Effect of solubilizing agent on properties of poly(3,4-ethylenedioxythiophene) (PEDOT) electrodeposited from aqueous solution

Eduard Nasybulin a,∗, Shu Wei a, Ioannis Kymissis b, Kalle Levon a,∗

a Department of Chemical and Biological Sciences, Polytechnic Institute of New York University, 6 Metrotech Center, Brooklyn, NY 11201, USA
b Department of Electrical Engineering, Columbia University, 500 West 120 Street, New York, NY 10027, USA

A R T I C L E   I N F O
Article history:
Received 17 February 2012
Received in revised form 23 June 2012
Accepted 23 June 2012
Available online 2 July 2012

Keywords:
Electrochemical deposition
Electropolymerization
Solubilization
Polymer solar cell

A B S T R A C T
PEDOT layers were electrodeposited from aqueous solutions in the presence of various solubilizing agents. A systematic study involving a large number of solubilizers was conducted. The six surfactants used were sodium dodecyl sulfate (SDS) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (both anionic), Tween 80 and Triton X-100 (both non-ionic), hexadecyltrimethylammonium p-toluenesulfonate (HDTMA) and hexadecyl(2-hydroxyethyl)dimethylammonium dibydrogen phosphate (HDHEDMA) (both cationic). Two polyelectrolytes, sodium polystyrene sulfonate (PSS) and κ-carrageenan were also used.

It was found that the nature of the solubilizing agent has a drastic effect on the polymerization conditions. The anionic solubilizing agents decreased the polymerization potential and eliminated the induction period of the polymerization. As a result, PEDOT layers with longer conjugation length as well as higher conductivity and transparency were deposited. These layers were incorporated into polymer solar cell as hole transporting layers and efficiencies close to the traditional spin-coated PEDOT:PSS layers have been reported. By contrast, cationic surfactants increased the polymerization potential by 0.21 V and a significant induction period was observed during the polymerization. In this case, PEDOT layers of poor quality were deposited and the efficiencies of the solar cells dropped by an order of magnitude. PEDOT layers deposited in the presence of non-ionic surfactants or without any solubilizing agent showed an intermediate performance. In addition to the strong effect of charge, the bulkiness of the solubilizing agent was also found to significantly affect the polymerization and properties of PEDOT.

1. Introduction

High conductivity, good stability and transparency have made PEDOT one of the most important polymers in organic electronics. It finds many applications in organic light emitting diodes (OLEDs), organic photovoltaic devices (OPVs), electroluminescent devices, anti-static coatings, organic field effect transistors (OFETs), printed boards, solid electrolyte capacitors, etc. Unlike other conductive polymers, some of the applications (electrolyte capacitors, anti-static coatings and printed circuit boards) have already been moved up to industrial manufacturing, making PEDOT the only conductive polymer produced commercially on a large scale. PEDOT is commonly used in the form of a water-soluble complex with poly(styrene-4-sulfonate) (PEDOT:PSS) prepared by oxidative chemical polymerization of EDOT in the presence of PSS [1]. Most of these applications utilize solid PEDOT films making an aqueous suspension of PEDOT:PSS a convenient and environmentally friendly material for their deposition by a number of techniques, such as spin-coating, doctor blading, spraying, printing, and roll-to-roll coating. Despite the processing advantages, the material suffers from relatively low conductivity due to the insulating nature of PSS. The highest conductivities achieved for PEDOT reach 1000 S/cm [2,3]. Without secondary doping and special curing, the conductivity of PEDOT:PSS is more than an order of magnitude lower (depending on its PSS content) [4]. PEDOT:PSS deposited on ITO is used as hole transporting layer in OPV and OLED applications. High acidity of PSS also causes degradation on the ITO interface, which shortens the lifetime of the devices.

