Charge Trapping in Poly(3,4-diphenylpyrrole) and Release by Trace Halocarbons in Water

Daniel L. Feldheim,‡ Susan M. Hendrickson, Michael Krejcik, and C. Michael Elliott*

Department of Chemistry, Colorado State University, Fort Collins, Colorado 80523-1872

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The sorption of trace organics from aqueous solution into the substituted pyrrole polymer, poly(3,4-diphenylpyrrole), has been investigated with cyclic voltammetry, UV–visible spectroelectrochemistry, flow-injection amperometry, and electrochemical quartz crystal gravimetry (EQCM). EQCM experiments revealed that the addition of the phenyl substituents improves the sorption capacity for dichloromethane by an order of magnitude over poly(*N*-methylpyrrole). Cyclic voltammetry showed no redox activity for poly(3,4-diphenylpyrrole) in pure aqueous electrolyte. When trace amounts of halocarbons are present in aqueous solution, however, the redox waves of poly(3,4-diphenylpyrrole) are observed and are well-behaved. This behavior was compared to a composite film consisting of poly(3,4-diphenylpyrrole) doped with the polyelectrolyte anion, poly(styrenesulfonate). The composite polymer displays "normal" voltammetric response in aqueous electrolyte with the current response only moderately increasing in the presence of trace halocarbons. The difference in the voltammetric behavior of the two polymers is discussed in terms of the relative hydrophobicities of the oxidized and reduced forms of each film.

Introduction

Several reports have appeared recently on the interactions between organic conducting polymers such as polypyrrole and organic vapors or trace organics dissolved in aqueous solution.[1–5] Potential applications of such interactions include sensors and separation membranes. Our work in this area has shown that the reduced form of poly(*N*-methylpyrrole) (PNMP) has a high affinity for trace halocarbons in water, while the oxidized form displays a much lower absorptivity for these molecules.[6,7] Concomitant with this change in halocarbon partitioning between the two polymer oxidation states are large shifts (i.e., 200 mV) in the cyclic voltammetric redox waves to more positive potentials. The shapes and the integrated areas under each wave remained, essentially, unchanged. This behavior was observed almost exclusively for halocarbons in water when compared to a number of small molecules containing other functional groups such as ketones, aldehydes, alcohols, and nitriles.

In an attempt to understand a structure–function relationship between the polymer and the amount and type of organic absorbed, the interactions between trace organics in water and another substituted pyrrole, poly(3,4-diphenylpyrrole), have been investigated by cyclic voltammetry, UV–visible spectroelectrochemistry, flow-injection amperometry, and flow-injection electrochemical quartz crystal microgravimetry. These techniques revealed surprising redox inactivity for the polymer when in contact with pure aqueous electrolyte solution. Electrochemical activity, however, was "turned on" when trace halocarbons (less than 1 mg/mL) were present in solution. The effect of incorporating a large polyelectrolyte dopant anion, poly(styrenesulfonate), was also explored and is reported herein.

Experimental Section

Chemicals. Acetonitrile (Baxter, Burdick & Jackson) and dichloromethane (Mallinckrodt) were used as received. Sodium perchlorate (Aldrich) was dried at 75 °C for at least 24 h prior to each experiment. Tetrahexylammonium poly(styrenesulfonate) (THAPSS) was prepared as described previously.[8]

The synthesis of 3,4-diphenylpyrrole was carried out with a slight modification to the procedure reported previously (Scheme 1).[9] In a three-neck round-bottom flask, 0.139 mol of iminodiacetic acid (Aldrich, 98%) were added to 100 mL of anhydrous methanol (Mallinckrodt), and the solution was saturated with HCl vapor. The mixture was refluxed until all the solid dissolved. With continued HCl bubbling, the solution was allowed to cool to room temperature. Upon cooling, white crystals of the hydrochloride salt of the bismethyl ester (**II**) formed which were filtered and recrystallized from hot methanol.

The crystals of **II** (0.0254 mol) were mixed with 0.0254 mol of triethylamine (Aldrich, 99%) in dichloromethane and anhydrous ethyl ether (Mallinckrodt). The solid triethylamine hydrochloride was filtered from the solution. The solution was

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[‡] Current address: Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, PA 16802.

[*] Corresponding author.

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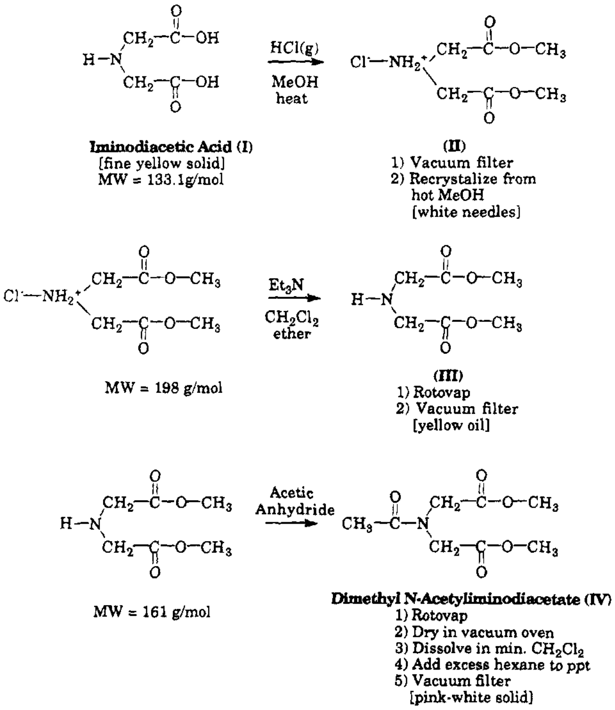
Scheme 1. Synthesis of Dimethyl *N*-Acetyliminodiacetate



dried to a yellow oil and acetic anhydride (Mallinckrodt) was added dropwise while cooling in an ice bath until no heat was produced. After recrystallizing in dichloromethane/hexanes dimethyl (*N*-acetylimino)diacetate (**IV**) was recovered in 50% yield. Otherwise, the synthesis of 3,4-diphenylpyrrole followed the literature procedure.[9]

