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Vapor Phase Polymerization of Pyrrole and Thiophene Using Iron(III) Sulfonates as Oxidizing Agents

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ABSTRACT: Vapor phase polymerization is a versatile technique that can be used to obtain highly conducting coatings of conjugated polymer on both conducting and nonconducting substrates. This is demonstrated here by preparation of polypyrrole, polybithiopene, and polyterthiophene, coatings that otherwise must be prepared electrochemically in order to achieve the desired high conjugation. The method is based on the use of organic ferric sulfonates as oxidant as these salts easily form smooth, noncrystalline films. By proper choice of the sulfonate anion, the oxidizing power of the ferric salt can be varied over a wide range. The described technique can easily be adapted to different patterning techniques.

Introduction

The majority of applications for conjugated polymers rely on the ability to deposit these materials as thin, even coatings. A number of routes are available for this purpose, depending on the polymer and substrates in question. Most common are solution processing in the form of spin-coating, solvent-casting, or printing. Conjugated polymer systems are, however, generally difficult to get into solution. It is often necessary to derivatize the polymer with soluble side chains or to dope the polymer with polyelectrolytes acting as solubilizers in order to be able to process these polymers. The choice of a conjugated polymer system for a given application may thus be restricted by the possibilities for finding a suitable compromise between functionality and processability.

Alternatively, a conjugated polymer can be deposited by in situ oxidative polymerization directly at the surface. On conducting substrates this can be achieved by electrochemical polymerization, which generally gives coatings of a high quality. This method is however rarely suited for large-scale applications and cannot be used to add electronic functionalities to nonconducting surfaces. Chemical oxidation, on the other hand, is more versatile and less restricted by the substrate. Chemical oxidation can be performed by coating the surface with a mixture of monomer and oxidant where the spontaneous reaction is suppressed in such a way that it will first occur after the mixture is spread onto the surface. Often such mixtures will have a limited pot life, and more freedom in the design of the coating process can be achieved if the monomer and oxidant are applied separately. One way to achieve this is to apply the oxidant by solvent coating and subsequently expose the coated surface to monomer vapor, a process that has been coined vapor phase polymerization (VPP).

The VPP method was first described by Mohammadi et al.[1] as a CVD process using $FeCl_3$ or H_2O_2 as oxidants for polymerization of polypyrrole films. It was later adapted for the formation of well-defined surface patterns of polypyrrole using copper converted to $CuCl_2$ as oxidants.[2] VPP has also been used for in situ polymerization of polypyrrole inside a number of different nonconducting polymers and rubbers, as first reported by Ueno et al.,[3] who made a conducting composite by exposing PVC blended with $FeCl_3$ to pyrrole vapors.

The homogeneity reported for surface films made by VPP has generally been inferior compared to films made by solvent processing. This is seen either in the topography of the films[4,5] or in a percolation-like behavior of the conductivity as a function of thickness, where the conductivity suddenly rises when individual grains coalesce.[5] One reason for the poor film quality is the preference for use of $FeCl_3$ as the oxidant. $FeCl_3$ crystallizes readily when the solvent evaporates, and the grainy structure of the deposit is then transferred to the polymer film formed in VPP process. The use of $FeCl_3$ was originally advocated[6] because the presence of trace amounts of chlorine showed up to be essential for production of conducting polypyrrole (PPy) under CVD conditions. To get smooth films it is, however, necessary to suppress crystallite formation in the dried layer of oxidant, and it will be shown here that the use of organic sulfonates, that does not readily crystallize, is a versatile route to both smooth and highly conducting films.

de Leeuw et al.[7] found that ferric *p*-toluenesulfonate (Fe(III) tosylate) was a well-suited oxidant for chemical polymerization of 3,4-ethylenedioxythiophene (EDT). Imidazole was used as inhibitor to suppress the polymerization until the solvent was evaporated. As Fe(III) tosylate did not crystallize under these conditions, smooth and well-conducting films were obtained. Later Fe(III) tosylate was tested in VPP of PPy in preformed polyurethane foams.[8] Although the results were promising, it appears that no other attempts to utilize Fe(III) sulfonates as oxidants in VPP processes have been reported. The present paper demonstrates how conducting films of PPy and polythiophenes can be prepared by VPP using various organic ferric sulfonates. These conjugated polymers systems are chosen because they

