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Comparison of the Charge-Transport Rate in Two Redox Levels of Polymers Derived from *N*,*N*′-Dibenzyl-4,4′-bipyridinium and *N*,*N*′-Dialkyl-4,4′-bipyridinium

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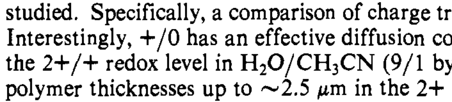
Abstract: Charge transport in electrode-confined polymers derived from *N*,*N*′-bis(*p*-(trimethoxysilyl)benzyl)-4,4′-bipyridinium dichloride, $[(BPQ^{2+/+/0})_n]_{surf}$, and *N*,*N*′-bis((trimethoxysilyl)propyl]-4,4′-bipyridinium dibromide, $[(PQ^{2+/+/0})_n]_{surf}$, has been studied. Specifically, a comparison of charge transport in the 2+/+ and +/0 redox systems of both polymers has been made. Interestingly, +/0 has an effective diffusion coefficient for charge transport, D_{CT}, that is significantly greater than that for the 2+/+ redox level in H_2O/CH_3CN (9/1 by volume) 1.0 M LiCl. Platinum disk electrodes have been studied that have polymer thicknesses up to ~2.5 μm in the 2+ state corresponding to a coverage of $\sim 7.5 \times 10^{-7}$ mol of monomer units per cm^2. Up to a 30–40% decline in thickness is observed upon reducing the polymer from the 2+ to the 0 state. Values of the products $D_{CT}C^2$, where C is the concentration of monomer units in the + or 0 state of the polymer, have been determined by measuring the current for reduction of $Ru(NH_3)_6^{3+}$ at polymer-coated rotating disks as a function of polymer coverage. The data support the conclusion that >20 mA/cm^2 can be maintained when the polymer thickness in the 2+ state is 1.0 μm, corresponding to a coverage of $\sim 2 \times 10^{-7}$ mol/cm^2 of monomers per cm^2.

We wish to report a significant difference in the charge-transport properties in the two reduction levels of polymers derived from the surface derivatizing reagents I and II. Charge transport through the polymers derived from I and II has been studied in aqueous electrolyte for the first reduction of each, $[(PQ^{2+/+})_n]_{surf}$ and $[(BPQ^{2+/+})_n]_{surf}$, respectively.[1] Such information is important as the rate of charge transport through an electrode-confined polymer derived from I or II may be current limiting in applications such as electrochromism,[2] photoassisted electrolysis of water,[3] or mediated reduction of biological molecules such as cytochrome *c*.[4] There has been relatively little study of the doubly reduced polymers derived from I and II, because the $[(PQ^0)_n]_{surf}$ and $[(BPQ^0)_n]_{surf}$ forms are not durable in aqueous electrolytes.[1] We have found conditions where the doubly reduced forms of the polymer are sufficiently durable to make measurements which establish that the polymer limited current, i_E, is about an order of magnitude larger for the second reduction level than for the first.



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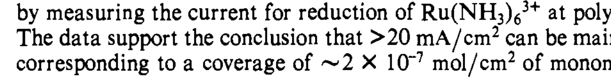

II

Charge transport in a variety of electrode-confined polymers has been studied.[5] The process can be regarded as a diffusion process where coupled electron and ion movement controls the value of the diffusion constant for charge transport, D_{CT}. When the observed steady-state current, i_{obsd}, at a polymer-modified electrode is the polymer-limited current, i_E, eq 1 relates i_{obsd} and D_{CT} where n is the number of electrons transferred, F is the Faraday constant, A is the area of the electrode, C is the concentration of charge carrier redox centers, mol/cm^3, in the polymer, Γ is the coverage of the polymer in units of moles of charge carriers per cm^2, and d is the thickness of the polymer.[5]

$$i_{obsd} = i_E = \frac{nFAD_{CT}C^2}{\Gamma} = \frac{nFAD_{CT}C}{d} \tag{1}$$

The value for C can be determined by measuring d and Γ. The difficulty, however, is that the thickness of a polymer should, a priori, be a function of the redox state of the polymer. Accordingly, i_{obsd} may vary with the redox state of the polymer because both *C and* D_{CT} are a function of redox state. We have determined i_{obsd} as a function of Γ under conditions where eq 1 applies for Pt electrodes modified with I or II, in order to determine $D_{CT}C^2$ for $[(PQ^{2+/+})_n]_{surf}$, $[(PQ^{+/0})_n]_{surf}$, $[(BPQ^{2+/+})_n]_{surf}$, and $[(BPQ^{+/0})_n]_{surf}$. Equation 1 applies in our case when the polymer is sufficiently thick and the electrode potential is sufficiently negative to hold the polymer in the + or 0 state for the mediated reduction of $Ru(NH_3)_6^{3+}$. Recent studies of M(2,2′-bipyridine)$_3^{2+}$-based polymers have shown that the more reduced polymers have a larger value of D_{CT}.[6] Our findings are similar in that the value of D_{CT} is significantly larger for the +/0 redox system than for the 2+/+ state of the polymers derived from I or II. We show additionally, however, that the value of C can change significantly with a change in redox state of the polymer. The diffusion coefficient for charge transport of Co(2,2′-bipyridine)$_3^{3+/2+}$ and Co(2,2′-bipyridine)$_3^{2+/+}$ has also been examined when these ions are electrostatically bound into Nafion films.[7] The diffusion coefficient found for the 2+/+ couple is greater than for the 3+/2+ couple, but the redox sites are not fixed as in our work or that of Murray and co-workers.[6]

Experimental Section

Materials. Reagents I and II were synthesized as previously described.[1-4] The H_2O solvent was triply distilled, and the CH_3CN was

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[1] Dominey, R. N.; Lewis, T. J.; Wrighton, M. S. *J. Phys. Chem.* **1983**, *87*, 5345.

[2] Bookbinder, D. C.; Wrighton, M. S. *J. Electrochem. Soc.* **1983**, *130*, 1080.

