

Effect of matrix domination in PANI interpolymer complexes with polyamidosulfonic acids

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Abstract Various polyaniline (PANI) interpolymer complexes with polyacids in the form of molecular solutions were synthesized by chemical oxidative polymerization of aniline in the presence of water-soluble poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (flexible backbone), poly-*p,p'*-(2,2'-disulfoacid)-diphenylene-terephthalamide (t-PASA, rigid backbone), and their mixtures in different ratios. The complexes were characterized by UV-Vis-near infrared spectroscopy in solutions; also, the films' drop-casts from these solutions were investigated by cyclic voltammetry, spectroelectrochemical, direct current (DC) conductivity, and atomic force microscopy (AFM) measurements. It was shown that the nature of polyacid affects the shape of spectra and the dynamics of their changes. The character of spectral changes during the matrix synthesis of PANI in the presence of mixtures of the rigid-chain and flexible-chain matrixes and the study of spectral properties of the obtained PANI solutions demonstrates the existence of the rigid-matrix domination effect in the process of formation of PANI interpolymer complexes. Spectral properties of the obtained PANI complexes with the mixtures of flexible-chain and rigid-chain polyacids of different ratios

(3:1, 1:1, 1:3, and 1:6) are very similar to those ones for the complex with rigid-chain t-PASA. At the same time, there is a correlation between the electrical conductivity and morphology of the films of PANI complexes and their composition, the conductivity passing through a minimum for the complexes with the polyacid mixtures (6:1, 3:1, and 1:1).

Keywords Polyaniline · Spectroelectrochemistry · Matrix synthesis · Conducting polymers

Introduction

Polyaniline (PANI) is one of the most promising conducting polymers possessing a wide range of interesting optical, electrochemical, and electrical properties as well as good environmental stability. PANI has been extensively studied for its application in sensors, batteries, light-emitting and electrochromic devices, solar cells, etc. [1]. However, the conducting state of PANI (emeraldine salt) is almost completely insoluble in common organic solvents and water. This limits PANI potential application. The main goal of recent studies was to obtain water-soluble or water-dispersed environment-friendly PANI. To prepare water-soluble PANI, a number of authors have carried out the chemical [2–14] and enzymatic [15–19] synthesis of PANI in the presence of polymeric acids of different structure. The polymer acid plays several important roles: (1) to preliminarily associate aniline with the polymer chain [9, 10] and to promote a more selective para-position reaction (head-to-tail aniline polymerization) [7, 16], (2) to provide a polyacid anion for doping of the synthesized PANI, and (3) to produce water-soluble polyaniline. Use of such high molecular weight dopants also improves morphology of the films and extends the electroactivity of the final polymer above pH 7 [12].

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Previously used polyacids, such as poly(styrenesulfonic acid) [3, 5, 13], poly(acrylic acid) [3–5], and poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) [3, 6–12], are distinguished by flexible polymeric backbone. The resulting PANI molecules are located along polyacid chains and form double-strand interpolymer complexes [3, 10]. In this case, the conformations of polyacid and PANI macromolecules changed to match each other.

In papers [10, 11], the matrix polymerization of aniline was carried out in the presence of aromatic polyamides containing sulfonic groups as substituents in the amine fragment of polyamides characterized by the structures with different rigidity [20]. The electronic structure of interpolymer complexes of PANI with these polyamides differs from that of PANI formed in the presence of flexible-chain polymeric sulfonic acids. We have assumed that, in the case of rigid-chain polyacid, only structures in which PANI macromolecules attached as side chains to polyacids (brush-type structure) are possible. In the case of semi-rigid-chain polyacid, the mixed structure is formed in which some of the PANI macromolecular units are situated along polyacid chains, while other units form side chains.

In paper [14], the effect of matrix domination was demonstrated for the first time. It was shown that, in the mixture of poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA, flexible backbone) and poly-*p,p'*-(2,2'-disulfoacid)-diphenylene-terephthalamide (t-PASA, rigid backbone) of the ratio 1:1, the rigid-chain acid exerts the dominant influence on the mechanism of synthesis of PANI interpolymer complexes and their spectral behavior.

In the present work, PANI was obtained by chemical matrix polymerization of aniline in the presence of PAMPSA, t-PASA (Scheme 1), and their mixtures in different ratios. PAMPSA has a high molecular weight (MW 2,000,000) and a flexible polymer backbone which allows it to form a random coil conformation in the presence of strong electrolytes. PAMPSA is distinguished by the presence of a single sulfonic group in each monomeric unit. The molecular weight of t-PASA is ~40,000. t-PASA is characterized by the presence of a pair of acidic groups in each monomeric unit,

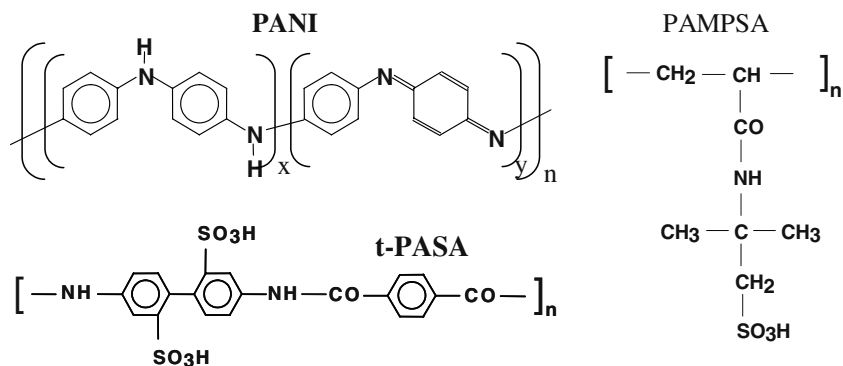
longer distances between the pairs of sulfoacid groups belonging to adjacent monomer units, and a rigid polymer backbone (scheme 1). As was shown in [20], t-PASA macromolecules in water present in the extended coil (or stick) conformation. This conformation remains unchanged with the increase of ionic strength of solution.