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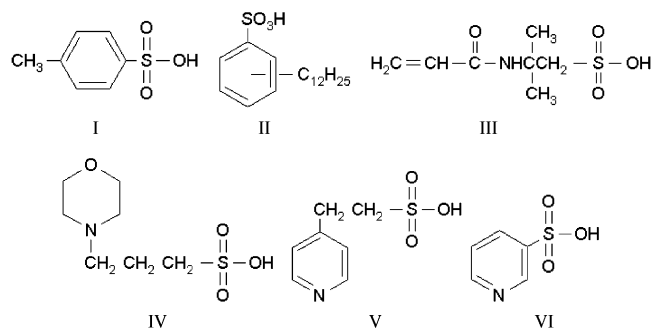§ University of Wollongong.
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Figure 1. Sulfonic acids used in the preparation of ferric sulfonate oxidants: (I) *p*-toluenesulfonic acid, PTS; (II) dodecylbenzenesulfonic acid, DBS; (III) 2-acrylamido-2-methyl-1-propanesulfonic acid, AMPS; (IV) 4-morpholinepropanesulfonic acid, MOPS; (V) 4-pyridineethanesulfonic acid, PES; (VI) 3-pyridinesulfonic acid, PS(3).
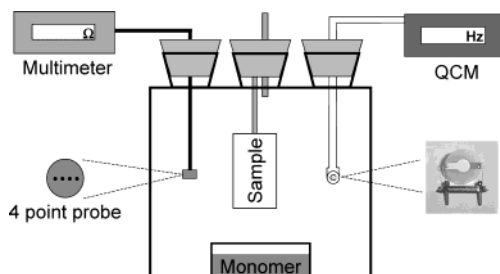

Figure 2. Schematic drawing of vapor phase polymerization chamber equipped with a sample holder, a four-point conductivity probe connected to a multimeter, and an oscillating quartz crystal used as quartz crystal microbalance (QCM).

are insoluble and cannot be prepared by conventional solvent processing. VPP appears to be the only alternative to electrochemical oxidation for the synthesis of well-conducting films of PPy.

Experimental Section

Fe(III) tosylate was received from Bayer AG as a 40% solution in butanol (Baytron C). All other chemicals were obtained from Aldrich and used as received.

Ferric 2-acrylamido-2-methyl-1-propanesulfonate (Fe(III) AMPS), ferric 4-morpholine propanesulfonate (Fe(III) MOPS), ferric dodecylbenzenesulfonate (Fe(III) DBS), ferric 4-pyridine ethanesulfonate (Fe(III) PES), and ferric 3-pyridinesulfonate (Fe(III) PS) were produced according to the following procedure: Ferric trichloride (FeCl$_3$·6H$_2$O) was dissolved together with 3 times the molar amount of the corresponding sulfonic acid in either butanol (AMPS, MOPS, and DBS) or water (PES and PS). The mixture was heated until the solvent was evaporated and subsequently treated in a vacuum at 60 °C. By this procedure it was possible to remove enough hydrochloric acid to give a pH value of the redissolved salt close to the pK_a of the corresponding sulfonic acid. The amount of HCl remaining in the salts was not determined, but the presence of residual chloride ions was too small to induce visible crystallization of the salts after coating onto a surface. The structure formulas of the corresponding sulfonic acids are shown in Figure 1.

Glass slides or PET foils were used as substrates for vapor phase polymerization. A solution of one of the Fe(III) salts was spread onto a substrate that was subsequently dried. The substrate with the Fe(III) sulfonate films was then exposed to monomer vapor directly over the liquid monomer. The reaction was carried out in a flask or bottle filled with air, without forced gas flow (see Figure 2). During polymerization of pyrrole the polymerization process was followed by in-situ measurements of the conductivity of the surface layer by a four-point probe used as a substrate. This four-point probe is made by embedding four parallel 0.1 mm Pt wires in epoxy

and exposing the cross section. By coating a quartz crystal with oxidant, the polymerization process could also be monitored by quartz crystal micro gravimetry (QCM). The QCM is based on a 10 MHz crystal (from ICM, Oklahoma City) connected to an Agilent E5100A network analyzer.

Slightly dissimilar procedures were followed in the preparation of different polymer coatings. Typical procedures are outlined below.

