

Conductive Polymers and Plastics



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Dedicated to my wife, Rena

Part I

Polymers

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Electrically Conductive Polymers

John R. Reynolds, Charles K. Baker, Cynthia A. Jolly, Paul A. Poropatic, and Jose P. Ruiz

Introduction

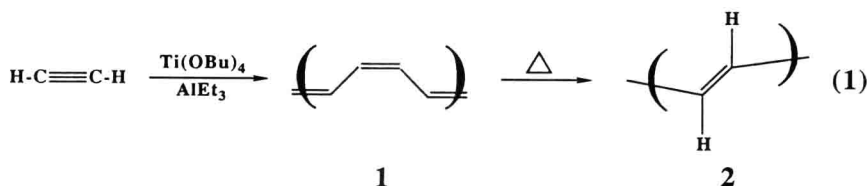
The 1977 report that polyacetylene,¹ a conjugated organic polymer, could attain high levels of electronic conductivity when oxidized by suitable reagents initiated a significant research thrust that has included the participation of chemists, physicists, and material scientists. Over the last decade, literally thousands of technical papers have been published in this field, which has now been expanded to include a multitude of polymer systems. In fact, a book entitled *Polyacetylene: Chemistry, Physics and Materials Science* has been published detailing significant research effort that has been dedicated to this polymer alone, and a set of handbooks treats the field in more detail.²

The concept of conductivity and electroactivity of conjugated polymers was quickly broadened from polyacetylene to include a number of conjugated hydrocarbon and aromatic heterocyclic polymers, such as poly(*p*-phenylene),³ poly(*p*-phenylene vinylene),⁴ poly(*p*-phenylene sulfide),⁵ polypyrrole,⁶ and polythiophene.⁷ An all-encompassing list would be quite extensive.

In this chapter we address the synthesis and electronic conductivity properties of conjugated organic polymers, using specific examples to illustrate our points. Further, we describe how transition metal ions, with suitably conjugated ligands, can be used to introduce charge carriers into polymers. Lastly, we describe some of the current and potential applications of these materials as they now approach a marketable form.

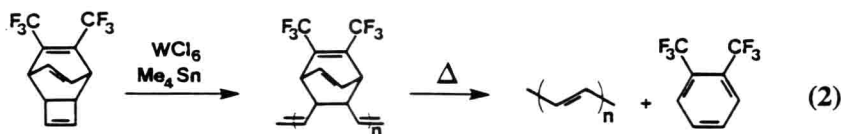
Polyacetylene: The Prototype Conducting Polymer

Polyacetylene, $(\text{CH})_x$, a simple conjugated polymer, can be synthesized by a variety of routes. Most research on $(\text{CH})_x$ as a conductive polymer has been performed on what is known as the "Shirakawa" type,¹ which is synthesized via the Ziegler–Natta polymerization of acetylene shown in Equation 1. The polymer forms as a highly crystalline, completely insoluble, mat of fibrils.



These fibrils have diameters on the order of 50–200 Å, which facilitates redox reactions used to impart conductivity to this polymer. At low temperature the polymer is synthesized as the *cis*-transoid isomer (1), which is easily thermally converted to the more stable *trans*-transoid form (2) as shown.

To obtain materials of a more controllable morphology, soluble precursor systems have been developed that, on elimination of some small molecule, leave the fully conjugated $(\text{CH})_x$ chain.^{8,9} This is illustrated in Equation 2 for a polymerization route developed by Feast. The elimina-

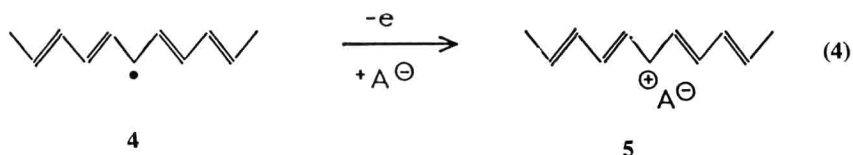
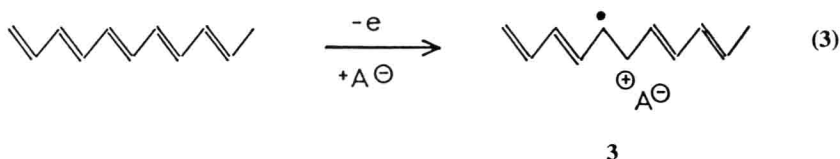


tion is carried out thermally and thus the polymer is obtained in the *trans*-transoid form by this method.