Experimental

PAMPSA (Aldrich, MW 2,000,000, 15% aqueous solution) was used without purification. Laboratory-synthesized t-PASA sodium salts [20] were converted into $[H^+]$ forms by means of passing their aqueous solutions through a column filled with a KU-2 cation exchange resin. Polyacids were diluted to the desired concentration and stirred for several days before use. Deionized water was used for diluting the acids. The compositions of PAMPSA/t-PASA mixtures were 12:1, 6:1, 3:1, 1:1, 1:3, and 1:6 with respect to sulfonic groups, taking into account that PAMPSA monomer unit has one sulfonic acid group and t-PASA monomer unit has two sulfonic groups. Molar ratio of aniline/sulfonic group was always kept as one aniline molecule per two sulfonic groups of the polyacids. Freshly distilled aniline was dissolved in the aqueous solutions of polyacids at constant stirring for 1–2 h. In all syntheses, the concentration of aniline was 0.003 M. pH of initial solutions of polyacids with aniline was about 2.8. The oxidative polymerization was started by the addition of ammonium persulfate (APS; 1:1 ratio of APS to aniline) at vigorous stirring for 1 min. Then some part of the reaction solution was transferred into the optical cuvette (1 mm). The polymerization of aniline in the presence of polyacids was performed at room temperature and controlled by in situ optical spectroscopy. The next day, the final solution was dialyzed using a cellulose membrane (ZelluTrans MWCO 8000-10000, Roth) against the deionized water at stirring for 3 days to remove oligomers and any traces of unreacted aniline, APS, and other by-products.

Fast spectroscopic studies in the spectral range 350–950 nm in the course of the synthesis were performed using

Scheme 1 Scheme of PANI, PAMPSA, and t-PASA



an AvaSpec 2048 diode array spectrophotometer (Avantes BV). Spectra in the range of 300–1,800 nm during the synthesis were recorded on a Shimadzu UV 3101 spectrophotometer. PANI films were prepared by drop-casting of a measured volume of the interpolymer complexes solutions onto substrates of equal size: for electrochemical and spectroelectrochemical measurements—onto glass substrates covered with a transparent conducting layer of SnO₂:F with the sheet resistance of approximately 7 Ω per square; for conductivity studies—onto glass substrates; for atomic force microscopy (AFM) studies—onto atomically flat mica substrates. The films were dried at 70 °C. For electrochemical measurements, PANI films were treated in 10% water solution of CaCl₂ to prevent dissolution of the films in aqueous electrolyte and to ensure better adhesion to the substrate. According to interferometric data (MII-4 by LOMO with CCD video camera), thicknesses of the films ranged within 500–900 nm. The measurements were executed in three different areas of the film, and the final averaged value was further used for DC conductivity calculations. Roughness of the films, according to the AFM measurements, does not exceed 30–40 nm, so it is negligible compared to the thickness. Cyclic voltammetry (CV) and spectroelectrochemical experiments were carried out in air in a three-electrode regime in a 1 M HCl (chemically pure) aqueous solution in a specially designed single-compartment spectroelectrochemical cell. A separate compartment for an Ag/AgCl reference electrode was connected to the main volume of the cell by a salt bridge. Pt foil with an area of approximately 10 cm² (double side) was used as a counter electrode. For spectroelectrochemical experiments, the cell was fixed in a variable-length cell holder of the AvaSpec 2048 equipped with flexible fiber-optic light guides. A computer-driven combination of an HA-501G potentiostat/galvanostat (Hokuto Denko Ltd.) and a digital storage oscilloscope Nicolet 2090 (Nicolet Inc.) was used for controlling and registering the electrochemical parameters. All the potentials in this paper are presented vs. Ag/AgCl reference electrode.

DC conductivity measurements were carried out by a four-probe method using a computer-controlled combination of Keithly 236 and Keithly 2601 source/measure devices. In order to ensure ohmic electrical contact with the films, a series of six parallel gold electrodes (7×1.5 mm), the distance between the electrodes being 1.0 mm, was deposited through a special mask onto each of the samples using a vacuum thermal evaporation technique. Each measurement consisted in performing of a linear sweep of current between 0 and 10 μA and registration of the voltage arising between the two inner electrodes. In each four-probe measurement, only four of the six electrodes were used followed by a displacement of the whole system of contacts by one electrode left or right. After three such measurements, the averaged

slope of the obtained current–voltage linear dependences was used for specific conductivity calculations, taking into account the length of electrodes, the distance between them, and the film thickness.

AFM topographic images of the films dried in ambient conditions were taken on a Nanoscope IV (Veeco).

Results and discussion

Typical evolution of the electron absorption spectra of PANI solutions in the course of chemical polymerization of aniline in the presence of various polyacids is presented in Fig. 1. For the flexible-chain PAMPSA (Fig. 1a), at the initial stage, we observe the growth of absorption near 375 nm and near 600 nm (quinone-imine form of PANI). At the second stage, we can see a rapid shift of absorption maximum to the long-wavelength area, which corresponds to the formation of localized polarons (750 nm) accompanied by simultaneous growth of absorption of localized cation radicals (430 nm) [21]. In the case of polymerization in the presence of rigid-chain t-PASA (Fig. 1d) in the initial stage, the growth of absorption in the range of 400 and 650–950 nm is observed. So, we see an intense absorption in the NIR region (950 nm and longer) which corresponds to the formation of delocalized polarons [22, 23]. In the second stage of polymerization, we do not observe absorbance shift, and the growth of radical cations absorption is weak.

The character of spectral changes during aniline polymerization in the presence of mixtures of PAMPSA and t-PASA (ratios 3:1, 1:1, 1:3, 1:6; Fig. 1c) is very similar to PANI synthesis in t-PASA. During the polymerization of aniline in the presence of polyacid mixture (6:1), the influence of flexible-chain PAMPSA is slightly observed (Fig. 1b). We may see the growth of absorbance of localized polarons and decrease of absorption in the NIR region. In the case of aniline polymerization in the presence of polyacid mixture with the ratio of 12:1, the character of spectral changes is almost the same as in PAMPSA.

