



# Templating effect of polymeric sulfonic acids on electropolymerization of aniline



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## ABSTRACT

The electrodeposition of polyaniline (PANI) was carried out in potentiostatic, galvanostatic and potential sweep regimes in the presence of water-soluble polymeric sulfonic acids with different structure. The course of polymerization was traced by chronoamperometry, chronopotentiometry, cyclic voltammetry and in situ AFM measurements. The rigidity of the polyacid backbone, the distance between sulfonic groups on the backbone, the length and rigidity of the side chains containing sulfonic groups were shown to affect the onset potential of aniline oxidation, the character and the rate of the initial stages of PANI/polyacid film growth. AFM data indicated that the structure of the polyacids has a direct influence on the shape of PANI “nuclei” and the morphology of the film in the early stages of the electropolymerization. The obtained films were characterized by UV-Vis-NIR spectroscopy and cyclic voltammetry.

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## 1. Introduction

Polyaniline (PANI) is one of the most actively studied conducting polymers because of great prospects of its application for the development of new electroluminescent and electrochromic devices, flexible polymer conductors, batteries, chemical and biosensors, coatings for electromagnetic shielding, as well as for antistatic and anticorrosion protection and other special devices [1]. This polymer is characterized by high chemical stability and ease of synthesis, low cost and availability of aniline as starting material. The nature of acidic dopant influences the kinetic of aniline electropolymerization and the properties, morphology and the structure of PANI films [2,3]. Thus the possibility of synthesizing and doping PANI with different types of protonic dopants is one of the key factors responsible for the versatility of this class of polymers. In the past few decades for PANI electrodeposition the following dopants were used: mixtures of polymer electrolytes containing sulfonic groups with inorganic acids [4–8] and pure poly(sulfonic acids) such as poly(vinylsulfonic acid) (PVS) [2,3], poly(styrenesulfonic acid) (PSSA) [9–12], and poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) [13–15].

The main advantages of thus prepared PANI interpolymer complexes are: stability of the properties of such complexes in aqueous media with high pH values [6,8], high aniline polymerization rate

at much lower concentration of the reagents (compared to the polymerization in aqueous solutions of inorganic acids) [14,15], environmental safety of the process (less harmful byproducts resulted from disturbance of head-to-tail coupling) and possibility to modify the structure of PANI to change its optical and electrochemical properties [15], improved morphology [3,5,6,15], structural uniformity and mechanical properties of the films. These complexes are electroconductive polymer-polymer composites in which ion-exchange group of the polyelectrolytes ( $-\text{SO}_3^-$ ) acts as immobilized dopants [10]. The polyelectrolyte is irreversibly incorporated in PANI and can not be leached out by cycling in aqueous acidic or nonaqueous solutions [4,6]. The addition of very small amount of the polyelectrolyte and its chemical structure [5] influences the film growth rate and morphology [5,7].

In our previous work [15] we have studied PANI electrodeposition at constant potential in the presence of the following poly(amidosulfonic acids): poly(2-acrylamido-2-methyl-1-propanesulfonic acid), poly(p,p'-(2,2'-disulfonic acid)-diphenylene-isophthalamide) (i-PASA), poly(p,p'-(2,2'-disulfonic acid)-diphenylene-*tere*-phthalamide) (t-PASA) and demonstrated the influence of the polyacid backbone rigidity on the character of synthesis, the electronic structure of resulting PANI complexes, their morphology and physico-chemical properties [15]. We have observed the acceleration of aniline potentiostatic electropolymerization in the presence of polyacids compared to the polymerization in inorganic acids in the same concentration [14]. We have supposed that the reason of the increase in PANI growth rate is the association of aniline monomer with the sulfonic groups of polyacid [14,15], which results in the formation of polyaniline clusters in the vicinity of

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electrode facilitating the nucleation of the polyaniline phase. Similar acceleration of aniline electropolymerization was observed by the authors of [4,5,7,8] in the mixed solutions of small amounts of polymer electrolytes and inorganic acids. It should be noted that earlier investigations of PANI electrodeposition in the presence of polyacids were performed at the aniline concentration higher by more than an order than this one in our works [2,3,9–13].

We have analyzed [16] some possible applications of the films of PANI interpolymer complexes with poly(amidosulfonic acids) and compared the operation characteristics of such complexes in electrochromic devices, in ammonia optical sensor, as well as tested their electroactivity at higher pH values in view of biosensing applications. It was shown that the films of complexes with the rigid-backbone polyacids are suitable for potential-controlled modulation of the absorption in the near-infrared region. The films of complexes with the semi-rigid-backbone polyacids exhibited best performance as ammonia sensors and demonstrated increased electrochemical stability at high pH values. The authors of [17] have investigated cation-exchanging properties of PANI composites with PSSA for rechargeable lithium batteries and demonstrated their improved charge/discharge characteristics.

In the present work, polyaniline was prepared by electrochemical polymerization of aniline in the presence of poly(sulfonic acids) at different regimes of the synthesis: potentiostatic, galvanostatic and linear potential sweep (cyclic voltammetry). For our experiments we have chosen the following poly(sulfonic acids): PAMPSA (flexible polymer chain); PSSA (flexible chain); i-PASA (semi-rigid chain); t-PASA (rigid chain) and a copolymer of the latter two acids with the monomers feed ratio 1:1 (co-PASA) (semi-rigid chain). Furthermore, the process of electrodeposition of interpolymer complexes of PANI films on atomically smooth substrate (highly oriented pyrolytic graphite (HOPG)) has been studied by in-situ atomic force microscopy (AFM) in solution to determine the effect of polymeric acid conformation on “nucleation” and the morphology of the films in the initial stages of their growth. We should underline that in this paper we use expansive interpretation of the terms “nucleation” and “nuclei” to describe the process of appearing on the HOPG-electrode of the smallest objects of the polymer phase, which can be registered by AFM using the chosen tip in the chosen experimental conditions.

