

Enhanced Molecular Order in Polythiophene Films Electropolymerized in a Mixed Electrolyte of Anionic Surfactants and Boron Trifluoride Diethyl Etherate

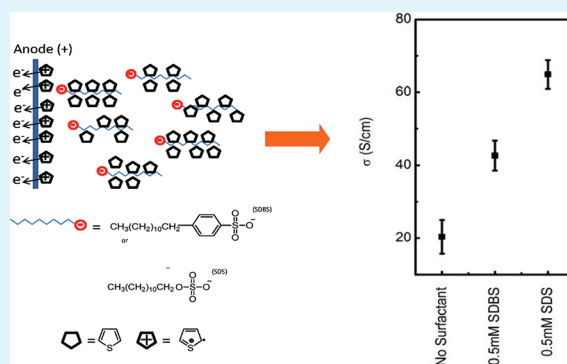
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S Supporting Information

ABSTRACT: We synthesized polythiophene (PTh) films on stainless steel electrodes using chronoamperometry in boron trifluoride diethyl etherate (BFEE) electrolyte with anionic surfactants. The presence of the anionic surfactants in BFEE reduced the oxidation potential of thiophene and increased the oxidation current during electropolymerization. The measured in-plane electrical conductivity of PTh films synthesized in the presence of anionic surfactants was up to 300% higher than that of films synthesized under similar conditions without surfactants. The observed increase in conductivity reflects the improved order and packing of polymer chains revealed by X-ray diffraction.

KEYWORDS: polythiophene, anionic surfactants, SDS, SDBS, electro-oxidation, BFEE, sonication, electrodeposition



1. INTRODUCTION

Among intrinsically conductive or conjugated polymers, polythiophenes (PThs) are especially attractive for several applications (e.g., thermoelectrics,^{1,2} electrochromic displays,^{3,4} corrosion protection,^{5,6} and others^{7–12}) because of their light weight, flexibility, structural diversity, and chemical, electrochemical, and environmental stability in both their doped and undoped states.^{13–15} Compared to other methods for chemical syntheses of conducting poly (heterocycles) such as PTh, anodic electropolymerization presents several distinct advantages, such as catalyst free synthesis, direct grafting of the doped conducting polymer onto the electrode surface, control of the film thickness by the deposition charge, and the possibility of in situ electrochemical characterization during the growth process. The structure and properties of the resulting polymer films are determined to a large extent by the electrosynthesis conditions.^{16–18}

Electrochemical routes offer the ability to control molecular arrangement, yet many difficulties exist when attempting to electrosynthesize PTh in aqueous media due to its poor solubility in water and higher oxidation potential than that of water.^{19–21} This problem has been addressed previously by using anionic surfactant solution to increase the solubility of thiophene and its derivatives (e.g., EDOT) in water, providing an electrocatalytic effect during polymerization^{19–22} and modifying the characteristics of the metal/electrolyte interface.²³ Alternatively, nonaqueous organic solvents such as acetonitrile (CH₃CN) with different supporting electrolytes have been used as the reaction medium for thiophene

electropolymerization.^{3,6,17,24,25} Electropolymerization of thiophene in acetonitrile (or nonaqueous solvents in general) can help prevent oxide formation on metal electrodes, which is especially attractive for corrosion protection applications,^{5,6} as well as deleterious effects of hydrogen evolution during the deposition process. However, polymer films synthesized in acetonitrile exhibit low conductivity (10–20 S/cm) and poor mechanical strength.

During the past decade, boron trifluoride diethyl etherate (BFEE) has been used as a novel solvent-electrolyte system for electropolymerizing suitable monomers into conducting polymers.^{26–32} The conductivity of BFEE is relatively low and ranges between 3×10^{-4} and 9×10^{-4} S/cm. The conductivity in this electrolyte results from the existence of polar molecules $[(C_2H_5)_3O^+][BF_4^-]$, which provide enough ions to produce a conducting medium; and the complexation of small quantities of water, which generate H^+BF_3OH species that behave as electrolyte.³³ PTh films produced in BFEE solution show great improvement in their electrical and mechanical properties because this Lewis acid reduces the oxidation potential of thiophene compared to PTh films made by deposition in a strong acidic solution or other nonaqueous solution, e.g., acetonitrile.²⁷ The complexation of thiophene and BF_3 from BFEE due to Lewis acid–base interactions between sulfur of the thiophene ring and BF_3 leads to

