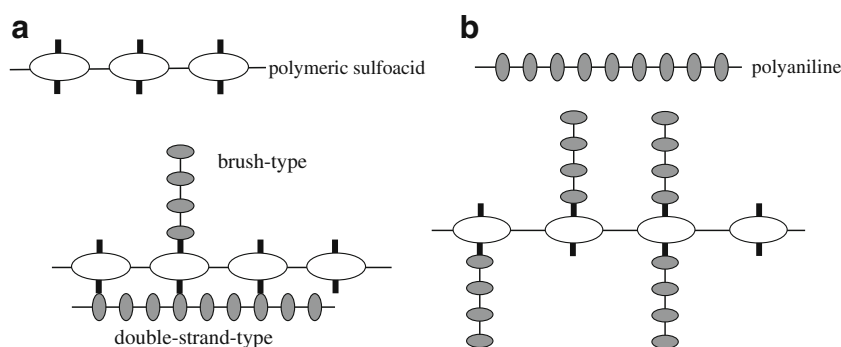


Fig. 2 Proposed structures of the interpolymer complexes of PANI: with semi-rigid-backbone i-PASA (a), and with rigid-backbone t-PASA (b)



cial by Aldrich, MW approx. 2,000,000), i-PASA, and t-PASA (synthesized in laboratory, MW approx. 40,000) was carried out according to the procedure described previously in [14]. The synthesis in the presence of co-PASA (synthesized in laboratory, MW approx. 40,000) is similar, for the most part, to that in t-PASA, but while calculating concentrations for the electrodeposition bath, we took into account that the copolymer is a quadruple-base acid as distinct from the double-base t-PASA. Conventional PANI–HCl films used for comparison were deposited potentiostatically from an aqueous solution of 0.1 M freshly distilled aniline in 1 M HCl. All the reagents were of analytical grade or higher, and deionated water was used as a solvent. The electrochemical synthesis of polyaniline was performed in a specially designed three-electrode spectroelectrochemical cell at the potential of 0.75 V relative to a saturated silver–silver chloride electrode (s.s.c.e.). All the values of potential in this paper are presented relative to this electrode. The PANI films were deposited onto glass substrates covered with a transparent conducting FTO layer ($\text{SnO}_2\text{:F}$) with the sheet resistance approx. $7 \Omega/\text{square}$. A platinum sheet located outside of the light path served as a counter electrode. The electrochemical parameters were controlled and measured by a computer-driven combination of HA-501G potentiostat/galvanostat (Hokuto Denko Ltd.) and a digital storage oscilloscope Nicolet 2090 (Nicolet Inc.). To ensure reproducibility of the film thickness, the course of the synthesis was also monitored by UV–vis in situ optical spectroscopy using an AvaSpec 2048 diode array spectrophotometer (Avantes BV) equipped with flexible light guides attached to the variable-length cuvette holder for the aforementioned spectroelectrochemical cell. According to interferometric data (MII-4 by LOMO with CCD video camera), thicknesses of the films (if measured ex situ in dry conditions) used in pH-dependent electroactivity studies and ammonia sensing experiments ranged within 50–60 nm and those of the films tested in the electrochromic experiments within 80–90 nm. The films were characterized by cyclic voltammetry (CV) in a 1 M HCl using the same electrochemical equipment.

Comparative studies of electrochromic properties of the films in the UV–vis–NIR range (350–1,700 nm) were carried out using a Shimadzu UV-3101PC spectrophotometer in the same spectroelectrochemical cell filled with a propylene carbonate (PC) solution containing 0.1 M HClO_4 and 0.9 M NaClO_4 . The spectroelectrochemical cell with the SnO_2 -glass substrate and the electrolyte inside was used as a background, which was arithmetically subtracted from the experimental spectra. The use of non-aqueous electrolyte in this experiment was dictated by intensive absorption of water in the NIR range of spectra, which makes it practically impossible to subtract the background. Nevertheless, even while using PC as a solvent, the recording range in our case is limited by 1,700 nm due to high absorption of PC in the longer wavelength area and rather long light path of the spectroelectrochemical cell (7 cm). The above described electrochemical equipment was used for controlling the potential.

CV experiments at different pH values were performed using the same electrochemical equipment and the cell in an aqueous solution of initially 1 M HClO_4 neutralized step-by-step by 30% aqueous ammonia to achieve desired pH. The pH values were measured using an OP-208/1 digital pH-meter (Radelkis). Perchlorate anion was chosen due to the following reason. Earlier, it was shown [18–20] that perchlorate anion practically does not participate in the charge compensation process because of the low diffusion coefficient. In this case, charge compensation after positive charging of the polymer during its electrochemical oxidation is achieved mainly by expulsion of protons instead of entering of the anions into the film. Therefore, in this respect, perchlorate anion is similar to unmovable polyacid dopant. This is particularly important while comparing the electrochemical response of common PANI with that of the interpolymer complexes. The films were sequentially tested in solutions with gradually increasing pH. For conditioning of the films in each of the solutions, the first six cycles were not taken into account. After cycling at the highest pH 5 used in this study, the films were returned into the bath with the lowest pH 0.5 in order to try to reproduce initial CVs.