VPP of Polypyrrole (PPy). The Fe(III) sulfonates were coated onto substrates from butanol or water solutions containing between 5 and 40 wt % salt.

When the coating was almost dry, but before the Fe(III) sulfonates form crystals, the samples were put into an oven or onto a hot plate at 50−100 °C. After heating for between $^1/_2$ and 3 min the color of the coating changes to a darker yellow, indicating that the solvent is now evaporated. The samples were then exposed to pyrrole vapor at room temperature. The reaction is quite fast as seen from the color change from yellow over green to brownish black. Normally the polymerization time was from 10 to 15 min for the more acidic sulfonates and up to 1 h for 2-pyridinesulfonate. After polymerization the samples were dried for half an hour before they were washed in ethanol.

VPP of Polybithiophene (PBTh). The oxidant, in this case Fe(III) tosylate, was coated onto the substrate from a 10% to 40% butanol solution. When the coating was almost dry, but before Fe(III) tosylate forms crystals, the sample was put into an oven at 75 °C. After approximately 3 min the solvent was evaporated, and the sample was exposed to bithiophene (BTh) vapor for 1 h at 75 °C (BTh melts at 33 °C) in a closed bottle in the oven. The sample was taken out of the bottle, and the oven and was left to cool to room temperature for half an hour before it was washed in ethanol.

VPP of Polyterthiophene (PTTh). Except for the polymerization temperature, the procedure was the same as used for PBTh. Terthiophene (TTh) melts around 95 °C, and PTTh becomes unstable at temperatures not much higher than this. If the polymerization temperature is too high, it is reflected in the UV−vis spectra of the polymerized film, with a huge peak below ∼450 nm and a brownish appearance of the polymer layer after wash.

The best results were obtained when the oven temperature was set to 95−100 °C and the bottle with TTh was placed in the bottom of the oven directly on top of the heating element. In this way, the TTh melted but the temperature of the substrate was kept below 100 °C.

Analysis of Polymer Films. Some coatings were characterized by cyclic voltammetry (CV) in a standard three-electrode cell. The conductivity of the samples was measured using a four-point probe from Jandel Engineering Ltd. connected to a Keithly 2400 source meter. The probe is equipped with four spring-loaded tungsten carbide needles spaced 1 mm apart. The bulk resistivity of the films is calculated from the surface resistivity using the film thickness. Coating thicknesses were measured by a DekTak profilometer.

The morphology of the coatings was characterized using scanning electron microscopy (SEM) or laser scanning optical microscopy (Zeiss LSM Pascal 5).