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decreased aromaticity of the thiophene ring, which lowers the oxidation potential of the monomer.³⁴ The shifts in frequency for C=C and C-C stretching bands in FT-Raman studies confirm the decrease in aromaticity of thiophene in BFEE.^{27,34} Despite improvements gained from electropolymerizing PTh in BFEE electrolyte,³⁵ the electrical conductivity and mechanical strength of PTh films are in general lower than that of most metals and inorganic semiconductors,^{7,36–38} which limits their use.

Surfactants are generally attractive for use in electropolymerization because of their potential to increase electrostatic diffusion to the electrode, improve the solubility of hydrophobic monomer in aqueous electrolyte, and serve as a soft template for molecular ordering.^{19–22} We investigate here the role of the anionic surfactants sodium dodecyl sulfate (SDS) and sodium dodecyl benzene sulfonate (SDBS) as supporting electrolyte in the electrochemical polymerization of thiophene in BFEE. We hypothesized that SDS and SDBS surfactant ions could increase the solution conductivity; lower the monomer oxidation potential and improve molecular alignment in PTh films synthesized in BFEE. Both surfactants were successfully solvated in BFEE by addition of sonic energy. Adding the surfactants to BFEE was found to increase the conductivity of the electrolyte medium and lower the monomer oxidation potential of thiophene. Wide-angle X-ray scattering revealed that molecular ordering was improved in PTh films electrosynthesized in the presence of surfactants, which produced polymer films with enhanced electrical conductivity and no change to mechanical strength.

2. EXPERIMENTAL SECTION

2.1. Materials. Stainless steel (AISI 304) with thickness of 0.025 mm and BFEE (46.5+%) in a sealed container under argon were purchased from Alfa Aesar. Thiophene (>99%) monomer, SDBS, and SDS (technical grade) were purchased from Sigma Aldrich. All materials were used as received unless otherwise specified.

BFEE is an extremely moisture-sensitive solvent. Therefore, the exposure of BFEE to air must be controlled in order to produce PTh films with consistent properties. Despite storing the solution under argon in a sealed container, we observed that the condition of the BFEE changed overtime during this work. In addition, different batches of the same type of BFEE purchased from Alfa Aesar resulted in PTh films with different properties. BFEE received from Alfa Aesar is reported to have less than 0.1% water; however, even small variations in water content can lead to inconsistent electrochemical behavior and make it difficult to synthesize PTh films with reproducible properties. Therefore, a control PTh film (i.e., PTh without surfactant) was synthesized every time a new batch of BFEE was used so that data could be normalized to the properties of this control. Another approach to control the quality of the BFEE used here was to freshly distill the BFEE before each experiment, which improved reproducibility. **Caution:** BFEE is toxic and corrosive and should be handled with proper protective equipment.

2.2. Electropolymerization of Thiophene in Anionic Surfactants/BFEE. PTh films were grown at a constant current of 0.5 mA/cm² in a one-compartment, three electrode cell using a Basi Epsilon C3 potentiostat. Cyclic voltammetry was performed from 1600 mV to -700 mV with a scan speed of 200 mV/s or 20 mV/s to study the electrochemical behavior of the system. The reference electrode was Ag/AgCl. Mirror-polished stainless steel (SS) sheets of size 5 × 2 cm, and 5.5 × 2.5 cm were used as the working and counter electrode, respectively. The polished SS electrodes were placed in an acetone bath that was sonicated for 30 min, and then dried under vacuum for 30 min prior to each experiment. The contact resistance between the electrodes and the lead wires connecting the electrodes with the energy source was measured to be 0.6 Ω. The distance between the

working and counter electrode was held constant at 5 mm. All solutions were deaerated by bubbling argon gas for 30 min and were maintained at a low overpressure during the polymerization process. Thiophene monomer was mixed in electrolyte solvent during the deoxygenation process to synthesize control samples. For mixed electrolyte, BFEE and surfactants were sonicated without monomer to improve the solvation (ionization) of the surfactants in the low polarity electrolyte (detailed in the Supporting Information). All electropolymerization experiments were performed at 21 ± 1 °C. Freestanding PTh films were washed with acetone and dried for 8 h under vacuum before characterization.

