



# Ultraviolet-Visible-Near Infrared and Raman spectroelectrochemistry of poly(3,4-ethylenedioxythiophene) complexes with sulfonated polyelectrolytes. The role of inter- and intra-molecular interactions in polyelectrolyte



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## ABSTRACT

Poly(3,4-ethylenedioxythiophene) (PEDOT) films were electrodeposited in galvanostatic mode in the presence of salt or acid forms of sulfonated polyelectrolytes distinguished by different rigidity of the polymer main chain and presence of amid fragments in their structure. The films obtained were characterized by cyclic voltammetry, as well as Ultraviolet-Visible-Near Infrared and Raman spectroelectrochemistry at fixed potentials in non-aqueous and aqueous media, respectively. It was found that bipolaronic fragments of PEDOT are hardly to be formed at high anodic potentials in the films prepared in the presence of acid forms of the rigid-chain amid-containing polyelectrolytes as distinct from all other polyelectrolytes regardless of amide-groups content. In situ Raman studies during PEDOT electrodeposition in the presence of the acid forms of the rigid-chain amid-containing polyelectrolytes showed domination and retarded delocalization of radical cations being the moving force of the electropolymerization. The results are discussed in terms of possibility/impossibility of proton-transfer inter- and intra-molecular interactions between sulfonic and amid groups in the polyelectrolytes. These result in the appearance of positive charges (confirmed by  $\zeta$ -potential measurements) on the polyelectrolyte chain, which create barriers for radical cations delocalization, their recombination into bipolarons, as well as prevents growth of long PEDOT chains. The prepared materials were studied as a hole-transport (buffer) layer in organic photovoltaic cells. The influence of polyelectrolyte structure on the cells performance is discussed.

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## 1. Introduction

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most widely used conductive polymers and practically the only representative of this class, successfully passed the way from scientific research to commercial application [1,2]. The polymer possesses high conductivity in the doped state, transparency in the visible region in thin, oxidized films and is characterized by relatively low band-gap and excellent stability in the oxidized state. Due to these advantages PEDOT is one of the most promising

materials for many applications such as antistatic or conductive coatings, components of electrochromic, electroluminescent and organic photovoltaic devices, capacitors, sensors, etc. [1].

PEDOT is commonly used in the form of a water-dispersible complex with poly(styrene-4-sulfonic acid) (PSSA) prepared by oxidative chemical polymerization of 3,4-ethylenedioxythiophene (EDOT) in the presence of PSSA [1,2]. Another polymerization method utilizes electrochemical oxidation of EDOT. This method combines polymerization and deposition onto different substrates into one step and is characterized by easy control of the polymerization parameters, thickness, morphology and oxidation state of the polymer layer that may be considered as the advantages over PEDOT chemical synthesis. Electrochemical polymerization of EDOT results in the formation of a highly

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conductive and transparent sky-blue, doped PEDOT film at the anode.

Due to low solubility and high oxidation potential of EDOT in water, many studies of PEDOT electrochemical synthesis are carried out in nonaqueous media [3–8]. Nevertheless, aqueous solutions are more preferable for environmental requirements. There are a number of studies of EDOT electrochemical polymerization in aqueous solutions [9,10]. At the same time, addition of surfactants and water-soluble polyelectrolytes during PEDOT electrochemical synthesis: 1) reduces the oxidation potential of the monomer [11–14]; 2) accelerates EDOT polymerization [12,14,15]; 3) produces some polyelectrolyte template effects at the electrode [13–15,19]; 4) stabilizes PEDOT radical cations [12,15] and 5) improves PEDOT electrocatalytic [15], mechanical, optical and hole-transport properties [16].

The electrochemical polymerization of EDOT in the presence of surfactants and polyelectrolytes is commonly carried out in aqueous-organic [16,17] and aqueous [11–15,18–20] media. PSSA [14,17], poly(sodium 4-styrenesulfonate) (PSSNa) [11–15,17–20], poly-(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPSA) [14–16,20] are the most widely used polyelectrolytes. However, majority of authors do not pay enough attention in what form (acid or salt) polyelectrolytes are present in the synthesis medium. Authors of [17] were the only ones who have down attempt of comparison of PEDOT film properties obtained in the presence of acid and sodium salt of poly(styrenesulfonate). The only difference noted was that the form (acid or salt) of PSS influences the conductivity of PEDOT films.

The commercially available “PEDOT-PSS” (Clevios) aqueous dispersion is one of the most widely used polymer in organic solar cells (OSC). It contains all the necessary ingredients in the right combination for a profitable use in OSC, as sufficient optical transparency in visible range; it is effective in transporting holes and blocking electrons to the anode, its high work function allows the formation of an ohmic contact with most of common donor polymers, and finally it is stable enough at ambient conditions [1,21]. However, “PEDOT:PSS” has some negative implications on OSC performance due to the extreme acidity of its dispersion (pH 1–2) causing ITO corrosion and the difficulty of reproducibility of PEDOT:PSS interlayer morphology [12,21]. To eliminate these drawbacks PEDOT electrochemical synthesis in the presence of polyelectrolyte salts may be used. A number of authors has reported about successful application of electrodeposition method for the preparation of PEDOT as an anode buffer layer in OSC [12,22–24].

