

Ion and Electron Transport in Stable, Electroactive Tetrathiafulvalene Polymer Coated Electrodes

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Abstract: A linear phenoxytetrathiafulvalene polymer is physically adsorbed onto a metallic substrate by spin coating to produce a polymer-modified electrode whose electrochemical and optical properties are distinctly different from those of the metallic substrate. A combination of electrochemical (cyclic voltammetry, coulometry, and chronoamperometry) and spectral (vis-near IR) measurements were used to characterize these films. The films were found to be reproducible in behavior, to be stable over a wide potential range, and to exhibit unchanging response over many thousands of cycles. The electrochemical activity of the polymer films results from the transport of electrons and charge compensating counterions through the polymer matrices. By varying the concentration and the nature of the electrolyte and from ac impedance measurements, the kinetics of oxidation in these films is shown to be limited by ionic flow into the polymer phase. Spectroelectrochemical data provide the first evidence for electronic interactions between sites on a modified electrode surface. Moreover, the optical data obtained as a function of potential strongly suggest that the electronic transport in these polymer films is not related to mixed valence induced electrical conductivity. A less specific process involving neighboring molecular group collisions which leads to electron transfer is suggested. The electrochemical properties of these polymer-modified electrodes are not limited solely to the TTF systems discussed in detail here, but rather are shown to be generally representative of a broad class of π -donor polymers.

I. Introduction

Polymeric coatings have recently become of great interest in the modification of electrode surface properties. Advantages offered by these systems over directly chemically bound monolayers include ease of preparation, stability, larger signals for more straightforward characterization, and complete surface coverage. Polymer-modified electrode surfaces have been prepared by glow-discharge polymerization,² oligomerization during surface chemical reaction,³ argon plasma polymerization,⁴ electrodeposition,⁵ functionalization of surface-bound polymers,⁶ and irreversible adsorption.⁷ Unfortunately, most of these methods suffer from a number of fundamental limitations such as difficulty in purifying or characterizing the polymer produced in situ and the requirement of specialized film deposition procedures which are unlikely to be of general utility. A previous report described a new class of electroactive polymers prepared by attaching a pyrazoline derivative to cross-linked chloromethylated polystyrene resins.⁸ We have recently discovered that the attachment of a variety of electroactive monomers to linear chloromethylated polystyrene backbones provides materials with vastly improved film-forming and electrochemical properties.

Our purpose in this paper is threefold. First, we show that a tetrathiafulvalene (TTF) functionalized polymer can be readily spin coated onto metal substrates to form uniform, stable modified electrode surfaces with film thicknesses from 50 Å to several microns. Second, we report the electrochemical and spectroscopic properties of these polymer electrodes and show how these properties depend on film thickness and the nature and the concentration of electrolyte. Last, we discuss a mechanism for the transport of electrons and charge-compensating ions into these polymer films. In particular, we show for the first time that the kinetics of oxidation is limited by ionic flow into the polymer phase.

The tetrathiafulvalene donor was chosen as the initial subject of study since the monomer exhibits two reversible redox waves and because the spectroelectrochemistry of similar TTF polymers in solution had been reported previously.⁹ In addition, it appeared that this donor was uniquely suited for the study of electronic interactions between electroactive sites in the film, since the absorption spectra of oligomeric forms of the cations are well characterized.¹⁰

II. Experimental Section

Materials. The TTF polymer used in this investigation was prepared¹¹ from linear poly(vinylbenzyl chloride) and the potassium salt of *p*-hydroxyphenyltetrathiafulvalene in a coverage of 70%.¹² Removal of the remaining benzyl chloride groups was effected by treatment with the potassium salt of phenol.¹³ The resulting TTF-substituted polystyrene copolymer was soluble in THF, DMF, and CH₂Cl₂ and was insoluble in acetonitrile, in which all electrochemical studies were conducted.

