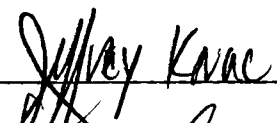
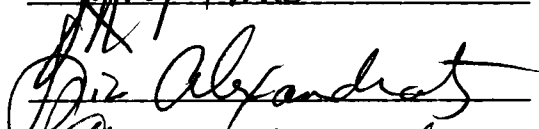
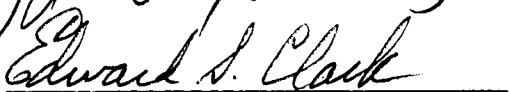


To the Graduate Council:

I am submitting herewith a dissertation written by Cecil V. Francis, entitled "Synthesis and Characterization of Tetracyanoquinodimethane Polyurethanes." 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.


James 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

SYNTHESIS AND CHARACTERIZATION OF TETRACYANOQUINODIMETHANE
POLYURETHANES

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

Cecil V. Francis

March 1986

DEDICATION

In memory of my father, Cecil V. Francis who died in 1978 and my sister Annette M. Francis-Sulaimana who died in 1983.

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ABSTRACT

Synthetic and eletrochemical studies directed towards electro-active polymers for fabrication of modified electrodes are presented. The monomer, 2,5-Bis(2'-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane (TCNQ diol) has well behaved electrochemical properties which have permitted us to carry out a systematic study of the extent to which polymer properties dictate the electrochemical behavior. This monomer is covalently incorporated in the backbone of polyurethanes via solution polycondensation reactions.

The polyurethanes are prepared by the polycondensation of TCNQ diol with methylene bis(4-phenylisocyanate), MDI, to give PU-MDI, 1,4-toluene diisocyanate, TDI, to give PU-TDI and 1,6-hexamethylene diisocyanate, HMDI, to give PU-HMDI.

The effects of different counter ions, solvents and pH on the electrochemical behavior of the polymers are examined. The characterization methods employed include spectrophotometric techniques, nuclear magnetic resonance, electrochemical methods, gel permeation chromatography, differential scanning calorimetry and electron spectroscopy for chemical analysis.

Financial assistance from The University of Tennessee, Department of Chemistry and The National Science Foundation is also gratefully acknowledged.

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CHAPTER I

INTRODUCTION

Like the vast number of compounds conventionally classified as organic materials, polymers have long been considered in terms of their good electrical insulating ability along with many other important industrial applications. In recent years a number of organic compounds have been shown to exhibit significant electrical characteristics. The term "Organic Semiconductors" has been used to describe these compounds which contain significant amounts of carbon-carbon bonding and show some capability of supporting electrical conduction. It is customary to consider organic semiconductors as materials that exhibit electronic conduction in between those of metals [10^4 to 10^6 (ohm cm) $^{-1}$] and insulators [10^{-22} to 10^{-10} (ohm cm) $^{-1}$], i.e., within a 10^{-9} to 10^3 (ohm cm) $^{-1}$ range.¹

Semiconducting organic solids are frequently grouped into three classes, namely: a) Molecular crystals, e.g., naphthalene and anthracene, b) charge transfer complexes, e.g., 7,7,8,8-tetracyanoquinodimethane(TCNQ) tetrathiafulvalene (TTF), and c) polymers, e.g., black orlon. The major aim of current research is to understand better the nature of the electron transport process in these solids, especially as related to their physicochemical structure. With such an understanding, one could envisage a "tailor made" semiconductor material with properties exactly matched to the requirements of specific applications. Thus fabricators of electronic devices can conceive of completely new films, filaments and molded shapes specially prepared to

best suit particular purposes.² Furthermore, such novel products would have the additional promise of lower material cost and easier fabrication compared to conventional inorganic semiconductors.¹

Generally, the better organic conductors are planar compounds which have delocalized, easily polarizable, π -electron clouds, free radicals, and charge transfer complexes.^{2,3} Although considerable experimental work has been carried out on the preparation and study of electronic properties of these materials, no comprehensive theory of the conduction mechanism in organic materials has been proposed, mainly owing to the limited knowledge of intermolecular interactions in the solid state. The most widely used explanation of the experimentally observed conduction of organic solids is in terms of a modified band model of these solids. The basis of the band theory is the existence of a forbidden energy gap. This energy gap is of prime importance in semiconductor theory. The band theory is essentially a quantum mechanical approach involving the calculation of the width of energy bands by calculating overlap integrals between π -electron molecular wave function on adjacent molecules.^{2,3,4}

The conductivity, σ , depends on the concentration of charge carriers, n , their charge, e , and mobility, μ .⁵ The concentration of carriers and hence the semiconductivity, increases with temperature, T , according to a Boltzmann type distribution with activation energy, E_A .^{3,5}

$$\sigma = n_0 e \mu \exp. (-E_A/kT) \quad (1)$$

Thus, semiconductivity with positive activation energy is distinguished from metallic conductivity which falls as the temperature is increased.

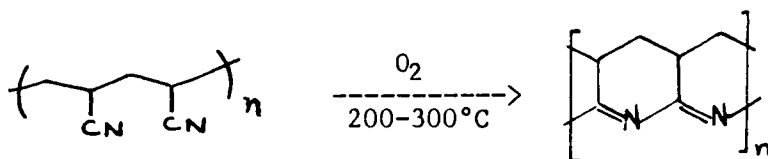
In a solid with long-range order or closely packed atoms, as in a metallic semiconductor, the energy levels form the conduction and valence bands and the separation between the two bands is the forbidden energy gap. On excitation of an electron from the valence band to the conduction band, a hole (or positive charge) is left in the valence band and both the hole and the electron can act as charge carriers and are free to move in the band where they have a high mobility.⁵ This is occasionally the case with close packed molecular solids. Most organic molecules are widely separated and hence, electronic coupling between molecules is poor. This wide separation between molecules is the major obstacle to conduction as it is difficult for electrons to pass between them. Electrons then move by thermally activated hopping, and, because they spend a long time on each molecule, the mobility is low, hence, the low conduction.^{4,5} Generally, mobility increases with long-range order and is highest in single crystals so that polymers start with a handicap since most polymers have a certain percent of amorphous domain.

Organic conductors can be divided into two major groups according to their means of conduction. Generally carriers are most readily formed by activation of non-bonded or π -electrons. If they are delocalized in a conjugated system, they form an internal conduction path of high mobility.⁵ Thus, long conjugated systems form one class of organic conductors. The second major class of organic conductors is comprised of stacked planar π -electron systems. In this class, the

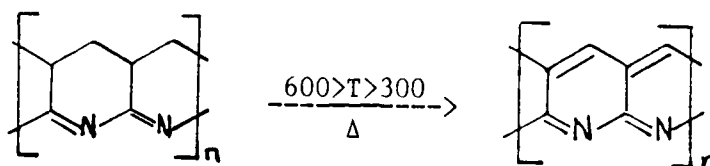
π -bonded electrons give better intermolecular orbital overlap than σ bonds, and hence we find that planar aromatic molecules, which can stack like cards with an interplanar spacing no greater than 0.335 nm, provide a conduction pathway normal to the molecular plane.²

In a polyene chain, $-(CH)_n-$, π -electron delocalization tends to make all the carbon-carbon bond lengths equal to facilitate good molecular orbital overlap. Thus, one might expect metallic conduction in true polyenes. However, only highly crystalline, stereoregular polyacetylenes show appreciable conductivity.^{3,5,6} Three reasons are cited for this: a) large intermolecular spacing; b) bonds are not all equal in length, but alternate; and c) rotation of the chain. Reason (b) stabilizes the polymer, but restricts electron delocalization; while reason (c) interrupts conjugation particularly where coplanarity of the substituents is prevented by steric interactions.

Interruption of the conjugation can be overcome by locking the bonds in a planar polyacene structure as is found in pyropolymers. One system which has been studied extensively is the pyrolysis product obtained from poly(acrylonitrile). Pyrolysis of this material takes place in three stages. a) Heating at 200°-300°C in the presence of



oxygen,^{7,8} results in formation of six membered rings via formation of conjugated imino functionalities.^{9,10,11} b) Heating at temperatures between 300°-600°C in an inert atmosphere causes dehydrogenation and results in a fully conjugated ladder polymer structure.⁷ c)

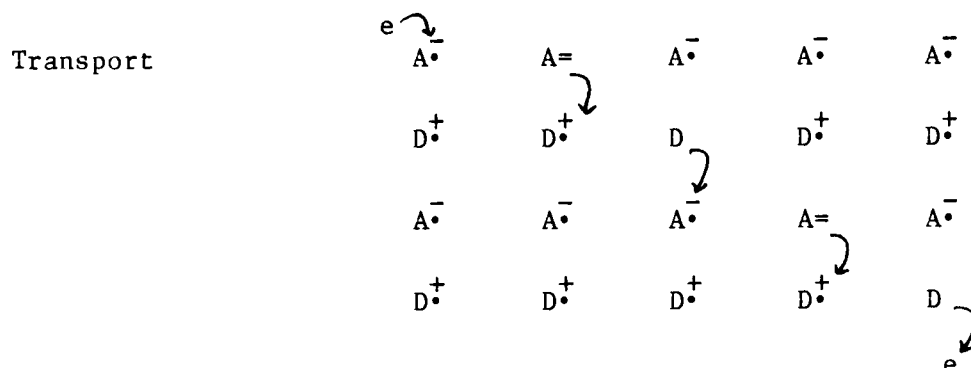


Formation of the extended planar graphitic structures which is believed to occur at temperatures greater than 600°C, with the loss of either NH_3 or HCN .^{9,11} The conductivity of this material can be controlled by the pyrolysis temperature.⁹ Generally, the final products are intractable materials which must be fabricated before pyrolysis. Conjugated polymers can give fairly high conductivities, but usually this is done at the expense of poor mechanical properties, refractory behavior and dark color.

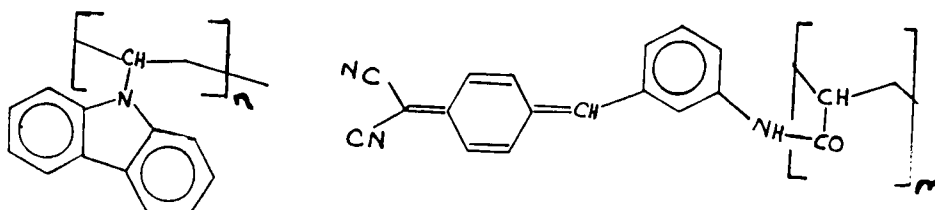
An alternative is found in the planar π -electron systems which include charge-transfer complexes and certain radical-ion salts. Partial formation of radical-ions occurs in donor-acceptor interactions leading to charge-transfer complexes which form rigid stacks of ...DADADA... and these determine the mechanical properties of the solid complexes. The conductivity is highly anisotropic, being greatest along the direction of the stacks and occurring by radical-ion disproportionation as suggested by Eley.¹²

formation: $D + A \longrightarrow D^+ A^-$

where D = donor molecule; A = acceptor molecule

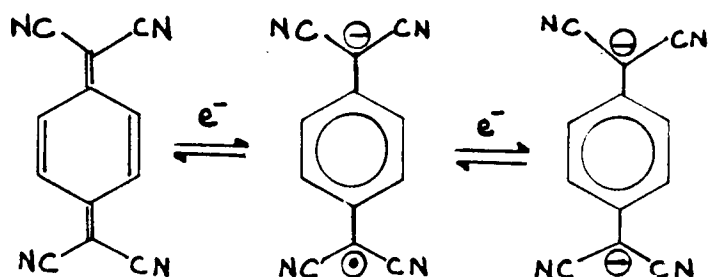


Many polymeric charge-transfer complexes have been synthesized, usually with the donor species being carried on a vinyl polymer^{5,13,14}. However, this often results in the conductivity being lower than that of the equivalent monomeric complex. This may be attributed to the incorrect spacing of the repeat units.¹³ This has to be a part of the solution since it was shown that complexes formed from polymeric donor and polymeric acceptor species such as that based on poly-(N-vinylcarbazole) (shown below) apparently form films with conductivity as high as $10^3 (\text{ohm}\cdot\text{cm})^{-1}$ ¹⁴.



Polymeric donor/acceptor complex

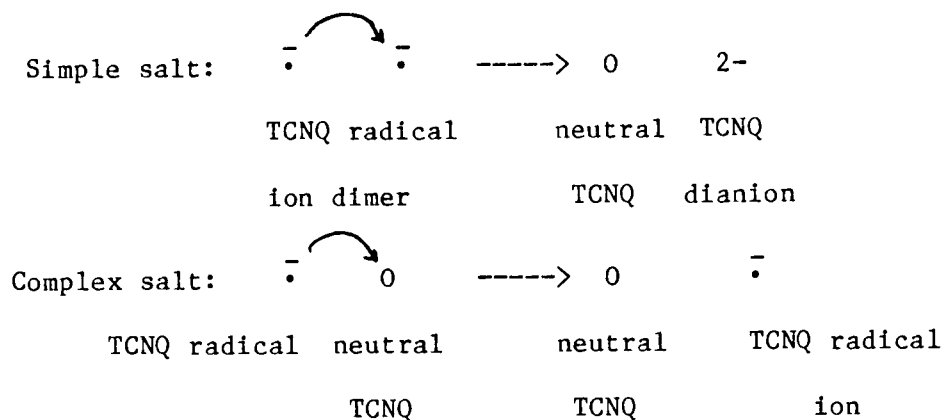
Central to the development of highly conductive materials based on radical-ion systems was the synthesis of TCNQ by Du Pont workers in 1960.¹⁵ Interconversion of $\text{TCNQ}^{\cdot-}$ and TCNQ^{2-} are characterized by reduction potentials of $E_1 = 0.127 \text{ V}$ and $E_2 = -0.219 \text{ V}$.^{16,17} That is:



The unusual stability of semi-reduced TCNQ (that is, $\text{TCNQ}^{\cdot-}$) with respect to the neutral TCNQ results from the concomitant change from a relatively unstable quinoid structure to the aromatic structure, allowing extensive delocalization of the π -electrons over the whole molecule. As a result of this TCNQ not only forms the typical charge transfer complexes, but also radical anion salts.⁶

With some cations, TCNQ will form both simple and complex salts, the latter containing an extra equivalent of the neutral TCNQ.⁵ The complex salts generally show higher conductivities than the simple salts.^{18,19,5} In the case of the simple salts, for an electron to move along the stack, coulombic forces have to be overcome in forming TCNQ^{2-} and so the conduction is poor. When neutral TCNQ is added however, it is not necessary to form a dianion when an electron is transferred. In both cases an energy barrier must be overcome to transfer the electron, however in the case of the complex salt, the overall change in energy (ΔE) when the electron is transferred from the

radical ion to the neutral TCNQ is zero. Thus, the complex salts have a higher conductivity.

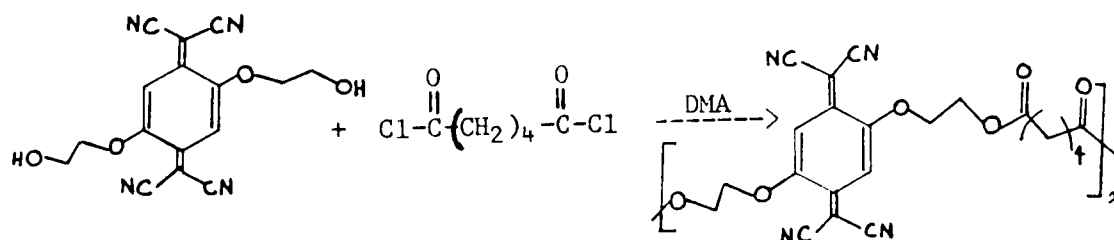


The metallic conductivity demonstrated for the charge-transfer complex between TCNQ and TTF would suggest that polymer containing these materials might also display metallic conductivity if properly oriented.²⁰⁻²³ Many synthetic schemes have been attempted in which TTF has been incorporated in the backbone of polymers or as pendant groups and then doped with TCNQ.²⁴⁻³² Most of these materials failed to form the required TTF-TCNQ charge transfer complex, and those that did form the charge transfer complex did not display the desired conductivity. So even though many TCNQ salts of polymeric cations and polymeric donor molecules have been synthesized and studied, conductivities reaching the metallic range are still elusive.

An approach taken by Hertler at synthesizing an organic polymer with metallic conductivity was to covalently bind TCNQ in the polymer backbone along with a donor comonomer like TTF.²⁵ The polymers showed very low conductivities and no solvent could be found to dissolve them. He attributed the failure of these covalently bound TCNQ polymers to show the very high electrical conductivity

characteristic of the non-polymeric charge-transfer complexes, to an unattainable preferred geometric position of the donor/acceptor molecules. The polymer is unable to achieve the high degree of orientation required to enable the donor and acceptor units in the polymer backbone to form the face-to-face stacks which are important in the conductivity of TCNQ salts.^{25,33,34}

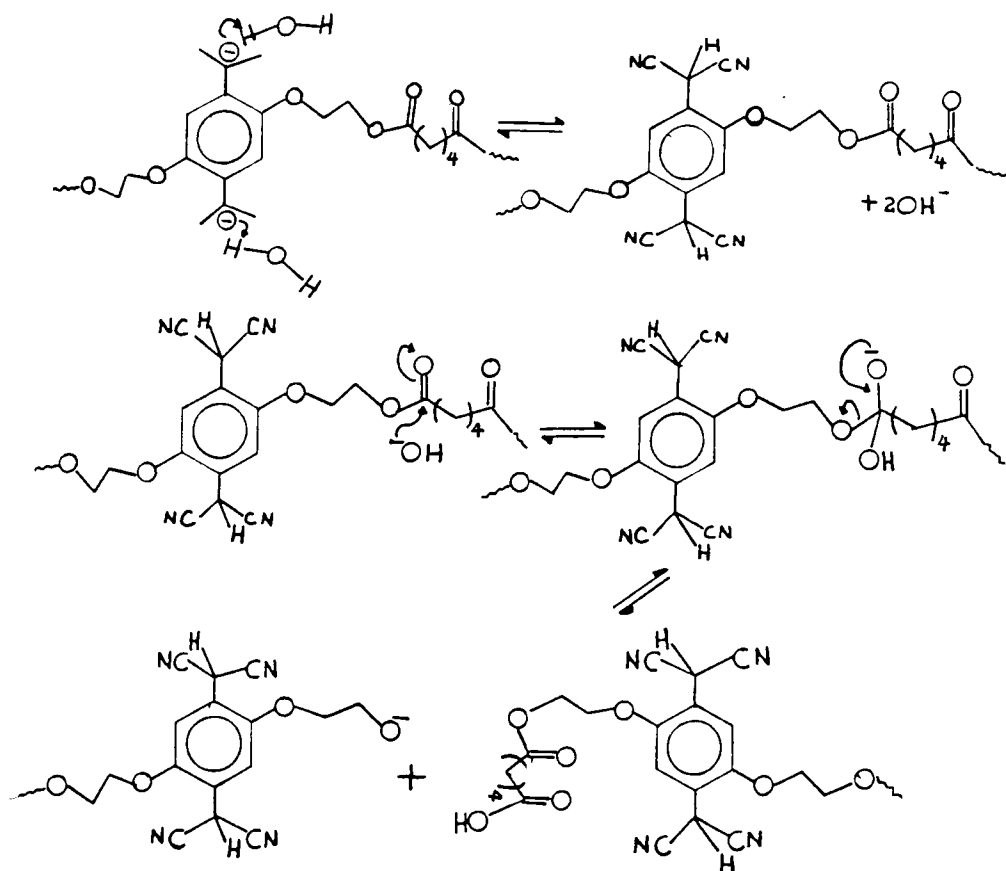
A similar synthesis of TCNQ covalently bonded in a polymer backbone was previously done in our laboratory. Specifically, 2,5-bis-(2'-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane (TCNQ diol) was copolymerized with adipyl chloride via low temperature solution polycondensation to yield a polyester, PE-TCNQ.^{35,36}



PE-TCNQ was a red solid which was partially soluble in acetonitrile and tetrahydrofuran, but completely soluble in more polar solvents like *N,N*-dimethylacetamide (DMA) and *N,N*-dimethylformamide (DMF). This polymer was cast into films on the surface of an electrode and its physicochemical behavior probed by various techniques.³⁷⁻³⁹

This polymer showed the expected electrochemical behavior of TCNQ namely, two reversible redox couples characteristic of EE systems, both in solution and as a film. It was noted that the film was destroyed when cycled to the second wave in unbuffered aqueous solutions.³⁷ This was attributed to a combination of dissolution

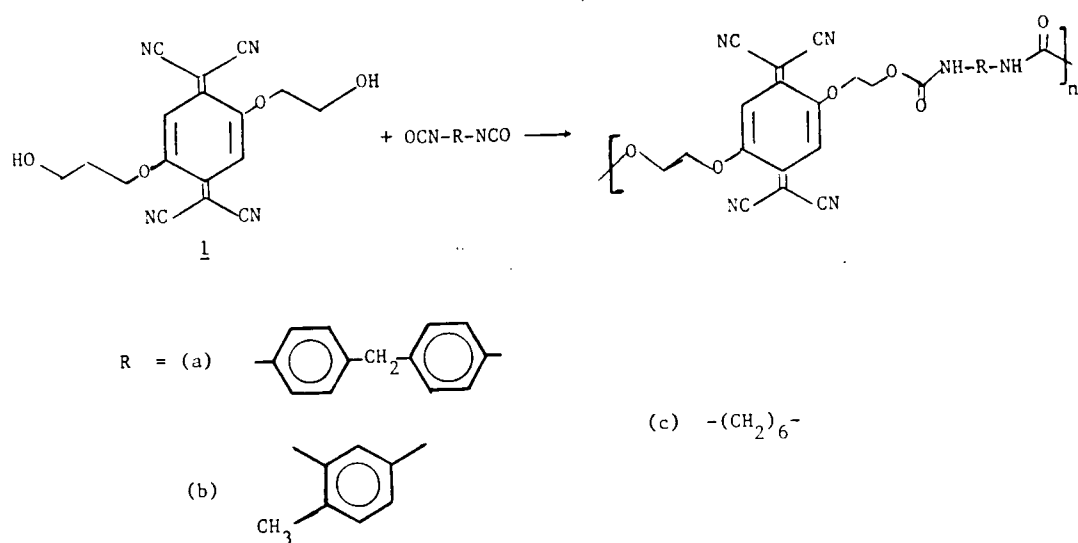
of the more soluble dianion, and also to hydrolysis of the polymer due to the relatively large hydroxide concentration generated in the film on cycling it to the fully reduced state:



The destruction of the PE-TCNQ films when TCNQ is fully reduced prompted us to seek other polymers which might be able to resist hydrolysis by the high hydroxide concentration generated by the formation of the fully reduced TCNQ^{2-} dianion. Several researchers have examined the hydrolytic stability of polyesters versus polyurethanes⁴⁰⁻⁴³ and also the hydrolysis of polyurethanes.⁴⁴⁻⁴⁹ They

have found that given the same conditions, the ester link, $\overset{\text{O}}{\parallel}\text{-C-O-}$, will hydrolyse at a much faster rate than the urethane, $\text{-NH-}\overset{\text{O}}{\parallel}\text{-C-O-}$, link.⁴³ With this in mind, we decided to synthesize and study TCNQ polyurethanes as the polymer to maintain a high TCNQ concentration and withstand hydrolysis when the TCNQ units are fully reduced. The diisocyanate comonomers chosen for this study are: methylene bis(4-phenylisocyanate), MDI; 2,4-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 because of the variation of structural features they impart to polymers. For example, MDI is a known "stiffening agent" that tends to make polymers rigid, while on the other hand, HMDI will act more like a plasticizer, adding flexibility to a polymer.⁴⁸ TDI will form polymers having properties lying between MDI and HMDI. This series of polyurethanes should give an indication of the effects of polymer structure on the electrochemical behavior. The similarity between HMDI and adipyl chloride as far the number of carbons are concerned should also enable us to see how the change from an ester to a urethane bond dictate electrochemical behavior of these polymers.

The synthetic approach taken was solution polycondensation of TCNQ diol and the diisocyanates in the presence of a catalyst like dibutyltin dilaurate (T-12) as shown follows:⁴⁸



The synthesis of polyurethanes is subject to many side reactions due to the reactivity of the isocyanate group. The various side reactions make it very difficult to obtain a stoichiometric balance of diisocyanate and diol to produce a linear polyurethane. Generally, a slight excess of the diisocyanate is required to overcome the stoichiometric imbalance caused by the side reactions. Temperatures in the range of 100-120°C along with a catalyst, usually tertiary amines or organometallic compounds are generally employed in polyurethane formation. High reaction temperatures are avoided because urethane polymers undergo several types of degradation at elevated temperatures. These side reactions are discussed in Chapter III.

CHAPTER II

SYNTHESIS AND CHARACTERIZATION OF 1,4 Bis(2'-HYDROXYETHOXY)-7,7,8,8-TETRACYANOQUINODIMETHANE

A. Introduction

One of the most widely studied charge-transfer complexes is that between the electron acceptor, 7,7,8,8-tetracyanoquinodimethane (TCNQ), and the electron donor, tetrathiafulvalene (TTF). This complex exhibits very high electrical conductivity of about $10^5 \Omega\text{m}^{-1}$.⁶ In recent years attention has been focused on making TCNQ derivatives which:

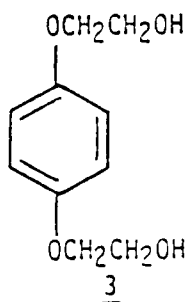
- a) can be polymerized,²⁵
- b) give improved metallic character of the charge transfer salt,^{16,18} and
- c) allow better understanding of the electron transport properties of these systems.^{35,37,39,50}

The synthesis of TCNQ and derivatives has been extensively reviewed by R. W. Day⁵¹ who synthesized a polyester containing TCNQ units covalently bound in the polymer backbone. Day's synthesis was based on a TCNQ diol, 2,5-bis(oxyethanol)-7,7,8,8-tetracyanoquinodimethane, compound first synthesized by Hertler.²⁵ A major substituted TCNQ derivative published since then is the synthesis of 11,11,12,12-tetracyano-9,10-anthraquinodimethane.⁵² In this dissertation the synthetic route followed is that which was proposed by Hertler²⁵ and later modified by R. W. Day.⁵¹ The major disadvantages of this synthesis route to TCNQ diol are:

- a) the overall yield of TCNQ diol is low,
- b) extremely poisonous reactants, leading to carcinogenic products, are used as starting materials at various steps in the synthesis.

A major advantage, however, of this route is that the starting materials are moderately inexpensive. We have been able to improve the overall yield of this ten-step reaction sequence seen in Figure 1, and characterize further the isolated intermediates. The details of this synthesis are described below.

1. Preparation of 1,4-Bis(hydroxyethoxy)benzene (3). The



first step in the synthesis of TCNQ diol requires the ethoxylation of hydroquinone. Several procedures are outlined in the literature for carrying out this reaction with yields that vary significantly. Dyer and Scott⁵³ prepared compound 3 in 24% yield by the reaction of ethylene carbonate on hydroquinone using a tertiary ammonium hydroxide catalyst; while on the other hand, Fujita reported a 96% yield using ethylene oxide and hydroquinone in the presence of an alkali or alkaline earth hydroxide catalyst.⁵⁴

We utilized the method of Fujita in our synthesis, using a dry ice-ethanol cooled condenser to prevent the escape of ethylene oxide

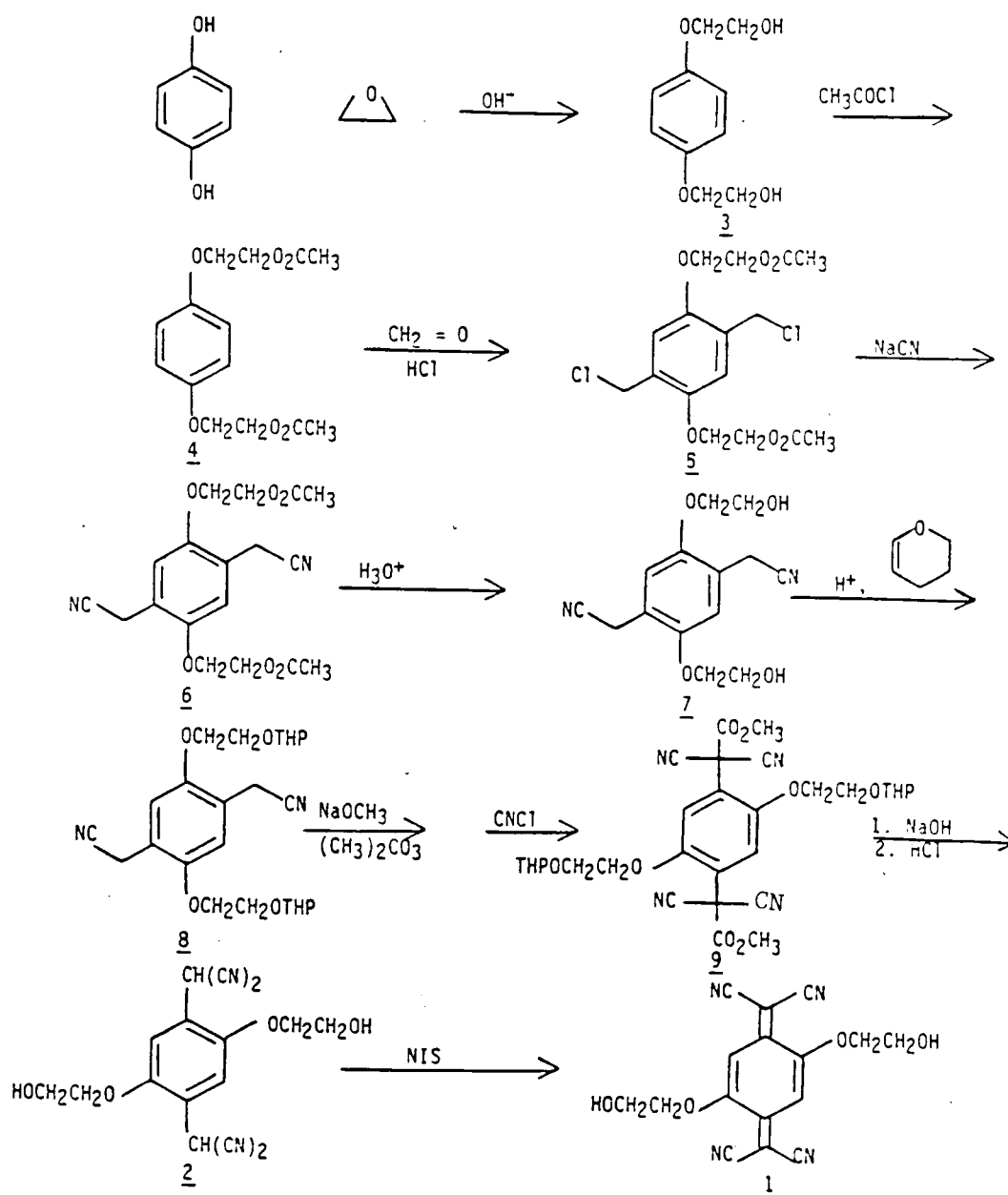


Figure 1. Synthesis of TCNQ diol.

from the reaction vessel. The yields of crude product were comparable to those reported by Fujita⁵⁴ and Day.⁵¹ However, on recrystallization the percent yield decreased significantly.

A mechanism of this reaction was not proposed by Fujita, but in view of the general reaction of phenols,⁵⁵ it is reasonable that the reaction should proceed via the formation of the sodium salt of hydroquinone which is a good nucleophile for the strained ethylene oxide ring. The phenoxy anion intermediates are quenched in aqueous media to regenerate the catalyst eventually resulting in the formation of the desired compound 3. The major side reaction is the attack of the phenoxy anions on ethylene oxide to form polymeric species. This side reaction is eliminated by slow introduction of the ethylene oxide into the reaction vessel. It was observed that subtle changes in the purity of the hydroquinone resulted in dramatic effects on the percent yields. In general, the reaction yielded bone-white crystals which were recrystallized to give white needles with a melting point of 103.5-104.5°C. The yields are summarized in Table I; the proton nuclear magnetic resonance (PNMR) data summarized in Table II and the major IR bands are summarized in Table III. The spectral data and melting point showed excellent agreement with literature data.¹⁰

2. Esterification and Bischloromethylation of 3. Chloromethylation of compound 3 invariably led to products which were difficult to isolate and purify. Under the extremely acidic conditions employed, one can envisage the formation of compound 10 which would react with compound 3 to produce a polymer.

Table I

Yields Obtained from the Ethoxylation Reaction After Recrystallization

Run	Yield	% Yield
1	170 g	41.6
2	345 g	84.4
3	320 g	78.2
4	340 g	83.1

Table II

PNMR Data of Compound 3 Dissolved in D₆ Acetone

Multiplicity	δ	Integration	Assignment
singlet	6.9	14 = 4H	b
multiplet	3.9	27 = 8H	a, a ¹
singlet	3.1		c

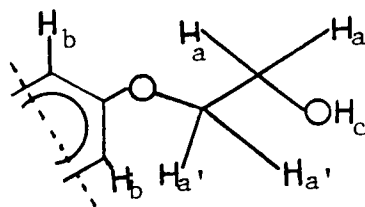
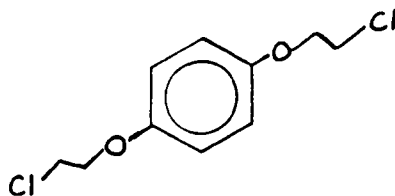


Table III

Major IR Bands Obtained for Compound 3

Wave Number (cm^{-1})	Shape/Intensity		Assignment
3265	b	vs	-OH
2955	s	M	aromatic - CH
2930	s	s	aliphatic - CH
2870	s	M	aliphatic - CH
825	s	vs	1,4-disubstituted benzenes



Compound 10

Many other potential reactions are possible that could irreversibly destroy the alcohol functionality.

To exclude reactions involving this alcohol functionality, it was protected by converting it to the acetate. The ester was chosen as the protecting group because:

- a) it was not expected to interfere with the reactivity of the aromatic nucleus,
- b) it can be prepared very easily in very high yields, and
- c) it could withstand the reaction conditions used in the chloromethylation reaction.

Chloromethylation reactions have been studied by a number of workers.^{56,57} It has been found that for aromatic systems bearing electron releasing substituents, chloromethylation is easier than for those systems bearing electron withdrawing substituents. This is very reasonable in view of the mechanism shown in Figure 2 in which the aromatic nucleus is acting as a nucleophile.

Generally, chloromethylation reactions are carried out using paraformaldehyde in the presence of a proton or Lewis acid catalyst at 30-50°C. At low temperatures Bide and Wilkinson⁵⁷ isolated a monochloromethylated derivative, while at high temperatures polymeric materials of the novalac type⁵⁸⁻⁶¹ in Figure 3 are formed.

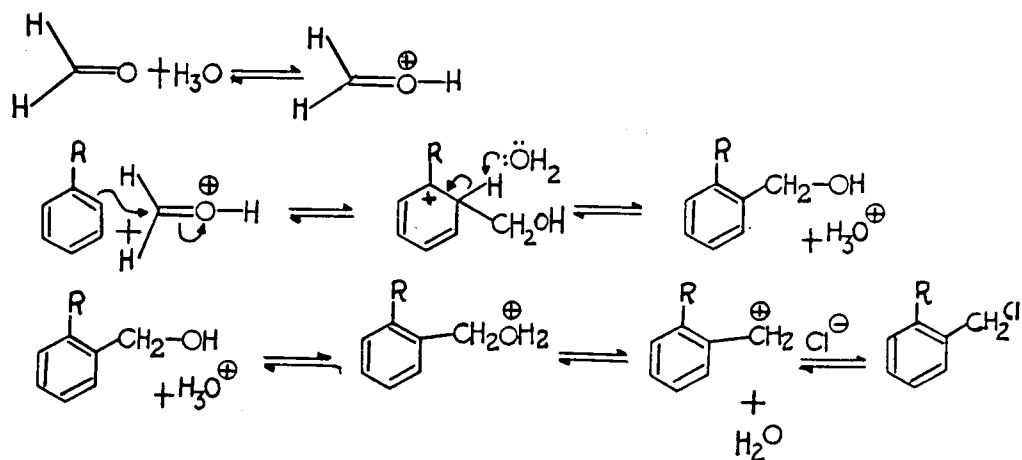


Figure 2. Chloromethylation reaction.

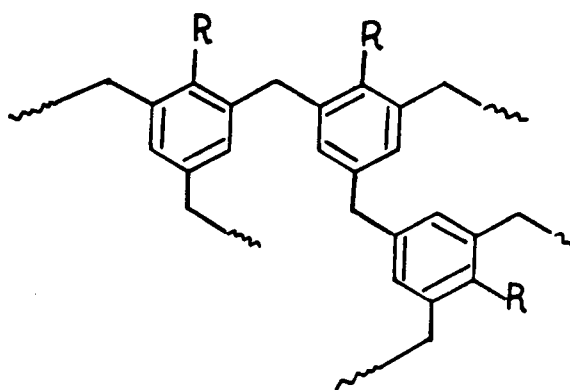
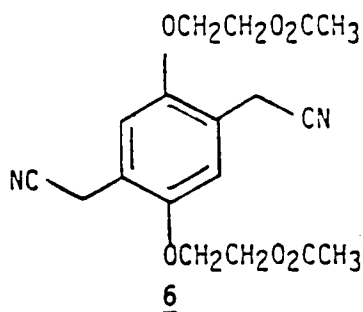


Figure 3. Novalac.

A very important side reaction here is the formation of the lung irritant, bis(chloromethyl) ether.⁶² This compound has been shown to display extremely high carcinogenic activity⁶³⁻⁶⁵ and so precaution should be observed when undertaking this reaction. Our reactions yielded white needles of compound 4 having melting point 95.0-96.0°C after recrystallization. The yield obtained for each reaction run, the PNMR data and the major IR bands are displayed in Tables IV-VI. On the other hand a white powder was obtained for compound 5 having a melting point of 127-129°C after recrystallization. The yields, the PNMR data, and the major IR bands are displayed in Tables VII-IX.

3. Preparation of 2,5-Bis(2'-acetoxyethoxy)-p-xylene dicyanide (6). Bischloromethylated compounds are notably unstable due to



the reactivity of the benzylic chloride.⁵⁷ This is exploited here by replacing the labile chloride with a cyanide group through nucleophilic attack of the cyanide ion on the benzylic carbon.⁶⁶ This is a potentially dangerous reaction due to the formation of hydrogen cyanide gas. To prevent this side reaction, the reactants and solvents are dried prior to use. Correct handling precautions must also be observed to prevent contact with DMSO used in this reaction because it will contain dissolved cyanide.

Table IV

Yields Obtained From Esterification Reaction

Run	Yield	%Yield
1	65.5g ^a	47.1
2	93.4	70.2
3	110.8	83.5

^aProduct was forced out the reaction flask when water at room temperature was added to reaction mixture thus, making yield low.

Table V

PNMR Data of Compound 4 Dissolved in CDCl₃Multiplicity

<u>Singlet</u>	<u>δ</u>	<u>Integration</u>	<u>Assignment</u>
multiplet	6.9	13 = 4H	b
multiplet	4.3	12 = 4H	a
multiplet	4.2	13 = 4H	a'
singlet	2.1	8 = 3H	c

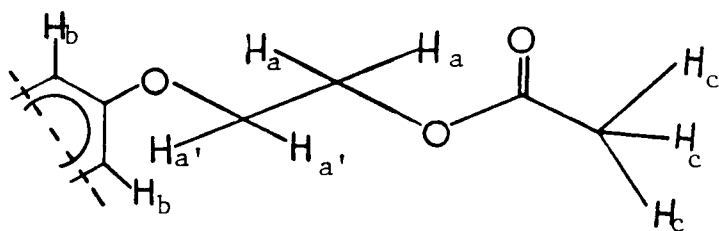


Table VI
Major IR Bands of Compound 4

Wavenumber(cm^{-1})	Shape/Intensity		Assignment
2960	S	M	aromatic C-H
2930	S	S	aliphatic C-H
2875	S	M	aliphatic C-H
1725	S	VS	ester C=O
825	S	VS	1,4-disubstituted benzene

Table VII
Yields Obtained from Bischloromethylation Reaction

Run	Yield	%Yield
1	44.4	82.6
2	47.9	89.1
3	77.5	84.6

Table VIII

PNMR Data of Compound 5 Dissolved in CDCl_3

Multiplicity	δ	Integration	Assignment
singlet	7.1	11 = 2 H	H_b
singlet	4.7	22 = 4 H	H_d
multiplet	4.4	66 = 12 H	$\text{H}_{a'}$
	4.3		H_a
singlet	2.1	33 = 6 H	H_c

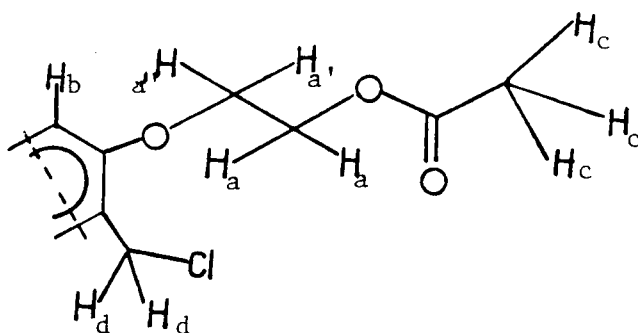


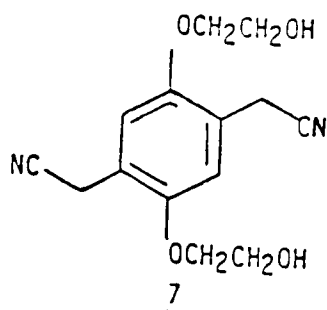
Table IX

Major IR Bands of Compound 5

Wavenumber (cm^{-1})	Shape/Intensity		Assignment
2980	S	M	aromatic C-H
2930	S	S	aliphatic C-H
2875	S	M	aliphatic C-H
1725	S	VS	ester C=O
885	S	M	tetrasubstituted benzene
740	S	S	C-Cl
700	S	M	C-Cl

The reaction yielded compound 6 as a white powder with a melting point of 170°C on a differential scanning calorimetry (DSC) thermogram as shown in Figure 4. The yields for each run, PNMR data and major IR data are summarized in Tables X-XII.

4. Preparation of 2,5-Bis(2'-hydroxyethoxy)-p-xylene dicyanide (7). Converting an ester to an alcohol is generally done by



hydrolysis⁶⁷ using an acidic or basic catalyst, or by reduction⁶⁸ using lithium aluminum hydride (LAH). In hydrolyzing compound 6, extreme care must be exercised because the cyanide group is also susceptible to hydrolysis and reduction.⁶⁹ Reduction using LAH would definitely reduce the cyanide group,⁶⁹ however mild acid hydrolysis should not attack this group. Basic hydrolysis would definitely lead to products where the cyanide group was replaced via SN_2 reaction to give the alcohol.⁶⁹ The logical choice thus, is an acid hydrolysis. Even though this is an equilibrium reaction, the equilibrium lies to the right because the product formed from the hydrolysis is insoluble; almost quantitative yields are obtained when the reaction is run at 30°C for seven days.

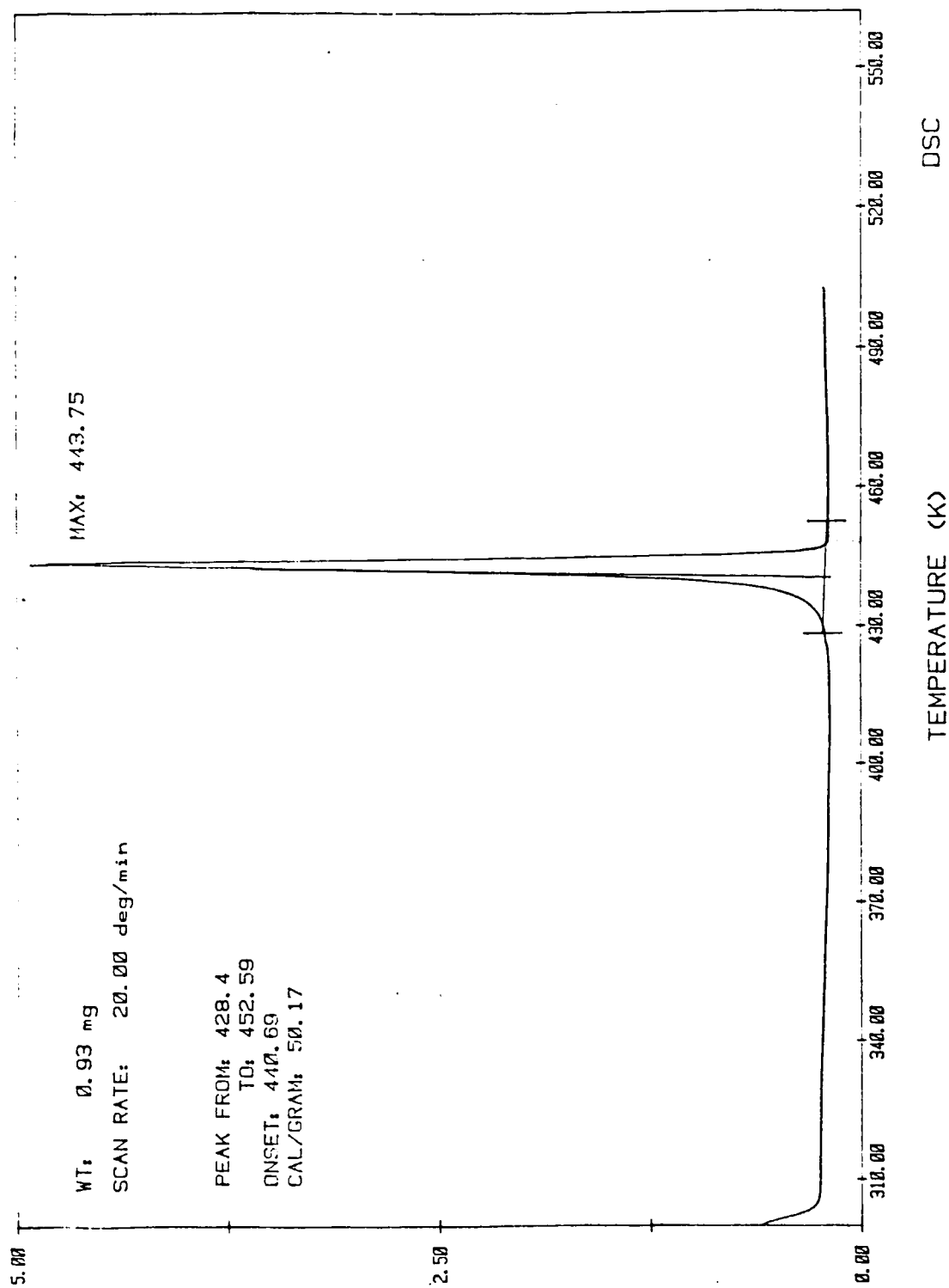


Figure 4. DSC thermogram of compound 6.

Table X

Yields Obtained for Compound 6

Run	Yield	%Yield
1	14.1g ^a	37.1
2	25.3	66.6
3	30.0	75.0

^aA portion was recrystallized from water but it oiled out. This accounts for the low percentage yield.

Table XI

PNMR Data of Compound 6 Dissolved in CDCl₃

Multiplicity	δ	Integration	Assignment
singlet	7.1	5 = 2 H	H _b
multiplet	4.4	20 = 8 H	H _a '
	4.3		H _a
singlet	3.6	11 = 4 H	H _d
singlet	2.1	16 = 6 H	H _c

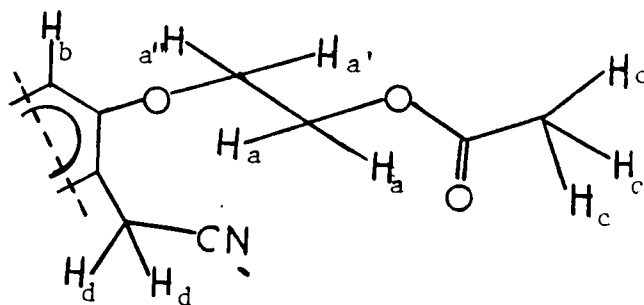
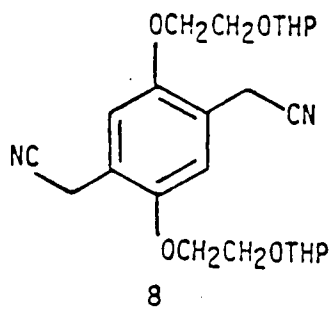


Table XII
Major IR Bands of Compound 6

Wavenumber(cm^{-1})	Shape/Intensity		Assignment
3060	S	W	aromatic C-H
2980	S	M	aliphatic C-H
2950	S	M	aliphatic C-H
2250	S	M	unconjugated $\text{C}\equiv\text{N}$
1725	S	VS	ester $\text{C}=\text{O}$
885	S	S	tetrasubstituted benzene

Compound 7 was isolated as a white powder which gave a melting point by DSC of 184.3°C (see Figure 5). The yield obtained for each reaction run, the PNMR data and IR data are summarized in Tables XIII-XV.

5. Preparation of 2,5-Bis[2'-(tetrahydropyranyloxy)ethoxy]-p-xylene dicyanide (8). The sequence of reactions for the conversion



of compound 7 into a TCNQ derivative would destroy the alcohol group of compound 7. Hence, it must be protected again, but now by a protecting group that is stable under highly basic conditions. Tetrahydropyran (THP) is the protective group of choice, because it reacts quickly and quantitatively under very mild conditions to yield a highly crystalline acetal which is easily purified and stable under basic conditions,⁶⁹ but easily removed under acidic conditions. The procedure outlined was employed by Day.⁵¹

Compound 8 was isolated as a white crystalline material with a melting point of 86.4°C (see Figure 6). The yields, PNMR data and mass spectrometry data are summarized in Tables XVI-XVIII.

6. Preparation of 2,5-Bis(2'-hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane (1) (TCNQ diol).

Table XIII

Yields Obtained From Hydrolysis Reaction

Run	Yield	%Yield
1	7.5	76.4
2	9.7	95.3
3	28.0	96.0

Table XIV

PNMR Data of Compound 7 Dissolved in CDCl_3

Multiplicity	δ	Integration	Assignment
singlet	7.1	5 = 2 H	H_b
multiplet	4.4	21 = 4 H	$\text{H}_{a'}$
	4.3		H_a
singlet	3.8	4 = 2 H	H_d
singlet	2.9		H_c

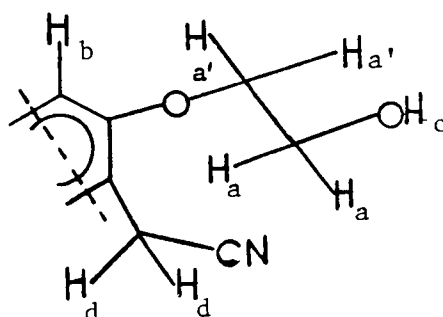


Table XV
Major IR Bands of Compound 7

Wavenumber(cm^{-1})	Shape/Intensity		Assignment
3260	b	S	H-bonded O-H
3170	b	S	unbonded O-H
3260	S	W	aromatic C-H
2940	S	S	aliphatic C-H
2880	S	M	aliphatic C-H
2255	VS	M	unconjugated $\text{C}\equiv\text{N}$
885	S	S	tetrasubstituted benzene

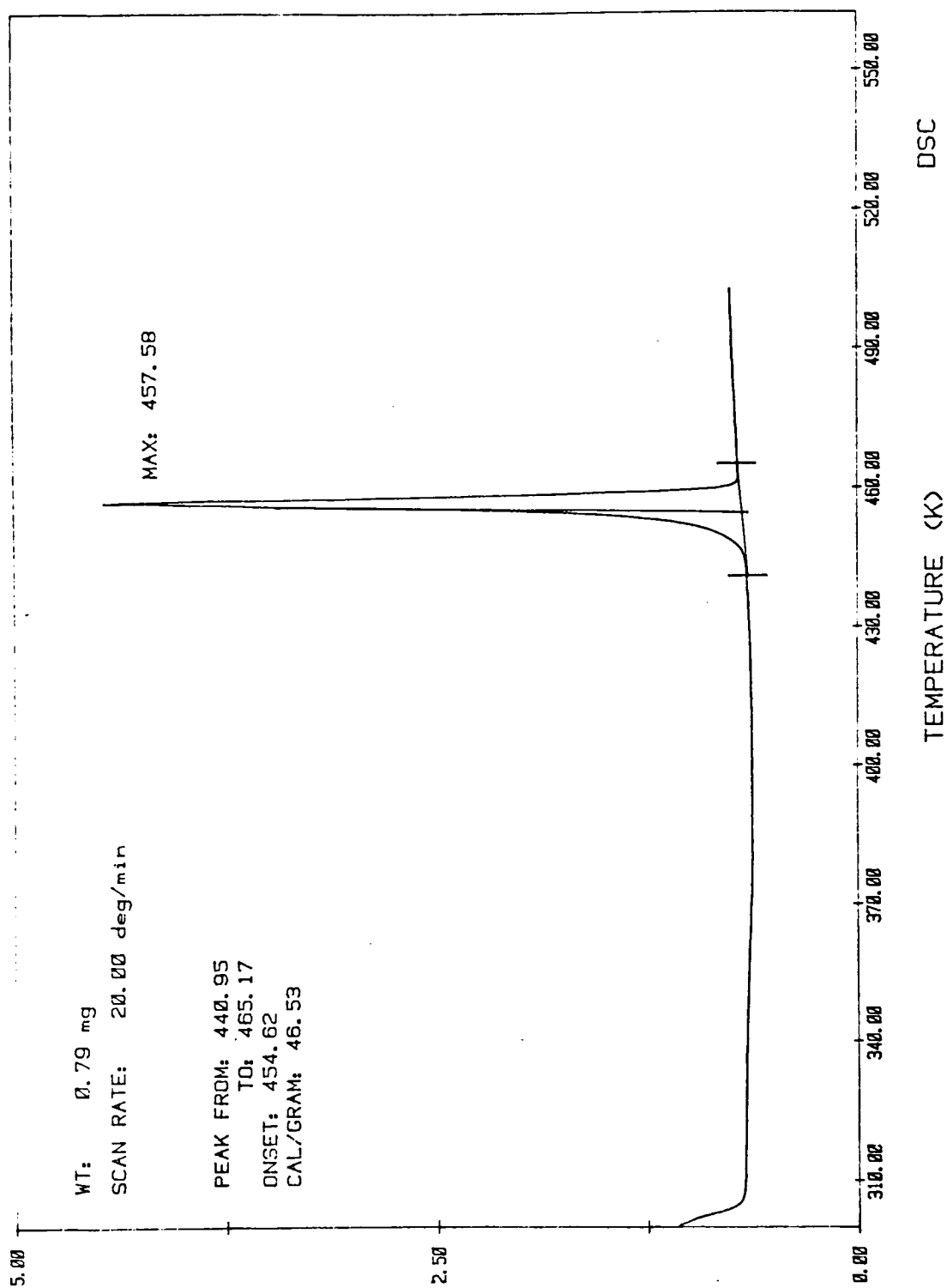


Figure 5. DSC thermogram of compound 7.

Table XVI

Yields Obtained For Tetrahydropyranylation Reaction

Run	Yield	%Yield
1	13.8	98.6
2	12.5	97.1
3	28.0	98.5

Table XVII

PNMR Data For Compound 8 Dissolved in CDCl₃

Multiplicity	δ	Integration	Assignment
singlet	7.1	5 = 2 H	H _b
singlet	4.7	5 = 2 H	H _f
multiplet	4.2	30 = 12 H	H _a , H _g , H _{a'}
singlet	3.8	11 = 4 H	H _d
multiplet	2.0	31 = 12 H	H _c

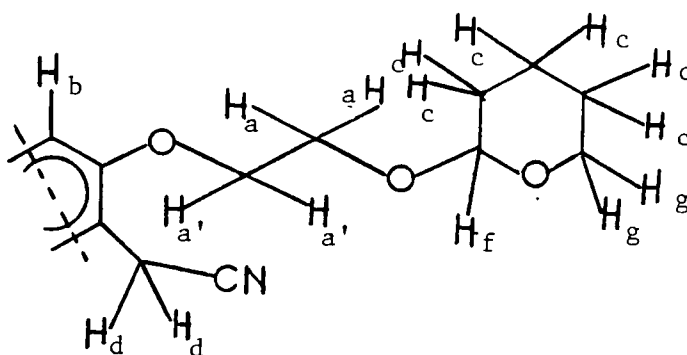


Table XVIII
Mass Spectrometry Data for Compound 8

Mass	% Abundance	Comment
445 (P)	1.3	parent
361	3.0	loss of C_5H_9O
276	20.5	loss of $C_{10}H_{18}O_2$
188	33.1	loss of $C_{14}H_{14}N_2O_3$
161	9.1	$C_9H_6NO_2$
85	100.0	C_5H_9O
84	21.2	C_5H_8O
83	8.9	C_5H_7O
77	22.2	C_6H_6
55	19.8	

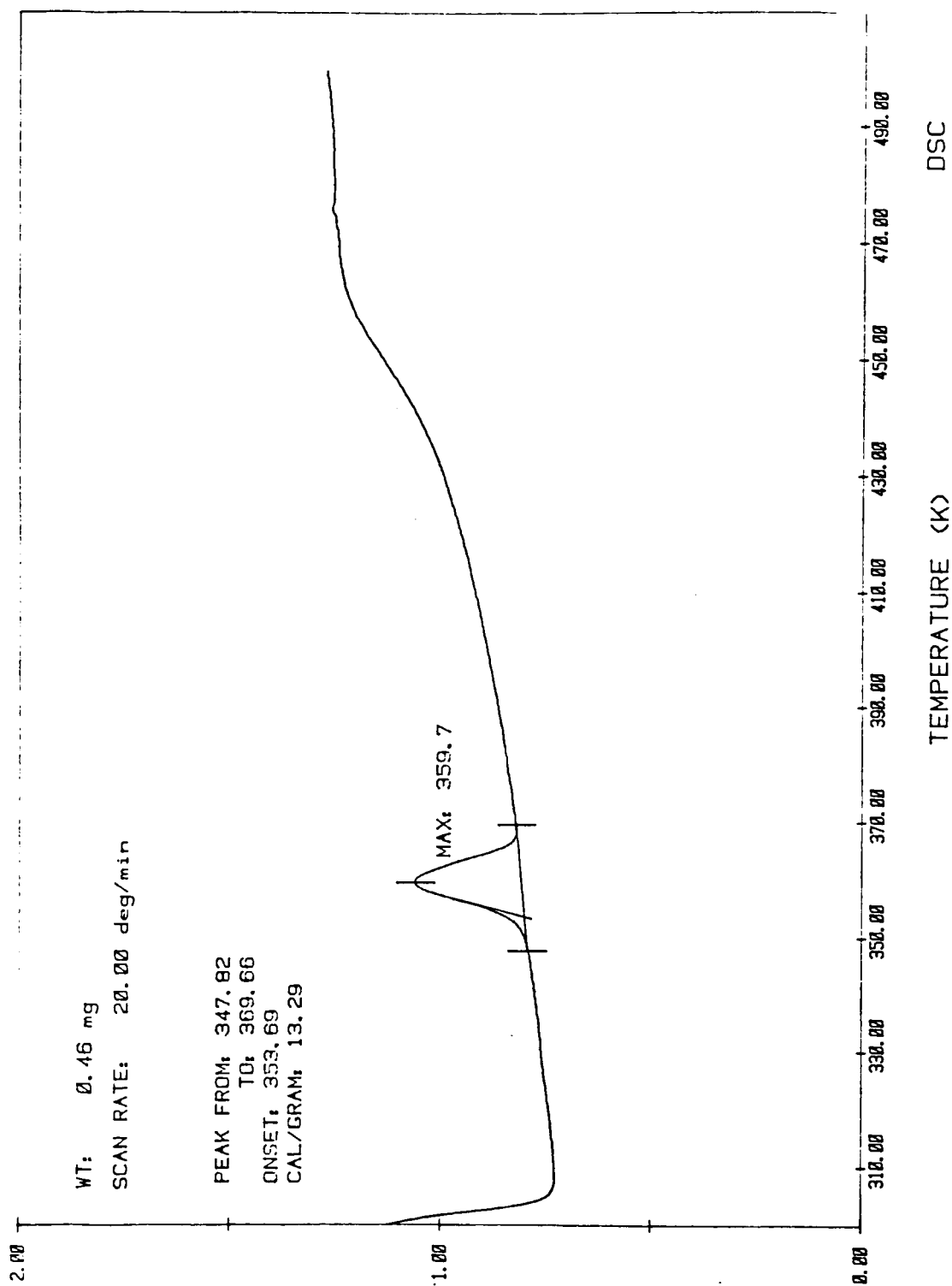
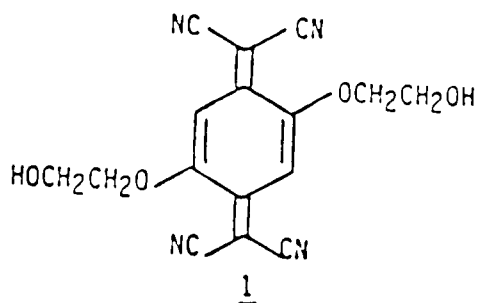


Figure 6. DSC thermogram of compound 8.



Going from compound 8 to the target compound 1 involves the use of fundamental organic reactions. The dianion of compound 8 is formed via the reaction of sodium methoxide on the neutral compound. This is followed by two consecutive Claisen condensations and two Claisen-type condensations involving cyanogen chloride to yield compound 9. Base hydrolysis of the ester group of compound 9, followed by acidification to decarboxylate and deacetalize the alcohol group, gives compound 2. The product can be isolated if the reaction mixture is allowed to stand overnight,⁷⁰ however purification of this unstable compound by recrystallization from ethanol gives compound 1. This is due to the air oxidation of compound 2 in solution. Compound 2 is not generally isolated, however, but is oxidized by N-iodosuccinimide, NIS, to give the desired product, compound 1. These reactions are summarized in the overall reaction scheme given in Figure 1, p 15.

Compound 1 was purified by recrystallization from acetonitrile to yield dark purple needles. The melting point obtained by DSC was 231.3°C followed by a decomposition temperature of 276.8°C. The intensity of the color was observed to be dependent on the rate of crystallization. If the recrystallization process is done slowly, very

dark needles are obtained. On the other hand, if it is done quickly a red powder is observed.

Extreme care must be exercised when adding cyanogen chloride to the reaction mixture. This deadly, colorless, gas is trapped as a colorless liquid at 0°C and then distilled into the reaction mixture which is also kept at 0°C. It was found that using an excess of cyanogen chloride resulted in significantly higher yields than was previously reported.^{25,51} A good indication of the extent of this reaction is reflected in the solubility of the product in sodium hydroxide. We have found that use of less than 100 ml of sodium hydroxide for a run with 7g of compound 8 produced yields for the cyanogen chloride reaction much higher than had previously been reported.^{25,51} (Table XIX.)

The PNMR spectrum shown in Figure 7 of TCNQ diol in solution does not give the resonance values expected for TCNQ diol based on δ values published by Wheland and Martin, for an extensive number of TCNQ derivatives.⁷¹ In all cases, they have found the quinone hydrogens exhibit resonances above $\delta = 6.40$ ppm. Figure 7 shows only one resonance above $\delta = 6.40$ ppm, $\delta = 8.02$ ppm corresponding to resonance contribution from the solvent. The spectrum was further complicated by the presence of inherent radical anions as reported by Wheland and Martin.⁷¹ A small iodine crystal was added to the solution which gave the spectrum of Figure 7 in order to oxidize the TCNQ radical anions via the following reaction:

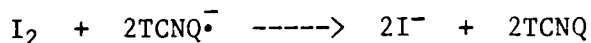


Table XIX

Yields Obtained For TCNQ Diol Based on 7g of Compound 8

Run	Yield	%Yield
1	—	—
2	1.6	31.3
3	0.95	18.6
4	0.85	16.6
5	1.2	23.5

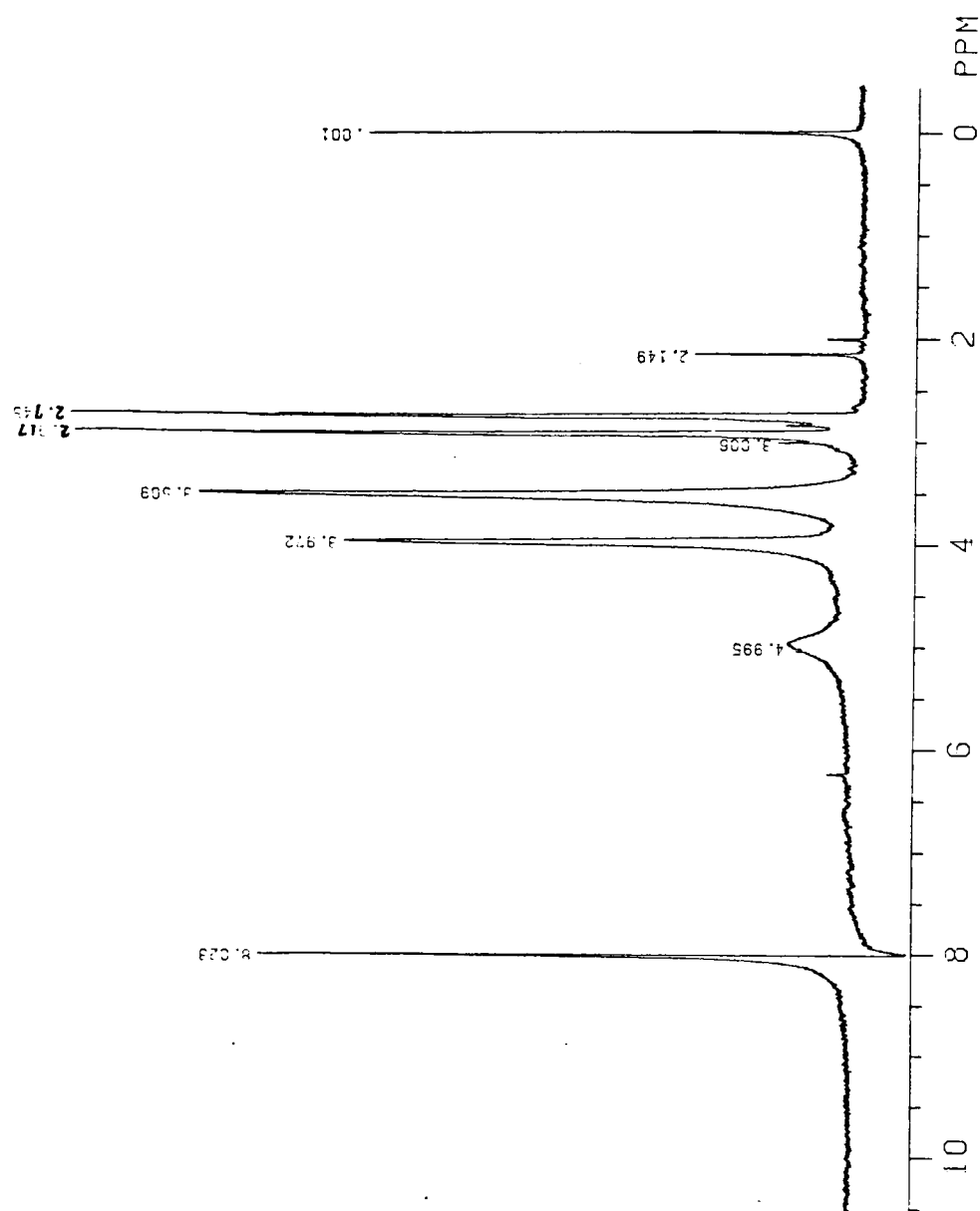


Figure 7. PNMN spectrum of TCNQ diol in d₇ DMF.