[3] (a) Bruce, J. A.; Murahashi, T.; Wrighton, M. S. *J. Phys. Chem.* **1982**, *86*, 1552. (b) Dominey, R. N.; Lewis, N. S.; Bruce, J. A.; Bookbinder, D. C.; Wrighton, M. S. *J. Am. Chem. Soc.* **1982**, *104*, 467.

[4] Lewis, N. S.; Wrighton, M. S. *Science (Washington, D.C.)* **1981**, *211*, 944.

[5] Pickup, P. G.; Murray, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 4510 and references therein.

[6] (a) Leidner, C. R.; Denisevich, P.; Willman, K. W.; Murray, R. W. *J. Electroanal. Chem.*, in press. (b) Pickup, P.; Kutner, W.; Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1991.

[7] Buttry, D. A.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 685.

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HPLC grade. The supporting LiCl electrolyte was reagent grade and used as received from commercial sources. $[Ru(NH_3)_6]Cl_3$ was used as received from Strem Chemical Co.

Electrodes. Pt disk electrodes, 4 mm in diameter and 0.2 mm thick, were used in all of the studies and configured for use as rotating disks as described elsewhere.[1] The Pt disks were pretreated prior to derivatization with I or II according to a published procedure.[8] Derivatization with I or II was carried out by cycling the potential of a pretreated Pt electrode linearly at 100 mV/s between 0.0 V vs. SCE and −0.7 V vs. SCE in an aqueous electrolyte (buffered to pH 8.9 with phosphate) solution containing 1–2 mM of I or II under N_2 or Ar.[1,2] Such solutions were used as soon as possible after preparation in order to reduce complications from polymerization of I or II. The cycling was continued until the integration of charge passed on a cycle showed approximately the desired coverage. The electrode was then removed from the derivatizing solution and dried. The coverage, Γ, was determined for each electrode by a slow potential scan from 0.0 to −0.7 V vs. SCE in aqueous 1.0 M LiCl while monitoring current for the $[(PQ^{2+})_n]_{surf} \rightarrow [(PQ^{+})_n]_{surf}$ or $[(BPQ^{2+})_n]_{surf} \rightarrow [(BPQ^{+})_n]_{surf}$ reduction.

For correlations of Γ and thickness d, smooth Au-coated glass slides or Pt flag electrodes were derivatized in a manner that would allow measuring the value of d by using a Sloan Dektak surface profile measuring system. This was accomplished by derivatizing an electrode partially coated with wax. The wax could be dissolved in an organic solvent after the derivatization procedure to produce a "step" of height d on the electrode surface. The value of d was measured in both the dry and wet state with less than a 15% difference in d. Selected surfaces having a step were examined by electron microscopy to confirm the value of d determined with the Dektak device. A spherical diamond tip stylus (4×10^{-4} cm diameter, 50-mg head pressure) was used in all measurements of thickness when using the Dektak device.

The thickness of $[(BPQ^{2+/+/0})_n]_{surf}$ was also measured at each of the three redox levels, 2+, +, and 0 by preparing modified electrodes that could be examined in situ by using the Dektak device. The electrochemical cell consisted of a smooth Au-coated glass slide partially modified with reagents I or II. The remaining, naked portion of the Au-coated slide was electrically insulated from the rest of the slide by scratching a line through the thin gold coating. This uncoated portion of the Au-coated slide was used as the counterelectrode. A Ag-wire quasi-reference electrode was positioned about 1 mm above the electrode surface. The solvent was confined to the surface cell by a ring of epoxy around the edge of the Au-coated slide. The stylus of the Dektak was then placed on the stationary polymer-coated surface, and its response was measured as the electrode potential was stepped to effect $2+ \rightleftarrows +$, $+ \rightleftarrows 0$, or $2+ \rightleftarrows 0$ interconversions. Alternatively, the electrode potential was cycled linearly in time from −0.3 to −1.1 V vs. SCE while recording stylus response associated with the $2+ \rightleftarrows + \rightleftarrows 0$ interconversions. The solvent/electrolyte was H_2O/CH_3CN (9/1) containing 1.0 M LiCl. Exclusion of O_2 is necessary to preserve the polymer in the + or 0 state, and all experiments were carried out under N_2, but, nonetheless, lifetime of the polymer is limited in such experiments because O_2 could not be completely excluded.

Procedures. Pt disk electrodes bearing $[(PQ^{2+})_n]_{surf}$ or $[(BPQ^{2+})_n]_{surf}$ were studied in deoxygenated solutions of 1.0 M LiCl by using H_2O/CH_3CN (9/1 by volume) as the solvent. The CH_3CN suppresses H_2 evolution from Pt and improves the durability of $[(PQ^0)_n]_{surf}$ and $[(BPQ^0)_n]_{surf}$. Steady-state current potential curves were recorded as a function of rotation velocity and polymer coverage in the presence of $[Ru(NH_3)_6]Cl_3$ in order to measure i_{obsd} for the mediated reduction of $Ru(NH_3)_6^{3+}$.

Results and Discussion

Pt electrodes derivatized with I or II show persistent electrochemical response consistent with the interconversions represented by eq 2 and 3 in H_2O/CH_3CN (9/1 by volume) solutions of 1.0 M LiCl. Figure 1 shows typical cyclic voltammograms for a

$$[(PQ^{2+})_n]_{surf} \underset{-ne^-}{\overset{+ne^-}{\rightleftarrows}} [(PQ^{+})_n]_{surf} \underset{-ne^-}{\overset{+ne^-}{\rightleftarrows}} [(PQ^{0})_n]_{surf} \quad (2)$$

$$[(BPQ^{2+})_n]_{surf} \underset{-ne^-}{\overset{+ne^-}{\rightleftarrows}} [(BPQ^{+})_n]_{surf} \underset{-ne^-}{\overset{+ne^-}{\rightleftarrows}} [(BPQ^{0})_n]_{surf} \quad (3)$$

$Pt/[(PBQ^{2+/+/0})_n]_{surf}$ electrode as a function of sweep rate. The fact that is interesting in connection with the present study is that the second reduction wave at ca. −0.9 V vs. SCE is somewhat sharper, with a larger peak current at the highest sweep rate compared to the first reduction at ca. −0.5 V vs. SCE. It was the observation of the disparate behavior for the two redox levels of the polymers from I and II that led us to measure the charge-transport properties of the two redox levels.