THF (Burdick & Jackson) was refluxed over LiAlH₄ and distilled under nitrogen prior to use. Acetonitrile (Burdick & Jackson) was dried and stored over 4 Å molecular sieves and bubbled with nitrogen before use. Tetraethylammonium perchlorate (TEAP) and tetrabutylammonium tetrafluoroborate (TBABF₄) (Southwestern Analytical Chemicals) were dried under vacuum prior to use. A sample of 1,2-(1',9'-dioxophenalenium)benzene tetrafluoroborate was generously supplied by Dr. Klaus Franz.¹⁴

Film Preparation. Approximately 20 μ L of a THF solution of the polymer was dropped onto a 1.0-in. diameter substrate spinning on a Headway Research, Inc., photoresist spinner at \sim 4000 rpm. The film was allowed to air dry while spinning for several minutes. Then the outer portion of the resulting polymer film was removed with a THF-soaked cotton swab in order to expose the electrode surface for making electrical contacts. For optical studies, the substrates were either thin, electron beam evaporated Pt (80 Å) or In₂O₃/SnO₂ (3000 Å) films deposited on quartz disks, and for electrochemical kinetic studies, thick Pt (5000 Å) coated disks were used. The thicknesses of the spin cast films were determined from mechanical surface profile measurements using a Tencor Alpha-Step Profiler. Thickness variations across films prepared in this way could be held to within \pm 10%. Films were prepared with thicknesses ranging from \sim 50 Å to greater than 1 μ , depending upon the concentration of the polymer solution used and the spin rate.

In a typical preparation, 1.25 mg of polymer was dissolved in 30 μ L of THF. One drop of this solution (15–20 μ L) was dropped from a disposable pipet onto a 1-in. substrate spinning at 3500 rpm. The thickness of the resulting film was 1600 Å. Film thickness is determined primarily by the viscosity of the spinning solution, so the solution concentration necessary to produce a given thickness depends strongly on the structure and molecular weight of the polymer. For a more detailed discussion of the spin coating process see Washo^{15a} and Meyerhof.^{15b}

Apparatus. The optically transparent coated electrodes were mounted in a Teflon cell equipped with quartz windows. The auxiliary Pt electrode compartment was separated by means of a frit, and the reference electrode (SCE) was employed with a Luggin capillary tip

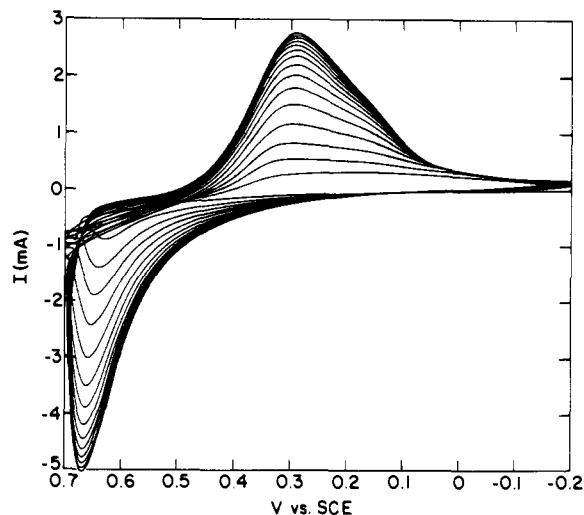


Figure 1. Cyclic voltammetric break-in of a fresh 4000-Å TTF polymer film: 0.1 M tetraethylammonium perchlorate in acetonitrile, 100 mV/s repetitive sweeps between -0.2 and $+0.7$ V vs. SCE (see text).

positioned immediately in front of the film. The absorption spectra of the films were recorded at constant potential on a Cary 14 recording spectrophotometer. For electrochemical kinetics studies, the coated electrodes were pressure sealed in a cylindrical Teflon cell such that only a 1.23-cm^2 area of the coated portion of the electrode made contact with the electrolyte solution. The auxiliary Pt electrode was positioned directly above the film and separated by a frit, and the reference electrode connection was made through a side hole in a design similar to that of Cahan et al.¹⁶

Cyclic voltammetry and chronoamperometry experiments were carried out with a PAR Model 173 potentiostat in conjunction with a PAR Model 175 programmer. Data were recorded on a Hewlett-Packard Model 7046A X-Y recorder or a Nicolet Model 206 digital storage scope. Resistance and capacitance measurements were made with an A-C impedance bridge balanced with a variable parallel R-C combination. Data were taken over the frequency range 0.5–100 kHz, and the ac voltage was varied during each measurement to verify that the balance condition was independent of the ac signal amplitude.

