MECHANISTIC ASPECTS OF THE ELECTROPOLYMERIZATION OF HETEROCYCLIC AROMATICS TO FORM CONDUCTING POLYMERS

by

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B.Sc., Trinity Western College, 1982

THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY in the Department of Chemistry

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MECHANISTIC ASPECTS OF THE

ELECTROPOLYMERIZATION OF HETEROCYCLIC

AROMATICS TO FORM CONDUCTING POLYMERS

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ABSTRACT

The study of electrically conducting polypyrrole, polythiophene and related compounds has attracted great interest because of the many possible applications of these materials. This work details the mechanistic studies of the electropolymerization of various heterocyclic monomers to form conducting polymers.

A study of the kinetic order dependence of the polymerization of 2,2'-bithiophene (BT) and of pyrrole was performed. This was measured by stepped potential experiments on glassy carbon and on Pt electrodes, and by monomer consumption experiments as measured by gas chromatographic analysis. The major conclusion from this work is that the reaction follows a first order dependence on monomer concentration. This is true except for the first 100 msec where background or transient current (non-faradaic) is significant. However, the results were not completely reproducible because of possible side-reactions and variable reaction conditions in heterogeneous systems.

Pyrrole-d5 was used in a deuterium isotope effect study in the polymerization. No primary effect was found at any applied potential (above and below the potential where the reaction becomes diffusion-limited) thus indicating that proton loss is not rate-limiting. A radical trap experiment revealed that polymer formation is completely inhibited by the presence of a radical scavenger, and thus a reaction with the scavenger is
more favourable than coupling with another radical cation. These studies are consistent with a radical coupling mechanism of polymerization.

A kinetic and molecular weight study of soluble poly(3-methoxythiophene) demonstrated nearly ideal first order dependence on monomer concentration, 50 to 70% faradaic efficiencies, and a remarkably narrow, low molecular weight distribution. The molecular weight is constant at all monomer conversions from 10% to 90%, and the molecular weight and its distribution are independent of the applied potential. This behaviour is unexpected for a polymerization proceeding by radical propagation, ionic propagation or a condensation-type mechanism, and thus the mechanism of polymerization is unique in polymer science. The limiting effect of the molecular weight is discussed in terms of the polaron / bipolaron theory for conduction in aromatic heterocyclic polymers. A kinetic and mechanistic model consistent with the data is presented.
TO MY PARENTS
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CHAPTER I

INTRODUCTION AND THEORETICAL CONSIDERATIONS

I.1 GENERAL INTRODUCTION

The study of electrically conducting polymers has generated much interest in recent years because of the novelty of these systems and their many potential applications. Although these polymers were known for many years, it was only in the mid to late 1970's that researchers discovered their metallic-like conductivity. Since then, there have been numerous publications describing the synthesis, characterization and applications of these materials. Several general reviews of the field have been written [1-6].

The polymers can exist in a neutral insulating state or an oxidized conducting state. Because there is extensive $\pi$-bonding throughout the polymer backbone, positive charges can be easily delocalized, and the conduction occurs via movement of these charges along the backbone. The polymer can be oxidized electrochemically via anodic processes or chemically via exposure to oxidizing agents such as $I_2$. In either case, the oxidized polymer must have some counter anion in the matrix to maintain electrical neutrality of the material.

Historically, most of the initial research centered on n-doped (reduced) and p-doped (oxidized) polyacetylene but later a pioneering study of electrochemically polymerized pyrrole demonstrated high conductivity in the polymer [7]. Some early
studies began to elucidate the electrochemical aspects of polypyrrole \[8,9\], and it was later determined that this was part of a new class of heterocyclic aromatic polymers which included polymers made from thiophene, furan, indole, azulene and related compounds \[10\]. The structures of some of these polymers are shown in Figure 1.

Polypyrrole and its analogues have been the most studied of this class of materials. There have been a number of reports on the electrochemical and chemical synthesis \[11-26\], and it has been well-characterized by electrochemical \[27-41\] and spectroscopic studies \[42-49\], and studies on differing reaction conditions \[60-73\]. The chief advantage of pyrrole-based polymers is their inertness to the atmosphere in their conducting state, but their disadvantage is their instability in their non-conducting state.

Polythiophene and its derivatives are the next most studied, and there have been a number of publications on the synthesis \[74-84\] and characterization \[85-116\] of these polymers. The advantages of polythiophenes over polypyrrole are in their greater stability and a better structural order, especially with the 3-substituted thiophenes.

Many papers have been published on the potential applications of these polymers. Much of the research has centered on their use in lightweight, rechargeable batteries \[117-127\] or on electro-optical devices \[128-131\]. However, there are also some applications in the medical field, especially in the controlled release of drugs or neurological agents into the bloodstream.
Figure 1: Structures of Some Aromatic And Heterocyclic Aromatic Polymers.
In addition, there have been studies in the chemical modification of electrodes for electrocatalysis [134-141], in the protection of various semiconductors from photocorrosion [142], and in the manufacture of novel microelectronic devices [143-149].

However, the mechanism of polymerization has never been clearly understood, and some disagreement exists in the literature. This work outlines several experiments which help to define some of the processes occurring in the formation of the polymers. Pyrrole, thiophene, and various derivatives of these two were chosen as monomeric materials because they are easily attained and because they have been well-characterized. It will be shown that the polymerization and the conduction mechanism are interrelated, and a mechanistic and kinetic scheme will be presented that best fits the results of this study.

I.2 THEORETICAL CONSIDERATIONS

I.2.1 Experimental Techniques

A) Cyclic Voltammetry

Cyclic voltammetry is a widely-used electroanalytical technique in the determination of reaction mechanisms and in the determination of the redox potentials of solution components. The potential of an electrode in a stationary solution is scanned from a potential where no reaction occurs to a potential higher than where the reaction occurs and the current is
recorded. The scan is then reversed.

A fundamental electrochemical equation is the Butler-Volmer relationship between the current and the overpotential:

\[ i = i_0 [e^{(1 - \beta)\eta F/RT} - e^{-\beta\eta F/RT}] \]  

(1)

where \( F \) is the Faraday, \( R \) is the gas constant, \( T \) is temperature, \( i_0 \) is the exchange current density, \( \beta \) is the symmetry factor which is related to the amount of electrical work an ion must use to approach the electrode, and \( \eta \) is the overpotential which is defined as the deviation of the reaction potential from the equilibrium potential. Thus the current has an exponential relationship to the applied potential, and the onset of current in the voltammogram resembles this relationship, but becomes limited by the diffusion of reactive species very quickly.

In a typical reversible voltammogram as shown in Figure 2, there is little or no current at the onset of the scan (very small currents may be observed due to the charging of the electrochemical double layer), but then the current begins to rise sharply near the redox potential of the solution species of interest. As the species in the vicinity of the electrode are depleted, a peak in the voltammogram is observed. The peak potential \( E_p \) is defined as the point where the rate of electron transfer to the species is equal to the rate of diffusion of the species to the electrode. A further increase in the potential causes the species to be depleted at a faster rate than the diffusion of new species to the electrode, and a depletion layer forms. When the scan is reversed, the species in the depletion layer are now the reactive species, and a reverse peak is seen.
Figure 2: A Typical Reversible Cyclic Voltammogram.
in the voltammogram.

The general oxidation-reduction reaction is given by:

\[ \text{O} + \text{ne} \rightarrow \text{R} \]  

(2)

The definition of electrochemical reversibility is that the rate of electron transfer at the electrode to species \( \text{O} \) and \( \text{R} \) is rapid, and thus the Nernst relationship describes the relationship between the potential and the concentration of species near the electrode:

\[ E = E_0' + \frac{RT}{nF} \ln \left( \frac{[\text{R}^\circ]}{[\text{O}^\circ]} \right) \]  

(3)

where \( E_0' \) is the formal potential of the redox couple and \( [\text{R}^\circ] \) and \( [\text{O}^\circ] \) are the activities in the electrode vicinity of species \( \text{R} \) and \( \text{O} \), respectively. For a one-electron transfer at 25°C, this equation reduces to:

\[ E = E_0' - 0.059 \log \left( \frac{[\text{R}^\circ]}{[\text{O}^\circ]} \right) \]  

(4)

A relationship for the peak current \( i_p \) is given by the Randles-Sevcik equation:

\[ i_p = 2.69 \times 10^5 n^{3/2} A D_o^{1/2} C_o^{1/2} \nu^{1/2} \]  

(5)

where \( C_o \) is the bulk concentration of the species, \( D_o \) is the diffusion coefficient of the species, \( \nu \) is the potential scan rate, and \( A \) is the electrode area. Thus, a plot of the peak current versus (scan rate)\(^{1/2} \) demonstrates whether the reaction is diffusion-limited. Occasionally, a linear relationship is found between the peak current and the scan rate; this is the case for surface-adsorbed species.

Nicholson and Shain [150] derived the following equations for the peak currents relative to the formal potentials at 25°C:

\[ E_{pc} = E_{1/2} - 28.5/n \text{ mV} \]  

(6)
\[ E_{p_a} = E_{1/2} + 28.5/n \text{ mV} \]  \hspace{1cm} (7)

where \( E_{p_a} \) and \( E_{p_c} \) are the peak potentials for the anodic and cathodic processes, respectively and where:

\[ E_{1/2} = E'_o - 0.059 \log \left( \frac{D_R}{D_0} \right)^{1/2} \]  \hspace{1cm} (8)

\( D_R \) and \( D_0 \) are the diffusion coefficients for the reduced and oxidized species, respectively, and \( E_{1/2} \) is the half-wave potential where the current is one-half the limiting value on a polarographic curve. Since \( D_R \approx D_0 \), \( E_{1/2} \approx E'_o \).

The peaks are thus separated by 59 mV for a one electron process in a totally reversible system. However, since few systems exhibit ideal reversibility at all scan rates, the peak separation widens with increasing irreversibility and the ratio of the peak currents deviates from unity. This is a result of slow electron exchange and an inability of the system to maintain equilibrium conditions.

Furthermore, the product produced in the electrochemical reaction may react chemically to form another product which itself may undergo another electron exchange. The reaction pathway may involve a variety of electrochemical (E) or chemical (C) steps. Some examples of such pathways are: \( E, EC, ECE, EEC \), or \( (EC)_n \). The nature of the reverse peak indicates the nature of the pathway.

Thus, the positions and magnitudes of the peak currents in cyclic voltammetry can yield thermodynamic, electrochemical, and mechanistic data.

B) **Rotating Disk Electrode Voltammetry**

The Rotating Disk Electrode (RDE) technique is a
controlled mass-transfer electroanalytical technique. In some respects it is similar to cyclic voltammetry, with the exception that no reverse scan occurs, and the rotation of the electrode causes controlled hydrodynamic movement of the electrolyte solution. In voltammetry, the current drops after the peak because of the depletion of reactive species, but in the RDE system, the current becomes constant due to the mass-transport limitations induced by the continual movement of fresh solution to the electrode. A typical current response is shown in Figure 3.

The solution in the vicinity of the electrode; i.e. the solution undergoing electrolysis, is considered to be motionless and the diffusion of species to the electrode is the operative mechanism for electron transfer. The current at the disk electrode is derived from hydrodynamic equations and is given by:

\[ i = 0.62nFAD^{2/3} \nu^{-1/6} \omega^{1/2} (C_o - C_e) \quad (9) \]

where \( \nu \) is the kinematic viscosity of the solution, \( \omega \) is the rotation rate, \( C_o \) is the bulk solution concentration and \( C_e \) is the concentration of the species at the electrode. At high potentials where \( C_e = 0 \), the limiting current \( i_l \) is described by the Levich equation:

\[ i_l = 0.62nFAC_oD^{2/3} \nu^{-1/6} \omega^{1/2} \quad (10) \]

A Nernstian relationship between the electrode potential and current has been derived and is given by the following:

\[ E = E_{1/2} - 0.059/n \log((i_l - i)/i) \quad (11) \]

Thus, the current behaviour of the RDE will yield \( E_{1/2} \) and \( n \) for
Figure 3: Typical Disk Current Behaviour in an RDE Experiment.
The rotating ring-disk electrode (RRDE) is closely related to the RDE, with the exception that another electrode in the shape of a ring is placed around the outside of the disk electrode, separated from the disk by about a millimeter or so. The potential of the ring is controlled independently from the disk. The hydrodynamic calculations of the RRDE technique show that products that form at the disk will flow to the ring electrode, where they can react further. Usually, a reverse potential is held at the ring, so that the products formed at the disk will be converted back to the reactants. The ring collection efficiency is defined as the ratio of the ring current to the disk current, and the maximum ring collection efficiency depends on the areas of the ring and disk and the separation distance between the two. The RRDE technique is useful to determine the stability of the products and more importantly to determine the reaction pathway.

C) Cell Designs

The general requirements for a controlled-potential electrochemical cell are that it must contain a working electrode, counter electrode and reference electrode and a solution with an excess concentration of a supporting electrolyte.

The working electrode may be either Pt, glassy carbon, or a glass slide coated with indium-doped tin oxide. The counter electrode is usually a coiled Pt wire or a large Pt gauze. The reference electrode is a non-polarizable electrode which is used
to keep a constant potential on the working electrode. In this work, the saturated calomel electrode (SCE) (Hg/Hg$_2$Cl$_2$) was used as the reference.

The reference compartment is separated from the working compartment through a Luggin capillary, which prevents mass transfer between the compartments but allows a small amount of electrical current. The reference compartment is filled with the electrochemical solution, and a salt bridge filled with 4 – 6% Agar in saturated KCl / water separates the aqueous reference from the organic electrochemical solution.

The working and counter compartments may be separated by a porous glass frit to prevent the mixing of products from the anodic and cathodic reactions. In addition, the cells may be sealed from the atmosphere through the use of tightly fitting teflon caps with O-rings. An inert gas such as argon may then be introduced in the cell which can deaerate the solution and provide a controlled atmosphere.

Examples and schematic diagrams of four of the cells used in this work are shown in Figures 4 to 7.

D) Gel Permeation Chromatography

Gel permeation chromatography (GPC) is a size-exclusion method for molecular weight measurements. The method has been reviewed [151]. The general concept of this technique is that a solution containing a distribution of molecular weights is passed through a column packed with particles which have controlled pore sizes. The lower molecular weight material is trapped and delayed by the pores and the higher molecular weight
Figure 4: Schematic Diagram of a Cell Used in Cyclic Voltammetry.
Figure 5: Schematic Diagram of a Cell Used in Monomer Consumption Analysis.

a) working electrode
b) counter electrode
c) reference compartment
d) Luggin capillary
e) Teflon caps
f) porous glass frit
Figure 6: Schematic Diagram of a Cell Used in RRDE Experiments.

a) Teflon casing  
b) ring electrode  
c) disk electrode  
d) counter electrode  
e) reference electrode  
f) salt bridge  
g) Luggin capillary  
h) porous glass frit  
i) Teflon cap
Figure 7: Schematic Diagram of a Cell Used in Spectrophotometric Studies.

a) tin-oxide glass electrode
b) counter electrode
c) reference compartment
d) Luggin capillary
e) glass cuvette
f) porous glass frit
g) Teflon caps
material is unaffected and passes through. Usually several columns packed with particles of different pore sizes are connected in series and thus a fractionation occurs of a wide range of molecular weight distributions. A detector is connected to the end of the column which measures the concentration of eluent materials either via differential refractive index measurements or via ultraviolet absorption.

