AD-A278 618

‖‖‖‖‖‖‖‖‖‖‖‖‖

OFFICE OF NAVAL RESEARCH

TECHNICAL REPORT

FOR

Grant N00014 91 J 1035

R & T Code 413302S

Technical Report No. 17

DTIC
ELECTE
S APR 2 6 1994
F
D

Ion Modulated Electroactivity in
Thin Film Metallopolymers

L. Andrew Lyon, Mark A. Ratner
and Joseph T. Hupp

Department of Chemistry and Materials Research Center
Northwestern University
Evanston, IL 60208.

94-12653

‖‖‖‖‖‖‖‖‖‖‖‖‖

94 4 25 065

REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	April 18, 1994	Technical Report, # 17

4. TITLE AND SUBTITLE	5. FUNDING NUMBERS
Ion Modulated Electroactivity in Thin Film Metallopolymers	G.N00014-91-J-1035

6. AUTHOR(S)

L. Andrew Lyon, Mark A. Ratner and Joseph T. Hupp

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)	8. PERFORMING ORGANIZATION REPORT NUMBER
Department of Chemistry Northwestern University 2145 Sheridan Road Evanston, IL 60208	17

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)	10. SPONSORING/MONITORING AGENCY REPORT NUMBER
Office of Naval Research Chemistry Division 800 North Quincy Ave. Arlington, VA 22217-500	

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT	12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Electroactivity in thin-film redox polymers derived from $Fe(2,2'\text{bipyridine})_3^{3+/2+}$ and $Fe(\text{phenanthroline})_3^{3+/2+}$ can be tremendously modulated by replacing conventional counter ions (such as perchlorate) with alkylsulfonates ($CH_3(CH_2)_nSO_3^-$, n=0-11). With large n species, the amount of charge passed during metal oxidation decreases (reversibly) by nearly an order of magnitude, while the rate of charge flow (as measured transiently by chronocoulometry) similarly decreases, again reversibly. Redox thermodynamic effects (systematic shifts in film-based formal potentials) are also seen. The unusual coupling of redox and ionic conductivity processes uncovered here appears to be related to: 1) the large free-volume demands of the alkylsulfonates, and 2) fundamental limitations on the ability of the metallopolymer to meet those demands.

DTIC QUALITY INSPECTED 2

14. SUBJECT TERMS			15. NUMBER OF PAGES
metallopolymer, redox processes, ionic conductivity			9
			16. PRICE CODE
			UL

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
unclassified	unclassified	unclassified	UL

Introduction

The potential uses of redox conductors in such areas as imaging[1], molecular electronics[2] and electrocatalysis[3] have led to a need for better understanding of the mechanism of conductivity. While it is generally acknowledged that electrons diffuse through the film via a series of hopping events,[4] the exact role of charge compensating counter ions is unclear. Available theory implies that intrapolymer ionic and electronic motion should be strongly correlated[5] yet there are only a handful of experimental observations to support this contention.[6] In the current study, some unusual and apparently unprecedented electrochemical effects, indicative of strong electron-ion coupling, have been uncovered. These effects are described below, together with preliminary explanations.

Experimental

Polymer films were grown on glassy carbon surfaces via reductive electropolymerization of the monomer $[Fe^{II}(vbpy)_3](PF_6)_2$ (vbpy = 4-methyl-4'-vinyl-2,2'-bipyridine).[7] Films were grown from an acetonitrile solution that was $0.1M$ in tetraethylammonium perchlorate (TEAP) and approximately $2mM$ in monomer. Continuous scanning between -0.5V and -2.0V vs. SSCE produced adherent red films. Electrochemical synthesis and subsequent measurements were made on a PAR 273 potentiostat with a standard three electrode arrangement consisting of a glassy carbon disk (area: 0.07 cm^2) (working), platinum wire (counter) and saturated sodium chloride calomel electrode (reference). All alkylsulfonates were purchased from Aldrich and used as received. TEAP (GFS) was recrystallized

from purified distilled water (Millipore system) and dried in vacuo. Acetonitrile (Fisher) was distilled in glass and stored over sieves.

