MWTP-72

FINAL REPORT—METAL ION REMOVAL FROM ACID MINE WASTEWATERS BY NEUTRAL-CHELATING POLYMERS: INITIAL INVESTIGATION AND MODELING STUDY

MINE WASTE TECHNOLOGY PROGRAM
ACTIVITY IV, PROJECT 4

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Final Report—Metal Ion Removal from Acid Mine Wastewaters by Neutral-Chelating Polymers: Initial Investigation and Modeling Study

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Foreword

Today industries are developing and modifying technologies to more efficiently produce their products. The waste generated by these industries, if improperly dealt with, can threaten public health and degrade the environment. The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the EPA strives to formulate and implement actions leading to a balance between human activities and the ability of natural systems to support and nurture life. These laws direct the EPA to perform research to define, measure the impacts, and search for solutions to environmental problems.

The National Risk Management Research Laboratory (NRMRL) of the EPA is responsible for planning, implementing, and managing research, development, and demonstration programs to provide an authoritative, defensible engineering basis. This supports the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. The Federal Energy Technology Center (FETC) of the Department of Energy (DOE) has responsibilities similar to the NRMRL in that FETC is one of several DOE centers responsible for planning, implementing, and managing research and development programs. In June 1991, an Interagency Agreement (IAG) was signed between EPA and DOE that made funds available to support the Western Environmental Technology Office's operating contractor, MSE Technology Applications, Inc. (MSE), and Montana Tech of The University of Montana for the development of the Mine Waste Technology Program (MWTP). This publication is one of the products of the research conducted by the MWTP through these two Federal organizations and provides a vital communication link between the researcher and the user community.

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1. Introduction

This final report presents the information and results compiled by Dr. Douglas Cameron (Principle Investigator), Dr. Doug Coe, and graduate students Mr. Robert D. Stickrod II and Mr. Raoul P. Gabhart from Montana Tech of the University of Montana (Montana Tech) for the Mine Waste Technology Program (MWTP), Activity IV, Project 4: Metal Ion Removal from Acid Mine Wastewaters by Neutral-Chelating Polymers—Initial Investigation and Modeling Study. The research described in this report was conducted in accordance with the work plan for the MWTP, Activity IV, Project 4, which addresses the research and design of new technology that will ultimately eliminate or minimize some of the economic or technical difficulties that exist in current treatment technologies for acid mine wastewaters. The novel technology is based on neutral-chelating polymers that can have their chelating property controlled. The chelate switch will be based on known electrochemical properties of electrically conducting polymers. This report describes the results from the literature review, molecular modeling studies, chemical and electrochemical syntheses, and spectroscopic studies.

1.1 Background

From the Bronze Age through current times, society has found a large number of uses for metals from weapons to food production and housing to transportation. Unfortunately, substantial environmental contamination has occurred from the mining of metals and minerals (Ref. 1-3) used in these technologies and through the production (Ref. 4), use (Ref. 5), and disposal (Ref. 6) of the materials used in these technologies. The popular press has been filled with reports of environmental problems, especially those associated with U.S. Government Agencies, and in particular the DOE (Ref. 7). The Government's interest in remediating these problems is exemplified by the steady increase in funding at the National Laboratories for programs in environmental management (Ref. 8, 9), and the joint efforts of the EPA with other governmental agencies, e.g., the MWTP. The magnitude of the expense for restoration work at facilities connected with agencies such as DOE is expected to be enormous. Consequently, the use of effective and cost-efficient remediation processes is necessary. Effective remediation processes are ones that remove a high (and desired) percentage of contamination and produce little, if any, waste. For the DOE, the technical problems of environmental remediation are compounded by the variety of wastes that have been produced over the past 40 years, e.g., low-level and high-level radioactive wastes, inorganic and organic hazardous wastes, and mixed (hazardous) wastes (Ref. 9).

Predictions of technologies that will be important in the future have been outlined in recent publications by the National Research Council (Ref. 10) and *Scientific American* (Ref. 11). Examples of these new or critical technologies are new ceramics for engines and power generation stations; catalysts for chemical production; construction and transportation material that is light weight, mechanically strong, and fire resistant; and new materials for computer systems, communications, and solar energy production. These new technologies will require the use of a variety of metals and metal-containing composites. Although current environmental regulations restrict or prohibit further contamination, effective and cost-efficient methods of waste treatment and disposal are not currently available for all types of metal-containing wastes. Therefore, the problem of what to do with the waste or used metals remains; however, the emphasis switches from restoration to abatement.

A significant portion of the metal contamination ultimately ends up in the water systems and industrial process waters of the U.S. and the World. The removal of contaminant metal ions and associated anions from aqueous solutions (particularly ground and surface waters) is one area of great importance and can be accomplished by a variety of chemical and electrochemical processes (Ref. 1, 3, 12). All of these techniques have distinct advantages in the appropriate situations, e.g., pH range, concentration range, matrix composition, temperature, etc. However, these processes suffer in not being economically viable or being technologically difficult when the operating conditions are not optimum. For example, reactions in ion-exchange columns replace the metal ions in solution with another cation (e.g., Na^+ or Ca^{2+}) from the ion-exchange medium (Ref. 13). This exchange reaction results in product solutions of high salt concentration. If the ion-exchange column is to be reused, recharging the ion-exchange resin is necessary, which creates additional waste. If the exchange column is not reused, disposal of the metal contaminated column is required.

Simple precipitation reactions require adding precipitating reagents to adjust the pH and/or to complex to the metal ions (Ref. 3, 12, 14). The precipitation reactions produce a sludge that must be treated, e.g., dewatered and stabilized, prior to disposal. The resulting solid waste may be classified as hazardous. Depending on the precipitating reagents used, the "cleaned" water may have a significant salt content, e.g., soluble Na^+ compounds. Additionally, as the metal ion concentration in the water decreases, the amount of precipitating agent required increases (Ref. 14), which adds to the cost of the remediation.

Removal of metal ions and various anions by adsorption to solids can also be used to improve water quality. However, this process produces a large volume of solid waste (potentially hazardous) that must be disposed of economically, safely, and legally.

Consequently, the development of newer technologies is required such that ground and surface water remediation and abatement/ recycling of process water can be accomplished, meeting the goals of reduced waste, reduced cost, and high water quality. The ability to recover strategic metals from the remediation or abatement processes would minimize the cost of the remediation, reduce the amount of new metal that must be mined, and thereby reduce the amount of future environmental contamination. This last point is amply demonstrated by the recycling of aluminum containers.

1.2 Research Objectives

The objective of Activity IV, Project 4, of the MWTP is to investigate the use of substituted electrically conducting polymers (ECPs) to remove metal ions and associated anions from water and to eliminate or reduce some of the technical and financial problems for remediation of aqueous systems. Electrically conducting polymers (Ref 15–18) have been studied for many years and have potential applications as molecular wires, electrochromics, batteries, sensors and indicators, electronics, and electromagnetic shielding. The substituents (functional groups) will be designed to remove metal ions and the associated anions from water without the addition of chemical reagents, to provide for the recovery of the aqueous contaminants, and to be reusable. Functional groups bonded to the backbone of the ECPs will be chosen so they can easily be oxidized or reduced.

Changing the electrical potential of the ECP will cause the oxidation or reduction (redox) reaction in the appropriately designed functional groups. One form of the functional group (oxidized or reduced) will have a strong affinity for the metal ion. Altering the oxidation state of the functional group will then lower the binding affinity for the metal ion. By altering the electrical potential applied to the polymer, it will be possible to turn the ion binding ability of the polymer system on or off. A corresponding polymer system will be used for the anions. Although described as an on/off process, the metal ion (or anion) binding affinity is simply altered between a high and a low value. However, depending on the chemical form of the functional group, the binding affinities can vary by many orders of magnitude (Ref. 19), thereby approximating on/off conditions. In the on mode, the aqueous effluent from the polymer system should be of high purity, since contaminants are being removed and no chemical agents are added. When the contaminant capacity of the polymer system is reached, the functional groups are turned off. The effluent during the off-cycle will be a highly concentrated solution that, in the ideal case, can be processed to reclaim the metals and anions. Reclamation of the metals and anions will defray some of the cost of the remediation. To enhance the metal removal efficiency, the chemical and structural features of the polymer/functional group system will be designed to take advantage of the chelate effect (Ref. 14, 19). A chelating (multidentate) compound is one that binds to the metal ion through more than one atom. The chelate or multidentate groups bind metal ions more strongly than monodentate groups. It is essential that the chelating groups be electrically neutral so that ion-exchange reactions are not the mechanism for metal ion removal. Neutral chelating systems are actually well known and studied, e.g., the iron-porphyrin system used to transport oxygen in blood (Ref. 20).

1.3 Project Description

The project is divided into several phases; literature review, molecular modeling, polymer syntheses, and polymer characterization. Testing of polymer systems, efficiency and economic comparisons to other treatment technologies, and photochemical polymer activation are future research areas. Additional work on this project is dependent on the availability of new funding sources.

1.4 Project Alterations

The original work plan for this project included funding and participation from Metanetix Corporation. Funding from Metanetix was to provide a full-time post-doctoral research assistant, chemicals, and some instrumentation. Metanetix personnel were experienced in a variety of chemical-chelating technologies and were to make chemicals, instrumentation, and services available to this project. Due to financial difficulties, Metanetix dropped out of the project soon after it was started. The loss of the financial, personnel, and instrumentation resources from Metanetix substantially reduced the rate at which the ECP project progressed. Consequently, about half of the original work plan was completed.

2. Literature Review

2.1 Electroactive Polymer

Polymers that are electrically active have been known for most of the 20th century; however, it was not until the late 1970s that a strong interest in these materials developed (Ref. 16). The electrically active polymers are divided into three general types: redox polymers, loaded ionomers, and electrically conducting polymers (Ref. 17).

Redox polymers are referred to as localized state conductors. The polymer backbone is electrochemically inactive; however, functional groups covalently bonded to the polymer are redox active (capable of undergoing oxidation/reduction reactions.) Electron transfer (electrical conductivity) occurs by a series of electron self-exchange reactions between neighboring redox groups. The electron transfer mechanism is referred to as electron hopping (Figure 2-1). The chemical structures presented in this Report are drawn using the PC program, ChemWindow (Ref. 21) or HyperChem (Ref. 22). Unless drawn for clarity of reaction mechanisms or chemical structures, hydrogen atoms are not presented in molecular structures. The number and location of hydrogen atoms are understood from the known valences of the other

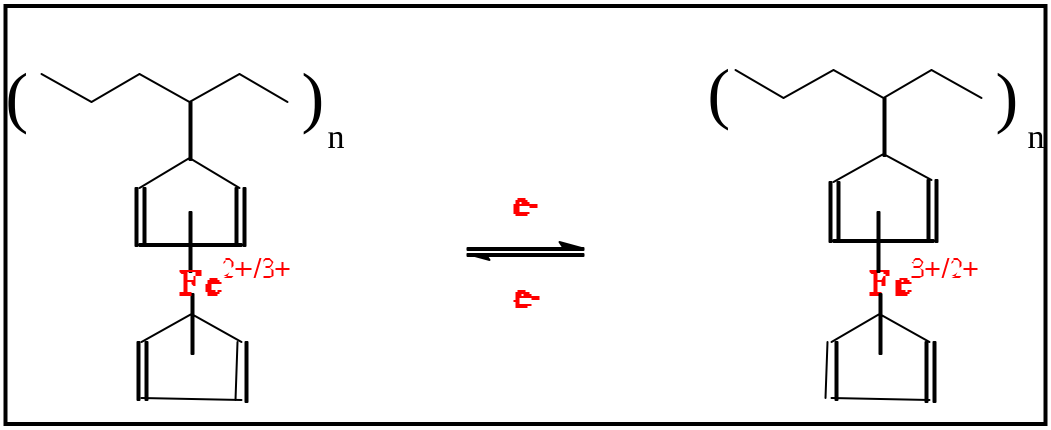


Figure 2-1. Redox polymer.

atoms in the molecules. The presence of carbon atoms is implicit in the structures at the juncture standard in organic and polymer chemistry.