Standard polystyrene samples with narrow molecular weight distributions are measured by this technique and then samples of unknown molecular weight can be calculated using the universal calibration:

$$\log ([\eta]_x M_x) = \log ([\eta]_s M_s)$$

(12)

where \([\eta]\) is the intrinsic viscosity of the sample, \(M\) is the molecular weight, and the subscripts \(x\) and \(s\) refer to the unknown polymer and the standard polymer. This relationship has been shown to be true for all polymers in a given solvent at isothermal conditions. The intrinsic viscosity is calculated by the Mark-Houwink expression:

$$[\eta] = K M^a$$

(13)

where \(K\) and \(a\) are constants for each given polymer. If these constants are known, then the universal calibration becomes:

$$\log M_x = (1+a_x)^{-1} \log(K_s/K_x) + (1+a_s)(1+a_x)^{-1} \log M_s$$

(14)

However, in cases where these values are unknown, as may be the case for new polymers, the viscosity can be approximated using viscometric measurements on varying polymer concentrations. The viscosity of the pure solvent is measured and the viscosity of the polymer at zero concentration is
determined by extrapolation. The ratio of the viscosity of the polymer at zero concentration to the viscosity of pure solvent is then approximated as the intrinsic viscosity.

Viscosity measurements are made by measuring the time needed for the solution to pass through a narrow capillary of fixed dimensions. The Ubbelohde viscometer is commonly used for this technique [151].

I.2.2 Kinetic Isotope Effects and Radical Trap Theory

A general treatment of isotope effects has been developed [152]. The isotopic substitution of an atom intimately involved in the transition state of a reaction will result in a change in the rate of reaction. Most commonly, the rate of reaction of a deuterium-substituted analog is compared with the rate of the normal hydrogen-containing molecule.

Since the primary difference between D and H is one neutron, the potential energy surface, electronic structure and binding forces remain identical. Thus, the isotope effect is due to the change in mass, which is measured and observed in the infrared vibrational frequencies.

The quantum mechanical description of energy levels for an small mass attached to a much larger mass is given by:

$$\epsilon_n = (n + 1/2)\hbar \nu \quad n = 0,1,2...$$  \hspace{1cm} (15)

where \( \nu \) is the vibrational frequency given by:

$$\nu = (2\pi)^{-1} k^{1/2} m^{-1/2}$$  \hspace{1cm} (16)

where \( m \) is the mass and \( k \) is the force constant (equal for all
isotopes of the same atom).

The zero-point energy levels of an C-H and a C-D molecular bond are proportional to $m^{-1/2}$, and thus the C-H bond has a higher zero-point energy than the C-D bond. Therefore, a lower activation energy is needed for C-H bond cleavage than for C-D cleavage; i.e. $k_H/k_D > 1$ for a primary isotope effect. The theoretical energy diagram is shown in Figure 8.

The frequency difference of the zero-point energy between C-H and C-D should be $(1/2)^{1/2}$ or 1/1.41, but is actually observed to be about 1/1.35 [152]. The activation energy difference is:

$$\epsilon_{H}^\dagger - \epsilon_{D}^\dagger = -(1/2)\hbar c(1 - 1/1.35) \nu_H$$

and the $k_H/k_D$ ratio is given by:

$$k_H/k_D = \exp \left(\frac{-\epsilon_H - \epsilon_D}{kT}\right) = \exp(0.1865 \nu_H T^{-1})$$

The value for $\nu_H$ is calculated from the C-H stretching vibration (ca. 3000 cm$^{-1}$), and so at $T=298$ K, the isotope effect is calculated to be 6.5.

However, equation (18) is an oversimplification of the isotope effect since it only accounts for the C-H bond stretching and neglects the other vibrations which may contribute. A more rigorous derivation of the relationship has the same form as equation (18), but includes more terms.

In addition, not all transition states involve perfectly linear cleavage of a C-H bond, and so the isotope effect will not be as dramatic in non-linear cases. In practice $k_H/k_D$ is between 3 and 7 for primary isotope effects.

Secondary isotope effects arise from isotopic substitution.
Figure 8: Theoretical Energy Diagram for a Molecule Containing C-H or C-D Bonds.
on bonds not broken in the transition state. A similar
relationship for \( k_\text{H}/k_0 \) can be derived and is given by:

\[
k_\text{H}/k_0 = \exp (-0.1865 \ T^{-1} \ (\nu_+ - \nu_\text{H}))
\]

(19)

where \( \nu_+ \) is the vibration frequency of the transition state and \( \nu_\text{H} \) is the vibration frequency of the reactant state. This
relationship shows that secondary effects are observed when
there is a change in hybridization in the transition state of
the molecule or a hyperconjugative effect in the transition
state. At 298 K, the maximum secondary effect for a molecule
undergoing a change from sp\(^3\) to sp\(^2\) is \( k_\text{H}/k_0 = 1.41 \). However, an
inverse secondary effect is observed when the
hybridization changes from sp\(^2\) to sp\(^3\) and \( k_\text{H}/k_0 \) is less than one
with a minimum value of 0.71 at 298 K. However, these values
reflect systems which change hybridizations completely in their
transition states. Experimentally, this is usually not the case
and typical \( k_\text{H}/k_0 \) ratios of 1.15 to 1.25 for normal and 0.8 to
0.9 for inverse effects are observed.

A general review of the spin trapping techniques has been
published [153]. The basic concept of radical traps is that a
species is added to a radical reaction which will form an adduct
containing an odd number of electrons. This adduct will
generally have a long lifetime (unlike most free-radicals) which
allows it to be measured by electron spin resonance (ESR). Most
commonly, the adduct species formed are nitroxides and the
trapping species are either nitroso compounds or nitrones.
A large number of papers have been published on the mechanism of conduction in polyacetylene, poly(p-phenylene sulfide), and the heterocyclic aromatic polymers such as polythiophene and polypyrrole [154-190]. A model was first proposed for polyacetylene in a paper by Su, Schrieffer and Heeger (the SSH model) [154,155]. Although there was some initial criticism [180], it has now generally been accepted as the best theory for explaining the conduction. Several reviews have been recently published [156-158].

The general concept of conduction in polyacetylene involves charge movement along the extended $\pi$ - network on the polymeric chain. However, the polymer must be doped first with some acceptor molecule $A \rightarrow A^-$ which will oxidize the polymer chain $P \rightarrow P^\prime$.

The ground state of $(CH)_x$ is a two-fold degenerate Peierls insulator, which has an occasional defect in the chain (Figure 9). This defect is known as a soliton. When the polymer chain is doped, many defects are induced into the polymer chain (positively or negatively charged solitons). Because the polymer has a Peierls instability, the bond lengths will alter to accommodate the defects, which lead to a new energy state in between the $\pi - \pi^*$ transition (see Fig. 9). This new energy state can be measured spectroscopically, and this level may contain one, two or no electrons for positively charged solitons, negatively charged solitons and neutral solitons,
respectively. In physicist's terminology, the solitons are "kinks" or domain walls in a lattice [157].

However, the degenerate state of polyacetylene is merely a special case of conducting polymers in general. For example, the quinoid structure of polythiophene has a higher ground state energy than the benzenoid structure (Figure 10), thus making this polymer non-degenerate. The basic premise is that the carbon-carbon bond lengths are different in each structure. Similar results are shown for the case of polypyrrole and 3-substituted polypyrroles [162-164,166-168] and poly paraphenylene [165,170].

Spectroscopic studies of the heterocyclic aromatic polymers have revealed that new absorptions occur in oxidized polymers at lower energies than the $\pi$ to $\pi'$ transition of the neutral polymer [160,167,171,172], similar to the mechanism of polyacetylene. Further, there is an unusual absence of an ESR signal (or at least no correlation of the ESR signal to the level of oxidation) of these polymers at oxidation levels greater than about 3% [162-164,168].

These data have been interpreted in a polaron/bipolaron model, which is simply an extension of the SSH soliton model. When the polymer is first oxidized, it forms a radical cation, just as in the mechanistic scheme shown earlier. However, this radical cation may reside in the middle of the chain rather than at the chain ends, making it chemically un-reactive. This is called a "polaron" and it can be delocalized over several units in the chain. If the chain is oxidized further, a "bipolaron" may form, which is simply a dication. Chemical structures for
Figure 9: Schematic Diagram and Band Energy Diagram of Polyacetylene.

a) neutral PA
b) soliton
c) mid-band gap energy of a soliton
d) mid-band gap energy of a negative soliton
e) mid-band gap energy of a positive soliton
Figure 10: Ground State Structures of Polythiophene.
the polaron and bipolaron are shown in Figure 11. The bipolaron has no radical character; the radicals have condensed, in a sense, in the quinoid structure.

There have been two suggestions for the mechanism of bipolaron formation. The first is that the polaron simply loses the radical to further oxidation, but the second is that two separate polarons form on the chain and then react together as shown in Figure 12. Although there is no decisive evidence for either model, most authors have recently favoured the latter model.

The energetics of the electron transitions are shown in Figures 13 and 14. The monomer has a $\pi$ to $\pi^*$ transition (i.e. valence band to conduction band) which occurs in the uv region. The same transition occurs in the neutral polymer, except that it occurs in the visible at about 460 nm, or 3.2 eV for poly(bithiophene). When the polymer is oxidized at low levels, new states form in between the $\pi$ to $\pi^*$ transition, which have a spin of $1/2$ (observed on ESR). At higher doping levels, these spins disappear. The $\pi$ to $\pi^*$ transition also widens (from 3.2 eV in the neutral state to 3.6 eV at very high doping levels for polythiophene), suggesting that the new states take on some of the characteristics of both the conduction band and the valence band. At low oxidation levels, the $h\omega_1$, $h\omega_1$, $h\omega_2$, and $h\omega_3$ transitions are all observed, but at higher levels the $h\omega_3$ transition disappears, consistent with the formation of spinless bipolarons. As more bipolarons are formed, the transitions become bands, and at very high doping levels, the bipolaron
Figure 11: Chemical Structures of the Polaron and the Bipolaron in Polythiophene.
polaron

bipolaron
Figure 12: Reaction of Two Polarons to Form a Bipolaron.
Figure 13: Band Energy Diagram for the Formation of a Single Bipolaron.
\begin{tikzpicture}
\draw[->] (0,0) -- (0,5) node[midway,above] {$\pi^*$};
\draw[->] (0,0) -- (0,-5) node[midway,above] {$\pi$};
\draw[->] (0,0) -- (0,-5) node[midway,above] {$E$};
\draw[->] (3,0) -- (3,5) node[midway,above] {CONDUCTION BAND};
\draw[->] (3,0) -- (3,-5) node[midway,above] {VALENCE BAND};
\draw[->] (6,0) -- (6,5) node[midway,above] {CONDUCTION BAND};
\draw[->] (6,0) -- (6,-5) node[midway,above] {VALENCE BAND};
\draw[->] (9,0) -- (9,5) node[midway,above] {CONDUCTION BAND};
\draw[->] (9,0) -- (9,-5) node[midway,above] {VALENCE BAND};
\draw[->] (3,0) -- (6,3) node[midway,above] {$\hbar \omega_1$};
\draw[->] (6,0) -- (9,3) node[midway,above] {$\hbar \omega_2$};
\draw[->] (9,0) -- (12,3) node[midway,above] {$\hbar \omega_3$};
\draw[->] (3,0) -- (6,-3) node[midway,above] {$\hbar \omega_0$};
\draw[->] (6,0) -- (9,-3) node[midway,above] {$\hbar \omega_0$};
\draw[->] (9,0) -- (12,-3) node[midway,above] {$\hbar \omega_0$};
\draw[->] (0,0) -- (3,-0.5) node[midway,above] {MONOMER};
\draw[->] (3,-0.5) -- (6,-0.5) node[midway,above] {NEUTRAL POLYMER};
\draw[->] (6,-0.5) -- (9,-0.5) node[midway,above] {POLYMER WITH TWO POLARONS};
\draw[->] (9,-0.5) -- (12,-0.5) node[midway,above] {POLYMER WITH A BIPOLARON};
\end{tikzpicture}
Figure 14: Band Energy Diagram for the Formation of Bipolaron Bands.
CONDUCTION BAND

VALENCE BAND

POLYMER WITH ONE BIPOLARON

POLYMER WITH SEVERAL BIPOLARONS

POLYMER WITH MAXIMUM # OF BIPOLARONS (50% QUINOID, 50% BENZENOID)

INCREASING OXIDATION
bands actually begin to merge with the valence and conduction bands, resulting in true metallic conductivity.

It has been shown through energy calculations using the Hückel theory with $\sigma$ bond compressibility, that the polymeric geometry relaxes around a localized charge; it is favourable to form a mixed benzenoid-quinoid structure as shown in Figure 10 [158]. The schematic diagrams shown in Figures 13 and 14 demonstrate an energy gain when going from the polaron to the bipolaron state; there is a binding energy of about 0.45 eV in the case of polypyrrole [158].

The conduction then occurs via bipolaron movement along the chain. It has been shown that the conductivity of polythiophene is highly anisotropic; the conductivity along the length of the chain is about 5 orders of magnitude greater than the conductivity perpendicular to the chain orientation [184]. Nevertheless, some interchain transfer must occur in a randomly-oriented sample, and a bipolaron chain hopping mechanism has been proposed [185,186].

However, the bipolaron model has been criticized recently [173-176]. The premise of the criticisms is that the ESR studies performed earlier were incorrect, and a spin correlation is indeed observed with the amount of oxidation. In addition, the electrochemical data demonstrate that there is no real energy gain in going from the polaron to the bipolaron state, thus making the formation of either state energetically equivalent. Further, the formation of the bipolaron was shown to be unfavourable due to simple Coulombic repulsions of like charges.
The bipolaron model also assumes that the heteroatom plays no role, due to the lack of evidence in the ESR of a g-factor resulting from the sulfur or nitrogen and due to the lack of evidence in the spectroscopic studies of a heteratom effect on the electron transitions. However, this has been criticized in a study which shows that the heteroatom indeed stabilizes and interacts with the carbon backbone [190].

A further weakness of the model is that any deviation from the regular carbon backbone structure would prevent the formation of bipolarons. The model applies only when all polymer units are linked in a regular $\alpha-\alpha'$ structure. Any deviation from this stereoregularity (e.g. an $\alpha-\beta'$ linkage) would destroy the conjugated chain. Some authors have suggested that these "mislinks" occur quite regularly [187,188], and thus bipolaron formation would rarely be favoured.

The final weakness of the model is that it does not satisfactorily explain the conduction mechanism at low doping levels; i.e. when the level of oxidation is small enough to only form polarons. The polymers do conduct electricity even at these low levels, although not nearly as much as the more oxidized samples.

Nevertheless, the bipolaron theory is still the best model to explain conduction mechanisms by the virtue of the fact that no better model has yet been proposed to interpret the spectroscopic results and the conductivity measurements of the polymers.
II.1 INTRODUCTION

II.1.1 General Remarks

When this project was initiated, it was known that a current passed through a solution containing an aromatic heterocyclic monomer produces an insoluble, electrically conducting, black polymer film on the anode, and that the amount of polymer film is stoichiometrically related to the amount of charge; i.e. about 2.5 charges are needed for every mer unit on the chain. The polymer was known to be neutral in the non-conducting state and oxidized in the conducting state, with a stoichiometric amount of counter anions in the film which stabilize the positive charges on the polymer. It was also known that 2,5-substituted pyrroles do not polymerize and thus polymer linkage occurs through the α-carbons on the monomer [191]. However, the mechanism of polymerization was only vaguely described as involving an oxidation of pyrrole and then a further reaction with another pyrrole unit [191].