Testing of ammonia sensing properties of the films was carried out in the same spectroelectrochemical cell containing a small amount of heavily diluted aqueous ammonia solution on the bottom. In these conditions in the closed cell, an equilibrium mixture of aqueous ammonia vapors and the air is formed above the solution. The values of partial pressure of ammonia in the cell were calculated by means of extrapolation to the near-zero range of the dependence built on the base of handbook tabular data [21] on ammonia partial pressure above the solutions of different concentrations. Thus, for the solution concentrations of 0.25%, 0.05%, and 0.01%, the partial pressures of ammonia above the solution were 2.4, 1.6 (~2,100 ppm), and 1.4 mmHg (~1,850 ppm), correspondingly. Since our goal was rather to compare the operation of different interpolymer complexes in this application than to achieve “record” sensitivities in ammonia sensing, such accuracy in the determination of ammonia partial pressure is quite enough. Samples of the films electrodeposited on FTO substrates were fixed inside the closed spectroelectrochemical cell, and their optical response to the ammonia vapors vs. time was registered in the UV–visible spectral area (350–1,050 nm) using the same AvaSpec 2048 spectrophotometer. Spectrum recording time was as low as 500 ms to ensure proper registration of rapid color transitions. Regeneration of the films after a single exposition to ammonia vapors was carried out by immersing them into 1 M aqueous HCl for 10 min. Following the regeneration, the films of interpolymer complexes were thoroughly rinsed with deionated water and then dried on air. Thanks to bulky unmovable acidic dopants, they successfully endured such a treatment without noticeable deprotonation in contrast to common PANI films, which were simply dried on air after the regeneration.

Results and discussion

The results of electrochemical characterization of the films by cyclic voltammetry presented in Fig. 3 show that PAN-PAMPSA films demonstrate behavior similar to the film prepared in hydrochloric acid. At the same time, in the case of polyacids with more rigid backbone, the second peak of current is much lower. Therefore, we may suppose that the formation of quinoid structures is sterically hindered in this case in full conformity with our suppositions about different conformational adaptabilities of the polyacids with different rigidities of the polymer backbone.

The results of CV experiments are summarized in Table 1. Comparison of the half-wave potential values ($E_{1/2}^1$) shows that this value for the rigid-chain t-PASA is much closer to common polyaniline than for other polyacids. This is another evidence in favor of the brush-type structure of the complex in this case. Close values of the half-wave potential of the complexes with i-PASA and co-PASA support our supposition about the similarity of their structure. Higher values of the peak-to-peak width (ΔE^1) for the interpolymer complexes most possibly are due to their lower conductivity because of the high volume portion of non-conductive unmovable polyacid.

First of all, we have tested the interpolymer complexes for their capability of modulating absorbance in the near-infrared (NIR) spectral area. It is well known that about 47% of energy in the solar radiation spectrum falls on the NIR range [22, 23]. Therefore, it would be advantageous during the summer months to decrease the total amount of solar energy entering a building and increase the total amount of solar energy entering a building during the winter months. This would provide a substantial energy savings for interior space heating and air conditioning.

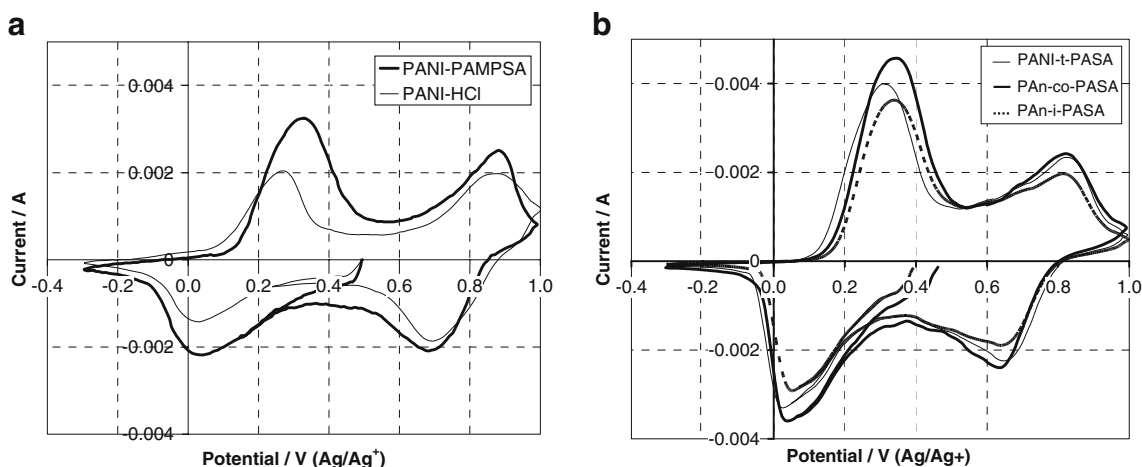


Fig. 3 CVs of electrodeposited matrix polyaniline films in 1 M HCl at 100 mV/s on SnO_2 electrode: flexible-chain polyacid (a), semi-rigid-chain and rigid-chain polyacids (b)