Loaded ionomers are ion-exchange polymers. The redox-active species are electrostatically incorporated into the ionomer. The redox-active material is a counter ion to the cation or anion bound to the polymer chain. Electrical conductivity occurs via an electron hopping mechanism or diffusion of the redox material followed by electron transfer (Figure 2-2). Electrically conducting polymers have extensive conjugation of pi (B) orbitals, which results in considerable delocalization of the B electrons (Figure 2-3). Charge transport along the polymer chain (intrachain) is rapid. Charge transport between chains was originally thought to be much slower; however, research has shown this interchain electron hopping can in some cases be the dominant conduction path (Ref. 23).

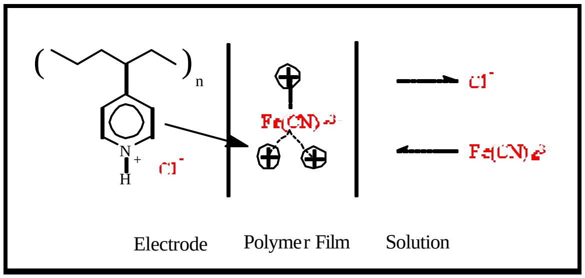


Figure 2-2. Loaded Ionomer.

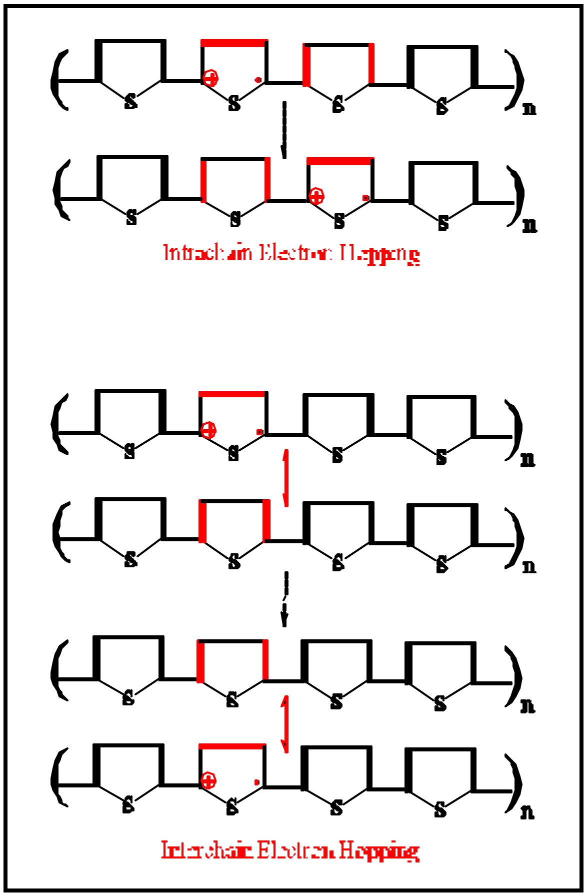


Figure 2-3. Electrically conducting polymers.

In some chelating polymer systems, the attached metal ion can be oxidized or reduced, similar to the redox polymers (Ref. 19, 24). This type of reaction is also found in a variety of natural biological systems (Ref. 20). The redox reactions of heteroatom containing groups, similar to chelating ligands, have been demonstrated in ECPs (Ref. 25, 26). Functional groups like these will be used in the work as chelating ligands to reversibly remove metals from solution.

2.2 Polypyrrole

The most well-characterized ECP is polypyrrole and as discussed below, polypyrrole is structurally and chemically very similar to the thiophene polymer systems investigated in the work (Ref. 16, 23, 27). The literature information concerning the formation, structure and electrical conductivity of polypyrrole is reviewed here since it is useful in understanding the data obtained on thiophene polymers.

2.2.1 Polymer Structure

Pyrrole (Figure 2-4) is a five-membered aromatic heterocyclic compound. The chemical formula for pyrrole is C_4H_5N, where nitrogen is the heteroatom. The " and $ subscripts, on the hydrogens, are one designation used to describe the positions on the ring. The prime marker (') is used to indicate the opposite side on a symmetrical molecule. The conjugation (overlap of the p-atomic orbitals) in this aromatic compound allows electrons (or electrical charge) to be shared between the four carbon atoms and the nitrogen atom. The valence p-atomic orbitals are shown in Figure 2-5. The five p orbitals are parallel to each other and perpendicular to the plane of the atoms.

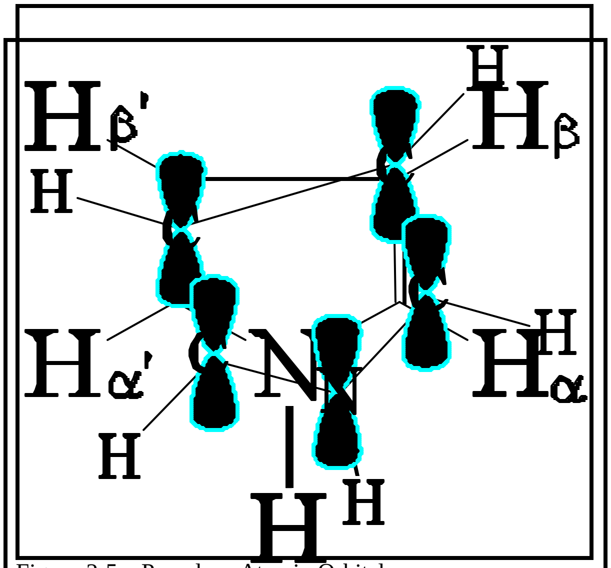


Figure 2-5. Pyrrole p-Atomic Orbitals.

Figure 2-4. Pyrrole structural formula.

The formation of polypyrrole could take several configurations with ","'; $,$'; or some combination of ",$ coupling of the pyrrole rings. However, spectroscopic studies have shown that the vast majority of the ring coupling is ","' and if the " positions are substituted, bonded to atoms other than hydrogen, little, if any, polymer is formed.

Consequently, most studies, and all of the work conducted on this project, deals with monomers substituted in the $ position. For optimal electrical conductivity between rings in a polymer chain (intrachain), the pyrrole rings must be planar. The rings can be oriented with the nitrogen atoms in the same (cis) or opposite (trans) directions (Figure 2-6).

Molecular modeling and experimental data suggests that the alternating orientation (trans) is preferred (most stable).

2.2.2 Electrical Conduction Mechanism

For most simple metals, the residence time that a charge spends on a given site within the metal lattice is very short compared to the time that the atoms vibrate (termed phonon vibration) within the lattice. The metal lattice appears rigid compared to the motion of the charge. In ECPs, the residence time for a charge, at a given site, is much longer than the vibrational time of the atoms within the polymer structure. As a result, the charge carriers (+ or -) cannot move as easily and must wait for the polymer to vibrate such that a pathway is produced to allow the charge to move to the next site.

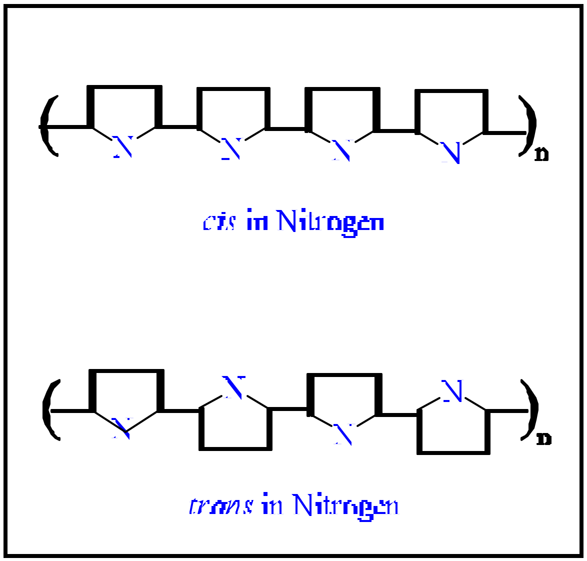


Figure 2-6. Nitrogen cis and trans conformations in polypyrrole.

The charge carriers are termed polarons, from POLAR phonONS, or bipolarons. Examples of positively charged polarons and bipolarons are given in Figure 2-7. Only one of the possible resonance forms is given for each charge carrier.

In the reduced form, polypyrrole is an insulator. Oxidation of the polymer, chemically or electrochemically, converts the polymer into a conductor. The process is often referred to as doping. At low doping levels, only polarons are formed in the polymer. As the amount of oxidation (doping) increases, bipolarons are formed. The electrical conductivity of a polypyrrole film increases with charge (oxidation) until there is approximately one charge per six monomer units. Additional doping (oxidation) produces no increase in polymer conductivity. Experimentally, it is observed that with increasing oxidation the number of bipolarons increases but the number of polarons reaches a maximum then decreases.

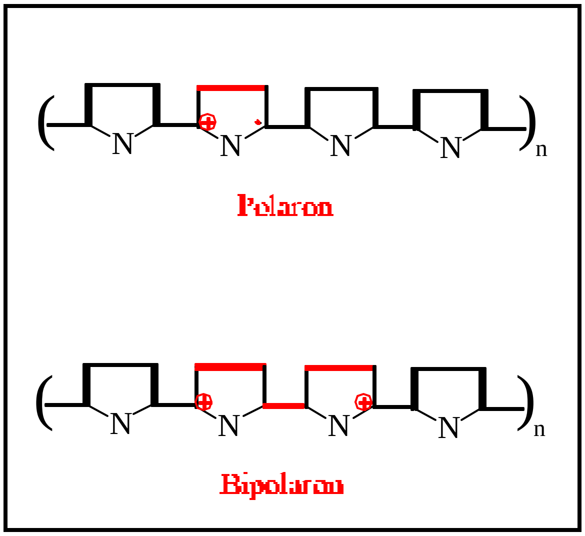


Figure 2-7. Polarons and bipolarons in polypyyrrole.

For polypyrrole, early work demonstrated that it was possible to have up to two charges per six monomer units. As a result, six monomer units have been referred to as a unit cell. As oxidation proceeds, it is energetically more favorable to add additional charges to different and separate unit cells (simple separation of like charges). As the unit cells become filled with single charges, addition of a second charge does not produce a second polaron (two charges and two unpaired electrons) but a bipolaron (two charges and no unpaired electrons). The best fit for the experimental data suggests that polarons are approximately 4.5 monomer units long and bipolarons are approximately 5 units long.

The relative number of polarons and bipolarons in a polymer is determined by the average conjugation length between defects or $-coupled monomer units, the distribution of conjugation lengths (i.e., number of monomer units) throughout the polymer film, and the size of the polarons and bipolarons. These polymer conditions appear to be highly dependent on the synthesis conditions, which explains the variation in results for inter- and intralab comparisons. These polymer conditions also affect the polymer conductivity. For example, in highly conducting polypyrrole films, it has been found that interchain hopping dominates over intrachain hopping as the mechanism for electrical conduction.

2.2.3 Polymer Film Production

For polypyrrole under a specific set of conditions (Ref. 23), there are three separate steps in the formation of the polymer film. Initially, oligomers are formed very rapidly in the solvent and precipitate onto the active sites of the electrode (anode) surface. The oligomers continue to grow homogeneously with time, until the potential (IR) drop along the chain becomes too great to support continued oxidation. At this point in the synthesis, the film is approximately 10 nanometers (nm) thick and is composed mainly of solvent and electrolyte. During the second step, there is very little change in the polymer thickness. However, polymer growth continues on the previously unoccupied sites on the electrode surface. As the polymer density on the electrode increases, the electrical conductivity of the polymer film increases. The third step begins when the conductivity is high enough to support continued growth of all the polymer chains. Chain growth continues until the potential drop throughout the film becomes too large to support the oxidative polymerization. Additional information on the electrochemical polymer synthesis is given in Section 3.2.