The resulting solution gave the spectrum shown in Figure 8 and summarized in Table XX. The spectrum shows resonances at $\delta = 8.01, 6.65, 4.64, 3.98, 3.85, 2.91, 2.74$ and 2.15 ppm. The resonances at $\delta = 8.01, 2.91$ and 2.74 ppm were due to the solvent. The resonance at $\delta = 6.65$ ppm was assigned to the quinone hydrogens, consistent with published PNMR of TCNQ and its derivatives.^{15-17,25,71} The resonances at $\delta = 4.64$ and 3.98 ppm were assigned to the methylene hydrogens, while the resonance at $\delta = 3.85$ was attributed to the hydroxyl hydrogen and water. The minor resonance at $\delta = 2.15$ ppm must be due to impurities since all the hydrogens have been accounted for.

The cyclic voltammogram, CV, shown in Figure 9 displays two reversible oxidation and reduction waves at peak potentials, $E_p^{c1} = -24\text{mV}$ and $E_p^{1a} = 44\text{mV}$ coupled with $E_p^{c2} = -550\text{mV}$ and $E_p^{a2} = -485\text{mV}$ giving $E_{1/2}^1 = 10\text{mV}$ and $E_{1/2}^2 = -517\text{mV}$ vs. Ag/AgI. The negative shift of the $E_{1/2}$ values of TCNQ diol when compared with $E_{1/2}$ values of TCNQ is as expected.^{16,37} The reasons for this shifting are discussed in Chapter III.

The UV-VIS spectrum shown in Figure 10 is in excellent agreement with published UV-VIS data TCNQ and its derivatives.^{16,17,35} A doublet is seen at $\lambda_{\text{max}} = 430 \text{ nm}$ ($\log \epsilon = 5.46$) and $\lambda_{\text{max}} = 410 \text{ nm}$ ($\log \epsilon = 5.44$). The IR spectrum displays major absorbances at $3550, 3440; 3060, 2950, 2980, 2230, 2220$ and 1540 cm^{-1} . The bands at 3550 and 3440 cm^{-1} were assigned to hydrogen bonded and free -O-H stretching frequencies. The band at 3060 cm^{-1} was attributed to the unsaturated C-H stretching frequency,¹⁷ while 2950 and 2980 cm^{-1} were assigned to the saturated C-H stretching frequencies. The $\text{-C}\equiv\text{N}$ stretching

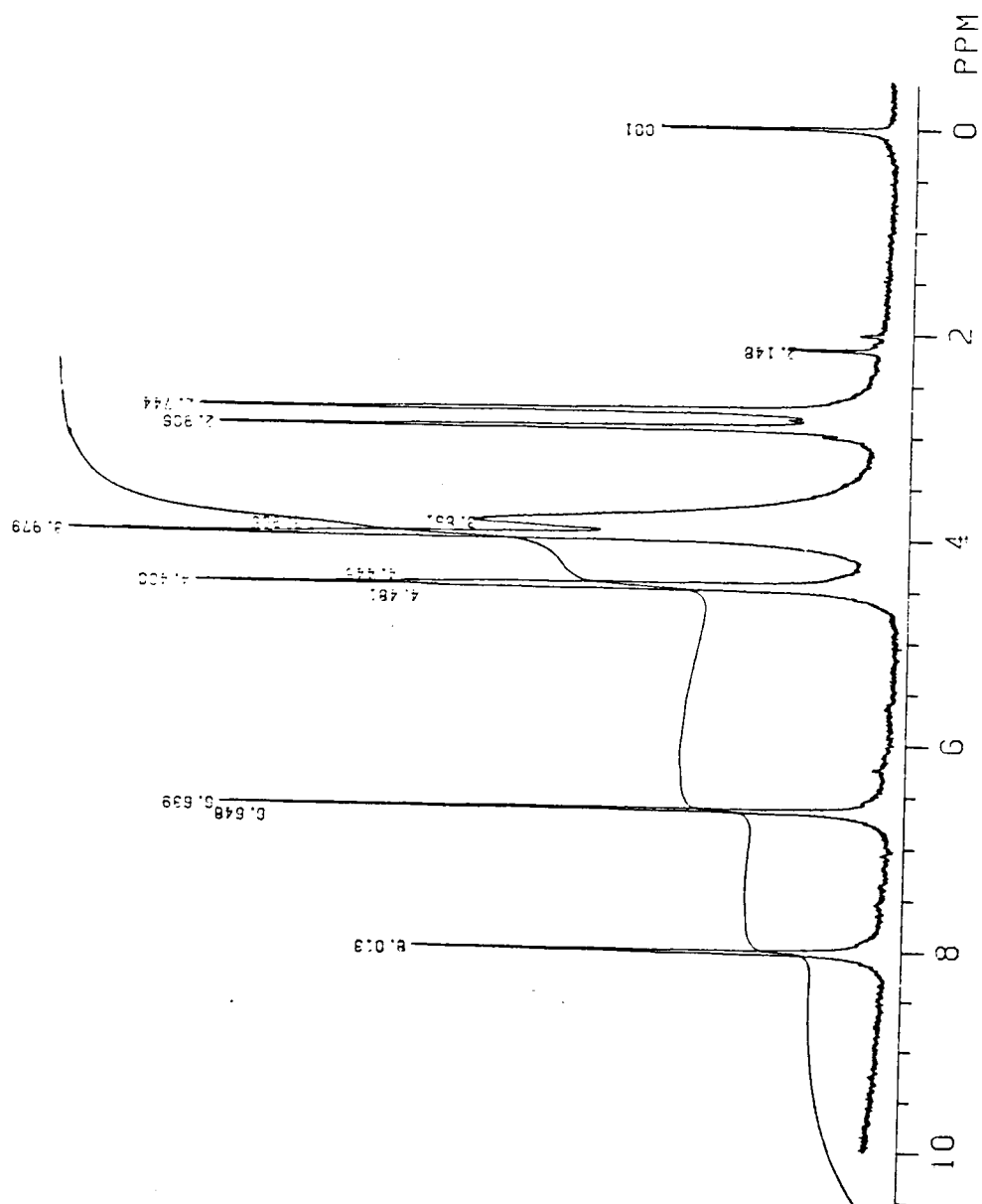
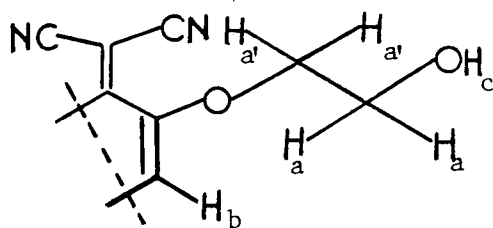


Figure 8. PNMR spectrum of TCNQ diol in d_7 DMF after the addition of iodine.

Table XX

PNMR Data of TCNQ Diol Dissolved in D₇ N,N,dimethylformamide

Multiplicity	δ	Integration	Assignment
singlet	6.65	2H	H _b
triplet	4.46	4H	H _{a'}
triplet	3.98	4H	H _a
singlet	3.85		H _c



↑
5μA
↑

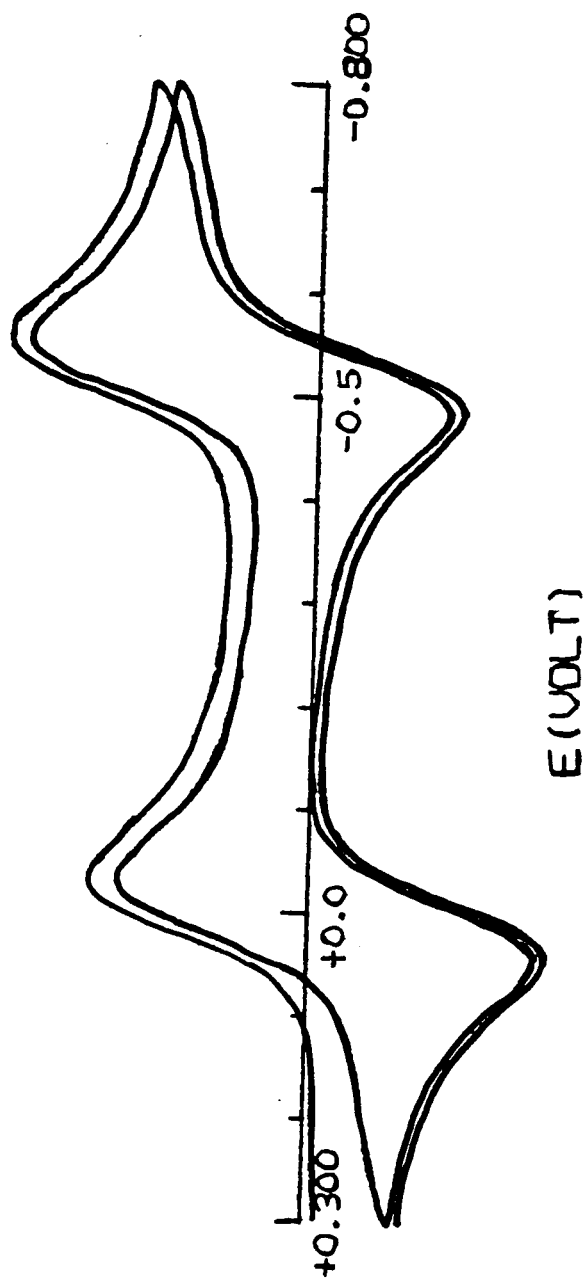


Figure 9. Cyclic voltammogram of TCNQ diol in 0.1M TEAP/DMA vs Ag/AgCl. 50 mV/S

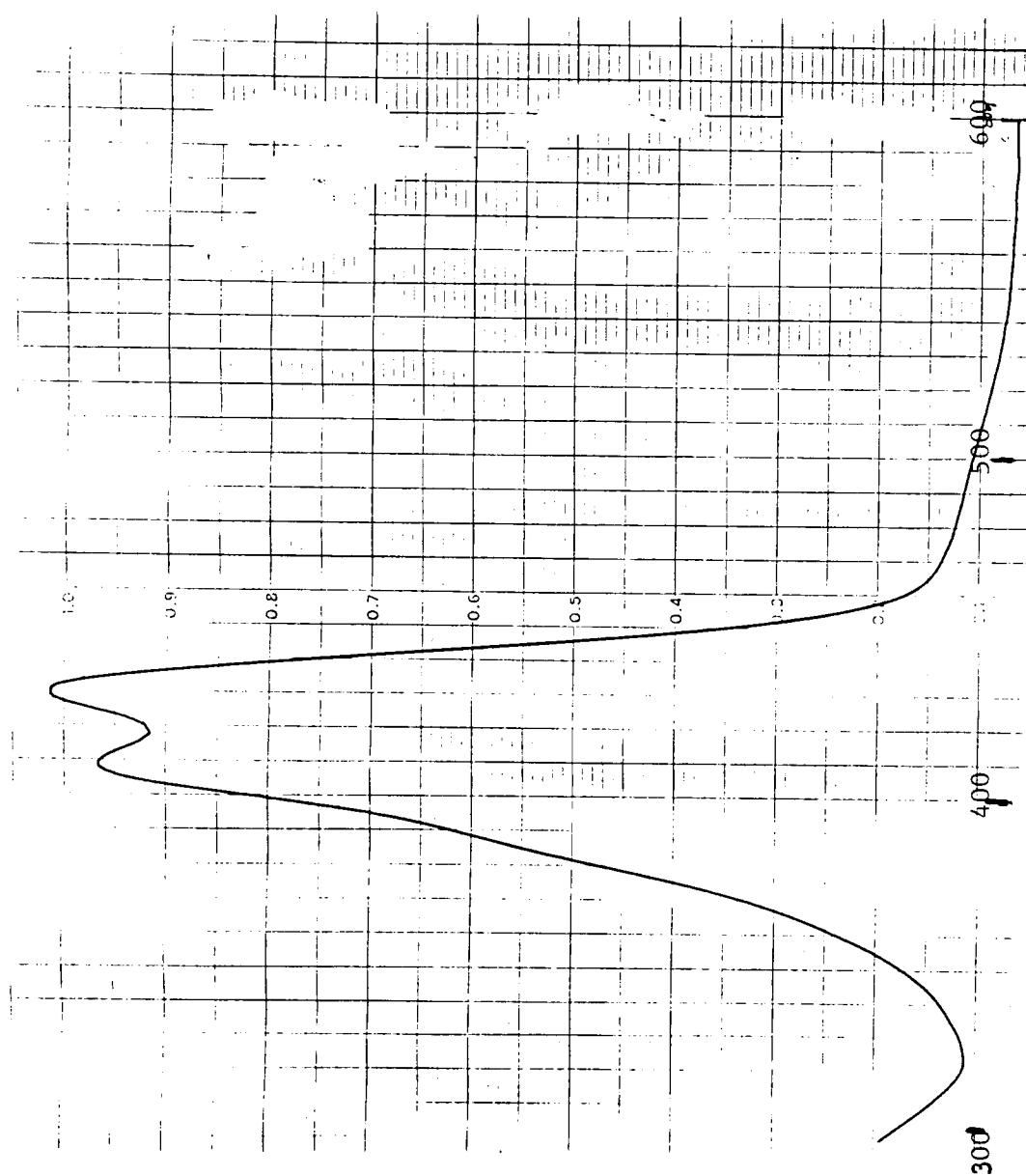


Figure 10. UV-VIS spectrum of TCNQ diol in acetonitrile.

frequencies were found at 2230 and 2220 cm^{-1} , as would be expected for a conjugated nitrile.¹⁷ The C=C stretching frequency at 1540 cm^{-1} is in the range expected for a conjugated cyanoolefin.¹⁷ These IR data are summarized in Table XXI.

The ^{13}C -NMR spectrum of compound 1 was also obtained, see Figure 11 and Table XXII. The assignments are based on standard ^{13}C -shifts of other molecules with similar functionalities. The resonance at $\delta = 149.3$ was assigned to C4 and C5. The C-5 assignment was based on chemical shifts reported for methylvinyl ether, $\text{CH}_2 = \text{CH}-\text{OCH}_3$, $\delta = 153.2$ and C-2 of 2-methyl-1,4-cyclohexadienedione, $\delta = 150.0$. The reason for the broadening of the signal at $\delta = 104.4$ ppm is not clear. It is possible that this line is broadened by the presence of radical species, but then the resonance at $\delta = 149.3$ should also have been broadened. Also, the concentration of radicals in the sample should be minimal (if any) because a small iodine crystal was dissolved in the solution to act as a radical scavenger. The absence of a signal assigned to C-7 may be due to C-7 having a longer relaxation time than either C5 or C6. This resonance should be evident if the time between pulses is increased ($\delta = 110$ -117 ppm).

B. Experimental Section

Apart from the ^{13}C CNMR and PNMR spectra of TCNQ diol (which were done on a 200 MHz NMR) all the PNMR spectra were obtained on a 90 MHz NMR. The IR of the samples were obtained by evaporating a solution on a KBr disc and using a Perkin Elmer 1330 spectrometer. The cyclic voltammograms were recorded on a BAS 100 Bioanalytical system.

Table XXI

Major IR Bands of TCNQ Diol Smeared on KBr Plate

Wavenumber(cm^{-1})	Shape/Intensity		Assignment	
3550	s	m	hydrogen bonded	O-H
3440	b	w	unbonded	O-H
3060	s	m	quinone	C-H
2950	s	s	aliphatic	C-H
2980	s	s	aliphatic	C-H
2230	s	s	conjugated	C=N
2220	s	s	conjugated	C $\equiv$ C
1540	b	s	conjugated	C=C

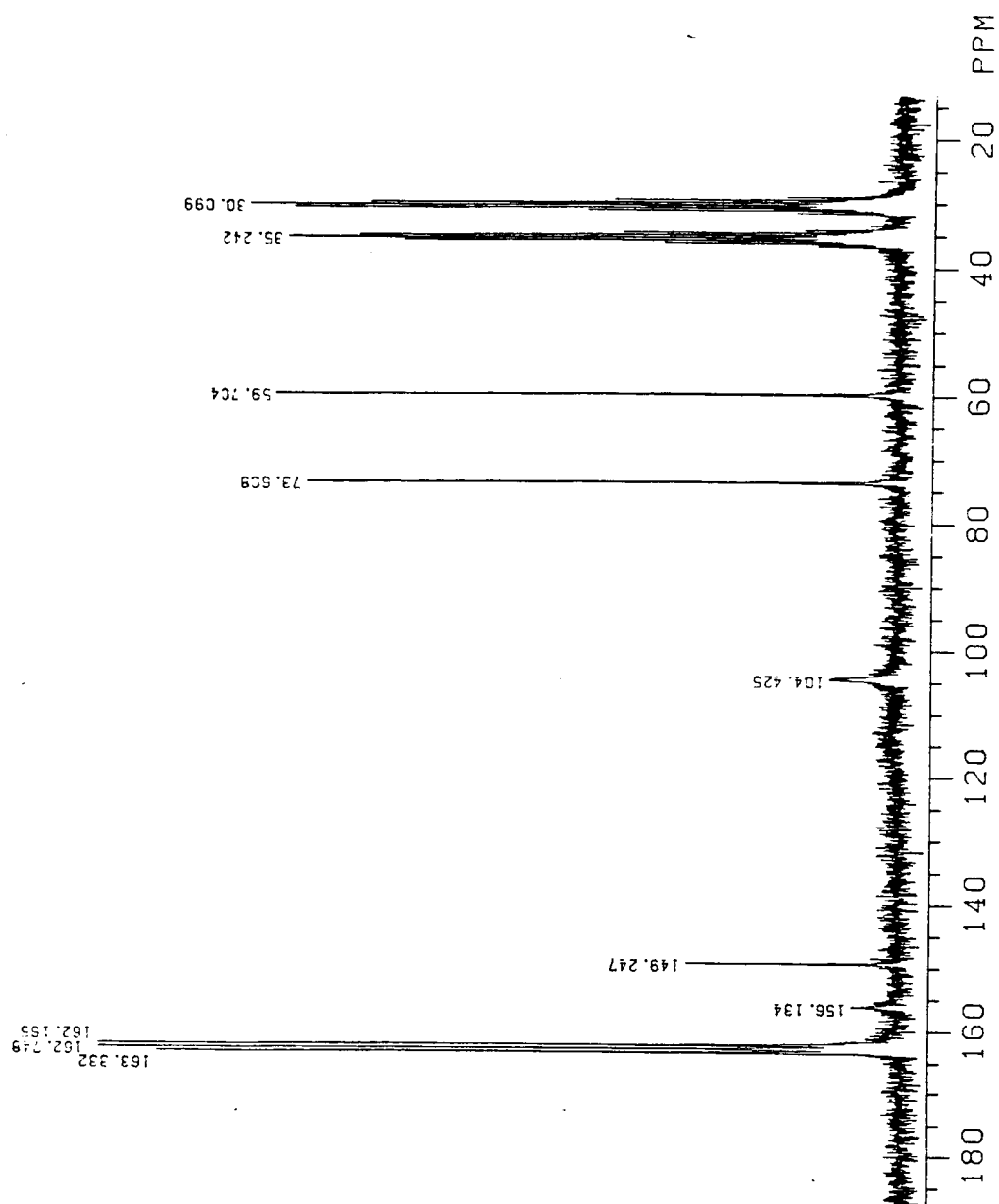
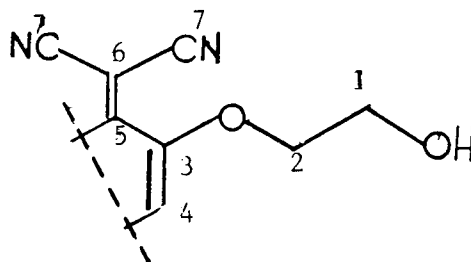


Figure 11. ^{13}C NMR spectrum of TCNQ diol in d_7 DMF.

Table XXII

 ^{13}C -NMR Data of TCNQ Diol Dissolved in D_7 DMF

δ	Assignment
59.7	C-1
73.6	C-2
104.4	C-6
149.3	C-4; C-5
156.1	C-3



a. Synthesis of 1,4-Bis(hydroxyethoxy)benzene (3). In a 1-liter 3-necked round-bottom (r.b.) flask equipped with a dry ice-ethanol cooled trap was dissolved 2.7 g (0.0675 mole) sodium hydroxide in 680mL distilled water. After bubbling nitrogen through the solution for 1/2 hour, 227 g (2.064 moles) of hydroquinone was added with vigorous stirring, and nitrogen bubbled through the slurry for an additional 1 hour. The reaction mixture was heated to 80°C and then 200 g (4.545 moles) of ethylene oxide was slowly distilled into the reaction mixture. After the addition of ethylene oxide was completed, the reaction mixture was stirred at 80°C for 3 hours, then poured into a beaker, and set to cool. This yielded bone-white crystals (yield = 82%) which were recrystallized from water or acetonitrile to give white needles with a melting point of 103.5-104.5°C after drying in a vacuum oven overnight at 50°C. The melting point and PNMR spectrum of the product showed excellent agreement with literature data.¹⁰

b. Synthesis of 1,4-Bis(acetoxyethoxy)benzene (4). To 93.2 g (0.47 mole) of compound 3 in a r.b. flask equipped with condenser and stirrer was slowly added 500 g (6.370 moles) acetyl chloride through the condenser. A sharp exotherm was observed. After the exotherm subsided, the reaction mixture was gently refluxed overnight. The mixture was then cooled to room temperature and diluted slowly by adding ice cold water through the condenser until the evolution of hydrogen chloride ceases. After cooling the reaction mixture, a white solid precipitated which was recrystallized from ethanol to give white needles with melting point of 95.0-96.0°C.

c. Synthesis of 2,5-Bis(2'-acetoxyethoxy)-p-xylene dichloride

(5). To a resin pot equipped with condenser, gas inlet for hydrogen chloride gas, overhead stirrer and thermometer were added 50 mL concentrated hydrochloric acid, 60 mL glacial acetic acid, 40 g of compound 4 (0.1418 mole) and 10 g of paraformaldehyde. The reaction mixture was rapidly stirred and a sharp exotherm, which was not allowed to exceed 30°C, was noted. A precipitate appeared after about 35 minutes. The temperature was raised to 45°C and kept at this temperature for 2 hours before the reaction mixture was set to cool to room temperature. The product was collected by vacuum filtration, washed with water to remove all traces of acetic acid, and then recrystallized from methylene chloride to yield a white solid. Its melting point was determined from a DSC thermogram to be 127-129°C (Tables VII-IX).

d. Synthesis of 2,5-Bis(2'-acetoxyethoxy)-p-xylene dicyanide

(6). In a 1-liter 3-necked r.b. flask flushed with nitrogen and equipped with a mechanical stirrer, thermometer, and reflux condenser were placed 72 mL dimethylsulphoxide (DMSO) previously dried over 4 Å molecular sieves and 13.6 g (0.2725 mole) sodium cyanide. After most of the sodium cyanide had dissolved, 40 g (0.1055 mole) of compound 5 was added and a sharp exotherm was observed. After the exotherm, which was not allowed to exceed 50°C, had subsided, the reaction mixture was heated with constant stirring to 50°C for one hour. Then the temperature was raised to 85°C for about 5 minutes and the reaction mixture set to cool to room temperature.

The mixture was poured into 300 mL distilled water and the solids collected by filtration. The filter cake was washed with copious

amounts of water and ether after which it was recrystallized from dioxane to give a white solid which showed a melting point of 170°C on a DSC thermogram. The structure was confirmed using PNMR and IR (Tables X-XII).

e. Synthesis of 2,5-Bis(2'-hydroxyethoxy)-p-xylene dicyanide (7). In a 1-liter flask, 12.78 g (0.0355 mole) of compound 6 was dissolved in a mixture of 200 mL acetonitrile, 200 mL dioxane and 80 mL 10% (V/V) hydrochloric acid. The solution was stirred at 30°C for 7 days. In some instances there was a precipitate after 45 mins, however in such cases the temperature was raised to increase the solubility and then brought back to 30°C after all the solid had dissolved. After 7 days, the cloudy solution was filtered to yield a white solid. A DSC thermogram revealed a melting point of 184.3°C. The structure was characterized by PNMR and IR (Tables XIII-XV).

f. Synthesis of 2,5-Bis[2'-(tetrahydropyranyloxy)ethoxy]-p-xylene dicyanide (8). In a 250 mL r.b. flask equipped with magnetic stirrer, reflux condenser and hot plate were placed 8.7 g (0.0315 mole) of compound 7, 40 mL tetrahydrofuran (THF), 24.5 mL dihydropyran (DHP) and 53.7 mg p-toluene sulphonic acid monohydrate. The reaction mixture was gently heated with stirring until a homogenous solution was obtained. This was then refluxed for 2 hours, after which it was poured into 225 mL benzene and then washed with three-100 mL portions of saturated sodium bicarbonate solution. The organic layer was dried over anhydrous magnesium sulfate, and then the solvent was removed on a rotary evaporator. This gave a waxy, yellowish solid which was recrystallized from cyclohexane to give a white crystalline material

with a melting point of 86.4°C. The structure was confirmed using PNMR and mass spectrometry (Tables XVI-XVIII).

g. Synthesis of 2,5-Bis(2'-hydroxyethoxy)-7,7,8,8-tetracyano-quinodimethane (1). A mixture of 7 g (0.0158 mole) of compound 8, 2.2 g of freshly prepared sodium methoxide and 32 mL dimethylcarbonate (DMC) was placed in a 100 mL r.b. flask equipped with overhead stirrer, reflux condenser and thermometer. The mixture was refluxed for 3 hours, 10 mL toluene added, and an azeotrope of toluene-methanol distilled off. The reaction mixture was cooled to 0-5°C and then 5.0 mL of cyanogen chloride, previously trapped in an ice bath, was distilled into the flask. The temperature was kept at 0-5°C for 2 1/2 hours and then slowly warmed to 50°C before it was brought back to room temperature.

The solvent was removed by rotary evaporation and the remaining solid dissolved in 80 mL of 10% sodium hydroxide. On acidification a gas evolved and a dark red-black oil floated on top of the solution. This oil was dissolved in 450 mL methylene chloride and dried over anhydrous magnesium sulphate. The methylene chloride was removed by rotary evaporation and the remaining oil dissolved in 200 mL acetonitrile. To this was added a warm solution of 1.5 g of NIS in acetonitrile. The temperature was maintained at 35-40°C for 30 minutes with constant stirring. After removal of the acetonitrile by rotary evaporation, the solid was dissolved in 30 mL methanol and water added slowly until no more solid precipitated from the methanol. The solid was recrystallized from acetonitrile to give reddish-purple needles with a melting point of 231.1°C and a decomposition temperature of

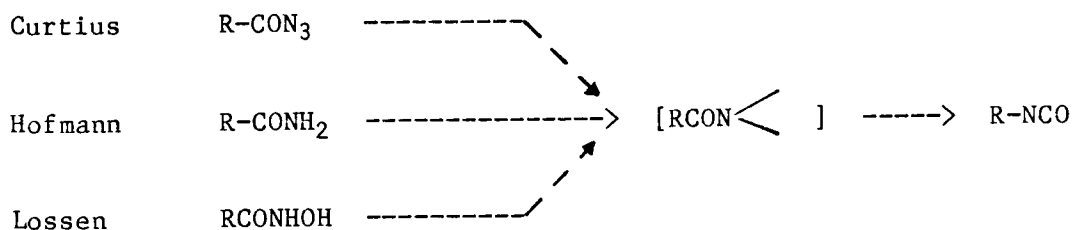
276.7°C The molecule was characterized further by UV-VIS, IR, NMR, and cyclic voltammetry (Tables XIX-XXII).

CHAPTER III

POLYMER SYNTHESIS AND CHARACTERIZATION

A. Introduction

Isocyanates are usually prepared by one of three reactions: Curtius rearrangement of azides, Hofmann rearrangement of amides, or Lossen rearrangement of hydroxamic acids. The method of choice is dependent on the type of isocyanate required.



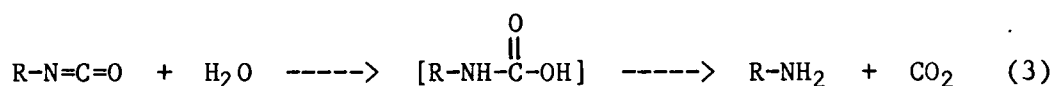
The reaction of isocyanates with alcohols to yield urethanes has long been studied and has been summarized in many excellent texts.^{48,72-74} The synthesis of polyurethanes was first reported in a 1947 paper from the laboratory of Professor Otto Bayer.⁷⁵ Soon after, many patents and papers appeared on the preparation of polyurethane via different synthetic routes including the reaction of diamines and bischloroformate at low temperature,^{76,77} and the reaction of 1,4-dichloro-2-butene with sodium cyanate and a diol.^{78,79} Additionally, the carbamate interchange reaction has also been utilized, especially in one-package type adhesive and coating formulations.^{80,81,82}

Industrial applications of polyurethanes are numerous and their importance cannot be over emphasized. They have found applications in

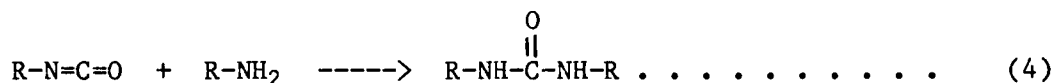
the area of adhesives,⁸³ coatings,⁸⁴ flexible and rigid foams,^{75,85-87} elastomers,⁸⁸ fibers,⁷⁹ waterproofing,⁹⁰ thermoset resins,⁹⁰ thermoplastic molding compounds,^{91,113} and rubber vulcanization.⁹² More recently polyurethanes are being examined for utility in reaction injection moulding (RIM) processes,⁹⁴ as absorbents,¹²⁴ and in the electronic industry.^{126,127}

The synthesis of polyurethanes via reaction of a diol and a diisocyanate has several special requirements due to the activity of the isocyanate towards a variety of reagents. This is further complicated by the influence of various catalysts on the reactivity of the isocyanate group. In order to appreciate the task of making a linear polyurethane, some of the more prominent side reactions are outlined below.

a. Reaction of Isocyanates With Water. Water reacts with isocyanates to produce a variety of compounds. The first product is the unstable carbamic acid, which usually reacts further by loss of carbon dioxide to form an amine:

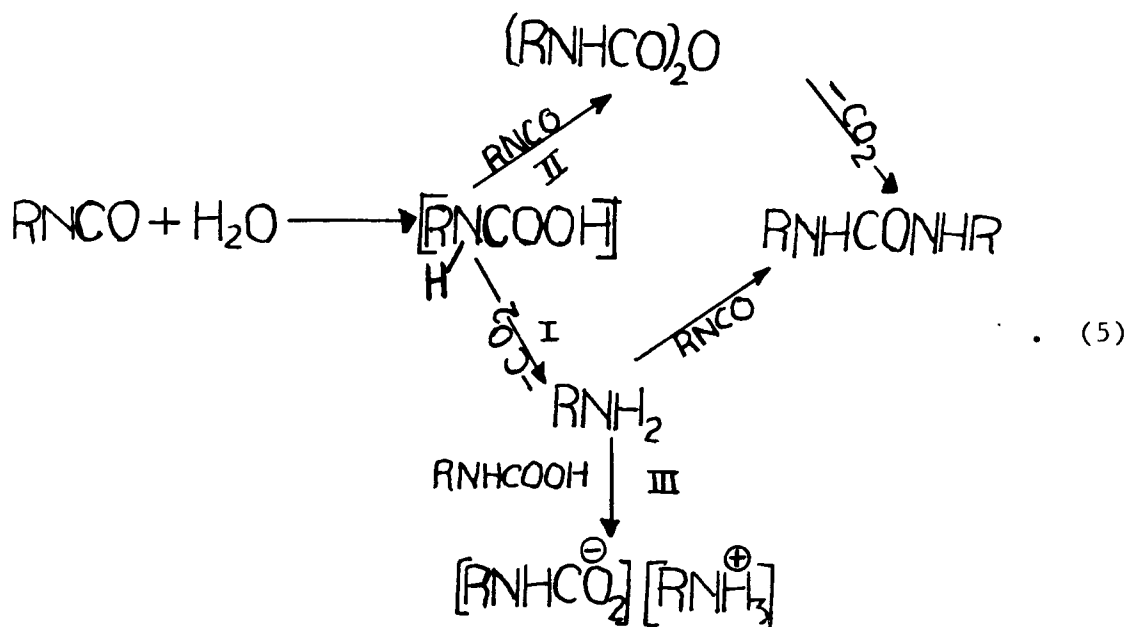


The amine reacts with more isocyanate to produce a disubstituted urea:



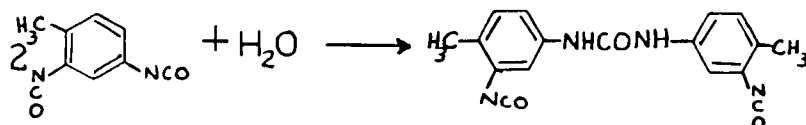
Even though equations (3) and (4) represent the principal pathway of the isocyanate-water reaction, it has been suggested that several other

pathways are possible to yield substituted ureas,⁴ as outlined in Equation (5).

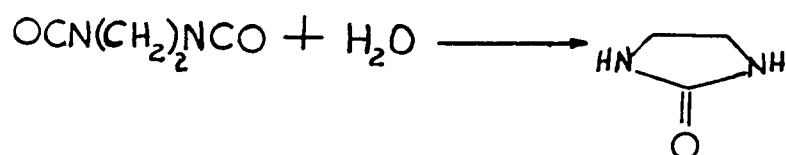


Saunders and Frisch⁴⁸ state that pathway I would be favored when the carbamic acid is very unstable. If the carbamic acid is fairly stable, the significance of pathway II increases. Pathway III may be significant when the reaction between the amine and the isocyanate is very slow. The slow reaction between the amine and the isocyanate can be attributed to several factors, of which steric hindrance seem to be the most important.

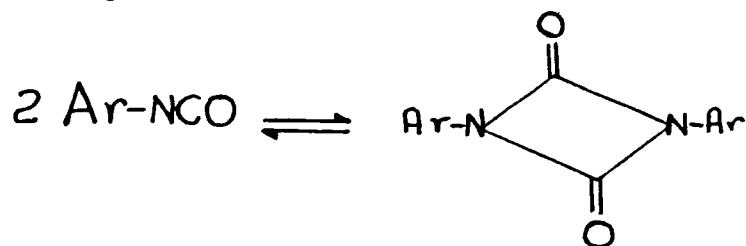
The reaction of aromatic diisocyanates, containing ortho methyl groups, with water can be specific. Dupont workers have shown that good yields of the corresponding urea can be prepared from two moles of toluene diisocyanate with one mole of water:^{95,96}



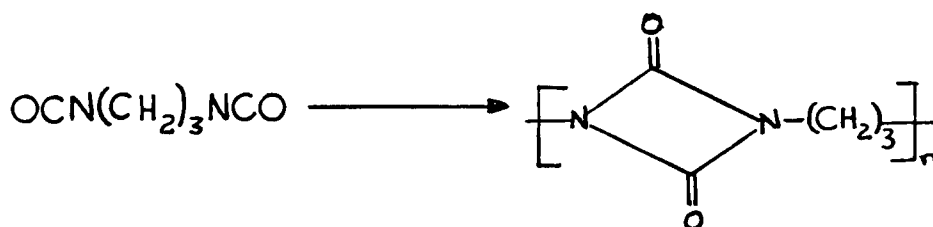
On the other hand, aliphatic diisocyanates of the form $\text{OCN}(\text{CH}_2)_n\text{NCO}$ react differently. If n is greater than or equal to three a 75:25 mixture of cyclic urea and polymer is formed. When n is equal to two a cyclic urea is obtained:^{97,98}



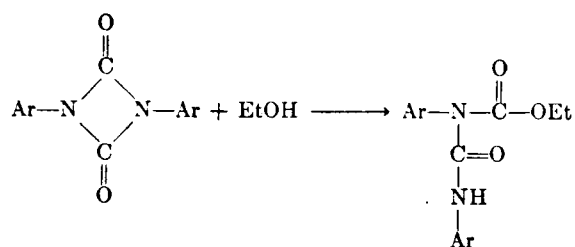
b. Dimerization Reactions. Aromatic isocyanates will dimerize quite easily to form 1,3-diazetidines-2,4-diones.^{72,99,100,102} Certain isocyanates, e.g., 4,4'-diphenylmethane diisocyanate, dimerize even on standing at room temperatures in the absence of a catalyst. The rate of dimerization is greatly retarded by ortho substitution on the aromatic ring.



Dimers from aliphatic isocyanates have been observed, but are very difficult to isolate.¹⁰¹ However, the formation of a polymeric dimer resulting from trimethylene diisocyanate has been reported:

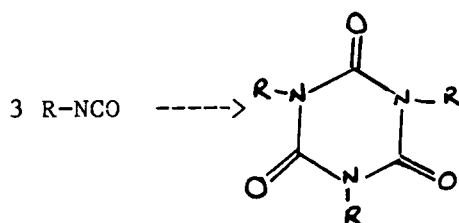


Fortunately, the dimerization of aromatic isocyanates is reversible, and can be minimized by a storage at low temperatures or raising the temperature to about 40–50°C.³⁰ However, these dimers may react with alcohols. The most common ring opening product is the corresponding allaphonate.⁹⁹



Dimerization of isocyanates is exploited in "blocked isocyanates."^{81,82}

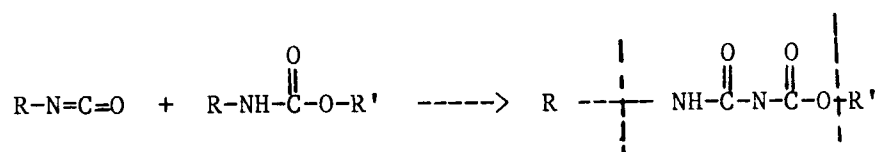
c. Trimerization of Isocyanates. Isocyanates also trimerize, but unlike dimerization, in an irreversible reaction to produce isocyanate rings or



perhydro-1,3,5-triazine-2,4,6 triones.^{47,104} The isocyanurates are exploited in the formation of high temperature resistant polyurethanes,^{47,105,106} however some isocyanurates have been reported to

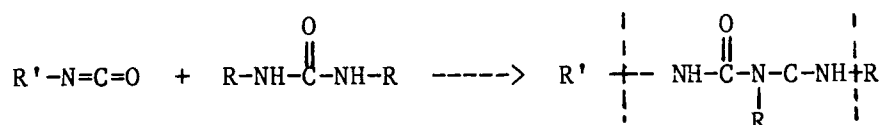
form carbodiimide on further heating.^{47,107,108,109} In general, electron-attracting groups substituted on a phenyl ring accelerate trimerization, whereas electron-donating groups retard the reaction. Steric factors also strongly influence trimerization of isocyanates.^{47,104}

d. Allophanate Formation. Allophanates are formed from the reaction of isocyanates and urethanes:¹¹⁵



This reaction generally occurs at elevated temperatures, however in the presence of a catalyst, this reaction will occur even at room temperatures.

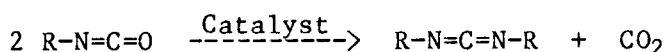
e. Biuret Formation. As discussed earlier, if water is present, isocyanates will react to form amines. Amines react very rapidly with isocyanates to form substituted ureas. The ureas can react further with isocyanates to form an addition product, a biuret:



This reaction generally requires temperatures at or above 100°C to be significant; however in the presence of certain metal catalysts, biuret may be formed at significantly lower temperature.¹²⁰

f. Carbodiimide Formation. When isocyanates are heated to elevated temperatures, or polyurethanes are thermally degraded,

carbodiimide or polycarbodiimide can be isolated.¹⁰⁹ Generally, carbodiimides result from heating the isocyanate in the presence of a phosphine-type catalyst.¹¹⁰ Neumann and co-workers¹¹¹ have



reported that the resistance to hydrolysis of polyester-based urethane elastomers can be significantly improved by the addition of small amount of polycarbodiimide.

g. Role of Catalyst. The role of the catalyst in polyurethane formation is very important, as the choice of catalyst will influence the formation of dimers, trimers, allophanates, biurets and many other side products. Numerous excellent reviews¹¹⁶⁻¹¹⁹ have been written on this subject. This section, like the previous sections in this chapter, is by no means intended to detail any specific area in the catalysis of isocyanates, but rather to give the reader a general view on the subject and some key references.

The catalysts most commonly used in polyurethane formation are tertiary amines and metal catalysts, especially tin catalysts. The efficiency of the tertiary amine catalysts is structure dependent. In general, the more basic amines with the least amount of steric shielding are more effective amine catalysts.¹¹² Organotin compounds are extremely effective; these include stannous octanoate, stannous oleate, dibutyltin dilaurate and dibutyltin di-2-ethylhexanoate. It is common practice to use a combination of a tertiary amine and a tin catalyst to exploit synergistic effects,^{120,121} especially in the synthesis of

flexible foams. A similar effect has been reported by Rogers for systems containing two tertiary amines.¹²²

It has been suggested¹²³ that the divalent metal-catalyzed isocyanate-alcohol reaction involves the formation of a tertiary complex between the metal compound, the isocyanate and the hydroxyl compound, in which the isocyanate and the hydroxyl compound are positioned on the same side of the metal compound, so that they reside in close proximity to each other. For tetravalent tin compounds, Frisch and Rumao suggest an intermediate donor-acceptor complex of the catalyst with the oxygen of the alcohol function.¹¹⁸ This renders the hydroxyl hydrogen very labile with respect to the isocyanate group, due to a decrease in the electron density of the hydroxyl oxygen. (See Figure 12.) This complex will now break down, due to the competing action of the carbon of the isocyanate for the complexed oxygen. This is in line with their observations that the effect of the catalyst appears to be more significant for less active isocyanates.

In general, the metal ion seems to fulfill a two-fold function, namely:¹¹⁸ 1) it increases the electrophilic character of the carbon in the isocyanate group by coordinating either at the oxygen or nitrogen, and 2) it brings both the isocyanate and the alcohol in closer proximity by forming a ternary complex.

h. Role of Solvent. When planning a solution polymerization, there are certain requirements which must be met by the solvent if the polymerization is to produce high molecular weight polymers. The solvent should be inert to the reactants and also be a good solvent for the reactants. This is especially critical in solution

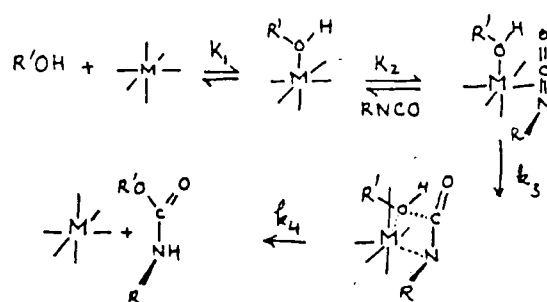


Figure 12. Proposed mechanism for the urethane formation catalyzed by organometallic compounds.

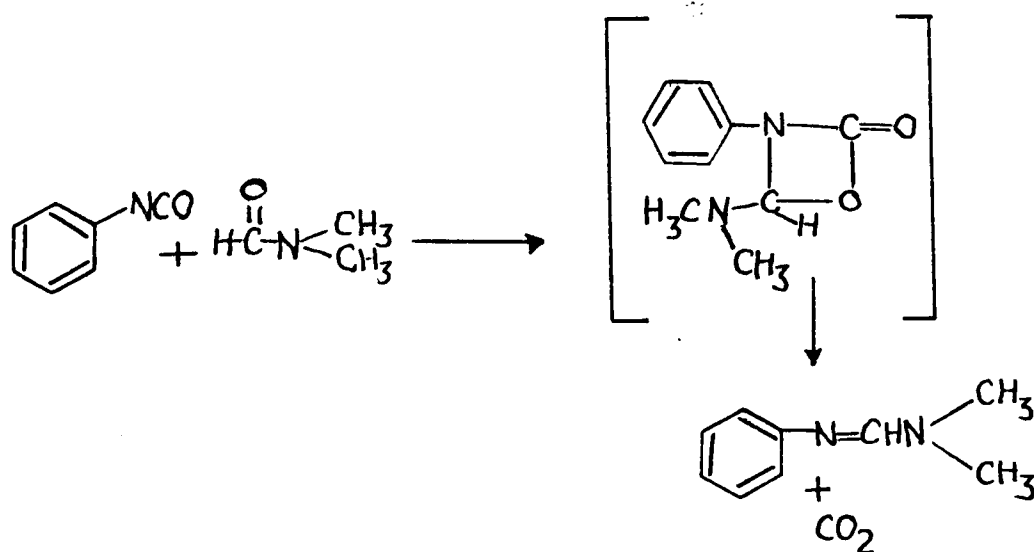
polycondensations where high reactant concentrations are essential. The solvent should also dissolve the polymer. Generally, if the polymer precipitates, low molecular weight materials will result. There are certain cases where only high molecular weight polymer precipitates. In these cases, this can be a great advantage, especially where narrow molecular weight distribution polymers are needed. So the role of the solvent in polycondensation reactions is to produce conditions which favor the formation of high molecular weight products, to allow for rapid mixing and homogenization of the reaction mixture, to dilute the reactants with consequent improvement in the rate of dissipation of the heat of reaction, and to increase the rate of chain propagation by lowering the viscosity of the reaction mixture.

In the case of polyurethanes, a polar aprotic solvent or a mixture of polar aprotic solvents is preferred.¹²⁸ A protic solvent cannot be used since the side reactions previously outlined would become dominant. As stated by Lyman, even when polymer solvents are used as reaction media, the molecular weight of the resulting polyurethanes vary considerably.¹²⁹ The extent of the side reactions governs the molecular weight of the resulting polymer. Lyman found that the side reactions were minimized in the reaction of a diisocyanate with ethylene glycol in either dimethylsulphoxide, DMSO, tetramethylene sulphone or DMSO/4-methyl-2-pentanone (50/50).¹²⁹

The polymerization of the TCNQ diol with a diisocyanate did not follow Lyman's findings owing to the reactivity of the diol. As a matter of fact, the model diol used to establish the reaction conditions for TCNQ diol was not really an ideal model monomer because

it could give no indication of the quinone moiety. It did however, give a good indication of the reactivity of the alcohol function in the solvents chosen.

Prior to this work, we were not aware of any work done on TCNQ or TCNQ diol in DMSO, and since this solvent fulfilled the solvent requirements outlined above, it seemed the ideal candidate for the reaction medium. Sorenson and Lyman of Du Pont had previously shown that diisocyanates could be polymerized in DMSO to yield polymers with an inherent viscosity (η) as high as 0.76 dl/g.^{129,130} Keeping these factors in mind, the polymerization conditions were worked out using the model diol, compound 3.¹²⁸ Solvents like N,N-dimethylacetamide, DMA, and N,N-dimethylformamide, DMF, were not given serious consideration originally because Weiner had shown that DMF reacted with phenylisocyanate to yield N,N-dimethyl-N'-phenylformamide as shown:¹³¹



1. Role of Temperature. The temperature is very important in isocyanate chemistry. The dominance of certain side reactions become more prominent as the temperature is increased. Also, like any other

polymerization, there is a ceiling temperature at which depolymerization takes place. This temperature is very dependent on the character of the monomers. Stability of the monomers at a given temperature is of utmost importance. TCNQ diol is not very stable in solution, especially at elevated temperatures.⁵¹ Knowing that TCNQ diol starts to decompose at about 75°C, the reaction temperature was set at 70°C and the reaction time varied. Importantly, even though isocyanate/alcohol reactions are exothermic, additional heat is required if high molecular weight polymer is desired.

j. Role of Reaction Time. Generally, long reaction times are needed to obtain high molecular weight polymers in polycondensation reactions. If short reaction times are employed, dimers, trimers and other oligomeric species predominate.

k. Role of Reagent Purity. To have a successful polycondensation, high purity reagents are essential. Monofunctional impurities act as chain stoppers, thus producing low molecular weight polymers. For a polycondensation taking place according to:



The total number of repeating AB units in the system would be:

$$\frac{N_A + N_B}{2} = \frac{N_A(1 + 1/q)}{2} \quad, \quad (7)$$

where $q = N_A/N_B$.

The amount of end groups of all polymers in the system is:

$$N_B - N_A = N_A \left(\frac{1-q}{q} \right) \dots \dots \dots (8)$$

Since each polymer molecule has two ends, the number of macromolecules will be:

$$\frac{N_A}{2} \left(\frac{1-q}{q} \right) \dots \dots \dots (9)$$

The degree of polymerization, D.P., will be the ratio of the number of monomers reacted to the number of macromolecules produced:

$$\text{D.P.} = \frac{\frac{N_A}{2} \left(1 + \frac{1}{q} \right)}{\frac{N_A}{2} \left(\frac{1-q}{2} \right)} = \frac{1+q}{1-q} \dots \dots \dots (10)$$

However, if N'_B moles of monofunctional component is added to the system, then:

$$\text{D.P.} = \frac{1 + \frac{N_A}{N_B + N'_B}}{1 - \frac{N_A}{N_B + N'_B}} \dots \dots \dots (11)$$

Assuming $N_A = N_B$

$$\text{D.P.} = \frac{2N_B}{N'_B} + 1 \dots \dots \dots (12)$$

The D.P. is therefore inversely proportional to the amount of monofunctional compound introduced.¹³² Multifunctional monomers, on the other hand, act as cross-linking agents, producing crosslinked polymers

which may not be desirable, especially if a highly soluble polymer is needed.

In polyurethane polymerization, the major impurity is adventitious amounts of water. Lyman has found that for the reaction of methylene bis(4-phenylisocyanate), MDI, with ethylene glycol in DMSO, a 0.4 mole percent addition of water resulted in a 66% decrease in inherent viscosity.¹²⁹ Acidic or basic impurities also promote the side reactions discussed previously.

B. Model Studies

The diol chosen for the model studies is compound 3. It is an intermediate in the synthesis of TCNQ diol and thus, was viewed as an ideal model monomer. The disadvantage of using compound 3 for model studies is that it gives no indication of the behavior the quinone moiety in TCNQ diol. It does, however give a good indication of the behavior of the alcohol group, as stated earlier. The other disadvantage of compound 3 is that it does not reflect the solubility of TNCQ diol. This monomer is soluble in polar organic solvents, however TCNQ diol is not very soluble, even in solvents as polar as DMA or DMF. The solubility of TCNQ diol was examined by Day.⁵¹

Model studies were carried out by polymerizing compound 3 with MDI, TDI and HMDI. For any given comonomer, polymerization of the series MDI, TDI and HMDI will reveal that the order of polymer "stiffness" is MDI > TDI > HMDI⁴⁸. Thus, a study of the electrochemical properties of these polymers using TCNQ diol as the comonomer, should give some indication of how configurational changes affect

electrochemical behavior. Also, a polyester was synthesized by Day,⁵¹ using TCNQ diol and adipyl chloride, so a polyurethane from HMDI and TCNQ diol should also give some indication of the effects of the urethane link versus the ester link, on the electrochemical behavior of the material.

As will be discussed in Chapter IV, the charge transport mechanism through redox polymer films is strongly influenced by the resulting polymer conformation. If the charge transport process involves an electron hopping mechanism, then the rigidity of the polymer should affect this process. The charge transport should be more facile in flexible polymers since they are able to curl and thus promote intra and intermolecular charge hopping. On the other hand, rigid polymers would rely mainly on the juxtapositioning of the redox sites to promote charge transport. Prior to this work, the question of polymer rigidity/charge transport mechanism relationship had not been asked or answered. Thus, it is hoped that this work will stir interest in this very important area of redox polymers.

C. Experimental Section

a. Materials. Compound 3 was recrystallized from acetonitrile; all the diisocyanates were distilled under reduced pressure through a vigreux condensor and stored in a refrigerator until ready for use. DMA was distilled from TDI and dibutyltindilaurate (T-12) was dried over 3 Å molecular sieves before use. DMSO was distilled and stored over 3 Å molecular sieves until ready for use.

b. Polymer Synthesis. In a 150 mL 3-necked r.b. flask previously dried overnight at 250°C and flushed with nitrogen dried over calcium chloride, was added 2.5039 g (0.01 mol) MDI in 10 mL DMSO. To this rapidly stirring solution were added 1.9822 g (0.01 mol) of compound 1 dissolved in 5 mL DMSO and 0.06 mL T-12 in a dropwise fashion. After the addition was completed, the solution was warmed to 70°C for 2h, and then stirred at 30°C for 17 h. The polymer was precipitated by pouring the solution in 80 mL methanol or 80 mL ice/water mixture. The white solid was dried in a vacuum desiccator at 60°C for 4 h to yield 2.9 g of a hard white solid. (See Table XXIII.)

c. Viscosity Measurements.¹³³⁻¹³⁶ The viscosity measurements were obtained using in an Ubbelohde dilution viscometer at a temperature of 25°C. The solvent and solutions were filtered through a No. 1 filter paper several times before the experiment. The initial polymer concentrations were determined by dissolving a known amount of polymer in a given amount of solvent. In each viscosity determination, at least five dilutions were usually made and four to five readings were taken for each dilution to obtain flow times within 2s of each other; these times were then averaged.

The intrinsic viscosity, (η), was obtained by double extrapolation using the Huggins equation (13) and the Kramer equation (14):

$$\eta_{sp}/C = [\eta] + \kappa'[\eta]^2C \quad \dots \quad (13)$$

$$\eta_{rel}/C = [\eta] + \kappa''[\eta]^2C \quad \dots \quad (14)$$

where: η_{sp} is the specific viscosity,
 C is the concentration of the polymer in g/dL,

Table XXIII

Yields of Model Polymers and Intrinsic Viscosity in DMSO

diisocyanate	wt. of polymer(g)	% yield	(η), dl/g intrinsic viscosity
MDI	2.9	64.6	0.12
^a MDI	3.6	78.6	0.13
^b TDI	2.5	63.9	0.12
HMDI	2.29	62.6	

^aReaction time was 30h.^bPrecipitated from ice/water mixture.

k' is the Huggins constant,
 k'' is the Kramer constant,
 η_{rel} is the relative viscosity.

Generally, the intrinsic viscosity of each polymer was determined as follows: 0.4991 g MDI polymer was placed in a 25 mL volumetric flask and the volume made up to 25 mL using DMSO. The solution was set at room temperature for a day after which it was filtered a few times to ensure it contained no suspended particles. The average time for the solvent to flow a given distance is measured for different dilutions. Both the Huggins and the Kramer equations are plotted on the same graph and a double extrapolation is done to obtain (η) . These (η) values are shown in Table XXIV.

d. Molecular Weight Determination.¹³⁴⁻¹³⁷ The molecular weight determinations of the polymers were carried out on a Waters GPC I Model 590 liquid chromatograph equipped with a differential refractometer detector using DMA as eluent. Flow rates of 0.8 mL min^{-1} and ultrastyagel columns 30 cm long with pore size 500Å and 10^3Å arranged in series were employed.

Since Moore used GPC in characterizing molecular weight distribution of polydisperse systems in nonaqueous media, polymer chemists have adopted this method as a means of estimating molecular weight and molecular weight distribution.¹³⁷⁻¹⁴¹ GPC separates molecules based on their size or, more precisely, hydrodynamic volume so a linear polymer and a branched or star polymer having different molecular weights may not be distinguishable by GPC if the appropriate standards are not available.

Table XXIV
Molecular Weight of Model Polymers

diisocyanate	retention time	(η)	molecular wt.
MDI	4.115	0.12	1.6×10^4
MDI	3.990	0.13	2×10^4
TDI	4.00	0.12	2×10^4
HMDI ^a	-	-	

^aHMDI polymer would not dissolve fully in DMA so its viscosity was not determined and also its molecular weight was not determined since this would only reflect the molecular weight of the soluble portion.

The theory of separation by GPC has been summarized in many excellent books and reviews¹⁴²⁻¹⁴⁵ and will not be given here. It was shown that the molecular weight of a polymer is proportional to its retention time, and so linear calibration can be made using known standards with a narrow molecular weight distribution. This calibration plot is not very useful when dealing with different polymers, so Benoit¹⁴⁶ and Contow¹⁴⁷ proposed a universal calibration plot based on the fact that the product of intrinsic viscosity and molecular weight is proportional to the retention time. (See Figure 13.) However, the intrinsic viscosity is related to the Mark-Houwink parameter through:

$$(\eta) = KM^a \quad (15)$$

where: (η) = intrinsic viscosity;

K = a constant,

a = Mark-Houwink parameter.

So, for accurate molecular weight determinations, the Mark-Houwink parameter of both standards and samples must be known. However, from a plot of intrinsic viscosity times molecular weight versus retention time for standards, at least an estimate of the molecular weight of an unknown sample can be made.

The polymers were dissolved in DMA to give concentrations of about 0.5% (w/v) and 50 μ L injected in the GPC. The retention time was taken for two to three injections and averaged and the molecular weight estimated from the calibration plot seen in Figure 13.

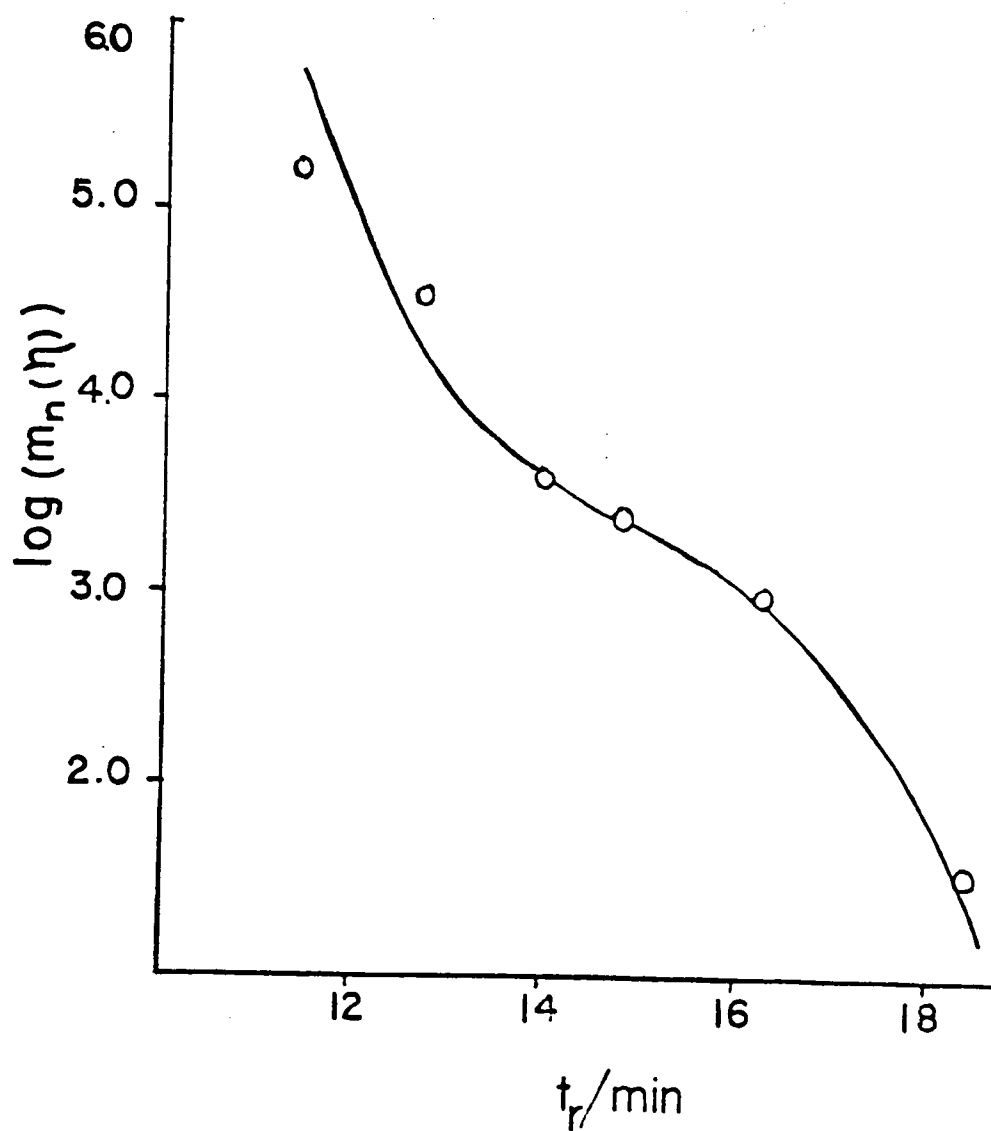


Figure 13. Log Calibration Plot for GPC using polystyrene standards.

e. Infrared Spectroscopy. The infrared spectra of the polymers were recorded on a Perkin Elmer 1330. The polymer was ground with dry KBr and a pellet made unless stated otherwise. The polystyrene peak at 1601 cm^{-1} was taken as the reference and the important bands in the infra-red spectrum of each polymer noted.

D. Results and Discussion

These model polymers were synthesized in order to establish conditions for the synthesis of high molecular weight TCNQ diol polyurethanes. Due to the temperature limitation, which was stated earlier, the temperature was kept constant and the reaction time varied to observe its effect on the viscosity. It was observed that the intrinsic viscosity did not show a significant increase as the reaction time increased from 17 h to 30h for the MDI polymer as shown in Table XXIV. The molecular weights estimated from Figure 13 are given in Table XXIV. The viscosity increase of 0.12 dL/g to 0.13 dL/g is not considered significant. This was taken as evidence that, for a 17h reaction period molecular weights in the region of 10K-20K could be expected. This would have been good for the TCNQ polymers, because even though large molecular weight is the aim, solubility of the polymer in a solvent from which a film can easily be cast must also be kept in mind.

The major infrared bands of each polymer are shown in Table XXV). A more detailed infrared characterization was not attempted since at this point we were mainly interested in making sure we could account for the urethane link.

Table XXV

IR Data for Model Polymers to Identify Urethane Bond

diisocyanate	Major IR Bonds	Assignment
MDI	3290 cm^{-1}	-NH
	1730 cm^{-1}	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}- \end{array}$
TDI	3295 cm^{-1}	-NH
	1730 cm^{-1}	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}- \end{array}$
HMDI	3285 cm^{-1}	-NH
	1732 cm^{-1}	$\begin{array}{c} \text{O} \\ \\ -\text{C}-\text{O}- \end{array}$

E. Synthesis of TCNQ Polyurethanes

A polyester TCNQ based on adipyl chloride and TNCQ diol was previously synthesized and studied in our laboratory.^{35,37,39,148} While this polymer, referred to as PE-TCNQ, showed interesting and understandable behavior based on the properties of monomer TCNQ, thin films of the polymer dissolved and decomposed under certain conditions.^{28,33} This was attributed to the solubility of the dianion and the high hydroxide concentration generated in the film by hydrolysis of the dianion. Attention was focused on the polyurethanes due to their hydrolytic stability.^{149,150}

It was initially decided to use the conditions established for the model polymers to synthesize the desired polymers. Accordingly, DMSO solvent was used to attempt the preparation of an electroactive polymer from TCNQ diol and MDI comonomers. This resulted in a dark green solid which gave absorption bands at $\lambda_{\text{max}}=640$ nm (very broad) and $\lambda_{\text{max}}=395$ nm in acetonitrile. These peaks are characteristic of $(\text{TCNQ})_2^{2-}$,³⁷ so a portion of this material was oxidized using nitroso-tetrafluoroborate in DMA. The green solution turned reddish/yellow on addition of the nitrosotetrafluoroborate and it was poured over ice/water mixture to precipitate a brown-reddish solid which was filtered and dried overnight at 60°C.

