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Electrocatalytic activity of poly(3-methylthiophene) electrodes

Abstract Poly 3-methylthiophene (P3MT) modified electrodes have shown an improvement for detecting catecholamines when compared to classical ones. Past work with this polymer electrode suggested the possible presence of "active sites," which are believed to be the polymer's center of electrocatalytic activity. The interaction of 1,5-anthroquinone-disolfonic acid (1,5-AQDS) at the P3MT electrode showed a nonreversible behavior resulting in the blocking of "the active sites," suggesting the specific electcatalytical activity of this polymer is limited to catechol and similar compounds. In order to improve catecholamine detection, two methods of electropolymerization for P3MT were compared under similar conditions; (1) a constant potential for a specific length of time, and (2) potential cycling. It was found that cycling provided a more sensitive CV, i.e. increased number of active sites. Under a controlled pH study (pH range 2–9), the polymer electrode maintained its superior performance, manifested as lower ΔE and higher i, toward catechol over the traditional electrodes. Two different supporting electrolytes were used, sulfate and phosphate, and it was found that in neutral or basic solutions containing phosphate, the oxidation and reduction potentials of catechol shifted to lower values. Solutions containing sulfate exhibited no shift in the oxidation potential at any pH value.

Keywords Poly-3-methylthiophene · Conducting polymer electrode · Supporting electrolytes · Cyclic voltammetry · Anthraquinone · Catecholamine

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Introduction

Cyclic voltammetry (CV) studies of catecholamines (a class of neurotransmitters) at poly(3-methylthiophene) (P3MT) modified electrodes showed unusual characteristics and properties compared to commonly used electrodes, such as Pt, Au, glassy carbon, and chemically modified electrodes [1–6]. P3MT exhibited improved electrochemical reversibility, sensitivity, and selectivity toward catechol(s), nicotineamide adenine dinucleotide (NADH), and other molecules of biological importance over the traditional electrode materials [6]. Further, the polymer is easily deposited on the substrate surface and is found to be chemically and mechanically stable. P3MT has been shown to eliminate the issues of adsorption fouling and passivation of electrode surface by large molecules or oxidative products that are so often encountered when using conventional electrodes in biological fluids. Wang and Li [7] reported that voltammograms of 2×10^{-4} M chlorophenol showed complete fouling of the working glassy carbon electrode within four cycles. However, when P3MT was used, a highly reproducible current peak was observed with no surface fouling after repeated cycles. They also reported improved catecholamine detection under flow injection and liquid chromatography conditions [7]. Other studies, based on diffusion coefficient measurements, have suggested that the electron transfer reaction of the catechol(s), NADH and ascorbic acid at P3MT film electrodes takes place at the organic surface/solution interface [8, 9].

Past research has shown that the electroactivity of the polymer can be changed when an electrochemically active molecule is incorporated into its matrix structure [10, 11]. Galal et al. [10] reported that when P3MT was polymerized in the presence of a ferrocene moiety, the activity of the polymer was enhanced, but the general structure of the polymer remained unchanged. They explained this behavior in terms of a lack of complexation of the ferrocene with the polymer backbone,

indicating that the ferrocene merely interacted with the polymer in a way that increased electroactivity. However, the presence of transition metal cations in or on the polymer film was found to completely hinder this electrocatalytic activity, even when the metal ion/sulfur atom ratio is quite small. This suggests that very specific sites are involved in the electron transfer with catechol(s) [7, 10]. It is believed that the explanation for the enhancement and the inhibition of the polymer's electroactivity is related to the chemical environment in the sulfur heteroatom, which is believed to be involved in the formation of active sites for electron transfer through the polymer. Previous studies on sulfur centers indicated that they play an important role in charge-transfer processes [12]. Similar enhanced analytical performance using voltametric measurements was reported on a thin film diamond electrode over the more traditional glassy carbon electrode for ferro/ferri cyanide solution [13].

An interesting characteristic of various conducting polymers that has been investigated by several groups is their use as pH sensors [14–16]. Conducting polymers that were under investigation included polypyrrole and polyaniline. It was found that the polymers lost activity at high pH values (>12). Talaie and Romagnoli [15] postulated that this is because these polymers require a certain movement of charge along the polymer chain for electroactivity to occur. At higher pH's, they claim that hydroxy groups interact with the polymer chain and inhibit the acidic response. Since the performance of the polymers used appears to be pH dependent, the authors [15] suggested that these polymers can be used as a basis of a new class of pH sensors. However, the use of P3MT in this context, or even the dependence of polymer's activity on pH, has not been reported in literature. One of the intentions of this work was to study the activity of the P3MT polymer in solutions of catechol in acidic, neutral, and basic electrolytes with different pH values. Determination of the effect of the supporting electrolyte on the electrocatalysis of the polymer will be presented as well.