Results

We have observed that changing the identity of the charge compensating counter ions from perchlorate to any of several ions of the type $CH_3(CH_2)_nSO_3^-$ (n=0-11) has striking effects on the film-based redox chemistry of poly-$Fe(vbpy)_3^{2+}$ – in particular, the reversible metal-centered (electrochemical) oxidation of the polymer backbone:

$$\text{poly-}Fe(vbpy)_3^{2+} + nX^- \rightleftharpoons \text{poly-}Fe(vbpy)_3^{3+},X^- + ne^- \text{ (electrode)} \qquad (1)$$

Both the kinetics and thermodynamics of the oxidation process are modulated, indicating strong coupling between electron hopping and ion diffusion. One of the more spectacular effects is shown in figure 1. A film is scanned via cyclic voltammetry (CV) from 0.3V to 1.2V vs. SSCE in an aqueous solution of TEAP (0.05M), yielding a large set of peaks corresponding to reaction 1. This voltammagram is then compared to one obtained with 0.05M aqueous 1-decanesulfonic acid, sodium salt (DSA) as electrolyte. A large decrease in current accompanies the replacement of TEAP by DSA, indicating that much of the film has now been rendered inaccessible electrochemically. A similar effect is observed to some degree for a number of other sodium alkylsulfonates (n=6-11) and is reversible over many changes of electrolyte. The magnitude of the effect is significantly dependent on film thickness. For example, a polymer film that is grown exhaustively from a 2mM solution (>50 scans; limiting coverage of ca. 500

monolayer equivalents) exhibits a much greater change in current response than a film grown for only 10 scans (coverage of ca. 100 monolayer equivalents). On the other hand, thinner polymer films exhibit fewer memory and time effects than the thicker (and presumably more cross-linked) assemblies.

Figure 2 shows that the electrolyte effects extend to the polymer-film redox thermodynamics. The apparent formal potential for (metal-based) polymer oxidation (determined from cyclic voltammetry peak potentials) exhibits a systematic negative shift with increasing n, for n=5 to 11 – but essentially no dependance for n=0 to 4. Interestingly, the break in the plot at n=4 is parallelled in the electroactivity attenuation studies above, i.e. *substantial* attenuation occurs only for n>4.

Preliminary studies of electron diffusion rates also reveal an electrolyte anion dependance. In particular, transient measurements (chronoamperometry) of charge transport diffusion coefficients (D_{CT}) during polymer oxidation show that D_{CT} diminishes as the alkyl chain length increases. While absolute quantification is unrealistic (due, in part, to film "memory" and time effects), we do find that D_{CT} undergoes an approximately five-fold relative decrease from TEAP to DSA. We can safely say, therefore, that the sulfonates are in some way limiting the fundamental dynamics of charge flow.

Finally, spectroelectrochemical experiments seem to present evidence that the observed losses of overall film electroactivity are related to reversible trapping of a fraction of metal centers in the oxidized (i.e. Fe(III)) form. Spectral interrogation of polymer metal-center oxidation-state distribution is possible when

film growth is carried out with conductive glass electrodes (indium tin oxide coatings; Delta Technologies). Particularly instructive are optical measurements at 520nm, where $Fe^{II}L_3^{2+}$ (but not $Fe^{III}L_3^{3+}$) absorbs strongly. As expected, the absorbance at 520nm (in TEAP as electrolyte) is maximized when the film is held at potentials significantly negative of the formal potential (i.e. at strongly reducing potentials), but is minimized – and indeed, completely bleached – when the film is subjected to oxidizing potentials. In striking contrast, the bleaching process as well as subsequent recovery, is substantially inhibited for a film equilibrated in a DSA-containing solution. Thus, it appears that the metallopolymer becomes trapped in a largely mixed-valent form – with changes in the external electrochemical potential causing only modest excursions away from mixed-valency.