Both the dark green solid and the reddish-brown solid were dissolved in DMA/0.1M TEAP and the cyclic voltammetry examined in separate experiments. Both solutions showed no indications of the electroactivity of the TCNQ moiety; no substantial faradic current resulted from either sample. A possible explanation is that TCNQ diol

was reduced in DMSO solution. This is supported by the green color which was presumably due to $\text{TCNQ}^{\cdot-}$. However, it is still not clear why the solutions did not show any electrochemical behavior if they were oxidized.

a. Synthesis of Poly[2,5-Bis(hydroxyethoxyl)-7,7,8,8-tetracyanoquinodimethane methylene bis(4-phenyl isocyanate)] PU-MDI. The failure of the first attempt at the preparation of a TCNQ polyurethane was attributed to reaction of TCNQ diol with DMSO, perhaps by oxidation of DMSO to the corresponding sulphone and interaction of the sulphone with the reduced TCNQ diol. It was therefore decided to repeat this experiment and replace DMSO with DMA. It was hoped that if a reaction similar to the reaction outlined above for phenyl isocyanate and DMF was possible in DMA, it would be considerably slower due to the steric effect of the methyl group. A similar procedure as the one outlined for the corresponding model polymers was applied to the MDI-TCNQ synthesis. After precipitation in methanol and drying at 60°C for 4 h a blue-black metallic-looking solid resulted. The percent yield was 60%. Elemental analysis showed: %C = 61.13, 63.02 %N = 13.13, 12.90 %H = 5.76, 5.75. The calculated values were %C = 63.0; %N = 14.2; %H = 4.0

b. Synthesis of poly[2,5-Bis(hydroxyethoxy)-7,7,8,8-tetracyanoquinodimethane 2,4-toluene diisocyanate] PU-TDI. An identical procedure to the one utilized for the preparation of PU-MDI was attempted in the synthesis of PU-TDI. This resulted in a blue-black metallic-looking solid. However, the UV-VIS in acetonitrile did not

show the expected peaks indicating the TCNQ moiety. Instead, it showed $\lambda_{\text{max}}=485$ nm and $\lambda_{\text{max}}=350$ nm. The cyclic voltammetry did not show the reproducible characteristic cyclic voltammetry (CV) of TCNQ. This experiment was repeated a number of times, but the results consistently agreed with the data obtained for the first attempt.

The synthesis was again attempted, however, this time the catalyst was omitted from the reaction. Again this yielded a blue-black metallic-looking solid. This solid partially dissolved in acetonitrile and the UV-VIS seen in Figure 14, indicates $\lambda_{\text{max}}=433$ nm and $\lambda_{\text{max}}=412$ nm, characteristic of the TCNQ moiety was obtained. The yield from this experiment based on 0.2105 g (0.0012 mol) TDI and 0.3244 g (0.001 mol) TCNQ diol was 56%.

c. Synthesis of poly[2,5-Bis(hydroxyethoxyl)-7,7,8,8-tetracyanoquinodimethane 1,6 hexamethylene diisocyanate] PU-HMDI. The original attempted synthesis of this polymer using the method as that used for PU-MDI resulted in a dark purple solid. The CV in DMA/0.1M TEAP showed the expected behavior for the TCNQ moiety. However, the UV-VIS spectrum in acetonitrile showed the following peaks: $\lambda_{\text{max}}=580$ nm; $\lambda_{\text{max}}=495$ nm and $\lambda_{\text{max}}=433$ nm. These peaks are not consistent with the published data for TCNQ and its charged species. This synthesis was repeated a number of times and on subsequent attempts, the UV-VIS in acetonitrile showed $\lambda_{\text{max}}=440$ nm and $\lambda_{\text{max}}=375$ nm. These numbers can be attributed to different charged TCNQ species, however it was felt that the UV-VIS should have showed the doublet at $\lambda=432$ nm and $\lambda=412$ nm for the neutral TCNQ diol. With this in mind, the synthesis was again attempted, but now the solvent was changed to nitrobenzene

and the catalyst omitted. The choice of nitrobenzene as a solvent was based on studies reported by Lyman where he states that for a reaction of MDI and ethylene glycol in nitrobenzene only high molecular weight polymer precipitated.¹²⁹ The experimental procedure used for the synthesis of HMDI-TCNQ was as follows: To a rapidly stirring solution of 0.1890 g (0.001 mol) HMDI in 2 mL nitrobenzene with a steady flow of nitrogen bubbling through the solution was slowly added 0.3289 g (0.001 mol) TCNQ diol dissolved in 8 mL nitrobenzene. After the initial exotherm had subsided, the reaction mixture was heated to 115-120°C for 2 h and then filtered after it cooled. This yielded a black solid and the filtrate was poured over methanol to precipitate another fraction. The percent yield of the solid which precipitated from nitrobenzene was 21.2% and the percent yield of the solid which precipitated from methanol was 51.3%.

F. Characterization of TCNQ Polyurethanes

Apart from the high electrical conductivity observed for TCNQ salts, there are other reasons for choosing TCNQ as the electroactive unit to be incorporated in the polymer for modification of electrode surfaces. These include the vast amount of literature available on this compound, the stability of TCNQ radical ion which is readily detected and characterized by ESR spectroscopy, and the striking color changes observed when TCNQ is reduced that allow the chemical activity of the films to be probed by UV-VIS spectrophotometry.

a. Elemental Analysis. The elemental analyses for PU-MDI and PU-TDI are shown in Table XXVI. Some possible end groups, depending

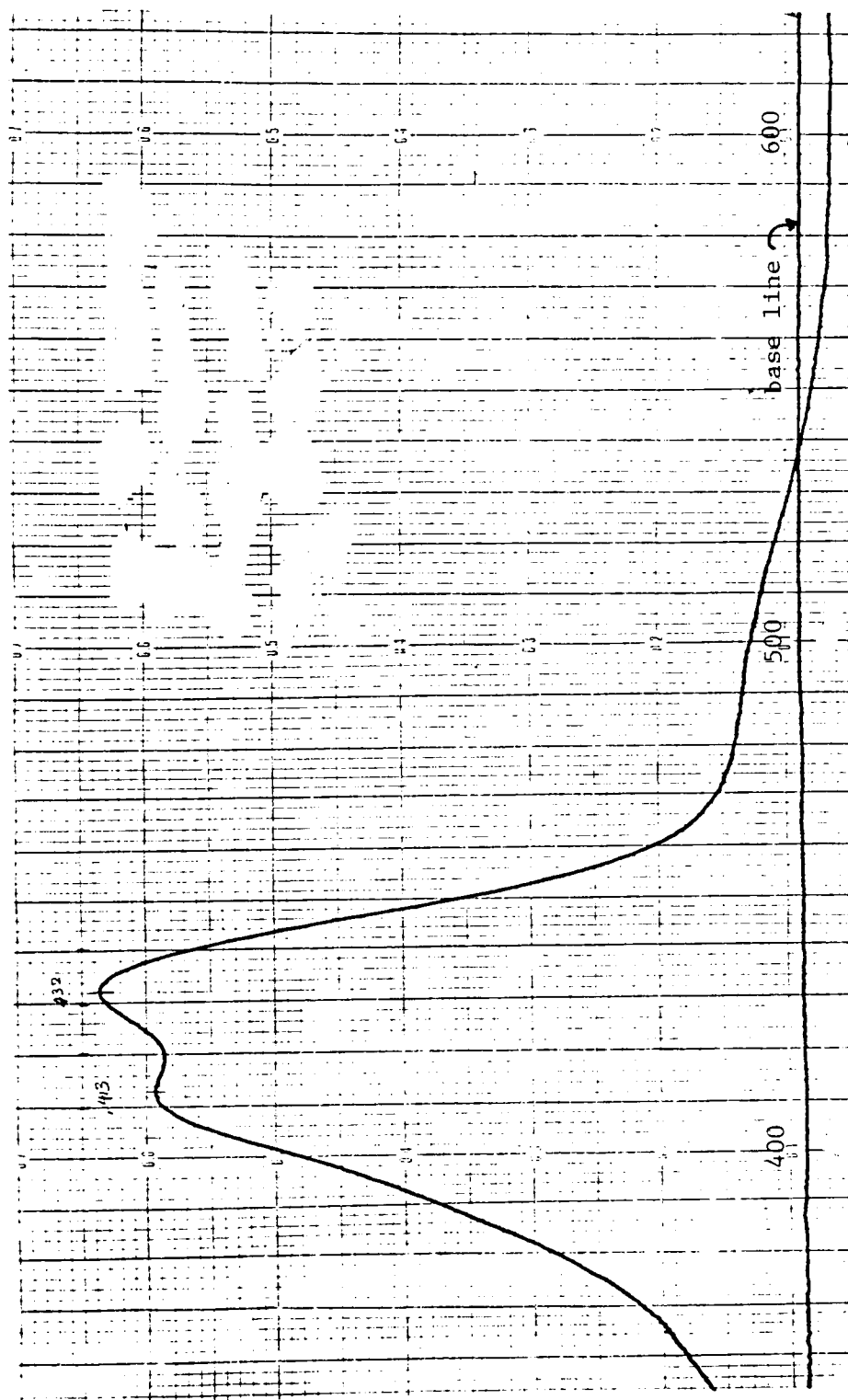


Figure 14. UV-VIS spectrum of PU-TDI in Acetonitrile.

Table XXVI
Elemental Analyses for PU-MDI and PU-TDI

Polymer	%C	%H	%N
PU-MDI ^a	63.0	5.8	12.9
PU-MDI ^b	67.1	4.0	11.6
PU-MDI ^c	63.0	4.0	14.2
PU-TDI ^c	60.0	3.7	17.0
PU-TDI ^b	62.8	3.8	13.4
PU-TDI ^a	60.0	3.7	17.0

^aAnalytical values.

^bCalculated values based on theoretical repeat unit.

^cCalculated values based on proposed end groups.

on the method of termination, and the repeat units are shown in Figure 15. The elemental analysis agrees quite well with the proposed structures seen in Figure 15, even though deviations from the values calculated for an ideal polyurethane of infinite length are observed. These deviations may be accounted for in the following manner:

1. End Groups. The polymers were precipitated in either methanol or water, thus the end groups are expected to be methyl carbamates or substituted amines. However, due to the relatively low temperature at which the reaction was carried out, it is conceivable that the end groups could also be an unreacted alcohol function from the TCNQ diol. If the polymer chains are very long, the contribution of these end groups to the elemental analysis may be neglected. However, if the polymer chains are not very long, end group contribution can become significant.

2. Branching. In calculating the percent of each element in the polymer, a linear repeat unit was assumed. This assumption is very rarely true in polyurethane chemistry, especially when one considers the number of potential side reactions that can occur in the polycondensation reaction between a diisocyanate and a diol. The PNMR spectrum of PU-MDI exhibits resonances, among others, at $\delta = 8.6$, 10.3, and 9.6 ppm, assigned to -NH from the carbamate link,¹⁵¹ to -NH from allophanate¹⁵³ and to biuret linkages,¹⁵³ respectively. This is an indication that all the polymer chains may not be linear.

3. Contamination. Contamination of the samples with DMA, which is the solvent used in the polymer synthesis, or methanol or water which are the precipitating media or even with the catalyst in

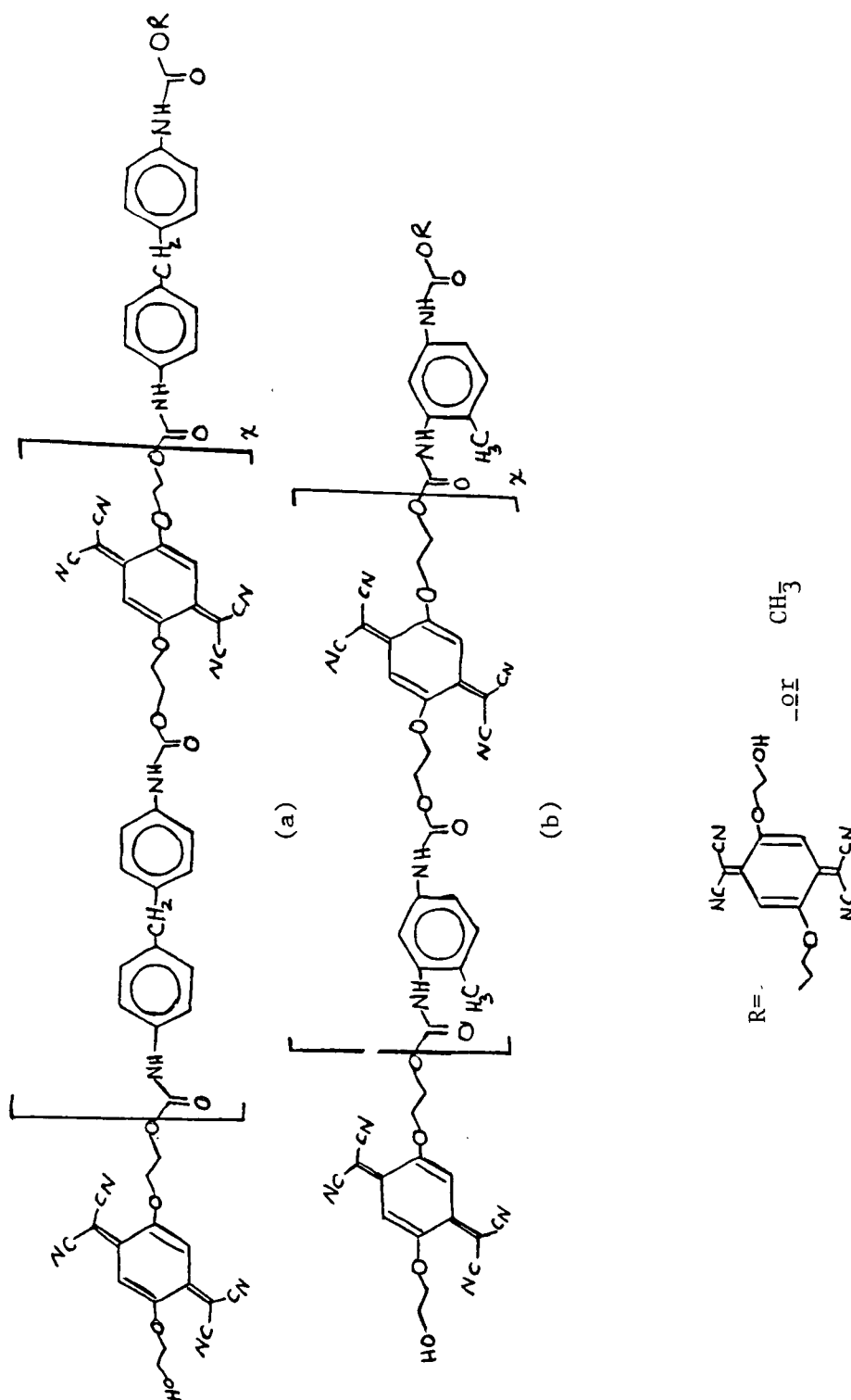


Figure 15. Proposed polymer structure for (a) PU-MDI and (b) PU-TDI.

the case of PU-MDI, could also cause disagreements between the calculated and analytical elemental analysis.

4. Presence of Catalysis. Interestingly, when PU-MDI was examined by ESCA, among the many interesting things revealed were two peaks having binding energies of 493 eV and 484.5 eV, as shown in Figure 16, which were assigned to tin. These peaks were more intense when the top layer of the film, after being doped with Cs^+ , was sputtered by an argon ion gun. This is strong indication for the incorporation of T-12 into the polymer. This would definitely alter the elemental analysis.

The percent tin in polymer was estimated from the ESCA data by observing the relative areas under the peaks for tin and nitrogen (see Table XXVII). It was also estimated simply, from the elemental analysis, assuming 100 g material and using:

$$x = \frac{(\%N)(M_p)}{(N_n)(\text{atm. wt. of N})} \quad (16)$$

where x is the weight of polymer/per 100 g sample; M_p is the molecular weight of the polymer; N_n is the number of nitrogen atoms in the polymer having molecular weight M_p . The molecular weight chosen was based on a proposed structure that gave a calculated element analysis fairly close to the analytical elemental analysis. The molecular weight estimated by electrochemical methods, discussed later, was also used. These calculations were checked by using the result obtained from equation 1 to calculate the percent carbon in the compound, using equation 17 below. The weight of polymer calculated using equation 16

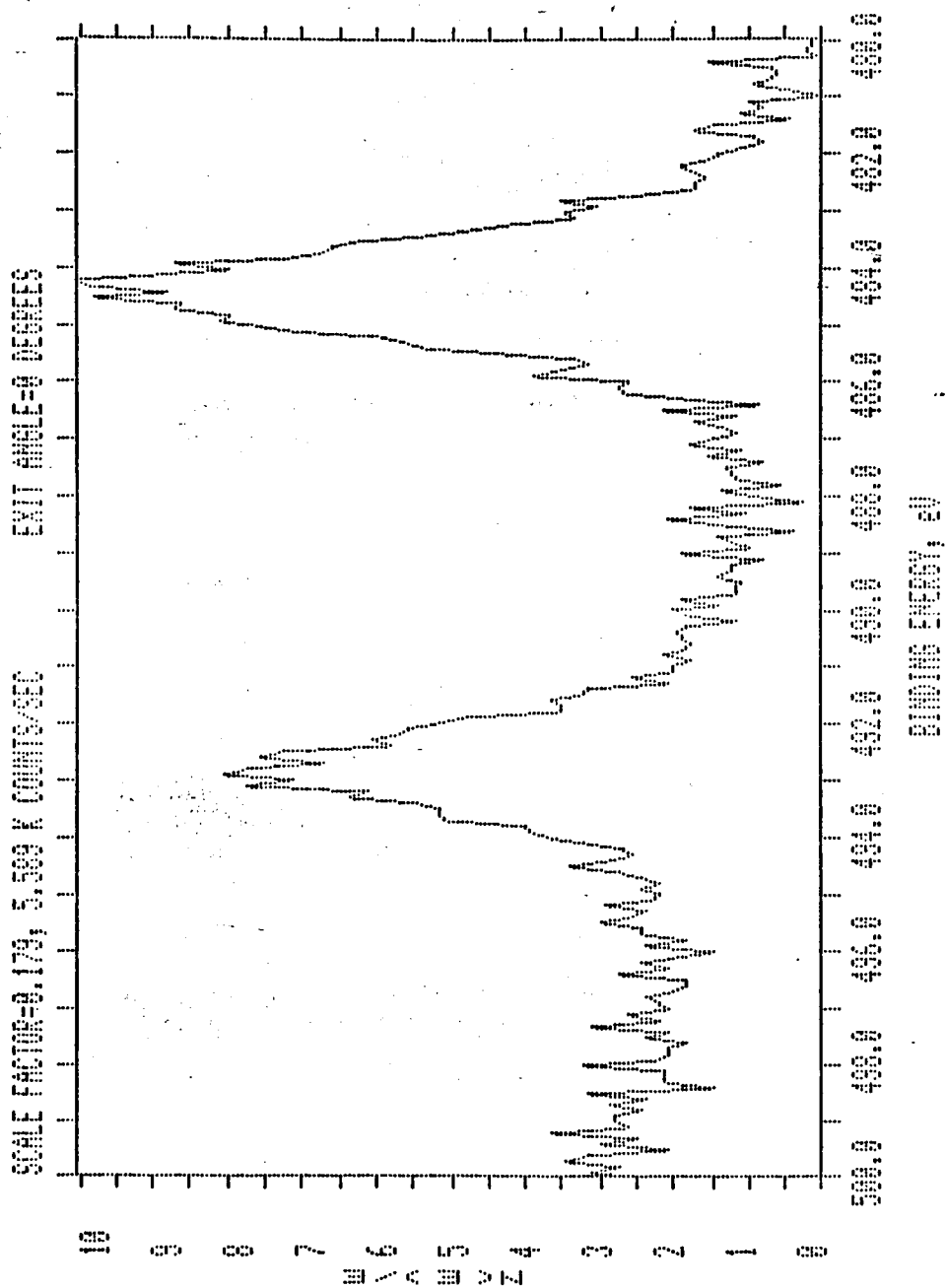


Figure 16. ESCA spectrum of Cs^+ doped PU-MDI film identifying Tin.

Table XXVII
Areas Calculated From ESCA Data

Element	Area (A) ^a	Sensitivity Factor (SF)	A/SF	Sn/N
N	3710	0.38	9736	0.17
Sn	5242	3.2	1638	

^aArbitrary Units.

$$\%C = \frac{x}{M_p} \times N_c \times \text{atm. wt. of C} + \frac{100 - x}{M_f} \times N_c \times \text{atm. wt. of C} \quad (17)$$

Where N_c is number of carbon atoms in the polymer.

N'_c is number of carbon atoms in T-12.

M_f is the molecular weight of the catalyst.

and a molecular weight of 3478 Dalton (D.P. = 6) was 89.7 g and using the molecular weight, estimated from electrochemical methods, of 6×10^4 Dalton (DP = 104) the weight of polymer was 88.8 g. These two weights are essentially the same and so they were rounded up to 90 g. Substituting this value in equation 2 and using a molecular weight of 3478 Dalton gave $\%C = 63.8$, while using $M_p = 6 \times 10^4$ Dalton gave $\%C = 64.4$ (analytical $\%C = 63.02$).

This remarkable agreement between ESCA data, which shows that the material contains about 10% T-12, and the other calculated data is strong evidence that T-12 is incorporated in the polymer. This incorporation is probably through coordinate covalent bonds from the nitrogen of the polymer to the tin in the catalyst. The catalyst-polymer interaction has to be fairly strong since T-12 did not dissolve in methanol, the precipitating medium, which is a good solvent of T-12. This also indicates that the pipette delivered more catalyst than was planned.

b. Infrared (IR) Data. The important IR absorption bands and assignments for these bands are shown in Tables XXVIII, XXIX and XXX. They confirm the presence of the TCNQ. Absorbances at about 2240 cm^{-1} and 1540 cm^{-1} are expected for a conjugated cyanoolefin.^{17,152}

Table XXVIII

IR Bands for PU-MDI in a KBr Pellet

Wave Number (cm^{-1})	Shape/Intensity		Assignment
3300	VB	M	N-H
2970	B	M	C-H
2440	S	S	$\text{-C}\equiv\text{N}$
2220	S	VS	$\text{-C}\equiv\text{N}$
2180	S	S	
1725	B	VS	C=O
1605	S	B	aromatic ring
1560	S	S	-C=C-
1530	S	VS	-C=C-
1510	S	S	aromatic ring
1415	S	S	
1310	S	S	
1260	S	M	C-O-
1220	B	VS	-C-O
1155	S	W	
1120	S	VW	
1080	S	S	-C-O
1015	S	VS	-C-O
920	S	M	
820	B	M	1,4 disubstituted benzene
755	S	M	aromatic C-H
515	S	S	

Table XXIX

IR Bands for PU-TDI in a KBr Pellet

Wave Number (cm ⁻¹)	Shape/Intensity		Assignment
3340	VB	VS	-NH
2960	S	S	aromatic -C-H
2930	VS	VS	aliphatic -C-H
2860	VS	S	aliphatic -C-H
2240	VS	S	-C≡N
2230	VS	S	-C≡N
2185			
1720	B	VS	-C=O
1615	S	VS	aromatic ring
1540	S	VS	-C=C
1420	S	M	
1385	S	M	
1305	S	M	
1265	S	W	
1215	B	VS	-C-O
1080	S	S	-C-O
875	B	M	Trisubstituted benzene
810	S	W	
620	B	M	
485	S	M	

Table XXX

IR Bands for PU-HMDI in a KBr Pellet

Wave Number (cm^{-1})	Shape/Intensity		Assignment
3320	VB	M	-NH
2940	S	M	-CH
2870	S	M	-CH
2235	S	S	-C $\equiv$ N
2210	S	S	-C $\equiv$ N
2195	S	M	
1725	B	VS	-C=O
1615	S	VS	
1555	S	VS	-C=C-
1530	S	VS	-C=C-
1485	S	M	
1390	VS	M	
1345	B	W	
1310	B	W	-C-O
1265	S	M	-C-O
1225	S	M	-C-O
1150	B	W	
1040	VB	W	
930	S	VW	
840	S	VW	
785	S	VW	-C-H
575	S	VW	

urethane link is expected for a conjugated cyanide characterized by absorbances at 1730 cm^{-1} , indicative of the carbonyl function and a broad absorbance band at about 3330 cm^{-1} . This broad absorbance (3220 cm^{-1} to 3640 cm^{-1}) could be due to water and/or -OH groups resulting from unreacted ends of TCNQ diol, and also definitely due in part to -NH bonds. The broadness of the band at about 1730 cm^{-1} may be an indication of allphonate and biuret linkages.¹⁵³

c. UV-VIS Spectra. The UV-VIS spectra for the polymers are very similar. Figure 17 shows the UV-VIS spectrum of PU-MDI in acetonitrile. The similarity between this spectrum and that of the TCNQ diol shown on page 44 is as expected, where the doublet is slightly shifted. A similar shift was also observed by Day for PE-TCNQ.⁵¹ Often the spectra for virgin polymers in acetonitrile or as a film on a transparent electrode exhibited minor absorbances at $\lambda_{\text{max}} = 730\text{ nm}$ and $\lambda_{\text{max}} = 670\text{ nm}$, indicative of the presence of radical anions species.¹⁷ For PU-MDI in DMA, a bathochromic shift is observed, whereby the peaks at $\lambda_{\text{max}} = 510\text{ nm}$ and $\lambda_{\text{max}} = 450\text{ nm}$ are attributed to the neutral TCNQ moiety.

d. Electron Spin Resonance (ESR). Reductive electrolysis of a solution of TCNQ diol in $0.1\text{M Et}_4\text{NClO}_4/\text{CH}_3\text{CN}$ produced a spectrum with 11-lines, showing an intensity pattern for interaction with four equivalent nitrogens and two equivalent hydrogen atoms, along with a g value of 2.0030.³⁷ Similarly, the ESR spectrum of $\text{Li}^+ \text{TCNQ}^-$ diol in water displayed the 11-line pattern found in acetonitrile and a g-value of 2.0029. When the ESR spectrum of reduced PU-MDI, PU-HMDI or PU-TDI was

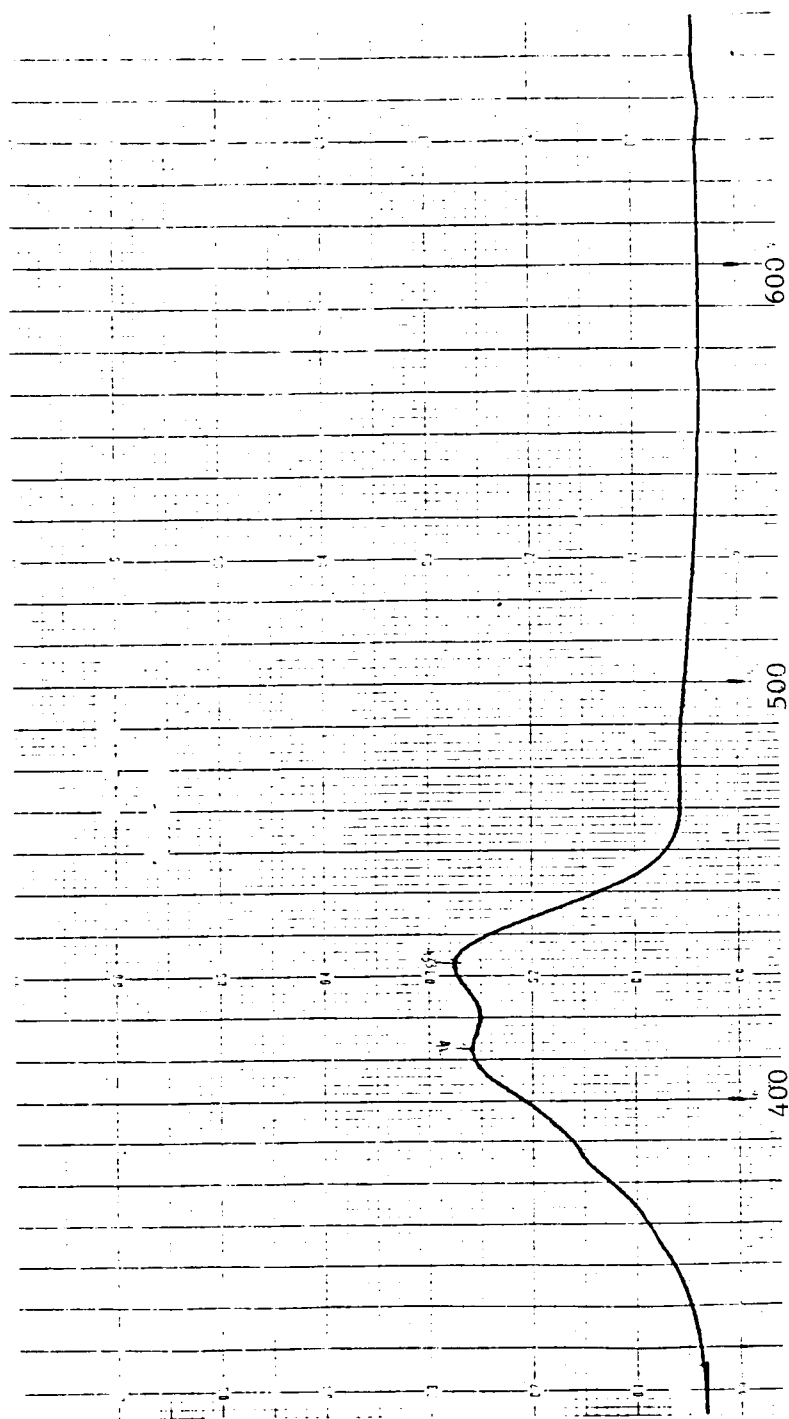
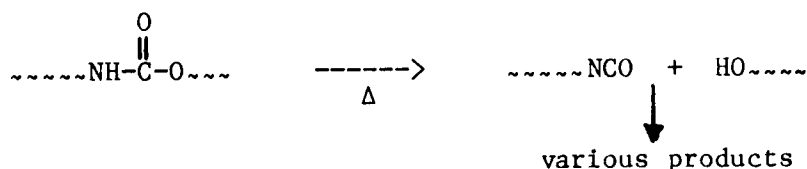


Figure 17. UV-VIS spectrum of PU-MDI in Acetonitrile.

examined a single line was observed. For reduced PU-MDI, the peak width was about 10G and a g-value of 2.0030 ± 0.0005 was obtained using DPPH ($g = 2.0036$) as reference. The absence of hyperfine splitting in the ESR spectrum resulted from the high concentration of $\text{TCNQ}^{\cdot-}$ sites in the film and the concomitant rapid exchange processes. Similar results were reported by Inzelt and coworkers for Day's polyester.³⁷

e. Differential Scanning Calorimetry (DSC). The DSC results for the polymers are given in Table XXXI. Figure 18 shows the DSC thermogram for PU-MDI. The endotherm at 141°C for PU-MDI was assigned as the glass transition temperature, T_g . No T_g was observed for the other polymers in the temperature range examined. However, all the polymers showed a major endotherm starting at temperatures above 200°C . This temperature was assigned as the "uncapping temperature," T_{uc} , of the urethane bond. That is, at this temperature the carbamate link is broken as shown below:



The differences between the uncapping temperatures of each polymer is in agreement with data published by Wicks,⁸¹ namely:

<u>Urethane</u>	<u>T_{uc}</u>
Alkyl - NHCOO - Alkyl	250°C
Aryl - NHCOO - Alkyl	200°C
Alkyl - NHCOO - Aryl	180°C
Aryl - NHCOO - Aryl	120°C

Table XXXI
Differential Calorimetry Data

Polymer	T _g /°C	T _{decomp} /°C
PU-MDI	141	207
PU-TDI	-	210
PU-HMDI	-	220

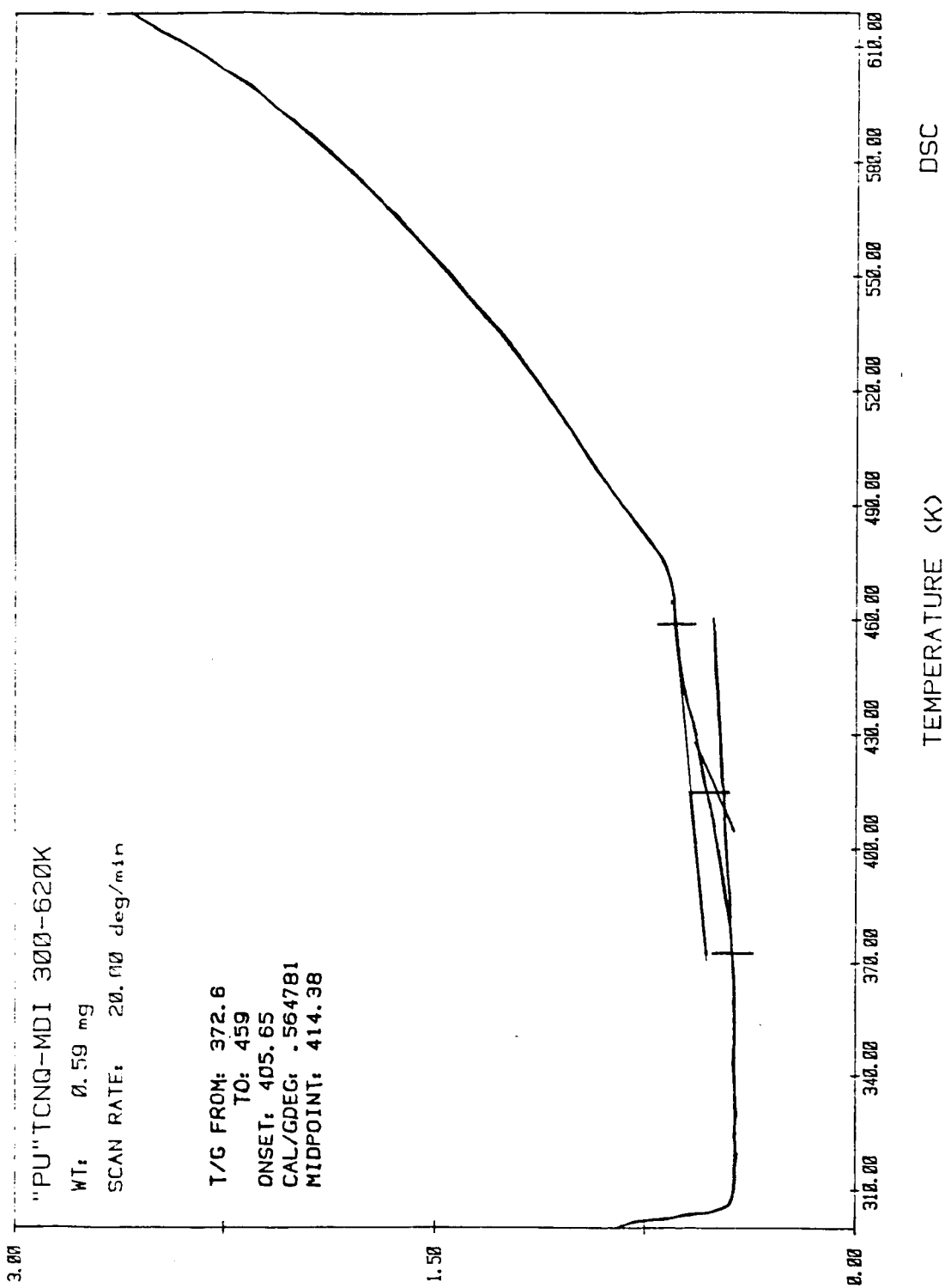


Figure 18. DSC thermogram of PU-MDI.

Similar uncapping temperatures were also reported by Pittman for polyurethanes containing tetrathiafulvalene instead of TCNQ in the polymer backbone.²⁷

f. Gel Permeation Chromatography (GPC). The polyurethanes containing TCNQ were excluded from a 500 Å column; Thus, a 10^3 Å column was connected in series with the 500 Å column and the calibration plot shown in Figure 13 obtained from the retention volume data shown in Table XXXII. Again the TCNQ polyurethanes were excluded from the column at 60°C, using DMA as eluent. Similar results were also observed for PE-TCNQ.³⁶

A comparison of the intrinsic viscosity of the model polymers and the TCNQ polyurethanes show them to be very close in DMA at 25°C. Thus, one would expect the molecular weights also to be close. So, the exclusion of these TCNQ polyurethanes from the column due to high molecular weight did not seem likely. Two possible explanations are offered here for this behavior.

First, there could be association of the polymer chains at the TCNQ or charged TCNQ sites to form high molecular weight aggregates. This is supported by electrochemical evidence that PE-TCNQ films adsorbed on metal substrates and TCNQ in solution will dimerize.¹⁵² However, this may not be the case here since a plot of peak current versus weight of polymer in solution, for PU-MDI, shows a linear relation. (See Figure 19.) This linearity indicates that at the concentration and temperature at which these experiments were carried out, very little, if any, association is taking place. It also indicates that the TCNQ units are behaving "ideally."

Table XXXII

Gel Permeation Chromatography of Polymers

Eluent, DMA; temperature, 60°C; flow rate, 1.0 mL/min.				
Sample	$t_R(\text{min})^b$	$M_n \times 10^3$	$[\eta](\text{dL/g})$	$\log\{[\eta] \times \text{MW}\}$
PS 2.35 ka	18.4	17.9	0.02	1.55
PS 15 ka	16.25	9.05	0.11	3.00
PS 19.6 ka	14.8	19.6	0.13	3.41
PS 34 ka	14.0	34.0	0.118	3.60
PS 110 ka	12.7	92.6	0.38	4.55
PS 200 ka	11.4	217.6	0.725	5.20
PU-MDI	7.9			
PU-TDI	8.1			

^aPolystyrene standard.

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

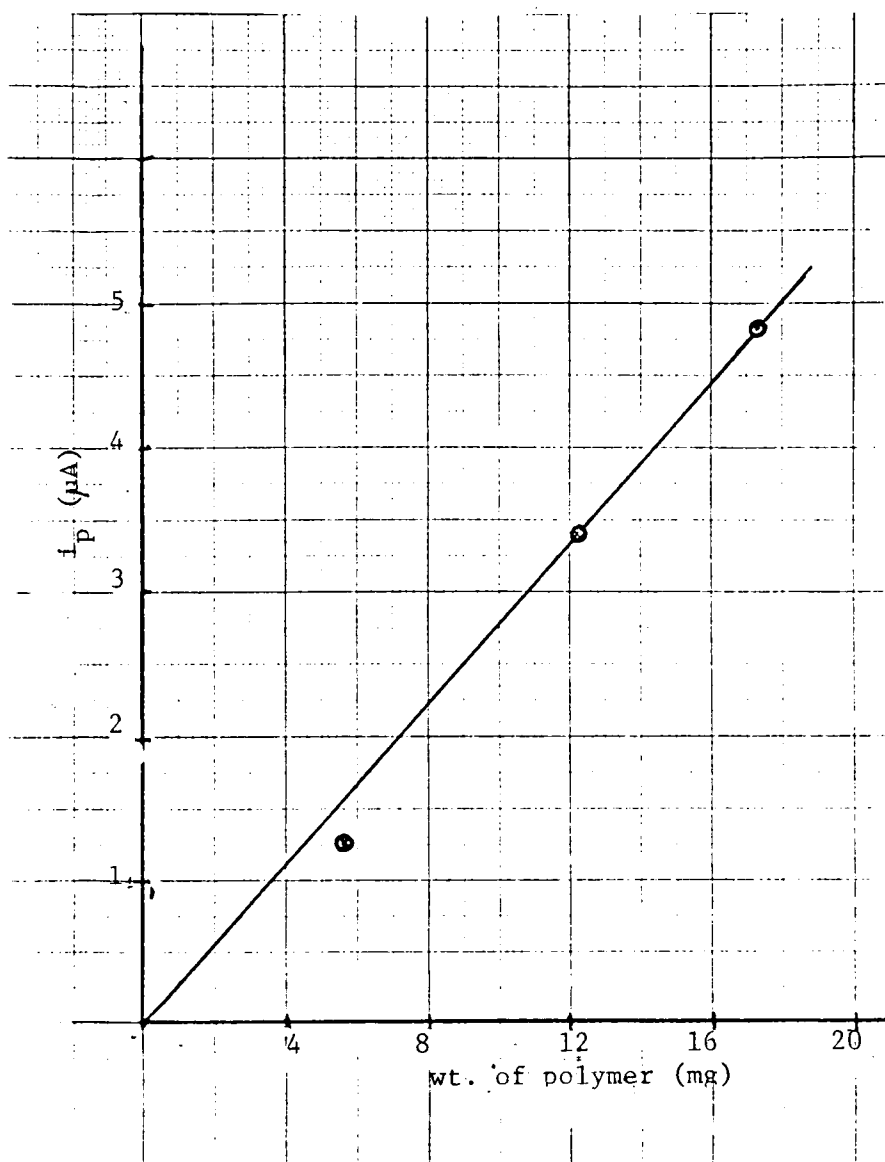
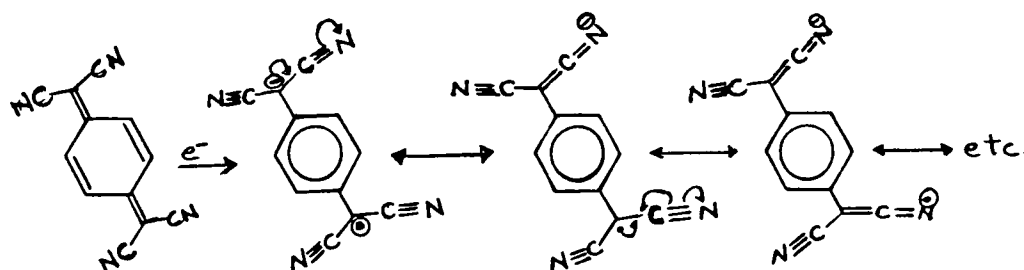


Figure 19. Plot of peak current vs wt of polymer in solution.

Another possibility is the existence of the polymer as a polyanion in solution. Indeed, absorption spectra for the virgin polyurethanes show weak absorbances at $\lambda_{\max} = 730 \text{ nm}$ and $\lambda_{\max} = 850 \text{ nm}$ where the semi-reduced TCNQ is known to absorb. Also these virgin films are paramagnetic, presumably due to radical anion groups in the polymers, as indicated by the ESR spectrum of a virgin film. Polyanions are known to be excluded from styragel columns, owing to their extended or rod-like conformation,¹³⁷ and thus this is a possible reason for the exclusion of these polymers.

g. Solution Electrochemistry. A DMA solution of TCNQ diol, 0.1M in TEAP, shows the expected two reversible peaks shown on page 43 with $E_{1/2}^{0/-} 10 \text{ mV}$ and $E_{1/2}^{-/2-} = -517 \text{ mV}$ vs. Ag/AgI. These values are slightly more negative than $E_{1/2}$ values reported for the unsubstituted TCNQ, but this is expected due to the electron donating ability of the 2'-hydroxyethoxy substituent of the TCNQ diol.¹⁶ The positive $E_{1/2}^{0/-1}$ value indicates the gain in stability of the semi-reduced TCNQ relative to the neutral TCNQ. This can be explained in terms of the resonance contributors one can draw for the TCNQ radical anion and the fact that the quinoid system is now converted to a more stable benzenoid system as shown below.



All three polyurethanes in DMA solution using TEAP as the supporting electrolyte also displayed the characteristic two quasi-reversible peaks expected of the TCNQ moiety. PU-MDI gave $E_p^{c1} = 45$ mV and $E_p^{c2} = -428$ mV coupled with $E_p^{a1} = +107$ mV and $E_p^{a2} = -257$ mV, giving $E_{1/2}^1 = 76$ mV and $E_{1/2}^2 = -343.5$ mV vs. Ag/AgCl (see Figure 20). PU-TDI displayed $E_p^{c1} = 41$ mV and $E_p^{c2} = -443$ mV coupled with $E_p^{a1} = 117$ mV and $E_p^{a2} = -274$ mV giving $E_{1/2}^1 = 79$ mV and $E_{1/2}^2 = -353.5$ mV vs Ag/AgCl; while PU-HMDI showed $E_p^{c1} = 45$ mV and $E_p^{c2} = -513$ mV coupled with $E_p^{a1} = 128$ mV and $E_p^{a2} = -256$ mV giving $E_{1/2}^1 = 86.5$ mV and $E_{1/2}^2 = -385$ mV vs. Ag/AgCl. These data are summarized in Table XXXII. The differences in the E_p values for the reduction of the TCNQ units may be a reflection of the chemical environment, however one has to refrain from making too much comparison between these data since important parameters like polydispersity and molecular weights are not known for all the polymers.

The size, shape and location of voltammetric waves reflect the environment in which the electroactive center is contained, and the extent to which interaction between neighboring groups hinder the process of electron transfer.¹⁵⁴ The electrochemical behavior of a molecule containing several electroactive sites can depend upon the extent of interaction between sites, solution condition, ion pairing, and structural changes of the molecule, but for molecules containing identical noninteracting centers, the successive electron transfer will follow simple statistics.¹⁵⁴ Electron transfer to or from polymeric molecules containing identical, noninteracting electroactive centers will involve as many electrons as there are centers and will yield a

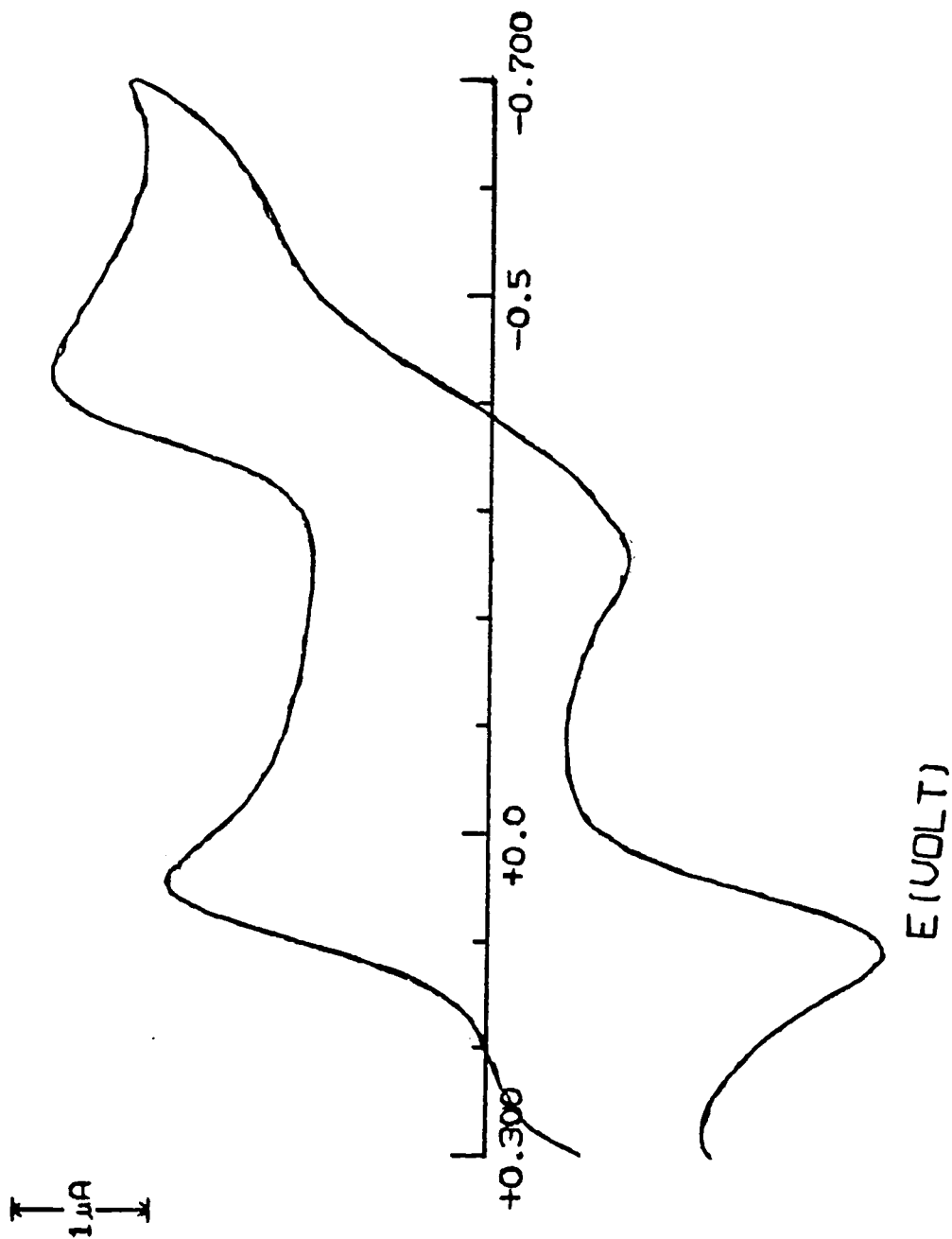


Figure 20. Cyclic voltammogram of PU-MDI in 0.1M TEAP/DMA potential vs Ag/AgCl.

Table XXXIII

Summary of Peak Potential Data^a for Polyurethanes in DMA, 0.1M TEAP

Polymer	E_{p1}^c /mV	E_{p1}^a /mV	E_{p2}^c /mV	E_{p2}^a /mV
PU-MDI ^b	45	107	-428	-257
	$E_{1/2}^{0/-} = 76$ mV		$E_{1/2}^{-1/-2} = -343$ mV	
PU-TDI ^b	37	104	-436	-259
	$E_{1/2}^{0/-1} = 71$ mV		$E_{1/2}^{-1/-2} = -348$ mV	
PU-HMDI ^b	45	128	-513	-256
	$E_{1/2}^{0/-1} = 87$ mV		$E_{1/2}^{-1/-2} = -385$ mV	
TCNQ diol ^c	-26	45	-549	-484
	$E_{1/2}^{0/-1} = 10$ mV		$E_{1/2}^{-1/-2} = -517$ mV	

^aPotentials vs. Ag/AgI.^bSweep rate vs. 30 mV/S.^cSweep rate is 50 mV/S.

voltammetric wave with a shape matching that of the corresponding molecule with a single electroactive center, but with a magnitude determined by the total number of centers present. Complications arising from absorption, precipitation or slow electron transfer kinetics will distort the voltammetric response. The current resulting from polymeric species will be attenuated relative to the monomer on a weight basis owing to the smaller diffusion coefficients of the polymers. This can permit an electrochemical estimation of the weight average molecular weight, $\bar{M}_w$, if the above conditions are applicable. Applications of this technique is found in the works of Funt,^{141,155,156} Flanagan,¹⁵⁴ Smith¹⁵⁷ and Morishima.¹⁵⁸ These measurements are simple, require very little material and can be combined with viscosity measurements to provide an estimate of $\bar{M}_w$ in the same manner as the "universal" GPC method of Benoit and coworkers.¹⁴⁶ Suitable electroactive standards remain to be synthesized and calibrated for this method, which in the best of cases has many pitfalls.¹⁵⁴

The Randles-Sevcik equation 18, shown below, can be rearranged to equation 19.

$$i_p = 2.69 \times 10^5 n^{3/2} A v^{1/2} C_b K_T M^{-b/2} \quad (18)$$

where i_p = cathodic peak current, μA

n = number of electrons transferred

A = Area of the electrode surface covered, cm^2

v = sweep rate, V/s

C_b = bulk concentration of the polymer mole/ cm^3

K_T = constant which is dependent on the polymer structure and solvent

M = molecular weight of the repeat unit

b = constant related to the Mark-Houwink parameter, a , through the relation $b = (a+1)/3$.

$$D.P = \frac{i_p^P/W_p}{i_p^m/W_m} \left[\frac{M_r}{M_m} \right]^{1.275} \quad (19)$$

Where: D.P. = degree of polymerization

i_p^P, i_p^m = cathodic peak current of polymer and monomer respectively

M_r, M_m = molecular weight of repeat unit and molecular weight of monomer respectively

Equation 18 has been applied quite successfully to linear sweep voltammetry to determine molecular weights of polymers.¹⁵⁴ The rearranged equation was applied to the cyclic voltammetric data for PU-MDI in order to estimate a molecular weight. The following assumptions were made:

1. The polymer behaves ideally in solution. The voltammograms of the polymer (PU-MDI) and TCNQ diol in 0.1MTEAP/DMA at room temperature are shown in Figures 21 and 22. The similarity of these two voltammograms suggest that this assumption may be valid. The linear plot observed for i_p versus weight of polymer in solution as shown in Figure 19 adds further credence to this assumption.

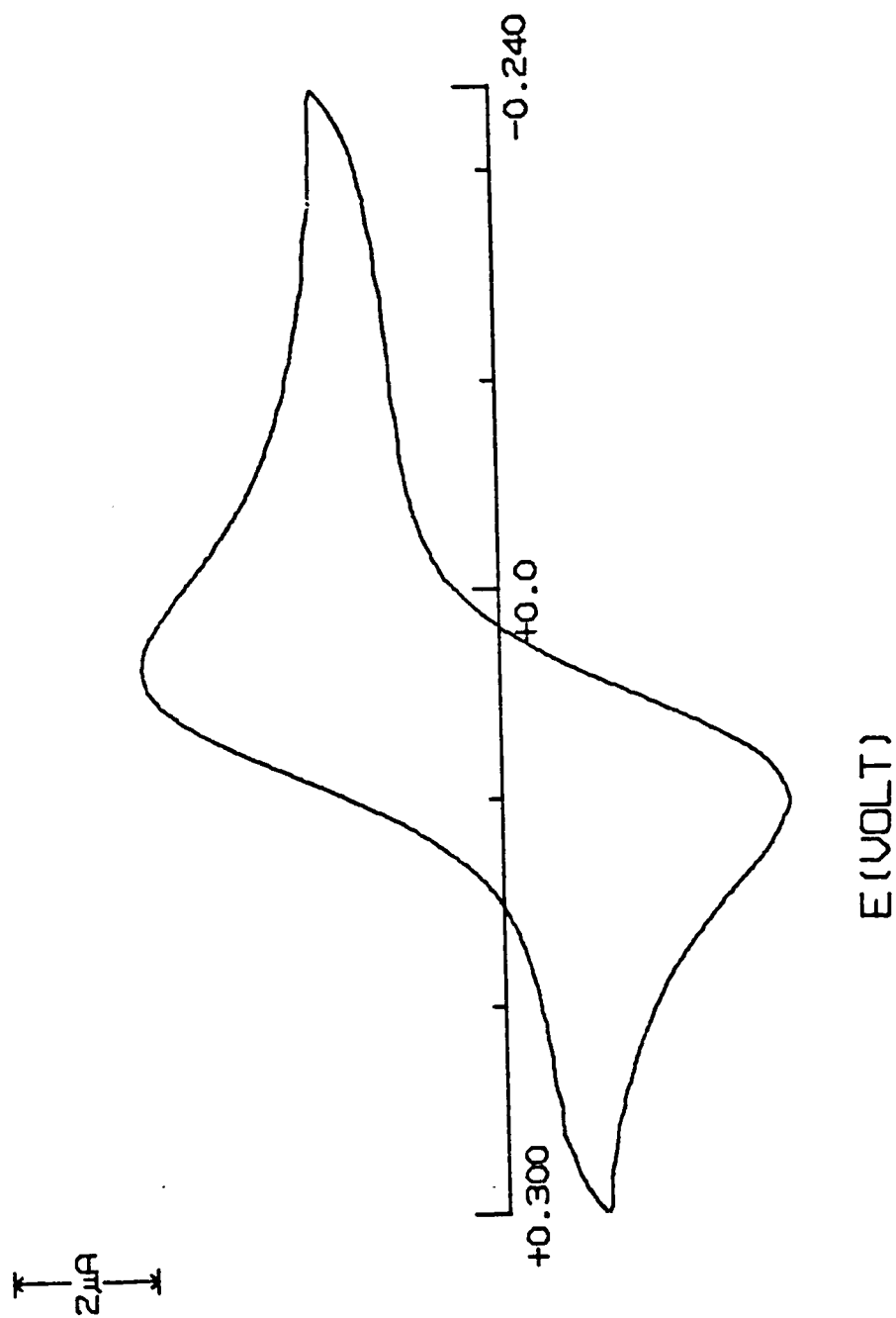


Figure 21. Cyclic voltammogram of PU-MDI in 0.1M TEAP/DMA potential vs Ag/AgCl.

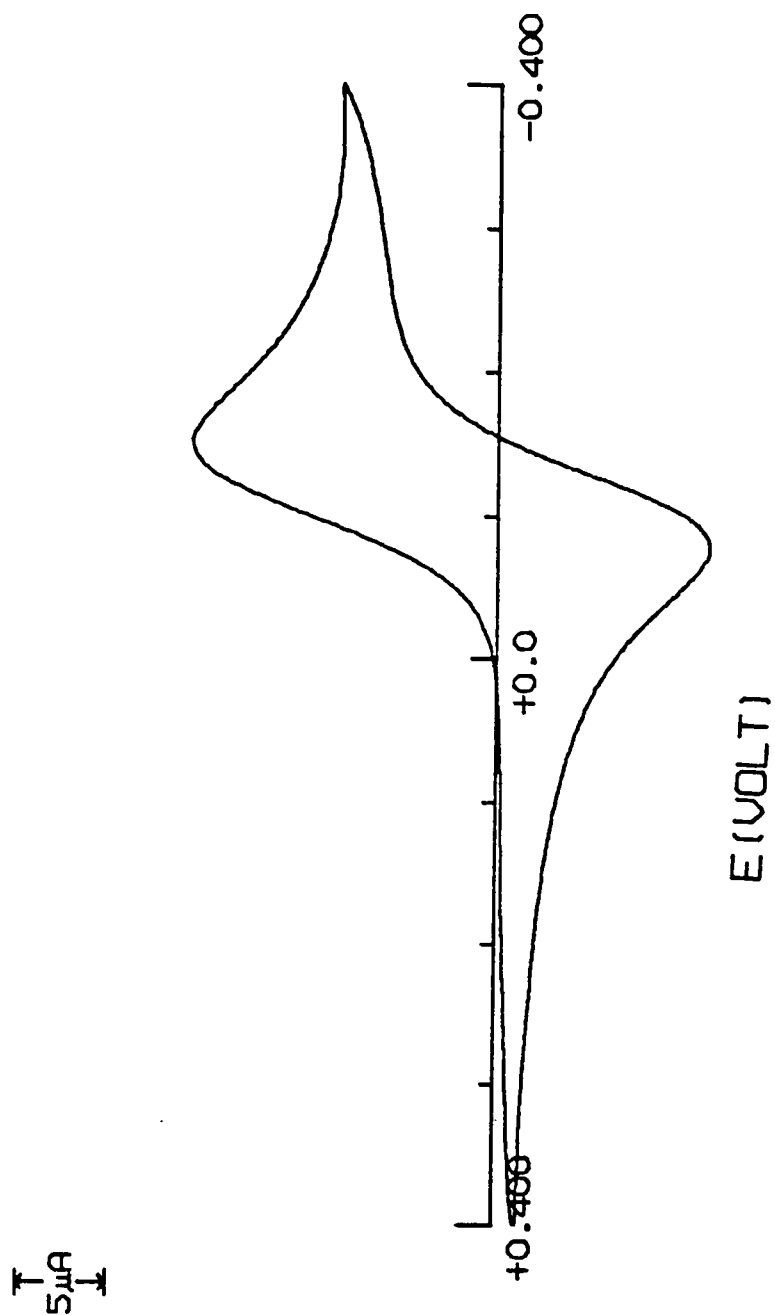


Figure 22. Cyclic voltammogram of TCNQ diol in 0.1M TEAP/DMA potential vs Ag/AgCl.

2. In DMA the polymer exists essentially as a fully extended rod-like molecule, thus making $b = 0.55$. This assumption is reasonable since DMA was found to be an excellent solvent for PU-MDI.¹³⁵

3. The polymer is linear. This may not be strictly correct since PNMR data and IR data indicates the presence of allophonate and biuret linkages.

In order to eliminate most of the above assumptions and to serve as a check on the method previously used, the electrochemical and viscosity measurements were combined in a fashion similar to Mark-Houwink treatment. For polymer molecules in dilute solution, the diffusion coefficient, D , is related to the molecular weight, M ,¹⁵⁴⁻¹⁵⁸ by:

$$D \propto 1/M^b \quad (20A)$$

where D is the diffusion coefficient and b is a constant for a given polymer-solvent system. Equation (20A) is often expressed in the more general form¹⁵⁵

$$D = K_T M^{-b} \quad (20B)$$

The value of D was calculated from the slope of Figure 23. An average D value of $4.1 \times 10^{-6} \text{ cm}^2/\text{s}$ was obtained when the experiment was performed four times. Using equation 20B, the value of K_T was calculated to be 1.0×10^{-4} for TCNQ diol. The value of K_T was assumed to be of the same order of magnitude for both the monomer and the

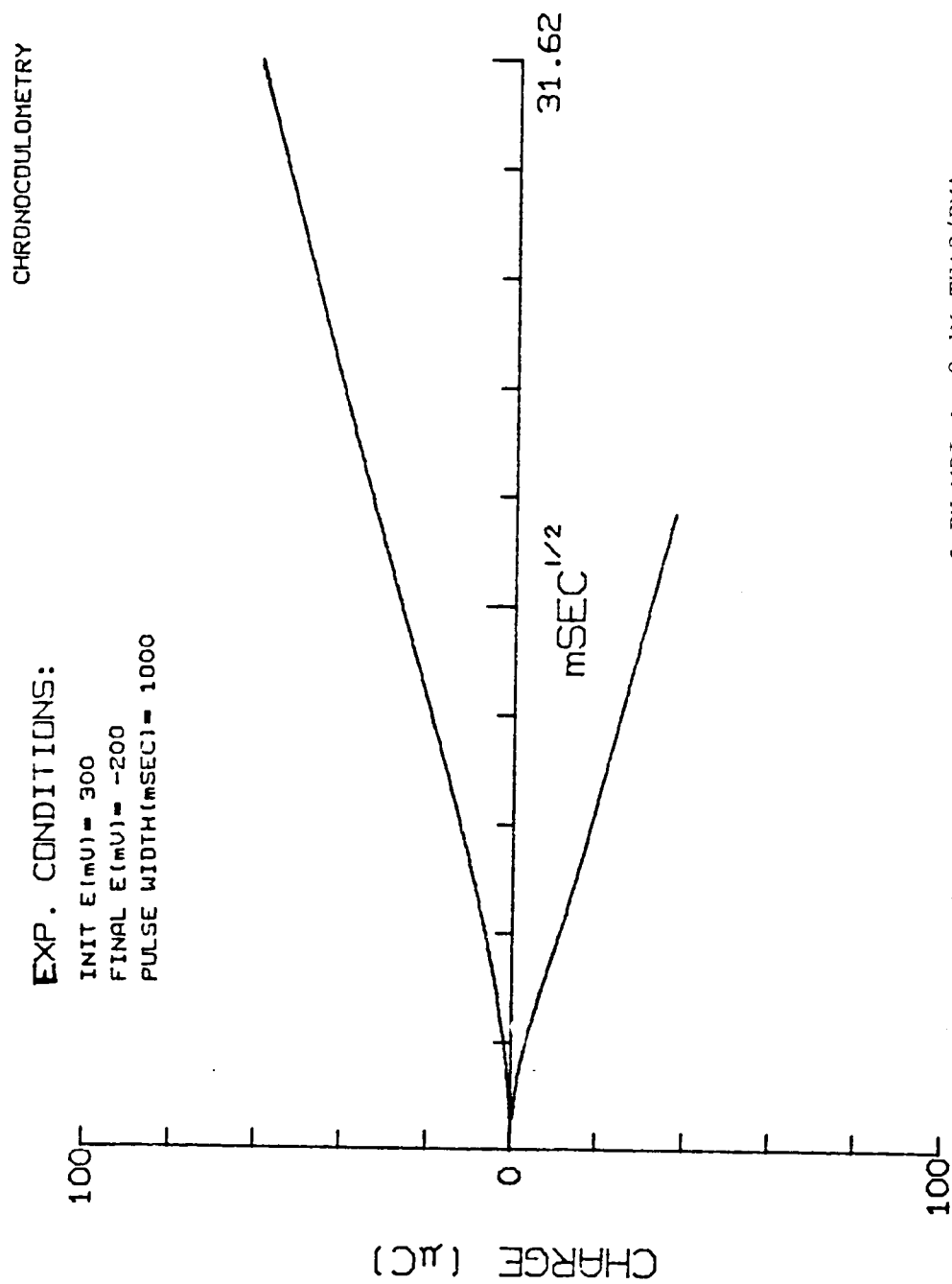


Figure 23. Chronocoulometry of PU-MDI in 0.1M TEAP/DMA.

polymer^{129b,155} and so it was used in the Mark-Houwink equation to calculate M , when b was set equal to 0.55. This gave a molecular weight, M , of 6×10^4 Daltons. Using the slope from i_p versus $v^{1/2}$ (see Figure 26) which reflects the diffusion coefficient for the monomer,¹⁵⁵ K_T can also be calculated. This value was calculated to be 1.1×10^{-4} , using equation 20. Substituting this value in equation 20B, gave $M = 5.0 \times 10^4$. Using the slope of i_p versus $v^{1/2}$ for the polymer (see Figure 24) in solution along with $K_T = 1.1 \times 10^{-4}$ gave $M = 2.0 \times 10^4$.