So, we may suppose that the structures of the interpolymer complexes of PANI and polyacid mixtures (3:1; 1:1; 1:3; 1:6) are the same as in the case of PANI complex with pure t-PASA (brush-type structure with PANI fragments attached as side chains). Thus, during PANI synthesis in the presence of the polyacid mixtures in certain range of PAMPSA/t-PASA ratios, the dominating influence of the rigid-chain polyacid is observed; even so, we use the mixture with higher content of the flexible-chain polyacid. Preliminary analysis of small-angle X-ray scattering (SAXS) in solutions shows that PANI–t-PASA complex is practically a monodispersed system and PANI–PAMPSA complex is a polydispersed system. PANI complexes with the polyacid mixtures (6:1; 3:1; 1:1; 1:3; 1:6) are close to

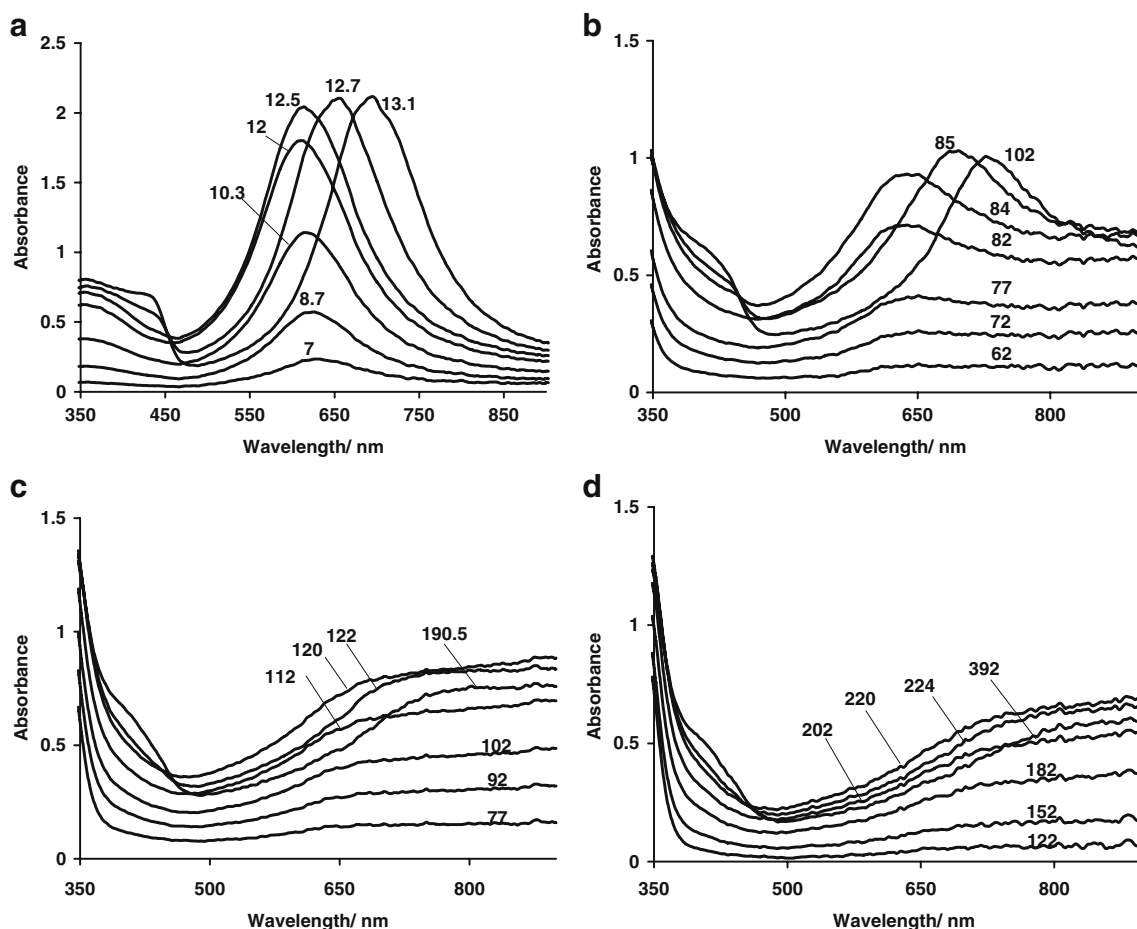


Fig. 1 Evolution of the electronic absorption spectra of reaction solutions during aniline polymerization in the presence of PAMPSA (a), PAMPSA-t-PASA mixture of ratios 6:1 (b) and 1:1 (c), and t-PASA (d). Numbers near the curves represent the time of synthesis in minutes

PANI-t-PASA complex (similar to the spectral characteristics). We are inclined to consider these results as an argument in favor of well-ordered brush-type structure of PANI-t-PASA complex with π -stacked PANI side chains. The more detailed data of these measurements will be discussed in the next paper.

The appropriate kinetic curves of the localized polaron absorption (750 nm) of the reaction solutions (Fig. 2) show that the fastest polymerization rate is observed in the presence of flexible-chain PAMPSA, while the lowest rate is observed in t-PASA with the rigid backbone. Considering limited rigidity of PANI chains in the conjugated emeraldine form, it is reasonable to assume that long duration of the induction period is associated with the difficulty of conformational changes in macromolecules of t-PASA necessary for proper spatial arrangement of sulfonic groups relative to PANI amine moieties. This process is additionally hampered by the longer distance between sulfonic groups belonging to neighboring monomer units (as is seen from their structural formulas) in t-PASA compared to PAMPSA. Evidently, all the factors mentioned above will provide not only increase of the duration of induction

period but also a decrease of the length of PANI molecules and a change in their electronic structure.