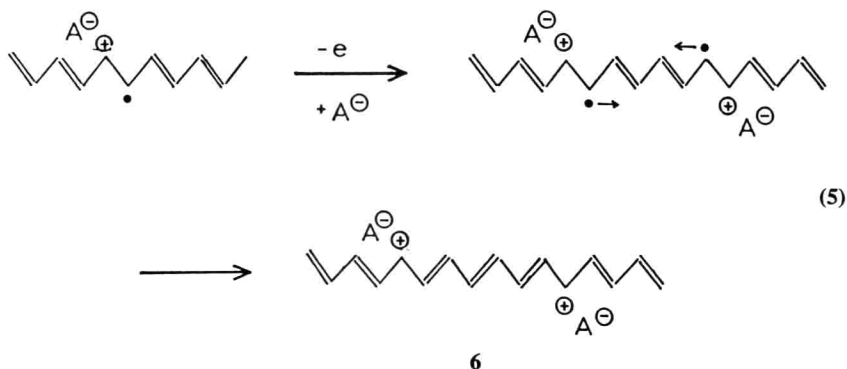
As synthesized, *trans*-($\text{CH})_x$ is a semiconductor having an electrical conductivity on the order of 10^{-5} – 10^{-6} $\text{ohm}^{-1} \text{cm}^{-1}$. The actual bond lengths alternate, half having more single-bond character and half having more double-bond character, as opposed to equal length if the system were perfectly conjugated. The polymer's structure is stabilized, via a phenomenon similar to a Peirels transition, leading to bond alternation.

The introduction of charged carriers is accomplished by redox reactions, which are commonly denoted as "doping reactions" in that they increase the conductivity of the polymer in a manner analogous to the

doping of inorganic semiconductors. Utilizing oxidative doping as an example, removal of an electron from the polymeric π system, as shown in Equation 3, leads to a delocalized radical ion. This radical ion is viewed as a polaron (3) in that it represents a charged and paramagnetic defect in the $(\text{CH})_x$ lattice. Also contained within the synthesized $(\text{CH})_x$ are a number of neutral paramagnetic defects termed solitons (4). Oxidation



of a neutral soliton yields a charged soliton (5), which is also delocalized along the polymer chain. A second oxidation of a chain containing a polaron, followed by radical recombination, yields two charged carriers on each chain (6), as illustrated in Equation 5.



These charged sites on the polymer backbone must be charge compensated, and during the doping process anions penetrate into the polymer matrix for this purpose. If the doping is carried out chemically, then the dopant anions are generated from the oxidizing agent, and if the doping is carried out electrochemically, an electrolyte anion is incorporated as the dopant anion. Chemical and electrochemical reduction can also be

used in a manner analogous to the preceding to yield polyacetylene with negatively charged (*n*-type) carriers.

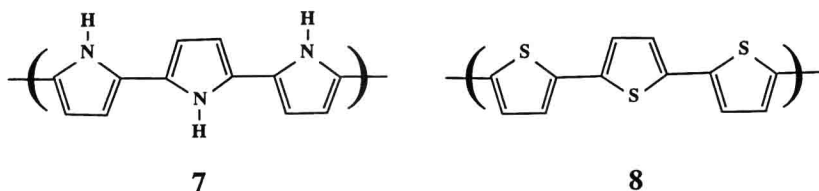
The delocalized charges on the polymer chain are mobile, not the dopant ions, and are thus the current-carrying species for conduction. These charges must hop from chain to chain, as well as move along the chain, for bulk conductivity to be possible. The actual mechanisms of conduction are quite complicated and still under debate, as will be discussed later. The preceding, relatively simplistic picture of charge creation in $(\text{CH})_x$ is given because it can serve as a model for understanding conductivity in the systems to be discussed further.

