Iron-Catalyzed Polymerization of Alkoxysulfonate-Functionalized 3,4-Ethylenedioxythiophene Gives Water-Soluble Poly(3,4-ethylenedioxythiophene) of High Conductivity

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Chemical polymerization of a 3,4-ethylenedioxythiophene derivative bearing a sulfonate group (EDOT-S) is reported. The polymer, PEDOT-S, is fully water-soluble and has been produced by polymerizing EDOT-S in water, using $Na_2S_2O_8$ and a catalytic amount of $FeCl_3$. Elemental analysis and XPS measurements indicate that PEDOT-S is a material with a substantial degree of self-doping, but also contains free sulfate ions as charge-balancing counterions of the oxidized polymer. Apart from self-doping PEDOT-S, the side chains enable full water solubility of the material; DLS studies show an average cluster size of only 2 nm. Importantly, the solvation properties of the PEDOT-S are reflected in spin-coated films, which show a surface roughness of 1.2 nm and good conductivity (12 S/cm) in ambient conditions. The electro-optical properties of this material are shown with cyclic voltammetry and spectroelectrochemical experiment reveals an electrochromic contrast (∼48% at $\lambda_{max} = 606$ nm).

1. Introduction

Since the discovery that polymers can be electrically conductive, much effort has been put in designing, synthesizing, and studying π-conjugated polymers. Their interesting conducting and/or electro-optical properties have been explored in a number of applications such as photovoltaic devices, photodiodes, printable electronics, and sensors. One of the most successful polymers combining these desired properties is poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT in it's pure form is an insoluble polymer that exhibits high conductivity, exceeding 1000 S/cm in a vapor-phase polymerized film,[1] good thin film transparency, and high stability.[2−4] The insolubility of PEDOT has been circumvented by using an excess of a water-soluble polyelectrolyte [poly(styrene sulfonic acid), (PSS)] as a charge-balancing dopant during polymerization, to yield the commercially available product PEDOT/PSS (Baytron) as an aqueous dispersion. The ability to couple the properties of PEDOT to the simple processability of soluble polymers is a necessity for the formation of homogeneous films in, e.g., optoelectronic applications. However, films formed from Baytron have a granular structure, due to the micellar character of the solution, with conducting particles surrounded by PSS.[5] The excess of PSS and the grains in PEDOT/PSS films give a material of lower conductivity compared to vapor-phase polymerized PEDOT. It has been shown that a separation occurs between PEDOT and PSS at surfaces.[5] The PSS segregated layer at the film/air boundary is estimated to be $\approx 30-40$ Å. This partly insulating layer with characteristics deviating from the bulk properties has several implications for device function, such as a changed charge injection conditions, and degradation caused by high concentration of the acidic groups on PSS. When critical dimensions in device applications are approaching the true nanoregime (<100 nm), an interfacial layer of up to 4 nm will have a significant impact on the overall characteristics. Therefore, new forms of PEDOT without these limitations are desirable.

An appealing idea is the integration between a soluble PEDOT and biomolecules in self-assembly processes. By utilization of both geometries, for example, wire-like features of misfolded protein in the form of amyloid, and available functional groups interacting with PEDOT, as well as organization in higher levels of hierarchy, alignment of nanosized wires into micrometer large patterns can be realized. Such systems may demonstrate new concepts in the fields of electronics and in tissue engineering.[6,7] The use of conjugated polymers as sensor materials has been extensively reviewed.[8] Both sensing and interactions with

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Scheme 1

templates are dependent on strong interactions with the conjugated material, implicating that a two-component material such as PEDOT/PSS, where the unconjugated PSS is in excess, is not an optimal choice. A single-species material with good solubility, for example, enabled by a side chain derivatization of PEDOT, would give a whole new range of possibilities in these applications. For combinations with biomolecules, either for sensing or template self-assembly, the polymer material should be fully water-soluble. Furthermore, to achieve close interaction between a polymer and a second species, it is preferred that the polymer is present as separated polymer chains or very small clusters in solution.

Despite the large number of potential applications, only a few examples of chemically polymerized, soluble, PEDOT derivates have been demonstrated. Zotti's group has reported a highly soluble, sulfonated PEDOT with good conductivity,[9] and Reynolds group has reported an alkane-substituted, chloroform-soluble PEDOT[10] and soluble derivates of the PEDOT-like PProDOT,[11] where the latter could demonstrate conductivities of 7 S/cm upon iodine doping.

