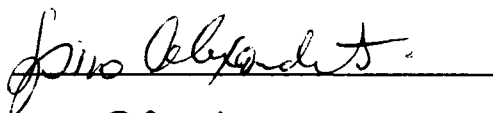


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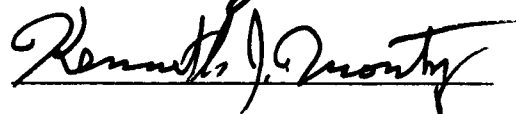
I am submitting herewith a dissertation written by Houshang Karimi entitled "A Study of Charge Transport Through Thin Films of Electro-active Polymers on Conductive Surfaces: Effect of Polymer Film Composition." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.


J. Q. Chambers, Major Professor

We have read this dissertation
and recommend its acceptance:







Accepted for the Council:


Vice Provost
and Dean of The Graduate School

A STUDY OF CHARGE TRANSPORT THROUGH THIN FILMS OF
ELECTROACTIVE POLYMERS ON CONDUCTIVE SURFACES:
EFFECT OF POLYMER FILM COMPOSITION

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Houshang Karimi

December 1986

DEDICATION

This dissertation is dedicated with love to my wife, Eleanor L. J. Karimi, whose help, understanding and continued patience made this work possible. Also to the memory of my late brother, Shahryar Karimi, whom I loved so much.

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ABSTRACT

The synthesis of a polyester is discussed which employs a mixture of the electroactive 2,5-bis(2'-hydroxyethoxy)-7,7,8,8, tetracyanoquinodimethane (TCNQ-diol) and electroinactive 1,4-bis(hydroxyethoxy)benzene (BOEB-diol) with stoichiometric amounts of adipyl chloride in dimethylacetamide via solution polycondensation at low temperature. The product of this polymerization is a terpolymer, which was characterized using electrochemical, rapid scanning spectrophotometric methods (uv-vis, IR), gel permeation chromatography (GPC), and elemental analysis.

Charge transport through polymer films containing the TCNQ structure in the polymer chain and swollen with acetonitrile solvent was studied as a function of film composition. Variation of the film composition was achieved by synthesis of TCNQ terpolymer and by casting blended films of the TCNQ polyester and an isomorphous polyester containing a benzene ring in place of the TCNQ structure. Formation of uniform blends was indicated for the neutral polymers, but phase separation took place on repeated cycling of the films between the 0 and -1 oxidation states.

Redox center site-site interactions were probed by following dimer formation of the $\text{TCNQ}^{\cdot -}$ radical anion and by the charge transport process as measured by chronocoulometric Cottrell slopes. Electron spin resonance and cyclic voltammetric data indicate that interchain, and not intrachain, interactions occur in the reduced films.

The charge transport rate in the region of the $\text{TCNQ}^-/\text{TCNQ}^{2-}$ couple relative to the rates for the $\text{TCNQ}/\text{TCNQ}_2^-/\text{TCNQ}^-$ region was found to be considerably retarded in films of the terpolymer and the blends.

The kinetics of the heterogeneous charge transfer step for the $\text{TCNQ}^-/\text{TCNQ}^{2-}$ process was studied using cyclic voltammetry at various scan rates. Limitations of the technique are pointed out.

Effect of film composition on chronocoulometry was studied. In all regards the chronocoulometric and cyclic voltammetric results were consistent. The limiting charge accepted by the films, estimated by the approach to thin layer behavior and the charge obtained by integration of the cyclic voltammograms were in agreement ($\pm 10\%$).

The Cottrell slopes displayed a temperature dependence as expected for a thermally activated diffusional process. Activation energies for the "apparent charge transport diffusion coefficient" were obtained for TCNQ polyester and blends.

Cyclic voltammetric and chronocoulometric studies of TCNQ polyester/PEG (PEG: polyethylene glycol) blend films on platinum electrodes and in contact with various combinations of solvent/electrolyte systems revealed further insight into the process of charge transport.

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CHAPTER I

INTRODUCTION

The study of "modified electrodes" has been one of the most active areas in electrochemical research in the past few years and has enjoyed a number of advancements in both experimental and theoretical regards (1-3). The term "modified" encompasses a rather wide range of strategies that have been used in the preparation and study of such systems. In a broad sense, three principal methods have been used to prepare "modified electrodes": (a) irreversible (strong) adsorption, (b) covalent bonding, and (c) coating, especially by a polymer (3).

A detailed coverage of the topics (a) and (b) is outside the scope of this presentation. However, due to their important role in directing attention towards area (c), a brief coverage of some historical developments will be given.

The main effort of electrochemists in the 1960s was centered on the development of new techniques for characterizing chemical systems. Cyclic voltammetry (see the section on Theory, p. 60) emerged in this era. New analytical techniques were made possible by the advent of sophisticated instrumentation such as x-ray photoelectron spectrometry, Auger electron spectrometry and secondary ion mass spectrometry (SIMS) that provided detailed chemical information about structures near surfaces (4). Initial attention was given to the understanding and "exploitation" of adsorption. Many aromatic nuclei were found to bind to graphite electrodes in the presence of an aqueous

electrolyte. In this case (i.e., chemisorption), the surface structure could be self-renewing in the presence of small equilibrium concentration of the adsorbate in solution. This method is known to be subject to impurities that can bind more strongly than the adsorbate (4). The discovery of adsorbed ionic species has also been an "empirical event," and its exploitation for useful purposes has found few "systematic" or "fundamental origins" (2).

Attention diverged from the above "traditional" field of adsorption on electrode surfaces, when the idea of "deliberately" modifying the electrode surface composition in a desired manner was envisioned (2). The most "essential" difference according to Murray (2) is that one purposely seeks in some rational manner to immobilize a chemical on an electrode surface so that the electrode thereafter displays the chemical, electrochemical, optical and other properties of the immobilized molecules (2).

The first "deliberately" modified electrode was prepared by Hubbard and Lane (5, 6) by the method of chemisorption (strong or irreversible adsorption of the electroactive substance) on the electrode surface. These workers demonstrated the notion of immobilizing a redox species by linking it to another chemical functionality, mainly olefins, with known chemisorption properties. They employed chemisorbed quinone-bearing olefins on Pt electrodes. Although chemisorption may involve covalent bond like interactions, in only a few cases have such interactions been usefully stable (2).

The limitations imposed by the method of chemisorption were then circumvented by the emergence of a new methodology based on "covalent binding" of electroactive molecules to electrode surfaces (7-10). Several approaches have been employed (11). Organic and organo-metallic compounds have been chemically bonded to the surfaces of suitable conductors. Modifiers, e.g., amines, were chemically bound to carbon electrodes via the surface oxides (10a, 12-16). Metal oxides, e.g., tin oxides, were modified by silylation (17, 8-9, 12, 18, 7, 19-20).

In all of the above cases, according to Miller et al., stable binding of both electroactive and electroinactive modifiers was achieved and new chemical properties imparted to the electrode surfaces (11). This method of covalent modification is still an effective means of modifying electrodes, but has several drawbacks (4): (a) it requires chemical pretreatment of the electrode surface and the use of special analytical techniques to characterize the small amounts (monolayers or less) of material involved (21); (b) structures synthesized in this way lack performance ability, and in practice on an operating electrode, the layers are usually lost "too quickly" to be effective (4).

The interest was shifted to polymeric coatings for modification of electrode surface properties because of the advantages offered by these systems over chemically bound monolayers: ease of preparation, stability, larger signals for more straightforward characterization, and complete surface coverage (22).

Polymer-modified electrode surfaces have been prepared by glow-discharge polymerization (23), argon plasma polymerization (24), functionalization of surface bound polymers (25), and electrodeposition (26, 27). Most of these methods, however, 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 (22).

Electroactive polymer-modified electrodes have been prepared by initiation of polymerization directly at the electrode to form an adherent deposit that incorporates the desired redox centers. Early work was done with ruthenium, osmium, and iron complexes of vinyl-substituted bipyridines. Upon reduction, the added electron is known to be ligand-localized (4). It has been suggested that this redistribution of charge would be capable of initiating anionic polymerization. Accordingly, films of almost any thickness can be grown. Furthermore, films with variable ratios of ruthenium to osmium can be grown by adjusting the mix of monomer complexes in the starting solution. Electrochemical formation of polymer modified electrodes has the advantage that, if thick layers are to be grown, the film will go down in the conducting state with the counterions and/or electrolyte "in place." This is also true when the films are prepared by simple electrodeposition of an insoluble form of a soluble electroactive polymer (26). A drawback of electrodeposition techniques, as opposed to other methods of film formation such as coating by droplet evaporation, spin

coating (22) or dip-coating (2), is that geometrically nonuniform films can be formed.

An alternative approach was reported in which films of preformed electroactive polymers (21, 26, 28, 11) were physically adsorbed onto untreated electrode surface with the subsequent observation of electrochemical charge transfer. Since then much effort has been spent on the development and characterization of new polymers for the modification process, on the theory and study of electrocatalysis using these electrodes, and on understanding the process of charge transport in the polymer film. These aspects are further enumerated in the remainder of this section.

Materials studied have included ion-exchange polymers such as Nafion (29, 30) and poly(vinylpyridine) (PVP) (31), and polymers with fixed electron transfer sites such as poly(vinylferrocene) (26), poly(bi-pyridine) metal complexes (32), poly(nitrostyrene) (28), poly(tetrathiafulvalene) (22, 33-34, 35).

Oyama and Anson's procedure, for example (36), involves attaching multiply charged transition metal complexes to electrode surfaces coated with various polyelectrolytes. Coordinatively saturated and substitutionally inert complexes could be readily attached by this procedure so that only electrostatic interactions between the polyelectrolyte layer and metal complexes carrying the opposite charge were responsible for the "strong" and "long-lived" attachments (36). With cationic polyelectrolyte coatings, such as poly(vinylpyridine) (PVP) at pH values below ~ 4 , anionic complexes such as $\text{Fe}(\text{CN})_6^{3-}$, $\text{Fe}(\text{CN})_6^{4-}$,

IrCl_6^{3-} and IrCl_6^{2-} can be attached to electrode surfaces. With polycationic coatings, such as polyacrylic acid at pH values above ~ 5 , cationic complexes such as $\text{Ru}(\text{NH}_3)_6^{3+}$ can be incorporated into the polymer coating. Catalytic properties of these types of polymer modified electrodes have been studied by the same group (36). Electrostatic binding is attractive because it offers "extreme synthetic simplicity" that facilitates experimentation, but is disadvantageous because the redox centers can leach out of the polymer matrix quite readily (4).

New organic materials have been reported that show high electronic conductivities (2). Electronic conductivity refers to electron transport through the polymer by a delocalized band structure, as distinct from redox conductivity by site-site hopping, which is the usual form of charge conductivity for the redox polymers discussed above. Several of the conducting polymers exhibit electrochemical reactions intrinsic to net oxidation or reduction of the polymer film. This can "drastically" alter the polymer conductivity. Polypyrrole films, for instance, on electrodes (2, 37-39) are electronic conductors in the oxidized state but are insulators when reduced (40). Molecular redox species have been attached to the surfaces of electronically conducting polymers (in a manner similar to the modification of carbon or Pt) and electroactivity of monolayer quantities of attached species observed (2). This was illustrated by Diaz et al. (38), who attached a tetrathiafulvalene derivative to a polypyrrole polymer film surface

(38). This and other electronically conducting polymers such as polyacetylene (PA), polythiazyl (SN)_x, polyphenylene (pph) are believed to have commercial potential (2, 41-42).

The processes that take place at electrode/solution interface have characteristic kinetic properties. While some are facile, others may be rather sluggish, although thermodynamically feasible. Electrode kinetics, however, depend on the electrode potential. What this implies is that a slow, but thermodynamically possible reaction may be enhanced by the imposition of extreme negative (for reduction) or positive (for oxidation) potentials. This approach, however, is not always desirable in view of the limitations that may be imposed by the stability of the solvent/electrolyte species in use. An alternative, therefore, has been to find an "electrocatalyst" that could speed up an electrode reaction in the same way as a conventional catalyst does at thermal reactions (4). This possibility has been coined as "electrocatalysis" and many workers are trying to identify appropriate materials for such exploitations (43).

As pointed out by Andrieux and Saveant (43), electrodes coated by redox polymer films may provide interesting possibilities for catalysis of electrochemical reactions. Regarding redox catalysis, redox polymer film electrodes may lead to efficient catalysis whereas monolayer derivatized electrodes are anticipated to give small catalytic effects if any (43). An experimental illustration of such capability of redox polymer has been reported for the reduction of meso-1,2-dibromo 1,2-diphenylethane as catalyzed by a poly(p-nitrostyrene) coated electrode (44).

Several other applications have also been envisioned for such polymer modified electrodes (45): electrochromic devices (46), electrochemical desalination electrolysis (47), neurotransmitter stimulating electrodes (48, 49), coatings for the stabilization of semiconductive photovoltaic electrodes (50-54), ion-gating devices (55) and bilayer electrodes having possible applications in microelectronics (56).

In part because the applications envisioned for polymer-coated electrodes require reasonably high current densities, there have been many studies directed at understanding the charge transport process through thin films of redox polymers on electrode surfaces (21, 57-59, 22, 33, 34, 62-64). For fixed-site redox polymers, this process involves electron hopping between electroactive centers in the polymer matrix which gives rise to Fickian diffusive behavior when the films are electrolyzed in contact with solvent/electrolyte (21, 43, 65, 57, 58). This mode of electron exchange "diffusion," which can also take place in solutions of redox couples, has been shown to be significant for redox couples electrostatically bound to ion-exchange polymers on electrode surfaces (59, 66-68).

As is well known, this process was treated several years ago by Dahms and Ruff (60, 69, 70) who considered diffusion of redox couples in solution and showed that the electron exchange contribution to the measured diffusion coefficient, D_{et} , is given by eqn. 1,

$$D_{et} = \text{Const } k_{ex} \delta^2 c, \quad (1)$$

where k_{ex} is the second-order rate constant for electron exchange between redox sites, δ is the distance between sites, and c is the site concentration. One experimental test of this relation for charge transport in electroactive polymer films is that of Murray and coworkers (68) who electrosynthesized bipyridyl copolymer films with variable concentrations of metal redox sites. Equation (1) was only partially successful in explaining the concentration dependence of the charge transport process in these polymer films. At high concentration of the electron exchange sites, the effective diffusion coefficient for charge transport was concentration dependent decreasing with dilution up to ca. $4 \text{ \AA}^\circ$ edge-to-edge separation of the electron exchange sites, at which point it became independent of concentration. In this region polymer self-diffusive motions were suggested to govern the charge transport process (68). At high dilution the observed diffusion constants decreased further for this system.

The electron hopping model, however, requires a concurrent uptake of counterions into the polymer matrix (71). As such, the overall electrochemical behavior may involve a number of other processes. Segmental motions of the polymer backbone which may either align redox sites for facile electron transfer or open pathways for incorporation of electrolyte and/or solvent become important in such studies (71).

In addition to electron exchange reactions, other types of redox site interactions are operative at the high concentrations that are present in redox polymer films. Dimerization of redox sites has been

documented in tetrathiafulvalene (TTF) donor polymers (22, 72) and in tetracyanoquinodimethane (TCNQ) acceptor polymers (73, 74). Interactions between redox sites are thought to be an important factor in determining the shape of voltammetric surface waves for electroactive polymer films (3, 75, 76). Energetically repulsive interactions give rise to voltammetric surface waves that are too fat, i.e., with half-peak widths greater than $3.53 RT/nF$. It has been suggested that solvent swelling plays an important role in determining the extent of deviation from ideal behavior.

The aspect of our approach that differs to a certain extent from that of others, discussed above, is the emphasis on variation of the chemical composition and the molecular structure of the polymeric interface. Our major goal has been and remains to be able to control and understand the charge transport process at the molecular level via synthetic methodology of polymer chemistry. The polymer interface has been varied at the molecular level by the synthesis of polyesters (77), polyurethanes (79) and copolymers (78) containing well behaved acceptor groups incorporated into a polymer backbone of variable flexibilities.

The synthetic methods employed here are based on the work of Day (77), who first synthesized polymers containing neutral TCNQ units. The choice of the TCNQ molecules as the acceptor groups appears to be very suitable in terms of the electrochemical properties of the polymer films: (a) the widely studied TCNQ molecule exhibits classical EE behavior (i.e., two successive reversible electron transfer

steps) and forms a variety of stable radical anion salts (80); these salts have been intensely studied owing to the significant solid-state electronic conductivities which are found in many cases, (b) TCNQ⁻ anion, but not the dianion (81), is relatively insensitive to water and oxygen.

Polyurethanes, synthesized by Francis, employed the comonomers methylene bis(4-phenylisocyanate) (MDI), 1,4-toluene diisocyanate (TDI), and 1,6-hexamethylene diisocyanate, HMDI. These specific diisocyanates, which are widely used in the synthesis of commercial polyurethanes and are readily available, were chosen for the variation of structural features they impart to polymers. For example, MDI is a known "stiffening agent" that tends to make polymers rigid, while HMDI will act more like a plasticizer to add flexibility to a polymer chain (79, 83-84).

In the studies reported here, a further variation of the molecular structure has been achieved by synthesis of TCNQ-BOEB copolymer (referred to in the remainder of this dissertation as terpolymer), containing electroinactive 1,4-bisoxymethanol benzene (BOEB), see Figure 1.

Variation of the polymer film composition was also achieved by casting films of Day's TCNQ-PE (77, 85) (Fig. 2) with BOEB-PE (Fig. 3). The common comonomer, adipylchloride, and the similar sizes of the benzene ring and the quinodimethane structure suggest that these polymers might be isomorphic leading to the formation of uniformly blended films. An important result of this study is the extent to which the electrochemical behavior of the blended films

Scheme for terpolymer synth

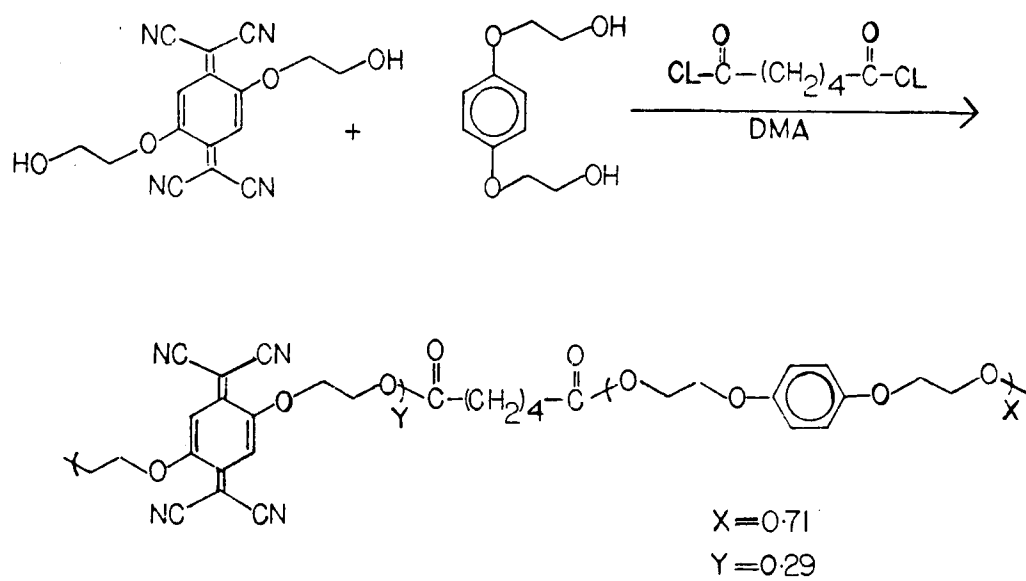


Figure 1. Reaction scheme for preparation of the terpolymer.

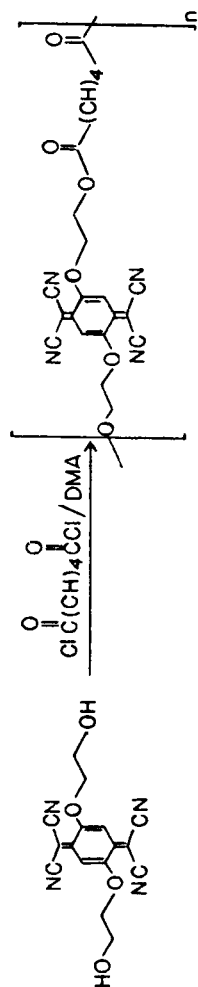
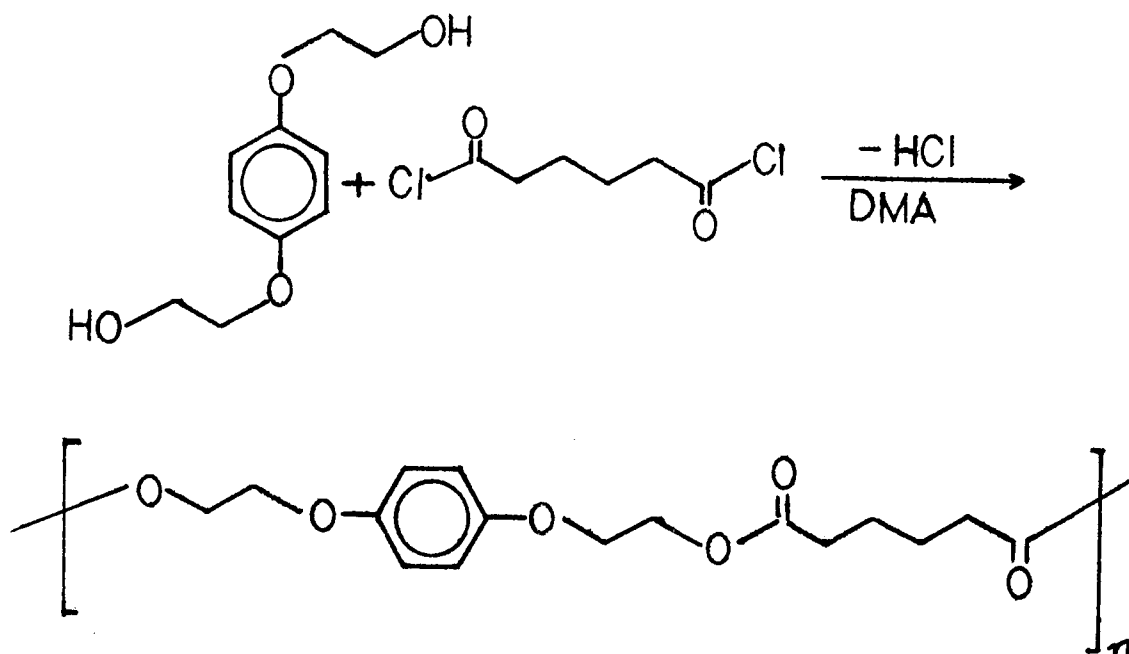


Figure 2. Reaction scheme for preparation of Day's TCNQ-PE.



POLY[(BIS)OXYETHANOLBENZENE-ADIPATE] = BOEB-PE

Figure 3. Reaction scheme for preparation of BOEB-PE.

corresponds to this expectation. Comparison of the electrochemistry of terpolymer with that of the blends has given information on this question (78). This is discussed in much detail in the present work. In addition, higher molecular weight materials have been obtained for the BOEB containing polymers since the bis-1,4-oxyethanol benzene monomer has significantly greater solubility than the TCNQ-diol. High molecular weight materials are favoured by high solubility of the comonomers in solution condensation procedures used for the polymer syntheses.

Variation of the polymer film composition has also been achieved by casting films of TCNQ-PE with a variety of "host" polymers such as polystyrene and poly(ethylene glycol), PEG. Charge transport through the films was markedly dependent on the nature of the host polymer in the "composite" films. While these films are not properly viewed as blends, since polymer blends are inherently unstable with respect to phase separation, nonetheless this approach provides a method of preparing modified electrodes for which the charge transport is dictated to a certain extent by the properties of the host polymer. Importantly, the polymeric nature of the film matrix seems to provide sufficient entanglement and other attractive forces may be responsible in maintaining the integrity of the film during the charge transport process. In this fashion it is possible to vary the molecular structure of the interface to a significant degree.

In view of mechanistic studies that were envisioned, PEG was chosen as a host polymer in the preparation of "composite" films. PEG is a known ionophore and PEG salt solutions are ionic conductors in

both liquid and solid state (86-89). It is also commercially available with a high degree of monodispersity and with a wide range of molecular weights. Murray's group recently reported solid state voltammetry of electroactive solutes codissolved in PEG polymer films on microelectrodes (87). Electrochemistry without liquid solvent is thought to be an attractive application of ionically conducting solids (87). The solids investigated so far have been primarily inorganic materials, most commonly β -alumina and silver salts (87-89). The use of ionically conducting polymers, according to Reed et al. (87), broadens the potential scope of "solid-state" electrochemical experiments. Use of polymer electrolytes such as salts of PEG with cations allows high ion transport rate to be achieved. Solvent free polymer electrolytes can be prepared by complex formation between a PEG and a simple alkali metal salt. Salts of a wide variety of anions may be incorporated in PEG (86).

Most studies of polymer electrolytes, such as PEGs, have focused on the factors influencing ion transport, with an emphasis on achieving high cation transport and negligible electronic conductivity or redox activity. The majority of solvent free polymer electrolytes have been prepared by complex formation between a polyether and a simple alkali metal salt. Hardy and Shriver (86) have utilized PEG as a host for alkali metal polyiodides. The polyiodides according to these workers, are potentially electrical conductors through ionic and electronic (or hole) charge transport. The conductivity of these materials, as well as other evidence (86) indicate that anion and cation are separated

by the polymer. This separation, according to Hardy and Shriver, appears desirable for the stabilization of polyiodide anions, because the polyiodide salts are known only in conjunction with large cations. For example, NaI_3 and higher sodium polyiodides are unknown, but a wide variety of tetraalkylammonium polyiodides are known (26).

A systematic study of the effects of polymer film composition on the process of charge transport through thin polymeric coatings has only been reported for a few systems (68, 62, 90). The reason for this void has been partly attributed to the difficulty associated with varying the polymer matrix composition in a controlled manner (68). The ideal behavior of TCNQ polyesters in acetonitrile/tetraethylammonium perchlorate (TEAP) as the supporting electrolyte allows such studies to be performed. The following sections deal with the application of cyclic voltammetry and chronocoulometry in the kinetic studies of charge transport through thin films of TCNQ polymer films of various compositions on platinum electrodes.

CHAPTER II

SYNTHESIS OF 2,5 BIS(HYDROXYETHOXY)-7,7,8,8-TETRACYANOQUINODIMETHANE

Introduction

Tetracyanoquinodimethane (TCNQ) has been one of the most thoroughly studied electron acceptor molecules since it was synthesized and characterized by Dupont chemists who reported its physicochemical properties in a series of publications (77, 80, 91-93). Much of the interest in this molecule, as discussed earlier, arose from the discovery that TCNQ formed stable radical anion salts which demonstrated significant solid state electronic conductivities in several cases. This discovery and the observation that these materials displayed anisotropic conductivities initiated the design of various synthetic schemes that described procedures for the preparation of different TCNQ derivatives. A comprehensive review of the above synthetic procedures has been given by Day (94).

The synthesis of 2,5-Bis(hydroxyethoxy)-7,7,8,8-Tetracyanoquinodimethane, (TCNQ-diol) 1, was reported by Hertler for use in the synthesis of semiconducting charge transfer polyurethanes (95). Day optimized the conditions and obtained somewhat higher yield for the preparation of TCNQ-diol (94). Day's work also included isolation and detailed characterization (UV-VIS, IR, C¹³-NMR and H¹NMR) of the intermediates in the overall reaction scheme shown in Figure 4.

This section describes the synthesis of TCNQ-diol according to Day's modification of Hertler's procedure.

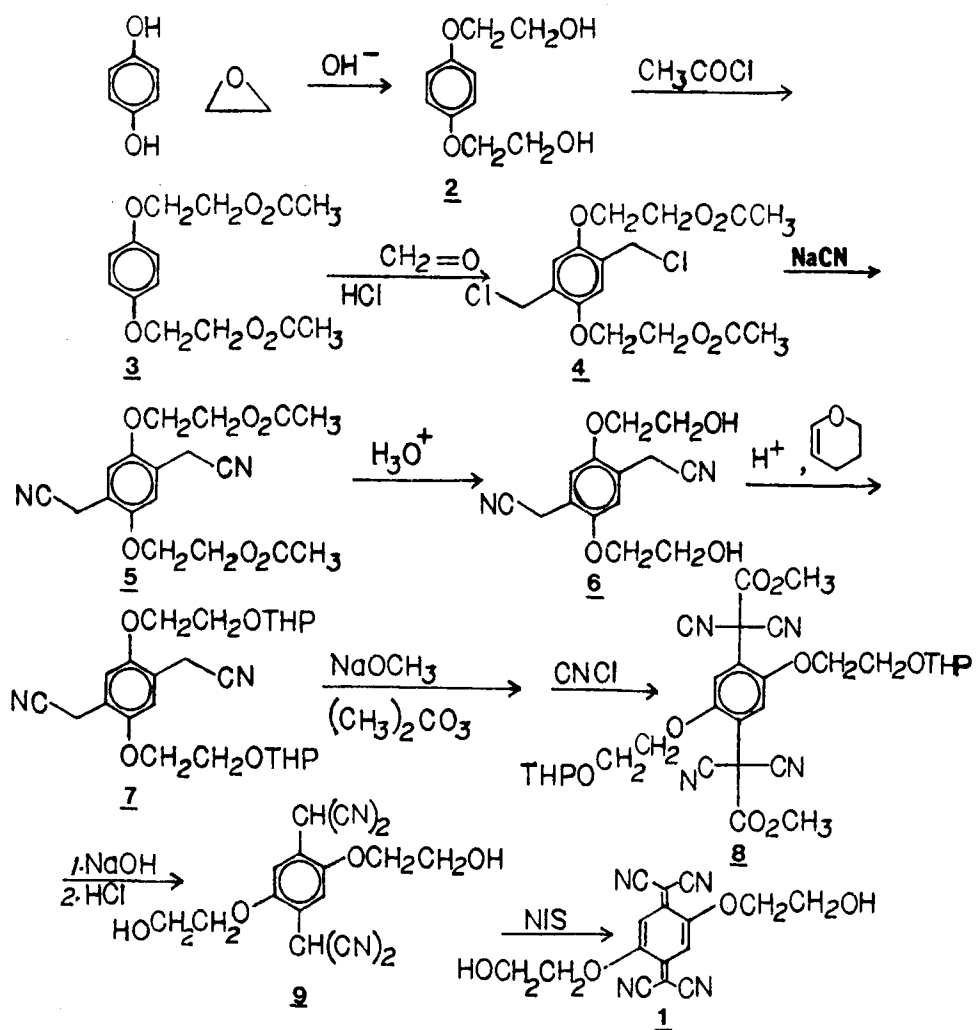


Figure 4. Reaction scheme for preparation of TCNQ diol.

The hydroxyl groups are introduced into the structure of the molecule in the first step of the reaction scheme. As pointed out by Day (94, p. 19), cyanodimethane groups are introduced in a series of steps that are similar to those described for the unsubstituted TCNQ. Therefore, the hydroxyl groups need to be protected from the strong electrophiles generated in the chloromethylation reaction by formation of the acetate ester. This protecting group must then be removed after the reactive dichloromethyl derivative, 4, has been converted to the more stable dicyano derivative, 5. The hydroxyl groups must then be reprotected with a base stable functionality that can withstand the subsequent reaction conditions involving alkoxides as reactant and carbanions as intermediates. This group is removed when, after the basic hydrolysis, the solution is acidified. The following sections will describe the above reactions in somewhat more detail.

Synthesis of 1,4-Bis(hydroxyethoxy) Benzene, 2

As pointed out by Day (94), Hertler's synthesis started with the esterification of 2 which was commercially available at the time of his work. This compound was no longer produced when Day started his synthetic work. However, several procedures were available in the literature that described the synthesis of this compound. The method of Fujita (96) was adopted which employed the reaction of hydroquinone (HQ) with ethylene oxide (EO) in the presence of catalytic amount of sodium hydroxide.

The initial attempts by Day to prepare 1,4-bis(hydroxyethoxy) benzene, BOEB-diol, proved to be challenging due to the volatile

nature of EO and the problems associated with side reactions that produced higher homologues of ethylene oxide adducts. The above problems, however, were circumvented by slow introduction of ethylene oxide into the reaction mixture containing deoxygenated aqueous sodium hydroxide and HQ at the temperature of 80°C. In this work, however, the reaction was performed at 50°C which resulted in higher yields and less impure products.

Day also suggested a mechanism which involved an acid-base reaction between hydroxide and HQ followed by nucleophilic attack on ethylene oxide. The reaction of phenoxyethoxide anion with the water then results in the regeneration of the catalyst.

The product of this reaction was a white solid which could be recrystallized to a high degree of purity in water and/or acetonitrile. The product melted at 103-106.5°C and showed absorption at 289 nm in acetonitrile corresponding to the benzene ring; see Figure 5. The IR spectrum (a KBr pellet) showed a broad band at $3,265\text{ cm}^{-1}$ corresponding to the hydroxyl groups. Bands corresponding to the aromatic ($2,955\text{ cm}^{-1}$) and aliphatic $-\text{CH}$ ($2,930$ and $2,870\text{ cm}^{-1}$) and 1,4-disubstituted benzene (825 cm^{-1}) were also present on the spectrum.

The intermediates in the overall reaction scheme were solids with distinct melting points. A high degree of correlation was observed, in all cases, between the spectroscopic data and the melting point range of the respective intermediates. Since detailed spectroscopic data were compiled by Day (94) and also reported by Francis (79), these data will not be given here.

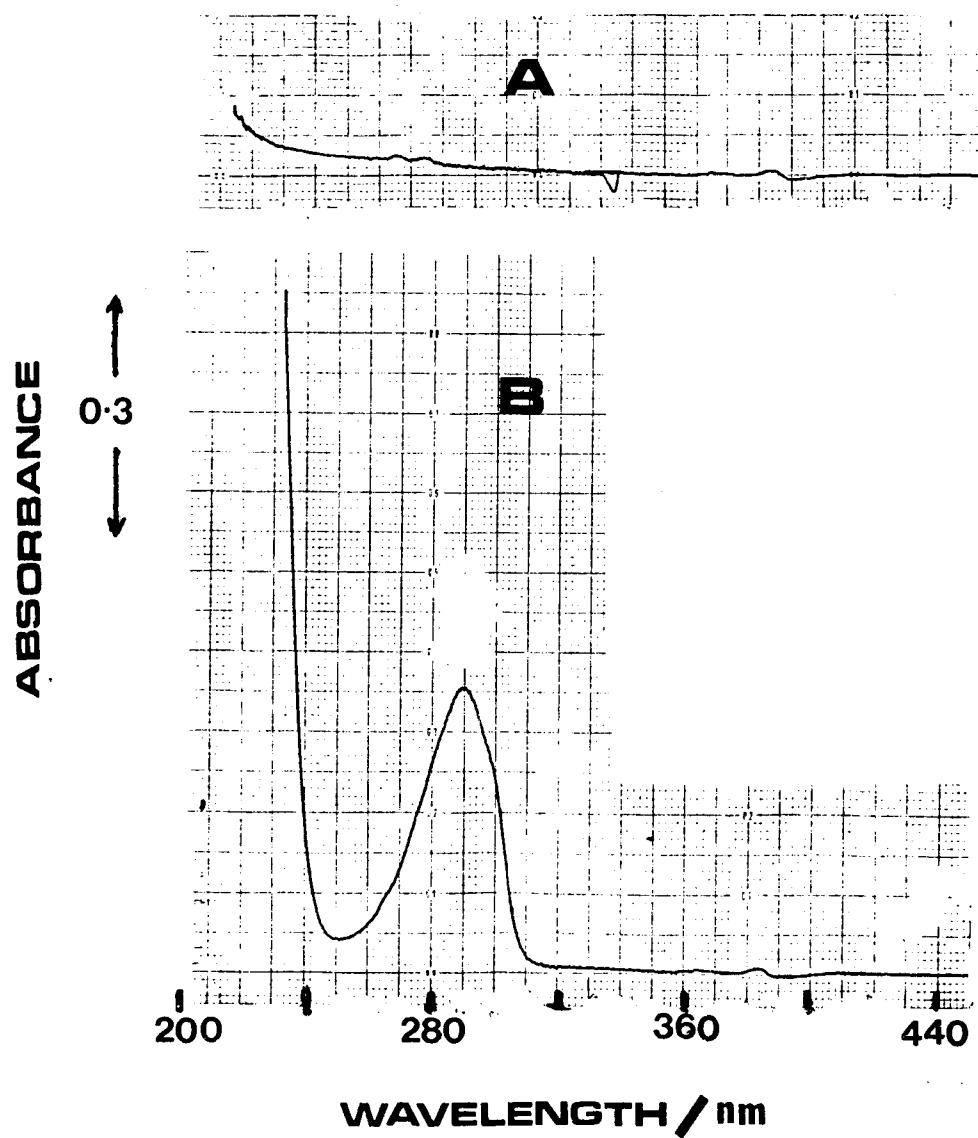


Figure 5. UV-VIS spectrom of acetonitrile (A) and UV-VIS spectrum of BOEB diol in acetonitrile (B).

Synthesis of 1,4-Bis(acetoxyethoxy) Benzene, 3

In order to chloromethylate 2, it was necessary to protect the hydroxyl groups from the electrophilic species present in the reaction medium. According to Day, for the chloromethylation of the phenolic compounds, esterification is usually the method of choice since esters are stable to the reaction conditions used and more importantly they do not lower the reactivity of the aromatic nucleus toward chloromethylation (94). Furthermore, since the hydroxyl groups are not directly attached to the aromatic ring, considerations of reactivity towards chloromethylation are not as important (94).

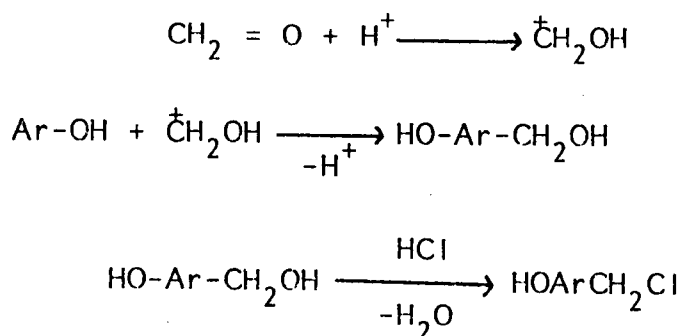
Acylation was achieved by treatment of 2 with acetylchloride. This rather nasty reaction, which should be performed with sufficient ventilation, is very facile and results in quantitative yields. The product was crystalline solid, white in color and melted at 97.5-99°C.

Synthesis of 2, 5-Bis(2'-acetoxyethoxy)-P-
Xylylene Dicyanide, 5

Although bis-chloromethylation of 3 was reported by Hertler, initial attempts to duplicate the reaction in our laboratory proved to be a very challenging task (94). The literature recipe lacked the details necessary for performing the reaction successfully. When the reaction was started by mixing the starting materials in the reaction vessel, it led to the formation of polymeric materials that were believed to consist of highly cross-linked insoluble species. A survey of the literature on chloromethylation reactions and a careful observation of the changes

taking place early in the course of reaction revealed that the reaction produced an exotherm in the initial stage. If this exotherm was controlled by external cooling, the desired product is formed.

Chloromethylation was carried out by the reaction of the substrate with p-formaldehyde and hydrochloric acid. A plausible mechanism for the chloromethylation of the aromatic substrate was discussed by Day (94). Accordingly, the reaction appears to proceed by the interaction of the hydroxymethyl carbonium ion with the aromatic nucleus:



The product of this reaction could be recrystallized from methylenechloride and melted at 129-133°C. The yield of this reaction varied in each different run (18.9-45.5%).