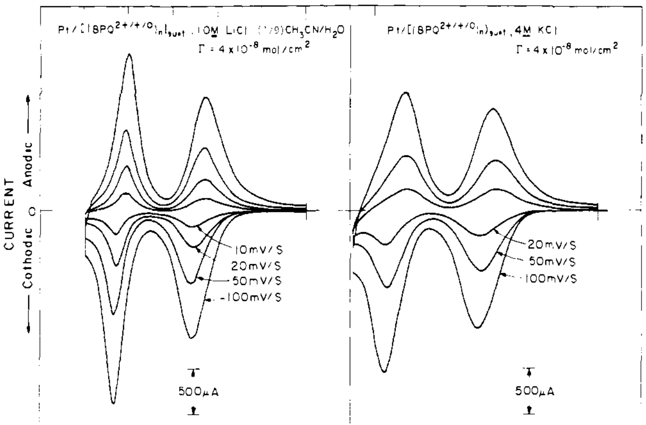
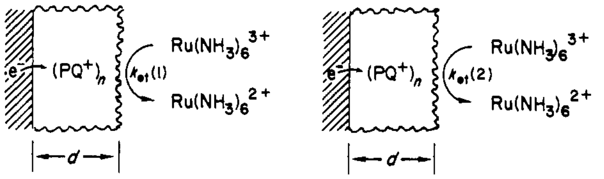


Figure 1. Typical scan-rate dependence of the cyclic voltammetric response of derivatized Pt electrodes. Data are shown for two different solvent/electrolyte systems for the same electrode: 1.0 M LiCl in H_2O/CH_3CN (9/1 by volume) and 4 M KCl in H_2O.

Scheme I. Mediated Reduction of $Ru(NH_3)_6^{3+}$ by Singly or Doubly Reduced Polymer from I



The electrochemical response of the modified electrodes does change somewhat upon variation in the medium. As shown in Figure 1, the cyclic voltammetry for a given electrode shows somewhat sharper waves in $H_2O/CH_3CN/1.0$ M LiCl than in $H_2O/4.0$ M KCl. Variation of this kind is expected, but the more significant consequence of adding CH_3CN to the solvent is that the half time for decay of $[(PQ^0)_n]_{surf}$ or $[(BPQ^0)_n]_{surf}$ is changed from ~1/2 h[1] to >3 h. Thus, the use of the H_2O/CH_3CN solvent system allows study of the doubly reduced polymers. Additionally, CH_3CN suppresses H_2 evolution at Pt and allows the use of more negative potentials to study the polymer than is possible with pure aqueous media.

In order to investigate the charge-transport properties of the polymers we have measured the current, i_{obsd}, associated with reduction of $Ru(NH_3)_6^{3+}$ at rotating Pt disk electrodes modified with polymers from I and II. In all cases reported here, we have used the $H_2O/CH_3CN/1.0$ M LiCl solvent/electrolyte system for the reasons cited above. The basic strategy is to effect the mediated reduction of $Ru(NH_3)_6^{3+}$ at the outermost surface of the singly or doubly reduced polymer, Scheme I, under conditions where i_{obsd} is controlled by the charge-transport rate through the polymer where equation 1 applies. $Ru(NH_3)_6^{3+}$ is chosen as an oxidant for several reasons: (i) it does not appear to diffuse through the polymer to be reduced at the Pt surface; (ii) the singly or doubly reduced polymers are capable of reducing $Ru(NH_3)_6^{3+}$ on thermodynamic grounds; (iii) at least the rate for reduction by the singly reduced polymer should be fast; the value of $k_{et}(1)$ is $>10^5$ M^{-1} s^{-1} for aqueous electrolytes;[1] and (iv) the solubility and durability of the $Ru(NH_3)_6^{3+/2+}$ couple are sufficient to make the measurements desired.

When the polymer is sufficiently thin and/or the concentration of $Ru(NH_3)_6^{3+}$ is sufficiently low, the value of i_{obsd} is controlled by the rate at which $Ru(NH_3)_6^{3+}$ becomes available at the surface. This conclusion is drawn from measuring i_{obsd} for a rotating disk electrode. When i_{obsd} for the reduction of $Ru(NH_3)_6^{3+}$ is recorded

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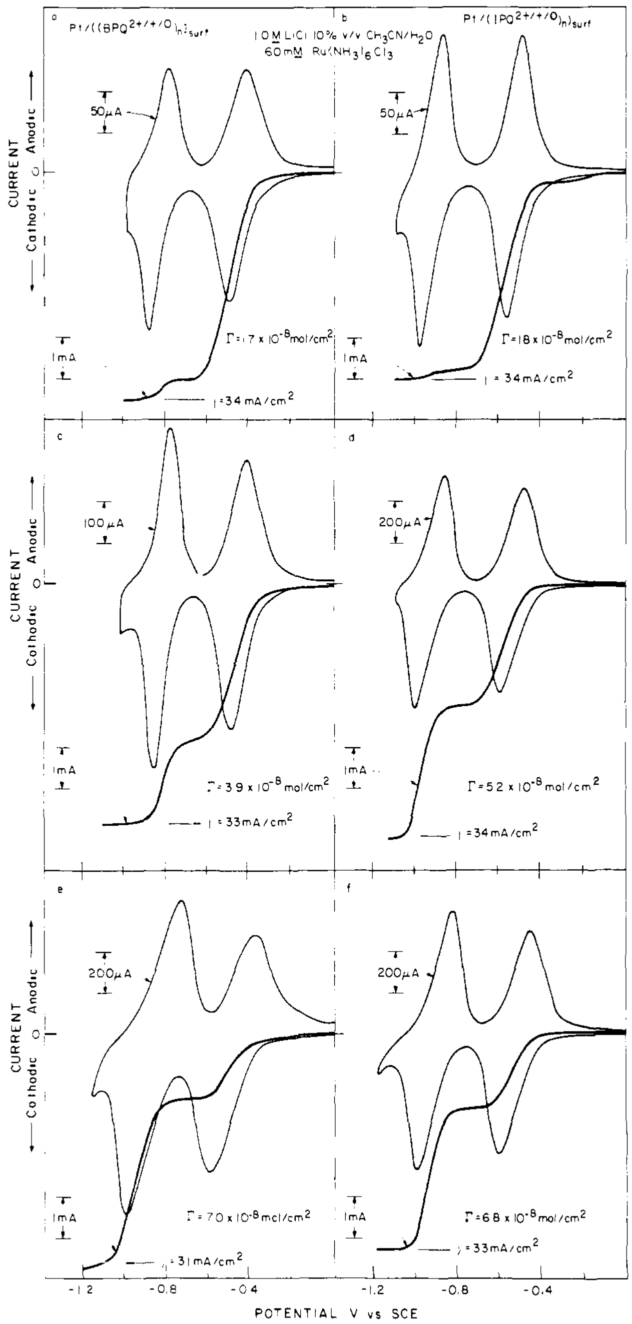

