Influence of Postsynthesis Heat Treatment on Vapor-Phase-Polymerized Conductive Polymers

Kamil Zuber,* Henry Shere,‡ Junaiz Rehmen,† Vivienne Wheaton,§ Manrico Fabretto,† Peter J. Murphy,† and Drew R. Evans†

†Thin Film Coatings Group, Future Industries Institute, University of South Australia, Mawson Lakes Boulevard, Mawson Lakes, South Australia 5095, Australia
‡Department of Chemistry, University of Bath, Bath BA2 7AY, U.K.
§Maritime Division, Defence Science and Technology Group (Australia), 506 Lorimer Street, Fishermans Bend, Victoria 3207, Australia

*Supporting Information

ABSTRACT: The effect of thermal treatment on the structure and electrical/optical properties of vapor phase-polymerized poly(3,4-ethylenedioxythiophene):tosylate (PEDOT:Tos) and polypyrrole:tosylate (PPy:Tos) polymer films was investigated. Thermal treatment was applied postpolymerization but prior to washing the embedded oxidant layer out of the polymer film. Structural and chemical changes arising from the treatment were studied in the context of their conductive and electrochromic behavior. Spectroscopic analysis indicated a rise in the doping levels of both conductive polymers when exposed to thermal treatment. Additionally, an increase in the film thickness was recorded after the oxidant and other unbound species were removed from the polymer layer using an ethanol rinse. As such, a strong indication that polymerization continued even in the absence of (external) monomer vapor was present. This film thickness increase was most pronounced for PPy:Tos but also present in the PEDOT:Tos film. Heat-treated films exhibited enhanced cohesion, making them more robust and therefore increasing the viability for the material to be used in the optoelectronics area. This robustness, due to additional (cross-linking) oligomer growth, came at the expense of lower conductivity relative to their untreated counterparts.

1. INTRODUCTION

Conductive polymers have been of great interest to researchers and industry alike because of their conductive and optical properties which can be altered by changing the dopant species and doping level, conjugation length, and the incorporation of additives. Various means of improving these materials have been keenly investigated, ranging from conductivity to optical and stability enhancement. Of the many conductive polymers which exist, poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) are arguably the two most studied. This gives them the potential of being exploited because of their favorable electrochromic behaviors. Thus, these polymers have been used in a variety of applications such as adaptive camouflage and other optoelectronic devices. For instance, because PEDOT is a p-type material it has been utilized as a hole injection layer in anodes for organic light-emitting diodes. Because these polymers are also optically active they have been utilized in so-called “smart windows” for automotive and building applications. These windows modulate the transmitted or reflected solar radiation and have the potential to reduce the demand for lighting and heating and hence energy consumption.

PPy and PEDOT have traditionally been synthesized via chemical oxidation or electrochemical polymerization methods. Both these methods rely on a solvent carrier to suspend the monomer and, in simple terms, can be thought of as a “wet” process. Vapor phase polymerization (VPP), however, does not utilize a solvent carrier but rather the monomer is transported to an oxidant layer in vapor form. This process has been described as a solvent-less or “dry” process and was first utilized in the pioneering work by Mohammadi et al. VPP overcomes problems associated with performance and processability, as polymerization occurs in situ negating any polymer insolubility issues. The procedure involves coating a substrate with an oxidant layer, usually an iron(III) salt (with or without other additives), which acts as both the polymerization and subsequently the doping agent for the forming...
polymer once it is brought into contact with the monomer vapor. The polymerization is initiated at the liquid—vapor interface as the monomer condenses on the substrate surface.\textsuperscript{15,16} Excess oxidant, unreacted monomer, and any by-products are then removed from the film by rinsing the polymer with an ethanol spray (or bath) to create the thin film conductive polymer.

