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Electrochemical polymerization of 3,4-ethylenedioxythiophene in the presence of dodecylsulfate and polysulfonic anions—An acoustic impedance study

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ABSTRACT

PEDOT layers are synthesized in aqueous solutions in the presence of one of the three different anionic species – polysterenesulfonate (PSS), poly(2-acrylamido-2-methyl-1-propane-sulfonate) (PAMPS) and dodecylsulfate without any addition of further inorganic anions. Simultaneous electrochemical and acoustic admittance measurements are carried out in the course of polymerization. The data from the admittance spectra are used to extract information on the mechanical shear storage and loss moduli of the three types of PEDOT layers. The anionic species are found to affect the polymerization kinetics, the surface morphology and most markedly the viscoelastic properties of the three types of layers. The latter depend primarily on the innate structure arising in the course of polymerization whereas the solution specifics play a secondary role. Dodecylsulfate imparts significant stiffness to the PEDOT layers with high rigidity preserved for relatively large polymerization charges. The *G* moduli in this case exceed 10^9 dyn/cm^2. Both polyanion-doped PEDOT layers are found to be softer but there is nevertheless a clear difference between them with PEDOT/PAMPS having a strong predisposition for swelling.

1. Introduction

Poly(3,4-ethylenedioxythiophene)(PEDOT) is one of the intensively studied conducting polymers due to the possibilities for its involvement in a large variety of applications ranging from organic LEDs, FETs and solar cells, electrochromic devices and solid electrolyte capacitors, to antistatic coatings, actuators and finally to electrocatalysts, and sensing materials in chemical and electrochemical sensor devices [1–3]. Due to the low solubility of the EDOT monomer in water PEDOT is obtained usually in non-aqueous solutions. The successful chemical synthesis of the aqueous dispersion of PEDOT with poly(styrenesulfonate) (PSS) [4,5] based on the formation of a polyelectrolyte complex between the two polymeric species initiated further attempts to use aqueous electrolytes for the polymerization of EDOT, especially in the electrochemical case. Together with polyanions such as PSS [6–10] and its alternative poly(2-acrylamido-2-methyl-1-propane-sulfonate) PAMPS [11], other surfactants were also used to increase the solubility of the monomer in water, e.g., the anionic dodecylsulfate [10,12–16], the non-ionic polyoxyethylene-10-lauryl ether [17–20], β-cyclodextrin [21] and sodium N-laurylsarcosinate [22]. In the cases when specific anionic species are used in the course of electrochemical synthesis they are expected to play a further important role for the PEDOT polymerization and properties. Through polyelectrolyte complex interactions and/or electrostatic (charge compensation of the oxidized PEDOT) and hydrophobic interactions the anionic species become immobilized in the polymer structure and further affect the PEDOT layer properties. It was demonstrated that conductivity and doping level [7], optical absorbance [10] and stability in biomedical applications [23] depend on the type of counterions used in the course of polymerization.

Almost all studies on electrochemical synthesis of PEDOT in aqueous solutions were carried out in electrolytes containing both the anionic solubilizing agent and an excess of small inorganic anions, usually ClO_4^-. These additional anions are also participating in the charge compensation of the PEDOT layers and compete with the bulky anionic surfactants used to increase the monomer solubility. Thus, it is difficult to isolate the effect of the different bulky anionic species on the polymerization kinetics and properties of the obtained PEDOT layers. One of the aims of the present investigation is to study the effect of three different organic anions (PSS, PAMPS and SDS) on the polymerization kinetics in aqueous solution in the absence of additional small inorganic anionic species. PSS and SDS are chosen as one of the most frequently used solubilizing species with different characters – a polyanionic one and a hydrophobic

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anionic surfactant. PAMPS was selected in order to be able to compare the role of two polysulfonate anions with different rigidities of the polymer backbone and possibly different interactions within the polyeletrolyte complex with PEDOT.

The electrochemical investigations on polymer film formation are often combined with microgravimetric studies in order to obtain data for the mass change in the course of electrochemical synthesis. Conventional EQCM measurements that provide only information for the frequency change of the quartz crystal upon surface mass loading were used in several studies on the anodic polymerization of EDOT [8,15,20,24,25]. In most cases the frequency change is used to calculate the mass change by using the well-known Sauerbrey equation [26]. The latter is strictly valid only for thin, homogeneous, rigid films deposited on the quartz crystal. Conducting polymers are, however, viscoelastic materials and therefore this simple way of transforming the data for the frequency into mass seems to a great extent limited. Therefore, a more complex experimental approach based on the registration of the whole acoustic admittance spectra of the quartz resonator was developed [27–33] and involved in studies of various conducting polymers, e.g., poly(3-methylthiophene) [30], polyaniline [34–36], PEDOT [32,37–39]. The interpretation of the experimental data for the admittance acoustic spectra based on models for the mechanical impedance of the loaded quartz crystal allows to extract information for the viscoelastic properties of the polymer layers, i.e., for the values of the shear storage and loss moduli, G' and G''. As far as the viscoelastic properties of the conducting polymer layers are expected to depend markedly on the type of the dopant used in the course of polymerization acoustic impedance measurements were the obvious method of choice for studying the effect of the three surfactants (PSS, PAMPS and SDS) on the PEDOT formation and properties.