The synthesis of fully water-soluble EDOT derivatives and polymers thereof, for example, poly(4-(2,3-dihydrothieno [3,4-b]-[1,4]dioxin-2-yl-methoxy)-1-butanesulfonic acid, sodium salt), (PEDOT-S, Scheme 1), is highly advantageous in terms of versatility of polymerization conditions and polymer processing. PEDOT-S was synthesized electrochemically by Stephán et al.,[12] as a copolymer with EDOT, and recently Reynolds and co-workers[13,14] have reported the successful chemical synthesis of water-soluble, self-doped PEDOT-S polyelectrolyte, for multilayer film depositions in conjugation with PAH (poly(allylamine hydrochloride)). However, this PEDOT-S showed low conductivity, 2.5×10^{-4} S/cm in as-deposited multilayer films.

In this work we report a synthetic route for chemically prepared, *fully* water-soluble PEDOT-S homopolymer (Scheme 1). We produce these chains via chemical oxidation by using an iron redox agent in a catalytic amount and a primary oxidant. Such a route has earlier been reported in a patent by Jonas and Kirchmeyer, using pure EDOT in dispersions of PSS,[15] but to our knowledge this concept has not been shown on a single-species polymer system.

We demonstrate by dynamic light scattering (DLS) measurements that this polymer is present as single polymer chains or as very small polymer complexes in solution, and we show its characterization by elemental analysis, X-ray photoelectron spectroscopy (XPS), cyclic voltammetry, UV−vis spectroscopy, atomic force microscopy (AFM), and conductivity measurements. The unique properties of the PEDOT-S reported here have been essential for generating conducting biotemplated nanowires, in the form of PEDOT-S coated amyloid fibrils, recently reported by Hamedi et al.[16] PEDOT-S/amyloid fibril nanowire networks were furthermore integrated as the electroactive material in fully functional electrochemical transistors operating at low voltages, between 0 and 0.5 V.

2. Results and Discussion

2.1. Polymer Synthesis and Characterization. EDOT-S[12] was kindly donated by HC Starck. The polymerization of EDOT-S was accomplished by dropwise addition of an aqueous mixture of $Na_2S_2O_8$ and a catalytic amount of $FeCl_3$ to a solution of EDOT-S in water, yielding PEDOT-S. We suggest a synthesis route according to Scheme 1 (Scheme 1).

Instantaneously upon addition of the oxidant mixture, the EDOT-S solution turned deep blue and after 3 h the reaction was quenched and the product precipitated by dilution with acetone. The precipitate was collected through centrifugation. The collected precipitate was dissolved in water and reprecipitated twice with acetone. Finally, the polymer was dialyzed with deionized water for 2 days using a 1000 g/mol cutoff membrane and freeze-dried, yielding PEDOT-S as a dark bluish powder prior to use. The overall yield of the polymerization is $\sim 45\%$. NMR spectroscopy in D_2O gave broad signals in agreement with doping of PEDOT-S; however, due to poor resolution, no good spectra were obtained. FT-IR transmission spectra (4000−1200 cm^{-1}) were taken on drop-casted PEDOT-S on CaF_2 windows. Absence of characteristic bands in the region 3600−1800 cm^{-1}, where the side-chain functionalities and incorporated hydroxide ions should appear, indicates doping of the material, similarly to what has been seen by Singh et al.[17]

Molecular weight determination was not possible using MALDI-TOF, but the dialysis procedure used in the purification removed the shortest oligomer chains.

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Table 1. Comparison of Elemental Composition in Neutral PEDOT-S and Experimentally Prepared Sulfate-Doped PEDOT-S

type of PEDOT-S	C (mass %)	H (mass %)	S (mass %)	O (mass %)	Na (mass %)	Fe (mass %)
neutral PEDOT-S (expected)	40.24	3.99	19.53	29.24	6.9	0
doped PEDOT-S (experimental)	39.7	4.3	19.9	33.2	0.21	0.038