2.3. Characterization. Electrical conductivity of PTh films (1 × 1 cm) was measured 8 h after the films were made using a Keithley 2400 multimeter and the inline four probe technique.³⁹ Film thickness was measured using a scanning electron microscope (SEM). Mechanical properties of 0.5 × 2 cm strips of polythiophene (PTh) films were measured under tension using dynamic mechanical analysis (DMA) (QA800 by TA Instruments). The strain rate and clamping pressure used during the testing were 2 mm/s and 13.8 kPa respectively. Wide-angle X-ray scattering (WAXS) patterns were obtained to calculate the molecular spacing of PTh in transmission mode with a Rigaku Micromax 002 X-ray generator ($\lambda = 0.15418$ nm) and R-axis IV+ detector system; the total exposure time was two hours for each sample.

3. RESULTS AND DISCUSSION

3.1. Electrochemical Behavior of Thiophene in Anionic Surfactants/BFEE Mixed Electrolyte. Panels a and b in Figure 1 show cyclic voltamograms (CVs) of 50 mM

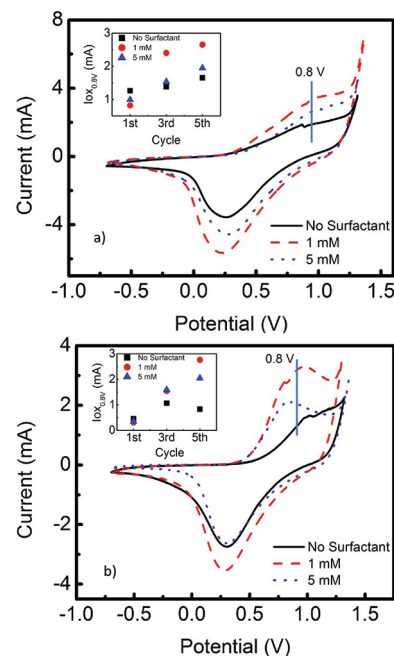
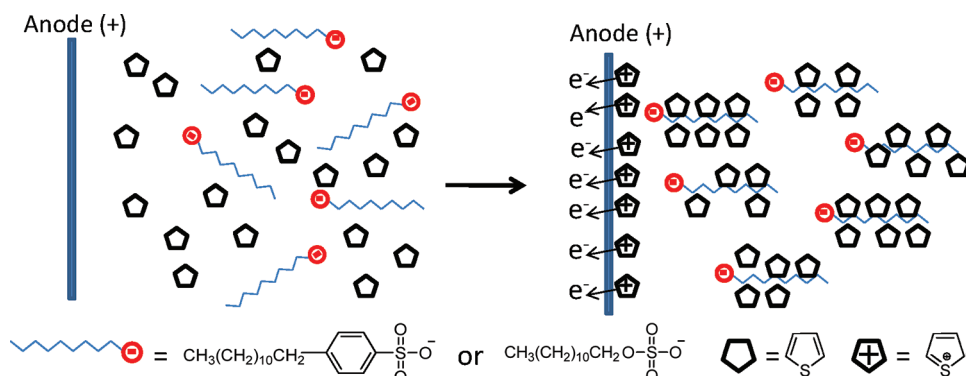


Figure 1. Cyclic voltamogram of thiophene in (a) SDS/BFEE and (b) SDBS/BFEE. Insets are the oxidation current densities at 0.8 V for 50 mM thiophene at 20 mV/s scan speed.

thiophene in SDBS/BFEE and SDS/BFEE electrolyte solutions, respectively. Five continuous CV sweeps were performed; the fifth cycle is shown in Figure 1, along with the oxidation current at 0.8 V for the first, third, and fifth cycle. The shape of the CVs is similar for solutions with and without surfactant; however, the oxidation potential for thiophene is lower in the presence of either SDBS or SDS. Despite the relatively small decrease in oxidation potential in the presence