The VPP process consistently produces conductive polymers exhibiting the highest conductivity values as exemplified by Cho et al.,\textsuperscript{17} who produced PEDOT nanowires with a conductivity exceeding 7500 S cm\textsuperscript{-1}. Other recent works on VPP PEDOT and PPy have demonstrated how additives, such as copolymers incorporated into the oxidant solution, have the ability to modify the conductivity and robustness of these polymers.\textsuperscript{18–20} Such work has been particularly important for PPy, where redox reactions are sensitive to the presence of oxygen, and a decay in electrical conductivity occurs due to the irreversible degradation of the polymer backbone.\textsuperscript{21} This loss in performance was investigated by Brooke et al.,\textsuperscript{22} who noted an increased resistance to degradation under oxidative and reductive conditions when the triblock copolymer poly-(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) (PEG–PPG–PEG) was incorporated into the oxidant solution.

Most oxidant solutions utilized in the VPP process consist of one (or more) solvent carriers (i.e., alcohols or water), additives (i.e., pyridine, glycol, etc.), and an oxidant, with the most common being iron(III) tosylate. Other alternatives exist and include (but are not limited to) iron(III) trimethylbenzenesulfonate and iron(III) chloride.\textsuperscript{16} Typically oxidant selection is based upon factors such as effective oxidative strength which the triblock copolymer poly-(ethylene glycol)–poly(propylene glycol)–poly(ethylene glycol) (PEG–PPG–PEG) was incorporated into the oxidant solution.

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2. RESULTS AND DISCUSSION

For the practical application of conductive polymer films synthesized using VPP, one needs a robust polymer film. Some polymers such as PEDOT exhibit sufficient flexibility while retaining film cohesion. Others, however, such as PPy can suffer cohesion issues, with films often disintegrating during the ethanol rinse process. This problem is less pronounced when “stronger” oxidants (having high effective oxidative strength) such as FeCl\textsubscript{3} are used in the polymerization process instead of “softer” oxidants such as iron(III) tosylate.\textsuperscript{6} The drawback, however, is that polymers synthesized with FeCl\textsubscript{3} typically exhibit lower conductivity levels, and in electrochromic applications, the presence of (residual) oxidant has been reported to etch the indium tin oxide (ITO) transparent electrode.\textsuperscript{6}

A possible solution for polymers exhibiting low cohesive strength could be to induce higher molecular weight growth by increasing the polymerization time. However, this has been shown to have detrimental effects on some conductive polymers.\textsuperscript{19} With this in mind, an alternative process is presented herein, in which the PEDOT and PPy samples were transferred from the VPP chamber to an oven set to 70 °C for various amounts of time, before ethanol rinsing any excess or unreacted oxidant from the sample. It was hypothesized that the elevated temperature(s) may allow for a degree of polymerization/cross-linking to occur, utilizing the short chain oligomers and residual monomer residing within the oxidant layer after removing the samples from the VPP chamber. Initial tests showed noticeable improvements in the cohesion of polymerized films when postpolymerization heat treatment was applied. A prior work has revealed that PEDOT is sufficiently robust when polymerized with iron(III) tosylate.\textsuperscript{31} Notwithstanding this, an improvement was observed when the film was deposited as a free-standing membrane onto a perforated plate (see Figure 1a\textsubscript{1},b\textsubscript{1}). The non-heat-treated sample fractured as the film dried while the heat-treated PEDOT:Tos remained intact. The PPy:Tos heat-treated for 7 h postpolymerization displayed vastly improved cohesion, whereas the non-heat-treated PEDOT:Tos coatings were prone to disintegration during the ethanol rinse process. This problem is less pronounced when “stronger” oxidants (having high effective oxidative strength) such as FeCl\textsubscript{3} are used in the polymerization process instead of “softer” oxidants such as iron(III) tosylate.\textsuperscript{6} The drawback, however, is that polymers synthesized with FeCl\textsubscript{3} typically exhibit lower conductivity levels, and in electrochromic applications, the presence of (residual) oxidant has been reported to etch the indium tin oxide (ITO) transparent electrode.\textsuperscript{6}

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integrity compared to those rinsed directly after polymerization as shown in Figure 1. As a consequence of the heat treatment, a distinct color change was observed for the PPy:Tos sample (not observed for PEDOT:Tos). To examine the cause of the color change, the polymers were studied by UV–vis–near infrared (NIR) spectroscopy.