Table 2. Calculations of the Level of Sulfate Based on the Elemental Analysis Results for Carbon and Sulfur

element distribution	total (experimental)	$(-C_{11}H_{13}O_6S_2Na-)_n$[a]	SO_4^{2-}[c]	unaccounted
C (mass %)	39.7	39.7		
H (mass %)	4.3	3.9		0.4
S (mass %)	19.9	19.3	0.6	
O (mass %)	33.2	28.8	1.2	3.2
Na (mass %)	0.21	6.9		
total mass in 100 g	97.31	98.6	1.8	3.6
molar mass (g mol^{-1})		328.34[b]	96.1	
amount (mol) in 100 g		0.30	0.018	
mole ratio of SO_4^{2-}			0.06	
presumed doping level of sulfate ions (%)			12	

[a] PEDOT-S. [b] For each monomer unit in PEDOT-S. [c] A calculation based on the assumption that the excess sulfur originates from incorporated sulfate ions acting as counterions.

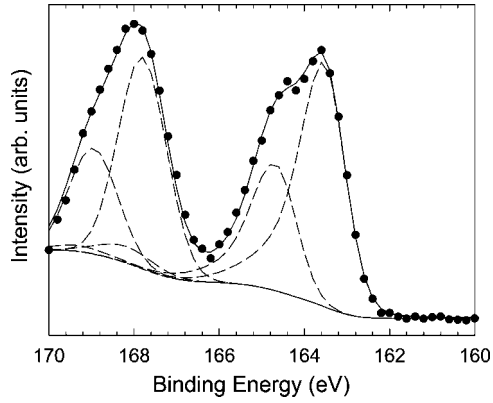

Figure 1. S(2p) signals from chemically prepared PEDOT-S. Experimental S(2p) spectrum (dotted line), fitted S(2p) spectrum (solid line), and individual peaks and background (dashed lines).

Tables 1 and 2 summarize the calculated percentage of each element expected in neutral PEDOT-S and the actual percentage of each element determined by elemental analysis. The observed elemental composition for PEDOT-S is in good agreement with that calculated for the elements C, H, S, and O. The observed data show a sulfur excess and that only a very small amount of sodium ions is present in the polymer. Considering the polymerization method, it is plausible that the sulfur excess is present in the form of sulfate ions, acting as charge-balancing counterions for the intrinsic doping of the PEDOT-S. As calculated in Table 2, sulfate ions alone could give a ~12% doping level of the material based on the observed mass ratios of carbon (39.7%) and sulfur (19.9%). This estimated sulfate level is in good agreement with that determined by means of S(2p) XPS spectrum, which is shown in Figure 1. Peak deconvolution of the S(2p) core level was carried out using three spin-split Gaussian doublets ($2p_{3/2}$, $2p_{1/2}$) representing PEDOT, SO_3^-, and SO_4^{2-} sulfur. A standard Shirley background was applied prior to deconvolution. All of the spin-split doublets are fixed in relative intensity (1:2) and binding energy split (~1.2 eV). The S(2p) doublet at 163.5 eV comes from PEDOT, where the asymmetric tail mimics the effect of p-doping according to the standard procedure.[18,19] The doublet at 167.8 eV is assigned to the SO_3Na functionality on PEDOT-S and the doublet at 168.2 eV to SO_4^{2-}. The relative concentration of the sulfate sulfur is 3% for the deconvolution in Figure 1, in agreement with the elemental analysis.

The element analysis furthermore shows a very low amount of iron, which is advantageous since iron, being a redox-active material, may cause unwanted electrochemical reactions in the polymer materials.

The results of Table 2 show that 3.6% of the mass of the polymer is not accounted for. This can be associated with species that contain hydrogen and oxygen because there are excess levels of these two elements, probably due to moisture absorbed by PEDOT-S during the synthesis. Although the polymer sample is dried in the preparation for element analysis, this level of moisture cannot be completely removed. There have also been suggestions by Seo and Chung[20] and Khulbe et al.[21] that an excess of oxygen in the elemental analysis result is due to overoxidation of PEDOT during the polymerization process.

The conductivity of the polymer and the low content of sodium suggest that additional counterions are present in the material. One appealing thought is that the covalently attached sulfonate group on the side chain might give rise to the doping; i.e., the PEDOT-S is a partly self-doped material.

