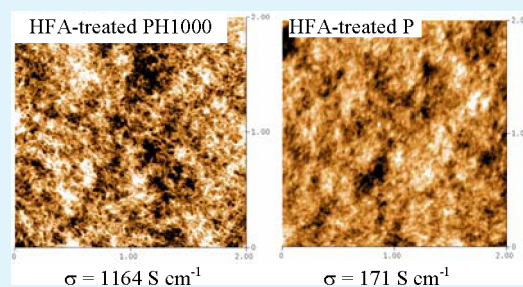


# Significant Different Conductivities of the Two Grades of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate), Clevios P and Clevios PH1000, Arising from Different Molecular Weights

Yijie Xia<sup>†,‡</sup> and Jianyong Ouyang<sup>\*,†</sup><sup>†</sup>Department of Materials Science & Engineering, National University of Singapore, Singapore 117576<sup>‡</sup>Institute of Materials Research and Engineering (IMRE), Singapore 117602

**ABSTRACT:** Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) is promising to be the next-generation transparent electrode of optoelectronic devices. This paper reports the differences between two commercially available grades of PEDOT:PSS: Clevios P and Clevios PH1000. The as-prepared PEDOT:PSS films from Clevios P and Clevios PH1000 solutions have close conductivities of 0.2–0.35 S cm<sup>-1</sup>. Their conductivities can be enhanced to 171 and 1164 S cm<sup>-1</sup>, respectively, through a treatment with hydrofluoroacetone trihydrate (HFA). The differences between Clevios P and Clevios PH1000 were studied by various characterizations on PEDOT:PSS aqueous solutions and PEDOT:PSS films. The gel particles are larger in Clevios PH1000 solution than in Clevios P solution as revealed by dynamic light scattering and fluorescence spectroscopy of pyrene in these solutions. These results suggest that PEDOT of Clevios PH1000 has a higher average molecular weight than that of Clevios P. The difference in the molecular weight of PEDOT for the two grades of PEDOT:PSS is confirmed by the characterizations on their polymer films, including atomic force microscopy and temperature dependences of the resistances of as-prepared and HFA-treated PEDOT:PSS films. The different molecular weights of PEDOT also gives rise to significant differences in the electrochemical behaviors of the two grades of PEDOT:PSS, as revealed by the cyclic voltammetry, in situ UV–vis–NIR absorption spectroscopy and potentiostatic transient measurements.

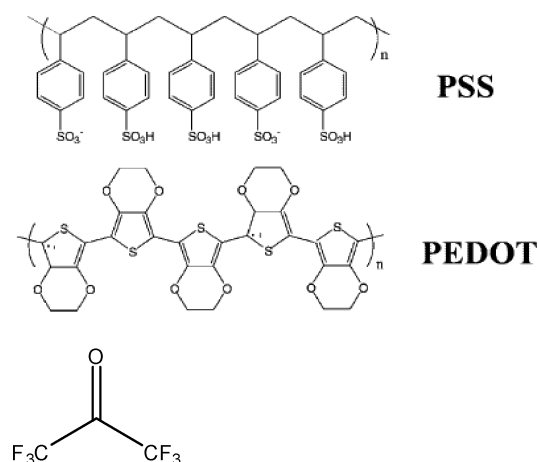
**KEYWORDS:** PEDOT:PSS, molecular weight, conductivity, transparent electrode, rigid



## INTRODUCTION

The demand for optoelectronic devices, such as liquid crystal displays (LCDs), light-emitting diodes (LEDs), solar cells, touch panel displays, lasers, and detectors, has been rapidly increasing, because they are indispensable units in many technologies. An optoelectronic device requires at least one transparent electrode so that light can pass through. Indium tin oxide (ITO) is the conventional material as the transparent electrode of optoelectronic devices. But it has problems of scarce indium on earth which leads to the skyrocketing of the indium price and high mechanical brittleness. These problems bring a concern of the long-term availability of ITO and cause ITO unsuitable for flexible electronic devices that are regarded as the next-generation electronic devices.<sup>1,2</sup> Hence, it is an imminent task to find new transparent conductive materials. A couple of materials have been proposed to substitute ITO as the transparent electrode, including conducting polymers,<sup>3–16</sup> carbon nanotubes,<sup>17–20</sup> graphenes,<sup>21,22</sup> and metal wires.<sup>22–25</sup> Among them, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, chemical structure shown in Scheme 1) is highly promising as the next-generation transparent electrode material, because PEDOT:PSS as a synthetic polymer can be available at low cost and PEDOT:PSS

## Scheme 1. Chemical Structures of PEDOT:PSS and HFA



films with high uniformity in a large area can be readily prepared by conventional solution processing techniques.

Received: May 17, 2012

Accepted: July 6, 2012

Published: July 6, 2012

PEDOT:PSS is the most successful conducting polymer in terms of the practical application because of its advantages in processability, mechanical, and optical properties. It can be dispersed in water and some organic solvents, and high-quality PEDOT:PSS films can be readily prepared on various substrates by conventional solution processing techniques, such as spin coating, spraying and printing.<sup>26–28</sup> Moreover, PEDOT:PSS films are highly transparent in visible range and highly flexible and have excellent thermal stability. Nevertheless, PEDOT:PSS does suffer a problem of low conductivity. As-prepared PEDOT:PSS films from PEDOT:PSS aqueous solution usually have a conductivity of less than  $1 \text{ S cm}^{-1}$ , which is saliently lower than that of ITO.<sup>27,29</sup> Hence, it is important to significantly enhance the conductivity of PEDOT:PSS films for its application as the transparent electrode of optoelectronic devices and other applications. Since Kim et al. reported the conductivity enhancement of Clevios P by about two orders in magnitude by adding dimethyl sulfoxide (DMSO) or dimethylformamide (DMF) into the Clevios<sup>TM</sup> P aqueous solution,<sup>30</sup> a couple of methods have been discovered to significantly enhance the conductivity of PEDOT:PSS.<sup>13,31–39</sup> The conductivity of PEDOT:PSS can also be significantly enhanced through a treatment of the PEDOT:PSS films.<sup>9,40–46</sup> The conductivity enhancement strongly depends on the grade of PEDOT:PSS. Several grades of PEDOT:PSS were developed and marketed by H. C Starck, which was taken over by Heraeus.<sup>47</sup> Though as-prepared PEDOT:PSS films from PEDOT:PSS aqueous solutions of different grades have almost the same conductivity, typically in the range of  $0.1–1 \text{ S cm}^{-1}$ , the conductivity of PEDOT:PSS films after a treatment is strongly dependent on the grades. For example, the conductivity can be enhanced up to  $200 \text{ S cm}^{-1}$  for Clevios P films, whereas it can be improved to  $600–700 \text{ S cm}^{-1}$  for Clevios PH1000 films after a treatment with DMSO or ethylene glycol (EG).<sup>48</sup> Conductivities exceeding  $1000 \text{ S cm}^{-1}$  were reported for treated Clevios PH1000 films. Kim et al. prepared PEDOT:PSS films from Clevios PH 1000 aqueous solution added with EG and then treated them in EG bath.<sup>49</sup> After the double treatments with EG, the conductivity of the PEDOT:PSS films were enhanced to  $1418 \text{ S cm}^{-1}$ . We recently reported that a treatment of Clevios PH1000 films with hexafluoroacetone trihydrate (HFA, chemical structure shown in Scheme 1) can enhance the conductivity to  $1164 \text{ S cm}^{-1}$ .<sup>50</sup> Moreover, the conductivity of Clevios PH1000 films can be further improved to more than  $3000 \text{ S cm}^{-1}$  through a treatment with  $\text{H}_2\text{SO}_4$ .<sup>51</sup> This conductivity is even higher than ITO on plastic substrate and comparable to ITO on glass substrate.