Results and Discussion

Polypyrrole Doped with *p*-Toluenesulfonate, PPy Tosylate. Figure 3 shows the polymerization of PPy on Fe(III) tosylate as followed with QCM and four-point conductivity measurements. Fe(III) tosylate is coated on the quartz crystal and the four-point probe from a 5% butanol solution. After drying the probes at 60 °C, they are moved to the container with pyrrole vapor (at time 320 s). Almost instantly there is a large weight gain due to condensation of pyrrole on the quartz crystal. Simultaneously at the four-point probe the resistance drops rapidly. At time ∼1250 s the resistance has reached a constant level, and the probes are removed from the pyrrole vapor. Instantly, the QCM
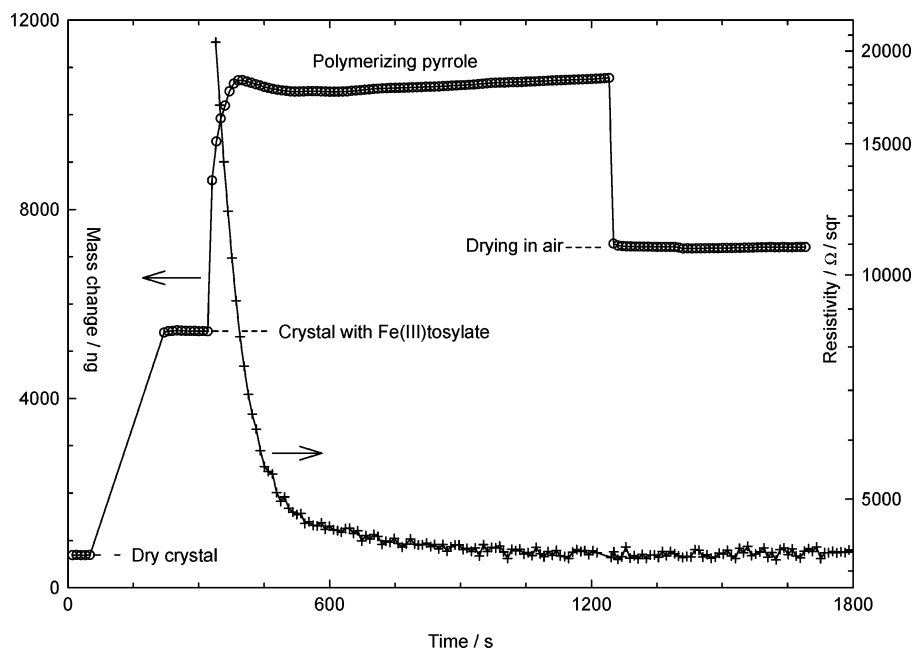
Figure 3. A vapor phase polymerization experiment followed by QCM (connected circles) and the four-point conductivity probe (connected squares).
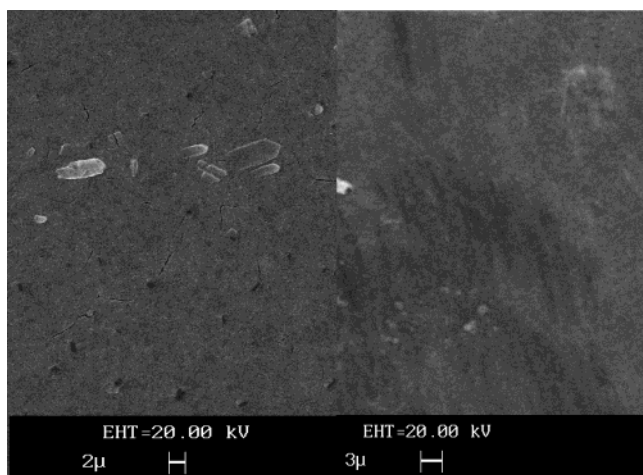

Figure 4. Scanning electron micrographs of PPy tosylate coated onto glass. The picture to the left shows the polymer layer directly after the oxidant was exposed to pyrrole vapor, and the picture to the right shows the same sample after wash in ethanol where the spent Fe(II) tosylate is extracted from the film.
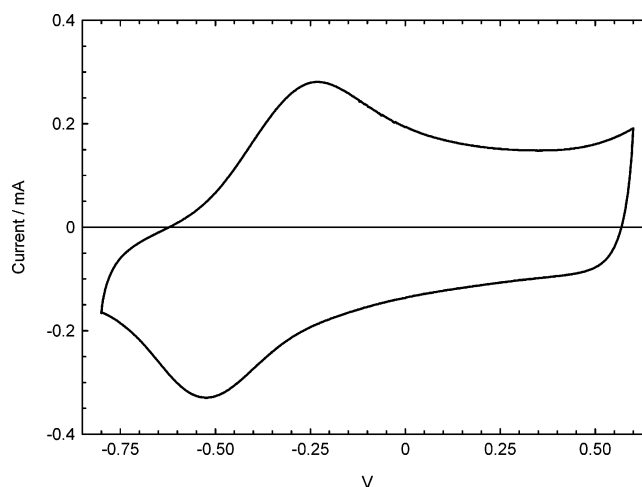

Figure 5. Cyclic voltammogram of PPy tosylate coated onto a strip of platinized PET foil. Sweep rate: 100 mV/s. Electrolyte: 1 M NaNO$_3$.

shows a weight loss due to evaporation of pyrrole, whereas the resistance stays constant. The weight gain during polymerization can be calculated from this curve. This weight change contains both the weight of the polymer, an amount of pyrrole dissolved or bound in the PPy film, and Fe(II) tosylate produced as a consequence of pyrrole oxidation. An accurate determination of the amount of polymer formed during the experiments can be obtained from the resonance frequency of the crystal determined after the coating is washed in ethanol. To make the calculations more accurate, a thicker polymer layer was deposited. The crystal was coated with 43.040 μg of Fe(III) tosylate, and the weight of the resulting polymer was 3.550 μg. Assuming that the redox equivalents are used either to polymerize pyrrole (two equivalents per monomer) or to overoxidize ("dope") the polymer, the degree of doping, y, of the poly(pyrrole^{y+} y × tosylate$^-$) can be calculated as 0.23. This is consistent with the doping levels obtained by electrochemical synthesis.