The reaction of 4 with sodium cyanide in DMSO was performed immediately after the preparation of the bis-chloromethylated compound. This minimized problems resulting from the instability of 4. The solution of cyanide in DMSO is poisonous and should be handled with care. The reaction of dichloride, 4, with sodium cyanide in DMSO is presumably an $\text{S}_{\text{N}}2$ displacement reaction.

The product of cyanide reaction could be crystallized from dioxane. The reaction yield was 63% and the product melted at 169-172°C.

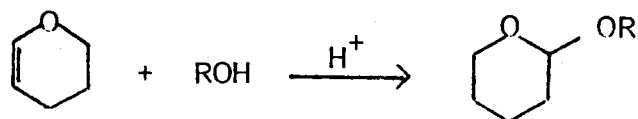
Synthesis of 2,5-Bis(2'-hydroxyethoxy)-P-
Xylylene Dicyanide, 6

Due to the susceptibility of the ester linkage to the harsh environment of the final steps in the reaction scheme shown in Figure 1 (p. 12) the protecting group had to be replaced. This was accomplished by removal of the acetyl group through hydrolysis of the ester linkage. Several methods are known for cleavage of esters (94). The most widely used method, however, is hydrolysis with basic or acidic catalysis. Since the use of basic hydrolysis may result in partial SN_2 displacement of the cyano groups from the active benzyl-positions, acid catalyzed hydrolysis, therefore, was used for removal of the ester groups. The hydrolysis was performed by subjecting compound 5 to dilute aqueous hydrochloric acid in a mixed solvent, dioxane-acetonitrile (50:50 v/v) solution. Since the ester is soluble in this solvent system and the free alcohol insoluble, the product precipitated as it is formed, thus driving the reaction equilibrium toward completion. The reaction was performed at room temperature and dilute acidic condition to avoid possible hydrolysis of the nitrile to an amide or acid which could occur under more harsh conditions (94).

The product of hydrolysis was a white solid that melted at 184-186°C and the yield was 77%.

Synthesis of 2,5-Bis[2'(tetrahydropyranyloxy)ethoxy]
-p-Xylylene Dicyanide, 7

The highly basic conditions of the last steps in the reaction require that the hydroxyl functionalities be protected with a suitable species that can survive the reaction conditions. Tetrahydropyranyl protecting group (THP) was chosen because of its ease of introduction and removal on the free hydroxyl groups.



The reaction of dihydropyran (DHP) with alcohols is catalyzed by acids and the resulting THP product is stable to a variety of conditions including strong bases (94). This reaction employed P-toluenesulfonic acid as a catalyst. Day reported that poor yields result, if the procedure outlined by Hertler (95) for the workout of the reaction mixture was followed. In this work the procedure employed by Day was followed closely. Quantitative yields of reasonably pure product can be obtained by a simple procedure. The reaction mixture was dissolved in benzene and washed several times with a saturated aqueous solution of sodium bicarbonate. The product of this reaction could be crystallized to a high degree of purity from cyclohexane. The reaction yield was 74.9% and the product melted at 89-90°C.

Synthesis of 2,5-Bis(2'-hydroxyethoxy)-7,7,8,8-Tetracyanoquinodimethane, 1 (TCNQ-diol)

Day has outlined the sequence of steps by which compound 8 can be converted to TCNQ-diol. According to the scheme shown in

Figure 6, the reaction proceeds via the delocalized anion, 10, which undergoes a Claisen condensation with dimethylcarbonate. A second Claisen condensation leads to 12. The anion, 13, which is produced by further reaction with methoxide, reacts with cyanogen chloride to produce the cyanodicarbonyl compound, 14. Base hydrolysis of the ester followed by acidification, which causes decarboxylation, and removal of the THP group yields the dihydro TCNQ derivative 9. N-Iodosuccinimide oxidation of this intermediate then gives 1. Methanol, one of the products in the reaction, is removed by distillation shifting the acid/base equilibria toward the product. As pointed out by Day, the use of benzene to aid in the removal of methanol as an azeotrope was found to be very advantageous. The reaction mixture which was very viscous became thinned by the addition of benzene, allowing efficient stirring and good heat transfer in the reaction medium. The completion of the removal of the methanol was marked by a sudden jump in the temperature of the reaction medium. Sodium methoxide was freshly prepared prior to the reaction. Cyanogen chloride, a colorless gas at room temperature, is very poisonous and must be handled with great care, under the hood. This compound can be handled safely if it is condensed at ice-temperature. Accordingly, this gas was trapped in a container, designed with safety precautions, which was immersed in an ice-water bath (see the Experimental section). The base catalyzed hydrolysis of the ester groups was also performed according to Day's outline (94). Hertler's procedure called for the addition of warm 10% aqueous sodium hydroxide to

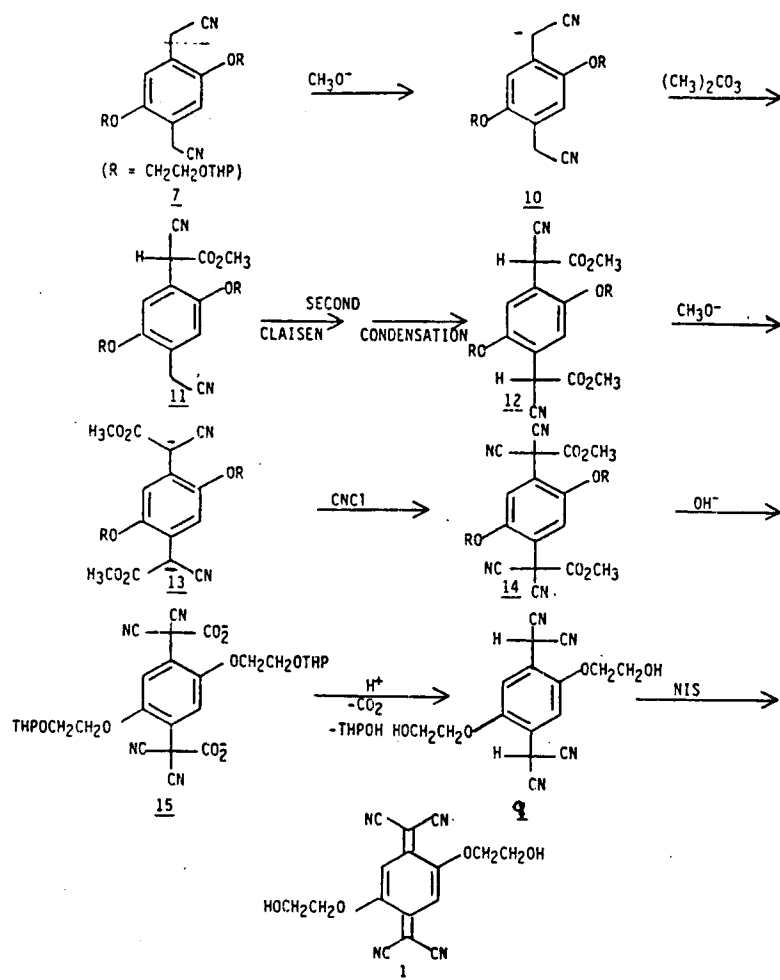


Figure 6. Reaction mechanism for TCNQ diol synthesis.

the dark colored gummy solid at this stage of the synthesis. In our hands the reaction proceeded exothermically and warming of the aqueous NaOH was not necessary to dissolve the solids.

The product, TCNQ-diol, could be recrystallized in acetonitrile to yield purple-red, very crystalline, needles that melted at 229.2-232°C. The uv-visible spectrum of TCNQ-diol (Figure 7) shows absorption bands at 415 nm and 432 nm in accord with the spectrum of neutral TCNQ-diol reported in the literature (95). Figure 8 shows the cyclic voltammogram of Hertler's monomer, 1, in acetonitrile and 0.1 M tetraethylammonium perchlorate (TEAP). The expected two-step reversible EE mechanism is evident with $E_{\frac{1}{2}}^{0/-} = -0.088 \text{ V}$ and $E_{\frac{1}{2}}^{-/2-} = -0.500 \text{ V}$ vs. Ag/AgCl.

Experimental Section (Monomer Synthesis)

Synthesis of 2

Sodium hydroxide (2.5 g) was dissolved in 682 ml of water in a 2 l round bottom (rb), three neck flask equipped with overhead stirrer, heating mantle, dry ice-ethanol condenser, thermometer, and nitrogen bubbler which was placed in a trap in the line. The solution was then purged with ultrapure N₂ for ½ hr to remove the dissolved oxygen. Addition of 1,4-benzohydroquinone (HQ, Merck), 227.3 g, was performed as quickly as possible to minimize O₂ contamination. Slight heating enhanced the rate of HQ dissolution which was marked by the appearance of dark brown color. Ethylene oxide (EO) introduction in to the reaction vessel was found to be a very critical step

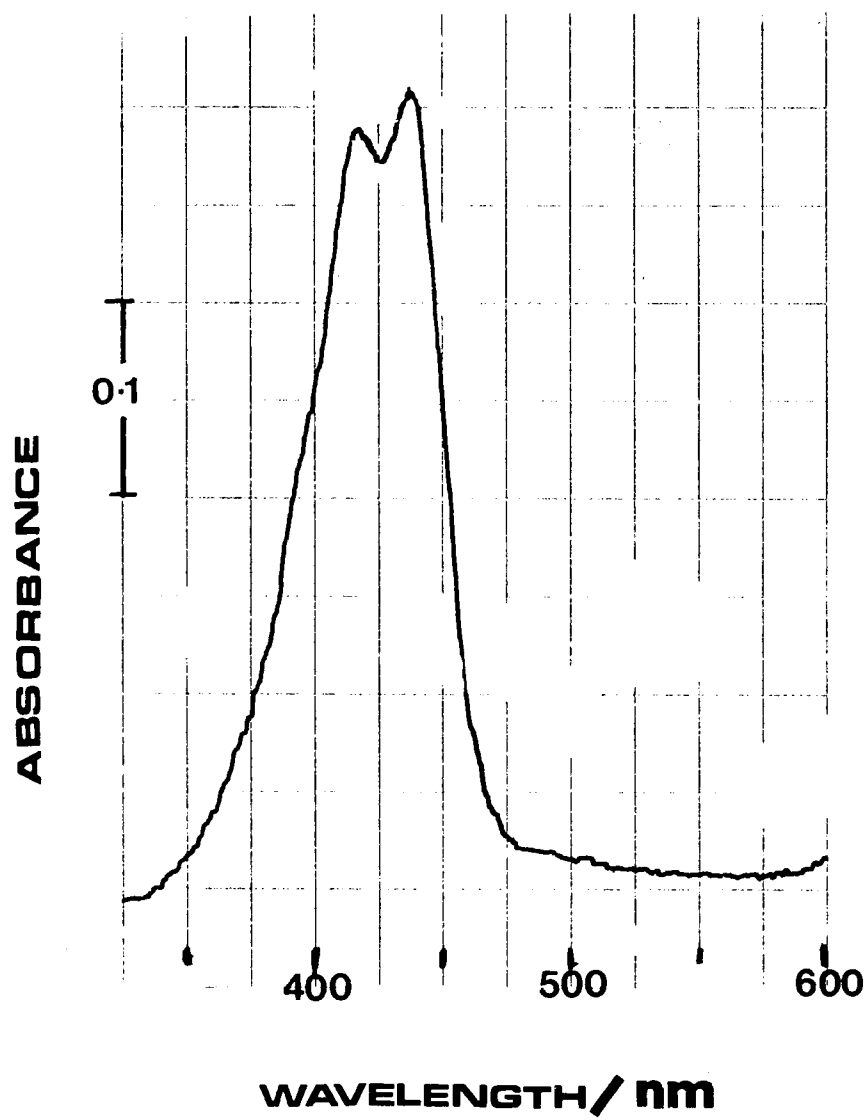


Figure 7. UV-VIS spectrum of TCNQ diol in acetonitrile.

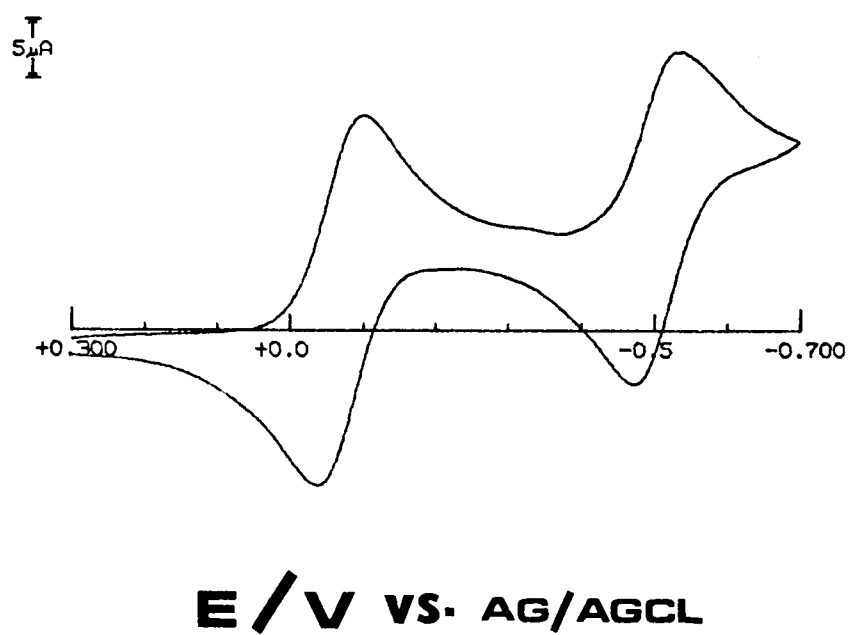


Figure 8. Cyclic voltammogram of TCNQ diol in acetonitrile/0.1 M TEAP solution; scan rate = 20 mV/sec.

and was performed at a very slow and continuous rate to avoid losses due to evaporation. The EO was condensed in the ice-cold trap and precautions were made to eliminate any losses through possible leaks at the junctions. Removal of the ice bath from the surroundings of the trap and introduction of a gentle/steady flow of N_2 gas allowed the diffusion of the EO into the reaction mixture which was held at $50^\circ C$. After the addition of EO was complete (approx. 5-7 hrs), the reaction was allowed to proceed for three more hours. The contents of the reaction vessel were then transferred to a wide mouth beaker to facilitate the work-up procedure. When the reaction mixture cooled to room temperature, a massive amount of white/beige solids precipitated from the solution. Although the yield of reaction at this stage proved to be rather high (87.9%), repeated recrystallization in water and/or acetonitrile yielded highly purified white crystalline solids of much lower yields.

The product melted at $103-106.5^\circ C$ and showed absorption at 289 nm in acetonitrile corresponding to the benzene ring.

The detailed spectroscopic data (IR, NMR, UV-Vis) corresponding to these intermediates were compiled by Day (94) and Francis (79).

Synthesis of Compound 3

Compound 2 (328.5 g) was placed in a 2 liter rb flask equipped with a magnetic stirrer, heating mantle and a condensor. Acetylchloride (1500 g) was then gradually added to the reaction vessel through the condenser. The reaction was exothermic and care was taken to keep the exotherm under control. After the solids were dissolved, the

reaction was brought to reflux by slow heating and was allowed to proceed overnight. The next day the olive black solution was transferred to a 2-liter beaker while still warm and cooled to room temperature. At this point white solids precipitated out of the solution. Great care must be taken during the product washes and the whole work-up procedure should be conducted under the hood with appropriate ventilation. The solids were collected by gravity filtration and cold water was used to perform the washes. The product was crystalline and white in color and quantitative yields were obtained. The product melted at 97.5–99°C.

Synthesis of Compound 4

In a 2-liter, 3 neck rb flask equipped with overhead stirrer, thermometer, heating mantle, condenser, and gas inlet were added compound 3 (176 g), paraformaldehyde (Aldrich) (47 g), 103 ml glacial acetic acid (Fisher) and 120 ml of concentrated HCl (Fisher). The contents of the flask were stirred while bubbling in dry gaseous HCl (electronic grade, MG scientific gases). After the exothermic reaction subsided, the temperature was gradually raised to 50°C and reaction was allowed to proceed for almost 2 hours. At the conclusion of the reaction, the product mix was dissolved in methylene chloride in a separatory funnel and the aqueous layer was discarded. The methylene chloride fraction was washed several times with water and then dried over magnesium sulfate (and decolorizing carbon) for a few hours. The clear, dark brown supernatant solution was then separated by filtration through fluted filter paper. All of the above

operations were performed under the hood. The creamy beige product was separated by rotoevaporation. The product was then recrystallized from methylenechloride. A second batch of product was also separated from the filtrate but was not used in the subsequent reactions. The product melted at 129-133°C. The yield of this reaction varied in several runs (18.9-45.5%).

Synthesis of Compound 5

A 1-liter, 3-neck rb flask was equipped with overhead stirrer, heating mantle, thermometer, condenser, and gas inlet (for generation of N₂ blanket). Compound 4 (98 g) and sodium cyanide (30 g) were dissolved in 175 ml of DMSO. The addition of the dichloride was performed in small portions and the reaction mixture was held at or below 40°C. After the addition of the dichloride was complete, the temperature was raised to 50°C and was allowed to proceed for 1 hour. The temperature was then raised to 80°C followed by cooling to room temperature. The product mixture was diluted by a large volume of water and the filtrate cake, orange in color, was separated by vacuum filtration and recrystallized from dioxane. Prior to recrystallization, an attempt should be made to remove NaCl from the reaction mix. Failure to do so will result in a tedious recrystallization procedure. The reaction yield was 63% and the product melted at 169-172°C.

Synthesis of Compound 6

A 1-liter rb flask was equipped with magnetic stirrer and a condenser. Compound 5 (23.5 g) was then added to a mixture of

225.8 ml of dioxane (Fisher-Cert ACS) and 225.8 ml of acetonitrile (Fisher-Cert. ACS). The above mixture was stirred with warming until the dicyanide dissolved. Then 90.5 ml 10% HCl (from Fisher by dilution) was added to the reaction vessel. The reaction was allowed to proceed for one week at 22°C. At the conclusion of reaction, the white precipitate was vacuum filtered and washed with water, dioxane and ether followed by drying. Temperature should be maintained at ~22-30°C during the course of the reaction. At lower temperatures (<15°C) the starting material precipitates out of solution and has the same appearance (white) as the desired product. The product of hydrolysis melted at 184-186°C and the yield was 77%.

Synthesis of Compound 7

A 250 ml Erlenmeyer flask was equipped with a magnetic stirrer and reflux condenser. The reaction vessel was then placed on a hot plate. Compound 5 (13.0 g) was placed in 73 ml of THF (Fisher) containing 96.21 mg of paratoluene sulfonic acid monohydrate (Aldrich). The reactants were stirred with gentle heating until dissolution took place and was then heated at reflux for an additional 1.5 hr. The reaction mixture was then cooled and dissolved in 400 ml of benzene (Fisher-Cert. ACS). The solution containing the product was then placed in a separatory funnel and washed three times with 100 ml portions of saturated NaHCO₃ solution. The organic phase was then dried over magnesium sulfate. After filtration, the solvent was removed by rotoevaporation and the solids were placed in a vacuum desiccator. The reaction yield was 74.9% and the product melted at 89-90°C.

Synthesis of Compound 1

In a 100 ml, three neck rb flask equipped with overhead stirrer, thermometer, heating mantle, and reflux condenser were placed 7 g of compound 7 and 32 ml of dimethylcarbonate (Aldrich, 99%) containing freshly prepared sodium methoxide (2.2 g). The temperature was gradually raised to 70°C, then 10 ml of benzene was added to the reaction mixture. The reaction was allowed to proceed, under reflux, for 3 hr. Methanol produced by the reaction was removed as an azeotrope with benzene by simple distillation. A gas inlet which was attached through an ice-cooled trap to a cyanogen chloride cylinder, was then substituted for the distillation apparatus. The reaction mixture was diluted by cold dimethyl carbonate to a temperature of 0-5°C. Cyanogen chloride (5.0 ml) was collected by condensation into a cool graduated cylinder used as a trap. Removal of the ice bath allowed slow distillation of the cyanogen chloride into the reaction mixture. When the addition of cyanogen chloride was complete, the mixture was stirred at 0-5°C for 2 hr, and then warmed to 50°C. At this point the heating mantle was removed, and the product was allowed to warm to room temperature and to stir overnight. The next day the reaction mixture was reheated to 50°C followed by recooling to room temperature. The contents of the reaction vessel were transferred to a 100 ml rb flask. Dimethylcarbonate was used to rinse the flask and the solution was evaporated to dryness on a rotary evaporator. After the removal of the solvents, a dark gummy solid was extracted with 100 ml of 10% aqueous sodium hydroxide and the extract

was acidified with 10% aqueous hydrochloric acid. Upon the addition of the acid, copious gas evolution was noticed which was also accompanied by the separation of an oily, gummy black-red material. The above oil was easily separated and dissolved in methylene chloride which yielded dark red-orange solution. Decolorizing carbon and anhydrous magnesium sulfate were added to the above solution. The solution was then filtered and the solvent was removed on a rotary evaporator to give an orange-red oil. The oily material readily dissolved in 100 ml of acetonitrile (Fisher-Cer. ACS) containing 1.5 g of N-iodosuccinimide (Pfaltz and Bauer). The solution color darkened as the solutions were mixed. The reaction vessel was gently stirred with occasional gentle heating for 30 minutes. The reaction mixture was rotoevaporated yielding a dark red gum which was washed with two 10 ml portions of water and hexane. The product was then dissolved in hot methanol. Upon cooling and addition of water large amounts of solid began to precipitate. The solids were collected by vacuum filtration and were then recrystallized in acetonitrile to yield approximately 1 g of purple-red needle (crystals) that melted at 229.2-232°C.

CHAPTER III

SYNTHESIS OF TCNQ-BOEB COPOLYMER (TERPOLYMER)

Introduction

TCNQ-diol is quite versatile in that it will lend itself to the synthesis of a wide variety of polymers using classical methods. Changing the comonomer will also affect the properties of the resulting polymeric TCNQ materials such as: solubility, viscosity, durability, resistance to hydrolysis, chain flexibility, etc. The electroactive monomer, TCNQ-diol, has well behaved electrochemical properties which have permitted a systematic study of the extent to which polymer properties dictate the electrochemical behavior. This monomer has been covalently incorporated in the backbone of polyesters (77) and polyurethanes (79) via solution polycondensation reactions. The polyesters were prepared by the low-temperature polycondensation of adipylchloride with TCNQ-diol, while polyurethanes were prepared by the polycondensation of TCNQ-diol with methylene-bis(4-phenylisocyanate) to give MDI-PU, 1,4(toluene diisocyanate) to give TDI and 1,6 hexamethylene diisocyanate to give HMDI-PU. These polyurethanes have rich electrochemistry and have been extensively studied in our laboratory (79).

In this section the synthesis of a polyester is discussed which employs a mixture of the electroactive TCNQ-diol and electroinactive BOEB-diol with stoichiometric amount of adipylchloride in DMA via

solution polycondensation at low temperature according to Day's procedure. The scheme for the synthesis of such a copolymer containing both TCNQ and benzene rings in the polymer backbone was envisioned in view of its ability to provide a strategy for the variation of the redox site concentration in the polymer backbone. The product expected for such a reaction would be a random copolymer with a fraction, x , TCNQ units and a fraction, $1-x$, aromatic units. The effective concentration of the acceptor sites is available from the electrochemical measurements (73). Since the extent of dimerization will depend on the concentration of the redox sites in the reduced state, it is of interest to see if simple dimer equilibria account for the electrochemical observations as the acceptor spacing is varied. The extent of dimerization has been well studied by spectroelectrochemical techniques by absorbance measurements at 660 nm and 730 nm, λ_{max} for the dimer (TCNQ_2^{2-}) and monomer ($\text{TCNQ}^{\cdot-}$) band respectively (74). Most importantly, by measurements on the extent of dimer formation in the reduced state and its effect on the electrochemical behavior, an indication of intra- vs. inter-chain interactions can be obtained. In view of the mechanistic implications that can be obtained regarding the process of charge transport through thin polymer films on electrode, the synthesis and study of the terpolymer was of special interest to us.

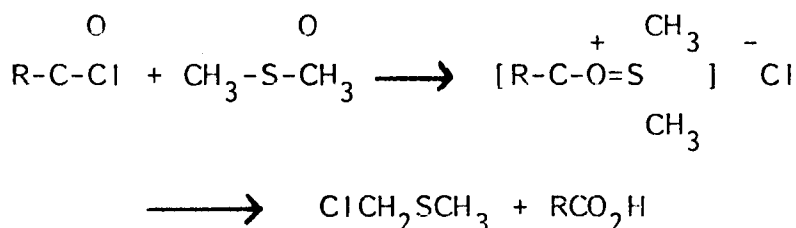
As pointed out earlier, the synthesis of a polyester, containing covalently attached neutral TCNQ units, was first accomplished by Day in our laboratory (77, 94). Although TCNQ radical anions had

previously been incorporated as counterions into polycationic matrices (97) and a low molecular weight TTF-TCNQ material (95), no polymer containing attached neutral TCNQ units had been reported previous to Day's initial communication (85). Day's synthesis described a low-temperature solution polyesterification procedure using aliphatic diacid chloride and aliphatic diols. Since such polycondensation reactions had previously resulted in only low-molecular weight products (94), a systematic study of the solution polyesterification of a model polymer system was first undertaken by Day. Reaction conditions such as the role of concentration, effect of reaction time, temperature, and solvent were established for the preparation of high molecular weight products and then applied to preparation of the "novel" TCNQ polyesters whose rich electrochemical properties have been the subject of extensive study in our laboratory in the past six years (72-74, 76, 45, 98, 85, 99).

The model monomer, 1,4-bis(2'-hydroxyethoxy)-benzene, 2, was employed in the above optimization studies. As discussed elsewhere, this compound was the first intermediate in the synthesis of the TCNQ-diol and that was readily purified by recrystallization from water and/or acetonitrile. Also, the hydroxyl groups are attached to a central nucleus by the same linking groups as in the TCNQ-diol. This aspect of the model monomer made it highly desirable for our purposes.

Aliphatic diacid chlorides were chosen as comonomers in the initial studies, because of their expected higher solubilities of the polyester

products. High yields and high molecular weight products have been realized under conditions where both monomer and polymer are soluble in the solvent used. It has been shown that increase in the solvent dielectric constant can result in higher molecular weight products from low-temperature solution polyamidization (94). But the low solubility of the TCNQ-diol in most common suitable organic solvents, as well as the intrinsic reactivity of some of the available polar solvents, limited Day in his choice of an appropriate solvent. Dimethylsulfoxide has been known to react with acid chlorides to give high yields of carboxylic acids and chloromethyl methylsulfide, the reaction proceeding



with initial formation of o-acylated complex. The formation of this side product will affect the stoichiometric balance that may result in low molecular weight product (94). N,N-Dimethylformamide (DMF) also undergoes reaction with acid chlorides, in this case the reaction proceeds via O-acylation. Pyridine was eliminated because it could form an insoluble complex with acid chlorides. Acetonitrile also introduced problems associated with solubility (94). N,N-Dimethylacetamide (DMA) was, therefore, chosen for these studies. Although a side reaction of acid chloride with DMA also occurs, by running the reaction at lower

temperatures, the side reactions could be suppressed and high molecular weight products could be prepared by low temperature polycondensation in this solvent (94). Furthermore, the synthesis of the polymer at low temperatures was desirable, because TCNQ-diol had been known to show signs of decomposition upon heating (94).

A series of polycondensation reactions was performed, at low temperatures, with the model monomer, and with various diacid chlorides in DMA. Day evaluated terephthalyl, isophthalyl, sebacyl and adipyl chloride as possible comonomers (94). The products of the aromatic diacid chlorides with model diol were found to be insoluble at room temperature in all solvents tested, and no molecular weight or viscosity determinations could be run on these products. The use of sebacylchloride also lead to products that precipitated at very short reaction times (<2 hrs). These precipitates were believed to be of low molecular weight (product was soluble in DMA and gave solutions with low viscosity) (94). Adipylchloride was the only comonomer tested which yielded products that did not precipitate from the DMA polymerization solvent. But, after several hours, the exact amount of time depending on the reaction variables, the reaction mixture, in the case of model systems, solidified into a gel-like mass. The possible consequences of this gelation, which was also seen for the synthesis of TCNQ-BOEB copolymer, has been discussed by Day (94).

The reaction was found to be very sensitive to the presence of even traces of atmospheric water. Accordingly all weighings and manipulations were done as recommended by Day, under a stream of ultrapure N_2 and inside of a glove bag.

Experimental Section

Apparatus

Voltammetry and chronocoulometry in solution were done on a BAS-100 and recorded with a Bausch and Lomb digital plotter (model no. DMP-40). The potential of this electrode was ca. 20 mV vs. SCE in the $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$ solution. All solutions were purged with high purity N_2 gas before use and an inert gas blanket was maintained throughout the voltammetric experiments.

Infrared spectrum of the polymer was recorded on a Perkin Elmer 1330. The polymer was dissolved in DMA/acetone (1:1) and aliquots were evaporated on NaCl plate. Very thick films were needed to see the band due to $-\text{C}=\text{N}$ ($2,240 \text{ cm}^{-1}$). The polystyrene peak at $1,601 \text{ cm}^{-1}$ was taken as the reference.

Viscosity measurements were obtained using an Ubbelohde dilution viscometer at a temperature of 25°C . The details and results of viscosity measurements on the standards used in analysis of GPC data are given elsewhere (see reference 79, p. 69).

UV-vis spectra were obtained with a Cary 17 spectrophotometer.

Gel permeation chromatography was performed on a Waters Model 590 gel permeation chromatograph equipped with two μ -Styragel columns (7.88 mm i.d. $\times$ 30 cm, $10^3 \text{ \AA}$ and $10^4 \text{ \AA}$, exclusion limit 200,000) in series using DMA as the eluent at 60°C . Polystyrene standards with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \approx 1.06$) were obtained from Polyscience or Water Associates.

Chemicals

The details of the synthetic procedure employed for the preparation of the monomers, TCNQ-diol and BOEB-diol was given in earlier sections. Adipylchloride (Aldrich, 98%) was fractionally distilled twice under vacuum prior to its use. DMA (Fisher certified) was purified by fractional distillation under reduced pressure and was stored over 3A molecular sieves. Tetraethylammonium perchlorate (TEAP) (Eastman) was recrystallized from H₂O and dried under vacuum. Spectral grade acetonitrile (Aldrich) used in the electrochemical studies was stored over 3A molecular sieves without any further purification.

Synthesis of the polymers used in this study, TCNQ-PE and BOEB-PE are given elsewhere (94, 77).

TCNQ-BOEB copolymer was synthesized by an identical procedure, as described for TCNQ-PE and BOEB-PE, and involved solution polycondensation of a mixture of 1 and 2 with stoichiometric amounts of adipylchloride in DMA at low temperatures.

Preparation of the Terpolymer

The synthetic procedure for the TCNQ-BOEB copolymer follows. Under the dry nitrogen atmosphere of a glove bag, 0.4735 g (2.587 mmol) of twice distilled adipylchloride, weighed into a syringe, was added to a frozen solution of 0.3254 g (1.6434 mmole) of recrystallized 2 and 0.3058 g (0.9438 mmole) of 1 in ca. 30 ml of DMA. After melting, the mixture was stirred at refrigerator temperature (ca. 4°C). After ca. 24 h, the reaction mixture solidified into a gel,

but stirring was continued for 5 days; the gel was then transferred to a beaker and dispersed in 120 ml of absolute ethanol. The solids were collected by vacuum filtration, washed exhaustively with ethanol, and dried under continuous high vacuum in an oven overnight. The product was a brown powder, 0.5365 g (56%), which could readily be cast as films and showed a somewhat lower solubility in DMA/acetone than the TCNQ polyester.

Results and Discussion

Spectroscopic Characterizations

An acetonitrile solution of the terpolymer absorbed light at 420, 438, and 290 nm (Fig. 9). The doublet observed in the spectrum is characteristic of neutral TCNQ moities, whereas the band at 290 nm was assigned to the absorption of benzene rings in the polymer backbone. The following procedure was used to estimate the mole fraction of TCNQ in the terpolymer backbone.

A solution of 1,4-bis(hydroxyethoxy) benzene, 2, in acetonitrile showed an absorption band at 289 nm corresponding to the benzene ring (see Fig. 5, p. 22). This absorption (0.16) was used to estimate a molar extinction coefficient of $3.4 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ for this compound. This extinction coefficient for BOEB and the literature value of ϵ for TCNQ absorption at 432 nm ($42,950 \text{ m}^{-1}\text{cm}^{-1}$) were used to estimate the concentrations of TCNQ and BOEB in the polymer backbone, which in turn allowed an estimation of the mole fraction of TCNQ (0.294) in the terpolymer backbone. In this procedure it was assumed that the

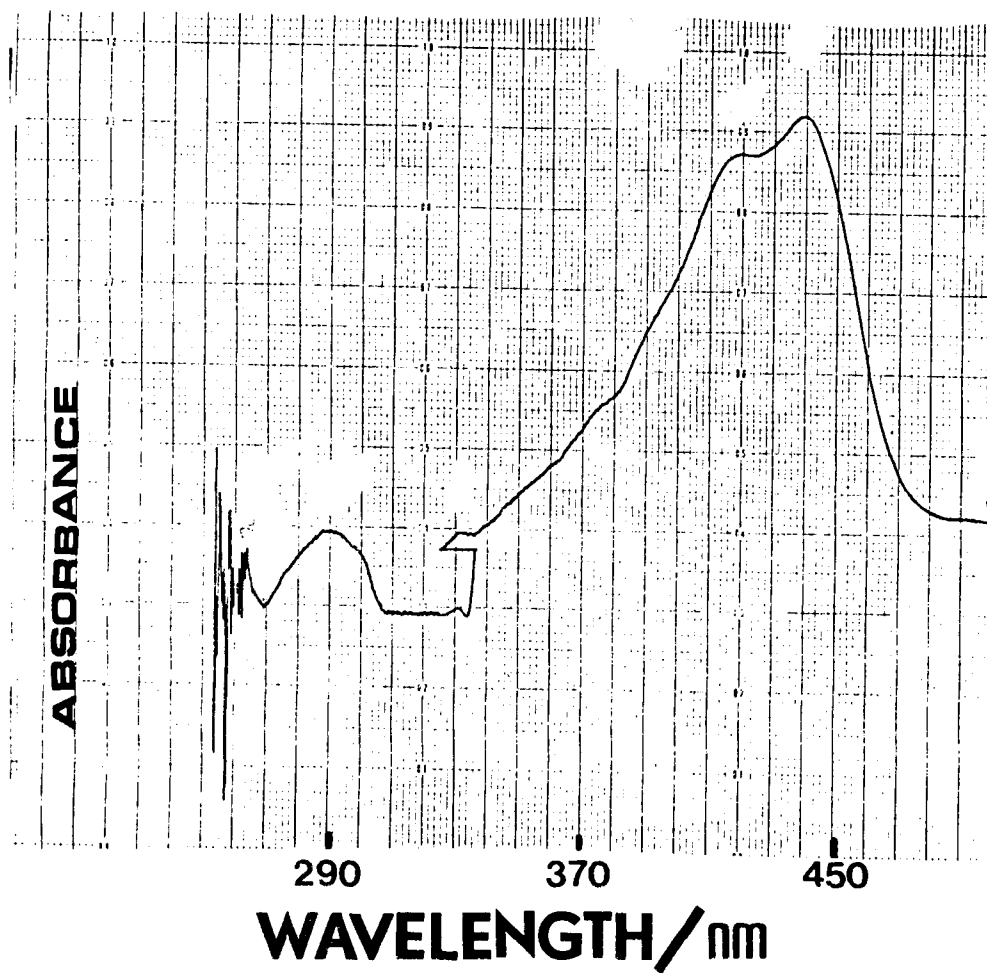


Figure 9. UV-visible spectrum of the terpolymer in acetonitrile.

absorptivity of the monomers, both TCNQ and BOEB, remains approximately unchanged after being incorporated into the polymeric backbone. This value is in excellent agreement with the results of elemental analysis (Galbraith, Knoxville, TN); calculated: %C = 61.7, %H = 5.52, %N = 5.33; found: %C = 61.3, %H = 5.59, %N = 5.29. The calculation of the above elemental composition assumed a mole fraction of 30% TCNQ in the repeat unit of the terpolymer backbone. The infrared spectrum of the terpolymer showed a strong ester carbonyl absorption at $1,740\text{ cm}^{-1}$, and absorptions attributable to the TCNQ monomer unit ($2,240\text{ cm}^{-1}$ for -C=N group) was beautifully observed, indicating that the TCNQ units had been incorporated into the polyester backbone (see Fig. 10). The IR spectrum also featured bands at $2,960\text{ cm}^{-1}$ (aromatic -CH), $2,880\text{ cm}^{-1}$ (aliphatic -CH), $1,570\text{ cm}^{-1}$ (-C=C) and $1,230, 1,080, 940\text{ cm}^{-1}$ (-CO-) and a band at 820 cm^{-1} is indicative of 1,4-disubstituted benzene structures (79, 94).

Electrochemical Behavior of the Terpolymer in Acetonitrile/0.1 M TEAP

Solution cyclic voltammetry. The voltammetric behavior in solution of diffusing polymers that possess noninteracting electron transfer sites is known to reflect that of the electroactive monomers (100). The current, however, will be attenuated relative to the monomer on a weight basis owing to the smaller diffusion coefficient of the corresponding polymer. The cyclic voltammetric behavior of the terpolymer demonstrated excellent agreement with this expectation. CV of this

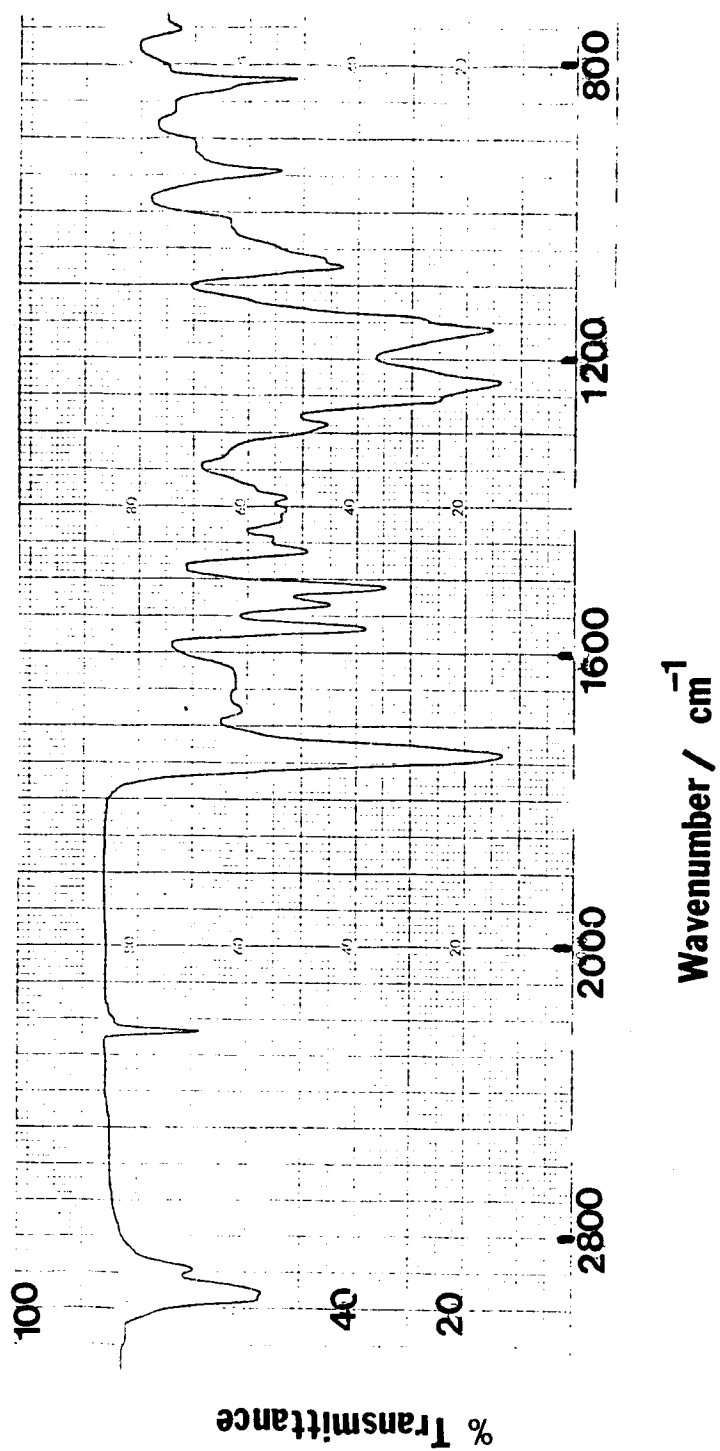


Figure 10. Infrared spectrum of the terpolymer film on NaCl plate.

polymer in solution of CH_3CN and 0.1 M TEAP is given in Figure 11A. The expected two-step quasi-reversible EE behavior is seen with $E_{\frac{1}{2}}^{0/-} \approx -0.05$ V and $E_{\frac{1}{2}}^{-/2-} = -0.53$ V vs. Ag/AgCl. The diffusional tails are more pronounced in the CV of the polymer in solution as compared to the monomer (same wt/volume) in solution of the same electrolyte; see Figure 11B. The peak currents were attenuated as compared to the monomeric form and the slope calculated from chronocoulometric Anson plot was smaller ($nD^{\frac{1}{2}}c \approx 3.99 \times 10^{-10}$ mole $\cdot$ cm $^{-2}$ $\cdot$ s $^{-\frac{1}{2}}$) than for the corresponding monomer ($nD^{\frac{1}{2}}c = 2.18 \times 10^{-9}$ mole $\cdot$ cm $^{-2}$ $\cdot$ s $^{-\frac{1}{2}}$).