The concept of self-doping conducting polymers has been introduced by Patil at al.[22] and a lot of effort has been put into development and characterization of self-acid-doped polyaniline by Chen and Hwang; although the latter is self-doped through a protonation process, a lot of insight has been

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reported on how alkoxy-sulfonate chains can be utilized as functional groups for self-doped polymers.[23,24]

However, the combined charge of sulfonate and sulfate groups in PEDOT-S would be 1.12 per monomer, much above what has been observed in other forms of PEDOT. The doping level, as estimated from conductivity and optical properties, is closer to the 0.2−0.3 level as found in other PEDOTs. Therefore, compensating cations must be present, in the form of protons or sodium. As sodium is present (0.03 sodium ions per EDOT), and the sulfate ion charge is 0.12, adding to 0.15, a more plausible doping level of 0.2−0.3 would require 1 proton on 10 EDOTs.

The low content of sodium in PEDOT-S, and its high solubility (over 40 mg/mL), suggest that an ion exchange has occurred between sodium and protons that has been released during polymerization.

However, the access of small, free counterions, such as sulfate ions, in solution during polymerization is likely to ease the solvation of the polymer, enabling the possibility for an increased interaction between water molecules and the ionic side chains.

Another cause of the low content of sodium is that the covalently attached functionalities are cross-linked between polymers, forming a charge neutral polymer complex during the formation of polarons (vide infra).

The earlier reported chemical synthesis of PEDOT-S was performed in chloroform with $FeCl_3$ as polymerization agent.[13] The polymerization was followed by chemical dedoping, ion exchange, and dialysis. Zotti's group has chemically prepared a water-soluble homopolymer of PEDTS by applying 3 equiv of $Fe(OTs)_3$ to a heated (80 °C) aqueous solution of EDTS (4-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethoxy)-butane-1-sulfonic acid)) under conditions of high concentration.[9]

To compare and elucidate the reaction mechanisms in our polymerization route, using a persulfate salt and catalytic amount of iron, we chemically polymerized EDOT-S with $FeCl_3$ and $Fe(OTs)_3$ respectively in water solutions. In this case the polymers formed precipitates from the aqueous reaction mixtures which were collected as dark green insoluble materials. It is possible when iron(III) is used as an oxidant in larger concentrations that iron cross-links the negative sulfonate groups on PEDOT-S and causes the precipitation of the polymers. Similar results have been reported.[25] In those cases the content of iron after polymerization was measured by elemental analysis, to reveal high amounts of iron left after purification of the polymer. In our novel approach for polymerization of EDOT-S the content of iron after polymerization is negligible (see Table 1). This not only ensures the solubility of PEDOT-S, by maximizing the interactions between the ionic side chains of PEDOT-S with the surrounding water, but also minimizes the time needed to obtain a pure product without iron contamination.

The use of peroxy salts as a primary oxidant for polymerization of EDOT (3,4-ethylendioxythiophen) from an aqueous solution has been reported successfully by Bowmakers group.[26]

Once more to shed light over the polymerization process we report in this work, we attempted to polymerize EDOT-S from an aqueous solution with sodiumpersulfate. The same procedure was accomplished by adding 2 equiv of $Na_2S_2O_8$ to an aqueous solution of EDOT-S. The final green material (after 72 h reaction) was soluble and could be spin-coated to uneven, insulating films. This is presumably not the same material that we obtain by the catalytic route.

2.2. DLS Measurements. Dynamic light scattering (DLS) experiments were performed to determine an averaged hydrodynamic radius of the polymer in solution. The signal strength was low (∼15 ± 5 kHz), probably because of the polymer absorbing the incident laser light. PEDOT-S is soluble in water up to very high concentrations, >40 mg/mL. The optimal concentration for DLS was evaluated over a range of concentrations to yield the best signal possible. The polymer concentration used (100 μg/mL) resulted in the highest measurable signal; increased polymer concentration resulted in total absorption and extinguishment of the scattered light. With use of the DLS software, the hydrodynamic radius (R_h) was calculated and weighted in relation to the number of particles in the samples. The measured values are shown in Figure 2(a,b), the averaged R_h measured on five samples with a main R_h of 2 ± 1 nm and minor peaks at 5 and 10 nm. However, the trace in the correlation curve (10−1000 ms) also shows a significant amount of larger polymer complexes ∼140 ± 40 nm but the signal in this region is suppressed when weighted against the number of scattering particles since the intensity of scattered light is proportional to R_h.[6] This value can be compared with the average particle size of the Baytron P dispersion, which is 80 nm, according to the manufacturer.