Treated PEDOT:PSS films with high conductivity have been investigated as the transparent electrode of optoelectronic devices. PEDOT:PSS films with different conductivities give rise to different device performances. For example, polymer solar cells with treated Clevios PH1000 films as the transparent anode can exhibit a photovoltaic efficiency of  $>3.5\%$ , which is comparable to that of control devices with ITO.<sup>50,51</sup> In contrast, polymer solar cells with treated Clevios P films as the transparent electrode have photovoltaic efficiencies below  $3\%$ .<sup>43,44</sup> Difference performances were also observed on organic light-emitting diodes (OLEDs) with treated PEDOT:PSS films of different conductivities. OLEDs with treated Clevios P films as the transparent electrode show a maximum luminance of  $1490 \text{ cd m}^{-2}$  and an external electroluminescence quantum efficiency of  $0.73\%$  at  $100 \text{ A m}^{-2}$ ,<sup>4</sup> whereas OLEDs with treated

Clevios PH1000 films can have a luminance of  $15\,000 \text{ cd m}^{-2}$  and an external electroluminescence quantum efficiency of  $1.71\%$  at  $100 \text{ A m}^{-2}$ .<sup>52</sup>

Though Clevios P and Clevios PH1000 can give rise to significantly different conductivities after a treatment, it is not well understood on the difference in the structure of the two grades of PEDOT:PSS. In fact, both Clevios P and Clevios PH1000 are prepared by polymerization of 3,4-ethylenedioxythiophene with persulfate and iron(III) in the presence of PSS in water. Both Clevios P and Clevios PH1000 aqueous solutions have the same concentration of  $1.3 \text{ wt } \%$  PEDOT:PSS and the same ratio of PEDOT to PSS ( $1:2.5$  by weight). Good understanding in the structure of these two grades of PEDOT:PSS can provide important guidance for the development of PEDOT:PSS with even higher conductivity and other high-performance conducting polymers. In this paper, we report our findings on the differences in the structure of Clevios P and Clevios PH1000 through various characterizations on both solutions and films. The experimental results indicate that PEDOT of Clevios PH1000 has a higher average molecular weight than that of Clevios P.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** PEDOT:PSS aqueous solutions (Clevios PH 1000 and Clevios P) were purchased from H. C. Starck that was taken over by Heraeus. The concentration of PEDOT:PSS was  $1.3\%$  by weight, and the weight ratio of PSS to PEDOT was  $2.5$  in both solutions. All other chemicals were obtained from Sigma-Aldrich. All the materials were used without further purification.

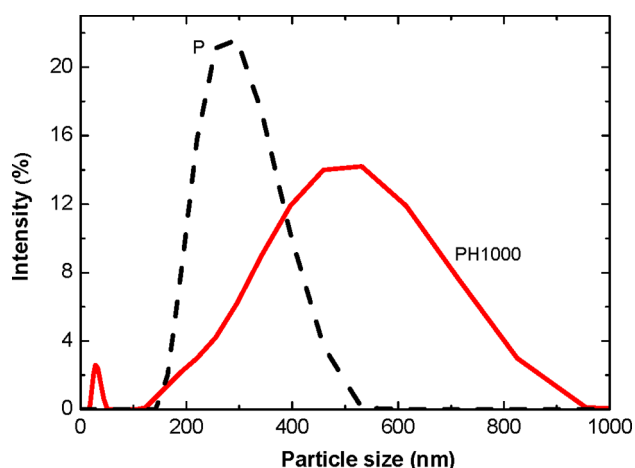
**2.2. Treatment of PEDOT:PSS Films with HFA.** PEDOT:PSS films were prepared by spin coating the Clevios<sup>TM</sup> PH 1000 or Clevios P aqueous solution on glass substrates of  $1.3 \times 1.3 \text{ cm}^2$ , which were precleaned sequentially with detergent, deionized (DI) water, acetone and isopropyl alcohol. The PEDOT:PSS films were dried at  $120 \text{ }^\circ\text{C}$  on a hot plate for  $15 \text{ min}$ . The treatment with HFA was performed by dropping  $100 \text{ } \mu\text{L}$  HFA on a PEDOT:PSS film on a hot plate at  $140 \text{ }^\circ\text{C}$ . The PEDOT:PSS films dried after about  $5 \text{ min}$ . They were cooled down to room temperature, and then were rinsed with deionized water and dried at  $140 \text{ }^\circ\text{C}$  again.

**2.2. Characterization of PEDOT:PSS Films.** The dynamic light scattering (DLS) measurements of PEDOT:PSS solutions were carried out with a Zetasizer Nano ZS by Malvern with a HeNe laser ( $633 \text{ nm}$ ) as the light source. The fluorescent spectra were acquired using a Shimadzu RF-5301 Spectrofluorophotometer. The conductivities of dried PEDOT:PSS films were measured by the van der Pauw four-point probe technique with a Keithley 2400 source/meter. The electrical contacts were made by pressing indium on the four corners of each PEDOT:PSS film on glass substrate. The temperature dependences of the resistivities of as-prepared and HFA-treated PEDOT:PSS films were tested using a Janis Research VPF-475 dewar with liquid nitrogen as coolant and a Conductus LTC-11 temperature controller. The UV–vis–NIR absorption spectra of the polymer films were taken with a Varian Cary 5000 UV–vis–NIR spectrometer, and the AFM images were obtained using a Veeco NanoScope IV Multi-Mode AFM with the tapping mode. The X-ray photoelectron spectroscopy (XPS) spectra were collected with an Axis Ultra DLD X-ray photoelectron spectrometer equipped with an Al  $K_{\alpha}$  X-ray source ( $1486.6 \text{ eV}$ ). The thicknesses of the polymer films were determined with an Alpha 500 step profiler. Cyclic voltammograms (CV) and potentiostatic transient currents were measured in  $0.1 \text{ M}$  NaCl solution with a ECO CHEMIE AUTOLAB PGSTAT 302N + FRA2 system. The working electrodes were prepared by dropping PEDOT:PSS aqueous solutions on Au discs with a diameter of  $2 \text{ mm}$  and subsequently drying at  $120 \text{ }^\circ\text{C}$ . A Pt wire and Ag/AgCl ( $3 \text{ M}$  NaCl) were used as the counter and reference electrodes, respectively. The scan rate was  $50 \text{ mV s}^{-1}$ . A potential of  $-0.6 \text{ V}$  vs Ag/AgCl was applied on the working electrode for the potentiostatic transient study.

The in situ electrochemical UV–vis–NIR absorption spectra were taken with a Varian Cary 5000 UV–vis–NIR spectrometer, and the potentials were applied on the working electrode by a Ivium-n-stat Voltammetric Analyzer.

### 3. RESULTS AND DISCUSSION

**3.1. Particle sizes of PEDOT:PSS in Clevis PH1000 and Clevis P Solutions.** Clevis™ PH1000 and Clevis™ P are two grades of PEDOT:PSS aqueous solutions. Their concentrations are 1.3 wt % in solutions. It has been reported that PEDOT and PSS form globular gel particles in water.<sup>53,54</sup> The particle sizes in PEDOT:PSS aqueous solution can be investigated by DLS.<sup>55–57</sup> Both Clevis PH1000 and Clevis™ P aqueous solutions were diluted to 0.013 wt % for the DLS study. Figure 1 presents the particle sizes of Clevis PH1000

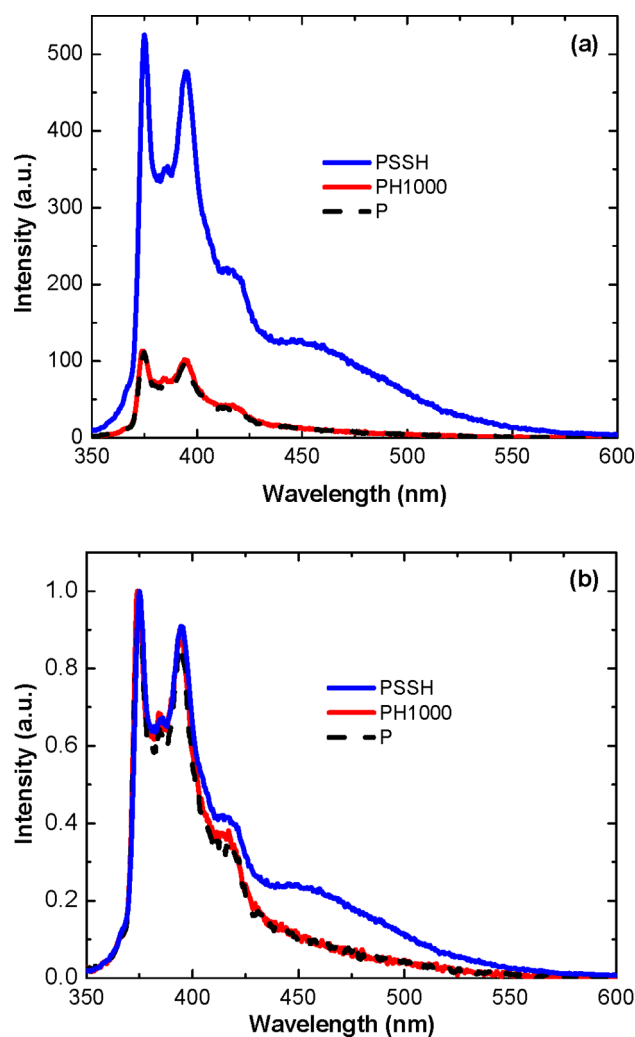


**Figure 1.** Gel particle size distributions of 0.013 wt % Clevis P and 0.013 wt % Clevis PH1000 solutions by DLS.

and Clevis P. The Clevis P solution has a size distribution from 170 to 520 nm with the maximum at 289 nm, and the average size is 285 nm. The sizes are consistent with those reported in literature.<sup>55–57</sup> In contrast, there are two size distribution peaks for the Clevis PH1000 solution. The majority (90%) has a size distribution of 160–940 nm with the maximum at 463 nm, and the average size is 486 nm. The minority (10%) has a size distribution of 16–51 nm, and the average size is 30 nm.