Scheme 1. Illustration of Diffusion of Anionic Surfactant in BFEE Electrolyte during Electropolymerization of Thiophene



of SDS compared to SDBS shown in Figure 1a, this trend was observed consistently in repeated CV experiments and in chronopotentiometry (CP) data (see Figure S1 in the Supporting Information). Mixing the surfactants and BFEE together increased the electrical conductivity of the electrolyte medium because the addition of energy via sonication facilitates the surfactant dissociation to DS^- and DBS^- , which provides additional charge to BFEE. Consequently, the decreased solution resistance lowers the oxidation potential of thiophene. A decrease in the oxidation potential of thiophene in the anionic surfactant medium can also be attributed to stabilization of the thiophene radical cation in the solvent due to electrostatic interactions of the thiophene radical cation ($\text{PTh}^{\cdot+}$) with the surfactant anions (DS^- and DBS^-).⁴⁰

The oxidation current during the deposition of PTh without anionic surfactants was higher during the first two cycles because diffusion of thiophene to the electrode surface is much faster than diffusion of the larger surfactants. The surfactant molecules are more than three times larger than that of thiophene; the molecular weights of thiophene, SDBS, and SDS are 84.14, 348.48, and 288.38 g/mol, respectively. Consequently, DS^- and DBS^- ions will need more time to diffuse into the polymer network. This conclusion is supported by the clear transition from lower to higher current at the fifth cycle when SDBS and SDS are included in the electrolyte (see insets of Figure 1), combined with the fact that the thicknesses of films with and without surfactants were approximately the same. The current density is expected to increase with increased concentration of anionic surfactants due to additional charge provided by SDS and SDBS. However, the current density decreases on further increase in surfactant concentration which could be due to steric effects of the micelles in the solution that limit diffusion of surfactant ions to the electrode. The oxidation data presented in insets of Figure 1 supports our explanation for the expected behavior in the CV plots using anionic surfactants. The current profile clearly shows that the current density increases in presence of surfactants, yet current density at 5 mM surfactant is lower than the density at 1 mM, suggesting the presence of micelles in the electrolyte.

PTh deposition using constant current density ($0.5 \text{ mA}/\text{cm}^2$), and SDS and SDBS as supporting electrolyte in BFEE results in lower oxidation potential than that for synthesis of PTh films in surfactant free BFEE electrolyte. The oxidation potential begins to increase when a critical surfactant concentration is reached, yet it is still lower than that of the solution without anionic surfactants (see Figure S1 in the Supporting Information). At a critical concentration, the

presence of bulky surfactant molecules hinders the diffusion of monomers or oligomers to the working electrode, which increases the effective solution resistance and eventually the oxidation potential. Fall et al. found the same trend in aqueous solution; increasing the concentration of anionic surfactant above critical micelle concentration (CMC) in anodic polymerization increased the monomer oxidation potential.²²

A proposed mechanism for the diffusion of anionic surfactants to the working electrode is depicted in Scheme 1. The diffusion of monomers to the electrode is faster than the diffusion of the surfactant anions. The surfactant is “late-arriving” because of its larger size compared to thiophene monomer. Hydrophobic interactions between the dodecyl chain of the surfactant (DS^- and DBS^-) and the thiophene monomers may add more to the size. These interactions can lead to chain alignment in the polymer network because the dodecyl chain acts as an aligning template for thiophene polymerization. The lower oxidation potential of surfactant/BFEE electrolyte results from additional charge and radical cation stability in the solution. At higher surfactant concentration, micelle formation takes place, leading to less dense films that exhibit poor mechanical and electrical properties.

3.2. Effect of Surfactants on the Electrical and Mechanical Properties of PTh Films. The in-plane electrical conductivity of PTh films synthesized using a mixed electrolyte of BFEE and surfactants at a constant current of $0.5 \text{ mA}/\text{cm}^2$ and a deposition time of 90 min is shown in Figure 2. X-ray

