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Synthesis, Characterization, and Redox Reactivity of Novel Quinone-Containing Polymer

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The synthesis of poly(vinyl hydroquinone), PVHQ, via stable free radical polymerization (SFRP) to give a low-dispersity (1.5) material is described. The electrochemical properties of the resulting material deposited as films onto glassy carbon electrodes have been investigated by cyclic voltammetry. In aqueous acetic acid solution, it was found that as the amount of material ostensibly deposited (Γ_{theo}) increased the ratio $\Gamma_{obs}/\Gamma_{theo}$ (where Γ_{obs} and Γ_{theo} represent the measured and the theoretical surface coverage values, respectively) drastically decreased, indicating that a significant fraction of the quinone sites are electrochemically inactive as the film thickness increases. This was attributed to a small electron transfer rate constant and to the fact that the electron transfer is coupled to proton transfer, so the hydrophobicity of the polymer backbone might adversely affect the accessibility of protons. Using Laviron's theory, the electron-transfer rate constant and the transfer coefficient were determined to be 2.1 s^{-1} and 0.5, respectively, for a PVHQ film ($\Gamma_{obs} = 4.3 \times 10^{-10}$ mol cm^{-2}) on a glassy carbon electrode in 0.10 M acetic acid solution. The formal potential of the PVHQ film shifted with pH at a rate of 59 mV/pH unit up to pH 6. At higher pH values, the slope decreased to ca. 30 mV/pH unit, suggesting a two-electron/one-proton reaction. The surface pK_a value for the first deprotonation reaction was estimated to be 7.8.

Introduction

Redox polymers that are capable of undergoing reversible reduction and oxidation reactions have a wide range of applications, including their use as redox agents, purification media to remove traces of small molecules, sensors, actuators, in drug delivery, and as models for biochemical systems.[1] These redox polymers can be coated onto electrode surfaces to mediate charge transfer to target solution species. The phenomenon of mediated charge transfer from a redox polymer-coated electrode has been employed in applications such as electrochemical synthesis and electrochemical sensors.[2] One of the key factors affecting the performance of polymer-coated electrodes is the structure of the polymer, which can in turn affect the rate of electron transfer, surface coverage (concentration) of redox active centers, charge transport and propagation, as well as diffusion and permeation of soluble species through the polymer.[2] Depending on their structure, redox polymers can be generally classified into those with redox groups that are part of the polymer chain backbone and those with redox group as substituents (pendant) to the chains.[1]

Poly(vinyl hydroquinone)s (PVHQs), which have quinone/hydroquinone (Q/QH_2) redox active groups as substituents on the chain, exhibit interesting electrochemical behavior in solution, since as with quinones, in general, their redox behavior involves proton-coupled electron transfer (two-electron/two-proton).[1] It would thus be of interest to modify electrode surfaces with PVHQ and explore their electrochemical properties and behavior. Although there have been numerous reports of poly(hydroquinone)-type modified electrodes,[3,4] to the authors knowledge, only one study of electrodes modified with poly(vinyl benzoquinone), the oxidized form of PVHQ, has been reported.[5] In that study, emphasis was placed on the electrochemical behavior, in nonaqueous solvents such as acetonitrile and DMSO, of electrodes modified with films of poly(vinyl benzoquinone). The voltammetric responses observed were quite broad and somewhat unstable and this likely arose, at least in part, from the thick films used (vide infra) and the synthesis method employed [conventional free radical polymerization with AIBN (2,2′-azobisisobutyronitrile) as initiator], which gave rise to rather broad molecular weight distributions. Although some preliminary studies were carried out in aqueous media, the modified electrodes were reported to be electrochemically inactive. We believe that this behavior arose from the fact that the films employed were rather thick, giving rise to slow rates of charge propagation, and that the potential

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window employed was not the most appropriate.

As will be described in detail below, we have found that glassy carbon (GC) electrodes modified with thin films of PVHQ exhibit quasireversible redox reactivity in aqueous media.

