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Highly transmissive and conductive poly[(3,4-alkylenedioxy)pyrrole-2,5-diyl] (PXDOP) films prepared by air or transition metal catalyzed chemical oxidation

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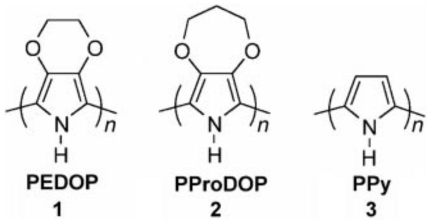
Poly[(3,4-ethylenedioxy)pyrrole-2,5-diyl] (PEDOP) and poly[(3,4-propylenedioxy)pyrrole-2,5-diyl] (PProDOP) were synthesized by *in situ* chemical polymerization yielding highly transmissive, conductive and electroactive thin films. PProDOP coatings exhibit a surface resistivity of $16\ \mathrm{k\Omega}\ \square^{-1}$ at 60% and $58\ \mathrm{k\Omega}\ \square^{-1}$ at 99.9% relative luminance (measured by colorimetry). Many factors were found to impact the formation of the films, including pH, temperature, nature of the dopant ion, and nature of the oxidizing agent. The best combination of dopant ion–oxidant was obtained for anthraquinone-2-sulfonic acid (AQSA)–copper chloride which yielded the most conductive films ($\sigma = 10\ \mathrm{S\ cm^{-1}}$). A doping level of about 25–30% was determined by X-ray photoelectron spectroscopy (XPS) for PEDOP and PProDOP films. Scanning electron microscopy (SEM) and profilometry indicate homogenous film deposition with total surface coverage attained in films as thin as 40–70 nm with a compact and smooth morphology. Spectroelectrochemistry of chemically prepared (oxidized) and subsequently electrochemically reduced PProDOP films showed the disappearance of the π–π^* transition, evident as two maxima at 485 nm and 518 nm upon electrochemical doping. The band gap, measured as the onset of the π–π^* transition was 2.2 eV. Since the oxidation potential of EDOP is relatively low (+0.6 V *vs.* $\mathrm{Ag/Ag^+}$), it was possible to obtain conducting films of PEDOP using air as the oxidizing agent for the polymerization. This result is of particular importance since very few conducting polymers can be obtained by such an environmentally friendly process.

Introduction

Conducting polymer-coated substrates produced by *in situ* chemical polymerization of pyrrole and aniline in aqueous electrolytes have aroused a great interest in both academia and industry over the past decade.[1–5] Simplicity, cost effectiveness and environmental friendliness (*i.e.* by avoiding the use of organic solvents) make this deposition technique of practical importance. The resulting products have substrate controlled mechanical properties, high electrical conductivities, along with environmental and thermal stabilities that allow their use in several applications including electrostatic dissipation (ESD) shielding,[6–8] electromagnetic interference (EMI) shielding, heating elements,[9,10] composite structures[11] and lightweight camouflage applications.[10,11–16]

In situ chemical polymerization corresponds to an oxidative process where the oxidation of the monomer is achieved with oxidizing agents containing a transition metal salt (*e.g.* $FeCl_3$, $CuCl_2$, $KMnO_4$, $(NH_4)_2Ce(NO_3)_6$) or non-metal containing oxidants (*e.g.* nitrates, peroxides, persulfates, peracids, *etc.*). The *in situ* oxidative polymerization of pyrrole in aqueous solution containing various sulfonated organic dopants, such as anthraquinone-2-sulfonic acid (AQSA), toluene-*p*-sulfonic acid (TSA), naphthalenesulfonic acid (NSA), benzenesulfonic acid (BSA), diphenylaminesulfonic acid (DPASA), dodecylbenzenesulfonic acid (DBSA) and (+)-camphor-10-sulfonic acid (DCSA), combined with various stabilizers, including benzophenones (BP) and 5-sulfosalicylic acid (SSA), has been reported to result in higher conductivity, along with enhanced environmental and thermal stability.[17–19] Under these conditions, coatings are obtained directly on a substrate during polymerization thus avoiding the use of organic solvents which may provide an environmental hazard and increase material preparation costs.