Electrochemical deposition of PEDOT layers represents a valuable alternative since it combines polymerization and deposition into one step, effectively eliminating solubility issues and PSS usage. Other advantages include: wide variety of available counterions, an almost quantitative conversion of the initial monomer to the functional PEDOT layer, the possibility of patterning, and control over thickness as well as the oxidation state and morphology of the polymer layer. PEDOT can be electrodeposited from various organic solvents using a number of electrolyte salts [5]. The highest conductivity of 850 S/cm was reported in the case of acetonitrile and perchlorate counterion [6,7]. There are several
studies in which an electrodeposited PEDOT layer was successfully incorporated into an organic solar cell as a hole transporting layer to replace conventional spin-coated PEDOT:PSS [8–12]. We have studied nanofibrillar PEDOT layers electrodeposited from mixed solvents and observed superior performance compared to spin-coated PEDOT:PSS [13]. Moreover, a functional polymer solar cell has recently been fabricated using exclusively electrochemical depositions [14,15].

Aqueous solutions are always preferable in industry for environmental and economical reasons. Due to the strong electron-donor properties of the ethylenedioxythiophene group, EDOT has considerably lower polymerization potential than other polythiophenes and can be electrochemically polymerized from the aqueous solutions. EDOT has low solubility in water (2.0 g/l at room temperature) and is usually electropolymerized with the help of surfactants or polyelectrolytes. Sodium dodecyl sulfate (SDS) [16–25], hydroxypropyl-β-cyclodextrin [25–27], sodium dodecylbenzenesulfonate (SDBS) [19,24,25], Triton X-100 [24,28] and X-405 [23], camphorsulfonic acid (CSA) [29], N-dodecyl-β-n-maltoside [24], cetyltrimethylammonium bromide (CTAB) [21], polyoxyethylene-10-lauryl ether [30], N-laurylsarcosinate (SLS) [31], PSS [32] and polyacrylic acid (PAA) [33] were used for this purpose. There are also a number of studies on electrochemical polymerization of EDOT from diluted solutions without using any solubilizing agents [19,20,23,24,34–36]. It was clearly shown in Lacaze et al’s early works that in the presence of SDS, the polymerization potential in aqueous solution is lower than in acetonitrile [17,18]. Later, it was revealed that the addition of SDS to the aqueous solutions of EDOT decreases the polymerization potential by about 100 mV [19,23]. The effect was attributed to strong electrostatic interaction between EDOT cation-radicals (EDOT⁺) and dodecyl sulfate anions [23]. Zhang et al. observed the same shift for another anionic surfactant SDBS [24]. Recently, Cho et al. electropolymerized EDOT in the presence of non-ionic hydroxypropyl-β-cyclodextrin and anionic SDS and SDBS [25]. Impedimetric studies and current sensitive atomic force microscopy reveal better ion-transport and conductivity for the film deposited in the presence of SDS.

It is obvious that nature of solubilizing agents (surfactant or polyelectrolyte) has a significant effect on the properties of the electrodeposited PEDOT. Even though there are many publications where PEDOT was electropolymerized from aqueous solutions, the results can hardly be correlated because of the different experimental conditions. In the present work, we aimed to build a systematic study involving a larger number of solubilizers. Six surfactants were used. These included: sodium dodecyl sulfate (SDS) and sodium bis(2-ethylhexyl) sulfosuccinate (AOT) (both anionic), Tween 80 and Triton X-100 (both non-ionic), hexadecyltrimethylammonium p-toluenesulfonate (HDTMA) and hexadecyl(2-hydroxyethyl)dimethylammonium dihydrogen phosphate (HDHEDMA) (both cationic), and two polyelectrolytes: sodium polystyrene sulfonate (PSS) and k-carrageenan. Polymerization conditions and spectroscopic properties were analyzed in relation to conductivity. The electrodeposited layers were incorporated as hole transporting layers into polymer solar cells to test their performance in functional electronic device.