Polypyrrole was reasonably well-characterized by electrochemical methods [192], but no work had yet been performed on polythiophene other than the first Tourillon & Garnier paper [10] which described the synthesis of the polymer.
and classified it along with polypyrrole. Nor was it conclusively proven that the mechanism of formation of polythiophene was the same as for pyrrole.

Thus, the initial studies of this project were designed to describe and compare the basic mechanistic processes of BT and pyrrole. This chapter studies the polymerization of 2,2'-bithiophene and pyrrole using stepped potential, voltammetric, RRDE, and macro monomer consumption experiments. These techniques qualitatively describe the kinetic order and the reaction pathway.

II.1.1 Key Mechanistic Studies

One of the first detailed mechanistic studies of the polymerization of pyrrole was published by Prejza, Lunstrom and Skotheim [193]. Their major conclusion was that polymerization was initiated by a radical produced by the oxidation of the supporting electrolyte anion, BF$_4^-$.

This statement was later refuted by several authors [194-196], but they utilized a valid electrochemical experimental technique to study the initiation. The general relationship between the current and the concentration of reactive species for any electrochemical reaction is given by:

$$i \propto [S]^\alpha$$  \hspace{2cm} (20)

where $S$ is the species and $\alpha$ is the kinetic reaction order. At various concentrations of $S$, the variation of the current should yield the reaction order as in the following equation:
The authors applied various stepped potentials to solutions containing varying concentrations of pyrrole and supporting electrolyte and measured the currents at \( t=0 \) using oscilloscope techniques. They found that \( \alpha = 0 \) for pyrrole and \( \alpha = 1 \) for the supporting electrolyte.

The first detailed proposal for a radical cation coupling mechanism was published by Genies, Bidan and Diaz [194]. It was found that the rate of polymer growth was not limited by the diffusion of pyrrole to the electrode, and since this behaviour was similar to that found in their earlier studies on the electrochemical dimerization of diphenylpyrazoline, they proposed the radical cation coupling as the rate-limiting step. This conclusion was based on a test of the integrated Cottrell equation where:

\[
Q_d = 2nFA D_0^{1/2} C_0 \pi^{1/2} t^{1/2}
\]

where \( Q_d \) = charge passed, and all other terms have their usual meaning. Thus, a linear plot of charge vs. \( t^{1/2} \) or absorbance vs. \( t^{1/2} \) (since absorbance \( \alpha \) charge) is indicative of a diffusion-limited reaction and since the authors found a linear relationship between absorbance and time, they concluded the polymerization was not limited by diffusion. Their mechanism involved the direct oxidation of the monomer at the electrode to form a radical cation species, followed by dimerization with another radical cation and then proton loss. The neutral dimer then is reoxidized at the electrode and the reaction repeats.

A further addition to this study was performed by Waltman.
and Bargon [197], who calculated the radical concentrations at each carbon in the pyrrole ring in monomeric and various oligomeric pyrrole species using INDO and CNDO molecular orbital calculations. It was found that $a-a'$ linkages were favoured, but some $\beta$ linkages were possible at higher chain lengths.

Several mechanistic studies have been published by Pletcher et al. [196,198-200] on the electropolymerization of pyrrole, N-methylpyrrole and thiophene. It was concluded that a three-dimensional nucleation mechanism was operative, and the current was found to be linear in $t^2$ at the onset of a stepped potential. However, the rate of film growth later became linear in $t^{1/2}$, indicative of a limitation imposed by the diffusion of monomer to the electrode. A mechanism was proposed involving neutral monomer addition to a monomer radical cation, followed by oxidation and proton loss, in contrast to the Genies et al. mechanism [194] of radical cation coupling. However, the authors admitted that their mechanism was simplistic since it did not account for three-dimensional growth.

Recently, a similar mechanism of neutral monomer - radical cation coupling has been proposed for the polymerization of pyrrole on an SnO$_2$ electrode [201]. However, this mechanism proposes an initiation step whereby a chemical bond is formed between Sn$^+$ sites on the electrode and a neutral pyrrole molecule. The initiation step was studied using the same technique as utilized by Prejza et al [193]; the kinetic order of pyrrole was calculated by the values of $(d \log i)/(d \log c)$. An order of 1.55 was found for pyrrole polymerized on a tin
oxide electrode, in contrast to the work of Prejza et al., who obtained an order of zero using a platinum electrode.

Polythiophene may be polymerized from thiophene monomers, 2,2'-bithiophene monomers, or monomers with even greater chain length. Two papers report the effect of monomeric chain length on the polymeric structure; in particular, the presence of α-α, α-β, and β-β linkages in the polymer [202,203]. It was found that differences in structural regularity occurred with different monomers, but the authors had conflicting conclusions as to which monomer produced the more regular polymer.

This brief review shows some of the extent of the disparity in the literature on the initiation and polymerization mechanism of the heterocyclic aromatics. However, most of the authors readily admit that this is a complex system. The experimental data in the literature do not unequivocally support any single mechanism.

II.2 EXPERIMENTAL

Pyrrole (Aldrich) was distilled in vacuo and 2,2'-bithiophene (BT) (Eastman) was sublimed under reduced pressure. Acetonitrile (AN) (Caledon, HPLC grade) was distilled over 4 Å molecular sieves and stored under N₂ or Ar, and propylene carbonate (PC) (Eastman) was distilled under reduced pressure in a rotating band column of ca. 100 theoretical plates. Tetrabutylammonium tetrafluoroborate (TBABF₄) (Aldrich) and tetrabutylammonium perchlorate (TBAP) (Eastman) were dried in
vacuo for several days.

The voltammetric and stepped potential experiments utilized either a three-compartment 50 ml. cell with a 1 cm² Pt working electrode or a 25 ml. cell with a ca. 2.5 mm² glassy carbon working electrode. In both cases, the counter electrode was a coiled Pt wire with a total area larger than the working electrode, and the reference was SCE.

The monomer consumption experiments utilized a three-compartment 150 ml. cell equipped with a large Pt gauze (ca. 2 x 4 cm) working electrode and a similar counter electrode and an SCE reference. The working compartment also contained a small magnetic stirring bar, which was used to control convection effects. The rotation rate of the stirring bar was held constant throughout all experiments and was measured by a stroboscope. The cell also contained a septum-covered sidearm attached to the working compartment, from which solution samples were withdrawn by syringe for gas chromatographic analysis. The samples were mixed with an appropriate internal standard and then quantitatively analyzed by a Hewlett-Packard model 5890A gas chromatograph equipped with capillary columns.

A three-compartment 50 ml. cell was used for the RDE and RRDE experiments with a removable 0.196 cm² Pt disk and a 0.126 cm² Pt ring. The counter electrode was a coiled Pt wire or coiled Pt gauze and the reference was SCE. The rotation apparatus, working electrode and associated electronics were constructed by Pine Instruments.

The spectrophotometric measurements utilized a three
compartment cell fitted with a cuvette. The working electrode was a glass slide coated with indium-doped tin oxide, the counter electrode was a large Pt gauze and the reference was SCE. The construction of the cell and the working electrode is described in more detail in Section III.2.

With the exception of the RDE and RRDE experiments, an EG&G PAR model 173 potentiostat / galvanostat with a model 179 digital coulometer along with a model 175 universal programmer was used for all experiments. The data for the stepped potential experiments were collected on an Apple II+ microcomputer equipped with Interactive Microware hardware and software.

All solutions were bubbled with either N₂ or Ar prior to use and an inert atmosphere was maintained throughout the course of the experiment.

II.2 RESULTS AND DISCUSSION

A) Voltammetric Experiments

A voltammogram of a growing film of polyBT is shown in Figure 15. This voltammogram was obtained by placing a bare Pt working electrode in the electrochemical solution and cycling from 0.0 V vs. SCE to 1.4 V vs. SCE twice. On the first scan, there is no current until about 1.2 V where the monomer begins to oxidize. The current then reaches a peak at 1.3 V, and this value is assigned as the peak potential for BT oxidation. An electrodeposition of polymer was observed to occur here, as evidenced by a colour change on the electrode.
Figure 15: Cyclic Voltammogram of a Growing PolyBT Film.

Solution species are $10^{-2}$ M BT, $10^{-1}$ M TBAP in AN. Scan rate = 50 mV/sec.
On the reverse scan, there is no peak at about 1.25 V, proving that an irreversible non-Nernstian oxidation has occurred. However, two broad peaks appear at 0.9 and 0.6 V which are due to the reduction of the newly formed polymer. The reason for two peaks is unclear, but they may be due to structural reordering of the polymer film to expel the counter anion.

On the second scan, the presence of neutral polymer on the electrode causes a peak at about 1.0 - 1.1 V. This peak is assigned as the peak potential for the oxidation of polyBT. The monomer oxidation peak then reappears at 1.3 V, but with a greater current magnitude. This is probably due to the presence of conducting polymer on the electrode which has the effect of increasing the total area of the electrode and thus providing more sites for the initiation of new polymeric chains. This is further indication of the three-dimensional growth observed in these polymers by the Pletcher group [196,198-200].

The reverse scan shows the same two reduction peaks but again with greater current magnitudes. This is indicative of a greater amount of polymer on the electrode on the second scan than on the first.

To prove that the oxidation peak at 1.0 V and the reduction peaks at 0.9 and 0.6 V are due to polymer and not monomer, a polyBT-coated Pt electrode was cycled in a BT-free solution. This voltammogram is shown in Figure 16. All of the peaks present in Figure 15 are in Figure 16, with the exception of the peak at 1.3 V. The peak at 1.0 V broadens somewhat due to a thicker polyBT film on the electrode.
Figure 16: Cyclic Voltammogram of a PolyBT Film.

Solution species are $10^{-1}$ M TBAP in AN.
Scan rate = 50 mV/sec.
Since the oxidation of polymer is lower than monomer, the polymer forms on the electrode in its oxidized state. PolyBT formation must always occur at potentials at or higher than about 1.2 V vs. SCE, and since the current has an exponential relationship to the potential (equation (1)), the oxidation of the polymer occurs very quickly. This is indeed advantageous for the formation of large quantities of polymer since the conducting polymer film will act as an electrode for further polymerization. If the polymer did not form in the conducting state, an insulating layer would quickly cover the electrode and polymerization would cease. Thus, the voltammetric studies give some indication of the electrode processes during polymerization.

B) RDE and RRDE Studies

A further clarification of the voltammetric experiments is provided by the RDE study of the polymerization of BT. Figure 17 shows the first and fifth scans of an RDE experiment. These scans were taken to 2.0 V vs. SCE, which is just before the limit at which the solvent begins to electrolyze. A large peak appears at 1.6 - 1.7 V vs. SCE, which was found by cyclic voltammetry to be completely irreversible. This peak diminishes with each scan, and no polymer oxidation peak ever appears at 1.0 V. This behaviour is due to an irreversible oxidation of the polymer film, which causes the film to become non-conducting. At the time of this work, a paper was published describing the infrared spectrum of polyBT at different potentials, and the irreversible potentials were shown to cause sulfone and sulfoxide absorptions
Figure 17: First and Fifth Scans in an RDE Study of

0.10 mM BT / 0.10 M TBAP in AN.

Rotation rate = 980 r.p.m.
in the polymer [111]. It is possible that the polymer becomes so heavily oxidized that it becomes very reactive. This also may be due to an inability of the anion to diffuse into the film quickly enough to stabilize the charge.

An RRDE study of the BT polymerization in acetonitrile is shown in Figure 18. A similar graph was found for the BT polymerization in propylene carbonate. The Levich equation (equation (10)) was used to plot the limiting current of the disk against the rotation rate as shown in Figures 20. Reasonably good Levich behaviour was found for the polymerization in either solvent, indicating that the electron transfer is limited by the diffusion of monomer species at potentials higher than 1.3 V. However, higher currents are observed for acetonitrile than for propylene carbonate; this may be due to the higher solution viscosity of propylene carbonate and thus slowing the diffusion of monomer.

Further, $E_{1/2}$ and $n$ (as given in equation (11)) were calculated by plotting $E$ versus $\log{(i_1-i)/i}$ for the disk current. It was found that $n = 1$ and $E_{1/2} = 1.3$ V vs. SCE for both solvents. This shows that on average the electrode receives only one electron from each monomer unit before the monomer proceeds to react chemically. In other words, at low enough potentials, the monomer will likely react before it receives a second charge.

The ring electrode was held at 0.0 V. vs. SCE, and thus it reduced any soluble species formed at the disk. The ring current parallels the disk current in each study, and the ring current
Figure 18: RRDE Study of 0.10 mM BT / 0.10 M TBABF$_4$ in AN at Several Rotation Rates.

Rotation rates shown in r.p.m.

Scan rate = 50 mV/sec.
Figure 19: RRDE Study of 0.10 mM Pyrrole / 0.10 M TBABF$_4$ in AN at Several Rotation Rates.

Rotation rates shown in r.p.m.
Scan rate = 50 mV/sec.
Figure 20: Levich Plots of the BT Polymerization in AN and PC.
appears to be reasonably constant when the disk potential is greater than about 1.3 V. This indicates that some soluble species are formed at the disk which can be reduced at the ring.

The ring current may be due to three factors. First, the presence of impurities in the electrolyte may cause some current at the ring. This certainly would account for the currents observed between 0.8 V and 1.3 V on the disk. However, the fact that the ring current increases sharply when the disk current increases at 1.3 V strongly suggests that the current here is related to the polymerization. Second, there may be soluble oligomeric products formed at the disk and the ring current is due to the reduction of these species. However, g.c – mass spectrometry, thin layer chromatography and Fourier Transform infrared spectroscopy all failed to detect any oligomeric products in solution. Third, the ring current may be due to the reduction of monomeric radical cation species which failed to polymerize at the disk. This is the most logical explanation for the ring current.

If the species collected at the ring are indeed monomer radical cations, a solvent effect should be observed in the ring collection efficiencies. It is predicted that radical cations would be more stable in a solvent with a higher dielectric constant. Thus, since propylene carbonate has a much higher dielectric constant than acetonitrile, larger ring collection efficiencies should be observed. This is generally the case, as evidenced by the data in Table I. It should be noted that the maximum collection efficiency for this RRDE was experimentally
Table 1

Comparison of RRDE Ring Collection Efficiencies

1mM BT / 0.1 M TBABF$_4$ in AN OR PC

1mM Pyrrole / 0.1 M TBABF$_4$ in AN OR PC

BT in AN Results

<table>
<thead>
<tr>
<th>Rotation Rate (rpm)</th>
<th>$i_{\text{ring}}/i_{\text{disk}}$ (percent)</th>
<th>BT in PC Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>107</td>
<td>1.97%</td>
<td>103</td>
</tr>
<tr>
<td>211</td>
<td>2.90%</td>
<td>205</td>
</tr>
<tr>
<td>312</td>
<td>2.75%</td>
<td>309</td>
</tr>
<tr>
<td>420</td>
<td>2.94%</td>
<td>407</td>
</tr>
<tr>
<td>518</td>
<td>2.79%</td>
<td>512</td>
</tr>
<tr>
<td>621</td>
<td>2.54%</td>
<td>613</td>
</tr>
<tr>
<td>717</td>
<td>2.88%</td>
<td>711</td>
</tr>
<tr>
<td>818</td>
<td>3.24%</td>
<td>818</td>
</tr>
<tr>
<td>927</td>
<td>3.22%</td>
<td>918</td>
</tr>
<tr>
<td>1019</td>
<td>3.22%</td>
<td>1015</td>
</tr>
</tbody>
</table>

Pyrrole in AN Results

<table>
<thead>
<tr>
<th>Rotation Rate (rpm)</th>
<th>$i_{\text{ring}}/i_{\text{disk}}$ (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>210</td>
<td>2.03%</td>
</tr>
<tr>
<td>410</td>
<td>3.25%</td>
</tr>
<tr>
<td>613</td>
<td>2.63%</td>
</tr>
<tr>
<td>819</td>
<td>1.64%</td>
</tr>
<tr>
<td>1014</td>
<td>1.85%</td>
</tr>
</tbody>
</table>
calculated to be about 17% through the use of a standard redox couple. The efficiencies are somewhat scattered due to difficulties in determining accurate limiting disk currents.