We report here the first results of the *in situ* chemical polymerization of two dioxypyrrole derivatives, 3,4-ethylenedioxypyrrole (EDOP) and 3,4-propylenedioxypyrrole (ProDOP), as examples of dioxypyrrole based monomers[20] and compare the properties of the films obtained with poly(pyrrole-2,5-diyl) (**3**) deposited under optimal conditions. PEDOP (**1**) and PProDOP (**2**) (Scheme 1) have already been demonstrated to have outstanding electrochemical and electrochromic properties when deposited by electrochemical polymerization.[21,22] Coatings of PEDOP prepared by dispersion of poly(styrene sulfonate) (PSS) doped PEDOP in a polymeric binder have proven useful for antistatic protection in the photographic film industry.[23] The lower oxidation potentials of EDOP and ProDOP compared to pyrrole allow chemical polymerization under milder conditions; for example air can be



Scheme 1 Structures of poly[(3,4-ethylenedioxy)pyrrole-2,5-diyl] (PEDOP, **1**), poly[(3,4-propylenedioxy)pyrrole-2,5-diyl] (PProDOP, **2**) and poly(pyrrole-2,5-diyl) (PPy, **3**).

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utilized as the oxidant. The electrical and optical properties of PEDOP and PProDOP thin films obtained by *in situ* chemical polymerization with various oxidizing agents including air, and in the presence of a variety of additives, were investigated. The possibility of using air as an oxidizing agent is remarkable since the resulting process is both environmentally friendly and cost efficient.

Experimental

Materials

Pyrrole, propylene carbonate (PC), ceric ammonium nitrate (CAN), ferric chloride, anthraquinone-2-sulfonic acid (AQSA), toluene-*p*-sulfonic acid (TSA), naphthalene-2-sulfonic acid (NSA), and 5-sulfosalicylic acid (SSA) were used as received from Aldrich without further purification. Potassium chloride, copper chloride, and sodium chloride were obtained from Fisher. Deionized water (18 MΩ) was used in all reactions. EDOP and ProDOP monomers were synthesized according to a procedure[21,22] adapted from Merz *et al.*[24–26] Methanol (MeOH) and acetonitrile (ACN) (Fisher) were used in minimal amounts to solubilize ProDOP. Custom-cut glass microscope slides (0.7 × 5 cm, Fisher) were used as substrates to prepare polymer films. For spectroelectrochemistry, ITO-coated glass slides (0.7 × 5 cm, $R < 10\ \Omega/\square$, Delta Technologies) were employed as the working electrode in a three electrode cell using a platinum wire as a counter and 10 mM Ag/AgNO$_3$ (Ag/Ag$^+$) as a reference.

Film synthesis

Cleaned glass slides were vertically introduced into aqueous solutions containing various concentrations of oxidant, dopant ion and stabilizing agent (if used) under gentle stirring. Typically, the polymerization medium consisted of an aqueous solution (10 ml) containing 0.05 M oxidant, 0.02 M monomer, 0.03 M dopant and 0.1 M stabilizer (if used). EDOP and ProDOP were found to be soluble in water up to about 0.10 M and 0.005 M at room temperature, respectively. ProDOP's somewhat lower solubility required that a small amount of MeOH or ACN (5–10% v/v) be used to help to dissolve the monomer. The polymerization solution was stirred and the temperature was kept constant. The pH was adjusted to the desired value by adding small amounts of 0.1 M NaOH to the mixture of oxidant, dopant and stabilizer. Note that this mixture is initially very acidic (pH = 1–3) and the optimal polymerization conditions are monomer dependent. Both poly(pyrrole-2,5-diyl) and PProDOP gave the best depositions when prepared at 0 °C, while PEDOP films are more conductive when polymerized at +20 °C with a transition metal oxidizing agent. However, for air polymerization, the best films were obtained at +40 °C. Depending on the reaction conditions, the polymerizations were allowed to proceed for 20 minutes to 6 hours. At the end of the polymerization, polymer coated substrates were removed from the solution, rinsed thoroughly with deionized water, and dried at room temperature in air before characterization.