The shape of the QCM and the resistance curves fits well with our understanding of the polymerization process; the amount of Fe(III) applied to the surface determines the amount of polymer deposited in the VPP process. When all Fe(III) is reduced to Fe(II), no more polymer can be formed. As the growth of the polymer is stopped, the resistance stops changing. The weight of the layer may still increase some time after the polymer growth has ceased due to the dissolution of monomers in the film. The decrease of resistance starts immediately after the substrate is exposed to the monomer vapor, and the decrease is smooth (Figure 3). This is a good indication that the film grows as a continuous sheet rather than as small coalescing islets nucleated at oxidant grains.

Figure 4 shows SEM pictures of a PPy tosylate layer coated onto glass after it is taken out of the VPP chamber and after it is washed in ethanol. The wash in ethanol removes reacted iron tosylate plus traces of
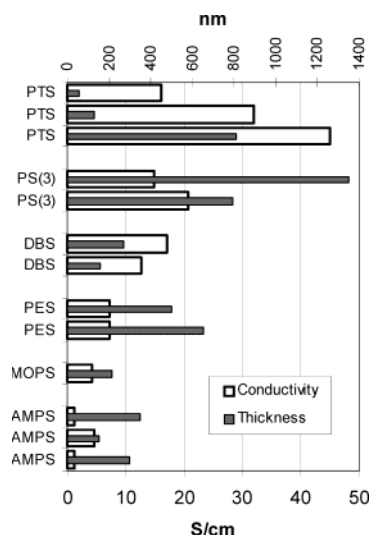
Figure 6. Conductivity of a polypyrrole doped with different organic sulfonates prepared by vapor phase polymerization on glass—the definition of the acronyms is given in Figure 1. The conductivity of the films is calculated from the sheet resistance and the thickness (also shown) measured by DekTak profilometry.

monomer dissolved in the polymer layer. As it can be seen, the resulting polymer film is very smooth and coherent, in contrast to films made by VPP using $FeCl_3$ as the oxidant. The thickness of this coating after washing was 400 nm.

Figure 5 shows a cyclic voltammogram (CV) of PPy tosylate grown by VPP onto a platinum-coated PET. Cyclic voltammetry is used to characterize the redox states and the electronic properties of conjugated polymers. The current measured is proportional to the number of sites that can be reduced or oxidized at a given potential, and this quantity depends not only on the chemical composition of the polymer but also on structural factors such as conjugation length and local order. CV's can thus be used as a kind of fingerprint to identify a given polymer type. The CV shown in Figure 5 is typical for PPy doped with small, inert anions and

is indistinguishable from the CV of PPy tosylate prepared by electrochemical oxidation.

Polypyrrole Doped with Other Organic Sulfonates. The VPP method described above can easily be extended to the preparation of PPy films with other dopants. We have synthesized ferric salts of a number of organic sulfonates. As the acidity of the salt is an important parameter because the oxidizing power of Fe-(III) is expected to increase with increasing acidity,[7] we have included several N-containing sulfonates. Pyrrole is relatively easy to oxidize, and it was possible to produce polymer coatings with all the ferric sulfonates shown in Figure 1. The polymerization time varied from a few minutes using the more acidic ferric tosylate to 1 h using the more alkaline iron(III) sulfonates (Fe(III)-MOPS and Fe(III)AMPS). The conductivities of the resulting polymer coatings are summarized in Figure 6.

It is seen that it is possible with this technique to obtain very thin coatings (<100 nm) that still have an appreciable conductivity. The conductivities of PPy–DBS and PPy–tosylate obtained by VPP compare well with literature values for materials prepared by other techniques.[8–10]