Two of the major drawbacks to the use of $(\text{CH})_x$ in practical applications are extreme air sensitivity and lack of processability. In the neutral, semiconductive form it irreversibly oxidizes, under exposure to air, degrading the π system along the backbone. The highly conducting doped polymer is also reactive in air, probably via a series of reactions involving moisture, with a corresponding precipitous conductivity drop. $(\text{CH})_x$ is also completely insoluble and infusible, which limits its ability to be used in typical polymer film and fiber operations. For this reason the bulk of this chapter is directed to describing conductive polymer systems in which these limitations are not so severe.

Electrochemical Polymerization of Aromatic Molecules

Electrochemical oxidation of resonance-stabilized aromatic molecules has become one of the principal methods used to prepare conjugated, electronically conducting polymers. Since the first reports that the oxidation of pyrrole at a platinum electrode in the presence of a supporting electrolyte will produce a free-standing electrically conductive film,^{6,10,11} many other aromatic systems have been similarly electropolymerized. These include thiophene,^{7,12-14} furan,⁷ carbazole,^{15,16} azulene,^{7,17} indole,⁷ aniline,¹⁸⁻²¹ selenophene,²²⁻²⁴ phenol,^{25,26} and thiophenol,²⁷ as well as many substituted, multiring, and polynuclear aromatic hydrocarbon systems such as 3-methylthiophene,^{28,29} bithiophene,³⁰ and pyrene.^{31,32} All the resulting polymers have a conjugated backbone and are oxidized electrochemically as they are formed on the electrode from a solution containing both electrolyte and monomer. This oxidation leads to the incorporation of charge-compensating anions into the oxidized film. These anions are thus the dopant ions. As in $(\text{CH})_x$, the resulting polymer films are electrically conducting when oxidized and electrically insulating when neutral.

The two most studied members in this group of polymers are polypyrrole (7)³³⁻³⁷ and polythiophene (8).^{38,39} For illustrative purposes we will



detail the data concerning their electropolymerization and electrochemical characterization in this section. It can be expected that other, comparable monomer systems will exhibit similar behavior. Figure 1.1 shows a typical cyclic voltammogram of pyrrole. Several important features should be noted. On the initial anodic sweep there is a single peak at 0.9 V versus the standard calomel reference electrode, which corresponds to the oxidation of pyrrole at the electrode surface. The lack of a reductive peak on the return sweep indicates that the oxidation is irreversible, and the highly unstable radical-cations formed during oxidation undergo an immediate chemical reaction. If additional cyclic voltammograms are performed on the same untreated electrode in the same electrolyte/monomer solution, the monomer oxidation peak current will continue to grow

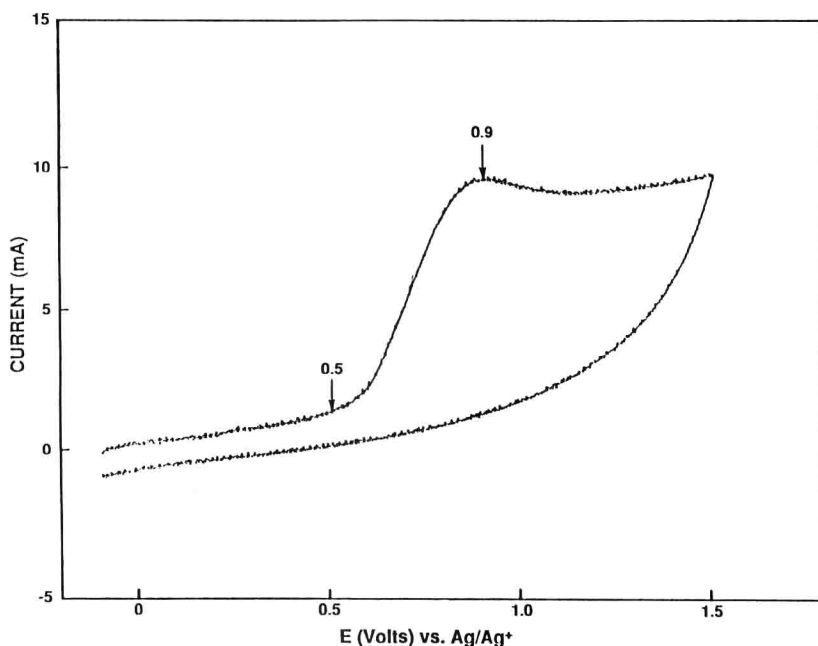


Figure 1.1 Cyclic voltammogram of pyrrole; scan rate = 25 mV s^{-1}

to progressively larger values, indicating that the polypyrrole produced remains on the electrode surface as it is produced. This also implies that the polypyrrole is produced with a high enough conductivity to participate in subsequent monomer oxidation and polymerization. Once a sufficient amount of polymer is deposited on the electrode, peaks due to polymer redox processes appear in the cyclic voltammogram.