In the previous work [14], we have performed studies of the influence of polysulfonic acid structure (hydrophobic nature, chain flexibility and distribution of sulfonic groups along polyacid macromolecule) on EDOT electropolymerization and the spectroelectrochemical properties of PEDOT films obtained.

In the present work, we aimed to elucidate the role of polyelectrolyte form (acid or salt) in EDOT electropolymerization and Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) and Raman spectroelectrochemical properties of PEDOT films obtained. For the first time we present in situ Raman spectroscopy studies during PEDOT electrosynthesis in the presence of polyelectrolytes with different structure. Additionally, electrodeposited PEDOT films were tested as buffer layers of bulk heterojunction (BHJ) organic solar cells.

The following polyelectrolytes were used: flexible-chain PSSA and PAMPSA, semi-rigid-chain poly(4,4'-(2,2'-disulfonic acid)-diphenylene-*iso*-phthalamide) (*i*-PASA) and rigid-chain poly(4,4'-(2,2'-disulfonic acid)-diphenylene-*tere*-phthalamide) (*t*-PASA) and their sodium salts (Fig. 1).

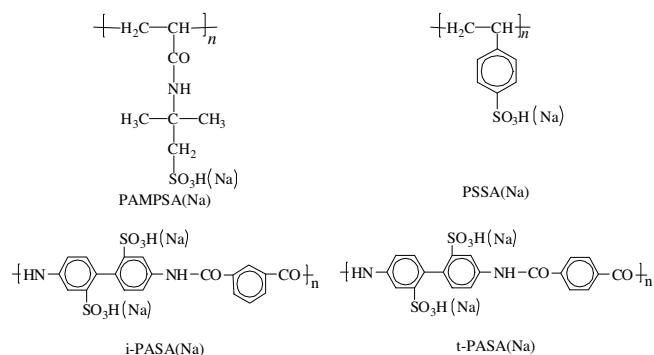


Fig. 1. Chemical structure of monomer units of polyelectrolytes used in the paper.

## 2. Experimental

Electrochemical polymerization of EDOT was carried out in eight aqueous solutions consisting of 10 mM EDOT and four polysulfonic acids with different structure and their sodium salts. PAMPSA (Aldrich,  $M_w = 2\,000\,000$ , 15% wt aqueous solution), PSSA (Alfa Aesar GmbH,  $M_w = 75\,000$ , 30% wt aqueous solution) and PSSNa (Aldrich,  $M_w = 70\,000$ , 30% wt aqueous solution) were purified *via* dialysis against distilled water (cellulose membrane ZelluTrans MWCO 8 000–10 000, Roth). PAMPSA was covered into Na<sup>+</sup>- form by titration. Laboratory synthesized Na<sup>+</sup>-salts of *i*-PASA and *t*-PASA ( $M_n = 40\,000$ ) [25] were converted into H<sup>+</sup>-forms using ion-exchange column. A constant ratio of concentrations of EDOT/sulfoacid groups was always kept as 1 mol/2 g-equivalent. The synthesis solutions were prepared in a similar procedure as in [14]. The EDOT electropolymerization was performed in a galvanostatic (0.02 mA cm<sup>-2</sup>) regime (GS). The electrodeposition charge of all films obtained in spectroelectrochemical studies was equal to 70 mC cm<sup>-2</sup>. For PEDOT films used as a buffer layer of OSC the electrodeposition charge was equal to 5 mC cm<sup>-2</sup>. All values of the potential in this paper are presented relatively a saturated silver-silver chloride electrode (Ag/AgCl). PEDOT films were electrodeposited onto glass substrates covered with a transparent conducting layer of SnO<sub>2</sub>:F with the sheet resistance ca. 7 Ohm/square for UV-Vis-NIR spectroelectrochemical measurements, polished Pt sheets for Raman spectroelectrochemical measurements and ITO-glass substrate (Kintec) for OSC fabrication. All the samples were thoroughly rinsed with deionized water after the synthesis. The surface area of all films was 2.25 cm<sup>2</sup>. The course of the synthesis was controlled both by electrochemical parameters and in situ optical and Raman spectroscopy. In situ spectroscopic monitoring in the UV-visible spectral area (350–900 nm) during the synthesis was performed using an AvaSpec 2048 diode array spectrophotometer (Avantes BV) as described in [14]. In situ Raman spectroscopic monitoring during the synthesis was registered using a Raman system consisting of a Maya2000 Pro diode array spectrophotometer (Ocean Optics Inc., USA) equipped with appropriate grating and controlled by Spectra Suite software, a 50 mW 532 nm laser DPSS-532 (Laserpath Technologies, USA) and a fiber optic Raman probe RPB-532 (InPhotonics Inc., USA). The Raman spectroelectrochemistry experimental setup was described in details elsewhere [14]. 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.).

UV-Vis-NIR spectroelectrochemical experiments of PEDOT films in a propylene carbonate solution containing 0.5 M NaClO<sub>4</sub> in the range up to 1700 nm were performed using a UV3101PC

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