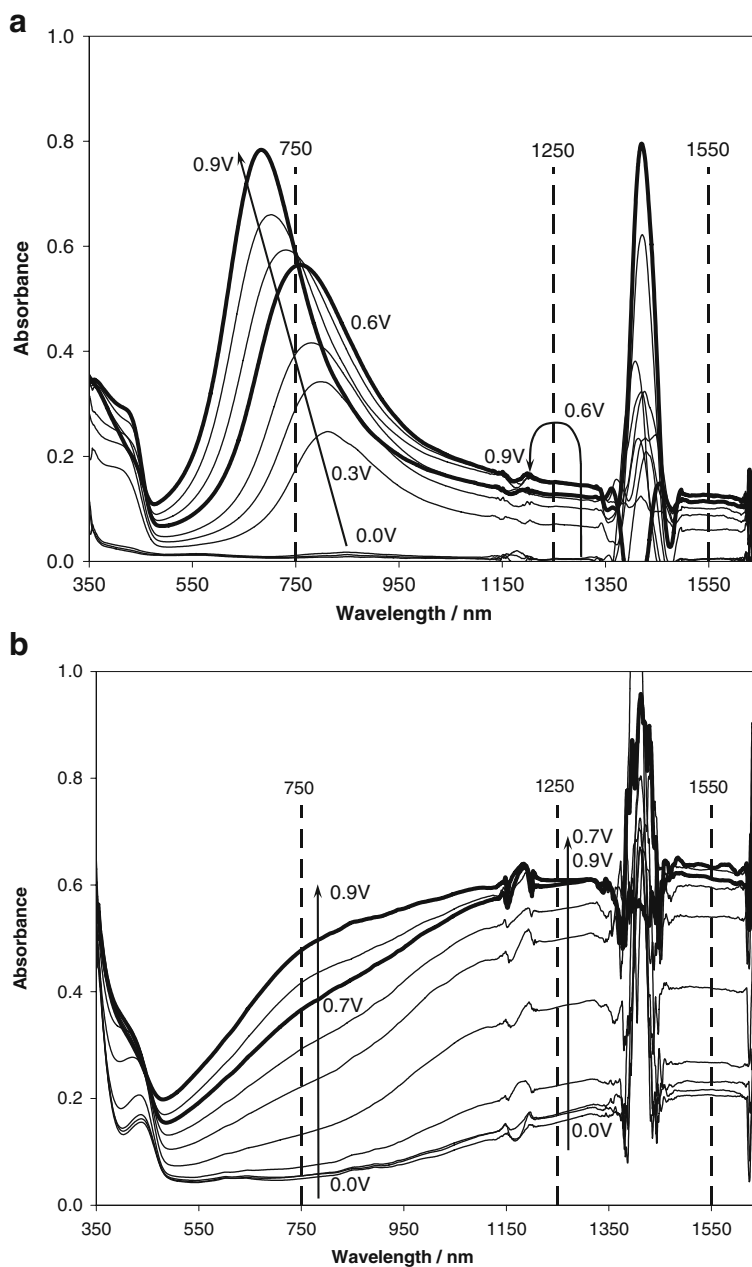
Table 1 Results of electrochemical characterization of the films

| | Potential (V) | | | | | |
|---------|---------------|---------|-------------|--------------|---------|---------|
| | E_a^1 | E_c^1 | $E_{1/2}^1$ | ΔE^1 | E_a^2 | E_c^2 |
| HCl | 0.268 | 0.026 | 0.147 | 0.242 | 0.882 | 0.694 |
| PAMPSA | 0.330 | 0.034 | 0.182 | 0.296 | 0.881 | 0.682 |
| t-PASA | 0.314 | 0.024 | 0.169 | 0.290 | 0.831 | 0.653 |
| i-PASA | 0.338 | 0.049 | 0.194 | 0.289 | 0.818 | 0.647 |
| co-PASA | 0.341 | 0.042 | 0.192 | 0.299 | 0.821 | 0.631 |

Lower index “a” denotes anodic peak, “c” cathodic peak, and “1/2” half-wave potential. Upper index “1” indicates the first oxidation stage and index “2” the second one

Fig. 4 Spectroelectrochemical phenomena in the UV–Vis–NIR range: PANI-HCl (a) and PANI-t-PASA (b). Medium: 0.1 M HClO₄ + 0.9 M NaClO₄ in PC; Electrode: SnO₂; Light path, 7 cm

Earlier [24], spectroelectrochemical studies were carried out for ordinary PANI in aqueous medium in the range of 800–2,000 nm. However, the electrochromic response of the film was quite low. In another publication [25], similar studies in the range between 1,200 and 3,000 nm were carried out in different aqueous acidic solutions. However, significant response in the NIR range observed in this paper cannot be compared with the response in visible area because there is no information about the films’ thickness. Figure 3 shows the results of spectroelectrochemical experiments in non-aqueous medium for common PANI and the interpolymer complex of PANI, with t-PASA being the most rigid one among the polyacids studied. First of all,



it should be noted that SnO₂-glass substrates used in this study are transparent enough in the NIR range up to 2300 nm. The noise in the region near 1,400 nm is due to an intense single absorption band of PC in this area. At the same time, PC optical absorption in the range of 1,450–1,700 nm is rather low, and the results obtained there are quite reliable. We should emphasize that the results presented here comprise only comparative spectroelectrochemical investigation of the electrochromic response in the NIR range in the model solution, while in a real electrochromic window, the electrolyte layer can be quite thin (several hundreds of microns), thus making no significant contribution to the total absorbance of the system in this spectral area.