Several studies of the electropolymerization of pyrrole and thiophene³⁵⁻⁴⁹ onto a number of supporting electrode substrates have been made in an attempt to elucidate both the mechanism during the initial stages of polymer film formation and the role that experimental conditions play in the mechanism. These studies have used a number of electrochemical techniques, including cyclic voltammetry, chronocoulometry, and chronoamperometry as well as optical absorption and gravimetric techniques. The cyclic voltammogram shown in Figure 1.2 is similar to the one shown in Figure 1.1 except that the switching potential is close to the monomer peak potential. In this experiment, a nucleation loop appears at the foot of the oxidation wave. This nucleation loop is characterized by a potential region in which the current on the reverse sweep is higher than that seen on the forward sweep and is evidence for the formation of polymer at the electrode surface. On subsequent scans, the foot of the oxidation wave starts at slightly lower potentials, suggesting that polymerization occurs more readily on polypyrrole than on the underlying metallic substrate.

Another electrochemical method used to study the nucleation and

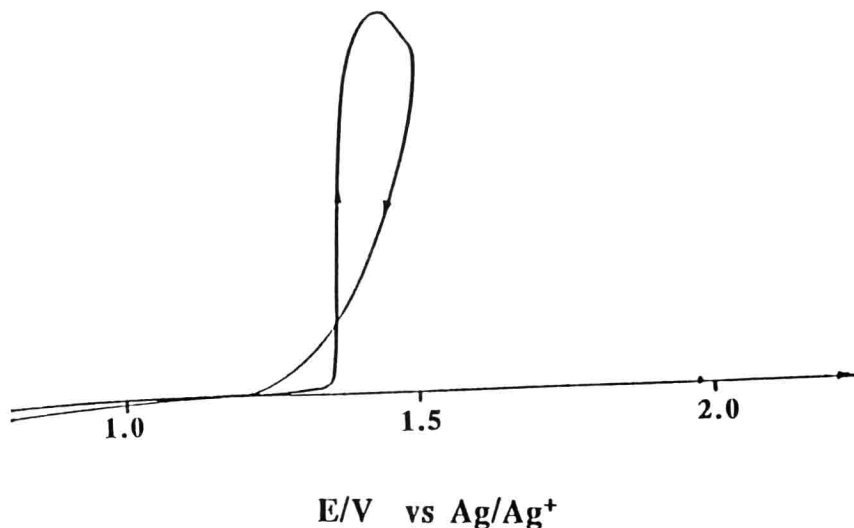


Figure 1.2 Cyclic voltammogram of pyrrole showing nucleation loop.

growth mechanism is chronoamperometry. In this technique, the potential at the working electrode is stepped from a rest potential to a potential where oxidation can occur and current is measured as a function of time. The current–time transient shown in Figure 1.3 is typical for the oxidation of pyrrole or thiophene and contains three distinct regions of behavior indicative of three separate stages involved during film formation. The first stage is characterized by a sharp initial current spike whose decay is potential dependent, nonexponential, and of time scales longer than that expected if it were due solely to charging of the ionic double layer at the electrode surface. Rotating ring–disc electrode and coulometric experiments of thiophene deposition on gold³⁷ suggest that this initial current spike has contributions from both a nucleation and growth process as well as from the formation of soluble oligomers. Quantitative analysis of the amount of charge passed and the duration of this spike suggest that this first stage corresponds to the coverage of the metallic electrode by a one-monolayer-thick polymer film. A separate study⁴⁰ has found similar results regarding monolayer coverage by using Tafel slope analysis and measurement of Pt electrode surface coverage by adsorbed pyrrole.