The above calculations assumed K_T for the monomer and polymer are of the same order of magnitudes. This assumption is reasonable since DMA was the solvent for both monomer and polymer.¹⁵⁹

The validity of the molecular weights calculated was tested by substituting them in equation 18 along with the other relevant data and calculating the peak currents. The calculated peak currents are shown in Table XXXIV along with the experimentally observed peak current for comparison. Table XXXIV would indicate that the molecular weights calculated are not the actual molecular weights of the polymer in solution. However, one has to be careful in making conclusions since the major contribution to i_p may be high molecular weight polymer adsorbed onto the surface of the electrode and thus not a true representative of the species in solution. The adsorption is indicated by the positive intercept of the i_p versus $v^{1/2}$ graph seen in Figure 24.

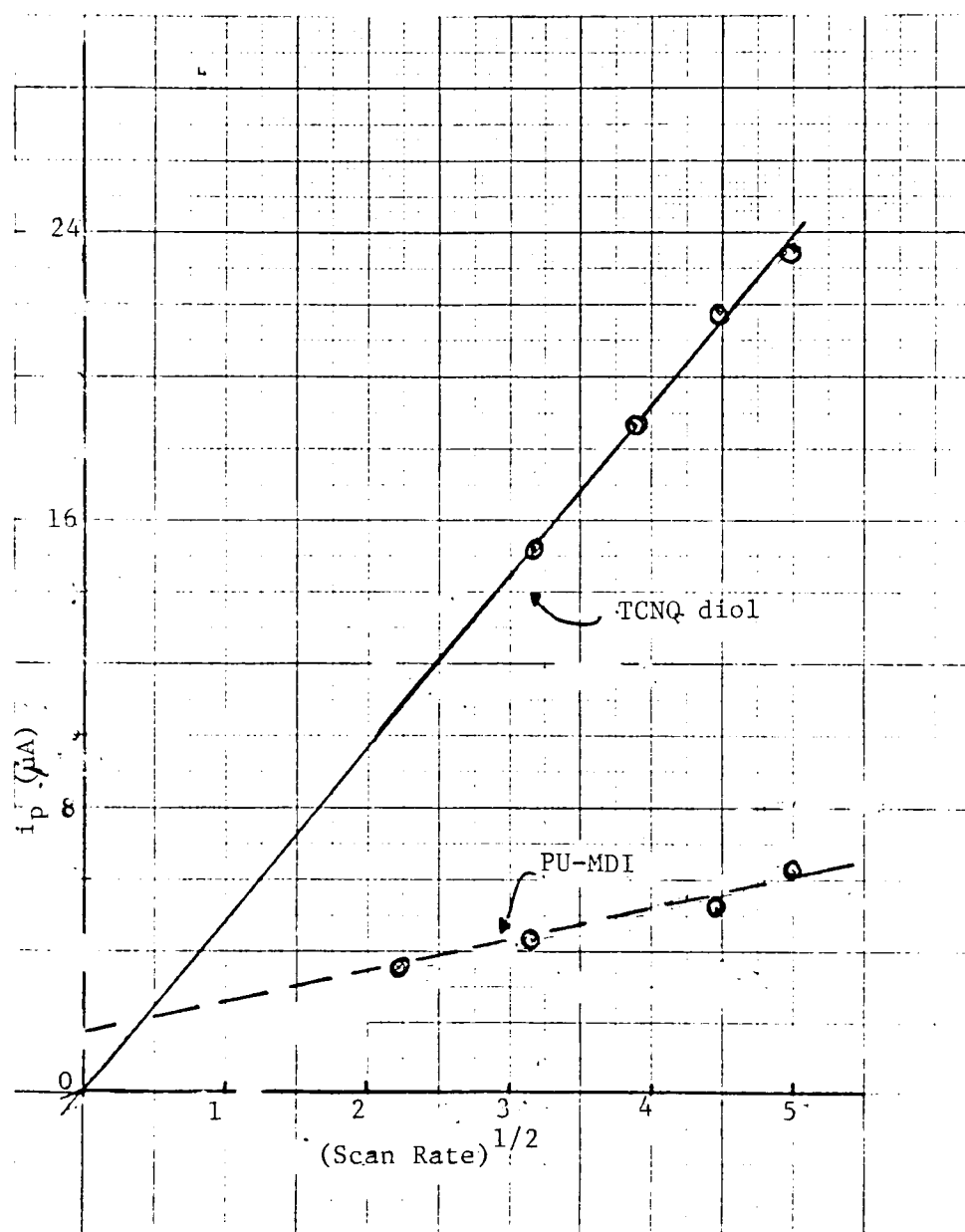


Figure 24. Peak potential dependence on scan rate for TCNQ diol and PU-MDI

Table XXXIV

Experimental and Calculated Peak Currents Based on Eq. 18

Molecular Weight	i_p Calculated	i_p from CV ^a
6.0×10^4	4.1×10^{-6}	1.3×10^{-6}
5.0×10^4	5.3×10^{-6}	1.3×10^{-6}
2.0×10^4	5.3×10^{-6}	1.3×10^{-6}

^aSweep rate = 10 mV/S, Area = $1.26 \times 10^{-5} \text{ m}^2$.

CHAPTER IV

ELECTROCHEMICAL STUDIES

As stated earlier, the electrochemistry of PE-TCNQ has been extensively studied in our laboratory. Due to the instability of the films when baked for short times at 130°C and fully reduced, attention was focused on the polyurethanes which are known to be more resistant to base hydrolysis.⁴³ The polyurethanes chosen were PU-MDI, which contains the "stiffening agent," methylene-1,4-bis(phenylisocyanate);⁴⁸ PU-TDI which also contains an aromatic ring, adding rigidity to the polymer; and PU-HMDI which contains six methylene groups acting like a plasticizer; adding flexibility to the polymer. It was hoped that the gradation of properties imparted to these polymers by the use of different diisocyanates would enlighten us on the effects of chemical structure on the electrochemical behavior of these polymers. The structural similarity between Day's polyester, PE-TCNQ, and PU-HMDI could show on a qualitative basis how the strong hydrogen bonding capability of the urethane group dictates the electrochemistry of these materials when compared to the weak hydrogen bonding capability of the ester group.⁴⁸

A. Experimental

a. Film Preparation. A number of methods have been developed to apply polymer films to electrode surfaces. For example, dip coating,^{160,161} spin coating¹⁶²⁻¹⁶⁴ oxidative or reductive deposition,^{165,164-167} droplet evaporation,^{168,169-171} electrochemical polymerization¹⁷²⁻¹⁷⁶ and RF plasma polymerization.¹⁷⁷ We utilized the droplet evaporation method. The disadvantage of this method is that films prepared in this manner can be topologically rough¹⁶⁸ unless the evaporation is very slow as in a container nearly saturated with solvent vapor.¹⁷⁸ Film uniformity can be improved by spinning the solution off, or otherwise removing it after only partial evaporation.^{179,180}

The films were prepared by dissolving the polymers in a DMA/Acetone (1/2, v/v) mixture and evaporating a few drops of the solution on the platinum surface of an electrode in a desiccator under vacuum. It was observed that the solution could be kept for a longer time if the polymer was dissolved in pure DMA, however the evaporation of the solvent took a longer time. All the films were baked for 2-3 minutes at 110°C unless stated otherwise.

b. Materials. Analytical grade LiCl, NaCl, KCl, RbCl, CsCl, NaClO₄, NaOH, CaCl₂, BaCl₂ and CdCl₂ (all from Fisher Scientific) were used without further purification, while NaH₂PO₄, Na₂HPO₄ (both from Fisher Scientific), tetraethylammonium chloride, TEACl, tetramethylammonium chloride TMACl and tetraethylammonium perchlorate, TEAP, (all from Eastman) were recrystallized and dried under vacuum prior to use.

All solvents, including distilled methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), n-butanol (BuOH), acetonitrile (99 +% Aldrich), reagent grade acetone and doubly distilled water, were purged with either argon or nitrogen before use for electrochemical experiments. All the solutions were 0.1M with respect to the electrolyte unless stated otherwise.

B. Baking Experiments

The effects of baking on Day's polyester was investigated at various temperatures and for various baking times.⁵¹ The baked films were examined by UV-VIS and IR spectra. Day found the appearance of new absorbance bands at 1437cm^{-1} and 1275cm^{-1} accompanied a decrease in the absorbance bands due to TCNQ in the IR spectrum. He also reported a significant decrease in the UV-VIS absorbance at 415nm and 432nm when the films were baked at 135°C for 90 min. From these findings he concluded that the baking process involved reactions of the TCNQ units.

Day also observed dissolution of the unbaked polyester ester film during cyclic voltammetry. Unlike the polyester films, the polyurethane films did not show significant changes in the CV for an unbaked film in aqueous media even after the film had been cycled a number of times. However, dissolution of the unbaked polyurethane films in nonaqueous media was obvious after a few cycles. Significant changes in the peak current for an unbaked film versus a baked film were observed along with an extended break-in time for baked film. These

observations prompted an extension of Day's work to examine the break-in phenomenon, described below, as a function of baking.

For virgin films, several cycles were required for the film to become fully electroactive and attain a state which yielded reproducible voltammograms. This is termed the break-in process and is illustrated in Figure 25 for a thick ($\geq 1.2 \text{ KÅ}$) PU-MDI film. The current, which was practically negligible, during the initial sweep gradually increased with each successive sweep until there was no significant changes in either the peak current or the peak voltage.

In these experiments, the same volume of PU-MDI solution was evaporated on a platinum disk electrode. The films were then baked at 120°C for various times and the voltammograms recorded for long enough times to capture the full break-in process on the same voltammogram. The cathodic peak current, i_p^c , was then graphed as a function of the break-in time, which is defined as the time from the start of the initial sweep to the time at a given i_p^c . The electrolyte used was aqueous 0.1M LiCl and the reference electrode was a saturated calomel electrode.

a. Break-in As A Function of Baking. For an unbaked film, after about five cycles the current was stabilized and the film fully broken-in as shown in Figure 26. Unlike the polyester films, these unbaked PU-MDI films could be cycled to large negative potentials (-1.0V) without any significant changes in the voltammogram when the potential range was returned to its original values ($+0.3\text{V}$ to -0.5V). When a film was baked for a long period of time (15min), the break-in shown in Figure 25 was obtained. Significantly, many more cycles were

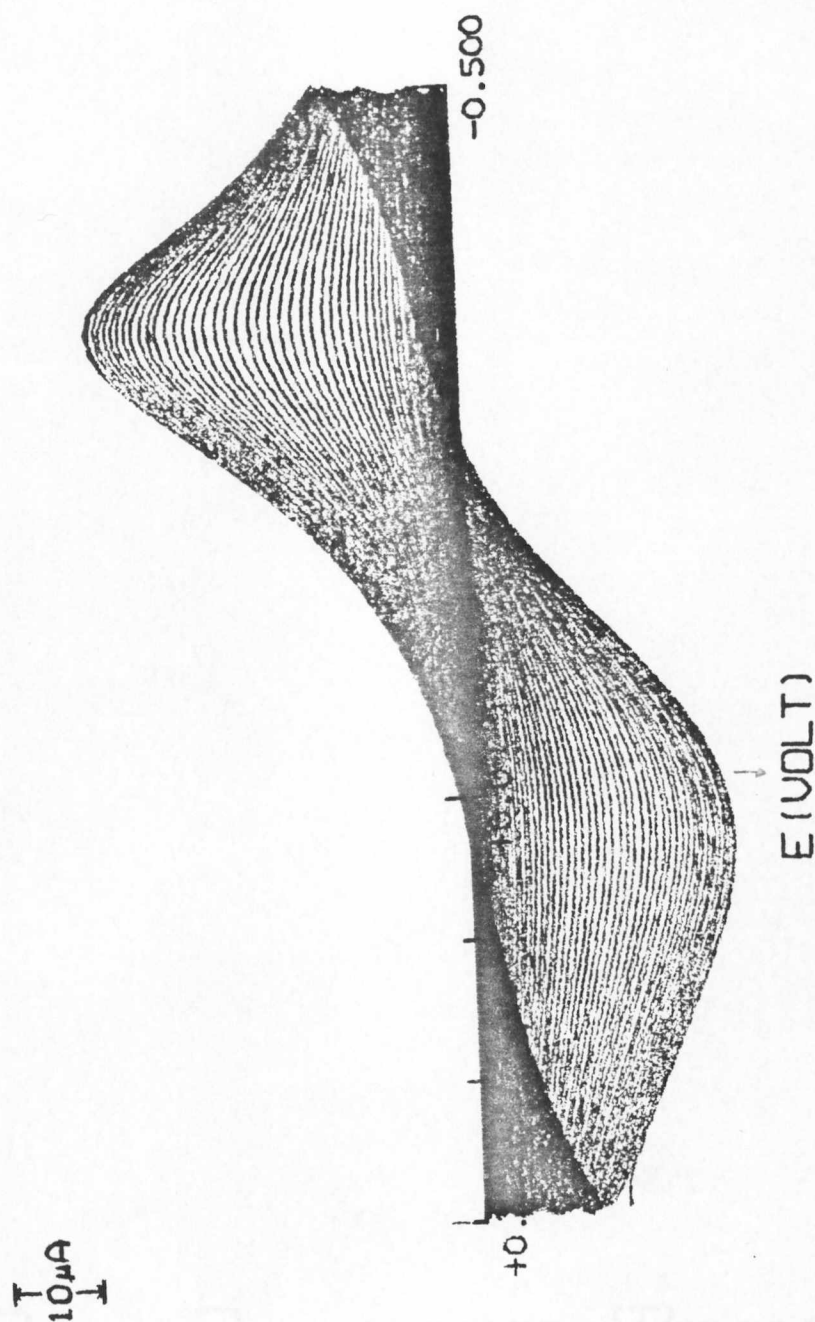


Figure 25. Break-in for PU-MDI film in 0.1M LiCl vs SCE baked 10 mins. 30mV/s.

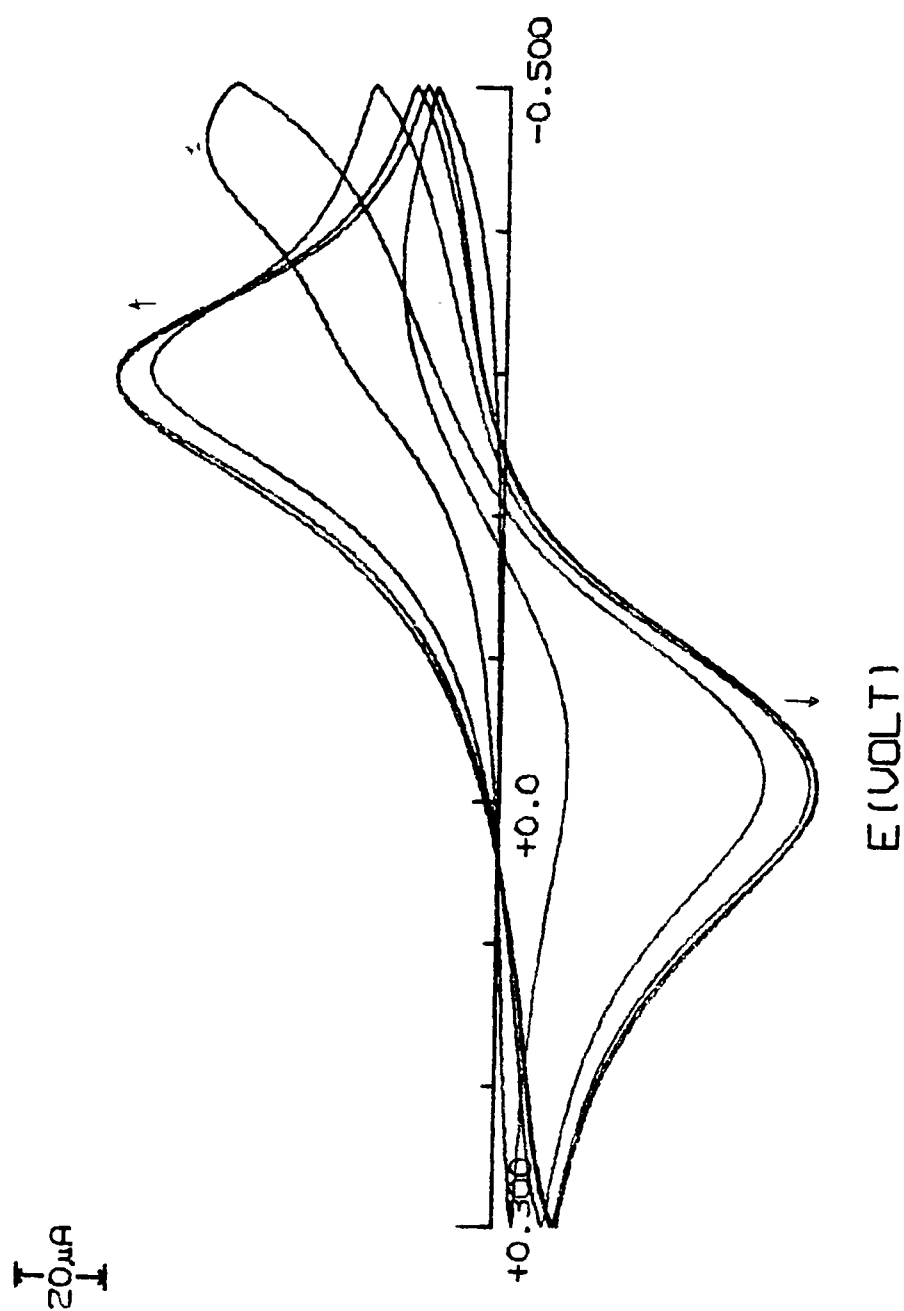


Figure 26. Break-in for unbaked PU-MDI film in 0.1M LiCl vs SCE; 30mV/s.

required for this film to be fully broken-in and the current scale decreased by a factor of two. Similar decreases in the current were observed for films baked for 5 min and 10 min. These results are summarized in Figure 27. These results show that an unbaked film was fully broken-in after about 3 min, while longer times were required for baked films. The i_p^c value for a fully broken-in film baked for 5-10 min was about 47% less than i_p^c observed for unbaked film, and 37% more than i_p^c observed for a film baked 15 min after a break-in time of 52 min. These results indicate that baking a film, to be used in an aqueous medium, for longer than 5 min, but less than 10 min, only increases the break-in time.

The number of cycles required for the break-in process to be completed was dependent on: a) the film thickness, thick films requiring many cycles to be fully broken-in, while thin films were broken-in in a few cycles¹⁶³; b) the baking time, the films baked for long times requiring many cycles before they were fully broken-in while unbaked films were broken-in in a few cycles; c) the solvent, the break-in process was completed in fewer cycles in nonaqueous solvents.

The break-in is thought to involve switching the polymer from an insulating film to a conducting medium, allowing the movement of solvent and counter-ions through the film as shown in Figure 28 in a layered fashion. Once the film was fully broken-in it could be reversibly reduced and oxidized.

The longer break-in time required for baked films may be due to a more compact structure of these films which makes the solvent swelling process which is assumed to be involved in the break-in process,

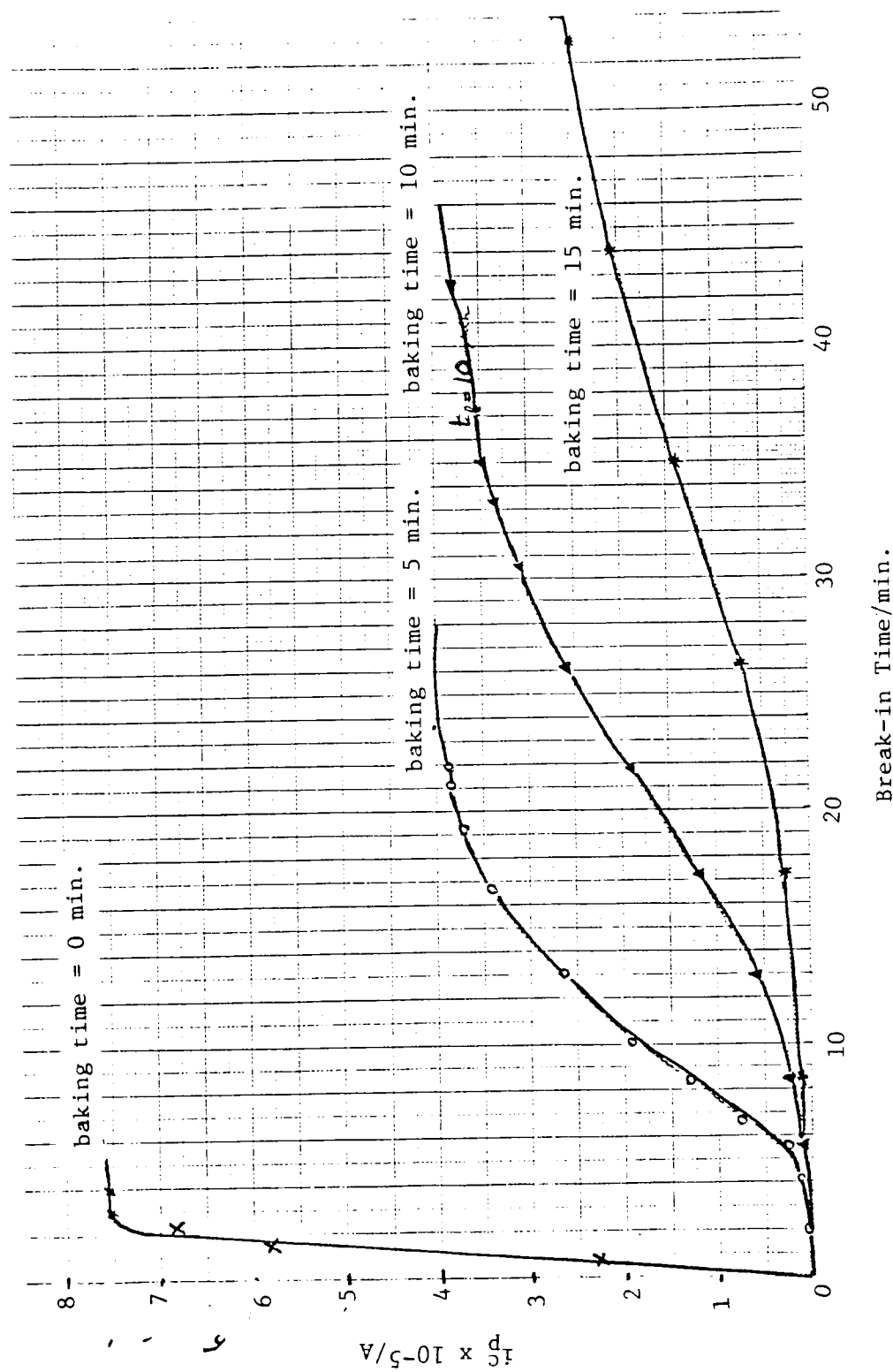


Figure 27. Plot of peak current vs Break-in time for PU-MDI film in 0.1M LiCl potential vs SCE.

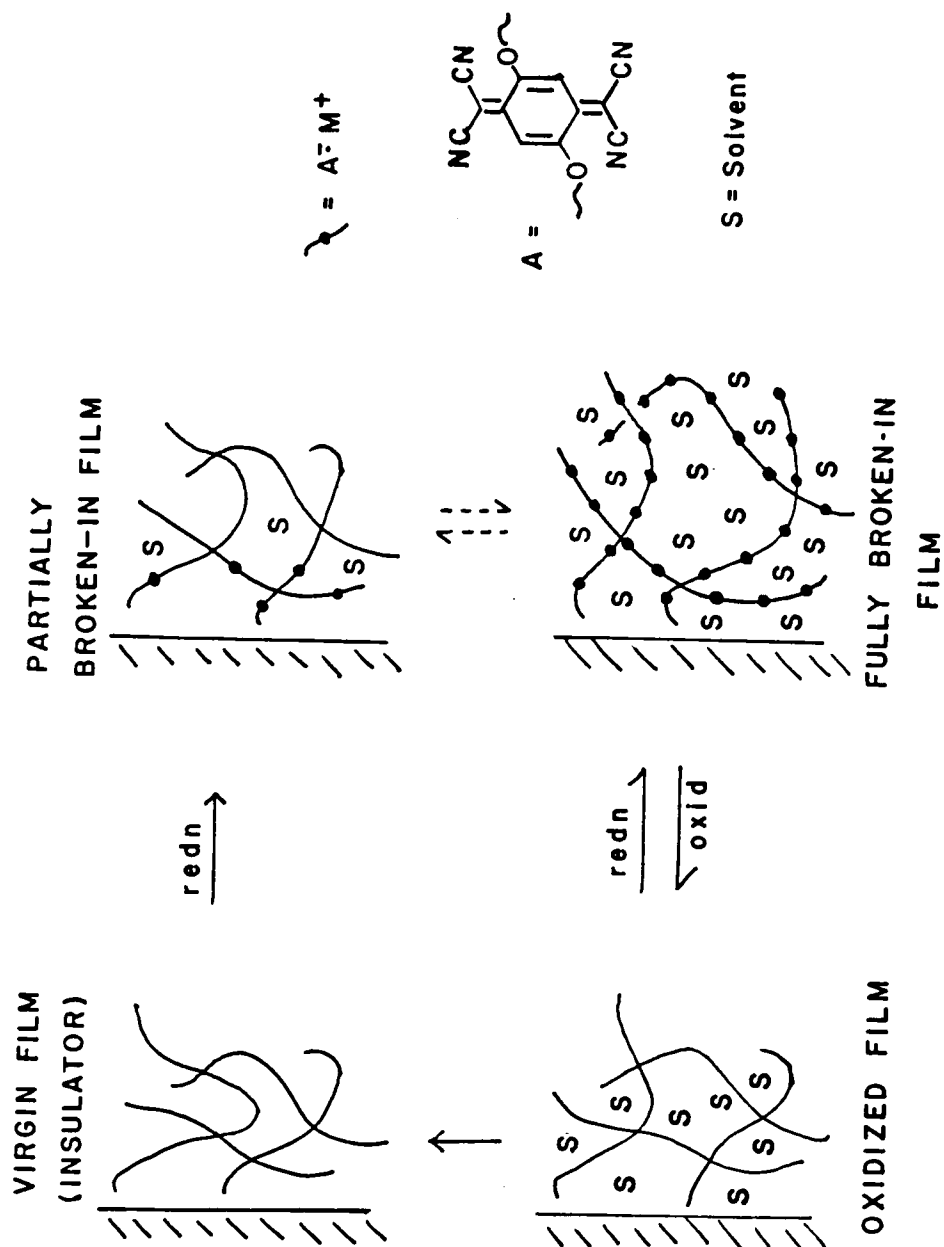
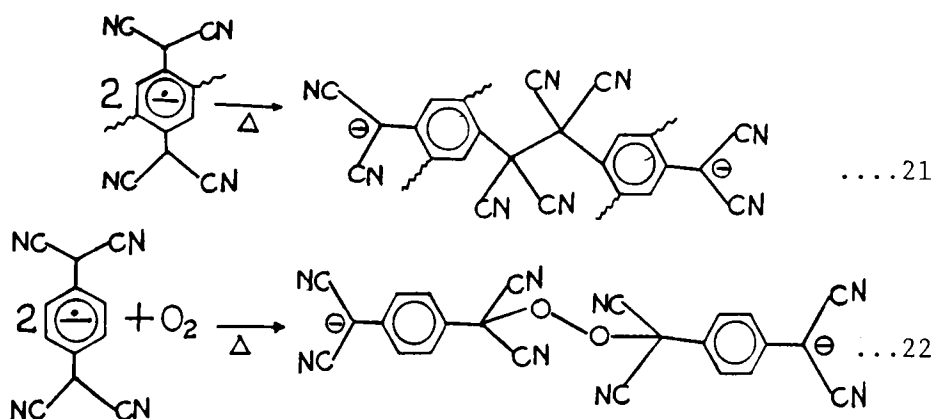


Figure 28. Electrochemically driven film swelling.

difficult. This swelling process may involve interaction of the solvent with the polymer by means of gross defects such as cracks, channels, or pores, or alternatively on a more microscopic scale, through uniform penetration into a homogeneous polymer phase.¹⁶³

In agreement with Day's baking experiments,⁵¹ a significant decrease in i_p^c for the baked films was observed. This decrease in i_p^c indicates that some of the TCNQ units were being irreversibly destroyed upon baking. A possible explanation for the current decrease is the reaction of trapped radical sites in the polymer on heating. The reactions taking place may be a combination of equations 21 and 22 below.



Conceivably, this decrease in i_p^c upon baking the film could also be due to cross-linking of the polymer via a transcarbamation reaction, causing a portion of the TCNQ units to be inaccessible.

Though not investigated further, appearance of an absorbance peak in the IR spectrum of the baked film in the region of 1600 cm^{-1} - 1700 cm^{-1} could indicate if such a process is occurring.¹⁵³ The further decrease of i_p^c upon baking the film for 15 min is not clear, but it may be a result of further reaction of unreacted radical sites, thermal decomposition of TCNQ units, or annealing of the polymer. Annealing of the polymer could result in the formation of crystallites, thus making some of the TCNQ units inaccessible if enough solvation energy is not provided to overcome the heat of crystallization.

b. Percent Radical As A Function of Baking. The ESR signal of a PU-HMDI film on a platinum grid electrode was observed as a function of baking at 120°C . The ESR signal of film was observed until no change was apparent in the intensity of the peaks when the film was baked for a certain period of time. The ESR signal, measured as the peak-to-peak distance of the baked film, was compared to the ESR signal obtained for an unbaked film.

The experiments revealed that after 2 min baking time the ESR signal decreased by 16%. This decrease doubled when the film was baked for an additional 13 min (total baking time = 15 min) and the decrease tripled when the total baking time of the film increased to 25 min. These results are summarized in Table XXXV. A mechanism for the decrease in the intensity of the ESR signal upon baking the film was proposed above. Equation 21 is probably the major reaction taking place in the film since Day¹⁵ reported that polyester films baked in a vacuum also showed a change in both the IR and UV-VIS spectra. Unfortunately Day did not report if he had degassed the solution before

Table XXXV

Percent Radical as a Function of Baking for a Dry PU-HMDI Film

Baking time (min)	Peak-to-Peak Signal(s)	% Decrease
0	72.0	0
2	60.8	15.7
15	45.4	36.8
25	34.9	51.2

he cast the films. If the solution was not carefully degassed, equation 22 cannot be eliminated. These results show that TCNQ units are being irreversibly changed to nonelectroactive molecules during the baking process. The stability of the film towards dissolution in nonaqueous solvents was also significantly improved upon baking the film possibly due to cross-linking.

c. Stability of Unbaked Film. Erratic, non-reproducible CV responses were observed when a film is cast from a DMA polyurethane solution which has been sitting a few days. If acetone is added to the solution, deterioration is even faster. Similar observations have been made by Karimi for Day's polyester and a terpolyester synthesized from compound 3, adipyl chloride and TCNQ diol.⁷⁰ It was decided to look at a film exposed to regular laboratory conditions for an extended period of time. A film was cast in the usual manner (see page 00) and the CV for this unbaked film in 0.1M LiCl recorded. After the break-in of this film was completed, it was removed from the aqueous electrolyte and placed on the laboratory bench for two months.

At the end of this period the CV was repeated. A break-in was observed as if it were a new film with only small changes observed in the peak potentials. The film was then exposed to sunlight for a week and the CV again repeated. The CV revealed a voltammogram for a virgin film in LiCl. A break-in was observed, however there was a shift in the cathodic and anodic peak potentials toward the positive direction as can be seen by comparing Figures 29 and 30. There is also a decrease for both the anodic and cathodic peak currents.

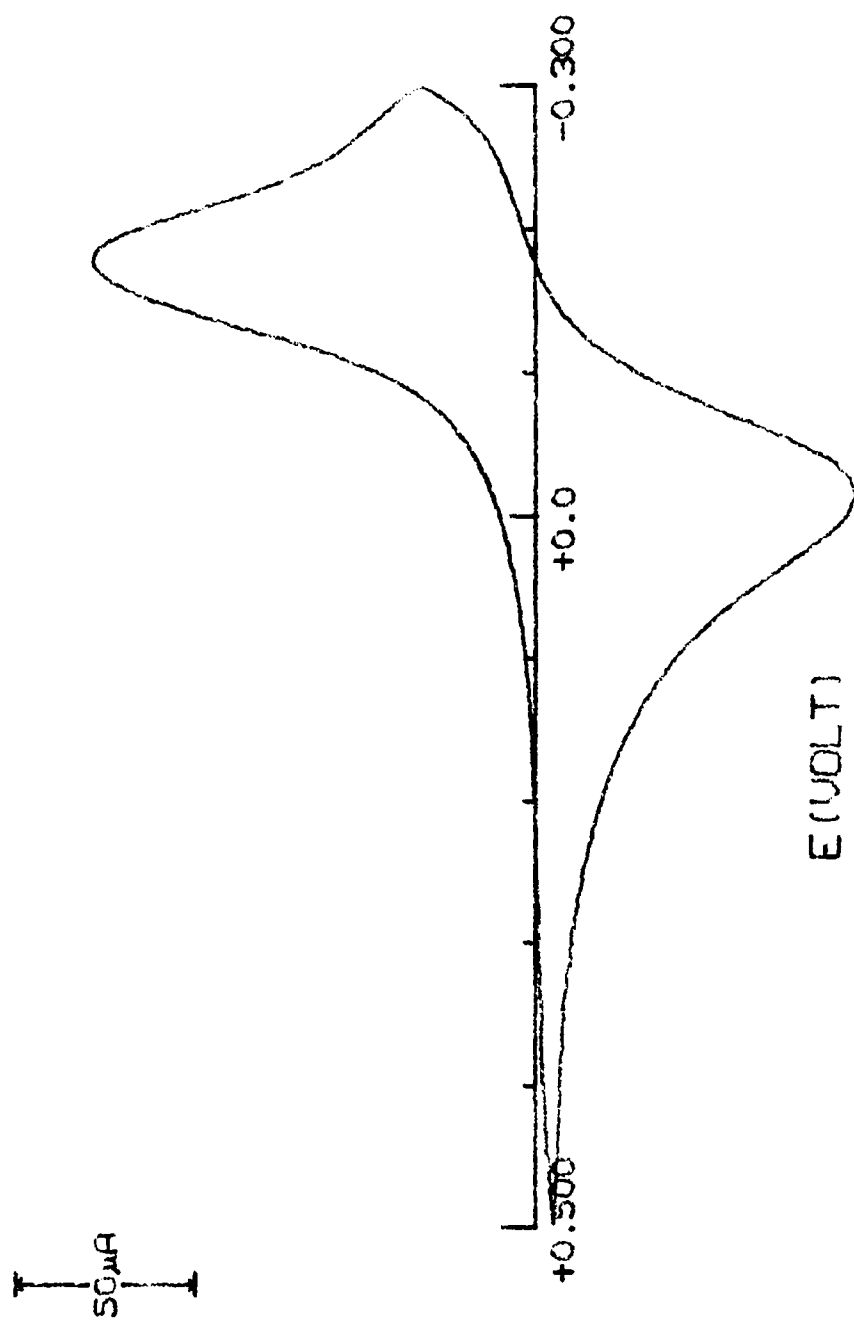


Figure 29. Cyclic voltammogram for unbaked PU-MDI film after 2 months exposure to air, 30mV/s.

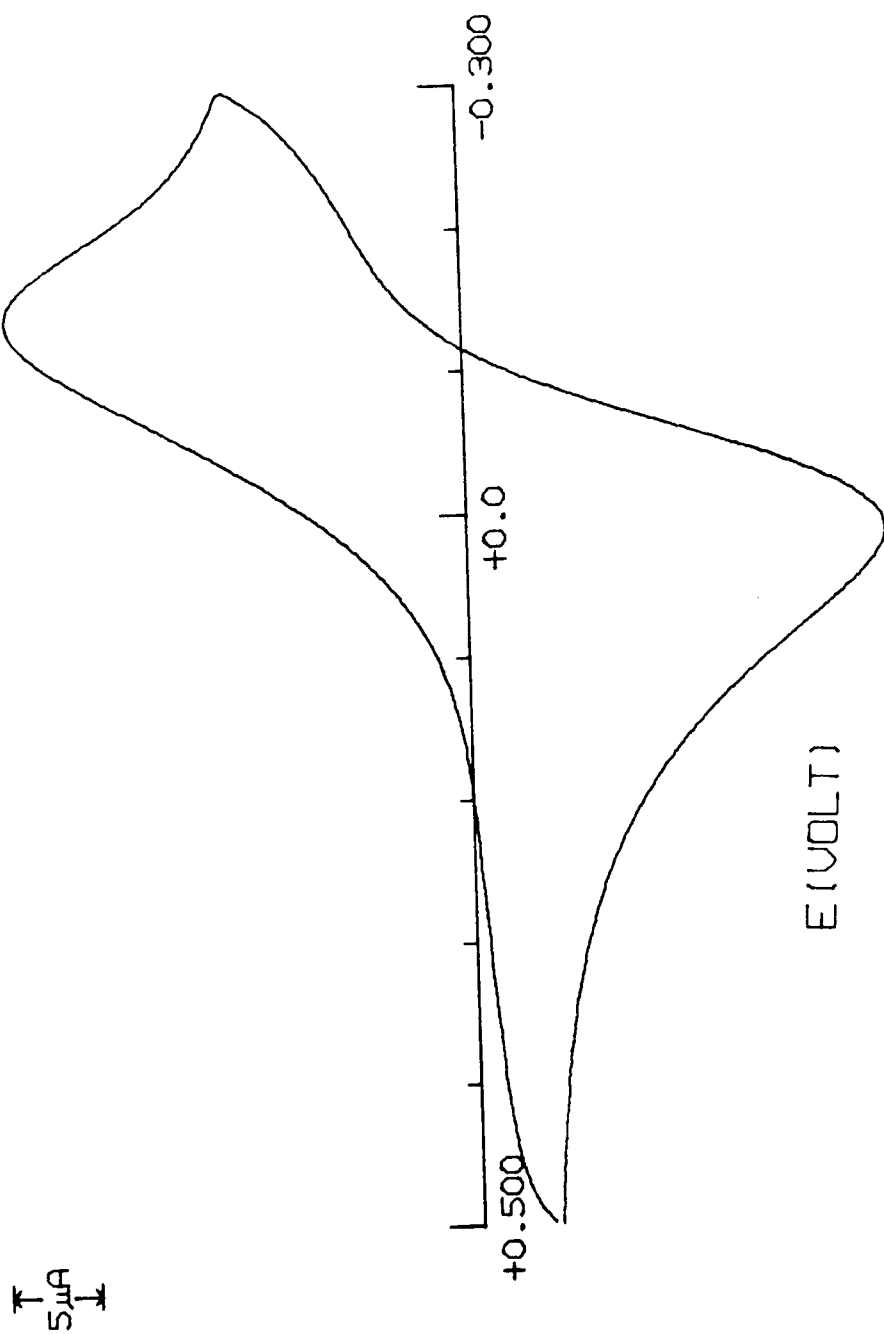


Figure 30. Cyclic voltammogram for unbaked PU-MDI film after 8 days exposure to sunlight, 30mV/s.

This simple and preliminary set of experiments demonstrate the remarkable stability of these TCNQ polymer films. They also suggest that over extended periods of time TCNQ $\cdot^-$ in solution reacts with either oxygen from the air or with the solution. A careful degassing of the solution was not carried out to eliminate deterioration due to oxygen from the air, but in light of these results of the unbaked film it would seem to suggest a reaction with the solvent is responsible for TCNQ's erratic behavior of old DMA solutions. The changes in the voltammogram when the film was exposed to sunlight maybe a result of a quinone-imide reaction occurring with the MDI units and the ultraviolet light from the sun.

C. Cation Effect

In aqueous LiCl solutions, the CV of a thick, virgin PU-HMDI film shows one quasi-reversible peak of $E_p^c = 205$ mV and one irreversible peak at $E_p^c = -395$ mV on the first cycle. On subsequent cycles, as shown in Figure 31, the first wave broadens and the second wave is severely diminished and drawn out. Subsequent cycling of the film to -0.5 V is also accompanied by a decrease in the peak current for the first wave. Interestingly, on repeated cycling of the film the second wave disappears. This second wave will reappear if the film is cycled only in the range of the first wave and then back to the range of the second wave, or if the film is allowed to sit in the solution for a while.

If a virgin film is cycled in Li^+ to -0.3 V, a voltammogram as shown in Figure 32 is typically obtained. Figure 32 shows a break-in

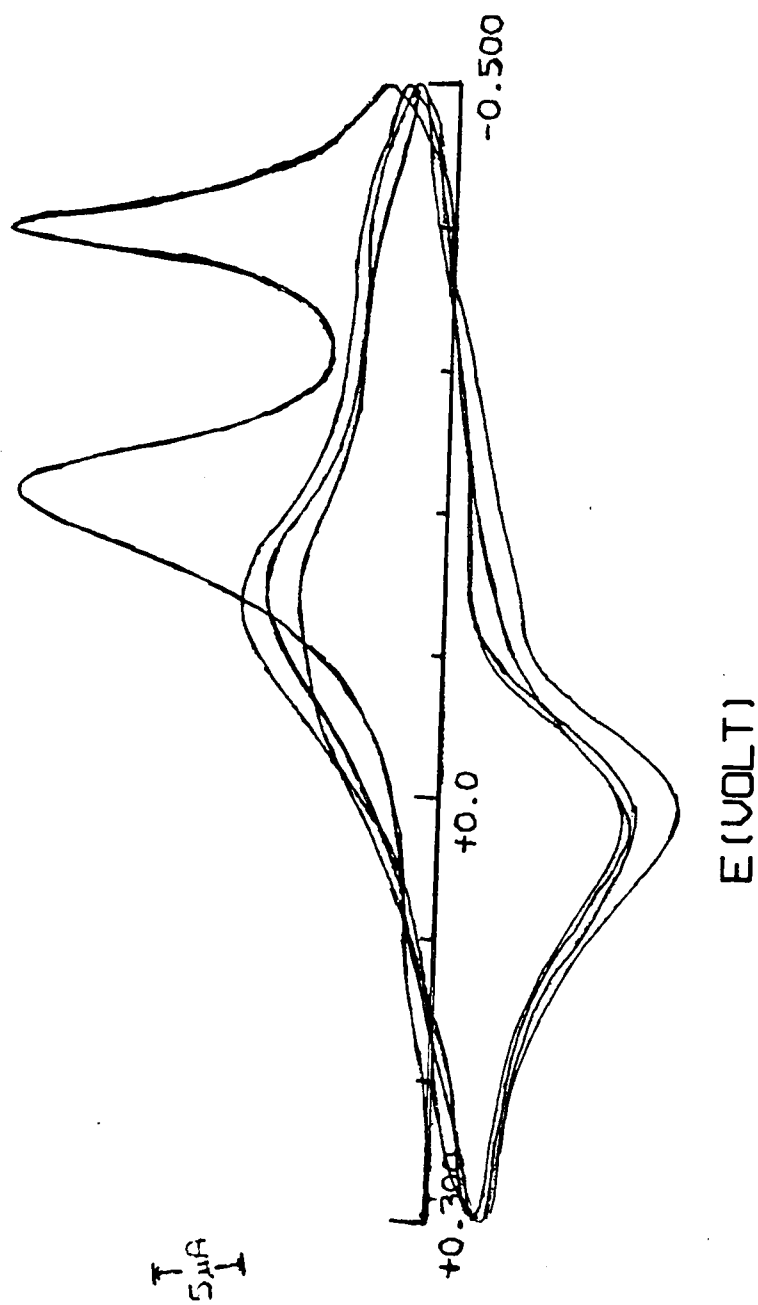


Figure 31. Cyclic voltammogram for PU-HMDI film in 0.1M LiCl potential vs SCE.

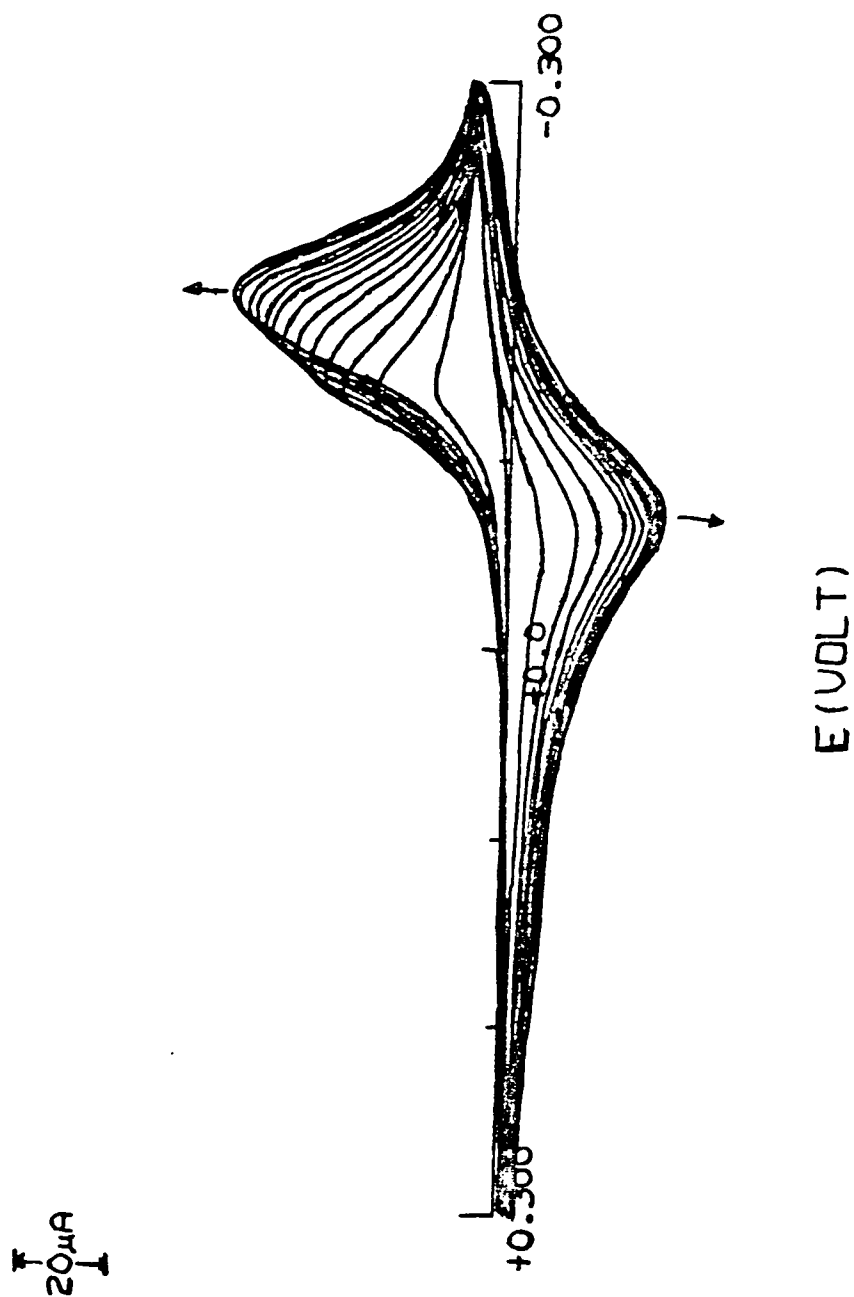
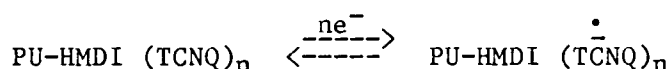


Figure 32. Cyclic voltammogram for PU-HMDI film in 0.1M LiCl when cycled between +0.3V and -0.3V, potential vs SCE.

process occurring for the PU-HMDI film. Like the tetrathiafulvalene polymer of Kaufman and coworkers,¹⁶² this break-in process could be reproduced a number of times for the same film, if it was allowed to sit in solution for a long enough period of time and then cycled again, or if the potential was held at a potential positive of the first wave, say +0.5 V, for a while before the film was recycled.

The quasi-reversible first wave observed for PU-HMDI may be represented by the following process:

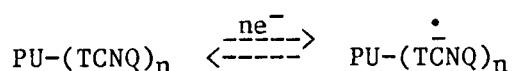


One could speculate that the second wave was due to formation of PU-HMDI (TCNQ)_n²⁻, via the transfer of ne⁻ to the radical anion, but further experiments are needed before this can be confirmed. It is clear from the CV that the effective diffusion coefficient for charge transport (D_{ct}) is very different for both waves. The second wave has a much smaller D_{ct} than the first wave and a correspondingly lower peak current. This may be related in part to the difficulty of incorporating a second large hydrated lithium ion $[\text{Li}(\text{H}_2\text{O})_n]^+$ into the film, which would be essential to maintain electrical neutrality in the film should the fully reduced TCNQ²⁻ species be formed.

Initially it was thought that the decrease in current when the film was continually cycled to -0.5 V was due to dissolution and/or degradation of the PU-HMDI film as was the case for PE-TCNQ.^{38,181} However, the UV-VIS spectrum of an aqueous solution of LiCl in which a number of films had been cycled many times did not indicate any strong

absorption characteristic of the TCNQ moiety. This was used as evidence that dissolution was not taking place and thus, could not be responsible for the decrease in peak current.

The electrochemical behavior of basically one quasi-reversible wave corresponding to the one-electron reduction of the TCNQ groups



in aqueous LiCl was also observed for PU-MDI and PU-TDI as shown in Figures 25 and 33. Again, a break-in process is observed for the virgin film (see Figure 25), and the film could be cycled numerous times after the break-in was completed without any significant changes in peak potential, (E_p) or peak current (i_p). The PU-TDI polymer shows a very attenuated second wave at about -440 mV, similar to that seen for PU-HMDI film which had been cycled a number of times. Further experiments are needed to confirm its origin.

Clearly, CVs which feature just one quasi-reversible wave even when the polyurethane films are cycled to large negative potentials (≤ 1.0 V) do not demonstrate the electrochemical behavior expected for the TCNQ monomer (see page 43) in that the second wave was absent. The film thickness was varied by diluting the solutions used to cast the films and repeating the CV. The results obtained were virtually the same. The sweep rate was also lowered (≥ 5 mV/s), however no second wave was observed. Spectroelectrochemical experiments were also performed in order to investigate the absence of the second wave. These experiments and results will be discussed in the

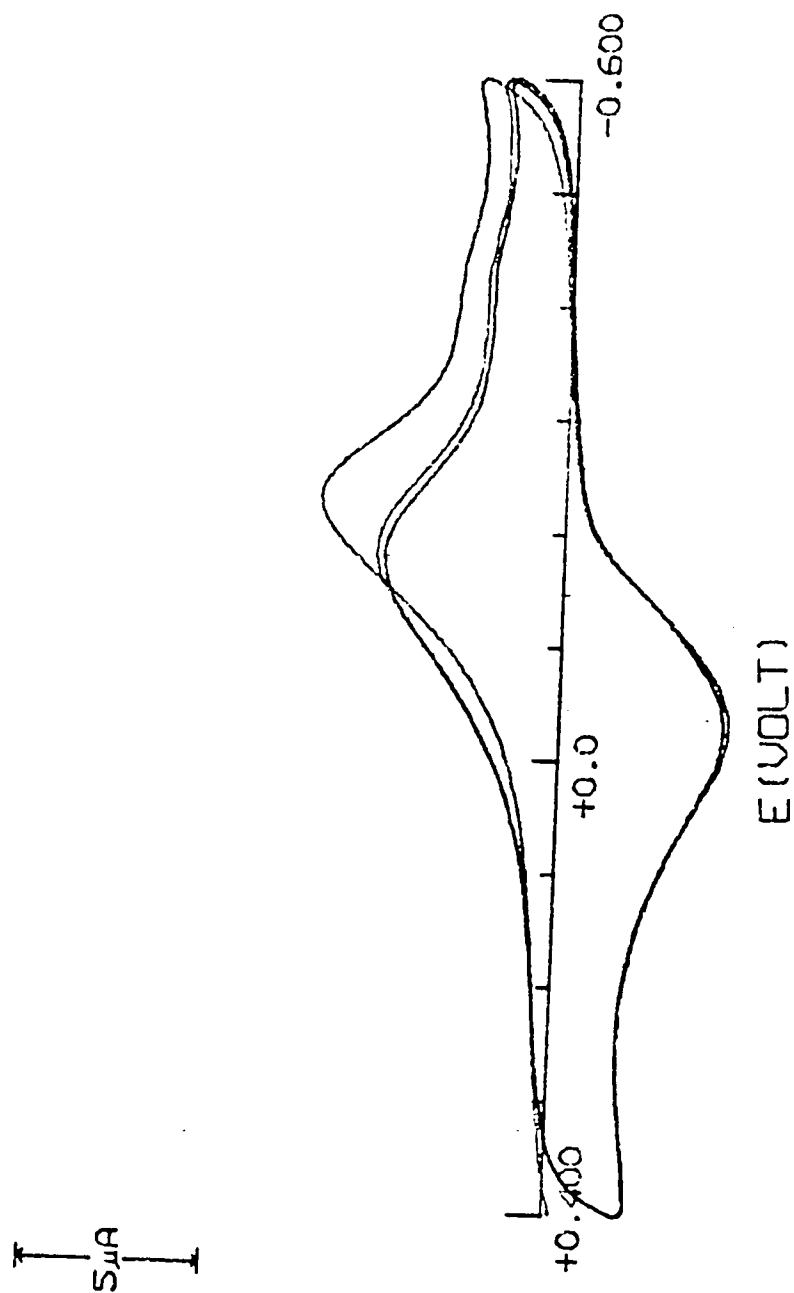


Figure 33. Cyclic voltammogram for PU-TDI film in 0.1M LiCl potential vs SCE; 30mV/s.

spectroelectrochemistry section. This behavior of the polyurethanes was a striking contrast to the behavior reported for PE-TCNQ under similar conditions.³⁵ Spectroelectrochemistry experiments indicate that the single wave observed for these polyurethanes in aqueous media is due to $\text{TCNQ}^{0/-}$ process. The $\text{TCNQ}^{\cdot-}$ absorbance does not exhibit a maximum in the negative-going sweep; a plateau is reached, indicating a single one-electron process.^{39,179}

D. Variation of Lithium Ion Concentration

For a reaction:



The Nernst equation can be written in the form:

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[\text{A}]}{[\text{A}^{\cdot-}]} \quad \quad (24a)$$

where: E = observed peak potential

E° = standard peak potential for the half reaction shown

F = Faraday constant

n = number of electron transferred

T = Temperature

R = universal gas constant

If a one-electron reduction is carried out at 25°C we can rewrite equation 23 as:

$$E = E^\circ + 59 \text{ mV} \log \frac{[\text{A}]}{[\text{A}^{\cdot-}]} \quad \quad (24b)$$

This equation assumes a simple one-electron transfer reaction in which dimerization and/or solvent interaction with any of the species involved is absent. If ion-pairing is involved, then we need to consider:



$$\text{From which } K_f = \frac{[A^{\bullet-} M^+]}{[M^+][A^{\bullet-}]} \quad \quad (26a)$$

$$\text{or } [A^{\bullet-}] = \frac{[A^{\bullet-} M^+]}{K_f [M^+]} \quad \quad (26b)$$

where K_f is the equilibrium constant. Substituting equation 26b in equation 24a and letting $M^+ = Li^+$ gives:

$$E = E^\circ + \frac{RT}{nF} \ln K_f [Li^+] + \frac{RT}{nF} \ln \frac{[A]}{[A^{\bullet-} \dots Li^+]} \quad \quad (27)$$

at $E = E_{1/2}$, $[A] = [A^{\bullet-} \dots Li^+]$ and if K_f is large we can write

$$E_{1/2} \approx E^\circ + \frac{RT}{nF} \ln K_f + \frac{RT}{nF} \ln [Li^+] \quad \quad (28)$$

Under ideal conditions at 25°C, a plot of E versus $\log [Li^+]$ should give a straight line having a slope of 59 mV, when $n = 1$. This Nernstian dependence of the peak potential as a function of electrolyte concentration was not observed for PU-MDI films in contact with aqueous LiCl. A considerable deviation was observed from the theoretical 59 mV slope. The slope calculated from Figure 34, by doing a least square fit of the data, was 78 mV ($\sigma = 18$). This 78 mV slope is consistent with ion-pairing of the $TCNQ^{\bullet-}$ sites in the polymer film. The process

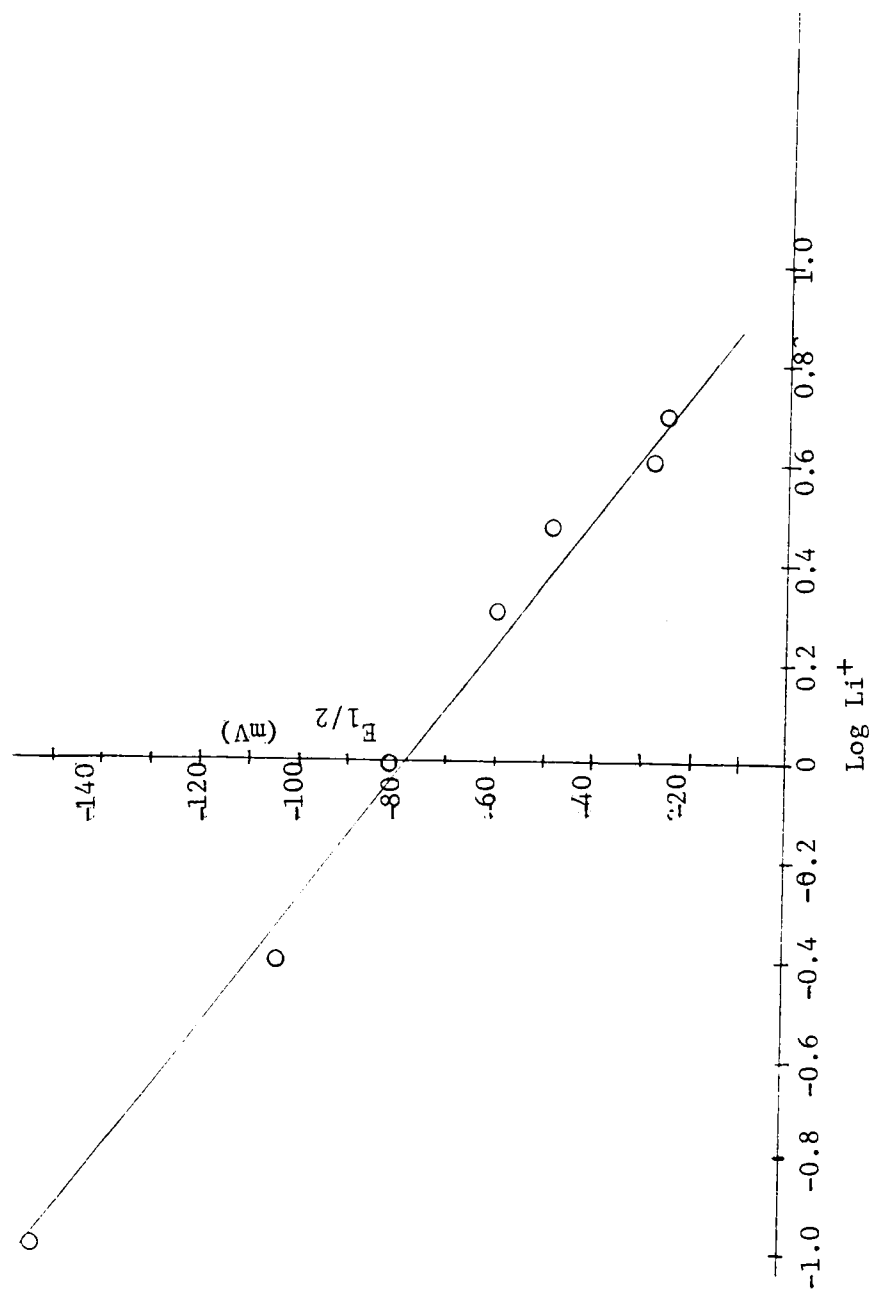
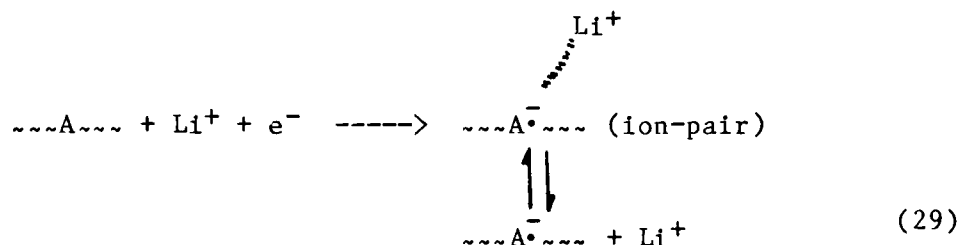


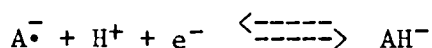
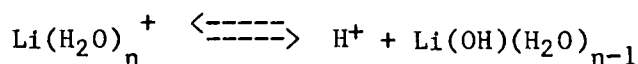
Figure 34. Graph of $E_{1/2}$ vs $\log[\text{Li}^+]$ for PU-MDI films.

occurring may be represented by equation 29 below. The large standard deviation does not reflect the reproducibility of the results, but rather the many factors which can influence the peak potential and the behavior of lithium as the concentration is increased.



Similar results were obtained by Inzelt and coworkers for Day's polyester.³⁹ The deviation could also be due to the quasi-reversible nature of the CV's which may be related to uncompensated resistance.

Interestingly, at high lithium concentration ($\geq 1\text{M}$) the voltammograms show a pre-oxidation wave at about -460 mV vs. Ag/AgI (See Figure 35). This may be due to the $\text{A}^{\cdot-}/\text{AH}^-$ couple, where the protons are supplied by the hydrated lithium cation:



In summary, a general shifting towards a more positive potential is observed for the cathodic peak as the lithium ion concentration is increased. This is an indication that the TCNQ units are being reduced more easily at the higher Li^+ concentrations and is consistent with ion-pairing of the $\text{TCNQ}^{\cdot-}$ sites. These results are summarized in Table XXXVI.

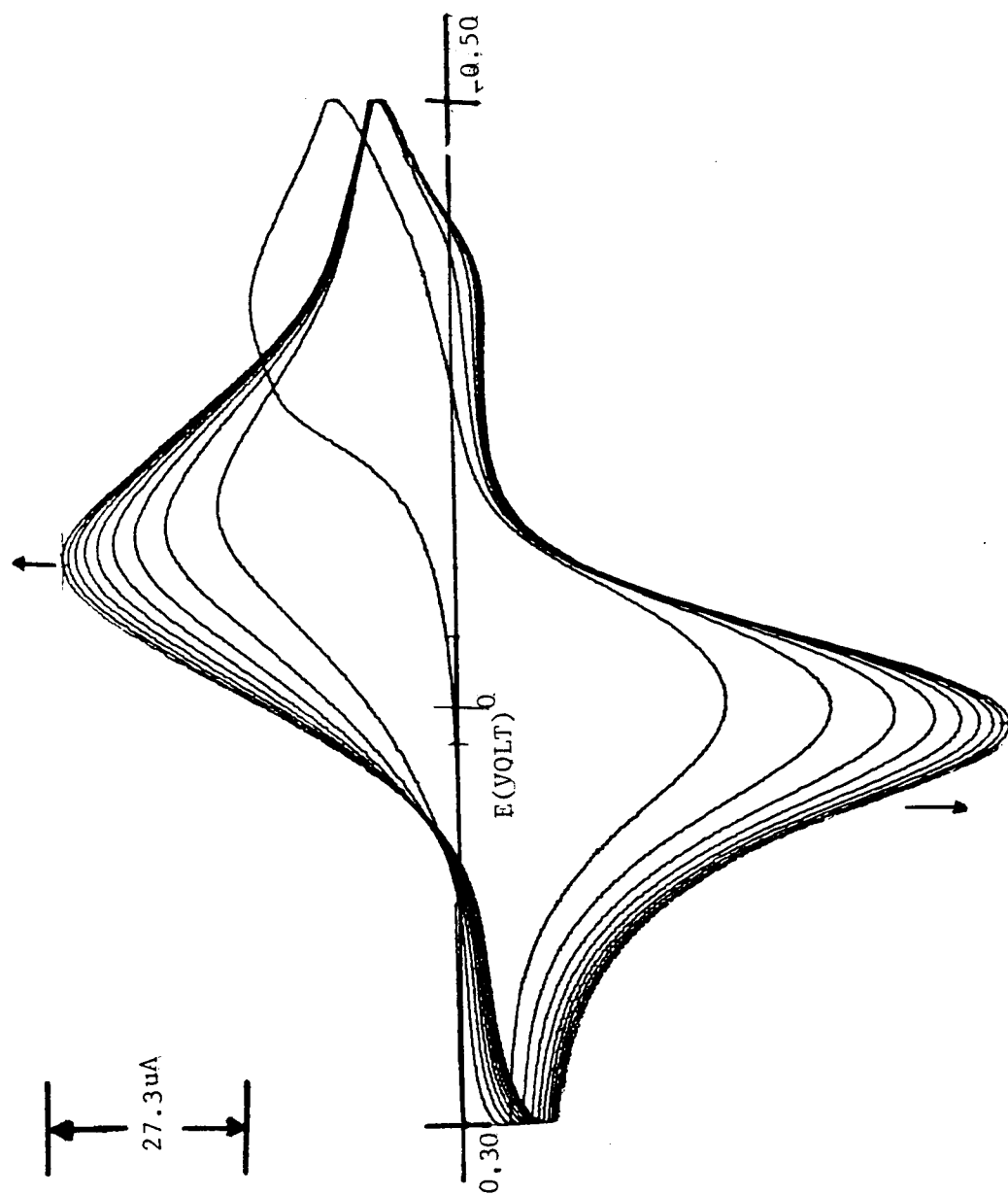


Figure 35. Cyclic voltammogram for PU-MDI film in 1.0M LiCl potential vs Ag/AgI, 30 mV/s .