It is obvious from Fig. 4 that more intense modulation of the NIR absorption is achieved by the film prepared in the rigid-chain polyacid. Moreover, ordinary PANI film exhibited even a drop in the NIR absorbance at the potentials above 0.6 V.

It is important that in the case of PANI-t-PASA film, we observe a synchronous change of the visible and NIR absorption (as distinct from PEDOT [26] for which the increase of absorption in the NIR range is accompanied by the decrease in the visible area). The evolution of spectra with potential for PANI complexes with i-PASA and co-PASA is similar to PANI-t-PASA complex except for lower contribution of the NIR absorption and higher contribution of localized polarons absorptions in the former two cases. The evolution of spectra for PANI-PAMPSA complex is similar to PANI-HCl film except for a slightly higher absorption in the NIR range in the former case.

To estimate the efficiency of NIR absorbance modulation for different films, we have used the values normalized to the absorbance of localized polarons (750 nm) [27] for each of them. Figure 5 presents the changes of normalized absorbance for standard polyaniline and the interpolymer complexes of PANI with flexible-chain and rigid-chain polyacids. As you can see, the most intense changes occur in the range of potentials 0.3–0.6 V. This is the evidence that the NIR-absorbing species probably have a radical cation nature.

The results for all the films studied in this paper are summarized in Table 2. The complexes with more rigid-chain polymeric acids (co-PASA and t-PASA) provide more intense modulation of absorbance in the NIR range.

Therefore, these materials may be considered as promising candidates for use in “smart windows” for thermal radiation flow control in architectural glazing.

For some, for example biological applications, it is important that the film remains electroactive at high pH of the medium. Figure 6 presents the results of cyclic voltammetry in NH₄ClO₄ solutions with different pH in

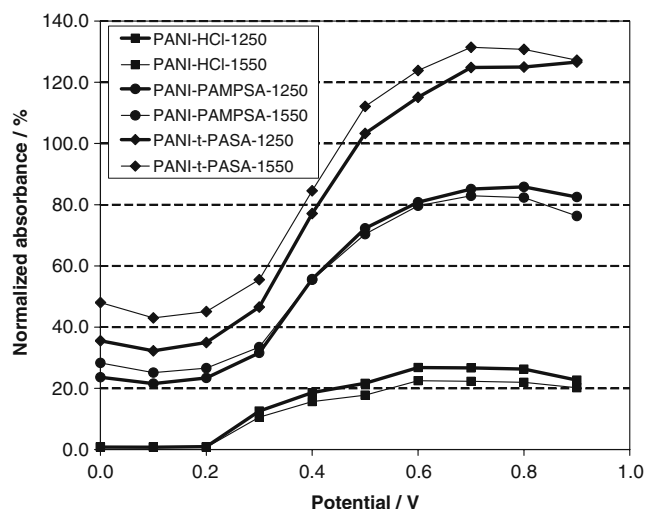


Fig. 5 Changes of normalized (to the absorbance of localized polarons 750 nm) absorbance at 1,250 and 1,550 nm depending on the potential for the films of ordinary PANI and different interpolymer complexes

the range of potentials, corresponding to the first oxidation stage.

Common polyaniline film exhibits “normal” cathodic shift [28] of the peak position only within the pH range 0.5–2. Moreover, after cycling at pH 5, where this film still exhibited some CV peaks, the film being transferred back into the 1 M acid solution (pH 0.5) completely lost its electroactivity. Similar phenomena were observed for ordinary PANI earlier in [19, 29]. However, in [29], the loss of electroactivity was not completely irreversible as in our case, possibly due to higher film thickness.

On the contrary, the interpolymer complex of polyaniline with, for example, co-PASA (Fig. 6b) exhibits “normal” cathodic shift of the peak position within the pH range 0.5–5. Probably, bulky unmovable acidic dopant adjusts the concentration of protons inside and in the vicinity of the film and serves as a “buffer” [30]. A similar widening of

Table 2 Maximum values of normalized (to the absorbance of localized polarons 750 nm) absorbance (A_{\max}) and dynamical ranges of absorbance modulation (ΔA) in the NIR range for the films of different interpolymer complexes

| | 1,250nm | | 1,550nm | |
|--------------|------------|------------|------------|------------|
| | ΔA | A_{\max} | ΔA | A_{\max} |
| PANI-HCl | 26.1 | 26.8 | 21.8 | 22.5 |
| PANI-PAMPSA | 64.3 | 85.8 | 57.8 | 82.9 |
| PANI-i-PASA | 84.4 | 108.8 | 77.4 | 113.4 |
| PANI-co-PASA | 99.8 | 121.1 | 92.6 | 119.9 |
| PANI-t-PASA | 94.3 | 126.6 | 88.4 | 131.4 |