2.2.4 Polymer Film Morphology

The polypyrrole film is noncrystalline and for specific synthesis conditions (Ref. 23) is approximately 30% thicker than is predicted. The extra thickness comes from entrained solvent and electrolyte. Measurements of the film thickness during cyclic voltammetry (CV) experiments indicate the film decreases in film thickness approximately 30% during oxidation. However, the process is reversible, and during the reduction portion of the CV experiment, the film expands in thickness. After several repetitive CV scans, a steady state is reached in terms of the shrinking and swelling of the polymer film.

There are two concurrent mechanisms for the constriction of the polymer film. There is a monotonic decrease in film thickness with increasing oxidative potential. As polarons are formed within the polymer, the positive charge on the polymer repels the cations of the electrolyte and associated solvent molecules. The initial rise in the CV anodic wave is due to the formation of the polarons. The transition from polarons to bipolarons as the dominant charge carriers in the polymer is noted by the peak maximum in the anodic wave. At this point there is also an electrostriction (electronic constriction) of the polymer film, and much of the remaining electrolyte and solvent is squeezed out of the film. During the reduction cycle of the CV experiment, the process is reversed, and the polymer expands allowing solvent and electrolyte to flow back into the film.

The cyclic voltammograms are asymmetrical, indicating that there are some differences in the system during the oxidation and reduction cycles. The asymmetry is believed to result from conformational changes in the polymer. The neutral polymer (nonconducting state) is thought to be most stable in a twisted configuration. However, when the polymer is oxidized (conducting state), the polymer becomes planar. (The topic of polymer planarity is discussed in more detail in Section 4.2, on Molecular Modeling). The planar form of the polymer stabilizes the positive electrical charge through conjugation (overlap of p-atomic orbitals over several atoms). The improved conjugation resulting from the planarity of the polymer reduces the reduction potential relative to the oxidation potential. When the reduction is complete, the polymer quickly, but not completely, reverts back to the twisted form. Continued cycling through the oxidation and reduction potentials in the CV experiment produces a steady state in the amount of twisted and planar sections within the polymer. This is noted in the CV data as a progression towards the same potential for the anodic and cathodic peak maxima. However, as noted in our data reported in Section 5.2, the steady-state condition usually does not contain the same amount of twisted and planar material. Consequently, the CV data remains asymmetrical.

2.3 Polythiophenes

In designing a polymer system for our initial studies of this project, substituted thiophenes were chosen for the starting monomers. The thiophene polymers are used here because of their stability in both an air and water environment (Ref. 28, 29). The monomer 3-methylthiophene (Section 3.3, Figure 3-1) was chosen for initial experiments since an abundant amount of information on synthesis conditions and electrochemical and spectroscopic data was available (Ref. 15). Note that thiophene is a five-membered aromatic heterocyclic compound very similar to pyrrole. The chemical formula is C_4H_4S, where sulfur is the heteroatom. Substitution on the 3-position corresponds to \$-substitution, which is the substitution pattern determined necessary to produce ECPs.

To develop a system that will attract and bind metals, it is necessary to have a functional group attached to the polymer that has electrons that can be shared with the metal ions. For the system to be able to reversibly bind and release the metal ions, it is necessary to be able to reversibly change the number of electrons that can be shared with the metal ions and the strength of the attraction between the electrons in the functional group and the metal ions. The functional group system chosen for the initial study is the oxidation of a primary alcohol (RCH_2OH) to the carboxylic acid (RCOOH), where R represents the polymer backbone. The polymer will be made from the 3-substituted thiophene monomer. The alcohol/acid system was chosen for a variety of reasons. The oxidation potential for this reaction is expected to be well within experimental boundary conditions (i.e., the electrical stability of the polymer system and that of water) based on the oxidation potential of methanol to formic acid (Ref. 30). Initial molecular modeling studies indicated that the 3-substituted polythiophene for both the alcohol and acid form will maintain planar thiophene rings. As noted in several literature references, ring planarity is essential for the polymer to maintain sufficiently high electrical conductivity (Ref. 23, 31, 32). In the oxidized (acid) form, the chelating ability of the polymer will be enhanced (turned on). The reduced (alcohol) form will have a lower binding affinity for the metal ions (turned off).

Substituted polymers will also be used to bind the aqueous anions associated with the metal ions since electrical neutrality must be maintained. Work reported in the literature suggests two potential polymer systems for binding anions: metal-polymer complexes and functional group-containing polymers. Anions will be attracted and bound to sites with electron deficiencies. These sites can be either metal ions bound within an ECP or functional groups that can be made electron deficient through oxidation. For the metal ion systems in the reduced state, the metal-polymer complex will be electrically neutral (turned off). Oxidizing the bound metal to a higher oxidation state will result in a site of positive charge (Ref. 33, 34), thereby attracting and binding the negatively charged anions. The functional group system could be based on the redox couple of nitrate to amine (RNO_2/ RNH_2). In acidic solutions like those found with many metal-bearing solutions, the amine would be protonated to form the quaternary amine, a positively charged species. The positively charged amines bound to the polymer will attract and bind soluble anions. There is some concern however that the metal ions will compete with the hydrogens bonded to the nitrogen of the amine (Ref. 35). This would minimize the anion removal efficiency.

For the polymer systems to be effective in removing metal ions and associated anions from solution, the polymers must be supported on a mechanically strong and porous material with sufficiently high electrical conductivity. Reticulated vitreous carbon (Ref. 36) is one material that meets these requirements.

3. Synthesis

3.1 Introduction

Synthesis of the ECPs was done using two principle methods: “classical” organic synthesis and electrochemical synthesis. A synopsis of each synthesis procedure is given in this section. Each method has its advantages and disadvantages. The organic synthesis can be used to produce significantly more polymer than the electrochemical method. However, the classical procedure uses much more solvent and reagents, is more time consuming (days), and is more difficult to accomplish. The electrochemical synthesis is fast (minutes) and easy to implement; however, the quantity of polymer produced using the current instrumentation is very small. Other advantages of the electrochemical procedure will be presented later in this section. As discussed later in this report, the monomer 3-thiophene methanol was derivitized to increase the amount of polymer that could be produced electrochemically. The synthesis conditions for the derivitization reaction are also presented here.

3.2 Chemical Polymerization

The “classical” chemical polymerization reactions were based on the procedure of Hotta, Soga, and Sonoda (Ref. 37). The reaction is a dehydrogenation condensation process where the iron in $FeCl_3$ (iron (III) chloride) acts as a Lewis acid (electron acceptor), and the chloride acts as a Lewis base electron donor. Like the electrochemical polymerization, this reaction proceeds more effectively to the desired product in the absence of water and oxygen. Consequently, the reaction was done in a glovebox under a nitrogen atmosphere.

3.2.1 Chemical Polymerization of 3-Methyl Thiophene

A total of 9.73 grams (g) of ferric chloride was added to a three-necked round bottom flask and heated at 100° C for 30 minutes while under vacuum and extreme agitation. After the $FeCl_3$ was dried, the vacuum line was removed, and dry nitrogen gas was allowed to flow, via side ports, through the reaction vessel and then through an NaOH trap. Then 100 milliliters (mL) of nitrobenzene were slowly added to the flask. Finally, 2 mL of 3-methyl-thiophene monomer were added via a dropping funnel while the reaction mixture was stirred vigorously. The reaction mixture turned a deep brown-black color after the monomer was added and became extremely viscous. Five grams of NaOH in a U-tube (trap) were used to eliminate the hydrogen chloride evolved when the monomer reacted with the $FeCl_3$. The reaction mixture was stirred for 50 hours under dry nitrogen flow. Upon completion, 100 mL of the flat black mixture was precipitated into 200 mL of methanol. A Buchner funnel, with vacuum, was used to collect the black precipitate. The precipitate was then washed with copious amounts of deionized water and methanol and cleansed for 21 hours with methanol via a Soxhlet extractor. The resulting precipitate was allowed to dry for 2 days, in which time it formed a solid cake of flat-black 3-methylthiophene polymer. The deep black color is a result of the doping of the polymer by $FeCl_3$ (Ref. 35). Approximately, 0.281 g of the polymer product was produced.

3.2.2 Chemical Polymerization of Derivatized 3-Thiophenemethanol

The chemical polymerization of derivatized 3-thiophenemethanol was carried out using the same procedure that was described in Section 3.2.1 with the exceptions listed below. The amounts of reagants and solvent were 6.34 g $FeCl_3$, 2 mL monomer, and 50 mL nitrobenzene. The derivatized alcohol was prepared using the procedure described in Section 3.4. The reaction mixture was stirred for 2 to 3 hours under dry nitrogen flow. The reaction mixture was precipitated into methanol. The precipitate was alternately washed with methanol and deionized water. A Soxlet extraction was not done. Approximately 0.949 g of product was obtained.

3.2.3 Chemical Polymerization of 3-Thiophenemethanol

The chemical polymerization of 3-thiophene-methanol was carried out using the same procedure that was described in Section 3.2.1 with the exceptions listed below. The amounts of reagents and solvent were 6.34 g $FeCl_3$, 2 mL monomer, and 50 mL nitrobenzene. The alcohol was used as purchased. The reaction mixture was stirred for 2 to 3 hours under dry nitrogen flow. The reaction mixture was precipitated into methanol. The precipitate was alternately washed with methanol and deionized water. Unreacted $FeCl_3$ was noted in the precipitate by a rust color on some of the particles. Three product forms are apparent as noted by the differences in color. The products are separated into a light brown, a medium brown, and a dark brown. The three products were physically separated using a spatula for future characterization. A Soxlet extraction was not done. Approximately 4.00 g of product was obtained.

3.3 Electrochemical Polymerization

The electrochemical syntheses were done using an EG&G, model 263A, Potentiostat/ Galvanostat with model 270 software. The procedures for the electrochemical polymerization of thiophene-type monomers are based on the methods reported in a review by Roncali (Ref. 15). The monomers 3-methylthiophene, 3-thiophenemethanol, trimethylsilyl derivitized 3-thiophenemethanol, and 3-thiophene-carboxylic acid have been used (Figure 3-1). The polymers are created by the oxidative electropolymerization of the monomer onto an electrode surface. Experimental variables such as applied current density; temperature; electrode (anode) material; and choice and concentration of monomer, electrolyte, and solvent allow control over the properties of the resulting polymer. The interdependence of these variables makes optimization of the electrosynthesis conditions a complex problem. However, the electrochemical method has the additional advantages of not needing a catalyst; direct grafting of the doped, conducting polymer onto the electrode surface; and control of the polymer film thickness (Ref. 15). The electrochemical polymerization reaction was described initially in Section 2.2.3 for pyrrole. The following information is generic to the aromatic ECPs and is taken from the review article by Roncali (Ref 15). The electrochemical polymerization reaction proceeds with an electrochemical stoichiometry in the range of 2.07 to 2.5 Faradays/mol or electrons/monomer molecule. The oxidation of the monomer for polymerization requires two electrons-molecule, as shown in the reaction mechanism of Figure 3-2. The excess charge is used in the reversible oxidation or doping of the polymer and makes the polymer electrically conducting.