Polymer Growth. Poly(3,4-diphenylpyrrole) (PDPP) films were grown electrochemically at a constant potential of +0.7 V vs Ag/Ag$^+$ from solutions of acetonitrile containing 0.1 M diphenylpyrrole and 0.1 M sodium perchlorate. Poly(3,4-diphenylpyrrole/poly(styrenesulfonate)) (PDPP/PSS) films were grown at a constant potential of +0.7 V vs Ag/Ag$^+$ from solutions of acetonitrile containing 0.1 M diphenylpyrrole and 0.5 M THAPSS.

Instrumentation. Electrochemical and electrochemical quartz crystal microbalance equipment has been described in detail previously.[7] A Bioanalytical Systems LC-44 electrochemical detector was used for the flow-injection amperometry experiments. UV–visible spectra were recorded with a Hewlett-Packard Model 8452A photodiode array spectrometer.

Results

Cyclic Voltammetry. The redox behavior of PDPP/ClO_4 films was investigated in acetonitrile, water, and dichloromethane-saturated water (Figures 1 and 2). In acetonitrile/0.1 M $NaClO_4$, the redox waves were sharp and stable to repeated potential cycling (Figure 1). When the same film was cycled in aqueous/0.1 M $NaClO_4$, however, the film was electrochemically inactive over the same potential range (i.e., no redox waves were observed; dashed curve in Figure 2). Upon introduction of dichloromethane vapor into the solution (solid curve in Figure 2), the redox waves of PDPP appeared and were well defined. Purging the solution with nitrogen to remove the dichloromethane reverted the redox behavior back to that illustrated by the dashed line in Figure 2.

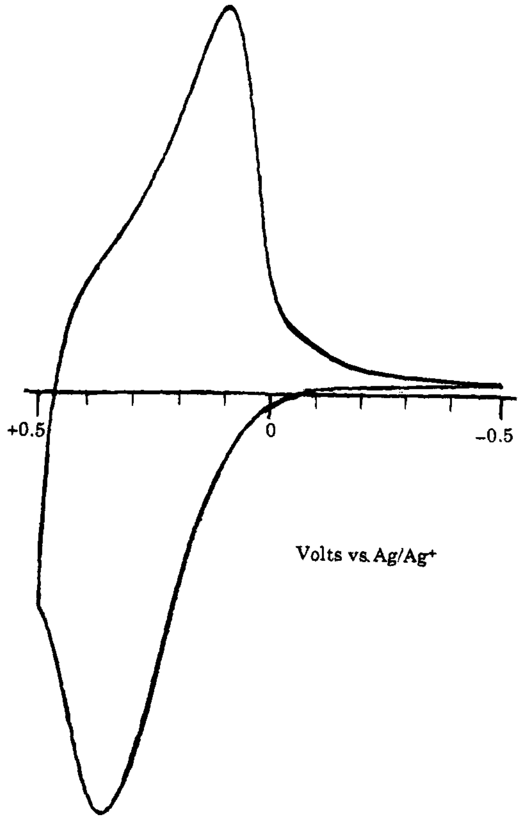


Figure 1. Cyclic voltammogram for a PDPP/ClO_4 film in acetonitrile/0.1 M $NaClO_4$. Working electrode was glassy carbon, auxiliary electrode platinum and reference electrode Ag/Ag$^+$ in DMSO. Scan rate was 50 mV/s.

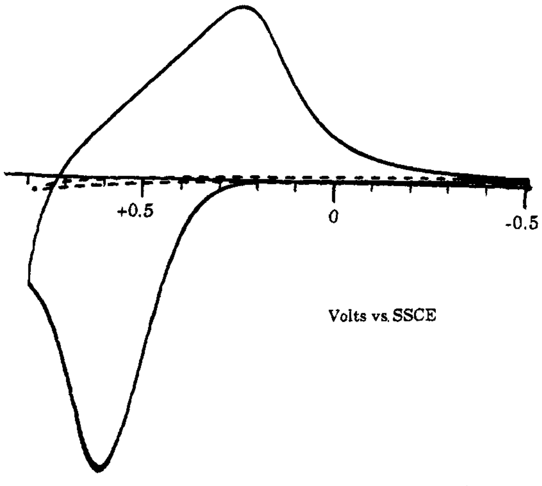


Figure 2. Cyclic voltammograms for a PDPP/ClO_4 film in contact with: aqueous/0.1 M $NaClO_4$ (dashed trace) and aqueous/0.1 M $NaClO_4$/saturated in dichloromethane (solid trace). Working electrode was glassy carbon, auxiliary electrode platinum and reference electrode an SSCE. Scan rate was 50 mV/s.

Small halocarbons appear to be unique in their ability to turn on the redox processes of PDPP in water with the exception of carbon tetrachloride which is much less soluble in water and has no dipole moment. Dichloromethane, 1,2-dichloroethane and chloroform each produced similar effects on the polymer voltammetry while carbon tetrachloride, acetone, acetonitrile, THF, benzene, toluene, and ethanol produced little or no effect at similar concentrations.