UV–vis–NIR spectroscopy is frequently used to analyze electron transitions and the band gap structure in semiconductors and conductive polymers. Typically, two major absorption bands can be observed in the spectra of conductive polymers in the 300–2000 nm range. The broad band found in the NIR region (i.e. >800 nm) refers to polaron and bipolaron transitions, while the peak in the visible region (i.e. 380–800 nm) typically refers to the band gap transition. In optical spectra of PEDOT:Tos, the peak energy gap is typically observed at approximately 600 nm, with single polaron transitions at 750–850 nm, followed by a broad absorption bipolaron band starting at approximately 1150 nm and extending to the medium wavelength IR region. Depending on the oxidation state of the conductive polymers, the energy gap ($E_g$) peak is more pronounced in the reduced state while the polaron and bipolaron excitations are more pronounced in the oxidized state. Given that PEDOT:Tos is naturally highly oxidized when synthesized using the VPP process, the $E_g$ peak in the UV–vis–NIR spectra (see Figure 2b) only manifests itself as a shoulder on the low wavelength slope of the polaron excitation, making it problematic if not impossible to determine its exact position. This peak was observed to be marginally lower in the intensity in spectra of PEDOT:Tos postpolymerization heat-treated for longer times. Typically, this could be an indication of a more oxidized polymer, and this hypothesis is explored further in the manuscript.

The energy gap for PPy is usually located in the range 3.2–3.6 eV (344–387 nm), and the polymer presents additional features in the visible range due to interband transitions at 0.7–1.0 eV: 1240–1770 nm, 1.4 eV: 885 nm, and 2.1–2.7 eV: 460–590 nm. Although the band gap structure changes in a similar way upon doping, as for other conductive polymers, the absorption peak at 2.1–2.7 eV (460–590 nm) relating to the transition from the VB to the antibonding polaron state becomes the dominant feature in the visible range. With increased doping/higher oxidation levels, absorption at 2.1–2.7 eV (460–590 nm) increases, making the polymer appear visibly darker. The PPy:Tos samples analyzed in this study displayed increased absorption in the 2.61–2.7 eV (460–475 nm) region as heat treatment times were increased. The absorption peak maximum was found to shift toward higher wavelength, and the calculated value of the respective energy level of the antibonding polaron state (see Table S2) also decreased (from 2.09 eV for nontreated to 1.98 eV for the sample heat-treated for 7 h). Additionally, in the sample treated for 7 h, the second absorption edge was found on the low energy side of the interband absorption peak which corresponds to an interband transition value of 2.15 eV, suggesting the presence of a second phase in the heat-treated PPy:Tos (see the Supporting Information for the Tauc plots and fittings). This is hypothesized to be related to a defected polymer formed upon prolonged heat treatment. The energy gap calculated from the spectra changed from 3.40 eV for nontreated to 3.18 eV for the sample posttreated for 7 h (see the inset in Figure 2a). These observations are likely to be related to changes in the chemistry of the polymer, and to explore it further, X-ray photoelectron spectroscopy (XPS) analysis was performed.

The XPS spectra of PEDOT:Tos and PPy:Tos samples were analyzed for atomic percentage and the fine structure of the peaks examined for specific elements. This analysis was performed to understand changes in the polymers chemistry induced by heat treatment. In PEDOT:Tos samples, no significant changes were observed in relative atomic concentrations apart from subtle variations in the concentration of carbon (see Figure S4). Because in the PEDOT:Tos system, both the polymer and dopant share the same elements, fine scans of 2p peaks were analyzed as per the methodology used by Bubnova et al. to analyze the doping levels. Two doublets were fitted to the spectra, with the 2p hybridization being set at 1.1 eV as a fixed parameter and the $2p_{3/2}$ area being half that of $2p_{1/2}$. These peaks were related to PEDOT with $2p_{3/2}$ being 163.8 eV and $2p_{1/2}$ 164.9 eV for charged PEDOT sites, with tosylate anions being in proximity of the polymer unit found at 167.1 eV for $2p_{3/2}$ and 168.2 eV for $2p_{1/2}$ (see Figure 3a). The ratios of PEDOT to tosylate calculated from these spectra and displayed in Figure 3c show higher doping levels in samples exposed to postpolymerization heat treatment at 70 °C, with tosylate to PEDOT ratios changing from 0.13 for the nontreated sample to nearly double: 0.22 in the sample treated for 7.5 h. This result is in line with the observations from the UV–vis–NIR spectroscopy displaying a decrease in the $E_g$ peak contributed to PEDOT:Tos becoming more oxidized upon heat treatment.