The sizes are related to the globular gel particle structure formed by PEDOT and PSS in water. PEDOT:PSS is a polyelectrolyte with the positively charged conjugated PEDOT and negatively charged nonconjugated PSS<sup>−</sup>. They are binded together due to the strong Coulombic attractions. The weight ratio of PSS to PEDOT is 2.5 in both Clevis PH1000 and Clevis P solutions, which corresponds to the molar ratio of 1.8 for their repeating units. Excess PSS is used to stabilize PEDOT in water. The average molecular weight of PSS is about 400 000 g mol<sup>−1</sup>, while the molecular weight of PEDOT is probably just about thousands g mol<sup>−1</sup>.<sup>53</sup> The PEDOT chains are much shorter than the PSS chains. The PSS segments or chains form globular particles to accommodate the rigid PEDOT chains. Thus, longer PEDOT chains will give rise to larger globular particles in water. The DLS results suggest that the particles are larger in Clevis PH1000 solution than in Clevis™ P solution. Hence, we can infer that the PEDOT chains in Clevis PH1000 have an higher average molecular weight than in Clevis P.

This conclusion is confirmed by the fluorescent spectroscopy of pyrene in dilute Clevis PH1000 and Clevis P solutions. Pyrene has strong fluorescence, and its fluorescence has been extensively used to study the micelle structure of surfactants.<sup>58,59</sup> PSS serve as a surfactant in PEDOT:PSS aqueous solution. Figure 2 presents the fluorescence spectra of  $5 \times 10^{-6}$



**Figure 2.** (a) Fluorescence spectra and (b) normalized fluorescence spectra of  $5 \times 10^{-6}$  M pyrene in 0.013 wt % Clevis PH1000, 0.013 wt % Clevis P, and 0.009 wt % PSSH solutions.

M pyrene in 0.013 wt % Clevis PH1000, 0.013 wt % Clevis P and 0.009 wt % poly(styrenesulfonate acid) (PSSH). The control experiments with 0.009 wt % PSSH solution were carried out to understand the fluorescence of pyrene in the two PEDOT:PSS aqueous solutions. The PSSH concentration is the same as that of PSS in the two PEDOT:PSS aqueous solutions. The sharp fluorescent bands at the low wavelength range are the fluorescence arising from pyrene monomer, while the featureless broad band in the long wavelength regime is the fluorescence from pyrene excimer due to the aggregation of the pyrene molecules.<sup>58,59</sup> Both the monomer and excimer fluorescences can be observed for pyrene in the PSSH solution, but only the monomer fluorescence appears for the PEDOT:PSS solutions. Moreover, the monomer fluorescence of pyrene in the PSSH solution is much stronger than in the two PEDOT:PSS solutions. The decrease in the fluorescenc

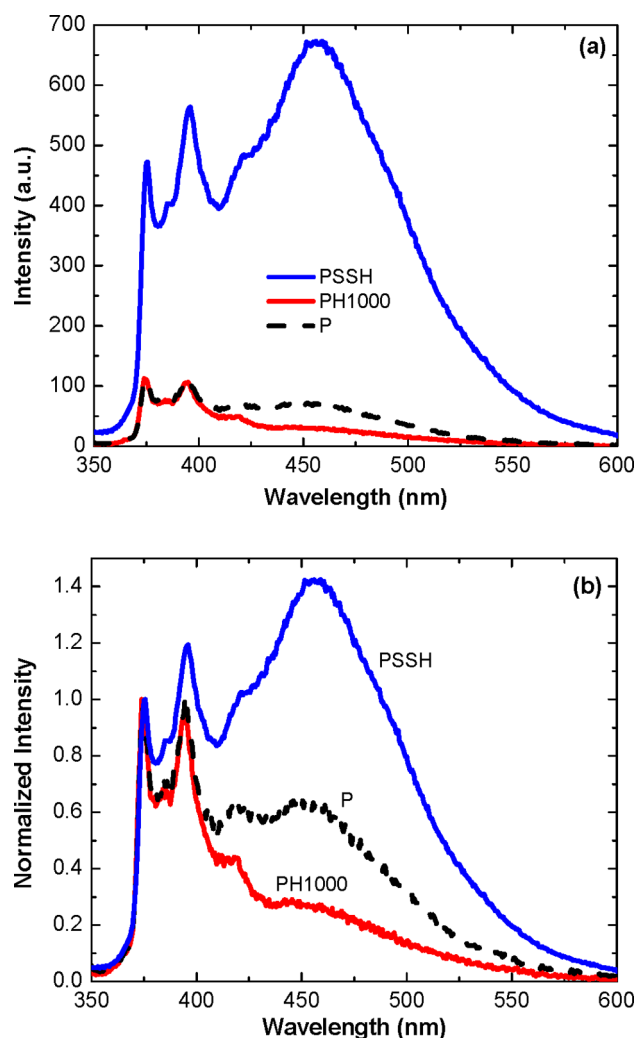
and disappearance of the excimer band in the two PEDOT:PSS solutions indicate that PEDOT can quench the fluorescence of pyrene. In fact, conducting polymers can almost completely quench the fluorescence because conducting polymers are metallic in nature.<sup>60</sup> The fluorescent spectra of pyrene in the two PEDOT:PSS solutions are almost identical. The pyrene molecules can be dispersed in the globular particles formed by PEDOT and PSS and the excess PSS segments without PEDOT adherent. The excess PSS chains may not participate in the globular particles, in stead they form a worm-like structure in water due to the Coulombic repulsion.<sup>61</sup> The fluorescence of the former is quenched by PEDOT, so that only the latter can be collected. Because the globular particles with conjugated PEDOT inside have a large size and PEDOT can have strong  $\pi$ - $\pi$  interaction with the conjugated pyrene molecules, these particles can accommodate more pyrene molecules than the excess PSS segments. Thus, most of pyrene fluorescence is quenched, and the fluorescence of pyrene in the PEDOT:PSS solutions is much weaker than in the PSSH solution. In addition, the absence of excimer fluorescence suggest that pyrene dispersed in the excess PSS segments has quite low concentration.

The excimer fluorescence of pyrene was observed in the PEDOT:PSS solutions when the pyrene concentration was increased to  $2 \times 10^{-5}$  M (Figure 3). The monomer fluorescence is almost the same for the two solutions, while the excimer fluorescence is stronger for the dilute Clevios P solution than the dilute Clevios PH 1000 solution. These results indicate that more pyrene molecules are dispersed in the excess PSS segments in the dilute Clevios P solution than in the dilute Clevios PH1000 solution. In other word, more pyrene is dispersed in the globular particles formed with PEDOT and PSS in the Clevios PH1000 solution than in the Clevios P solution. This also suggests that the globular particles in the Clevios PH1000 solution are larger than in the Clevios P solution. Thus, the fluorescence spectra are consistent with the DLS observations.

### 3.2. Morphology and Electrical and Optical Properties of As-Prepared and HFA-Treated Clevios P and Clevios PH1000 Films.

As discussed above, PEDOT has different molecular weights, which give rise to different gel particles sizes in Clevios PH1000 and Clevios P aqueous solutions. The core/shell structure of PEDOT/PSS is reserved in as-prepared PEDOT:PSS films. The different PEDOT molecular weights can lead to different morphologies for the as-prepared PEDOT:PSS films. As shown in Figures 4(a) and 4(b), the surface morphologies of as-prepared PEDOT:PSS films are different. The Clevios P film is very smooth while grains can be observed for the Clevios PH1000 film. Because of the grains, the rms roughness of the Clevios PH1000 film is 1.20 nm, greater than that (1.06 nm) of the Clevios P film.