The redox response of a composite PDPP film with poly(styrenesulfonate) was also investigated in acetonitrile, water and dichloromethane-saturated water (Figures 3 and 4). The voltammetry of the composite film in acetonitrile/0.1 M $NaClO_4$ was similar to the

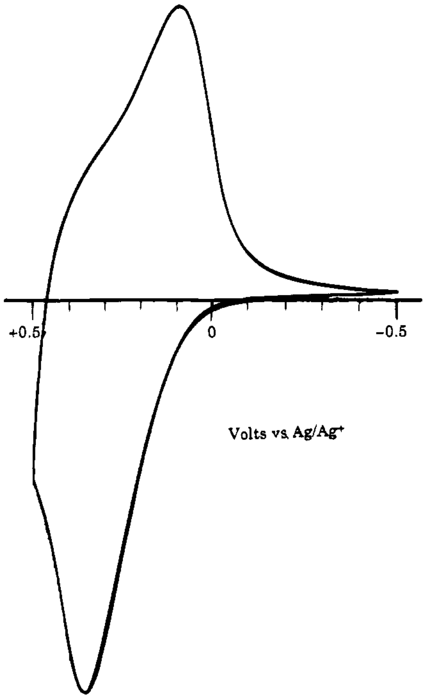


Figure 3. Cyclic voltammogram for a PDPP/PSS film in acetonitrile/0.1 M $NaClO_4$. Working electrode was glassy carbon, auxiliary electrode platinum and reference electrode Ag/Ag^+ in DMSO. Scan rate was 50 mV/s.

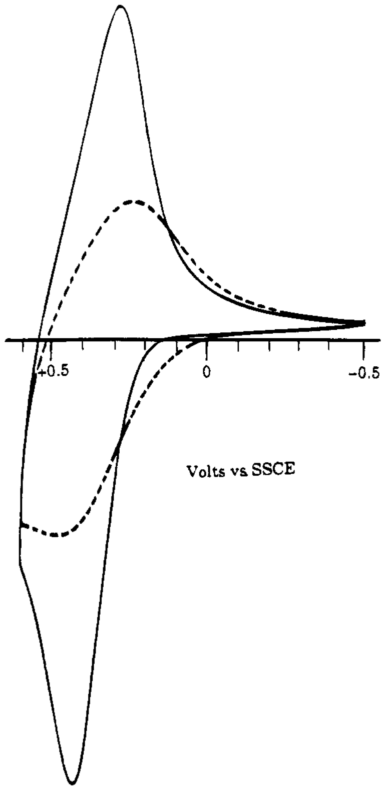


Figure 4. Cyclic voltammograms for a PDPP/PSS film in contact with: aqueous/0.1 M $NaClO_4$/pH = 1.2 (dashed trace) and aqueous/0.1 M $NaClO_4$/pH = 1.2/saturated in dichloromethane (solid trace). Working electrode was glassy carbon, auxiliary electrode platinum and reference electrode an SSCE. Scan rate was 50 mV/s.

noncomposite film, well behaved and stable to repeated cycling (Figure 3). In aqueous/0.1 M $NaClO_4$ at pH values greater than ca. 2, however, the current response slowly decreased upon potential cycling until no waves

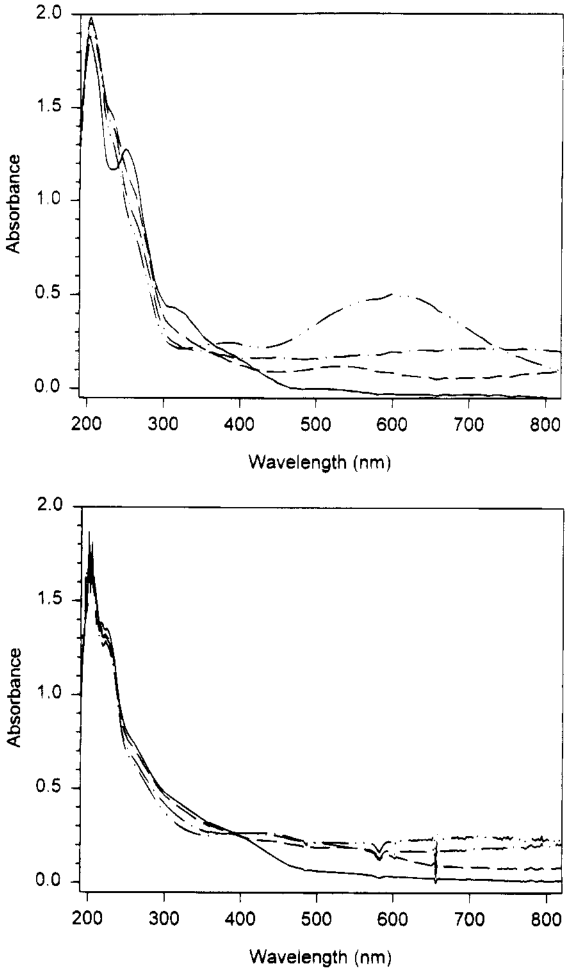


Figure 5. UV–visible spectra for PDPP/ClO_4 (top) and PDPP/PSS films (bottom) as a function of applied potential. The solution was acetonitrile/0.1 M $NaClO_4$. The working electrode was gold-coated CaF_2, auxiliary was platinum grid and reference a silver wire. In the PDPP/ClO_4 data, the spectra were acquired at potentials of −0.5 V (—), +0.5 V (– –), +0.65 V (– • –), and +0.9 V (– •• –). In the PDPP/PSS data, the spectra were acquired at potentials of −0.3 V (—), +0.3 V (– –), +0.5 V (– • –) and +0.75 V (– •• –).

were observable. At pH values less than ca. 2, redox waves were observed which were stable to repeated potential cycles, although they were much broader than those in acetonitrile (Figure 4, dashed curve). When dichloromethane was introduced into the solution of pH less than 2, the waves sharpened and the peak current increased (Figure 4, solid trace). As with noncomposite PDPP, dichloromethane can be introduced and purged repeatedly from solution and the voltammetric response will cycle between that of the solid and dashed curves, respectively, of Figure 4.