**Figure 2.** Change in UV–vis–NIR absorbance spectra for 70 °C heat-treated samples. (a) PPy and (b) PEDOT samples. Note: black—0 h (not treated); blue = 2.5 h; red = 5 h; green = 7 h. The arrows indicate the position of the energy gap peak (in PEDOT not observed clearly due to polymers being in the oxidized state, in PPy partly obstructed by the absorption from the substrate), and in PPy:Tos, the additional sharp absorption peak in the visible region is related to electron transition from valence band (VB) to antibonding polaron state.
Two complementary methods were used to analyze the doping level in PPy. As PPy does not contain sulfur in the polymer backbone, while being present in the tosylate dopant, the atomic ratio of S 1s to N 1s was used as a simple means of measuring the change in the doping level. Additionally, N 1s spectra were analyzed and fitted with two peaks: 399.8−400.0 eV related to neutral pyrrole rings and 401.8−402.0 eV related to oxidized pyrrole rings (see Figure 3b). Examining the results of both methods and by comparing the ratios of N to S and analyzing the fine structure of the N 1s peaks, one can reasonably conclude that the thermal treatment has increased the doping level of the PPy polymer (see Figure 3d), similar to what was observed for PEDOT:Tos.
To confirm the changes in the PPy film are particular to post-synthesis heat treatment, as most significant changes were observed in this polymer, an additional study regarding the effect of polymerization temperature was conducted and examined using XPS. PPy:Tos samples were synthesized at polymerization temperatures between 60 and 110 °C, in 10 °C increments and rinsed immediately after polymerization. The data are summarized in Table S3, and no significant changes and trends in the data were observed. This confirmed that the changes observed when using post-synthesis heat treatment are particular to that process rather than simply a difference due to the temperatures during VPP synthesis.

XPS only examines the surface of the polymer thin film (approximately 10 nm depth). Therefore, further investigation using Fourier-transform infrared spectroscopy (FTIR) was performed to shed some light on the structure of the “bulk” volume of the polymers and to establish whether the changes were a surface phenomenon or indicative of the entire polymer.

The FTIR spectra are presented in Figure 4 (background was subtracted for better presentation) and the full peak assignment with original spectra is presented in Tables S4 and S5. These spectra were confirmed to be typical for PEDOT and PPy when compared to the spectra presented in the literature.24,35 Figure 4a for PEDOT showed no measurable differences in the fingerprint region between pristine and heat-treated samples. Both PEDOT and PPy displayed higher absorption of the broad bipolaron absorption band (above 2000 cm⁻¹ and typically extending to the NIR region; see nonsubtracted spectra in Supporting Information S5 and S6) in the non-heat-treated samples, which is in contrary to higher doping levels observed in XPS and UV–vis–NIR analysis, suggesting other effects present in the polymers.

PPy:Tos samples, however, displayed several changes in the fingerprint region: peaks related to C=N stretching at 1384 cm⁻¹, SO₃⁻ at 1174 cm⁻¹, C=N‘ bending at 1088 cm⁻¹, and C–H vibrations at 929 cm⁻¹. These peaks are related to the doped form of PPy and they exhibit increased absorption for the heat-treated samples compared to the nontreated sample. Even though this observation aligns with the XPS results confirming a larger doping level in the polymer, it would typically lead to the contrary response in the bipolaron band region to what was observed. This might suggest that other changes in the polymer are occurring with heat treatment, such as cross-linking, leading to disruption of conjugation. Such a mechanism could explain higher rigidity of PPy:Tos observed in the heat-treated polymer.