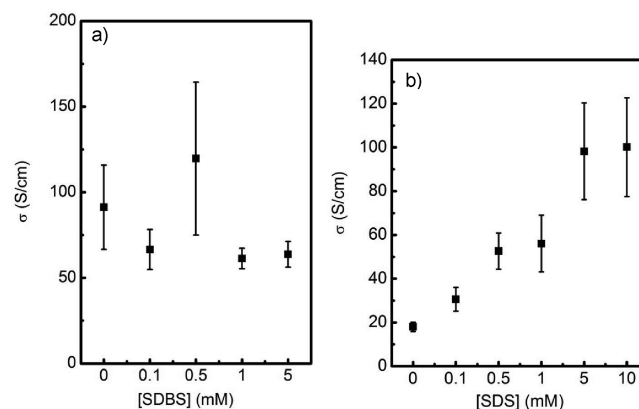


Figure 2. In-plane conductivity of PTh films grown at $0.5 \text{ mA}/\text{cm}^2$ for 90 min using 50 mM thiophene in (a) SDBS/undistilled BFEE/, (b) SDS/undistilled BFEE. The film thickness is $4.1 \pm 0.3 \mu\text{m}$. Each data point is an average of four measurements from two films.

photoelectron spectroscopy (XPS) confirmed that SDS and SDBS are incorporated in PTh films synthesized in the presence of surfactants (see the Supporting Information). In general, the addition of surfactants to the polymerization electrolyte increased electrical conductivity. However, the presence of surfactant showed no effect on the conductivity of PTh films when the deposition time was less than a critical value (approximately 13 min) that corresponds to the time that was required for the surfactant molecules to diffuse into the polymer films. This is in agreement with the solid-state polymerization process in which “late-arriving” surfactant molecules can influence molecular ordering at the electrode–film interface.¹⁶ Figure 2a shows that there is a critical concentration of SDBS of ~ 0.5 mM at which the conductivity reaches a maximum. This is in agreement with CP data, which shows that the oxidation potential during polymerization increases at 1 mM and 5 mM SDBS from the value produced at 0.5 mM (see Figure S1a in the Supporting Information). These results suggest that micelles form at concentrations higher than 0.5 mM, and that they are large enough to produce steric hindrance effects that reduce electrical conductivity as discussed above. The CP data for SDS also suggests micelle formation at 1 mM and 5 mM concentrations (see Figure S1b in the Supporting Information); however, the electrical conductivity of the PTh films synthesized at these concentrations is higher than that of films synthesized at lower concentrations (see Figure 2b). We attribute this difference to the smaller size of DS^- anions in SDS compared to the larger DBS^- in SDBS, which likely produce smaller micelles and more densely packed films. In this case, steric hindrance from micelles during growth affects the properties of the films less than the extra charge added to the films from the higher DS^- concentrations.

BFEE is a suitable solvent for PTh electropolymerization because it is a strong Lewis acid; this characteristic also makes it extremely sensitive to moisture. The different electrical conductivities of the control samples in Figure 2 are caused by different amounts of water in the respective BFEE batches. The higher conductivity of the control for the SDBS experiments suggest that there was more water in this batch than in the batch used for the SDS experiments. This higher water content may have caused increased interaction between DBS^- anions and water ($H^+BF_3OH^{33}$) leading to lower doping levels in films synthesized with SDBS relative to the control sample. This explains the unexpected decrease in electrical conductivity when the film is deposited in 0.1 mM of SDBS in BFEE. We made several PTh films without surfactant (i.e., controls) using different bottles of the same batch of as received BFEE. We could not quantify the amount of water in BFEE due to the sensitivity limits on our titrator. However, as seen in Figure 3, the electrical conductivity of control PTh films ranges from 18 to 140 S/cm. This observation suggests that a small change in water content can produce significantly different electrical conductivities.

The reproducibility of our experiments was improved significantly by using freshly distilled BFEE. However, the conductivities of PTh films synthesized in freshly distilled BFEE were relatively low compared to those of films synthesized in undistilled or “as-received” BFEE (see Figures 2 and 4). This could be due to low dopant concentrations (mainly H^+BF_3OH) in films synthesized in freshly distilled BFEE. Synthesis of PTh films in freshly distilled BFEE reduced the data scatter for electrical conductivity measurements (see