Table XXXVI

Variation of Peak Potential with Lithium Ion Concentration for PU-MDI^a

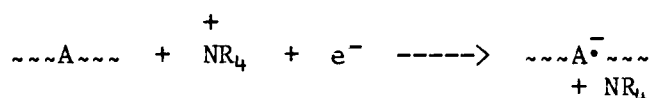
E_p^c/mV	E_p^a/mV	$E_{1/2}/\text{mV}$	$E_{1/2}/\text{mV}$	$\text{Log}[\text{Li}^+]$
-128	77	-26	5.0	0.699
-113	59	-27	4.0	0.602
-129	31	-48.8	3.0	0.477
-132	11	-60.5	2.0	0.301
-137	-29	-54.0	1.0	0.0

^aSweep rate is 20 mV/S.

E. Variation of the Cation

The electrochemistry of the polymers, PU-HMDI and PU-MDI, was studied in the presence of organic and inorganic cations. The organic salts used were tetraalkylammonium chlorides and the inorganic salts examined were the group I alkali chloride salts along with three divalent chloride salts, Cd^{2+} , Ca^{2+} and Ba^{2+} .

In the presence of the tetraalkylammonium salts, the films cast from any of the polyurethanes were passivated (see Figure 36), except the film from PU-HMDI which was electroactive in the presence of TMACl (see Figure 37). The electroactivity in of PU-HMDI the presence of TMACl suggests some kind of hydrophobic interaction between the methyl groups of the cation and the PU-HMDI chains. Also, the results with PU-MDI again indicates the possible role of $\text{M}^+ \dots \text{A}^-$ interactions. Passivation for these films can be viewed as a result of forming a reduced insulating layer at the film/solution interface. That is,



Thus, the CV should have shown a reduction peak on the first cycle if the film was thick ($\geq 100 \text{ \AA}$). We do not observe this behavior. This could be due to a very thin insulating film or simply a very slow reduction process characterized by a small D_{ct} -value. The latter proposition could be what is happening since close examination of Figure 36 shows a broad oxidation peak which increases as the number of cycles increase. Thus, the reduction process is probably slow, and as such the reduction wave is drawn-out.

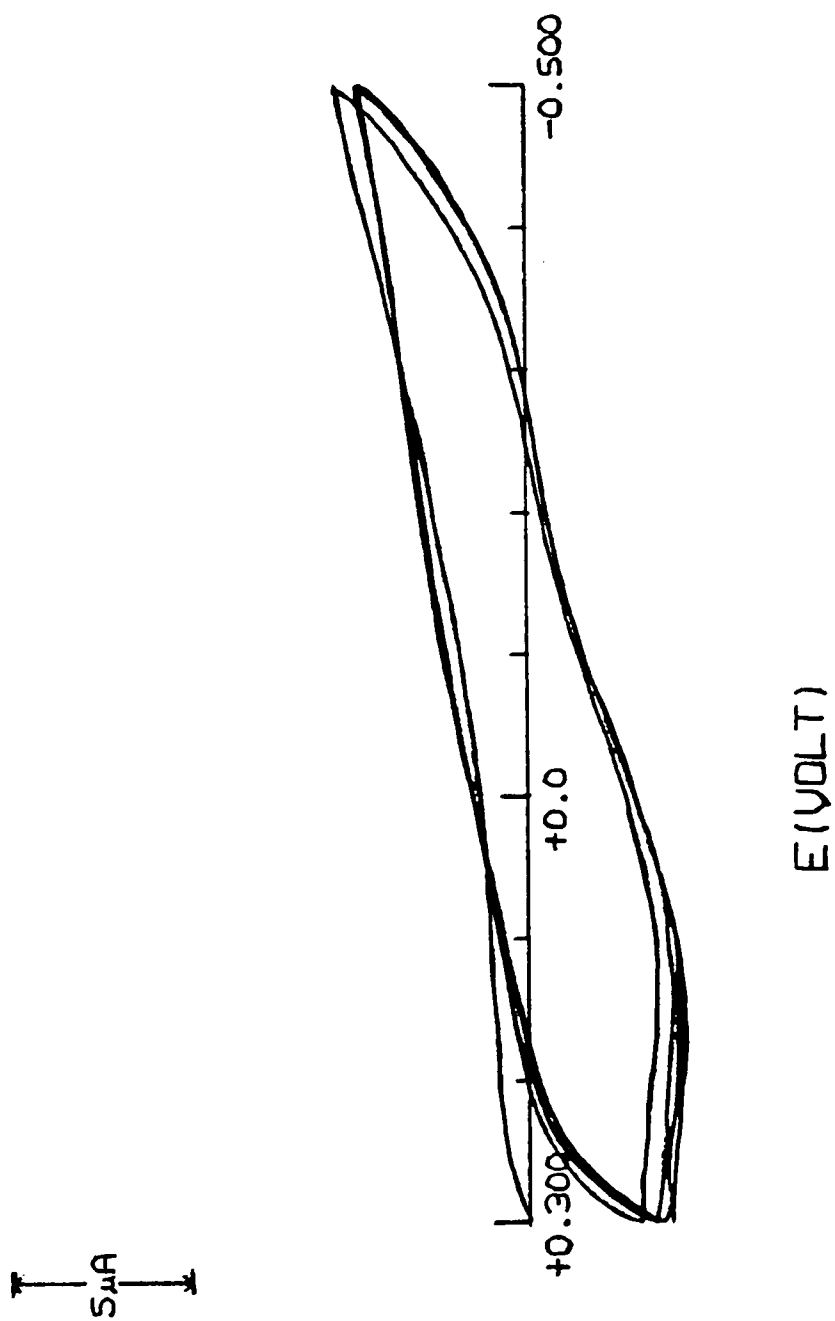


Figure 36. Cyclic voltammogram for PU-MDI film in 0.1M TEAP/H₂O potential vs SCE; 30mV/s.

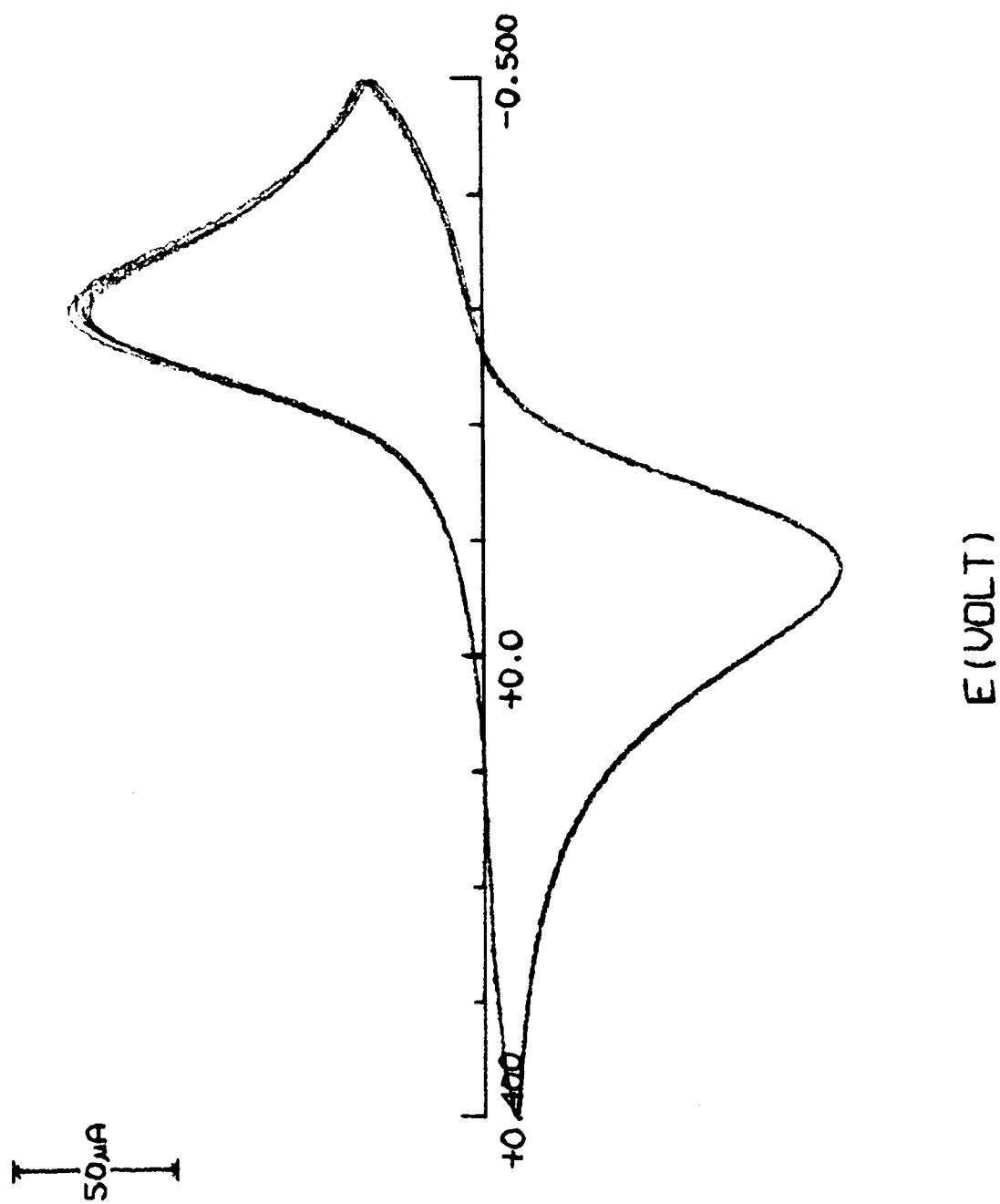


Figure 37. Cyclic voltammogram for PU-HMDI film in 0.1M TMACl/H₂O potential vs Ag/AgCl; 30mV/s.

A number of explanations have been offered for the general broadening of voltammetric peaks.¹⁸²⁻¹⁸⁵ For example, in an ensemble of attached species, slight variations in surface structure, solvation, and so on, can cause a spectrum of peak potential values rather than a unique value.

The electroactivity of these films could be regenerated by rinsing the film in water and cycling it in, say, Li^+ . The "loss of electroactivity" of these polyurethanes in the presence of aqueous solutions indicate that these polymers may be applicable in areas where one would like to discriminate against organic cations in an aqueous medium. Interestingly, PE-TCNQ films are electroactive in the presence of these tetraalkylammonium salts.³⁹ This result may be an indication of the differences in the structure of PU-HMDI and PE-TCNQ, probably a reflection of the hydrogen bonding capability of the urethanes as opposed to the ester, or the flexibility of the ester group as opposed to the urethane group. However, this is a speculation because in order to have a good comparison of both class of polymers, reliable molecular weights, polydispersity and cross-link density data for the polymers would be needed.

In the presence of the alkali cations, PU-HMDI shows very little change in the peak potential as the electrolyte is changed from Li^+ through to Cs^+ (see Table XXVII). This would tend to indicate that the structure of the polymer network is not very tightly packed. Similar data was reported for PE-TCNQ.³⁹ More importantly, in the presence of the smaller cations namely, Rb^+ and Cs^+ , the second wave indicative of TCNQ^{2-} formation becomes more persistent (see Figure 38). Again, this

Table XXXVII

Variation of Peak Potential with Cation for Polymers^a

Cation	<u>PU-MDI</u> E_p^c/mV	<u>vs.</u>	<u>PU-HMDI</u> SCE	^b Hydration Radius Å
Li ⁺	-288		-108	3.40
Na ⁺	-272		-118	2.76
K ⁺	-256		-106	2.32
Rb ⁺	-242		-103, -388	2.28
Cs ⁺	-224		-111, -379	2.28
^c Cd ²⁺	-1329		- -	-
^c Ba ²⁺	-		-320, -564	-
^c Ca ²⁺	-		-146, -418	-

^aSweep rate is 20 mV/S.^bTaken from Advanced Inorganic Chemistry by Cotton and Wilkinson.^cThese solutions are 0.05 M.

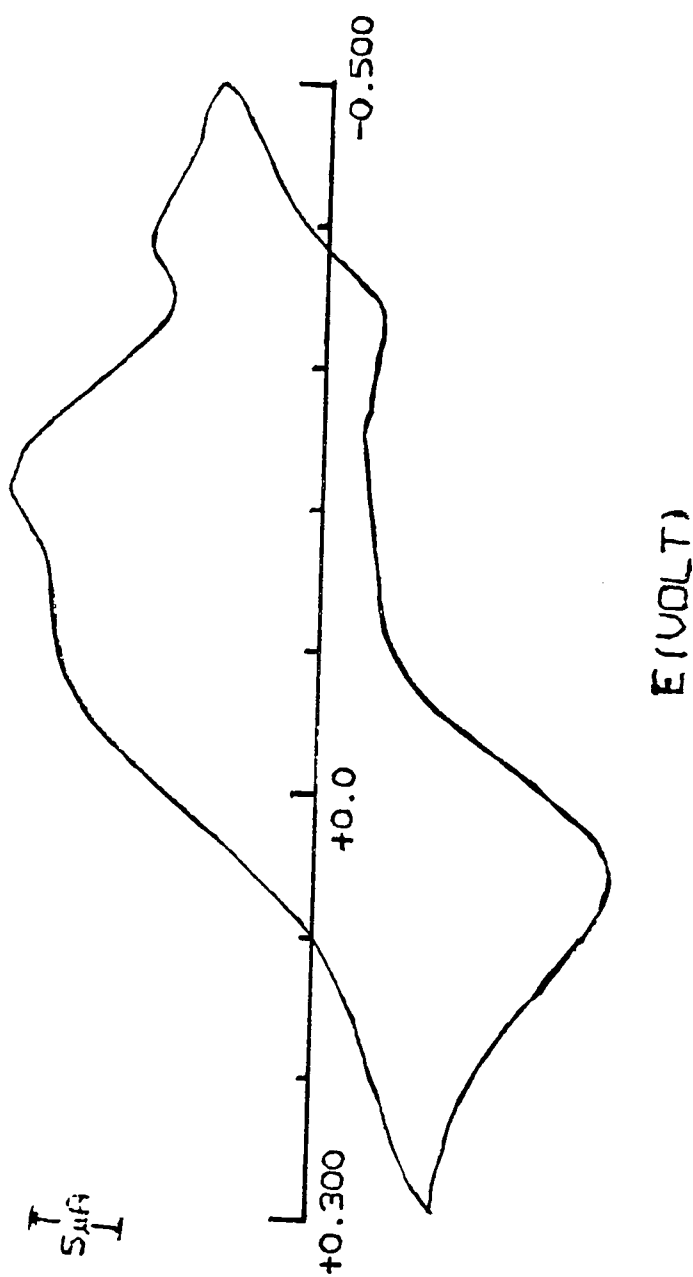


Figure 38. Cyclic voltammogram for PU-HMDI film in 0.1M CsCl potential vs SCE; 30mV/s.

indicates the role of the counter ion migration is controlling the relative values of D_{ct} for the first and second wave. The behavior of PU-HMDI versus PU-MDI (discussed below) on platinum surfaces does suggest that cation migration is more freely accomplished in the former polymer than in the latter. However, the immediate conclusions from the independence of $E_{1/2}$ values with variation of cation for PU-HMDI is that $A^{\cdot-} M^+$ formation is not as significant as it is in the case of PU-MDI films. Figure 31 and 32 (see pages 129 and 130) show typical voltammograms obtained for PU-HMDI in either Li^+ , Na^+ or K^+ electrolyte solution and Table XXXV summarizes the relevant data obtained by variation of the cations. Interestingly, in the presence of Cs^+ or Rb^+ the first wave seen in Figure 38 is broadened and practically separates into two waves, suggesting the formation of mixed valence species in the film. The mixed valence species, $A_2^{\cdot-}$, has also been observed and discussed for PE-TCNQ.³⁸

A typical CV for PU-MDI films in the presence of the group I cations is shown in Figure 25 (see page 117). Typically the CV shows a break-in for the initial cycles. When the film was stabilized a constant shifting of 16 mV per cation into the positive direction was observed for the reduction potential when the electrolyte was varied in the sequence, LiCl to CsCl. A new film was used for each electrolyte. These results are summarized in Table XXXVII. This shifting of the peak potential was attributed in part to the change in size of the cations. The smaller the cation, the easier it will be to reduce the film. This cation effect is seen in Figure 39 where the peak potential is plotted as a function of the log hydration radius. These results

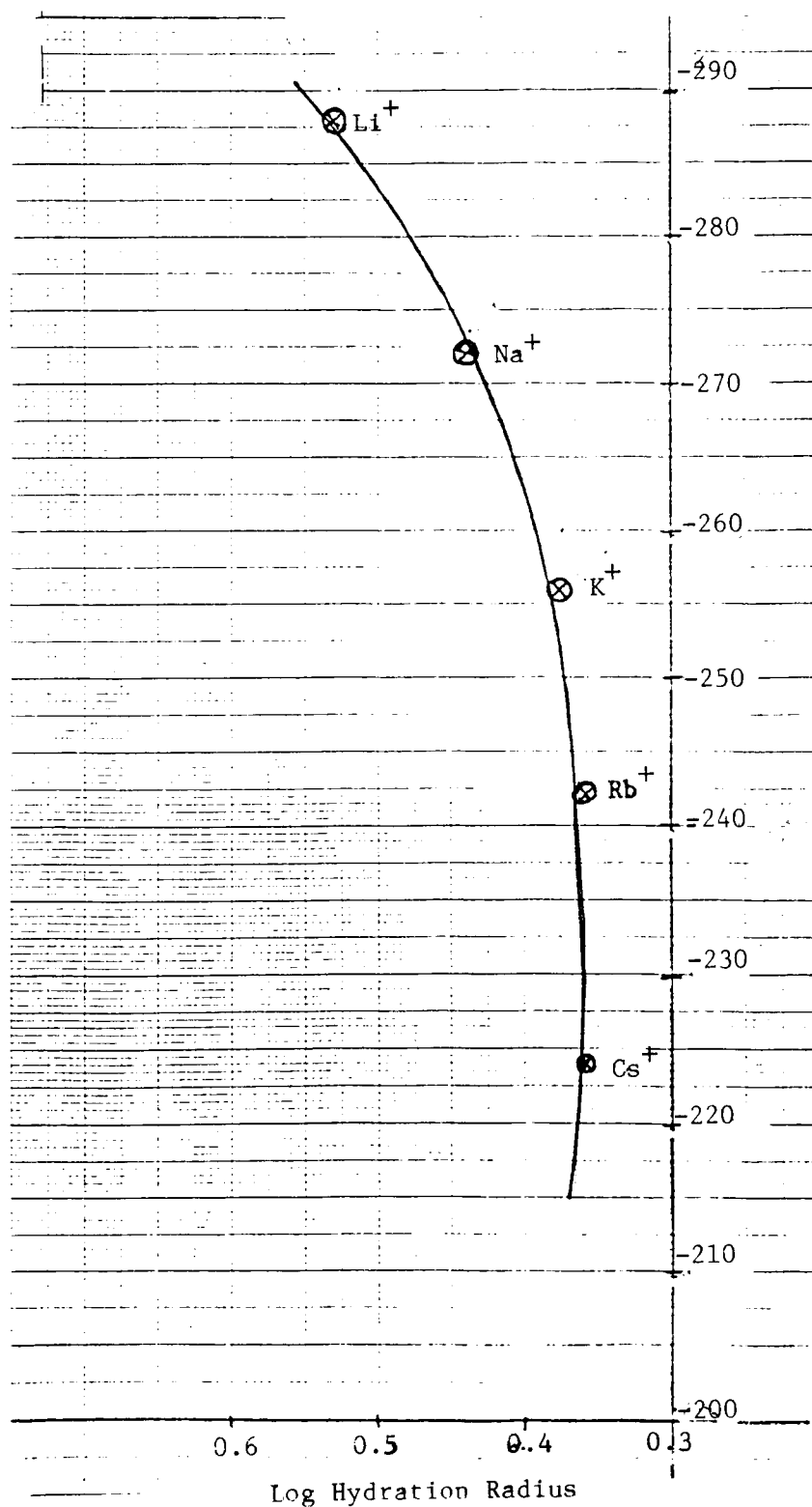


Figure 39. Graph of peak potential vs log hydration radius for PU-MDI films in 0.1M aqueous alkali chloride salts.

again indicate that, as the size of the cation decreases, reduction of the TCNQ sites becomes easier which is consistent with the above ideas on ion-pairing in the film.

On repeated cycling of a PU-HMDI film in 0.05 M Ca^{2+} solution the voltammogram shown in Figure 40 was obtained. A break-in is observed for both waves, with the second wave being extremely attenuated. When this experiment was repeated in 0.1M Ca^{2+} solution, similar CV's were obtained, except that both the first and second wave gave approximately the same i_p^c values. A similar behavior was reported for PE-TCNQ.³⁹ The second wave here is probably the $\text{A}^{\cdot-}/\text{AH}^-$. Similar behavior was displayed for PU-HMDI in Ba^{2+} as shown in Figure 41. The reduction peaks in 0.1M Ba^{2+} are significantly broader than those obtained from the CV in 0.1M Ca^{2+} . Also, the reduction potentials are more negative in Ba^{2+} than in Ca^{2+} .

For PU-MDI in the presence of Ba^{2+} , in the range of +0.3V to -1.4V, the voltammogram was complicated by the presence of many sharp anodic peaks. In the presence of Ca^{2+} , the waves were drawn-out and very little faradic current was observed. However, in the presence of Cd^{2+} , a most interesting voltammogram is observed as shown in Figure 42. The reduction wave of Figure 42 is far more negative than expected for TCNQ, but the oxidation wave occurs just about at the right potential. Interestingly, the films cycled in Ca^{2+} or Ba^{2+} solutions did not regain their original behavior when placed in aqueous Li^+ , however the film cycled in Cd^{2+} solution behaved like a virgin film when transferred to aqueous Li^+ .

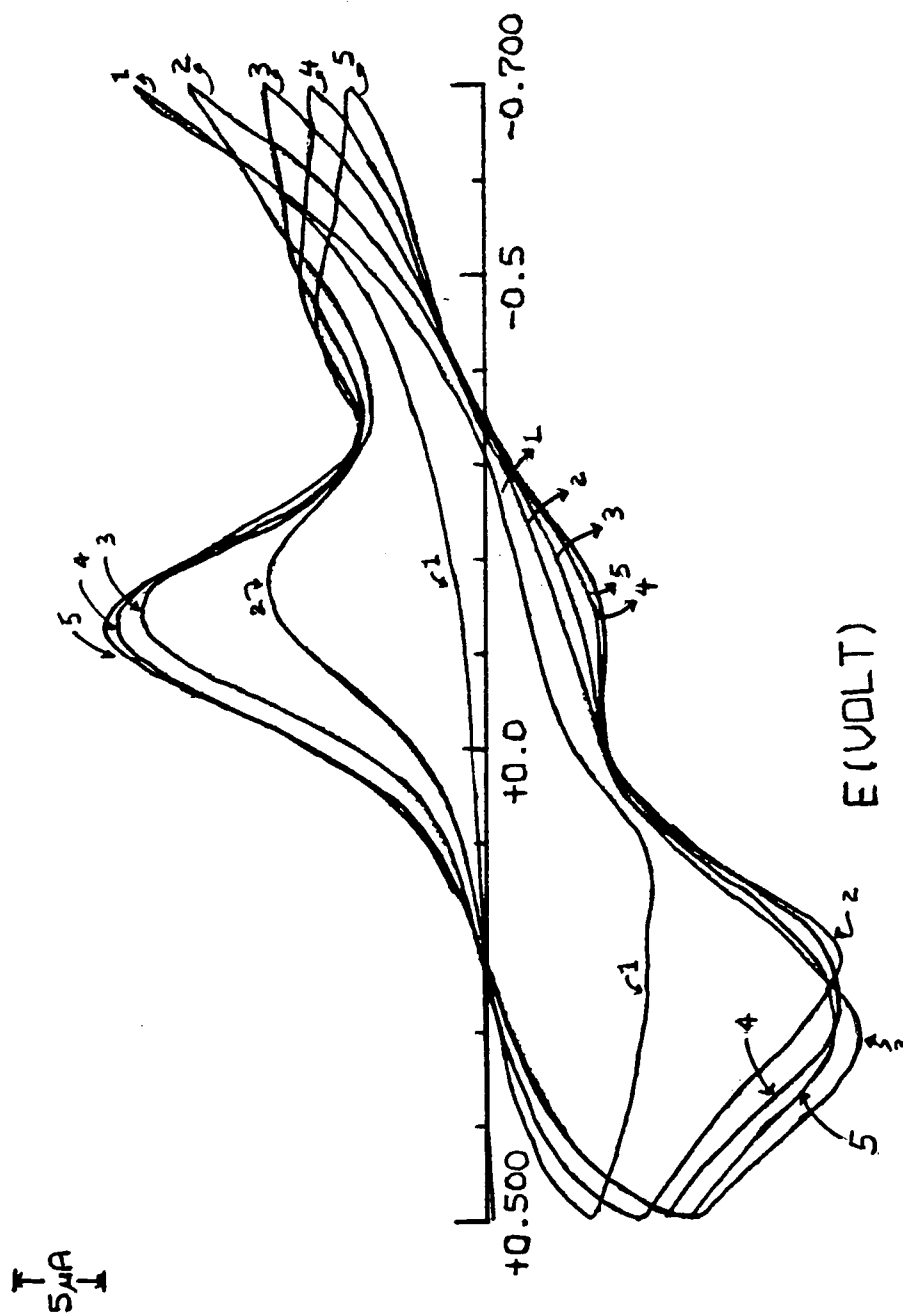


Figure 40. Cyclic voltammogram for PU-HMDI film in 0.05M $CaCl_2$ potential vs SCE; 30mV/s.

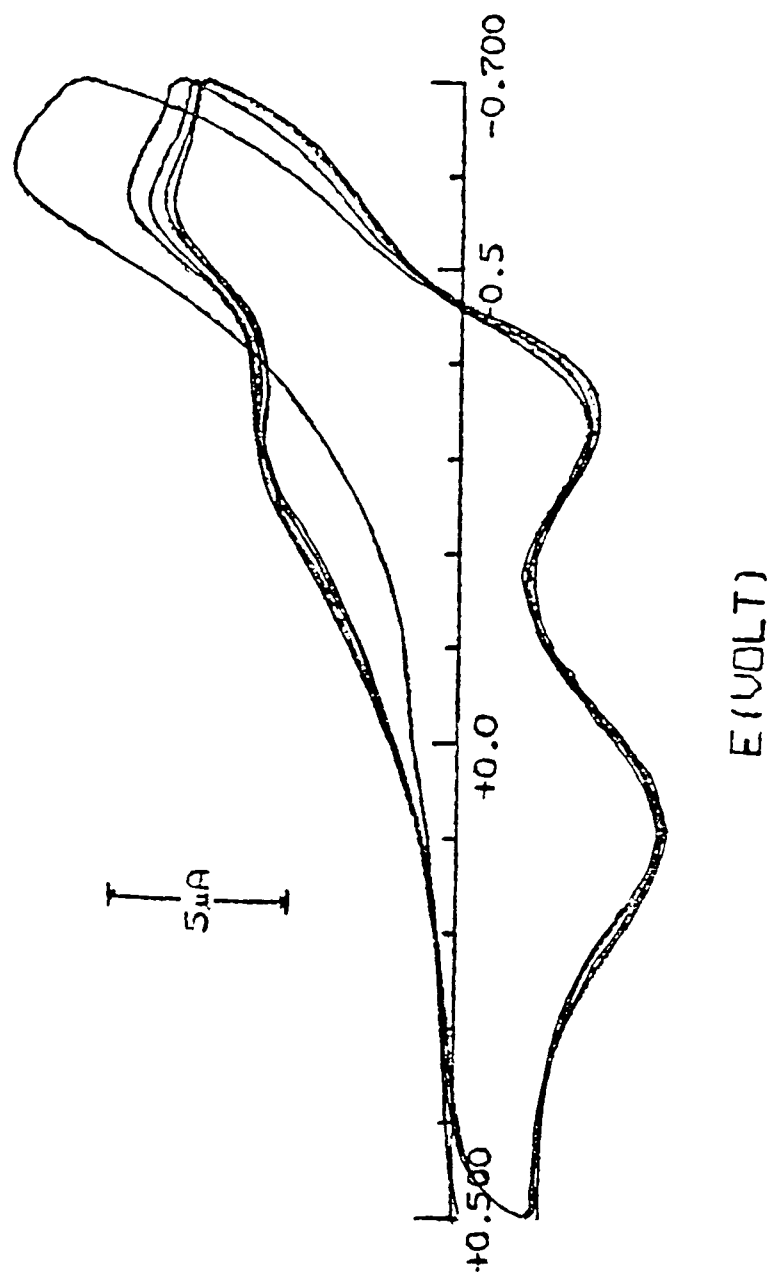


Figure 41. Cyclic voltammogram for PU-HMDI film in 0.1M BaCl₂ potential vs Ag/AgCl; 30mV/s.

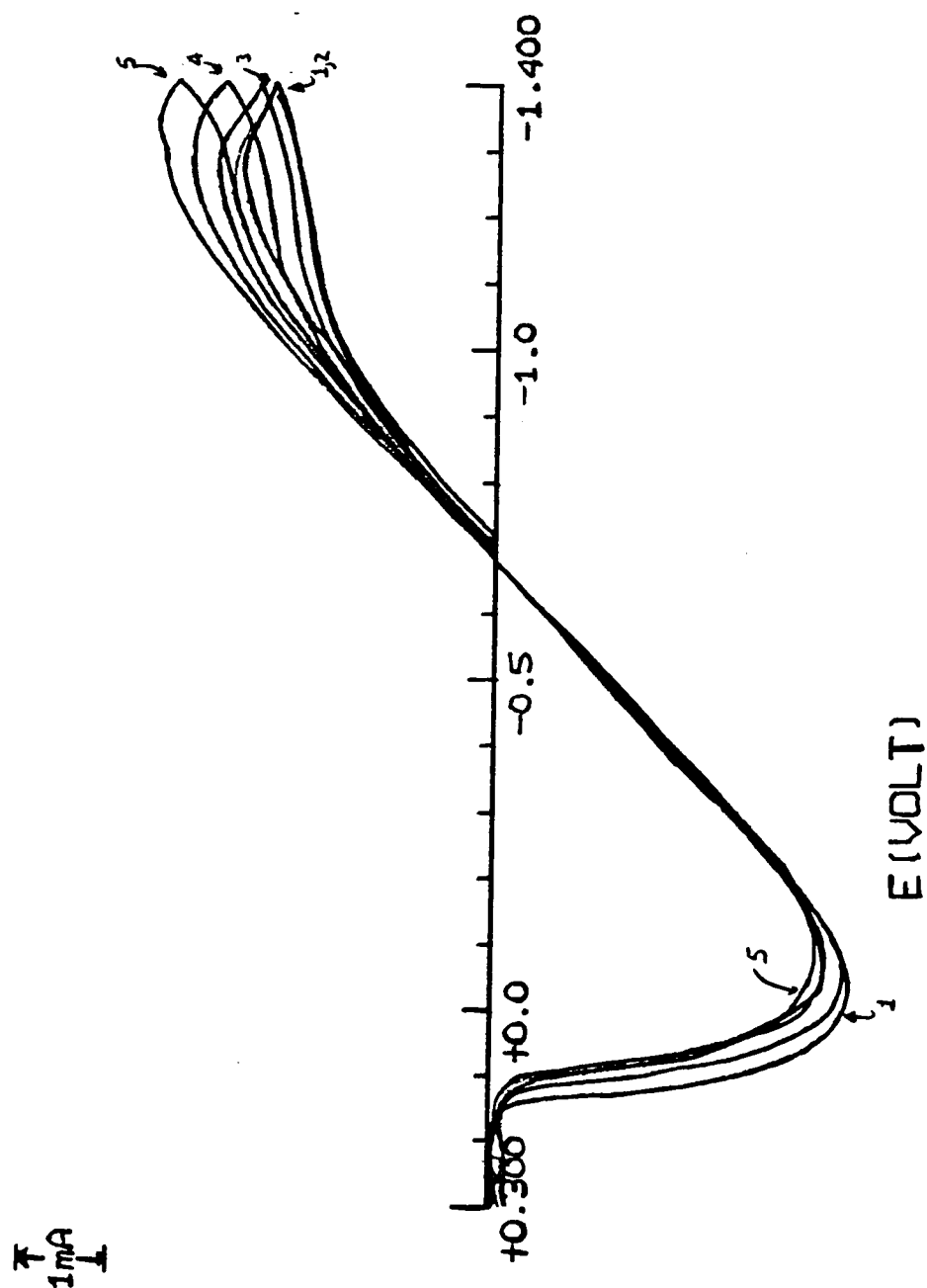
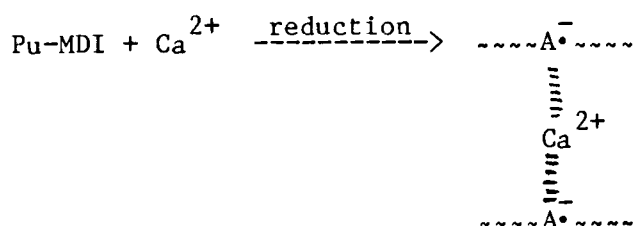


Figure 42. Cyclic voltammogram for PU-MDI film in 0.05M CdCl₂ potential vs SCE; 30mV/s.

The irreversible behavior of PU-MDI in Ca^{2+} or Ba^{2+} indicates that the film is being chemically altered when cycled in these solutions. A possible mechanism explaining these results may be a cross-linking at the surface of the film by either calcium or barium as follows:



Once this cross-linked material is formed, the charge transport is retarded considerably and the oxidation of the TCNQ units is not observed. The deviation of Cd^{2+} from this behavior is not clear. The large current observed for the CV in Cd^{2+} may suggest that a conducting complex is being formed between the reduced TCNQ units and cadmium. Further detailed experiments are needed with cadmium and other group IIB elements to illuminate this interesting phenomenon.

F. Analysis of Wave Shape

a. Charge Transport. By virtue of low mobility, due for instance to being affixed to a cross-linked polymer film matrix, many of the redox centers in electrochemically reactive polymer films cannot rapidly contact the electrode directly.¹⁷⁹ Kaufman and coworkers¹⁶² proposed that such sites become oxidized or reduced by a succession of electron transfer self-exchange reactions between neighboring redox sites. Since the redox center ionic charge is changed, a flow of

counterions and associated solvent must accompany electron transport. Segmental motions of the polymer chains occur with, or antecedent to, the ion and solvent motions and the juxtapositioning motions of redox centers producing electron transfers.¹⁷⁹ The intrinsic thermal barrier to electron transfer may also be important. Collectively these ideas are termed, charge transport.^{168,186}

It has been proposed by various workers that this charge transport in polymer films conforms to the laws of diffusion.^{165,168,186,187,188,189} This then enables a systematic study of charge transport process by measuring the rate at which a polymer film becomes oxidized or reduced in response to a potential or current applied to an electrode.¹⁷⁹ For conditions at which the rate of charge transport through a polymer film is important, cyclic voltammograms of redox films lose their peak symmetry common to voltammograms of monolayers where charge transport is much faster, and instead assume a shape reminiscent of the voltammetry of a dissolved electroactive species diffusing to the electrode.¹⁹⁰ For thin films, large diffusion coefficients, or slow sweep rates, charge transport through the film yields voltammetric peak current, i_p , directly proportional to the sweep rate, v .

The shape of the voltammograms obtained for all the polyurethane films in contact with aqueous electrolytes indicated diffusional character. The diffusion character was indicated by the lack of symmetry between the anodic and cathodic peaks, and the fact that i_p was not directly proportional to the sweep rate. The diffusion

character of the waves was investigated by studying i_p^c as a function of v , utilizing the equation:

$$i_p^c = k v^a \quad \quad (30)$$

where i_p^c = cathodic peak current

v = sweep rate

k = proportionality constant

a = a constant; $a = 0.5$ indicates a diffusion wave, while $a = 1.0$ indicates a surface wave¹⁸⁶.

The graphs of i_p^c versus $\log v$ are shown in Figures 43 and 44 for a PU-MDI film in contact with Li^+ and a pH 7 solution (10 mL 0.5M NaH_2PO_4 /6 mL 0.5 M NaOH) respectively. A linear regression was performed on the data in Tables XXXVIII and XXXIX and a slope calculated to be 0.6 ($\sigma = 0.2$) in Li^+ and 0.4 ($\sigma = 0.2$) at pH 7. So i_p^c was found to be approximately proportional to $v^{1/2}$ and conforms to the same equation as that used for species dissolved in solution and diffusing to the electrode, namely:

$$i_p = 2.69 \times 10^5 n^{3/2} A D_{ct}^{1/2} v^{1/2} C_b \quad \quad (31)$$

where all the terms have been previously defined.

The wave shapes also exhibit distinctive "diffusional tail." All this evidence suggest that $D_{ct} \tau / d^2 \ll 1$, a condition necessary for slow charge transport.¹⁷⁹ This behavior is promoted by small D_{ct} (low temperature),¹⁸⁶ polymer film cross-linking,¹⁷⁹ fast scan rates^{186,191} and thick films.¹⁸⁷

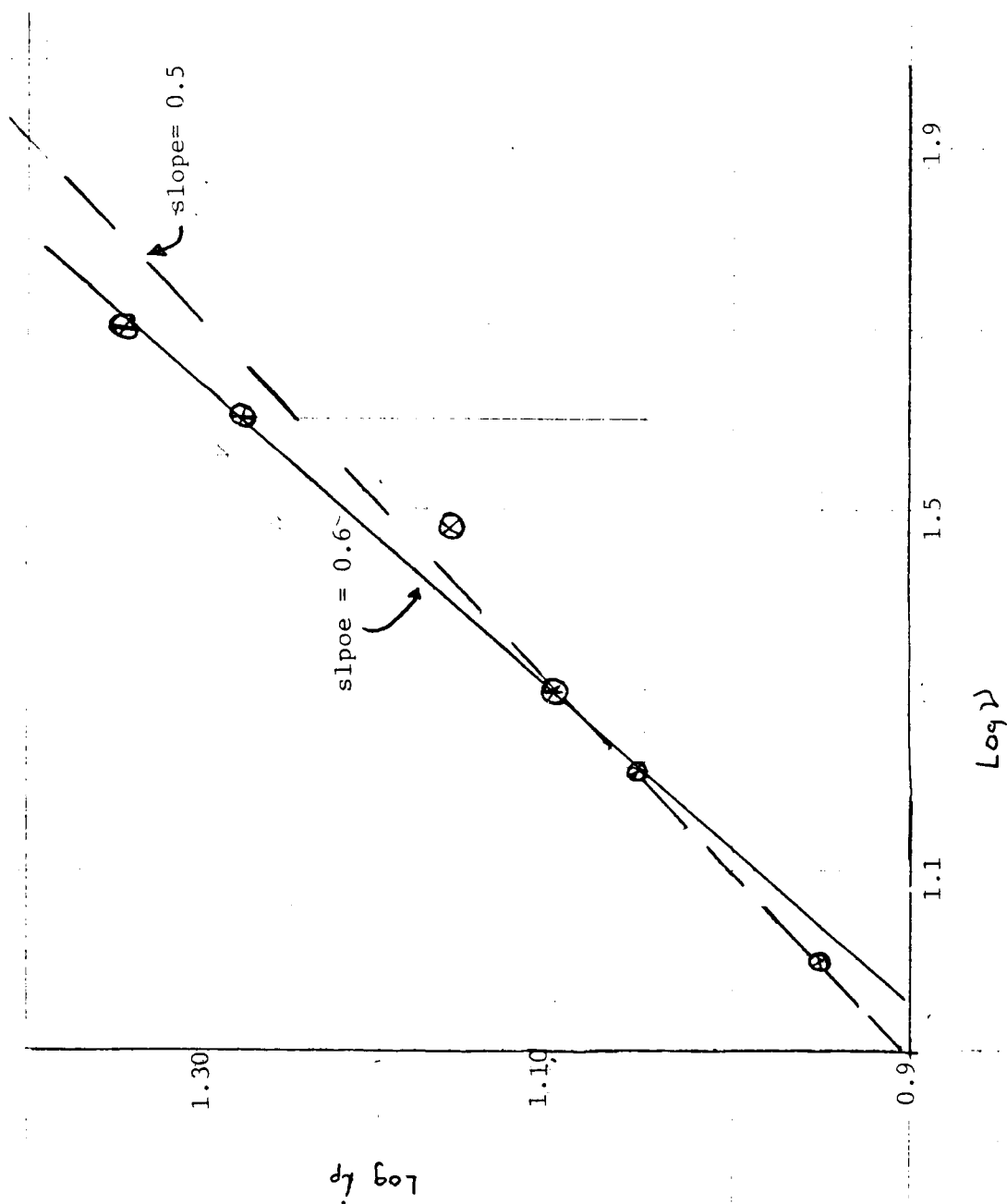


Figure 43. Cathodic peak current-sweep rate dependence for PU-MDI film in 0.1M LiCl.

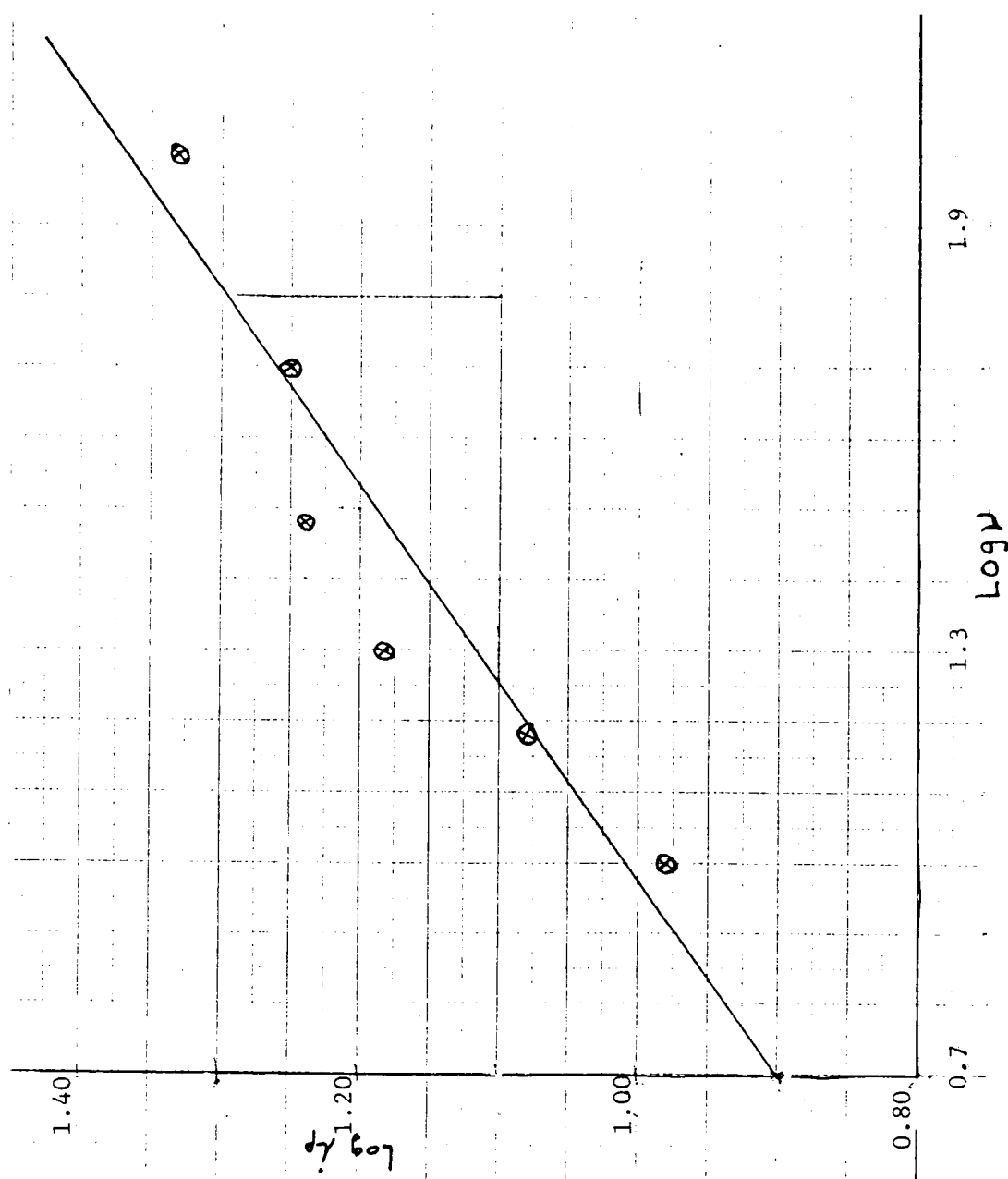


Figure 44. Cathodic peak current-sweep rate dependence for PU-MDI film in phosphate buffer at pH 7.

Table XXXVIII

Sweep Rate Results for PU-MDI in 0.1 M LiCl vs SCE

$i_p/\mu\text{A}$	$\log i_p$	$v/\text{mV/S}$	$\log v$
22.4	1.35	50	1.70
12.7	1.10	20	1.30
14.3	1.16	30	1.48
8.9	0.95	10	1.0

Table XXXIX

Sweep Rate Results for PU-MDI in pH 7 Solution vs SCE

$\mu p/\mu\text{A}$	$\log i_p$	$V/\text{mV/S}$	$\log v$
21.4	1.33	100	2.0
17.6	1.25	50	1.70
17.5	1.24	30	1.48
15.0	1.18	20	1.30
12.0	1.08	15	1.18
9.8	0.98	10	1.0
8.0	0.90	5	0.70

The diffusion coefficient for the charge transport through PU-MDI film in $\text{Na}^+(\text{aq})$ was calculated from chronocoulometric data shown in Figure 45, which is a plot of the charge, Q , versus $t^{1/2}$ (t is time).^{187,192} The total concentration of TCNQ units was estimated as follows: using a Tencor Alpha-Step profiler, the average thickness of a dry virgin film cast on a transparent platinum electrode was estimated and the absorbance measured at 432 nm. Chronocoulometry was then performed on the electrode in a Teflon cell and the amount of charge, given by $\Gamma = Q_T/FA$, accepted by the film calculated, when n was set equal to unity. Knowing Γ , the concentration of TCNQ units can be calculated by utilizing:

$$\Gamma = C_b d \quad \quad (32)$$

where d is the film thickness.³⁷

The value of C_b was also checked by calculating Γ from absorbance measurements, knowing:

$$\Gamma = \text{Abs}^{432}/\epsilon^{432} \quad . . . \quad (33)$$

$$\epsilon^{432} \text{ was taken as } 43000 \text{ M}^{-1} \text{ cm}^{-1},^{37}$$

These calculations resulted in an average concentration of 3.15 moles/dm³. This value was viewed as an estimate and not an absolute number since the surface of the film was not smooth. Also, the UV-VIS give absorbance for all neutral TCNQ units in the film, but not all these units are electrolyzed in an aqueous medium as will be discussed later. Thus, the actual concentration of active TCNQ units will be

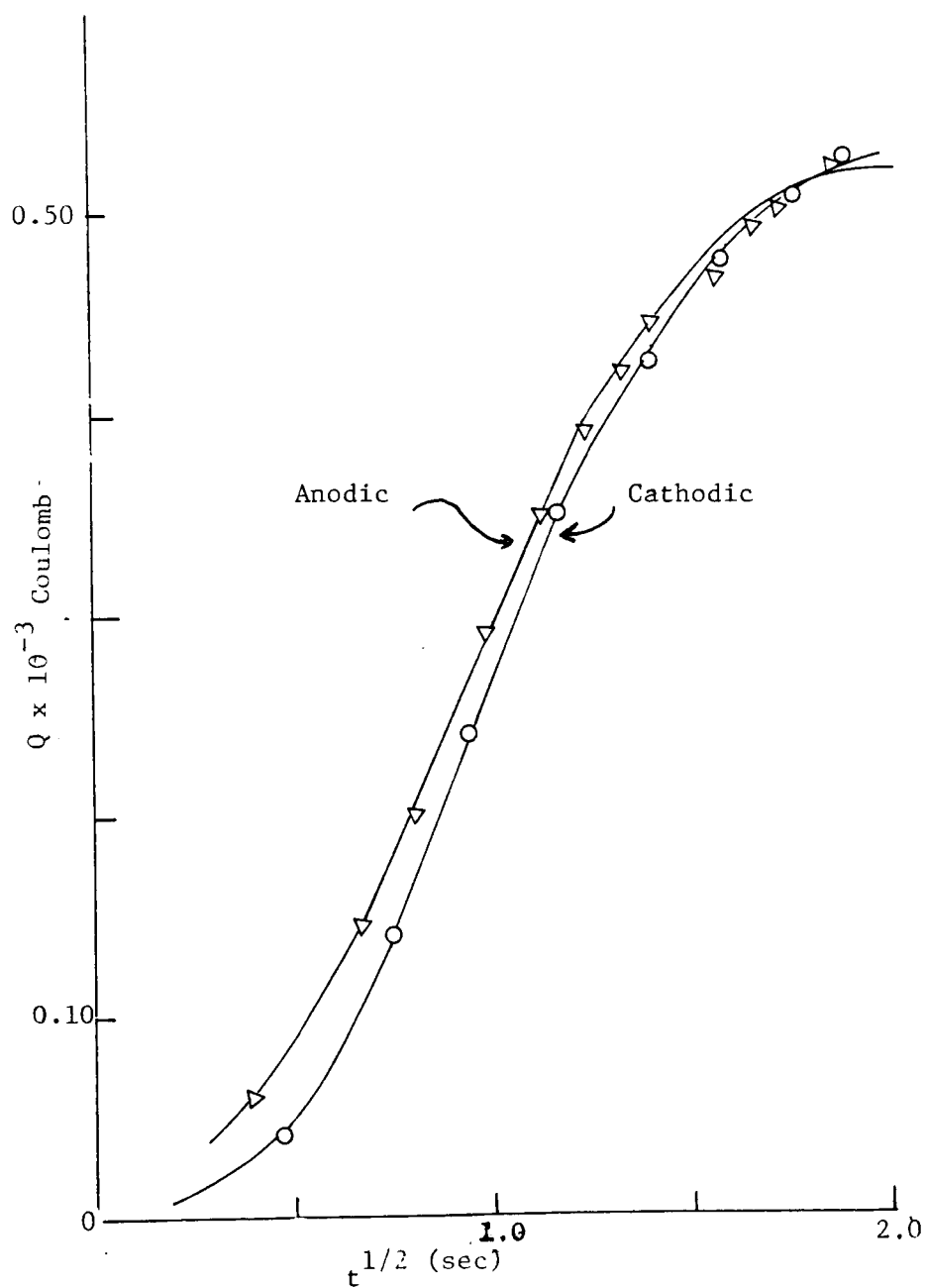


Figure 45. Chronocoulometric data for PU-MDI film in 0.5M NaClO₄.

somewhat lower. This allowed us to calculate a diffusion coefficient for charge transport through the film.^{186,192,193}

The diffusion of charge transport, D_{ct} , through the film in contact with 0.5M NaClO_4 was calculated to be $5 \times 10^{-11} \text{ cm}^2/\text{s}$. The value of D_{ct} calculated for the film in contact with 0.1M LiCl was almost the same as that calculated for the film in contact with NaClO_4 , but ten times less for a film placed in a phosphate buffer at pH 4. These values are summarized in Table XL. Qualitatively, these numbers are in agreement with the formation of a hydroquinone analogue, TCNQH_2 , which acts as a non-conducting layer, insulating the TCNQ sites in the bulk of the film and thus making charge transport more difficult.³⁸ This will be discussed further when the pH experiments are discussed.

G. Solvent Effects

The CV of the MDI polyurethane films showed one quasi-reversible diffusional wave for aqueous electrolyte solutions at room temperature. Furthermore, even when the films were cycled to potentials as far negative as -1.0V, no second wave was observed. Even though Rb^+ and Cs^+ showed an attenuated second wave with PU-HMDI, it was thought that the size of the cation was not the only factor involved in the absence of the second wave. These results also imply that the reactions of these polymer films are more complex than those of monolayer redox films, requiring mechanism(s) for charge transport in case where the redox sites are too immobile or remote in the polymer film to contact the electrode directly that involve associated motions

Table XL

Diffusion Coefficient for Charge Transport Through
PU-MDI in Different Electrolyte Solutions

Electrolyte	$D_{ct}(\text{cm}^2/\text{S})$
0.5 M NaClO_4	5×10^{-11}
0.1 M LiCl	4×10^{-11}
0.5 M $\text{Na}_2\text{H}_2\text{PO}_4$ (pH 4)	3×10^{-12}

of the polymer chains, charge-compensating counterions and solvent molecules.¹⁷⁹ With this in mind, we decided to investigate the solvent's role in the electrochemical behavior of these films. The solvents chosen were acetonitrile, the homologous series of alcohols ranging from methanol to n-butanol and acetone. For the films to be stable, they had to be baked for a minimum of 10 min at 120°C (see discussion on baking, p 115).

a. Electrochemistry in Acetonitrile (ACN). In ACN/TEAP solution, a PU-MDI film exhibits two quasi-reversible peaks, $E_p^{cl} = -64\text{mV}$ and $E_p^{c2} = -369\text{ mV}$ coupled with $E_p^{al} = 120\text{ mV}$ $E_p^{a2} = -284\text{ mV}$ giving $E_{1/2}^1 = 28\text{ mV}$ and $E_{1/2}^2 = -326.5\text{ mV}$ vs SCE. The CV shown in Figure 46 exhibits a break-in phenomenon for both the first and second wave. Interestingly, the break-in observed for a film baked for 2-3 minutes (see Figure 47) and an unbaked film are very similar. It should be noted that thick films are used in these experiments and so uncompensated resistance may be a problem.

For the film baked for 2-3 minutes, and the unbaked film, the break-in is accompanied by a decrease in peak current on subsequent cycling along with a change in shape of the second wave which is highly visible for the film baked 2-3 minutes. This second wave is broadened and then sharpens up again when the wave is stabilized, during this time the shape of the first wave remains basically unchanged. It is very important to note here the well-behaved electrochemistry of two reduction and two oxidation waves exhibited by PU-MDI, characteristic of the TCNQ diol. The second wave was confirmed to be due to TCNQ^{-/2-} process by absorbance measurements at 720 nm. The absorbance at 720 nm

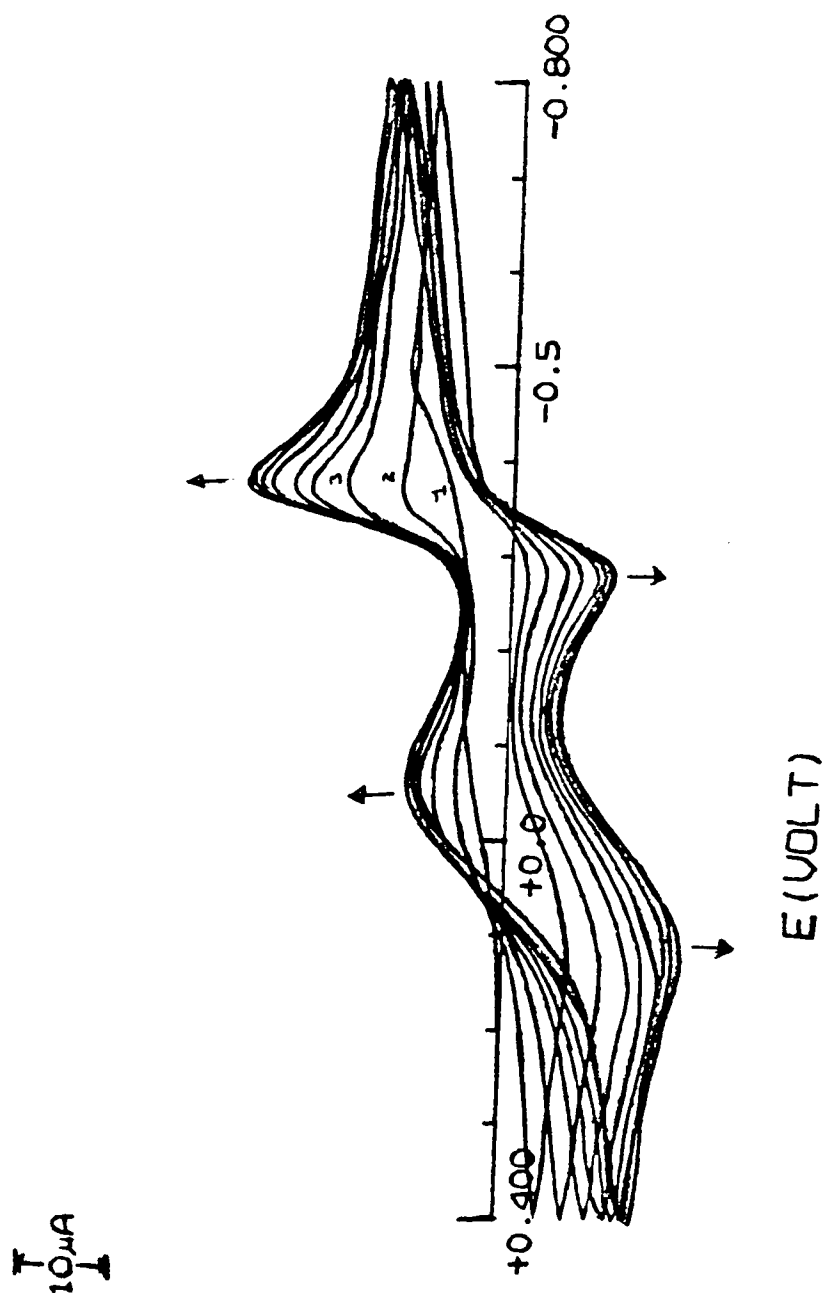


Figure 46. Cyclic voltammogram for PU-MDI film (baked 10 min) in 0.1M TEAP/ACN potential vs SCE; 30 mV/s.

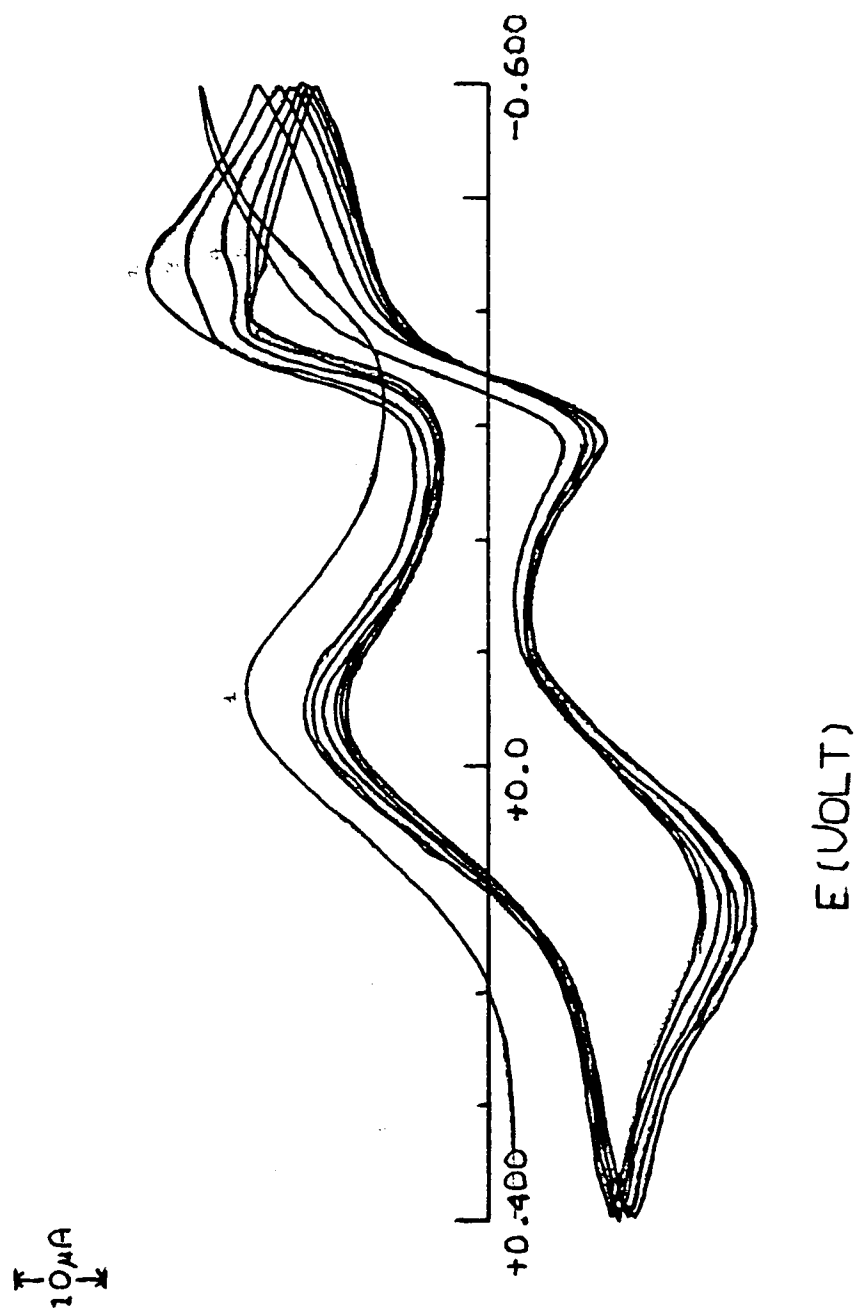


Figure 47. Cyclic voltammogram for PU-MDI film baked 2-3 min. in 0.1M TEAP/ACN potential vs SCE; 30mV/s.

characteristic of $\text{TCNQ}^{\cdot-}$ was observed to decrease and reach a minimum as the potentiostat scanned to the region of the second wave.

The appearance of the second wave when the solvent was changed from water to acetonitrile definitely implies that the solvent swelling process plays a very important role in the charge transport mechanism. It has been reported by Leddy and Bard that electrodeposited poly(vinylferrocene) films in contact with acetonitrile underwent an increase in film thickness of 80%,¹⁹⁴ and Inzelt has even reported a dry reduced film to be somewhat thicker than a corresponding dry neutral film.¹⁹¹ It is thought that solvent swelling will favor motions of the electron acceptor sites, migration of counterions in and out the polymer film, and accordingly, will promote electrochemical charge transport.¹⁷⁹

To test this hypothesis the following transfer experiments were conducted. A PU-MDI film was broken-in in ACN/TEAP and then transferred to aqueous LiCl after it was dried with a paper towel. The voltammogram shown in Figure 48 was obtained. As expected the CV revealed one oxidation and one reduction wave corresponding to $\text{TCNQ}^{0/-}$ couple. Also, the voltammetric response characteristic of aqueous electrolytes was developed on the very first cycle as was found by Joo and Chambers for PE-TCNQ films when the transfer was from PrOH to water.¹⁸¹ Close examination of Figure 48 show very minor waves in the region where the second wave was expected. This indicates that the film never returned to its original conformation after being fully reduced in ACN. This could be a result of solvent trapped in the bulk of the film when it was fully reduced in ACN.