Another aim of this work was to further study the existence and specificity of the P3MT active sites toward catechol/catecholamines. This concept has not been extensively explored previously nor has the actual interaction of the polymer with organic redox couples, other than phenolic compounds, been studied. The results of this investigation further characterize the active sites and their role in the electron transfer step on the P3MT electrocatalytical behavior. Anthraquinone-based molecules have been used to probe the electron transfer step in kinetic studies of several electrode materials. They have also been used to investigate the process of adsorption onto the surface of these electrode materials. [17–20]. This work shows the results of probing the polymer's reaction with 1,5-anthraquinonedisulfonic acid (1,5-AQDS).

Images of the P3MT electrode surface were made using an atomic force microscope (AFM). AFM images can be used to discern structural differences at the nano-scale. Another possible use of this technique is to determine the film thickness, a measurement that can be made by measuring a cross section of the film profile over partial coverage on a flat substrate. An investigation into the method of electropolymerization was also carried out. Traditionally, the polymer has been deposited on the substrate by applying a constant potential at the metal electrode in a monomer solution. This method was evaluated against cycling the applied potential at the metal electrode in an identical solutions. The performance of polymers formed by each method has been evaluated based on the reversibility and sensitivity that was probed by the response of CV of catechol.

Materials and methods

Materials

The 3-methylthiophene and tetrabutylammoniumtetrafluoroborate (TBA-TFB) were obtained from Aldrich (Milwaukee, WI, USA). Acetonitrile (AcN), HPLC grade, was also obtained from Aldrich and was stored over a molecular sieve. Concentrated sulfuric and phosphoric acids (A.C.S. Reagents) were obtained from Fisher Scientific Company (Pittsburgh, PA, USA) and were diluted to 0.01 M. Phosphate and sulfate buffer components, as well as sodium ferrocyanide and 1,5-anthraquinone disulfonic acid, were obtained from Aldrich, and Catechol was obtained from Acros Chemicals (NJ, USA). All chemicals were used as received. All aqueous solutions were prepared with deionized water (>18 MΩ) obtained from Service Deionization Column, US Filters (Warrendale, PA, USA).

Instrumentation

Cyclic Voltammetry was done on an EG&G Princeton Applied Research Potentiostat/Galvanostat Model 263 A (Oak Ridge, TN, USA). The instrument was controlled through software packages PowerSuite and Virtual Potentiostat 32. AFM images were taken on a Park Scientific Instruments Autoprobe CP (Santa Barbara, CA, USA) coupled with TM Microscopes ProScan version 1.7.02.

Methods

Electropolymerization

Each electrode was polished for a minimum of 6 min on a polishing pad in an alumina polishing solution (<12% by volume) (Bioanalytical Systems, W. Lafayette, IN, USA) mixed with deionized water. After polishing, it

was rinsed with deionized water and sonacated in a methanol bath for 5 min. Polymerization took place in a one compartment three-electrode cell containing argon-deaerated acetonitrile, 0.125 M TBA-TFB, and 0.05 M 3-methylthiophene. All potentials were measured against an Ag|AgCl saturated reference electrode. The auxiliary electrode was a flag Platinum wire. The working electrodes used were Pt electrodes obtained from Bioanalytical Systems (0.0113 cm^2) and Ametek (Paoli, PA, USA) or a Glassy Carbon electrode obtained from Ametek. In the cycling method for electropolymerization, the potential applied to the working electrode was cycled between 0.4 and 2.0 V eight times to obtain a polymer film. For the other method, a constant potential (which was varied during the trials) was applied to the working electrode and then the electrode was doped at −0.2 V for 3 min in the same solution.

For the pH study, all pH reading were taken on a Corning pH Meter 440 (Woburn, MA, USA). The phosphate buffer was constructed in deionized water by dissolving fixed amounts of Na_2HPO_4 and NaH_2PO_4, and the pH was adjusted to 7 using concentrated phosphoric acid and 0.1 M NaOH. The sulfate buffer was simply a solution of 0.1 M sodium sulfate with the pH adjusted to 7 using 0.1 M sulfuric acid and 0.1 M NaOH. The pH 2 solution was 0.01 M sulfuric or phosphoric acid. The pH 7 and 9 solutions were made from the phosphate and sulfate buffers, and the pH was adjusted with 0.1 M NaOH and either phosphoric of sulfuric acid.