Discussion

The profound film-based redox effects accompanying counter ion replacement are most logically ascribed to steric phenomena. In particular, the diminution in redox capacity (Figure 1) is likely connected to an inability to place, within the available free volume, the full number of alkylsulfonate ions required for complete metallopolymer oxidation. An extreme, of course, would be absolute steric blocking of counter ion incorporation – a case examined previously by Elliott and co-workers in their studies with a poly-xylylviologen electrolyte.[4(b)] Obviously, in the present study, electroactivity is not *completely* eliminated, implying that counter anions are not entirely excluded. An interesting possibility, however, is

that the required transient charge compensation occurs not by bulky anion incorporation and expulsion (oxidation and reduction processes, respectively: see eq. 1), but by cation (Na⁺) motion in the opposite direction. This, of course, would ultimately require net salt incorporation. Nevertheless, if anion transport were sufficiently *dynamically* hindered, cation transport might represent a viable charging mechanism.

To evaluate this idea in a quantitative fashion, we measured film redox potentials as a function of electrolyte concentration in each of several electrolytes (including TEAP and DSA). After correction for small liquid junction potentials associated with the SSCE reference, we found that the poly-$Fe^{III/II}(vbpy)_3^{2+}$ potential shifted in the negative direction by 58 to 68 mV per decade increase of electrolyte concentration (independent of electrolyte identity). If the metallopolymer behaved as a perfect cation-exclusion membrane, rigorous Donnan behavior (-59.2 mV per decade) would have been seen.[8] Our results clearly are sufficiently close to the ideal that only anions can be participating significantly in the film charging and conduction processes.

With the identity of the charge compensating ion now more satisfactorily established, it seems reasonable to ascribe the diminution of apparent electron transport rates with increasing anion size (relative D_{CT} measurements, above) directly to polymer-based steric constraints on anion motion.

The behavior illustrated by figure 2 also appears to be connected to steric effects, as the large potential shifts appear only under conditions where decreases in electroactivity are dramatic (n>4). Significant counter ion effects on

metallopolymer electrochemistry have been observed by Bocarsly and co-workers,[4(c)] but these observations were attributed to the well defined lattice vacancies in their polymers (semicrystalline prussian blue analogues) and hence extreme spatial requirements for counter cation incorporation. Our results, however, do not lend themselves to an identical interpretation since they are derived from amorphous materials that presumably lack such well defined vacancies.

Conclusions

The substantial changes in polymer film electroactivity induced by counter-ion size manipulation are unusual and, apparently, largely unprecedented. The microscopic origin of the changes may lie in ion-gated electron hopping effects, hydrophobic/hydrophilic effects, ion trapping effects or, perhaps more likely, some combination of the above. Further studies, including steady state conductivity assessment, electrochemical quartz crystal microbalance measurements and Auger spectroscopy studies, are planned, and should eventually resolve the remaining mechanistic questions.

References

1.   See, for example: (a) Zhang, H.-T.; Subramanian, P.; Fussa-Rydel, O.; Bebel, J.C.; and Hupp, J.T., *Solar Energy Mater. and Solar Cells*, **25**, 315, (1992). (b) O'Toole, T.R.; Sullivan, B.P. and Meyer, T.J., *J. Am. Chem. Soc.*, **111**, 5699, (1989). (c) Elliott, C.M. and Redepenning, J.G., *J. Electroanal. Chem.*, **197**, 219, (1986).

2.   (a) White, H.S.; Kittlesen, G.P. and Wrighton, M.S., *J. Am. Chem. Soc.*, **106**, 5375, (1984). (b) Pickup, P.G. and Murray, R.W., *J. Electrochem. Soc.*, **131**,

1922, (1991). (c) Mirkin, C.A. and Ratner, M.A., *Annu. Rev. Phys. Chem.*, **43**, 719, (1992). (d) Natan, M.J. and Wrighton, M.S. in *Progress in Inorganic Chemistry*, Ed. S.J. Lippard, **37**, 391, New York, Wiley, (1989).

3. Representative work: (a) Andrieux, C.P.; Haas, O. and Saveant, J.-M., *J. Am. Chem. Soc.*, **108**, 8175, (1986). (b) Nishihara, H.; Pressprich, K.; Murray, R.W. and Collman, J.P., *Inorg. Chem.*, **29**, 1006, (1990). (c) O'Toole, T.R.; Meyer, T.J. and Sullivan, B.P., *Chem. Mater.*, **1**, 574, (1989) (d) Stoessel, S.J.; Elliott, C.M. and Stille, J.K., *Chem. Mater.*, **1**, 259, (1989).