The results of a similar RRDE study of pyrrole is shown in Figure 19 and Table I. The behaviour of pyrrole is similar to the BT studies (within experimental error), and it is concluded that a similar mechanism is operative in both systems.

C) Spectrophotometric Studies

The rate of polyBT growth can be measured spectrophotometrically since the polymer has absorptions in the visible region. Spectra of neutral and oxidized polyBT are shown in Figure 21. The neutral polymer has a π-π* transition at 470 nm and the oxidized polymer shows this transition at 380 nm, indicative of the formation of bipolaron and polaron bands from the π and π* bands. The bipolaron transitions in the oxidized polymer are not shown; they probably occur in the Raman and infrared frequencies.

The growth of polyBT under a constant potential of +1.45 V was monitored at 720 nm for eight minutes. The absorbance was linear in t^{1/2} even over this long period as shown in Figure 22. This is in contrast to the results reported by Genies et al. [194] for the pyrrole polymerization, where the absorption was linear in t. However, the results for BT are consistent with the voltammetric and RDE data and thus it can be concluded that the reaction is limited by the diffusion of monomer to the electrode region, except at potentials low enough where the electron transfer becomes kinetically limiting.
Figure 21: Visible Spectra of Neutral and Oxidized PolyBT Coated on an SnO₂ Electrode.
Figure 22: Absorbance of a Growing PolyBT Film Plotted as a Function of $t^{1/2}$.

$\lambda = 720$ nm

Applied potential = +1.4 V vs. SCE
D) **Stepped Potential Experiments**

A technique similar to the one used by Prejza et al. [193] was used to study the initiation mechanism of BT and pyrrole. A series of stepped potentials was applied to a Pt electrode immersed in a solution containing the monomer, supporting electrolyte and solvent. The concentrations of monomer and supporting electrolyte were systematically varied throughout the experiment; concentrations of monomer ranged from $1.0 \times 10^{-4}$ M to $1.0 \times 10^{-1}$ M and concentrations of supporting electrolyte ranged from $1.0 \times 10^{-1}$ M to $1.0 \times 10^{0}$ M. The current responses were measured using fast data acquisition techniques on the Apple microcomputer, which is an improvement over the Prejza et al. technique of photographing oscilloscope traces. Examples of the current responses for the BT polymerization are shown in Figure 23. The initial currents were calculated by plotting $\log i$ versus $\log t$ and extrapolating to $\log t = 0$. The kinetic rate order for each species was determined by the relationship between $\log i$ and $\log [\text{monomer}]$ and $\log [\text{electrolyte}]$. This was calculated by data analysis (i.e. least-squares fitting programs on the computer). The results are shown in Table II.

Pyrrole and BT monomer have an apparent order of zero. This may be interpreted as indicative of an adsorption mechanism on the electrode, where the current is dependent on the adsorption isotherm and not the solution concentration of species. However, the first few msec of the stepped potential includes some non-faradaic current used to charge the electrode
Figure 23: Examples of Current Responses to Stepped Potentials of 0.2, 0.4, 0.6, 0.8, 1.0, 1.2 and 1.4 V vs. SCE.

\[ [\text{BT}] = 10.0 \text{ mM}, \ [\text{TBAP}] = 0.10 \text{ M in AN} \]
double layer. The time constant for the double layer charging can be estimated roughly from the RC values for the cell and the solvent. With $C \approx 20 \, \mu F$ and $R \approx 100 \, \Omega$ (estimated values for the system based on known values for double layer charging in a H$_2$O solution), the time constant is 2 milliseconds. This may explain a zero order initially, but it does not explain the near-zero order observed within 100 msec or so. Even though there is some capacitative current, it is still significant that no concentration dependence is seen for monomer, and it can be concluded that the reaction appears to have a zero order initially.

A further test of this zero order was performed with the BT monomer using a glassy carbon electrode instead of Pt. Similar current responses were obtained, and a zero order was found for the initial currents. A plot of log $i$ versus log $c$ ($c$ is the concentration of BT) is shown in Figure 24, with theoretical slopes of 1 and 2 also included. The data best fits around the zero slope. This figure is typical for all data performed using Pt or glassy carbon. Thus, if adsorption is operative, no difference is observed in the adsorption on Pt or glassy carbon electrodes.

However, for the BT polymerization at potentials greater than the voltammetric oxidation potential, the current develops a dependence on the monomer concentration at longer times. Table III shows apparent kinetic orders taken at 39 msec intervals of the applied potential. The kinetic orders may not be absolute here, because the current becomes diffusion-limited and the
Table II
Apparent Reaction Order at Various Applied Electrode Potentials for Monomer and Supporting Electrolyte

Reaction order at $t \to 0$ from $(d \log i)/(d \log c)$

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>0.2</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
<th>1.4</th>
<th>1.6</th>
<th>1.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,2'-Bithiophene System</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apparent Order ($\pm 0.1$) BT</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
<td>-0.1</td>
<td>0.1</td>
<td>-0.1</td>
<td>-0.1</td>
</tr>
<tr>
<td>Apparent Order ($\pm 0.1$) TBAP</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.3</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Pyrrole System</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Apparent Order ($\pm 0.1$) Pyrrole</td>
<td>0.1</td>
<td>-0.3</td>
<td>-0.2</td>
<td>-0.2</td>
<td>-0.3</td>
<td>-0.2</td>
<td>0.2</td>
<td>0.1</td>
<td>0.0</td>
</tr>
<tr>
<td>Apparent Order ($\pm 0.1$) TBABF$_4$</td>
<td>0.2</td>
<td>0.4</td>
<td>0.4</td>
<td>0.4</td>
<td>0.6</td>
<td>0.8</td>
<td>1.1</td>
<td>0.9</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Table III

Apparent Reaction Order for BT at Various Times

Applied Potential = +1.4 V vs. SCE
Reaction order at t=n from (d log i)/(d log c)

Results from the BT polymerization on a glassy carbon and a platinum electrode

<table>
<thead>
<tr>
<th>BT on Glassy Carbon</th>
<th>BT on Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>n (msec)</td>
<td>Apparent Order</td>
</tr>
<tr>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>39.0</td>
<td>0.2</td>
</tr>
<tr>
<td>78.0</td>
<td>0.4</td>
</tr>
<tr>
<td>117.0</td>
<td>0.5</td>
</tr>
<tr>
<td>156.0</td>
<td>0.5</td>
</tr>
<tr>
<td>195.0</td>
<td>0.6</td>
</tr>
<tr>
<td>234.0</td>
<td>0.7</td>
</tr>
<tr>
<td>273.0</td>
<td>0.8</td>
</tr>
<tr>
<td>312.0</td>
<td>0.9</td>
</tr>
<tr>
<td>351.0</td>
<td>0.9</td>
</tr>
<tr>
<td>390.0</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Figure 24: Log $i$ at $t \to 0$ vs. Log $c_{BT}$ for the BT Polymerization on a Glassy Carbon Electrode.

Applied potential = +1.4 V vs. SCE.
concentration of monomer around the electrode is continually depleted, nevertheless, this data shows that the reaction does not remain at zero order.

Table II shows that the supporting electrolyte has only a small apparent reaction order for the BT polymerization, but has an order of about 1 in the pyrrole polymerization at potentials higher than the pyrrole oxidation potential. These results are probably due to the presence of polymer on the electrode. Since the electrode was cycled back to 0.0 V after each potential step, any polymer that may have formed will have been reduced. Thus, the next potential step would involve the reoxidation of polymer, which is limited by the diffusion of anion into the film. The reaction order is not interpreted as being due to the oxidation of supporting electrolyte to form a radical species, as was concluded by Prejza et al. [193].

E) Monomer Consumption Experiments

To further clarify the reaction order of monomer, a macro experimental approach was undertaken. The rate of monomer consumption during polymerization was measured using g.c. analysis on samples of the polymerizing solution held at a constant potential. If the reaction is indeed zero order, then a linear relationship will be observed between the change in concentration of monomer and time. However, if the reaction is first order, a linear relationship should be observed between log concentration and time.

Initial studies of BT monomer depletion in an acetonitrile solution containing TBAP showed zero order in monomer
Figure 25: Changes in [BT] During Polymerization at a Constant Potential of +1.45 V vs. SCE.
Table IV

Experimental Results for the Polymerization of BT
Measured by G.C. Analysis

<table>
<thead>
<tr>
<th>Expt. Name</th>
<th>[BT]₀ /M (x 100)</th>
<th>[TBABF₄] /M</th>
<th>[TBAP] /M</th>
<th>% Conversion</th>
<th>$\frac{d\ln(BT)}{dt}$ (x 10000 sec⁻¹)</th>
<th>Charges per BT</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.248</td>
<td>0.10</td>
<td>-</td>
<td>34</td>
<td>3.73</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>1.020</td>
<td>0.10</td>
<td>-</td>
<td>27</td>
<td>2.64</td>
<td>2.2</td>
</tr>
<tr>
<td>C</td>
<td>0.945</td>
<td>0.10</td>
<td>-</td>
<td>32</td>
<td>3.37</td>
<td>2.2</td>
</tr>
<tr>
<td>D</td>
<td>0.844</td>
<td>0.10</td>
<td>-</td>
<td>41</td>
<td>4.67</td>
<td>2.1</td>
</tr>
<tr>
<td>E</td>
<td>0.602</td>
<td>0.10</td>
<td>-</td>
<td>45</td>
<td>5.07</td>
<td>2.3</td>
</tr>
<tr>
<td>F</td>
<td>0.392</td>
<td>0.10</td>
<td>-</td>
<td>36</td>
<td>4.41</td>
<td>3.6</td>
</tr>
<tr>
<td>G</td>
<td>1.441</td>
<td>-</td>
<td>0.10</td>
<td>43</td>
<td>4.96</td>
<td>1.5</td>
</tr>
<tr>
<td>H</td>
<td>1.076</td>
<td>-</td>
<td>0.10</td>
<td>33</td>
<td>3.46</td>
<td>1.8</td>
</tr>
<tr>
<td>I</td>
<td>0.724</td>
<td>-</td>
<td>0.10</td>
<td>31</td>
<td>3.46</td>
<td>2.7</td>
</tr>
<tr>
<td>J</td>
<td>0.598</td>
<td>-</td>
<td>0.10</td>
<td>47</td>
<td>4.40</td>
<td>1.9</td>
</tr>
</tbody>
</table>

Average of charges per BT = 2.3
concentration to conversions of 60% or better. An example of such a result is shown in Figure 25. However, these results were not always reproducible; repeat experiments did not show such ideal linearity.

However, further studies of BT demonstrated good first-order behaviour. Table IV shows the results of several polymerizations of BT varying the initial concentrations and varying the supporting electrolyte. A constant potential of +1.45 V was used in each run. Figures 26 and 27 show the plots of \( \ln [\text{BT}] \) versus time for each experiment. Identical slopes were plotted for comparison purposes. Thus, a good first-order behaviour is demonstrated. There seems to be no effect of supporting electrolyte, thus the electrolyte is not involved in the polymerization via a chemical reaction.

The percent conversion was calculated as the concentration of monomer used in the reaction divided by the initial monomer concentration. The charges per BT are calculated by dividing the total number of faradays passed by the number of moles of monomer used in the reaction. Even though there appears to be considerable scatter, the average number of charges per BT is about 2.3.

In the polymerization, two charges are needed for every monomer, since the polymer may grow at the 2 and 5' positions on the monomer. One charge is needed for coupling at the 2 position and another is needed for coupling at the 5' position. The additional 0.3 charges reflect the simultaneous oxidation of the polymer; one positive charge is delocalized over 3 to 5 monomer
Figure 26: First-Order Plots of BT Polymerization
(Experiments A to F).

Applied potential = +1.45 V. vs. SCE

$[\text{TBABF}_4] = 0.10 \text{ M}$
Figure 27: First-Order Plots of BT Polymerization
(Experiments G to J).

Applied potential = +1.45 V. vs. SCE

[TBAP] = 0.10 M
units in the chain.

However, even though the concentration profiles appear to be ideally first-order, the current behaviour in each experiment does not lead to the same conclusion. The rate of reaction in any normal first-order system decreases as the reactant conversion increases. Since the current is defined as the rate, it would be expected to approach zero as the reaction proceeds. This was seldom the case in these experiments; the current either remained constant or actually increased. For example, in experiment # I the current initially started at 25 milliAmperes, and nearly doubled by the end of the run after 31% of the monomer had been depleted. The current suggests that the rate of reaction is accelerating as more monomer is used up, and this does not fit into any proposed kinetic scheme. This particular problem was never solved; the electrodes were made smaller, the total solution volume was decreased, the RDE system was used in the same type of experiment to improve the hydrodynamic movement of solution, and the initial concentrations of monomer were decreased, all to no avail.

This particular difficulty can be attributed to the heterogeneous nature of the polymerization. As the polymer is formed, it deposits on the electrode and increases the total electrode area since it forms a conducting surface. Further, some of the charge may be used in polymer reactions (such as $\beta-\beta$ coupling, causing crosslinking) rather than monomer oxidation; this may be the reason for some of the scatter seen in the charges per BT calculations. There may be additional
reactions of the polymer with impurities in the solution. It was not possible to identify and control these factors, and thus this study was abandoned in favour of the experimental approaches which are presented in Chapters III and IV.

II. CONCLUSIONS

The irreversibility of the polymerization of BT was shown in the voltammetric data and the polymer was shown to have a lower oxidation potential than the monomer meaning that the polymer forms on the electrode in an oxidized, conducting state.

The polymerization appears to be first-order in monomer except in the very initial stages of the polymerization, where it is zero order. The zero order may be due to the occurrence of adsorption of monomer or double layer charging prior to faradaic charge transfer. The macro monomer consumption experiments show mostly first-order reactions, but the irreproducibility of repeat runs and the conflicting current behaviour does not allow an indisputable conclusion. The data are interpreted as due to the heterogeneous nature of the reaction.
CHAPTER III

PHYSICAL ORGANIC STUDIES OF THE POLYMERIZATION OF PYRROLE

III.1 INTRODUCTION

III.1.1 General Remarks

Some of the studies of the mechanism of the polymerization of pyrrole and related compounds were reviewed in the previous chapter. Although various mechanistic pathways are possible, the one gaining the greatest interest involves oxidative coupling of monomer molecules [194]. In general, to form polymer the monomer must diffuse to the electrode surface, lose an electron from the \( \pi \)-electron system and form a radical cation which by resonance will distribute some radical character to the \( \alpha \)-carbon [197]. Subsequently these radical cations will dimerize and then lose two protons (see Figure 28). A high concentration of radical cations at the electrode surface ensures the formation of high molecular weight species.