III. Results

Cyclic Voltammetry. For freshly deposited films, several cyclic potential sweeps were required for the films to become fully electroactive and reach a state which yielded reproducible current-voltage curves. This break-in period is illustrated in Figure 1 for a thick (4000 Å) film. The currents passed during the initial sweep were almost negligible, and gradually increased with each successive sweep until a steady state i - V curve was obtained. The number of cycles required for this process depended on the film thickness, thick films requiring many cycles, while thin (≤ 200 Å) films were broken in in a single sweep. Upon standing in their neutral forms, the films slowly reverted back to their initial states over the span of several minutes and again required a break-in. After being broken in, as described above, the films exhibited remarkable electrochemical stability. For instance, it was seen that cycling between -0.2 and $+0.7$ V many thousands of cycles did not cause any decrease in the amount of current passed. Furthermore, these films could be removed from solution, stored in a dry state, and reused, at which point they exhibited behavior identical with that of freshly spun films.

TTF in solution exhibits two reversible redox waves at $+0.33$ and $+0.70$ V vs. SCE.¹⁷ Qualitatively, the same behavior was observed for thin films of the TTF polymer (Figure 2a), which also showed two waves at nearly the same potentials. The peak currents of the polymer waves were directly proportional to the sweep rate, indicative of surface-bound species. The peak shapes, however, were very complex and did not conform to

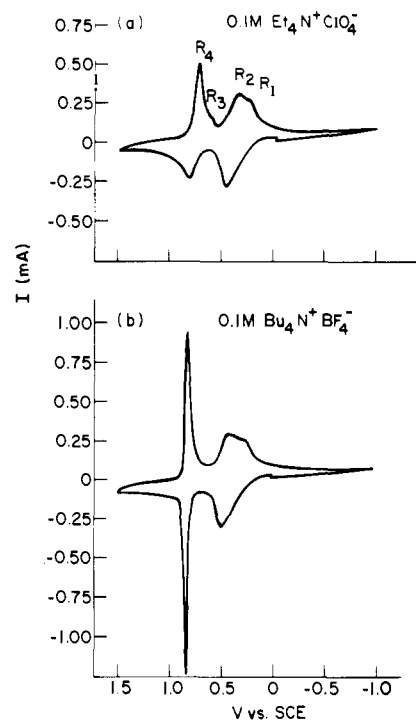


Figure 2. Cyclic voltammograms of a 400-Å TTF polymer film at 20 mV/s in acetonitrile: (a) 0.1 M tetraethylammonium perchlorate; (b) 0.1 M tetrabutylammonium tetrafluoroborate.

the simple, symmetric contours predicted theoretically for surface waves.¹⁸ Similar CV waves have been observed for TTF covalently bound to metal oxide surfaces.¹⁹

The appearance of the current-voltage curves exhibited a striking dependence on the electrolyte. Figures 2a and 2b show CVs of the same thin film obtained with acetonitrile solutions of TEAP and TBABF₄, respectively. In the presence of the fluoroborate salt, the second wave becomes much sharper and is shifted anodically by nearly 100 mV. Film thickness also had a major effect on the appearance of the voltammograms. As thickness increased, the first wave became broader, the peak-to-peak separation increased, and the second wave became far less pronounced (compare Figures 1 and 2). The origins of these unusual features of the TTF polymer films CV will be discussed at length below.

Chronoamperometry. Figure 3 shows the current-time curves for a broken-in film following an applied voltage pulse from -0.2 to $+0.65$ V (oxidation to the monocation) and the reverse pulse (reduction to the neutral TTF). The oxidation process is clearly much slower than the reduction. For films not yet broken in, the oxidation was even slower (requiring up to 5 min for very thick films), but the reduction process was just as fast. By varying the delay time between cathodic and anodic pulses it was found, that, whereas the reduction step always exhibited the same i - t behavior, the rate of oxidation depended upon the length of time the film was held at the neutral potential. Thus, the oxidation rate could be increased by applying the anodic pulse shortly after the reduction current from the cathodic pulse had diminished. This behavior correlates with the break-in and reverse break-in phenomena observed in the CV, and indicates that some process is occurring in the film following reduction which is much slower than the reduction process itself.