UV–Visible Spectroelectrochemistry. UV–visible spectra as a function of potential for the noncomposite and composite 3,4-diphenylpyrrole polymers are shown in Figure 5. The noncomposite film held at −0.50 V vs Ag(s) showed a sharp absorption at 252 nm and less intense absorptions at 312, 382, and 510 nm. At +0.50 V vs Ag(s), the bands at 252 and 312 nm decreased in intensity while the band at 382 nm disappeared completely. Concomitant with these losses was the formation of a new broad band centered around 550 nm. These changes are consistent with the formation of polarons in the film.[5,6] Shifting to a potential of +0.65 V vs Ag(s) further oxidized the film and marked

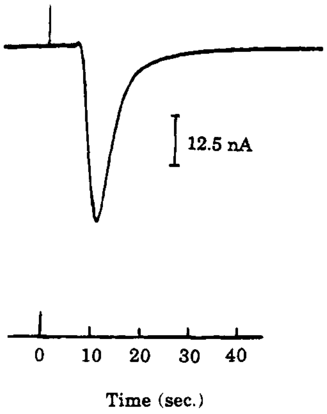


Figure 6. Current transient for a 2 mC PDPP/ClO_4 film in contact with a flowing solution of aqueous/0.1 M $NaClO_4$. Upward-going line marks the 20 μL injection of aqueous/0.1 M $NaClO_4$/saturated in dichloromethane. Working electrode was glassy carbon, auxiliary was stainless steel, and reference was Ag/AgCl. Prior to the injection, the film was equilibrated in acetonitrile/0.1 M $NaClO_4$ at 0.0 V vs Ag/Ag^+ in DMSO. The film was then transferred to the aqueous electrolyte solution and held at +375 mV vs Ag/AgCl.

the appearance of a band from ca. 700 to greater than 820 nm which indicated the onset of bipolaron production in the polymer. At an even higher oxidizing potential, +0.90 V vs Ag(s), new transitions appeared at 385 and 600 nm which are atypical of most pyrrole-based conducting polymers [i.e., polypyrrole, poly(*N*-methylpyrrole)]. It is possible that this involves the reversible oxidation of the phenyl rings. Unlike the overoxidation of polypyrrole films,[10] this oxidation step did not render the film electroinactive. The observed spectra for the PDPP/PSS composite film are similar to the noncomposite polymer except that all major bands were red shifted and were lower in intensity.

Flow-Injection Amperometry. To better understand the ability of counterions to move into and out of a PDPP film, dichloromethane-saturated aqueous electrolyte solutions were injected over a film held at constant potential. Figure 6 shows the current response of a noncomposite PDPP film which was perchlorate-doped in acetonitrile to a level required at 0.0 V vs Ag/Ag^+ in DMSO. The film was transferred to an aqueous solution 0.1 M in $NaClO_4$ and held for several minutes at a potential of +375 mV vs Ag/AgCl. Prior to injection aqueous/0.1 M $NaClO_4$ was flowing over the polymer. When the dichloromethane-saturated aqueous/0.1 M $NaClO_4$ plug (ca. 20 μL) was injected over the film, a sharp anodic current spike appeared which subsequently decayed back to zero. Serial injections showed a diminution of the magnitude of each successive current spike. Figure 7 shows the identical experiment on the same PDPP film but after the potential had been set back to +250 mV vs Ag/AgCl following injections of dichloromethane-saturated electrolyte. Notice that the dichloromethane injection under these conditions resulted in a cathodic current spike. Again, subsequent injections showed decreasing magnitudes of current response. After approximately six injections the magnitude of the current in each of the above experiments decayed to less than 4% of that for the initial injection.

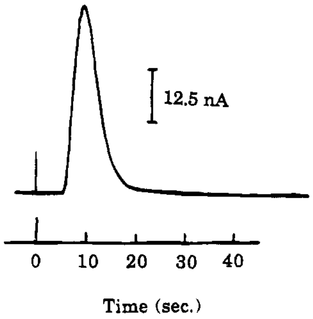


Figure 7. Current transient for same film in Figure 6 in contact with a flowing solution of aqueous/0.1 M $NaClO_4$. Upward-going line marks the 20 μL injection of aqueous/0.1 M $NaClO_4$/saturated in dichloromethane. Working electrode was glassy carbon, auxiliary stainless steel and reference Ag/AgCl. Prior to the injection, the film was equilibrated at +375 mV vs Ag/AgCl and changed to +250 mV vs Ag/AgCl.

Flow-Injection Electrochemical Quartz Microgravimetry: Undoped Film. A frequency vs time plot for a 200 nm thick reduced PDPP film is shown in Figure 8. This film was equilibrated at −0.4 V vs SSCE in acetonitrile/0.1 M $NaClO_4$ and transferred to aqueous/0.1 M $NaClO_4$ where it was held at a potential of 0.0 V vs Ag(s). Both of these potentials are sufficiently negative that the film should remain fully undoped (as evidenced by cyclic voltammetry); thus, none of the mass change considered below is due to changes in doping level of the film. At times less than ca. 10 s aqueous/0.1 M $NaClO_4$ was flowing over the film. Approximately 10 s into the run, a continuous plug of aqueous/0.1 M $NaClO_4$/saturated dichloromethane was injected over the film. At this point, the frequency decreased (i.e., mass increased) as dichloromethane was absorbed into the film. Once the mass of the film became constant (after ca. 15 s), the flow solution was changed back to aqueous/0.1 M $NaClO_4$ and the frequency increased indicating dichloromethane desorption from the film. Mass transients of this type yield information on the kinetics of absorption/desorption and equilibrium mass uptakes. For the moment, we will focus on the latter quantity.