PVHQ has been previously synthesized via conventional free radical polymerization, resulting in broad product polydispersity. In such cases, the measured properties will necessarily reflect and represent the average of such a broad distribution. The advantage of a narrow distribution polymer is that having such well-defined macromolecules makes evaluation of various physical and electrochemical properties more meaningful. Various techniques including living anionic, living cationic, living ring opening, and living free radical polymerization have been applied to the preparation of narrowly dispersed polymer samples. The popularity and use of “stable free radical polymerization” (SFRP) methods[6,7] have grown tremendously in the past few years, mainly because of the versatility they offer in terms of the broad range of monomers and polymerization conditions possible. Nitroxide-mediated controlled free radical polymerization can be easily carried out for functionalized styrenic monomers under less stringent conditions when compared to living anionic techniques.[8]

In this study we have applied nitroxide-mediated stable free radical polymerization to prepare narrow-polydispersity PVHQ by the hydrolysis of poly(2,5-diacetoxystyrene) or poly(2,5-bis[(4-*n*-butylbenzoyl)oxy]styrene), PBBOS. PBBOS is a mesogen-jacketed liquid-crystalline polymer with the mesogenic groups laterally attached to the polymer backbone.[9] We polymerized 2,5-bis[(4-*n*-butylbenzoyl)oxy]styrene (BBOS) via stable free radical polymerization (SFRP) to obtain narrow-dispersity PBBOS. BBOS is an ideal starting material for the synthesis of PVHQ, primarily because it has unusually high reactivity for styrenic monomers under these conditions.[9] The high reactivity of BBOS allows us to achieve a molecular weight of 80 000 under SFRP conditions in less than 8.0 h. Narrow-dispersity PVHQ could be readily obtained by subsequent hydrolysis of PBBOS. This enabled the preparation of PVHQ with a molecular weight as high as 20 000−30 000 g mol^{-1}. An alternative pathway to PVHQ is through hydrolysis of poly(2,5-diacetoxystyrene). However, this was found to be relatively difficult, as it resulted in substantial amounts of insoluble red byproduct. Hence, the material described in this report is derived from hydrolyzed PBBOS. The application of stable free radical polymerization to obtain PVHQ makes it feasible to prepare well-defined block copolymers of PVHQ with styrene and other functional monomers by saponification of the corresponding protecting ester. In this paper we report on the synthesis of narrow-dispersity (ca. 1.5) PVHQ and on the evaluation of its electrochemical properties when coated, as a thin film, on an electrode surface.

Experimental Section

Materials. 1-Phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane was used as received from Birnard Industry. Water was purified with a Millipore Milli-Q-System. All other reagents were purchased from Aldrich and were used as received.

Apparatus for Electrochemical Measurements. Electrochemical experiments were carried out at room temperature with a BAS CV-27 potentiostat. Three-compartment electrochemical cells (separated by medium porosity sintered glass disks) were employed. GC electrodes (geometric area = 0.20 cm^2) were used as working electrodes. The electrodes were polished prior to use with 1 μm diamond paste (Buehler) and rinsed thoroughly with water and acetone. After the electrode was dried, it was modified with PVHQ by casting from a typically 0.1 mM (monomer unit) PVHQ ethanol solution. The volume cast varied depending on the desired coverage of the PVHQ. A large-area platinum wire coil was used as a counter electrode. All potentials are referenced to a saturated Ag/AgCl electrode without regard for the liquid junction potential. Acetate or phosphate buffers (0.10 M) were used as supporting electrolytes.

Synthesis and Characterization of PVHQ. *Synthesis of Monomer*. The monomer 2,5-bis[(4-*n*-butylbenzoyl)oxy]styrene, BBOS (**1**) (Scheme 1), was synthesized by the reaction of 2-vinyl-1,4-dihydroxybenzene and 4-butylbenzoyl chloride according to the method described by Zhou et al.[10]

^{1}H NMR ($CDCl_3$): $\delta = 0.95$, 6H for CH^a3, $\delta = 1.35$, 4H for CH^b2, $\delta = 1.65$, 4H for $CH_2{}^c$, $\delta = 2.70$, 4H for CH^d2, $\delta = 5.10-5.90$, 2H for $=CH^e2$, $\delta = 6.60-6.95$, 1H for $-CH^f=$ and $\delta = 7.00-8.30$, 11H for the phenylene rings.

Synthesis of Poly{2,5-bis[(4-n-butylbenzoyl)oxy]styrene} (PBBOS). BBOS was polymerized by a controlled free radical technique using 1-phenyl-1-(2′,2′,6′,6′-tetramethyl-1′-piperidinyloxy)ethane as initiator. Typically a 1000:3 molar ratio of monomer:initiator was taken in a glass tube containing a stir bar and purged with nitrogen for 15 min. The tube was subjected to four freeze−pump−thaw cycles to get rid of any residual oxygen and subsequently sealed under vacuum. The mixture was heated in a water bath at 95 °C for 2 min to uniformly mix the initiator and the monomer in the isotropic state of the monomer.[9] The sealed tube was placed in an oil bath at 120 °C and polymerized for 6 h (Scheme 1).