Figure 2. Polymer coverage dependence of the cyclic voltammetry of Pt/[$(BPQ^{2+/+/0})_n$]$_{surf}$ and Pt/$(PQ^{2+/+/0})_n$]$_{surf}$ disk electrodes at 100 mV/s sweep rate (no added $Ru(NH_3)_6^{3+}$) and of the steady-state current–potential behavior at a rotation velocity of 2500 rpm ($\omega^{1/2} \approx 16$ s$^{-1/2}$) in the presence of 60 mM $Ru(NH_3)_6^{3+}$. Note that the mass transport limited current is 31–34 mA/cm^2 and that at the lowest coverages this current is obtained (or nearly so) just negative of the first reduction of the polymer. However, at the higher coverages the steady-state current is lower than mass transport limited just negative of the first reduction but is at the mass transport limit just negative of the second reduction.

for a rotating Pt/[$(PQ^{2+/+/0})_n$]$_{surf}$ or Pt[$(BPQ^{2+/+/0})_n$]$_{surf}$ electrode, i_{obsd} is directly proportional to (rotation velocity)$^{1/2}$, $\omega^{1/2}$, when (i) the electrode is held >70 mV negative of $E^{\circ\prime}$ for [$(PQ^{2+/+})_n$]$_{surf}$ or [$(BPQ^{2+/+})_n$]$_{surf}$ and (ii) the polymer is thin and/or the $Ru(NH_3)_6^{3+}$ concentration is low.[1] It is the strict linearity of plots of i_{obsd} vs. $\omega^{1/2}$ that establishes that reduction of the $Ru(NH_3)_6^{3+}$ is mass transport limited. Figure 2 illustrates the cyclic voltammetry response in the absence of $Ru(NH_3)_6^{3+}$ and the steady-state current–potential curves for a rotating disk ($\omega^{1/2} = 16$ s$^{-1/2}$) in the presence of 60 mM $Ru(NH_3)_6^{3+}$. In all cases shown, the mass transport limited current density is obtained at the most negative potential. However, only in a and b is the polymer thin enough to allow the reduction of $Ru(NH_3)_6^{3+}$ to be mass transport limited (or nearly so) via mediation by the singly reduced polymers. For the larger coverages of polymer the mediated reduction via the doubly reduced polymer remains at the mass transport limit, whereas mediation via the singly reduced polymer clearly occurs at a rate less than the mass transport limit. At the highest coverage shown, 7 × 10^{-8} mol/cm^2, the singly reduced polymer seriously impedes the reduction compared to the doubly reduced polymer, since the steady-state current at ca. −0.7 V vs. SCE (where the surface species is only [$(PQ^+)_n$]$_{surf}$ or [$(BPQ^+)_n$]$_{surf}$) is approximately one-third of that at ca. −1.1 V vs. SCE (where the surface species is only [$(PQ^0)_n$]$_{surf}$ or [$(BPQ^0)_n$]$_{surf}$). $E^{\circ\prime}$ for the $Ru(NH_3)_6^{3+/2+}$ couple is ca. −0.2 V vs. SCE; the lack of a cathodic current onset near this potential is consistent with the conclusion that $Ru(NH_3)_6^{3+}$ does not penetrate the [$(PQ^{2+})_n$]$_{surf}$ or [$(BPQ^{2+}]_n$]$_{surf}$ polymers.

Because the onset of H_2O reduction is just negative of the second reduction wave of [$(PQ^{2+})_n$]$_{surf}$ and [$(BPQ^{2+})_n$]$_{surf}$, it is difficult to experimentally determine, in aqueous or partially aqueous solution, if solution redox species can penetrate through the polymer coatings in their fully reduced and neutral states, [$(PQ^0)_n$]$_{surf}$ and [$(BPQ^0)_n$]$_{surf}$. However, rotating disk studies at Pt/[$(BPQ^{2+})_n$]$_{surf}$ in CH_3CN/0.1 M [n-Bu_4N]ClO_4 containing either $Ru(bpy)_3^{2+}$ or $Co(\eta^5\text{-}C_5H_5)_2^+$ have demonstrated that neither of these species is reduced at Pt/[$(BPQ^{2+})_n$]$_{surf}$ at significant rates compared to our observations made for $Ru(NH_3)_6^{3+}$ in H_2O/CH_3CN solutions. Because the reduction potentials for $Ru(bpy)_3^{2+}$ and $Co(\eta^5\text{-}C_5H_5)_2^+$ are negative of the second reduction potential for [$(BPQ^{2+})_n$]$_{surf}$ or [$(PQ^{2+})_n$]$_{surf}$, permeation of these cations through the neutral film is the only possible mechanism for their reduction. Thus, the lack of reduction indicates insignificant diffusion through the neutral polymer. It is unlikely, therefore, that the more highly charged cation, $Ru(NH_3)_6^{3+}$, would penetrate the neutral, presumably more hydrophobic, polymer coatings. The measurements for $Ru(bpy)_3^{2+}$ and $Co(\eta^5\text{-}C_5H_5)_2^+$ have been made at a polymer coverage where the reduction of $Ru(NH_3)_6^{3+}$ in H_2O would be significantly limited by charge transport in the polymer, i.e., coverages greater than 5 × 10^{-8} mol/cm^2.