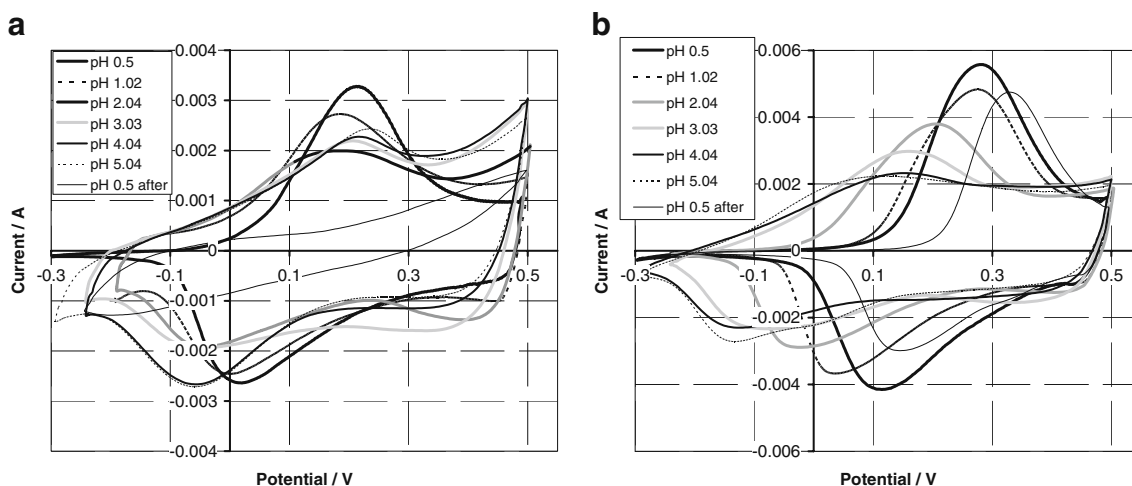


Fig. 6 Dependence of electroactivity in the range of potentials of the first oxidation stage on pH of aqueous solutions of 1 M (HClO₄ + NH₄ClO₄) for different PANI films on SnO₂ electrode: common PANI–HCl (a) and interpolymer complex PANI–co-PASA (b)

the electroactivity range, but only up to pH 3, was observed in [19] for ordinary PANI in the electrolytes containing low molecular sulfonic acids. Therefore, the nature of the acidic group seems to play an important role in this case. It is interesting that after cycling at pH 5, when returned into the initial solution of pH 0.5, the interpolymer complex still retains electroactivity, although with a lesser redox charge. This fact deserves a special investigation, which will be the subject of our future work. In [31], reversible electrochemical behavior up to pH 4 was demonstrated for PANI films prepared in the presence of poly(styrene sulfonic acid), which also has flexible backbone.

Table 3 summarizes the results of cyclic voltammetry at high pH. It is seen that if we take as a criterion cathodic (negative) shift ($\Delta E_{1/2}$) of the half-wave potential ($E_{1/2}$) depending on pH, PANI–co-PASA interpolymer complexes have the widest pH range of electroactivity, followed by PANI–i-PASA, which also possesses close value of the

half-wave potential in HCl (Table 1). Most possibly, this due to the mixed structure of the interpolymer complex in this case. PANI–HCl films exhibited the worst results, followed by PANI–t-PASA and PANI–PAMPSA, which, in accordance with the above discussion on the structure of interpolymer complexes and the results of electrochemical characterization in HCl, resemble common PANI most of all. Another interesting observation is the fact that when the films were returned again into 1 M HClO₄ (pH 0.5) after cycling at pH 5, PANI–co-PASA and PANI–i-PASA exhibited the smallest anodic shift of the half-wave potential among the films tested, indicating that they suffered the least damage.

At the same time, paper [32] reports that the range of electrochemical activity for the films prepared from chemically synthesized PANI–PAMPSA extends up to pH 9, which is much higher than for the electrodeposited PANI–PAMPSA films in our case. This may be due to the

Table 3 Values of the half-wave potential ($E_{1/2}$) determined from CV experiments at different pH and shifts of the half-wave potential ($\Delta E_{1/2}$) at every pH step for common PANI and PANI interpolymer complexes studied

| | $E_{1/2}$ (V) | | | | | | |
|------------------|---------------|--------|--------|--------------|--------------|--------------|-------|
| pH | 0.5 | 1.02 | 2.04 | 3.03 | 4.04 | 5.04 | 0.5 |
| PANI–HCl | 0.115 | 0.094 | 0.071 | <i>0.078</i> | <i>0.079</i> | <i>0.088</i> | – |
| $\Delta E_{1/2}$ | | –0.021 | –0.023 | <i>0.007</i> | <i>0.001</i> | <i>0.009</i> | – |
| PANI–PAMPSA | 0.165 | 0.159 | 0.079 | 0.038 | 0.027 | <i>0.065</i> | 0.212 |
| $\Delta E_{1/2}$ | | –0.007 | –0.080 | –0.042 | –0.011 | <i>0.038</i> | 0.047 |
| PANI–t-PASA | 0.171 | 0.143 | 0.078 | 0.023 | <i>0.032</i> | <i>0.028</i> | 0.226 |
| $\Delta E_{1/2}$ | | –0.029 | –0.065 | –0.056 | <i>0.009</i> | –0.004 | 0.055 |
| PANI–i-PASA | 0.202 | 0.164 | 0.108 | 0.069 | 0.006 | –0.005 | 0.244 |
| $\Delta E_{1/2}$ | | –0.038 | –0.056 | –0.039 | –0.063 | –0.011 | 0.042 |
| PANI–co-PASA | 0.199 | 0.156 | 0.091 | 0.040 | 0.012 | –0.012 | 0.236 |
| $\Delta E_{1/2}$ | | –0.043 | –0.065 | –0.051 | –0.028 | –0.024 | 0.039 |