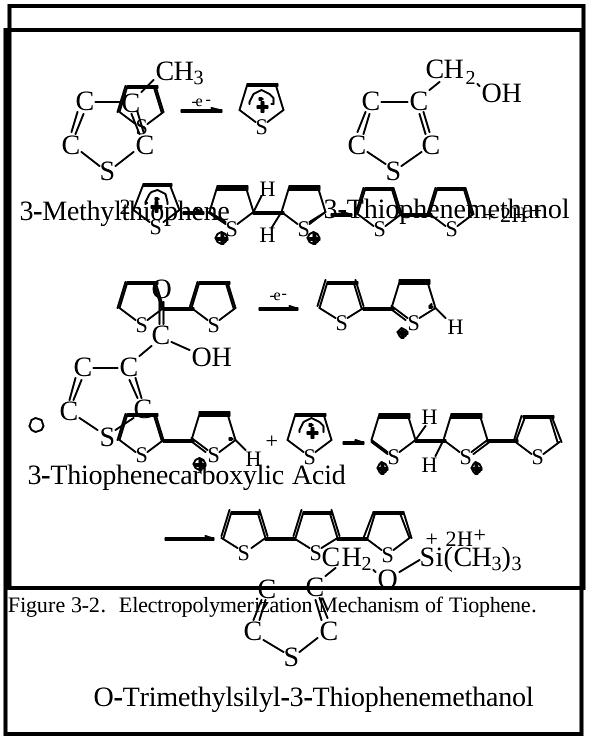


Figure 3-2. Electropolymerization Mechanism of Tiophene.

Figure 3-1. Structural Formulas for Thiophene Monomers

As shown in Figure 3-2, the first electrochemical step is the oxidation of the monomer to its radical cation. One electron is lost from each monomer molecule that is oxidized. A high concentration of the monomer radicals is maintained near the electrode surface since the oxidation reaction is much faster than the diffusion of the radicals to the bulk solution. The second step is a chemical reaction and involves the coupling of two radicals to produce a dihydro, dimer dication intermediate. The intermediate quickly loses two protons (hydrogen ions) and rearomatizes to form the dimer. The rearomatization constitutes the driving force of the chemical step, an energetically more stable product. The dimer is more easily oxidized than the monomer, which results in a rapid increase in the concentration of dimer radicals. This is the third step in the reaction and shows the loss of the second electron from the terminal monomer unit. The forth step in the reaction is the chemical reaction where the dimer radicals couple with monomeric radicals to form trimers and two protons. It is possible that some dimer-dimer coupling occurs to form tetramers. However, due to the high concentration of the monomer radicals, monomer addition is the highest probability process for continued polymerization. Electropolymerization proceeds then through successive electrochemical and chemical steps according to this general scheme until the oligomer becomes insoluble in the electrolytic medium and precipitates onto the electrode surface. As discussed in Section 5.1, the solubility of the oligomer in the solvent is critical to the formation of the polymer film on the electrode.

Previous work (Ref. 15) has demonstrated that the applied electrical conditions exert considerable effects on the structure and properties of electrogenerated polythiophenes. The “best” polymers in terms of homogeneity and electrical conductivity are generally obtained using constant current conditions and electrical potentials approximately 0.5 volt (V) more positive than the oxidation potential of the monomer. The 0.5-V overpotential causes the instantaneous creation of a larger number of initial nucleation sites, improving the compactness and thus conductivity of the polymer. Synthesis using high current densities, and the necessary higher voltages, causes a decrease in electrical conductivity. It is believed that the decrease in conductivity is related to the instability of the polythiophenes at the electrical potentials near and above that required for their formation. This is termed the “polythiophene paradox,” and the consequence is that degradation of the polymer may compete with its electrodeposition. The paradox is noted for two specific conditions: high anodic potentials and when the monomer concentration is too low to sustain the rate of polymer deposition imposed by the applied electrical conditions (Ref. 15). Alternately, high monomer concentrations [> 0.5 to 1 molar (M)] tend to produce loose, poorly conducting films containing significant amounts of soluble oligomers (Ref. 15).

Work reported in the literature indicates that the most conductive polymers have been obtained on bulk platinum electrodes. This is presumably because thiophene adsorbs more efficiently on platinum and because platinum presents a larger number of potentially active sites (Ref 15). However, for the synthesis of (poly) 3-methylthiophene, good results were obtained using a glassy carbon electrode (Section 5.2).

The solvent in the electrochemical polymerization reactions, as in all chemical reactions, has a strong effect on the structure and properties of the ECP films. The solvent must have a moderate to high solubility for the monomer and electrolyte, have a low solubility for the oligomers and polymer, have a high dielectric constant to ensure the ionic conductivity of the electrolytic medium, be chemically unreactive, and be electrochemically stable at the potentials required to oxidize the thiophene rings. Numerous works have reported the deleterious consequences that trace amounts of water in the synthesis medium have on the electropolymerization reaction. During synthesis, the presence of water adversely affects the conjugation length and conductivity of the polymer. However, on completion of the synthesis, the polythiophene-type polymers are stable in both air and water environments (Ref. 15).

Using the literature information as a guide, over 70 electrochemical syntheses were performed using a variety of chemical and electrochemical conditions. A summary of the experimental conditions is given in Table 3-1. Not included in the summary table are the experiments where an attempt was made to place the polymer of 3-thiophenemethanol on top of an existing film of (poly) 3-methylthiophene.

In every experiment, tetrabutylammonium hexfluorophosphate was used as the electrolyte; however, as noted, the concentration was varied. The temperature of each experiment was that of the ambient conditions. The laboratory does not have temperature regulation capabilities, and the laboratory temperatures were not recorded. For the majority of the syntheses, nitrobenzene was the solvent, and platinum foil was used as the anode (or working electrode). However, a series of experiments were done by varying the solvent and keeping the other experimental conditions constant. The platinum electrodes were made in Montana Tech's laboratory. The platinum foil was cut to 0.5 centimeters (cm) by 0.5 cm to give a total surface area of approximately 0.5 cm^2. The platinum foil was 0.08 millimeters (mm) thick. Therefore the edges of the foil had a negligible impact on the surface area of the electrode. The reference and auxiliary electrodes were silver/silver chloride (Ag/AgCl) saturated in AgCl and 3 M in NaCl. A commercial glassy carbon electrode (EG&G) was used in some of the reactions. This electrode had a working surface area of 0.3 cm^2. The Table 3-1 Summary of the Electrochemical Reaction Conditions volume of solution (mainly solvent) for each reaction was 5 mL. The reaction solutions were sparged with dry nitrogen gas to remove any dissolved oxygen prior to the start of each synthesis. Oxygen is known to interfere with the synthesis. The reaction vessel was maintained with a blanket of nitrogen gas during the reaction.

3.4 Silylation Derivitization Reaction

The electrochemical polymerization of 3-

thiophenemethanol and 3-thiophene-carboxylic acid, as described in Section 5.1, has produced very little polymer that adheres to the platinum electrode. The occurrence of a reaction with these monomers is obvious by the appearance of a dark, wispy material in the solvent near the electrode and a discoloration of the reaction solution. The formation of the ECPs, as discussed previously, involves oxidation and bonding of the five-membered rings of the monomers. The oxygens in the alcohol and acid functional groups are areas within the monomers of high electron density. The functional groups therefore are potential areas for competitive oxidation or chemical reaction. In addition, these polar functional groups enhance the solubility of the oligomers in the solvent. As a consequence, several experiments were done on derivitized 3-thiophenemethanol. The derivitization was done to reduce the solubility of the oligomers and reduce the reactivity of the alcohol. The derivitization reaction chosen is a quite facile formation of the trimethylsilyl-3-thiophenemethyl ether (Ref. 38). For this reaction, 5 mL of 3-thiophenemethanol were combined with 10 mL of the weak base, triethylamine, in a round bottom flask under a dry nitrogen atmosphere. With vigorous agitation of the solution, 8 mL of chlorotrimethylsilane were added to the flask, dropwise, through a separatory funnel.

Table 3-1. Summary of the electrochemical reaction conditions.

Variable	3-Methylthiophene	3-Thiophene-methanol	Derivitized 3-Thiophenemethanol	3-Thiophene-carboxylic Acid
Platinum Electrode	10 Experiments	21 Experiments	27 Experiments	6 Experiments
Carbon Electrode	2 Experiments	3 Experiments	0 Experiments	0 Experiments
Solvent	Nitrobenzene	Nitrobenzene, DI Water, pH 10 Water, Pyridine, Methanol, 2-Methylfuran	Nitrobenzene, Acetonitrile,DI Water, Pyridine, Methanol, 2-Methylfuran, Dimethyl Formamide Dimethyl Sulfoxide	Nitrobenzene, DI Water, pH 10 Water, Pyridine, Methanol, 2-Methylfuran
Monomer Concentration	0.05-0.15 M	0.025-0.05 M	0.05 M (est.)	0.05 M
Electrolyte Concentration	0.02 M	0.02-0.03 M	0.02 M	0.02 M
Current	0.15-15 mA	0.15-15 mA	0.15-17 mA	2.0 mA
Time	100,300,400 s	100,400 s	100 s	100 s

Immediately a cloud of a fine white powder was emitted from the flask. The powder is thought to be triethylammonium chloride. A thick, creamcolored slurry was observed in the reaction flask. The reaction mixture was filtered through a Buchner funnel and the filtrate distilled to remove the solvent. The distillation yielded approximately 15 mL of a light amber colored distillate. Analysis of the distillate by gas chromatography/mass spectrometry determined the distillate was a mixture of the solvent, triethylamine, unreacted 3-thiophenemethanol, and the major component, trimethylsilyl-3-thiophenemethyl ether.

As discussed in Section 5.2, the amount of polymer produced from the derivatized 3-thiophenemethanol is approximately twice that produced by the underivatized alcohol.

4. Moleculecular Modeling

4.1 Molecular Modeling Introduction

Molecular modeling (or computational chemistry) uses molecular and quantum mechanical calculations to determine the energies and energy derivatives of atoms within molecules. Varying the relative three-dimensional positions of the atoms, these calculations can construct a potential energy surface for the molecule. The computer program, HyperChem (Ref. 21), has been used for the molecular modeling calculations. Within the HyperChem program, there are three types of calculations: single point, geometry optimization, and molecular dynamics; within each type, there are several calculation methods.

The single-point calculations provide information on the static properties of the molecule, such as relative atomic charges, electron density, electrostatic potential, potential energy, and ground and excited electronic state molecular orbital energies. This latter information can be used to calculate the appearance of ultraviolet, visible, and infrared spectra of molecules.

Geometry optimization calculations determine the three-dimensional Cartesian coordinates for the atoms at local and global minima on the potential energy surface of the molecule. These calculations are the precursors to the single-point calculations and the molecular dynamics calculations. Information concerning bond lengths and angles, torsional angles, and interatomic distances are also determined from the geometry optimizations.

The molecular dynamics calculations simulate the positions and velocities of atoms in molecules. These calculations account for the effects of thermal energy and solvents on the conformations and dynamics of molecules and some thermodynamic properties.

Molecular modeling is used here as a guide in studying the synthesis of ECPs and the effects of various functional groups on the syntheses and polymer properties. Where possible, the molecular modeling data is correlated with electrochemical, spectroscopic, and experimental data on the polymer systems. The results from the modeling studies and the correlations are used to maximize our understanding of the polymer systems and to guide us in what polymer systems to evaluate.

4.2 Polymer Planarity

Maximum conductivity along the conjugated polymeric chains of unsaturated rings requires that the rings be nearly coplanar (Ref. 23, 31). Electronic communication with conjugated chelating groups will require these groups also be effectively coplanar with the polymeric backbone. Substitution in the 3 position of the heteronuclear pentacyclic rings has in some cases been shown to force the rings out of planarity (Ref. 15). Modeling can determine whether the minimum energy conformations of both substituted and unsubstituted polymers are expected to be planar.