Additional information in relation to the heat treatment process was obtained from the waste material after the treated samples were rinsed with ethanol. To our knowledge, this is the first report of such an examination. Typically, the last step of the VPP process is rinsing the surface with ethanol to remove the spent oxidant, untreated monomer, and other byproducts in an attempt to “purify” and compact the polymer film. The waste material was collected, pelleted in KBr, dried (in ambient conditions), and analyzed using FTIR (see Figure 4c,d). When compared with spectra of basic starting compounds used in the VPP process (see Supporting Information), the possible content of the waste material must be the oxidant (iron(III))Tos, and/or reduced iron(II)-Tos), the block copolymer PEG–PPG–PEG, monomer, and small oligomers.

The differences observed in the PEDOT:Tos waste material postpolymerization were larger than those in the waste material from PPy:Tos. In the non-heat-treated sample of PEDOT:Tos, a larger relative absorption was observed for several peaks related to the major peaks in the PEG–PPG–PEG copolymer (refer to Figure S8) at 2969 cm⁻¹, 2869 cm⁻¹ (C–H vibrations), 1159 cm⁻¹, 1348 cm⁻¹ (C–H), and 1107 cm⁻¹ (C–O–C). This suggests that there is a higher concentration of PEG–PPG–PEG remaining in the heat-treated PEDOT:Tos polymer (as less PEG–PPG–PEG was rinsed off into the waste material). The most pronounced change in the FTIR spectra for the waste material from PPy:Tos polymer was the larger relative intensities in the non-heat-treated sample for peaks characteristic of iron(III) tosylate: at 1089 and 1047 cm⁻¹. This result is consistent with the larger doping levels recorded for the heat-treated samples observed in the XPS spectra. Such differences between PEDOT:Tos and PPy:Tos suggest that the changes upon heat treatment in two polymers are noticeably different. Lower changes in the heat-treated PPy:Tos waste material compared to those in the polymer suggest structural defects and possible cross-linking combined with higher doping level being responsible for observed macroscopic changes. In contrast, PEDOT:Tos did not present noticeable accumulation of defects upon heat treatment, though still, a larger concentration of dopant and PEG–PPG–PEG was observed in the polymer. Such differences between PEDOT and PPy polymers are consistent with the stability studies found in the literature, with PPy being found less stable under ambient atmospheric conditions than PEDOT.37,38

Following the analysis of structural changes, the electrical properties of the conductive polymers were analyzed. The conductivity, σ, of the polymeric films was calculated as per the protocol described in the Supporting Information, by measurement of film sheet resistance and thickness, and is presented in Figure 5. All samples exhibited a drop in conductivity during postpolymerization heat treatment, accompanied by an increase in film thickness. Thicker films are most likely the result of residual monomer being present within the oxidant (and/or polymer) layers39,40 as the substrates are removed from the VPP chamber. While exposed to the heat treatment, the polymerization process is able to continue. The conductive polymer growth mechanism proposed by Diaz,41 followed by Mueller,42 suggests that the polymer chain starts as a dimer, followed by the addition of subsequent units onto the forming polymer chain. On the basis of the observation of enhanced film cohesion and increased film thickness, it is not unreasonable to expect polymers with...
longer chains. The lower conductivity values are contrary to the higher doping levels observed with XPS, FTIR, and UV–vis. To some extent, this result may be explained by the growth of side chains, cross-linking, or branching of the polymers having the major effect on disturbing the conjugation and intrachain charge transfer. In addition, a larger concentration of PEG−PPG−PEG was observed in heat-treated samples. The PEG−PPG−PEG copolymer resides at the conductive polymer grain boundaries, impairing intergrain hopping and hence decreasing the conductivity.

Finally, conductive polymers have the ability to display an electrochromic effect—a change of color upon electrochemical oxidation and reduction. The effect of the postpolymerization heat treatment on the performance of electrochromic devices, made using PEDOT:Tos and PPy:Tos conductive polymers (each individually), was investigated. Both polymers displayed differences in the UV−vis−NIR spectra due to heat posttreatment, and further analysis was performed to examine the effect of these changes on the electrochemistry of the polymer and their spectra. To analyze the electrochemical response and spectral changes, the polymers were tested in a three-electrode cell, with transparent electrodes, allowing the measurement of optical spectra while simultaneously being electrochemically oxidized and reduced in a reversible manner.