The AFM images were made of a freshly electropolymerized P3MT, following the fixed potential method described above, on a platinum disk of a modified wet cell (TM Microscope, Santa Barbara, CA, USA).

Results and discussion

Optimization of polymerization

Polymerization of the 3-methylthiophene onto the substrate electrode (Pt or GC) was achieved using two different methods. One was cycling the applied potential and the other was applying a constant potential for a fixed period of time. Preliminary results comparing the polymer response by the two methods of electropolymerization showed a difference in the catechol redox reversibility and sensitivity, indicating structural differences between the two polymers. Although there have been studies on the optimization of polymerization conditions for the constant potential methods [8], it was deemed necessary to optimize each method for our own purposes and compare the optimal conditions to each other to see if the discrepancy in reversibility and sensitivity still existed. For cycling, the factors varied were number of cycles and potential range, and the overall optimized conditions for this method were 8 cycles (at scan rate of 0.05 V/s) in a 0.05 M monomer solution between 0.4 and 2.0 V versus Ag|AgCl. The resulting film had an estimated thickness of 4.5 μm with 0.5 μm roughness from the AFM study. For the constant potential method, the factors varied were polymerization time, applied potential, and concentration of the monomer solution. The overall optimized conditions for the constant potential method are polymerization at 1.903 V for 30 s in a 0.05 M monomer solution.

To compare the performances of P3MT formed by each of these methods of polymerization, cyclic voltammograms of 0.004 M catechol in 0.01 M sulfuric acid solution were carried out. When the data collected, shown in Fig. 1, were compared, they were found to have comparable reversibility, both showing a ΔE of slightly less than 0.10 V. The polymer that was made by cycling did exhibit enhancement in sensitivity over the polymer that was made by constant potential. This difference in sensitivity between the two polymers could be due to the number and to the accessibility of the active sites available on the surface. It is possible that in the cycling method, the strands of the P3MT produced are layered on top of each other; leading to a better chance for the generation of more active sites that are available for electrolysis, this conclusion was manifested as an increased current flow and sensitivity. A thinner film, produced by less than 8 cycles, would not generate maximum number of active sites while a thicker film, more than 8 cycles, causes higher impedence for the current flow. Further AFM investigation may shed more light on the relative effect of the film thickness on this property of the polymer.

Effect of active sites

The enhanced performance of the P3MT electrode over the traditional ones for the analysis of phenolic molecules is explained in terms of active site formation within the polymer that will play a role as catalyst for the
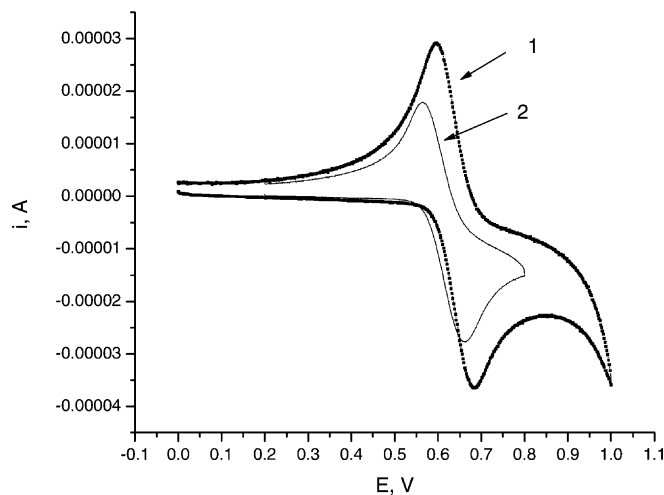