Cyclic voltammetry of the terpolymer in adsorbed state. Cyclic voltammetric behavior of this polymer in adsorbed state is shown in Figure 11C. The behavior manifested by this voltammogram is discussed in much detail in later sections. As expected, the voltammograms feature two redox waves characteristic of an EE mechanism corresponding to the TCNQ moieties ($E_{\frac{1}{2}}^{0/-} = 0.0 \pm 0.05$ V and $E_{\frac{1}{2}}^{-/2-} = -0.420 \pm 0.005$ V vs. Ag/AgCl) which at moderately slow scan rates (<50 mV/sec) has the characteristic of reversible surface wave.

Gel Permeation Chromatography

GPC analysis of the Day's polyesters (TCNQ-PE and BOEB-PE) was discussed in a recent publication from this laboratory (77). These polyesters were subjected to GPC analysis on μ -Stryagel columns using DMA as the eluent. BOEB-PEs gave broad peaks that encompassed the low molecular weight limit and extended into the middle of the linear portion of the log (MW) vs. retention time (t_R) curve; see Figure 12.

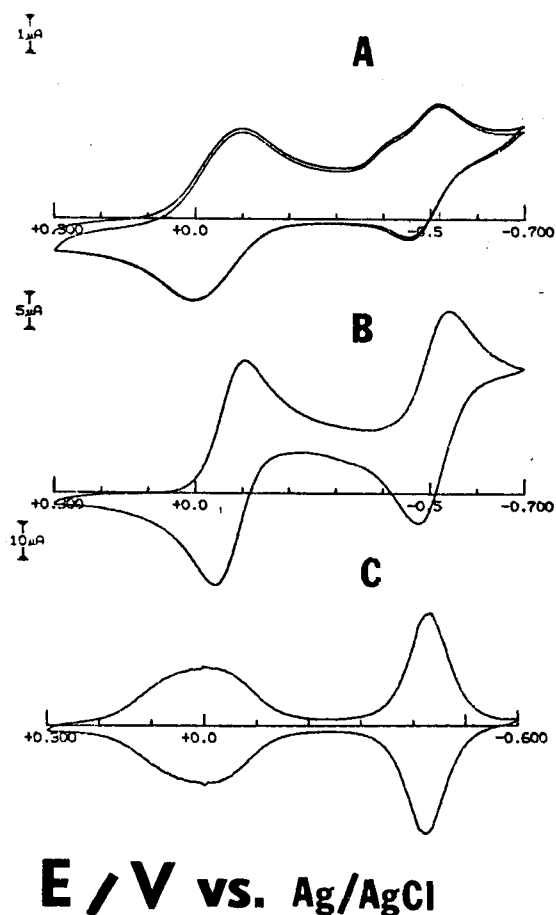


Figure 11. Cyclic voltammograms recorded in acetonitrile/TEAP solution. The terpolymer in solution (A); TCNQ-diol in solution (B); terpolymer film on platinum electrode (C). All recorded at scan rate of 20 mV/sec.

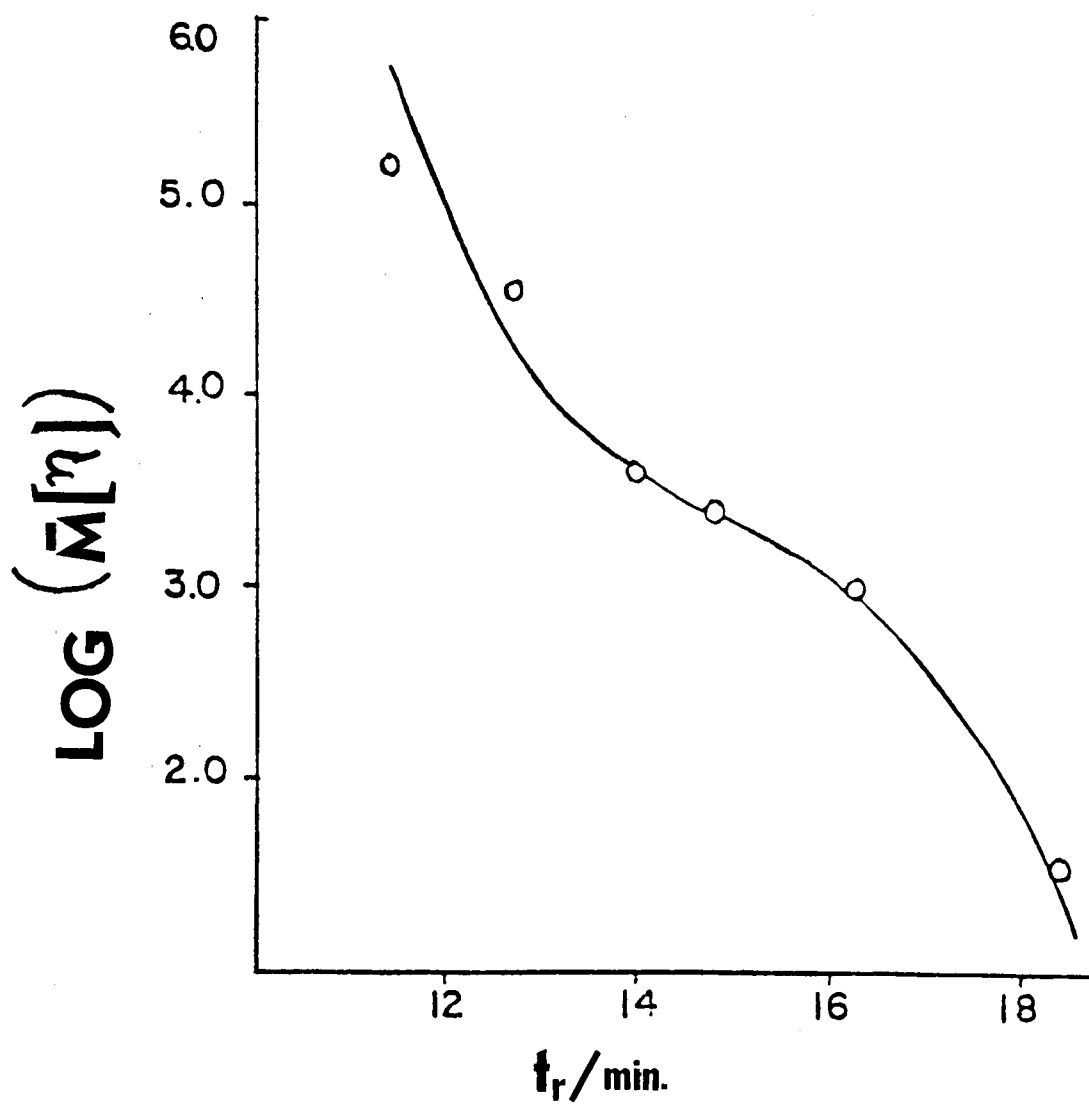


Figure 12. GPC calibration curve for polystyrene molecular weight standards.

The GPC results were consistent with the viscosity data in that similar trends were observed: products with the highest viscosities gave the shortest retention times; see Table I. As pointed out elsewhere (77), the GPC data do not permit valid estimates of the MW for the polyesters to be made, since reliable Mark-Houwink parameters are not available for a suitable model polymer (77). An indication of the molecular weight distribution (MWD) was obtained by analysis of the elution curves following the approach outlined by Yau et al. (101). Using the log MW vs. t_R curves for the polystyrene standards polydispersity indexes (i.e., M_w/M_n) in the range of 2.5-2.9 were calculated for BOEB-PEs of Day (77). Furthermore, results of the GPC analysis were reported to be consistent with what was expected of a "solution condensation" reaction and are indicative of the presence of a sizable fraction of low-molecular weight oligomers. The GPC data also suggested that the high molecular weight fraction contained an appreciable amount of polymers in the molecular weight range of 10,000-15,000 ($\bar{DP} \approx 30-50$).

The TCNQ polyester and terpolymer samples were excluded from the columns under the above conditions, i.e., DMA eluent, 60°C. This was the case not only for the polyesters, but also for several TCNQ-polyurethanes recently synthesized in our laboratory (79). As pointed out elsewhere (77) this observation was found to be somewhat "bewildering" in that it was unlikely that high molecular weight polyesters were prepared from TCNQ-diol and not from BOEB-diol via adipylchloride condensation reactions. Several explanations were given for this observation (77). One possibility was thought to be that TCNQ-PEs

Table 1. Gel permeation chromatography of aliphatic polyesters^a and polystyrene molecular weight standards.

Sample	^b t_R (min)	$[\eta]$ (dL/g)	$\log\{[\eta] \times Mwt\}$
PS 2.35 K ^c	18.4	0.02	1.67
PS 15 K	16.25	0.11	3.21
PS 19.6 K	14.8	0.13	3.41
PS 34 K	14.0	0.118	3.60
PS 110 K	12.7	0.38	4.62
PS 200 K	11.4	0.725	5.16
PE-A (64 h) ^d	15.95	ca. 0.1	3.08 ^g
PE-B (38 h) ^d	15.7	ca. 0.1	3.14
PE-C (12 h) ^d	15.9	ca. 0.1	3.10
PE-D (2 h) ^d	16.9	ca. 0.1	2.70
TCNQ.PE ^e	10.5	--	--
TPE ^f	9.87	--	--

^aEluent, DMA; temperature, 60°C; flow rate, 1.0 mL/min.

^bAverage of two values; reproducibility, ± 0.1 min.

^cPolystyrene standards.

^dPoly[(bis)oxyethanol benzene Adipate] samples from η_{inh} versus reaction time study of Figure 3, reference 94. Reaction time is given in parentheses.

^eTCNQ polyester.

^fTerpolymer.

^gEstimated from polystyrene data; see discussion in text.

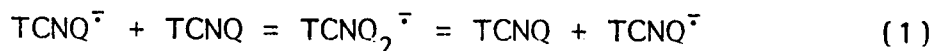
are partially reduced and behave as polyanions in solution. Anionic polymers are known to be excluded from the Styragel columns (102). Since absorption spectra of the TCNQ-PEs in solution was found to exhibit weak bands at 730 and 850 nm (where the $\text{TCNQ}^{\cdot-}$ radical anion is known to absorb) the above possibility could not be disregarded. Furthermore, the virgin polymers were also found to be weakly paramagnetic, presumably due to radical anion groups in the polymer. Another possibility that was given was based on the process of dimerization. The TCNQ esters associate in solution via dimer formation at the $\text{TCNQ}^{\cdot-}$ sites to form crosslinked high molecular weight aggregates. Firm electrochemical evidence was presented earlier that this takes place in TCNQ ester films adsorbed on metallic substrates (73).

As indicated elsewhere, the major emphasis in this work will be on the effect of the polymer matrix composition on the process of electron and ion transport in polymer films on electrodes in contact with solvent/electrolyte. As such it was envisioned that BOEB-PE, being isomorphous with TCNQ-PE and containing a benzene ring in place of the TCNQ structure, could provide an easy way to manipulate the polymer film composition in terms of the redox site concentration in the film. Such studies are of much interest, both experimentally and theoretically, and may provide a better understanding of the process of charge transport through electroactive polymer films. Most importantly, it would be interesting to compare the behavior of the terpolymer with films prepared from polymer blends. The results of such studies are presented and discussed in the following sections.

CHAPTER IV

ELECTROCHEMICAL STUDIES: EFFECT OF POLYMER FILM
COMPOSITION ON SITE-SITE INTERACTIONSElectrochemical Studies of TCNQ Containing Polymer
Films of Various Composition on Pt Electrode
In Contact with Acetonitrile/Electrolyte:
Use of BOEB-PE as Host PolymerIntroduction

The TCNQ polymers that we have studied extensively (45, 98) are an attractive system for study of the role of redox site interactions on polymer film electrochemistry. In contact with aqueous electrolytes, $\text{TCNQ}^{\cdot -}$ radical anion, TCNQ_2^{2-} dianion, and $\text{TCNQ}_2^{\cdot -}$ dimer radical anion sites can be formed by electrochemical reduction. The existence of the latter species is interesting in view of its possible role in the electron relay process by which charge is transported through these films, eqn. 1.



In aqueous systems, e.g., for films in contact with concentrated LiCl solutions, the dimerization is visually announced by the appearance of a decidedly blue coloration to the electrode surface due to the dimer dianion. In contact with acetonitrile solutions, while the extent of dimerization is less than for aqueous electrolytes, the formation of dimer radical anion sites is especially clear in the cyclic voltammetry of the TCNQ polymer films. Accordingly, this system is well suited for a

study of the effect of film composition and site concentration on the electrochemistry of electroactive polymer films.

In this section a simultaneous electrochemical/electron spin resonance spectroscopic (SE/ESR) study of TCNQ-PE films in acetonitrile/TEAP is also presented. As pointed out by Inzelt et al. (73), ESR spectroscopy has been used in the last 20 years for detection and identification of electrochemically generated radical ions. The sensitivity and the molecular structure information in the hyperfine splitting pattern of the spectra make the ESR technique a powerful tool for the study of organic electrode reactions. The ESR studies of Inzelt et al. (73) have supported the mechanistic conclusions of complementary voltammetric and spectroelectrochemical studies of these TCNQ modified electrodes. Prior to Inzelt's report no such studies were reported in which the dependence of an ESR signal on electrochemical parameters (electrode potential, current) was used to obtain information concerning electrode reaction at a polymer film electrode. One reason for this void, according to Inzelt et al., has been the nature of the most widely used polymer film materials. The technique pioneered by Anson and co-workers (57, 31), in which the electroactive ions, often inorganic species such as $\text{Fe}(\text{CN})_6^{3-/4-}$, are exchanged into polymeric ion-exchange resin films on electrodes, does not lend itself to ESR spectroscopic characterization. Other systems, such as poly(nitrostyrene) (28), involve radical ions which are, unlike TCNQ^- , air and moisture sensitive, and therefore difficult to study. For electroactive polymers, however, if the radicals formed are stable, ESR

spectroscopy can provide valuable insight into the nature of the polymer film electrolysis process. This is the situation for electroactive polymers based on TCNQ acceptor molecules (73).

Experimental Section

Chemicals. Details of the synthetic procedure for the preparation of TCNQ polymers used in this study are given elsewhere (see Chapter II). The synthesis of poly(bis-oxyethanol benzene adipate), BOEB-PE, used in this study has also been described elsewhere (77, 94). In all cases the polymers were synthesized by solution polycondensation of the diol(s) with stoichiometric amounts of adipyl chloride in diethylacetamide, DMA, at low temperatures.

Tetraethylammonium perchlorate (Eastman), TEAP, was recrystallized from water and dried under vacuum. Spectral grade acetonitrile (Aldrich) was stored over 3 Å molecular sieves and used without further purification. DMA (Fischer Certified) was purified by fractional distillation under reduced pressure and was also stored over 3 Å molecular sieves.

Film casting. The polymer film electrodes were prepared by placing a desired quantity of the polymer solution in DMA/acetone (50:50 vol %) on the electrode surface followed by vacuum evaporation of the solvent. Platinum disk substrates (area = 0.21 cm^2) were employed to obtain the results described below. Baking of the film at 125°C for 30 min was shown to improve markedly the adherence and stability of

the film for the subsequent electrochemical studies. It is believed that this baking process stabilizes the TCNQ polyester films by a cross-linking process involving a fraction of the TCNQ sites. While the spectral features of the film, both in the neutral and reduced states, remain unchanged for films treated in this manner, the absorbance in the 410-430 nm region due to the TCNQ groups decreases as does the total electrochemical charge accepted by the films (94). Without this baking process, in contact with acetonitrile solution the TCNQ polyesters slowly desorb from the electrode substrates upon repeated cycling between the 0 and -1 oxidation states. In contact with aqueous electrolytes, TCNQ films prepared in this manner gave evidence of somewhat decreased charge transport rates relative to films baked for shorter periods at lower temperatures. While the outer layers of the polymer film may remain attached to the electrode through the above cross-linking, the actual mechanism of adsorption on to the substrate material, at the molecular level, is an intriguing phenomenon which is poorly understood. Aside from the possible insolubility of the resulting cross-linked polymer film, another possible mechanism may involve the formation of charge transfer complexes at the surface of the substrate. Studies of solvent effect on adsorption of TCNQ on metal oxides by Esumi et al. (132) have revealed very interesting phenomena. These workers studied the TCNQ adsorption on to metal oxides such as alumina and titania from three basic solvents (acetonitrile, ethylacetate, and 1,4-dioxane). The TCNQ anion radicals were formed as a result of electron transfer from the metal oxide surfaces to the

adsorbed TCNQ. It is likely that long lasting baking at high temperature and in air may help the formation of PtOH and/or PtO.

Films of polymer blends were prepared essentially in the same way as described above. A solution of the BOEB polyester was prepared in the DMA/acetone mixture and mixed with a solution of the TCNQ polyester in the desired ratio. The resulting solution was gently stirred to homogeneity prior to film casting. The electrodes, which were treated as above, showed exceptional adherence of the polymer film to the platinum substrate surface.

Apparatus. Voltammetry was done on a BAS-100 Electrochemical Analyzer. Generally a Ag/AgCl quasi-reference electrode was employed. The potential of this electrode was ca. +0.02 V vs. SCE in the $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$ solution. All solutions were purged with high purity nitrogen gas before use and an inert gas blanket was maintained throughout the voltammetric experiments. For the low-temperatures studies, the cell was immersed in an ethanol-dry ice bath; a Fluke Model No. 2100A digital thermometer/thermocouple combination was used to measure temperature.

Chronocoulometric charge was taken in digital form and stored in the memory of a digital oscilloscope (Explorer II, Nicolet). A PAR Model 173/179 potentiostat/coulometer was used for the chronocoulometry. Electrode loadings, in mol cm^{-2} , were determined either from the limiting chronocoulometric charge or by integration of the charge under a slow sweep voltammogram between 0.3 V to -0.3 V vs.

Ag/AgCl. The latter method gave less ambiguous, more reproducible values.

The simultaneous electrochemical electron spin resonance (SEESR) experiments were performed on polymer films that had been dip-coated on a Pt grid substrate. The measurements were made using the intra muros technique (73).

Theory

Cyclic voltammetry of surface films. Cyclic voltammetry is a versatile electrochemical technique in which a stationary working electrode is immersed into a quiescent solution. In this work all the experimental cyclic voltammetric studies were performed in a three-electrode electrochemical cell where the other two electrodes were a platinum flag counter electrode and a reference electrode (Ag/AgCl or Saturated Calomel Electrode, SCE). The major advantage of this cell configuration is that no current flows between the working and the reference electrodes, thereby improving the accuracy of the potential impositions on the working electrode as compared to that of the reference electrode. The absence of separators such as frits or membranes also improves the instrumental problems associated with the uncompensated resistance which plagues all voltammetric measurements (103).

A potential of triangular waveform is applied between the reference and working electrodes. The current-voltage (I-E) relationships are plotted to give a voltammogram. The data from the voltammogram yields useful information, both thermodynamic and kinetic, on electron transfer and redox reactions at the electrode/solution interface.

An immobilized monolayer of a substance can (directly or indirectly) exchange electrons with the electrode surface. The electrode displays electrochemical responses for oxidation or reduction of the substance. In their current-potential representation, these responses are called surface waves; the reaction does not involve semi-infinite diffusional mass transport, at least within a certain time frame (2).

The reactions of polymer films, however, are more complex than those of monolayer redox films, requiring mechanism(s) for motion of electrons to/from redox sites in cases where these are too immobile or remote in the polymer film to contact the electrode directly, plus associated motions of polymeric chains, charge-compensating counterions, and solvent molecules for solvation. These events are "collectively" referred to as "motion" or "transport" of electrochemical charge in the polymeric film and all have kinetic and thermodynamic implications (2).

In most films, electrochemical charge transport is thought, as indicated earlier (22), to occur by "electron self-exchange" reactions between neighbor oxidized and reduced sites. Although electron hopping may be a mechanism for charge transport, it is possible that either ion transport or electron hopping can constitute the rate controlling event for overall charge transport (58).

Despite the above complexities, however, polymer film electrolysis can be mathematically represented by diffusional laws in which an "effective charge transport diffusion coefficient", D_{ct} , is introduced to measure its rates (57, 58, 63). An electrode coated with a redox polymer film of uniform composition and thickness, d , which does

exhibit diffusive charge transport may do so at a rate fast, slow, or intermediate with respect to the experimental time scale:

Thin-layer electrochemical behavior. If the charge transport is significantly faster than the experimental time scale, the oxidized reduced sites concentration ratio will be both uniform throughout the film and in thermodynamic equilibrium with the applied electrode potential. Cyclic voltammetric current-potential peaks will have a symmetrical shape in this case and the theory derived for thin layer behavior can be applicable within certain limits.

The following derivation yields an equation for the peak current, i_p , which is based on the following assumptions: (a) homogeneous concentrations in the film; (b) absence of interactions between the redox sites; (c) mass transport contributions of all sorts are absent (i.e., transport of electrons via hopping, transport of the counterions or of the solvent are not limiting factors); and finally (d) charge transfer is fast.

Consider the reaction and initial conditions,



$$C_{Ox}(x,0) = C_T \quad t = 0; \quad 0 \leq x \leq d$$

for the situation where the working electrode potential is swept from an initial E_i where no reaction occurs, toward negative values. Under conditions cited above, the current is given by equation 3.

$$i = -nF V \frac{dC_{ox}}{dt} \quad (3)$$

For a Nernstian reaction we can write,

$$E = E^{o'} + \frac{RT}{nF} \ln \frac{C_{ox}}{C_R} \quad (4)$$

where surface concentration, C_T , can be written as

$$C_T = C_{ox} + C_R \quad (5)$$

Combination of equations 4 and 5 yields:

$$C_{ox} = C_T \{1 - [1 - \exp(\frac{nF}{RT}(E - E^{o'}))]^{-1}\} \quad (6)$$

Differentiation of equation 6, and substitution in equation 3 with the sweep rate $v = -(dE/dt)$ yields the expression for the current:

$$i = \frac{n^2 F^2 v V C_T}{RT} \frac{\exp[(\frac{nF}{RT})(E - E^{o'})]}{1 + \exp\{[(\frac{nF}{RT})(E - E^{o'})]\}^2} \quad (7)$$

The peak current, i_p , occurs at $E = E^{o'}$ and is given by

$$i_p = \frac{n^2 F^2 v A \Gamma}{4 RT} \quad (8)$$

where n = number of electrons,

F = Faraday Constant, C/mole,

v = scan rate, V/sec,

A = electrode area, cm^2 ,

Γ = surface coverage, mole/cm^2 ,

R = gas constant, $\text{J mole}^{-1}\text{K}^{-1}$,

T = temperature, $^{\circ}\text{K}$,

V = volume of the surface film.

The significant aspects of this equation are that a proportionality exists between i_p and potential sweep rate v , that the peak potentials and waveshapes for the cathodic and anodic surface waves are identical ($\Delta E_p \approx 0$), and the peak width at half maxima, $\Delta E_{p/2} = 90.6 \text{ mV}/n$. The location of the peak on the potential axis (at $E = E^{\circ}$) is a direct measure of the redox potential of the couple on the surface. This potential is usually close to that found for the same couple in solution. For thicker films, the electrochemical response will show larger integrated areas, representing greater amounts of material on the electrode (104).

It should be pointed out that the voltammetric responses of polymer films, although very complex, can in some cases be described by the above equation.

Slow charge transport. Under conditions of slow charge transport, a negative potential scan traverses the wave before sites at the film's outer boundary are reduced. In this case semi-infinite diffusion governs the process and an electrochemical peak current is obtained which is proportional to $v^{1/2}$ and given by the same equation as that used for species dissolved in solution and diffusing to the electrode:

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{ct}^{1/2} v^{1/2} C_{ox} \quad (9)$$

The waveshape also exhibits a distinctive "diffusional tail."

At intermediate values of D_{ct} , intermediate i_p vs. v dependence occurs, and a less pronounced diffusional tail appears.

Kinetic analysis. At sufficiently high values of the potential scan rate, where irreversible behavior dominates, theory predicts a linear dependence of current peak potential, E_p , on the logarithm of the scan rate when voltammetry is applied to the study of surface reactions. By measuring current-potential curves at different values of scan rate, plots of E_p vs. $\ln v$ can be used to estimate values for kinetic parameters, α (transfer coefficient) from the slope, and k^0 from the critical scan rate, v_i , corresponding to the condition $E = E^0$. In practice v_i is obtained by extrapolating the linear portion of the E_p vs. $\ln v$ plot observed at high values of v .

The peak potential data in this work was analyzed with the help of the theory of Daifuku et al. (105) for surface electrochemical reactions as outlined below:

1. Voltammograms are recorded over a wide range of scan rates.
2. A plot of E_p vs. $\ln v$ should yield a straight line whose slope is given by,

$$s = \frac{RT}{\alpha nF} \quad (10)$$

3. The value of v_i was also extracted from the above plot.
4. The magnitude of the term $\alpha nF/RT \Delta E_{1/2}$ at v_i was determined, where $\Delta E_{1/2}$ corresponds to the width of the peak at half

maxima. This term allows an estimation of the value of χ , the interaction parameter, using a working curve developed by Daifuku et al. (34) (5). The following equation can be used to calculate k^0 (sec^{-1}):

$$k^0 = \frac{\alpha n F}{2RT} v_i e^{-A} \quad (11)$$

where,

$$A = 0.0119 - 0.2358 \chi + 0.0049 \chi^2 - 0.00086 \chi^3 \quad (12)$$

Chronocoulometry. In chronocoulometry (cc) the current response to the potential step excitation signal is integrated. The planar working electrode coated with polymer film is held at some potential E_i where no electrolysis takes place. At $t = 0$, the potential is shifted to E_f , which is sufficiently negative to enforce a diffusion limited current (103). The monitored response in cc is charge, Q .

$$Q = \int_0^t i(t) dt \quad (13)$$

Substitution of Cottrell's equation for current and its integration yields equation 14:

$$Q = \frac{2nFA C D^{\frac{1}{2}} t^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \quad (14)$$

A plot of Q vs. $t^{\frac{1}{2}}$ should yield a linear response with a slope, s , as:

$$s = \frac{2nFAC D^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \quad (15)$$

$$nD^{\frac{1}{2}}c = \frac{S \pi^{\frac{1}{2}}}{2FA} \quad (16)$$

Therefore, analysis of chronocoulometric response gives a derived experimental parameter $nAD^{\frac{1}{2}}c$ which includes the diffusion coefficient associated with other terms, where for the polymer case, n is the number of electrons transferred per accessible redox sites, A is the electrode area, and C is the apparent concentration of redox sites.

In this dissertation chronocoulometric charge (Q) vs. time curves were also analyzed by the procedure outlined by Chambers (71). This procedure is based on analysis of the existing theory for coulometry of thin layers of solution and permits D_{eff} to be derived from chronocoulometric charge (Q) vs. time curves without a knowledge of n , A , or c . The polymer film is assumed to have a uniform thickness, d . The slope of the plot of $-\ln(1-Q/Q_T)$ vs. time allows calculation of the time constant τ by equation 17.

$$\tau = \frac{\pi^2}{S^2} \quad (17)$$

With τ in hand, the effective diffusion coefficient can be calculated via equation 18.

$$nD^{\frac{1}{2}}c = \frac{2\Gamma}{\tau^{\frac{1}{2}}} \quad (18)$$

Chronocoulometry offers some advantages over chronoamperometry for the measurement of diffusion coefficients. The measured chronocoulometric signal grows with time, and hence the later parts of the transient, which are most accessible experimentally and are least distorted by nonideal potential rise, offer better signal-to-noise ratios than the early time results. The opposite is true for chronoamperometry. The act of integration smooths random noise on the current transients, and hence the chronocoulometric records are inherently cleaner.

Extraction of the activation energy, E_a . If the barrier, E_a , to charge transport in the film is formulated as for thermally activated diffusion (58) and expressing the diffusion constant in terms of the experimentally measured $D^{\frac{1}{2}}C$, we have

$$D^{\frac{1}{2}}c = D_0^{\frac{1}{2}}c \exp\left(-\frac{E_a}{2RT}\right) \quad (19)$$

$$\ln D^{\frac{1}{2}}c = \ln D_0^{\frac{1}{2}}c - \frac{E_a}{2R} \frac{1}{T} \quad (20)$$

A plot of

$$\ln D^{\frac{1}{2}}c \text{ vs. } \frac{1}{T} \quad (21)$$

yields the slope given in equation 22.

$$\text{slope} = - \frac{E_a}{2R} \quad (22)$$

Results and Discussion

In this section, variation of the polymer film composition and the corresponding redox site density was achieved in two ways. The first method was by the synthesis of a copolymer containing electroactive TCNQ and nonelectroactive bis-ethoxy-benzene sites designated as terpolymer. The mole fraction of TCNQ sites in the terpolymer was estimated to be 0.294 from the ratio of the absorbance at 290 nm for the benzene ring to the absorbance at 430 nm for the TCNQ unit in the neutral polymer; see Chapter III, p. 45. The elemental analysis was in good agreement with this value.

The second method of varying the film composition involved casting films from homogeneous solutions of the TCNQ polyester and the BOEB polyester. The common comonomer, adipyl chloride, and the similar sizes of the benzene and quinodimethane structures suggested that these polymers are an isomorphic polymer pair (106) and that uniformly blended films will result from this procedure. An important result of the present study is the extent to which the electrochemical behavior of the blended films corresponds to this expectation.

Cyclic voltammetry of TCNQ polyester in contact with CH_3CN . In Figure 13A is shown a cyclic voltammogram of Day's TCNQ polyester (85) in contact with a 0.1 M TEAP/ CH_3CN solution. In contrast to

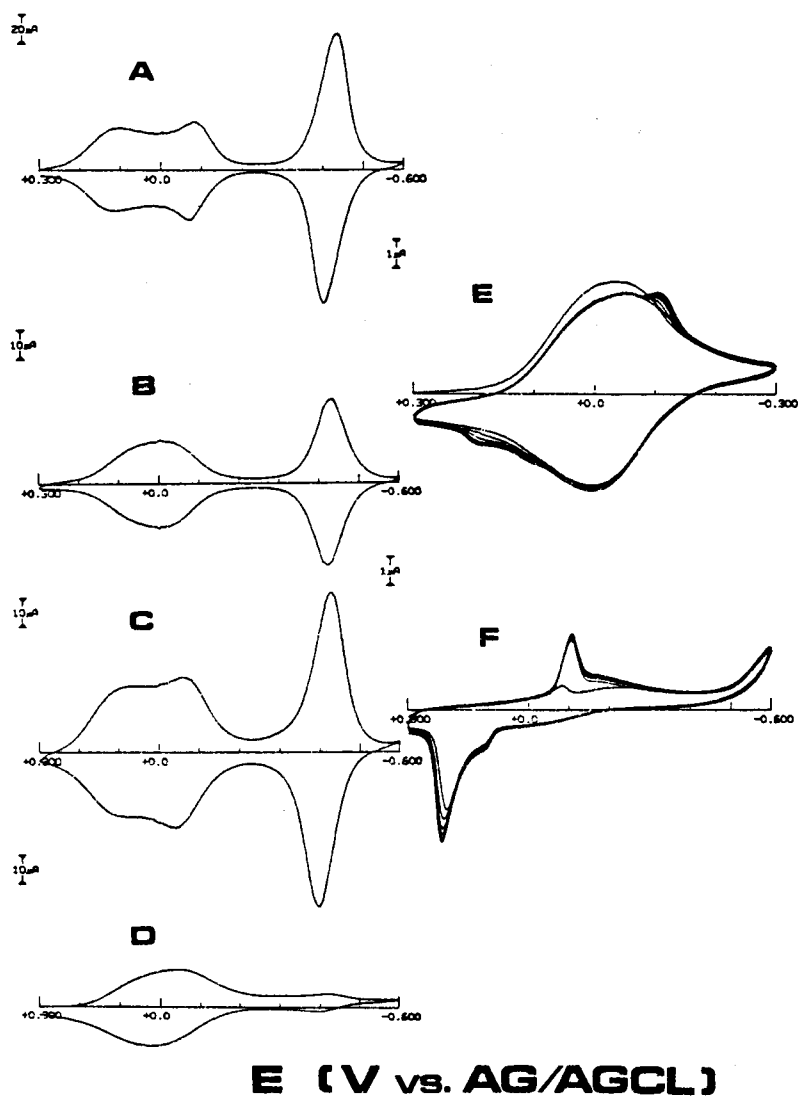
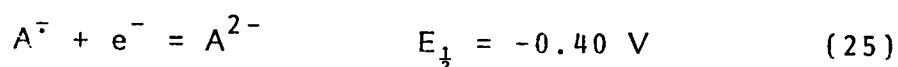
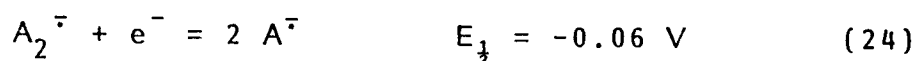
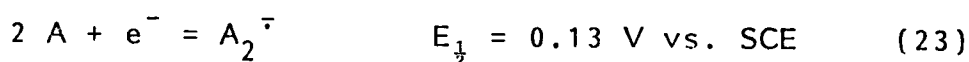


Figure 13. Cyclic voltammogram of TCNQ polymer film electrodes in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$; sweep rate, 20 mVs^{-1} . (A) TCNQ polyester, $\Gamma = 20 \text{ nmol}\cdot\text{cm}^{-2}$; (B) TCNQ terpolymer, $\Gamma = 8.1 \text{ nmole}\cdot\text{cm}^{-2}$; (C-F) TCNQ-BOEB polyester blends at 70%, 50%, 30%, and 10% TCNQ polyester, respectively.

film preparation methods used previously, films prepared as described above adhered strongly to the electrode and could be studied in contact with a variety of nonaqueous solvents. The electrochemical response did not degrade significantly when the films were repeatedly cycled between the 0, -1 and -2 oxidation states, and furthermore film "break-in" effects were not evident in the voltammetry for the electrode loadings examined in this study. The implication is that the films are rapidly swollen by the acetonitrile/supporting electrolyte.

In Figure 13A three reversible, or nearly reversible, surface waves are evident. Previous work and the evidence presented below allows identification of these waves with the A/A_2^- , A_2^-/A^- and A^-/A^{2-} couples, where A represents the neutral TCNQ acceptor site.



The nearly symmetrical waves observed for these processes are typical for fast charge transport to and from surface bound species (3). Of note is the height of the first two waves relative to the third. The latter one-electron wave for the A^-/A^{2-} couple is roughly 3 to 4 times the peak currents for two "0.5-electron" waves, as would be expected for reversible surface waves where the peak currents are proportional

to n^2 . Exact agreement with this relationship is not expected since the first two waves involve the dimer radical anion and are not one-to-one 0.5-electron processes. The expected peak current ratio for a reversible thin-layer electrodimerization, eqn. 23, relative to a simple one-electron reduction, eqn. 24, is ca. 0.34. (This value was calculated numerically assuming Nernstian behavior and mass balance on the total concentration of TCNQ sites in the polymer film.) The measured values of this ratio for the two 0.5-electron waves in Figure 13A are 0.31 and 0.32. It is significant that the general cyclic voltammetric behavior exhibited in Figure 13A is independent of electrode loadings for films for a few effective monolayers up to films of ca. 100 nm thickness.

The above behavior parallels that found in methanol (99) where evidence for dimer radical anion sites was also found. In water, however, dimerization is slower, giving rise to slowly increasing cathodic currents in the $E_{1/2}$ region for eqn. 4 and asymmetrical voltammetric waves (73, 74). More pronounced break-in effects were also seen in water underscoring the importance of solvent swelling to the polymer film charge transport process.

The splitting of the one-electron reduction of TCNQ (per TCNQ site) is reminiscent of the behavior of TTF polymer films (22, 72) and the thionine-coated electrodes of Alberly and co-workers (107). The latter workers found a series of $E_{1/2}$'s for one-electron oxidation of thionine electron relay sites in slightly differing environments, which accounted for the broadening of the thionine surface waves. However, the separation and definition of the waves for the A/A_2^- and A_2^-/A^-

couples is much better for the TCNQ polymers than for the corresponding waves in the cyclic voltammetry of TTF polymers (22).

Particularly interesting is the nearly quantitative formation of the $A_2^{\cdot -}$ dimer in the $CH_3CN/TEAP$ system. Since ion association with the tetraethylammonium counterion is expected to be minimal under these conditions, a charge transfer pi-complex is indicated for the structure of the "mixed-valence" dimer. Evidence is presented below suggesting that this dimerization interaction occurs between separate polymer chains.

Electron spin resonance of TCNQ polyester electrodes. Since SE/ESR techniques proved to be highly diagnostic of the electrode process in the previous studies of Inzelt et al. on the behavior of TCNQ polyester electrodes in contact with aqueous solutions (73) the method was applied here. When a platinum grid electrode coated with the TCNQ polyester, in contact with $CH_3CN/0.1 \text{ M TEAP}$, was subjected to cathodic electrolysis, a single-line ESR signal was obtained similar to that observed in aqueous systems. The potential dependence of the intensity, however, did not exhibit a maximum at intermediate potentials in the region where the dimer radical anion is stable; see Figure 14. (In this figure the intensity is measured by $Y' (\Delta H_{pp})^2$, where Y' is the maximum of the derivative ESR signal and ΔH_{pp} is the peak width.)