Values in italics indicate abnormal (positive or zero) shift of $E_{1/2}$ with the increase of pH

higher PANI/PAMPSA ratio in the chemically prepared interpolymer complexes where this ratio is determined only by the composition of initial solution, while in the electro-deposited films, this ratio may depend on many other parameters and may differ from the electrochemical bath composition. However, it should be noted that the shape of CVs at different pH presented in [32] look rather strange, and no attempts were made to reproduce initial CV of the film after cycling it at high pH. In any case, according to our own experience, the electrodeposited PANI–PAMPSA films possess much better adhesion to, for example, FTO glass substrates than the solution-cast analogs, which is also true for other interpolymer complexes studied in our paper.

Also, the films of interpolymer complexes were tested for ammonia sensing by using their optical response. Optical response sensor has one serious advantage before the electrical response sensor: Its operation is practically independent of the humidity [8].

The main drawback of common polyaniline film, which contains hydrochloric acid, is the formation after exposition to ammonia vapors of solid ammonium chloride, which increases scattering in the film and reduces the accuracy. To eliminate a scattering influence of solid ammonium chloride or aqueous vapors, which sometimes formed dew on the samples during the exposition, for each of the films, the values of optical absorbance were normalized to the absorption at the red edge of spectrum recording range (1,050 nm) taken as 50%. The influence of scattering, which usually increases with the decrease of the wavelength of light, is clearly seen for PANI–HCl film in the higher energy part of Fig. 7a. On the contrary, the films of interpolymer complexes, which can be completely washed off the hydrochloric acid without any significant deprotonation, exhibit much more clear response (Fig. 7b).

In Fig. 8, optical response curves (at 650 nm) are presented for the films of ordinary polyaniline and the interpolymer complex with i-PASA. Initial absorbance of the film before the exposition was taken as zero. It is clear that the interpolymer complex PANI–i-PASA outperforms ordinary polyaniline in this application concerning the amplitude of response, demonstrating comparable response rate. Unfortunately, at the moment, we cannot give adequate explanation for the decrease in the response curves at long exposition times.

The values of optical response time (Δt) and amplitude (ΔA) were determined at the end of a “rapid” stage of response (as shown in Fig. 8), after which a slower relaxation stage begins. Although PANI–HCl films exhibited fastest response in this experiment, the response amplitude is comparable with experimental error. If we analyze the operation characteristics thus calculated for different interpolymer complexes in this application (Table 4), we can notice that the complexes with flexible and semi-flexible polyacids exhibit the best results. Surprisingly, PANI–i-PASA complexes were a leader in this application also, similarly to the previous CV tests at high pH.

If we are going to compare our results with those published in the literature, we should take into account several important points. First of all, this is humidity of the atmosphere. In [33], films of ordinary HCl-doped chemically synthesized PANI were used for sensing NH_3 content in NH_3/N_2 mixture and demonstrated fast (up to 15 s) linear optical response in the range of ammonia concentrations from 180 to 18,000 ppm. However, the gas mixture used in this paper seems to contain no water vapors at all. In our case, the fast response observed for ordinary electro-deposited PANI film is in rather good agreement with this paper, but the above discussed scattering in the presence of

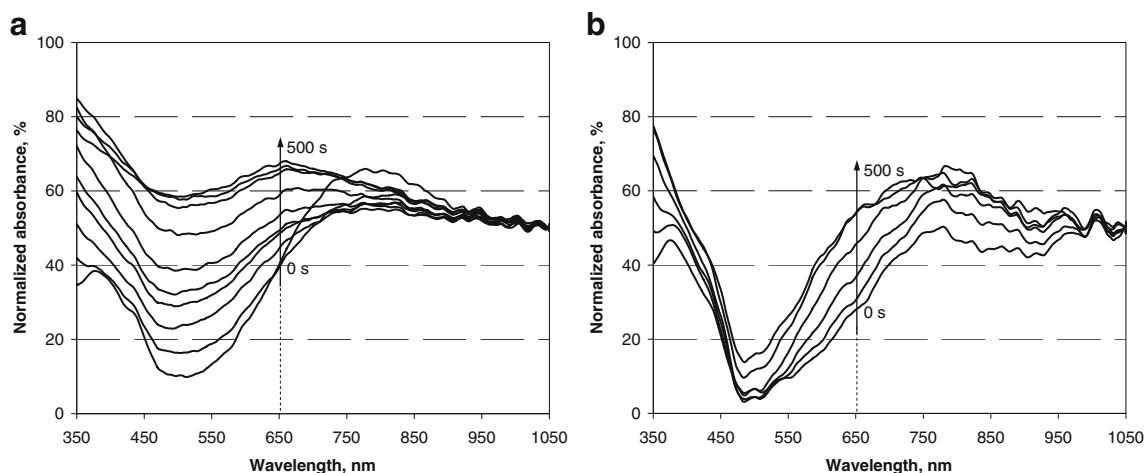


Fig. 7 Evolution of normalized absorption spectra for the films of ordinary PANI–HCl (**a**) and interpolymer complex PANI–PAMPSA (**b**) during exposition to aqueous ammonia vapors with ammonia partial pressure of 1.4 mmHg (~1,850 ppm)