The fact that a mass transport limited reduction of low concentrations of $Ru(NH_3)_6^{3+}$ can be effected at $\omega^{1/2} = 16$ s$^{-1/2}$ for derivatized electrodes of modest coverage held at −0.7 or −1.1 V vs. SCE means that both $k_{et}(1)$ and $k_{et}(2)$ (cf. Scheme I) exceed 10^5 M^{-1} s^{-1}. This argument follows from the strict linearity of a plot of i_{obsd} vs. $\omega^{1/2}$ up to $\omega^{1/2} = 16$ s$^{-1/2}$ (highest rotation rate used).[9] The fact that i_{obsd} can fall below the mass transport limit by increasing the $Ru(NH_3)_6^{3+}$ concentration or by increasing polymer coverage is consistent with the conclusion that the charge-transport rate through the polymer can limit i_{obsd}. In such a situation the observed current, i_{obsd}, is given by eq 4[10] where i_l is the mass transport limited current due to $Ru(NH_3)_6^{3+}$ reduction at a bare electrode of equal area, i_k is the kinetic current associated with the rate constants $k_{et}(1)$ and $k_{et}(2)$, and K is the equilibrium constant for the polymer–substrate cross reaction (Scheme I) given by $(RT/F) \ln K = E^0/(Ru(NH_3)_6^{3+/2+}) - E^{\circ\prime}$ (polymer). Values

$$\frac{1}{i_{obsd}} = \frac{1}{i_E} + \frac{1}{i_l} + \frac{1}{i_k} + \left(\frac{1}{K} - 1\right)\frac{i_{obsd}}{i_l i_E} \tag{4}$$

of K for the mediated reduction of $Ru(NH_3)_6^{3+}$ at [$(PQ^{2+})_n$]$_{surf}$ and [$(BPQ^{2+})_n$]$_{surf}$ are greater than 10^4 for the singly reduced polymers and even larger, >10^{10}, for the doubly reduced polymers, allowing simplification of eq 4 to eq 5.

$$\frac{1}{i_{obsd}} = \frac{1}{i_E} + \frac{1}{i_k\left(1 - \dfrac{i_{obsd}}{i_l}\right)} \tag{5}$$

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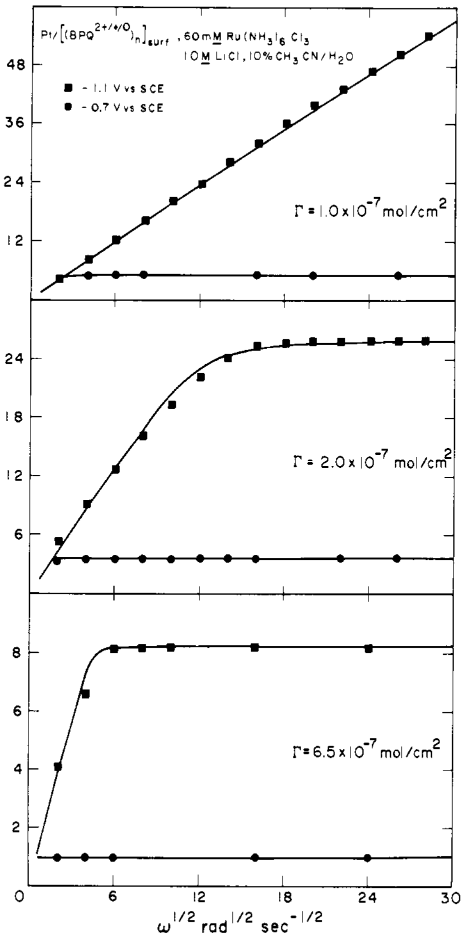

Figure 3. Comparison of the measured current density, *j*, as a function of $\omega^{1/2}$ and surface coverage, Γ, at $Pt/[(BPQ^{2+})_n]_{surf}$ with current density calculated (smooth curves) from eq 5 (see text). Experimental points were determined in H_2O/CH_3CN (9/1 by volume) with 1.0 M LiCl, containing 60 mM $[Ru(NH_3)_6]Cl_3$. Squares (■) and circles (●) correspond to the doubly and singly reduced polymer. The smooth curves were obtained by using eq 5 with i_k = 2000 mA/cm^2 and $D(Ru(NH_3(_6{}^{3+})$ = 4.5×10^{-6} cm^2/s. The values of i_E were calculated from eq 1 by using $D_{CT}C^2$ values from Table I.

Figure 3 shows plots of i_{obsd} vs. $\omega^{1/2}$ for $Pt/[(BPQ^{2+/+/0})_n]_{surf}$ rotating disk electrodes for the mediated reduction of 60 mM $Ru(NH_3)_6{}^{3+}$. Data for three different electrodes having different amounts of polymer are shown and in each case data are given for the electrode held at −0.7 and −1.1 where the polymer is in the $[(BPQ^+)_n]_{surf}$ and $[(BPQ^0)_n]_{surf}$ state, respectively. Clearly, and consistent with the data in Figure 2, the $[(BPQ^0)_n]_{surf}$-mediated reduction gives rise to larger values of i_{obsd} compared to the $[(BPQ^+)_n]_{surf}$-mediated current. Further, the data show that higher coverages of polymer give lower values of i_{obsd}.