This behavior can be understood on the basis of the equilibrium analysis presented previously. The ESR signal tracks the sum of the radical anion and dimer radical anion concentrations,

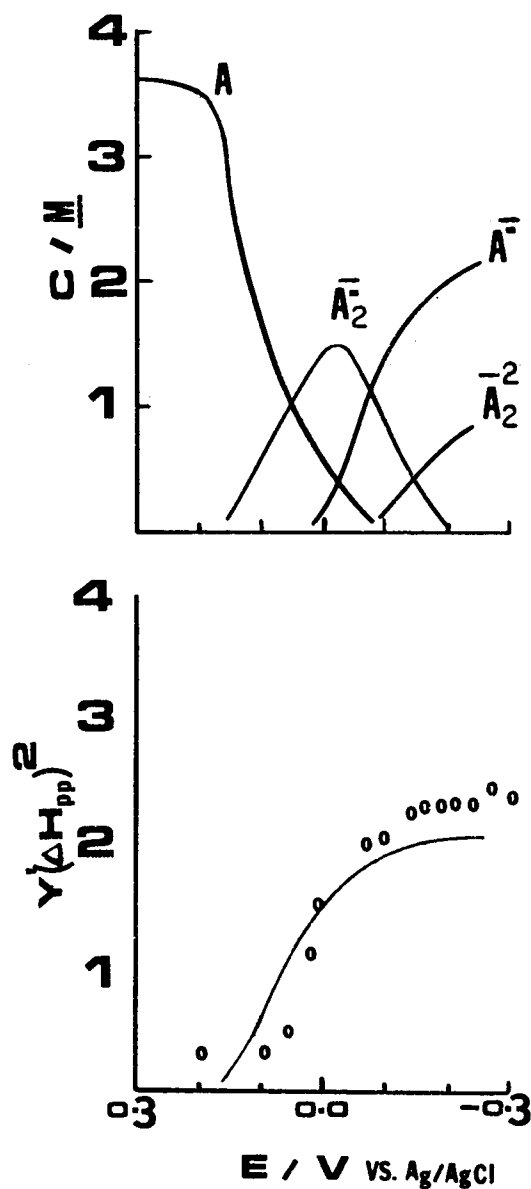


Figure 14. Results of the simultaneous electrochemical/electron spin resonance experiments. Potential dependence of the ESR signal, $Y'_{\max} (\Delta H_{pp})^2$, in arbitrary units, for a TCNQ polyester film in contact with $CH_3CN/0.1 M$ TEAP (bottom); and calculated equilibrium distribution of neutral and reduced sites in a TCNQ polyester film: $C_T = 3.6 M$, $K_D = 0.1635 M^{-1}$, $E_2^0 - E_1^0 = -0.12 V$.

$$S = [A^{\cdot-}] + [A_2^{\cdot-}], \quad (26)$$

obtained from the distribution diagram of Figure 14. This diagram was constructed with the following parameters: $K_D = 0.16 \text{ M}^{-1}$, degree of dimer dianion dissociation (α) = 0.59, $E_1 = -0.034 \text{ V}$ for the $A/\dot{A}^-$ couple, and $E_2 = -0.153 \text{ V}$ for the $A_2^{\cdot-}/A_2^{2-}$ couple. The value of K_D (or α) used to construct Figure 14 was estimated by trial-and-error adjustment of the calculated and experimental potential dependence of the ESR signal. These values are only approximate since the total concentration of acceptor sites is based on an estimate made on the dry film state. However, the correspondence of the voltammetric and ESR behaviors gives support to the above interpretation of the cyclic voltammetry.

It is of interest to compare these values with those obtained in aqueous LiCl solutions (73). The most striking difference is that the extent of dimer formation is significantly less for the nonaqueous solvent in agreement with the behavior of unsubstituted TCNQ $^{\cdot-}$ radical anion salts (108). The E^0 values are also somewhat more positive in water perhaps due to ion-pairing with the Li^+ counterion (74). Finally, in accord with the voltammetry, there is much less hysteresis in the SE/ESR response, Figure 14, than previously found for the aqueous studies.

Effect of film composition on cyclic voltammetry. When the film composition is varied in the fashion described above, several interesting effects are seen in the cyclic voltammograms; see Figure 13.

(1) In the voltammogram of the terpolymer, Figure 13B, the waves due to the A/A_2^- and A_2^-/A^- couples are merged into a single broad, symmetrical surface wave with a peak width of ca. 200 mV. A similar effect can be noted in the voltammograms of the TCNQ and BOEB polyester blends, Figure 13C to 13E. Significantly, there is good agreement between the position and shape of the $A/A_2^-/A^-$ wave in the CV of the terpolymer (Fig. 13B) and the first cycle for the 30% blend (Fig. 13E) where the nominal TCNQ site concentrations are approximately the same. (2) A striking difference between the terpolymer and the blend voltammetry, however, is the disappearance of the second wave due to the A^-/A^{2-} couple. Even at the 50% blend composition (Fig. 13D), the $A/A_2^-/A^-$ wave is much larger than the second wave under these conditions (sweep rate, 20 mV/s; Γ , ca. 8 nmol cm⁻²). At high loadings for the blended films, $\Gamma > 10$ nmol cm⁻², the cyclic voltammograms were distorted and "break-in" effects were evident. (3) For the very dilute blends, Figure 13F, the voltammetry is considerably altered. Here small, somewhat distorted peaks are observed with a peak separation of ca. 300 mV. Also a noticeable "break-in" is evident in Figure 13F where the cathodic peak current on the first potential sweep is considerably less than on subsequent cycles. These three phenomena are considered in the following paragraphs of this section.

The merging of the A/A_2^- and A_2^-/A^- waves as the TCNQ sites are diluted is in qualitative agreement with the above data derived from the ESR and CV of the TCNQ polyester films; see the predominance area diagram in Figure 15. In this figure the circles and

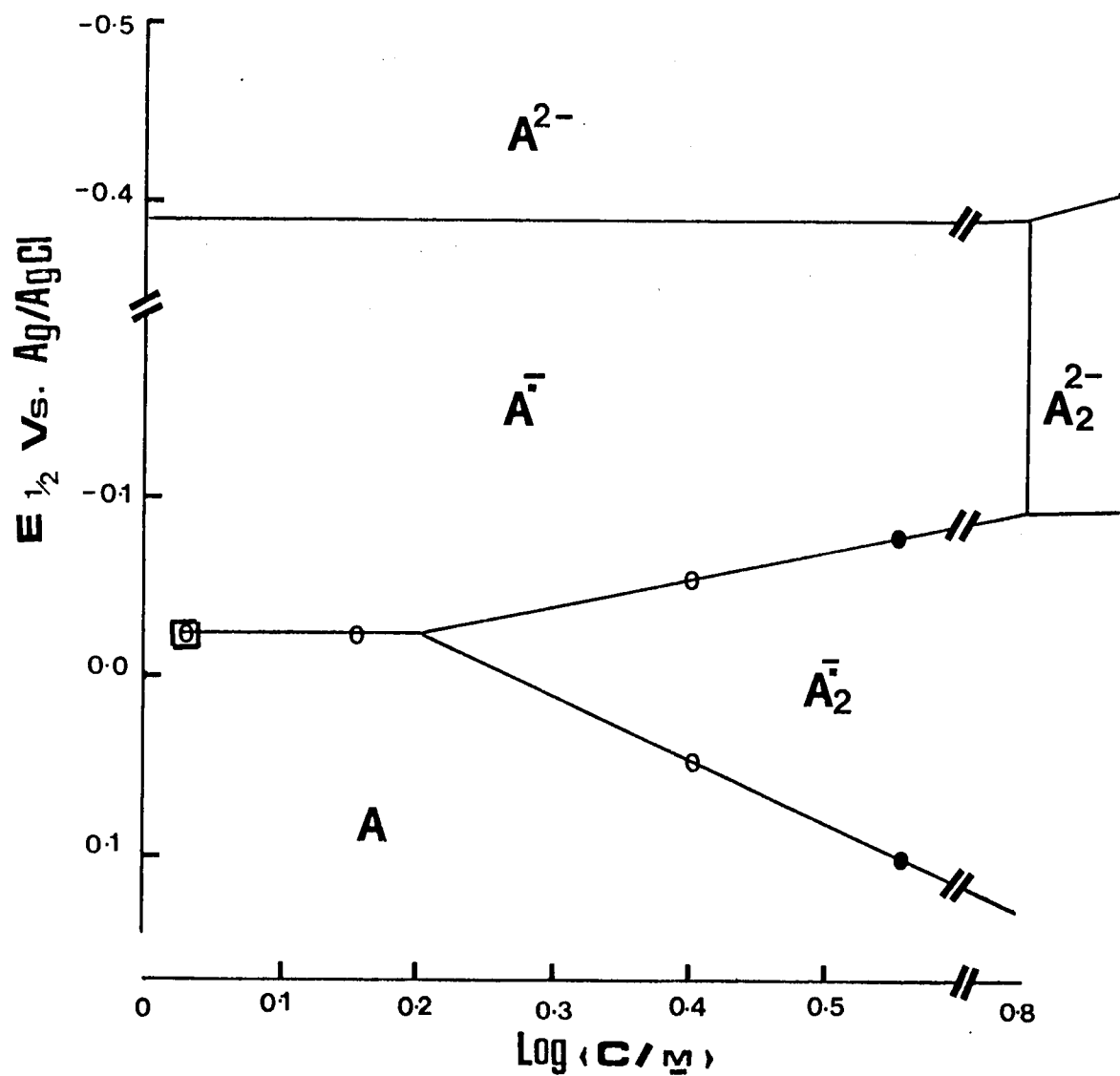


Figure 15. Predominance area diagram for TCNQ polymer films in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$. Solid circles, TCNQ polyester; open circles, TCNQ-BOEB polyester blends; square, TCNQ terpolymer.

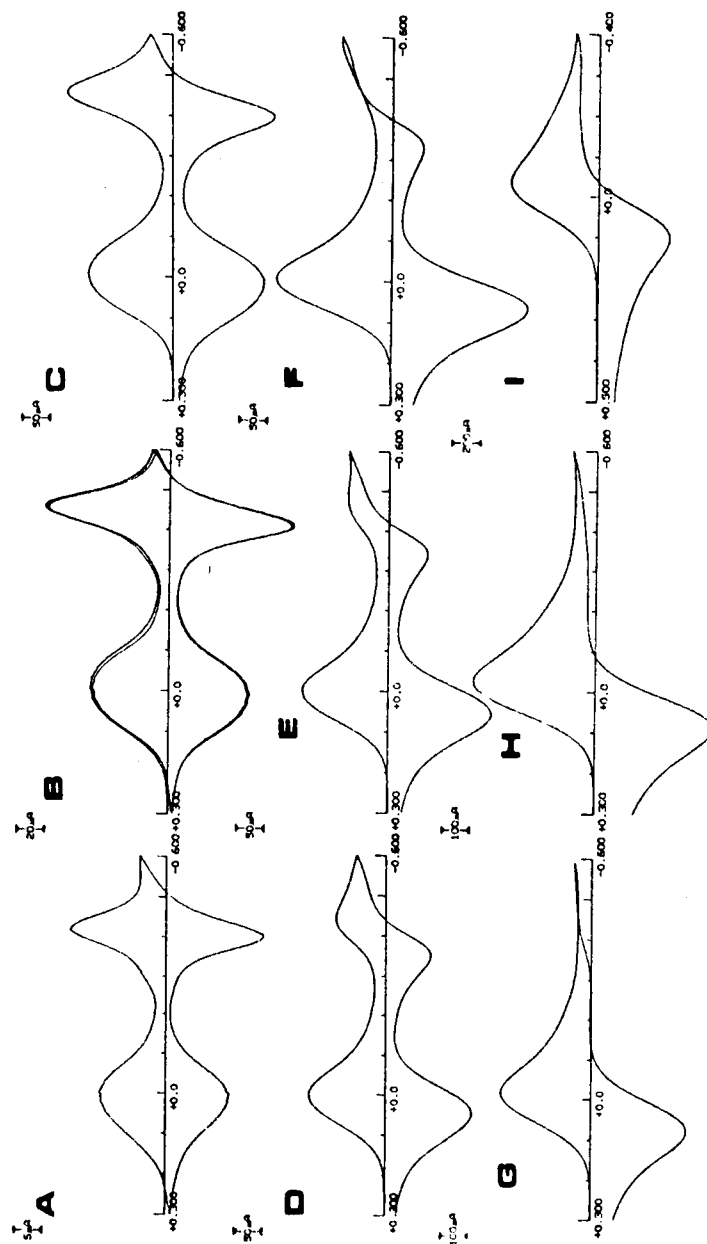
squares are measured $E_{1/2}$ values from Figure 13 (p. 70), given by the average of the nearly symmetrical cathodic and anodic peak potentials; the border between the $A^{\cdot-}$ and A^{2-} regions is set by the $E_{1/2}$ of the $A^{\cdot-}/A^{2-}$ wave; and the border between the $A^{\cdot-}$ and A_2^{2-} regions is set by the value of the dimer formation constant (K_D) and the total concentration of film acceptor sites in the TCNQ polyester. While the qualitative picture given in Figure 15 is satisfying, distinctly non-Nernstian slopes are observed for the $A/A_2^{\cdot-}$ and $A_2^{\cdot-}/A^{\cdot-}$ borderlines. Part of the discrepancy can be attributed to the gross assumptions necessary to estimate TCNQ site concentrations in the highly swollen films. In addition numerical deconvolution of the $A/A_2^{\cdot-}/A^{\cdot-}$ waves in the voltammograms, especially in Figures 13B, 13D and 13D, was not attempted.

Two related and important conclusions can be made on the basis of these results. First, the uniform variation of the $E_{1/2}$ values with film composition is consistent with the above treatment of the polymer film as a homogeneous phase with a uniform distribution of TCNQ sites. The indication is that the TCNQ polyester and the BOEB polyester form uniformly blended films as cast from the DMA/acetone solutions. In this regard the multicycle CV of Figure 13E is most interesting. On repeated cycling between the 0 and -1 oxidation states, postwave peaks develop on the symmetrical surface wave. Repeated cycling of the terpolymer, which has the same nominal concentration of TCNQ sites as the 30% TCNQ-BOEB blend, does not produce this distortion. The position and shape of the new postwave peaks on the CV

of Figure 13F (p. 70) closely match the peaks in Figure 13F for the 10% blend. A likely explanation of this behavior is that redox cycling the TCNQ sites induces phase separation and composite formation in these films such that the electrode substrate/polymer film interface is depleted of the TCNQ polyester. This is understandable since most polymer blends are inherently unstable with respect to phase separation (106) and since the BOEB and reduced TCNQ polyesters are less likely to meet the requirements of an isomorphous pair than the neutral polymers.

A related conclusion is that the TCNQ radical anion site interactions, i.e., the formation of dimer anions, are interchain in nature. Intrachain dimer formation, on the other hand, would not be strongly dependent on dilution of the TCNQ sites. Thus formation of dimeric acceptor sites in these TCNQ polymers represents a reversible cross-linking process.

Decreased charge transport rates in the region of the $A^{\cdot-}/A^{2-}$ couple relative to the rates for the $A/A_2^{\cdot-}/A^{\cdot-}$ region are consistent with previous work on the TCNQ polyester (45) and TCNQ polyurethanes (79) which have shown that the effective diffusion coefficient for the $A^{\cdot-}/A^{2-}$ process is especially dependent on the nature of the solvent, the solution pH, and the counter ion. The dramatic effect of differing charge transport rate constants for the two waves is shown in Figure 16, which depicts a sweep rate study on terpolymer film. As the sweep rate is increased, the first wave retains its surface character ($i_p = kv$) while the second wave becomes diffusional ($i_p = kv^{\frac{1}{2}}$) at sweep rates as low as 80 mV/s for the electrode loading of



E (V vs. AG/AGCL)

Figure 16. Cyclic voltammograms of TCNQ terpolymer in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$. $\Gamma = 25.6 \text{ nmole}\cdot\text{cm}^{-2}$; sweep rate (A-I): 5, 20, 60, 80, 100, 150, 300, 500, and $1000 \text{ mV}\cdot\text{s}^{-1}$.

Figure 15. At 1 V/sec only the first wave is seen in the CV, which no longer has the thin-layer or surface shape. For equivalent loadings, films of the TCNQ polyester display both the $A/A_2^-/A^-$ and the A^-/A^{2-} waves at sweep rates up to 40 V/sec. While the waves of the TCNQ polyester are distorted at these sweep rates with peak separations of ca. 200 mV, all three couples are clearly evident. Comparison of Figures 13B and 13C, p. 70, reveals that the charge transport rate for the A^-/A^{2-} process in films of the blends is decreased to a greater extent than for the terpolymer.

The sweep rate dependence of the ratio of the peak current for the second wave to that of the first wave (i_p^2/i_p^1) was a function of the surface coverage. This ratio was proportional to $v^{-0.7}$ for thick films and to $v^{-0.2}$ for thin films. If the first wave is in the thin-layer time domain and the second in the diffusional domain, a proportionality to $v^{-0.5}$ would be expected. The indication is that for very thin films, both waves display surface behavior over a limited range, while the second wave is diffusional in nature under most experimental conditions. The $v^{-0.7}$ dependence for thick films may be related to uncompensated resistance effects.

Several explanations are possible for the marked sweep rate dependence of the A^-/A^{2-} couple based on the electron hopping/counter ion migration scheme for charge transport in redox polymer films. The possibility that the blend is actually a composite of TCNQ and BOEB polyester phases, and that electron transfer between A^-/A^{2-} islands is slow relative to the terpolymer films, is discounted by the

qualitative observation that the charge transport rate is relatively fast for the $A/A_2^{\cdot-}/A^{\cdot-}$ process. Another possibility is that the blends form tighter, less swollen films than the TCNQ polyesters, and consequently incorporation of a second equivalent of counter ion becomes more difficult in these films. It is also likely that the interchain crosslinking that exists in the -1 oxidation state decreases the flow of counter ion necessary for reduction to the -2 oxidation state.

Effect of film composition on chronocoulometry. In order to probe further the effect of film composition on the charge transport process, chronocoulometric experiments were carried out on the terpolymer and polymer blends over a wide temperature range. The Cottrell slopes derived from the Anson plots (109) of Q vs. $t^{\frac{1}{2}}$ give a more quantitative estimate of the rate of the charge transfer process than the qualitative shape of the cyclic voltammograms in Figure 13 (p. 70). Typical experimental results are shown in Figures 17 and 18, and Table II contains values of $nD^{\frac{1}{2}}c$ for the polyester, the terpolymer, and the 50% TCNQ-BOEB polyester blend. In these experiments in order to avoid the $A^{\cdot-}/A^{2-}$ region the potential step was applied between 0.3 V, where the film is in the neutral state, to -0.3 V where the film is in the $A^{\cdot-}$ state.

In all regards the chronocoulometric and the cyclic voltammetric results are consistent. The limiting charge accepted by the films, estimated by the approach to thin layer behavior seen in Figures 17 and 18, and the charge obtained by integration of the cyclic voltammograms were in agreement (+ or -10%). Furthermore the form of the

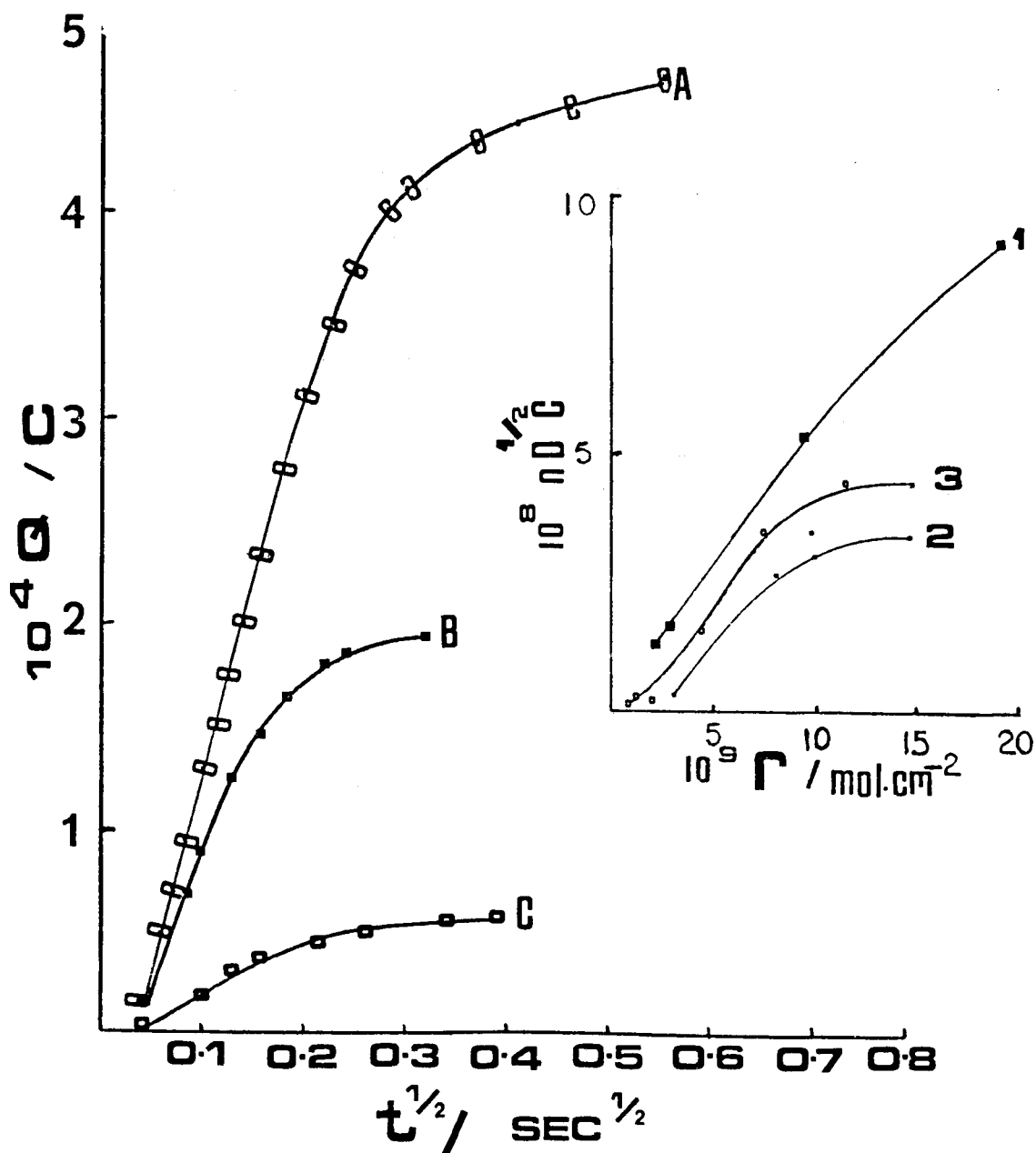


Figure 17. Chronocoulometric Anson plots for the reduction of TCNQ polymer films in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$ at $22 \pm 2^\circ\text{C}$. Surface coverages: (A) 19, (B) 9.47, (C) $3.1 \text{ nmol} \cdot \text{cm}^{-2}$. Inset shows Cottrell slope variation with electrode loading; (1) TCNQ polyester, (2) TCNQ terpolymer, (3) TCNQ-BOEB blends.

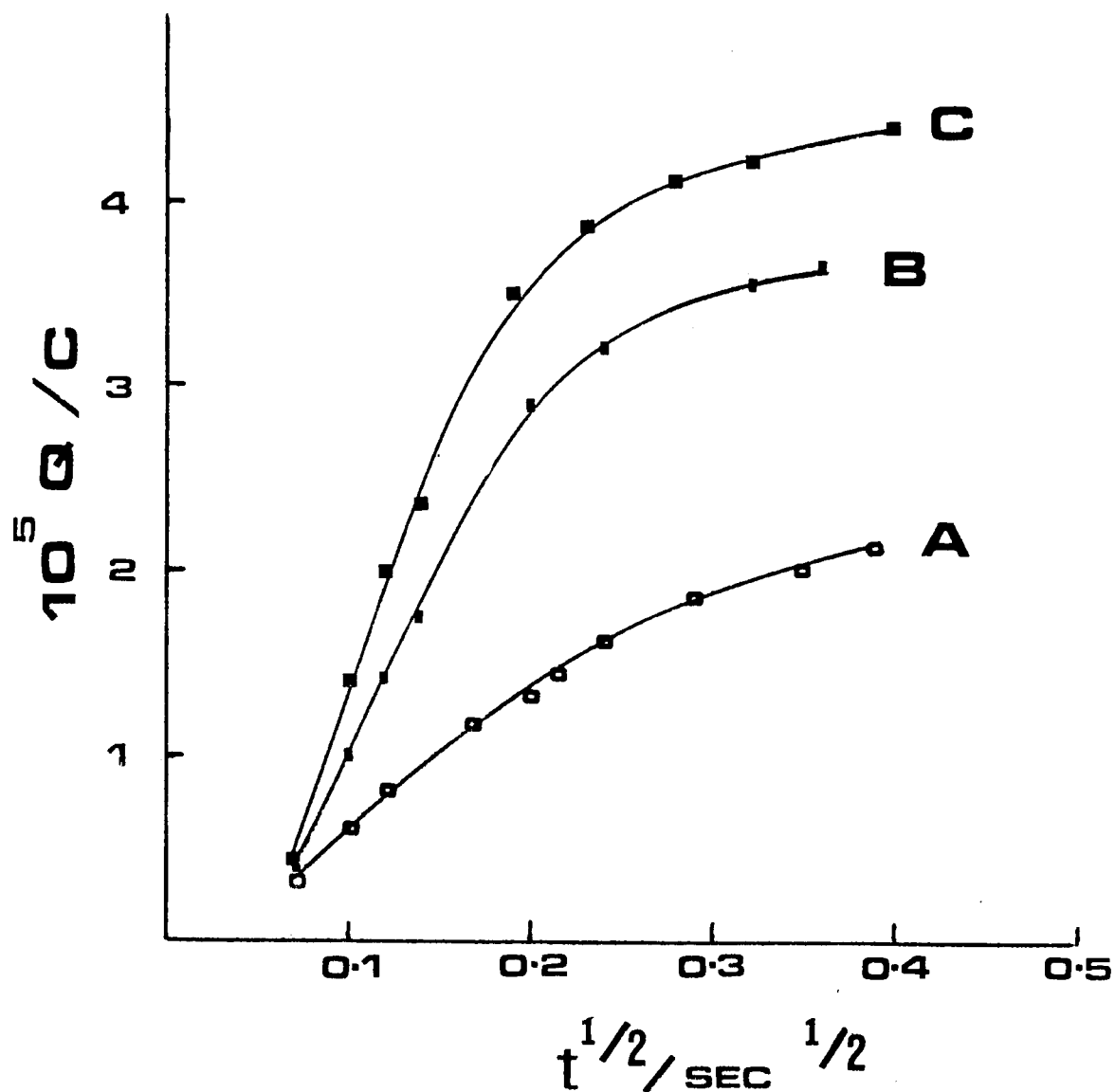


Figure 18. Chronocoulometric Anson plots for the reduction of TCNQ polymer films in contact with $CH_3CN/0.1$ M TEAP. $\Gamma = 2.33$ nmole $\cdot$ cm $^{-2}$, at (A) -21.0°C , (B) -1.8°C , and (C) 20.0°C .

Table II. Chronocoulometric Cottrell function data for TCNQ modified electrodes in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$.

$\Gamma/\text{nmol cm}^{-2}$	$T/^\circ\text{C}$	$10^8 nD^{\frac{1}{2}}c/\text{mol cm}^{-2} \text{ s}^{-\frac{1}{2}}$
<u>TCNQ polyester</u>		
19.0	22	9.1 (4) ^a
9.5	22	5.4 (2)
3.1	22	1.6 (1)
2.3	20	1.30 (3)
2.3	-1.8	0.92 (3)
2.3	-21.7	0.42 (4)
<u>TCNQ terpolymer</u>		
14.7	22	3.4 (3)
10.2	22	3.0 (3)
9.8	20.8	3.5 (1)
9.8	-4.6	0.99 (1)
9.8	-27	0.44 (2)
8.1	22	2.7 (3)
3.2	22	0.32 (1)
<u>50% TCNQ-BOEB blend</u>		
14.7	25	4.4 (2)
11.6	25	4.5 (3)
7.5	25	3.5 (2)
3.9	25	1.25 (2)
2.0	22	0.12 (3)
1.1	25	0.20 (2)
0.69	25	0.15 (2)

^aNumber of determinations given in parentheses.

Anson plots is that expected for an uncomplicated redox polymer film electrochemical process where the time scale extends from the diffusional to the thin-layer region (71). This is shown in Figure 19 in which complete Q vs. time curves are analyzed by plotting $\ln[1 - (Q/Q_T)]$ vs. time (71) for several chronocoulometric experiments on TCNQ polyester films. Linear slopes were obtained indicating that the films were of uniform thickness, d , and composition and could be described by a single charge transport time constant, $\tau = (2d)^2/D$. The derived values of $nD^{1/2}c$ presented in Table III were quite consistent with the data of Table II. (The positive intercept of the $t^{1/2}$ axis evident in Figures 17 and 18 is due to either uncompensated resistance in the cell or slow charge transfer effects. Cottrell slopes were evaluated from the linear segments of the curves as shown in Figures 17 and 18.) While interpretation of Cottrell slopes for polymer film electrode experiments is almost always clouded by the ambiguity of the solvent swelling influenced concentration term, careful inspection of the data reveals some interesting features.

Before comment is made on the influence of film composition, however, the dependence of the Cottrell slopes on the electrode loading evident in Figure 17 and Tables II and III must be addressed. As the amount of polymer on the electrode surface increases, the apparent charge transport diffusion coefficient increases. This behavior was observed for both TCNQ and terpolymer films. The implication is that, as the films become thicker, the charge transport rate constant increases. This phenomenon, which is opposite to the expected effect

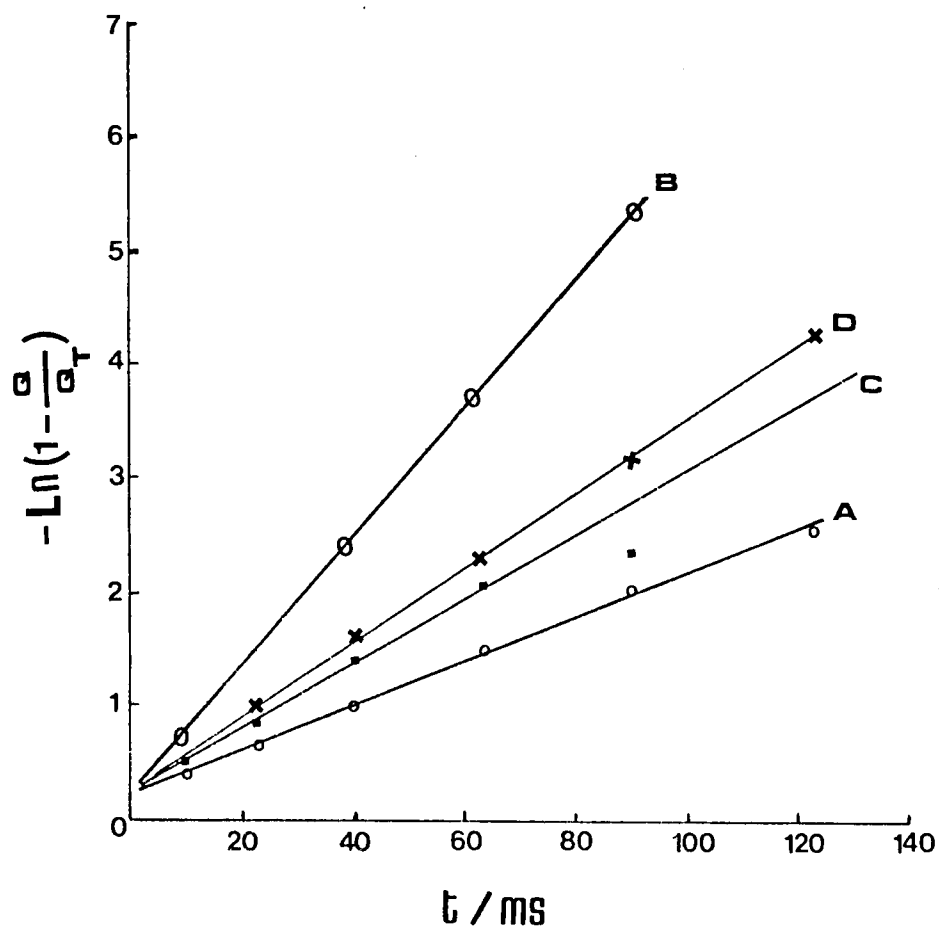


Figure 19. Analysis of chronocoulometric data for TCNQ polyester at $22 \pm 2^\circ\text{C}$ in finite diffusion regime. Γ : (A) 23.8, (B) 9.7, (C) 2.93, (D) 2.23 nmol/cm^2 .

Table III. Chronocoulometry (in finite diffusion regime) of TCNQ polyester films in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$.

$\Gamma/\text{nmol cm}^{-2}$	$T/^\circ\text{C}$	Slope/ sec^{-1}	$10^8 nD^{1/2}c/\text{mol cm}^{-2} \text{ s}^{-1/2}$
23.8	22	23.7	7.4
9.7	22	59	4.8
2.93	22	30.5	1.03
2.23	20	35	0.84

of uncompensated resistance, is difficult to explain. Interestingly, others have found similar thickness-dependent diffusion coefficients in redox polymer films; e.g., Pearce and Bard simulated the polyvinylferrocene voltammetry with a diffusion coefficient that increased with the square root of the film thickness (110). A possible explanation of this phenomenon is that the polymer film is ordered by the surface of the electrode substrate in the region of the substrate polymer film interface, and as a result the thin films are poorly swollen and the charge transport process is slowed. Based on the previously determined dry thickness vs. charge dependence of the TCNQ polyester (73, 74) the approximate thicknesses of the thinnest films examined is ca. 5 + or -2 nm. This interpretation is supported by the observation that the width of the $A^{\cdot-}/A^{2-}$ wave in the cyclic voltammograms of the TCNQ polyester films is also dependent on the amount of material on the electrode surface. The thicker films exhibit narrower peaks, decreasing from 77 mV (width at half-peak height) for $\Gamma = 2.3 \text{ nmol cm}^{-2}$ to 64 mV for $\Gamma = 19 \text{ nmol cm}^{-2}$, which is indicative of a decrease of repulsive interactions between redox sites and a greater degree of solvent swelling in the thicker films (76). Other interpretations of this effect are possible and the interaction of the TCNQ sites with the electric field (111) especially for the thin films, cannot be ruled out. At any rate, this dependence of the charge transport rate on loading further complicates the comparison of the data in Table II.

When allowance is made for the above dependence on Γ (see inset in Figure 17), the Cottrell slopes for the TCNQ polyester, terpolymer,

and TCNQ-BOEB polymer blends are consistent with each other and the Dahms-Ruff equ. 1. At room temperature, the Cottrell slopes for the terpolymer are ca. 50% of those for the TCNQ polyester films. When allowance is made for the uncertainties in the degree of solvent swelling for the two films, this is in good agreement with the nominal concentration of TCNQ sites in the two films. The Cottrell slopes for the 50% blend are also in accord with this description, indicating further that the blends contain a homogeneous distribution of TCNQ sites as originally cast from the DMA/acetone solvent.

The Cottrell slopes displayed a temperature dependence (see Figure 18) as expected for a thermally activated diffusional process. Activation energies for the "apparent charge transport diffusion coefficient" were obtained from equ. 27 neglecting the (likely?)

$$nD^{1/2} c = \text{Constant} \times \exp\left(-\frac{E_{\text{act}}}{2RT}\right) \quad (27)$$

temperature dependence of the concentration term. For the TCNQ polyester and terpolymer, the data of Table I, p. 53, give E_{act} values of 7.1 Kcal mol⁻¹ and 9.3 Kcal mol⁻¹, respectively. If counter ion motion is controlling the charge transport process, the slightly larger value for the terpolymer is understandable by the increased energy required for the ion to move from site to site in the terpolymer where the intersite distance is greater than in the TCNQ polymer.

Effect of film composition on the $A^{\cdot-}/A^{2-}$ process. The well behaved appearance of the $A^{\cdot-}/A^{2-}$ wave in the cyclic voltammograms of

the TCNQ polyester and terpolymer films prompted us to examine the kinetics of this process in greater detail. For thin films of the TCNQ polymer that approach monolayer coverage of the electrode surface, the surface wave character is retained at sweep rates up to ca. 40 V/s; see Figure 20 which shows a sweep rate study of the TCNQ polymer in contact with $\text{CH}_3\text{CN}/0.5 \text{ M TEAP}$. Although there is a considerable separation of the anodic and cathodic peak potentials, very little diffusional tailing of the surface voltammetric waves is evident. Qualitative inspection of the voltammograms reveals that the $\text{A}^\cdot/\text{A}^{2\cdot-}$ process is slower than either the $\text{A}/\text{A}_2^\cdot$ or the $\text{A}_2^\cdot/\text{A}^\cdot$ process. For example at a sweep rate of 15.8 V s^{-1} the $\Delta E_p (= E_p^a - E_p^c)$ for the former is 140 mV, while the latter processes have ΔE_p 's of ca. 100 mV.

The peak potential data were analyzed with the help of the theory of Daifuku et al. (105) for surface electrochemical reactions. The electrode loadings significantly influence the experimental results as is shown in Figure 21. Here the cathodic and anodic peak potentials of the $\text{A}^\cdot/\text{A}^{2\cdot-}$ wave are plotted as a function of sweep rate for different values of Γ and supporting electrolyte concentration. For the thicker films both diffusion and uncompensated resistance effects contribute to the peak separation. Only for the thinnest film examined do the data correspond to a true surface process. Table IV and Figures 22 to 25 summarize the results obtained for a number of different electrode preparations and for different supporting electrolyte concentrations in acetonitrile. Note that in most cases the transfer coefficients α_c and α_a are seen to deviate from the normally assumed value of 0.5 and

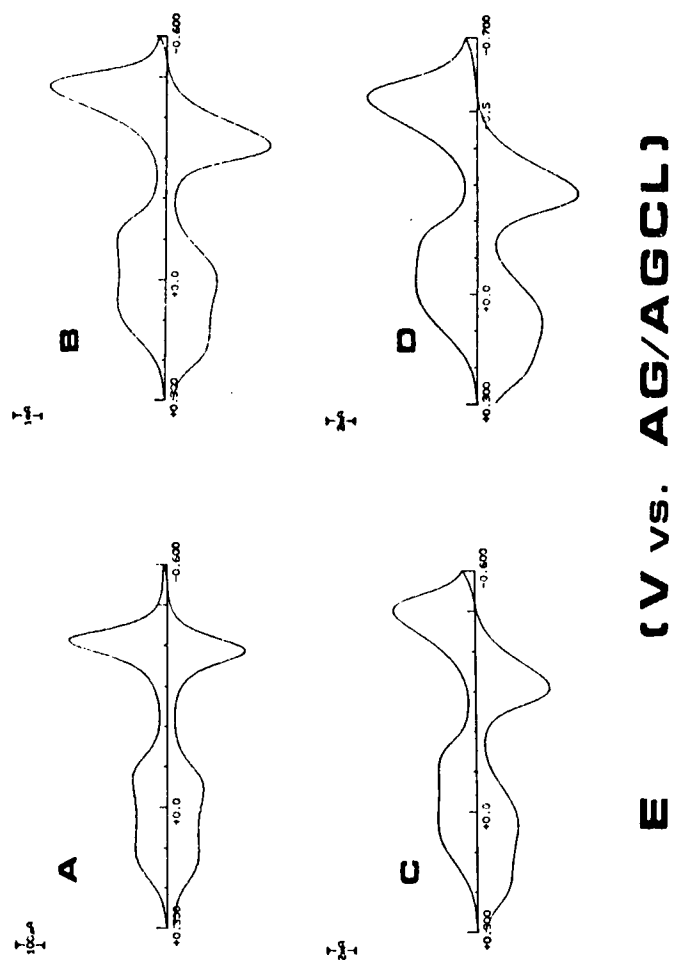


Figure 20. Cyclic voltammograms of TCNQ polyester film electrode in contact with $\text{CH}_3\text{CN}/0.5 \text{ M TEAP}$. $\Gamma = 1.7 \text{ nmol} \cdot \text{cm}^{-2}$, 25.3°C , sweep rates (A-D): 1.00 , 15.8 , 25.6 , and $41.0 \text{ V} \cdot \text{s}^{-1}$.