The morphologies of the as-prepared PEDOT:PSS films are strongly affected by the presence of excess PSS chains.<sup>57</sup> They make the PEDOT:PSS films smooth. The excess PSS chains can be reduced through a treatment with various compounds as reported in literature.<sup>12–16,34–46,50,51</sup> In this research work, PSS was reduced by treating the Clevios PH1000 and Clevios P films with HFA. As we reported before, the HFA treatment can remarkably lower the PSS amount and significantly enhance the conductivity of the PEDOT:PSS films.<sup>50</sup> The morphologies of the Clevios PH1000 and Clevios P films become more different after they are treated with HFA as shown in images c and d in Figure 4. Grains with an elliptical shape can be observed for the



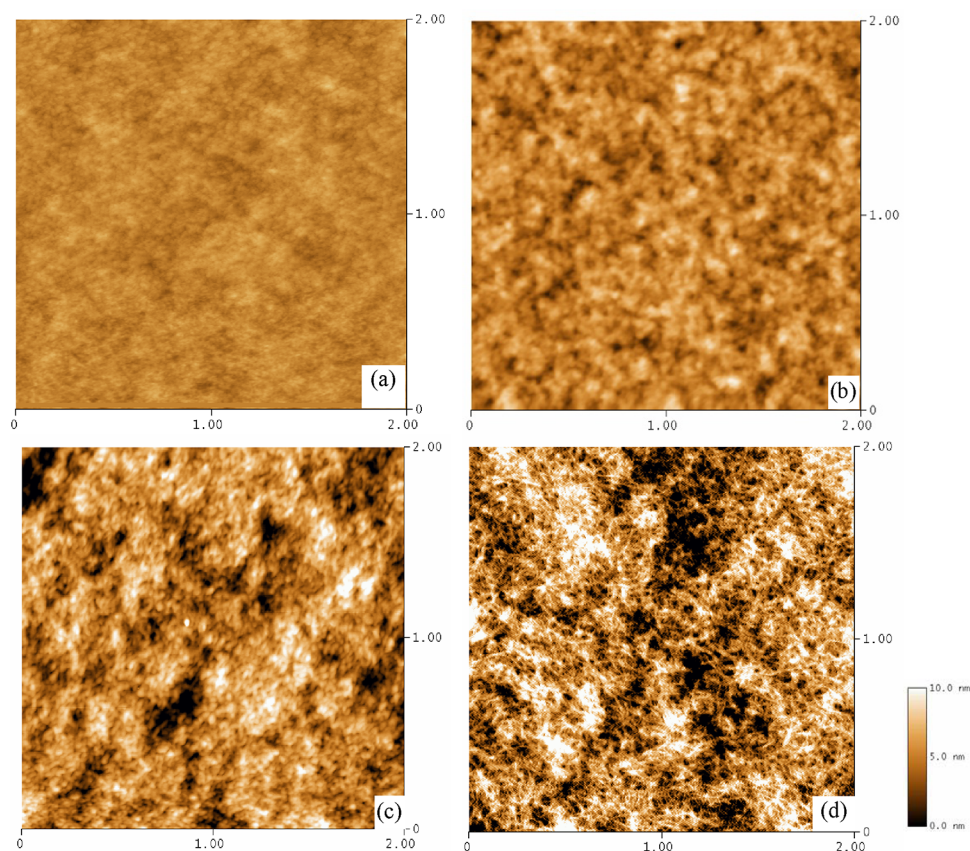
**Figure 3.** (a) Fluorescence spectra and (b) normalized fluorescence spectra of  $2 \times 10^{-5}$  M pyrene in 0.013 wt % Clevios PH1000, 0.013 wt % Clevios P, and 0.009 wt % PSSH solutions.

HFA-treated Clevios P film, while fibrous structures appear for the HFA-treated Clevios PH1000 film. The different grain shapes can be attributed to the different lengths of the rigid PEDOT chains. Long rigid polymer chains favor the formation of the fibrous structure.

The as-prepared Clevios P and Clevios PH1000 films have close conductivities. The conductivity is  $0.25$ – $0.30$  S  $\text{cm}^{-1}$  for as-prepared Clevios P films, and it is  $0.30$ – $0.35$  S  $\text{cm}^{-1}$  for as-prepared Clevios PH1000 films. The resistances of Clevios PH1000 and Clevios P films were studied from room temperature down to 110 K. Figure 5a shows the temperature dependences of the normalized resistances of the two PEDOT:PSS films. Both resistances increase as the temperature is cooled down. As shown in Figure 5b, the temperature dependences of both resistances can be fitted well by the one-dimensional variable range hopping (VRH) model,<sup>62</sup>

$$R(T) = R_0 \exp \left[ \left( \frac{T_0}{T} \right)^{1/2} \right]$$

where  $T_0 = 16/k_B N(E_F) L_{\parallel} L_{\perp}^2$  is the energy barrier between localized states and is a measurement of the degree of disorder in disordered regions,  $N(E_F)$  is the density of the states at the



**Figure 4.** AFM images of polymer films. (a) As-prepared Clevios P, (b) as-prepared Clevios PH1000, (c) HFA-treated Clevios P, and (d) HFA-treated Clevios PH1000.

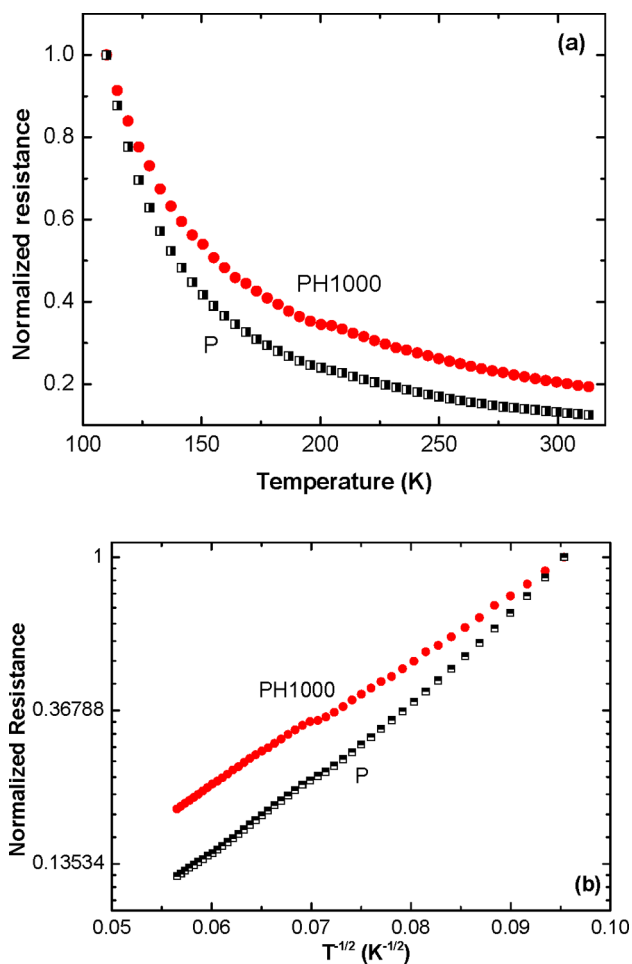
Fermi level, and  $L_{//}(L_{\perp})$  is the localization length in the parallel (perpendicular) direction. The best fittings of the  $R-T^{1/2}$  data indicate that the  $T_0$  values are 2660 and 1901 K for the Clevios P and Clevios PH1000 film, respectively. The  $T_0$  value of the Clevios<sup>TM</sup> PH1000 film is slight lower than that of the Clevios P film. It is consistent with the conductivities of the two PEDOT:PSS films at room temperature.

The conductivities of Clevios P and Clevios PH1000 films increase to 171 and 1164 S cm<sup>-1</sup>, respectively, after a treatment with HFA. The resistances of a HFA-treated Clevios PH1000 film and a HFA-treated Clevios<sup>TM</sup> P film were studied from room temperature down to 110 K (Figure 6). The resistance of the latter monotonically increases with the elevating temperature which is similar to the temperature dependence of as-prepared PEDOT:PSS films, while the resistance of the former has only a weak dependence on the temperature. The resistance of the HFA-treated Clevios PH1000 film increases with the decrease in the temperature at  $T < 220$  K, it then becomes almost insensitive to the temperature as  $T > 220$  K. The resistance of the Clevios<sup>TM</sup> P film can be fitted well with the one-dimensional VRH model except the slight deviation at temperature higher than 250 K. The best fitting indicates a  $T_0$  value of 199 K. In contrast, the  $R-T$  relationship of the Clevios PH1000 film can be analyzed by the one-dimensional VRH model only at  $T < 220$  K. The  $T_0$  value is 99 K for this temperature range. The difference in the  $T_0$  values of the HFA-treated Clevios PH1000 and Clevios P films is more remarkable than that of the as-prepared PEDOT:PSS films.