The beginning of the second stage is marked by a minimum in the

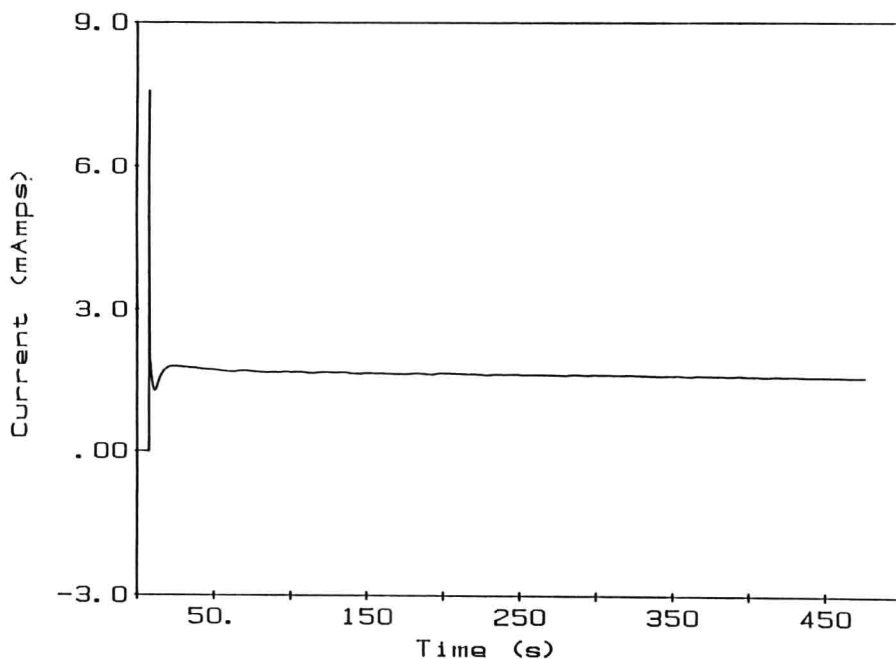
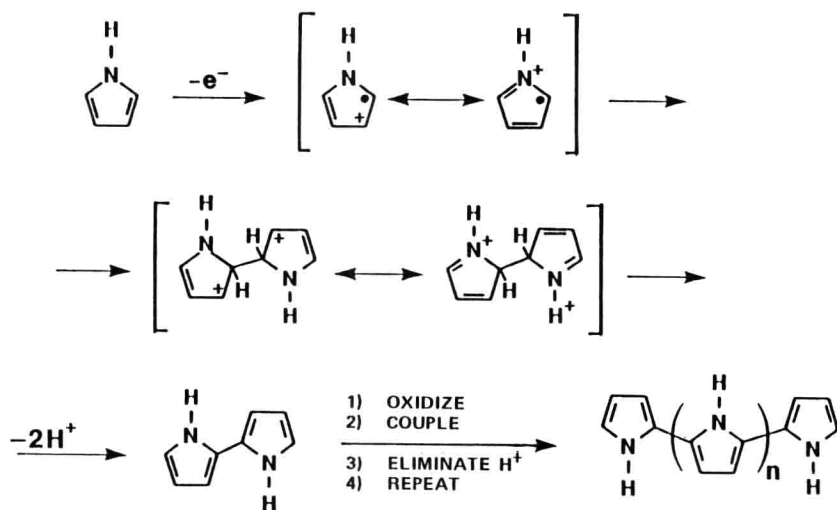


Figure 1.3 Current-time transient for the polymerization of pyrrole.

current-time transient followed by a rising current that levels off relatively quickly. During this stage, the rise in current is proportional to t^2 , which indicates that the growth of the surface phase is determined by the rate of electron transfer at the surface of the expanding phase. This is characteristic of instantaneous formation of nucleation sites on the polymer monolayer followed by a three-dimensional growth until these sites overlap. The beginning of the third stage corresponds roughly with this overlap of nucleation sites and additional growth perpendicular to the underlying substrate. The current response in this region is independent of time, when diffusional constraints are absent, which is generally the case over the bulk of film formation. The fact that polymerization in this region is not diffusion limited is confirmed by the linear charge-time,^{42,44,49} mass-time,^{42,49} and absorbance-time⁴⁴ results obtained from chronocoulometric, chronogravimetric, and spectroelectrochemical measurements, respectively.