4. Chidsey, C.E.D. and Murray, R.W., *J. Phys. Chem.*, **90**, 1497, (1986).

5. (a) Saveant, J.-M., *J. Phys. Chem.*, **92**, 1011, (1988). (b) Anson, F.C.; Blauch, D.N.; Saveant, J.-M. and Shu, C.-F., *J. Am. Chem. Soc.*, **113**, 1922, (1991). (c) Blauch, D.N. and Saveant, J.-M., *J. Am. Chem. Soc.*, **114**, 3323, (1992).

6. (a) Surridge, N.A.; Zvanut, M.E.; Keene, F.R.; Sosnoff, C.S.; Silver, M. and Murray, R.W., *J. Phys. Chem.*, **96**, 962, (1992). (b) Elliott, C.M.; Redepenning, J.G. and Balk, E.M., *J. Am. Chem. Soc.*, **107**, 8302, (1985) (c) Amos, L.J.; Duggal, A.; Mirsky, E.J.; Ragonesi, P.; Bocarsly, A.B. and Fitzgerald-Bocarsly, P.A., *Anal. Chem.*, **60**, 245, (1988).

7. (a) Abruna, H.D.; Denisevich, P.; Umana, M.; Meyer, T.J. and Murray, R.W., *J. Am. Chem. Soc.*, **25**, 315, (1981). (b) Elliott, C.M.; Baldy, C.J.; Nuwaysir, L.M. and Wilkins, C.L., *Inorg. Chem.*, **29**, 389, (1990).