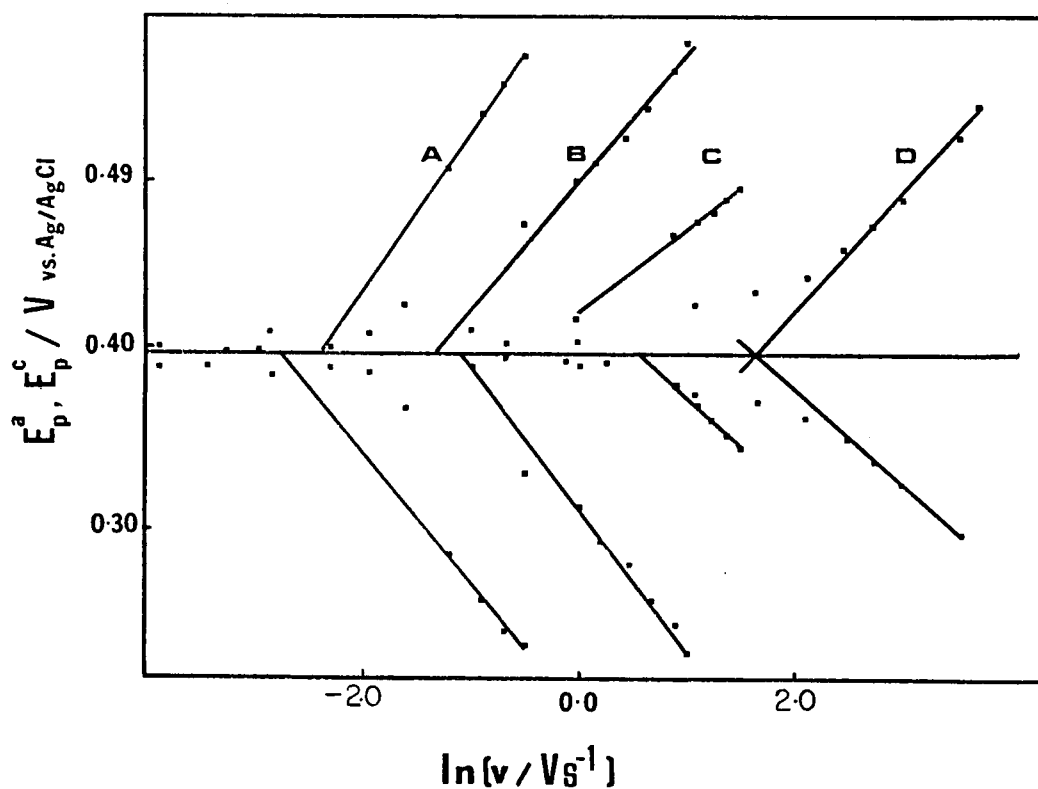


Figure 21. Variation of anodic (E_p^a) and cathodic (E_p^c) peak potentials for the $A^{\cdot-}/A^{2-}$ wave of TCNQ polyester films in contact with $CH_3CN/0.1\text{ M}$ (A-C) or 0.5 M (D) TEAP. $\Gamma = 11.5, 7.3, 1.88$, and $1.70\text{ nmol} \cdot \text{cm}^{-2}$ (A-D).

Table IV. Summary of the kinetic analyses of $A^{\cdot-}/A^{2-}$ couple for TCNQ polyester films of various surface coverages ($\Gamma/\text{mole}, \text{cm}^{-2}$) on Pt in acetonitrile and different concentrations of TEAP.

$\Gamma/\text{nmol}\cdot\text{cm}^2$	$[\text{TEAP}]/M$	$v_i/V\cdot\text{sec}^{-1}$	α_c	α_a	$k_{app}^\circ/\text{s}^{-1}$	Temp/ $^\circ\text{C}$	Ea/Kcal $\cdot\text{mole}^{-1}$
7.3	0.1	0.3	0.34	0.38	3.18	R.T.	--
1.88	0.1	0.548	0.59	0.73	7.84	R.T.	--
0.410	0.1	0.6	0.48	0.54	6.38	R.T.	--
2.38	0.5	3.67	0.45	0.49	26.6	R.T.	--
1.70	0.5	6.0	0.40	--	64.5	25	15.6
1.7	0.5	2.46	0.36	--	28.2	5	
1.7	0.5	1.32	0.275	--	12.5	-4	
1.7	0.5	0.462	0.337	--	3.68	-13	

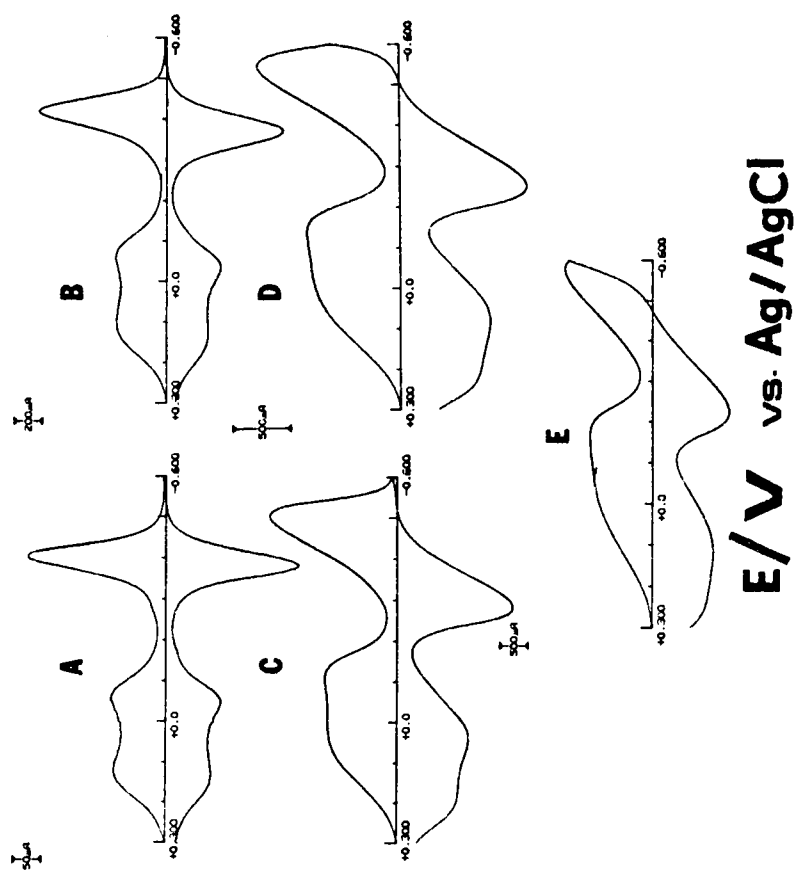
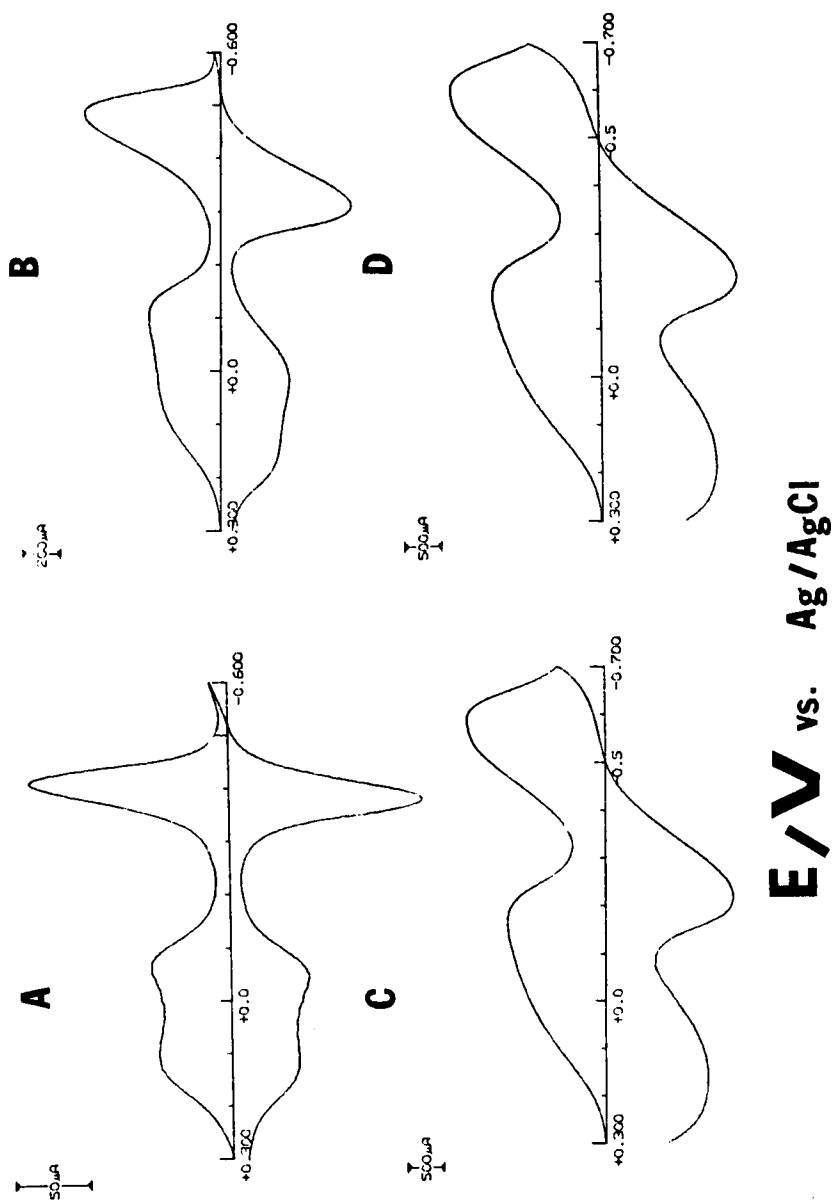


Figure 22. Cyclic voltammograms of Day's TCNQ-PE in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$, $\Gamma = 11.5 \text{ nmole/cm}^2$. Sweep rates (A-E): 50, 200, 300, 500, and 700 mV/sec.



E/V vs. Ag/AgCl

Figure 23. Cyclic voltammograms of Day's TCNQ-PE in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$, $\Gamma = 7.3 \text{ nmole/cm}^2$. Sweep rates (A-D): 100, 800, 3500, and 4000 mV/sec.

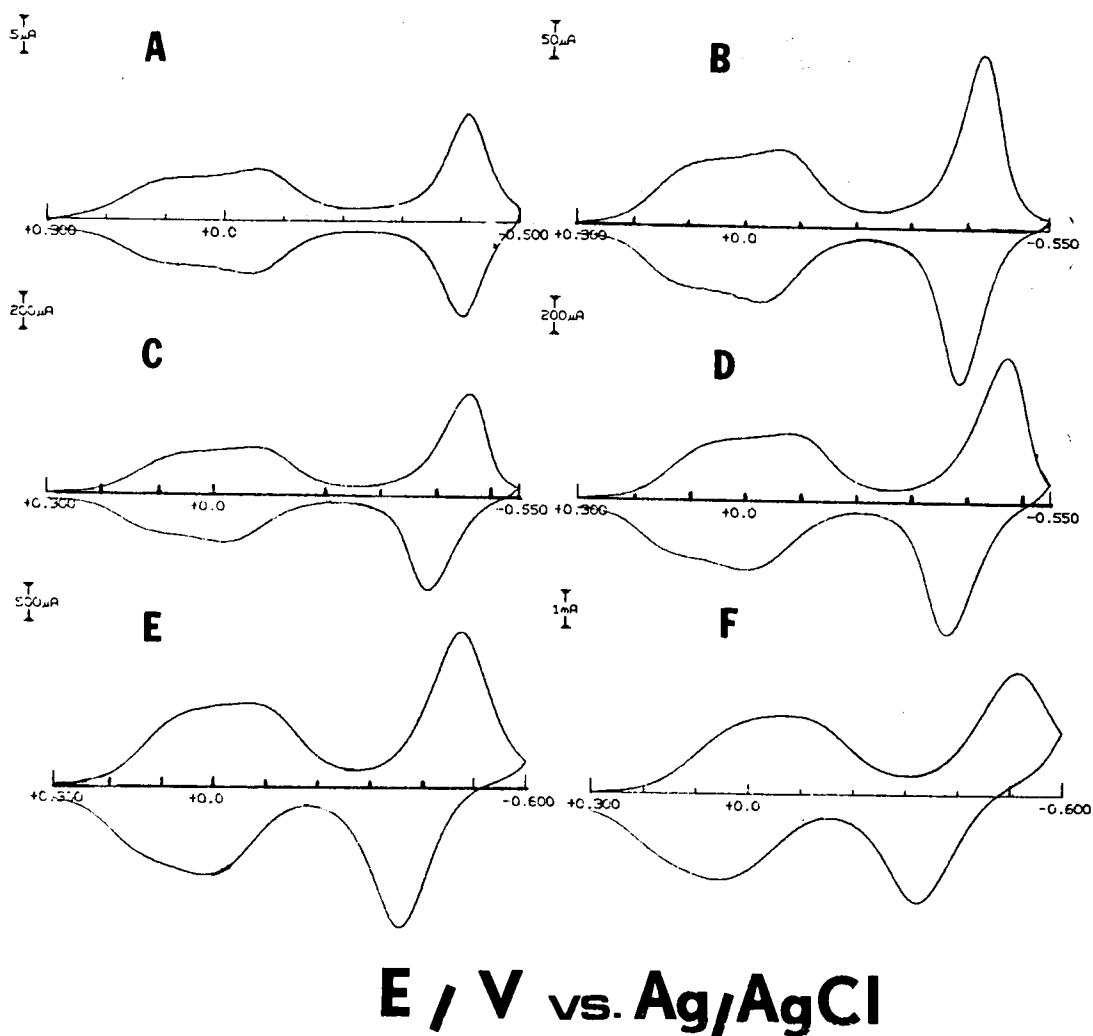


Figure 24. Cyclic voltammograms of Day's TCNQ-PE in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$. $\Gamma = 1.88 \text{ nmole/cm}^2$; sweep rate (A-F): 50, 800, 2000, 3000, 10,000, and 20,000 mV/sec.

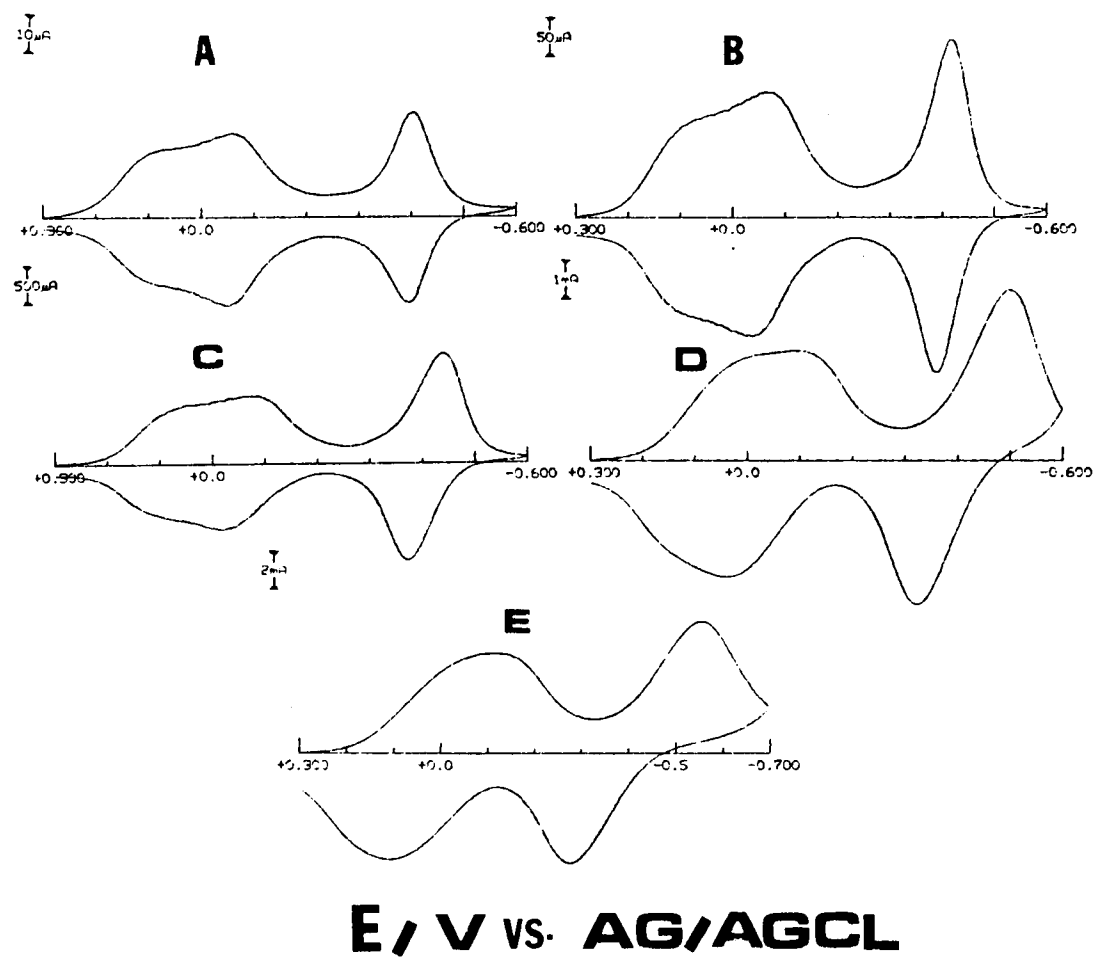


Figure 25. Cyclic voltammograms of TCNQ-PE in contact with $\text{CH}_3\text{CN}/0.5 \text{ M TEAP}$. $\Gamma = 2.38 \text{ nmole/cm}^2$; sweep rate (A-E): 100, 800, 5000, 20,000, 40,000 mV/sec.

their sum $\alpha_c + \alpha_a \neq 1$. Possible reasons for the above deviations will be discussed in this section.

Surface rate constants for electron exchange were obtained from the following equation,

$$k^{o'} = \left(\frac{\alpha n F}{2RT}\right) v_i \exp(-A)$$

where v_i is the sweep rate at the intersection of the straight line segments in Figure 21, and $A = [0.0119 - 0.2358 \chi + 0.0049 \chi^2 - 0.00086 \chi^3]$. The interaction parameter in this treatment, χ , is obtained from the peak width using the working curve of Daifuku et al. (105). This treatment was applied to the $A^{\cdot-}/A^{2-}$ wave over the temperature range, -13° to 25°C . At 25° the experiment of Figure 21D gave $k^{o'} = 64 \text{ s}^{-1}$, with α and $(1 - \alpha)$ values of 0.48 and 0.52 respectively. An activation energy of 15 Kcal mol^{-1} was derived from the temperature dependence.

The above value of the rate constant for the $A^{\cdot-}/A^{2-}$ process is of the same order of magnitude as the transition metal couples examined by Daifuku et al. (105). Comparison with the corresponding value for the TCNO terpolymer, $k^{o'} = 6.4 \text{ s}^{-1}$, is more pertinent to this study. The order of magnitude difference in rate constants suggests that the $\text{TCNQ}^{\cdot-}$ radical anion sites in the terpolymer overlap less with the electrode surface than the $\text{TCNQ}^{\cdot-}$ sites in polyester films. While this might be due to differences in the orientation or spacing of the TCNQ sites at the electrode surface for the two materials, further work is necessary to establish this conclusion.

It should be pointed out that the method of Daifuku et al. employed here for the evaluation of heterogeneous rate constants was developed for surface reactions and does not take into account the possible effects of diffusion. As pointed out by Peerce and Bard (110), such a theoretical procedure can not be applied "directly" to the determination of rate constants for most polymer films. This is because the theory not only neglects mass transport problems inherent in multilayer surface films, but also the possible presence of electrochemically nonequivalent redox sites and any changes in the extent of swelling or in the structure which may occur upon reduction and oxidation. Furthermore, the use of cyclic voltammetry for this purpose requires a great deal of care in that the effect of "ohmic drop" and the "irreversibility" of the reaction are often very similar (3). Despite the above limitations, however, the electrochemical studies of the behavior of these redox polymer films have proved to be very constructive and have provided further insight into the nature of charge transport in the polymer film.

Measurements of the rate of heterogeneous electron transfer to a polymer film has only been reported in few cases (110). The monolayer discussed by Daifuku (105) showed contributions from the space distributed redox sites which are not in direct contact with the electrode surface, owing to the surface roughness. This possible effect is similar to polymer coated electrodes, for which, due to conformational characteristics of the polymers, diffusional contributions are unavoidable (1, 3) and can only be minimized. These authors

report values in the range of 71 to 100 s^{-1} for "Ruthenium Complex" and "Osmium Complex" respectively. Peerce and Bard (110) have proposed a model for the oxidation and reduction of electronically non-conductive surfaces and calculated the current-potential characteristics by digital simulation techniques. The effect of factors such as those discussed above on the electrochemistry of the surface films was examined and the simulated results were compared to the experimental data for electrodeposited poly(vinyl ferrocene) (PVF) films in 0.1 M tetrabutylammonium perchlorate (TBAP) solutions over a wide range of the scan rate. The simulated voltammograms obtained by Peerce and Bard reproduced the "essential" features of the observed cyclic voltammetry of electrodeposited PVF films rather well. The values obtained from the simulation for the heterogeneous rate constants were $100\text{--}250 \text{ s}^{-1}$ (110). These authors also pointed out that the values of the diffusion coefficients which fit their data were very sensitive to the value for the film thickness, increasing as the square of the film thickness. According to Peerce and Bard the diffusion coefficient of ca. $10^{-10} \text{ cm}^2/\text{s}$, assumed for their system, is of the order of the diffusion coefficients for small dissolved reactants diffusing through these films under similar conditions, so that "counterion diffusion and self-diffusion of the polymer segments" are probably important in limiting the rate of reduction or oxidation of the film. Although, all the kinetic parameters extracted are highly approximate, they do, however, seem to indicate that the electron transfer to redox polymers can become very slow (112).

Permeability studies. Several simple electrochemical experiments were performed to obtain some crude idea about the permeability of TCNQ-PE, BOEB-PE and PEG to some solvent/electrolyte systems. Both solvent and electrolyte play a significant role in the kind of electrochemical behavior seen for solution and adsorbed species. A typical experiment would involve the separation of the electrode from solution constituents by a relatively thin coating of the respective polymer. After the usual baking procedure, the polymer modified electrode is then used to study the electrochemical behavior of a solution species whose electrochemical behavior is well known. In the case of electroinactive polymers such as BOEB-PE and poly(ethylene glycol) (PEG), demonstration of electroactivity of the solution constituents will depend on how easily these species can pass through the polymeric matrix and reach the electrode surface. For polymers with good affinity for the solvent, uptake of solvent from the solution will result in the swelling of the polymer matrix which in turn may generate open channels through which the solution constituents can move towards the electrode surface where the electron exchange can take place. A poor affinity of the polymer for the solvent in use, however, may result in more compact structures that could seriously retard the above transport processes.

In the case of electroactive polymer modified electrodes, such as TCNQ-PE film electrodes, other interesting possibilities may arise with respect to the mechanism by which the electroactive solution constituents react at such electrodes. A full discussion of the above processes is outside the scope of this presentation, but due to its very

important relevance to the phenomenon of electrocatalysis a brief summary of Murray's account will be provided (2). There are basically three ways for the solution constituent to react at the polymer/electrode interface:

1. Reduced or oxidized constituents of the polymer film can act as " e^- transfer mediators (catalyst)" to drive electrochemical reactions of solution components. If such a mediation is possible, the large quantity of mediator sites in a polymer film will potentially enhance the electrocatalytic rate (113-115) as compared to monolayers. For such mediation to be fully effective, the ability of the substrate to penetrate the polymer film and encounter an appropriate oxidized or reduced catalyst site becomes a serious limiting factor in that several rate determining steps come into picture (114-118).

2. When the polymer film redox sites do not act as a catalyst, electroactive species of the solution "must" partition into and diffuse through the polymer film, or progress through pinholes or channels in the film, to reach the electrode surface in order to express their intrinsic electrochemical reactivity. Examples of cases where both the solution constituent electroactivity occurs freely (28, 116, 119), and cases where it is partially or totally retarded (116, 120, 36, 121, 122) were also given by Murray. He has interpreted the above behavior to reflect the inability of the species to penetrate the film or diffuse very slowly in the film. The charge of the dissolved reactant, its steric bulk, and the thickness and solvent swelling of the polymer film are some of the relevant factors.

3. The third mode of reaction of a dissolved electroactive substance at a polymer-coated electrode occurs when the film is electronically conductive and becomes the "electrode" surface. References to systems demonstrating such abilities have also been cited in Murray's review (40, 23).

In view of the above discussion, the experimental results presented in this section were found to be interesting and are in accord with our expectations based on other electrochemical observations.

Cyclic voltammetry of TTF at TCNQ-polymer modified Pt electrode in acetonitrile/0.1 M TEAP. The cyclic voltammetric behavior of TTF (1.6 mM) in acetonitrile/0.1 M TEAP solution was studied at a TCNQ-PE film electrode. Figure 26 shows the voltammograms corresponding to the following systems: CV A corresponds to that of TTF in solution and was recorded at a bare Pt electrode; CV B was recorded for the same solution (1.6 M TTF in acetonitrile), using a TCNQ-PE film Pt electrode (the film was baked at 125°C for 30 min.); the voltammogram of virgin TCNQ-PE/Pt was also recorded and is shown in Figure 26C.

The voltammogram of TTF in solution (Fig. 26A) and at a bare Pt electrode, in acetonitrile/0.1 M TEAP was recorded at scan rate of 100 mV/sec. As expected, this voltammogram exhibits two reversible waves at $E_{\frac{1}{2}}^{0/+} = +0.315$ and $E_{\frac{1}{2}}^{+/2+} = +0.68$ V vs. Ag/AgCl. The peak shapes in this voltammogram are characteristics of a diffusional process as expected for mass transport limited electroactivity.

A cyclic voltammogram corresponding to the above solution was then recorded at a TCNQ-PE film Pt electrode. Interestingly, this

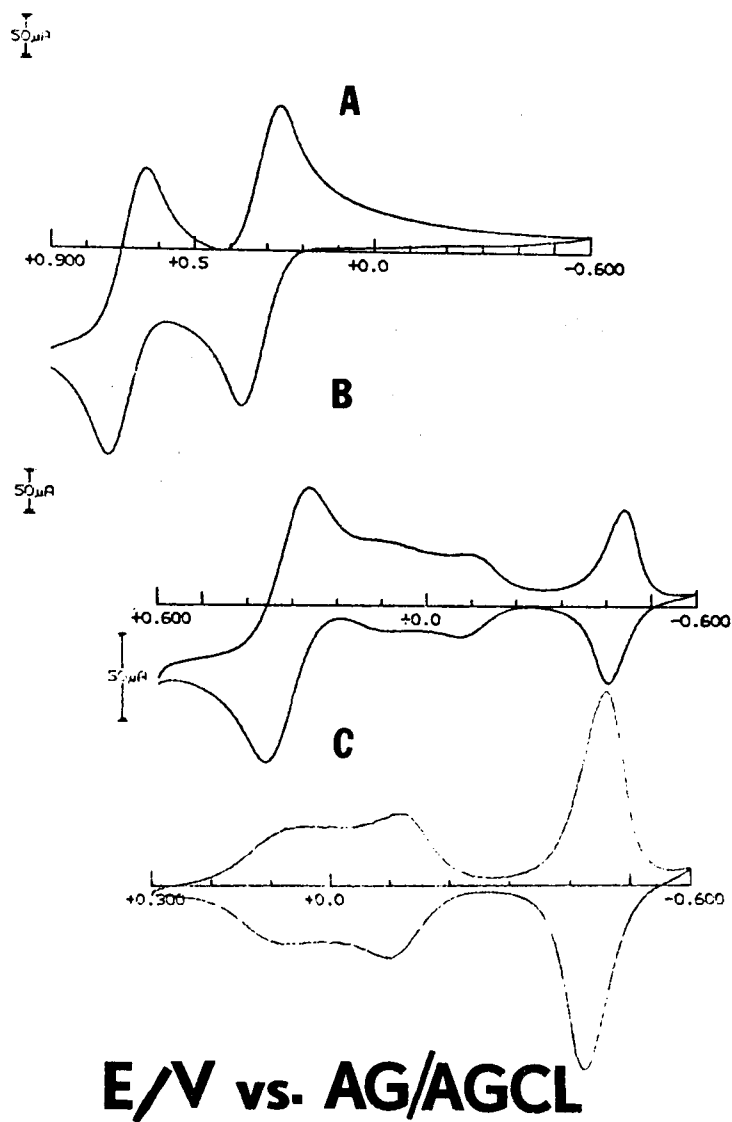


Figure 26. Results of permeability studies. Cyclic voltammograms of (A) TTF in solution recorded at Pt electrode, (B) TTF in solution recorded at Pt/TCNQ-PE film electrode, and (C) TCNQ-PE in acetonitrile/0.1 M TEAP; sweep rate = 100 mV/sec.

voltammogram (Fig. 26B) shows the typical redox wave as that seen in Figure 26A. The $E_{1/2}$ corresponding to TTF/TTF^+ couple was seen at approximately the same potential ($E_{1/2}^{0/+} = +0.31 \text{ V vs. Ag/AgCl}$). The potential excursion limits included the region where two typical voltammetric waves were seen that corresponded to A/A_2^- , A_2^-/A^- and A^-/A^{2-} couples at the expected $E_{1/2}$ values. The diffusional tail of the wave corresponding to TTF/TTF^+ overlaps with currents from reduction of TCNQ sites. The voltammogram of TCNQ-PE film electrode in solution of acetonitrile/0.1 M TEAP is also given for comparison purposes.

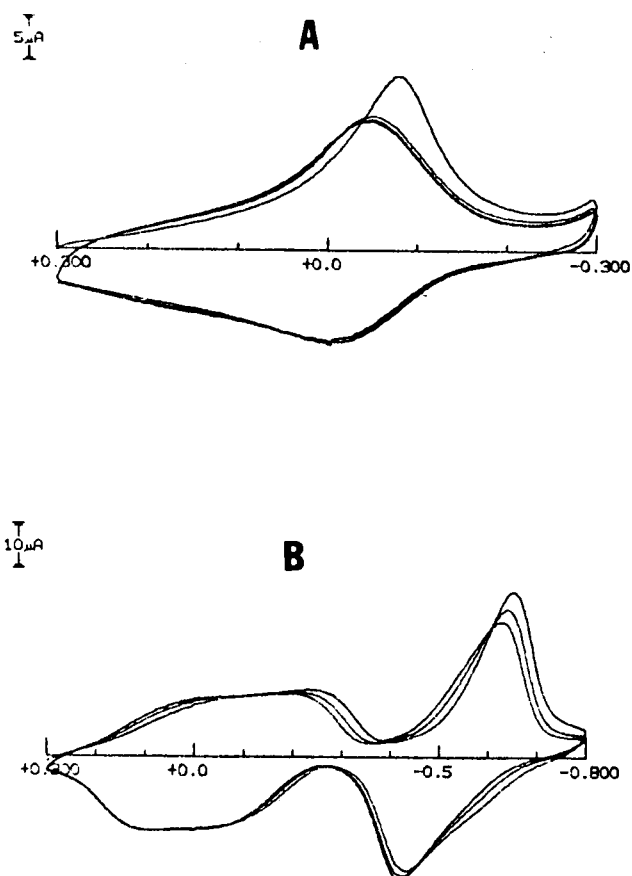
The above observations imply that TCNQ-PE film is highly swollen and that TTF/electrolytes easily permeate through the polymer matrix toward the electrode surface. The potential scan was started at a point where the oxidation of solution TTF moieties takes place at the rate controlled by diffusional mass transport to the electrode surface. The TCNQ redox sites are present in their neutral state, therefore, excluding any electrocatalytic effect and also eliminating the possibility of polymer/solution interface as being the locus of electron exchange. The presence of pinholes or defects in the film homogeneity is thought to play insignificant role in this observation as judged from similar studies that were performed with BOER-PE film Pt electrodes. The above coating totally insulated the electrode surface which was known to swell poorly in the presence of acetonitrile and is probably also impermeable to TEAP.

Cyclic voltammetric and chronocoulometric studies performed at Pt/TCNQ-PE/PEG in contact with solvent/electrolyte systems. The

experiments discussed in this section were aimed at studying the permeability of PEG polymer matrix to aqueous and organic solvents containing various counterions.

The electrode was fabricated in the following manner: a thin film of TCNQ-PE was coated on a Pt electrode and baked for 1 hr at 115°C. This Pt-TCNQ-PE electrode was then cooled to room temperature and a few drops of PEG in DMA/acetone was layed on top of it followed by removal of the solvent by evaporation. This electrode designated as Pt/TCNQ-PE/PEG was then used to determine the permeability of acetonitrile/TEAP and water/KCl through the exterior PEG matrix. The electroactivity of TCNQ-redox sites in contact with Pt will depend on the ability of solvent/electrolyte to cross the PEG barrier and diffuse or migrate to TCNQ sites. In the absence of penetration, no electrochemical activity can be expected to take place, based on known behavior of TCNQ-polymer films (72-74, 76, 45, 98, 77).

The results of such studies were found to be interesting and were consistent with other observations. Figure 27A shows the voltammogram recorded in water containing 0.5 M KCl. This voltammogram ($\Gamma = 1.2 \times 10^{-8}$ mole/cm²) features both cathodic and anodic waves at the expected potential ($E_{\frac{1}{2}}^{0/-} = 0.070$ V vs. SCE). Note that there is no break-in process observed and that the overpotential effects in the initial cycle usually seen for TCNQ-PE films on Pt are absent here. The CV is nearly identical to those of Inzelt et al. obtained on broken-in TCNQ-PE films. The magnitude of peak current



E, V vs. $Ag/AgCl$

Figure 27. Cyclic voltammograms of Pt/TCNQ-PE/PEG film electrode in (A) $H_2O/0.5 M$ KCl, $v = 10$ mV/sec; (B) acetonitrile/ $0.1 M$ TEAP, $v = 20$ mV/sec.

and the value of peak width at half maximum show a slight dependency on the length of time the potential was held at +0.3 V vs. SCE before the excursion was started. The peak currents increased and $\Delta E_{p/2}$ decreased with time.

In order to obtain a more quantitative idea about charge transport through this film, potential step chronocoulometry was performed on both the cathodic and anodic process. Interestingly the magnitude of $(nD^{1/2}c)^{cath}$, $(2.06 \pm 0.61) \times 10^{-8}$, was significantly smaller than that measured for the anodic process, $(6.07 \pm 0.35)10^{-8}$.

The above results imply that the PEG film becomes readily swollen and the transport of the solvent/electrolyte through TCNQ polymer matrix becomes the limiting factor in the overall electrochemical activities.

At the conclusion of the above CC experiments the above electrode was pulled out of the water/KCl solution, shaken to remove the excess solvent, and reinserted into acetonitrile/TEAP solution. The voltammogram obtained is shown in Figure 27B. The qualitative features of this CV resemble those expected for a virgin TCNQ-PE film in contact with $CH_3CN/TEAP$. The larger size of TEAP and its slower mobility in PEG may explain the above behavior.

Electrochemical Studies of TCNQ-PE/PEG Blend Films on Pt Electrode in Contact with Acetonitrile/Electrolyte Systems

Introduction

In earlier sections of this dissertation the effect of the film composition on cyclic voltammetric and chronocoulometric behavior of TCNQ

polyester (TCNQ-PE) was discussed in some detail. When the film composition was varied by using BOEB-PE as a host polymer, CVs recorded at slow scan rates in acetonitrile/0.1 M TEAP demonstrated several interesting features: there was a good agreement between the position and shape of the $A/A_2^{\cdot-}/A^{\cdot-}$ wave in the CV of the terpolymer (Fig. 13B, p. 70) and that seen for BOEB blend film (Fig. 13E) where the nominal TCNQ site concentration was approximately the same. However, there was a striking difference between the terpolymer and the blend voltammetry with respect to the behavior corresponding to the second wave ($A^{\cdot-}/A^{2-}$). As pointed out previously, decreased charge transport rates in the region of the $A^{\cdot-}/A^{2-}$ couple relative to the rates for the $A/A_2^{\cdot-}/A^{\cdot-}$ may play a significant role in the above observation. Slow reduction of the TCNQ sites in thick virgin films in contact with solvents of poor swelling power is believed to be in part due to slow ion transport from solution to the nonpolar polymer phase (74). This kinetic limitation was attributed to an uncompensated resistance which decreased as the film incorporated more solvent and electrolyte species, thus increasing the ionic mobility (break-in process) in the film.

As also pointed out by Murray (2), electroactivity of the redox centers in most redox polymer films depends on the film's ionic conductivity. Either enough supporting electrolyte solute ions must penetrate the film through pores, or the film must contain many fixed charged sites plus mobile counterions. This ionic conductivity is needed so that a potential applied to the electrode can develop a sufficient potential gradient at the electrode-polymer interface to drive

electron transfer there between the electrode and adjacent redox centers in the polymer (2). Solvent penetration into the polymer (i.e., swelling) in many cases, probably, facilitates adequate ionic mobility, penetration and conductivity. A polymer film that is unable to incorporate the necessary counterions, for whatever reason, can be electrochemically inert or less than freely reactive because of the ohmic resistance of the film between the electrode polymer and polymer-solution interfaces (2).

The idea that the failure of the second reduction process could be related to the impermeability of the polymer matrix to solvent and/or counterion transport was strengthened by experiments with BOEB-PE coated electrodes. Coatings of this polymer almost insulated the electrode surface to electroactive species.

The transport processes which are necessary for the electrochemical activity of polymer-coated electrodes are also known to be strongly dependent on the morphology of the polymer matrix (34). The free volume concept and the extent of swelling by solvent, discussed above, have been used to explain this morphological effects (34). According to Schroeder and Kaufman (34), the permeation of a polymer film by solvent and electrolyte is an "activated diffusion" process which is sensitive not only to the polymer and the electrolyte, but also to the nature of the electrochemically generated ion-counterion pair. Accordingly, the ionized films swell to a far greater extent than do the neutral films. Therefore, the electrochemical characteristics of a particular polymer film will depend on the relative and absolute rates of

both "electron (hole)" transport and rapid counter ion transport. The former is favoured by high density of the electroactive groups, whereas the latter is favoured by high free volume contents and larger ionic diffusion coefficients (34). The single most important characteristic influencing the above rates according to Schroeder and Kaufman is the morphology of polymer film. Parameters that are cited by these workers to affect the morphological state of the polymer are: (a) the nature of the electroactive group, (b) the size and structure of the side chain linking the electroactive group to the backbone, (c) polymer backbone, (d) extent of ionization, (e) the presence of dopants, and (f) the conditions of the film preparation. As indicated earlier there has been a great deal of effort to assess the degree to which some generalizations can be made with respect to the behavior of various electroactive polymer modified electrodes. As such many different types of electroactive moieties have been employed by various research groups (see Chapter I). The rapid electron-transfer reactions of the TCNQ acceptors, as discussed elsewhere, render the film fully electroactive and thus has permitted the observation of the effects of various parameters such as (b-d) on the film electrochemistry (85, 79, 78).