Figure 4 summarizes a more complete set of data, giving observed current density at $\omega^{1/2} = 16$ s$^{-1/2}$ vs. polymer coverage for mediated reduction of $Ru(NH_3)_6{}^{3+}$ at polymer-modified rotating disk electrodes where polymer coverage has been varied over a wide range and for both polymers. Data are given for reduction via $[(BPQ^+)_n]_{surf}$ and $[(PQ^+)_n]_{surf}$ when a derivatized electrode is held at −0.7 V vs. SCE and for reduction via $[(BPQ^0)_n]_{surf}$ and $[(PQ^0)_n]_{surf}$ when a derivatized electrode is held at −1.1 V vs. SCE. The smooth curves in Figure 4 are calculated current densities from eq 1 and 5 as a function of $D_{CT}C^2$ and Γ for an electrode of an area that would give a mass transport limited current of i_l = 32 mA/cm^2 at $\omega^{1/2} = 16$ s$^{-1/2}$ without polymer or kinetic limitations. A kinetic current of i_k = 2000 mA/cm^2 yields good agreement between calculated and observed currents for the mediated reduction of $Ru(NH_3)_6{}^{3+}$ via both singly and doubly reduced $[(PQ^{2+})_n]_{surf}$ and $[(BPQ^{2+})_n]_{surf}$ polymer-modified electrodes, although reasonably good fits could be obtained by using i_k = 500–5000 mA/cm^2, Figure 5. Taking i_k = 2000 mA/cm^2, the bimolecular rate constants for the electron-transfer cross reactions in Scheme I, $k_{et}(1)$ and $k_{et}(2)$, can be estimated from eq 6,[10] where $\Gamma°$ is the surface coverage of one monolayer at the polymer solution interface. Assuming a value of $\Gamma° = 10^{-10}$

$$i_k = C_{Ru(NH_3)_6{}^{3+}} k_{et} A F \Gamma° \qquad (6)$$

mol/cm^2, $k_{et}(1)$ and $k_{et}(2)$ are $\geq 10^6$ M^{-1} s^{-1}. Our lower limit of 10^5–10^6 M^{-1} s^{-1} for $k_{et}(1)$ and $k_{et}(2)$ from mediated reduction at low $Ru(NH_3)_6{}^{3+}$ concentration is thus in accord with the value of i_k = 2000 mA/cm^2. As expected, the consequence of fast kinetics at the polymer–solution interface is that the calculations based on eq 5 are not strongly affected by the value of i_k at moderate and large surface coverage. Thus, the calculated curves in Figure 4 are, at $\Gamma > 2 \times 10^{-7}$ mol/cm^2, essentially independent of changes in i_k, Figure 5. The product $D_{CT}C^2$ was thus determined from the i_{obsd} values in the range $2 \times 10^{-7} < \Gamma < 8 \times 10^{-7}$ mol/cm^2. Table I summarizes the essential findings for the polymers derived from I or II. The smooth curves in Figure 3 represent calculated i_{obsd} vs. $\omega^{1/2}$ values using $D_{CT}C^2$ and i_k = 2000 mA/cm^2. The close fit between calculated and measured i_{obsd} for all ω, three coverage, and both redox levels of the polymer allow us to conclude that eq 5 applies to this situation.

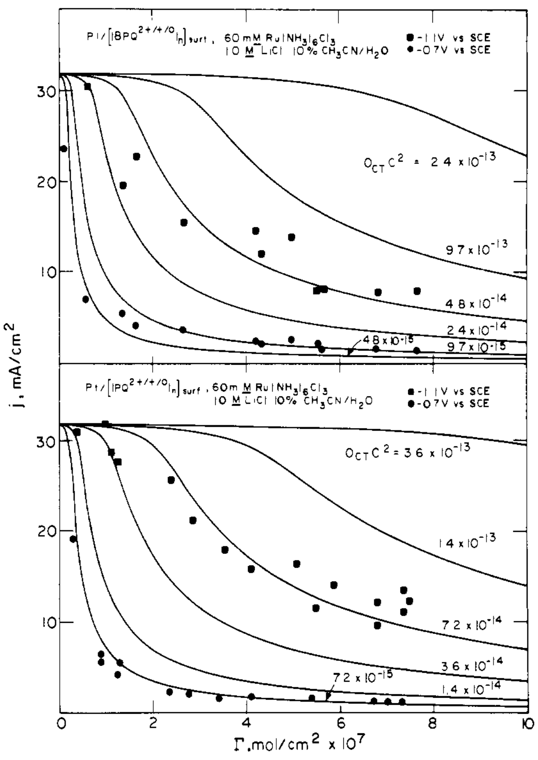

Figure 4. Comparison of the measured current density, *j*, vs. polymer coverage, Γ (data points), at $Pt/[(BPQ^{2+})_n]_{surf}$ and $Pt/[(PQ^{2+})_n]_{surf}$ rotating disk electrodes ($\omega^{1/2}$ = 16 s$^{-1/2}$) with those calculated (smooth curves) assuming different values of $D_{CT}C^2$. Experimental points were determined in H_2O/CH_3CN (9/1 by volume) with 1.0 M LiCl, containing 60 mM $[Ru(NH_3)_6]Cl_3$. Squares (■) and circles (●) correspond to the doubly and singly reduced polymers, respectively. The theoretical curves werre obtained by using eq 5 for a situation where the mass transport limited current would be 32 mA/cm^2 and i_k = 2000 mA/cm^2. Values of $D_{CT}C^2$ are given for each theoretical curve.

Table I. Summary of Relevant Properties of Polymers Derived from I or II[a]

system	$E°'$, V vs. SCE	$D_{CT}C^2$, mol^2/(s cm^4)[b]
$[(BPQ^{2+/+})_n]_{surf}$	−0.48 ± 0.05	7.3×10^{-15}
$[(BPQ^{+/0})_n]_{surf}$	−0.86 ± 0.05	4.8×10^{-14}
$[(PQ^{2+/+})_n]_{surf}$	−0.55 ± 0.05	7.2×10^{-15}
$[(PQ^{+/0})_n]_{surf}$	−0.95 ± 0.05	7.2×10^{-14}

[a] All data are for H_2O/CH_3CN (9/1) 1.0 M LiCl solutions for Pt electrodes modified with I or II. Cf. Figure 3. [b] Estimated error is ±30%.