8. (a) Naegli, R.; Redepenning, J. and Anson, F.C., *J. Phys. Chem.*, **90**, 6627, (1986). (b) J. Redepenning, personal communication.
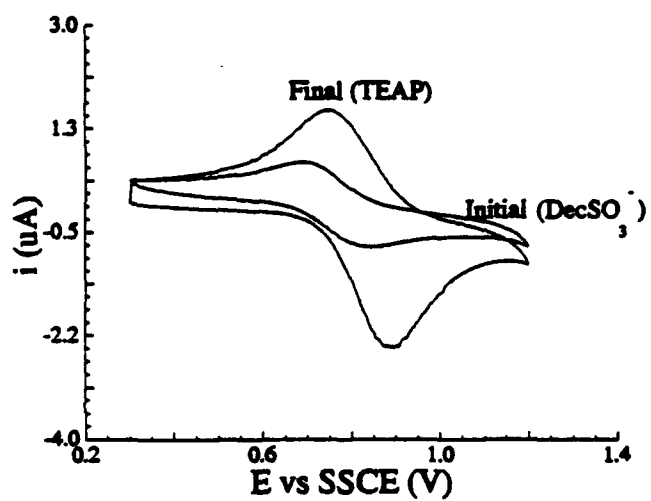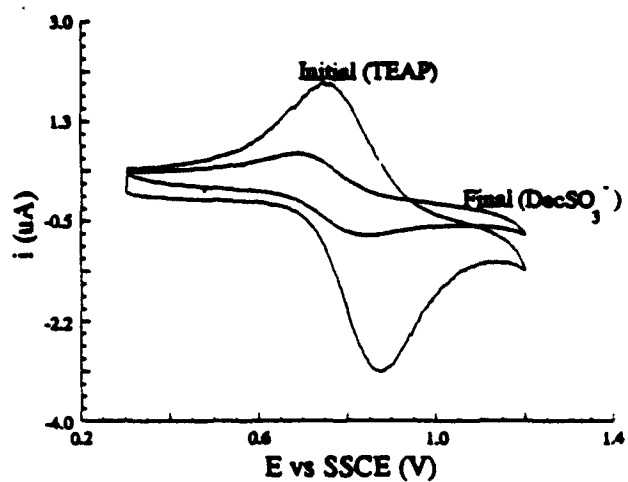
Figure 1. Top panel: Modulation of electroactivity by DSA. Bottom panel: Regeneration of voltammagram in TEAP.
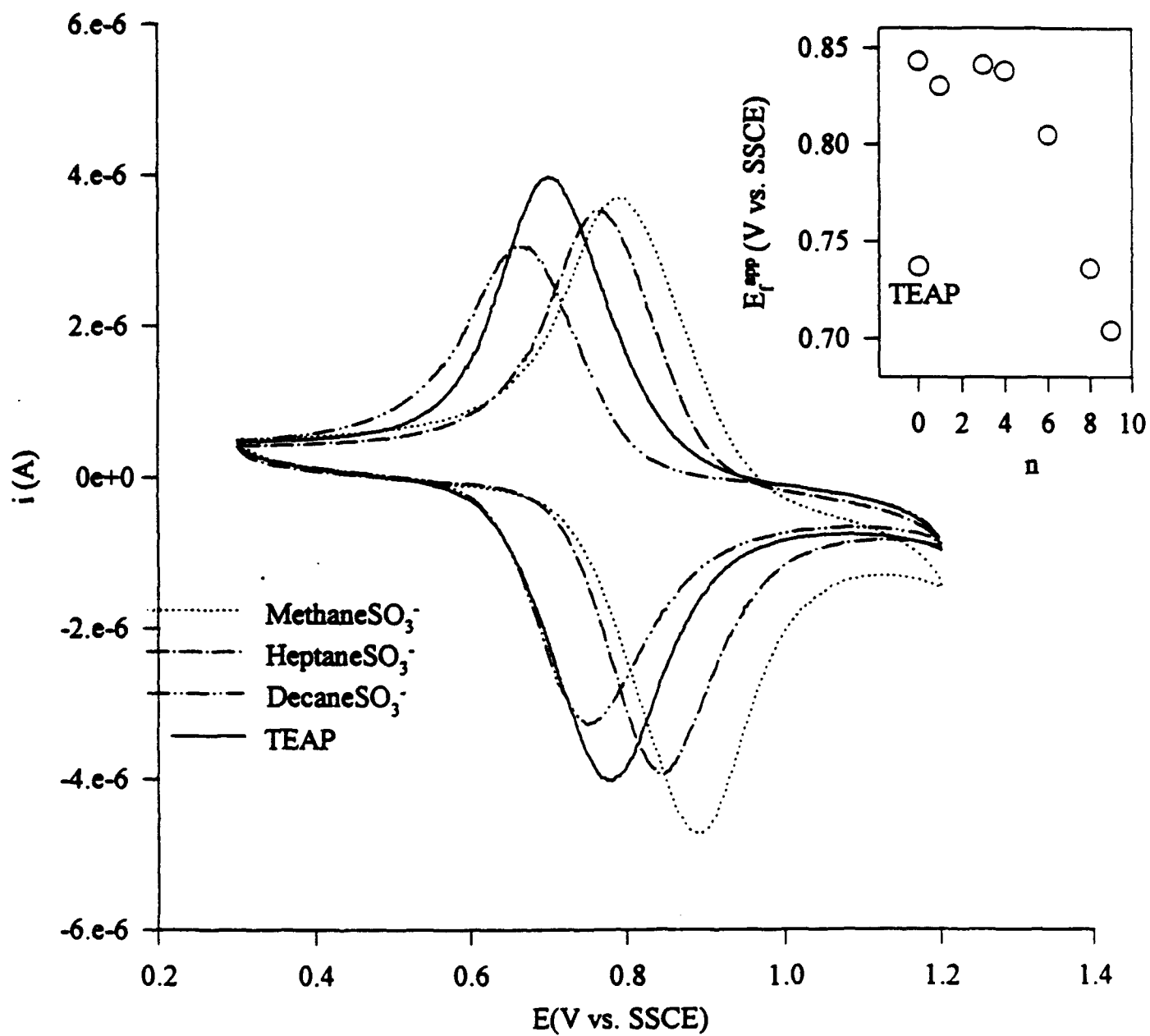
Figure 2. Dependance of the apparent formal potential (E_f^{app}) on alkylsulfonate size.