As for the polyacid mixtures, we may assume that a growing PANI chain is capable of forming ionic bonds

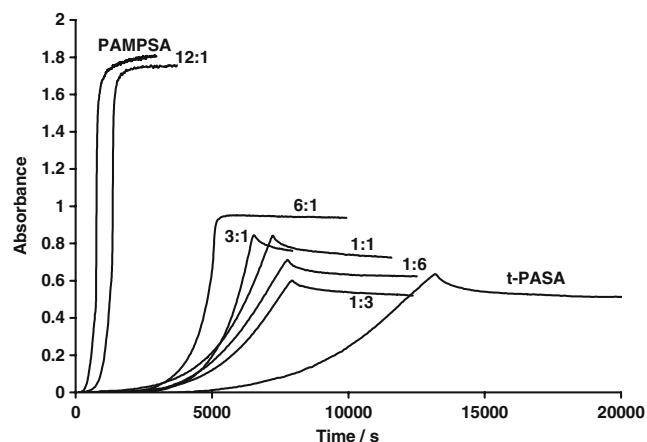


Fig. 2 Kinetics of the absorbance changes of solutions at 750 nm during aniline polymerization in the presence of PAMPSA, t-PASA, PAMPSA/t-PASA mixtures of different ratios

simultaneously with the flexible-chain PAMPSA and the rigid-chain t-PASA. In these conditions, the presence of rigid-chain t-PASA may force PAMPSA (or a part of its macromolecule) to change its conformation from random coil to the extended coil, thus making the whole structure to look more like PANI–t-PASA complex. Therefore, the PANI synthesis in the presence of polyacid mixtures proceeds more or less similarly to that in the presence of rigid-chain t-PASA, which is characterized by longer induction period. On the other hand, PAMPSA has higher molecular weight, and this results in a higher local concentration of monomeric aniline near its macromolecule. This leads to decreasing of the induction period. Due to the competition of these two opposite influences, the rates of aniline polymerization in the presence of polyacid mixtures (ratios 6:1, 3:1, 1:1, 1:3, 1:6) and durations of the induction period are close to each other and occupy intermediate position between the syntheses in pure PAMPSA and t-PASA. Moreover, this competition is additionally complicated by a nonlinear autocatalytic character of PANI synthesis, which results in unpredictable fluctuations in the matrix synthesis rate in the presence of the polyacid mixtures. These fluctuations are responsible, in particular, for “abnormal” sequence of the kinetic curves for 1:6 and 1:3 complexes in Fig. 2; however, this fact cannot alter our main conclusion about intermediate rates of the matrix syntheses in the presence of the polyacid mixtures. Finally, in the case of polyacid mixture 12:1, the influence of rigid-chain t-PASA is so small that the synthesis rate is close to that of PANI synthesis in the presence of pure PAMPSA.

The UV-Vis-NIR spectra of the final solutions of PANI interpolymer complexes after dialysis are presented in Fig. 3. We may see that the absorption of localized polarons (near 750 nm) is most intensive in the case of the flexible-chain polyacid and mixture of PAMPSA with t-PASA 12:1. On the contrary, the absorbance in the NIR region is much more intensive in the case of rigid-chain polyacid. The absorbance spectra of PANI solutions prepared in the presence of mixtures (3:1, 1:1, 1:3, and 1:6) are very similar to the spectrum of interpolymer complex PANI with t-PASA. PANI complex with the mixture 6:1 represents a transitional state of the system.

One can see from Table 1 that the ratios of absorption of the localized polarons (750 nm) to that of the radical cations (430 nm) and delocalized polarons (1,700 nm) are the biggest in the interpolymer complex PANI–PAMPSA. In the case of PANI complexes with polyacid mixtures (3:1, 1:1, 1:3, 1:6), these values are smaller and close to the PANI–t-PASA complex.

In the paper [22], it was shown that correlation between absorption of localized and delocalized polarons depends on electronic interaction between adjacent PANI chains. Weak interaction leads to higher absorption of localized polarons.

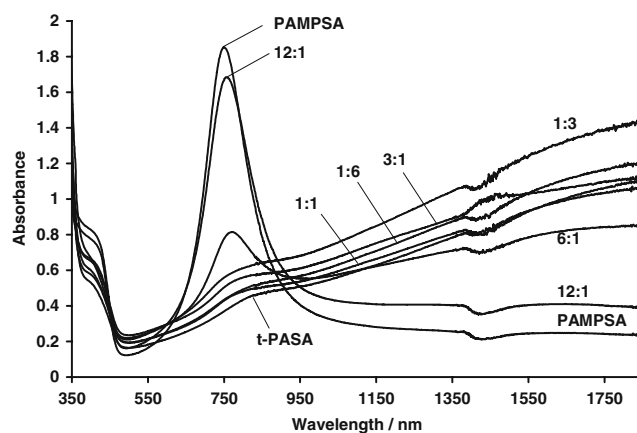


Fig. 3 UV-Vis-NIR absorption spectra of solutions of PANI–polyacid complexes prepared by chemical polymerization of aniline in the presence of PAMPSA, t-PASA, and PAMPSA–t-PASA mixtures of different ratios

This is the case for flexible polyacid which gives double-strand macromolecular structure of the interpolymer complex [3, 10] and has a longer conjugation length. High absorption of delocalized polarons may be due to π – π stacking of adjacent PANI molecules [11, 22]. The PANI complex with rigid-chain t-PASA may have the structure with PANI fragments as side chains of the polyacid macromolecule (brush-type structure) [10, 11], and the π – π stacking in such structure is more probable. So, the PANI complexes with t-PASA and polyacid mixtures (3:1, 1:1, 1:3, and 1:6) have probably the same brush-type structure with π – π stacking of adjacent PANI molecules. But PANI fragments in such side chains presumably have a shorter length.

The electrochemical and spectroelectrochemical properties of the films of interpolymer complexes are influenced by the structure of polyacids also. Before these experiments, the films were cycled in the range of potentials corresponding to the first oxidation peak until obtaining a stable reproducing CV curve.