Characterization

The electrical conductivity of the films was measured using the four point probe technique.[27] A Signatone four point probe with an adjustable head was used to make electrical contact with the films. Constant current (microamperes) was applied between the external probes using a Keithley 224 programmable current source, while the resulting voltage was measured between the two central probes with a Keithley 181 nanovoltmeter. At least 15 measurements were taken and averaged to calculate the conductivity. Film thickness and roughness were measured with a Dektak 3030 Profilometer across several places on each sample to yield the average thickness. In order to demonstrate the reproducibility of the conductivity values, 3 to 10 different samples were used for each set of conditions reported. A Cary 5E UV-Vis-NIR Spectrophotometer was used to monitor the optical properties of the polymer films. Electrochemical characterizations were carried out with an EG&G 273 Potentiostat. Corrware II software from Scribner Associates was used for data acquisition and instrument control. A JEOL JSM-6400 scanning electron microscope (SEM) was used to investigate the morphology of the films. A Perkin-Elmer PHI 5100 ESCA System/Kratos Analytical Surface Analyzer XSAM 800 model was used for X-ray photoelectron spectroscopy (XPS).

Colorimetry measurements were obtained by use of a Minolta CS-100 chromameter and CIE recommended normal/normal (0/0) illuminating/viewing geometry for transmittance measurements.[28] The sample was illuminated from behind by a D50 (5000 K) light source in a light booth designed to exclude external light. A background measurement was taken using a blank glass substrate. The color coordinates are expressed in the CIE 1931 *Y*xy color space where the Y value is a measure of the luminance in Cd m^{-2}. The relative luminance, expressed in %, was determined as the ratio between the Y value measured on the sample and the Y_0 value corresponding to the background. Note that the relative luminance is frequently reported, as opposed to absolute luminance, as it gives a more meaningful value in terms of the materials properties.[29]

Results and discussion

Polymerization conditions

Polymerization rate, deposition characteristics on the substrate, and the conductivity of the polymer coated on the substrate are influenced by many factors, particularly pH, reaction temperature, nature of the oxidizing agent, concentrations of reactants, the ratio of surface area of the substrate to the solution volume, the presence of surface active agents, polymerization time and agitation.[19] It should be noted that polymerization rate and deposition rate increase with oxidant concentration. With such a multitude of variables, determination of the ultimate optimal deposition conditions will be quite time intensive. It is the intent of this first publication to indicate the applicability of this deposition method to new dioxypyrrole derivatives, to indicate that highly conductive continuous thin films can be deposited, and illustrate the aqueous compatibility and ease of oxidation (air oxidant) of the dioxypyrroles.

Ferric chloride is the most widely used oxidizing agent for *in situ* chemical polymerization of pyrrole due to its oxidation potential and low cost.[30] By optimizing the deposition conditions, *i.e.* the nature of the dopant ions and addition of additives, researchers at Milliken Corporation have developed a method to provide highly conductive poly(pyrrole-2,5-diyl) (PPy, **3**) coated textiles.[2] The efficient polymerization with concurrent deposition in this method is obtained by using a large aromatic dopant bearing a sulfonate group (AQSA, TSA, NSA, BSA, DPASA or DBSA) and a stabilizer (SSA or BP and derivatives). In order to compare the properties of PEDOP (**1**) and PProDOP (**2**) films with state-of-the-art PPy (**3**) coatings, we have prepared PPy films using the Milliken method. PPy films (*ca.* 130 nm thick) were prepared on glass substrates by *in situ* chemical polymerization using three different dopant ions (TSA, NSA and AQSA) according to their known ability to form the most conductive materials films.[2] The conductivities measured on fresh films, and after 45 days of ambient air exposure, are presented in Fig. 1 and summarized in Table 1. The results confirm the efficiency of this method for the production of highly conductive PPy films.[17] As noticed by the Milliken researchers, there is a strong dopant ion dependence,

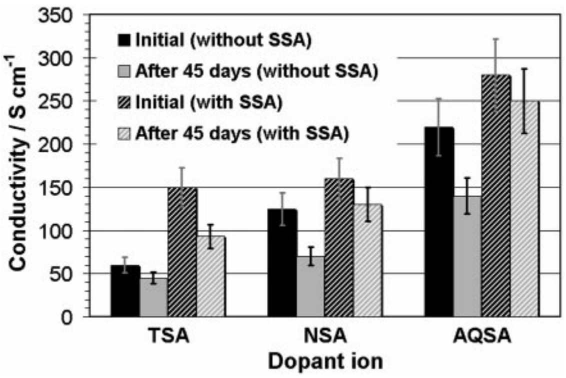

Fig. 1 Effect of dopant ion and stabilizer (SSA) on conductivity of poly(pyrrole-2,5-diyl) films prepared with $FeCl_3$.