The polymerized solid was dissolved in tetrahydrofuran and purified by reprecipitating twice from methanol to remove the unreacted monomer.

GPC analysis gave a $\bar{M}_n$ value of 71 600 and a PDI (polydispersity index) of 1.56.

Synthesis of PVHQ. PVHQ was synthesized by saponification of PBBOS by modifying the method described by Cassidy et al.[1] To carry out the reaction in the absence of oxygen, an H-shaped vessel was fabricated with one leg attached to a condenser (with stopcock) and the other leg attached to a vacuum adapter. The two tubes were connected through a cross tube containing a Teflon stopcock. Dry polymer (360 mg) was fed into the leg attached to the condenser, and 10 mL of 0.2 N NaOH in ethyl alcohol was fed to the other leg. These two compartments were isolated by the stopcock in the cross tube. Both compartments were purged with nitrogen gas and subjected to four freeze−pump−thaw cycles to exclude any oxygen. The sodium hydroxide solution was brought into contact with the polymer by tipping the reactor and opening the stopcock. The resulting mixture was refluxed on a water bath for 48 h at 90 °C, and 6 mL of 1 N sulfuric acid was introduced into the empty leg of the reactor, subjected to freeze−pump−thaw cycles, and transferred, under vacuum, to the reaction mixture. After stirring for 15 min, the reaction mixture was cooled and precipitated in an excess of water. The saponified polymer was centrifuged and purified by dissolving in 90% acetic acid and precipitating in water. The NMR of the product obtained showed the presence of 4-butylbenzoic acid

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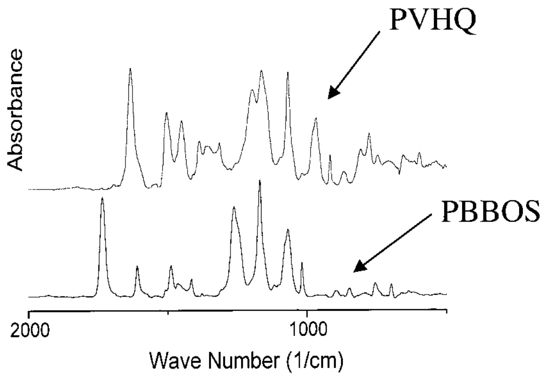

Figure 1. IR spectra of PVHQ (top) and PBBOS (bottom) showing the complete hydrolysis of PBBOS to PVHQ.

in the polymer. Further purification was carried out by dissolving the polymer in acetone, followed by precipitating in petroleum ether. Following this step, the NMR spectrum showed the complete removal of 4-butylbenzoic acid. The polymer was centrifuged and washed with 5% sodium hydrosulfite solution in an inert atmosphere to obtain the completely reduced form. The final yield was 85 mg (81%).

The expected molecular weight of the hydrolyzed polymer based on the molecular weight of the starting polymer (PBBOS) is 21 500.

Characterization. A Varian XL 400 MHz NMR using deuterated chloroform or acetone as solvent, with tetramethylsilane as internal standard, was used to record the NMR spectra. Quantitative hydrolysis of PBBOS to PVHQ was confirmed by both IR and NMR. Representative IR spectra of PBBOS and PVHQ are shown in Figure 1. As would be anticipated, the ester carbonyl peak at 1735 cm^{-1} is absent in the spectrum of PVHQ. In the case of PVHQ, a broad −OH peak appears from 3000 to 3500 cm^{-1}.

The measurement of molecular weight and polydispersity of the polymer sample were carried out using Waters Ultrasyragel HT columns operating at 40 °C. THF was used as the solvent and the GPC was operated at 1 mL min^{-1}. The molecular weight was calculated from GPC elution volume data using monodisperse polystyrene standards.