The similar conductivities and  $T_0$  values of the as-prepared Clevios PH1000 and Clevios P films imply that the energy

barriers for charge transport are similar for the two polymer films. These results indicate that the insulator PSS shell is the dominant factor for the energy barrier for the charge transport through the as-prepared Clevios P and Clevios PH 1000 films. But the energy barrier changes after the HFA treatment of the PEDOT:PSS films. The HFA treatment can induce the phase segregation between the hydrophobic PEDOT and hydrophilic PSSH and lead to the wash-away of some PSSH chains from the PEDOT:PSS films. The insulator PSSH shell is thus significantly reduced. As a result, the PEDOT chains become the dominant factor for the charge transport after the HFA treatment. The lower  $T_0$  value of the HFA-treated Clevios PH1000 film than that of the HFA-treated Clevios P film suggests that the charge hopping among the PEDOT chains is easier for the HFA-treated Clevios PH1000 film than for the HFA-treated Clevios P film. This implies that the localization length(s) ( $L_{//}$  and/or  $L_{\perp}$ ) for the HFA-treated Clevios PH1000 film is longer than that for the HFA-treated Clevios P film. Hence, the PEDOT chains of Clevios PH1000 are longer than those of Clevios P.

The effect of the PEDOT chain length on the conductivity can be understood in terms of the model by Pike and Seager on the conductivity of assemblies formed by conductive widthless sticks.<sup>63</sup> Longer sticks can give rise to lower critical percolation concentration for charge transport and higher conductivity. The effectiveness of that model has been evidenced by the conductivity of carbon nanotubes and metal nanowires.<sup>64–66</sup> A rigid PEDOT chain can be regarded as a conductive stick. Longer PEDOT chains can render higher conductivity for the PEDOT:PSS films.

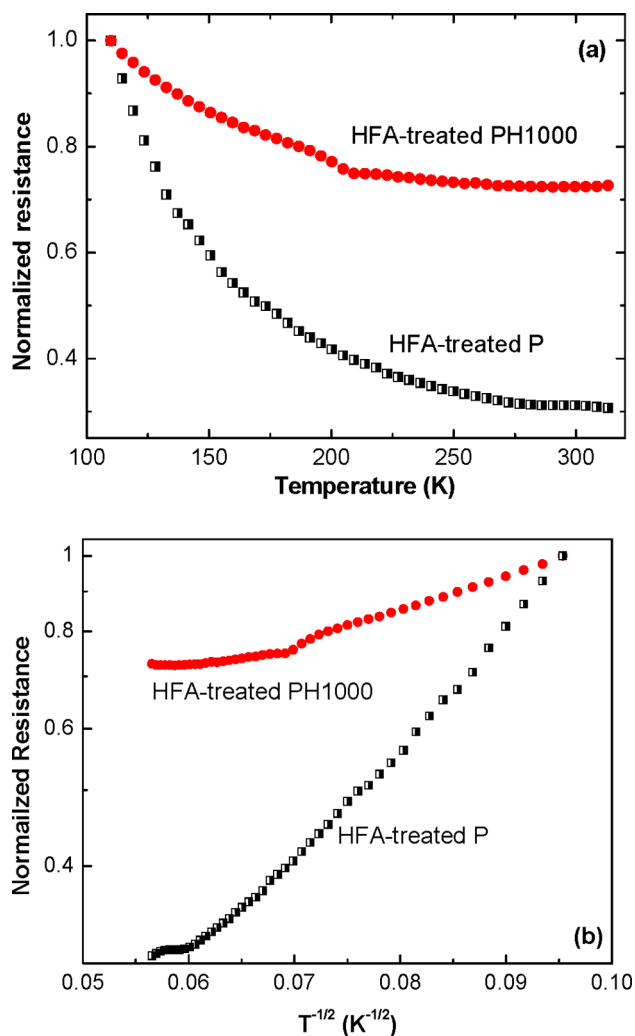


**Figure 5.** (a) Temperature dependences of the resistances of as-prepared Clevis P and Clevis PH1000 films. (b) Analyses with the one-dimensional VRH model. The resistances are normalized to those at 110 K.

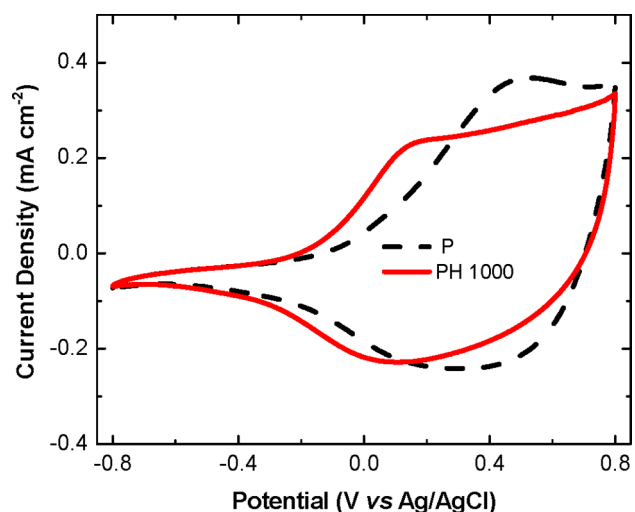
These results suggest that PEDOT of Clevis PH1000 has higher average molecular weight than that of Clevis P. The rigid PEDOT chains of Clevis P are too short to form fibrous structure. Though remarkable fiber structures were observed on HFA-treated Clevis PH1000 films, no crystalline structure was observed by XRD. We also studied the as-prepared Clevis P and Clevis PH1000 films by XPS and UV-vis-NIR absorption spectroscopy and did not observe any appreciable difference between them.

**3.3. Electrochemical Behaviors of Clevis P and Clevis PH1000 Films and Polymer Solar Cells with HFA-Treated Clevis P and Clevis PH1000 Films As the Transparent Electrodes.** As-prepared and HFA-treated Clevis P and Clevis PH1000 films were investigated by electrochemical characterizations. Figure 7 presents the CVs of as-prepared Clevis PH1000 and Clevis P films in the potential range from  $-0.8$  to  $0.8$  V vs Ag/AgCl. Both films exhibit similar electrochemical behavior. But the cathodic and anodic peaks appear at lower potentials for the Clevis PH1000 film than the Clevis<sup>TM</sup> P film. They are  $0.15$  and  $0.12$  V vs Ag/AgCl for Clevis PH1000, respectively, whereas they appear at  $0.52$  and  $0.33$  V vs Ag/AgCl for Clevis P, respectively.

The electronic structure of the Clevis PH1000 and Clevis P films during the electrochemical reduction were studied by the in situ UV-vis-NIR absorption spectroscopy (Figure 8).

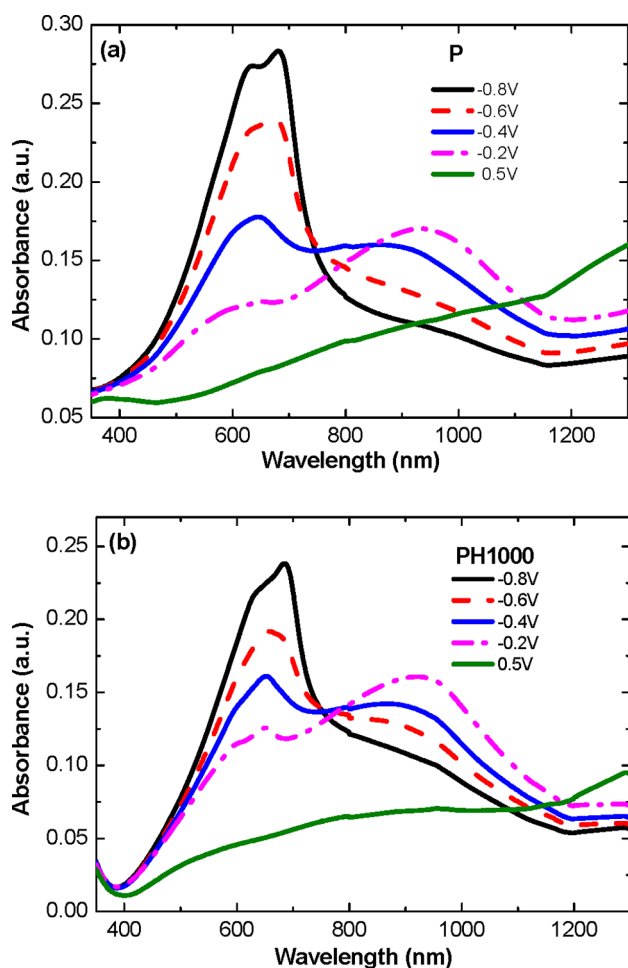


**Figure 6.** (a) Temperature dependences of the resistances of HFA-treated Clevis P and Clevis PH1000 films. (b) Analyses with the one-dimensional VRH model. The resistances are normalized to those at 110 K.