2. Experimental

2.1. Materials

Sodium dodecyl sulfate (SDS), Tween 80, Triton X-100, hexadecyltrimethylammonium p-toluenesulfonate (HDTMA), hexadecyl(2-hydroxyethyl)dimethylammonium dihydrogen phosphate (HDHEDMA), sodium nitrate, 3,4-ethylenedioxythiophene (EDOT), anhydrous 1,2-dichlorobenzene and regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) were purchased from Aldrich. Regioregular P3HT showed a single 1H NMR peak at 6.977 ppm (head-to-tail regioregularity) [37,38]. M₀ = 29,000 and PDI = 2.2 were measured by GPC using polystyrene standards in chloroform. Phenyl-C₆₃-butyric acid methyl ester (PCBM) was purchased from Luminescence Technology Corp. Sodium bis(2-ethylhexyl) sulfosuccinate (AOT) and k-carrageenan were received from Fluka Chemie. Sodium polystyrene sulfonate (PSS) (Mₐ = 70,000) was ordered from Polysciences, Inc. All the chemicals were used as received. Millipore deionized (DI) water was used in the experiments.

Indium tin oxide (ITO) coated glass slides, Rₐ = 5–15 Ω, 7 mm × 50 mm × 0.7 mm, were ordered from Delta Tech., Inc. Custom-made ITO glasses for solar cell fabrication, Rₐ = 15 Ω, 25 mm × 25 mm × 0.7 mm, were purchased from Luminescence Technology Corp.

2.2. Instruments

The electrochemical depositions and characterization were done using a model 660D workstation (CH Instruments, Inc., TX). UV–Vis–NIR spectra were recorded with a UV-3101PC spectrophotometer (Shimadzu Scientific Instruments, Inc., MD). Morphological studies were performed by Nanoscope IIIa Atomic Force Microscope (AFM) (Veeco, Inc., CA). The solar cell testing was done using Keithley 2400 source meter (Keithley Instruments, Inc., OH) and standard AM 1.5 solar simulator, 100 mW/cm² (Newport, Inc., CA); an aluminum cathode was evaporated in an Angstrom Engineering vacuum deposition system at pressure of 2 × 10⁻⁶ Torr.

2.3. Electrochemical polymerization of PEDOT

Before the electrochemical depositions, ITO working electrodes were cleaned by sonication in aqueous Kleensonic solution (Ted Pella, Inc.), rinsed with water and dried in a nitrogen stream. A one-compartment cell with a three-electrode configuration was used in the experiments. Ag/AgCl in 3 M NaCl (0.197 V vs SHE) and platinum wires were employed as reference and counter electrodes, respectively. Aqueous solutions contained EDOT monomer (10.0 mM), NaNO₃ as a supporting electrolyte (0.5 M) and solubilizing agent. The concentration of the solubilizing agent was 10.0 mM for the low molecular weight compounds (SDS, AOT, HDTMA and HDHEDMA) and 2.5 g/l for the high molecular weight compounds (Tween 80, Triton X-100, PSS and k-carrageenan). A solution without any solubilizing agent was also prepared. Polymerization was done either potentiodynamically (cyclic voltammetry) or potentiostatically (chronocoulometry). The former technique was used to measure the oxidation potential of EDOT (onset of the polymerization), while the latter was used to deposit the layers of equivalent thicknesses and monitor the kinetics of polymerization. Cyclic voltammetry was run from 0.0 to 1.0 V at 100 mV/s scan rate; potentiostatic deposition was performed at 1.0 V by passing a charge of 6.25 mC/cm². After that, the layers were rinsed thoroughly in water to remove excess of solubilizing agent and dried in a nitrogen stream. As-prepared samples were used for further characterization and solar cell fabrication.

2.4. Fabrication of polymer solar cells

PEDOT layers electrodeposited on ITO in the presence of various solubilizing agents were applied as hole transporting layers to build polymer solar cells. All the layers were deposited by passing the same charge of 6.25 mC/cm². The P3HT–PCBM mixture was used as the photoactive layer. P3HT and PCBM were dissolved in 1,2-dichlorobenzene by mixing at 80 °C for 30 min. The concentration of each component was 20.0 mg/ml. The solution was cooled down to...
to room temperature and filtered through a 0.45 μm Teflon syringe filter on PEDOT-coated ITO slides. The slides were spun at 300 rpm for an initial 30 s, then the speed was increased to 500 rpm for the next 3 min and finally to 2000 rpm for another 3 min to dry completely. Uniform reddish layers were obtained. Aluminum cathodes (60 nm) were thermally evaporated through the mask at 1 Å/s. The cells were annealed for 10 min at 90 °C after the Al evaporation. The design is shown in Fig. 1. For better accuracy of testing 6 individual cells (0.15 cm²) were fabricated on each slide.