Table 1 compares the amount of dichloromethane absorbed by the reduced forms of PDPP, poly(*N*-methylpyrrole), and poly(*N*-methylpyrrole/poly(styrenesulfonate)) as determined by EQCM.[6] As can be seen from these data, the addition of the phenyl groups to the pyrrole ring increased the absorption capacity of the reduced form of the polymer by over an order of magnitude. An explanation for this observation may lie in the data of Figure 9 in which the dichloromethane solution concentration is plotted vs dichloromethane mass uptake by a reduced PDPP film. The shape of the curve is indicative of type II, or BET, adsorption.[11] Type II adsorption describes multilayer adsorption. This behavior is in contrast to PNMP films which were characterized as adsorbing only a monolayer of dichloromethane (type I or Langmuirian isotherm).[6] This observation could reasonably account for the difference in the amount of dichloromethane absorbed by the two films. It is important to note that the frequency response of a bare quartz crystal to an aqueous/electrolyte solution saturated in dichloromethane is ca.

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(10) Beck, F.; Braun, P.; Oberst, M. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 967.

(11) Adamson, A. W. *Physical Chemistry of Surfaces*, 5th ed.; John Wiley & Sons: New York, 1990.

Table 1. Relative Amounts of Dichloromethane Absorbed into Reduced Polymer Films

polymer	thickness (nm)	DCM absorbed (μg)	g of DCM absorbed/ mol of polymer	mol of DCM/ mol of polymer
PNMP/PSS$^-$Na$^+$	240	0.78 ± 0.06	25 ± 2.0	0.294
PNMP	200	0.9 ± 0.05	11 ± 0.06	0.129
PDPP	80	1.64 ± 0.13	129 ± 10	1.52

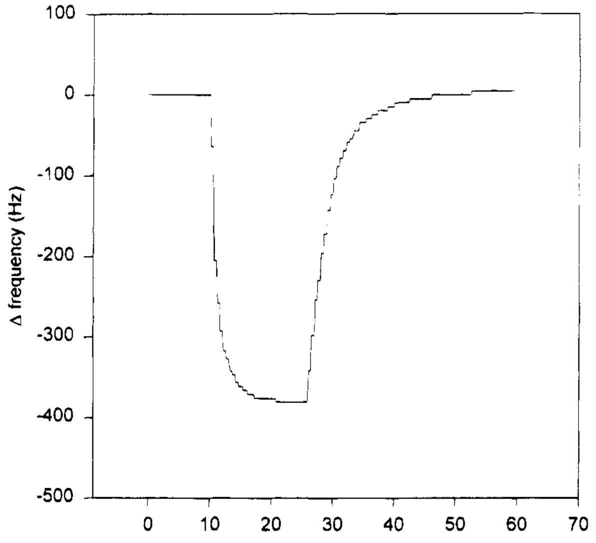

Figure 8. Frequency transient for a 200 nm thick reduced PDPP/ClO_4 film in contact with a flowing solution of aqueous/0.1 M $NaClO_4$ and injected with aqueous/0.1 M $NaClO_4$/saturated in dichloromethane. Working electrode was gold, auxiliary was platinum and reference a silver wire. The potential of the working electrode was held at 0 V.

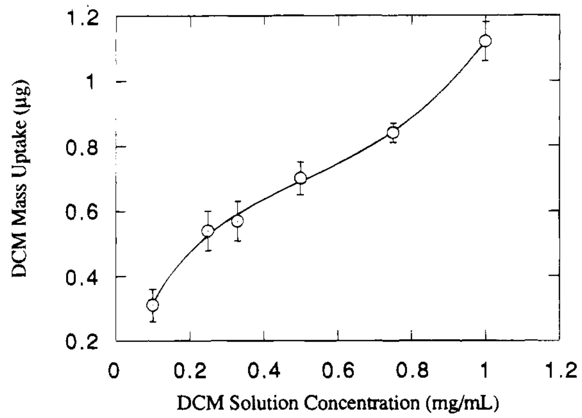

Figure 9. Plot of dichloromethane mass uptake vs dichloromethane solution concentration for a 80 nm thick reduced PDPP film. Conditions are identical to those in Figure 8.

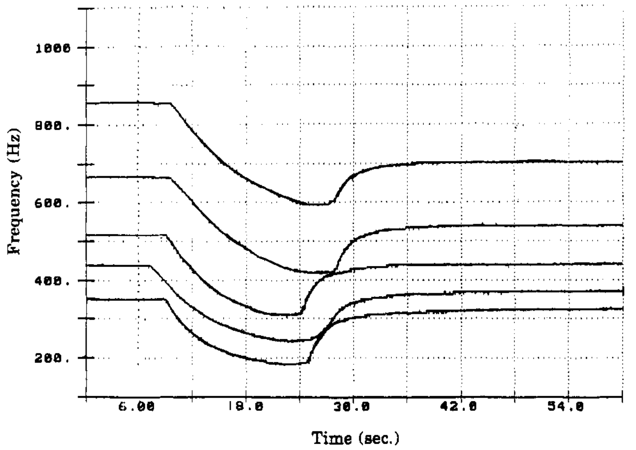

Figure 10. Absolute frequency vs time for successive injections of aqueous/0.1 M $NaClO_4$/saturated in dichloromethane over a PDPP film which was equilibrated at 0 V vs Ag(s) and switched to +0.5 V vs Ag(s) (see text for details).

10 Hz (most likely due to solution density changes). Additionally, the Sauerbrey relation was tested by monitoring mass uptake vs film thickness.[12] The plots were linear for all films investigated suggesting bulk, rather than surface adsorption, and film rigidity during absorption.

Finally, because these are bulk-sorption rather than true surface-sorption processes, characterizations such as type I or type II should not be taken too literally at the molecular level. The mathematical form of the sorption isotherm for PDPP is simply the same as that of a type II surface isotherm. While the analogy to a true two-dimensional process is imperfect, these results do imply that the sorption of dichloromethane into reduced PDPP is not sorption-site limited. A more molecular-level model of the sorption process will be presented for consideration in a later section.