The polymers in which we are interested are synthesized chemically or electrochemically from a solution of monomer. For the case of unsubstituted heterocyclic monomers, not only are "-"', "-$', and $ -$' linkages between the monomers possible (and not insignificant in the case of polythiophene (Ref. 39), but all trans, all cis, or mixtures of cis-trans polymers, with respect to the relative positions of the heteroatoms, are also possible (Ref. 27). For asymmetrically 3-substituted monomers, the number of possible substitutional patterns or tacticity in the synthesized polymers is much greater (Ref. 27). Steric interactions between adjacent 3-substituted monomers may provide some control over the conformation and tacticity of the resultant synthetic polymer. Modeling can predict which of these linkages, cis-trans, and substitutional patterns represents a minimum energy conformation and is therefore most likely to represent the most favorable structure of the synthesized polymer.

Internal rotation about inter-ring bonds has the potential to convert the polymeric backbone among different cis-trans patterns. Internal rotation about the functional group-ring bond can similarly alter the orientation of the functional group with respect to the ring atoms or with respect to neighboring functional groups and hence affect the ability of these groups to complex metals. Molecular modeling can predict the magnitude of the energy barriers that must be surmounted to accomplish these internal rotations. Preliminary modeling studies in this laboratory indicate that the barriers to internal rotation are sufficiently large (> 40 kcal) to prevent internal rotation about either inter-ring or functional group-ring bonds, although other studies suggest that internal rotation about the inter-ring bond is possible for bithiophene in the liquid state (Ref. 40).

The ability of the functional groups to complex metal ions is expected to be strongly influenced by the electron density in the molecular orbitals associated with these groups (Ref. 41). The electron density is in turn expected to be strongly affected by the chemical form or oxidation state of the group. Molecular modeling should allow placement of these groups in a particular charge condition, e.g., fix all carboxylic acid groups as carboxylate anions, and then determine how the electron density associated with this introduced charge redistributes along the polymer chain. Information like this will be useful for selecting functional groups and experimental conditions for study.

4.3 Computer Hardware and Software Information

The initial molecular modeling work was done using HyperChem version 3.0 on a 486 PC with 8 Mbytes of RAM and a 33-MHZ clock speed. Geometry optimization calculations were done by a two-step process. A molecular mechanics method, MM+, was used to calculate an initial optimized geometry. The results from this calculation were then used as the starting point for the AM1, semi-empirical, calculations. Calculations on the thiophene octomers typically required in excess of 7 or 8 days of continuous operation. Unfortunately, the calculations were often halted by power interruptions to the computer. It was then necessary to restart the calculations at the beginning.

Our initial molecular modeling studies indicated that oligomeric (with up to eight rings) 3-thiophenemethanol and 3-thiophenecarboxylic acid are planar and hence may be expected to be conducting. As a result, these monomers were chosen for experimental study.

The computer hardware and software have been upgraded for the modeling studies. The current computer is a 586 PC with 16 Mbytes of RAM and a 90-MHZ clock speed. Version 4.5 of HyperChem is used for the calculations. It is no longer necessary to use a MM+ precalculation to expedite the geometry optimizations. However, in comparing the final modeling results with and without the precalculation, the results are indistinguishable. The results reported here are based on the semi-empirical AM1 method using the following conditions: self-consistent field convergence limit of 0.0001, RHF spin pairing, no configuration interaction, the Poak-Ribiere (conjugate gradient) calculation algorithm, a termination condition of 0.1 kcal/D mol, and in vacuo (no solvent or other boundary conditions).

4.4 Geometry Optimization Results

The focus of our recent modeling work has been the 3-thiophenemethanol system. This system was chosen because of the difficulties encountered in electrochemically forming polymer on the electrode. The cis and trans forms of the octomer, with respect to the sulfur atom, show some interesting differences. Disk plots of the trans form of the 3-thiophenemethanol octomer are shown in Figures 4-1 and 4-2. The two perspectives of this molecule are given to demonstrate the molecule is linear and planar. Figure 4-1 is an edge view of the molecule where the yellow disks represent the sulfur atoms, red is oxygen, blue is hydrogen, and black is carbon. Four of the eight sulfur atoms are pointed toward the front of the molecule, while the other four sulfur atoms are oriented 180E from the front-facing sulfurs. From this figure, it is obvious that with respect to the thiophene rings the molecule is planar. Figure 4-2 is similar to Figure 4-1 except the molecule has been rotated approximately 60E toward the viewer to provide a partial view of the backside of the molecule. The planarity of the molecule is noted, for example, by the horizontal alignment of the sulfur atoms in the front and back of the molecule. A quantitative measure of the planarity is the torsional angle between adjacent sulfur atoms. From left to right in Figure 4-2, the torsional angles are measured as: 178.29E, 177.22E, 178.09E, 178.98E, 179.42E, 178.63E, and 179.37E (average value 178.57E). Torsional angles of 180E are required for a completely planar system. It is obvious from the numbers, that the trans octomer is very close to planar. As discussed below in more detail for the cis conformation, the neutral form of the polymer is nonconducting. When the polymer is oxidized (ionized), it becomes conducting. Calculating the torsional angles for the trans 3-thiophenemethanol octomer containing two positive charges indicates slight improvements towards planarity. The torsional angles for the dication of the trans isomer are: 179.01E, 178.83E, 179.76E, 179.76E, 179.00E, 179.02E, and 178.77E (average value 179.16E).

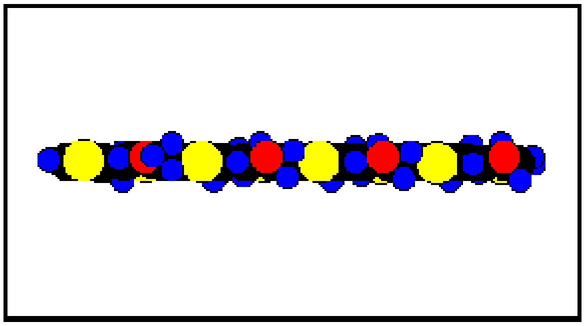


Figure 4-1. AM-1 geometry optimized trans form of octomer of 3-thiophenemethanol - edge view.

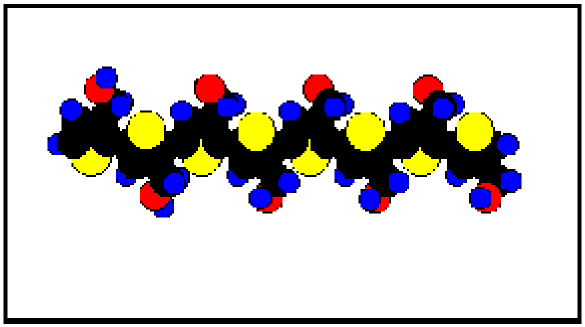


Figure 4-2. AM-1 geometry optimized trans form of the octomer of 3-thiophenemethanol - rotated.

Figures 4-3 and 4-4 show the geometry optimized structure of the cis form of the 3-thiophenemethanol octomer. Figure 4-3 is an edge view of the molecule with the sulfur atoms in the back. It is obvious from this figure that the molecule is not planar. This is confirmed by measuring the torsional angles between the adjacent sulfur atoms. For a planar molecule in the cis form, the torsional angle would be 0E. From left to right in Figure 4-3, the sulfur torsional angles are -55.75E, -37.21E, +47.36E, -35.74E, -35.93E, +41.26E, and -38.31E (average absolute value 41.65E). In Figure 4-4, the lack of planarity in the octomer is noted by the position of the sulfur atoms rotating from front to back in going from left to right in the figure. It is also noted from this figure that the molecule is not linear but is bent. The octomer is "U" shaped and twisted. The electrical conductivity for this conformer would be expected to be much less than that of the trans form.

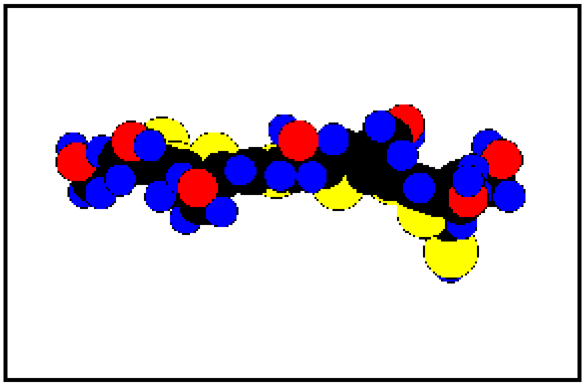


Figure 4-3. AM-1 geometry optimized cis form of the octomer of 3-thiophenemethanol - edge view.

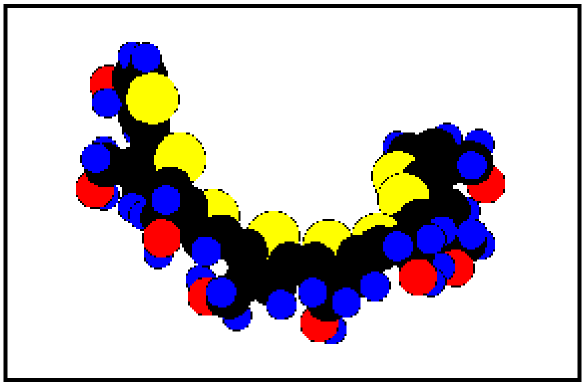


Figure 4-4. AM-1 geometry optimized cis form of the octomer of 3-thiophemememethanol - rotated.

Figures 4-5 and 4-6 show the geometry optimized structures of the +2 ion of the cis 3-thiophenemethanol octomer. The +2 charge was chosen based on literature data indicating a maximum single charge (polaron) every four monomer units or a maximum double charge (bipolaron) every six monomer units (Ref. 15, 23). The edge view of the dication of the molecule (Figure 4-5) shows that the ion conformation is still not planar. However, the ion is not twisted as much as the neutral octomer. This result is seen more quantitatively by looking at the torsional angles between adjacent sulfur atoms. From left to right in Figure 4-5, these values are: -55.75E, -37.21E, +10.36E, -6.41E, -5.05E, -2.35E, and -24.60E(average absolute value 20.20E). The torsional angles are smaller than those of the neutral molecule particularly in the center of the octomer. Figure 4-6 is a face view of the dication. The enhanced planarity, as compared to the neutral molecule, is observed by looking at the number of the sulfur atoms that are totally visible. Although the dication is still "U" shaped, there is less twist in the structure than in the neutral molecule.

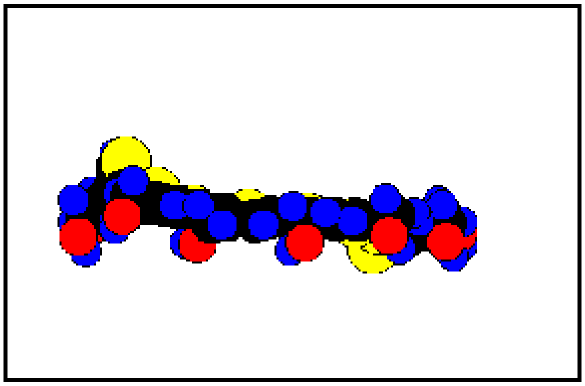


Figure 4-5. AM-1 geometry optimized cis form for the +2 ion of the octomer of 3-thiophenemethanol - edge view.

In considering potential structures for the modeling study, the ",$ combinations were not evaluated. This decision was based on literature information that indicates this coupling does not have a significant contribution in ECPs. The cis and trans forms studied, so far, are both isotatic. This means the substituents are all on the same side of the thiophene ring. Complimentary studies need to be done on the syndiotatic forms of the cis and trans isomers.