### 3. Results and discussion

The standard oxidation potential of water is 1.23 V vs SHE (25 °C, pH 0). Even though the pH of the NaNO₃ electrolyte solution used in the experiments is close to neutral, a potential value higher than 1.0 vs Ag/AgCl (1.197 V vs SHE) should be avoided. Cycling voltammetry was run up to 1.0 V for all the solubilizers (Fig. 2). Oxidation potential of EDOT (Eₘox) was calculated from voltammograms as the point where current increased by 0.1 mA compared to background level. The values are provided in Table 1. Eₘox increases in the order of PSS–SDS–Twee 80–AOT–κ-carrageenan–no solubilizer–Triton X-100–HDTMA–HDHEDMA from 0.79 to 1.00 V. The nature of the solubilizing agent has a significant effect on EDOT polymerization. It can be concluded that the charge of solubilizer plays an important role. It is a general trend that Eₘox increases moving from anionic to non-ionic to cationic molecules. Apparently, the bulkiness of the solubilizer also contributes as Eₘox(κ-carrageenan) > Eₘox(PSS).

![Fig. 2. Cyclic voltammograms for 10.0 mM EDOT solutions in 0.5 M NaNO₃ recorded in the presence of various solubilizing agents. [b], [d], [h], [i] = 10.0 mM; concentrations of a, c, e, g = 2.5 g/l.](image)

### Table 1

<table>
<thead>
<tr>
<th>Solubilizer</th>
<th>tₘox (s)</th>
<th>tₑad (s)</th>
<th>Eₘox (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSS</td>
<td>5</td>
<td>No</td>
<td>0.79</td>
</tr>
<tr>
<td>SDS</td>
<td>5.9</td>
<td>No</td>
<td>0.81</td>
</tr>
<tr>
<td>κ-Carrageenan</td>
<td>8.8</td>
<td>1.5</td>
<td>0.87</td>
</tr>
<tr>
<td>No solubilizer</td>
<td>9.3</td>
<td>1.5</td>
<td>0.91</td>
</tr>
<tr>
<td>Tween 80</td>
<td>12.7</td>
<td>2.5</td>
<td>0.85</td>
</tr>
<tr>
<td>AOT</td>
<td>13.7</td>
<td>No</td>
<td>0.87</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>22.2</td>
<td>8</td>
<td>0.93</td>
</tr>
<tr>
<td>HDTMA</td>
<td>41.7</td>
<td>25</td>
<td>0.94</td>
</tr>
<tr>
<td>HDHEDMA</td>
<td>263.5</td>
<td>?</td>
<td>1</td>
</tr>
</tbody>
</table>

Eₘox(AOT) > Eₘox(SDS) and Eₘox(HDHEDMA) > Eₘox(HDTMA). Electrochemical polymerization of PEDOT from aqueous solution in the presence of SDS was first performed by Sakmeche et al. [18]. The same Eₘox of 0.81 V (0.76 V vs SCE) was measured on a Pt electrode for a solution containing 50 mM EDOT and 70 mM SDS. Later, a 90 mV negative shift compared to control solution without SDS was reported by the same group [23]. Zhang et al. observed 110 mV decrease in Eₘox for anionic SDS [24]. In addition to anionic surfactants, both authors tried non-ionic Triton X-100 and no significant shift was measured. A 100 mM decrease in Eₘox for SDS (from 0.91 to 0.81 V) and a slight 20 mV increase for Triton X-100 (from 0.91 to 0.93 V) were observed in the present study, finding excellent agreement with the data discussed above. Herein, we aimed to conduct systematic study involving a larger number of solubilizers, including cationic surfactants and polyelectrolytes. It is important that the negatively charged polyelectrolytes also decreased the Eₘox. Moreover, in the case of PSS, the lowest value of Eₘox (0.79 V) was measured. Cationic surfactants in opposite were found to significantly increase Eₘox and the highest value of 1.00 V was measured for HDHEDMA. It is obvious that the solubilizers interact with EDOT before and during the polymerization. The cation-radical mechanism of the polymerization is responsible for such behavior. Apparently negatively charged solubilizers stabilize the oxidized monomer units (EDOT•⁺) and the growing macromolecular chain bearing positive charge before the polymer reaches critical molecular weight and deposits on the electrode surface. In the case of cationic surfactants the same species are destabilized by the environment due to strong electrostatic repulsion. Non-ionic surfactants have a rather intermediate effect.