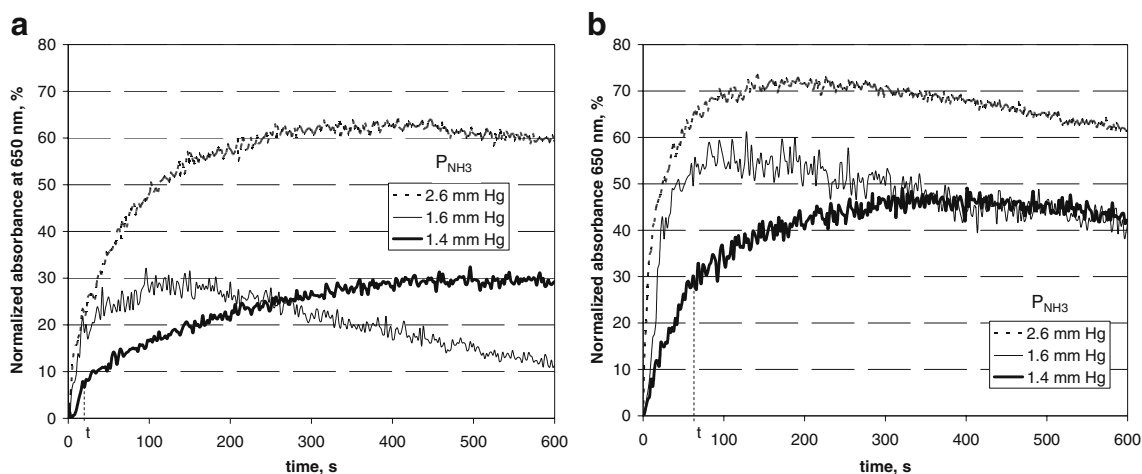


Fig. 8 Optical response at 650 nm of the films of PANI–HCl (a) and interpolymer complex PANI–i-PASA (b) after exposition to aqueous ammonia vapors at different ammonia partial pressure

water vapors significantly limits the applicability of ordinary PANI in humid atmosphere. Similar results in similar dry NH₃/N₂ atmosphere were obtained for PANI–PMMA (polymethylmethacrylate) composite in [8] in the range of concentrations of 10 to 4,000 ppm. But the response time was much longer in this case (1 min and more), which is due to the presence of inert PMMA in the composite. In this respect, our interpolymer complexes resemble the PANI–PMMA composite: The polyacids are inert to the influence of ammonia, while the presence of unmovable sulfonic groups may even interfere with the detection. Nevertheless, some of our films for 1,850 ppm concentration demonstrated faster response (42 s). PANI doped with camphorsulfonic acid (CSA) is a closer analog to our interpolymer complexes due to the presence of sulfonic groups. In [8], PANI–CSA films were tested for their NIR optical response to ammonia at conditions of controlled (30–70% RH) humidity of the gas mixture. However, the response times reported in this paper for 400 ppm concentration of ammonia are rather long—up to 5 min.

Therefore, the optical response characteristics demonstrated by the interpolymer complexes of PANI with

flexible and semi-flexible polyacids studied in this paper are quite comparable with those reported earlier notwithstanding that we made no special attempts to optimize their operation.

Conclusions

Thus, in this paper, we have analyzed some possible applications of the films prepared from interpolymer complexes of PANI with poly(amidosulfonic acids) distinguished by different rigidities of the polyacid matrix and different distance between the sulfonic groups. We have compared the operation characteristics of such interpolymer complexes in electrochromic devices modulating absorption in the near-infrared region in ammonia optical sensor as well as tested their electroactivity at higher pH values in view of biosensing applications.

Thanks to intensive potential-controlled absorption in the near-infrared spectral range, PANI interpolymer complexes with rigid-chain polyacids can be considered as promising candidates for “smart” windows for thermal radiation control.

Table 4 Optical response times (Δt) and normalized amplitudes (ΔA) for the films of different interpolymer complexes after exposition to aqueous ammonia vapors with different ammonia partial pressure

| PANI acid | 1.6mmHg (~2,100ppm) | | 1.4mmHg (~1,850ppm) | |
|--------------|---------------------|----------------|---------------------|----------------|
| | Δt (s) | ΔA (%) | Δt (s) | ΔA (%) |
| PANI–HCl | 18 | 21.8 | 18 | 7.8 |
| PANI–t-PASA | 38 | 15.4 | 87 | 15.3 |
| PANI–co-PASA | 34 | 19.0 | 106 | 20.3 |
| PANI–PAMPSA | 10 | 19.8 | 42 | 22.2 |
| PANI–i-PASA | 24 | 42.9 | 62 | 30.2 |

Due to the presence of bulky unmovable polyacid anion, which can serve as a buffer of protons, the interpolymer complexes of polyaniline with polymeric sulfonic acids possess much wider pH range of electroactivity than common PANI. In this application, the complexes with semi-rigid-chain polyacids and flexible-chain polyacids exhibited the best results.