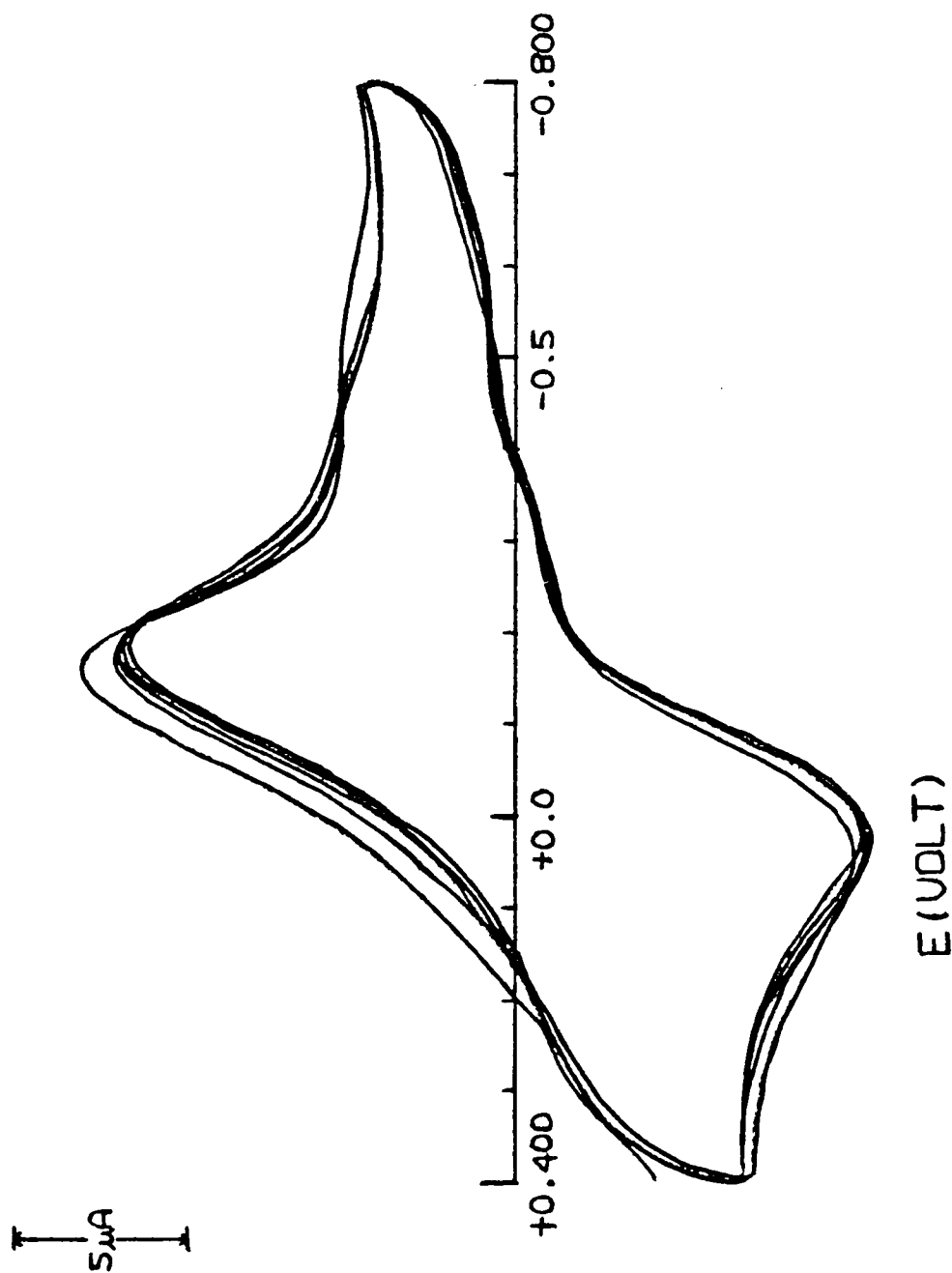
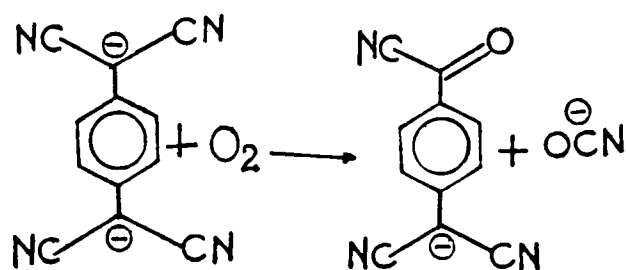


Figure 48. Cyclic voltammogram for PU-MDI film after broken-in in 0.1M TEAP/ACN and then transferred to 0.1M LiCl potential vs SCE; 30mV/s.

When the same film was removed from the aqueous electrolyte, gently dried in a paper towel, and then transferred to a saturated solution of EtOH/TEAP, two waves are again observed as shown in Figure 49. These two waves had the characteristics of waves generated in ACN/TEAP and not those of waves observed in EtOH/LiCl. Interestingly, the second wave was broadened and no dissolution was indicated by either a change in color of the electrolyte to the characteristic gold color of TCNQ in solution, or by any significant change in i_p upon subsequent cycling of the film. This could be an organic ion effect but further experiments are needed for conformation. Noteworthy is the stability of the film when transferred from the aqueous solution to the alcoholic solution. This may be an indication of a possible chemical change occurring in the film concomitant with the formation of TCNQ dianion. It is possible that the chemical change may involve:¹⁹⁵



This is very possible since the dianion is very sensitive to oxygen.

In ACN/TEAP, PU-TDI displayed the very interesting voltammogram shown in Figure 50. A break-in for three reduction waves having peak potentials at $E_p^{c1} = 62\text{mV}$, $E_p^{c2} = -244\text{mV}$ and $E_p^{c3} = -418\text{mV}$ coupled with $E_p^{a1} = 171\text{mV}$ and $E_p^{a2} = -177\text{mV}$ giving $E_{1/2}^1 = -54.5\text{mV}$ and $E_{1/2}^2 = -210.5\text{mV}$ vs. Ag/AgCl is observed. A close examination of Figure 50 indicates there may be an E_p^{a3} wave developing, however slower sweep rates and

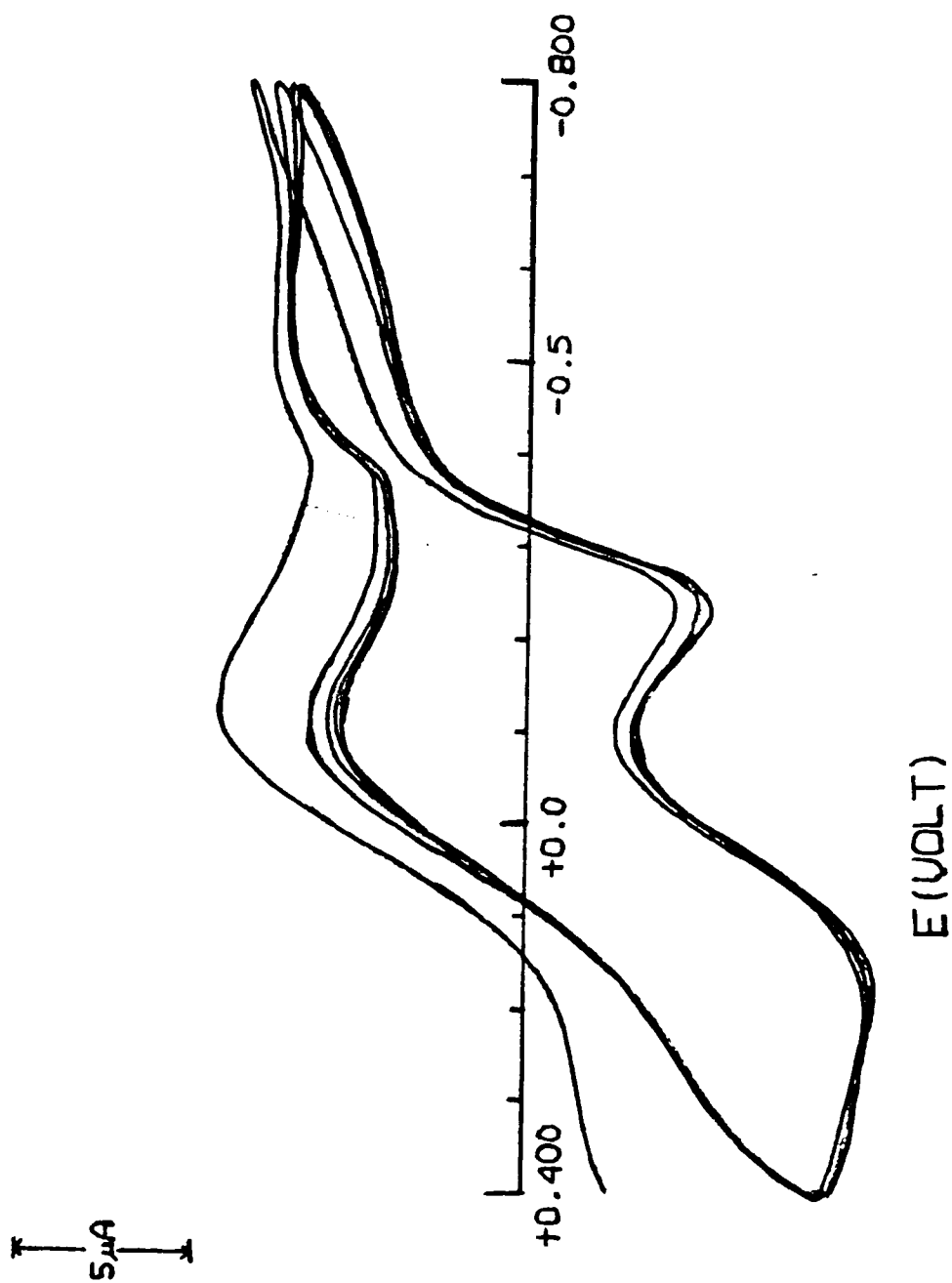


Figure 49. Cyclic voltammogram for PU-MDI film after being cycled in 0.1M LiCl and then transferred to a saturated solution of LiCl/EtOH; potential vs SCE; 30mV/s.

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5 μ A
I

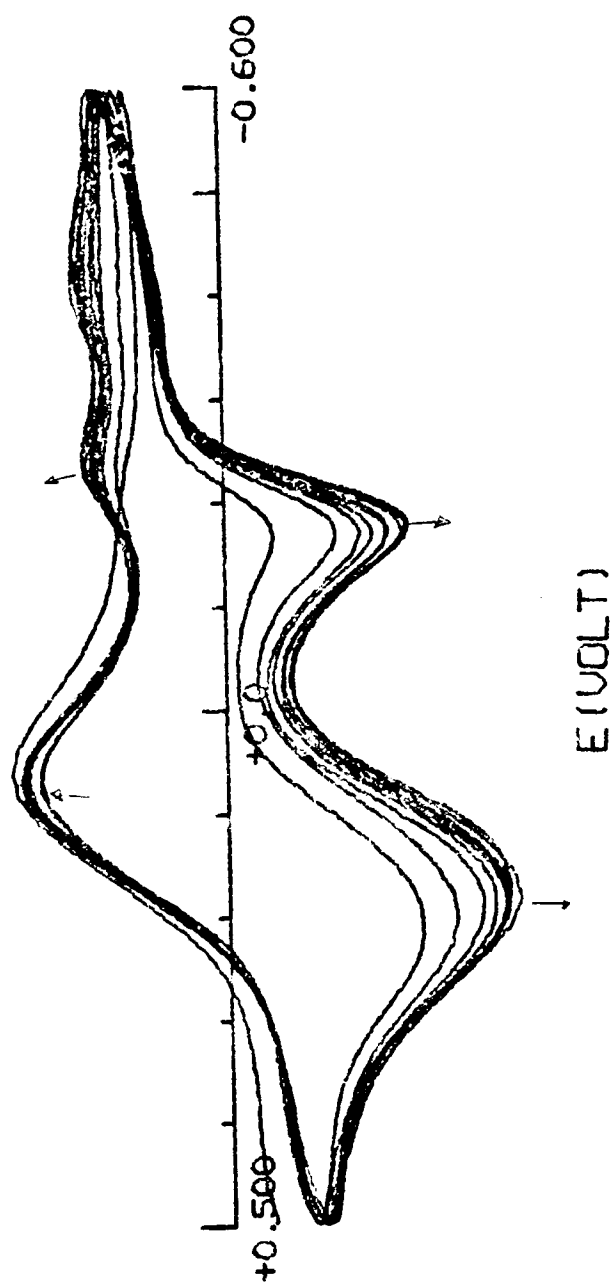
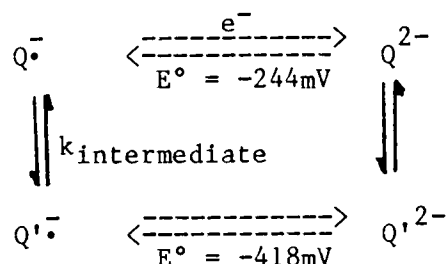


Figure 50. Cyclic voltammogram for PU-TDI film in 0.1M TEAP/ACN, potential vs AgAgCl; 30mV/s.

many more cycles would be needed to clarify this matter. Interestingly, at high scan rates, the reduction wave at $E_p = -418$ mV disappears as shown in Figure 51, where the scan rate was 500 mV/S.

This unexpected behavior of PU-TDI in ACN/TEAP is not clear, however the three reduction waves does imply that a square scheme of the sort shown below may be operating. This scheme depicts the charged



TCNQ units as existing in two different conformations, Q and Q', which are in equilibrium. $Q^{\cdot-}$ representing one conformation of the monomer radical anion and $Q'^{\cdot-}$ representing another conformation of the radical anion. This is seen as an extreme case of Figure 47 which shows the second wave for PU-MDI in ACN/TEAP broadening and separating into two waves as the film is cycled. Certainly, further work is needed here before precise and definite conclusions can be drawn, however noting the similarities of these results with work done by Evans,¹⁹⁵ it is definitely reasonable to make these speculations.

b. Electrochemistry in Alcoholic Solvents. With the hope of understanding the role of the solvent in the electrochemistry of these polyurethanes, the series of n-alcohols, MeOH-BuOH, was examined using a common supporting electrolyte. Physical data for these solvents are

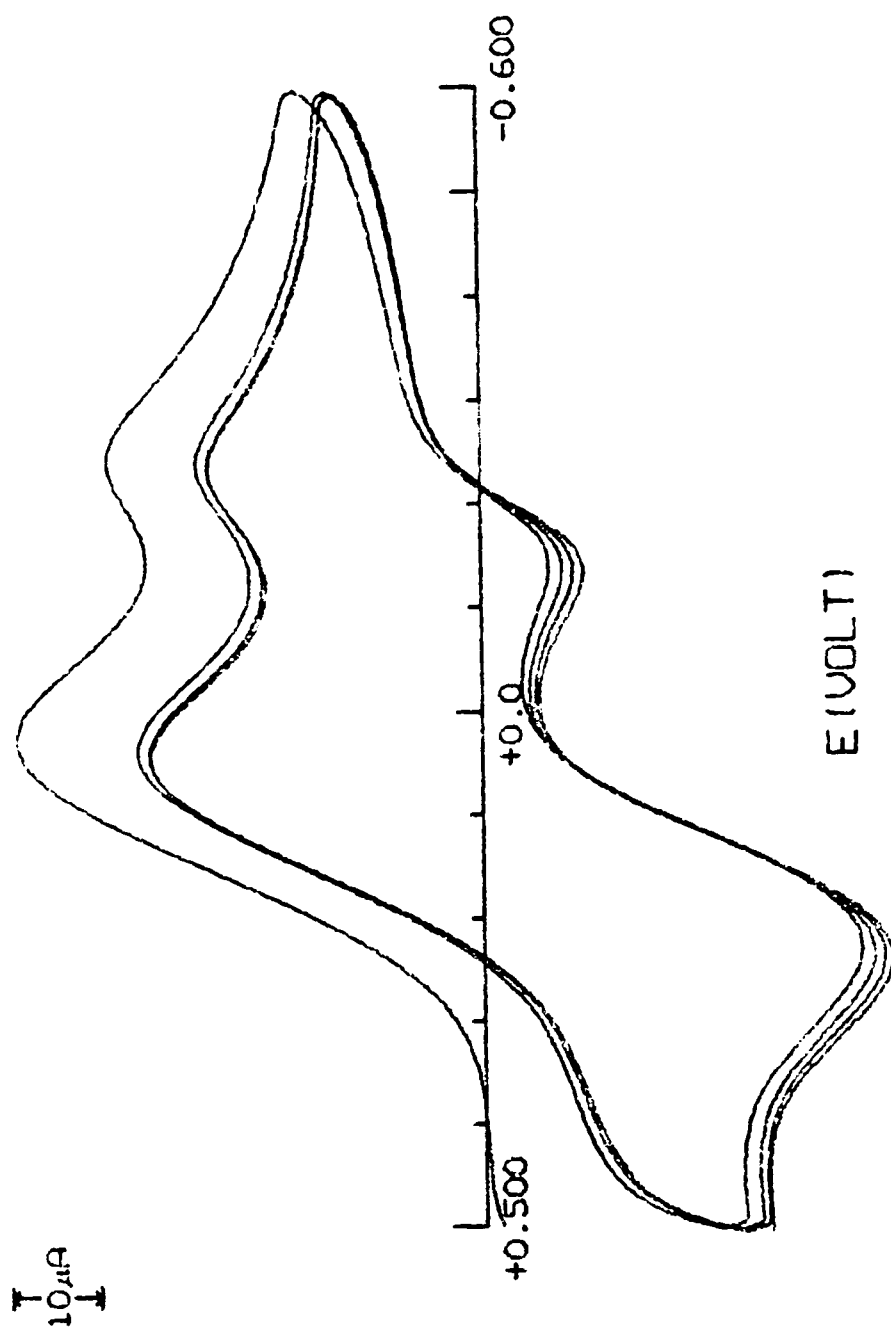


Figure 51. Cyclic voltammogram for PU-TDI film in 0.1M TEAP/ACN, potential vs Ag/AgCl; 500mV/s.

given in Table XLI, water, acetone and acetonitrile are included for comparison.

The CV's for PU-MDI film adsorbed on platinum substrates in the series MeOH-EtOH are shown in Figures 52 and 53. In MeOH/LiCl, two peaks are observed and partial dissolution follows on continuous cycling of the film (see Figure 52). The peak potentials observed on cycle #4 of the CV shown in Figure 52 are $E_p^{c1} = -54$ mV and $E_p^{c2} = -282$ mV coupled with $E_p^{a1} =$ mV and $E_p^{a2} = -252$ mV giving $E_{1/2}^1 = -27$ mV and $E_{1/2}^2 = -267$ mV vs Ag/AgCl. In EtOH/LiCl, the CV for PU-MDI, shown in Figure 53, displays a break-in accompanied by partial dissolution. The peak potentials are: $E_p^{c1} = 6$ mV $E_p^{c2} = -286$ mV coupled with $E_p^{a1} = 93$ mV and $E_p^{a2} = -209$ mV giving $E_{1/2}^1 = 49.5$ mV and $E_{1/2}^2 = -247.5$ mV vs Ag/AgCl. These data along with the data from MeOH/LiCl are summarized in Table XLII. The data observed for TCNQ diol in these solvents are summarized in Table XLIII for comparison. The peak separation was greater in EtOH than in MeOH. However, in general, similar behavior was observed for PU-MDI in contact with EtOH/LiCl and MeOH/LiCl. The wave exhibited in EtOH/LiCl showed more diffusion character than those of PU-MDI in contact with MeOH/LiCl. This slower charge transport in EtOH may be a result in MeOH being able to swell the film more than EtOH. (MeOH is assumed to be a better swelling agent for the film since dissolution was more rapid in MeOH.)

In the presence of PrOH/LiCl and BuOH/LiCl no significant faradic current was observed; the films were passivated. This passivation did not seem reasonable in the light that the films were electroactive in other solvents having similar physical properties (see Table XLI). It

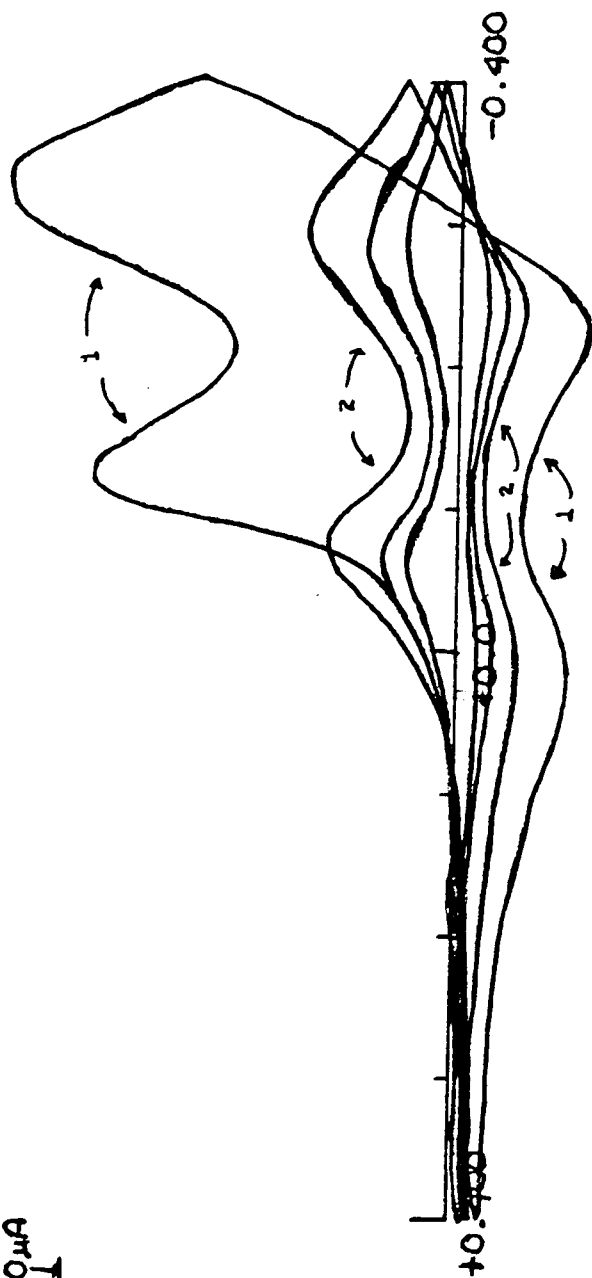
Table XLI

Physical Data for Solvents Used in Electrochemical Studies^a

Solvent	δ_o	δ_d	δ_p	δ_H	Dielectric constant	Dipole moment D	η Viscosity cp
Acetonitrile	11.9	7.50	8.8	3.0	36	3.37	0.34
Acetone	9.77	7.58	5.1	3.4	20.7	2.72	0.30
Butanol	11.30	7.81	2.8	7.7	17.1	1.68 (20°)	2.27 (30°)
Ethanol	12.92	7.73	4.3	9.5	24.3	1.68	1.08
Methanol	14.28	7.42	6.0	10.9	32.6	1.66	0.54
Propanol	11.97	7.75	3.3	8.5	20.1	1.66	2.00
Water	23.5	6.0	15.3	16.7	78.54	1.84	0.89

^aTaken in part from Polymer Handbook, Brendrup, J. and Immergut, E. H. Eds. Wiley Interscience Publication, New York 1975.

T
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I



E (VOLT)

Figure 52. Cyclic voltammogram for PU-MDI film in 0.1M LiCl/MeOH potential vs Ag/AgCl 30mV/s.

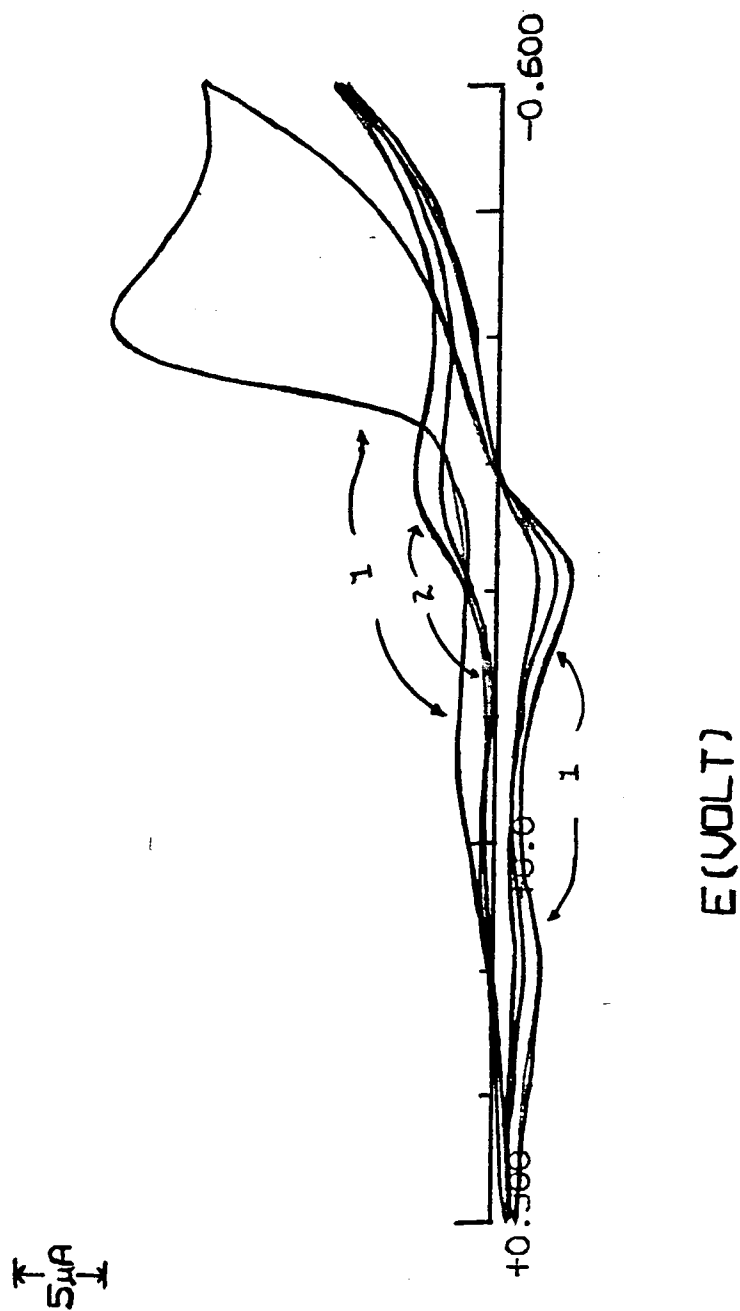


Figure 53. Cyclic voltammogram for PU-MDI film in 0.1M LiCl/EtOH potential vs Ag/AgCl; 30mV/s.

Table XLIII

Voltammetric Parameters for PU-MDI in Alcoholic Solvents Containing
0.1 M LiCl Supporting Electrolyte vs. Ag/AgCl^a

Solvent	E_p^{c1} (mV)	E_p^{a1} (mV)	$E_p^{c1} - E_p^{a1}$	$E_{1/2}^1$ (mV)	E_p^{c2} (mV)	E_p^{a2} (mV)	$E_p^{c2} - E_p^{a2}$	$E_{1/2}^2$	ΔE^b
CH ₃ OH	-54	0	54	-27	-282	-252	30	-270.0	228
CH ₃ CH ₂ OH	6	93	87	49.5	-286	-209	77	-247.5	292
CH ₃ CH ₂ CH ₂ OH	2	124	122	63.0	-342	-220	122	-281.0	340
CH ₃ CH ₂ CH ₂ CH ₂ OH	4	124	120	64.0	-340	-228	112	-284.0	336

^aSweep rate is 30 mV.

^b $\Delta E = E_p^{c1} - E_p^{c2}$.

Table XLIII

Voltammetric Parameters^{a, b} for TCNQ diol in Alcoholic Solvents Containing
0.1M LiCl Supporting Electrolyte vs. Ag/AgCl

Solvent	E_p^{c1} (mV)	E_p^{a1} (mV)	$E_p^{c1} - E_p^{a1}$	$E'_{1/2}$ (mV)	E_p^{c2} (mV)	E_p^{a2} (mV)	$E_p^{c2} - E_p^{a2}$	$E_{1/2}^2$	ΔE^c
CH ₃ OH	13	77	64	45	-265	-155	110	-210	278
CH ₃ CH ₂ OH	98	170	72	130	-286	-219	67	-250	384
CH ₃ CH ₂ CH ₂ OH	99	158	59	130	-304	-236	68	-270	403
CH ₃ CH ₂ CH ₂ CH ₂ OH	102	173	71	140	-317	-243	74	-280	419

^aTaken in part from reference 181.

^bSweep rate is 20 mV/s.

$$c_{\Delta E} = E_p^{c1} - E_p^{c2}$$

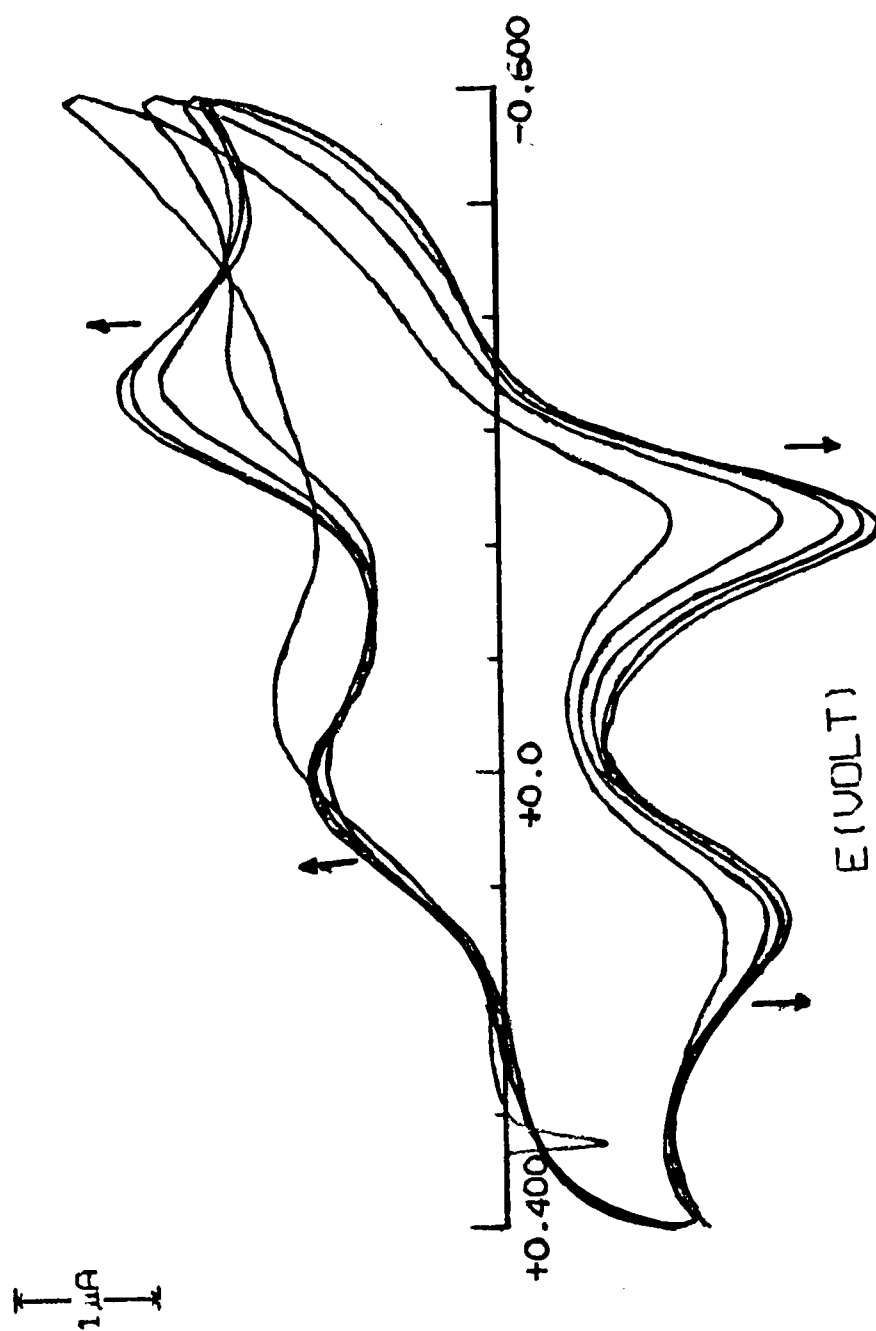


Figure 54. Cyclic voltammogram for PU-MDI film in 0.1M LiCl/PROH potential vs Ag/AgCl; 30mV/s.

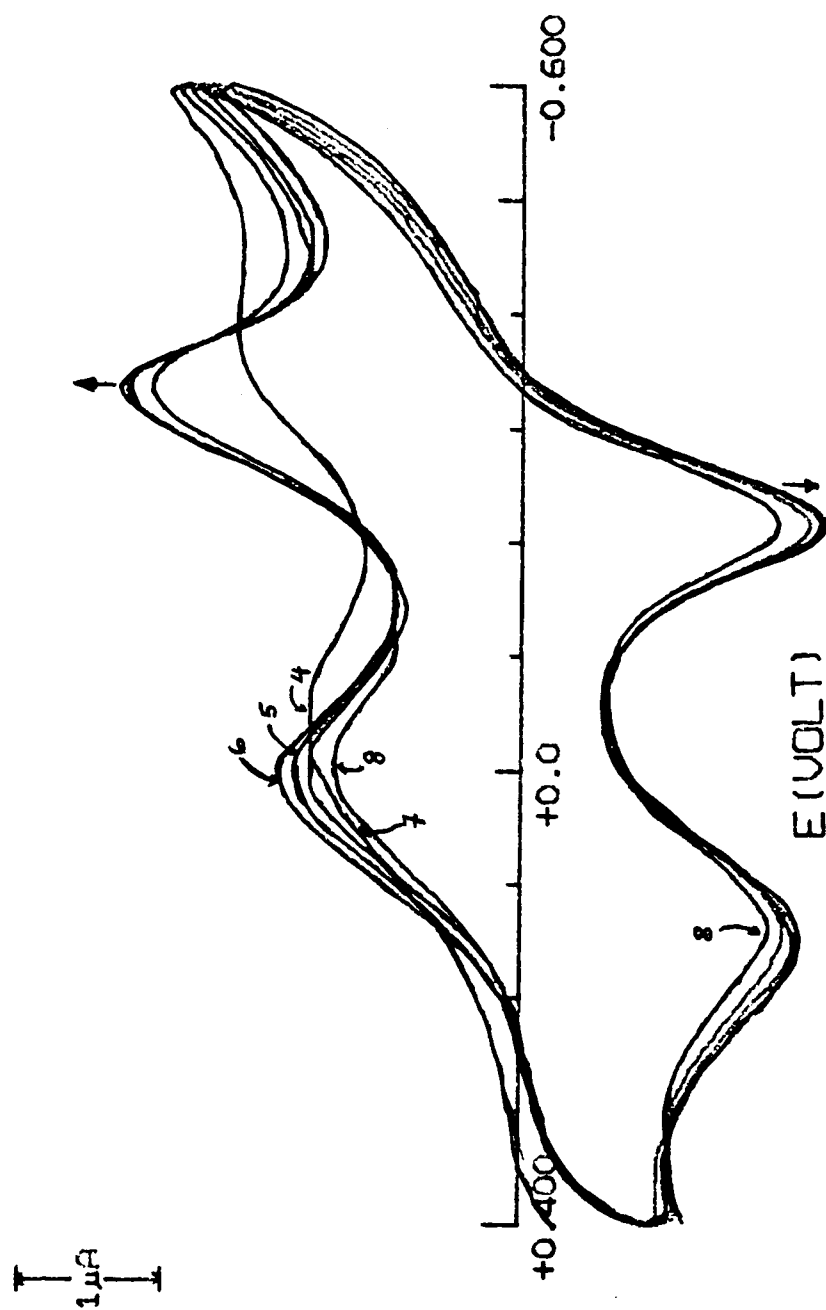


Figure 55. Cyclic voltammogram for PU-MDI film in 0.1M LiCl/BuOH potential vs Ag/AgCl; 20mV/s.

was assumed that the problems were due to uncompensated resistance as a consequence of the films being thick and the low solubility of LiCl in PrOH and BuOH. Thus, the solution was diluted with DMA and a thinner film cast to study the CV response in these solvents. The film used in these solvents was first broken-in in LiCl.

When the film was transferred to PrOH/LiCl, a break-in was observed as if it was a virgin film. Like PE-TCNQ films, the break-in was observed for both waves and very different from the break-in observed in aqueous electrolytes.¹⁸¹ From Figure 54, the waves are observed at $E_p^{c1} = 2$ mV and $E_p^{c2} = -342$ mV coupled with $E_p^{a1} = 124$ mV and $E_p^{a2} = 220$ mV giving $E_{1/2}^1 = 63$ mV and $E_{1/2}^2 = -281$ mV vs Ag/AgCl. For the same film in BuOH/LiCl, a break-in is again observed for both waves, however like PE-TCNQ, the second wave develops at the expense of the first wave.¹⁸¹ The waves are observed at $E_p^{c1} = 4$ mV and $E_p^{c2} = -340$ mV coupled with $E_p^{a1} = 124$ mV and $E_p^{a2} = -228$ mV giving $E_{1/2}^1 = 64.0$ mV and $E_{1/2}^2 = -284$ mV vs Ag/AgCl. (See Figure 55.)

A striking feature of these voltammograms in alcoholic solvents, for PU-MDI films, is the formation of the fully reduced TCNQ²⁻ dianion species which was not observed in aqueous electrolytes. These voltammograms also exhibited more symmetrical peaks than the voltammograms observed in acetonitrile. The asymmetry could be due to uncompensated resistance.¹⁸¹ The symmetric nature of the peaks is probably a reflection of the better swelling ability of these alcoholic solvents over acetonitrile or may be an indication of the relative hydrogen bonding ability of the solvents to the polyurethane chains. A dramatic effect is observed on the electrochemical reversibility of

the film's redox process. As the solvent changes from methanol to n-butanol, there is an increase in the peak widths. Similar results were noted for PE-TCNQ.¹⁸¹ Another interesting revelation of these experiments, similar again to PE-TCNQ,¹⁸¹ is that the films are more stable in the higher molecular weight alcohols. The second wave was assigned to TCNQ⁻/2⁻ couple since similar observations were confirmed for PE-TCNQ.¹⁸¹

In MeOH/LiCl and EtOH/LiCl, PU-TDI films dissolved rapidly. The dissolution was indicated by the MeOH/LiCl solution becoming gold and a rapid decrease in the peak current values. In MeOH/LiCl $E_p^{c1} = -66\text{mV}$, $E_p^{c2} = -304\text{mV}$ coupled with $E_p^a = 26\text{mV}$, as $E_p^{a2} = -350\text{mV}$, giving $E_{1/2}^1 = -20\text{mV}$ and $E_{1/2}^2 = -327\text{mV}$. In PrOH/LiCl and BuOH/LiCl, PU-TDI showed no significant faradic current, the films were passivated. The passivation may be a result of the film not being thin enough to observe any significant electrochemical behavior as was the case when PU-MDI films were first cycled in PrOH/LiCl and BuOH/LiCl. Thinner films were made but the results were similar, so probably an electrolyte more soluble than LiCl in these solvents along with very thin film are needed to observe good electrochemical behavior of PU-TDI films in these solvents.

Shown in Figures 56 are the CV's for PU-HMDI adsorbed on platinum substrates in contact with the series of alcohol solvents MeOH-BuOH/LiCl. Solvent effects are observed on the reversibility of the TCNQ reduction process, the film break-in process, and the stability of the fully reduced film. The peak potentials, $E_{1/2}$ values and peak separation, $E_p^a - E_p^c$, are summarized in Table XLIV.

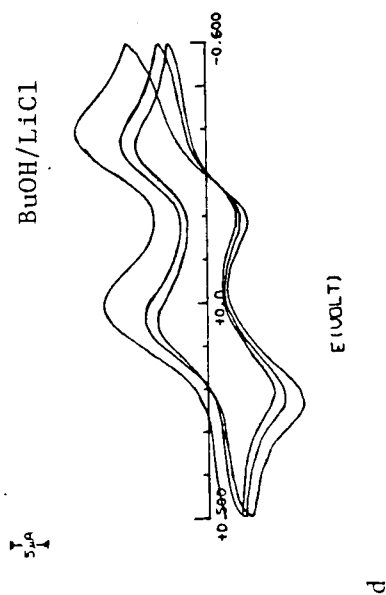
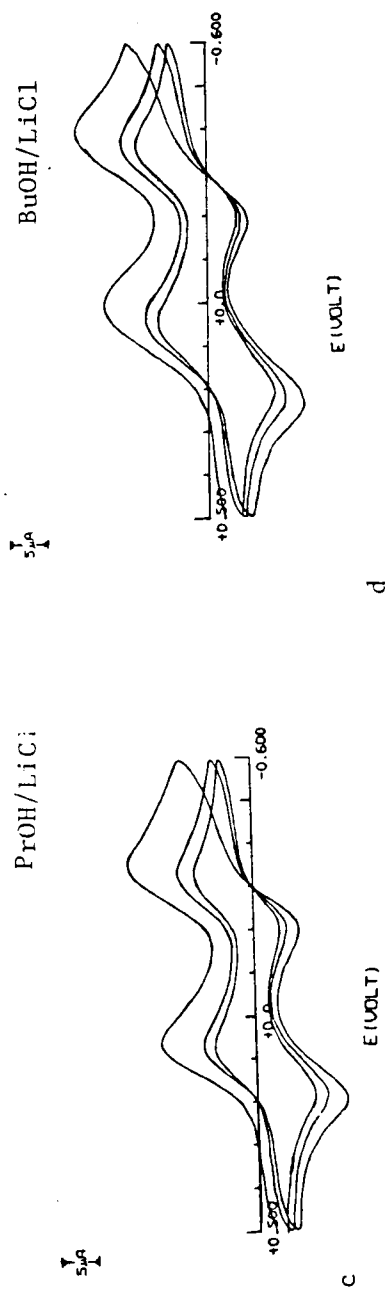
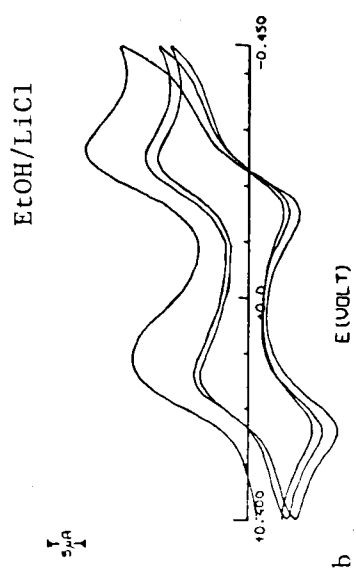
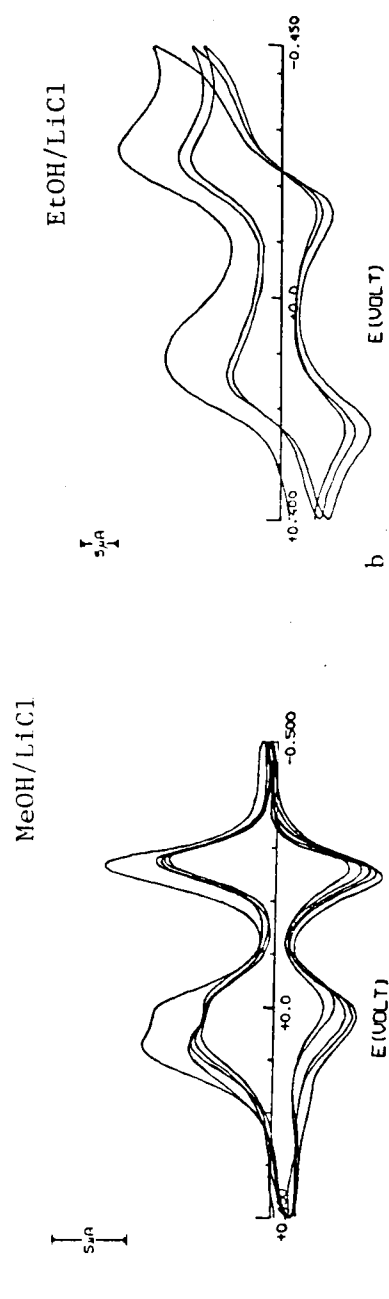


Figure 56. Cyclic voltammogram for PU-HMDI film in alcoholic 0.1M LiCl potential vs Ag/AgCl ; 30mV/s.

Table XLIV

aVoltammetric Parameters for PU-HMDI in Alcoholic Solvents Containing
0.1 M LiCl Supporting Electrolyte vs. Ag/AgCl

Solvent	E_p^{c1} (mV)	E_p^{a1} (mV)	$E_p^{c1} - E_p^{a1}$	$E_{1/2}^1$ (mV)	E_p^{c2} (mV)	E_p^{a2} (mV)	$E_p^{c2} - E_p^{a2}$	$E_{1/2}^2$	ΔE^b
CH ₃ OH	76	16	30	46	-258	-246	12	-252	334
CH ₃ CH ₂ OH	114	237	123	175.5	-260	150	110	-205	374
CH ₃ CH ₂ CH ₂ OH	56	195	139	125.5	-357	-200	157	-278.5	413
CH ₃ CH ₂ CH ₂ CH ₂ OH	56	188	132	122	-364	-206	158	-285	420

^aSweep rate is 30 mV/S.

^b $\Delta E = E_p^{c1} - E_p^{c2}$.

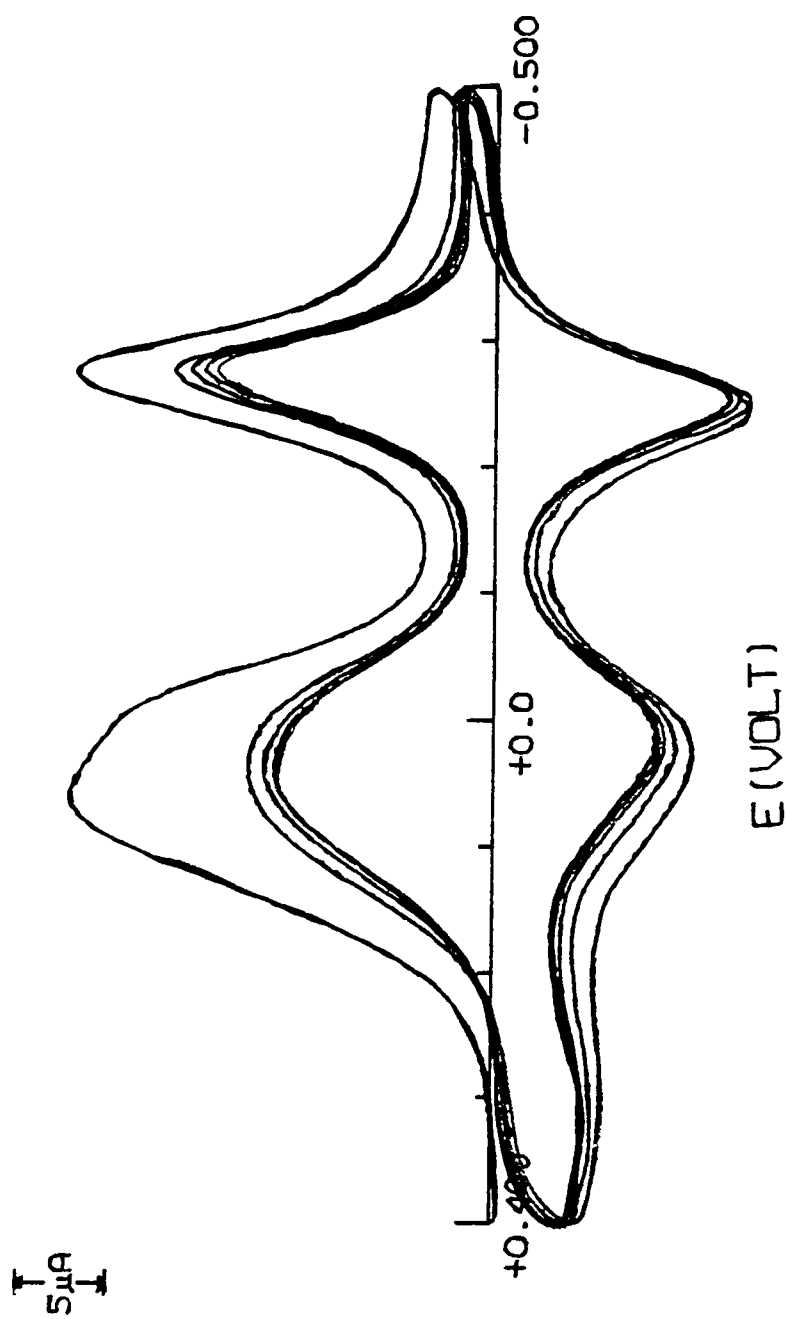


Figure 57. Cyclic voltammogram for PU-HMDI film in 0.1M LiCl/MeOH, potential vs Ag/AgCl; 100mV/s.

PU-HMDI films in contact with MeOH/LiCl show well-developed surface waves for both the first and the second electron transfer steps, for the first time. Again with repeated cycling as in the case of PU-MDI and PE-TCNQ,¹⁸¹ the film gradually dissolves, giving the solution a color characteristic of the TCNQ diol in solution. At slow sweep rates a prewave is observed on the first wave. Sometimes, at very slow sweep rates (≤ 10 mV/S), the prewave forms two fully developed waves $E_p^{c1} = 136$ mV and $E_p^{c2} = 26$ mV coupled with $E_p^{a1} = 193$ mV and $E_p^{a2} = 31$ mV giving $E_{1/2}^{c1} = 165$ mV and $E_p^{c2} = 29$ mV vs. SCE. At higher sweep rates the prewave coalesces with the first wave as shown in Figure 57. Interestingly, these results are quite similar to PE-TCNQ films in contact with ACN electrolytes.⁷⁰

In EtOH/LiCl, PU-HMDI displayed a very similar behavior to that displayed in MeOH/LiCl except that here the film could be cycled between TCNQ^{0/-} oxidation states without any significant dissolution (if the film was baked for at least 20 minutes prior to use). Also in EtOH the second wave had more diffusion character than that for the film in MeOH.

The CV's in PrOH/LiCl and BuOH/LiCl shown in Figures 56 are very similar, yet different from the CV's obtained in either MeOH/LiCl or EtOH/LiCl. Even though two oxidation and two reduction waves are observed in these solvents, the CV's would tend to indicate that as the molecular weight of the solvent increases, the diffusion character of the waves also increases. The peak separation is also larger in these solvents than in either MeOH or EtOH. This result is certainly

indicative of the important role the solvent swelling process plays in the charge transport rate.

Surprisingly, PU-HMDI in these alcoholic solvents did not display the break-in phenomenon observed for this material in aqueous LiCl (see Figure 32, p 130). In aqueous electrolytes, several cycles are required before any significant current is observed and the peak sharpened on subsequent cycles with generally, a shift in peak potential until the break-in process is completed. The shift in peak potential may be due to uncompensated resistance as the film is charged. On the other hand, in alcoholic solvents, the very first cycle is representative of the voltammograms obtained with only minor changes occurring in the peak potentials as the current increases on subsequent cycles. These results may be an indication that PU-HMDI is swollen almost instantaneously in alcoholic solvents. It was observed that in the presence of the higher molecular weight alcohols, the films could be cycled for a much longer time before any visible dissolution. The reason for this is not clear, however it may be indicating the differences in the swelling characteristic of these solvents towards these polyurethanes.

The differences between PU-HMDI and PU-MDI are clearly demonstrated in the electrochemical response of these films in the alcoholic solvents. Unfortunately quantitative conclusions cannot be made from these experimental results since important molecular parameters like molecular weight, cross-link density and polydispersity are not known for these polymers. However, some qualitative conclusions may be drawn. First, only small changes are observed in the

peak potential for the first wave of PU-HMDI while PU-MDI shows a shift of almost 50 mV in the peak potential of the first wave as the solvent is changed from MeOH-BuOH. This may be a manifestation of the importance of association ($A^{\cdot-} M^+$) which was discussed earlier (p 134). Secondly, the similarities observed in the electrochemical response for PE-TCNQ and PU-HMDI, and the significant differences with PU-MDI, indicate that the electrochemistry of these polymers is strongly influenced by the rigidity of the polymers. This conclusion is supported by work from Funt and others who noted that electroactive polymers of varying degrees of polymerization gave electrochemical behavior consistent with the electroactive monomer.^{141,155,156,196,197} This of course assumes noninteracting redox centers.¹⁵⁴ The rigidity will also grossly affect morphological changes and kinetics in solution.¹⁹⁸ Thirdly, for both polymers there seem to be a change in the wave shapes indicating more diffusional character in PrOH and BuOH, while more surface wave type behavior is observed in MeOH and EtOH. That is, the rate of the charge transport process is greater in the more strongly hydrogen bonded and lower molecular weight solvents.

c. Electrochemistry in Acetone. The CV behavior of PU-MDI and PU-TDI adsorbed on platinum substrates in contact with acetone/ $NaClO_4$ is shown in Figures 58 and 59. The background CV for acetone/ $NaClO_4$ is also shown in Figure 60 since the acetone was not purified before use. Two reversible surface waves are observed for PU-MDI showing $E_p^{c1} = -10$ mV and $E_p^{c2} = -301$ mV coupled with $E_p^{a1} = 56$ mV and $E_p^{a2} = -27$ mV giving $E_{1/2}^1 = 23$ mV and $E_{1/2}^2 = -286$ mV vs SCE.; PU-TDI showed $E_p^{c1} = -14$ mV and $E_p^{c2} = -371$ mV coupled with $E_p^{a1} = 94$ mV and $E_p^{a2} =$

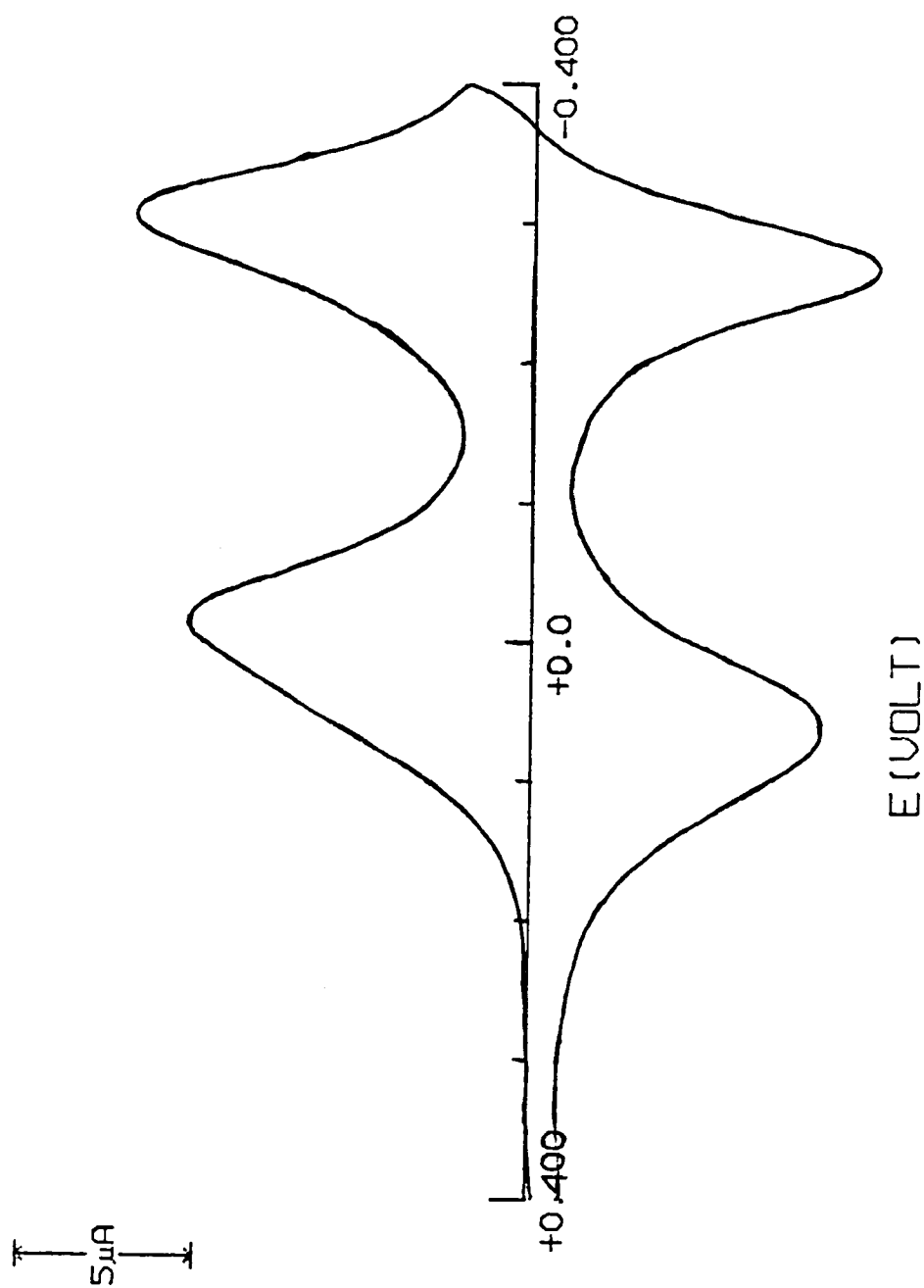


Figure 58. Cyclic voltammogram for PU-MDI film in 0.1M NaClO_4 /Acetone, potential vs SCE 30mV/s .

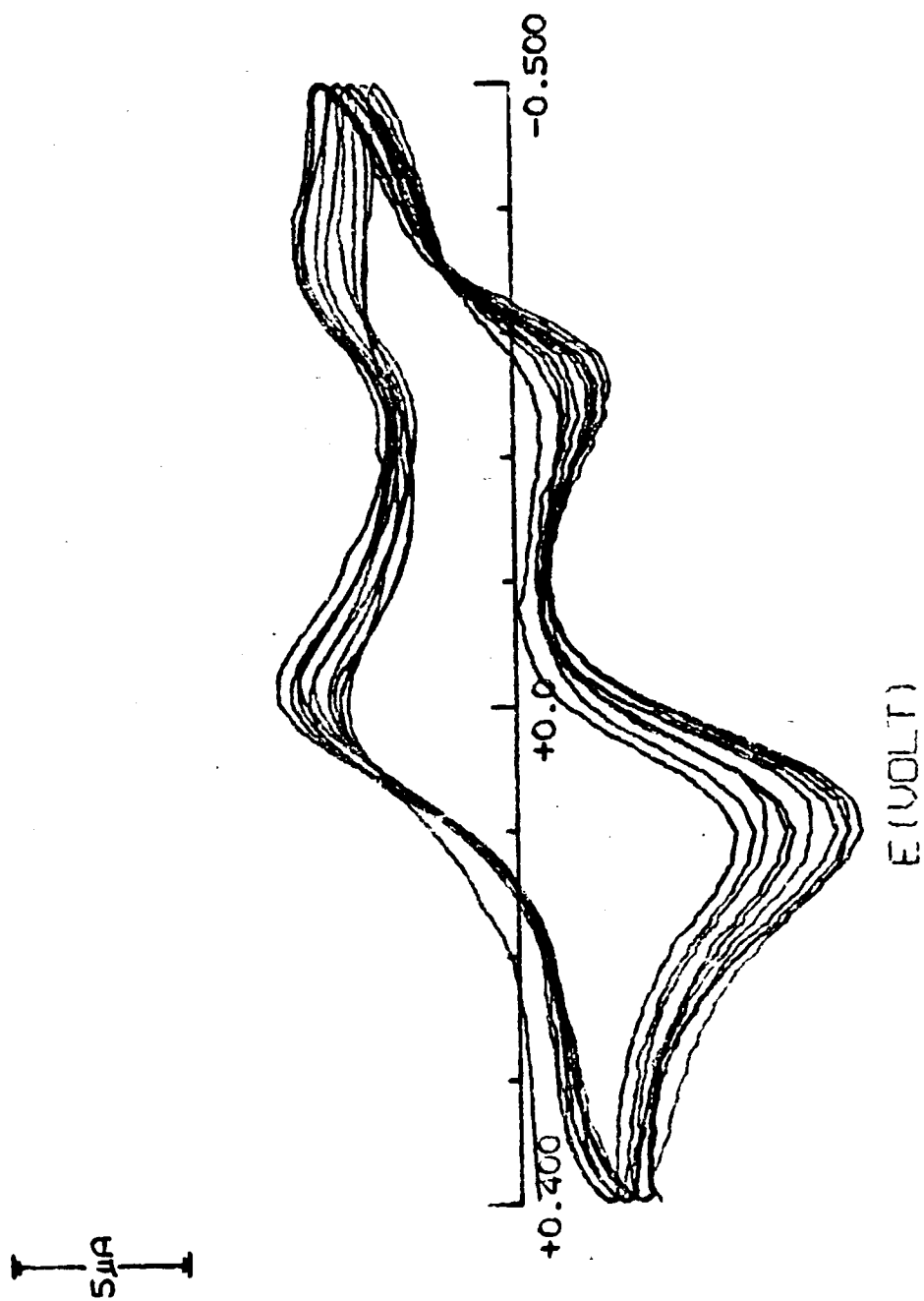


Figure 59. Cyclic voltammogram for PU-TDI film in 0.1M NaClO_4 /Acetone potential vs Ag/AgCl ; 30mV/s.

↑
5μA
↓

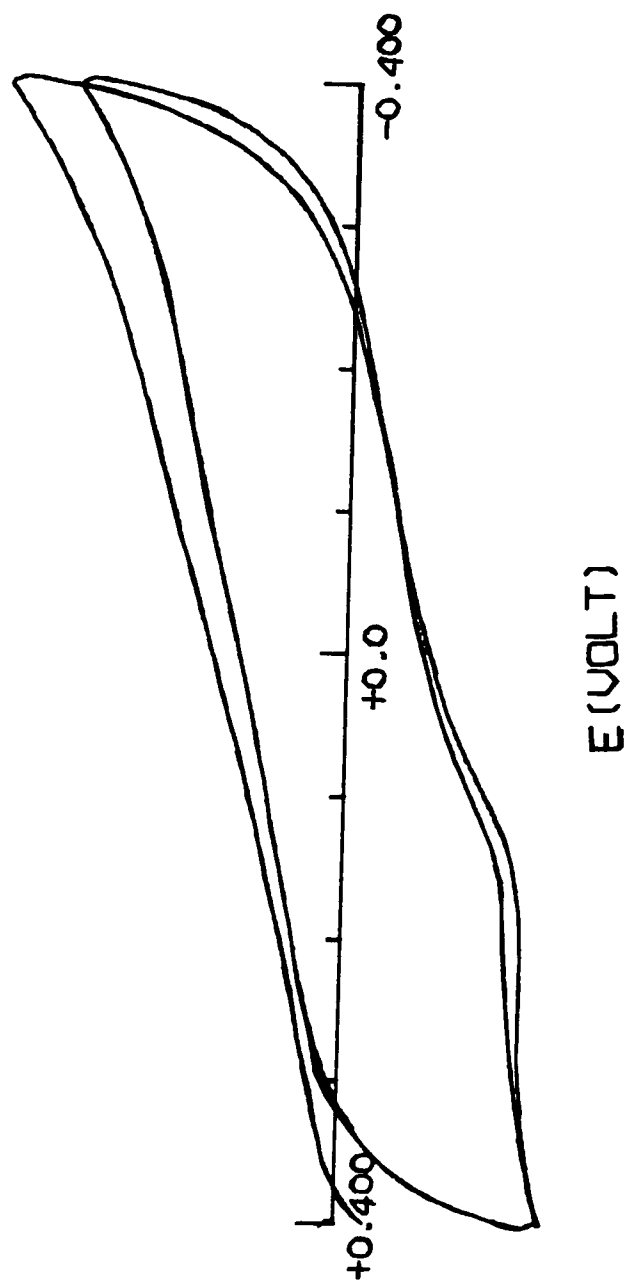


Figure 60. Background CV for 0.1M NaClO₄/Acetone, potential vs SCE, 30mV/s.

Table XLV

Voltammetric Parameters^a for PU-MDI and PU-TDI in Acetone
Containing 0.1M NaClO₄ Supporting Electrolyte

Polymer	E_p^{cl} (mV)	E_p^{al} (mV)	$E_p^{cl} - E_p^{al}$	$E_{1/2}^1$ (mV)	E_p^{c2} (mV)	E_p^{a2} (mV)	$E_p^{c2} - E_p^{a2}$	$E_{1/2}^2$	ΔE^b
PU-MDIC	-10	56	46	23	-301	-271	30	-286	291
PU-TDId	-11	94	83	41.5	-371	-260	111	-315.5	291

^aSweep rate is 30 mV/S.

^b $\Delta E = E_p^{cl} - E_p^{c2}$.

^cPotential vs SCE.

^dPotential vs Ag/AgCl.

-260 mV giving $E_{1/2}^1 = 41.5$ mV and $E_{1/2}^2 = -315.5$ mV vs Ag/AgCl. These data are summarized in Table XLV.

On cycling PU-MDI films in acetone/ NaClO_4 , there was an initial dissolution indicated by a reduction in peak current and the yellowing of the acetone solution. However, after a few cycles the film was stabilized, indicated by no significant i_p change on cycling, and two well-developed reversible surface waves are observed for both the first and second electron transfer steps. These waves are persistent as the electrode is cycled between the 0 and -2 oxidation states. Interestingly, this is the first time PU-MDI exhibited surface wave behavior similar to both PE-TCNQ and PU-HMDI.

On the other hand, PU-TDI surprisingly showed waves with a more diffusional character, especially for the second wave. PU-TDI films also showed a break-in in acetone electrolytes for both waves. This behavior was surprising since acetone was thought to be a good swelling agent for these polymers based on the performance of PU-MDI in acetone/ NaClO_4 . It is possible that PU-TDI may contain crystalline domains which are not swollen immediately in acetone, but rather in a gradual manner, and thus explain the voltammogram shown for PU-TDI/Acetone (see Figure 59). These results are preliminary and further work would be needed to explain the differences here for PU-TDI and PU-MDI.

The percent electroactivity of PU-MDI films in water and in acetone was estimated. These calculations were based on a 1:1 TCNQ/MDI molar ratio in the polymer. The molar weight of the repeat unit was used to calculate the number of moles of TCNQ units on the electrode

surface. That is, knowing the volume of the casting solution along with its concentration the moles of TCNQ units on the electrode surface could be calculated. The theoretical number of coulombs expected from the moles of material used was calculated as follows:

$$n F m = C_T \quad \quad (39)$$

where m = moles of polymer per repeat unit, C_T = theoretical number of coulombs. The actual charge in coulombs was obtained by comparison of the weight of the area under the reduction peak obtained from the CV to the weight of a known area corresponding to a known charge. The calculations revealed that only 44% of the TCNQ units are active for an unbaked film in water and a mere 32% active for a film baked for 5 minutes. The film was however, fully electroactive in acetone. These data are summarized in Table XLVI. This full activity of all the TCNQ units in acetone is consistent with the surface wave behavior exhibited in Figure 58.