In short, the presence of BOEB-PE as a host in TCNQ-PE films is interpreted to hinder the ionic mobility in the polymer matrix, partly due to the poor affinity of the polymer for the solvent and/or impermeability to the counterions. The employment of a host polymer which is more compatible with the solvent/electrolyte system will therefore

provide further support for the above interpretation. Such a host can provide an attractive system that would allow one to monitor the redox site concentration in the polymer film with minimal effects on the film ionic conductivity.

The choice of poly(ethylene glycol), PEG, (Polysciences, Inc., Warrington, PA; Mwt = 11,250; Mw/Mn < 1.07, and Lot no. 33978) was found to be ideal for such studies. The results were consistent with the above discussion and also with some of the known properties of these well studied PEGs that are commercially available. PEGs of low molecular weight are thought to predominantly exist in "zigzag" form, resulting in an open-coil extended conformation (123). Chains longer than nine repeat units have a more compact helical coil. The interactions between the polymer and metal ions (specially alkali metal ions) are believed to involve the same kind of ion-dipole interactions observed in cyclic polyethers (123). Proton, carbon-13 and sodium-23 magnetic resonance experiments have confirmed that the ethereal oxygens on the oxyethylene units of both PEGs and crown ethers are actually the site of interactions with the metal ions. The reaction of noncyclic PEG with alkali and alkaline earth metal ions was investigated by Yanagida et al. (124) by means of solvent extraction. PEGs with more than 23 oxyethylene units showed a strong extracting power, comparable to those of the crown ethers, and the power increased with increasing number of oxyethylene units. Yanagida et al. (124) also showed that high-molecular weight PEGs have some hydrophobic properties as judged from the high-percent extraction

obtained by dichloromethane, implying that the helical conformation is energetically favorable in an organic solvent (124). Noncyclic PEGs may take, on the average, a helical conformation even in the liquid state and therefore may favorably complex with cations, or the cations may induce an "energetically" favorable helical structure and, as a result, show a fair extracting power for the cationic species.

Solid state ionic conductivity of complexes of PEG with various salts has been actively pursued by several groups (87, 125-127). These solid state studies have concentrated on evaluating the ion mobility in the polymer matrix. Studies in the liquid state, however, have put more emphasis on the affinity of PEG for various cationic species. The higher the affinity of the cation for the ethereal oxygens of PEG, the lower would be the mobility of the cation in the polymer matrix. Ion pairing is also known to retard ion mobility in the polymer matrix in both cases, solid and liquid states. In the following sections an attempt will be made to correlate the electrochemical behavior of the films, containing PEG as a host, with the above phenomena.

The following sections deal with electrochemical studies of these blends (TCNQ-PE/PEG) in acetonitrile and aqueous solutions of various electrolytes.

Results and Discussion

Cyclic voltammetric and chronocoulometric studies of TCNQ-PE/-PEG blend films on Pt electrodes in contact with ACN/TEAP. When the

film composition is varied by blending TCNQ-PE with PEG of well-defined molecular weight and high degree of monodispersity, several interesting observations are made in view of the earlier findings with the BOEB polyester blends.

Cyclic voltammograms (CVs) of TCNQ-PE/PEG blend (33% in TCNQ-PE), with $\Gamma = 1.03 \times 10^{-8}$ mole/cm², in acetonitrile/0.1 M TEAP recorded at various scan rates are shown in Figure 28. At scan rate of 20 mV/sec, the CV features two waves that are presumably due to $A/A^{\cdot-}$ ($E_{1/2} = +0.030$ V) and $A^{\cdot-}/A^{2-}$ ($E_{1/2} = -0.386$ V vs. Ag/AgCl) couples. The two waves due to $A/A_2^{\cdot-}$ and $A_2^{\cdot-}/A^{\cdot-}$ couple are merged into a single broad ($\Delta E_{p/2} = 194$ mV) wave. There is a good agreement between the position and shape of the $A/A_2^{\cdot-}/A^{\cdot-}$ wave in the CV of the terpolymer (Fig. 13B, p. 70) and the behavior observed for the 33% blend (Fig. 28A) where the nominal TCNQ site concentration is approximately the same. CVs recorded over repeated cyclings in the potential range +0.3 to -0.6 V did not show any major changes. Unlike the behavior of TCNQ-PE/BOEB-PE blend film (Fig. 13E), no postwaves were seen in the voltammogram after many cyclings. Also the peak separation between the cathodic and anodic waves is slightly larger for BOEB-PE blend films ($\Delta E_{pp} \approx 40$ mV) as compared to the voltammetric behavior shown in Figure 28A ($\Delta E_{pp} \approx 0.0$). The second wave, as seen in Figure 28A, is at a more positive potential compared to the value of $E_{1/2}$ corresponding to the terpolymer. But charge transport rate in the region of $A^{\cdot-}/A^{2-}$ couple relative to the rates for the $A/A_2^{\cdot-}/A^{\cdot-}$ region showed the same trend as that discussed for the

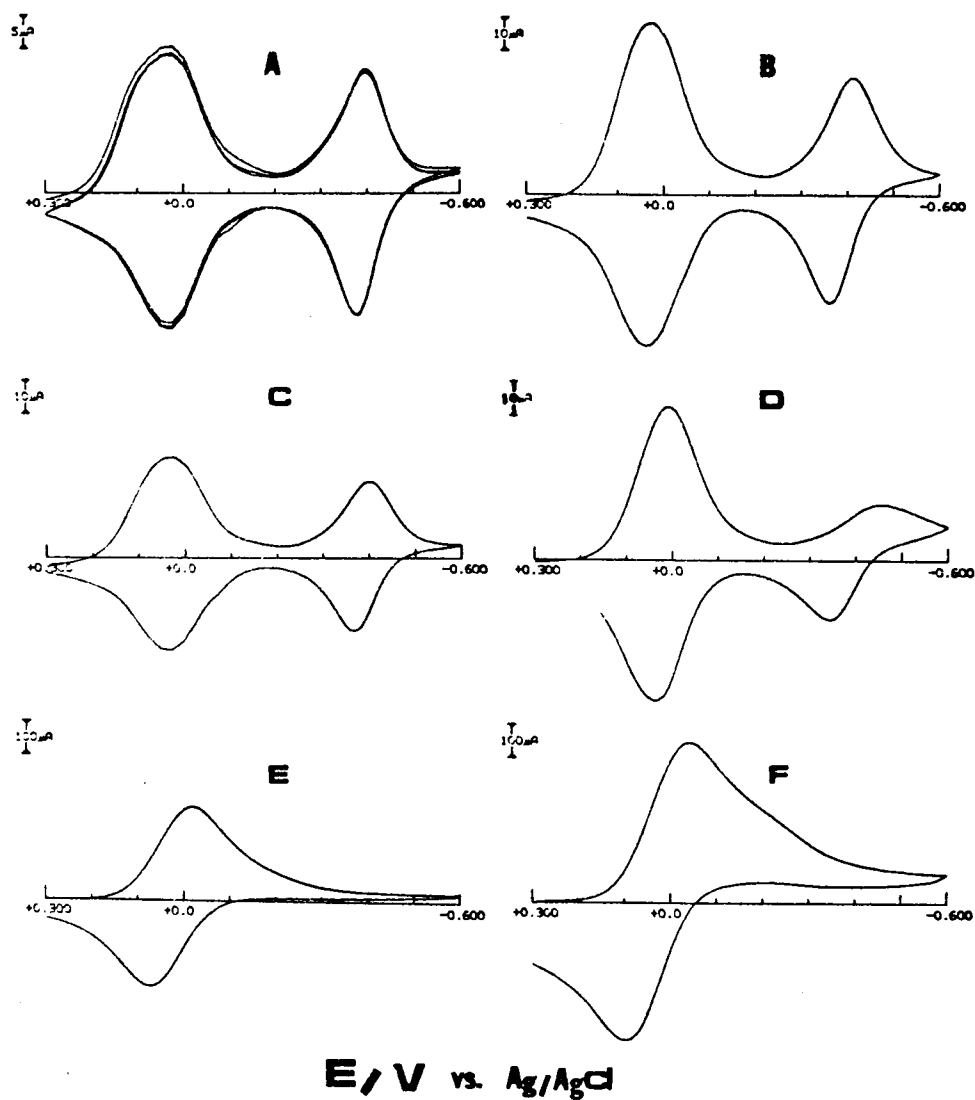


Figure 28. Cyclic voltammograms of TCNQ-PE/PEG (33% TCNQ-PE) in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$. $\Gamma = 10.3 \text{ nmole}/\text{cm}^2$; sweep rates (A-F): 20, 30, 50, 100, 500, and 2000 mV/sec.

terpolymer (see Fig. 16, p. 80). As the sweep rate was increased, the first wave retained its characteristic features, whereas, the second wave first assumed a diffusional appearance and then disappeared at relatively slow scan rates ($v = 100$ mV/sec). The peak to peak potential difference for both waves showed a strong dependence on the sweep rate, indicative of slow kinetic effects. This trend, i.e., the dependency of ΔE_{pp} on the sweep rate, and the overall behavior of the second wave (see Table V) showed a high degree of similarity to that seen for the terpolymer, studied under similar conditions (see Fig. 16).

In order to obtain a more quantitative idea about the process of charge transport in films with PEG as a host polymer, chronocoulometric experiments were carried out on the TCNQ-PE/PEG Pt electrode over a wide temperature range. As pointed out earlier, the Cottrell slopes derived from the Anson plots of Q vs. $t^{\frac{1}{2}}$ give a more quantitative estimate of the rate of the overall charge transfer process than the qualitative shape of the CVs. As the temperature is lowered (Fig. 29), the peak voltammogram for the first reduction process becomes diffusional in shape and ΔE_{pp} approaches 69.7 mV. Overall the voltammograms at lower temperature resemble those of a diffusionally controlled process. These effects are even more serious for the second wave which disappears totally at temperatures below -15°C (see Fig. 20D, p. 92). The quantity of TCNQ reduced at -15°C was found to be 43% of that known to exist on this electrode as judged from the magnitude of manually integrated charge above the baseline of CV

Table V. Effects of scan rate on voltammograms of TCNQ-PE/PEG blend (33% TCNQ-PE), $\Gamma = 10.3$ nmole/cm², and the terpolymer, 25.6 nmole/cm², in contact with acetonitrile/0.1 M TEAP.

v/mV/sec	TCNQ-PE/PEG (33% TCNQ-PE)		Terpolymer	
	A/A^+ $\Delta E_{pp}/mV^*$	A^-/A^{2-} $\Delta E_{pp}/mV$	A/A^+ $\Delta E_{pp}/mV$	A^-/A^{2-} $\Delta E_{pp}/mV$
5	--	--	0.0	20
20	0.0	18	20	47
60	--	--	27	60
100	24	diffusional	60	absent
500	88	absent	93	--
800	110	--	--	--
1000	--	--	133	--

*Anodic, cathodic peak separation.

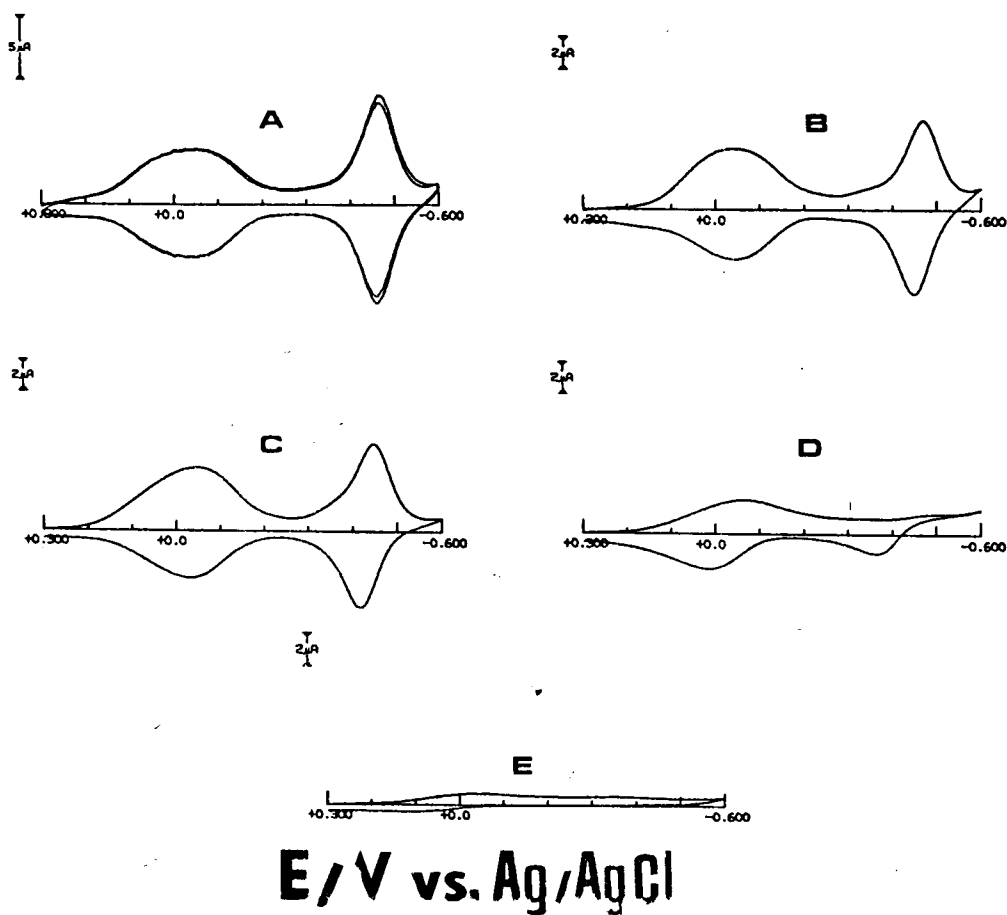


Figure 29. Cyclic voltammograms of TCNQ-PE/PEG blend film in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$. $\Gamma = 2.1 \text{ nmole/cm}^2$. Temperatures (A-E): 27.0, 15.2, -0.4, -15.0, and -26.0°C.

recorded at low scan rate at room temperature. This implies that the TCNQ sites are not exhaustively reduced at low temperatures, because the rate of charge transport is now slower than the experimental time scale (116). Chronocoulometric measurements corresponding to above CVs at various temperatures further supported this conclusion.

In all cases the chronocoulometric and cyclic voltammetric results were consistent. At temperatures not too much below room temperature, as seen earlier, the limiting charge accepted by the films, estimated by the approach of thin layer behavior and the charge obtained by integration of the CVs were in agreement. In this regard the overall features of the chronocoulometric Anson plots prepared for the data collected at higher temperatures were as expected for polymer film electrolysis. That is, the plot featured three regions: the early portion of the plot, usually with a nonzero time axis intercept; a linear region from which the useful CC Cottrell slopes are obtained; and the deviation from the linear behavior due to the finite volume of the film (Fig. 30). At lower temperatures, however, subtle changes were observed when Q vs. $t^{\frac{1}{2}}$ plots were constructed. The major difference was the positive intercept on the Y axis when the linear portion of the plot was extrapolated to $t = 0$ (see Figs. 30 and 31). Also note that, in agreement with the CVs recorded at lower temperatures, no deviation from linear behavior was observed in the time scale of the experiment. Actually, this is a typical behavior observed when double layer and/or adsorption of electroactive species become significant compared to the faradaic current due to diffusing species, and is known to be common to solution phase electrochemistry (103, p. 203).

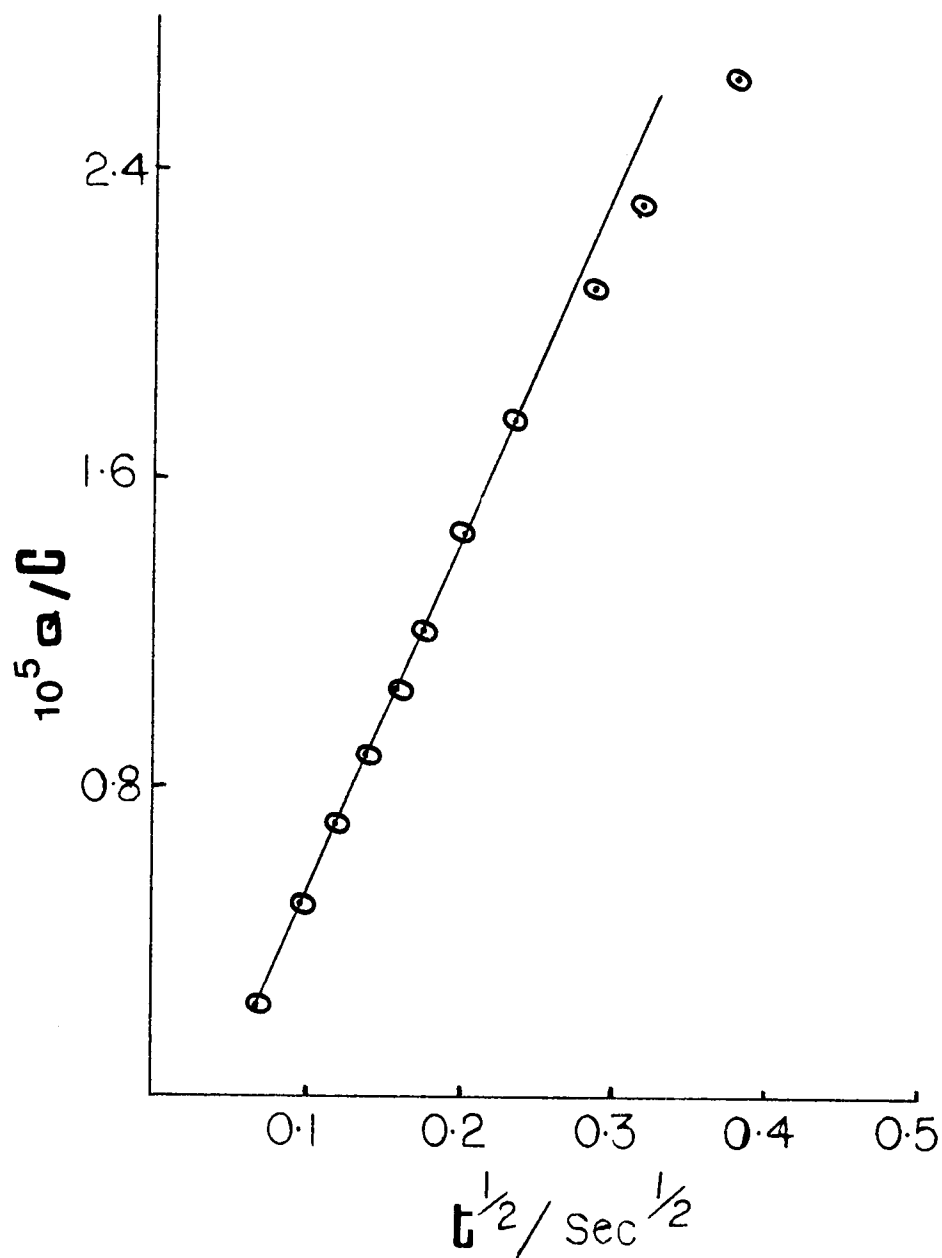


Figure 30. Chronocoulometric Anson plot for the reduction of TCNQ-PE/PEG blend (25% TCNQ-PE) film electrode in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$ at $15.2 \pm 0.5^\circ\text{C}$. $\Gamma = 2.1 \text{ nmole} \cdot \text{cm}^2$.

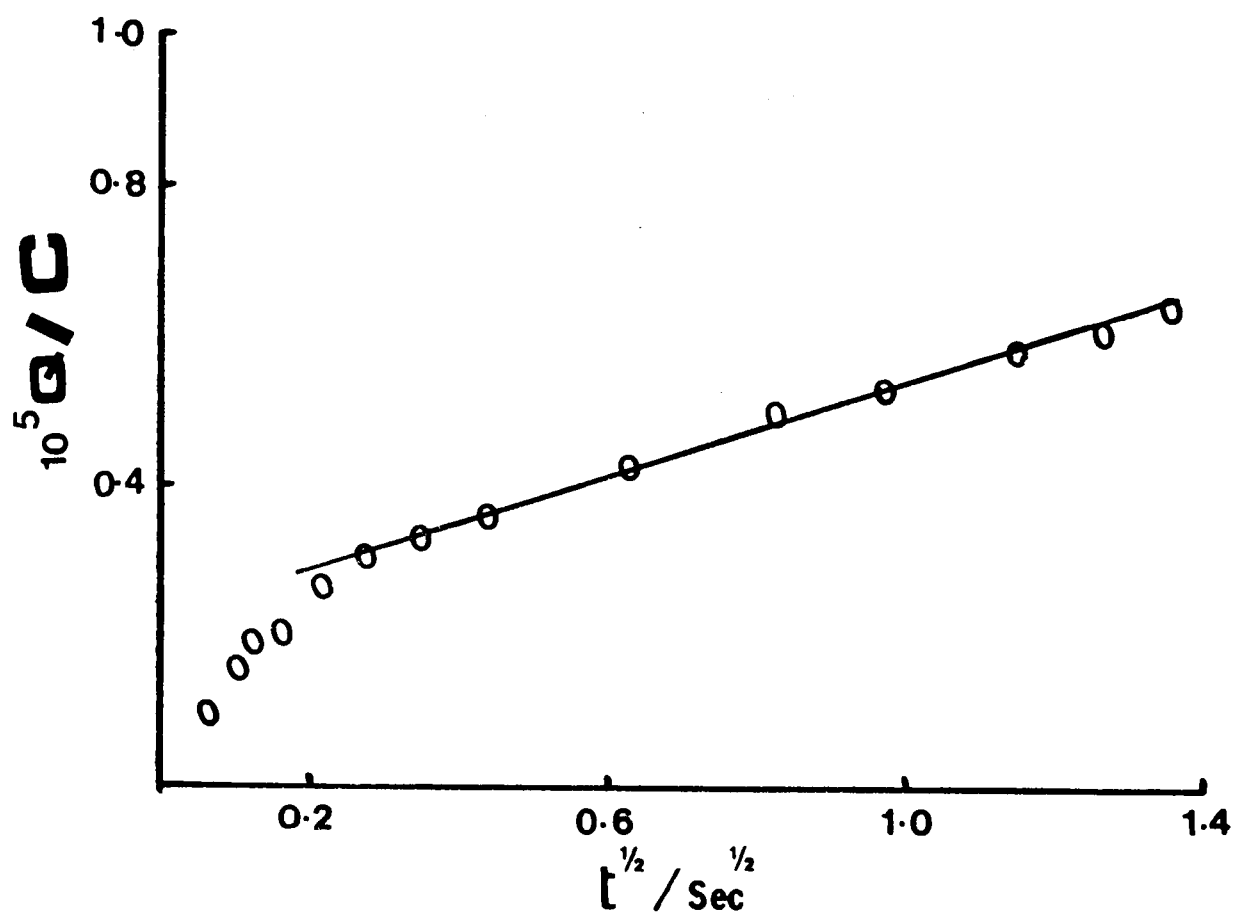


Figure 31. Chronocoulometric Anson plot for the reduction of TCNQ-PE/PEG blend (25% TCNQ-PE) film electrode in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$ at -26.0°C .

Note that the dependence of the Cottrell slopes on the electrode loading is also evident and is consistent with our previous observations. The Cottrell slopes also displayed a temperature dependence, see Table VI, as expected for a thermally activated diffusional process. Activation energies for the "apparent charge transport diffusion coefficient" were obtained as discussed elsewhere (p. 68). The data of Table VI were analyzed by linear regression method which gave E_{act} of 8.34 Kcal/mole, slightly smaller than that measured for terpolymer (9.3 Kcal/mole).

The expected merging of the A/A_2^- and A_2^-/A^- waves as the sites were diluted with PEG is in qualitative agreement with the data derived from the ESR and CV of the TCNQ polyester films. This behavior is also consistent with our previous treatment of the polymer film as a homogeneous phase with a uniform distribution of TCNQ sites. The indication is that the TCNQ polyester and the PEG form uniformly blended films as cast from the DMA/acetone solutions.

Charge transport rates in the region of the A^-/A^{2-} couple relative to the rates for the $A/A_2^-/A^-$ region was much less affected compared to blends with BOEB-polyester.

Finally a comparison of the chronocoulometric results given in Table VII with those obtained for TCNQ-PE, terpolymer and TCNQ-BOEB blend films deserves some discussion. As indicated earlier, the Cottrell slopes show a dependence on the electrode loading. As the amount of the TCNQ-PE in the blend film is increased (keeping the ratio of PE/PEG constant in the stock solution), the apparent charge

Table VI. Chronocoulometric Cottrell function data for TCNQ polyester and TCNQ-PE/PEG blend films in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$.

$\Gamma/\text{nmole}/\text{cm}^2$	$T/^\circ\text{C}$	$(10^8 n D^{1/2} c)^a / \text{mole cm}^{-2} \text{s}^{-1/2}$	$(10^8 n D^{1/2} c)^b / \text{mole cm}^{-2} \text{s}^{-1/2}$
6.40 (50% TCNQ-PE)	27 ± 0.5	3.58 ± 0.26	4.87 ± 0.021
3.60 (50% TCNQ-PE)	27 ± 0.5	2.27 ± 0.1	2.73 ± 0.16
2.1 (25% TCNQ-PE)	27 ± 0.5	0.29 ± 0.025	--
2.1 (25% TCNQ-PE)	15.2 ± 0.2	0.39 ± 0.033	--
2.1 (25% TCNQ-PE)	-0.4	0.18 ± 0.001	--
2.1 (25% TCNQ-PE)	-15.0	0.0386	--
2.1 (25% TCNQ-PE)	-26.0	0.0171	--

^aCathodic process.

^bAnodic process.

Table VII. Chronocoulometric Cottrell function data for TCNQ polyester, the terpolymer, and TCNQ-PE/PEG blend films in contact with $\text{CH}_3\text{CN}/0.1 \text{ M TEAP}$.

System	$\Gamma/\text{nmole}/\text{cm}^2$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})_{\text{cath}}^{-2} \text{ s}^{-\frac{1}{2}}$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})_{\text{anod}}^{-2} \text{ s}^{-\frac{1}{2}}$
TCNQ-PE	3.1	1.6	--
TCNQ-PE	2.3	1.3	--
Terpolymer (30% TCNQ)	3.2	0.32	--
TCNQ-PE/PEG (50% TCNQ-PE)	3.60	2.27 ± 0.10	2.73 ± 0.16
TCNQ-PE/PEG (25% TCNQ-PE)	2.1	0.29	--

transport diffusion coefficient increases. The value of $nD^{1/2}_c$ corresponding to various film compositions are compiled in Table VII for comparison purpose. The results indicate that even before the magnitude of the concentration term is adjusted, TCNQ-PEG blend films of a comparable surface coverage show a larger value for the derived $nD^{1/2}_c$ than the corresponding TCNQ-BOEB films. Another important aspect of the results shown in Table VII is the relative magnitude of the $nD^{1/2}_c$ values for the cathodic and anodic processes derived for blend films containing PEG as a host polymer. In the following sections an attempt will be made to correlate these observations with the available literature on the properties of PEG and ion-exchange polymer film electrodes. Although the interpretation will be speculative, some insight on the process of charge transport in polymer films in contact with solvent/electrolyte will be obtained.

Earlier it was pointed out that (34) the permeation of a polymer film by solvent and electrolyte is an "activated diffusion" process and that the electrochemical characteristics of a particular polymer film will depend on the rate of counter ion transport in response to electrochemical perturbations. According to Yanagidi et al. (124), high-molecular weight PEGs have some hydrophobic properties in that the helical conformation is energetically stabilized in an organic solvent. Solid state voltammetry of electroactive solutes in PEG polymer films on microelectrodes indicated larger rates of charge transport when the electrode was exposed to acetonitrile vapor (87). This observation was interpreted to be due to the plasticizing effect of the acetonitrile

following its adsorption onto the polymer matrix containing the electro-active species along with the counterions.

Stainer et al. (125) have determined the conductivity of PEG materials in their "crystalline" and "metastable," amorphous states. In the amorphous state, conductivity enhancement at room temperature was roughly 10^3 ($\Omega^{-1}\text{cm}^{-1}$) greater than for the corresponding crystalline state of these polyelectrolytes. This behavior, according to these workers, further strengthens the assumption that cooperative polymer conformation fluctuations are responsible, at least in part, for the transport process in these conductors.

Irregular cross-linking of the polyether backbone through interactions with the cations may induce the amorphous structure discussed above. If the ions can reside in the helical tunnel of PEG through coordination to oxygen atoms, where hydrogen binding may also play a significant role, the resulting structure will most likely be very crystalline. On the other hand, in the presence of larger cations that do not fit inside the helical cavity, the structure will be irregular and therefore not crystalline (125). Several possibilities for ion transport in these polymer materials have been envisaged (127). The simplest involves ion hopping in the helical pipes and might be similar to ionic motion in tunnel-type framework ionic conductors. This would imply simple Arrhenius behavior in the logarithmic conductivity-temperature plot, as well as a strong dependency on stoichiometry. A second mechanism, which has been used to explain transport and relaxation processes in fused salts, polymers, and other glass-forming materials,

involves local, liquid-like motions of the solvent (polyether) with the ions moving in an amorphous, locally disordered (liquid) environment (127).

Strong ion pairing may effectively trap the mobile cations, significantly reducing the observed ionic conductivity relative to non-ion paired complexes of similar structure (127).

As pointed out earlier, regardless of whether the overall diffusion process is described in terms of electron hopping through the polymer film from reduced to the neutral sites or in terms of true diffusion, migration of ions must occur if electroneutrality in the film is to be maintained upon electrochemical perturbations. This process may therefore require fast motions, if larger charge transport is operative (128).

In the blend films with PEG as a host, the polymer matrix can possibly extract the electrolyte ions and their accompanying solvent molecules from the contacting solution. This process will preconcentrate the electrolyte ions in the polymer matrix. The permeation of counterions and solvent molecules are therefore less likely to limit the charge transport process in the PEG blends than in the BOEB blends under the above conditions. This model provides a simple explanation for the lack of a break-in in the CV of virgin TCNQ-PEG polymer films. Furthermore, the larger size of the tetraalkylammonium cation and the good solvating ability of acetonitrile may induce a more amorphous polymer matrix and provide a low resistance to ionic motions that result from the electrochemical perturbations.

Cyclic voltammetric and chronocoulometric studies of TCNQ-PE/-PEG blend film electrodes in acetonitrile/0.5 M LiClO₄. A cyclic voltammogram of TCNQ-PE/PEG blend film electrode (50% TCNQ-PE, $\Gamma = 7.69 \times 10^{-9}$ mole/cm²) is shown in Figure 32A. This voltammogram was recorded at a scan rate of 20 mV/sec and features two waves with $E_{\frac{1}{2}}^{0/-} = 0.0$ V and $E_{\frac{1}{2}}^{-/2-} = -0.30$ V vs. Ag/AgCl. In this voltammogram, the waves due to the A/A_2^- and A_2^-/A^- couple are merged into a single broad ($\Delta E_{\frac{1}{2}} = 187$ mV), symmetrical surface wave ($\Delta E_{pp} \approx 0.0$). The position of $E_{\frac{1}{2}}$ corresponding to the A/A^- couples is approximately the same as that discussed earlier for the acetonitrile/TEAP system (see Fig. 28A, p. 116), but the second wave takes place at a potential 86 mV more positive. This observation may reflect stronger ion-association of the TCNQ dianion with Li⁺ as compared to the tetra-ethylammonium cation. Also note that the second wave has a slightly larger peak to peak separation ($\Delta E_{pp} = 24$ mV) compared to the CV recorded for the TEAP system at the same scan rate ($\Delta E_{pp} = 18$ mV). However, although the peak separation for Li⁺ electrolytes is larger at 20 mV/sec, the value of ΔE_{pp} is not as strongly dependent on the scan rate as for the TEAP system. Figure 32B shows the voltammogram of the blend in Li⁺/acetonitrile that was recorded at 50 mV/sec and the magnitude of ΔE_{pp} was measured to be 27 mV compared to 50 mV seen for TEAP/acetonitrile system.

For comparison purposes, the voltammetric behavior of TCNQ-PE film electrode was studied under similar conditions. An attempt was made to prepare a TCNQ-PE film electrode containing a comparable

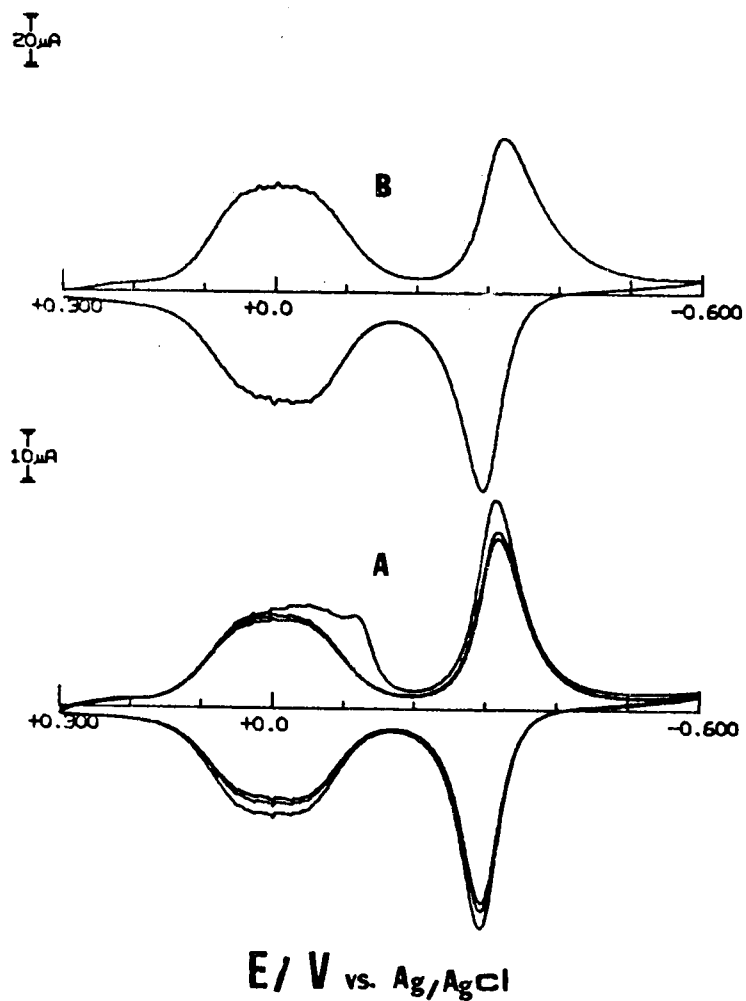


Figure 32. Cyclic voltammograms of TCNQ-PE/PEG (50% TCNQ-PE) blend film electrode in contact with acetonitrile/0.5 M $LiClO_4$. $\Gamma = 7.69$ nmole/cm²; sweep rates (A-B), 20 and 50 mV/sec.

amount of TCNQ sites as that of the blend film. The corresponding voltammogram which is shown in Figure 33A ($\Gamma = 7.89 \times 10^{-9}$ mole/cm²) features two waves that are qualitatively similar to those observed for the blend film ($E_{\frac{1}{2}}^{0/-} \approx 0.0$ V, $E_{\frac{1}{2}}^{-/2-} = -0.322$ V vs. Ag/AgCl). The voltammetric parameters are compiled in Table VIII.

At the conclusion of the scan rate studies performed on TCNQ-PE film electrode, the electrode was removed from the LiClO₄ solution and shaken to remove the solvent/electrolyte. The electrode was then immersed into a fresh solution of acetonitrile/0.1 M TEAP and the voltammogram was recorded at 20 mV/sec; see Figure 33. Interestingly, the typical behavior expected in acetonitrile/TEAP is evident in this CV for the behavior corresponding to A/A_2^- and A_2^-/A^- couples. This voltammogram was obtained on the initial cycle with no break-in process observed. The implication of this experiment is that upon reoxidation total ejection of the Li⁺ cations occurs. The shorter life time of the mixed valence species in the presence of LiClO₄/acetonitrile may also be responsible for the absence of the split waves in the region of first reduction wave. Chronocoulometric results further supported this interpretation. Although the voltammogram in Figure 33A has qualitatively the same shape as that of terpolymer discussed earlier, the scan rate dependencies are markedly different.

Chronocoulometry. In order to determine the magnitude of $nD^{\frac{1}{2}}c$ for charge transport in the presence and absence of PEG as a host polymer, potential step chronocoulometry was performed. The corresponding data are shown in Table IX. Interestingly, when allowance

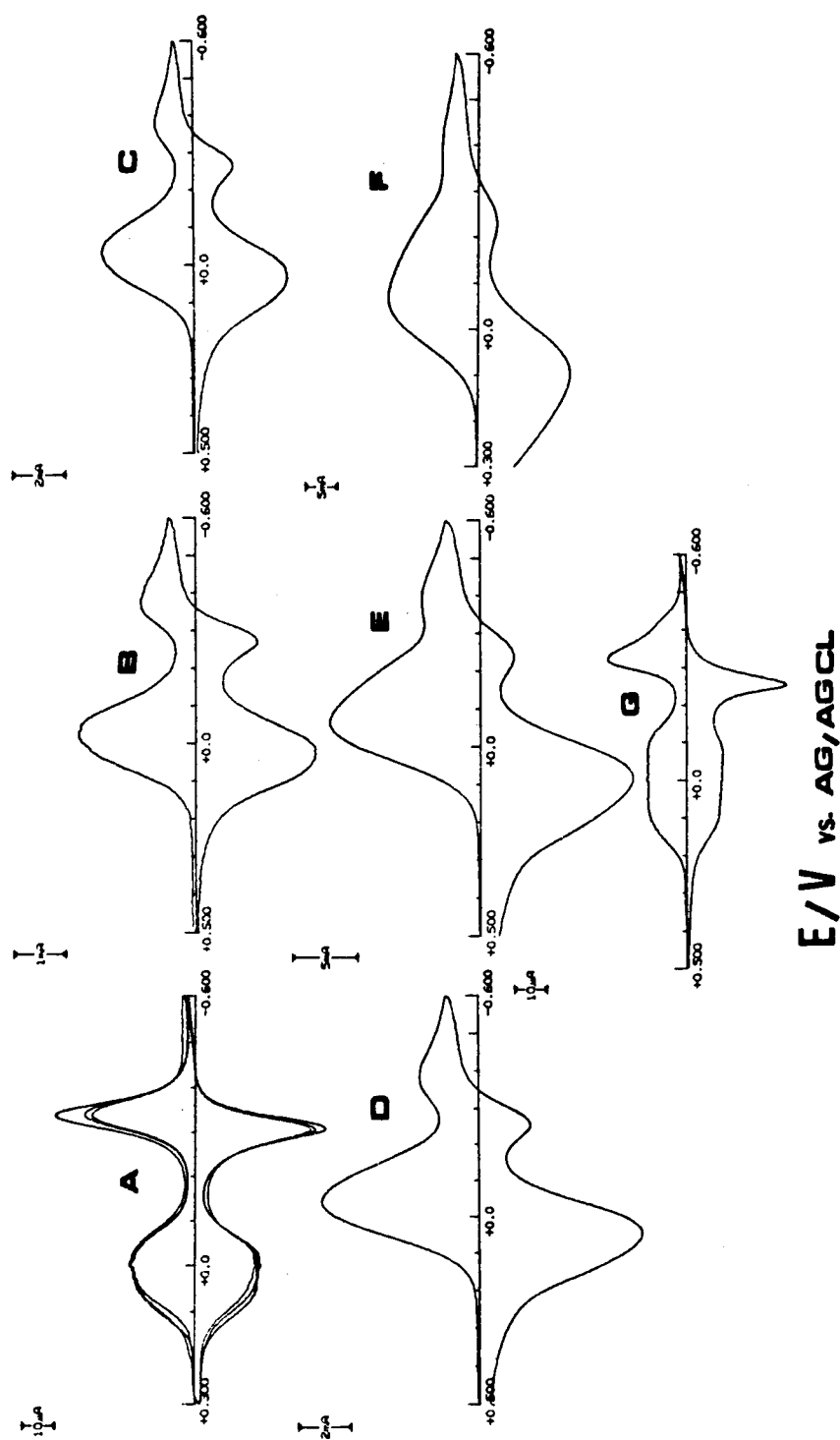


Figure 33. Cyclic voltammograms of Day's TCNO-PE in contact with $\text{CH}_3\text{CN}/0.5 \text{ M LiClO}_4$; $\Gamma = 7.89 \text{ nmole/cm}^2$, sweep rate (A-G): 0.02, 3.0, 5, 10, 25.6, and 34.1 V/sec. G. Transferred to acetonitrile/0.1 M TEAP; scan rate; 20 mV/sec.