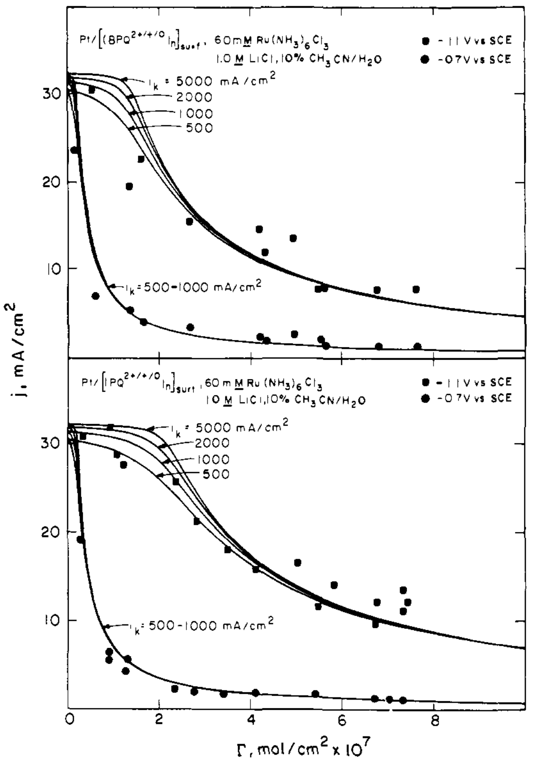

Figure 5. Comparison of the measured current density, j, vs. polymer coverage, Γ (data points), at Pt/[$(BPQ^{2+})_n$]$_{surf}$ and Pt/[$(PQ^{2+})_n$]$_{surf}$ rotating disk electrodes ($\omega^{1/2} = 16\ s^{-1/2}$) with those calculated (smooth curves) assuming different value of i_k. Experimental points were obtained in H_2O/CH_3CN (9/1 by volume) with 1.0 M LiCl, containing 60 mM $Ru(NH_3)_6Cl_3$. Squares (■) and circles (●) correspond to the doubly and singly reduced polymers, respectively. The theoretical curves were obtained by using eq 5 for a situation where the mass transport limited current would be 32 mA/cm^2. Values of $D_{CT}C^2$ used in the calculation of i_E were taken from Table I. Values of i_k are given for each theoretical curve.

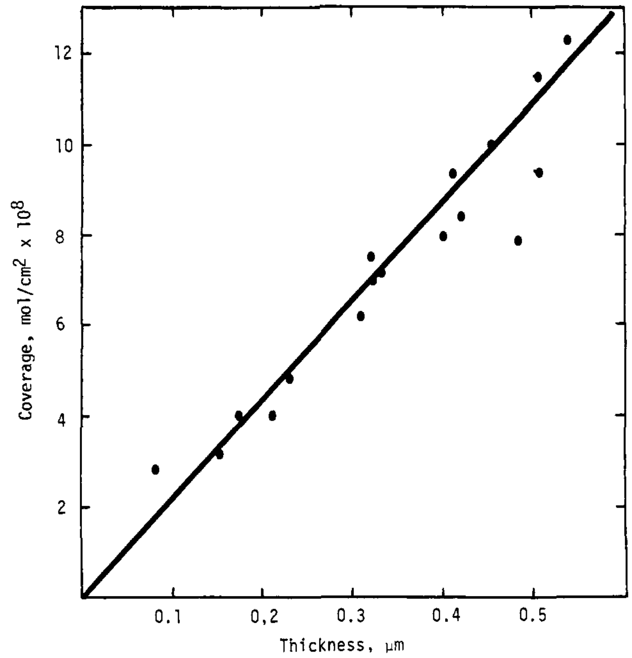

Figure 6. Correlation of polymer coverage from electrochemical determination and film thickness measured by using a surface profile measuring device for the [$(BPQ^{2+}\cdot 2Cl^-)_n$]$_{surf}$ system.

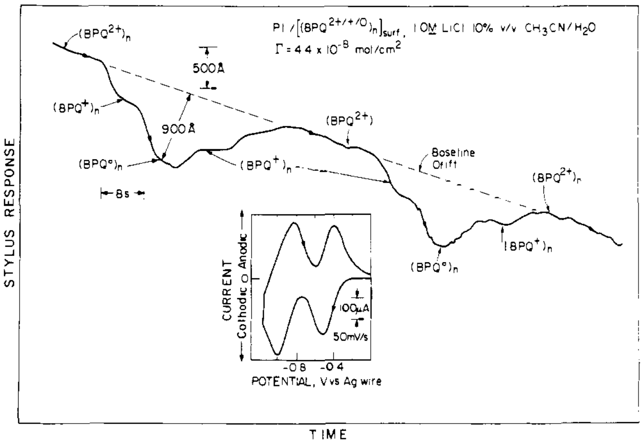

Figure 7. Change in the thickness of the [$(BPQ^{2+})_n$]$_{surf}$ polymer upon reduction to [$(BPQ^+)_n$]$_{surf}$ and to [$(BPQ^0)_n$]$_{surf}$ measured by using a Dektak surface profile device. The inset shows a cyclic voltammogram for the electrode characterized. The plot of stylus response vs. time during two cyclic voltammograms is shown.

The quantitative measurement of $D_{CT}C^2$ values for [$(BPQ^{2+})_n$]$_{surf}$ and [$(PQ^{2+})_n$]$_{surf}$ in their doubly reduced states by the mediation experiments described above is complicated by the fact that a small portion of the polymer film nearest to the solution must exist in the fully oxidized, 2+, form. This gives rise to a more complicated set of concentration profiles for the 2+, +, and 0 states of the polymer than during the mediation to $Ru(NH_3)_6^{3+}$ via the singly reduced polymers. Because the observed values of $D_{CT}C^2$ are considerably larger (×10) for the doubly reduced polymer we expect that only a small fraction of the film exists in the 2+ form during the mediated reduction of $Ru(NH_3)_6^{3+}$ via the doubly reduced polymers and that neglecting this complication, at worst, causes our $D_{CT}C^2$ values (Table I) for the *doubly reduced polymers* to be somewhat lower than the true value.