Upon changing the electrolyte concentration (dashed line in Figure 3) or using a different electrolyte (dotted line) the rate of oxidation changes drastically, whereas the reduction rate is affected only slightly. These results suggest that sol-

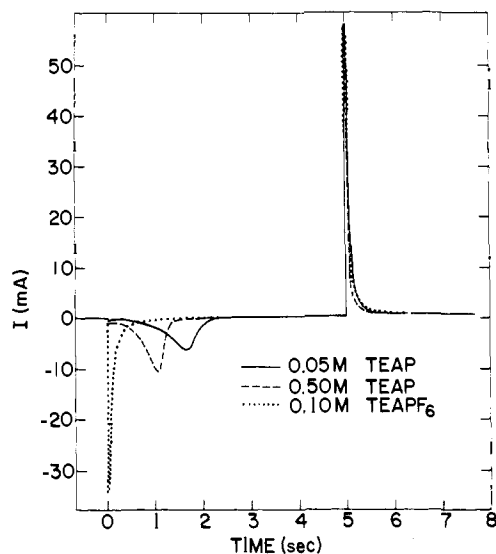


Figure 3. Current-time curves for a 1200-Å TTF polymer film following an applied potential pulse from -0.2 to $+0.65$ V and back again after a 5-s delay. Solid line, 0.05 M TEAP; dashed line, 0.5 M TEAP; dotted line, 0.1 M TEAPF₆.

vent-electrolyte becomes incorporated into the film during oxidation, but is slowly expelled following reduction. This interpretation is supported by the results of ac impedance measurements of both neutral and oxidized films. In its oxidized form, a 1300-Å TTF film-coated electrode (1.23 cm^2) exhibited a capacitance of $6 \mu\text{F}$ and no additional resistance could be detected above that of the electrolyte solution. The neutral film, however, exhibited a low-frequency impedance component with an unusually low capacitance ($\sim 0.1 \mu\text{F}$) and a resistance between 1 and 2 k Ω . Furthermore, this resistance was found to increase with time following reduction of the oxidized film.

Coulometry. The density of TTF groups and thickness of these films provide a medium which can accommodate extremely large amounts of charge. Thick films ($\sim 5000 \text{ \AA}$) have been prepared which have accepted up to 20 mC/cm^2 . In order to determine how many of the TTF units in these films are electrochemically active, the number of coulombs passed at $+0.60$ V (monocation) was determined. The films were then reduced back to their neutral form and dissolved completely in 1.0 mL of DMF, and the optical density of the solutions was determined at 390 nm (neutral TTF absorption band). For three films of different thicknesses, this procedure yielded ratios of charge (in mC) per absorbance unit of 25.3 (300 Å), 29.6 (6500 Å), and 26.4 (8500 Å). The extinction coefficient of the polymer was determined from standard DMF solutions and, assuming a single charge per TTF unit, corresponds to 27.6 mC per absorbance unit. These data reveal that, within an experimental error of $\sim 15\%$, all of the TTF substituents present in the film can be oxidized, regardless of the film thickness. Using the amount of charge injected at $+0.60$ V, and using the film area and thickness to calculate the film volume, the effective TTF⁺ClO₄⁻ concentration within the polymer is ~ 3.5 M. This corresponds to an average distance between TTF groups of $\sim 8 \text{ \AA}$. This high density of TTF units suggests an explanation for the facile electronic conduction through these amorphous films, since motions over very small distances would be sufficient to allow electron exchange between individual TTF molecules. Studies are currently underway to determine the effects of varying this distance by preparing a series of polymers with different extents of TTF functionalization.

Spectroelectrochemistry. Previous studies of the optical properties of the TTF radical cation, both in solution and in

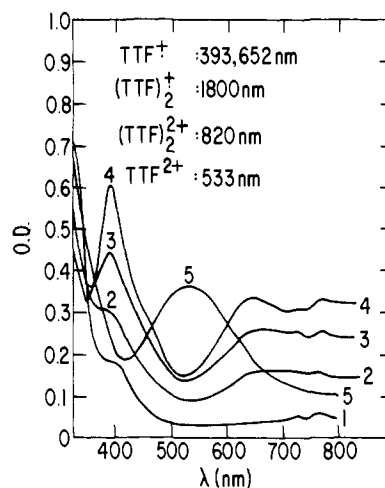


Figure 4. Optical absorption spectra for a thin TTF polymer film at different potentials: (1) -0.20 , (2) $+0.28$, (3) $+0.40$, (4) $+0.64$, (5) $+0.90$ V. (A weak TTF₂⁺ mixed-valence absorption at 1800 nm is not shown.)