Results and Discussions

Electrochemical Response. Figure 2 shows cyclic voltammograms of a PVHQ-modified GC electrode in 0.10 M aqueous acetic acid solution (pH 2.9) at various potential scan rates. It should be noted that the peak height of the cyclic voltammogram at 500 mV s^{-1} obtained 1 h later was virtually identical to the one at 500 mV s^{-1} presented in Figure 2. This indicates that the PVHQ film is stable, at least over such a time period, under the conditions employed. As is evident from Figure 2, the voltammograms exhibit a single redox couple centered at +290 mV vs Ag/AgCl. The fact that only a single redox process is observed implies a simultaneous multielectron transfer of all the quinone centers at the same potential. In addition, the relatively large ΔE_p (peak separation) value of 160 mV at 10 mV s^{-1} between anodic and cathodic peaks indicates a slow electron-transfer rate (detailed electron-transfer kinetics

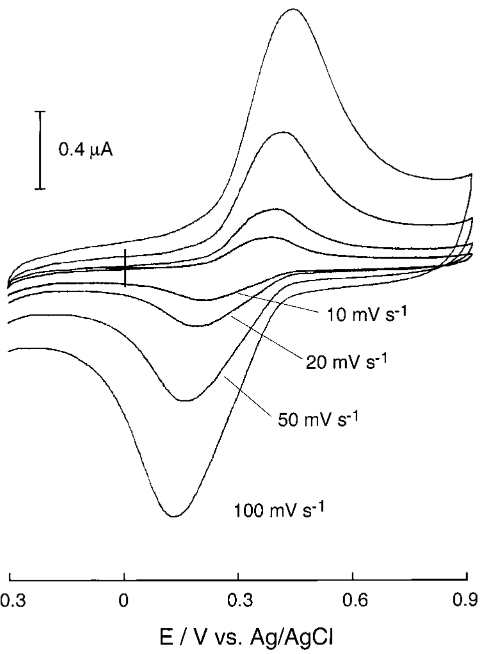

Figure 2. Typical cyclic voltammograms of a PVHQ-modified GC electrode (4.5×10^{-10} mol cm^{-2}, monomer unit) in a 0.10 M acetic acid aqueous solution at various potential scan rates.

Scheme 1. Reaction Scheme Depicting the Stable Free Radical Polymerization of BBOS to PBBOS and Its Hydrolysis to PVHQ

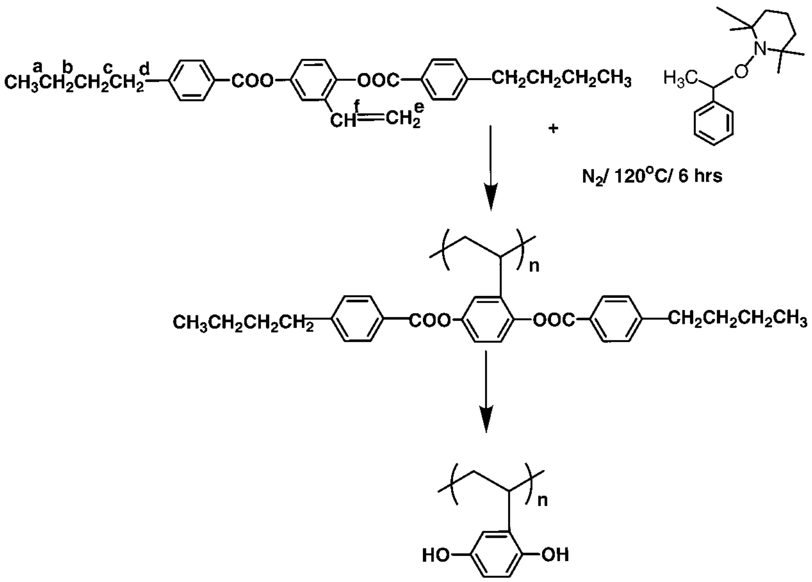

Table 1. Values of Expected (Γ_{theo}) and Observed (Γ_{obs}) Surface Coverages and Their Ratio

Γ_{theo} (mol cm^{-2})	Γ_{obs} (mol cm^{-2})	ratio ($\Gamma_{obs}/\Gamma_{theo}$)
6.4×10^{10}	4.5×10^{10}	0.71
6.4×10^{9}	8.8×10^{10}	0.14
6.4×10^{8}	4.2×10^{10}	0.007

will be discussed later). The actual surface coverage (Γ_{obs}) was determined to be 4.5×10^{-10} mol cm^{-2} (monomer unit) from integration of the charge under the cyclic voltammetric peaks obtained at a slow potential scan rate, where the peak current is directly proportional to scan rate, as anticipated for a surface immobilized reagent. The coverage of a monolayer equivalent of PVHQ was estimated to be 3.6×10^{-10} mol cm^{-2} using the molecular dimensions of vinyl hydroquinone and assuming a hexagonal close-packed structure. Thus, for the electrode described above, the surface coverage is slightly over 1 (ca. 1.25) equivalent monolayer.