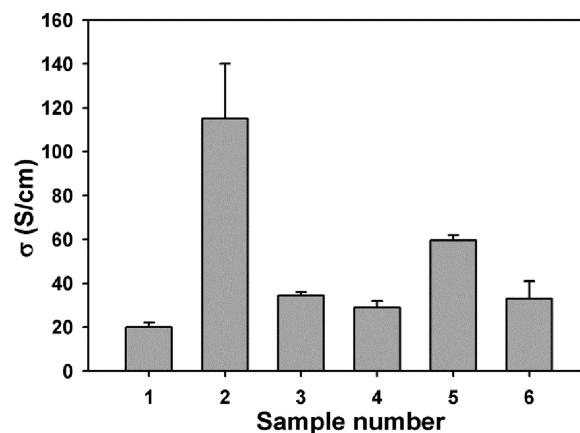


Figure 3. In-plane conductivity of PTh films grown at 1.0 mA/cm^2 for 90 min using 50 mM thiophene in different bottles (age) of as-received BFEE without surfactant. The film thickness is $4.1 \pm 0.3 \mu\text{m}$.

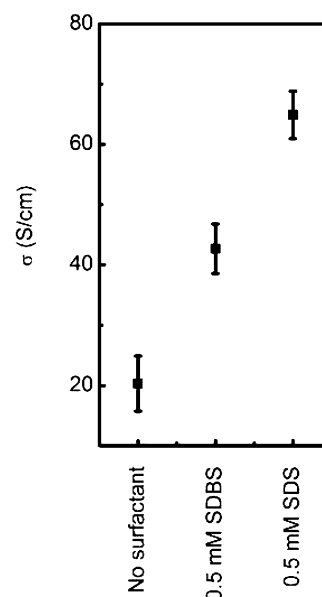


Figure 4. In-plane conductivity of PTh films without surfactant and at critical concentrations of SDS and SDBS grown at 0.5 mA/cm^2 for 90 min using 50 mM thiophene and distilled BFEE. Each data point is an average of four measurements from two films. The film thickness is $4.1 \pm 0.3 \mu\text{m}$.

Figure 4) compared to the values measured on films synthesized in as received BFEE (Figure 2). This result illustrates the significance that small variations in moisture content can have on film properties. The critical concentration of SDS reduced to 0.5 mM when freshly distilled BFEE was used (Figure 4). The critical concentration of SDBS in distilled BFEE appears to be approximately similar to that in undistilled BFEE (0.5 mM). The change in critical concentration of SDS is likely caused by the reduced water content in distilled BFEE, which reduced reactions between SDS and water.

Addition of SDS and SDBS improved the conductivity of PTh films synthesized in freshly distilled BFEE, which is similar to the results from synthesis in undistilled BFEE with surfactant. Figure 4 shows a clear 2- to 3-fold increase in conductivity for PTh films synthesized at the critical SDS (0.5 mM) and SDBS (0.5 mM) concentrations in distilled BFEE with respect to the control sample.

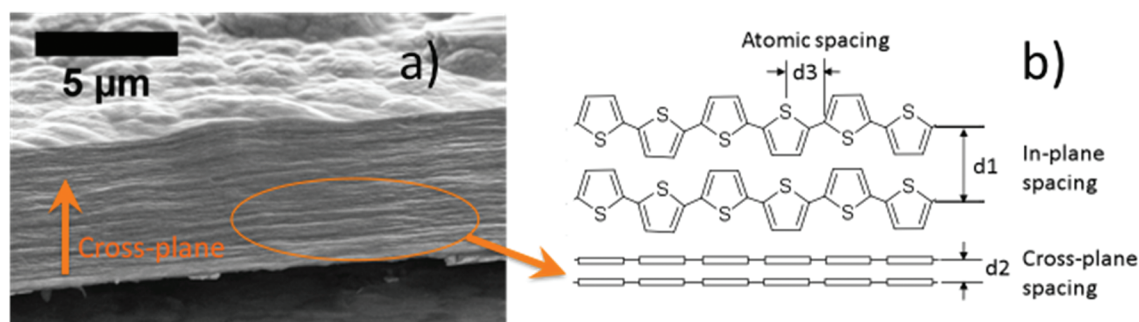


Figure 5. (a) PTh film synthesized in 0.5 mM SDBS in BFEE. The layer-by-layer structure shown here was typical of all PTh films synthesized with and without surfactants. (b) Illustration of molecular packing and interatomic spacing in a PTh film.