These results suggest that PEDOT-S exists primarily as single chains or in very small aggregates in water solution.

2.3. Polymer Electrochemistry. The electrochemical characteristics of PEDOT-S were obtained on spin-coated films of PEDOT-S on Pt electrodes and using Pt as a counter electrode and a Pt wire as a quasi reference electrode. The measurements were made in a $LiClO_4$ (0.1 M) acetonitrile electrolyte, bubbled with a nitrogen gas to ensure minimal background signals. The scan rate dependence suggests non-diffusion-limited redox processes, up to at least 600 mV/s, and there is a positive shift in the oxidation potential at faster scan rates as seen from Figure 3. The redox processes are centered at −0.15 V vs Pt quasi reference electrode at 100 mV/s.

2.4. Optical Properties. Spectroelectrochemistry experiments of PEDOT-S spin-coated on ITO were performed in 0.1 M $LiClO_4$ in acetonitrile. Spin coating was done as described in section 2.5. Upon switching of the film from the neutral state to the oxidized, a distinct color change from purple to pale blue occurred. This is a consequence of the decrease of absorption of the $\pi-\pi^*$ transition ($\lambda_{max} = 606$ nm), followed by increased absorption in the IR region due

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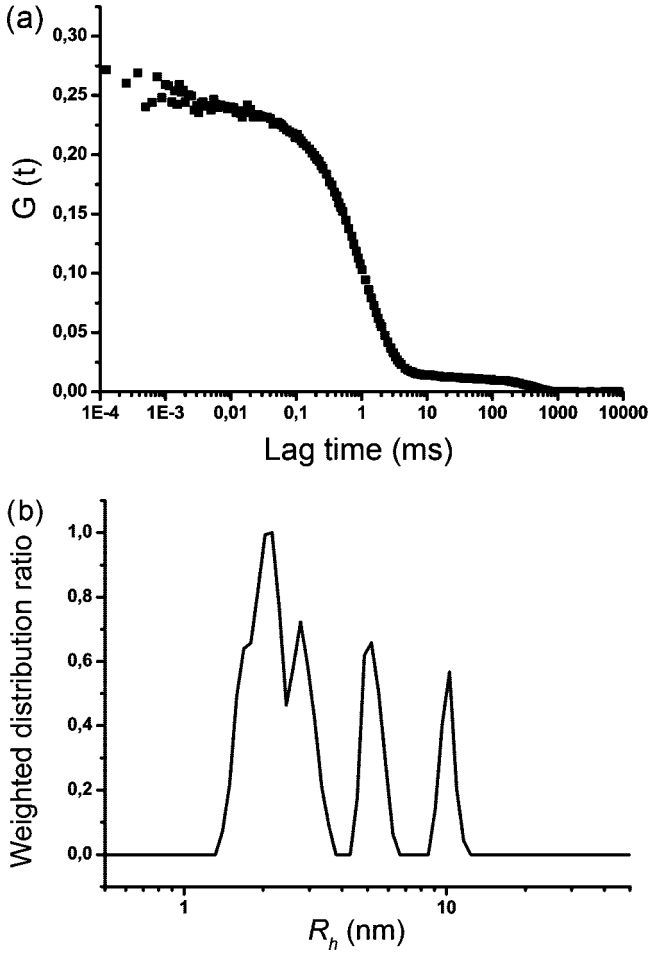

Figure 2. (a) Typical correlation curve of DLS with PEDOT-S. (b) Averaged hydrodynamic radius from five experiments (number weighted).