It should be noted that as the thickness of the PVHQ film was increased, by increasing the volume (or concentration) of solution cast, the ΔE_p increased significantly. For example, for a film with an expected (from volume cast) surface coverage (Γ_{theo}) of 6.4×10^{-8} mol cm^{-2}, ΔE_p was found to be about 700 mV at 10 mV s^{-1}. This value is not only exceedingly large but also it is 540 mV larger than that for the film shown in Figure 2, (at the same sweep rate) that, based on the volume of the solution cast, had a Γ_{theo} of 6.4×10^{-10} mol cm^{-2}. This behavior is typical of redox reactions with a small electron-transfer rate constant. In addition and as the above data indicate, Γ_{obs} was generally smaller than Γ_{theo} estimated from the concentration and the volume cast, especially when Γ_{theo} was high. Surface coverage values are summarized in Table 1 as well as their ratio ($\Gamma_{obs}/\Gamma_{theo}$). It can be noted that as the Γ_{theo} increased, the ratio decreased dramatically, indicating that a large fraction of the quinone sites are electrochemically inactive as the film thickness increases. As mentioned previously, we believe that this is due to a small electron-transfer rate constant and/or apparent diffusion coefficient. On the basis of these results, all subsequent experiments were performed on electrodes with PVHQ films prepared to have an expected surface coverage of 6×10^{-10} mol cm^{-2}. As mentioned earlier, this gives rise to experimentally determined surface coverages that were in the 1−2 equivalent monolayer regime.

Funt and Hoang have reported that a Pt electrode, modified with poly(vinyl benzoquinone), is electrochemically inactive in aqueous media.[5] The surface coverage value, determined in DMSO solution, was reported to be ($\Gamma_{obs} = 5.2 \times 10^{-9}$ mol cm^{-2}). Assuming that this coverage value is also applicable to measurements in aqueous media, the observed inactivity is likely due to the thickness of the film (estimated to be on the order of 10 equivalent monolayers). Also, the higher hydrophobicity of the benzoquinone polymer used by them, compared with the hydroquinone polymer used in our investigations, could also lead to electrode inactivity in aqueous media. Both of these effects, increased film thickness and hydrophobicity, would tend to lower the electron-transfer rates and decrease the movement of protons, which are necessary to compensate for the negative charges of the reduced quinone sites, throughout the polymer film.

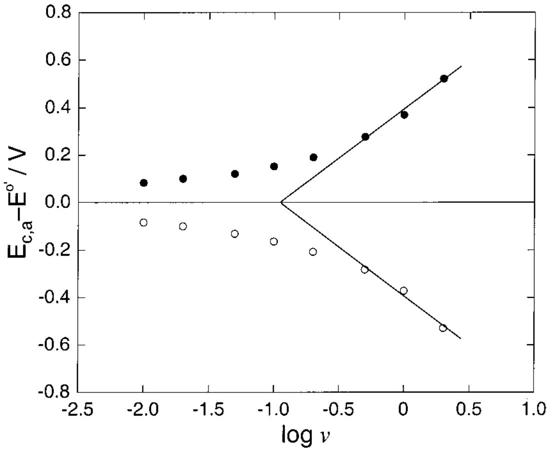

Figure 3. Laviron plot ($E_p - E^{\circ\prime}$ vs log potential scan rate) of a PVHQ-modified GC electrode in a 0.10 M acetic acid aqueous solution.

Electron-Transfer Kinetics. Since the redox reaction of electrodes modified with PVHQ was that of a surface-confined process, the electron-transfer rate constant, k_s, and the transfer coefficient, α, were determined from the relationship between ΔE (defined as $E_p - E^{\circ\prime}$; E_p is the peak potential value for the anodic or cathodic wave, and $E^{\circ\prime}$ is the formal potential taken as the average of the anodic (E_a) and cathodic (E_c) peak potentials) and the log of the potential scan rate (v) based on Laviron's theory.[11] According to this theory, α and k_s can be calculated using eqs 1 and 2

$$\alpha/(1 - \alpha) = v_a/v_c \tag{1}$$

$$k_s = nF\alpha v_c/RT = (1 - \alpha)nFv_a/RT \tag{2}$$

where F is the Faraday's constant, n is the number of electrons, and v_a and v_c are the potential scan rates at intercepts of the straight line fits to anodic and cathodic data, respectively, when ΔE_p is greater than $200/n$ mV. Figure 3 shows plots of ΔE vs log v (Laviron plots) for a PVHQ film on a GC electrode ($\Gamma_{obs} = 4.3 \times 10^{-10}$ mol cm^{-2}) in a 0.10 M acetic acid aqueous solution (pH 2.9) From the plot, values of α and k_s were determined to be 0.5 and 2.1 s^{-1}, respectively. The small value of $k_s = 2.1$ s^{-1} is fully consistent with the behavior discussed above in terms of ΔE_p values in the cyclic voltammograms.[12] We believe that the slowness of the electron-transfer kinetics is due, at least in part, to the fact that the electron-transfer reactions are proton-coupled. In addition, the hydrophobic nature of the film could affect the accessibility of protons and, thus, k_s.