Flow-Injection Electrochemical Quartz Microgravimetry: Doped Film. In the previous section the conditions considered were such that the doping level of the PDPP film did not change upon exposure to aqueous dichloromethane. In this section we consider the situation where first the film was brought to an equilibrium doping level, the solution was changed to pure aqueous electrolyte (where no measurable current flows), and then the potential was changed to a value corresponding to a different equilibrium doping level. Under these conditions, as with the amperometric data presented earlier, the frequency response to injections of dichloromethane-saturated aqueous electrolyte were history dependent. The data in Figure 10 were acquired for a PDPP film that was first equilibrated in aqueous/0.1 M $NaClO_4$ at 0.0 V vs Ag(s) (fully undoped) and then held at +0.5 V vs Ag(s). In the absence of dichloromethane, no measurable current flowed on a time scale of minutes so the film remained, initially, undoped. Figure 10 shows the frequency response when this film was alternately subjected to injections of dichloromethane-saturated aqueous electrolyte followed by pure aqueous electrolyte. Upon the initial injection of dichloromethane/electrolyte the frequency first decreased and then reached a constant value. When the flow solution was changed back to dichloromethane-free electrolyte the frequency increased, but it did not return to the initial value. With subsequent injections of dichloromethane/electrolyte the constant absolute frequency reached was smaller (i.e., higher mass) than for the previous cycle and the difference got smaller with each injection. Also the frequency hysteresis upon returning to pure electrolyte decreased with each subsequent injection, as well.[13]

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(12) Buttry, D. A. The University of Wyoming, personal communication, 1992.

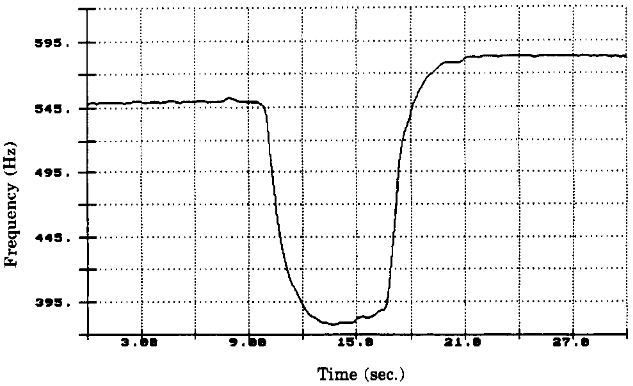

Figure 11. Frequency transient for an injection of aqueous/0.1 M $NaClO_4$/saturated in dichloromethane over a PDPP film which was equilibrated at +0.5 V vs Ag(s) and switched to 0 V vs Ag(s). (See text for details.)

Figure 11 shows the frequency response of this same film, subsequent to the above series of injections, after the potential was changed back to 0.0 V vs Ag(s) in pure electrolyte. Initially, when the potential was changed no current flowed; thus, the doping level remained the same as it was at +0.5 V vs Ag(s). When the film was then alternately exposed to dichloromethane/electrolyte followed by pure electrolyte, the final frequency in pure electrolyte was higher than before the dichloromethane/electrolyte injection indicating an overall mass loss.

Finally, it should be noted that for each change of solution a constant frequency was reached after ca. 12 s. Therefore, on the time scale of these experiments a single solution cycle was insufficient to bring the film to the full equilibrium condition. It was only after ca. 10 cycles that there was no longer a hysteresis in frequency vs time curves upon switching the solutions back and forth.

Discussion

Kinetics of Dichloromethane Adsorption into Reduced PDPP Films. We have previously developed an equation which describes pseudo-first-order adsorption kinetics for solution phase molecules binding at specific sites on a polymer chain to form sorbent-site pairs.[7] This equation is

$$1 - M_t/M_\infty = \exp(-kt) \qquad (1)$$

where M_t and M_∞ are the masses of dichloromethane adsorbed at time t, and at equilibrium, respectively; t is time, and k is the rate constant for single-site adsorption. This model was compared with a diffusional model developed by Crank assuming diffusion in a plane sheet:[14]

$$1 - M_t/M_\infty = {}^1/_4[0.81 \exp(-At) + 0.09 \exp(-9At) + 0.032 \exp(-25At)] \qquad (2)$$

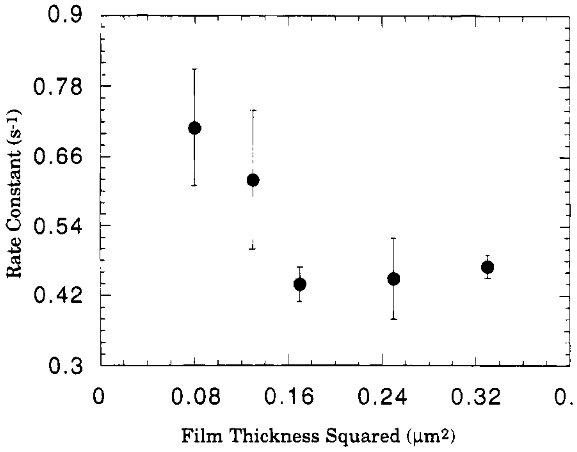

Figure 12. Rate constant of dichloromethane absorption calculated from eq 1 vs film thickness squared for five reduced PDPP films.

where

$$A = D\pi^2/L^2 \qquad (3)$$

D is the diffusion coefficient of sorbent molecules in the polymer phase and L is the film thickness. Since the diffusional model contains the film thickness while the kinetic model is thickness independent, then, to the extent that either of these are applicable, a study of the rate constant vs film thickness yields information about the rate-limiting step in the absorption.