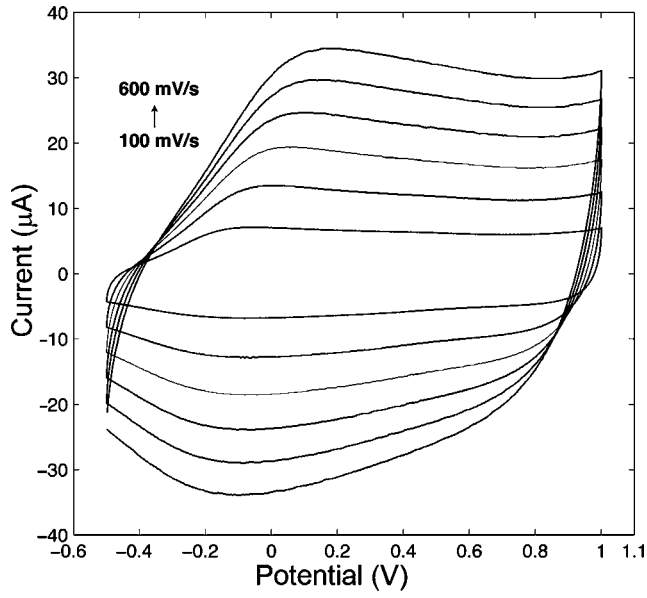

Figure 3. Cyclic voltammograms of PEDOT-S films at scan rates between 100 and 600 mV/s in $LiClO_4$ (0.1 M)/acetonitrile.

to the formation of polarons (Figure 4a). The electrochromic contrast of PEDOT-S was ~48%, calculated as the change in transmission at 606 nm between the reduced and oxidized state, which is comparable to PEDOT having a contrast of 44%.[26]

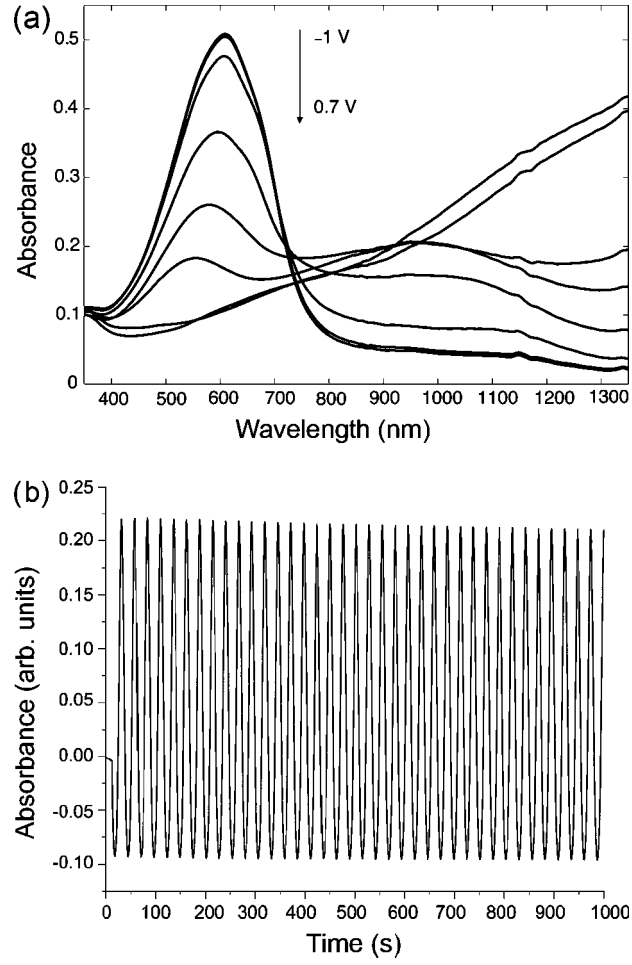

Figure 4. (a) Spectroelectrochemistry of spin-coated PEDOT-S on ITO in $LiClO_4$ (0.1 M) in acetonitrile. A three-electrode system with a Ag/AgCl quasi reference electrode was used. (b) Repeated switch cycles 0 to −1 V, while measuring the absorption at 606 nm.

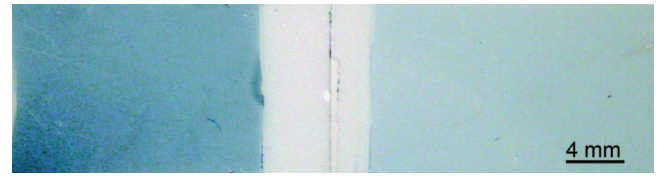

Figure 5. Spin-coated films: (left) PEDOT-S (thickness 60 nm); (right) PEDOT/PSS (Baytron P) (thickness 120 nm).

In addition to the spectroelectrochemistry a repetitive cycling was made, by switching the film between 0 and −1 V and continuously measuring the absorption values at the absorption peak maximum (see Figure 4b). The result demonstrates good electrochemical stability and redox reversibility of the PEDOT-S films. No visible change in the performance of the switching can be observed over the time range of the experiment (1000 s).