In addition, the heats of formation and the ultraviolet/visible (UV/VIS) and infrared (IR) spectra of these octomers need to be calculated. As discussed in Section 5.3, there is experimental evidence that suggests the polymer changes confirmation as it is oxidized and reduced. Additional modeling studies need to be done to confirm and better understand this conformational change with electronic conditions.

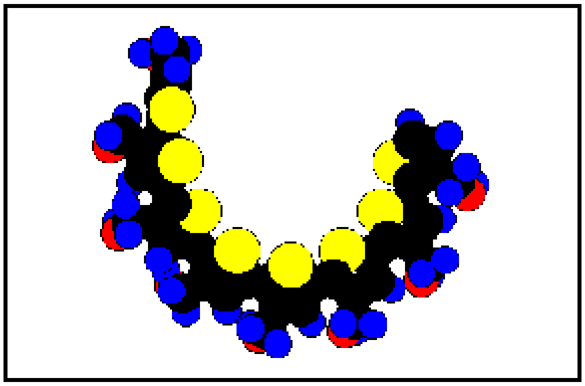


Figure 4-6. AM-1 geometry optimized cis form of the +2 ion for the octomer of 3-thiophenemethanol-rotated.

4.5 Electron Density and Atomic Charge Results

The electron distribution within a molecule determines the site and type of reactions that can occur in that molecule (Ref. 42). The determination of electron distributions can be obtained by calculating electron density maps and atomic charges for molecules (Ref. 43). The electron density contour maps and atomic charges presented here are based on single-point calculations of the AM1 geometry-optimized molecules.

Figure 4-7 shows the atomic charges and Figure 4-8 shows the electron density map for 3-methylthiophene. The atomic charges are best used as relative numbers for comparisons and not as absolute values. The atomic charges in Figure 4-7 indicate excess negative (electron) charge on the "-carbons. The electron density map in Figure 4-8 shows the highest density about the unsubstituted 3-position on the thiophene ring (the $ carbon bonded to a hydrogen). However, high electron density is also noted on the two " carbons (1 and 5 positions on the ring). The combination of these two sets of information would suggest that the "-carbons would be the most probable site for an oxidative (electron removal) reaction. This is observed experimentally in the chemical and electrochemical synthesis of poly (3-methylthiophene)

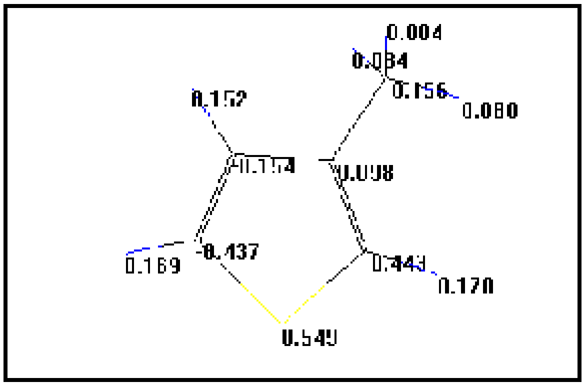


Figure 4-7. Atomic Charges in 3-Methylthiophene.

Figures 4-9 and 4-10 contain the atomic charges and the electron density map, respectively, for 3-thiophenemethanol. Comparing the atomic charges in Figures 4-7 and 4-9, it is seen that the charges on the " carbons have not changed significantly. However, the charge on the oxygen of the methanol group is comparable to that on the "-carbons. Viewing the electron density map of Figure 4-10, it is observed that the area about the oxygen atom has a noticeably higher electron density than that found around the "-carbon atoms. The combination of results in Figures 4-9 and 4-10 indicates that the oxygen atom is an area that must be considered strongly as a site for electrophilic (electron loving) type reactions and may be a preferential site for oxidation reactions (Ref. 44).

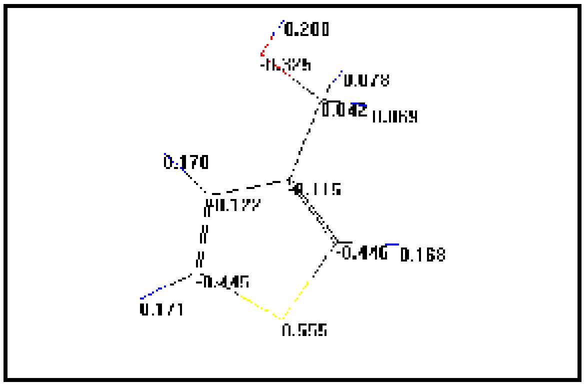


Figure 4-9. Atomic Charges in 3-Thiophenemethanol.

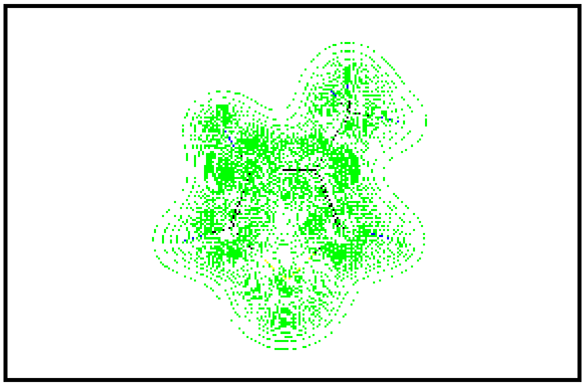


Figure 4-8. Electron Density Contour Map of 3-Methylthiophene.

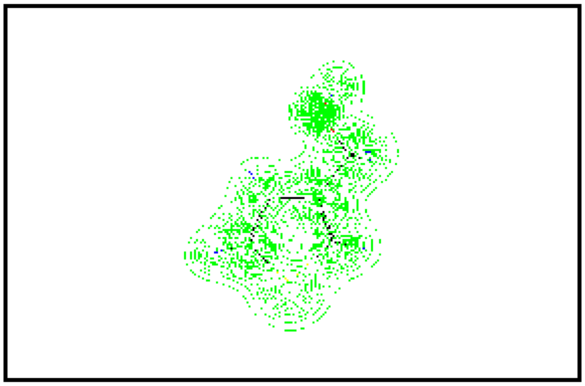


Figure 4-10. Electron Density Contour Map of 3-Thiophenemethanol.

Derivitization of functional groups has been known to protect these groups from chemical reaction (Ref. 45,46). Figures 4-11 and 4-12 show the atomic charges and the electron density map, respectively, for the trimethylsilyl derivative of 3-thiophene-methanol (O-trimethylsilyl-3-thiophene-methanol). Comparing the atomic charges in Figures 4-7, 4-9, and 4-11 reveals little change in the values on the "-carbons, however there is a slight increase in the negative charge on the derivitized oxygen atom. Looking at the electron density map in Figure 4-12, it is seen that the greatest density still lies about the oxygen atom. One would predict that the oxygen atom may still be the site of greatest electrophilic activity. However, as discussed below, derivatizing groups often function by sterically blocking reactions.

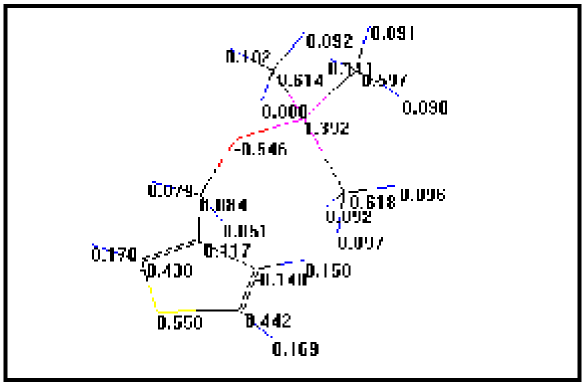


Figure 4-11. Atomic Charges in O-Trimethylsilyl-3-Thiophenemethanol.

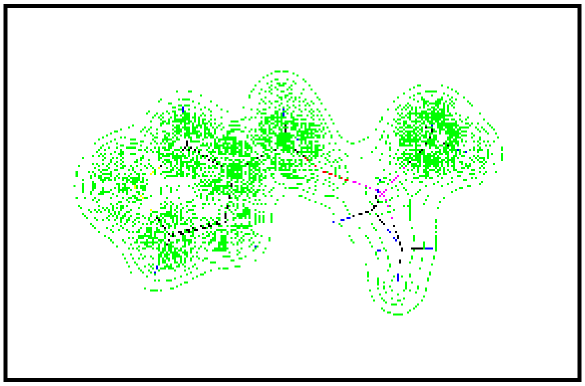


Figure 4-12. Electron Density Contour Map of O-Trimethylsilyl-3-Thiophenemethanol.

The apparently high electron density about one of the methyl groups on the siliconatom in Figure 4-12 is an artefact of the three-dimensional structure of the molecule. Since the methyl groups on the silicon atom are above and below the plane of the thiophene ring and the oxygen, the electron densities on these groups are positively and negatively exaggerated relative to the other atoms.

Derivatizing (or protecting) groups can prevent or minimize certain chemical reactions by altering the energy necessary for the reaction (a thermodynamic effect) or by physically preventing or slowing reactants from reaching a reactive site (a kinetic effect.) By comparing the structures of the derivatized and underivitized alcohol in Figures 4-13 and 4-14, respectively, it is observed that the oxygen (shown in red) in the derivatized molecule is sterically protected from reaction. In terms of energy, the oxygen is still probably the preferred site for reaction, but the kinetics of reactions at the oxygen are decreased substantially because the oxygen is physically inaccessible.

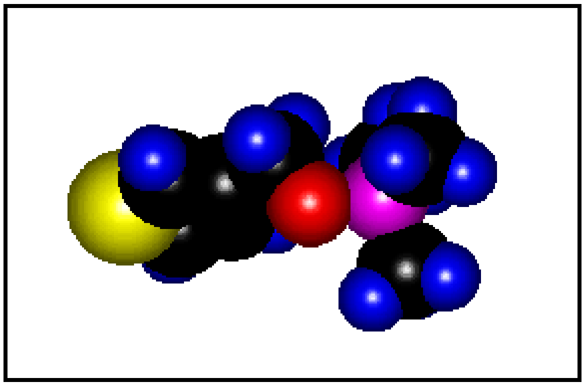


Figure 4-13. 3-D Rendering of O-Trimethylsilyl-3-Thiophenemethanol.

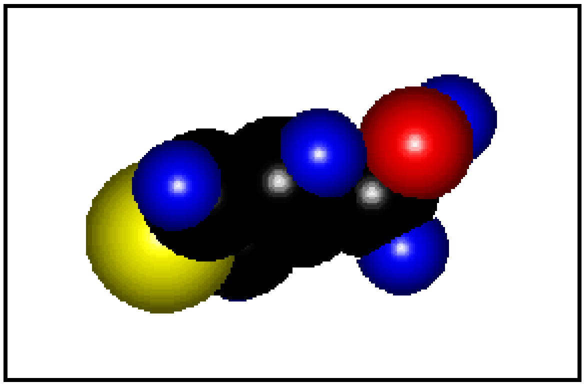


Figure 4-14. 3-D Rendering of 3-Thiophenemethanol.

In addition to protecting the alcohol group from reaction, the derivitve will also lower the solubility of any oligomer in polar solvents such as nitrobenzene. From these modeling results, it was decided to experiment with derivitized alcohols as a means to increase the amount of polymer formed at the working electrode. As noted in Section 5.3, the amount of polymer formed from the derivitized monomer is approximately twice what was observed with the underivitized 3-thiophenemethanol.

A significant amount of work remains to be done in the modeling studies. As more information is gained in the modeling work and correlated to experimental data, greater improvements will be realized in the quality and quantity of ECPs produced.