Equations 1 and 2 were used previously to investigate the rate-limiting step in the absorption of dichloromethane into reduced poly(N-methylpyrrole) and poly(N-methylpyrrole/poly(styrenesulfonate)) films.[7] For both films, the absorption was found to be independent of thickness for film thicknesses ranging from 0.15 to 0.50 μm.

In Figure 12 the rate constant for absorption is plotted vs film thickness squared for five reduced PDPP films. For film thicknesses less than ca. 0.4 μm the rate constant decreases with increasing film thickness. Above these thicknesses, the rate constant is independent of film thickness. While the data in this figure might initially suggest that there is a transition from a case where the sorption rate is diffusion-controlled, for thin films, to one where it is site-sorption controlled, this simple interpretation appears unlikely.

First, at equilibrium saturation for a dichloromethane-saturated electrolyte solution, there are three dichloromethane molecules in the polymer for every two pyrrole units. Since eq 1 was derived assuming noninteracting sites, it is highly unlikely that this equation would bare relevance to such a high loading. Second, since the processes of diffusion into the polymer and sight binding would be sequential processes the absolute overall rates presented in Figure 12 are difficult to rationalize in a sensible way from these models. If site-binding were fast relative to diffusion for thin films, it should remain the fast relative-process for thick films since diffusional transport would be even slower (in absolute terms). Nonetheless, the quantity $1 - M_t/M_\infty$ is a good exponential function of time over approximately 4 half-lives for all of the films examined to generate Figure 12.

It is possible that morphological differences exist between thin and thicker films. These differences could be responsible for the transition from thickness-depend-

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(13) There is a slight frequency difference between the end of one cycle and the beginning of the next. This is most pronounced between the first and second cycle (ca. 35 Hz). Roughly 3 min elapsed between each cycle during which time the sample loop was refilled with solution. We speculate that this offset is due to a combination of instrument drift and some slight changes in doping level which will occur in aqueous electrolyte even in the absence of dichloromethane over long periods of time.

(14) Crank, J. *The Mathematics of Diffusion*; Clarendon: Oxford, 1956.

ent to thickness-independent sorption kinetics. Possibly thin films are denser than thick films[15] and, consequently, they might exhibit simple plane-diffusion-limited sorption. It is possible, also, to rationalize thickness independent sorption kinetics by considering a microporous structure for the polymer as we have done previously in our studies of PNMP.[7] Whatever the origins of the thickness independence of the sorption kinetics for thick films of PDPP, it is almost certainly not due to simple slow sight-binding kinetics.

Charge Trapping and Release in PDPP Films. On the basis of the voltammetry alone it is not possible to determine whether the effects of dichloromethane on the polymer are thermodynamic or kinetic in origin. In previous studies on poly(*N*-methylpyrrole) we have shown that changes in the voltammetry which occur upon introduction of dichloromethane into solution are largely due to thermodynamics.[6] Results from the flowing solution experiments (both EQCM and amperometry) indicate strongly that for the case of PDPP films the effects of dichloromethane are primarily kinetic (vide infra). This argument is supported by the fact that if sufficient time is allowed to elapse (e.g., 30 min) these films will partially dope or undope even in pure aqueous electrolyte. The presence of dichloromethane in solution, however, appears to greatly speed the process.

Proceeding with this assumption, it appears that on the time scale of the cyclic voltammetry experiment (e.g., Figure 2) in aqueous electrolyte charge cannot pass. When dichloromethane is introduced into the solution the film becomes electroactive and charge can pass into and out of the film.

The flow amperometric experiments represented in Figures 6 and 7 and the flow EQCM experiments of Figures 10 and 11 are entirely consistent with a kinetically based explanation. The current response shown in Figure 6 is entirely dependent upon the fact that the film was first equilibrated (doped) at a more negative potential than the potential applied during the current measurement and that charge did not pass at a measurable rate when the film was not exposed to dichloromethane-saturated electrolyte. Moreover, the current flow was only in one direction—in other words, under this particular set of conditions there was no re-reduction of the film once the dichloromethane plug passed out of the cell; thus, there was a net charging of the film. Likewise, in Figure 7 once the film was partially doped at a more positive potential and examined at a more negative potential the sign of the charge flow was reversed. This behavior is in sharp contrast to the behavior observed for PNMP films where the film was electroactive in both the presence and absence of dichloromethane. As can be seen from Figure 13 when dichloromethane-saturated electrolyte was injected over a PNMP film, both anodic and cathodic currents passed. Furthermore, when the current was integrated the total charge change per injection for the PNMP film was zero.

The flow EQCM experiments illustrated in Figure 10 add additional insight into the behavior of the film. With the first injection of dichloromethane-saturated electrolyte the mass of the film increased *but reached a constant value.* When the flow was changed back to pure electrolyte, as pointed out previously, there was a mass hysteresis. These results are qualitatively consistent with influx of both dichloromethane and ClO_4^- dopant ions and the efflux of only dichloromethane. The fact that the residual mass continued to increase (along with the residual charge) with each subsequent solution cycle (up to ca. 10 cycles) suggests that a single exposure to dichloromethane is not sufficient to allow the film to fully charge equilibrate. Apparently, the film must be swollen and unswollen several times to reach charge equilibrium. A schematic representation of this model is shown in Figure 14.