Different in-situ probe techniques (AFM and scanning tunneling microscopy (STM) [18]) have been used to study the process of electrosynthesis of polyaniline and its derivatives [19–24]. In some works performed on HOPG, authors [21–23] in addition to the visual observation of morphological changes during aniline electropolymerization in the presence of inorganic [21,22], and low molecular weight organic [23] acids have analyzed chronoamperometric dependencies to determine the growth mechanism of the polyaniline phase. However, the size of AFM images in the latter six works, at best, was  $500 \times 500$  nm, which, in combination with rather low resolution, greatly complicated the analysis of the shape of objects smaller than 10 nm. In addition, these studies used a non-standard molar ratio of aniline: acid (1:1.5 or 1:2). As shown by our study [14] low acid concentration leads to a violation of the standard autocatalytic nature of the synthesis, which certainly affects the nature of morphological transformations in the initial stage of the film growth.

PANI electrosynthesis in the most “classical” conditions (0.1 M An + 1 M HClO<sub>4</sub>) was studied by in-situ AFM on HOPG in [20]. However, the size of the AFM image here is  $1 \times 1$  μm, and the picture was not of high quality. In addition, the in-situ AFM method was not used to study PANI electrosynthesis in the presence of polymeric acids.

In order to demonstrate the differences in conformations of the poly(sulfonic acids) resulted from their different structure, which may influence the nucleation mechanism of PANI, we have carried

**Table 1**

Values of pH in the electropolymerization baths, the duration of induction period in the potentiostatic regime ( $T_{ps}$ ), the onset potential of aniline oxidation ( $E'_{cv}$ ) in the CV-regime and the plateau potential in the galvanostatic regime ( $E'_{GS}$ ) for PANI electrodeposition in the presence of different polyacids.

Polyacid	pH	$T_{ps}/s$	$E'_{cv}/V$	$E'_{GS}/V$
PAMPSA	2.10	600	0.70	0.64
PSSA	1.70	365	0.70	0.71
i-PASA	1.90	50	0.40	0.73
co-PASA	1.85	160	0.60	0.66
t-PASA	1.85	230	0.65	0.63

\* Potential vs. (Ag/AgCl)

out molecular modeling of their oligomeric fragments using semi-empirical PM3 method (Fig. 1). It should be emphasized that the simulation was performed without the environment (under vacuum) and the resulting structures are just some of the possible ones (except for t-PASA, which always has a stick conformation). Molecular modeling of the PANI/polyacids complexes would require much more computing power.

Structures of the monomer units and the results of molecular modeling for the studied polyacids are presented in Fig. 1.

PAMPSA and PSSA are distinguished by the regular distribution of sulfonic groups along the main chain of the macromolecules, shorter distance between them and a flexible polymer backbone, which allows these polyacids to form a random coil conformation in the presence of strong electrolytes [25,26]. However, short benzene-containing side chains in PSSA may hinder the backbone bending resulting in a bigger radius of gyration. Contrarily, i-PASA, co-PASA and t-PASA are distinguished by irregular distribution of the sulfonic groups along the macromolecule, bigger distances between the groups belonging to adjacent monomer links and different rigidity of the polymer backbone. Semi-rigid-chain i-PASA and co-PASA can change their conformation to a coil one in the presence of strong electrolytes [27]. Our computer simulation demonstrates a possibility of ring-shape structure of i-PASA octamer (Fig. 1). t-PASA macromolecules in water exists in the extended coil (or stick) conformation (rigid backbone). This conformation remains unchanged with the increase of ionic strength of the solution [27].

## 2. Experimental

PAMPSA (Aldrich, molecular weight (MW) 2 000 000, 15% wt aqueous solution) and PSSA (Alfa Aesar GmbH, MW 75 000, 30% wt aqueous solution) were used without purification. Laboratory synthesized Na<sup>+</sup>-salts of i-PASA, co-PASA and t-PASA (ca. MW 40 000, measured by end-group titration method) [27] were converted into H<sup>+</sup>-forms according to the procedure described earlier [15]. In all syntheses the concentration of aniline was 25 mM. A constant ratio of concentrations of aniline/sulfoacid groups was always kept as 1 mol/2 g-equivalent. The synthesis solutions were prepared in a similar procedure as in [15,28]. pH-values in the synthesis baths (after adding aniline) are presented in Table 1. pH values were measured using an OP-208/1 digital pH-meter (Radelkis, Hungary) within the accuracy of measurements  $\pm 0.05$  pH. The aniline electropolymerization was performed in a potentiostatic (0.75 V), galvanostatic (50 μA) and cyclic voltammetry (−0.3 ÷ 0.9 V, sweep rate 50 mV/s) regimes in a specially designed three-electrode spectroelectrochemical cell [28]. PANI films were electrodeposited onto glass substrates covered with a transparent conducting layer of SnO<sub>2</sub>:F (FTO) with the sheet resistance of ca. 7 Ohm/square. A platinum foil was used as a counter electrode and a saturated silver–silver chloride electrode (Ag/AgCl)–as a reference electrode. All values of potential in this paper are presented relative to this electrode. The electrochemical parameters were

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