H. Summary and Conclusions of Solvent Effects

The electrochemical behavior of these polyurethanes is significantly affected by the solvent in which the experiments are performed. Whereas in aqueous electrolytes only one reduction and one oxidation peak are seen, corresponding to the $\text{TCNQ}^{0/-}$ couple, two reduction and two oxidation peaks, corresponding to $\text{TCNQ}^{0/-}$ and $\text{TCNQ}^{-1/2-}$ are observed in nonaqueous solvents. The differences in behavior of the films as the solvent is changed is definitely related to the ability of the solvent to swell the polymer. If the polymer is only partially

Table XLVI

Percent Electroactivity of PU-MDI Films in Different Solvents^a

<u>Mole of Polymer^b</u>	<u>% Electroactivity</u>
6.54 x 10 ^{-9c}	32
6.54 x 10 ^{-9c}	32
6.54 x 10 ^{-9c,d}	44
6.54 x 10 ^{-9e}	100
6.54 x 10 ^{-9e}	100

^aSweep rate is 10 mV/S.^bThe true moles of polymer would be these numbers divided by the degree of polymerization.^cSolvent is water.^dUnbaked film.^eSolvent is acetone.

swollen, then facile charge transport is not accommodated. This is thought to be the case for aqueous electrolytes. If the solvent is able to swell and solvate the polymer to a good extent, then the behavior as shown in acetone is observed. At this point the film can be cycled reversibly between the fully reduced and oxidized states.

Interestingly, the second wave, relative to the first wave, is a sensitive indication of the charge transport through the film. As discussed earlier, if $(\frac{D_{ct}\tau}{d^2})$ is large, surface wave behavior is observed and i_p is proportional to v . If $(\frac{D_{ct}\tau}{d^2})$ is small, diffusion behavior is seen and i_p is proportional to $v^{1/2}$. For these polyurethanes, the indications are that D_{ct} for the second wave is smaller than D_{ct} for the first wave. Thus, conditions can be found, even for fast electron transfer for the TCNQ⁻/2⁻ hop, where the second wave will not be seen as in the case of aqueous electrolytes.

CHAPTER V

SPECTROELECTROCHEMISTRY AND pH STUDIES

In aqueous electrolytes the polyurethanes displayed one reduction and one oxidation peak. This behavior was not consistent with the behavior expected of either TCNQ diol or PE-TCNQ, both of which exhibited two reduction and two oxidation peaks. Studies of the optical properties of TCNQ have revealed absorption band characteristic of neutral TCNQ molecule,^{16,39,200,201} the radical anion^{16,20,39} the dianion²⁰² and the dimer dianion species.^{39,152} Thus, it was decided that if the fully reduced TCNQ^{2-} is being formed and not detected by CV, an absorption band characteristic of this species should appear in the UV-VIS spectrum. Furthermore, additional manipulation of the data obtained from spectroelectrochemical experiments in the form of derivative cyclic voltabsorptometry, DCVA, should indicate conclusively if two electrons are being transferred to TCNQ under these experimental conditions.

A. Film Preparation and Apparatus

The films were prepared by the droplet evaporation procedure described on page 114. The optically transparent coated electrodes were mounted in a Teflon cell equipped with a quartz window. The absorption spectra of the films were recorded on a Cary 17 recording spectrophotometer with an uncoated Pt-on-quartz disc in the compartment of the reference beam. These films were made thick ($> 1.2 \text{ kÅ}$) in order to increase their absorbance and get a good UV-VIS response.

B. Optical Spectrum and its Potential Dependence

In agreement with the literature, the absorption spectrum of neutral PU-MDI featured two peaks at $\lambda_{\max}$ 432 nm and $\lambda_{\max}$ 412 nm,^{16,39,200,201} while the electrogenerated PU-MDI (TCNQ $^{\cdot-}$)_x polyanion spectrum at -0.5V showed bands at $\lambda_{\max}$ 720nm and $\lambda_{\max}$ 432 nm for the radical anion, TCNQ $^{\cdot-}$,^{16,39,201} bands at $\lambda_{\max}$ 640 nm and $\lambda_{\max}$ 395 nm for the dimer dianion, TCNQ $_2^{2-}$,^{29,152} and bands at $\lambda_{\max}$ 480nm and $\lambda_{\max}$ 385 nm characteristic of the oxygen decay product of the dianion, α,α -dicyano-p-toluoylecyanide anion.^{202,203}

Figure 61 shows the absorption spectra of a PU-MDI film in aqueous 0.1N LiCl at different potentials. The absorption bands evident in these spectra can be assigned to previously characterized TCNQ species. As the film becomes reduced, the dimer dianion band at 640 nm grows more prominent relative to the radical anion band at 720 nm. This is consistent with the extensive dimerization of TCNQ $^{\cdot-}$ as reported by Boyd and Phillips¹⁵² and Inzelt and coworkers for PE-TCNQ.³⁹ At more negative potentials bands are observed at 480 nm and 345 nm. The intensity of these bands increase as the potential becomes more negative. These bands are thought to be due to the oxygen decay product of the dianion.^{202,203}

In order to monitor the decay of the radical anion and the dimer dianion, two further experiments were performed. First, the absorbance at 720 nm, Abs⁷²⁰, was monitored as a function of the applied potential, E. This was done in two stages as outlined below.

a. Cyclicvoltabsorptametry, (CVA) and DCVA. The CVA technique involves keeping the wavelength of the spectrometer constant and

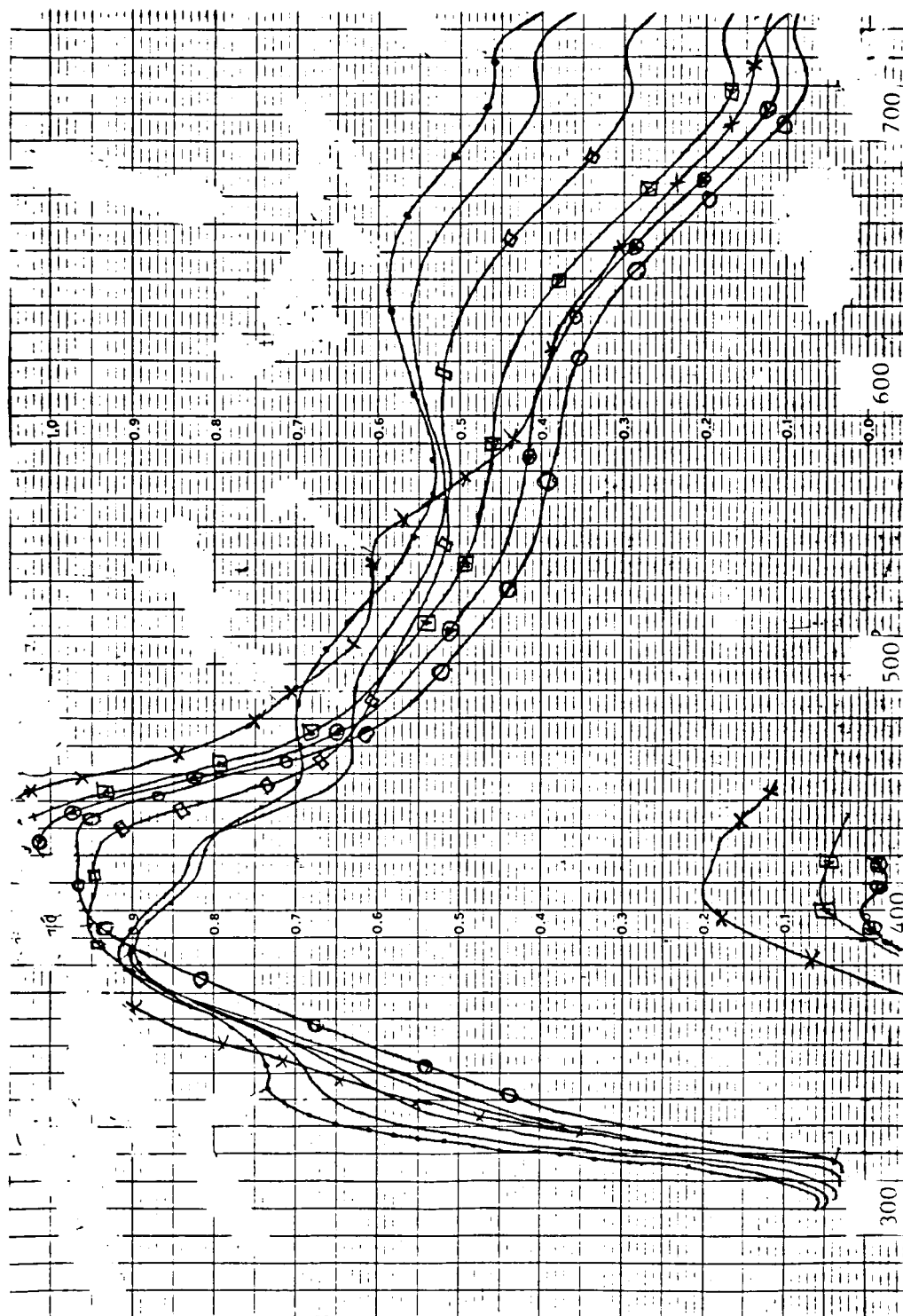


Figure 61. UV-VIS spectra for PU-MDI film at different potentials in 0.1M LiCl.

simultaneously performing the CV. The changes in absorbance should give an indication of the changes in chemical species responsible for the absorbance at that given wavelength.²⁰⁴ The absorbance versus applied potential in a derivative format leads to a response similar to CV and is known as DCVA. The theoretical basis for this technique, developed by Blount and coworkers,²⁰⁵ is described by the following equation:

$$\frac{dAbs}{dE} = \beta n^{1/2} \epsilon_D^{1/2} C_v^{-1/2} \quad \quad (40)$$

where β is $-0.08810 \text{ mV}^{-1/2}$ and all the other terms have been previously defined. This technique has been used to study chemical reactions of intermediates generated at optically transparent electrodes.²⁰⁶

The CVA experiment was carried out at 720 nm in 0.1M LiCl, Figure 62 was obtained. On the negative going sweep a maximum in the absorbance is observed at about -0.7V. This maximum remains with very little change until about -0.1V when oxidation of the $\text{TCNQ}^{\cdot-}$ is noticable. The DCVA curve was then derived from Figure 62 by plotting dA/dE versus E as shown in Figure 63. The DCVA curve is a very good indication that on the time scale at which these experiments are performed the fully reduced TCNQ^{2-} is not formed. If such a process was taking place, then the characteristic crossing pattern of an EE electrode process would be observed, as was shown for PE-TCNQ.³⁹ The CVA experiment was also performed at 625 nm where TCNQ_2^{2-} absorbs. A DCVA curve from these data yielded similar results to the DCVA curve

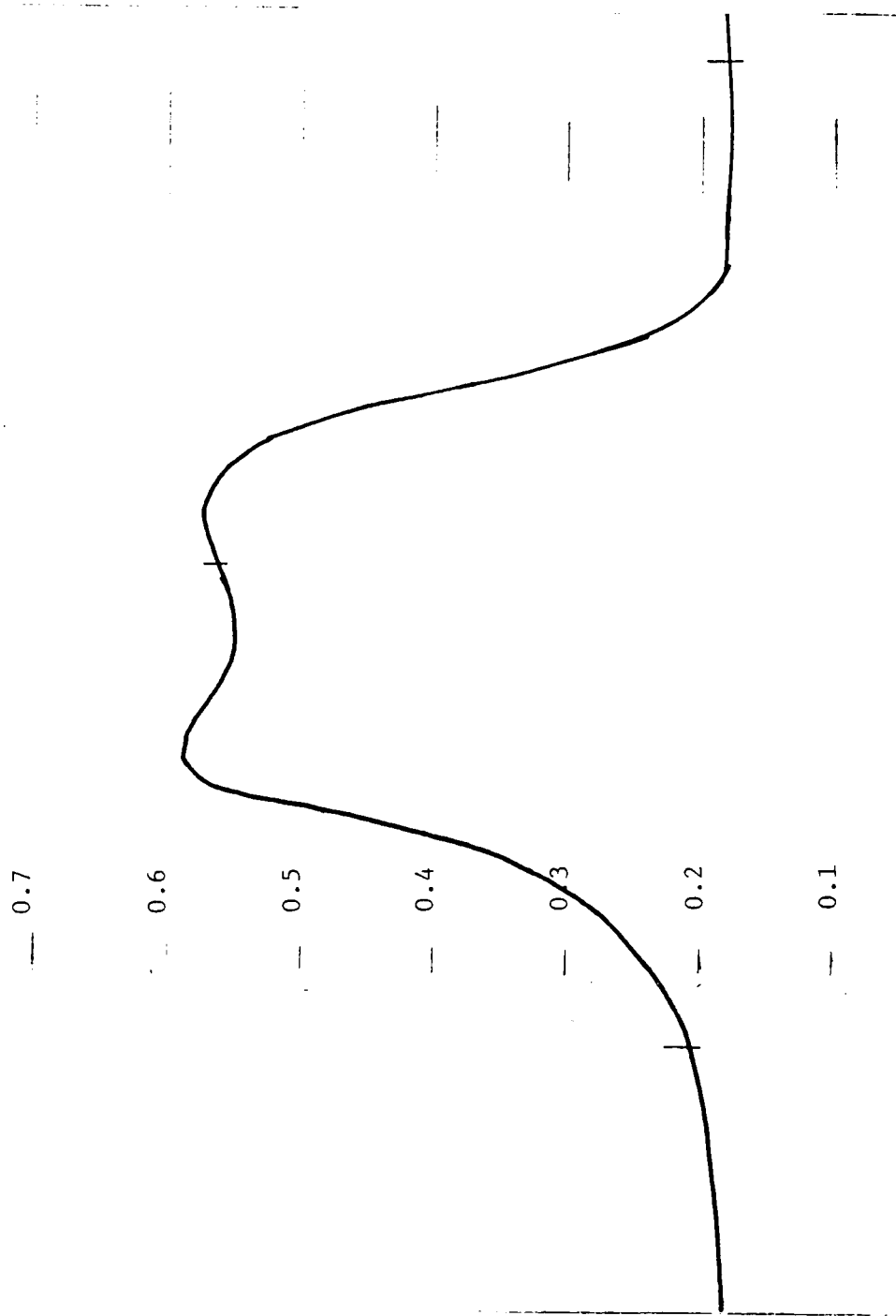


Figure 62. UV-VIS spectrum for PU-MDI film being cycled between +0.3 and -0.85V at $\lambda = 725\text{nm}$.

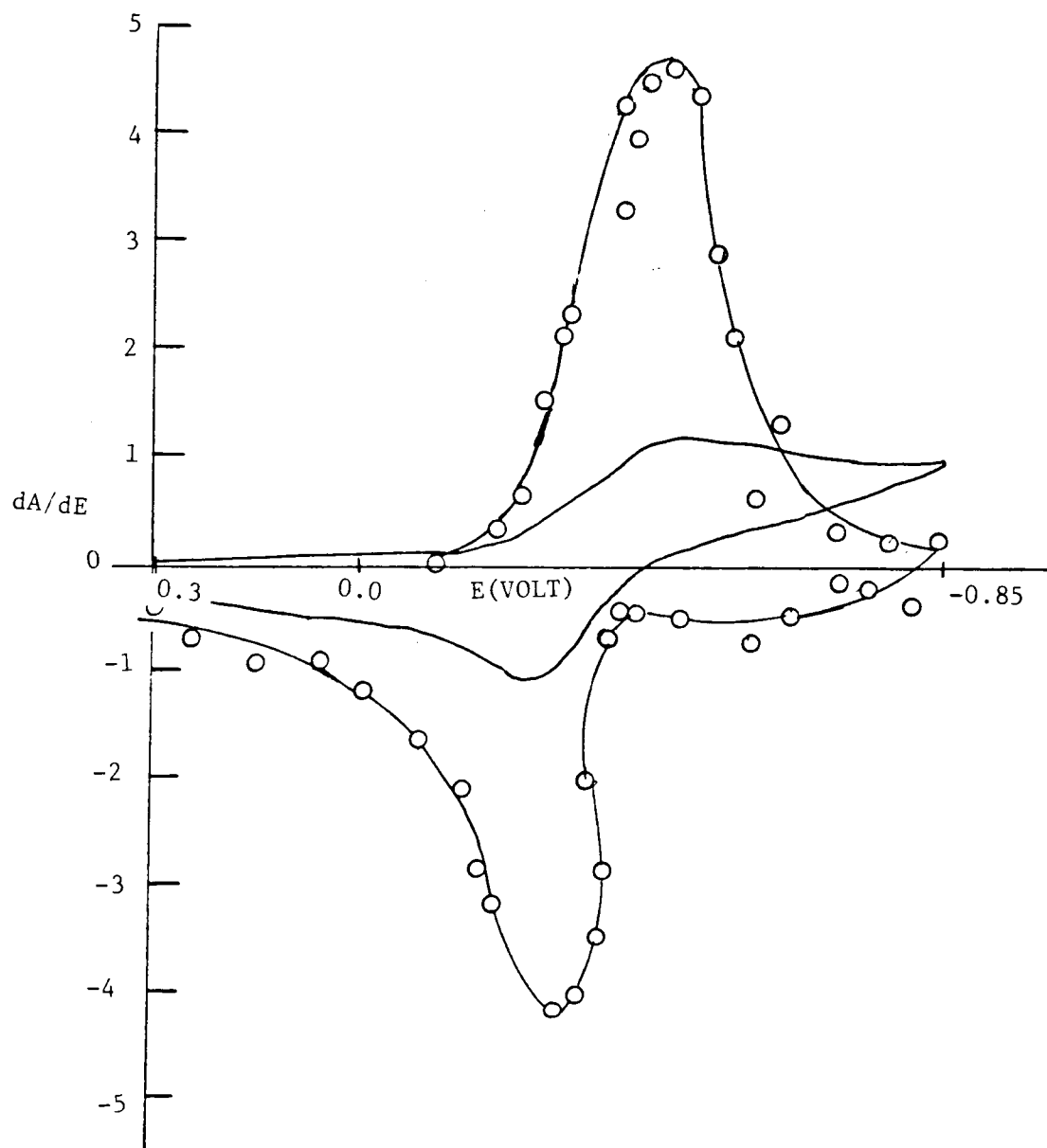
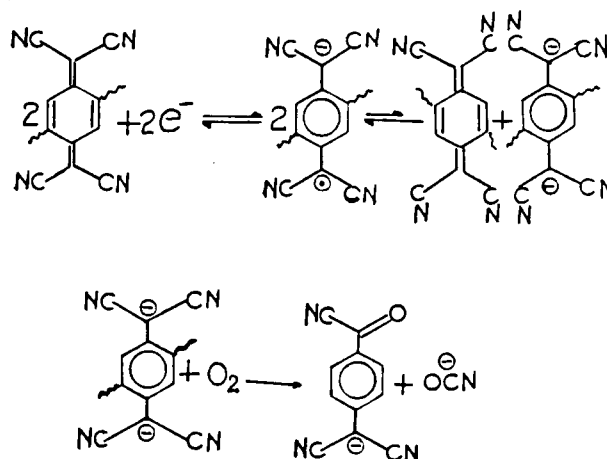


Figure 63. DCVA curve for PU-MDI film in 0.1M LiCl, potential vs Ag/AgCl.

obtained at 725 nm. These results are strong evidence in support of $\text{TCNQ}^{\cdot-}$ not being converted to TCNQ^{2-} on the time scale of these experiments.

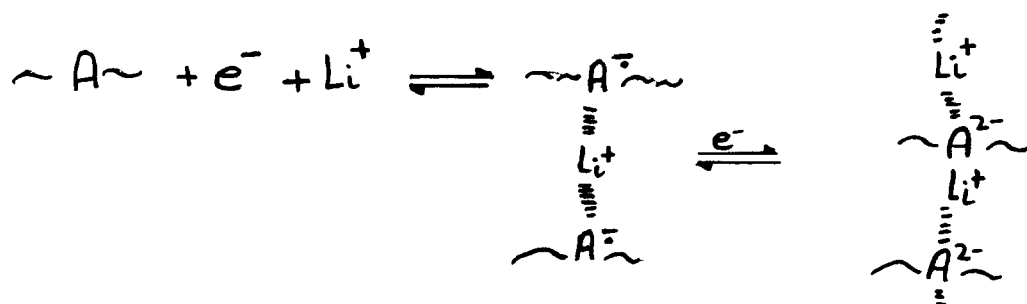
Three explanations are proposed here for the absorbances seen at 480 nm and 345 nm, indicative of the oxygen decay product of TCNQ^{2-} . If the film contains residual oxygen trapped in it, then the following processes can be visualized:



Such processes could conceivably occur at the potential at which the radical anion is formed and produce low concentrations of the dianion. The irreversible reaction of residual O_2 with the dianion would drive the equilibrium disproportionation step to the right.

Another possibility is the conversion of a small fraction of the radical anions to the dianion at -0.5V . This could then trigger a cross-linking of the film via a chelating effect, and thus render the charge transport for the second wave zero.

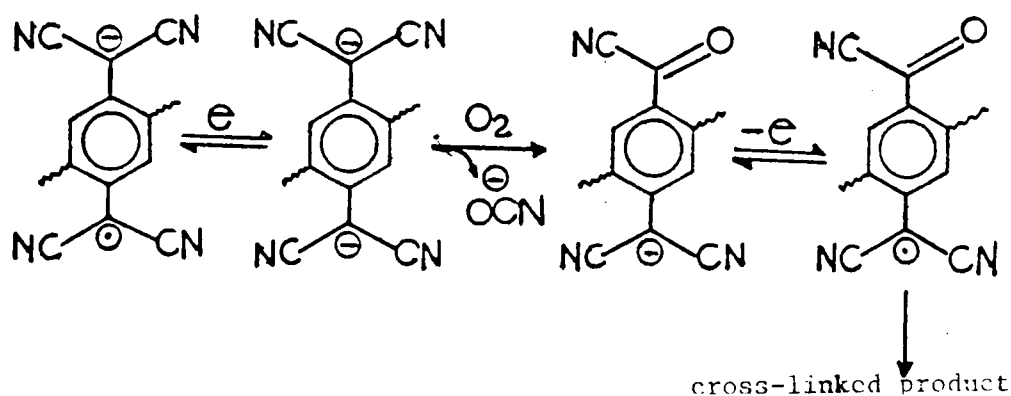
That is:



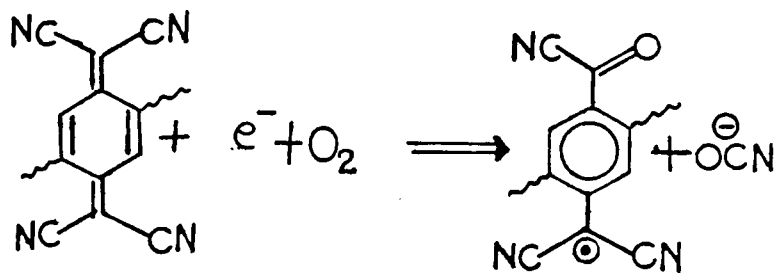
where A represents TCNQ

The A^{2-} can now react very quickly with oxygen to produce α,α -dicyano-p-toluoyl cyanide anion.²⁰³

Yet a third possibility may be that there is an initial formation of the dianion from the reduction of the radical anion at -0.5V. This dianion, which is extremely sensitive to oxygen,^{203,204} reacts immediately with oxygen followed by a one electron oxidation to a neutral radical which cross-links immediately to prevent the formation of more fully reduced sites. That is:



Overall, this sequence of reaction may be represented as:



The second explanation seems more likely, in light of the results obtained from the transfer experiments and variation of cation experiments discussed earlier. The cross-linked products obtained via the chelating ion effect would be soluble in nonaqueous solvents and thus, allow the transfer of the second electron to produce TCNQ^{2-} in say, acetone.

b. Equilibrium Step Potential Spectroelectrochemistry. In this set of experiments the wavelength was set at the 725 nm absorbance band of $\text{TCNQ}^{\bullet-}$. The film was then potentiostated at a certain potential for 5–10 min, in 0.1M LiCl, to allow the film to reach equilibrium. The change in absorbance is then measured as a function of the potential.²⁰⁶ These data are summarized in Table XLVII. The results of this experiment reveal that the plot of change in absorbance vs E (see Figure 64) shows a drawn-out wave that resembles the CV in the essential features. The corresponding Nernst plot seen in Figure 65 is linear, but the n-value derived from the slope is only 0.41. The $E_{1/2}$ value calculated from the Nernst plot is -0.245V vs Ag/AgCl or 0.198V vs SCE. These results clearly demonstrate that the radical anion is formed in the reduction process and it is not reduced further

Table XLVII

Equilibrium Absorbance data for PU-MDI in 0.1M LiCl

E	Abs.	Δ Abs	$\log \frac{\lim_{\Delta \text{Abs}} \text{Abs} - \Delta \text{Abs}}{\Delta \text{Abs}}$
open	0.393	0	
-0.10	+0.404	0.0045	1.00
-0.12	0.408	0.0065	0.82
-0.14	0.412	0.0085	0.68
-0.16	0.414	0.0095	0.62
-0.10	0.420	0.0125	0.465
-0.20	0.427	0.106	0.31
-0.22	0.433	0.019	0.20
-0.24	0.440	0.0225	0.07
-0.26	0.450	0.0275	-0.10
-0.28	0.460	0.0325	-0.29
-0.30	0.464	0.0345	-0.38
-0.32	0.469	0.037	-0.49
-0.34	0.474	0.0395	-0.62
-0.36	-0.480	0.0425	-0.815
-0.38	0.480	0.0425	-0.815
-0.40	0.480	0.425	
-0.45	0.487	0.046	-1.19
-0.50	0.490	0.0475	
-0.55	0.494	0.0495	
-0.60	0.493	0.049	

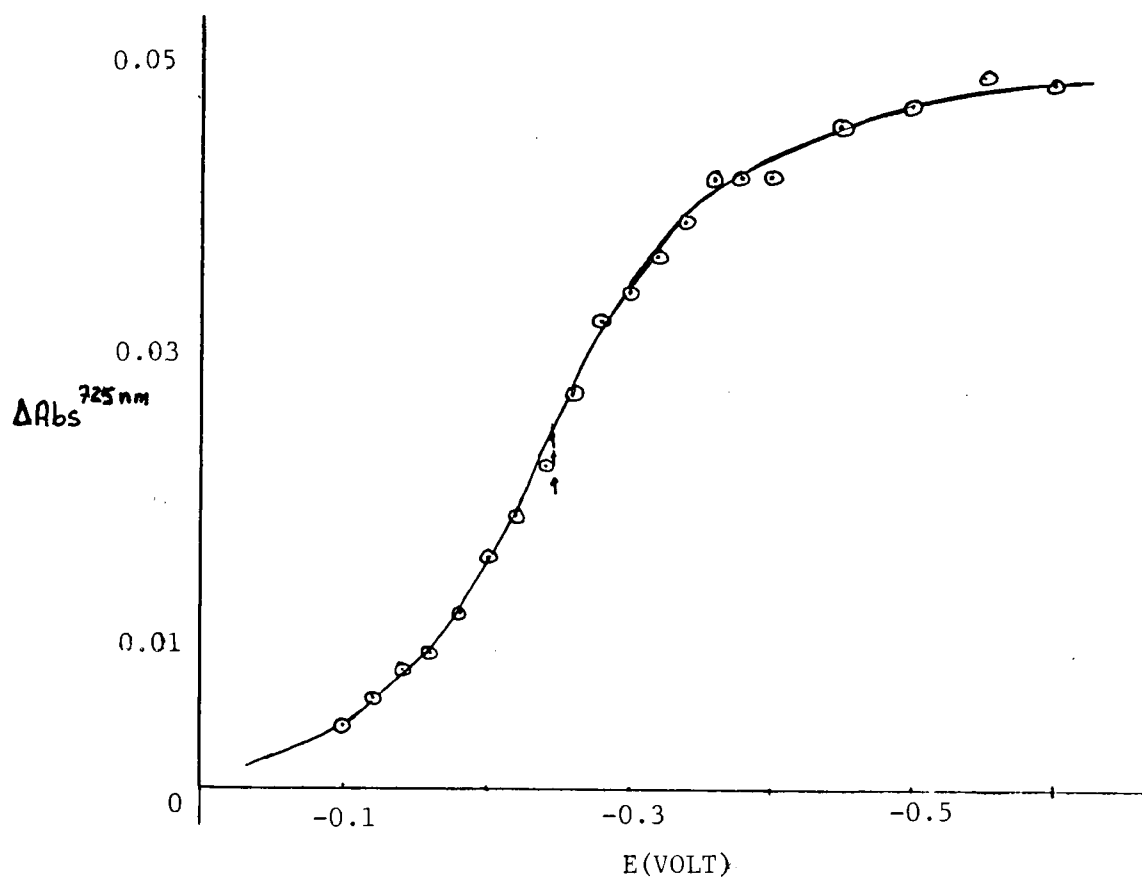


Figure 64. Graph of change in absorbance vs potential in 0.1M LiCl.

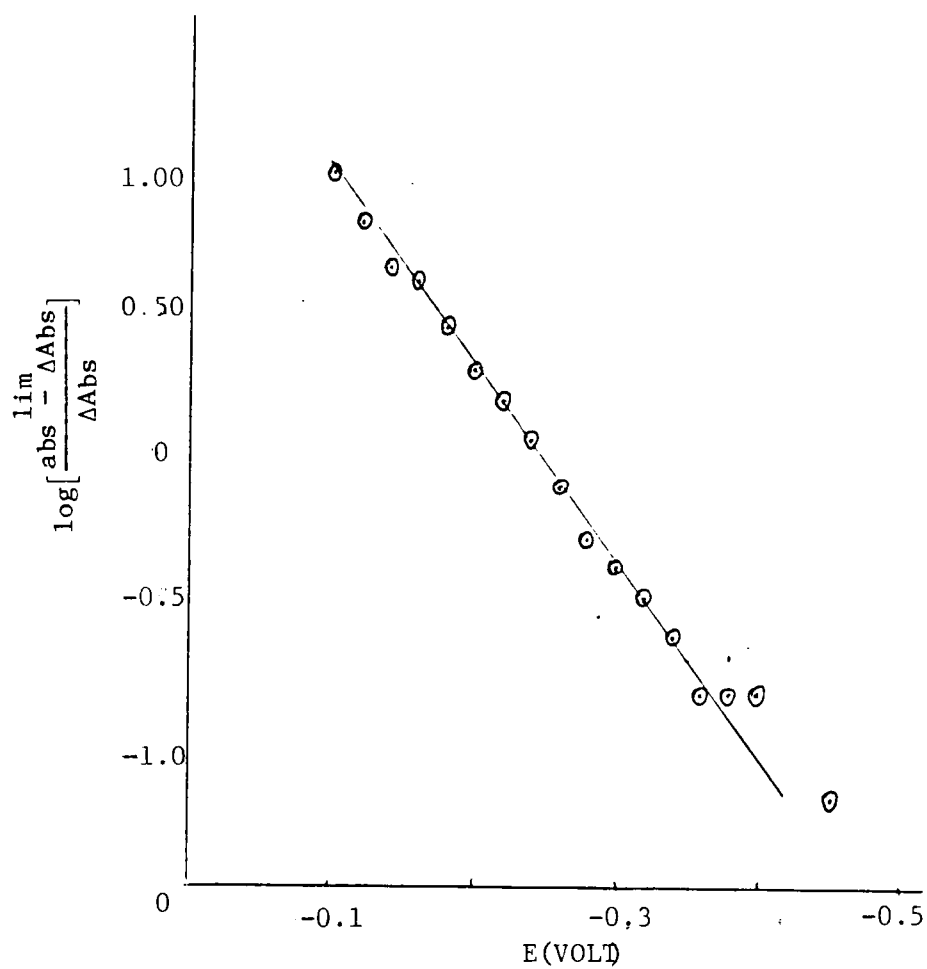
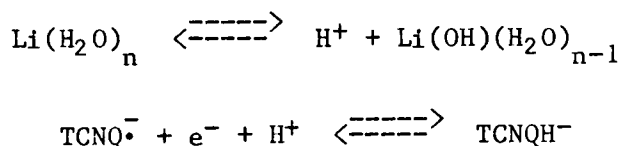


Figure 65. Nernst plot of change in absorbance vs potential in 0.1M LiCl.

or chemically decomposed during the long term electrolysis of the spectroelectrochemical experiment.

This experiment was repeated using 1.0M LiCl in order to investigate the dependence on the concentration of the counter ion. The results obtained from this experiment are displayed in Table XLVIII and Figures 66 and 67. Again the plot of ΔAbs^{720} vs E revealed a drawn out wave that resembled the CV in the essential features. However, now a small decrease in absorbance was observed at about -0.3V. The corresponding Nernst plot was divided into regions, giving n-values of 0.55 and 0.70. The $E_{1/2}$ value was -0.130V vs Ag/AgCl or -0.124 vs SCE. These results again demonstrate that the redox process is not a simple one electron step. An $n < 1$ value is consistent with dimer formation, but $n = 0.42$ or 0.55 is much too low to be explained entirely by dimerization. The low n value may be an indication of the existence of negative solitons in the film where, say, there are three electrons per seven TCNQ units.

The decrease in absorbance at about -0.3V could be due to $\text{TCNQ}^{\cdot-}/\text{TCNQH}^-$ couple, whereby:



Indeed the CV's done in high concentration ($\geq 1.0\text{M}$) of LiCl often show a small preoxidation wave similar to that seen at pH 6.2; see Figure 35, p 138.

Table XLVIII

Equilibrium Absorbance data for PU-MDI in 1.0M LiCl

E	Abs.	Δ Abs	$\lim_{\Delta \text{Abs} \rightarrow 0} \log \left[\frac{\text{Abs} - \Delta \text{Abs}}{\Delta \text{Abs}} \right]$
open	0.300		
-0.02	0.319	0.0095	1.00
-0.04	0.328	0.014	0.81
-0.06	0.337	0.0185	0.67
-0.08	0.350	0.025	0.505
-0.10	0.368	0.034	0.32
-0.102	0.372	0.036	0.28
0.120	0.391	0.0455	0.12
-0.140	0.416	0.058	-0.09
-0.160	0.440	0.070	-0.30
-0.180	0.467	0.0835	-0.59
-0.200	0.482	0.091	-0.81
-0.220	0.493	0.0965	-1.055

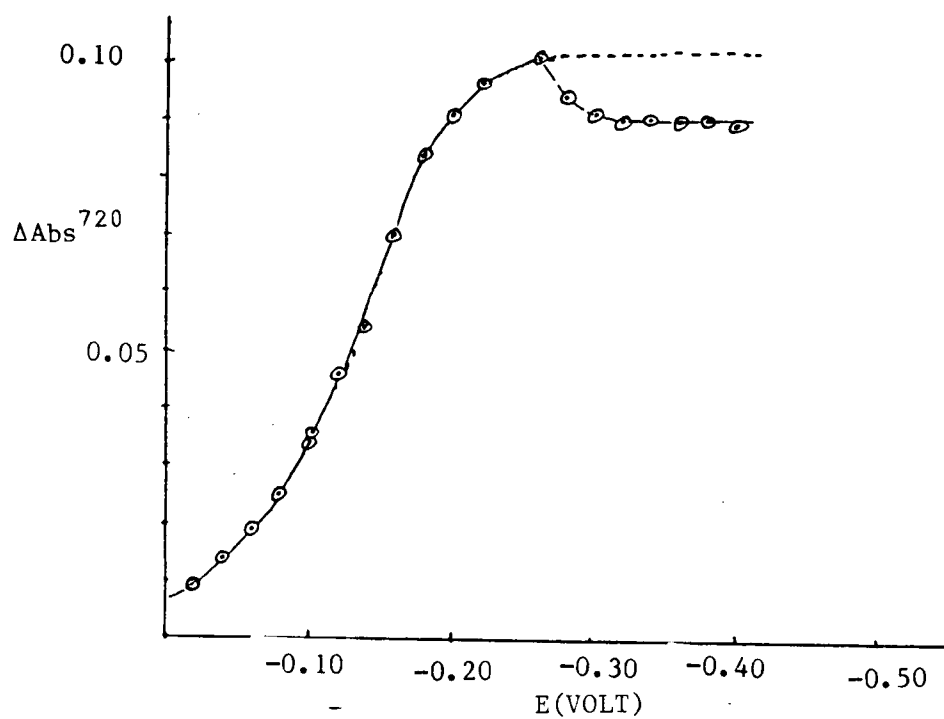


Figure 66. Graph of change in absorbance vs potential for PU-MDI film in 1.0M LiCl.

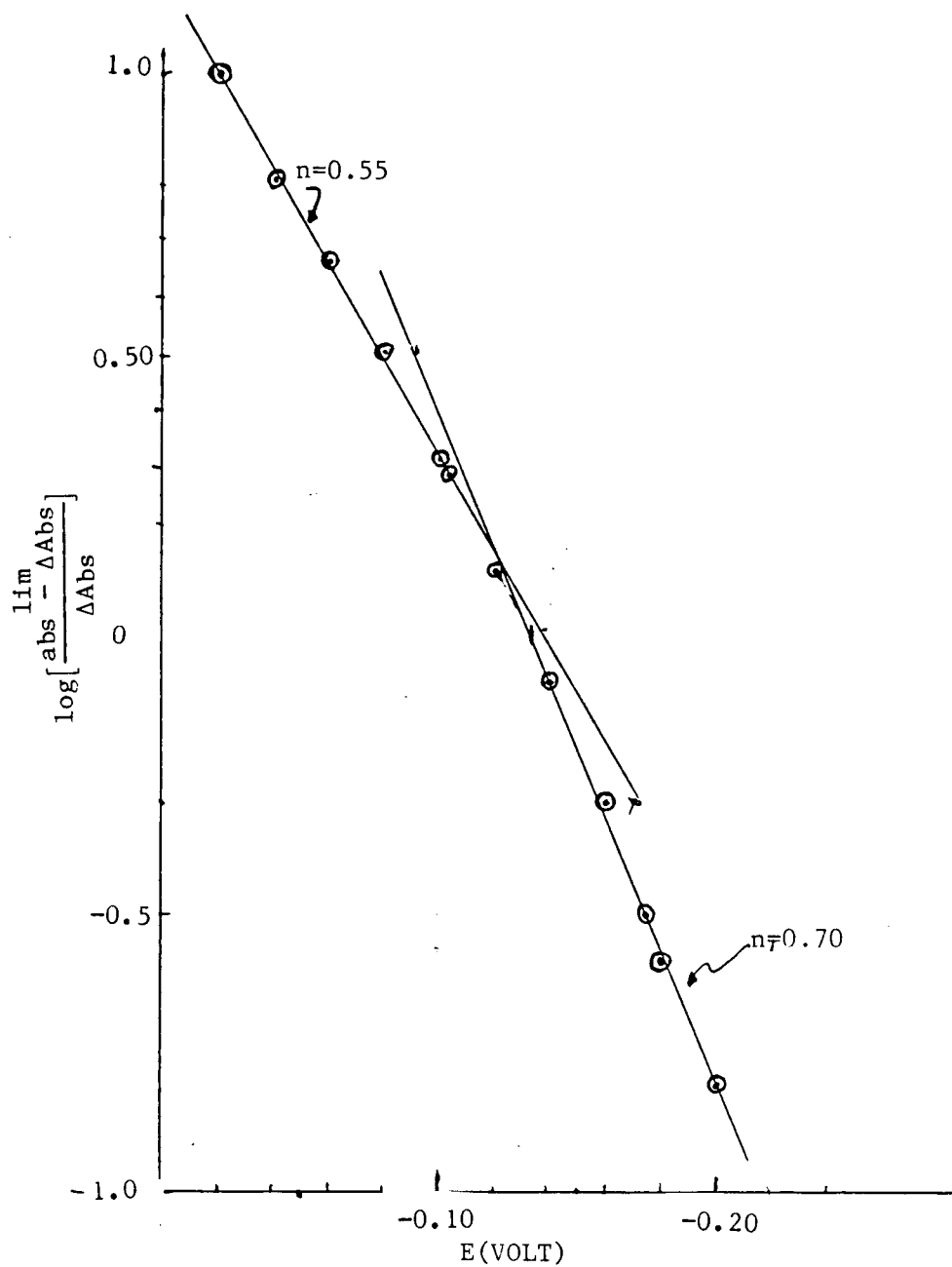
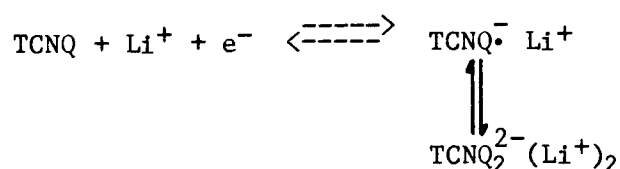
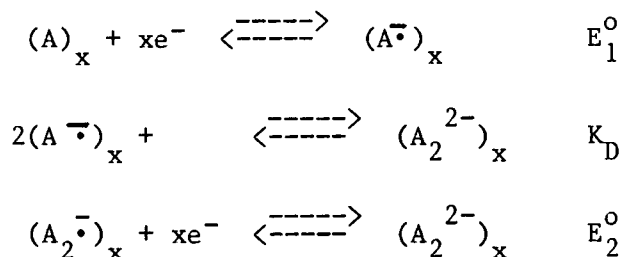


Figure 67. Nernst plot of change in absorbance vs potential for PU-MDI film in 1.0M LiCl.

The disagreement with theoretical Nernstian slope, that is $n = 0.70$ vs 1.0, is probably due to extensive dimerization that takes place during the reduction process. Furthermore, the decrease of 74 mV in $E_{1/2}$ value as the Li^+ concentration is changed from 0.1M to 1.0M is also consistent with dimerization. That is,



Indeed, in aqueous LiCl electrolytes a principal absorption band appears about 640 nm during reduction where the dimer dianion is known to absorb.^{39,152} The absorbance versus E plot, taking into account dimerization, was simulated using the computer program developed previously.³⁷ This simulation plot shown in Figure 68 assumes the following simple reactions³⁷:



where K_D is the formation constant of the dimer dianion:

$$K_D = [(\text{A}_2^{2-})_x] / [(\text{A}^{\cdot-})_x]^2$$

and

$$C_T = [\text{A}] + [\text{A}^{\cdot-}] + 2[\text{A}_2^{2-}] + 2[\text{A}_2^{\cdot-}]$$

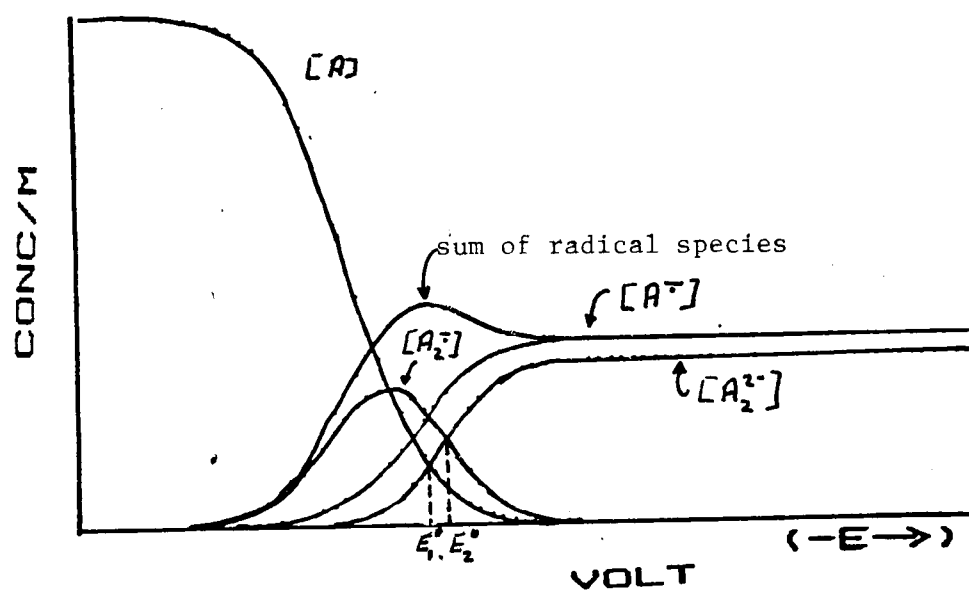


Figure 68. Computer simulation of conc. of TCNQ species vs potential.

where C_T is the total concentration of TCNQ units. It does not take into account solvent swelling, morphological changes or other factors affecting the bulk properties of the film.

Of particular interest is the effect of the dimerization equilibrium constant on the shape of the absorbance vs E curve for the monomeric radical anion band. These results seen in Figure 68 show qualitative agreement with the low n values. It shows a slight maximum for the sum of all the radical containing species and a bit less dimer formation than what was observed for PE-TCNQ.³⁷ The degree of dimer dissociation, α , and the formation constant for the dimer dianion, K_D , were estimated according to a procedure outlined by Inzelt and coworkers.³⁷ Measurements were made at $Abs_1 = 725$ nm where $\epsilon^M = 1.98 \times 10^4$, $\epsilon^D = 5.0 \times 10^5$ and at $Abs_2 = 640$ nm where $\epsilon^M = 4.5 \times 10^5$ and $\epsilon^D = 3.36 \times 10^4$.^{152,37} At -0.4V, α was calculated to be 0.33 while K_D was estimated to be $1.0 \text{ dm}^3/\text{mol}$.

Simultaneous ESR-electrochemical experimental results seen in Figure 69 shows a maximum resulting from the overlap of the radical anion and dimer radical anion spectra, similar to that seen in the computer simulation plot. However, this maximum is not pronounced to the extent necessary to explain fully the abnormally low n values. It should be noted that the ESR measurements were also taken under equilibrium conditions. Repetitive scans were carried out at each potential until no change was detected in the peak to peak distance. Also, there was very little change in the peak widths of the ESR signals, so this was not taken in consideration for this plot.

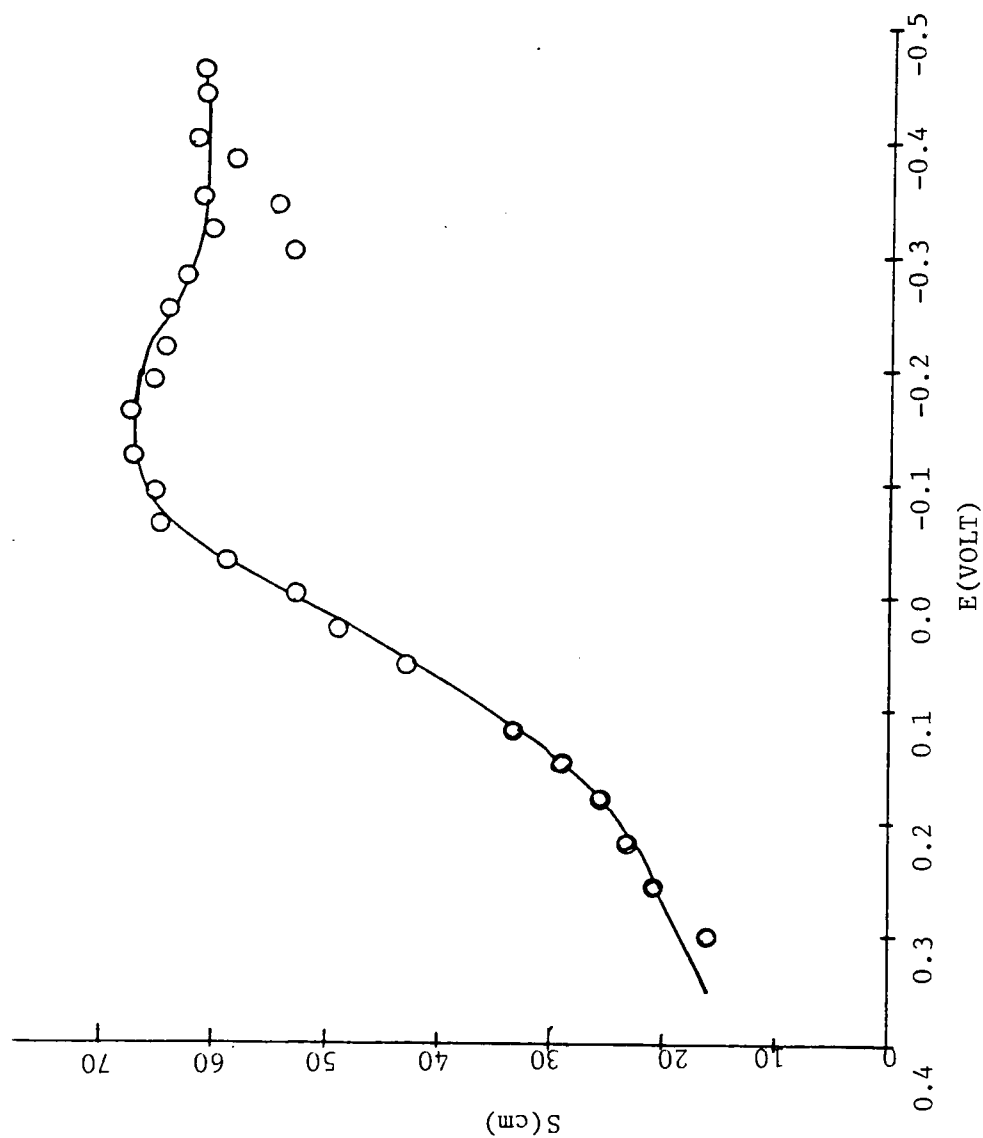


Figure 69. ESR signal peak-to-peak height vs potential for PU-MDI film in 0.1M LiCl.

c. Evidence for Formation of Dianion in Aqueous Electrolytes.

In Figure 61, p 00, at a potential of $-0.4V$, absorbances at 480 nm and 345 nm indicative of the oxygen decay product of $TCNQ^{2-}$ are observed in the spectrum of a PU-MDI film.^{202,203} These absorbance became more pronounced as the potential was shifted to $-0.5V$. Furthermore, for the equilibrium step potential spectroelectrochemical experiments done in $1.0M LiCl$, a decrease in the absorbance at 720 nm was observed. A possible reason for this decrease was discussed earlier, but the possibility of the $TCNQ^{2-}$ cannot be ruled out. Solvent studies discussed earlier, indicate the possibility of $TCNQ^{2-}$ formation by a very slow process depending on the solvent and counter ion. To understand further the absence of the second wave, the absorbance at 725 nm and $-0.85V$ in $0.5M NaClO_4$ was monitored.

The CVA was performed in the usual manner and the results are displayed in Figures 70 and 71. This experiment was interrupted at $-0.85V$ such that the CV and the chart measuring absorbance were stopped. After 20 min at $-0.85V$ a decrease in absorbance of 18% was observed and the CV showed a small preoxidation wave. The decrease in absorbance was attributed to a very slow conversion of $TCNQ^{\cdot-}$ to $TCNQ^{2-}$. The long time required for such small decrease in absorbance at $-0.85V$ is in full agreement to our previous discussions surrounding this second wave. That is, $(D_{ct} \tau / d^2) \ll 1$ for the second wave so it is not observed in aqueous solvents unless τ is large. So actually, the TCNQ units in the polyurethane can be converted to $TCNQ^{2-}$ however, this process is kinetically very slow and cannot be observed on the CV time scale.

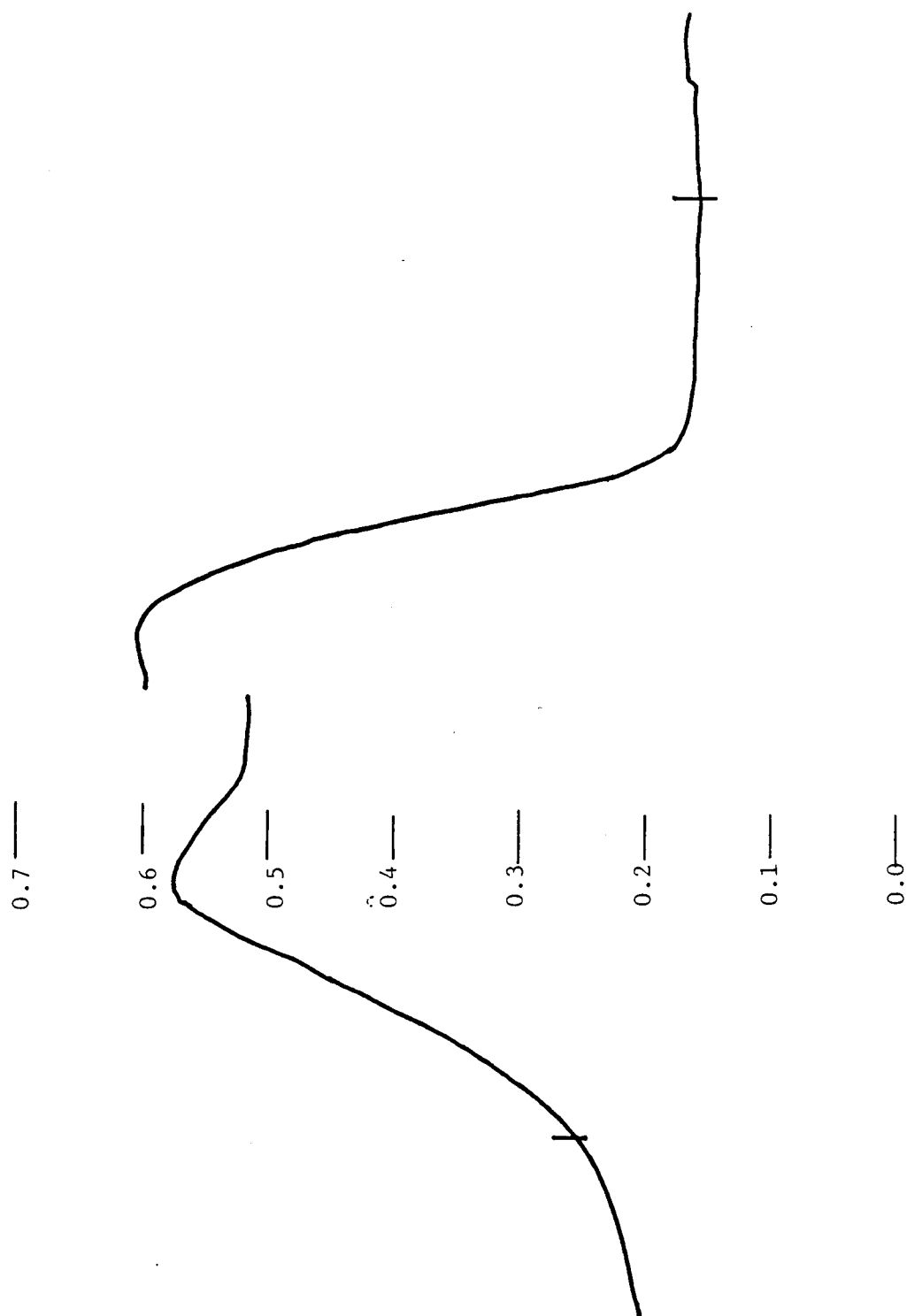


Figure 70. UV-VIS absorbance for PU-MDI film in 0.5M NaClO₄ held at -0.85V for 20 min.

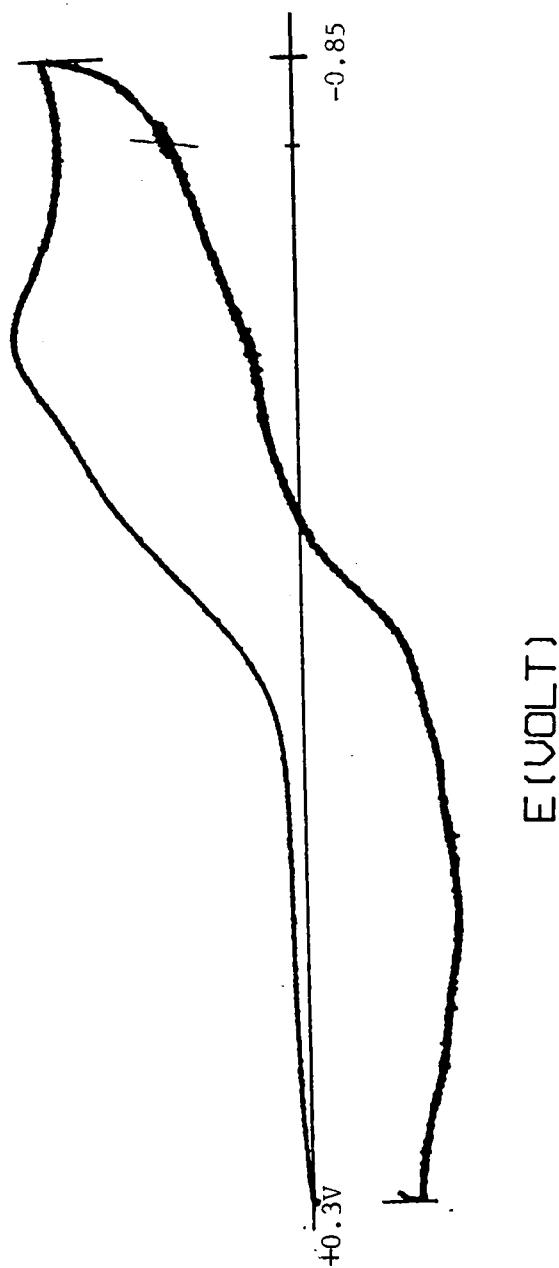


Figure 71. Cyclic voltammogram for PU-MDI film in 0.5M NaClO₄ when the potential was held at -0.85V for 20 min.

C. pH Studies

A key reason for the synthesis of the TCNQ polyurethanes was the better base stability of the carbamate link as opposed to the ester link, as stated earlier. With this in mind it was desirable to study the effects of pH on the electrochemical behavior of PU-MDI films. The rate of charge transport, as manifested in the square root of the effective diffusion coefficient, $nD_{ct}^{1/2}$, was monitored along with the peak currents and peak potentials as the pH of a monobasic sodium phosphate/sodium hydroxide buffer solution was changed by the addition of sodium hydroxide or hydrochloric acid.

The factors governing the magnitude of $nD_{ct}^{1/2}$ for various electroactive polymers are not well understood. For fixed-site electroactive polymers, an electron-hopping charge-transport mechanism is operative, in the absence of mediators. Charge propagates through these films by electron-exchange reactions between adjacent sites in the polymer matrix. For the fixed electron-transfer sites, the effective charge-transport diffusion is given by:

$$D_{ct} = (\text{constant}) k_{ex} \delta^2 C$$

where k_{ex} is the second order exchange rate constant, δ is the distance between exchange sites and C is the concentration of exchange sites. Thus, rapid charge transport is favored by high density and proper alignment of exchange sites in the polymer matrix.³⁸

The effects of acidity on the electrochemistry of PU-MDI was demonstrated by observing the CV in a buffered phosphate solution at

different pH values. The pH was varied by the addition of 0.1M HCl or 0.1M NaOH. The pH was measured with a Corning pH/ion meter model 150 using a Corning combination X-EL electrode. The same film was used for all the experiments and cycled through 20 segments at 30 mV per second and the relevant data abstracted from the last cycle.

Figure 72 shows the CV of the partially broken-in film at pH 6.7 in $\text{NaH}_2\text{PO}_4/\text{NaOH}$ buffer system. This break-in process is basically the same as that observed for PU-MDI films in unbuffered aqueous solutions as shown in Figure 25, p 117. However it is quite different from the break-in observed for PE-TCNQ in a buffer solution. In a buffer solution PE-TCNQ exhibits a wave due to the $\text{TCNQ}^\bullet/\text{TCNQH}^-$ couple when broken-in at pH 7.³⁸ The absence of this wave is a further indication that the charge transport rate of the second wave is much slower for the PU-MDI films than the PE-TCNQ films of Day.

When the pH of the buffered solution was decreased to pH 6.64 the CV shown in Figure 73 was observed. There is a short break-in time for the reduction of the TCNQ units followed by the break-in for an oxidation wave X at about -460 mV. This wave X becomes more pronounced as the pH is lowered to pH 6.4 and then to pH 6.1 when it becomes a fully developed wave having $E_p^a = -392$ mV (see Figures 74 and 75). Unlike PE-TCNQ, a reduction couple is not observed for this wave. As the pH of the solution is further lowered to pH 5.6, wave X disappears and a reverse break-in is observed. This reverse break-in is also accompanied by a broadening of the waves as shown in Figure 76. Figure 77, p 226, shows the extreme broadening effect of the wave as the pH is lowered to pH 3.2. This broadening began to be reversed when the pH of

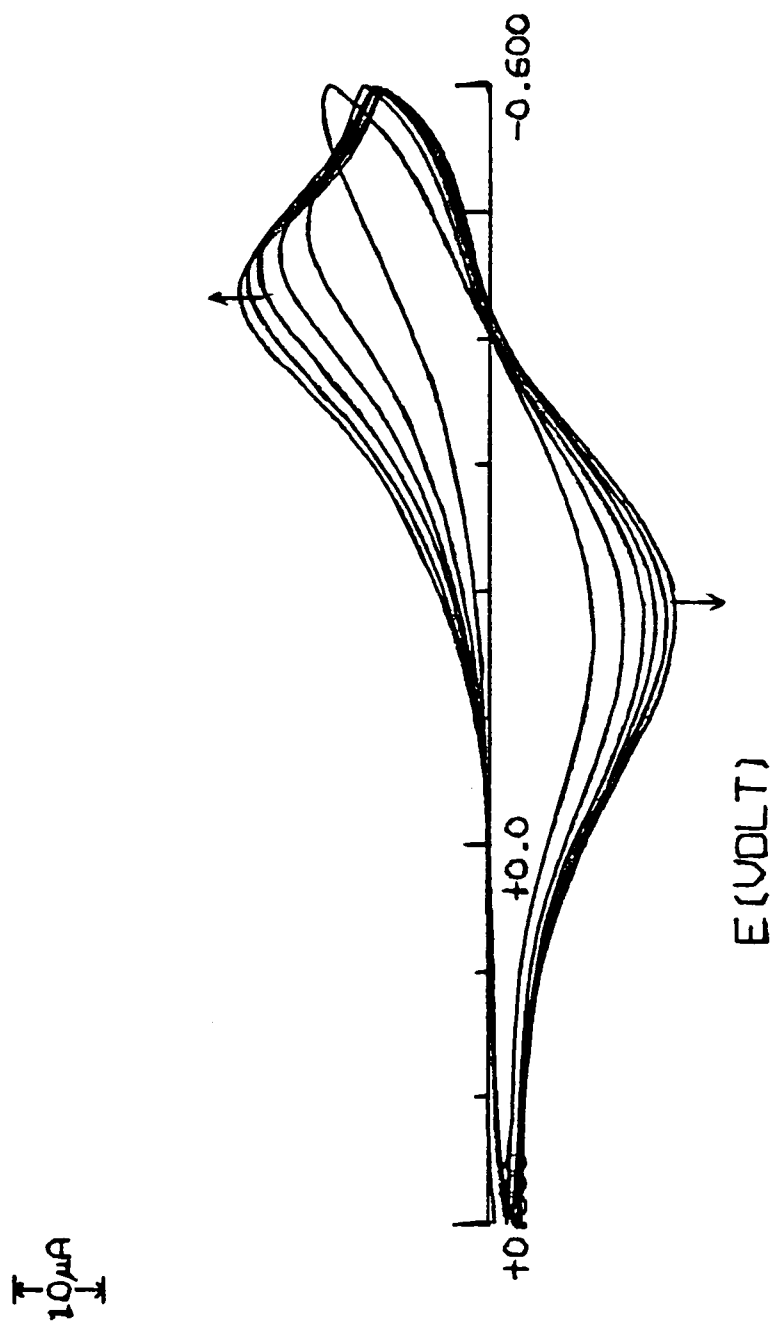


Figure 72. Cyclic voltammogram for PU-MDI film at pH 6.7 potential vs Ag/AgCl.

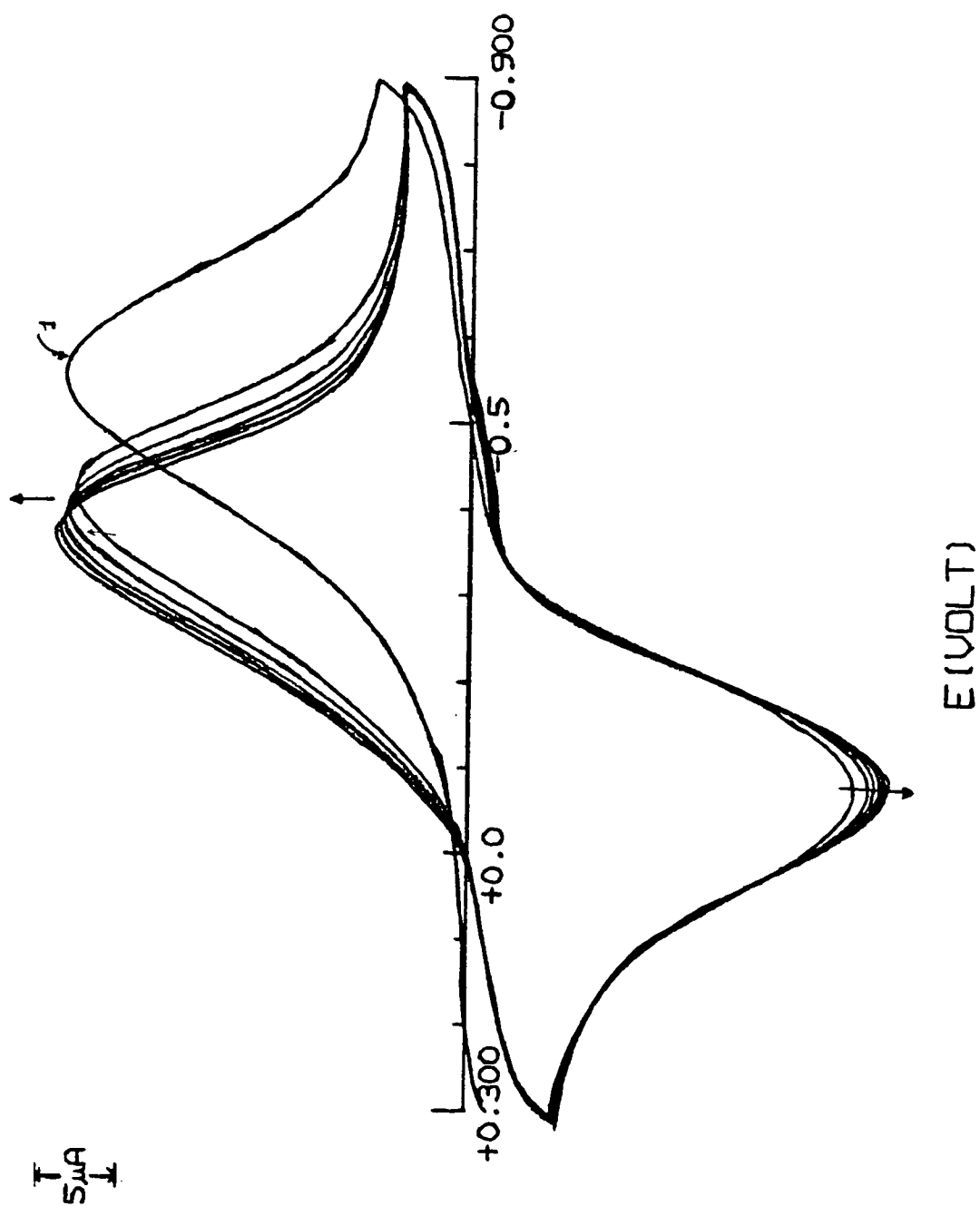


Figure 73. Cyclic voltammogram for PU-MDI film at pH 6.64 potential vs Ag/AgCl.