Chronocoulometry was applied in order to control the amount of the electrodeposited PEDOT. Thin light blue layers were deposited by passing charge of 6.25 mC/cm² at 1.0 V (Fig. 3). Similarly to CV, the nature of the solubilizing agent significantly affected the
kinetics of the depositions. The deposition time \(t_{\text{dep}}\) was strongly influenced by the charge and the bulkiness (steric effect) of the solubilizing agent. In the case of anionic surfactants and polyelectrolytes \(t_{\text{dep}}\) was about 10 s (Table 1). The fastest deposition was observed in the presence of PSS \(t_{\text{dep}} = 5.0\) s which can be attributed to the strong template effect of the polyelectrolyte. Importantly, cationic surfactants drastically slowed down the kinetics of the polymerization. The longest \(t_{\text{dep}}\) of 263.5 s was measured for HDHEDEMA due to the 90 mV shift of \(E_{\text{ox}}\) Basically, in the case of HDHEDEMA the electrodeposition was done on the onset of the polymerization potential. Overall kinetics is consistent with the oxidation potential values. The deposition of the PEDOT layer without any solubilizing agent was achieved in less than 10 s, despite the relatively high \(E_{\text{ox}}\). This phenomenon can probably be attributed to the short induction period, compared, for example, to Tween 80 (Fig. 3, right). The induction period in the initial step of the polymerization is common for many conjugated polymers and is attributed to the formation of dimers and other intermediates, which have lower oxidation potentials. It makes the polymerization an autocatalytic reaction [39,40]. It is interesting that negatively charged solubilizers have no induction period or very short ones, as in the case of \(\kappa\)-carrageenan (Table 1). AOT has no induction period but relatively slow polymerization kinetics apparently due to its bulkiness.

UV–Vis–NIR spectroscopy is a simple and powerful technique to validate the quality of PEDOT. For most applications, including photovoltaics, the polymer should be in a conductive oxidized (doped) state. Conductivity depends on a number of free charge carriers (polaron and bipolarons). The carriers have a signature in the spectrum, namely absorbance in the NIR region [41,42]. Another important property of PEDOT utilized in optoelectronics is its transparency in the Vis region. An ideal PEDOT layer should mostly absorb above 800 nm. The spectra of the layers electrodeposited in the presence of various solubilizers are shown in Fig. 4a. Table 2 summarizes all the data including other solubilizers not shown in Fig. 4a. The layer deposited in the presence of SDS had the best spectrum with a strong absorbance in NIR region. NIR absorbance decreased in the order of SDS–PSS–no solubilizer–Triton X-100–HDTMA, following the kinetics of deposition and \(E_{\text{ox}}\) discussed above. In addition, a shoulder at 500 nm appeared in the case of Triton X-100 and the absorbance shifted to the Vis region. The layer deposited in the presence of HDTMA had a darker color as a result of the large absorbance in the Vis region with a peak at 640 nm. It is important that other surfactants had a similar effect on the spectroscopic properties in accordance with their charge (Table 2). AOT and \(\kappa\)-carrageenan raised the shoulder at 500 nm in addition to the strong absorbance in NIR because of the bulkiness. It can be concluded that the number of free charge carriers in the electrodeposited PEDOT layers greatly depends on the nature of the solubilizing agent.