Fig. 1 Cyclic voltammograms i–E of 1.0 mM catechol in 0.01 M H_2SO_4 at P3MT films electrodeposited; by cycling *curve no. 1*, and by poteniostatic method *curve no. 2*

conversion reaction. Several experiments were carried out in which the anodic current was measured with varying concentrations of the analytes such as catechol. A property of the "active sites", similar to that found in enzymes, is that the sensitivity of the reaction aided by the active sites does not increase as concentration increases after a certain point. This is because there are only a limited number of active sites, and once they are all in use, an increase in concentration cannot improve the performance. This is true for the case of the active sites in the polymer. At high concentrations of catechol, $> 1.0\times10^{-3}$ M, P3MT-modified electrode has shown a significant departure from the linear behavior between the current peak intensity and concentration of the analyte. Figure 2 shows a calibration plot of the anodic current measured for a range of catechol concentrations (1.0×10^{-5}–1.0×10^{-2} M) on a polished glassy carbon and P3MT electrodes. The leveling-off of the current has shown on the P3MT above the one millimolar concentration is a result of the active sites saturation that were addressed above. Since the same GC electrode was used as a substrate to deposit the P3MT in this study, the surface area of the polymer can be approximated to the glassy carbon's area. The GC electrode showed a linear response with current values on the same magnitude of the theoretical ones. A theoretical current value for a semi-infinite diffusion condition can be calculated using the Cottrell equation. Assuming a value for the diffusion coefficient of 10^{-6} cm^2 s^{-1} would give a current around 3.00×10^{-6} A on an electrode area of 0.03 cm^2 [9]. It should be mentioned here that the alumina-polishing of the GC surface is not considered to be the optimal method for this purpose; however it is the common method of surface preparation. Extensive work has been carried out to investigate the effect of surface pretreatments on the electron kinetics on GC electrode by the McCreery research group. They showed that alumina polishing pretreatment alone would leave a significant
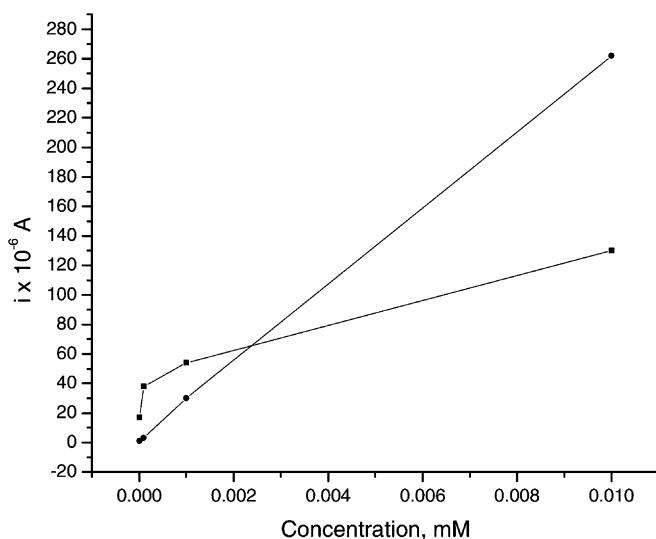

Fig. 2 Calibration curves for catechol at bare glassy carbon (linear) and at P3MT electrodes

part of the electrode surface covered with oxide.[21–23] A typical ΔE value associated with catechol on the polymer electrode was measured around 0.095 V and it stayed the same through a concentration range of 10^{-5}–10^{-2} M, whereas the observed ΔE value on the GC electrode was a function of concentration ranging from 0.090 V to about 0.175 V within the same concentrations. Also, from Fig. 2 (at lower concentrations 0.001 and 0.01 mM) it can be seen that current intensity associated with the catechol reaction is enhanced significantly over the glassy carbon electrode. At the lower catechol concentrations (10^{-5} and 10^{-4} M) this sensitivity enhancement was more evident since the contribution of the ohmic current is minimal. In other set of experiments where differential pulse voltammetry (DPV) was used to scan 0.10 and 0.01 mM solutions of catechol in 0.01 M sulfuric acid at the P3MT, GC, and Pt electrodes, the P3MT electrodes showed an oxidation peak for the analyte ca. 0.680 mV that was more intense than the peaks produced by the other two electrodes (results are not shown here). In previous reports the authors have addressed the catechol's behavior on the P3MT in some detail with diffusion coefficient measurement, other theoretical concepts, and the presence of active sites by showing x-ray photoelectron spectroscopic evidence of the sulfur heteroatom's possible involvement in these active sites. [9, 24].