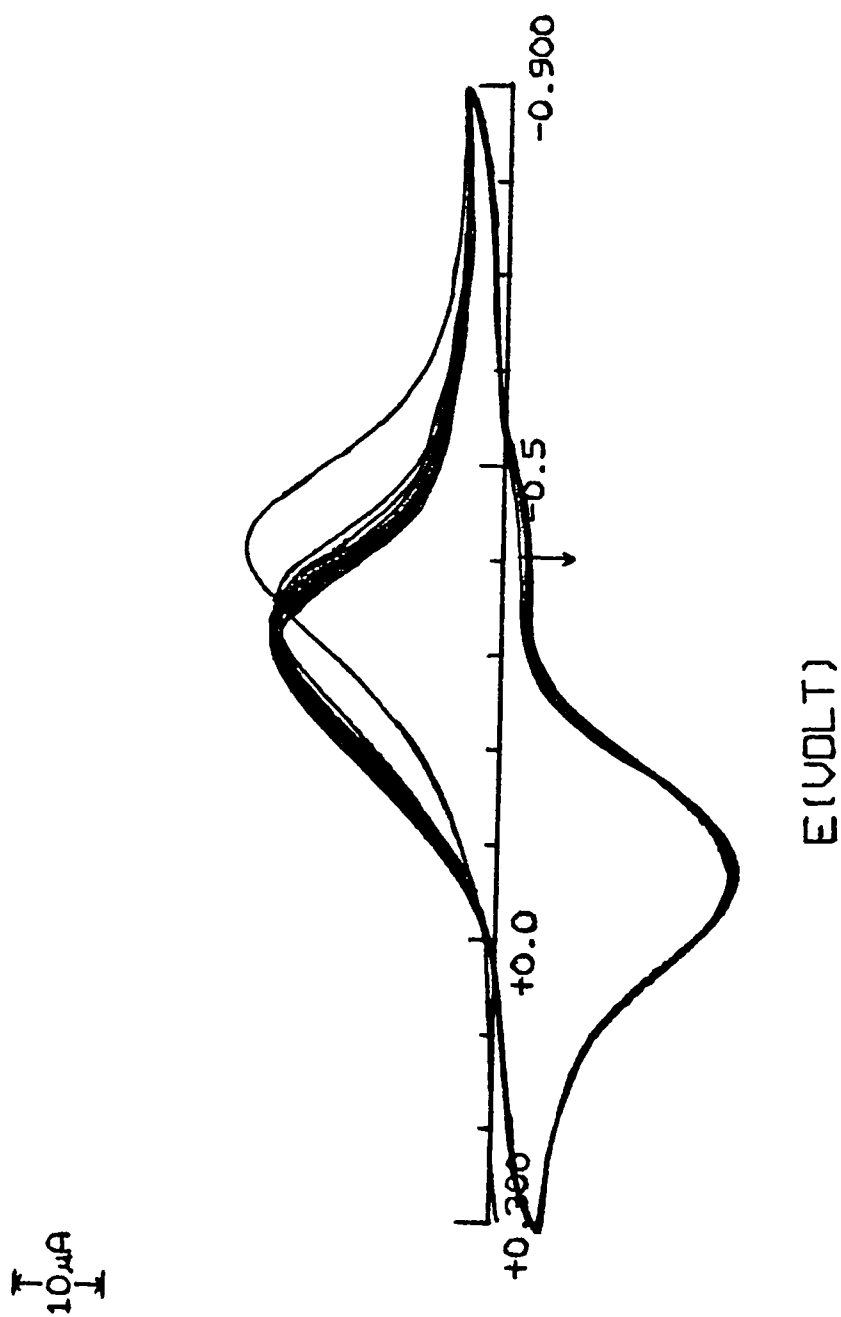
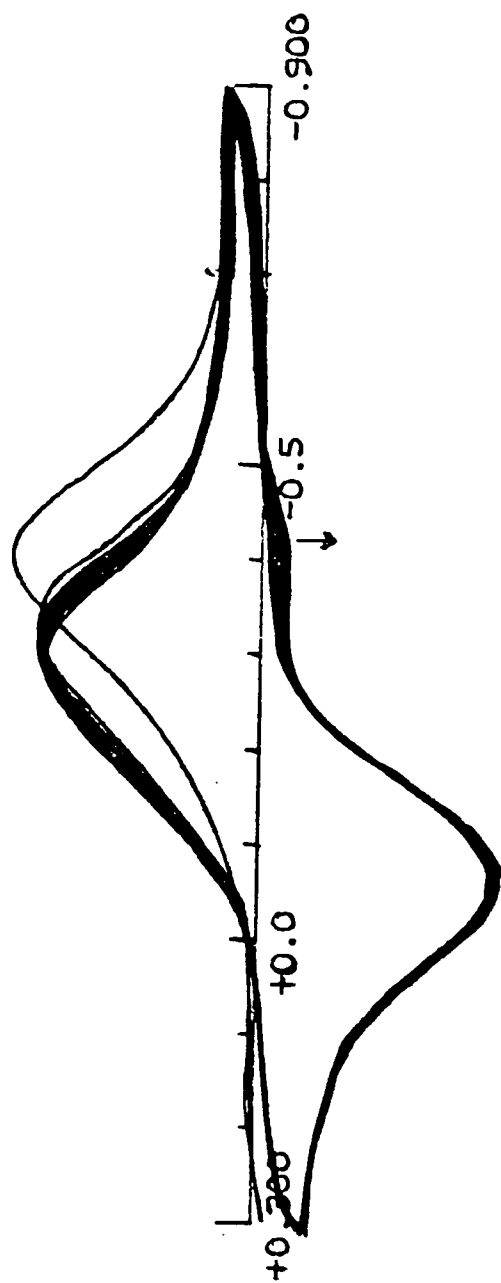


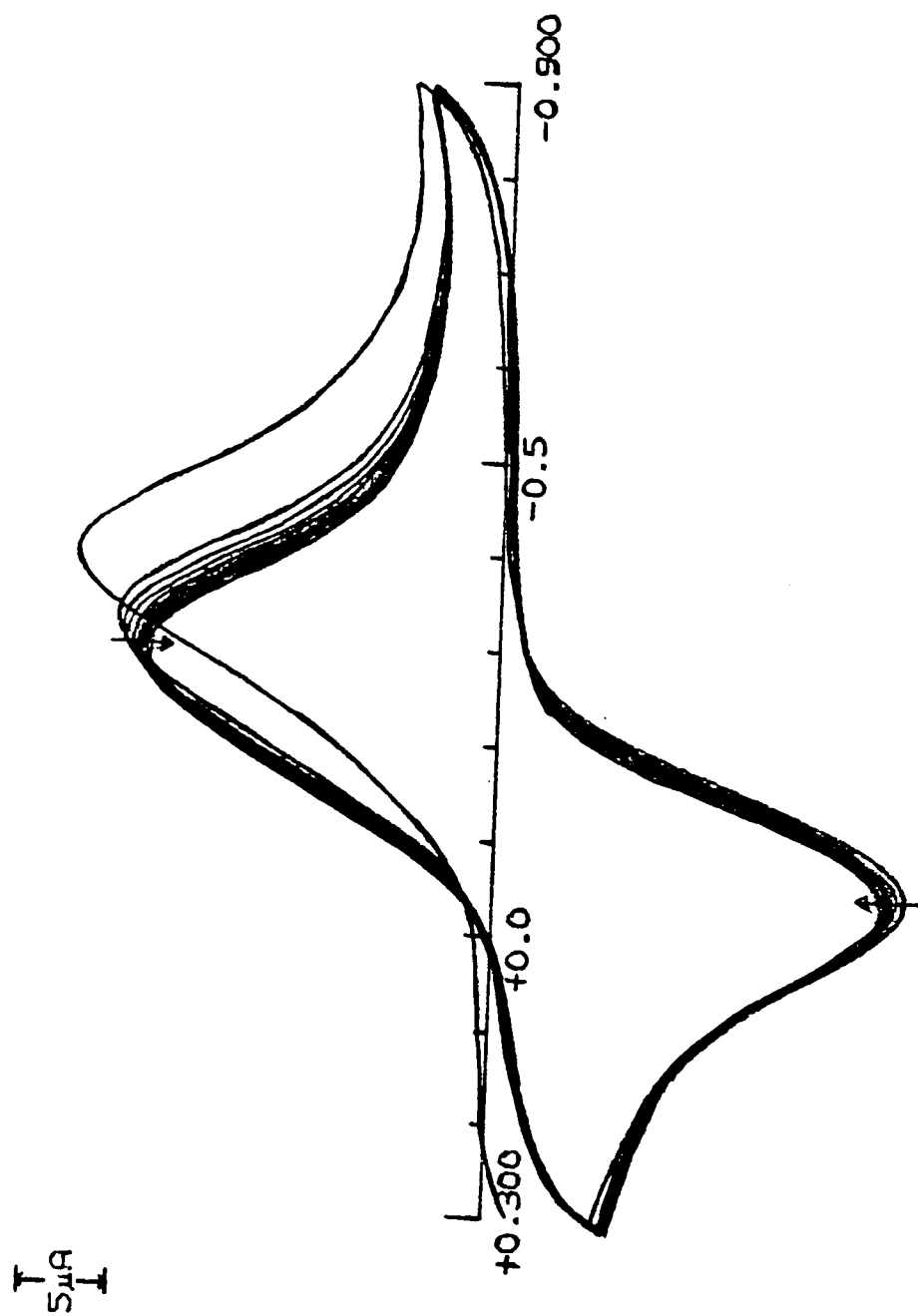
Figure 74. Cyclic voltammogram for PU-MDI film at pH 6.4 potential vs Ag/AgCl.

↑
10 μ A
↓



$E(VOLT)$

Figure 75. Cyclic voltammogram for PU-MDI film at pH 6.1 potential vs Ag/AgCl.



E (VOLT)

Figure 76. Cyclic voltammogram for PU-MDI film at pH 5.6 potential vs Ag/AgCl.

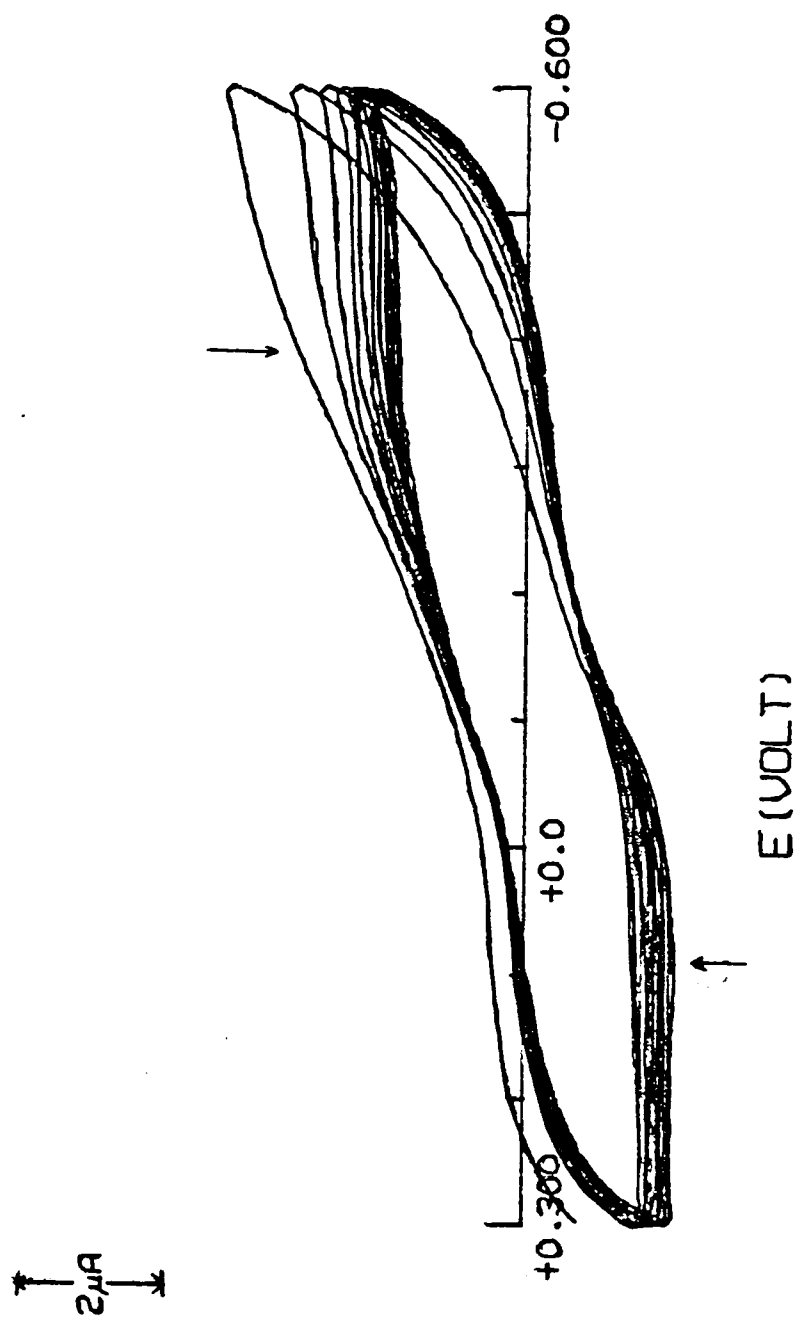
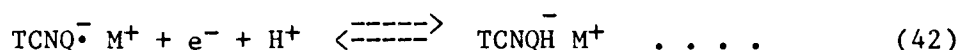
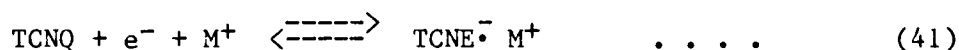


Figure 77. Cyclic voltammogram for PU-MDI film at pH 3.4.

the buffer was increased to pH 4.7, as shown in Figure 78, through to pH 7.0.

When the pH of the buffer solution was increased to pH 7.2, a behavior similar to that observed at pH 5.6 is seen. The CV (Figure 79) displays a reverse break-in, again accompanied by a broadening of the waves. The peak broadening is more evident on the reduction wave and becomes more prominent as the number of cycles increases. This is clearly demonstrated in Figure 80 where the first three cycles are shown for the film at pH 10.0.

The fact that a reduction couple was not observed for wave X may be a result of the TCNQH^- anion being formed in very low concentration relative to $\text{TCNQ}^\bullet$. Theoretically, if one could subtract the contribution due to the formation of the radical anion, then one would observe the reduction contribution of wave X to the reduction wave observed. The process occurring may be summarized as follows:²



As for PE-TCNQ, wave X was assigned to the half-reaction of equation (42). As the pH of the buffer is lowered further, TCNQH^- is converted to the hydroquinone analogue, TCNQH_2 , and the currents decrease and the peaks broaden. This hydroquinone analogue forms a nonconducting, fully reduced, protonated TCNQH_2 layer, which insulates the TCNQ sites in the bulk of the film.³⁸ This is consistent with Laviron's square scheme.²⁰⁷ The portion relevant to our system is summarized in

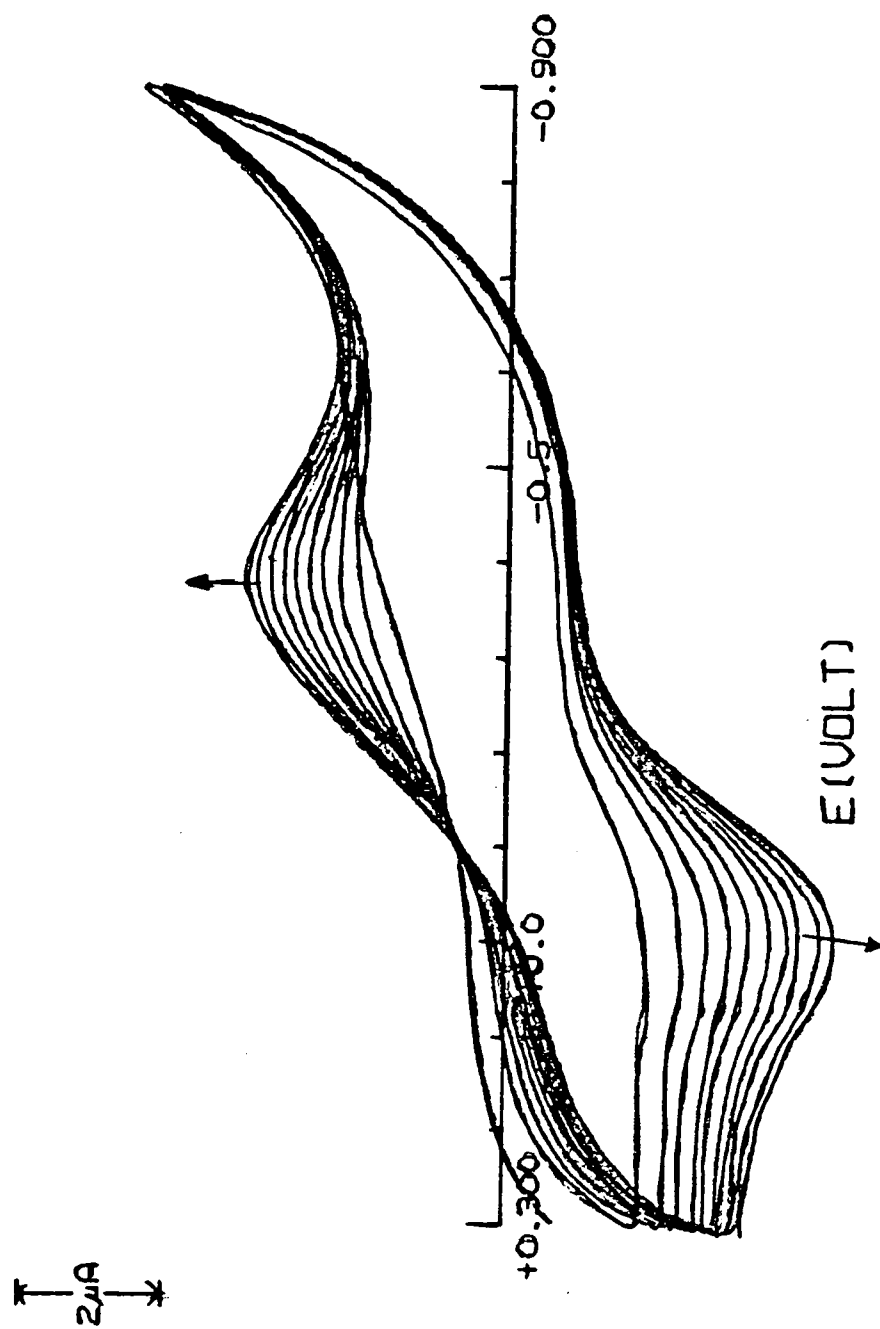


Figure 78. Cyclic voltammogram for PU-MDI film when pH was increased from 3.2 to 4.7.

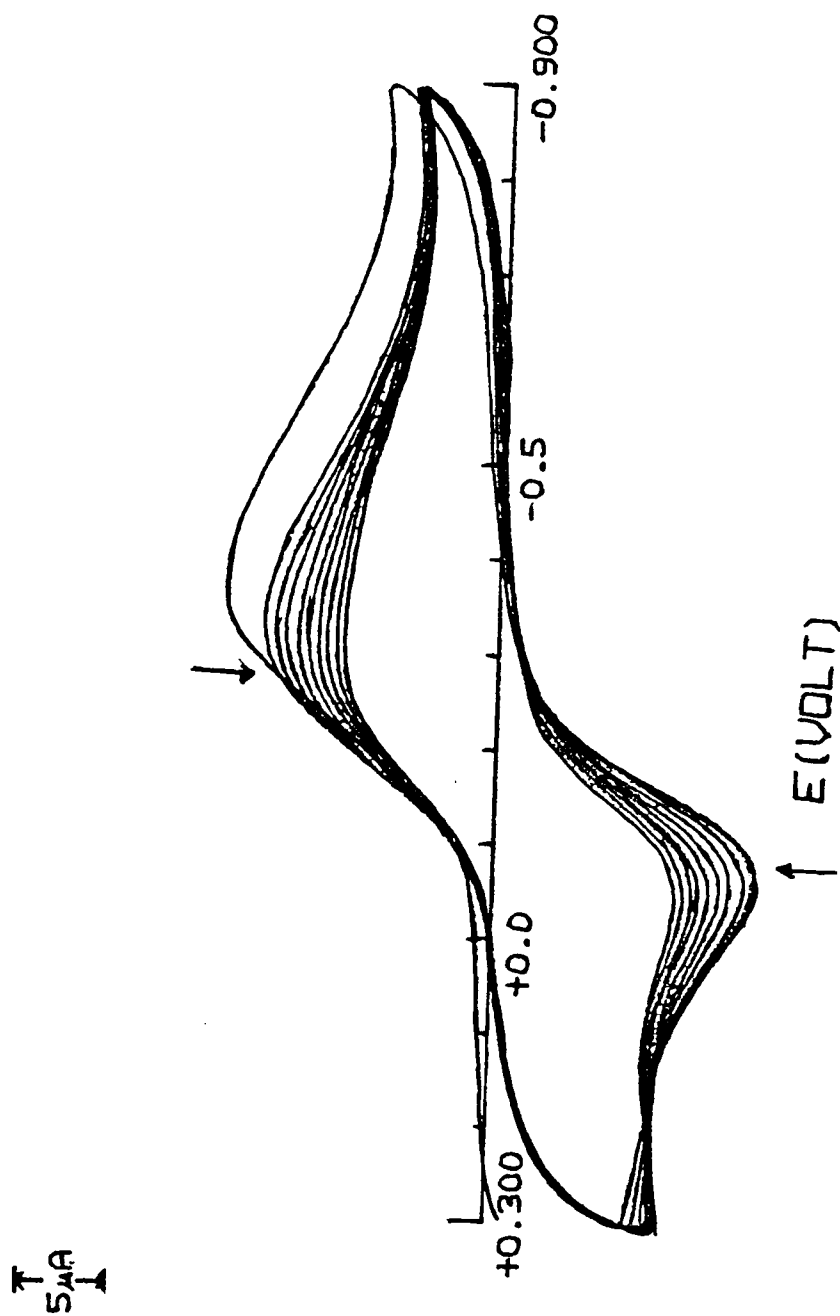


Figure 79. Cyclic voltammogram for PU-MDI film when pH was increased from 4.7 to 7.2.

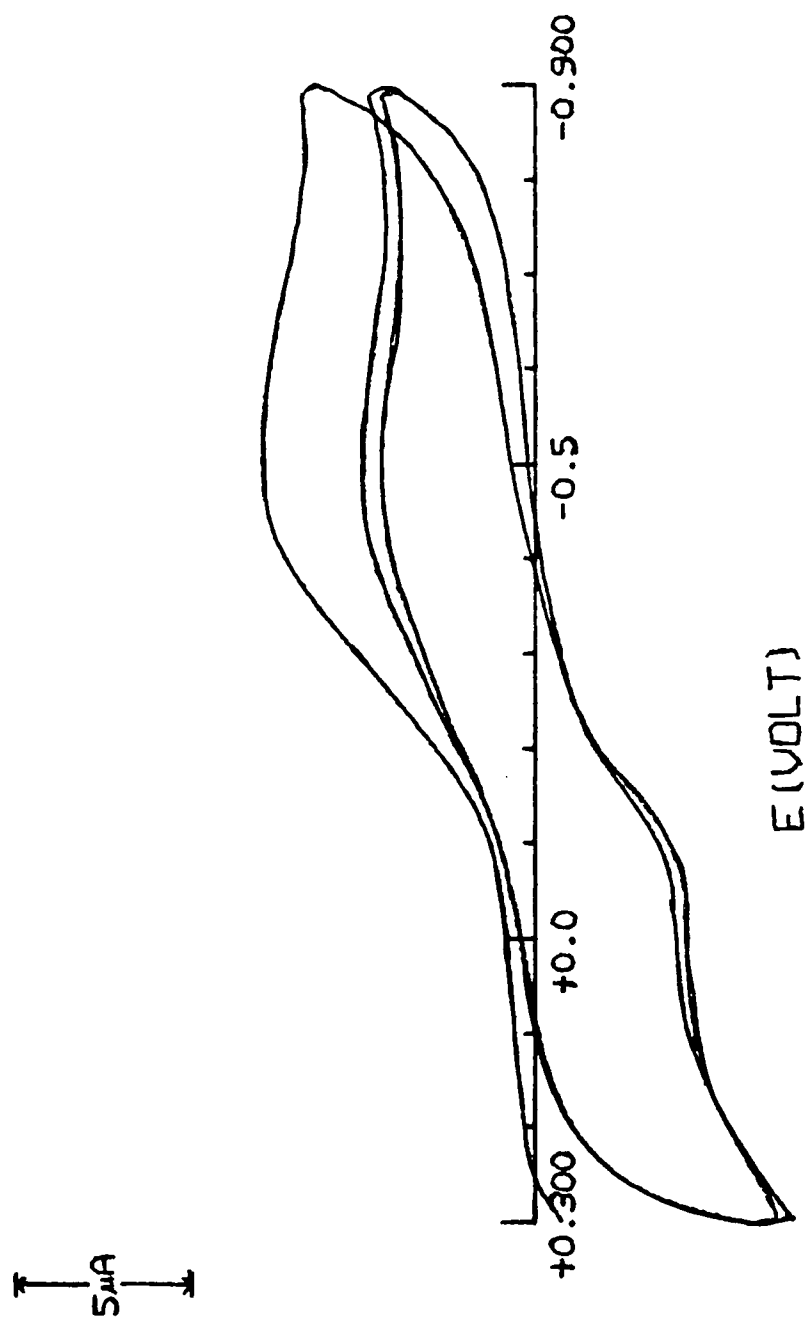


Figure 80. Cyclic voltammogram for PU-MDI film when pH was increased from pH 7.2 to pH 10.0.

Figure 81. The expected disappearance of wave X as the pH is increased is due to the low concentration of TCNQH^- expected in the system. Thus, the couple corresponding to $\text{TCNQ}^\bullet/\text{TCNQH}^-$, responsible for wave X, will disappear. Similar results have been reported for PE-TCNQ.³⁸ The gradual broadening of the waves may be a result of the TCNQ species being in different microenvironment at extreme pH values.

Interestingly, the cathodic peak potential shows a slight shift in the positive direction as the pH decreases and then increases negatively after the disappearance of the wave X. This behavior is summarized in Table XLIX. It should be noted however, the $E_{1/2}$ values are practically independent of the pH changes. In Figure 82, which displays a plot of $E_{1/2}$ versus pH, the points at pH 6.7, and pH 6.64 may be neglected if we consider that the film may not have been fully broken-in in the time it was cycled. The independence of $E_{1/2}$ and pH is consistent with equation 41 above, which does not involve a proton.

Another interesting point to note in Table XLIX, is that the anodic peak current (i_p^a) increases, on lowering the pH, to a maximum which corresponds to the pH at which wave X was fully developed. This peak then decreases as wave X disappears when the pH is lowered further. On increasing the pH of the buffer solution from pH 3.2 to pH 10.0, a similar trend is observed. First, i_p^a increases to a maximum value at pH 7.0, where wave X has become negligible, and then decreases as the pH is increased. This is summarized in Figure 83.

On lowering the pH of the buffer and then raising it, i_p^a never regained its original value and the smooth parabolic behavior is

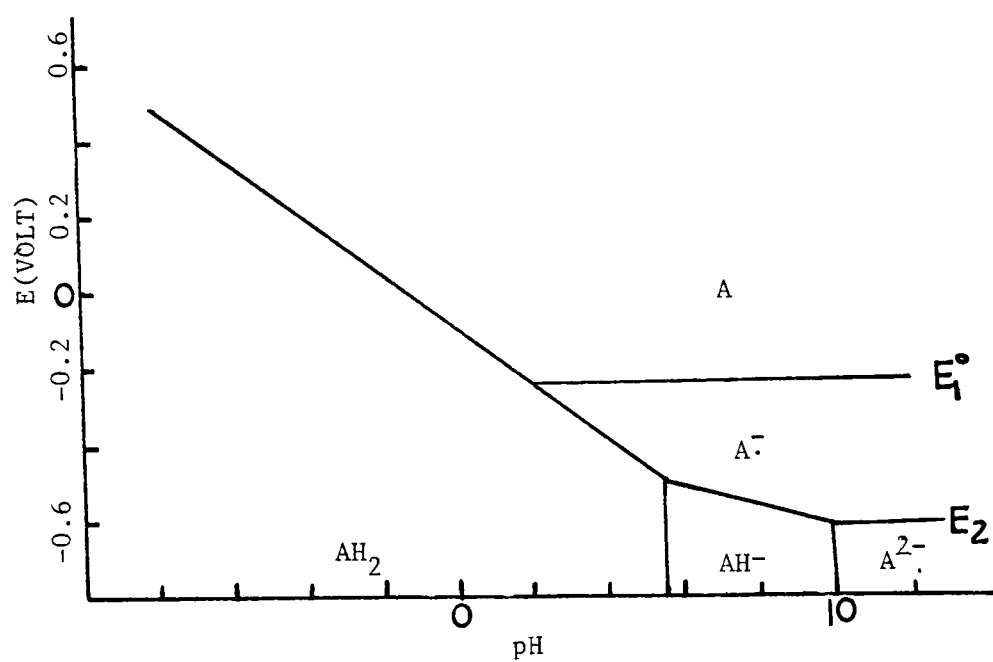


Figure 81. Potential-pH equilibrium diagram.

Table XLIX
Data Obtained From CV of a PU-MDI Film at Different pH's

pH	$i_p^c/\mu A$	E_p^c/mV	$i_p^a/\mu A$	E_p^a/mV	Slope ^c from chronocoulometry	$E_{1/2} = \frac{E_p^c + E_p^a}{2}$
6.7	9.3	-432	14.1	-204	7.90	-318
6.64	3.5	-356	16.8	-112	7.84	-234
6.4	3.5	-308	20.3	-92	7.63	-200
6.1	5.0	-296	21.7	-92	6.33	-194
5.6	2.6	-304	15.2	-60	5.30	-182
3.4	-	-344	-	6	0.96	-
3.2	-	-	-	-	0.50	-175
3.4	-	-	-	-	0.34	-
4.7	-	(-381) ^b	3.8	-22	1.10	-201.5
5.5	-	(-375)	-	-35	1.33	-205
6.0	-	(-369)	-	-	-	-
6.4	-	(-336)	6.55	-36	2.39	-186
7.0	-	(-335)	12.0	-69	3.78	-202
7.2	-	(-323)	9.22	-61	3.12	-186.5
7.7	-	(-348)	8.51	-71	2.85	-204
8.3	-	(-435)	5.65	-61	2.29	-242.5
9.0	-	-	-	-	1.85	-
10.0	-	-	-	-	1.41	-

^bBrackets indicate calculated values.

^cValues were averaged from at least three runs.

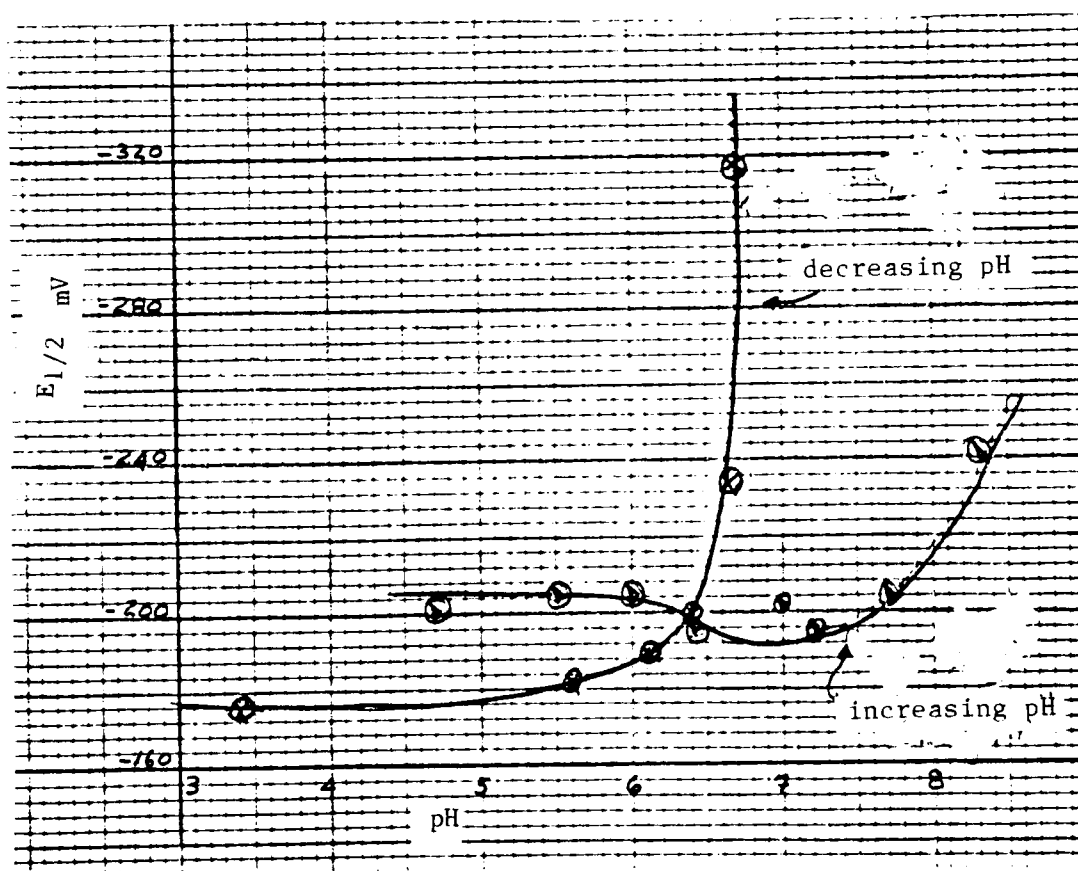


Figure 82. Graph of $E_{1/2}$ vs pH for PU-MDI film.

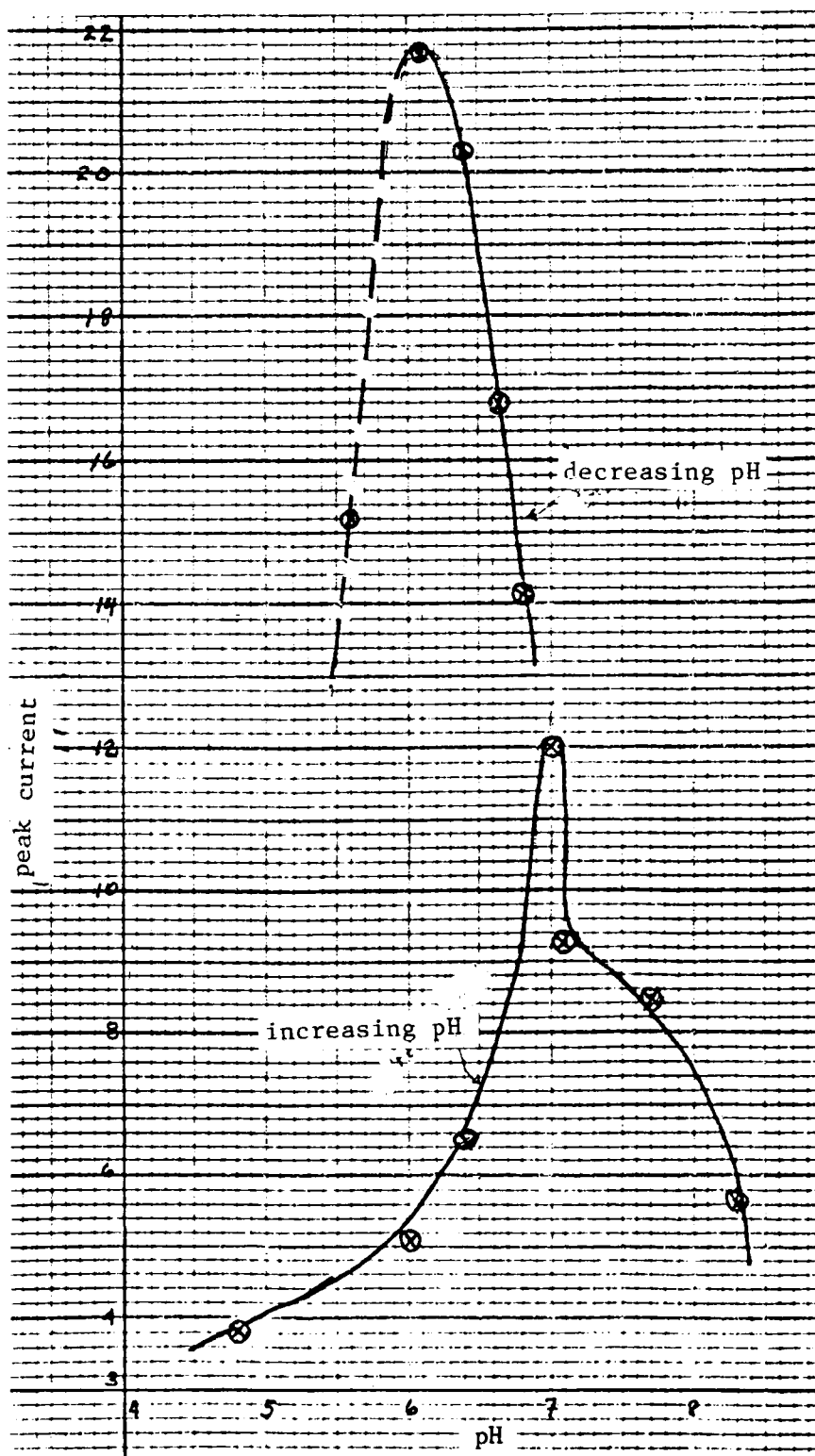
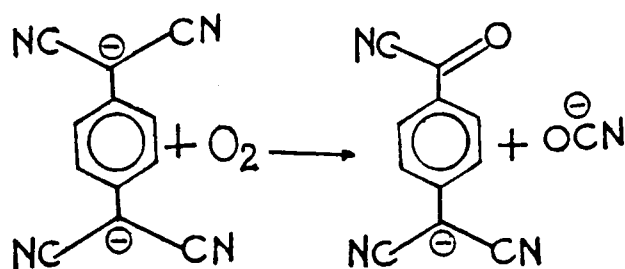


Figure 83. Graph of anodic peak current vs pH for PU-MDI film.

severely distorted. This may be due to a number of things of which three are given below.

1. Partially irreversible chemical changes taking place in the film under extreme pH conditions. For example, at high pH values where the fully reduced TCNQ dianion should be formed, if the potential is correct, there may be a reaction taking place with oxygen. That is:



or there may be an intra- or intermolecular reaction within the bulk of the polymer involving the TCNQ dianion. Figure 84 shows the CV of a virgin PU-MDI film which has been cycled in a pH 9.2 buffer solution which was saturated with air. The first three cycles show the break-in, as expected, however subsequent cycling indicate that the film was being passivated. This same film, when transferred to an acetone/ NaClO_4 solution, as Figure 85 indicates, gives the behavior expected of a new film in acetone except that the waves have been broadened (compare with Figure 58 on page 188) and the peak currents attenuated. This again, indicates that a reaction, which was not reversible at pH 9.2, had taken place.

2. Perhaps the film was not cycled long enough to be fully broken-in at the low pH values where the rate of charge transport is slow. This is indeed very possible since the film was cycled for the same length of time at each pH value in order to have as few variables as possible.

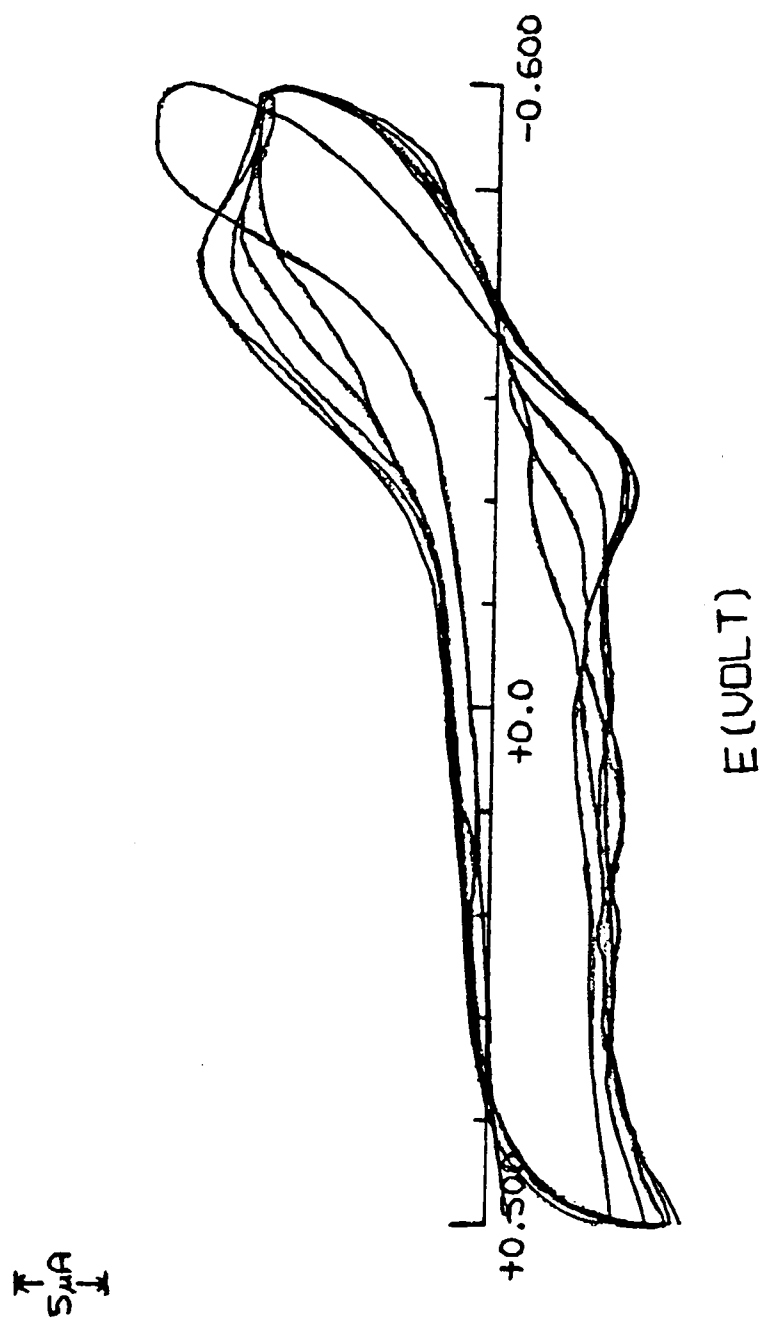


Figure 84. Cyclic voltammogram for virgin PU-MDI film at pH 9.2 when air was blown in the solution.

T
5μA
I

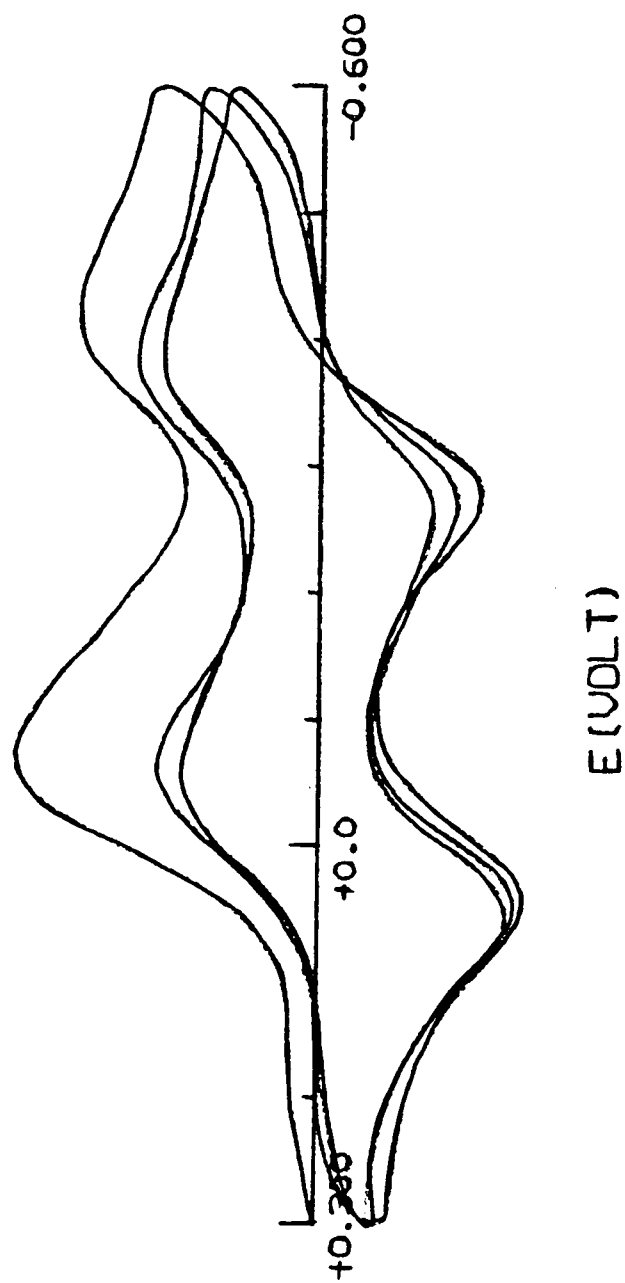


Figure 85. Cyclic voltammogram for PU-MDI film in 0.1M NaClO₄/Acetone after being broken in at pH 9.2; 30mV/s.

3. Dissolution of the low molecular weight fraction of the polymer at extreme pH's is possible, thus losing a portion of the TCNQ units.

Included in Table XLIX, and also summarized in Figure 86 are the slopes from the charge versus square root time obtained from chronocoulometric data. Qualitatively, these numbers are in agreement with the gradual passivation of the film by the formation of TCNQH₂. On increasing the pH from pH 3 the D_{CT} values increase to a maximum at pH 7.0, and then decrease at higher pH values.

When the film used to carry out this pH study was transferred to aqueous NaClO₄ electrolyte, the behavior observed after many cycles was that expected of a PU-MDI film in aqueous NaClO₄, except that the waves were broadened and the peak currents severely attenuated. On the other hand, when a virgin film was cycled in carefully degassed pH 9.2 solution, the behavior shown in Figure 87 was observed. A regular break-in is observed and the peak broadening is not prominent. When this film was transferred to aqueous NaClO₄, the regular behavior was observed. Interestingly, when this film was cycled to -0.75V, a second wave was observed, $E_p^c \approx -560\text{mV}$ and $E_p^a = -510\text{ mV}$ giving $E_{1/2} = -535\text{ mV}$ vs Ag/AgCl. The position of this wave (compare with data given on page 191) would indicate it is due to the formation of the TCNQ²⁻, again being very consistent with Laviron's scheme.²⁰⁷ However, further experiments, namely spectroelectrochemistry, would be needed for confirmation.

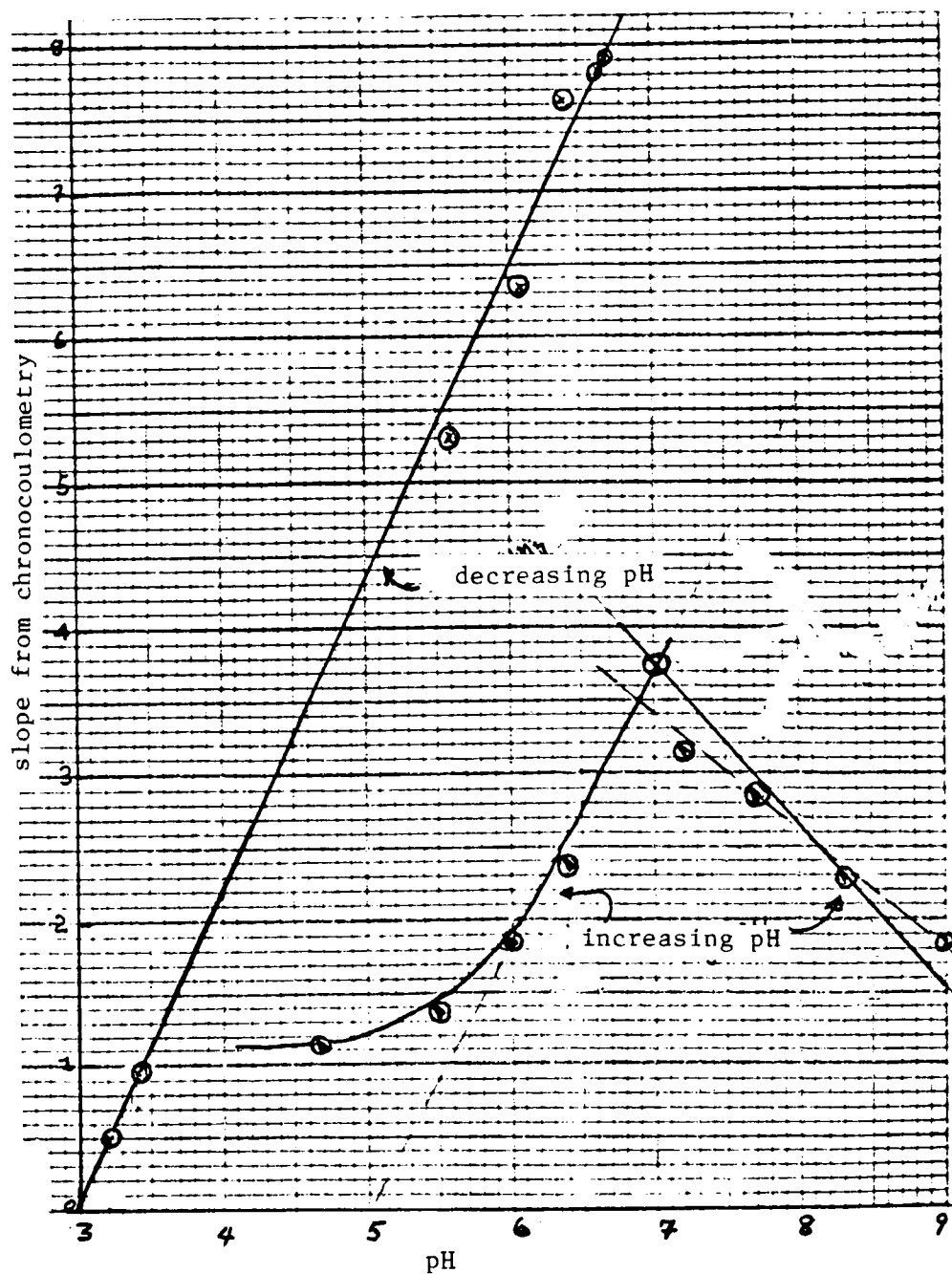


Figure 86. Graph of slope from chronocoulometry vs. pH.

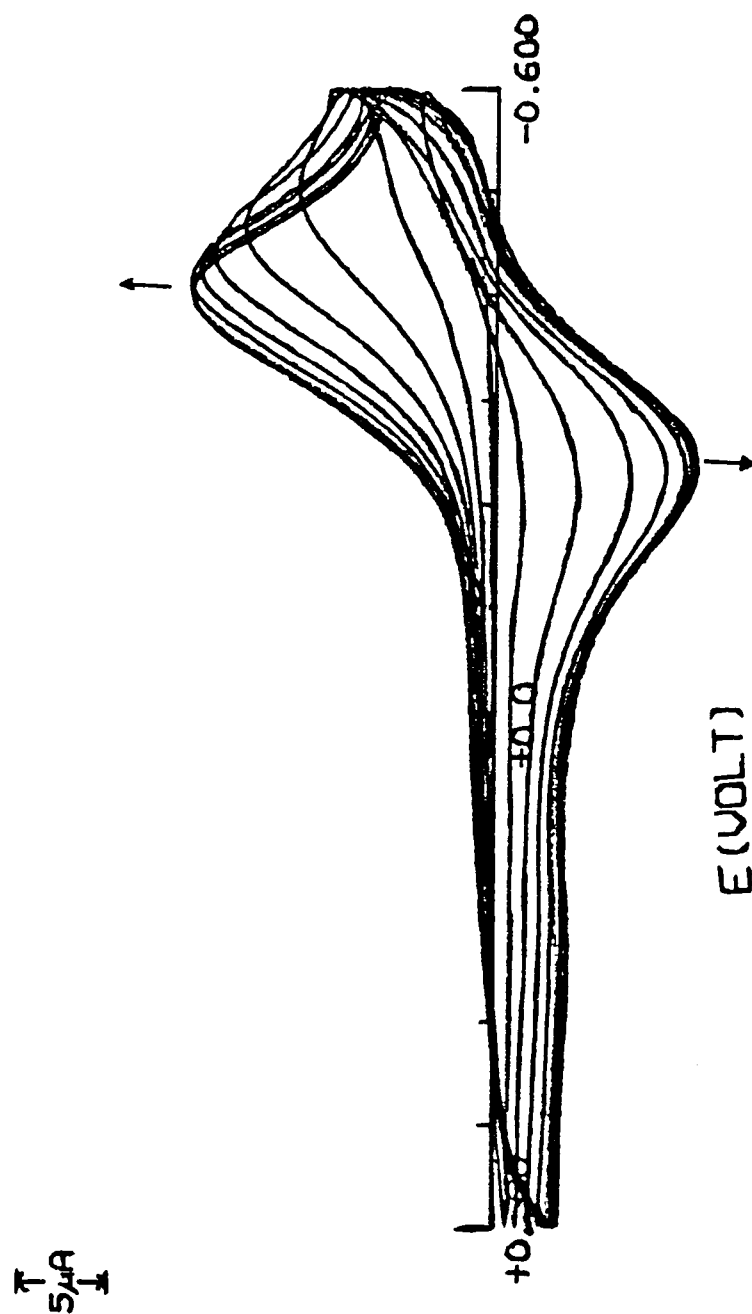


Figure 87. Cyclic voltammogram for virgin PU-MDI film at pH 9.2 when solution was carefully degassed; 30mV/s .

CHAPTER VI

CONCLUSIONS AND FUTURE DIRECTIONS

A. Conclusions

The synthesis and characterization of TCNQ diol and its copolymers from methylene diisocyanate (giving PU-MDI), 2,4-toluene diisocyanate (giving PU-TDI) and 1,6-hexamethylene diisocyanate (giving PU-HMDI) have been discussed in this dissertation. Even though the overall yield of TCNQ diol has been significantly improved over the original work performed by Hertler²⁵ and later by Day,⁵¹ new and improved methods of synthesizing this compound must be sought if this compound or its derived materials are to become prominent in research. Unfortunately, important molecular parameters, like molecular weight, for the polymers were not determined because the polymers were excluded from 10^3Å ultrastyrigel column. However, an attempt was made to estimate the molecular weight from electrochemical methods proposed by Flanagan¹⁵⁴ and Funt.¹⁵⁵ The molecular weights obtained for PU-MDI using this electrochemical method were in the range of 50,000 to 60,000 Daltons. It is thought that these numbers are a reflection of the molecular weight of species adsorbed onto the electrode surface and not a true representation of the average molecular weight of the polymer as a whole.

The electrochemical behavior of the polymers in the presence of a variety of solvents and cations at different concentrations have been examined. These preliminary experiments have revealed that the second wave, representing $\text{TCNQ}^{-/2-}$ couple, is a sensitive indication of the

charge transport through the polymer film. The indications are that the value of the effective diffusion coefficient for charge transport for the second wave is smaller than that of the first wave. Thus, conditions could be found, even for fast electron transfer for the $\text{TCNQ}^{-/2-}$ hop, where the second wave will not be seen. These results may be complicated by slow electron transfer kinetics associated with the second wave, but more elaborate experiments like those performed by Schroeder, Kaufman and coworkers would be required to investigate fully this phenomenon.¹⁶³ Intuitively it seemed that the electrochemical behavior of these polymers in the various solvents would be strongly influenced by the solubility parameter, δ_o , of the solvents since the electrochemical process involves film swelling. No simple correlation was found between the electrochemical behavior of the films and δ_o . However, from Table XLII it appears as if there has to be a compromise between the solubility component due to polar forces, δ_p , and the solubility component due to hydrogen bonding, δ_h , in order to observe both waves. Even though water has high δ_p and δ_h values, only one wave is observed in aqueous electrolytes. The absence of the second wave may be due to a combination of factors which include: (a) water being unable to interact with the hydrocarbon portions of the polymer chains, thus making the solvent swelling process not very effective; (b) water supporting large solvation spheres of the cations, rendering them too large to move through the film easily; (c) water supporting extensive ion-pairing, thus forming a "cross-linked" network of the sort $\text{M}^+(\text{A}^-)_n$ where A represents a TCNQ molecule from either the same polymer chain or from neighboring chains.

Studies on PU-MDI in a wide range of pH values have shown that the behavior of this polymer is in good agreement with Laviron's quinone scheme.²⁰⁷ Unfortunately, the same film studied under low pH conditions proved not very useful for high pH conditions due to irreversible changes which occur in the film at extreme pH values. At low pH values, however, waves representing $\text{TCNQ}^{0/-}$ and $\text{TCNQ}^{\bullet-}/\text{TCNQH}^-$ appeared, and at high pH values waves representing $\text{TCNQ}^{0/-}$ and $\text{TCNQ}^{-/2-}$ were observed. The second wave attributed to $\text{TCNQ}^{-/2-}$ was not confirmed by UV-VIS experiments.

A qualitative look at the electrochemical behavior of Day's polyester⁵¹ and these polyurethanes gives preliminary indications of the extent to which the behavior of the electroactive units depend on the polymer structure and conditions of film formation. For example, the polyester maintained its electroactivity in the presence of aqueous solutions of tetraalkylammonium salts while only PU-HMDI showed any significant electrochemical response in tetramethylammonium chloride. Significant differences are also observed in the electrochemistry of the polyurethanes. For example, in aqueous solutions of Rb^+ or Cs^+ salts, PU-HMDI shows an attenuated second wave, PU-TDI shows reproducible indentations in the region where the second wave is expected in aqueous 0.1M Li^+ , but PU-MDI shows no sign of a second wave in solutions of any of the alkali cation salts at 0.1M concentrations. Thus, the nature of the electrochemical response seems to be very sensitive to the polymer structure.

The polyurethanes were found to be remarkably stable in solution. As a film, preliminary results have shown that they maintain

their integrity for months without significant loss of electrochemical activity, provided the film is not subjected to extreme pH conditions and severe potential changes for long periods of time. The polyradical anion film, formed by the semi-reduced quinone units, has been found to be also exceptionally stable in air or in contact with electrolyte solutions. However, the polydianion, formed by the fully reduced quinone units, was found to be extremely air sensitive and rapidly decomposed in contact with electrolyte solutions which were not carefully degassed, to form α,α -dicyano-p-toluoyl-cyanide anion. This was confirmed by UV-Vis spectroscopy.

A variety of applications can be envisioned for these polymers. One under active investigation in a collaborative effort is their use as ion stimulation electrodes in neurophysiological studies.²⁰⁸ Here neurotransmitter ions, such as calcium or acetylcholine can be loaded into the reduced film on a microelectrode which is then inserted in the brain of a rat. Subsequently, the ions can be released from the electrode surface by the appropriate current or potential pulse. This concept can be applied to the controlled release of almost any ionic species from a suitable polymer modified microelectrode. Applications in the area of electrochromic devices have been demonstrated in our laboratory using PU-HMDI coated on a platinum flag electrode. Murray has suggested applications of these type of polymers in the area of ion gating devices.²⁰⁹ Other possible applications include electrochemical desalination electrolysis,²¹⁰ coatings for the stabilization of semiconductor photovoltaic electrodes,²¹¹ bilayer electrodes in

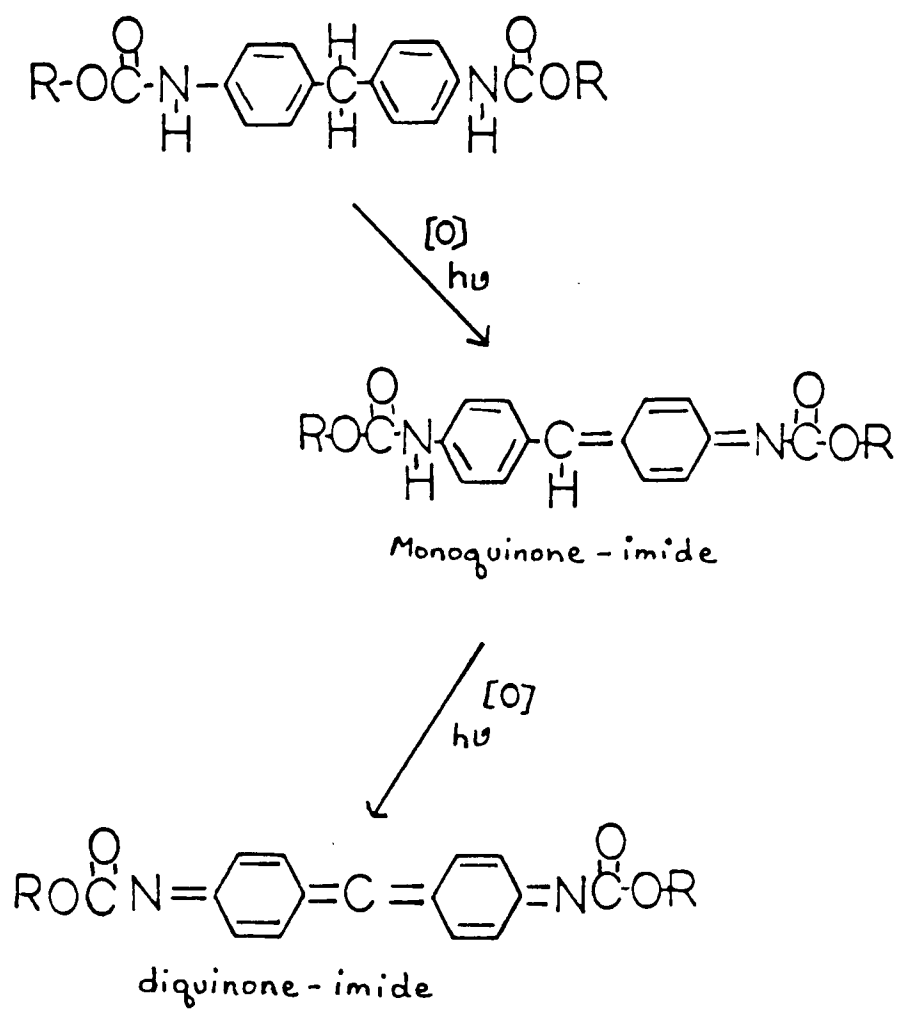
microelectronics,²¹² electrocatalysis²¹⁰ and electronically conducting polymers.²¹³

B. Future Work

An interesting property of electroactive polymers is their conductivity. The conductivity of these polyurethanes was not examined and even though they are not expected to exhibit high conductivity, it would still be of interest to know how the conductivity of these materials depend on the counter ion, molecular weight of the material, polydispersity and cross-linked density. Dielectric measurements are also needed for these materials in order to explore their applicability as organic capacitors or rectifiers. These parameters, which have not been seriously addressed for electroactive polymers in general, in the open literature, require attention if these materials are to become applicable in the electronics industry.

Of particular interest in polyurethane chemistry is the quinone-imide formation of aromatic polyurethanes. It has been shown by Osawa and coworkers that polyurethanes resulting from MDI will undergo a quinone-imide transformation of the sort known in Figure 88, when exposed to ultraviolet radiation.²¹⁴⁻²¹⁶ This undesirable reaction which results in the yellowing of polyurethanes could be exploited to produce redox polymers as shown in Figure 88. These polymers will now have more than one quinone unit per repeat structure and could display some extremely interesting redox properties.

Preliminary examination of PU-MDI in the presence of Cd^{2+} has revealed a most interesting voltammogram. This voltammogram displays a



Figures 88. Quinone-imide formation of MDI polyurethanes.

linear region reminiscent of a Ohm's law type behavior where the currents are in the milliampere range. It is thought that cadmium is complexing with reduced TCNQ $\cdot^-$ to form a conducting layer. Definitely, further work is needed with these polymers in the presence of group IB and IIB cations to illucidate this very interesting phenomenon.

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LIST OF REFERENCES

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