However, no detailed studies have been performed on the individual steps of the polymerization to determine the rate-limiting step. It has been suggested that proton loss in the above sequence is rate-determining. This fact can best be established by an examination of the kinetic isotope effect of the monomer and its deuterium-substituted analog. If the transition state in the polymerization mechanism proceeds by the
Figure 28: Proposed Mechanism for Oxidative Coupling Polymerization to Form Conducting Polymers.
Step:

1. $\text{monomer oxidation}$

2. $\text{radical coupling}$

3. $\text{expulsion} + 2H^+$

4. $\text{dimer oxidation and coupling with a monomer radical cation (chain growth)}$

$X = \text{NH(D), S, O}$
breaking of a C-H bond, then a large difference in the rate of the reaction will be observed when deuterium is substituted for hydrogen.

The coupling of radical cations has been proposed as the rate-limiting step \[194\]. If the reaction proceeds by a radical coupling or radical propagation mechanism, then the addition of a radical trapping agent to the polymerization will have the effect of inhibiting or retarding the reaction. However, if a cationic mechanism is involved, the addition of a radical trapping agent will have no effect. In a normal free-radical polymerization, a trapping agent has the effect of inhibiting the polymerization initially, then chain growth proceeds when the trap is depleted.

The first study in this section is the comparison of the rate of the polymerization of pyrrole and the rate of pyrrole-\textsuperscript{d5} (all protons are replaced by deuterium). Of particular interest is the presence or absence of a primary isotope effect which will suggest whether proton loss in the final step of the sequence is rate-determining. Three separate methods were chosen to measure these rates: cyclic voltammetry, quantitative gas chromatographic analysis of monomer uptake, and visible spectrophotometric analysis of the rate of polypyrrole growth.

The second study is a comparison of the rate of polypyrrole formation and the rate of polypyrrole formation in the presence of a radical trapping agent: 5,5-dimethyl-1-pyrroline-N-oxide (DMPO). A difference in the rates demonstrates whether the reaction proceeds by a radical
mechanism. This was measured by spectrophotometric analysis.

III.1.2 Isotope and Radical Trap Studies

There have been several publications which examine the isotope effect in electrochemical reactions [204-213]. These include deuterated solvent effects on the oxidation of water [204,205,207] and anodic oxidations of various organic compounds [206,208-211].

In the solvent effect studies, Salomon [204] performed a theoretical study on all of the steps involved in the anodic water-splitting reaction where oxygen is evolved. He found that various isotope effects could occur depending on the reaction conditions.

Kuhn and Byrne [205] studied the deuterium isotope effects in the hydrogen evolution reaction on gold electrodes. They found similar exchange current densities for the deuterated and non-deuterated compounds, and suggested a mechanistic model consistent with their results.

Weaver et al. [207] found that the electron transfer kinetics to various transition-metal complexes was affected by the deuteration of the water solvent. Values of $k_H/k_D \approx 2$ were obtained, and it was concluded that electron transfer was affected by the hydrogen bonding on the ligands to the solvent molecules.

In the anodic oxidation studies, Shono et al. [206] found an isotope effect in the oxidation of carbamates and determined
that proton loss in an oxidized carbamate occurred through a
direct electron transfer process rather than through abstraction
by another species.

Van Effen and Evans [208] found primary deuterium isotope
effects in the oxidation of aldehydes, and suggested a mechanism
based on the cleavage of the α-carbon-hydrogen bond as the rate-
limiting step. This was studied using linear sweep voltammetry,
and equations were derived to calculate the values of $k_H/k_D$ from
the currents of the deuterated and non-deuterated compounds.

There have been several studies of isotope effects in
outer-sphere electron transfer reactions [211-213]. In general,
this technique was not used to study a C-H or O-H bond breaking,
rather, it was used to demonstrate the proton coupling in the
electron transfer and to determine the reaction kinetics.

Several other publications describe deuterium isotope
effects in various polymerizations [214-220]. Polymerization by
a free radical mechanism generally yields no isotope effect
[219,220] as no C-H bond is broken in the transition state.
However, isotope effects were seen in termination, chain-
transfer, or branching reactions [214-218].

While this work was in progress, a study on the isotope
effect in the electropolymerization of thiophene was published
[221]. The peak oxidation potentials, the conductivities and the
doping levels of non-deuterated and deuterated polythiophenes
were compared and no difference was observed for any of the
samples. No isotope effect was found and thus proton loss is
not rate-limiting, and the authors concluded that a mechanism of
neutral monomer addition to a radical cation species was consistent with their results.

The technique of spin trapping in electrochemical systems is gaining acceptance as a useful tool in studying reaction mechanisms. One such study examined the electrochemical behaviour of various nitroso compounds and their application as traps in the reduction of alkyl halides [222]. It was found that a nucleophilic attack of the halide by the nitroso radical anion occurred under certain conditions.

Radical scavengers have been used in polymerization studies; for example in the study of the emulsion copolymerization of acrylonitrile and butyl acrylate [223]. The kinetics of the copolymerization and the molecular weights were affected by the presence of hydroquinone.

III.2 EXPERIMENTAL

Pyrrole (pyr) (Aldrich) was distilled in a rotating band column of ca. 100 theoretical plates. Pyrrole-d5 (pyr-d) (MSD Isotopes) was used as received, but stored at 0°C in the dark and under Ar atmosphere in a vial sealed with a silicone rubber disk to allow withdrawals by syringe. The radical trapping species 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) (Aldrich) was stored under Ar at 0°C.

Acetonitrile (AN) (Caledon, HPLC grade) was distilled over CaH₂ and stored over 4 Å molecular sieves and under argon. Tetrabutylammonium tetrafluoroborate (TBABF₄) (Aldrich) was dried
for several days in vacuo. All electrochemical solutions were thoroughly bubbled with argon and kept under an argon atmosphere throughout the course of the experiment.

The voltammetric experiments utilized a small (25 ml) two-compartment cell fitted with a 2.3 mm\(^2\) Pt disk working electrode and a Pt wire counter electrode.

Quantitative gas chromatographic measurements were undertaken on a solution undergoing electrochemical polymerization in a 150 ml. three-compartment H-cell with a septum-covered sidearm. The working electrode was a 2.6 cm\(^2\) Pt gauze and the counter was a 7.8 cm\(^2\) Pt gauze. The solutions in the working compartment were stirred by a magnetic stirrer at a constant speed of 634 r.p.m. Solution samples for g.c. analysis were withdrawn through the sidearm by syringe and then mixed with an internal standard and injected into the gas chromatograph.

The spectrophotometric experiments utilized an H-type cell fitted with a 1 cm spectro-cell. Because of the configuration of the cell, it was not possible to stir these solutions. A 0.4 x 1.2 cm indium-doped tin-oxide coated glass electrode (Applied Physics Specialties, resistivity ca. 6 \(\Omega\)/square) was used as the working electrode, and a large Pt gauze was used as the counter. The working electrode was positioned in the beam of the spectrophotometer so that the polymer buildup on the electrode would be measured continuously. The glass electrode was constructed by masking a 0.4 x 1.2 cm area with electricians' tape, connecting a wire to the surface with an Electrotrag
contact, and then covering all exposed areas with epoxy resin. The tape was pulled off leaving a well-defined surface area when the epoxy had cured enough to prevent any flow, but prior to complete cure. The electrodes were cleaned with acetone prior to use. Variations in electrode area were within 5%.

All experiments employed an SCE reference, connected to the cell by an aqueous Agar bridge and a Luggin capillary filled with the organic electrochemical solution.

An EG&G PAR model 173 potentiostat / galvanostat was used, along with a model 175 universal programmer and a model 179 digital coulometer. A Perkin-Elmer Lambda 3A uv/visible spectrophotometer was used for the spectrophotometric experiments, and a Hewlett-Packard model 5890A gas chromatograph for the monomer uptake experiments. Some of the data were collected on an Apple II+ computer with Interactive Microware hardware and software.

All experiments were kept to low conversion to minimize the polymer buildup on the electrode surface. At higher conversions with correspondingly higher film thicknesses, the current is increasingly variable and the rate data are less consistent. This is attributed to an increased surface area available for polymerization. Electron micrographs clearly show surface non-uniformity of conducting polymer films [222,224]. The inconsistency of results especially at higher conversions is explained by variations in the morphology of the film.
III.3. RESULTS

III.3.1 Isotope Studies

A) Voltammetric Experiments

Several voltammograms at different scan rates were performed on pyrrole and pyrrole-d5 (see Figures 29 and 30). A freshly polished electrode was used for each scan. The electrode was conditioned prior to each experiment by electrochemical cycling in 6 M H₂SO₄ for several scans.

The voltammograms show diffusion-limited peak currents (ip), as shown by the linear relationship between ip and (scan rate)¹/² (Figure 31). In fact, the peak currents of both monomers are nearly identical (within experimental error). Therefore, the mass transport limited current is approximately the same for both monomers.

A relationship between k_H/k_D and the current in the voltammogram as previously derived [208] is given by:

\[ \frac{k_H}{k_D} = \frac{i_H/i_D}{(i_{p,H}/i_{p,D})(i_{p,D} - 0.773i_D)/(i_{p,H} - 0.773i_H)} \]  

(23)

The 0.773i_H and 0.773i_D terms in this equation are corrections for the diffusion-limited current. The mass-transport limited current is approximated as the peak current giving rise to some scatter in the results. The rate constant ratio was evaluated using the pyrrole and pyrrole-d5 data at several potentials between 0.5 V and 1.0 V vs. SCE at scan rates of 10, 20, 50, 100 and 200 mV/sec. Table V provides an summary of the voltammetric results for all scans. The average k_H/k_D for all scan rates over
Figure 29: Cyclic Voltammograms of 1.0 mM Pyrrole / 0.10 M TBABF₄ / AN at Scan Rates of 100, 200 & 500 mV/sec.
Figure 30: Cyclic Voltammograms of 1 mM Pyrrole-d5 / 0.10 M TBABF₄ / AN at Scan Rates of 100, 200 & 500 mV/sec.
Figure 31: Plot of Peak Current ($i_p$) of Pyrrole and Pyrrole-d5 Versus (Scan Rate)$^{1/2}$.

Square symbols = pyrrole, diamond symbols = pyrrole-d5.
the whole range of potentials was found to be 1.2±0.8. At potentials just below the peak potential where faradaic charge transfer is still significant (ie. between 0.6 and 0.7 V vs. SCE), \( k_\text{H}/k_\text{D} \) is 1.5±0.9. At potentials above the peak, the ratio is 0.8±0.3.

**B) Monomer Consumption Experiments**

The rate of monomer consumption was measured by quantitative gas chromatographic analysis. Small samples were withdrawn from the polymerizing solution and an internal standard was added prior to injection into the g.c.

Figures 32 and 33 show examples of the rate of monomer consumption of pyrrole and pyrrole-d5 at 1.0 V vs. SCE. The graphs were plotted as log concentration versus time to compare the first-order rates, but the values of the calculated rates are dependent on factors such as electrode area and the applied potential. Nevertheless, since the experimental conditions are
constant in each run, the values are comparable. Assuming a first order rate dependence for monomer consumption (rate = \( k[\text{monomer}] \)), the average values of \( k_0 \) and \( k_d \) were measured at \( 3.8 \times 10^{-5} \pm 1.3 \times 10^{-5} \text{ sec}^{-1} \) and \( 6 \times 10^{-5} \pm 3 \times 10^{-5} \text{ sec}^{-1} \), respectively. Error values report the standard deviations of repetitive runs. Our calculation of experimental error is approximately 4% due to sampling and g.c. errors. Thus the variation seen in these results is due to other factors, one of which we assume is the inconsistent manner with which polymer is coated onto the electrode. The average value for the \( k_0/k_d \) ratio is about 0.7 but may vary from 0.3 to 1.7.

An underlying assumption in the monomer consumption experiments is that the rate of monomer uptake and polymer formation are equal. This is true if there is no build-up of intermediate species after the monomer oxidation. In each of the experiments, polymer is observed to form on the electrode quickly, and the g.c. trace shows no evidence of dimeric, trimeric, or tetrameric materials; thus this assumption appears valid.

C) Rate of Polymer Growth Experiments

The polymer growth rate was measured in situ at a potential of +1.40 V. vs. SCE and at a wavelength of 460 nm which is close to the absorbance maximum of oxidized polypyrrole [225]. The spectra of polypyrrole and polypyrrole-d are nearly identical, so the comparison of polymer growth at this wavelength is valid, and needs no normalization. The monomer shows no significant absorbance at 460 nm.
Figure 32: Decrease in Monomer Concentration During the Polymerization of Pyrrole.

Applied potential = +1.0 V vs. SCE.
Figure 33: Decrease in Monomer Concentration During Polymerization of Pyrrole-d5.

Applied potential = +1.0 V vs. SCE.
Examples of the coulombic uptake and absorbance responses in the polymerization of pyrrole and pyrrole-d5 are shown in Figures 34 and 35 respectively. For this particular series, values of $i_H/i_D$ ($k_H/k_D$) were calculated along the curve at various times, and the average value was found to be $1.6 \pm 0.7$. Repeated experiments show similar scatter.

On a short time scale ($0 - 10$ seconds), the current ratio $i_H/i_D$ was measured at $1.02 \pm 0.03$. Repeated experiments generally yield values of close to one for $i_H/i_D$ at short initial time intervals.

In the early seconds of a stepped potential electro-polymerization, the current is nearly ideally diffusion limited, convection effects are minimal and the growing film is still very thin. Thus the errors which produce variability in results are reduced in comparison to longer experiments. We thus assume that for polymer growth experiments the $k_H/k_D$ ratio ideally is one.

The polymer growth rate was also measured at $0.75$ V vs. SCE (slightly lower than the peak potential), where the transport of monomer to the surface is not limiting. The results from this experiment (see Figure 36) yield a $k_H/k_D$ of approximately 1.

All of the data for the isotope studies is summarized in Table VI.
Figure 34: Charge Passed to Pyrrole and Pyrrole-d5 During the Spectrophotometric-analyzed Polymerization.

Applied potential = +1.4 V. vs. SCE.
Figure 35: Absorbance Response of Pyrrole and Pyrrole-d during the Spectrophotometric-analyzed Polymerization.

Applied potential = +1.4 V. vs. SCE

\( \lambda = 460 \text{ nm} \).
Figure 36: Absorbance Response of Pyrrole and Pyrrole-d5
During the Spectrophotometric-analyzed
Polymerization.

Applied potential = +0.75 V. vs. SCE

$\lambda = 460 \text{ nm.}$
TABLE VI

Summary of the Isotope Effect Results

<table>
<thead>
<tr>
<th>Technique</th>
<th>$k_H/k_D$</th>
<th>$k_H/k_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;0.75 V</td>
<td>&gt;0.75 V</td>
<td></td>
</tr>
</tbody>
</table>

Technique:

- Voltammetry
  - a) comparison of $i(t)$: 1.5 ± 0.9
  - b) peak current: 1.0
- G.C. Monomer Consumption Analysis
- Spectrophotometric Measurements: $\approx 1 $ 1.02 ± 0.03

III.3.2 Radical Trap Studies

Figure 37 shows the rate of growth of polypyrrole measured by spectrophotometric analysis in the DMPO-containing and DMPO-free solutions. The experiment was repeated several times and similar results were obtained. No polypyrrole growth ever occurred in a solution containing DMPO; the polymerization was completely inhibited.