**Figure 7.** CVs of as-prepared Clevis P and Clevis PH 1000 films.

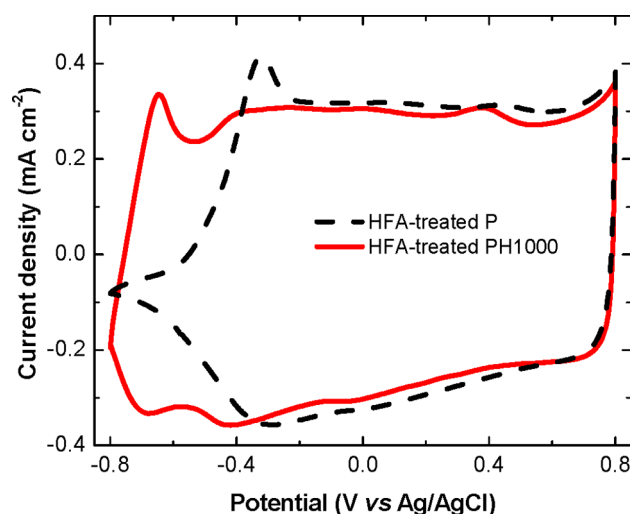
The absorption is strong in the infrared range and weak in the visible range at  $0.5$  V vs Ag/AgCl, that is, PEDOT is in the oxidized state. When the electrochemical potential is lowered



**Figure 8.** In situ UV-vis-NIR absorption spectra of as-prepared (a) Clevios P and (b) Clevios PH1000 films.

from 0.5 V down to  $-0.2$  V vs Ag/AgCl, the absorption at the wavelength range of longer than 1150 nm, which is related to the bipolarons, decreases. In addition, two new bands, one between 700 and 1150 nm and another between 400 and 800 nm, appear. The former band is due to the polarons, and the latter band is the  $\pi$ -to- $\pi^*$  transition of PEDOT.<sup>33</sup> The polaron band is the most remarkable one at  $-0.2$  V vs Ag/AgCl. When the potential is further lowered to  $-0.8$  V, the  $\pi$ -to- $\pi^*$  transition band becomes the strongest, while the bipolaron absorption band disappears and the polaron absorption band becomes weak. This indicates that the PEDOT:PSS films cannot be completely reduced. This is because the PEDOT chains are surrounded by a thick shell rich of PSS chains for both grades of PEDOT:PSS. Both the as-prepared Clevios PH1000 and Clevios P films exhibit similar change in the absorption during the electrochemical reduction of PEDOT:PSS by scanning the electrochemical potential from 0.5 V down to  $-0.8$  V vs Ag/AgCl.

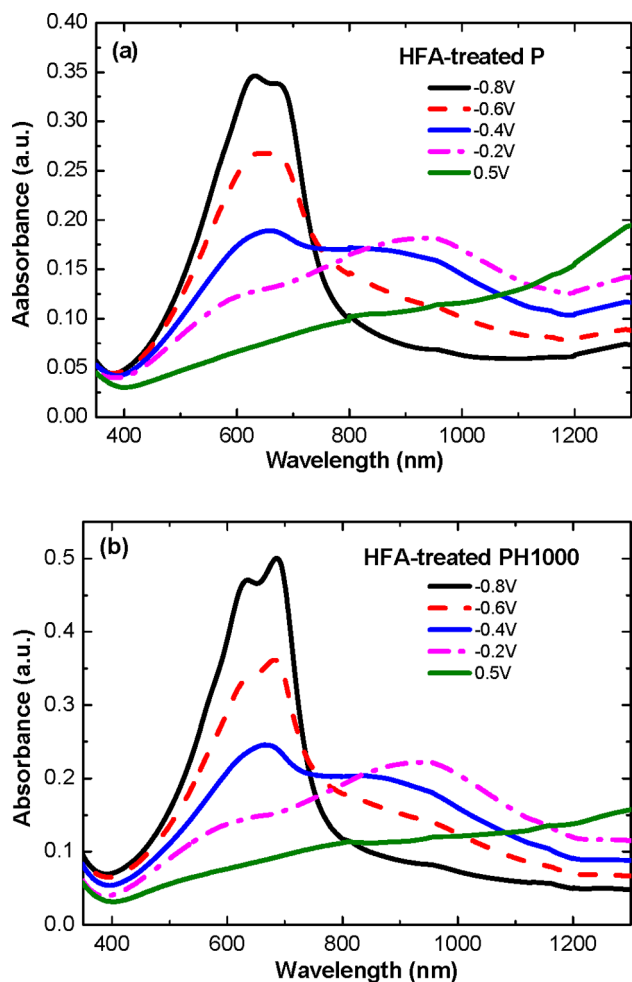
The difference in the CVs of the two PEDOT:PSS films becomes more significant after the treatment with HFA. Both CVs become quite broad after the HFA treatment (Figure 9). The broadenings of the CVs can be attributed to the HFA-induced phase segregation between PEDOT and PSS, which facilitates the electron transport between the external circuit and the PEDOT:PSS films. But the HFA-treated Clevios PH1000 film has additional electrochemical activity in the low potential range. A redox couple with cathodic and anodic peaks



**Figure 9.** CVs of HFA-treated Clevios P and HFA-treated Clevios PH1000 films.

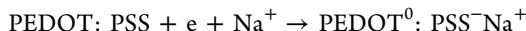
at  $-0.64$  and  $-0.70$  V vs Ag/AgCl, respectively, appear for the HFA-treated Clevios PH1000 film, whereas it is absent for the HFA-treated Clevios P film. Presumably, the difference in the CVs of the two HFA-treated PEDOT:PSS films is related to the molecular weight of PEDOT and interactions among the PEDOT chains. It was observed that high molecular weight and high crystallinity of conducting polymers can lead to broad electrochemical behavior.<sup>67,68</sup> For example, poly(3-hexythiophene) with higher molecular weight have broader electrochemical activity than that with lower molecular weight. Regioregular poly(3-hexythiophene) has higher crystallinity than random poly(3-hexythiophene), and correspondingly the former has additional electrochemical behavior in comparison with the latter. We studied the as-prepared and HFA-treated Clevios PH1000 and Clevios P films with X-ray diffract and did not observe any XRD pattern for them. But the crystallinity is related to the interaction among the polymer chains. Higher crystallinity corresponds to stronger interchain interactions. The interactions among the PEDOT chains are much stronger for the HFA-treated PEDOT:PSS films than the as-prepared PEDOT:PSS films as a result of the HFA-induced phase segregation between PEDOT and PSS. Longer rigid PEDOT chains can give rise to stronger interchain interactions. Thus, there is additional electrochemical behavior in the low potential range for the HFA-treated Clevios PH1000 films.

The electronic structures of the HFA-treated Clevios PH1000 and Clevios P films were investigated by UV-vis-NIR absorption spectroscopy (Figure 10). The spectra are different from that of the as-prepared PEDOT:PSS films, particularly at  $-0.8$  V vs Ag/AgCl. The polaron band disappear, and the  $\pi$ -to- $\pi^*$  transition band becomes stronger than that of the as-prepared PEDOT:PSS films at  $-0.8$  V vs Ag/AgCl. The maximum absorptions are 0.34 and 0.48 for the HFA-treated Clevios P and HFA-treated Clevios<sup>TM</sup> PH1000 films at  $-0.8$  V vs Ag/AgCl, saliently higher than those (0.26 and 0.24) of the as-prepared PEDOT:PSS films. The stronger  $\pi$ -to- $\pi^*$  transition absorption for the HFA-treated Clevios PH1000 film than for the HFA-treated Clevios P film can be attributed to the stronger inter-PEDOT interactions. It has been observed that higher crystallinity of conjugated polymer films can give rise to stronger absorption.<sup>69-71</sup>



**Figure 10.** In situ UV-vis-NIR absorption spectra of (a) HFA-treated Clevis P and (b) HFA-treated Clevis PH 1000 films.