PEDOT has two redox states like other polythiophenes. The reduced (undoped) state was achieved by subjecting the deposited layers to −1.0 V until the current dropped to zero. The color changed from light blue to dark blue. In the case of cationic surfactants, it changed from blue to purple. The spectrum of PEDOT in its reduced state provides important information about the conjugation length in the polymer [43,44]. The peak at 580 nm (\(\lambda_{\text{max}}\)) observed for PEDOT deposited in the presence of SDS (Fig. 4b) corresponds to the \(\pi−\pi^*\) transition. Overoxidation, branching, twisting and cleavage create defects in the polymer backbone, shortening the conjugation length. As a result, the characteristic peak shifts hypsochromically.

Fig. 3. Potentiostatic deposition of PEDOT layers on ITO in the presence of various solubilizers. Deposition potential 1.0 V vs Ag/AgCl, [PEDOT] = 10 mM; [NaNO3] = 0.5 M; [b], [f], [h], [i] = 10 mM; concentrations of a, c, e, g = 2.5 g/l.

Fig. 4. UV–Vis–NIR spectra of the PEDOT layers electrodeposited in the presence of solubilizing agents: (a) as deposited oxidized; (b) reduced at −1.0 V.
There was a 30 nm shift from 580 to 550 nm depending on the nature of the solubilizing agent (Fig. 4b and Table 2). PEDOT layers deposited in the presence of SDS, PSS and without any solubilizing agent had the longest conjugation lengths with the \( \lambda_{\text{max}} > 570 \) nm. In the case of the non-ionic Tween 80 and Triton X-100 and the cationic HDTMA and HDHEDMA, the \( \lambda_{\text{max}} \) was measured to be at 550 nm while the use of large anionic AOT and \( \kappa \)-carrageenan generated the peaks at 560 nm. It is obvious that a longer conjugation length increases the delocalization of polaron and bipolarons in an oxidized state. Indeed, there was a correlation between \( \lambda_{\text{max}} \) of the reduced layers and NIR absorbance of the oxidized layers (Fig. 4a and b). Reduced PEDOT layers deposited in the presence of anionic solubilizers also showed maxima at 1000 nm corresponding to polarons [41]. This can probably be attributed to the difficulty of complete dedoping. The PEDOT layer deposited without solubilizer represented a special case. Despite relatively low NIR absorbance, the layer had the \( \lambda_{\text{max}} \) at 575 nm, just slightly less than in the case of SDS.

One would expect that negatively charged surfactants (SDS and AOT) act not only as templates but also as counterions affecting the properties of PEDOT in its doped state. However, this is questionable since concentration of surfactants was 50 times less than \( \text{NO}_3^- \). At the same time, polyelectrolytes (PSS and \( \kappa \)-carrageenan) strongly interact with PEDOT due to the formation of interpolyelectrolyte complexes and were found to effectively incorporate into the electrodeposited PEDOT layers [45].

PEDOT has many interesting applications and it is important to correlate the properties of the PEDOT layers with the performance in a functional device. PEDOT layers electrodeposited in the presence of various solubilizing agents were incorporated into P3HT–PCBM polymer solar cells as hole transporting layers. Equivalent thicknesses were achieved by passing the same amount of charge (6.25 mC/cm²). Typical I–V curves of PEDOT layers are shown in Fig. 5 and the characterization is summarized in Table 3. In the case of anionic SDS and AOT, the highest overall efficiency was observed. Both cells showed a current above 6 mA/cm². The highest \( V_{\text{oc}} \) of 0.58 V was measured for SDS and the highest FF of 58.2% for AOT. In the case of the layer deposited without solubilizer efficiency decreased to 1.43% mainly because of the lower \( J_{\text{sc}} \). Nevertheless, the performance was significantly better than it was for the layers deposited in the presence of any other surfactant. The phenomenon can be attributed to a longer conjugation. Even though the density of the free charge carriers is relatively low (NIR absorbance), their mobility is still high because of the long conjugation length (\( \lambda_{\text{max}} = 575 \) nm). This should keep the conductivity at a high level. Conductivity of the electrodeposited PEDOT layers is proportional to the slope of I–V curves recorded in the dark (Fig. 5b) since all the solar cells were fabricated and tested under the same conditions. It can be concluded that only the layers deposited in the presence of SDS and AOT have conductivity significantly higher than the layer deposited without any solubilizer. As was expected, the worst performance was observed in the case of HDHEDMA. The use of Tween 80, PSS, HDTMA, \( \kappa \)-carrageenan and Triton X-100 resulted in \( V_{\text{oc}} \) ranging from 0.28 to 0.42 V and \( J_{\text{sc}} \) ranging from 3.87 to 4.53 mA/cm². Higher \( V_{\text{oc}} \) and slower polymerization kinetics in the presence of Triton X-100 compared to another non-ionic surfactant Tween 80 found reflection in the performance of corresponding solar cells. Efficiency decreased from 0.86 to 0.44%.