Effect of pH and supporting electrolyte

The effects of the supporting electrolyte and the pH of the solution on the electrocatalytic behavior of the P3MT deposited on Pt or GC electrodes were determined by using sulfate and phosphate solutions at pH values of 2, 7, and 9 and monitoring the results of CV of 4.0 mM catechol in these solutions. Changes in the potential of the oxidation and reduction peaks (ΔE), the anodic current intensity, and/or any loss of electroactivity due to these changes were observed. Throughout the trials, the substrate, whether it was the glassy carbon or the platinum that was employed for the deposition of P3MT did not have a significant effect on the catechol CV. At pH 2, CV's obtained on GC and Pt in phosphate and sulfate were almost identical, signifying that at this pH these supporting electrolytes do not have an effect on the electroactivity of the polymer electrode. Each ΔE was approximately 0.1 V. At pH 7, the CV's done in a phosphate buffer showed a shift in potential in the negative direction. The oxidation peak occurred at approximately 0.4 V and the reduction peak occurred at approximately 0.26 V. Figure 3 shows the results obtained in pH 7 using the GC substrate for the polymer electrode in curve 1 (phosphate) and curve 2 (sulfate). Curves 3 and 4 were obtained using a bare GC electrode in the same solutions respectively. The electroactivities of the glassy carbon electrode appears to be extremely diminished at this pH. On a platinum substrate P3MT electrode in sulfate buffer, pH 7 caused only a slight
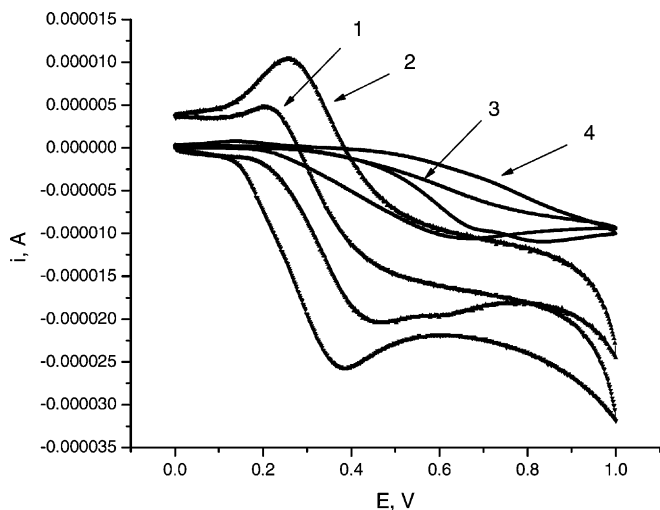
Fig. 3 Cyclic voltammograms *i–E* of 4.0 mM catechol at P3MT buffer solutions at pH 7, *curves 1* and *2* obtained in phosphate and sulfate respectively, *curves 3* and *4* obtained at GC electrode in sulfate and phosphate, respecyively

Fig. 5 Cyclic voltammetries *i–E* of 4.0 mM catechol in buffer solutions at pH 9 obtained on P3MT coated on GC and Pt substrates, *curves 1 & 2* in phosphate and *curves 3 & 4* in sulfate

negative shift in the oxidation potential peak of the catechol without any change to ΔE. On a bare platinum electrode the change in pH of the electrolyte caused a shift only in the reduction potential (ca. 90 mV) without a significant change to the oxidation potential that resulted in an increase in ΔE. Figure 4 compares the performances of the polymer on both Pt and GC substrates at pH 7 in both supporting electrolytes. At pH 9, the potentials obtained from all electrode materials in either supporting electrolyte solution were similar to those obtained at pH 7. The only difference was that the reaction became more sluggish and less reversible at pH 9, as shown in Fig. 5. This behavior showed more dramatically in the phosphate solution.
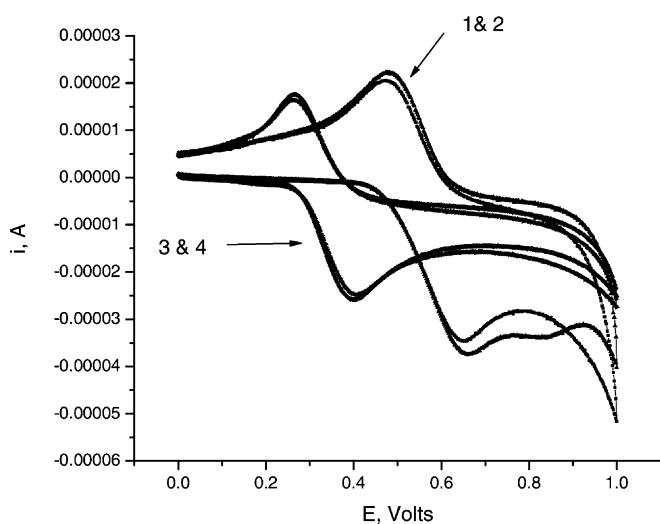