The significant finding revealed by the data in Figures 3 and 4 is that $D_{CT}C^2$ for the fully reduced polymers is ~10 times larger than for the one-electron reduced state. In order to determine a value for D_{CT} it is necessary to determine C in each of the redox states of the polymers. The value of C can be determined by measuring the thickness d and the coverage Γ. This is most easily done for the fully oxidized polymers. The relationship between polymer coverage, Γ, and d is illustrated in Figure 6 for the [$(BPQ^{2+})_n$]$_{surf}$ system. The fact that there is a linear relationship between Γ and d and that the line passes through the origin is consistent with the conclusion that rather uniform films of polymer can be deposited. Examination of polymer film surfaces by microscopy does reveal texture not apparent to the unaided eye, but the point is that there are apparently not large variations in d over a surface of macroscopic dimensions. Data like that in Figure 6 can also be obtained for electrodes immersed in H_2O; the value of d does not vary by more than 15% for the wet vs. dry state of the polymer. Thus, from the data in Figure 6, the value of C can be calculated and is 2.2 ± 0.2 M. Similar measurements for the [$(PQ^{2+})_n$]$_{surf}$ system have been made[2] and give a value for C of 3.0 ± 0.3 M.

The value of d for the one-electron and two-electron reduced polymers has been measured by actually following the stylus response of a surface profilometer as a function of electrode potential. Figure 7 shows the type of data that can be obtained for an electrode functionalized with II. In this case the [$(BPQ^{2+})_n$]$_{surf}$ → [$(BPQ^+)_n$]$_{surf}$ conversion results in a diminution of ~300 ± 100 Å, and further reduction to [$(BPQ^0)_n$]$_{surf}$ results in an additional shrinkage of ~600 ± 100 Å. Thus, the values of C do change significantly. The in situ measurement of d is somewhat difficult, owing to the extreme O_2 sensitivity of the reduced polymers. The thickness changes are somewhat irreproducible, but the 2+ → + reduction typically results in a 10–20% diminution in thickness and the 2+ → 0 reduction results in a 30–40% diminution in thickness. Thus, the change in C can account for some of the difference in the variation of $D_{CT}C^2$ with changes in the redox state of the polymer. However, the change in C upon reduction of the one-electron reduced polymers to the fully reduced polymer cannot account for the nearly 10-fold change in $D_{CT}C^2$. It is noteworthy that such large changes in the thickness

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of the polymer occur. This may be a negative factor in situations where there is the need to rapidly cycle the polymer from one redox state to another, as in electrochromism. Such may not be important in constant current applications, since the overall polymer structure would be fixed.

Since the variation in C is too small to account for the changes in $D_{CT}C^2$, the value of D_{CT} must also be larger for the +/0 state of the polymer than for the 2+/+ state. The fundamental reason for the larger value of D_{CT} for the more reduced system is not clear. With the view that charge transport occurs via a self-exchange process, the change in the fundamental rate constant can be attributed to the change in the structure of the polymer. Changes in the structure of the polymer are likely the significant factor in changes in the cyclic voltammetry waves for the first and second reduction illustrated in Figure 1. Whatever the explanation, the changes in the charge-transport rate in the various redox levels may have practical consequence. Note that >20 mA/cm^2 can be sustained for $[(PQ^{2+})_n]_{surf}$ or $[(BPQ^{2+})_n]_{surf}$ film thicknesses exceeding 1 μm. This establishes that thick films of redox polymer derived from a viologen can yield significant steady-state current that might be required in energy conversion and storage or synthetic applications. Additionally, the greater value of D_{CT} for the +/0 form of the polymers compared to the 2+/+ form suggests that the purple/yellow colors associated with the +/0 forms might prove more valuable in electrochromism applications where speed is an important concern. The lack of long-term durability of the doubly reduced polymers derived from I and II in aqueous electrolytes,[2] however, remains a practical limitation in any application despite the improved rate of charge transport.

The results for the polymers derived from I or II accord well with results[6] from polymers having $M(2,2'\text{-bipyridine})_3^{2+}$ redox centers in that the value of D_{CT} is larger for the more reduced redox state. It may be that the similar increase in D_{CT} for the more reduced state of the polymes is due to the fact that all of the systems studied give lower electrostatic repulsions between the redox centers for the more reduced state. Studies of polymers that can increase electrostatic repulsions between redox centers by reduction will be undertaken in this laboratory to establish factors influencing charge transport in redox polymers.

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A Pulse Radiolysis Study of the Azulene Triplet State

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Abstract: The triplet state of azulene has been produced in benzene by pulse radiolysis and a lifetime of 11 ± 1 μs determined. This is longer than previously reported values. The identity of this species has been confirmed by witnessing its formation and quenching via essentially diffusion-controlled triplet energy-transfer processes involving respectively 1,3-cyclohexadiene as donor and perylene as acceptor. A triplet energy of 40.1 ± 0.2 kcal mol^{-1} has been determined by establishment of an equilibrium for triplet energy transfer between anthracene and azulene.

I. Introduction

Over the last 2 decades the non-alternant hydrocarbon azulene (Az) has played an important role in mechanistic organic photochemistry as a triplet quencher.[1] In spite of this diagnostic use the two key characteristics of $^3Az^*$, its triplet energy and its lifetime, have been subjects of considerable discussion. Experimental values for the triplet energy of <43,[2] 31–39,[3] 30,[4] 40,[5] 38.6,[6] and close to 39[7] kcal mol^{-1} have been quoted, and, perhaps more understandably, molecular orbital calculations have also yielded a wide range of values, 34,[8] 35,[9] 37,[10] and 41[11] kcal mol^{-1}. Although a triplet lifetime of less than 1.5 μs has been reported,[5,6] the most reliable lifetime data appear to be those published recently by Görner and Schulte-Frohlinde as a result of a pulsed laser study.[12] In this work $^3Az^*$ was produced by triplet energy transfer from various sensitizer molecules and an absorption spectrum with λ_{max} 360 nm and a lifetime of 4 ± 2 μs in benzene reported. However, according to these authors the transient appeared within the rise time of the laser pulse (10 ns) and was formed in the same yields in deaerated and aerated benzene. Neither of these facts appears consonant with quoted concentrations and rate constants for electronic energy transfer from sensitizer triplets to azulene and oxygen. In this work we have addressed ourselves to the

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