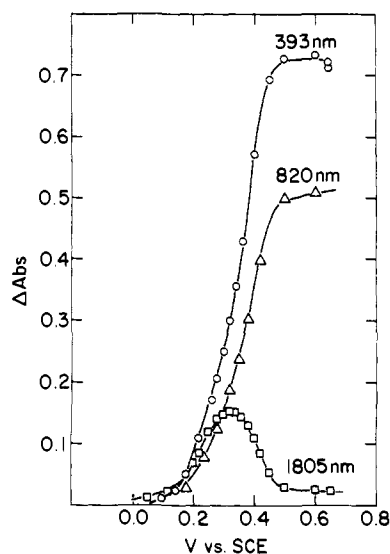


Figure 5. Absorbance (V) - absorbance (-0.20 V) as a function of potential (V) at 1805 ((TTF)₂⁺), 820 (TTF)₂²⁺, and 393 nm (TTF⁺).

the monovalent and mixed-valence solids, have identified absorptions characteristic of the isolated TTF⁺, the mixed-valence dimer (TTF)₂⁺, and the dimer dication (TTF)₂²⁺.¹⁰ Figure 4 shows absorption spectra of a thin TTF polymer film at a number of different potentials. Each of the absorptions exhibited by this film corresponds to one of these previously characterized species, with small shifts to lower energies relative to the unsubstituted TTF caused by the phenoxy substituent. The appearance of absorptions due to aggregated forms of the oxidized TTF groups contrasts with the monomer in solution which does not aggregate at room temperature, and constitutes the first direct evidence for electronic interactions between sites on a modified electrode surface.

Plots of the absorbance at each characteristic wavelength as a function of potential (Figure 5) show that as oxidation commences both the TTF radical cation (λ_{max} 393 and 650 nm) and the mixed-valence dimer²⁰ (λ_{max} 1800 nm) are formed. As the first half-wave potential is passed, the dimer dication absorbance (λ_{max} 820 nm) increases at the expense of that due to the mixed-valence dimer. The potential at which each absorbance is half of its maximum value should correspond to $E_{1/2}$ for the species giving rise to that absorption. The potentials at half-maximum absorbance from Figure 5 are

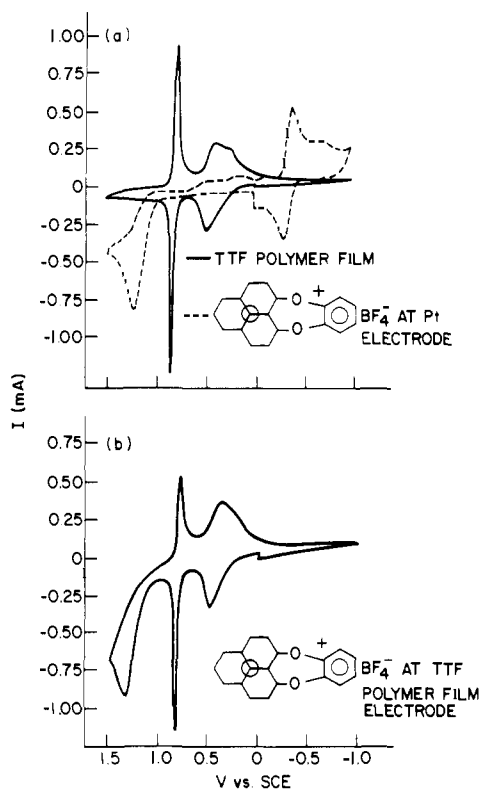
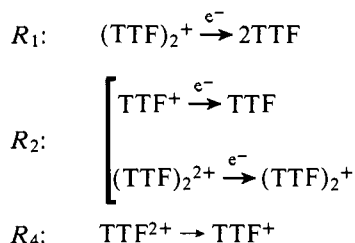


Figure 6. (a) 400-Å TTF polymer film in 0.1 M TEAP-acetonitrile, 20 mV/s (solid line). 1,2-(1',9'-Dioxophenalenium)benzene tetrafluoroborate in 0.1 M TEAP-acetonitrile solution at a Pt electrode (dashed line—note: current scale applies to polymer only). (b) The same phenalenium salt in 0.1 M TEAP-acetonitrile at the TTF polymer coated electrode shown in a.

+0.34 V for TTF⁺, +0.35 V for (TTF)₂²⁺, and +0.23 V for the mixed-valence dimer (TTF)₂⁺. These potentials correspond quite well to those of the reduction peaks labeled R₂ (+0.34 V) and R₁ (+0.20 V) in Figure 2. Thus, the following assignments can be made for the multiple reduction waves observed during the cathodic sweep of the TTF polymer film CV:



The process responsible for the peak labeled R₃ has not yet been identified.