In general, the performance of solar cells is consistent with the electrochemical and spectroscopic characterization. The only
exception is with the polyelectrolytes. Indeed, all the parameters and efficiencies of the solar cells are rather low, despite their fast polymerization kinetics, low 

<table>
<thead>
<tr>
<th>Solubilizer</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF</th>
<th>ε (%)</th>
<th>Jmax (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOT</td>
<td>0.51</td>
<td>6.73</td>
<td>58.2</td>
<td>2.1</td>
<td></td>
</tr>
<tr>
<td>SDS</td>
<td>0.58</td>
<td>6.6</td>
<td>51.6</td>
<td>1.98</td>
<td>20</td>
</tr>
<tr>
<td>No solubilizer</td>
<td>0.49</td>
<td>5.67</td>
<td>51.5</td>
<td>1.43</td>
<td>9</td>
</tr>
<tr>
<td>Tween 80</td>
<td>0.41</td>
<td>4.53</td>
<td>46.5</td>
<td>0.86</td>
<td>8</td>
</tr>
<tr>
<td>PSS</td>
<td>0.42</td>
<td>4.13</td>
<td>46.8</td>
<td>0.81</td>
<td>349</td>
</tr>
<tr>
<td>HDTMA</td>
<td>0.35</td>
<td>4.33</td>
<td>38.8</td>
<td>0.59</td>
<td>19</td>
</tr>
<tr>
<td>κ-Carrageenan</td>
<td>0.36</td>
<td>4.13</td>
<td>39.2</td>
<td>0.58</td>
<td>189</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>0.28</td>
<td>3.87</td>
<td>40.8</td>
<td>0.44</td>
<td>15</td>
</tr>
<tr>
<td>HDHEDMA</td>
<td>0.2</td>
<td>2.27</td>
<td>29.1</td>
<td>0.13</td>
<td>5</td>
</tr>
</tbody>
</table>

4. Conclusions

The nature of the solubilizing agent has a dramatic effect on the polymerization conditions and the properties of the electrodeposited PEDOT. Anionic solubilizing agents favor polymerization by lowering the oxidation potential of EDOT and by eliminating the induction period. Conversely, cationic surfactants increase the oxidation potential and exhibit slow polymerization kinetics. Non-ionic surfactants have an intermediate effect. The difference in the oxidation potential reaches 210 mV. As a result, PEDOT layers deposited in the presence of anionic solubilizing agents demonstrated longer conjugation length, higher transparency and increased conductivity. The PEDOT layers were applied as hole transporting layers in P3HT–PCBM polymer solar cells. The performance of these solar cells was found to be consistent with the electrochemical and spectroscopic studies. A maximum overall energy conversion efficiency of 2.0% was measured for the PEDOT layers deposited in the presence of anionic surfactants. In the case of cationic surfactants, efficiency decreased more than an order of magnitude.

We speculate that the cation-radical mechanism of the polymerization is the reason for the aforementioned effect. The charge of the solubilizing agent affects the polymerization by either stabilizing or destabilizing the oxidized monomer units (EDOT•+) and/or growing macromolecular chains. In addition to the primary effect of charge, the bulkiness of the solubilizing agent also plays an important role in the polymerization process.

References