PPy–DBS prepared electrochemically from aqueous solutions shows very pronounced hysteresis phenomena that have been attributed to conformation changes in the polymer–detergent complex involving the uptake of a relatively large amount of water when the polymer is reduced. The water uptake is responsible for the very large changes in volume that can be observed when these materials are switched between their oxidized and neutral forms.[9] It is interesting to note that although PPy–DBS prepared by VPP has the same characteristic nodular surface topology as the electrochemically prepared material, the electrochemical behavior is quite different (see Figure 7). The material prepared with the VPP process does not show the same high degree of hysteresis at the material prepared from aqueous, micellar solutions. This is in accordance with the finding that the properties of PPy–DBS can be tuned by changing the micellar structure of the synthesis medium.[10] In the present case, the absence of water during
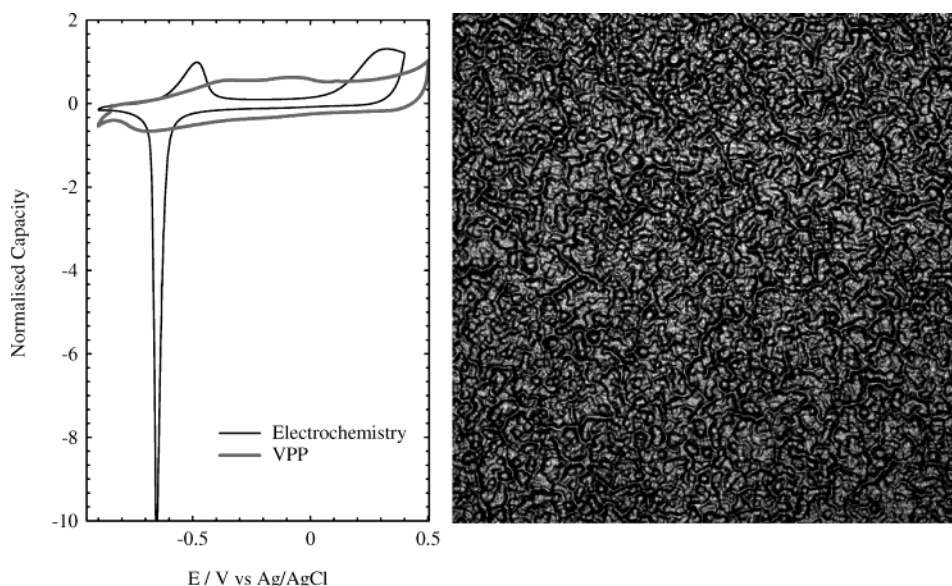

Figure 7. Cyclic voltammograms of PPy–DBS prepared electrochemically (thin black curve, 25 mV/s) and by VPP (gray curve, 10 mV/s). The curves are normalized to give the same integral capacity. The laser scanning micrograph to the right shows the surface topography of a 2 μm PPy–DBS VPP layer on PET. The calculated roughness is Ra = 0.05 μm.
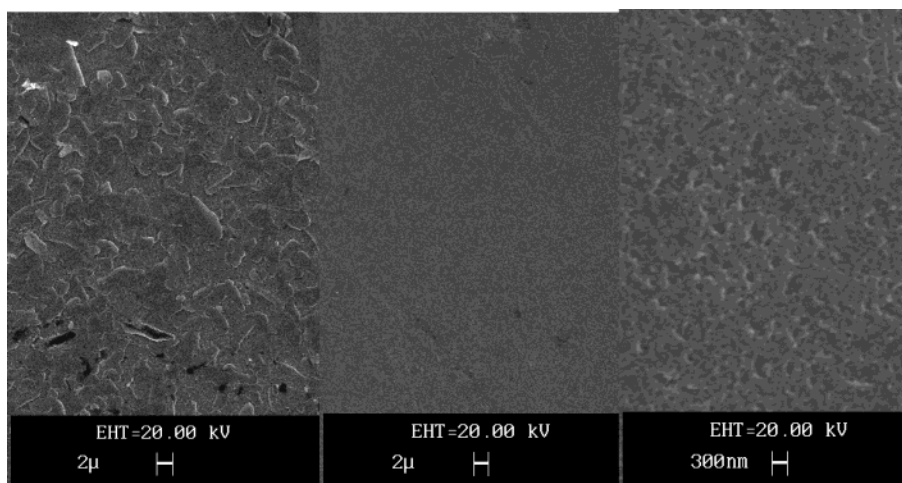
Figure 8. SEM micrographs of PTTh prepared by VPP before (left) and after wash (middle and right) in ethanol. Note the different length scales on the right micrograph. Thickness of the coating after wash is 120 nm.
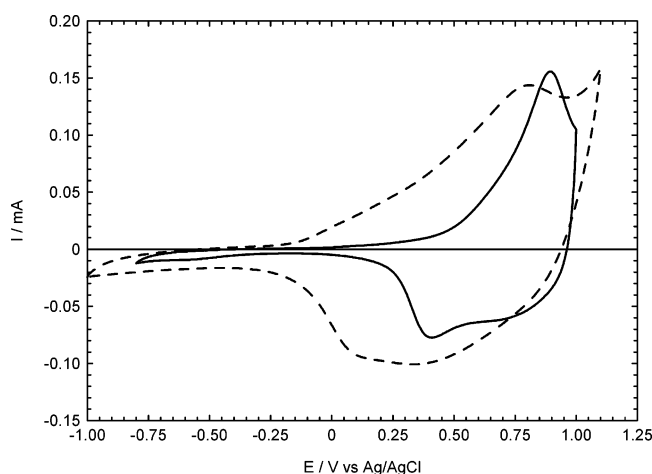