Fig. 4 Cyclic voltammetries *i–E* of 4.0 mM catechol in buffer solutions at pH 7 obtained at P3MT coated on GC and Pt substrates, *curves 1 & 2* in phosphate and *curves 3 & 4* in sulfate
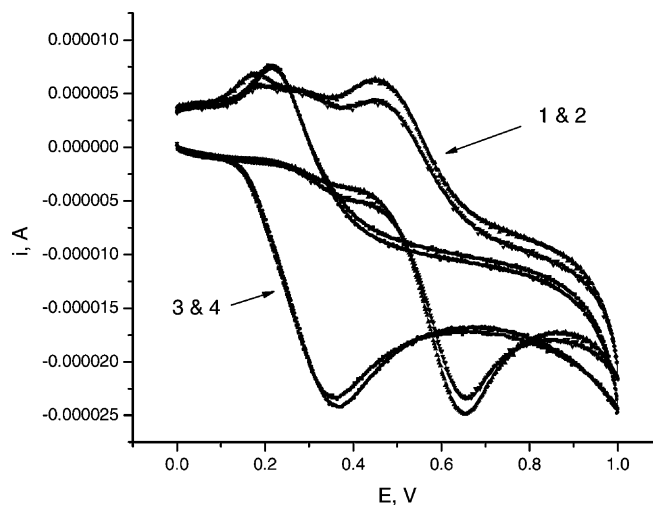
The shift in potential observed as the pH increases is caused by several factors including the availability of the protons that are involved in the catechol oxidation-reduction reaction, and the form of the supporting electrolyte. The form of the supporting electrolytes (sulfate and phosphate) and the concentrations of the protonated versus the deprotonated species have a great impact on the makeup of the double layer and the transport mechanism in the bulk solution. Since the catechol-polymer reaction is diffusion controlled, based on the linear dependence of the peak current on the square-root of scan rate [9], the capacitance behavior of the double layer has an effect on the potential of oxidation and reduction. At the basic pH the reversibility of the catechol redox reaction is severely limited due to the lack of hydrogen ions which are reactants in the reduction reaction. At pH~2, most of the hydrogen sulfate and all of the dihydrogen phosphate electrolytes exist in the protonated form due to the greater concentration of H^+ ions in the solution. As the pH increases, these species of the supporting electrolytes solution would exist in the deprotonated form carrying negative charges. The double layer involves more charged species at higher pH values and the polymer itself does not appear to be affected by the pH of the solution. In fact, it shows much less dependency on pH than the traditional Pt and GC electrodes. The traditional electrodes lost their electroactivity as the pH of the solution increased, possibly due to adherence of the negatively charged electrolytes to the positively charged electrode surface. While the polymer did lose some electroactivity in solutions with higher pH values, this loss was not nearly as significant as that of the Pt and GC electrodes, and overall the polymer retained most of its activity. This effect was particularly striking on the glassy carbon electrode, which by itself lost almost all activity, but when coated with the polymer retained a good deal of

that activity. The only effect the pH seems to have is a shift in the oxidation and reduction potentials when a phosphate electrolyte is used. Again, this phenomenon can be explained through the presence of the active sites. The majority of the polymer surface is organic in nature and would not carry charges like the platinum or the glassy carbon would at a positive potential, and the change in the thickness of the double layer is minimal making the effect on the active sites of the P3MT is much less severe than on the charged other surfaces at the same potential. This finding presents a clear advantage of the P3MT over the traditional electrodes for the detection of catecholamine in neutral or basic solutions.