and the presence of stabilizer (SSA) improves the film conductivity in all cases. The initial conductivity of PPy films without using SSA is maximum ($\sim 220\ S\ cm^{-1}$) when AQSA is used as dopant ion, whereas the conductivity was reduced somewhat to $125\ S\ cm^{-1}$ and $60\ S\ cm^{-1}$ for NSA and TSA dopants respectively. Higher conductivities are achieved in the presence of SSA with 280, 160 and $150\ S\ cm^{-1}$ measured for AQSA, NSA, and TSA respectively. It is noteworthy that AQSA, NSA and TSA are relatively planar molecules and likely enhance the planarity and π-overlap of the PPy segments which are responsible for the increase in the conductivity. Consequently, a larger dopant molecule gives a higher conductivity. In terms of film properties, SSA has proven useful for improving both the conductivity and ambient atmosphere stability of PPy coatings.[17] It should be noted that, even after 45 days of exposure to ambient atmosphere, the samples prepared in the presence of SSA display a higher conductivity than fresh samples obtained without SSA.

As emphasized in the Milliken method,[2–4] the monomer solution should be acidic, with a pH lower than 5, in order to obtain the optimum chemical polymerization conditions for pyrrole. The highest conductivity PPy coatings are generally reported for films deposited between pH 1 and 3. This is likely due to the fact that protons are acting as catalysts in the pyrrole polymerization.[31,32] We have adopted this method for the *in situ* chemical polymerization of EDOP and ProDOP, though the pH sensitivity is slightly different in the case of PEDOP and PProDOP film formation. At a pH below 3, no conductive PEDOP could be formed. Under these conditions, the coatings were of poor quality and inhomogeneous. Relatively smooth and continuous conductive coatings were obtained, though thin (40–80 nm) at pH values between 4 and 6. On the other hand, ProDOP's pH dependence is similar to that of pyrrole, giving the highest conductivities for pH values between 1 and 3. This difference in pH sensitivity between EDOP and ProDOP may stem from the water solubility of the oligomers formed during the polymerization; EDOP is significantly more soluble in water than ProDOP and this effect likely extends to the growing chains. As a result, the EDOP oligomers may be more soluble than those of ProDOP and therefore deposit less easily on the glass substrate. Consequently, a higher pH provides a way of controlling the polymerization and transfer rate and thus allows a more homogenous growth of the PEDOP films.

The selection of appropriate oxidant is one of the most important factors for deposition and conductivity of these polymer films. If an oxidizing agent with an oxidation potential too high is selected, the polymerization is quite rapid and precipitation of polymer particles takes place in solution. On the other hand, when the oxidation potential is too low, polymerization does not occur. As a result of their electron rich character stemming from the 3,4-alkylenedioxy substitution, EDOP and ProDOP are more easily oxidized than pyrrole[21,22] (pyrrole: +0.92, ProDOP: +0.64 and EDOP: +0.58 V *vs.* Ag/Ag^+ in 0.1 M $LiClO_4$/PC). In this study, we used four different oxidizing agents: CAN, $FeCl_3$, $CuCl_2$ and O_2. The oxidizing power of the transition metal salts can be empirically ranked as follows: $CAN > FeCl_3 > CuCl_2$ according to their standard redox potentials $E°$ ($Ce^{4+}/Ce^{3+} = 1.44$ V; $Fe^{3+}/Fe^{2+} = 0.77$ V; Cu^{2+}/Cu^0: 0.34 V *vs.* NHE at 25 °C).[33] It should be noted that the mechanism involving these oxidants and monomer are complex and may involve interaction with the solvent (H_2O) and counterion.[34] Moreover, not only thermodynamic factors (redox potentials) but also kinetic factors (*e.g.* concentration of oxidant, electron transfer rates) need to be taken into account. Since only a small amount of oxygen ($E°$ $[O_2/H_2O] = 1.23 - 0.059$ pH) is present in the polymerization medium, the oxidation reaction will take place at a much slower rate than when transition metal salts are used. Therefore, oxygen can be considered as the mildest oxidant of the series employed.