PTh films synthesized in the presence of surfactants exhibited necking in tensile tests that was not observed for films without surfactants (Figure S3 in the Supporting Information). This necking behavior suggests more ductile behavior and a greater degree of chain alignment and chain length in PTh films with surfactants.⁴¹ The Young's modulus and tensile strength of PTh films with surfactants were essentially the same as that of films without surfactants (see Table S2 of the Supporting Information). The Young's modulus and tensile strength of all PTh films were ~ 3 GPa and ~ 100 MPa, respectively. The phenomena and mechanisms responsible for the enhancement of the mechanical properties are different than those behind the improvement in electrical conductivity. Thus, as expected the presence of surfactants increases the conductivity of the PTh films but does not affect the mechanical properties such as tensile strength and modulus.

3.3. Effect of Surfactants on the Structure of PTh Films. X-ray diffraction (XRD) is used commonly to determine the molecular structure of PTh.^{17,18} Similar to earlier reports,^{13b,20} we observed three distinct peaks in the scattering pattern of PTh films synthesized with and without anionic surfactants. The three peaks represent intermolecular spacing of d_1 , d_2 , and d_3 as illustrated in Figure 5b. The d_1 , d_2 , and d_3 spacing is calculated by applying Bragg's law to the 2θ peaks in the XRD spectra. PTh films with and without surfactant viewed in SEM show the results of layer-by-layer deposition (Figure 5a), which supports the arrangement proposed by Jin et al. (Figure 5b) and confirmed by XRD data.¹⁸ Jin et al. observed two types of molecular packing (d_1 and d_2) for polymer chains in PTh films as shown in Figure 5b.¹⁸ This packing results in highly anisotropic electrical transport in the films because of the orientation of thiophene rings on the electrode.¹⁸ The peak observed at $2\theta = 38^\circ$ has not been discussed in prior studies. It is proposed here that the d_3 distance represents the distance between two thiophene rings because the d_3 peak corresponds to the larger values of angles (i.e., shortest d -spacing) compared with the other two peaks.

Wide-angle X-ray scattering (WAXS) data for PTh films made with and without SDBS and SDS anionic surfactants are shown in Figure 6 and Table 1. The broad peaks in the WAXS pattern of the PTh films synthesized in the presence of SDBS and SDS show that the PTh films are amorphous. As discussed above, the anion tail from the surfactant is thought to create steric effects that reduce the packing density of PTh chains in the film. This hypothesis is supported by the larger d_1 and d_2 spacing (i.e., larger full width at half-maximum for the d_1 and d_2 peaks) for films synthesized with 5 mM SDS (Figure 6d) compared to that of films synthesized without surfactant

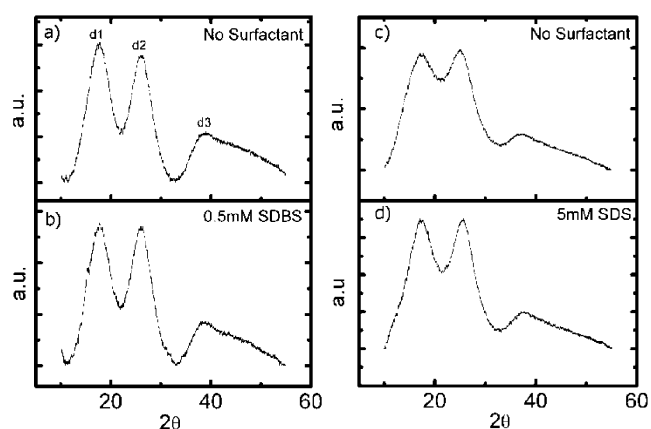


Figure 6. WAXS pattern in transmission mode of PTh film electrochemically synthesized using 50 mM thiophene with current density of 0.5 mA/cm^2 at 5 mm interelectrode distance in anionic surfactants/BFEE electrolyte.