Polymer-Mediated Electron Transfer. Previous studies of electron-transfer mediation by surface-bound species have suffered from the drawback that surface coverages have not been high or uniform enough to eliminate the possibility of competing processes occurring at portions of the metal surface directly exposed to the solution. Complete coverage of the electrode surface has been demonstrated for the TTF polymers with experiments of the kind pictured in Figure 6. The upper CV trace shows a 400 Å film (solid line) and the solution electrochemistry of 1,2-(1',9'-dioxophenalenium)benzene tetrafluoroborate¹⁷ at a Pt electrode. The lower trace shows the CV obtained with the modified electrode exposed to a solution of the phenalene salt. The absence of the depolarizer reduction wave at the modified surface indicates that at these potentials the metal surface is uniformly covered with an effectively insulating layer of neutral polymer which is devoid

of channels large enough to allow penetration of the electroactive solute to the metal surface. Complete surface coverage has been demonstrated in this way for films as thin as 150–200 Å. The observation of an oxidation wave through the same film which completely inhibits the reduction is strong evidence for mediation of electron transfer by the oxidized, ionic film. (The magnitude of the oxidation wave peak current is significantly smaller than that at a metal electrode of the same area, however. This may be due to passivation of the film by the products of the irreversible phenalene oxidation, in which case the current peak may reflect loss of film activity rather than a true mass transport limited current. Subsequent cycles showed progressively lower currents, both for the bound TTF and solute species consistent with this interpretation.)

IV. Discussion

Our experiments have shown that a TTF polymer, made by covalent attachment to a polystyrene backbone, can be easily spin coated onto a conducting electrode to form physically adsorbed electroactive polymer films. Such films, even when rather thick, can take up large quantities of charge, are remarkably stable over many thousands of cycles, and do not suffer from loss of film adhesion or inefficient electronic contact to the metal electrode surface. Since the preparation of these polymer-modified electrodes requires virtually no surface pretreatment and can be accomplished in a few minutes, it is of considerable importance to determine if these results are limited to the single polymeric material reported here. We have found that this phenomenon is rather general. Specifically, we have attached other TTF derivatives, as well as different donors such as triarylpyrazoline, ferrocene, and *N,N*-dimethylphenylenediamine to polystyrene backbones and found that all give soluble polymers¹¹ which can be spin coated to yield electroactive polymer films.

In the first section below we discuss the way in which solvent and electrolyte are incorporated into the film to give the initial electroactivity and to provide charge neutrality. A more detailed comparison of the observed CV wave shapes with those theoretically predicted follows. Finally, the mechanism of electron transport in these polymeric film phases is considered.

Mechanism of Polymer Film Ion Transport. The coulometric measurements on the polymer films showed that the number of equivalents passed in the oxidation step was equal to the number of bound TTF molecules regardless of film thickness. For the thickest films discussed (~5000 Å), the experimentally observed complete oxidation to the TTF⁺ state involves many hundreds of layers of bound donor molecules. This indicates that electrons and appropriate counterions for charge neutrality move through the bulk polymer matrix in response to changes in the applied potential. In this regard, we can ask whether solvent, electrolyte, or solution depolarizers interact with the electroactive polymer by means of gross defects such as cracks, channels, or pores or, alternatively on a more microscopic scale, through uniform penetration into a homogeneous polymer phase.

With the specific TTF copolymer and film preparation conditions discussed here, it is clear that a macroscopic, permanent physical pore structure is not necessary for the electrochemical activity of the films. This is based on three types of experimental evidence. First, scanning electron microscopy (SEM) micrographs of both the neutral and oxidized polymer films reveal that down to a resolution of several hundred ångstroms the polymer films are smooth and defect-free and show no evidence of pore structure. Secondly, the polymer films have been shown to be highly insulating prior to the break-in process, and after break-in demonstrate a remarkable sensitivity to the nature of the electrolyte anion. Finally, the complete inhibition of solute depolarizer waves through the

unoxidized film proves that the neutral film is devoid of channels large enough to allow solute penetration to the metal surface.

In considering polymer–electrolyte interactions in the absence of gross film defects it is useful to refer to studies on the penetration of nonsolvents into glassy, amorphous polymers.²¹ The picture that has emerged from these physical studies is that nonsolvents can penetrate into polymer films by a process which involves local segmental motions of the polymeric backbone.²² In addition, it has been found that pendant groups attached to these backbones experience a considerable degree of flexibility in the presence of such penetrating nonsolvents.²² These processes are important to the present discussion since they provide a straightforward mechanism by which the solvent, electrolyte, and other solutes can make contact to the electroactive polymer phase without the requirement of a permanent pore structure. Field-promoted ion incorporation into the polymer film by this mechanism should be subject to rather severe kinetic restraints relative to ion transport in solution. We suggest that the observed sluggish nature of the oxidation process in these TTF polymer films is due to ion transport rate limitations of this kind.