Cyclic voltammetry of DMPO revealed no anodic oxidation of the compound in the potential ranges used for pyrrole oxidation and thus no interfering oxidation of DMPO occurs when pyrrole is oxidized. ESR studies were attempted, but they failed because of the signal interference of the high dielectric solvents.

DMPO was chosen for this study because of its inertness to self-dimerization, ready availability and similarity in structure to pyrrole. DMPO bonds with other radical species at
the α-carbon, similar to the pyrrole reactions. The structure of DMPO is shown in Figure 38.

Figure 38 also shows the reaction pathways available for the pyrrole radical cation. The results indicate $k_r >> k_0$.

III.4 DISCUSSION

A mechanism for the polymerization is shown in Figure 28. The three possibilities for the rate-limiting step are: 1) the monomer oxidation, 2) the radical coupling, or 3) the proton expulsion. None of the measurements in this study approach a value of $4 - 7$ indicative of a primary isotope effect. Thus, proton loss (step 3) is not the rate-determining step in oxidative polymerization. The rate-limiting step must be either step 1 or step 2.

An alternative mechanistic scheme has been recently proposed [192,201]. This mechanism has two steps: 1) monomer oxidation and proton loss and 2) radical propagation on a neutral monomer molecule accompanied by oxidation and proton loss. This is shown in Figure 39. The electrochemical stoichiometry in this mechanism is the same as in Figure 28, but one would expect to find a primary isotope effect if this mechanism were true, since each step includes the loss of a proton. As this is not the case, it is not a realistic mechanism.

These results suggest that either a normal or inverse secondary isotope effect is present in these polymerizations.
Figure 37: Growth of Polypyrrole in DMPO and DMPO-free Solutions Measured Spectrophotometrically.

$\lambda = 460$ nm.

Applied potential = +1.45 V vs. SCE

$[\text{Pyrrole}] = [\text{DMPO}] = 1.0$ mM
Figure 38: Structure of DMPO and Reaction Pathways of Pyrrole and DMPO.
5,5-dimethyl-1-pyrroline-N-oxide (DMPO)

\[
\text{CH}_3\text{N}\overset{\text{O}}{\text{H}} + \text{C}_3\text{H}_6\overset{\text{O}}{\text{N}} \stackrel{k_T}{\longrightarrow} \text{C}_3\text{H}_6\overset{\text{N}}{\text{N}}\text{H} + \text{CH}_3\text{N}\overset{\text{O}}{\text{H}} - \text{H}^+ 
\]

\[
\text{C}_3\text{H}_6\overset{\text{N}}{\text{N}}\text{H} + \text{C}_3\text{H}_6\overset{\text{N}}{\text{N}}\text{H} \stackrel{k_D}{\longrightarrow} \text{C}_3\text{H}_6\overset{\text{N}}{\text{N}}\text{H} - 2\text{H}^+ 
\]

\[k_T \gg k_D\]
The voltammetric experiments possibly indicate a normal secondary effect below the peak potential and an inverse secondary effect above the peak. The stirred monomer consumption experiments suggest an inverse secondary effect at a mass transport - limited potential. The spectrophotometric experiments suggest a normal secondary effect over a long time period but no isotope effect in the first few seconds of the run. In all cases, the uncertainties in the calculated $k_h/k_d$ values are large enough to preclude a firm conclusion on the presence or absence of a secondary effect. Secondary effects are normally associated with hybridization changes in the transition state or hyperconjugative effects [152] none of which are predicted by the mechanism for electrochemical polymerization in Figure 28. Thus, evidence of secondary effects (normal or inverse) may simply be due to experimental errors.

According to Figure 28, oxidation of monomer at the electrode involves diffusion of monomer to the electrode followed by oxidation. As the potential increases the rate of monomer oxidation increases steadily and eventually the rate of monomer transport to the electrode becomes rate-limiting. At potentials below the peak potential, the electron-transfer is slow relative to mass transport. The absence of a primary isotope effect here (shown in the voltammetry and spectrophotometric experiments) suggests that electron transfer limits the entire scheme.

Much of the data has been gathered at potentials where mass transport of monomer is limiting; i.e. potentials above the
Figure 39: Proposed Mechanism for Free Radical Propagation Polymerization to Form Conducting Polymers.
Step:

1. \[
\text{monomer oxidation & proton loss}
\]

2. \[
\text{radical propagation oxidation & proton loss}
\]

3. chain growth

\[X = \text{NH(D), S, O}\]
peak. All of these results show no primary isotope effect. Thus it is concluded that at potentials higher than the peak potential proton loss is not the rate controlling step.

The rate of polymer growth at 0.75 V experiments and the voltammetric experiments demonstrate no isotope effect. There is some scatter in the results, nevertheless, it is concluded that proton loss is also not the rate controlling step at potentials where mass-transport is not limiting.

The voltammetric experiments reveal that the peak currents of pyrrole and pyrrole-d5 are approximately equal at several scan rates. This fact alone demonstrates the absence of a primary isotope effect. Results by Beltowska-Brzezinska and Vielstich [209] show that a primary isotope effect in the oxidation of alcohols can be seen by the comparison of the peak currents of the deuterated and non-deuterated compounds. In their study, the peak currents yielded an \( i_\text{H}/i_\text{D} \) ratio of close to 7. However, the results in this work do not demonstrate this.

The second step in the mechanism for oxidative coupling is proposed as a radical coupling between \( \alpha \) - carbons where the radical is present in a p-orbital. It was previously suggested that a hybridization change must take place to allow formation of a \( \sigma \) - radical at the \( \alpha \) - position before coupling occurs [195]. However, INDO calculations by Waltman and Bargon [197] indicate that radical coupling at the \( \alpha \) or \( \beta \) - carbon takes place preferentially between \( \pi \) - radicals. Their calculations imply coupling without the prior formation of a \( \sigma \) - radical, and thus a high energy step is avoided. Figure 40 shows the
mechanism of coupling. However, it should be noted that the $\alpha - \alpha'$ bonds are not through the $p_z$-orbitals on the carbon; a $\sigma - \sigma$ bond must form. This coupling mechanism must be accompanied by an electron promotion to the $\pi$-system in each ring and proton loss. Nevertheless, the initial attraction of radical species may occur through the $p_z$-orbitals.

Mechanistically it is possible that steps 2 and 3 might be concerted, with the $\sigma - \sigma$ bond forming as the proton leaves. Thus the mechanism would consist of two steps rather than three. The absence of a primary isotope effect then indicates that monomer oxidation is the rate-determining step in the reaction sequence.

Although the radical coupling step or the radical propagation step may be the rate-determining step as suggested previously [4,194,221], the radical trap experiments only show that the oxidized monomer species reacts with the trap at a faster rate than it reacts with another monomer species; they do not necessarily suggest that radical combination or propagation are rate-determining. However, there is some evidence in this study that the oxidized pyrrole behaves more as a pure radical than a cation or even a radical cation. A species with cationic character would not be expected to react with DMPO in the same manner as a radical. If the cation is extensively delocalized in the $\pi$-system, the cationic character becomes minimal. Alternatively, proton expulsion and rearomatization of the ring may occur before the coupling. In this case, steps 2 and 3 in Figure 28 would be reversed, and the radical would not be in the
Figure 40: Proposed Mechanism of Radical Coupling.
\[ X = \text{NH}_2, \text{OH} \]
π - system but would reside in a localized σ - orbital on the α - carbon. Such a mechanism has been previously proposed for the polymerization [226].

On the other hand, it is not surprising that the radical cation would prefer to react with DMPO rather than with another radical cation. Coulombic repulsions between charged species make dimerization electrostatically unfavourable and thus a reaction with a reactive neutral species is favoured.

Conceptually, when the pyrrole is first oxidized at the electrode, a depletion layer forms and neutral pyrrole monomer begins to diffuse in from the bulk. DMPO is unaffected by the anodic potential, but it reacts with the oxidized pyrrole in the depletion layer and thus both pyrrole and DMPO are depleted in the layer next to the electrode. DMPO and pyrrole then must both diffuse in from the bulk and the spin adduct diffuses away into the bulk solution. Pyrrole is then oxidized and once again reacts with the DMPO. The fact that the polymerization is completely inhibited indicates that the diffusion rates of pyrrole and DMPO are either equal or that the rate of DMPO is greater than the rate of pyrrole. If this were not the case, an excess of reactive pyrrole radical cations would build at the surface and some polymerization would occur. This was not observed.

However, it may be concluded that the radical recombination is the rate-limiting step in the chemical steps of the polymerization, and that the entire polymerization is limited by slow diffusion of the monomer to the growing polymer.
film.

III.4 CONCLUSIONS

The rate of polymerization of pyrrole and pyrrole-d$_5$ by electrochemical oxidation has been shown to be similar by voltammetric experiments, rate of monomer consumption experiments, and rate of polymer growth experiments. There is certainly no primary effect, but it cannot be statistically determined whether a secondary effect is present or absent. At low potentials the monomer oxidation step may be the rate-determining step, and at high potentials, the polymerization becomes limited by the diffusion of monomer to the electrode after the voltammetric peak potential.

The rate of polymerization of pyrrole is completely inhibited by a radical trapping species. These experiments do not necessarily indicate radical coupling is the rate-determining step, but they prove that the pyrrole is reacting by a mechanism which requires free radicals.
CHAPTER IV

STUDIES OF SOLUBLE POLY(3-METHOXYTHIOPHENE)

IV.1 INTRODUCTION

IV.1.1 General Remarks

Poly(3-methoxythiophene) (Poly(MeOT)) is classified as an organic conducting polymer, in the same class as polypyrrole, polythiophene and related compounds. However, unlike most of the conducting polymers, poly(MeOT) is soluble in most organic solvents in either the oxidized or reduced form or both and thus molecular weight analysis can be performed.

Poly(MeOT) is formed in an electrochemical cell by applying a constant potential to a solution containing MeOT monomer and some supporting electrolyte, or alternatively by applying a constant current. The polymer will either form in solution or precipitate on the anode surface, depending on the choice of solvent and the choice of supporting electrolyte. Most of the other conducting polymers (e.g. thiophene, pyrrole, etc.) will precipitate on the electrode.

The mechanism of formation of poly(MeOT) is thought to be the same as for the polypyrrole or polythiophene polymers; i.e. by an oxidative coupling mechanism. The monomer diffuses to the electrode, loses an electron to form a radical cation, couples with another radical cation, then expels two protons to form a
neutral dimer. The dimer then reoxidizes at the electrode (at a lower potential than the monomer) and then will couple with another radical cation species to propagate the polymerization. This mechanism predicts a large range of molecular weights since nothing is expected to limit the random addition of radical cation species to polymer chains. In addition, the solution should show evidence of very low molecular weight species (e.g. dimers, trimers, tetramers, etc.).

IV.1.2. Studies of Soluble, Conducting Polymers

The initial studies of soluble conducting polymers utilized novel solvents such as AsF₃ to dissolve normally insoluble polymers such as polyacetylene, poly(p-phenylene sulfide) and the polyheterocycles [227,228]. The reasons for the solubility are unclear, but it appears as if there is an electronic interaction between the solvent and the polymer in its conducting state; specifically, an interaction occurs between the inorganic dopant ions and the solvent. However, this does not satisfactorily explain the nature of the solubility of the organic polymer backbone. Nevertheless, the most remarkable feature of this work was that all electronic and characterization studies were performed in solution rather than in the less-versatile solid state.

Poly(3-methylthiophene) and polythiophene prepared by catalytic coupling of the brominated monomer using the Grignard reagent were shown to have a small fraction soluble in organic
solvents [229,230]. These polymers were then characterized in solution using voltammetric and spectroscopic techniques.

Two studies of soluble polyaniline have been published. First, soluble polyaniline was synthesized by a long-time extraction into a NaOH-THF solvent mixture, but the solubility was quite low [231]. Second, polyaniline was synthesized using large size organic proton acids as a supporting electrolyte [232]. However, only the protonated (oxidized) polyaniline was soluble in this method. Nevertheless, the gel permeation chromatography technique was used to determine molecular weights, which was probably the first use of this technique for conducting polymers.

The polymers made from 3-alkylthiophenes have generated the greatest research interest in soluble conducting polymers [233-248]. In general, the monomers are synthesized using a nickel-catalyzed Grignard coupling of 3-bromothiophene and an alkylmagnesium bromide. The polymers were then synthesized electrochemically by the method described previously. Both the environmental stability (i.e. insensitivity to air) and the solubility increased with increasing chain length of the alkyl substituent [235,236].

Several papers report that 3-(alkylsulfonate thiophenes) are water-soluble [237-239]. These polymers exist as sodium or lithium salts and are thus soluble in their ionized form. The unique feature of these polymers is that a negative charge resides on the sulfonate group when dissociated in solution which in turn stabilizes the positive charge on the conducting
polymer backbone. Thus, these polymers are called "self-doped".

Two molecular weight studies have been performed on the 3-alkylthiophenes. Using vapour phase osmometry, Sato et al. [240] found that the degrees of polymerization of poly(3-hexylthiophene), poly(3-octylthiophene) and poly(3-dodecylthiophene) were 230, 140 and 90, respectively. Using HPLC techniques, Hotta et al. [244] found that the weight-average molecular weight of poly(3-hexylthiophene) was 48,000, corresponding to a degree of polymerization of 300.

Only a few studies exist on poly(3-methoxythiophene) [248-253], and only four of these [248,250,252,253] discuss the solubility of this polymer. The reduced (neutral) polymer was found to be soluble in several organic solvents including acetonitrile, dichloromethane, acetone and dimethylformamide, but the oxidized polymer was found to be soluble only in dimethylformamide [250]. A molecular weight analysis of the material formed in a water-acetonitrile solvent mixture showed that the chain length was only 5 or 6 units in length [252,253]. It is thus classed as an oligomer rather than a polymer.

A potential application of a poly(3-methoxythiophene) film was described by Blankenspoor and Miller [250], who used it for the controlled release of the neurotransmitter glutamate.

The only bipolaron study of soluble conducting polymers was performed on poly(3-hexylthiophene) [246]. It was found that the spinless bipolaron was the lowest energy charge storage configuration, but that polarons were formed as a result of odd numbers of charges in a single chain or as a result of
interchain interactions.

IV.2 EXPERIMENTAL

MeOT monomer was synthesized using the synthesis described previously [254]. The monomer was purified by vacuum distillation and was found to contain only a small fraction (< 2%) of the isomer 2-methoxythiophene by gc/mass spectrometry results.

Dimethylformamide (DMF) (BDH) was distilled in a vacuum spinning band column of ca. 1000 theoretical plates. Acetonitrile (AN) (Caledon, HPLC grade) was used without further purification. Distilled water from the SFU distilling system was used without further purification.

Tetrabutylammonium tetrafluoroborate (Aldrich) was dried for several days in vacuo and was used in the polymerizations in DMF. Lithium perchlorate was used without further purification in all polymerizations with water as a solvent or co-solvent. In all cases, the concentration of supporting electrolyte was $1.0 \times 10^{-1}$ M and the initial concentration of monomer was about 10 mM.

The monomer depletion and molecular weight experiments initially used a small (15 ml) one-compartment cell with a large (ca. 2 cm. x 4 cm.) unimesh Pt gauze working electrode and a large coiled Pt gauze counter electrode. However, it was found that the products from the counter electrode (presumably some reduced species) interfered with the oxidized products from the working electrode, and therefore all the data from these runs were discarded.
For the results described here a 50 ml. three-compartment electrochemical cell was used. The cell was fitted with the same electrodes as described before and with an SCE reference electrode connected to the cell with an external Luggin capillary. A EG&G PAR Model 173 potentiostat with a model 179 coulometer were utilized in these experiments. The currents were recorded on an x-t chart recorder.