(Figure 5c) where both film types have similar values of electrical conductivity. The PTh films in panels a and b in Figure 6 were produced with a different batch of BFEE than the one used to produce the films in panels c and d in Figure 6, so it is only useful to compare the percent improvement in electrical conductivity achieved due to addition of SDBS or SDS in the respective BFEE batches. The Bragg's angles and full width at half-maximum (fwhm) of peaks in the WAXS spectrum of the films made with SDBS are comparable to the angles and fwhm for films made with no surfactant as shown in panels a and b in Figure 6 and Table 1. The important differences are that the ratio of d_1/d_2 is closer to one when SDBS is in the PTh film, which means that the thiophene ring has approximately the same periodicity of d_1 and d_2 packing; and that the fwhm of the d_3 peak is significantly lower when SDBS is in the film. The sharper d_3 peak in films made with 0.5 mM SDBS suggests increased ordering, and possibly increased chain length, compared to films synthesized without surfactants, which is further corroborated by measured improvement in electrical conductivity at the same concentration of SDBS compared to the control sample. Films synthesized with SDS exhibited a more than 400% increase in electrical conductivity compared to films made with no surfactant. The fwhm of the d_2 and d_3 peaks are narrower in films synthesized with 5 mM SDS than in films made with no surfactant. The films with 5 mM SDS also show larger d_1/d_3 and d_2/d_3 peak ratios. The sharper d_2 peak indicates closer out-of-plane packing of polymer chains, and the sharper d_3 peak suggests increased conjugation length; this hypothesis is

Table 1. X-ray Diffraction Data of PTh in Anionic Surfactant/BFEE Electrolyte^a

ID	σ (S/cm)	2θ			fwhm			peak intensity ratio			
		d1	d2	d3	d1	d2	d3	d1/d2	d1/d3	d2/d3	
a	no surfactant	86–129	17.6	26.0	38.7	5.1	4.6	13.2	1.1	3.0	2.7
b	0.5 mM SDBS	163–184	17.7	26.0	38.3	5.2	4.8	10.8	1.0	3.5	3.4
c	no surfactant	18–21	17.0	24.9	37.2	6.3	7.2	12.7	1.0	3.6	3.7
d	5 mM SDS	90–135	17.3	25.5	36.8	6.3	5.9	12.0	1.0	4.1	4.0

^aElectrical conductivity data are from Figure 2.

based on assigning the d3 peak to the unit spacing between thiophene rings.

4. CONCLUSIONS

The solvation of anionic surfactants SDS and SDBS in nonaqueous BFEE electrolyte was improved by sonication. Mixing anionic surfactants in BFEE was demonstrated as an effective method to improve the electrical conductivity of PTh films electropolymerized in BFEE. The improvements to electrical conductivity were maximized at critical concentrations of SDS and SDBS because of increased micelle formation with increased surfactant concentration. X-ray scattering revealed improved molecular ordering and packing density of polymer chains for PTh films synthesized in the presence of anionic surfactants. Mixtures of SDS and freshly distilled BFEE produced PTh films with a maximum conductivity of 64.9 ± 3.9 S/cm, which is approximately 3-fold larger than the conductivity of PTh films synthesized without surfactant under similar conditions. This improvement in electrical conductivity was achieved without change to the modulus and tensile strength of the films, and it is attributed to the dual role of surfactants as dopants and templates for molecular ordering. The larger conductivities achieved by use of SDS compared to SDBS in freshly distilled BFEE are mainly attributed to the smaller size of DS⁻ compared to that of DBS⁻, which reduces steric hindrance effects during growth and facilitates closer packing of polymer chains. PTh films with the largest conductivities were produced from synthesis in mixtures of surfactants with BFEE that was not distilled because the presence of water increased the conductivity of the electrolyte and increased the amount of dopant ions available to the film. However, these data were not easily reproduced because small variations in moisture content were demonstrated to affect film properties significantly. Further investigation of the role water content in BFEE plays in the electropolymerization of PTh in BFEE is recommended for future studies.

■ ASSOCIATED CONTENT

Supporting Information

Estimation of energy required for solvation of SDS and SDBS in BFEE. Chronopotentiometry data for PTh deposition in surfactant/BFEE electrolyte mixtures. Representative stress–strain curve for PTh films with and without surfactants. Young's modulus and tensile strength as a function of surfactant concentration in PTh films. X-ray photoelectron spectra of PTh films with surfactants. This material is available free of charge via Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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