2.5. Conductivity Measurement and Film Surface Characterization. Freeze-dried PEDOT-S was easily dissolved in water and spin-coated into homogeneous films on glass substrates. Figure 5 shows a 60 nm thick PEDOT-S film spin-coated from a 20 mg/mL PEDOT-S solution and as a comparison a 120 nm thick Baytron P film. The mass fraction between PEDOT backbone and the sulfonate functionality in PEDOT-S is 139/310, which gives a content of 45% versus

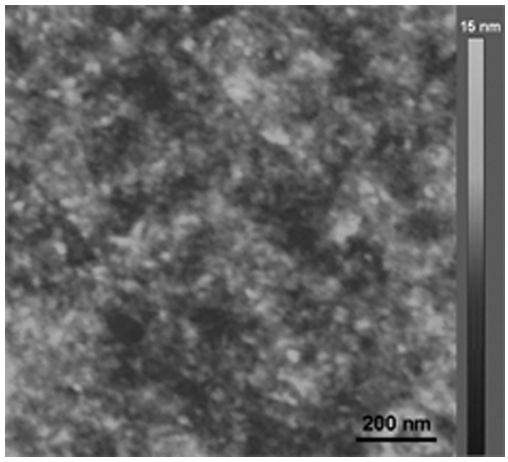

Figure 6. AFM micrograph (1.1 μm × 1.1 μm^2) of a spin-coated PEDOT-S film obtained in tapping mode under ambient conditions.

30% PEDOT of the solid content in Baytron P. This can explain the visible differences in contrast between the films.

The conductivity of spin-coated PEDOT-S films was determined to be 12 S/cm with four-point-probe measurements in ambient conditions, and a sample of Baytron P demonstrated a conductivity of 0.03 S/cm under identical conditions. It should however be noted that higher values of Baytron P conductivity has been reported elsewhere[27,28] and that the combined chemical and thermal treatment can give much higher conductivities.

Optical microscopy revealed a smooth and domain-free PEDOT-S film. The nanostructure of the film was studied with AFM, giving a root-mean-square roughness of 1.2 nm. This value can be compared with reported values of PEDOT/PSS. Jönsson et al. showed 4.9 nm in average height variation of pristine PEDOT/PSS,[18] whereas others have demonstrated smoother PEDOT/PSS.[27,28] A low density of larger aggregates, domains approximately 100 nm in diameter and up to 10 nm in height, could also be found in the PEDOT-S film. Presumably, these aggregates are larger insoluble particles of PEDOT-S, which could be circumvented in further optimization of the synthesis or through filtration. The surface morphology was not changed notably by moderate heating (100 °C, 10 min).

Roughness analysis done on areas of the same size as Figure 6 gave an average R_q of 1.2 nm. In this value larger aggregates were avoided. Roughness analysis on larger areas with the aggregates included gave an R_q of 2.7 nm.

3. Conclusion

In conclusion, we report a chemically polymerized PEDOT derivate, which shows high conductivity in as-prepared spin-coated films. The PEDOT-S exhibits high yield, full water-solubility, and good electrochromic contrast.

The polymerization route we report here can be compared with the known Fenton's reaction (Fe salts and hydrogen peroxide). Apart from regenerating Fe(III), the persulfate salt ensures the possibility of incorporation of free sulfate ion as charge-balancing counterions of the oxidized polymer. Importantly, persulfate salts can be used under nonacidic conditions, implying that other molecules, such as biomolecules, can be present during the polymerization.

DLS measurements reveal an average polymer cluster size in the range of 2 ± 1 nm. This can effectively be associated with single polymer chains in solution, or with small polymer complexes.

PEDOT-S offers opportunities for nanopatterning, as biomolecular nanotemplates may be used to shape the material. The absence of insulating nanodomains in PEDOT-S is advantageous, as such domains may dominate conduction in nanostructured materials. Furthermore, the possibility to form films of PEDOT-S alone or in combination with PEDOT/PSS has the potential of giving high contrast in very thin layers of polymer, necessary for efficient electrochromic devices.