The properties of the films obtained from the chemical polymerization of pyrrole, EDOP and ProDOP are summarized in Table 1. It is noteworthy that CAN, the strongest oxidant, did not yield polymer films on the glass substrate for any of the studied monomers. In each case, aggregates were formed in solution and the formation of these species was too fast to allow a transfer of the polymer to the substrate. As noted earlier, too mild an oxidant is also a problem, as noted by the lack of pyrrole polymerization by $CuCl_2$ or O_2 (air). Ferric chloride yielded homogeneous polymer coatings in all cases with a conductivity of about $3\ S\ cm^{-1}$ for PProDOP and $0.7\ S\ cm^{-1}$ for PEDOP. Note that a milder oxidizing agent ($CuCl_2$) is preferable for EDOP and ProDOP polymerizations thus providing slightly higher conductivities for the films of 7 and $8\ S\ cm^{-1}$, respectively.

Interestingly, the polymerization of EDOP can be achieved in the presence of air (O_2) without the addition of another

Table 1 Comparison of thickness and conductivity results for poly(pyrrole-2,5-diyl), PProDOP and PEDOP films doped with AQSA and prepared with different oxidizing agents

Polymer	Oxidant	Thickness / nm	Initial σ / S cm^{-1}	Final σ^a / S cm^{-1}
PPy	CAN		no film, polymer in solution	
	Fe^{3+}	130 ± 15	280 ± 45	250 ± 40
	Cu^{2+}		no film, polymer in solution	
	Air		no film, no polymer in solution	
PProDOP	CAN		no film, polymer in solution	
	Fe^{3+}	80 ± 12	3.0 ± 4.0	0.3 ± 0.04
	Cu^{2+}	90 ± 10	8.0 ± 1.0	3.0 ± 0.4
	Air		no film, polymer in solution	
PEDOP	CAN		no film, polymer in solution	
	Fe^{3+}	40 ± 5	0.7 ± 0.1	0.03 ± 0.005
	Cu^{2+}	70 ± 9	7.0 ± 0.9	0.05 ± 0.006
	Air	50 ± 6	0.3 ± 0.05	0.1 ± 0.017

[a] Final conductivity was measured after 45 days.

oxidant. On the other hand, ProDOP yields a polymer in solution when polymerized under similar conditions, but does not give a coating on the glass substrate. The slightly lower oxidation potential, as well as the higher hydrophilicity and lower steric hindrance of EDOP are likely to be the key factors in this different behavior upon air oxidation. The ability to be polymerized by air oxidation is a remarkable feature which has been reported, to our knowledge, only once for conducting polymers.[35]

As shown in Table 1, PPy's conductivity decreases from 280 to 250 S cm^{-1} after 45 days of exposure to air and shows the best stability to ambient atmosphere. For PEDOP and PProDOP, the drop is more pronounced, but the conductivities remain in the same range as obtained initially. For the case of air polymerized PEDOP, the conductivity changed from 0.3 S cm^{-1} (initial value) to 0.1 S cm^{-1} after 45 days. It should be noted that both the PEDOP and PProDOP films are thinner than the PPy films prepared in these studies. As a result, the bulk of the film in PEDOP and PProDOP is more exposed to moisture and air which may increase the aging rate.

XPS characterization

X-Ray photoelectron spectroscopy (XPS) was used in order to estimate the doping level in PEDOP and PProDOP films. The full XPS spectrum of AQSA doped PEDOP prepared with $CuCl_2$ (and in the absence of SSA) is shown in Fig. 2. Since sulfur is only present in the sulfonate group of the dopant (AQSA) and nitrogen is only found in the polymer backbone, the ratio of these elements is an approximation of the doping level[36–38] and represents the number of positive charges induced per pyrrole ring. This ratio between the atomic concentration (%) of nitrogen N(1s) and sulfur S(2p) was integrated from the corresponding XPS spectrum. Polymerization with $CuCl_2$ gives almost the same doping level for both PEDOP and PProDOP films with 27 and 28% measured respectively. In the case of air oxidation, this ratio is slightly lower at about 23% and may explain the lower conductivity reported for the film. The values obtained are in agreement with the common ratios measured in PPy films (25–33%) as measured in bulk and at the surface. It is important to note that no signals are observed for Cl (201 eV) which indicates the efficiency of the doping process. While a small amount of Cu is detected, this value is less than 2%.