Table VIII. Effect of scan rate on voltammograms of TCNQ-PE, $\Gamma = 7.89 \text{ nmole/cm}^2$, in contact with acetonitrile/0.5 M LiClO_4 .

$v/\text{V sec}^{-1}$	A/A^-	A^-/A^{2-}
	$\Delta E_{pp^*}/\text{mV}$	$\Delta E_{pp}/\text{mV}$
0.02	20	25
0.050	25	26
3.0	37	102
		(diffusional)
5.0	60	105
15.7	110	133
25.6	144	highly diffusional

*Anodic, cathodic peak separation.

Table IX. Chronocoulometric Cottrell function data for TCNQ polyester and TCNQ-PE/PEG blend films in contact with $\text{CH}_3\text{CN}/0.5 \text{ M } \underline{\text{LiClO}_4}$.

System	$\Gamma/\text{n mole}/\text{cm}^2$	$(10^8 n D^{\frac{1}{2}} c)_{\text{cath}} \text{ mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$	$(10^8 n D^{\frac{1}{2}} c)_{\text{anod}} \text{ mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$
TCNQ-PE/PEG Blend (50% TCNQ-PE)	7.7	3.63 ± 0.007	5.1 ± 0.21
TCNQ-PE	7.89	3.44 ± 0.21	8.24 ± 2.8

is made for the surface coverage, $(nD^{\frac{1}{2}}c)^{\text{cathodic}}$ for the blend is approximately the same as that measured for the undoped film, despite the 50% effective dilution caused by inclusion of PEG in the film.

Several possibilities can be envisioned which may account for the above observations. The binding of alkali metal cations with PEG was studied by means of conductometry in methanol. Apparent binding constants, K_A , were determined by assuming the existence of discrete binding sites distributed every a monomer units along the polymer chain. The value of K_A increased in the order $\text{Li} < \text{Na} < \text{K} < \text{Cs} < \text{Rb}$ (129).

For large anions, such as thiocyanate or perchlorate, the formation of an ion pair complex was indicated. K_A and α increased rapidly with decreasing salt concentration. This result was interpreted to be due to an increase in electrostatic repulsion between the bound ions (129).

These observations suggest that electrostatic interactions between ions which can form a complex with the different sites on the polymer chain can affect ionic mobility in the polymer matrix.

It should also be pointed out that cation solvation also plays an important role, especially for lithium and sodium ions. The low binding constant for these ions has been rationalized as being due to strong solvation of solvent molecules (methanol) which in turn makes it difficult to interact with PEG. Under these conditions, Li^+ ions are expected to be more mobile in the polymer composite matrix.

The above results indicate that the value of $nD^{\frac{1}{2}}c$ is no longer a function of the redox site concentration as we expected. In the case

of $\text{Fe}(\text{CN})_6^{3-}$ coordinately attached to PVF films (62), it was also found that D_{ct} values were relatively insensitive to changes in concentration of the complex until this concentration dropped below about 1% of the total available coordinating sites. Below this level, an abrupt drop in D_{ct} was observed.

Martin et al. have reported that the diffusion coefficients in the presence of the large ions (H^+ and p-toluene sulfonate) were the same as those in the presence of smaller ions (K^+ and SO_4^{2-}). This observation, over the range of ion sizes studied by Martin and co-workers (128), implies that in an ion-exchange membrane, motion of the counterions or co-ions does not affect the rate of the overall process. Since electrochemical activity observed does not include contribution due to gross ionic motion, faster rates of charge transport is likely to be measured. In the case of dilution with BOEB-PE, however, the ion transport, as discussed earlier, was seriously retarded and was responsible for the type of electrochemical observations made.

Finally, the enhancement of charge transport rate was significantly larger for TCNQ-PEG blend film in acetonitrile/TEAP solution than that observed in acetonitrile/ LiClO_4 . As pointed out earlier an amorphous structure is thought to be less resistant to ionic mobility than a crystalline structure. The opposite is true for electronic conduction. Salts of Li^+ ions complexed to PEG, have been known to have a more crystalline structure than the bulkier cations, such as TEAP, which may induce a more amorphous polymer matrix.

Electrochemical Studies of TCNQ-PE/PEG Blend Films
on Platinum in Water/Alkali Metal Salts

Introduction

In order to gain more insight into the role of PEG in the "overall" observed electrochemical behavior, it was decided to extend the above studies to aqueous solutions of alkali metal ion electrolytes and non-buffered systems. The rationale for such studies is briefly discussed here. As pointed out by Inzelt et al. (74), the stability of the reduced TCNQ films can be related to interactions with counterions. Earlier studies have revealed that TCNQ-PE films exhibit identical behavior in solutions containing monovalent alkali metal ions, showing only a slight shift in the negative direction for the sequence Li^+ to Rb^+ . No anion dependence was found using chloride and perchlorate salts (74). Another interesting observation has been the solvent effect on the electrochemistry of TCNQ-PE films in aqueous, nonbuffered systems. In the case of TCNQ polyesters studied in our laboratory, solvent has been shown to have a significant role in the overall electrochemical behavior, particularly on the stability of the film in the -2 oxidation state, where protonation of the TCNQ^{2-} groups was suggested to occur in aqueous solutions of alkali electrolytes (27). When the potential sweep was extended into the region of the second wave, in the absence of buffered aqueous media, the film was seen to dissolve as evidenced by the irreversible $\text{TCNQ}^{-/2-}$ wave. The greatly diminished $\text{TCNQ}^{0/-}$ wave on subsequent cycles was accompanied by the appearance of the characteristic color of TCNQ and $\text{TCNQ}^{\cdot-}$ in

solution. This phenomenon was ascribed to the hydrolysis of the ester linkages in the TCNQ polyester by the hydroxide ions formed by hydrolysis of the reduced acceptor sites (85).

In view of the above observations, the behavior of TCNQ-PE films doped with PEG on Pt and in H_2O /alkali metal ions was found to be very interesting. The films containing PEG as a host polymer in the "-2" oxidation state were significantly more stable than the undoped films, but the cyclic voltammograms underwent subtle changes in wave shape upon repeated cycling. The effects of film composition and delay time between cycles in multisweep voltammograms were also studied.

Another motivation for the experiments presented in this section was the well studied affinity of PEGs for various alkali metal ions. The "solution-phase" ion-polymer interactions between PEG's and alkali metal ions (in glycerol) were studied by electrohydrodynamic ionization mass spectrometry (123). This technique was reported to be capable of resolving metal complexes of different oligomers with degree of polymerization (n) as low as 4. According to Chan and co-workers, mass spectral intensities of these complex ions supported the prediction of multi-ion association by larger oligomers. Furthermore, the minimum n required for this multiple-ion association correlated positively with the size of the metal ion. Preferential complexation by PEG oligomers for one metal over another was also observed. From the total spectral intensities of each metal complex, bulk selectivity of PEG for alkali metal ions was found to follow the order $K^+ > Cs^+ > Rb^+ > Na^+ > Li^+$. These

findings by Chan et al. generally agreed with studies by other methods. Ono et al. (129) observed maximum binding for the rubidium ion and the binding strengths for potassium and cesium were found to be comparable for PEG complexes. The relatively strong interaction of large cations with PEG was related to the possible flexibility in the structure of the PEG chain which enables the chain conformation to change with the ionic diameter of the cation. It was also pointed out that solvation to cations plays an important role specially for lithium and sodium ions. The low binding constants for these ions were, in part, explained by the strong solvation effects which in turn makes it difficult to interact with PEG (methanol was used as solvent by Ono et al.).

Results and Discussion

Cyclic voltammetric and chronocoulometric studies of TCNQ-PE films with PEG as a host polymer on platinum in contact with water/0.5 M LiClO_4 . In Figure 34A is shown a cyclic voltammogram of Day's TCNQ polyester (24, 26) in contact with a 0.5 M $\text{LiClO}_4/\text{H}_2\text{O}$ solution. Both EE processes are seen on the first reductive cycle. However, when the direction of the potential scan is reversed at -0.6 V vs. Ag/AgCl, the film was seen to dissolve as evidenced by the irreversible $\text{TCNQ}^{-1/2-}$ wave. It was also noticed that the $\text{TCNQ}^{0/-}$ wave diminished on subsequent cycles and the characteristic color of TCNO and TCNQ^- appeared in solution. This phenomenon, as pointed out earlier, was observed and reported from our laboratory (99) and has

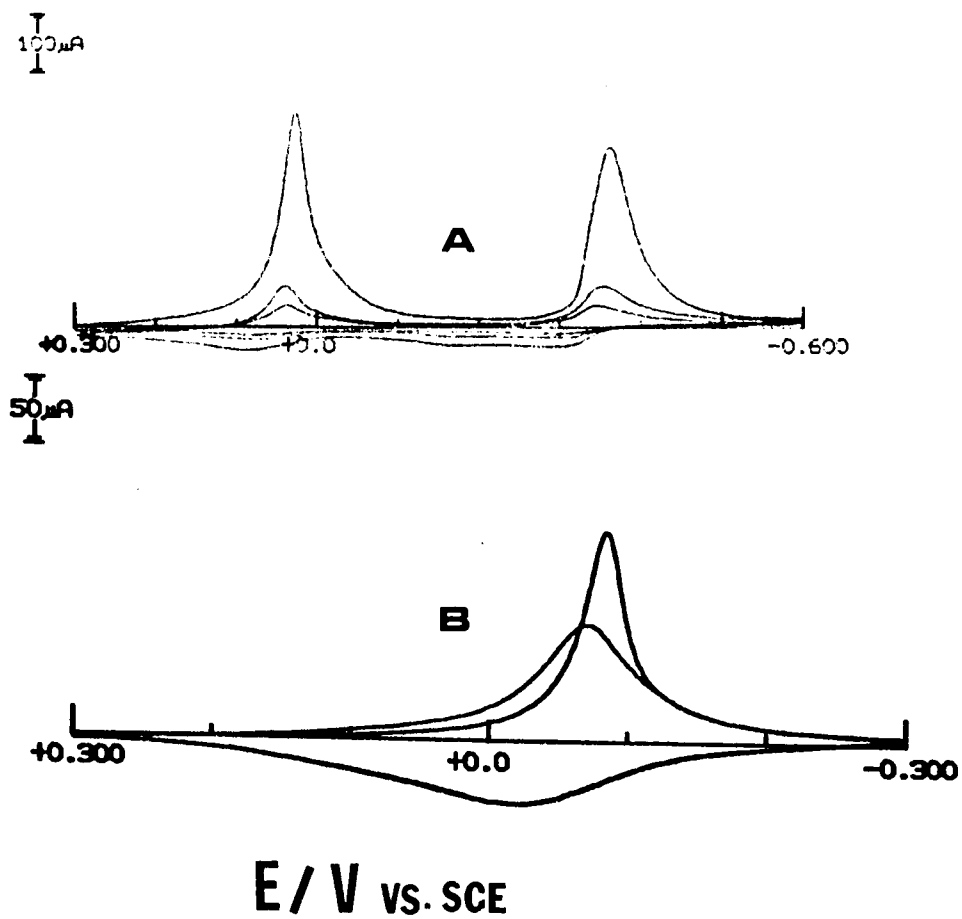


Figure 34. Cyclic voltammogram of Day's TCNQ-PE in contact with water/0.5 M LiClO_4 . Scan rate = 20 mV/sec.

been ascribed to hydrolysis of the ester linkages in the TCNQ polyester by the $\bar{\text{O}}\text{H}$ ions formed by hydrolysis of the reduced acceptor sites in the absence of buffer species. When the potential excursions were maintained within the limits of Fig. 34B, however, the TCNQ polymer film retained its full electrochemical activity over many potential cycles. The CVs had features similar to those observed by Day et al. (85). Initial scans in the negative direction resulted in a narrow cathodic peak (peak width ca. 36 mV), which was replaced by a broader peak (width 80 mV) on subsequent cycles, see Figure 34B. Holding the potential at +0.3 V for 3-5 min. restored the film to the original state.

Spectroelectrochemical (74) and simultaneous electrochemical/ESR (73) experiments were performed in order to explain the voltammogram shown in Figure 34B, which is more or less similar to those observed for alkali metal salts (74). These studies revealed that the voltammetric response includes contributions from overlapping Faradaic processes that lead to the formation of a mixture of TCNQ radical anion and dimer dianion sites in the reduced films. Little cathodic current is observed in the CVs in the potential region where the mixed valence species is stable (reaction 23, p. 71). The current becomes appreciable at potentials negative enough to reduce acceptor sites to the radical anion state. The $\text{TCNQ}^{\cdot -}$ sites then undergo dimerization. It was found that the absorbances of the dimer and the radical anion increase simultaneously, indicating that the equilibrium of equation is established on the time scale of the spectroelectrochemical

measurements (74). At the switching potential therefore, the film is fully reduced, oxidation of the dimer dianion leads to the formation of $\text{TCNQ}_2^{\cdot-}$ sites in a fast reaction. At more positive potentials $\text{TCNQ}^{\cdot-}$ and $\text{TCNQ}_2^{\cdot-}$ sites are oxidized. The rather broad feature of the anodic wave reflects the separation of the dimer dianion and the radical anion oxidation (Fig. 34B). These conclusions were also supported by the SEESR experiments (73).

On the second and subsequent cycles, a positive displacement and broadening of the reduction wave is evident. This behavior is considered to be consistent with the formation of a mixture of radical anion and dimer dianion sites in the reduced film (74). The observed peak widths are intermediate between theoretical values for a reversible dimerization process (47 mV) and a simple reversible one-electron wave (91 mV) (130).

There are several possible explanations for this difference between the first and second cycles for a "broken-in" film. The uptake of electrolyte in the cathodic film charging process could lead to decreased film resistance and a change in the polymer morphology that facilitates the charge transport process. Upon completion of a cathodic/anodic cycle, supporting electrolyte is incorporated in the films as indicated by secondary ion mass spectroscopy of virgin and cycled electrodes (131). This "presumably" occurs by migration of ions, both cations and anions, out of and into the film in order to maintain charge neutrality upon oxidation of the reduced film (74). Since the cations are implicated in the film reduction process by the electrolyte effects, the decreased overpotential on the second cycle,

relative to the first cycle, can be understood on the basis of the increased cation concentration in the film on the second cycle and related ion association effects (74).

In view of the above discussion, electrochemical results obtained, under similar conditions, when films were prepared from blends of PEG with TCNQ-PE are interesting (see Fig. 35).

A film of TCNQ-PE/PEG blend (25% TCNQ-PE) containing $\Gamma = 1.39 \times 10^{-8}$ mole/cm² electroactive redox sites in 0.5 M LiClO₄/water exhibits both EE processes on the initial potential scan. Both waves are at potentials characteristic of reduction and re-oxidation of TCNQ sites in the polymer film ($A/A^{\cdot-} E_{1/2} = -0.003$, $A^{\cdot-}/A^{2-} E_{1/2} = -0.333$ V vs SCE). A feature of this voltammogram, however, which contrasts to the behavior of the pure TCNQ-PE films, is the behavior of the film on the reverse cycle. Effectively, no film dissolution was observed upon repeated cycling in the potential region that encompassed both EE processes. Furthermore, the general appearance of the voltammograms recorded over repeated cycling undergoes some changes in the wave-shape. Whereas the first wave reached a steady-state behavior on the first cycle, the second wave was severely affected when repetitive potential scans were made. In the case of first wave (Fig. 35A), an initial scan in the negative direction resulted in a narrow cathodic peak (peak width ca 72 mV), which was replaced by a broader peak (width 103 mV) on subsequent cycles. There was also a slight decrease in the magnitude of the charge corresponding to both cathodic and anodic processes. Steady state voltammograms were recorded

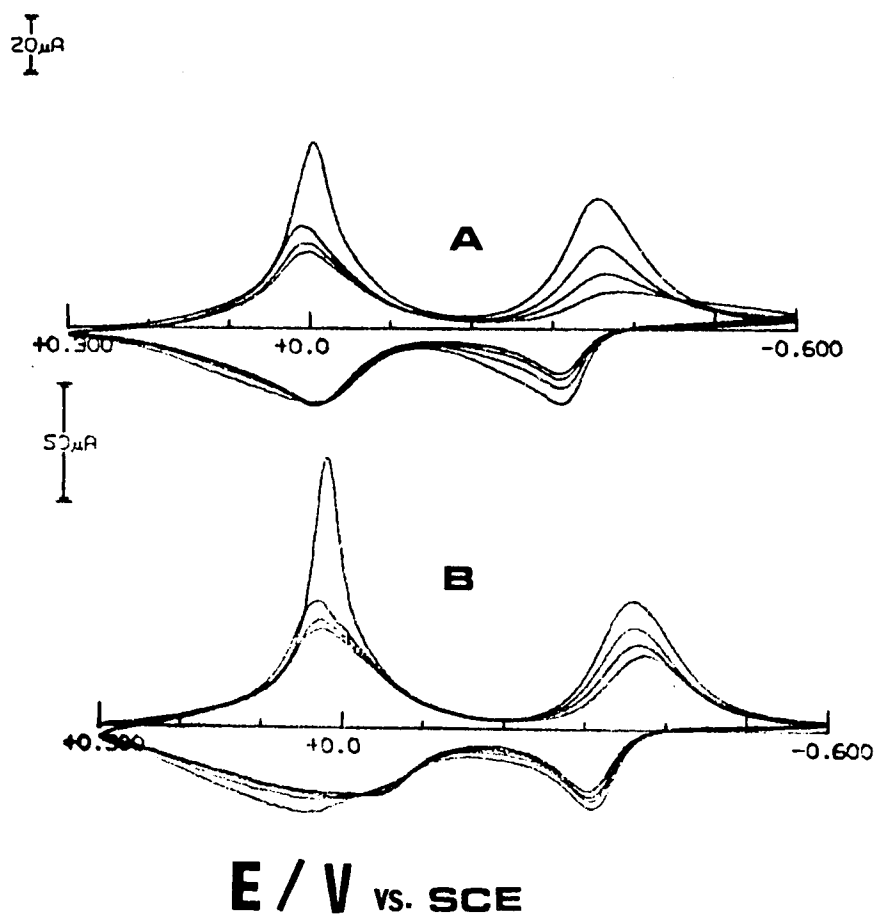


Figure 35. Cyclic voltammogram of TCNQ-PE/PEG blend film electrode in contact with water/0.5 M LiClO_4 . Scan rate = 20 mV/sec. (A) 25% TCNQ-PE, (B) 50% TCNQ-PE.

after a few cycles only for the first wave. Upon repeated cycling, the second wave assumed a more diffusional character which transformed into a featureless voltammogram when the potential scan was continued without interruption. Qualitatively, the electrochemical activity of the second wave could be restored by allowing a longer relaxation time before subsequent voltammograms were recorded, indicating that the above process was reversible. The CVs have several features that indicate slow potential dependent changes in the film structure and/or uptake of electrolyte without complete ejection of electrolyte upon oxidation. In addition, upon repeated cyclings, isopotential points (or prewaves) developed in the cyclic voltammograms as seen ($E_{iso}^o = -0.023$ V vs. SCE) in Figures 35A-B. The position of this isopotential point was seen to be at a more negative potentials and more pronounced when films of higher concentration and surface coverage (50% TCNQ-PE, $\Gamma = 2.40 \times 10^{-8}$ mole/cm²) were studied under similar conditions; see Figure 35B.

In order to study further the effect of PEG on the charge transport process, chronocoulometric experiments were carried out on the TCNQ-PE/PEG blend films. In order to compare the magnitude of $nD^{\frac{1}{2}}C$, measured for blends, with those of the corresponding values for the pure films, it was decided to first study the CC behavior of TCNQ-PE films in the same solvent/electrolyte system.

The derived Cottrell slopes were determined for a range of surface coverages, simply because $nD^{\frac{1}{2}}C$ values were found to be dependent on Γ . These data, which are compiled in Table X, are consistent

Table X. Chronocoulometric Cottrell function data for TCNQ-PE and TCNQ-PE/PEG blend films in contact with $\text{H}_2\text{O}/0.5 \text{ M } \underline{\text{LiClO}}_4$ and $0.5 \text{ M } \underline{\text{LiCl}}$.

System	Electrolyte	$\Gamma/\text{n mole}/\text{cm}^2$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})^{\text{cath}}$ $\text{mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})^{\text{anod}}$ $\text{mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$
TCNQ-PE	LiClO_4	21.8	7.32 (3) ^a	8.61 (3)
TCNQ-PE	LiClO_4	9.71	4.19 (3)	--
TCNQ-PE	LiClO_4	9.35	4.47 (3)	--
TCNQ-PE	LiClO_4	7.69	3.63 (2)	5.10 (2)
TCNQ-PE	LiCl	27.1	9.06 (3)	11.6 (2)
TCNQ-PE	LiCl	19	6.99	9.09
TCNQ-PE/PEG (50% TCNQ-PE)	LiClO_4	8.17	1.19	1.27

^aNumber of determinations given in parentheses.

with earlier findings with respect to the magnitude of $nD^{\frac{1}{2}}C$ values corresponding to the anodic vs. cathodic process. The anodic data were collected for films which were initially in the reduced state (more conductive state) and oxidation was accomplished by stepping the potential to +0.3 V, where the film was transformed to its neutral form.

The $nD^{\frac{1}{2}}C$ values calculated for a TCNQ-PE/PEG blend (nominal concentration of 50% TCNQ-PE), with $\Gamma = 8.17 \times 10^{-9}$ mole/cm², were 1.19×10^{-8} and 1.27×10^{-8} for the cathodic and anodic waves respectively. This observation (i.e., the relative magnitude of $nD^{\frac{1}{2}}C$ measured for the cathodic and anodic processes) is in contrast with what was obtained for the TCNQ-PE films, where the anodic Cottrell slopes were approximately twice the cathodic slopes. The $nD^{\frac{1}{2}}C$ values were almost equal for both the cathodic and anodic processes. It should be pointed out that the effective concentration of the redox sites was 50% lower in the blend film.

Lithium ions demonstrated the largest $nD^{\frac{1}{2}}C$ for the TCNQ-PE/PEG films as compared to other alkali ions and the order was $\text{Li}^+ > \text{Na}^+ > \text{K}^+ \approx \text{Rb}^+$ (Table XI). In all of the above cases, the magnitude of $nD^{\frac{1}{2}}C$ showed some dependence on the electrode surface coverage and this was taken into consideration in the above comparisons. The rate of ionic migration through a polymer matrix in this case seems to be related to the size of the diffusing ion. The results imply that the rate is controlled by ionic migration and the value of $nD^{\frac{1}{2}}C$ obtained in the presence of larger ions is smaller than those obtained in the

Table XI. Chronocoulometric Cottrell function data for TCNQ-PE in water/alkali metal salts.

System	Electrolyte	$\Gamma/\text{nmole}/\text{cm}^2$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})^{\text{cath}}$ $\text{mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})^{\text{anod}}$ $\text{mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$
TCNQ-PE	LiCl (0.5 M)	27.1	9.06	11.6
TCNQ-PE	LiClO ₄ (0.5 M)	21.8	7.32	8.61
TCNQ-PE	NaClO ₄ (0.1 M)	13.7	3.66	--
TCNQ-PE	NaClO ₄ (0.1 M)	27.2	4.4	8.92
TCNQ-PE	KCl (0.5 M)	13.7	2.0	6.08
TCNQ-PE	RbCl (0.1 M)	11.0	2.0	--

presence of smaller ions. The results also imply that although the effective size of Li^+ in water is the largest ($\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$), upon permeation into the polymer matrix, especially to the redox sites in the TCNQ-PE domain, the solvents may have to be stripped off. The smaller size of naked or partially solvated Li^+ and its higher affinity for the redox sites may, in part, explain the above observations.

The above results also imply that the ionic conductivity of the TCNQ-PE/PEG blend is the same in both oxidation states. Since this is not true for TCNQ-PE film electrodes, PEG seems to improve the film swelling in the sense described by Schroeder and Kaufman (34).

One way to explain the improvement in the stability of the film in the -2 oxidation state is to consider the effective dilution that is caused by doping the TCNQ-PE solution with PEG solution prior to film casting. Actually, this interpretation is consistent with the kind of reasoning that was given for film dissolution, i.e., the generation of high local concentrations of hydroxide ion due to hydrolysis of A^{2-} . The blend films studied here were doped with significant amount of PEG that effectively diluted the redox site concentration in the polymer matrix, thereby decreasing accumulation of high levels of $\overline{\text{OH}}$ in the film. Since the events that lead to hydrolysis take place predominantly in a polymer matrix, it is also reasonable to consider the possible effects cations may have on the ester hydrolysis. Stronger association of the cations with PEG may decrease the rate of hydrolysis of the ester in the polymer film.

The electrochemical behavior and electron spin resonance of thin films of TCNQ-PE in aqueous buffers have been studied earlier and reported from this laboratory. The results indicated that the coupling of electron and proton transfer steps in the classical 3×3 square scheme, which also describes quinone electrochemistry, can significantly influence the charge-transport rate through the film, limiting the electroactivity to a fraction of the available electron-transfer sites and decreasing the effective diffusion coefficient for charge transport through the polymer film by 100-fold for specific conditions. The acid-base chemistry of the reduced acceptor sites in the film matrix was cited to account for the pH dependence of the voltammetric waves, the film passivation in acidic solutions, and the film dissolution at negative potentials in simple salt electrolytes. It is not unreasonable to think that A^{2-} hydrolysis over repeated cycling can partly account for the above observations. The effect of repeated cycling was particularly severe for the second wave, similar to that seen for TCNQ-PE in buffered systems (45).

It was found that the appearance of the prewave on the oxidative cycle (Fig. 35B) was dependent on the potential range used during the experiment. When the direction of the potential scanning was reversed before reaching the region of the second wave, the prewave disappeared and no more film passivation could be observed. The dianion A^{2-} has been known to react with oxygen. The possibility that the prewave may be due to the oxidation of oxygen decay products can not be ruled out (74). But the prewave on the oxidative cycle is more

likely due to the oxidation of TCNOH^- formed from TCNQ^{-2} at negative potentials.

Electrochemical behavior of TCNQ-PE/PEG blend films on Pt in contact 0.1 M NaClO_4 , 0.01 M $\text{NaCl}/\text{H}_2\text{O}$. A cyclic voltammogram of virgin TCNQ polyester film on Pt ($\Gamma = 2.7 \times 10^{-8}$ mole/cm²) and in contact with a 0.1 M NaClO_4 , 0.01 M $\text{NaCl}/\text{H}_2\text{O}$ solution is shown in Figure 36A. The potential scan was switched at a potential where the formation of the dianion (A^{2-}) was avoided. Current corresponding to the foot of the second wave, however, is seen in the voltammogram. This behavior is similar to that discussed for the 0.5 M $\text{LiClO}_4/\text{H}_2\text{O}$ system. An initial scan in the negative direction resulted in a narrow cathodic peak ($\Delta E_{\text{P}/2} \approx 71.4$, $E_{\text{P}}^{\text{S}} = -0.059$ V vs. SCE), which was replaced by a broader peak ($\Delta E_{\text{P}/2} = 114$ mV) on subsequent cycles, see Figure 36A. When the potential scan was extended into the region where A^{2-} was formed, the film dissolved.

When a similar study was performed with TCNQ-PE films that were doped with PEG on Pt, markedly different behavior was observed compared to the undoped films (Fig. 36B). Although there is a slight decrease in the magnitude of the peak currents, steady-state voltammograms can be recorded after several cycle. Several features of this voltammogram (Fig. 36B) are interesting. The pattern of film stability is distinctly different from the undoped film under similar conditions (no immediate dissolution was seen when the potential range studied included A^{2-} species). The first scan in the negative direction resulted in a narrow cathodic peak (69 mV peak width at half

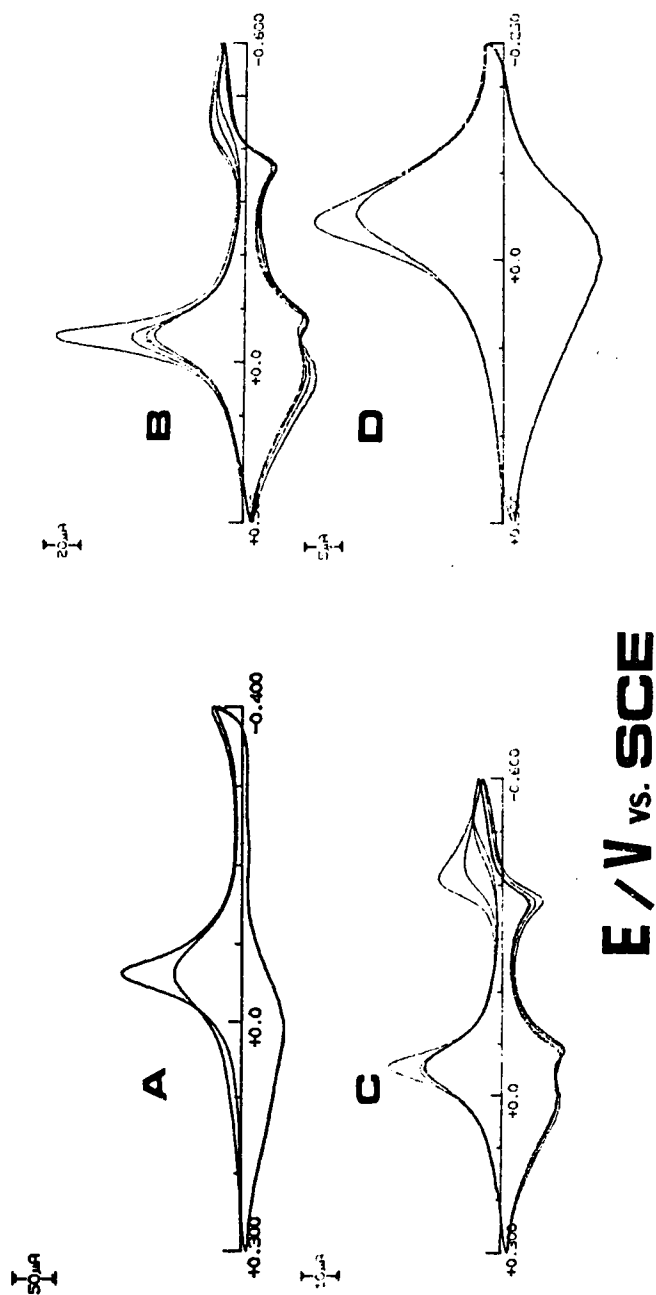
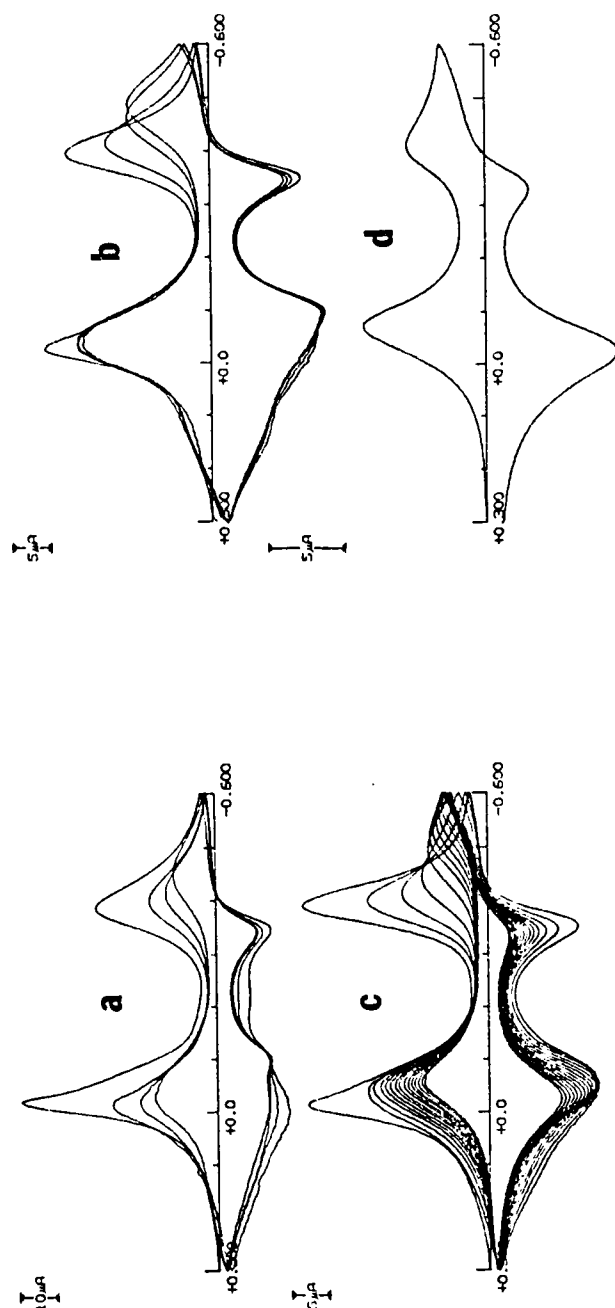


Figure 36. Cyclic voltammograms of (A) TCNQ-PE, $v = 20$ mV/sec, (B-D) TCNQ-PE/PEG (50% TCNQ-PE). Scan rates: 20, 10 and 20 mV/sec; in contact with $\text{H}_2\text{O}/0.1 \text{ M } \text{NaClO}_4$.

maxima, $E_p^S = -0.054$), which became broader ($\Delta E_{p/2} = 103$ mV) over repeated cyclings. The electrochemical activity corresponding to the second wave is highly suppressed. The qualitative features of the second wave were a function of the scan rate (see Fig. 36B). At lower scan rates the first voltammogram recorded is rather well-developed. Also there are signs of isopotential points developing over repeated cyclings, which disappear when the potential scanning is reversed prior to the formation of the A^{2-} species (see Fig. 36D). Figs. 36C and 36D correspond to the same film. When the potential excursion was maintained within the limits of Fig. 36D, $\Gamma = 1.38 \times 10^{-8}$ mole/cm², the isopotential points and the developing prewave both disappear and the total electroactivity of the film remained constant. Also note that the anodic wave, although still broad, is less so compared to the undoped film (Fig. 36A). An initial scan in the negative direction resulted in a narrower ($\Delta E_{p/2} \approx 88$ mV, $E_p^C = 0.059$ V vs. SCE) anodic wave compared to subsequent cycles ($\Delta E_{p/2} = 118$ mV).

As pointed out earlier, the behavior of second reduction step and the overall changes in the waveshape of the voltammograms over repeated cyclings showed a strong dependence on the scan rate at which the electrochemical process was being performed. On the initial scan at a scan rate of 10 mV/sec, the second wave is well defined compared to the corresponding behavior at larger scan rates. Figure 37A shows the CV of a virgin film of TCNQ-PE/PEG blend ($\Gamma = 2.6 \times 10^{-8}$ mole/cm²) on Pt and in contact with NaClO₄ in water. Note that both waves are seen in the voltammogram ($E_p^{0/-} = -0.018$ V, $E^{-1/2-} =$



E/V vs. SCE

Figure 37. Cyclic voltammograms of TCNQ-PE/PEG (50% TCNQ-PE) blend film electrode in contact with water/0.1 M NaClO_4 , 0.01 M NaCl . Scan rate: 10 mV/sec. (See the text for details on a-d.)

-0.38 V Ag/AgCl) on the first cycle. When the potential scan range included both $A/A^{\cdot-}$ and $A^{\cdot-}/A^{-2}$ couples, repeated cycling resulted in severe change in the wave shape of both EE processes (see Fig. 37a). Figures 37a-d were all recorded for the same film in the course of detailed electrochemical studies that were intended to test the behavior of the film over continuous cycling.

Isopotential points are distinctly evident on the anodic branch of the first wave in Fig. 37b. This CV was recorded after the film corresponding to Fig. 37a was allowed to remain in the neutral state for a few minutes. The magnitude of the current in the region of the pre-wave is much more pronounced on the anodic branch of the first wave (see Fig. 37b). Also note that the $E_p^{\cdot-}$ corresponding to the second wave shifts to more negative potentials, whereas the position of E_p^a remains more or less the same. When the film was allowed to cycle between oxidation states of "-1" and "-2" for 15 cycles with no interruptions ($v = 10$ mV/sec), the behavior seen in Figure 37c was observed. The CV shown in Fig. 37d was recorded at the conclusion of the experimental results shown in Fig. 37c, with approximately 50 minutes interruption.

Chronocoulometric experiments were carried out on the doped vs. undoped TCNQ-PE films to obtain more insight into the nature of charge transport in these films. The Cottrell slopes derived from the Anson plots of Q vs. $t^{\frac{1}{2}}$ are shown in Table XII for blend and TCNQ-PE films. In all regards the chronocoulometric and cyclic voltammetric results are again consistent. The dependence of the Cottrell slopes on

Table XII. Chronocoulometric Cottrell function data for TCNQ-PE and TCNQ-PE/PEG (50% TCNQ-PE) blend films in contact with water/0.1 M NaClO_4 , 0.01 M NaCl .

System	$\Gamma/\text{mole}/\text{cm}^2$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{c})_{\text{cath}}^{-2} \text{ s}^{-\frac{1}{2}}$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{c})_{\text{anod}}^{-2} \text{ s}^{-\frac{1}{2}}$
TCNQ-PE	2.72×10^{-8}	4.4 ± 0.420	8.92 ± 0.25
TCNQ-PE	1.37×10^{-8}	3.66 ± 0.140	--
TCNQ-PE/PEG ^a	1.46×10^{-8}	2.66	4.22 ± 0.2
TCNQ-PE/PEG	1.37×10^{-8}	--	4.73
TCNQ-PE/PEG ^b	4.89×10^{-9}	0.8 ± 0.02	0.7 ± 0.04

^a Figure 37B.

^b Corresponds to the voltammogram 37D.

the electrode loading, discussed earlier, is also evident from the results presented in Table XII. The value of $nD^{\frac{1}{2}}C$ measured for the blend is slightly smaller than the undoped film. If the ionic mobility is not the limiting factor, the decrease in TCNQ redox site concentration alone can account for this difference. Also the relative magnitude of $nD^{\frac{1}{2}}C$ for the cathodic vs. anodic process shows trends similar to those seen for the Li^+ electrolytes.