Other theoretical and electrochemical studies involving the relationship between electropolymerization conditions and the properties of the resulting film have led to conclusions about the efficiency and mechanism of the oxidation/deposition process. The picture that emerges from these studies for the polymerization during the bulk of film formation is shown in Scheme 1 for polypyrrole.



Scheme 1

Polymerization is initiated by the oxidation of monomer to yield a radical-cation species. Although some⁴⁴ have suggested that the next step may be formation of a covalent bond between this radical cation and a neutral monomer, followed by an electron transfer from this product, this seems unlikely because of the potential dependence found in the copolymerization of pyrrole with substituted pyrroles.⁵⁰ Therefore, the second step is more likely to be the coupling of radical cations to yield dimers. These resulting dimers can then be oxidized at a lower potential⁵¹⁻⁵³ to yield a radical-cation dimer in which the highest spin density is found at the terminal carbons alpha to the pyrrole nitrogens. These dimer radical ions (or at later stages, oligomers) may couple with another radical-ion monomer, dimer, or oligomer species, eventually precipitating and leading to an insoluble film. This lack of solubility is inherent to unsubstituted polymers containing a polyconjugated planar backbone. This planarity is due to the energy minima associated with the overlap of adjacent π -orbitals that is necessary to achieve efficient electron transport along the polymer chain. The insolubility of these materials limits the number of analytical techniques that can be employed for characterization.

In practice, the highest-quality electrically conducting polymer films are prepared in an inert atmosphere using a three-electrode electrochemical cell. The reaction mixture usually includes 0.01 to 0.2 molar pyrrole in an unreactive aprotic solvent and an electrolyte such as tetraethylammonium tosylate, tetrabutylammonium tetrafluoroborate, or lithium perchlorate. In addition, a small percentage of water, typically 2%, can be added, as it has been shown to enhance the mechanical properties of the resulting film.⁵⁴ The water is thought either to provide a labile counter electrode reaction or to participate in the initial stages of film formation, although the exact mechanism of this enhancement is still unclear.

Variation of the identity of the dopant or counter anion used in the synthesis provides a means to modify chemically the physical, electrochemical, and conductivity properties of these polymer films. A number of papers^{29,55-59} have treated this topic. One study⁴⁶ has found that films with superior mechanical properties (smoothness and flexibility) possessed higher conductivities. These mechanical properties were found to be related to anion size, with the larger organic atoms (i.e., large amphiphilic aromatic sulfonates such as dodecylsulfonate) producing higher-quality films by increasing the order of the polymer chains during the polymerization and deposition process. This study also found a correlation between the acid strengths of the dopant anions and conductivity, with weak acid anions giving lower conductivities. The cyclic voltammograms of thin polypyrrole films prepared and characterized in different anion-containing solutions were used as an estimate of film quality by examining the sharpness of the reduction peak on the first

scan. Again, the larger organic dopants gave higher-quality electrochemical responses in addition to higher conductivities.

Similar studies⁵⁸ on 3-methyl thiophene concluded that the nature of the anion plays a primary role in determining the structure of the polymer during synthesis. The nature of the cation affects the electrochemical behavior of the polymer but not its structure.

Other experimental variables affecting the properties of the electrochemically deposited conducting polymers include different methods of electrochemical synthesis—i.e. constant potential, constant current, and potential sweep, solvent choice, atmospheric conditions, e.g., N₂ or air, and electrode material (e.g., Pt, Au, indium-tin oxide, and glassy carbon).

Electrochemistry of Conducting Polymer Films

The electrochemical properties of organic conducting polymers are critical to any potential electrode applications. When the polymer films are left in contact with the substrate on which they were formed, they can be cycled repeatedly between the oxidized and neutral forms. In general, the oxidized form of the polymer is highly conducting because of the formation of polarons and bipolarons and insulating in the reduced, or neutral, state. Several common electrochemical techniques are used to examine the nature of the oxidation or doping process that controls the level of conductivity—namely, cyclic voltammetry and chronocoulometry—because of their ease of application and ability to control accurately the oxidation state of the polymer.