2. Experimental

The combined equipment for electrochemical and microgravimetric studies used in this investigation consisted of a potentiostat (263A, EG&G Instruments) and a network analyzer (Advantest R3753BH, Tokyo, Japan). The experimental set-up provides simultaneously electrical data (current, charge and potential) and acoustic impedance data (resonance frequency, f and damping, w of the resonance signal) measured at the working electrode. The damping is defined as full width at half height at the resonance frequency maximum of the resonance curve of the quartz crystal. The home-made program for data acquisition provides a single file that stores all data. Details on the experimental set-up are given in [29].

The polymerization of EDOT (Aldrich) was carried out in aqueous solutions containing 10 mM EDOT and 34 mM of the corresponding dopant: sodium polystyrenesulfonate (Aldrich, $M_w = 70{,}000$), poly(2-acrylamido-2-methyl-1-propanesulfonic) acid (Aldrich, 0.15 wt% in water, $M_w = 2{,}000{,}000$) or sodiumdodecylsulfate (Aldrich) without any addition of further supporting electrolyte. The amount of monomer (10 mM) in the solutions used in our study is below the solubility limit (15 mM) of EDOT in water. This means that the studied effects on the polymerization and characteristics of the various PEDOT layers are expected to relate not to increased concentration of EDOT but mainly to the incorporation of different counterions in the course of the polymer layers formation.

The layers obtained in the presence of the various dopants will be further denoted as PEDOT/SDS, PEDOT/PAMPS and PEDOT/PSS. The solutions were de-aerated by bubbling of Ar before starting the measurements. The electrochemical experiments were carried out in a three-electrode set-up using gold-coated quartz crystals (10-MHz AT-cut quartz, Vectron International) as working electrodes (with mass sensitive surface area, $A = 0.22\ \text{cm}^2$), platinum counter electrodes and a Ag/AgCl/KCl(sat.) reference electrode. The working electrodes were cleaned by immersing in concentrated nitric acid for several hours. A pretreatment step at 0.1 V for 30 s was used for conditioning the electrode before applying the polymerization potential.

Despite the fact that cyclic voltammetry is widely employed for electropolymerization of conducting polymers, potentiostatic deposition was used as a method of choice in our experiments in order to avoid additional effects arising from recurrent dedoping of the PEDOT layers taking place in each potentiodynamic cycle. The polymerization was carried out at 0.84 V in the three types of solutions. After polymerization the PEDOT layers were thoroughly rinsed with water and transferred to 0.1 M sodium phosphate buffer solution (PBS), pH 7. Several cyclic voltammetric curves were measured for each polymer layer in the potential interval −0.73 to +0.8 V at a scan rate 20 mV/s.

The resonant frequencies of the quartz resonator were measured both in air and in the solution before starting the polymerization experiment. The values of the frequency and the damping, f_0 and w_0, measured before applying the polymerization potential in the solution are used as reference values for each experimental run. The rough results from the microgravimetric experiments are presented in terms of frequency shift, $\Delta f = f - f_0$ and normalized damping, w_0/w. These data are used as input in a computational program designed to model acoustic impedance of viscoelastic layers. A brief description of the procedure and mathematical model used to obtain data for the shear storage and loss moduli is given below.

Acoustic impedance data were recorded also in the course of potentiodynamic cycling in PBS as well as after rinsing and drying the various PEDOT layers in an argon flux. These data were used to estimate the volume fraction of solute species in the polymer layers and the extent of their swelling. Several (typically five) voltammetric scans were measured in PBS until a stable electrochemical and acoustic impedance response was obtained in order to guarantee a complete exchange of the loose (not immobilized) counter ions present initially in the polymer layers with the PBS-containing anions. Only in the case of PEDOT/SDS a complete stabilization of the acoustic impedance data was not achieved within these scans. Weak further loss of mass (with subsequent scans) was observed indicating very probably continuous release of dodecylsulfate anions.

In all cases several combined electrochemical and microgravimetric experiments were carried out at fixed conditions and typical data of Δf and w_0/w are shown in the figures. As before [36] the quantity w_0/w is considered as a first qualitative indicator to estimate the PEDOT layer rigidity by assuming that for w_0/w close to unity the layer is rigid and with decreasing w_0/w it becomes viscoelastic.

The surface morphology of the PEDOT layers obtained in the different polymerization solutions was studied by SEM (DSM 982, Gemini from Zeiss, Germany).

3. Modeling of the experimental data for the acoustic admittance

The complex frequency shift, Δf^*, resulting when an acoustic wave is traveling across a thin viscoelastic layer deposited on a quartz resonator is given by [28]:

$$\Delta f^* = f - f_0 + i\frac{w - w_0}{2} \quad (1)$$

where f_0 and w_0 are the resonance frequency and the damping of the quartz electrode before the deposition of the viscous layer. In