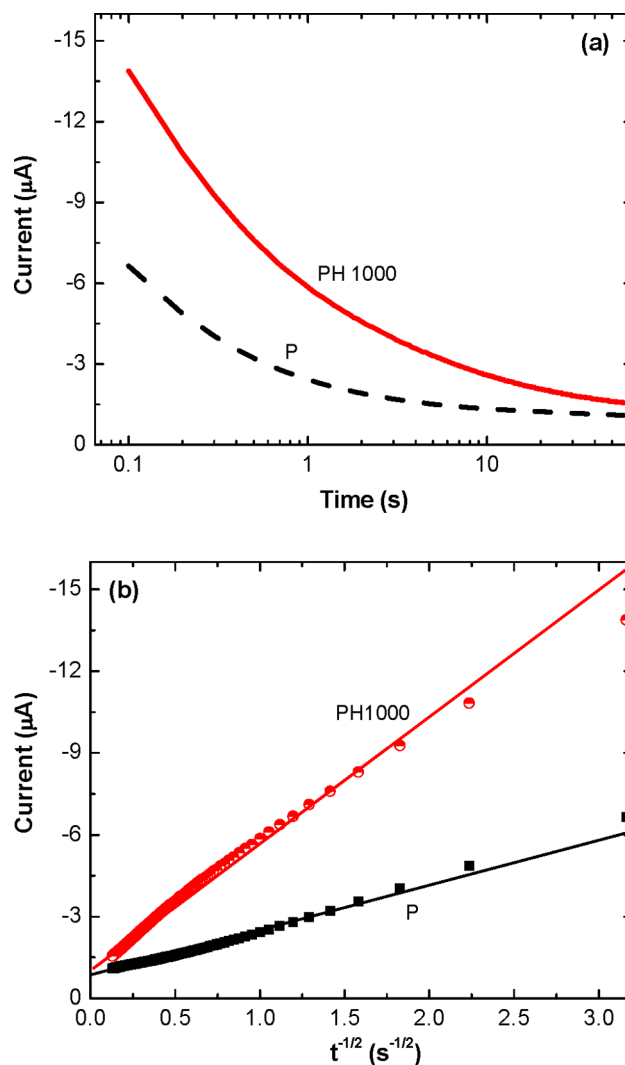
The as-prepared Clevis PH1000 and Clevis P films were investigated by the potentiostatic transient technique. A potential of  $-0.6$  V vs Ag/AgCl was applied to reduce the PEDOT:PSS films, and the currents during the electrochemical reduction were monitored. As shown in Figure 11, the current decay is faster for the Clevis™ PH1000 film than the Clevis P film. The current is the reduction of PEDOT,



which is related to the electron transfer from the external circuit to PEDOT and the cation diffusion from the electrolyte into the polymer films. The current is predominantly affected by the cation diffusion from the electrolyte into PEDOT:PSS. The ion diffusion constants ( $D_0$ ) can be estimated by analyzing the currents by the equation

$$i(t) = \frac{FAD_0^{1/2}C}{\sqrt{\pi t}}$$

where  $F$  is the Faraday constant,  $A$  the area of the working electrode,  $C$  the charge of an electron, and  $t$  the time. The  $D_0$  values are  $7.4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$  and  $9.3 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$  for the Clevis™ PH1000 and Clevis P films, respectively. These  $D_0$  values are reasonable for conducting polymers.<sup>72,73</sup> The ion diffusion constant is greater for the Clevis PH1000 film than the Clevis P film. It can be attributed to the different lengths of the PEDOT chains in the two grades of PEDOT:PSS. The



**Figure 11.** (a) Potentiostatic transient currents of as-prepared Clevis P and Clevis PH1000 films in 0.1 M NaCl aqueous solution. A potential of  $-0.6$  V vs Ag/AgCl was applied on the PEDOT:PSS films. (b) Estimation of the  $\text{Na}^+$  diffusion constants for as-prepared Clevis P and Clevis PH1000 films. The dots are the experimental data, and the straight lines are the best fittings of the data.

longer rigid PEDOT chains can make the polymer film rougher as observed by AFM, which facilitate the cation diffusion from the electrolyte into PEDOT:PSS.

HFA-treated Clevis P and Clevis PH1000 films were used as the transparent electrodes of polymer solar cells. The device fabrication and characterization were followed our previous work.<sup>43,44,50,51</sup> The active layer of the polymer solar cells were prepared by spin coating a 1,2-dichlorobenzene solution of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl- $\text{C}_{61}$ -butyric acid methyl ester (PCBM). The photovoltaic performance of the polymer solar cells with HFA-treated Clevis P films as the transparent electrode is similar to those with cosolvent-treated Clevis P films.<sup>44</sup> The photovoltaic efficiency is around 2.8% at AM1.5G illumination ( $100 \text{ mA cm}^{-2}$ ). The photovoltaic efficiency increases to 3.57% for the polymer solar cells with HFA-treated Clevis PH1000 films as the transparent electrode.<sup>50</sup>



## CONCLUSIONS

The differences between Clevios P and Clevios PH1000 were studied by various characterizations on PEDOT:PSS aqueous solutions and films. The DLS and fluorescence spectroscopy of pyrene in these solutions indicate that the gel particles are larger in Clevios PH1000 solution than in Clevios P solution. These results suggest that PEDOT of Clevios™ PH1000 has higher average molecular weight than that of Clevios™ P. The different average molecular weights of PEDOT in the two grades of PEDOT:PSS are confirmed by the atomic force microscopy and temperature dependences of the resistances of as-prepared and HFA-treated PEDOT:PSS films. The different average molecular weights of PEDOT also gives rise to significant difference in the electrochemical behavior of the two grades of PEDOT:PSS. The HFA-treated Clevios™ PH1000 films have broader electrochemical activity than the HFA-treated Clevios™ P film. The  $\pi$ -to- $\pi^*$  transition band of HFA-treated Clevios™ PH1000 films are stronger than that of HFA-treated Clevios™ P films when both films are electrochemically reduced to neutral state. The cations diffuse faster for Clevios™ PH1000 films than for Clevios™ P films. This understanding can provide guidance for the development of PEDOT:PSS films with even higher conductivity and other high-performance conducting polymers.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: mseoj@nus.edu.sg

### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

This research work was financially supported by a research grant from the Agency for Science, Technology and Research, Singapore.