1,5-Anthraquinonedisulfonic acid

The use of 1,5-AQDS was another attempt to probe the P3MT electrode's behavior with a phenolic molecule that is much larger than the catechol's, and has the ability to form hydrogen bonding. The electroactivity of the P3MT electrode in a solution containing 1,5-AQDS was limited to a nonreversible process with an oxidation peak at ca. $+200$ mV. The CV obtained by a bare platinum electrode in the same solution gave a reduction peak around -0.16 V and an oxidation peak around -0.44 V, both of which are well-defined. A CV of 1,5-AQDS on Pt electrode when compared to a CV of 1,5-AQDS on the polymer electrode would make it appears similar to the one obtained from a blank solution. Furthermore, it was found that when the same P3MT electrode that was cycled in a 1,5-AQDS solution was immediately used to detect catechol, the electrochemical activity of the P3MT was significantly blocked even at a very low concentration (1.0×10^{-5} M) of 1,5-AQDS. To investigate this phenomenon, the potential of a fresh polymer electrode was cycled in a 0.01 mM 1,5-AQDS solution between -0.5 V and $+0.6$ V several times with constant decreasing current density. The peak that was found around 0.23 V was presumed to be the oxidation peak for the analyte, its current intensity started to become smaller with each successive cycle. This suggests that the 1,5-AQDS was adsorbing to the polymer in a way that appears to follow a nonreversible process. It is possible that the 1,5-AQDS is covalently bonded to the polymer through the sulfite ($-SO_3^-$) part of the molecule as recently described by Arslan Udum et al. [25]. To determine the extent of the inhibition of 1,5-AQDS to the active sites of the polymer electrode a fresh P3MT electrode was used to obtain a catechol CV before cycling it in a 0.01 mM 1,5-AQDS solution and one after cycling it in the 1,5-AQS solution. Lower concentrations of the 1,5-AQDS were also tested. The results are shown in Fig. 6. The catechol CV obtained after cycling the electrode in 1,5-AQDS solution resembles a background CV. This apparent fouling of the P3MT active sites by trace amounts of 1,5-AQDS is similar to what has been found by using an active metal such as Mo, Ni, or Fe.[24]. This finding suggests that the polymer's
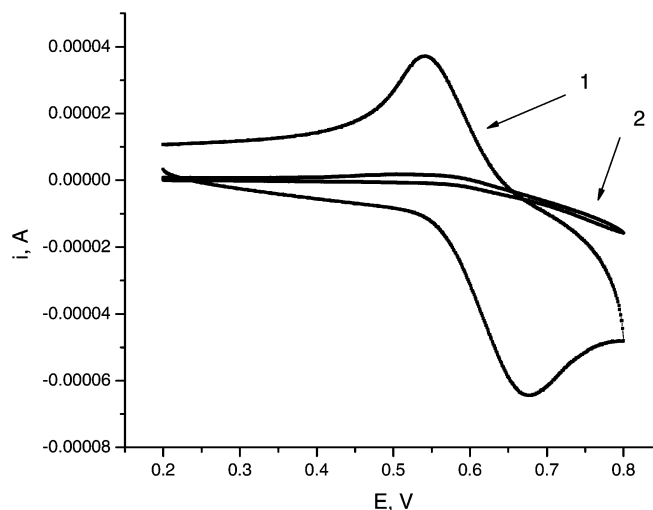

Fig. 6 Cyclic voltammetry (CV) i–E of 4.0 mM catechol in 0.01 M H_2SO_4 solutions at P3MT electrode, *curve no. 1* before and *curve no. 2* after treatment with 1,5-AQDS

enhanced electrocatalysis toward catechol and similar molecules is not applicable to all organic redox couples.

It is possible that the electron transfer reaction of the 1,5-AQDS on the P3MT electrode is taking place at spots that are different than the ones usually involved in the catechol or this activity involves the adsorbed 1,5-AQDS molecules on the surface. The reaction of the 1,5-AQDS on P3MT electrode follows a model that has been described by He, et.al. for a GC electrode with the difference being that it is not as efficient a process at the P3MT [17]. Clearly the reaction of the 1,5-AQDS with the "active sites" that have been proposed for the catechol is permanent and nonreversible, the subsequent inhibition of the catechol catalysis is further evidence for that.

Atomic force microscope study

Images were taken of the bare platinum substrate, a dry polymer electrode, and a wet polymer (which is the state it would be in while detecting analytes). The dry polymer images were taken in contact mode, in which the AFM tip actually drags across the surface. The wet polymer measurements were taken in non-contact mode, in which the tip oscillates at a microscopic distance above the surface and generates the image. Figures 7 and 8 are AFM images showing some structural detail difference between the dry and wet surfaces respectively. The results demonstrate a rod-like formation of the polymer on the surface of the substrate. And as predicted earlier, the wet polymer appears more swollen than the dry polymer, which could make the "active sites" conformation more accessible to the redox couple from solution. The wet film thickness was measured by this method and found to be about 4.5 Mm. The AFM images of the polymers obtained by the two methods of