Figure 4 shows the results of spectroelectrochemical experiments in 1 M HCl at different potentials for the

Table 1 The ratios of absorption of the localized polarons (750 nm) to absorption of the radical cations (430 nm) and delocalized polarons (1,700 nm) in the interpolymer complexes of PANI with polyacids

	Absorbance ratio	
	$A_{750/430}$	$A_{750/1,700}$
PANI–PAMPSA	2.80	7.50
PANI–PAMPSA–t-PASA 12:1	2.40	4.10
PANI–PAMPSA–t-PASA 6:1	1.38	0.93
PANI–PAMPSA–t-PASA 3:1	0.92	0.47
PANI–PAMPSA–t-PASA 1:1	0.90	0.42
PANI–PAMPSA–t-PASA 1:3	1.08	0.41
PANI–PAMPSA–t-PASA 1:6	0.89	0.38
PANI–t-PASA	0.87	0.38

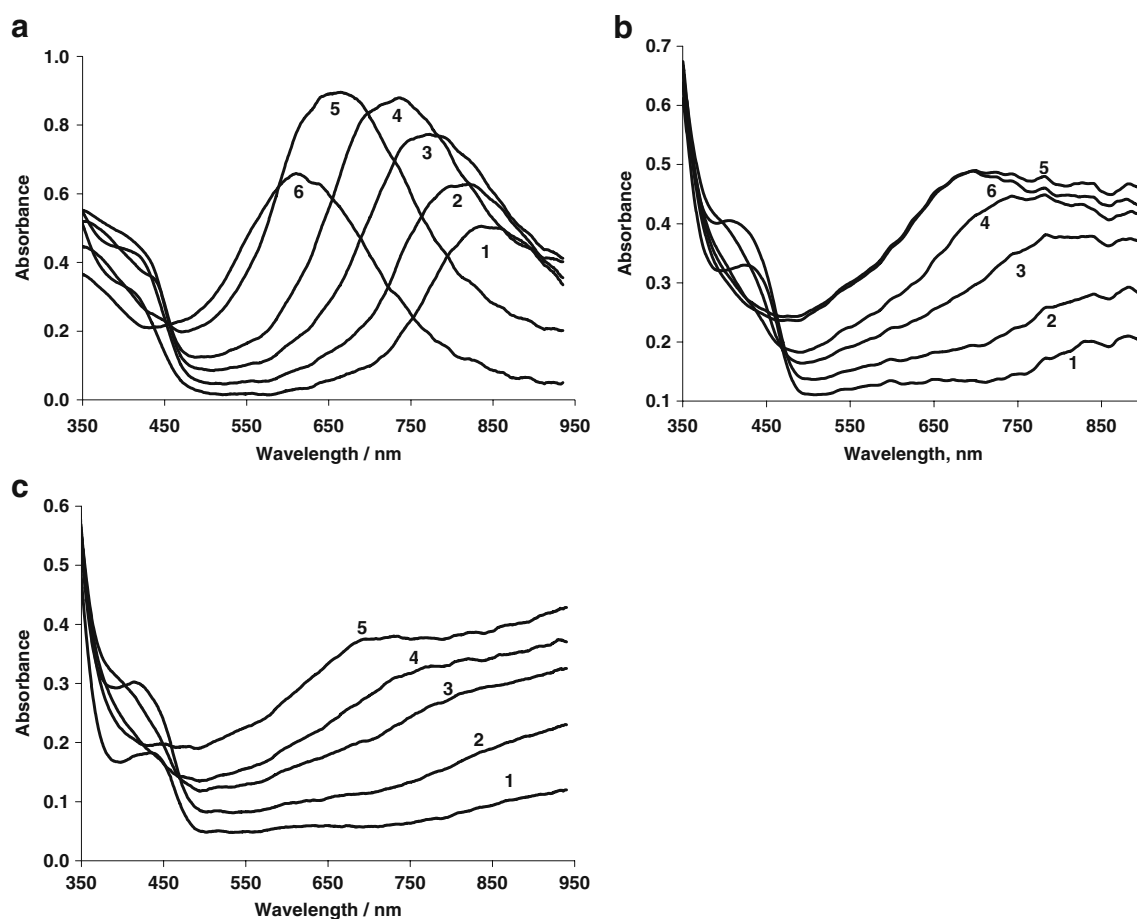


Fig. 4 Absorption spectra of the films of PANI complexes with PAMPSA (a), PAMPSA–t-PASA mixture of ratio 3:1 (b), and t-PASA (c) cast on transparent SnO_2 glass electrodes measured at different potentials: 0.0 V (1), 0.2 V (2), 0.4 V (3), 0.6 V (4), 0.8 V (5), 1.0 V (6) in 1 M HCl

films of interpolymer complexes of PANI with PAMPSA, t-PASA, and PAMPSA–t-PASA (3:1). For PANI–PAMPSA films (Fig. 4a), while increasing the potential up to 1.0 V, we observe a regular shift (analogous to PANI obtained in the presence of inorganic acids) of the well-defined absorption band from the region near 800 nm to the region near 650 nm, indicating the formation of quinoid structures in polyaniline. In contrast to this observation, the corresponding shift of absorption for PANI–t-PASA complexes (Fig. 4c) is very small, and the absorption bands are much less defined. We observe the same situation for the complexes of PANI with the polyacid mixtures (3:1, 1:1, 1:3, and 1:6; Fig. 4b). So, we may suppose that the formation of quinoid structures is hampered for these films.

In Table 2, we can see that the ratio of absorption of the localized polarons (at 0.4 V, 750 nm) to absorption of the delocalized polarons (at 0.4 V, 900 nm) is most intensive in the cases of PANI–PAMPSA and PANI–PAMPSA–t-PASA (12:1). PANI complexes with t-PASA and mixtures (3:1, 1:1, 1:3, 1:6) have much smaller values of this ratio. The PANI complex with polyacid mixture (6:1) represents the transitional state of the system after which the rigid-matrix

domination begins. The ratios of absorption of the localized polarons to the absorption of quinone-imine fragments (0.8 V, 600 nm) are practically the same for all polyacids and their mixtures, so we may suppose about direct conversion of the localized polarons into the quinoid fragments.