CV Wave Shapes. The rather complex nature of the voltammetric curves for the TTF polymer films can now be examined. The oxidation process is hampered by the slow ion transport from solution into the nonpolar polymer phase. This kinetic limitation is effectively an uncompensated resistance which decreases as the film incorporates more solvent–electrolyte and the ionic mobility increases (break-in process). This variable resistance is never completely eliminated during the anodic sweep of a CV experiment because solvent–electrolyte begins to migrate out of the film again as soon as the film is reduced. Thus the oxidation waves appear shifted and asymmetric, and show a very marked sweep rate dependence. However, with high concentrations of an electrolyte which allows rapid oxidation (see Figure 3), these effects can be minimized, and multiple oxidation waves due to the various aggregate species have been detected which are very nearly symmetric with those in the cathodic sweep (Figure 7).

Ion mobilities are much higher in the polar, oxidized film, so the reduction waves should appear more ideal. The first reduction wave is a superposition of waves due to the various aggregates, but the second wave (R_4 in Figure 2), due to reduction of the dication, provides an opportunity for comparison with the theory. In fact, with TEAP electrolyte this wave has a peak at the reversible potential of +0.70 V and the predicted¹⁸ peak width at half-height of ~ 90 mV. With TBABF₄ electrolyte, however, the peak shifts to +0.78 V and narrows to 48 mV at half-height. The origin of these effects with the BF₄⁻ counterion is not yet understood.

Mechanism of Polymer Film Electron Transport. Mixed-valence interactions are known to give rise to high electrical conductivities in a number of crystalline ion radical salts composed of TTF donor molecules. Experiments on dry, solid TTF polymer films have shown that partial oxidation to produce a solid which exhibits⁹ near-infrared absorption characteristic of mixed-valence aggregates leads to considerable enhancement of the electrical conductivity. In view of the fact that the TTF polymer film coated electrodes also exhibit this mixed-valence absorption, it is of interest to determine the extent to which facile electron transport in these polymers is dependent upon the presence of the mixed-valence structural unit within the film.

The experimental results of our spectroelectrochemical investigations (Figure 5) indicate that it is only in a narrow potential range that a relatively high concentration of these mixed valence states exist. If the polymer film's electrochemistry were dependent on the intermediacy of these mixed-valence states, a rather unusual i vs. V behavior due to electron transport

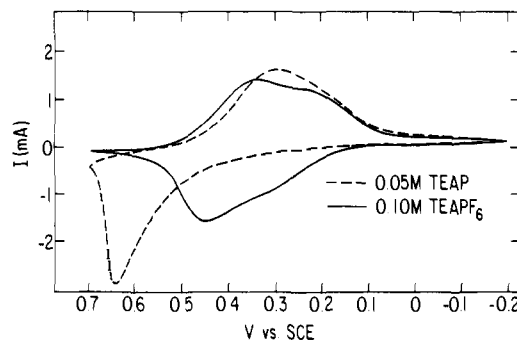


Figure 7. CV of a 1200-Å TTF polymer film at 100 mV/s. Dashed line, 0.05 M TEAP; solid line, 0.1 M TEAPF₆.

limitations would be observed in the potential region positive of +0.5 V, where the amount of mixed-valence species present is negligible. Limited, if any, electrochemical activity would be expected in the dication potential regime (0.6–0.8 V). In fact, electroactivity is observed throughout the entire potential range studied and is readily interpretable in terms of ion transport limitations. In none of the experiments reported here was any evidence for electron transfer rate limitations discovered.

The data in this paper indicate that sites on the TTF polymer can undergo rapid electron transfer without forming stable mixed-valence clusters. Electronic transport via hopping or tunnelling modulated by means of neighboring molecular group collisions would be consistent with these observations. Solvent-induced pendent group motion, as discussed previously, could provide the necessary dynamic interactions to allow rapid electron transfer to occur. The seemingly nonspecific nature of this mechanism is consistent with the reported experimental observations of electron transport in a number of chemically different polymeric materials.