Electrochemical studies of TCNQ-PE/PEG blend film electrode on Pt in water/0.5 M KCl. A cyclic voltammogram of TCNQ-PE film in contact with a 0.5 M KCl/water solution is shown in Figure 38a. As long as the potential excursion was limited to the potential region shown in this figure, the film was stable and almost no electrochemical activity was lost, as judged from the appearance of steady-state i - E curves recorded upon many cycles. Again, as for other alkali salt solutions, the initial scan in the cathodic cycle resulted in a narrow peak ($\Delta E_{p/2} = 68 \text{ mV}$, $E_p^c = -0.071 \text{ V vs. Ag/AgCl}$), which was replaced by a broader peak ($\Delta E_{p/2} = 124 \text{ mV}$) on subsequent cycles (see Figure 38a). The anodic process is rather sluggish ($E_p^a = -0.026 \text{ V vs. Ag/AgCl}$) judged from the broad feature of the oxidative wave. In agreement with the results discussed earlier for other alkali ions, the film dissolved as evidenced by the irreversible $A^{-/2-}$ wave, when the potential excursion was extended into the region of the second wave.

Figure 38b shows the voltammogram recorded at scan rate of 20 mV/sec for a TCNQ-PE/PEG blend film electrode under the same

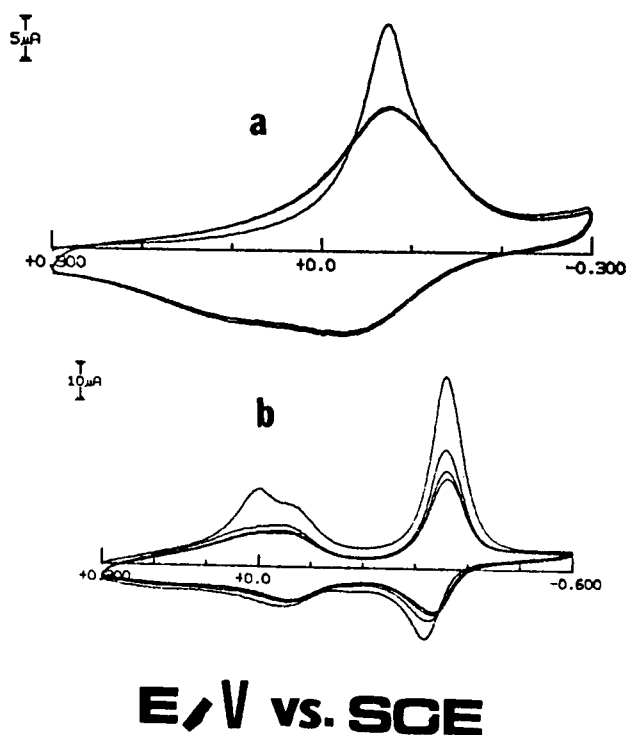


Figure 38. Cyclic voltammograms of (a) TCNQ-PE, (b) TCNQ-PE/PEG (50% TCNQ-PE) blend film electrode in contact with water/0.5 M KCl. Scan Rate = 10 mV/sec.

conditions as discussed for the undoped film. This CV features both waves ($E_{\frac{1}{2}}^{0/-} = -0.012$ V, $E_{\frac{1}{2}}^{-/2-} = -0.336$ V vs. SCE) and manifests a distinctly different behavior under continuous cycling compared to the undoped film and to the other alkali metal ion systems discussed earlier. The second wave retains its surface characteristics and when the film is subjected to repetitive cycling. There is, however, a decrease in peak current, i_p , corresponding to this wave (A^-/A^{2-}). The smaller magnitude of i_p^a may partly explain this drop over repeated cycling. Also note that, unlike the behavior discussed for doped films in $H_2O/NaClO_4$ system, the position of $E_{\frac{1}{2}}$ for the $A^{-/2-}$ wave remains almost the same over repeated cycling. Also $E_p^{0/-}$ shifts positive and there is an indication of mixed valence dimer formation.

Chronocoulometric Cottrell function data for both TCNQ-PE and TCNQ-PE/PEG blend (50% TCNQ-PE) in contact with water/0.5 M KCl is given in Table XIII. The Cottrell slopes are significantly small for the PEG blend than for the TCNQ-PE film in this case.

Electrochemical studies of TCNQ-PE/PEG blend films on platinum in water and other alkali metal salts. A CV of TCNQ-PE film adsorbed on platinum substrate in H_2O and 0.1 M RbCl is shown in Figure 39a ($E_p^C = -0.071$ V vs. SCE, $\Delta E_{p/2} = 57$ mV for A/A^- couple and $E_p^C = -0.410$, $\Delta E_{p/2} = 60.7$ mV for A^-/A^{2-} couple). The film instability in the "-2" oxidation state is similar to other alkali ions discussed before. When the potential sweep was switched at least 100 mV more positive of the $E_{\frac{1}{2}}$ corresponding to A^-/A^{2-} wave, the film showed exceptional stability over many cycles (Fig. 39b).

Table XIII. Chronocoulometric Cottrell function data for TCNQ-PE and TCNQ-PE/PEG blend (50% TCNQ-PE) in contact with water/0.5 M KCl (room temperature).

System	$\Gamma/\text{n mole/cm}^2$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})^{\frac{1}{2}}_{\text{cath}} \text{ mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})^{\frac{1}{2}}_{\text{anod}} \text{ mole} \cdot \text{cm}^{-2} \cdot \text{s}^{-\frac{1}{2}}$
TCNQ-PE	13.7	2.0 (2)	6.08 (2)
TCNQ-PE	6.09	1.92 (3)	7.7 (1)
TCNQ-PE/PEG (50% TCNQ-PE)	6.56	0.097 ± 0.004	--
TCNQ-PE/PEG (50% TCNQ-PE)	5.73	0.0733 ± 0.0075	--

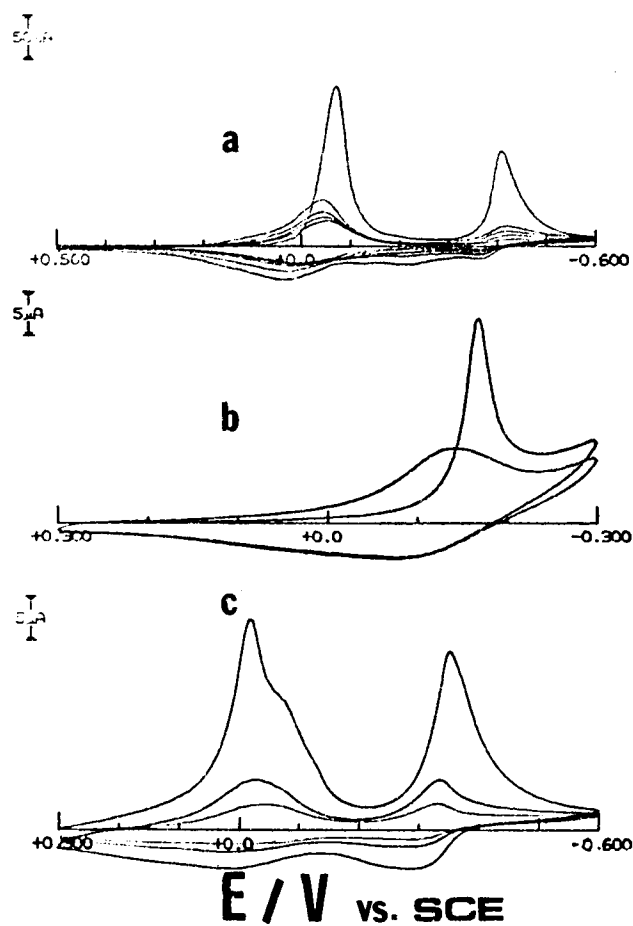


Figure 39. Cyclic voltammograms of (a-b) TCNQ-PE and (c) TCNQ-PE/PEG (50% TCNQ-PE) in contact with water/0.1 M RbCl. Scan rates = 20 mV/sec and 10 mV/sec, respectively.

The differences between the position of $E_{\frac{1}{2}}^C$ corresponding to $A/A^{\cdot-}$ couples in the two voltammograms (i.e., Fig. 39a-b) is thought to be related to the length of time the virgin film electrode is allowed to stay in contact with the solvent prior to initial potential application. The length of time the potential was kept at 100 mV more positive of the $E_{\frac{1}{2}}$ for $A/A^{\cdot-}$ also resulted in differences in the magnitude of overpotential seen in the first voltammogram of the virgin film. Also note that there is lack of symmetry in the two halves of the wave corresponding to $A/A^{\cdot-}$ couple (Fig. 39b), the trailing segment of the cathodic wave does not fall to the baseline ($\Delta E_{p/2} \cong 36$ mV, $E_p^C = -0.168$; $E_p^a = -0.141$ V vs. Ag/AgCl) and remains at a diffusional tail. The anodic process is rather sluggish as judged from the featureless anodic wave.

A CV of a TCNQ-PE/PEG blend (50% TCNQ-PE) film is shown in Figure 39c. In this case the film appeared to dissolve in the A^{2-} state as judged from the appearance of the characteristic color of TCNQ/TCNQ $^{\cdot-}$ in solution. This is in marked contrast to other alkali ions where the loss of electroactivity was thought to take place by passivation of the redox sites while they remained adsorbed on the electrode surface (this conclusion was supported by lack of any absorption, in the uv-vis region, of the solvent/electrolyte after passivation). Again it appears that the $A/A_2^{\cdot-}$ wave becomes kinetically facile in the presence of PEG. Significant cathodic current is observed in the CVs in the potential region where the mixed valence species is stable. Also note that the film "break-in" effects are not evident in the voltammogram shown in Figure 39c. The reason for the film dissolution is not clear at this point.

Chronocoulometric experiments were also carried out in $\text{H}_2\text{O}/0.1 \text{ M}$ RbCl . The Cottrell slopes derived from the Anson plots of Q vs. $t^{\frac{1}{2}}$ for blend and TCNQ-PE films are shown in Table XIV. Again, the chronocoulometric and cyclic voltammetric results of TCNQ-PE films are consistent. The dependence of the Cottrell slopes on the electrode loading, observed in all previous cases, is also evident (in the case of TCNQ-PE films) from the results presented in Table XIV. Also the relative magnitude of $nD^{\frac{1}{2}}c$ for the cathodic and anodic processes (corresponding to TCNQ-PE films) shows trends similar to those discussed earlier for other alkali metal ion solutions. Also note that the Cottrell slopes are significantly smaller for the PEG blend than for the TCNQ-PE film in this case. The possible formation of irregular cross-linking of the polyether backbone through interactions with large cations such as Rb^+ ions may induce a more compact structure. The lower affinity of the TCNQ-PE film for water can significantly reduce the ionic mobility in the polymer matrix.

In short, strong cation binding to the ethereal oxygens of PEG (128) and the resulting decreased ion mobility is suggested as the cause of the low charge transport rates for the PEG blends in contact with aqueous alkali metal electrolytes. Furthermore, in contact with water the degree of TCNQ_2^{2-} dimer formation is larger, which in turn may result in tighter and more compact films. Ionic mobility can be seriously affected under these conditions. The above observations can also be related to the polyelectrolyte nature of the polymer film matrix (135). The strong extracting power of PEG for larger alkaline ions,

Table XIV. Chronocoulometric Cottrell function data for TCNQ-PE and TCNQ-PE/PEG blend (50% TCNQ-PE) in contact with water/0.1 M RbCl.

System	$\Gamma/\text{n mole/cm}^2$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})_{\text{cath}} \text{ mole} \cdot \text{cm}^{-2} \text{ s}^{-\frac{1}{2}}$	$(10^8 \text{ nD}^{\frac{1}{2}} \text{ c})_{\text{anod}} \text{ mole} \cdot \text{cm}^{-2} \text{ s}^{-\frac{1}{2}}$
TCNQ-PE	1.44	1.70 ± 0.09	3.40 ± 0.44
TCNQ-PE	11.0	2.09 ± 0.13	--
TCNQ-PE/PEG Blend (50% TCNQ-PE)	6.0	0.238 ± 0.09	--

as indicated earlier, may preconcentrate the ions in the polymer film. With increasing concentration of the counterions the reduced film adopts a more compact structure and the diffusion of the counterions and/or the segmental motion of the polymer becomes hindered (135).

The voltammograms corresponding to a TCNQ-PE/PEG (50% TCNQ-PE) film electrode in contact with water/0.1 M CsCl are shown in Figure 40a-b. The voltammogram recorded for a virgin film manifested both waves on the initial cycle. The anodic process, as seen in Figure 40a, is very sluggish and the subsequent voltammograms showed signs of decrease in both reduction waves. When the potential was scanned repetitiously, however, a more or less steady-state behavior was obtained for both waves. The second wave became diffusional, upon repeated cycles, but never disappeared. The position of E_p^C for A/A^+ , unlike the behavior of undoped films shifts to slightly more negative values and the fraction of current in the anodic cycle, is also significantly larger in the region where mixed-valence species may be generated from the dimer dianion oxidation.

Cyclic Voltammetry of Terpolymer in H₂O
and 0.5 M LiClO₄

Figure 41A shows the cyclic voltammogram recorded at a scan rate of 20 mV/sec for a relatively thick virgin film of terpolymer on Pt electrode in contact with water and 0.5 M LiClO₄ solution. Although there are some residual currents on both cycles, the voltammogram has no features. A visual inspection of the electrode after its removal

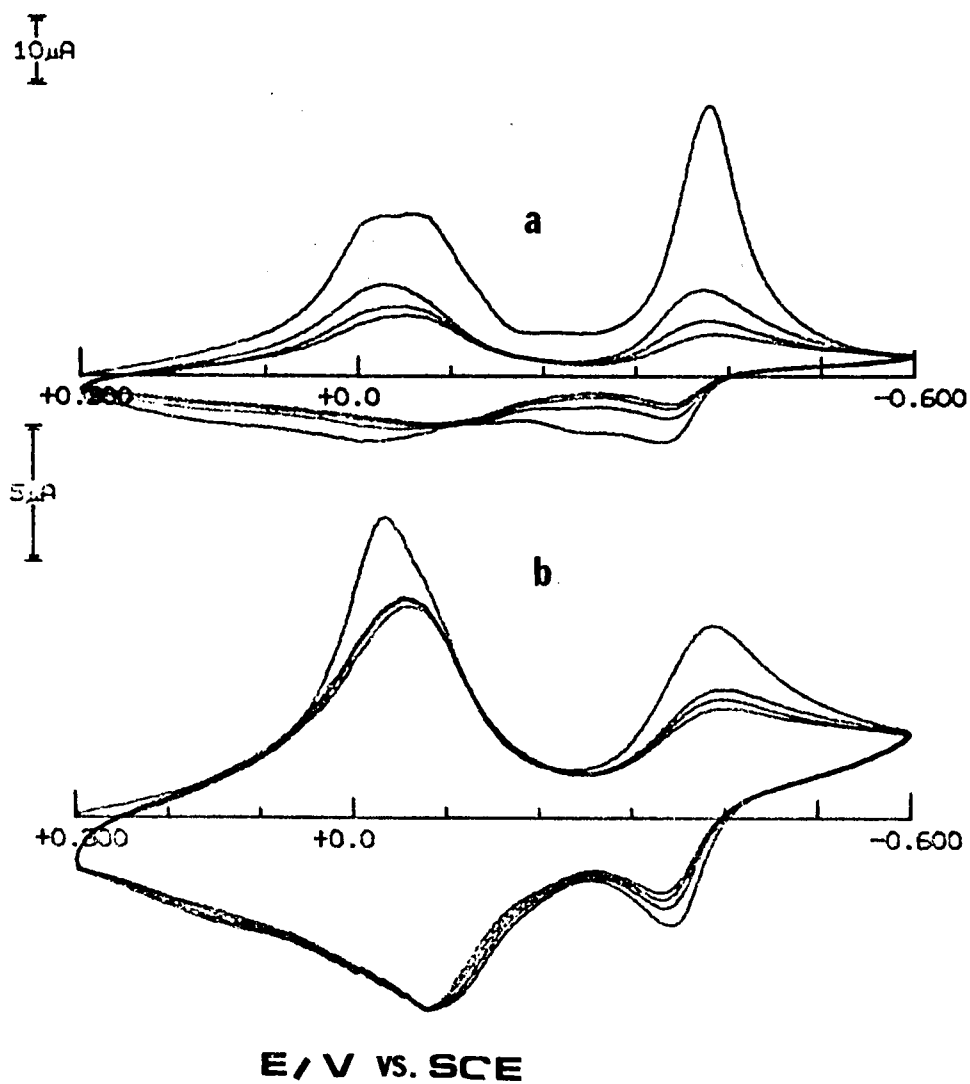


Figure 40. Cyclic voltammograms of TCNO-PE/PEG (50% TCNQ-PE) in contact with water/0.1 M CsCl (a-b repetitive cycles). Scan rate = 10 mV/sec.

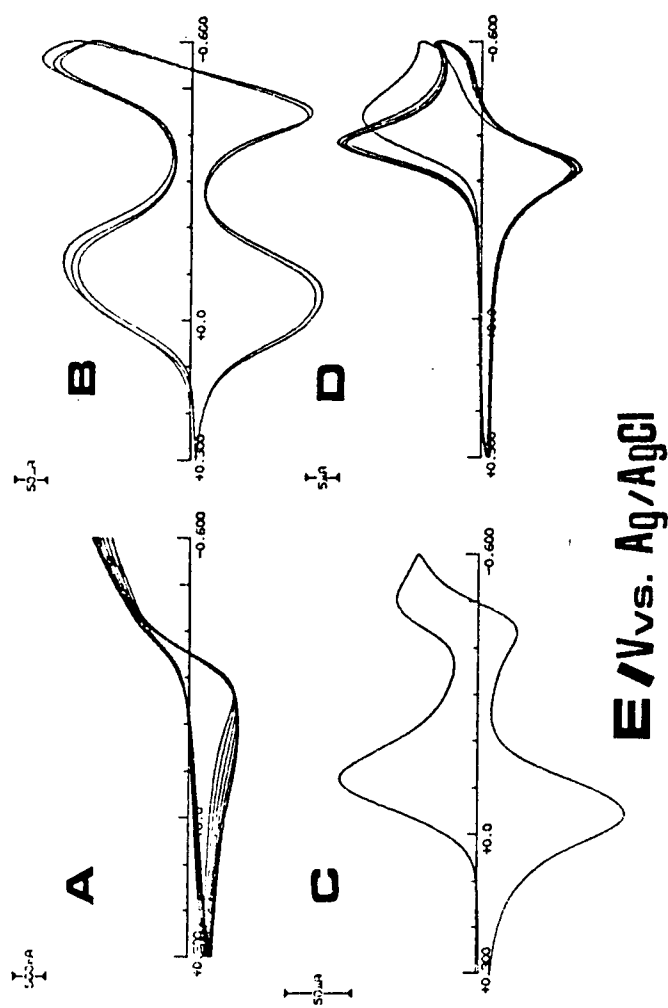


Figure 41. Cyclic voltammograms of the terpolymer. (A) thick virgin film of the terpolymer in $\text{H}_2\text{O}/0.5 \text{ M LiClO}_4$, (B-C) transferred to acetonitrile/ 0.1 M LiClO_4 , and (D) thin virgin film of terpolymer in $\text{H}_2\text{O}/0.5 \text{ M LiClO}_4$. Scan rate = 20 mV/sec .

from the cell indicated that the film was still present and no dissolution had taken place. The solvent/electrolyte solution was also reasonably colorless.

The above electrode was then pulled out of cell and was inserted into a solution of freshly prepared acetonitrile containing 0.5 M LiClO_4 . Figure 41B shows the voltammogram recorded at the same scan rate. Note that the electrochemical behavior, Figure 41B, did not show any "break-in" that both waves are present, and that significantly larger charges are obtained. This voltammogram for an acetonitrile/0.5 M LiClO_4 solution is similar to the behavior of the well studied acetonitrile/TEAP system discussed elsewhere. The position of the peak potentials are slightly shifted in this case to more negative values. Unlike the behavior in acetonitrile/TEAP, the voltammetric wave shape changes in the presence of LiClO_4 when repeated cyclings were performed. This observation may be related to the higher solubility of the Li^+ salts of TCNQ in this solvent. After several cycles the behavior shown in Figure 41C was recorded for the same film. The magnitude of peak currents for the second wave decreases relative to the first wave, perhaps due to electrochemical cross-linking.

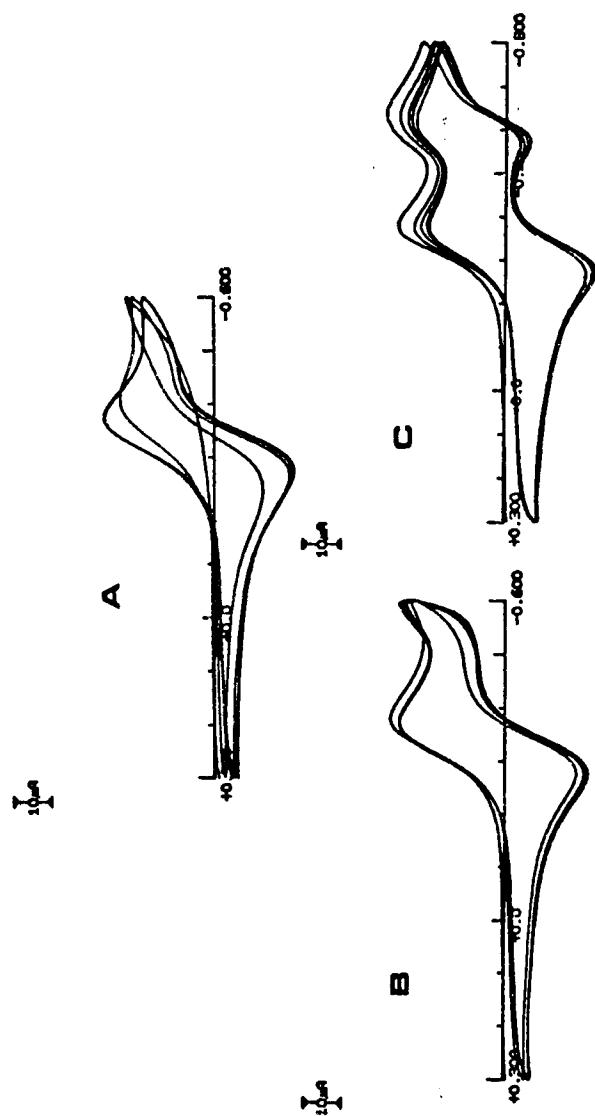
The above results shine some light on the importance of solvent uptake for the overall electrochemical response of TCNQ polymer films. The role of solvent on polymer film electrolysis was discussed in some detail in earlier sections. The degree of deviation from ideal behavior can be minimized and facile charge transport can take place if the

polymer matrix can swell by an optimum uptake of the solvent (99). The poor solvating ability of water may result in a rather compact film which can seriously retard the ion migration needed for electroactivity. This interpretation is supported by the results shown in Figure 41B, where the change of solvent renders the film electroactive, indicating rather fast swelling and counterion uptake.

On the basis of the method of preparation, it was believed that the polymer film on the above electrode (Fig. 41A-C) was rather thick. An attempt was made to prepare an electrode with a smaller surface coverage. The cyclic voltammetric behavior of this thinner film was markedly different than the above film. Figure 41B shows the CV recorded at scan rate of 20 mV/sec for a thin virgin film of terpolymer on Pt in $\text{H}_2\text{O}/0.5 \text{ M LiClO}_4$ ($E_{1/2}^{0/-} = -0.35 \text{ V vs. Ag/AgCl}$). A striking feature of this voltammogram is the relatively narrow cathodic and anodic peakwidths. Films of TCNQ-PE under the same conditions yield CVs with much broader anodic waves. The degree of dimer formation in aqueous systems and the effects of slow kinetics on the oxidative cycle are believed to be responsible for this behavior. In the case of terpolymer, however, due to much smaller effective concentration of TCNQ in the polymer matrix, dimer formation is not as pronounced and therefore the cyclic voltammetric behavior is consistent with these conclusions. In this respect, the exceptional stability at the extremely negative potentials supports this interpretation. Note that the $E_{1/2}$ corresponding to the $\text{A/A}^{\cdot-}$ couple is shifted to more negative values. This effect is thought to be due to the difficulty involved with incorporating counterions into the polymer matrix.

Electrochemical Behavior of the Terpolymer Films
Doped with PEG on Pt in H₂O and 0.5 M LiClO₄

The CV of a film of the terpolymer doped with PEG was recorded in H₂O and 0.5 M LiClO₄ (see Fig. 42A). An interesting break-in behavior is observed for this film. On the first reductive cycle only a small residual current was seen. Subsequent cycles, however, yielded both cathodic and anodic waves, presumably corresponding to A/A⁻ couple ($E_{1/2} = -0.32$ V vs. Ag/AgCl). The CV corresponding to the blend features greater diffusional character compared to the undoped film. The film demonstrated excellent stability judged by the very small decrease in the magnitude of cathodic and anodic charges over repeated cyclings. Furthermore, a second wave started to show up which is most probably due to the second reduction process. The $E_{1/2}$ for this wave, extracted from the voltammogram shown in Figure 42C, was ~ -0.6 V vs. Ag/AgCl. This second wave also has characteristics of a diffusional process. The features of the second wave were lost when attempts were made to further dilute the blend with respect to terpolymer. After several repeated cyclings, the electrode was visually inspected and it was noticed that it had green spots. This is in contrast to the dark blue coloration that is seen for TCNQ-PE studied under similar conditions. At such a low concentration of the redox sites, one does actually expect a smaller degree of dimer formation. Another interesting aspect of this voltammogram is the exceptional stability of the film in the potential range employed. The voltammogram shown here is a good example of electron hopping/ diffusion contribution to the observed electrochemical behavior.



E/V vs. Ag/AgCl

Figure 42. Cyclic voltammograms of TCNQ-PE/PEG blend film in $\text{H}_2\text{O}/0.5 \text{ M } \underline{\text{LiClO}_4}$. (A-C) Repetitive cycles.

CHAPTER V

CONCLUSIONS AND FUTURE DIRECTIONS

All of the synthetic procedures employed in this work were adopted from the existing literature (77, 95, 94). The synthesis of TCNQ-diol was performed according to Day's modification of Hertler's procedure (95). The terpolymer was synthesized via solution polycondensation at low temperature according to Day's procedure and employed a mixture of the electroactive TCNQ-diol and electroinactive BOEB-diol, and a stoichiometric amount of adipyl chloride in DMA (77, 95).

The major emphasis of this work was on the effect of polymer film composition on the process of electron and ion transport in polymer films on electrodes in contact with solvent/electrolyte systems. Such studies have revealed several interesting phenomena.

Careful analysis of the cyclic voltammograms indicated that the electron hopping process was intermolecular between sites on different polymer chains, and not intrachain in nature (108). The electrochemical response of the blends indicated uniform distribution of acceptor sites and association of reduced sites down to compositions of ca. 30% TCNQ-PE. Below ca. 20% TCNQ-PE abrupt changes in the voltammetry were observed: multicycle "break-ins" were required and large peak potential separations appeared between relatively narrow voltammetric peaks. In one example, a relatively thick blended film containing 5% TCNQ-PE, ca. 100 slow sweep potential cycles were required to obtain any indication of a faradaic response. The more concentrated blends

developed patterns similar to the dilute ones. This observation was interpreted to be a possible indication of electrochemically driven phase separation in the "-1" oxidation state.

Decreased charge transport rate in the region of the $A^{\cdot-}/A^{2-}$ couple was specially evident in the voltammogram of TCNQ-PE/BOEB-PE blend films of low TCNQ-PE concentration. This slow rate of the reduction of TCNQ sites was interpreted to be, at least in part, due to a slower ion transport from solution to the nonpolar polymer phase (74).

The employment of poly(ethylene glycol) as a host polymer strengthened the above interpretation. In this regard, the charge transport enhancements that were observed in acetonitrile/TEAP when the films were prepared with PEG as a host polymer, were specially interesting. Increased Cottrell slopes were found even before the concentration effect was taken into account. This observation was interpreted to signify the important role of ion and/or solvent permeation, which is driven by electrochemical perturbations, on the overall electrochemical activity measured. Regardless of whether the overall diffusion process is described in terms of electron hopping through the polymer film from reduced to the neutral sites or in terms of the true diffusion, migration of ions must occur if electroneutrality in the film is to be maintained upon electrochemical perturbation. If this process is fast, larger charge transport rates are likely to be measured.

In the blend films with PEG as a host, the polymer matrix can possibly extract the electrolyte ions and their accompanying solvent

molecules from the contacting solution. This process can of course precede the electrochemical perturbations if the permeation process is fast and spontaneous. Large cations such as TEA^+ possibly cannot fit inside the helical cavity of PEG and therefore may induce a more irregular, amorphous structure. Mobility of ions in such amorphous materials is known to be faster. Lack of strong ion-pairing with perchlorate ions under these conditions may also contribute to higher mobility of the TEA^+ and ClO_4^- in response to electrochemical perturbations.

The relatively smaller enhancement factor for Li^+ ions under exactly the same conditions was interpreted in terms of a higher crystalline structure that can be induced by lithium cations. The behavior in the presence of acetonitrile/ Li^+ was similar to electrochemical studies performed in ion exchange polymer films (62, 128). To some extent, the magnitude of $nD^{1/2}c$ does not show a significant dependence on the concentration of the redox sites in the polymer matrix. As pointed out earlier, this behavior is similar to the case of $\text{Fe}(\text{CN})_6^{3-}$ coordinately attached to PVF films (62). In the case of ion exchange polymer films of Martin et al., it was reported that the motion of the counterions or co-ions does not affect the rate of the overall process. Since the electrochemical activity observed does not include contributions due to gross ionic motion, faster rates of charge transport are likely to be measured. More detailed studies with various LiX salts can be very revealing in that a correlation between conductivity values and the extent of ion pairing can be made.

The behavior of blend films containing PEG as a host polymer in water/alkali metal ions was also studied. In this regard, the most significant finding was that the stability of these films in the "-2" oxidation state compared to the pure TCNQ-PE films under similar conditions. The cyclic voltammograms, however, underwent subtle changes in waveshape upon repeated cycling. The effects of film composition and delay time were also studied and discussed in detail. In our interpretations of the results, strong cation binding to the ethereal oxygens of PEG and the resulting decreased ion mobility was suggested as the cause of the low charge transport rates for the PEG blends in contact with aqueous alkali metal electrolytes. In contact with water the results indicated that the ions are probably less solvated upon permeation into the polymer matrix, at least in the TCNQ-PE regions of the composite films containing PEG as a host polymer. This is of course, due to the known low affinity of TCNQ-PE for water. Also in water the degree of TCNQ_2^{2-} dimer formation is larger, which in turn may result in tighter and more compact films. Ionic mobility can be seriously affected under these conditions.

As indicated above, the film stability was found to depend on the presence of the host polymer. This is probably related to dissolution of the films in the reduced or ionic form. This aspect of these electrodes will require further careful studies.

Preliminary experiments described in this work indicate that other polymers can be used to prepare film electrodes that may manifest the properties of the host polymer. Polystyrene (PS, MW = 15,000)

(Fig. 43), for example, gives different behavior than BOEB and PEG host polymers. It would be of interest to use low capacity polyelectrolytes or lightly cross-linked polystyrene as the host polymers. The significant point here is that polymer films with a wide variety of charge transport properties can be easily fabricated in which both electron and ion injection is facilitated. In future work the above studies should also be extended to other electroactive polymers such as: poly(vinylferrocene), polyimides (108), the polymeric quinones of Funt (134), poly(vinyl pyridine) (46, 47) and sulfonated polystyrene (48). These are soluble species and may allow the preparation of blends of variable composition and properties. The above studies will determine the degree of generality in the observations.

The above studies should especially be extended to the polyurethanes prepared in our laboratory (79). Careful examination of the electrochemistry of TCNQ-PU's have revealed fascinating questions on the charge transport process (79). The variation of solvent and counter ions have revealed significant difference between films of TCNQ-MDI, TCNQ-TDI and TCNQ-HMDI polyurethanes. In solution (DMA/acetone is a good choice) all three polymers exhibit the classical EE electrochemistry characteristic of TCNQ (99). However, as films in contact with aqueous or alcohol solvents, different voltammetric patterns were observed for thin films of the above polymers. The "second" wave corresponding to the $\text{TCNQ}^{-/2-}$ process is a sensitive indication of the charge transport through the polymer layer. For the MDI polymer in the presence of aqueous solutions of alkali metal counter ions, no second wave was present in the voltammograms; even at

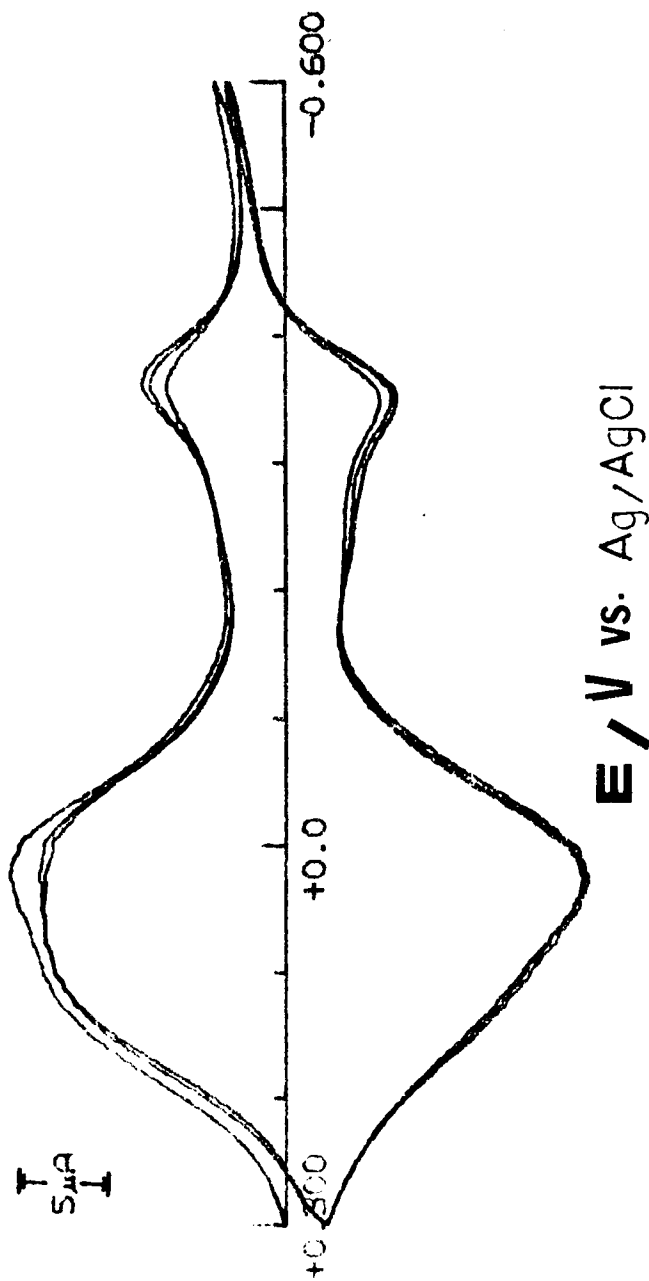


Figure 43. Cyclic voltammogram of TCNO-PE/PS blend film (30% TCNQ-PE) in acetonitrile/0.1 M TEAP. Scan rate = 20 mV/sec.

extremely slow sweep rates or long electrolysis time. Only a diffusion controlled wave was evident corresponding to the partial reduction of the film to the radical anion state as confirmed by spectroelectrochemistry. Transfer of the electrode to an acetone solvent resulted in the reappearance of the EE pattern in the voltammograms. In aqueous solutions of Rb(I) or Cs(I) salts, films of TCNQ-TDI-PU showed reproducible indentations in the region where the second wave is expected, while films of TCNQ-HMDI-PU showed an attenuated second wave (79). TCNQ-PE under the above conditions exhibits a well developed second wave on the first potential sweep in the negative direction which, results in film destruction via hydrolysis due to high film pH generated by the TCNQ^{2-} dianion sites (99). As expected, the polyurethane, terpolymer and blends of TCNQ-PE/PEG films exhibited better stability under above conditions. A general observation resulting from the above studies is that the electrochemical response is very sensitive to the polymer structure.

There are several other aspects of the charge transport process through the TCNQ polymer films that deserve further study. The process is remarkably dependent on the concentration of the supporting electrolyte, increasing as expected for increasing electrolyte concentration, but then decreasing at higher concentrations (135). This effect was interpreted in terms of a qualitative polyelectrolyte picture of the polymer film in which, with increasing concentration of the supporting electrolyte, the reduced film adopts a more compact structure and the diffusion of the counterions and/or the segmental

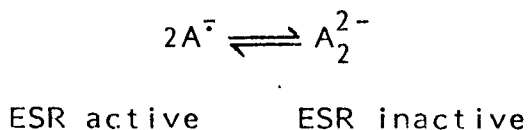
motion of the polymer chain becomes hindered. Since this phenomenon is a common property of polyelectrolyte gels (136, 137), it should be general for the polymer film electrodes discussed above.

Preliminary ESR studies of the above blends by Chiu has revealed interesting phenomena which deserve further study in the future (138).

Gaudiello et al. (139) have reported the application of simultaneous electrochemical and electron spin resonance techniques for the study of two viologen-based chemically modified electrodes. ESR studies of electrochemically generated radical ions can provide information concerning the environment and mobility of redox species in chemically modified electrodes and on the electron-transfer rates in these films. These authors discovered that for the $[(MV^{2+})]_{\text{surf}}$ films, where the redox species were covalently anchored to the polymer chain, the ESR spectrum was broad and featureless, similar to the case of TCNQ-polymers discussed earlier. A quantitative assessment of the rate of self-exchange was not possible, because of the absence of fine structure in these spectra. The ESR signal intensity as a function of the extent of film reduction indicated that the rate of electron transfer (self-exchange) was high. Electrodes covered with the perfluorosulfonate polymer Nafion in which MV^{2+} (methyl viologen) was incorporated through electrostatic binding, displayed ESR spectra upon reduction that were similar to those of MV^+ in solution, suggesting that the radicals were free to tumble on the ESR time scale and that their exchange rate in the polymer film was relatively smaller. Chiu (138) has made

ESR measurements on TCNQ-PE films of various compositions with BOEB-PE and PEG as the host polymers. In all cases studied, electrolysis was performed outside the ESR cavity.

For the TCNQ-BOEB blends, one-line signals were observed in the ESR spectra of films containing more than 20% TCNQ-PE. No signals were observed for the more dilute films. For the TCNQ-PEG blends also a one-line signal was observed. The signal from a film electrolyzed in TEAP/acetonitrile was about three times stronger than in LiCl/H₂O. This observation is consistent with the results presented in this work and can, partly, be due to the formation of dimers in the reduced state which results in a decrease in the spin concentration through the reaction,



All of the ESR spectra obtained for reduced blend films showed a one-line pattern, indicating the occurrence of fast spin exchange process in these films. As Chiu has pointed out (138), although the total amount of TCNQ sites adsorbed on the surface may be low, in the order of nmoles/cm², the local concentration of TCNQ sites could still be high. In general, spin exchange occurs in radical concentrations greater than $\sim 10^{-3}$ M.

Further attempts should be made to study the "solid state" (solvent free) conductivity of the above polymer films of various compositions. Cu Phung (82) has recently reduced thin films of TCNQ

polymer adsorbed on NaCl disks and glass plates by the controlled potential generation of the radical anion of chloranil. The E^0 of this mediator is appropriate for the reduction of the TCNQ sites to the radical anion state. This has permitted FTIR and conductivity measurements to be made on the dried reduced films (solvent free) for the first time. Very tentative results for the reduction of TCNQ-PE in the presence of TEA^+ counterions indicated specific conductivity in the 10^{-3} to 10^{-2} Scm^{-1} range (82). Attempts should be made to refine the above techniques for the measurements of the solid state conductivity of the various polymer blend films described above.

Finally, much of the effort in this work was dedicated to the understanding of charge transport in electroactive polymer films. A considerable progress has been achieved in this respect; many questions, however, need to be answered before "general" conclusions can be drawn.

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