5. Experimental Results

Our initial literature work led us to investigate the polythiophene ECP systems. This decision was based on the polymer stability in air and water, the availability of appropriate monomers, and the relatively high electrical conductivities for this class of compounds. As discussed in Section 4, the first modeling calculations indicated the substituted thiophenes of interest would maintain planar thiophene rings after polymerization. Our initial synthetic work was the electrochemical synthesis of poly (3-methylthiophene). This system was chosen because it has been well characterized electrochemically and spectroscopically (Ref. 47). We have used both glassy carbon and homemade platinum electrodes in the syntheses. Characterization of the polymers synthesized in our laboratory, to date, has been done using CV, UV/VIS absorption spectroscopy, and IR absorption spectroscopy.

5.1 Electrochemical Synthesis Monitoring

The electrochemical synthesis of the polymers has been done under constant current conditions. Constant current synthesis has been the electrochemical method of choice in the literature (Ref. 15, 16, 23). The EG&G potentiostat hardware and software alter and record the potential on the working electrode to maintain the constant current conditions in the elctrochemical cell. Plots of the electrode potential as a function of reaction time are given in Figure 5-1 for four representative synthesis experiments: solvent/electrolyte blank, 3-methylthiophene monomer, 3-thiophenemethanol monomer, and derivitized 3-thiophenemethanol monomer. For a "well- behaved" electrochemical system, the time versus potential plot should be a step function. At time zero, the electrode potential is zero. With the start of the reaction, there is an instantaneous rise in the electrode potential from zero volts to the potential required to conduct the preset current in the cell. At this point, the cell current, and hence the electrode potential, is determined by the diffusion rate of the analyte to the electrode. As long as the bulk concentration of the analyte remains constant, the cell potential will not change with time. This discussion assumes the electron transfer rate between the electrode and the analyte is much faster than the diffusion rate of the analyte from the bulk solution to the electrode/solution interface.

The electrode potential profile for the synthesis blank (tetrabutylammonium hexafluorophosphate, TBAPF6, in nitrobenzene) is very near this ideal response, as seen in Figure 5-1. The potential versus time plot for 3-methylthiophene is also near the ideal profile, although the electrode potential does show a slight increase with time. The large difference in required potential between the blank and the 3-methylthiophene data (ca. 8 V) indicates the current flow is caused by the oxidation reaction of the 3-methylthiophene.

The electrode potential profiles for the 3-thiophenemethanol monomer and derivatized 3-thiophenemethanol monomer show deviations from the ideal with the large curvatures in the signal in the 5 to 20 second time range and by the continued rise in the potential with increasing reaction time. These nonidealized potential profiles correlate well with the poor adhesion of the polymer to the working electrode. It is proposed that the curvatures are the result of oxidation reactions occurring away from the electrode surface.

In the production of poly (3-methyl-thiophene), the formation of the polymer is obvious by the initial discoloration on the working electrode and the buildup of the polymer film. The formation of oligomer and possibly small polymer is noted in the reactions of the 3-thiophenemethanol monomer and derivatized 3-thiophenemethanol monomer by an initial discoloration on the working electrode, followed by the formation of dark, wispy-looking material near the electrode surface. This dark material, having the appearance of cirrus clouds, quickly moves and dissolves into the solvent. It is not known at this time whether diffusion or some other process is responsible for the movement of the material; however, the movement of the material away from the electrode can be visually observed. Dissolution of the dark brown matter is noted as the solution changes from clear to a light yellow-brown color. The formation and dissolution of oligomer is also noted in the experiments using 3-methylthiophene monomer. However, the relative amount of material dissolved is much less than that found with the polar-substituted monomers.

As noted in Section 5.2, the derivatized 3-thiophenemethanol monomer produces more polymer attached to the working electrode than the underivitized monomer. Observing the potential profiles in Figure 5-1, it is noted that the 3-thiophenemethanol potential profile shows a more significant deviation than the derivitized monomer. The shape of these time versus potential plots may be an indication of the difference between having reactions at or near the electrode surface. Additional experimental and literature work needs to be done to understand this data more completely.

5.2 Cyclic Voltammetry Results

A comparison of our CV data for poly (3-methylthiophene) to that reported in the literature (Ref. 22) is given in Figure 5-2. The close agreement in the general appearance of the voltammograms is an indication of our ability to reproduce the 3-methylthiophene polymers as reported by others. Minor differences between the two voltammograms occur because the literature data is reported as current not current density, the saturated calomel electrode (SCE) is used for reference not a Ag/AgCl electrode, and was scanned to only 1,000 millivolts (mV) not 1,500 mV.

A cyclic voltammogram is produced by systematically changing the potential between the working and reference electrodes and monitoring the current that is produced at the working electrode (Ref. 23, 48, 49). Cyclic voltammogram is useful for studying the mechanism and kinetics of reversible oxidation/reduction (redox) reactions (Ref. 23, 50). The potential is “scanned” (changed monotonically) from its starting voltage to some preselected positive voltage to oxidize the material of interest. The potential difference is then decreased, to some preset value, to cause the reduction reaction to occur. The electrode potential is then returned to the starting voltage, ending the first CV scan. The voltage range scanned is determined by the material being studied and the electrochemical stability of the solvent and electrolyte in the CV cell. We used the electrochemical synthesis solution as the first solution for obtaining cyclic voltammograms of the synthesized polymers. Solutions using lithium per chlorate as the electrolyte and either water or acetonitrile as the solvent have also been used to obtain cyclic voltammetry data.

To determine the CV results are from the polymer systems and not the solvent/electrolyte solutions, blank cyclic voltammograms were recorded. The potential range of -500 mV to +1,500 mV (versus the Ag/AgCl reference electrode) was chosen because the solvent/electrolyte system is electrochemically stable in this range, the substituted thiophene polymers can be oxidized and reduced in this range, and any residual monomers will not react appreciably at these voltages. The CV data for the TBAPF6/nitrobenzene solution is given in Figure 5-3. The current density recorded is nanoamps (nA) per square centimeter of working electrode surface. This current density is several orders of magnitude less than those observed when polymer films coat the electrode, for example Figures 5-4 to 5-6. These results indicate the CV data for the polymers represent redox reactions within the polymer systems and not from the solvent or electrolyte.

For reversible, one-electron transfer reactions, the cyclic voltammograms should be symmetrical. The symmetry occurs in that the reverse (reductive) scan should be a mirror image of the oxidative (forward) scan but changed in sign. The mirror (or plane) of symmetry is at the half-wave potential ($E_{1/2}$) (Ref. 49) for the redox reaction. The half-wave potential is equivalent to the cell potential when the electrolytic cell current is equal to the diffusion limited current of either the oxidized or reduced electroactive species. The lack of symmetry is readily noted in the CV data of Figure 5-2, where the oxidation scan contains one maximum and the reduction scan contains two maxima.

Figures 5-4, -5, and -6 are the cyclic voltammograms of the polymers from 3-methylthiophene, 3-thiophenemethanol, and derivitized 3-thiophenemethanol, respectively. Although difficult to see in Figures 5-3 and 5-4 due to the broad features of the curves, the CV data in these three figures also shows an asymmetry. The asymmetric nature of the ECPs has been attributed to a change in the polymer conformation between the oxidized and the reduced forms (Ref. 21). It is postulated that the reduced nonconducting forms of the polymers have a twisted conformation. This means the monomer units within the polymers are not planar. When the polymers are oxidized (conducting), the polymer becomes more planar, which gives better overlap of the B orbitals and hence better conductivity. The planar form of the oxidized polymer is then in a lower energy configuration, and as a result, requires less energy for the reduction reaction. The lower energy of the polymer leads to a lower reduction potential. In the reduced form, the polymer conformation twists again, raising the energy of the system and shifting the oxidation potential to higher values. The changing of the polymer conformation and the resulting changes in energy cause the asymmetric appearance in the CV data. Our molecular modeling data, as reported in Section 4.3, supports this postulate. A significant amount of additional work needs to be done to better understand the CV data and the resulting affects on ECP performance.

The general profiles of the CV data for the three polymer systems are different. One valuable piece of information from these results is the area of each cyclic voltammogram. Since the current flow is determined only by the polymer system and the amount of current is determined by the amount of polymer oxidized or reduced, the area of the cyclic voltammogram is a measure of the amount of polymer on the electrode. We currently do not have a good measure for the number of polarons and bipolarons formed for each polymer type or experimental synthesis/ analysis; therefore, we cannot quantitatively determine the amount of polymer from the CV data. However, we can qualitatively determine having more or less polymer based on the voltammogram areas. From the data in Figures 5-4, -5, and -6, we can say that the 3-methylthiophene produced the most polymer on the electrode. The derivitized 3-thiophenemethanol produced more polymer on the electrode than the 3-thiophene-methanol. This latter result is critical since the purpose of the derivitization was to increase the amount of polymer on the electrode. The CV area results are confirmed by visual observation of the electrodes. There is an obvious difference in the amount of polymer that is formed on the electrodes with the 3-methylthiophene producing the most polymer and the derivitized 3-thiophenemethanol producing the second largest amount of polymer. The reasons for the other differences in the CV profiles are still being investigated.

An obvious difference in the appearance of the CV data for 3-methylthiophene is noted by comparing the profiles in Figures 5-2 and 5-4. Our data in Figure 5-2 was obtained using a commercial, glassy-carbon electrode, while the literature results were obtained using a platinum electrode. The data presented in Figure 5-4 was collected using a homemade platinum electrode. It appears that our platinum electrode broadens the features of the CV profiles relative to commercial carbon and platinum electrodes. We are exploring the cause for this apparent broadening.

5.3 Ultraviolet and Visible Absorption Spectroscopy Results

Ultraviolet and visible (UV/VIS) absorption spectroscopy has been used in the chemical characterization of polymers and electrically conducting polymers (Ref. 15, 47, 51). Ultraviolet and visible spectra provide information on the electronic structure of the polymers and in many cases the chemical form of functional groups within the polymers.

The UV/VIS spectra for the 3-methylthiophene monomer and chemically and electrochemically generated poly (3-methylthiophene) are given in Figure 5-7, in the range of 190 to 450 nm. The spectra were recorded in the range of 190 to 1,100 nm; however, only the range showing absorption of radiation was printed in the figure. The spectra were recorded on a Hewlett Packard model 8453A UV/VIS/NIR spectrometer with a diode array detector. As was expected, the spectra of the polymers are different from the spectrum of the monomer. However, the two polymer spectra show significant differences, and the polymer spectra are different than those reported in the literature (Ref. 15, 47). Most of the literature spectra were recorded using reflectance techniques or transparent electrodes. The spectra in Figure 5-7 were recorded by dissolving the monomer and polymers in acetonitrile. The dissolution technique is disadvantaged for characterizing ECPs because the polymers are not very soluble in any solvent and there is very little control over the oxidation state, and hence the electronic environment, of the polymers. The reflectance (Ref. 52, 53) or transparent electrode (Ref. 54, 55) techniques allow the spectra to be obtained in situ under any experimental oxidation condition and the polymer does not have to be dissolved.

Consequently, the differences between our experimental spectra and that found in the literature is understandable. The differences in the wavelengths of maximum absorption (lambda max, 8_{max}) are what would be expected. Since the wavelength of maximum absorbance is dependent on polymer chain length (Ref. 55), the spectra of the dissolved polymers or oligomers should have 8_{max} values at shorter wavelengths than those of the intact polymer films. The shift to lower 8_{max} values in our data occurs because the solubility of the polymer increases as the chain length decreases.

The differences between the two polymer spectra are not understood but may result from the differences in the synthesis conditions. The chemical synthesis could potentially incorporate some iron and/or chloride into the polymer film, while the electrochemical synthesis could cause some TBAPF6 to be present within the polymer film. These ionic compounds could then interact with the dissolved polymer. A second and more probable explanation deals with the degree of oxidation of the polymers. The degree of oxidation is not easily controlled when the polymer is dissolved in the acetonitrile. Acetonitrile was chosen as the solvent because in is transparent in the UV/VIS region of the electromagnetic spectrum. Additional work needs to be done in this area to make the current instrumentation useful for the UV/VIS characterization.