4. Experimental Section

4.1. Chemicals and Reagents. Pure 4-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethoxy)-butane-1-sulfonic acid sodium salt (EDOT-S) was kindly donated by HC Starck. $FeCl_3$ and $Na_2S_2O_8$ were purchased from Aldrich. All other chemicals were reagent grade and used as-received.

4.2. Poly(4-(2,3-dihydro-thieno[3,4-b][1,4]dioxin-2-ylmethoxy)-butane-1-sulfonic acid sodium salt). EDOT-S (0.200 g, 0.61 mmol) was solved in water (3 mL). A mixture of $Na_2S_2O_8$ (0.29 g, 1.22 mmol) and $FeCl_3$ (0.005 g, 0.031 mmol) solved in water (3 mL) was dropwise added to the stirred solution. After 3 h the reaction was quenched by dilution with acetone (40 mL). When the product precipitated, it was centrifuged (5 min, 3500 rpm). The collected precipitate was dissolved in water (7 mL) and precipitated from acetone (40 mL). The procedure was repeated twice. Finally, the polymer was dialyzed against deionized water for 2 days using a 1000 g/mol cutoff membrane (Spectra/Por) and freeze-dried prior to use. Yield ∼ 45% (with respect to monomer unit).

4.3. Elemental Analysis. The elemental analysis was performed at MIKRO KEMI AB, Uppsala, Sweden, and at ALS Analytica, Luleå, Sweden. The elemental analysis of doped PEDOT-S samples was used to calculate the doping level with respect to sulfate ions in the samples. The doping level is defined as the average number of positive charges per monomer unit in the polymer, expressed as a percentage. The doping level with respect to a double-charged anionic dopant (e.g., SO_4^{2-}) is twice the number of anions per monomer unit.

4.4. X-ray Photoelectron Spectroscopy. The experiments were carried out using a Scienta ESCA 200 spectrometer. The vacuum system consists of an analysis chamber and a preparation chamber. X-ray photoelectron spectroscopy (XPS) was performed in the analysis chamber at base pressure of 10^{-10} mbar, using monochromatized Al Kα X-rays, at $h\nu$ = 1486.6 eV. The experimental conditions are such that the full-width at half-maximum (fwhm) of the gold Au($4f_{7/2}$) line is 0.65 eV. The binding energies are obtained with an error of ±0.05 eV.

4.5. Conductivity and Film Surface Measurements. Freeze-dried PEDOT-S was dissolved in Milli-Q water at a concentration of 20 mg/mL. Spin coating was done on clean glass substrates or ITO-coated glass at 2500 rpm, which resulted in a film thickness of 110 nm measured by a profilometer (Dektak). As a reference sample Baytron P was spin-coated at 2000 rpm, resulting in a thickness of 120 nm. The conductivity measurement was made by

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using a four-probe setup with four identical metal needles with 1 mm spacing, connected to a Keithley parameter analyzer. The thickness of the spin-coated films was measured using a Dektak profilometer from Veeco. AFM measurements were performed on spin-coated PEDOT-S on clean glass in tapping mode under ambient conditions with a Dimension 3100 (Veeco).

4.6. Spectroelectrochemistry. The spectroelectrochemistry measurements were done by placing the PEDOT-S film inside an acetonitrile electrolyte $LiClO_4$ (0.1 M) in a quartz cuvette and measuring absorbance with a spectrophotometer (Lambda 950, PerkinElmer).

4.7. DLS Measurements. The hydrodynamic radius (R_h) of PEDOT-S was determined by dynamic light scattering (DLS) and averaged from five measurements. PEDOT-S (0.1 mg) was dissolved in Milli-Q water (final concentration 0.1 mg/mL). The setup used was based on the ALV/DLS/SLS-5022, compact goniometer system (ALV-Gmbh, Germany) with a HeNe laser (632 nm, power 22 mW) as light source and two avalanche photo diodes (PerkinElmer, Canada) working in cross auto correlation mode. The temperature was kept constant (293.25 ± 0.05K) in the surrounding toluene bath ((Sigma Aldrich) filtered trough a Whatman Anotrop/Anopore syringe filter (0.02 μm VWR, Sweden)). The scattered light was collected at 90° from the incident laser. The intensity correlation curves were analyzed with the ALV-500/E/EPP + ALV-60XO-win V3.0.2.3 software based on standard CONTIN analysis.

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