Table 2 The ratios of absorption of the localized polarons (750 nm) to absorption of the delocalized polarons (900 nm) and quinone-imine forms (600 nm) in interpolymer complexes of PANI with polyacids

	Absorbance ratio	
	$A_{750/900}$	$A_{750/600}$
PANI–PAMPSA	1.50	1.05
PANI–PAMPSA–t-PASA 12:1	1.72	0.99
PANI–PAMPSA–t-PASA 6:1	1.28	1.04
PANI–PAMPSA–t-PASA 3:1	1.04	0.92
PANI–PAMPSA–t-PASA 1:1	0.92	1.02
PANI–PAMPSA–t-PASA 1:3	0.95	0.89
PANI–PAMPSA–t-PASA 1:6	0.89	1.03
PANI–t-PASA	0.87	1.00

The results of the conductivity measurements of the films prepared by drop-casting of the interpolymer complexes of PANI are presented in Table 3.

It is seen that PANI-t-PASA, PANI-PAMPSA, and PANI-PAMPSA-t-PASA (12:1) exhibit significantly higher conductivity than other complexes. The reason for high conductivity of PANI-PAMPSA complexes is higher concentration of conjugated polarons. In this case, charge transport occurs preferentially along the system of large molecules, and the number of intermolecular barriers is minimized. For PANI-t-PASA, there is quite a different situation. Charge transport is probably realized via the system of well-ordered π - π -stacked PANI side chains existing in this brush-type complex. Also, as these complexes comprise straight beams due to the rigidity of t-PASA, an interpenetrating network may be formed between adjacent brush-type complexes located in parallel to each other. This structure decreases the height of intermolecular barriers. The conductivity of PANI-PAMPSA-t-PASA (12:1) is slightly higher than the conductivity of PANI-PAMPSA. The complexes with the polyacid mixtures (6:1, 3:1, 1:1) apparently have neither large content of polaronic fragments nor intense π - π stacking, which results in their lower conductivity.

The results of DC conductivity studies are in good agreement with the AFM data. First of all, it should be emphasized that all films were prepared in the same drop-casting experiment (identical water-saturated atmosphere, identical temperature resulting in identical drying speed). In Fig. 5a, one can see that the intermolecular complex with flexible-chain PAMPSA gives films of well-ordered globular morphology with the globule size of 100–200 nm, while the films of highly conductive PANI-PAMPSA-t-PASA (12:1) complex (Fig. 5b) has even slightly larger globules. At the same time, PANI complexes with the polyacid mixtures (6:1, 3:1, 1:1) give poorly conductive films with poor morphology (Fig. 5c, d, e) represented by a chaotic distribution of smaller nanostructures (about 40 nm). So, it seems that the presence of large quantities of flexible-chain polyacid in the mixture worsens mutual arrangement of molecules in the film. Finally, the well-ordered morphology gradually appears

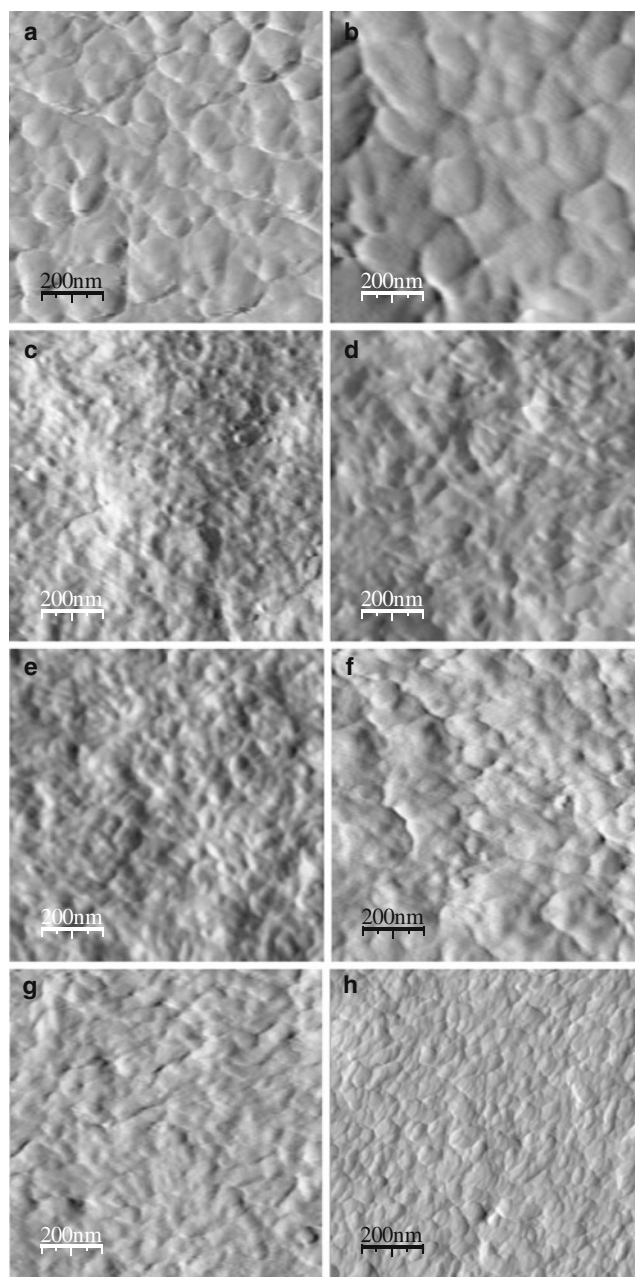


Fig. 5 AFM images of drop-cast films of the interpolymer complexes PANI-PAMPSA (a), PANI-PAMPSA-t-PASA (12:1) (b), PANI-PAMPSA-t-PASA (6:1) (c), PANI-PAMPSA-t-PASA (3:1) (d), PANI-PAMPSA-t-PASA (1:1) (e), PANI-PAMPSA-t-PASA (1:3) (f), PANI-PAMPSA-t-PASA (1:6) (g), and PANI-t-PASA (h)