## REFERENCES

- Inganäs, O. *Nat. Photon.* **2010**, *5*, 201.
- Chipman, A. *Nature* **2007**, *449*, 131.
- Na, S. I.; Kim, S. S.; Jo, J.; Kim, D. Y. *Adv. Mater.* **2008**, *20*, 4061.
- Kim, W. H. *Appl. Phys. Lett.* **2002**, *80*, 3844.
- Zhang, F.; Johansson, M.; Andersson, M. R.; Hummelen, J. C.; Inganäs, O. *Adv. Mater.* **2002**, *14*, 662.
- Lee, C. S.; Kim, J. Y.; Lee, D. E.; Koo, Y. K.; Joo, J.; Han, S.; Beag, Y. W.; Koh, S. K. *Synth. Met.* **2003**, *135*, 13.
- Argun, A. A.; Cirpan, A.; Reynolds, J. R. *Adv. Mater.* **2003**, *15*, 1338.
- Ouyang, J.; Chu, C. W.; Chen, F. C.; Xu, Q.; Yang, Y. *Adv. Funct. Mater.* **2005**, *15*, 203.
- Ouyang, J.; Yang, Y. *Adv. Mater.* **2006**, *18*, 2141.
- Yoo, J. E.; Yoo, J. E.; Lee, K. S.; Garcia, A.; Tarver, J.; Gomez, E. D.; Baldwin, K.; Sun, Y.; Meng, H.; Nguyen, T. Q.; Loo, Y. L. *Proc. Nat. Acad. Sci.* **2010**, *107*, 5712.
- Huang, J. H.; Kekuda, D.; Chu, C. W.; Ho, K. C. *J. Mater. Chem.* **2009**, *19*, 3704.
- Na, S. I.; Wang, G.; Kim, S. S.; Kim, T. W.; Oh, S. H.; Yu, B. K.; Lee, T.; Kim, D. Y. *J. Mater. Chem.* **2009**, *19*, 9045.
- Hsiao, Y. S.; Whang, W. T.; Chen, C. P.; Chen, Y. C. *J. Mater. Chem.* **2008**, *18*, 5948.
- Chang, Y. M.; Wang, L.; Su, W. F. *Org. Electron.* **2008**, *9*, 968.
- Lee, M. W.; Lee, M. Y.; Choi, J. C.; Park, J. S.; Song, C. K. *Org. Electron.* **2010**, *11*, 854.
- Elschner, A.; Lövenich, W. *MRS Bull.* **2011**, *36*, 794.
- Wu, Z. C.; Chen, Z. H.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. *Science* **2004**, *305*, 1273.
- Zhang, M.; Fang, S.; Zakhidov, A. A.; Lee, S. B.; Aliev, A. E.; Williams, C. D.; Atkinson, K. R.; Baughman, R. H. *Science* **2005**, *309*, 1215.
- Gruner, G. *J. Mater. Chem.* **2006**, *16*, 3533.
- Mei, X.; Ouyang, J. *J. Mater. Chem.* **2011**, *21*, 17842.
- Kim, K. S.; Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J. H.; Kim, P.; Choi, J. Y.; Hong, B. H. *Nature* **2009**, *457*, 706.
- Becerril, H. A.; Mao, J.; Liu, Z.; Stoltenberg, R. M.; Bao, Z.; Chen, Y. *ACS Nano* **2008**, *2*, 463.
- Lee, J. Y.; Connor, S. T.; Cui, Y.; Peumans, P. *Nano Lett.* **2008**, *8*, 689.
- Yu, Z.; Zhang, Q.; Li, L.; Chen, Q.; Niu, X.; Liu, J.; Pei, Q. *Adv. Mater.* **2011**, *23*, 664.
- Yu, Z.; Li, L.; Zhang, Q.; Hu, W.; Pei, Q. *Adv. Mater.* **2011**, *23*, 4453.
- Heywang, G.; Jonas, F. *Adv. Mater.* **1992**, *4*, 116.
- Groenendaal, L.; Jonas, F.; Freitag, D.; Peilartzik, H.; Reynolds, J. R. *Adv. Mater.* **2000**, *12*, 481.
- Pei, Q.; Zuccarello, G.; Ahlsgott, M.; Inganäs, O. *Polymer* **1994**, *35*, 1347.
- Cao, Y.; Yu, G.; Menon, R.; Heeger, A. J. *Synth. Met.* **1997**, *87*, 171.
- Kim, J. Y.; Jung, J. H.; Lee, D. E.; Joo, J. *Synth. Met.* **2002**, *126*, 311.
- Pettersson, L. A. A.; Ghosh, S.; Inganäs, O. *Org. Electron.* **2002**, *3*, 143.
- Jönsson, S. K. M.; Birgersson, J.; Crispin, X.; Greczynskib, G.; Osikowiczb, W.; van der Gonc, A. W. D.; Salaneckb, W. R.; Fahlman, M. *Synth. Met.* **2003**, *139*, 1.
- Ouyang, J.; Xu, Q.; Chu, C. W.; Yang, Y.; Li, G.; Shinar, J. *Polymer* **2004**, *45*, 8443.
- Crispin, X.; Jakobsson, F. L. E.; Crispin, A.; Grim, P. C. M.; Andersson, P.; Volodin, A.; van Haesendonck, C.; van der Auweraer, M.; Salaneck, W. R.; Berggren, M. *Chem. Mater.* **2006**, *18*, 4354.
- Nardes, A. M.; Kemerinka, M.; de Kokb, M. M.; Vinkenc, E.; Maturovaa, K.; Janssen, R. A. J. *Org. Electron.* **2008**, *9*, 727.
- Nardes, A. M.; Janssen, R. A. J.; Kemerink, M. A. *Adv. Funct. Mater.* **2008**, *18*, 865.
- Döbbelin, M.; Marcilla, R.; Salsamendi, M.; Pozo-Gonzalo, C.; Carrasco, P. M.; Pomposo, J. A.; Mecerreyes, D. *Chem. Mater.* **2007**, *19*, 2147.
- Fan, B. H.; Mei, X. G.; Ouyang, J. *Macromolecules* **2008**, *41*, 5971.
- Reyes-Reyes, M.; Cruz-Cruz, I.; Lopez-Sandoval, R. *J. Phys. Chem. C* **2010**, *114*, 20220.
- Xia, Y.; Ouyang, J. *ACS Appl. Mater. Interfaces* **2010**, *2*, 474.
- Xia, Y.; Ouyang, J. *Macromolecules* **2009**, *42*, 4141.
- Xia, Y.; Ouyang, J. *Org. Electron.* **2010**, *11*, 1129.
- Xia, Y.; Zhang, H. M.; Ouyang, J. *J. Mater. Chem.* **2010**, *20*, 9740.
- Xia, Y.; Ouyang, J. *J. Mater. Chem.* **2011**, *21*, 4927.
- Sun, K.; Xia, Y.; Ouyang, J. *Sol. Energy Mater. Sol. Cells* **2012**, *97*, 89.
- Peng, B.; Guo, X.; Cui, C.; Zou, Y.; Pan, C.; Li, Y. *Appl. Phys. Lett.* **2011**, *98*, 243308.
- Information about Clevios PEDOT:PSS can be found at the website by Heraeus, <http://clevios.com/en/conductivepolymers/pedot-pss-conductive-polymers.aspx>
- Zhou, Y.; Cheun, H.; Choi, S.; Potscavage, W. J.; Fuentes-Hernandez, C.; Kippelen, B. *Appl. Phys. Lett.* **2007**, *97*, 153304.
- Kim, Y. H.; Sachse, C.; Machala, M. L.; May, C.; Müller-Meskamp, L.; Leo, K. *Adv. Funct. Mater.* **2011**, *21*, 1076.
- Xia, Y.; Sun, K.; Ouyang, J. *Energy Environ. Sci.* **2012**, *5*, 5325.
- Xia, Y.; Sun, K.; Ouyang, J. *Adv. Mater.* **2012**, *24*, 2436.

- (52) Cai, M.; Xiao, T.; Liu, R.; Chen, Y.; Shinar, R.; Shinar, J. *Appl. Phys. Lett.* **2011**, *99*, 153303.
- (53) Lang, U.; Müller, E.; Naujoks, N.; Dual, J. *Adv. Funct. Mater.* **2009**, *19*, 1215.
- (54) Bagchi, D.; Menon, R. *Chem. Phys. Lett.* **2006**, *425*, 114.
- (55) Friedel, B.; Keivanidis, P. E.; Brenner, T. J. K.; Abrusci, A.; McNeill, C. R.; Friend, R. H.; Greenham, N. C. *Macromolecules* **2009**, *42*, 6741.
- (56) Friedel, B.; Brenner, T. J. K.; McNeill, C. R.; Steiner, U.; Greenham, N. C. *Org. Electron.* **2011**, *12*, 1736.
- (57) Vacca, P.; Petrosino, M.; Miscioscia, R.; Nenna, G.; Minarini, C.; Sala, D. D.; Rubino, A. *Thin Solid Films* **2008**, *516*, 4232.
- (58) Turro, N. J.; Kuo, P. L. *Langmuir* **1986**, *2*, 438.
- (59) Winnik, F. M. *Chem. Rev.* **1993**, *93*, 587.
- (60) Ramanavicius, A.; Kurilcik, N.; Jursenas, S.; Finkelsteinas, A.; Ramanavicien, A. *Biosens. Bioelectron.* **2007**, *23*, 499.
- (61) Teraoka, I. *Polymer Solutions: An Introduction to Physical Properties*; Wiley: New York, 2002.
- (62) Joo, J.; Long, S. M.; Pouget, J. P.; Oh, E. J.; MacDiarmid, A. G.; Epstein, A. J. *Phys. Rev. B* **1998**, *57*, 9567.
- (63) Pike, G. E.; Seager, C. H. *Phys. Rev. B* **1974**, *10*, 1421.
- (64) De, S.; Coleman, J. N. *MRS Bull.* **2011**, *36*, 774.
- (65) Hecht, D.; Hu, L. B.; Gruner, G. *Appl. Phys. Lett.* **2006**, *89*, 133112.
- (66) Hu, L. B.; Wu, H.; Cui, Y. *MRS Bull.* **2011**, *36*, 760.
- (67) Trznadel, M.; Pron, A.; Zagorska, M. *Macromolecules* **1998**, *31*, 5051.
- (68) Skompska, M.; Szkurlat, A. *Electrochim. Acta* **2001**, *46*, 4007.
- (69) Ouyang, J.; Xia, Y. *Sol. Energy Mater. Sol. Cells* **2009**, *93*, 1592.
- (70) Padinger, F.; Rittberger, R. S.; Sariciftci, N. S. *Adv. Funct. Mater.* **2004**, *13*, 85.
- (71) Peet, J.; Heeger, A. J.; Bazan, G. C. *Acc. Chem. Res.* **2009**, *42*, 1700.
- (72) Li, Y.; Qian, R. *Synth. Met.* **1994**, *64*, 241.
- (73) Ouyang, J.; Li, Y. *J. Appl. Polym. Sci.* **1996**, *59*, 1827.