For the monomer depletion experiments, a 25 μl sample of the electrochemical solution was withdrawn from the working compartment using syringe techniques at regular time intervals and mixed with 25 μl of a solution of an internal standard (specifically, 1.0 x 10^{-2} M naphthalene in AN) and a 1 μl sample of this sample was injected into a Hewlett-Packard Model 5890A gas chromatograph for concentration analysis. The data were collected on an Apple II+ computer equipped with Interactive Microware hardware and software.

For the molecular weight experiments of polymer formed in a completely soluble system, 0.5 to 2.0 ml samples were withdrawn from the working compartment at various times, filtered and then injected a Waters Associates gel permeation chromatograph (GPC) equipped with a differential refractometer detector and three columns packed with Styragel with pore sizes ranging from 500 to 5000 Å. In the experiments where the polymer precipitated on the electrode, the electrode was withdrawn and washed with about 2 ml of DMF to dissolve the polymer. The DMF solution was then injected into the GPC.
IV.3 RESULTS AND DISCUSSION

IV.3.1 Polymerization of MeOT in DMF

A) Monomer Depletion and Coulombic Efficiency Experiments

MeOT and poly(MeOT) are completely soluble in DMF. Two separate experiments measured the rate of monomer depletion; one measured to 50% monomer depletion and the other to 86% monomer depletion.

The first experiment (to 50% completion) demonstrated a current behaviour typical of an electrochemical reaction where the reactant is being depleted at a first order rate (Figure 41). The rate of monomer depletion is shown in Figure 42. A nearly ideal first order reaction is observed with \( k = 8.11 \times 10^{-5} \ \text{sec}^{-1} \), using the expression \( \text{Rate} = k [M]^a \) where \([M]\) = monomer concentration, \(k\) = rate constant and \(a\) = order of the reaction. This is only an estimate of the rate constant, since this is a relative rate, dependent on factors such as the electrode area, rate of stirring, etc.. These values are not meaningful on an absolute scale, and should only be used on a comparison basis. A graph of the extent of monomer conversion during the course of the experiment is shown in Figure 43.

The coulombic efficiency was measured by comparing the number of Faradays passed with the amount of monomer used. A graph of the concentration of monomer versus the charge passed is shown in Figure 44. The monomer initially is depleted at the same rate as the charge, but then at later times, more charge is
Figure 41: Current Response of the MeOT Polymerization in DMF (to 50% Conversion).

Applied potential = +1.6 V vs. SCE
Figure 42: First-Order Plot of [MeOT] During the Polymerization in DMF (to 50% Conversion).

Applied potential = +1.6 V vs. SCE
Figure 43: Extent of MeOT Conversion During the Polymerization in DMF (to 50% Conversion).
Figure 44: Concentration of MeOT versus Charge for the MeOT Polymerization in DMF (to 50% Conversion).
passed than monomer is depleted. This can be understood as follows: the initial solution only contains monomer and supporting electrolyte but as the reaction proceeds, polymer is formed and will compete with monomer for oxidation. Thus, at higher conversions, some of the charge will be absorbed by the polymer. The average number of electrons passed per monomer molecule is 3.76. This is higher than the expected value of about 2.20 – 2.30, and results in a coulombic efficiency of only 65%. This is in contrast to the earlier bithiophene experiments where the efficiency was close to 100%. However, it should be noted that this is a completely soluble system whereas the bithiophene was completely insoluble. Also, since DMF is a solvent with basic character, it may act as a Lewis base toward the conducting polymer and some solvent interaction with the polymer may serve to "dedope" the chain, thereby necessarily causing a greater amount of electron transfer to the polymer. In addition, the presence of water and other impurities in the solution may account for the low efficiency.

A summary of the data from this experiment is shown in Table VII.

The second experiment (to 86%) was nearly identical to the first, except that the polymerization was allowed to proceed much longer. Table VIII shows a summary of this data, Figure 45 shows the current response, Figure 46 shows the rate of monomer depletion with time, Figure 47 shows the reaction conversion with time and Figure 48 shows the nonlinear relation between the monomer concentration and the charge passed. The constant in
### TABLE VII.

Data From the Polymerization of MeOT in DMF to 50% Conversion

| Time (min) | Time (sec) | Current (mA) | Charge (Coul.) | Conc'\n| MeOT mole/L | % Conv'n | Charges per molec. | % Effic. |
|------------|------------|--------------|----------------|-----------------|
| 0          | 0          | 12.0         | 0.00           | -               | 0.0% | - | - |
| 4          | 240        | 6.3          | 1.40           | -               | - | - | - |
| 7          | 420        | 5.9          | 2.48 9.46E-03  | 3.0%            | 3.68 | 61.2% |
| 10         | 600        | 5.7          | 3.56 9.55E-03  | 2.0%            | 7.73 | 29.1% |
| 18         | 1080       | 5.4          | 6.12 8.91E-03  | 8.6%            | 3.16 | 71.2% |
| 25         | 1500       | 5.1          | 8.27 8.54E-03  | 11.4%           | 3.22 | 69.8% |
| 42         | 2520       | 4.8          | 13.23 7.74E-03 | 20.6%           | 2.84 | 79.3% |
| 60         | 3600       | 4.6          | 18.33 7.32E-03 | 24.9%           | 3.26 | 69.0% |
| 76         | 4560       | 4.4          | 22.62 6.60E-03 | 32.3%           | 3.10 | 72.6% |
| 100        | 6000       | 4.0          | 28.90 5.94E-03 | 39.0%           | 3.28 | 68.6% |
| 151        | 9060       | 3.9          | 40.97 4.76E-03 | 51.1%           | 3.55 | 63.4% |

Average charges per molecule = 3.76
Average % efficiency = 64.9%
Figure 45: Current Response of the MeOT Polymerization in DMF (to 86% Conversion).

Applied potential = +1.6 V vs. SCE
Figure 46: First-Order Plot of [MeOT] During the Polymerization in DMF (to 86% Conversion).

Applied potential = +1.6 V vs. SCE
Figure 47: Extent of MeOT Conversion During the Polymerization in DMF (to 86% Conversion).
Figure 48: Concentration of MeOT versus Charge for the MeOT Polymerization in DMF (to 86% Conversion).
Concn. Meq/L / mole L⁻¹ (× 10⁻³)

Charge / coul
Figure 49: Coulombic Efficiency Changes During the Course of the Polymerization of MeOT.
### TABLE VIII

Data From the Polymerization of MeOT in DMF to 86% Conversion

<table>
<thead>
<tr>
<th>Time min</th>
<th>Time sec</th>
<th>Current mA</th>
<th>Charge Coul.</th>
<th>Conc'n MeOT mol/L</th>
<th>% Conv'n</th>
<th>Charges per molecule</th>
<th>% Effic.</th>
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<td>37.000 4.72E-03</td>
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<td>86.3%</td>
<td>4.64</td>
<td>48.5%</td>
<td>-</td>
</tr>
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</table>

Average charges per molecule = 3.93
Average % efficiency = 58.0%
this experiment was found to be $9.2 \times 10^{-5}$ sec$^{-1}$.

The average number of electrons per molecule is 3.93 which corresponds to an average efficiency of 58%. However, the efficiency decreases as the reaction proceeds (Figure 49). Again, this would be due to the competing reactions of the polymer at higher conversions.

B) Molecular Weight Experiments

A typical GPC trace of poly(MeOT) and three polystyrene standards is shown in Figure 50. The poly(MeOT) peak is much narrower than expected for the proposed mechanism.

The molecular weight experiment was performed by withdrawing samples at 10.8 Coulombs, 40.0 Coulombs, 62.2 Coulombs and 92.0 Coulombs, which correspond to conversions of about 10%, 50%, 65% and 90%. The applied potential was +1.6 V vs. SCE. Each GPC trace showed polymer peaks in identical positions, with molecular weights of approximately 3000. This corresponds to a chain length of about 30 units. The remarkable feature of this data is that there is no change in molecular weight from low conversions to high conversions.

A typical peak was digitized and entered into a spreadsheet program. Mw was calculated by the relationship:

$$M_W = \frac{\sum \alpha_i M_i}{\sum \alpha_i}$$  \hspace{1cm} (24)

where $\alpha_i =$ height of the trace and $M_i =$ molecular weight according to the polystyrene standards. The molecular weights are converted using the universal calibration:

$$\log(\eta_{\text{polyMeOT}} M_{\text{polyMeOT}}) = \log(\eta_{\text{polystyrene}} M_{\text{polystyrene}})$$  \hspace{1cm} (25)

The viscosities of polyMeOT and polystyrene were measured by the
Figure 50: A Typical GPC Trace of Three Polystyrene Standards of 63,000, 17,500, and 4000 Molecular Weight, and PolyMeOT.
Ubbelohde viscometer at 21.1°C.

Mw for the typical poly(MeOT) experiment in DMF was calculated to be $2.9 \times 10^3$, and Mn was taken to be the molecular weight at the peak maximum, which was $2.7 \times 10^3$. Mw/Mn was calculated to be 1.07.

Two additional experiments were performed at +1.55 V and +1.65 V. The results of these experiments should demonstrate if a limiting electronic effect would be affected by a change in potential; specifically, whether a change in the level of oxidation of the polymer would result in a change in the radical cation density at the chain ends. Since the current is proportional exponentially to the applied potential, a 50 mV change should yield a significant change in the molecular weight if this model were true. The +1.55 V experiment yielded an Mn of $2.9 \times 10^3$, Mw of $2.9 \times 10^3$, and Mw/Mn of 1.01. The +1.65 V experiment yielded an Mn of $3.2 \times 10^3$, Mw of $3.3 \times 10^3$ and Mw/Mn of 1.04. These values are considered to be within the experimental error of the technique; the calibration peaks are less sensitive than the poly(MeOT) peaks and even a difference of 0.1 ml in the elution volume can significantly alter the molecular weights. The standard deviation is around 10%, which is reasonable for the GPC technique, especially at such low molecular weights.

The results of the molecular weight studies are initially quite surprising. A broad distribution and a random chain length are expected, since nothing should limit the addition of another monomer unit to the end of the growing chain, with the
exception of a termination reaction proceeding by the disproportionation of two radical cations.

It is even more surprising that a change in the potential would not cause a change in the molecular weight. A change in the radical cation character of the growing polymer chain is expected to change the molecular weight. For instance, a higher potential should result in a polymer with a greater level of oxidation and thus with more localized radical cation character. The growth of the polymer would then be facilitated, as there is a greater (or less delocalized) concentration of radical cations at the chain end. The fact that this does not occur must indicate that there is an additional mechanism operative in the polymerization.

The polaron / bipolaron model may help to explain some of these phenomena. All of the literature studies were performed in a monomer-free solution which contains only dissolved polymer or a polymer film. In the formation of the polymer, the monomer adds onto a growing chain and polymer is oxidized simultaneously. The polymer may be oxidized to form a radical cation (polaron) either in the middle of the chain or near the chain ends. Only the radical cation near the chain ends would be chemically reactive.

However, a bipolaron near the chain end will result in a chemically unreactive polymer since there is no radical character. If the polymer has enough bipolaron character, it can be considered essentially terminated. During the formation of the polymer, units will continue to add to the growing chain
until bipolarons form.

The work of the Diaz group [194], Tourillon and Garnier [88] and this work has shown that the oxidation of polythiophene and polypyrrole is limited by the diffusion of anions. The rate of polaron recombination to form bipolarons in polypyrrole has also been found to be limited by the diffusion of anions [163]. A similar mechanism would be expected for soluble polymers, except for the fact that the diffusion would be much faster because the anion would not have to diffuse through a solid layer.

Therefore, the formation of the bipolaron is limited by the rate of anion diffusion. Subsequently, the magnitude of the molecular weight may also be limited by the anion diffusion. The low degree of polymerization of poly(3-methoxythiophene) (25-30 units) as compared to estimated values for polypyrrole (100 units) [255] is a result of easier diffusion.

In addition, the methoxy group is well-known as an electron-donative group, and should stabilize the formation of a polaron or bipolaron, thus resulting in the faster formation of bipolarons and subsequently limiting the molecular weights to low values.

Two explanations may account for the narrow molecular weight distributions. The first is that the polymer must reach a limiting molecular weight before bipolaron formation is favoured [256]. The premise of this is that the potential needed to form a bipolaron on the polymer chain decreases with increasing chain length. At about 30 units, the potential may be low enough to
produce enough bipolaron character on the chain which then becomes non-reactive. This is outlined in Figure 51.

Figure 51 is a continuation of the mechanistic scheme presented in the previous chapter. Step 1 is the oxidation of newly-formed polymer to form a radical cation (polaron) near the chain end. Step 2 is the oxidation of monomer to form a radical cation. In step 3, the chain end and the monomer couple and lose two protons to form a chain which has grown by one unit. This chain may then go back to step 1. At some point in the polymerization, step 4 begins to occur and two polarons form. Because of the coulombic repulsions of the cations, this step would not be expected to occur until the chain is at a minimum length which could accommodate two charges. The polarons migrate and form a bipolaron in step 5. If the bipolaron resides near the chain end as the scheme suggests, no radical character exists on the chain, no coupling can occur and thus the polymerization is terminated. It is possible that bipolaron formation may occur well before the termination; it is only when the bipolaron is at or near the end of the chain that the polymerization ceases.

The second possible explanation for the narrow molecular distribution is that the polymer reaches its bipolaronic state at about 30 units simply because enough anion has diffused and the charge is stabilized enough by the methoxy substituents to form bipolarons. As the polymer is forming, it continually adds units at a rate limited by the diffusion of monomer, but it also forms polarons in the body of the chain which is limited by the
Figure 51: Schematic Diagram of the Proposed Polymer Termination Mechanism.
two polarons

bipolaron (inert)

1

- 124b -
rate of anion diffusion. At a certain point, which just happens to be 30 units, the polymer becomes oxidized enough so that it becomes unreactive.

The fact that the molecular weight is identical at all extents of monomer conversion indicates that new polymer is continually formed. Once the polymer has reached its limiting molecular weight, it becomes chemically unreactive and diffuses away, and a new chain is initiated at the electrode.

The substituent has a profound effect on the molecular weight of the soluble thiophene based polymers. This work has shown that molecular weights of 3000 are obtained for the MeOT polymer, while others have shown molecular weights of 38000, 27000 and 22500 for 3-hexyl-, 3-octyl- and 3-dodecyl-substituted thiophenes, respectively [240,241]. No clear correlation has yet been determined between the electronic effects of the substituent and the molecular weights.

IV.3.2 Polymerization of MeOT in AN/H₂O

A) Monomer Depletion and Coulombic Efficiency Experiments:

A potential of +1.4 V vs. SCE was applied to the water/AN cosolvent system, and the polymer precipitated on the electrode during the formation. The current response shown in Figure 52 shows similar behaviour to the DMF experiment, but the concentration profiles shown in Figures 53 and 54 demonstrate no clear order dependence. The plot of the MeOT concentration versus the charge passed (Figure 55) demonstrates again the
Figure 52: Current Response of the MeOT Polymerization in 
$\text{H}_2\text{O} / \text{AN}$.

Applied potential = +1.4 V vs. SCE
Figure 53: Changes in \([\text{MeOT}]\) During the Polymerization in \(\text{H}_2\text{O} / \text{AN}\).