The UV−vis−NIR spectra of polymers analyzed in the previous part of the manuscript (Figure 2) were of the "as-synthesized" polymers, which were in the oxidized state, and the three-electrode test allowed us to extend these observations to reduced forms of polymers. As the changes due to heat treatment were observed in the optically visible range of the spectrum, it produced a permanent change in the color. For the PPy:Tos, there has been observed the difference in color as presented in the insets of Figure 6a. Additionally, the cyclic voltammograms of PPy:Tos samples showed distinctively different patterns for oxidation potentials in treated and nontreated samples (see Figure 6c). Given that the shift in the value of the antibonding state (expressed as change in the absorption peak in the visible range of the UV−vis−NIR spectrum) is permanent such that it does not change upon subsequent oxidation and reduction, this difference has most likely been caused by structural changes in the polymer, rather than simply a change in the doping state. For the PEDOT:Tos samples, reducing the polymer electrochemically (with optical spectrum presented in Figure 6b) allowed the measurement of the position of the energy gap peak, which was not possible in the "as-synthesized" polymers. No measurable change in the position of the energy gap was observed, and minor changes in the optical performance were attributable to variations in the film thickness. However, a noticeable shift in the reduction potential (see Figure 6a,b) toward lower potentials for heat-treated samples was observed in the cyclic voltammetry tests. This is in line with other measurements for PEDOT:Tos, with this polymer showing less degradation upon postpolymerization heat treatment, while improving the cohesion of the polymer.

3. CONCLUSIONS

The influence of postpolymerization heat treatment on the structure and properties of vapor-phase-polymerized conductive polymers: PEDOT:Tos and PPy:Tos was investigated. It was shown that the postsynthesis heat treatment enabled the polymerization process to continue even though the samples had been removed from the monomer source. This growth continuation resulted in increased film robustness and...
integrity, especially with respect to the PPy:Tos but also to the PEDOT:Tos film, albeit to a lesser extent. Heat-treated polymers were shown to possess a band gap structure characteristic of polymers having a higher oxidation level compared to nontreated samples. This was confirmed by means of compositional analysis, performed using XPS and FTIR, which showed the heat-treated polymers to have a higher doping level. A higher concentration of PEG–PPG–PEG block copolymer was also present, most notably for the PPy:Tos sample. As a result of the incorporation of additional block copolymer, the drawback was that the conductive polymers exhibited lower film conductivity. Other likely additional factors such as an increase in the polymer structure defects or cross-linking polymer chains may have contributed to the overall observed changes as indicated by the spectroelectrochemical analysis.

4. MATERIALS AND METHODS

Iron(III) tosylate (Clevios CB54, 54 wt % in butanol) was received from Heraeus. 3,4-Ethylendenedioxioxyphene monomer, PEG–PPG–PEG ($M_n = 5800$ and $2900$ g mol$^{-1}$), and pyrrole, were purchased from Aldrich. Butanol and 100% undenatured ethanol were purchased from Chem-Supply Pty. Ltd. Potassium bromide (KBr) powder was supplied by Merck. 3,4-Ethylenedioxythiophene monomer, Iron(III) tosylate (Clevios CB54, 54 wt % in butanol) was made for the synthesis of PPy doped with tosylate (PPy:Tos) containing 3 g of Baytron CB54, 3 g of PEG (PEG $M_n = 5800$ g mol$^{-1}$), and 1 g of ethanol. The oxidant solution was pipetted onto the substrates and spin-coated (400B-6NPP, Laurel Technologies Inc.) at a speed of 2685 rpm for 25 s. The substrates were then placed into a VPP chamber in the presence of monomer.

The synthesis of PPy:Tos was performed in a VPP chamber composed of a 16 L glass bell desiccator resting on a hot plate. The chamber temperature was 70 °C and left to equilibrate for 60 min. Four drops of pyrrole monomer were pipetted onto a microscope slide and placed within the polymerization chamber 3 min prior to polymerization, in order to saturate the chamber with monomer. The oxidant-coated substrate was then placed in the chamber for 7 min while adding an additional four drops of pyrrole monomer (to ensure a saturated vapor environment).