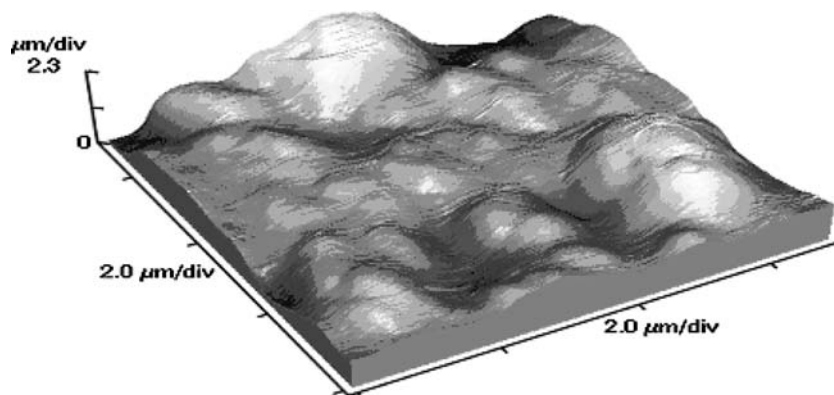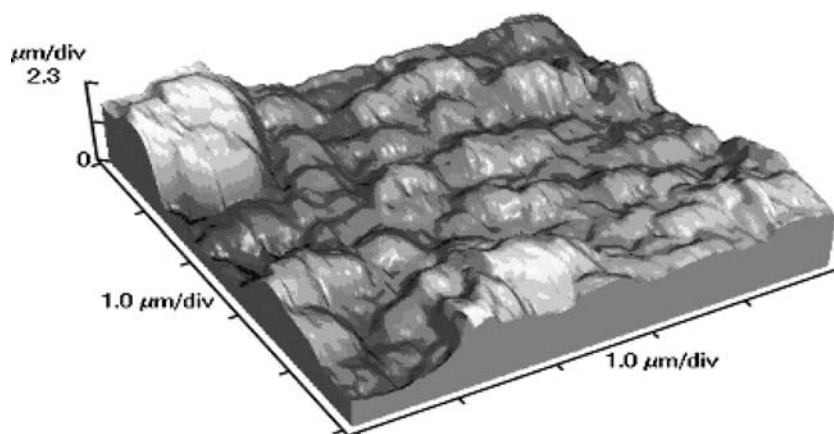**Fig. 7** A contact mode AFM image of a dry P3MT surface on Pt substrate

Fig. 8 A non-contact mode AFM image of a wet P3MT surface on Pt substrate

electropolymerization described above have revealed that the constant potential method would generate a smaller number of sites of polymerization initiation (polymer initiated on the substrate from which the polymer coating can grow) than the method with cycling technique. It has been proposed previously that the polymer is initiated on the substrate surface and grown in a rod-like form, causing what has been termed "edge effect" [9].

The layered structure shown by the AFM could be a key to understanding the involvement of the heteroatom in the electrocatalysis process of the P3MT. It is possible that the nonbonding electrons of the sulfur form an intermediate complex with certain phenols such as catechol while the polymer is in the reduced state (undoped). Based on these results, not every thiophene ring gets involved in this complex formation that leads to catalysis. Only such a confirmation of the layered polymer may form an active site. Similar processes take place in proteins and peptides containing sulfur atoms.

Conclusions

The electrocatalytical activities of poly-3-methylthiophene electrode have been further investigated. Several new evidences have been presented in support of the unique structure of the polymer toward the electrocatalysis of catechol and similar molecules. The term "hot spot" has been coined for this uniqueness and it is believed to be composed of some structural conformation involving possibly more than one sulfur heteroatom that provide the suitable environment for the electron transfer step for this class of molecules. These sites are completely deactivated when a molecule such as 1,5-AQDS binds to them, a result that is similar to what has been seen for the effect of transition elements. It is believed that the sulfite groups on the 1,5-AQDS are responsible for this phenomenon, because the polymer has previously proved able to detect plain phenol molecules. The pH sensitivity of P3MT appears to depend on the supporting electrolyte. This suggests that the mechanism of P3MT does not depend on surface charge or movement of charge along the polymer, but rather on the confirmation of its structure. In the sulfate supporting electrolyte, the polymer demonstrated activity that was only decreased by a small amount at basic pH's. In the phosphate electrolyte, the polymer still did not lose activity at neutral and basic pH's, but merely experienced a shift in oxidation and reduction potential. This shift is most likely due to the ionic form of the phosphate ions in the solution that depends on the pH, because it did not occur in the sulfate solution. Furthermore, it appears that the P3MT polymer would

not be suited for work as a pH detector, as other conducting polymers are being considered for, because the change in activity as pH increases is not significant. To elucidate a detailed mechanism of the polymer activity, further investigation needs to be carried out using various other organic and inorganic molecules.

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