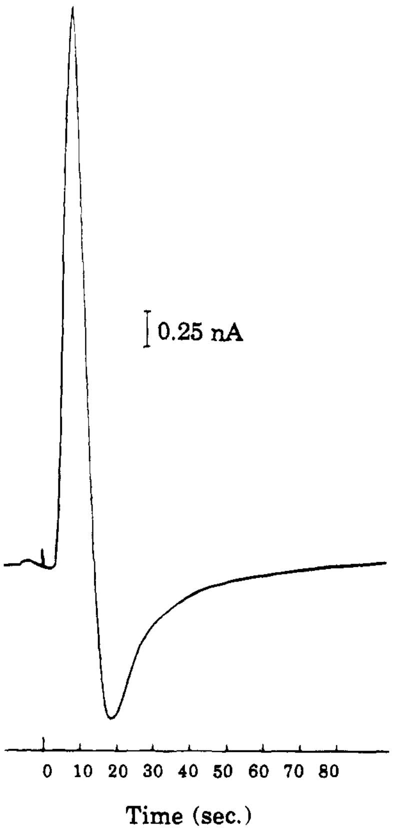

Figure 13. Current transient for a 2 mC PNMP/ClO_4 film in contact with a flowing solution of aqueous/0.1 M $NaClO_4$. Upward-going line marks the 20 μL injection of aqueous/0.1 M $NaClO_4$/saturated in dichloromethane. Working electrode was glassy carbon, auxiliary was stainless steel, and reference was Ag/AgCl. The potential of the working electrode was held at +250 mV.

A more quantitative examination of the mass data from Figure 10 reveals that the total mass increase is much larger than is required to account for the intake of sufficient ClO_4^- to compensate for the charge passed. This observation indicates that there is a net transport of other species into and out of the film: most probably water or possibly some fraction of the dichloromethane which becomes irreversibly entrapped.

Redox Behavior of PDPP/PSS Films. It is interesting to compare the voltammetric response of PDPP/PSS films with those PNMP[6] and PDPP/ClO_4 films. The voltammetry for PDPP/PSS in water would suggest that ion transport to the bulk of the film is only partially blocked (Figure 4). This accounts for the decrease in total charge passed and the broadening and separation of the anodic and cathodic current waves compared to the voltammetry in water saturated with dichloromethane. This response can be compared to the voltammetry for PNMP in which ion transport *is* observed in

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(15) Cai, Z.; Martin, C. R. *J. Electroanal. Chem.* **1991**, *300*, 35.

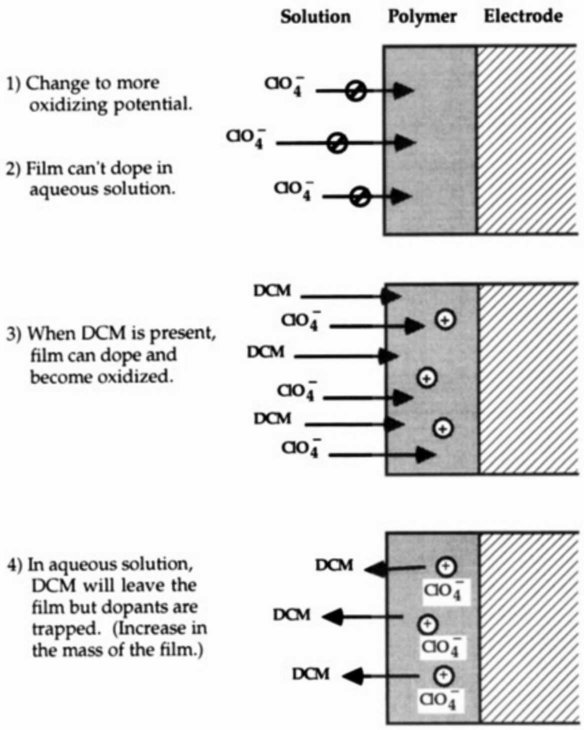

Figure 14. Schematic illustration of a model for the charge-trapping process observed in PDPP films.

water and that for PDPP in which ion transport is *completely* blocked. An explanation for the differences in the observed voltammograms for PDPP/ClO_4 and PDPP/PSS films in pure aqueous electrolyte solution may lie in the ionic compositions of each film. Films of PDPP/ClO_4 are ionic when in the oxidized form but non-ionic when reduced. Films of PDPP/PSS, however, are ionic irrespective of the oxidation state of the film. PSS^- is the counteranion to the oxidized form of PDPP, but when the PDPP is reduced the polyelectrolyte cannot leave the film. As a result sodium cations must enter the film to maintain charge balance. Upon oxidation of either film, counterions must enter or leave the film along with any associated water molecules. The ionic composition of PDPP/PSS films, both oxidized and reduced, provides a more hydrophilic environment; thus it is more likely to experience some water swelling. This environment should allow solvated dopant ions to pass more freely. Reduced PDPP films, on the other hand, provide a non-ionic, hydrophobic environment which likely does not swell in pure aqueous electrolyte. It is only when hydrophobic dichloromethane is present in solution to swell this polymer that ion transport can occur. This difference in behavior illustrates the dramatic influence that ring substitutions and the use of composite materials can have on the physical properties and, possibly, the morphology of the resulting polymer.

Conclusions

It is well established that adding ring substituents in polypyrrole or polythiophene can have a profound influence on the conductivity of these polymers.[16] Reasonably, adding or changing substituents can influence other physical and chemical properties as well, such as the sorption properties studied here. In some sense, other properties are more easily and rationally tailored in these materials than are their conductivities. We have found that increasing the lipophilic nature of polypyrrole by adding two phenyl groups to the β-positions increases, by an order of magnitude, the amount of dichloromethane which will partition into the reduced form of the polymer. In the absence of dichloromethane or some related compound, this polymer is so hydrophobic (and presumably unswollen) that it is electrochemically inactive in pure aqueous electrolyte. On the other hand, the polymer can be made hydrophilic enough to become electroactive by incorporating a polyelectrolyte anion such as poly(styrenesulfonate). The general observations presented here suggest that, by careful tailoring, it may be possible to design specific properties into conducting materials. Such specifically designed materials would have potential applications in many areas including selective sensors and separation membranes.

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