Table 3 Conductivity of the films of PANI interpolymer complexes

	Conductivity, Scm^{-1}
PANI-PAMPSA	1.5×10^{-2}
PANI-PAMPSA-t-PASA 12:1	2.7×10^{-2}
PANI-PAMPSA-t-PASA 6:1	5×10^{-3}
PANI-PAMPSA-t-PASA 3:1	1×10^{-3}
PANI-PAMPSA-t-PASA 1:1	1×10^{-3}
PANI-PAMPSA-t-PASA 1:3	2×10^{-2}
PANI-PAMPSA-t-PASA 1:6	3×10^{-2}
PANI-t-PASA	5.3×10^{-2}

again, first in the films of 1:3 and 1:6 complexes (Fig. 5f, g) and then in the highly conducting films of PANI-t-PASA complexes (Fig. 5h), the characteristic size of objects growing up to 150 nm. We may reasonably suppose that this improvement of the morphology is due to the above-noted π - π stacking.

It is a very interesting fact that there is an obvious correlation between the uniformity of morphology of the films (Fig. 5) and their conductivity (Table 3).

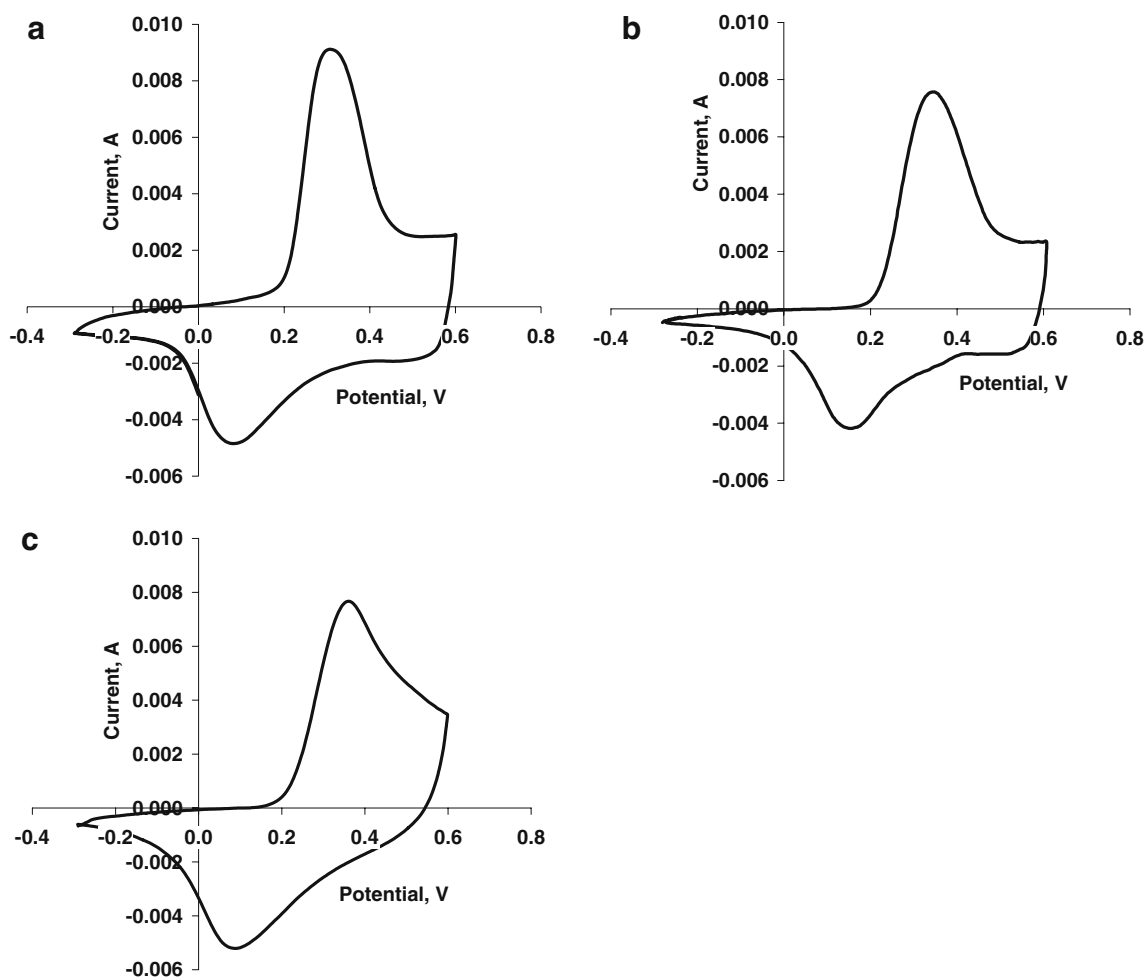
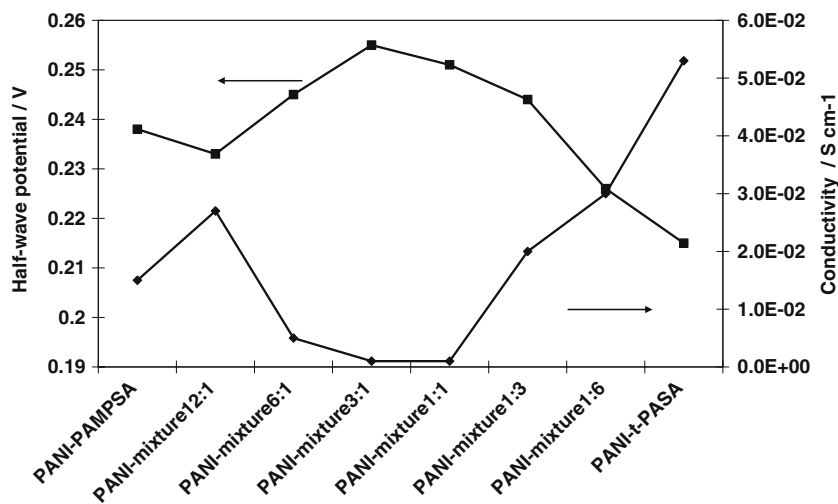