V. Conclusions

This paper describes how modified electrodes having uniform and controllable thickness can be prepared by the simple procedure of spin coating certain electroactive polymers from solution. Electrochemical and spectroscopic measurements on these electrodes have shown them to be reproducible in behavior, stable over a wide potential range, and exhibiting unchanging response over many thousands of cycles. The ability to reversibly oxidize films of the TTF phenoxy copolymer material is shown to be independent of mixed-valence effects. The kinetics of oxidation in these films is shown to be limited by ionic flow into the polymer phase. Electron-transfer mediation to a species in solution is demonstrated and the results of these and other experiments indicate that these electroactive films completely cover the metallic surface without pore or channel defects. The ability to readily vary materials' (electroactive substituent, extent of polymer functionalization) and film preparation parameters should make this novel approach to modified electrodes useful in terms of elucidating further the mechanism of electron and ion transport and the mechanism of mediation to solution species in polymers of this type. Work is currently in progress to utilize this approach in the design and study of electrodes with unique electrochemical, electrocatalytic, electrochromic, and photoelectrochemical properties.

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The Isomer Dependence of Oscillator Strengths in Retinal and Related Molecules. Spectroscopic Assignments

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Abstract: The spectroscopic properties of the higher excited states of retinal isomers and related molecules are considered in detail. A simple graphical description is used to characterize the transition moments to various excited states and it is shown that the isomer dependence of oscillator strengths is a particularly reliable parameter for making spectroscopic assignments. We show that the 280-nm (β) band of retinal isomers is the cis band corresponding to a transition to the lowest A_g^+ state. It derives intensity from the s-cis ring chain conformation in all retinal isomers and is further enhanced by cis conformations along the polyene chain. It is particularly intense for conformations with central cis double bonds in keeping with the classical behavior expected for cis bands. Our assignment of the cis band allows us to explain a large number of experimental observations including the appearance of vibrational structure for this band alone at low temperature. The 250-nm (γ) band in retinals is not assigned; however, we show that previous assignments for this transition are incorrect. Based on our results for retinals we are able to identify the cis (β) and γ bands in the spectrum of both rhodopsin and bacteriorhodopsin.

Introduction

Polyene spectroscopy and photochemistry have become areas of considerable interest over the past few years. Much of the impetus has come from interest in retinal isomers which play a central role as chromophores in visual pigments and bacteriorhodopsin.² Our major concern in this study is the assignment of the spectroscopic transitions of the higher excited states of retinal isomers. In addition to the intrinsic interest in this controversial problem a proper state assignment is required for the evaluation of theoretical studies of the excited-state manifold of these complex molecules.

It has become common practice in polyene spectroscopy to use symmetry labels appropriate to all-trans isomers which belong to the C_{2h} point group. The main strongly allowed absorption band in all polyenes results from an excitation into the lowest B_u^+ state. At approximately the same energy, although generally at longer wavelengths, a weakly allowed A_g^- state has been identified in a number of polyenes.³ A proper theoretical description of this state requires the inclusion of multiply excited configurations in an SCF-CI molecular orbital scheme. Another important state which can be easily assigned in many polyenes is the A_g^+ state which corresponds to the "cis" band identified by Zechmeister.⁴ In addition to these well-studied transitions, further B_u^- , A_g^- , and B_u^+ states are calculated to be present 1 or more eV above the main absorption band and

thus should be considered in any assignment of higher excited states.⁵

In this paper we first review the spectroscopic properties of polyenes and consider the extent to which it is possible to reproduce the relative intensities and transition energies of their observed absorption bands with standard π electron calculations. The isomer dependence of oscillator strengths is then explained qualitatively in terms of localized dipoles positioned at each nucleus and these are used in a qualitative interpretation of polyene spectra. Turning to the absorption spectra of retinals and closely related molecules, we find that the 280-nm band system can best be assigned as the A_g^+ cis band while the third absorption band, which has no obvious analogue in polyene spectra, remains somewhat of a mystery band.

Features of Polyene Spectra

Long polyenes exhibit consistent behavior with respect to both the intensity and position of their three lowest absorption bands.⁴ The first optically allowed transition corresponds to the intense B_u^+ state and exhibits a characteristic red shift with increasing chain length.⁶ The transition is most intense in trans isomers and is weakened somewhat by the presence of cis bonds in the chain.⁴ The second allowed absorption band in long polyenes is the cis band which corresponds to a transition to the A_g^+ state. The transition gains intensity in cis isomers,