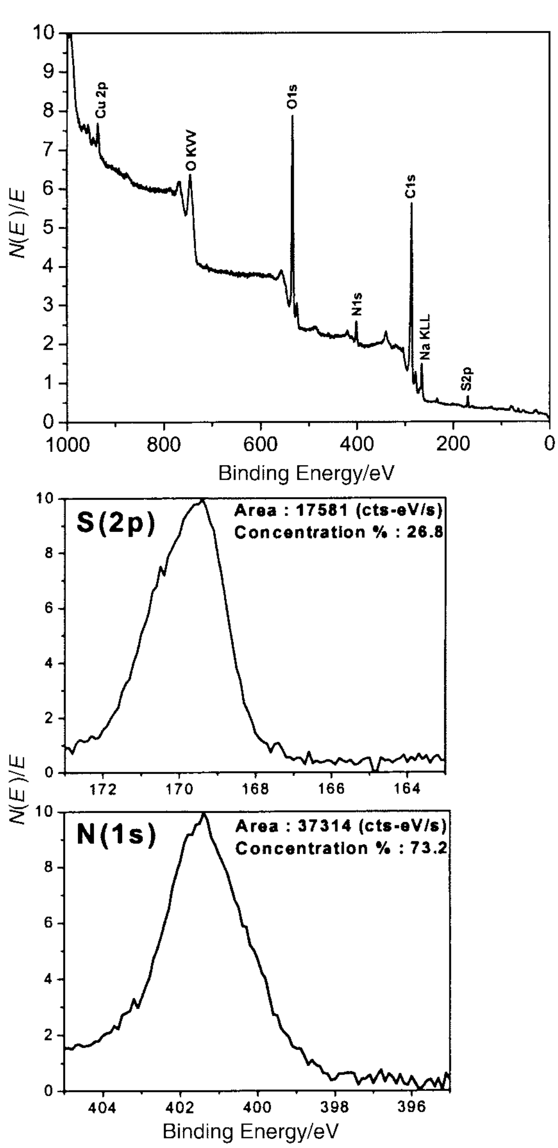

Fig. 2 Complete XPS spectrum of an AQSA doped PEDOP prepared with $CuCl_2$. The regions corresponding to the N(1s) and S(2p) XPS spectra are expanded and presented.

Optical properties

Colorimetry measurements were performed in order to determine the dependence of visible light transmissivity as a function of film thickness. The results are given in Fig. 3 as relative luminance (%*Y*) to uncoated glass. This value is a measurement of the optical transparency of the film throughout the entire visible range of light and corresponds to the lightness of the color. Note that it provides different information than optical absorbance at a fixed wavelength because it takes into account the sensitivity of the human eye over the entire visible spectrum.[29] PProDOP and PEDOP films appear light blue/gray colored whereas PPy of comparable thickness gives a dark gray coating. Fig. 3 shows that $CuCl_2$ prepared PEDOP and PProDOP thin films (20 to 40 nm) are highly transmissive and have a relative luminance above 80%. These optical properties are expected as both PEDOP and PProDOP have lower band gaps (2.0 and 2.2 eV respectively) than PPy.[21,22] As a result, the optical transitions in the doped films associated with the charge carriers are located in the near infrared (NIR). The slight gray coloration observed stems from the tail of the NIR absorption. Surprisingly, PProDOP($CuCl_2$), (note the reagent in parentheses is the oxidant used for polymerization) and especially PEDOP(air) gave darker films than PEDOP($CuCl_2$) for a comparable thickness. In the case of PProDOP($CuCl_2$), this may suggest the presence of more ordered (compact) films than PEDOP($CuCl_2$) since the doping level is almost identical (about 27%). In the case of PEDOP, the significant difference in luminance between air-polymerized and $CuCl_2$-polymerized samples could also find its origin in the fact that PEDOP(air) has a lower doping level than PEDOP($CuCl_2$) (as shown by XPS).

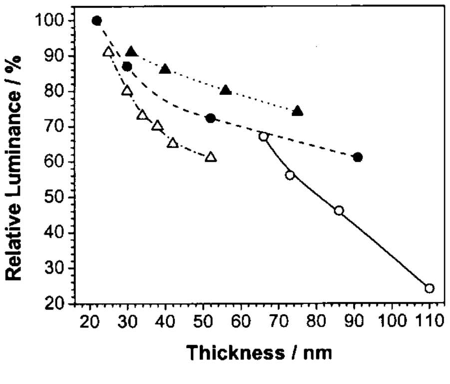

Fig. 3 Relative luminance measured by colorimetry of (○) PPy($FeCl_3$); (●) PProDOP($CuCl_2$); (▲) PEDOP($CuCl_2$); (△) PEDOP(air) as a function of film thickness.