Effect of pH. Since the redox centers are quinones, the redox reaction of PVHQ would be anticipated to be pH dependent. That is, the formal potential is predicted to shift with pH at a rate of 59 mV/pH unit (for a two-electron/two-proton process). To ascertain this, the voltammetric response of a PVHQ-modified GC electrode was obtained at 10 mV s^{-1} in phosphate solutions of pH varying from 1.4 to 12.4. Figure 4 presents the

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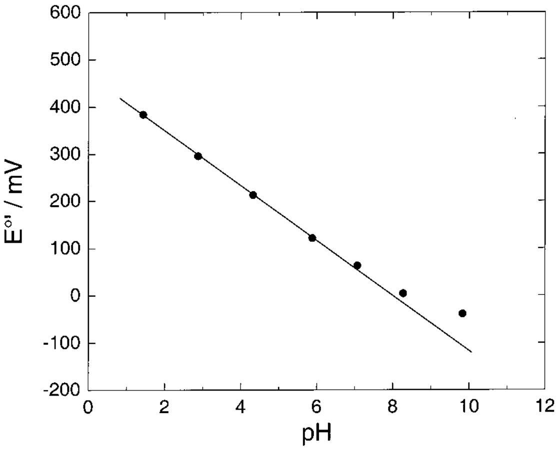

Figure 4. Dependence of the $E^{\circ\prime}$ on pH for a PVHQ-modified GC electrode in 0.10 M phosphate solutions at various pH values.

dependence of the formal potential on the solution pH. Up to about pH 6, the formal potential was found to be linearly pH dependent with a slope of 59 mV/decade, which is in good accordance with the theoretical Nernstian value. At higher pH values, there was a clear deviation as the slope decreased to about half (ca. 30 mV/pH unit). We attribute this to deprotonation of the hydroquinone moieties at higher pH, so the process is a two-electron/one-proton reaction that would give rise to a decrease in the slope to 30 mV/pH unit, as was indeed observed. It should be noted that whereas a small and broad wave was observed on the first scan at pH 12.4, it disappeared on the second and subsequent scans. This would suggest that the film is displaced from the surface of the electrode or that the polymer is not stable under these conditions, so the redox activity is rapidly lost. From the intersection of the two linear regions, we estimate that the pK_a value for the first deprotonation of the PVHQ is about 7.8. This pK_a value is significantly lower than that of hydroquinone (9.9 for the first deprotonation). These differences might arise, in part, from the ring substitution, which would lower the pK_a.[13] In addition, the pK_a value of the hydroquinone centers in the film might be different from that in bulk solution, since the charge distribution on the electrode surface and the environment within the film are expected to be significantly different from those in bulk solution, due to double-layer effects and differences in the solvation of the polymer backbone. Unfortunately it is experimentally difficult to unambiguously measure the pK_a value, since PVHQ is confined to the electrode surface and it is difficult to factor out the various effects present.

Conclusions

Poly(vinylhydroquinone) has been synthesized via SFRP to give a low dispersity (1.5) material whose electrochemical properties have been studied by cyclic voltammetry. In aqueous acetic acid solution, it was found that as the Γ_{theo} increased, the ratio $\Gamma_{obs}/\Gamma_{theo}$ drastically decreased, indicating that a significant fraction of the quinone sites are electrochemically inactive as the film thickness increases. This was attributed to a small electron-transfer rate constant. The electron-transfer rate constant and the transfer coefficient were determined to be 2.1 s^{-1} and 0.5, respectively, for a PVHQ film ($\Gamma_{obs} = 4.3 \times 10^{-10}$ mol cm^{-2}) using Laviron's theory. The formal potential of PVHQ shifted with pH at a rate of 59 mV/pH unit up to pH 6. At higher pH, the slope decreased to be ca. 30 mV/pH unit, suggesting a two-electron/one-proton reaction. From the intersection of the two lines, the surface pK_a value was estimated to be 7.8.

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