The interpolymer complexes of PANI with semi-rigid-chain polyacids and flexible-chain polyacids can be considered as promising materials for the development of optical sensors for ammonia.

At the same time, during this study, we have found many interesting phenomena, each of them deserving a special investigation. We purposely did not present here more detailed studies on these phenomena because the volume of a single paper is not at all enough for careful investigation of the mechanisms leading to the described differences in behavior of the interpolymer complexes of polyaniline. This will be the subjects of our several future papers.

Acknowledgments This work was supported by the International Science and Technology Center, project ISTC 3718 and the Russian Foundation for Basic Research, grant 07-03-92176-NTsNI. The authors are very thankful to Prof. V.A. Tverskoj from Moscow State Academy of Fine Chemical Technology for providing us with the rigid-chain and semi-rigid-chain polymeric sulfonic acids used in this study.

References

- Gribkova OL, Nekrasov AA, Isakova AA, Ivanov VF, Vannikov AV (2006) *Russ J Electrochem* 42:1085–1092
- Ljutov V, Georgiev G, Tsakova V (2009) *Thin Solid Films* 517:6681–6688
- Bernard MC, Hugot-Legoff A (1999) *Synth Met* 102:1342–1345
- Jelle BP, Hagen G (1999) *Sol Energy Mat Sol Cells* 58:277–286
- De Paoli M-A, Nogueira AF, Machado DA, Longo C (2001) *Electrochim Acta* 46:4243–4249
- Hechavarria L, Hu HL, Rincon ME (2003) *Thin Sol Films* 441:56–62
- Trojanowicz M, Krawczyk TKV, Zmorzynska M, Campanella L (1997) *Electroanalysis* 9:1062–1066
- Chabukswar VV, Pethkar S, Athawale AA (2001) *Sens Actuat B* 77:657–663
- Nicho ME, Trejo M, Garcivalenzuela A, Saniger JM, Palacios J, Hu H (2001) *Sens Actuat B* 76:18–24
- Christie S, Scorsone E, Persaud K, Kvasnik F (2003) *Sens Actuat B* 90:163–169
- Simon E, Halliwell CM, Toh CS, Cass AEG, Bartlett PN (2002) *Bioelectrochemistry* 55:13–15
- Yu X, Sotzing GA, Papadimitrakopoulos F, Rusling JF (2003) *Anal Chem* 75:4565–4571
- Snejdarkova M, Svobodova L, Evtugyn G, Budnikov H, Karyakin A, Nikolelis DP, Hianik T (2004) *Anal Chim Acta* 514:79–88
- Nekrasov AA, Gribkova OL, Eremina TV, Isakova AA, Ivanov VF, Tverskoj VA, Vannikov AV (2008) *Electrochim Acta* 53:3789–3797
- Guseva MA, Isakova AA, Gribkova OL, Tverskoj VA, Ivanov VF, Vannikov AV, Fedotov YuA (2007) *Polym Sci A* 49:4–11
- Sun L, Liu L-M, Clark R, Yang SC (1997) *Synth Met* 84:67–68
- Kirsh YuE, Fedotov YuA, Iudina NN, Katalevskii EE (1990) *Polym Sci B* 32:403–404
- Benyaich A, Deslouis C, ElMoustafid T, Musiani MM, Tribollet B (1996) *Electrochim Acta* 41:1781–1785
- Pruneanu S, Csahók E, Kertész V, Inzelt G (1998) *Electrochim Acta* 43:2305–2323
- Koziel K, Lapkowski M, Vieil E (1997) *Synth Met* 84:91–92
- Rabinovich VA, ZYa K (1977) *Kratkii khimicheskii spravochnik (Short chemical handbook)*. Khimiya, Moscow, p 271
- Thieste D, Byker HJ, Baumann K, Srinivasa R (2001) *US Patent* 6,193,912
- Granqvist CG (2002) *Handbook of inorganic electrochromic materials*. Elsevier Science B.V., Amsterdam, p 14 (Second impression)
- Yang SC, Clark RL, Liao H, Sun L (1995) *Proc SPIE* 2528:198–208
- Abd-Elwahed A, Holze R (2003) *Russ J Electrochem* 39:391–396
- Lapkowski M, Pron A (2000) *Synth Met* 110:79–83
- Nekrasov AA, Ivanov VF, Vannikov AV (2000) *J Electroanal Chem* 482:11–17
- Huang W-S, Humphry BD, MacDiarmid AG (1986) *J Chem Soc Faraday Trans 1* 82:2385–2400
- Hirai T, Kuwabata S, Yoneyama H (1989) *J Chem Soc Faraday Trans 1(85)*:969–976
- Yue J, Epstein AJ (1992) *J Chem Soc Chem Commun* 21:1540–1542
- Kang Y, Lee MH, Rhee SB (1992) *Synth Met* 52:319–328
- Tarver J, Yoo JE, Dennes TJ, Schwartz J, Loo Y-L (2009) *Chem Mater* 21:280–286
- Jin Z, Su Y, Duan Y (2001) *Sens Actuat B* 72:75–79