Fig. 6 CV curves for drop-cast films of the interpolymer complexes PANI–PAMPSA (a), PANI–PAMPSA–t-PASA (3:1) (b), and PANI–t-PASA (c) in 1 M HCl aqueous solution, at 50 mV/s within the range of potentials of the first oxidation stage. The electrode (SnO_2 glass) area is 2 cm^2

Figure 6 presents cyclic voltammetry (CV) curves for the drop-cast films of the interpolymer complexes PANI–PAMPSA (a), PANI–PAMPSA–t-PASA (3:1) (b), and PANI–t-PASA (c) in the first oxidation peak. The PANI complexes

with polyacid mixtures (6:1, 3:1, 1:1, 1:3, and 1:6) give very similar CV curves. However, there are differences in the values of half-wave potential of the first redox stage, which are presented in Fig. 7 together with the conductivity values.

Fig. 7 Half-wave potential of the first redox stage and conductivities of the films of PANI interpolymer complexes with PAMPSA, t-PASA, and their mixtures



One can see (Fig. 7) a correlation between the half-wave potential values, AFM, and the conductivity data. Maximum of conductivity corresponds to the minimum of half-wave potential and conversely. The film of PANI–PAMPSA–t-PASA (12:1) complex is composed of larger well-ordered nanostructures and has higher conductivity and lower $E_{1/2}$ ¹ than PANI–PAMPSA complex. This interesting phenomenon will be the subject of a future investigation.

Conclusions

Based on the above-presented experimental data, we may conclude that the rigid-chain polyacid matrix has a predominant influence on the spectral and spectroelectrochemical properties of PANI complexes with mixtures of rigid-chain and flexible-chain polyacids in the range of PAMPSA/t-PASA ratios from 3:1 to 1:6. Judging from the character of synthesis and the spectral data, we may assume that PANI complexes with the polyacid mixtures (3:1, 1:1, 1:3, and 1:6) have structure similar to that of PANI–t-PASA. The complex (6:1) represents a transitional state, while PANI–PAMPSA–t-PASA (12:1) complexes are very much alike PANI–PAMPSA. A weaker effect of the rigid-chain matrix domination is observed for electrochemical, electrical, and morphological properties of these complexes. The electrical and morphological properties of PANI complexes with the polyacid mixtures (6:1, 3:1, 1:1, 1:3, and 1:6) differ from those of PANI–t-PASA. The conductivity and half-wave potential dependences on the complexes composition are complicated and nonmonotonous, an obvious correlation being observed between them.

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References

1. Skotheim TA, Reynolds JR (eds) (2007) *Conjugated polymers: processing and applications*. Handbook of conducting polymers, 3rd edn. Taylor & Francis, London
2. Liu J-M, Yang S (1991) *J Chem Soc Chem Commun* 1529
3. Sun L, Liu L-M, Clark R, Yang SC (1997) *Synth Met* 84:67–68
4. Hu H, Saniger JM, Banuelos JG (1999) *Thin Solid Films* 347:241–247
5. Yang SM, Chen WM, You KS (1997) *Synth Met* 84:77
6. Hechavarria L, Hu H, Rincon ME (2003) *Thin Solid Films* 441:56–62
7. Yoo JE, Cross JL, Bucholz TL, Lee KS, Espe MP, Loo Y-L (2007) *J Mater Chem* 17:1268–1275
8. Yoo JE, Bucholz TL, Jung S, Loo Y-L (2008) *J Mater Chem* 18:3129–3135
9. Ivanov VF, Gribkova OL, Cheberjako KV, Nekrasov AA, Tverskoj VA, Vannikov AV (2004) *Russ J Electrochem* 40:299
10. Guseva MA, Isakova AA, Gribkova OL, Tverskoi VA, Ivanov VF, Vannikov AV, Fedotov YuA (2007) *Polym Sci A* 49:4–11
11. Gribkova OL, Nekrasov AA, Ivanov VF, Sazikov VI, Razova AB, Tverskoj VA, Vannikov AV (2010) *Polymer* (in print)
12. Tarver J, Yoo JE, Dennes TJ, Schwartz J, Loo Y-L (2009) *Chem Mater* 21:280–286
13. Tengstedt C, Crispin A, Hsu C-H, Zhang C, Parker ID, Salaneck WR, Fahlman M (2005) *Org Electron* 6:21–33
14. Ivanov VF, Isakova AA, Gribkova OL, Nekrasov AA, Bogdanov AN, Vannikov AV, Tverskoj VA (2009) *Protection of Metals and Physical Chemistry of Surfaces* 45(5):548–552
15. Caramyshev AV, Evtushenko EG, Ivanov VF, Ros Barcelo A, Roig MG, Shnyrov VL, van Huystee RB, Kurochkin IN, Vorobiev AKh, Sakharov IYu (2005) *Biomacromolecules* 6:1360
16. Liu W, Kumar J, Tripathy S, Senecal KJ, Samuelson L (1999) *J Am Chem Soc* 121:71–78
17. Samuelson LA, Anagnostopoulos A, Alva KS, Kumar J, Tripathy SK (1998) *Macromolecules* 31:4376
18. Liu W, Cholli AL, Nagarajan R, Kumar J, Tripathy S, Bruno FF, Samuelson L (1999) *J Am Chem Soc* 121:11345
19. Nagarajan R, Tripathy S, Kumar J, Bruno FF, Samuelson L (2000) *Macromolecules* 33:9542
20. Kirsh YuE, Fedotov YuA, Iudina NN, Katalevskii EE (1990) *Polym Sci B* 32:403
21. Nekrasov AA, Ivanov VF, Vannikov AV (2000) *J Electroanal Chem* 482:11–17
22. Gospodinova N, Dorey S, Ivanova A, Zhekova H, Tadjer A (2007) *Int J Polym Anal Charact* 12:251–271
23. Pron A, Rannou P (2002) *Prog Polym Sci* 27:135–190