The synthesis of PEDOT:Tos was performed using the VPP technique as per the protocol in the literature.$^9$ EDOT monomer (four drops) was added to the polymerization chamber (Binder 115L vacuum oven), and the oxidant-coated substrates were then placed into the VPP chamber, kept at a pressure of 45 mbar and a temperature of 35 ± 1 °C for 30 min.

Batches of four conductive polymer samples were synthesized during each run, to minimize the sample to sample variation in each experiment. The control sample (not subjected to heat treatment) was removed and spray-rinsed with ethanol and then dried with (filtered) compressed air in order to remove any remaining oxidant, by-products, or unreacted monomer. The rinsing procedure was repeated to afford a dry conductive polymer film. This sample is also referred to as treated for “0 h” when presented in the figures. The samples heat-treated for 2.5, 5, and 7 h were removed at the same time as the nontreated sample but were transferred directly into an oven where they were kept at 70 °C. Once removed from the oven, the treated samples were rinsed in the same manner as previously described.

The films were characterized by UV–vis–NIR spectroscopy (Agilent Technologies, Cary), with the absorbance recorded in the range of 300–2000 nm. Energy gap was calculated using the Tauc method$^{45}$ with more detailed description included in the Supporting Information. Elemental analysis was performed using XPS (SPECs SAGE, Phoibos 150-HSA) using a Mg anode at a power setting of 200 W, with the samples cut into 2 × 2 cm squares. Samples were grounded to the sample stage with carbon tape during the measurements in order to minimize sample charging. CasaXPS software was used for quantification of the results, with which the relative atomic percentage change and doping levels recorded for each sample.

Film thickness was measured using a mechanical profilometer (Dektak model from Bruker). The polymer samples were scribed using a soft scalpel in the central parts of microscope slides, and the step height between the glass substrate and the film surface was recorded. The depth profile was measured at 10 different locations in order to obtain an average measurement.

The sheet resistance ($R_s$) of each sample was measured using a four-point probe from Jandel Engineering (RM3 Drive Unit, 500 μm tip, 60 g load, 1 mm tip spacing), and the value was calculated as the average of 10 measurements across the substrate. The current applied was varied from 5 μA up to 10 nA, depending on the sample so as to obtain a voltage in the range of 1–10 mV (optimal equipment range). Conductivity of the polymer films was calculated as per the procedure described in the Supporting Information, and the standard deviations were calculated using the propagation of uncertainty principle.

FTIR spectra were collected in transmission mode using a Nicolet Model Magna-IR 750. The PEDOT:Tos samples analyzed with FTIR were transferred as membranes onto a support Al mesh so that only the polymer was analyzed (no substrate interference). The PPy conductive polymers were ground with potassium bromide (KBr) and pressed into pellets for analysis.

The electrochemical and spectroelectrochemical studies were performed in an in-house-built three-electrode cell with a VoltaLab PGZ100 All-In-One potentiostat controlled by VoltaMaster 4 Electrochemical Software and a HunterLab Pro spectrophotometer. The working electrode was ITO-coated glass (from Kaivo) ($R_s < 7 \Omega$/sq, T > 80%), with conductive polymers deposited onto this electrode. Clear ITO-coated glass was used as the auxiliary electrode, and silver wire (99.9% Ag from Sigma-Aldrich) was used as the reference electrode. The reference electrode was polished with 600 grit abrasive paper and rinsed thoroughly with ethanol before each test. The electrolyte was [BMP][TFSI], obtained from Merck Millipore.
Calculation for the conductivity of conductive polymer films; film thickness of PPy:Tos at different postprocessing times; energy gap calculation; relative concentrations of the principal elements observed in PPy:Tos; and additional characterization data including FTIR spectra with peak assignments, and XPS results (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: kamil.zuber@unisa.edu.au. Phone: +61 8 830 26319.*

**ORCID**
Kamil Zuber: 0000-0003-0579-1983
Drew R. Evans: 0000-0002-1525-2249

**Notes**
The authors declare no competing financial interest.

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