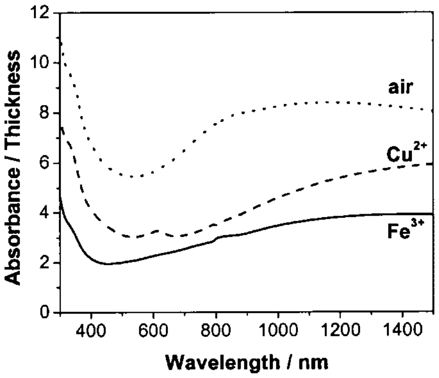

Fig. 4 Comparison of normalized absorption spectra of AQSA doped PEDOP films prepared with $FeCl_3$ (solid line), $CuCl_2$ (dashed line) and air (dotted line). Note the absorbance measured was normalized by film thickness measured in microns.

UV-visible spectroscopy provides a method for comparing the conductivity of conducting polymer thin films as there is a direct relationship between conductivity and the tail of the absorbance in the near-infrared (NIR) (corresponding to the transitions associated with the charge carriers) as reported previously for PPy.[17,39,40] Absorption spectra of AQSA doped PEDOP coatings obtained by *in situ* chemical polymerization using three different oxidants ($FeCl_3$, $CuCl_2$ and O_2) are presented in Fig. 4. It should be noted that PEDOP($CuCl_2$) exhibits an absorption band in the NIR with a maximum at a lower energy (longer wavelength) than PEDOP($FeCl_3$) and PEDOP(air), respectively. As expected, the conductivities of the coatings follow the same order with 7.0, 0.7 and 0.3 S cm^{-1}, respectively. In the case of PProDOP, respective conductivities of 3 and 8 S cm^{-1} for $FeCl_3$ and $CuCl_2$ were obtained for the corresponding coatings.

Spectroelectrochemistry

Spectroelectrochemical results for PProDOP films prepared on ITO glass using $FeCl_3$ and $CuCl_2$ are given in Fig. 5. The absorption band localized at about 2.5 eV corresponds to the π–π* transition and the neutral polymer coatings are orange in color. The two maxima observed at 2.6 (485 nm) and 2.4 eV (518 nm) due to vibronic coupling, have been reported for electrodeposited PProDOP,[21,22] and suggest a certain degree of order in the polymer film. The band gap of PProDOP calculated at the edge of the π–π* transition in the neutral form is 2.2 eV, identical to the value reported by us for electrochemically prepared PProDOP. This value is, of course, much lower than that reported for PPy (about 2.8 eV)[41] and reflects the higher electron rich character of the PProDOP due to the presence of the 3,4-dioxy substituent. As expected, the π–π* transition is depleted upon doping with the creation of lower energy transitions associated with charge carriers. The spectroelectrochemical results nicely illustrate the enhanced transmissivity of PProDOP conducting films relative to PPy. The lowered band gaps in PProDOP cause the charge carrier absorptions to be pushed outside the visible spectral region and into the near IR. PPy, on the other hand, retains a higher level of absorption throughout the visible region. The 3,4-dioxy substituents also serve to reduce the oxidation potential of PProDOP relative to PPy. This is evident in the spectroelectrochemical series as complete oxidation is obtained at −0.2 V *vs.* Ag/Ag^+.

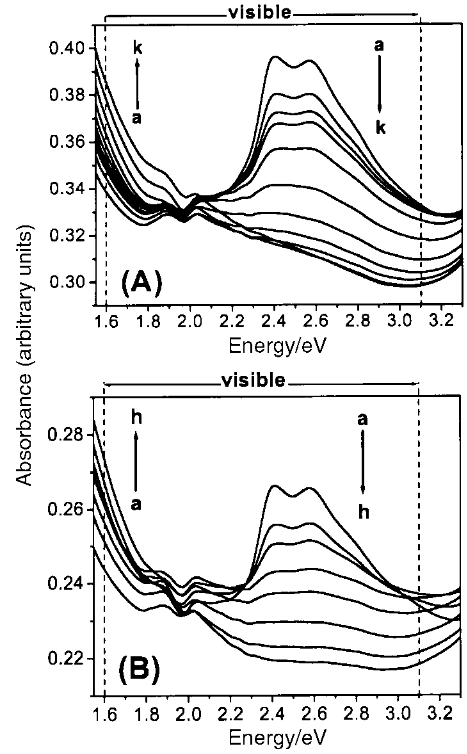

Fig. 5 Spectroelectrochemistry of AQSA doped PProDOP films prepared with $FeCl_3$ (**A**) and $CuCl_2$ (**B**). The optical spectra shown correspond to an applied potential of: a) −1.2 V, b) −1.1 V, c) −1.0 V, d) −0.9 V, e) −0.8 V, f) −0.7 V, g) −0.6 V, h) −0.5 V, i) −0.4 V, j) −0.3 V, k) −0.2 V *vs.* Ag/Ag^+ in 0.1 M $LiClO_4$/PC.