Figure 9. Cyclic voltammetry of PBTh (gray, broken line) and PTTh (black, full line) on Pt-coated PET foils. The electrolyte is 0.1 M tetrabuthylammonium perchlorate in acetonitrile, and the sweep rate is 100 mV/s.

synthesis prevents the formation of micelles, and it is most likely that the resulting polymer coating is representative of a nonstructured PPy−DBS.

Polybithiophene and Polyterthiophene. Even the most acidic Fe(III) sulfonate did not have sufficient oxidative power to produce coherent and conducting polythiophenes from the thiophene monomer. It is well-known that oligomers of thiophene are more easily oxidized than the monomer and that the polymers produced from e.g. bithiophene or terthiophene are much less degraded due to overoxidation than polythiophenes produced from the monomer.[11]

By proper choice of synthesis temperature, it was possible to produce both polybithiophene (PBTh) and polyterthiophene (PTTh) by VPP using Fe(III) tosylate as the oxidant. Both polymers are formed in their oxidized, blue state but are spontaneously reduced to the neutral, yellow-orange state when washed in ethanol. The reduction is due to the decrease in acidity caused by washing out Fe(II)/Fe(III) tosylate with ethanol. The reduced PBTh and PTTh are poor conductors (over 500 Mohm/sq for the coatings produced here). Figure 8 shows SEM micrographs of PTTh right after it is produced by VPP and after it is washed in ethanol. The as-prepared rough film becomes very smooth when the spent oxidant and excess tosylate is removed in the washing process. It can be seen from the figure that the size of the morphological features decreases in the range of an order of magnitude. XPS analysis on both sides of a similar film shows that the amount of iron in the washed film is at or below the detection limit, 0.1 atom %.

The electrochemical response of PBTh and PTTh is shown in Figure 9. The characteristic difference in electrochemical response previously reported for electrochemically prepared PBTh and PTTh[11] is accurately reproduced by the VPP coatings. This stresses the fact that the VPP route is well-suited for preparation of conjugated polymer coatings with a low defect density. In this sense it mimics electrochemical synthesis although it is much more versatile with respect to the choice of substrates.

Conclusion

It has been shown here that vapor phase polymerization is a versatile technique that can be used to obtain conjugated polymer coatings on both conducting and nonconducting substrates. The use of ferric salts of organic sulfonates is a good source for oxidants with a wide range of pK_a values governed by the acidity of the sulfonate anions, but also other oxidant systems may be of interest—a number of alternatives to both the ferric oxidant and the film forming organic modifier are readily available. The anion of the oxidant is built into the polymer as dopant, and the spent oxidant can easily be washed out of the polymer film with alcohol, leaving very smooth and coherent coatings. Except in cases where structuring of the synthesis medium influences the properties of the conjugated polymer, coatings obtained by VPP have properties that fully match the properties of polymers prepared by electrochemical oxidation. VPP is however a much more versatile technique. It can be used on nonconducting surfaces, and it can readily be adapted to a number of patterning techniques, where the oxidant is selectively applied to the surface by ink jet printing, stamping, or other printing technologies.

The freedom in formulation using VPP can lead to polymers that are not limited by the restrictions in the present synthesis route. It is now possible by VPP techniques to produce poly(ethylenedioxythiophene) (PEDT) coatings with conductivities exceeding 1000 S/cm.[12]

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