5.4 Infrared Absorption Results

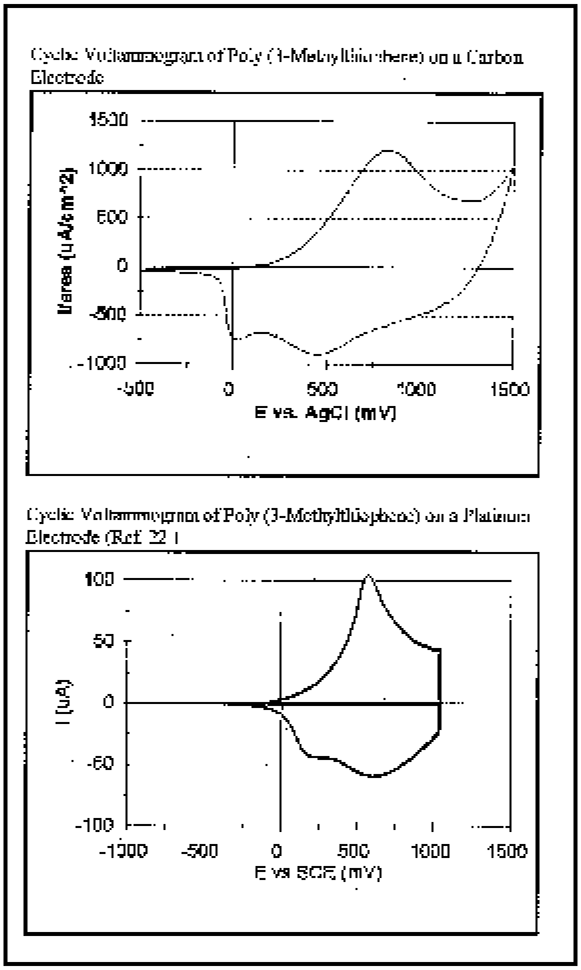
Infrared absorption spectroscopy is used to identify functional groups and isomeric forms of molecules and has been used in the study of ECPs (Ref. 51, 55, 56). The IR spectra of 3-methylthiophene monomer and electrochemically generated poly (3-methylthiophene) are given in Figure 5-8. The IR spectra were recorded on a Perkin Elmer model 1310 dispersive spectrometer; this instrument is not interfaced to a computer data acquisition system. Figure 5-8 was obtained by photoreducing the original spectra and physically "cutting and pasting" the copies. Some spectral data was removed in this process to make the results fit the figure. The numerous, sharp peaks in the monomer spectrum correspond to the various stretching and bending vibrations of the 3-methylthiophene molecule. A few sharp peaks are noted in the IR spectrum of the poly (3-methylthiophene); however, the dominate features of the polymer spectrum are the two broad peaks centered at 3,400 cm^{-1} and 1,050 cm^{-1}. These peaks indicate the presence of the polarons and the bipolarons in the polymer and are not associated with the molecular vibrations (Ref. 23). Repeated drying of the polymer did not change the relative abundance of the 3,400 cm^{-1} peak compared to the 1,050 cm^{-1} peak. This result indicates the peak at 3,400 cm^{-1} is not from water. The sharp peaks in the spectrum are due to molecular vibrations; however, their positions are shifted with respect to the monomer. Classical correlation tables are not useful in assigning the identity of these peaks, as a result their identity is presently unknown (Ref. 57).

5.5 Miscellaneous Characterizations

Visible light microscopy has been used to evaluate the morphology of the polymers (Ref. 58). Photomicrographs of many of the polymer/electrode systems have been obtained, although the photos are not represented in this report. Evaluation of the microscopy data does not indicate the presence of any crystal formation in the polymer films. The films appear completely amorphous. Polymer film growth appears in "clumps," which is consistent with the proposed mechanism of precipitation followed by polymer chain extension.

Matrix-assisted laser desorption and ionization (MALDI) mass spectrometry (Ref. 59) was used in an attempt to identify polymer composition on an electrode surface. This work was done at the Chemistry Department of Montana State University in Bozeman, Montana, by Dr. Joe Sears. The resulting mass spectrum was unfortunately inconclusive and is not reproduced here.

Figure 5-1. Reaction time vs. Electrode potential for four electrochemical synthesis experiments.



Cyclic Voltammogram of Poly (3-Methylthiophene) on a Carbon Electrode

Cyclic Voltammogram of Poly (3-Methylthiophene) on a Platinum Electrode (Ref. 22)

Figure 5-2. Experimental (top) and Literature (bottom) Cyclic Voltammograms of Poly(3-Methylthiophene).

Figure 5-3. Cyclic voltammogram of tetrabutylammonium hexafluorophosphate in nitrobenzene.

Figure 5-4. Cyclic voltammogram of poly(3-methylthiophene) in nitrobenzene.

Figure 5-5. Cyclic Voltammogram of poly(3-thiophenemrthanol) in nitrobenzene

Figure 5-6. Cyclic voltammogram of o-trimethylsilyl-3-thiophenemethanol in nitrobenzene, 1st and 19th scans.

Figure 5-7. Normalized UV/VIS spectra of the 3-methylthiopnene monomer and chemically and electrochemically synthesized poly(3-methylthiophene.

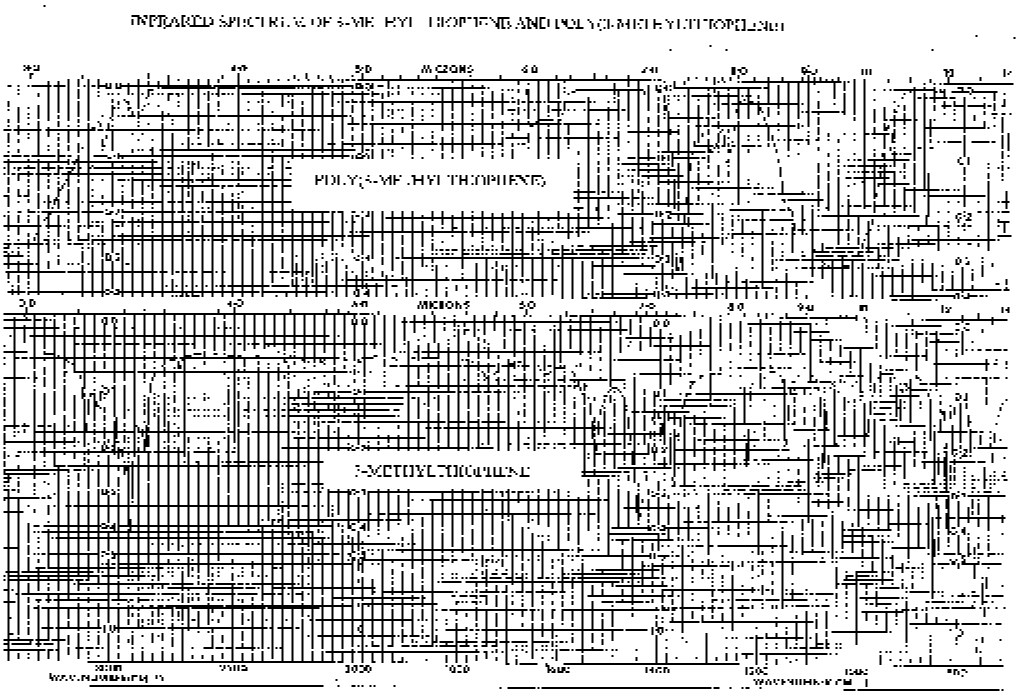


Figure 5-8. Infrared Spectra of 3-Methylthiophene (bottom) and Poly(3-Methylthiophene) (top).

6. Future Work

6.1 Electrical Conductivity

Determination of the electrical conductivity of the polymer systems is one important characterization technique that needs to be implemented in the Montana Tech laboratory. For the polymer systems to be effective in oxidizing and reducing the functional groups, it will be necessary for the polymer backbone to be highly conductive. We will use the standard four-probe technique for conductivity measurements (Ref. 21, 49).

6.2 Spectroscopic Studies

To spectroscopically study the redox reactions of the polymer chains and the functional groups, it is necessary to add the capability of diffuse reflectance to our UV/VIS spectrometer and to acquire a fourier transform infrared spectrometer (FTIR) with reflectance capabilities. This instrumentation will allow us to characterize and monitor changes with the polymer system as a function of electrode potential, pH, temperature, and metal ion and anion composition and concentration. These spectroscopic capabilities will give us information to better understand the chemistry of the ECP ion removal system, and as a consequence, design a more efficient process.

6.3 Modeling Studies

Modeling work to date has led to a better understanding of some of our experimental data and helped in the design of some experiments and polymer systems. Additional modeling work must be done to determine the energies (enthalpies) of the polymer systems and energies necessary to convert from one structure to the next or between confirmations. These studies are necessary in helping to design the functional groups and their positions on the monomers to maximize the binding of ions. Work must be done on oligomers larger than 8 monomer units to more correctly model experimental systems. It is possible that some of this work on “large” oligomers (or small polymers) can be done on the current PC system. However, the exactness of the calculations and the speed of the work could be improved substantially using a computer workstation and the appropriate software.

6.4 Synthesis Conditions

Our work to date has demonstrated that we can make substituted thiophene electrically conducting polymers via chemical or electrochemical means. Our electrochemical procedures need to be optimized when using monomers with polar functional groups. The solvent for the polymerization reaction plays a deciding factor on whether the forming oligomers precipitate onto the electrode or diffuse and dissolve into the solution. Better solvent systems need to be discovered. The chemical synthesis produces a significant amount of polymer for study and use. However, the polymer is not soluble in any of the solvents studied to date. We need to develop the information and techniques to work with the polymers after they have been chemically produced.

6.5 Photochemical Polymer Activation

In addition to electrically activating the polymer systems to bind metal ions and anions, photochemical reactions can be used. Photochemical reactions of polymeric systems can produce electron transfer (redox) reactions. These light-initiated electron transfers may proceed at sites many atoms away from the photoreceptor (chromophore) in electrically conducting polymers. Although these reactions have been demonstrated, we have not found literature showing these reactions applied to the oxidation and reduction of metal chelating groups. It is possible that a combination of a conducting polymer containing the appropriate chromophore will provide the best or most convenient mechanism for turning off and on the chelating properties of the polymer. The chelate switch would then be operated by a combination of electric fields and photons.

A second photochemical reaction that could be used to alter the chelating properties of a polymer is that which causes cis-trans isomerization. In the cis form, the polymer would exist as a bidentate (two binding sites) chelating compound. After irradiation with the appropriate wavelength of light, the polymer would isomerize to the trans form. This reduces the polymer to a monodentate ligand. The reduced binding strength of the trans form would then allow the metal ions to be released. With appropriate design of the polymer, the chelating groups could be arranged to be tridentate or higher in the cis form. This would increase the binding strength of the chelating polymer for metal ion removal. These polymers could also be designed to be electrically conducting such that redox reactions could be incorporated into the on/off chelate switch. The ability to model these systems prior to any synthetic work will be essential. The knowledge of bond and rotation energies, bond and torsional angles, planarity of conjugated systems, electron densities, etc., in various polymer systems will help determine which polymers are most worthwhile to attempt to synthesize.

6.6 Efficiency and Economic Comparisons

A variety of remediation processes are available for removing metal ions and anions from aqueous systems. Once we have developed an ECP system for removing ions from aqueous systems, we will compare the ECP systems to a number of other remediation techniques, including ion exchange using zeolites, precipitation processes, sulfate-reducing bacteria, and constructed wetlands. These processes are all currently being evaluated at Montana Tech through research funded by the MWTP. As a result of the proximity of this other work, comparative samples and data will be easily available.

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