Applied potential = +1.4 V vs. SCE
Figure 54: First-Order Plot of [MeOT] During the Polymerization in H₂O / AN.

Applied potential = +1.4 V vs. SCE
Figure 55: Extent of MeOT Conversion During the Polymerization in H₂O / AN.
Figure 56: Concentration of MeOT versus Charge for the MeOT Polymerization in $H_2O$ / AN.
presence of a secondary reaction at higher conversions similar to the experiments in DMF. The extent of monomer conversion as shown in Figure 56 is much smaller than the DMF experiments.

The applied potential is 200 mV smaller in this experiment than in the DMF work. The monomer oxidation potential is around +1.3 V vs. SCE. It was found that polymer buildup on the electrode proceeded quite rapidly in the water/AN system at +1.4 V, but little or no reaction occurred in DMF at +1.4 V. On the other hand, the polymerization in DMF proceeded satisfactorily at +1.6 V, but a similar potential in the water/AN system resulted in the destruction of the electrodeposited polymer. Similar results were also observed with the electrochemical polymerization of anisidine [256].

The extent of monomer conversion is quite low in the water/AN system. The polymerization was continued for 2 1/2 hours (the same as for the DMF polymerization to 50%) but the extent of conversion was less than half of the DMF polymerization. One reason for this is that the applied potential is lower, but another reason is that the electrodeposited polymer somehow impedes the current flow to the monomer in solution through the formation of an insulating layer on the electrode at later stages of the polymerization. In addition, secondary reactions within the polymer film may occur such as β-β' coupling. A comparison of Fig. 44 and Fig. 55 shows that the insoluble system deviates from linearity at much lower conversions than the totally soluble system. This may indicate that the presence of the polymer on the electrode adversely
<table>
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<tr>
<th>Time</th>
<th>Time</th>
<th>Current</th>
<th>Charge</th>
<th>Conc'n</th>
<th>% Conv'n</th>
<th>Charges per molecule</th>
<th>% Effic.</th>
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<td>mA</td>
<td>Coul.</td>
<td>MeOT</td>
<td>mole/L</td>
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Average charges per molecule = 3.47
Average % efficiency = 66.6%
affects the charge transfer processes and the kinetics of the polymerization.

It was not possible to obtain an order dependence for this reaction as no relationship was found between the concentration changes and the time of the reaction or the charge passed.

The average charges per molecule was found to be 3.47, which leads to an overall efficiency of 67%. A summary of the data for this polymerization is shown in Table IX.

B) Molecular Weight Experiments

Unfortunately, the polymer synthesized in the water/AN system was too unstable too be measured in the GPC. The electrode with the deposited polymer was removed from solution, dried slightly by dabbing it with a KimWipe, then dissolved in 2 ml. of DMF, immediately filtered and finally injected into the GPC. No peaks due to polymer were observed except for one experiment where a slight irregular blip occurred approximately where the polymer should have been seen. The molecular weight here was estimated to be 4300, but this value is not defensible. This experiment was attempted at different conversion limits and at different water/AN ratios. All failed to give a molecular weight.

IV.4 A KINETIC MODEL FOR CONDUCTING POLYMER FORMATION

The results from this chapter and previous chapters can be fit into a general kinetic scheme for the polymerization of heterocyclic aromatics. A kinetic scheme can be drawn for the
various proposed mechanistic pathways, but the data in this work and the literature most strongly support the radical cation coupling mechanism. This work has found the following:

a) the polymer oxidizes at a lower potential than the monomer and thus the polymer forms in its oxidized, conducting state during the polymerization.

b) the reaction appears to be first order for the MeOT and BT polymerizations (at long times).

c) there is no primary isotope effect in pyrrole, and thus the proton loss is not rate-limiting.

d) a complete inhibition of polymerization occurs with pyrrole in the presence of a radical trap.

e) the molecular weight of polyMeOT is identical at all conversions and potentials.

These observations are assumed to be true for all heterocyclic aromatics.

The mechanism can be written as follows:

\[ M \xrightarrow{k_1} M^{+*} \text{ (oxidation)} \]  
\[ M^{+*} + M^{+*} \xrightarrow{k_2} M_{2}^{++} \text{ (dimerization)} \]  
\[ M_{2}^{++} \xrightarrow{k_3} M_2 + 2H^{+} \text{ (H\textsuperscript+ expulsion)} \]  
\[ M_{2} \xrightarrow{k_4} M_{2}^{+*} \text{ (dimer oxidation)} \]

The rate of monomer depletion is given by:

\[ - \frac{d[M]}{dt} = k_1[M] \]  

(30)
This is a first order reaction which is experimentally observed in this work.

In free radical polymerization kinetics, a steady-state assumption is applied where the concentration of all intermediate species (i.e. the concentration of radicals) remains constant. This yields the conclusion that the rate of polymer formation is equal to the rate of monomer depletion. However, in the conducting polymer mechanism, this conclusion is not readily apparent.

The following rate equations are derived:

\[
\frac{d[M_2^+]}{dt} = k_3 [M_2^{++}] - k_4 [M_2] \tag{31}
\]

\[
\frac{d[M_2^{++}]}{dt} = k_2 [M^{**}]^2 - k_3 [M_2^{++}] \tag{32}
\]

\[
\frac{d[M^{**}]}{dt} = k_1 [M] - k_2 [M^{**}]^2 \tag{33}
\]

Assume that \( \frac{d[M_2^{++}]}{dt} = \frac{d[M^{**}]}{dt} = 0 \) (steady-state assumption).

This assumption may be proven valid by the RRDE experiments; the magnitude of the ring current was proportional to the disk current, and the collection efficiencies were reasonably constant (within the experimental scatter). Thus, the concentration of intermediate species remains constant.

Thus a combination of (32) and (33) yields:

\[
k_2 [M^{**}]^2 - k_3 [M_2^{++}] = k_1 [M] - k_2 [M^{**}]^2 \tag{34}
\]
Solving for $[M_2^{++}]$:

$$[M_2^{++}] = \frac{2k_2}{k_3} k_2[M^*]^2 - \frac{k_1}{k_3} [M]$$  \hspace{1cm} (35)

Substituting (35) into (31):

$$\frac{d[M_2]}{dt} = 2k_2[M^*]^2 - k_1[M] - k_4[M_2]$$  \hspace{1cm} (36)

Thus, the rate of dimer formation is proportional to the rate of monomer depletion. If it is assumed that $[M^*]^2 \ll [M]$ and $[M_2] \ll [M]$,

$$\frac{d[M_2]}{dt} \approx - \frac{d[M]}{dt}$$  \hspace{1cm} (37)

If the reaction stopped at the dimer stage, equation (37) would be invalid since it cannot be assumed that the concentration of dimer is much less than the concentration of monomer. However, the dimer further goes on to react to the trimer as outlined in the following scheme:

$$M_2 \xrightarrow{k_6} M_2^{++}$$  \hspace{1cm} (38)

$$M_2^{++} + M^* \xrightarrow{k_5} M_3^{++}$$  \hspace{1cm} (39)

$$M_3^{++} \xrightarrow{k_6} M_3 + 2H^+$$  \hspace{1cm} (40)

$$M_3 \xrightarrow{k_7} M_3^{++}$$  \hspace{1cm} (41)

The rate expressions are as follows:

$$\frac{d[M_3^{++}]}{dt} = k_5 [M_2^{++}][M^*] - k_6 [M_3^{++}]$$  \hspace{1cm} (42)

$$\frac{d[M_2^{++}]}{dt} = k_4 [M_2] - k_5 [M_2^{++}][M^*]$$  \hspace{1cm} (43)
Assume that \[
\frac{d[M_3^{++}]}{dt} = \frac{d[M_2^{++}]}{dt} = 0 \quad \text{ (steady-state)}
\]

Thus,

\[
k_5[M_2^{++}][M^{++}] - k_6[M_3^{++}] = k_4[M_2] - k_5[M_2^{++}][M^{++}] \quad (45)
\]

Solving for \([M_3^{++}]\),

\[
[M_3^{++}] = \frac{2k_5}{k_6} [M_2^{++}][M^{++}] - \frac{k_4}{k_6} [M_2]
\]

Substituting (46) into (44),

\[
\frac{d[M_3]}{dt} = 2k_5[M_2^{++}][M^{++}] - k_4[M_2] - k_7[M_3]
\]

If one assumes \([M_2] \gg [M_2^{++}]\) and \([M^{++}]\) and \([M_3]\), then

\[
\frac{d[M_3]}{dt} = -\frac{d[M_2]}{dt} = \frac{d[M]}{dt}
\]

In general, for n mer units,

\[
\frac{d[M_n]}{dt} = k_a[M_{n-1}^{++}][M^{++}] - k_\beta[M_{n-1}] - k_7[M_n]
\]

where \(k_a\), \(k_\beta\), and \(k_7\) are general rate constants as expressed in (47) and (36).

This expression assumes that only monomer is adding to the growing chain, and that there is negligible dimer combination, dimer plus trimer, etc. This certainly does occur to some degree in the reaction, but the concentration of oligomeric species is extremely low compared to the concentration of monomer and thus the probability of monomer addition to the
growing chain is much larger than the probability of oligomeric reactions. However, if these reactions were considered, the rate expression would have the same form as equation (49), but more terms would be included to account for these other processes.

Nevertheless, the conclusion of equation (49) is:

\[
\frac{d[M_n]}{dt} = -\frac{d[M]}{dt} \tag{50}
\]

However, as \(n\) approaches its limiting value, the final term in (49) becomes significant since \([M_n]\) is growing constantly compared to \([M]\). In the case of polyMeOT, \(n \approx 30\) and after 50% conversion there is a 20:1 ratio of \(M\) units to \(M_n\) units.

The rate constant \(k_7\) must be further defined. In the examples given earlier (i.e. examples using chain lengths of 1, 2, and 3 units), each oxidation of species yielded a chemically reactive radical cation. However, as the chain length increases, the probability increases for the occurrence of a competing oxidation forming a chemically unreactive species; i.e. a polaron in the middle of the chain or a bipolaron.

\[
M_x--M--M_y \xrightarrow{k_p} M_x--M^+--M_y \quad \text{(polaron)} \tag{51}
\]

\[
M_x--M^+--M_y \xrightarrow{k_b} (M_x--M--M_y)^{++} \quad \text{(bipolaron)} \tag{52}
\]

where \(k_p\) is the rate constant for polaron formation and \(k_b\) is the rate constant for bipolaron formation.

Therefore, as \(n\) approaches its limiting value, \([M_n]\) indeed becomes significant, but \(k_7\) (the rate constant for the
formation of chemically reactive radical cations) becomes extremely small and approaches zero at the limiting value of n.

The addition of a radical trap merely provides an alternative reaction pathway. As discussed in Chapter III, the reaction of the radical cation with the trap is kinetically favoured over the reaction with another radical cation. Thus, the concentration of dimer is zero, and polymer formation is inhibited.

The overall kinetic scheme is complex and the model presented here is likely an oversimplification of the many steps involved in polymer formation, Nevertheless, this model fits the results obtained in this work.

IV.5 CONCLUSIONS

The studies of soluble polyMeOT have shown that the reaction follows a nearly ideal first-order dependence on monomer when synthesized in DMF, with Faradaic efficiencies of 50 to 70%. The formation of polyMeOT in the insoluble form on the electrode demonstrated the effect of the adsorbed polymer on the reaction kinetics.

The remarkable aspect of the narrow molecular weight results is explained by a limitation due to bipolaron formation in the conducting chain. A comparison of the literature and this work shows a substituent effect in the molecular weights of conducting polymers. The mechanism of the formation of conducting polymers has been more clearly elucidated by this work.
CHAPTER V

CONCLUDING REMARKS

The mechanism of the electropolymerization of derivatives of pyrrole and thiophene was elucidated in this work. The results are most consistent with a schematic model involving the formation and coupling of radical cations to eventually form polymer.

Electrochemical and kinetic order dependence studies were performed on pyrrole and BT. Since the polymer was found to oxidize at a potential lower than the monomer oxidation potential, the polymer forms on the electrode in an oxidized, conducting state which facilitates further oxidation of the monomer. Some soluble species, presumably monomeric radical cations, are produced in the polymerization as evidenced by the RRDE studies. The kinetic order of pyrrole and BT was found to be zero using a stepped potential technique, and the order of the supporting electrolyte in some cases was found to be one. An adsorptive mechanism or a capacitative charging mechanism may account for the zero order, and the kinetic order of the supporting electrolyte is interpreted as a result of the diffusion-limitation of the anions into an oxidized polymer film. However, at times greater than approximately 100 msec past the application of the potential, the kinetic order of BT was found to be between 0.5 and 1, depending on the reaction conditions. A macro experimental approach involving the
measurement of the monomer concentration during polymerization yielded a first order relationship in the monomer, and nearly 100% faradaic efficiencies. However, the results were somewhat inconsistent and some conflicting data was obtained. This is due to the heterogeneous nature of the polymerization; the reaction site at the electrode is continually changing due to the presence of growing polymer.

The electropolymerization of pyrrole was studied using physical organic methods. A kinetic isotope study demonstrated no primary effect, leading to the conclusion that proton loss is not the rate-determining step in the polymerization and that proton loss occurs as a separate step. It was not possible to conclude whether a secondary effect was present because of the experimental errors, but it is thought that a secondary effect is improbable due to the lack of hybridization changes in the transition state of any of the mechanistic proposals. A radical trap study showed that polymerization is completely inhibited by the presence of a trapping species. This does not necessarily indicate that the combination of radical cations is rate limiting, rather, the alternative mechanistic pathway involving the combination of the radical cation with the trap is more favourable than the dimerization reaction.

In the study of the electropolymerization of 3-methoxy-thiophene to form a soluble conducting polymer, an ideal first order dependence on monomer was observed and 50 to 70% faradaic efficiencies were observed. The reproducibility of much of the data was greatly improved because of the fact that polymer forms
in a DMF solution rather than depositing on the electrode, thus making the locus of the reaction less variable.

The most remarkable aspect of this work is that a highly monodispersed polymer forms in solution which has a uniform molecular weight throughout the course of the polymerization. The degree of polymerization is approximately 30, and $\text{Mn/Mw}$ ranges from about 1.01 to 1.10. This behaviour is interpreted as a result of the formation of a chemically non-reactive species produced by the formation of bipolarons in the chain.

Although the radical cation coupling mechanism is the model most consistent with these results, it has not been completely proven that this mechanism is correct or complete. Additional studies may be performed to further develop the mechanistic picture.

For instance, the radical trap results may be developed further by modifying the system so that ESR spectra can be obtained of the spin adduct. A structural determination of the adduct would yield information on the nature of the monomer radical cation. In addition, the radical trap study may also be performed using the RRDE technique.

Several interesting studies can yet be performed on soluble polymers. The bipolaron limitation of the molecular weight can be further elucidated by repeating the experiments with other thiophene derivatives which will form soluble polymers. In particular, the stabilization of the bipolaron is expected to be affected by the nature of the substituent, and thus a substituent with a large electron-donative character would be expected to lower the molecular weight.
The development of a conducting solution of the polymer would also be interesting. This work has produced only dilute polymer solutions which are non-conducting without a supporting electrolyte. A concentrated solution would cause chain entanglement which may facilitate interchain bipolaron hopping. This type of system would improve the processability and increase the applications of these polymers.

In conclusion, although there was some irreproducibility, this work has developed a clearer understanding of the mechanism of the electropolymerization of heterocyclic aromatics.
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