The cyclic voltammogram produced from a polypyrrole film in a monomer free supporting electrolyte shown in Figure 1.4 contains a peak for the oxidation of the film at ca. -0.1 V on the anodic sweep and a corresponding reduction peak at ca. -0.3 V on the cathodic sweep. The peak current values for the anodic process, i_{pa} , scale linearly with the sweep rate as expected for electron transfer to surface-bound species. The peaks are also displaced toward higher positive potentials with an increase in sweep rate. The peak currents for the reductive process are much broader and are difficult to analyze. This has been attributed to inhomogeneities of the polypyrrole in the potential regions of interest.⁶⁰ Although this redox reaction is electrochemically reversible over many scans, the peak shapes and separation indicate that this process deviates from a strictly Nernstian behavior and has kinetic limitations.

Several works appear in the literature that attribute the non-Nernstian behavior of the polymer redox process to ion mobility, as seen in the unsymmetrical appearance of the cyclic voltammogram. Early work^{56,61}

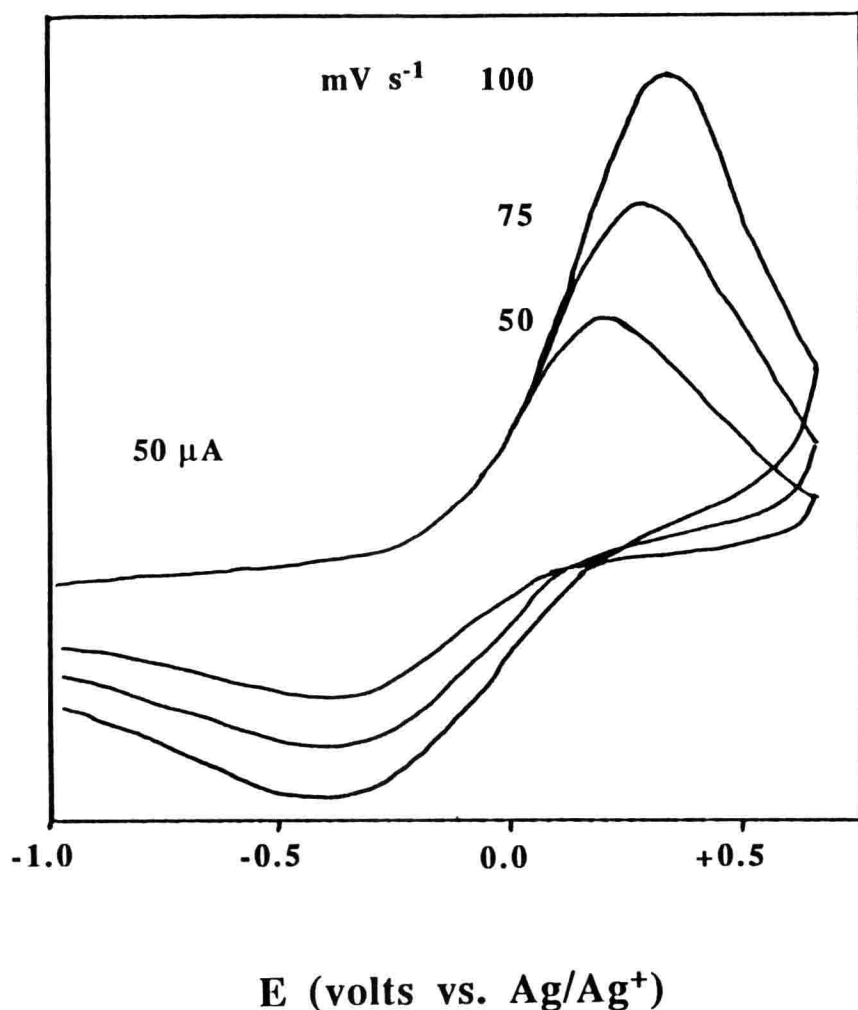


Figure 1.4 Cyclic voltammogram for polypyrrole at varied scan rates.

found significant changes in the shifts of the E_{pa} values and peak shapes as a function of anion identity that was attributed to changes in the kinetics of the redox process. Experiments in which only the anion was replaced during analysis of the polymer film suggested that any anion-dependent differences in peak characteristics occur primarily as a result of the electrochemical synthesis.⁵⁸ They also found that the electrochemical characteristics of the film are enhanced as the size of the anion used during synthesis increases. Further investigations brought to light the effects of the cation in the polymer redox process.⁵⁸ By replacing the