Surface morphological properties

Surface morphological properties of the polymer coatings were investigated by scanning electron microscopy (SEM) and a representative set is presented in Fig. 6. It should be noted that all PProDOP and PEDOP films exhibit a total surface coverage in films as thin as 40–70 nm, which indicates a homogenous film deposition. A compact and smooth surface morphology is obtained using the mild oxidants ($CuCl_2$ or air) as illustrated by Fig. 6a for PEDOP(air), whereas the use of $FeCl_3$ as oxidant yields a somewhat more disordered PProDOP film (Fig. 6b) probably resulting from a less controlled polymerization

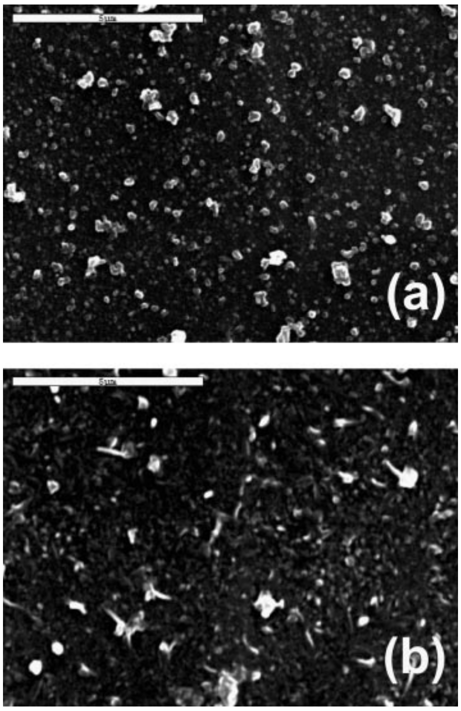

Fig. 6 Comparison of SEM pictures of AQSA doped (**a**) PEDOP(air) and (**b**) PProDOP($FeCl_3$) films.

reaction. The increased disorder in PProDOP($FeCl_3$) compared to the other PEDOP and PProDOP films is further supported by the profilometry results which show an average surface roughness of about 30% and 10%, respectively. Consequently, it is not surprising to observe a lower conductivity in films polymerized with $FeCl_3$ compared to the values observed when $CuCl_2$ is used. Even though conducting polymers usually start to grow by island-type nucleation in the early stages of polymerization,[42] smooth surfaces can be obtained as reported for poly(pyrrole-2,5-diyl) films.[43] The use of a planar dopant such as AQSA, combined with mild polymerization conditions, are important variables for achieving high conductivities and for obtaining homogenous film coatings.

Conclusion

In summary, the poly[(3,4-alkylenedioxy)pyrrole-2,5-diyl]s PEDOP and PProDOP have been shown to form homogenous conductive coatings with a high degree of transparency when deposited as thin films on glass substrates by *in situ* chemical polymerization. Despite a lower conductivity when compared to PPy coatings using the same dopant ion (AQSA), the films appear smooth and are light blue/gray colored as opposed to dark gray. Because of their electron rich character, ProDOP and EDOP monomers are more readily oxidized and therefore require a milder oxidizing agent such as $CuCl_2$. A remarkable feature of EDOP is its ability to be polymerized using air as an oxidant to yield a PEDOP doped with AQSA with a conductivity of $0.3\ S\ cm^{-1}$. The potential environmental and cost improvements using this type of deposition are an important step towards providing highly transparent conductive polymer coatings for various industrial applications. It should be noted that the lack of stability of the doped PEDOP and PProDOP films prepared under the conditions employed here precludes their present industrial application. Based on the fundamental electrochemical properties of these systems (especially their low redox potential), further work may lead to significantly more stable conducting polymer films. The deposition of PEDOP and PProDOP films can be easily transposed to substrates other than glass, including textiles and plastic films.

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