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SYNTHESIS AND ELECTROCHEMICAL STUDY OF COPOLYMERS
CONTAINING FERROCENE AND IMIDAZOLE

A Thesis Submitted to the Graduate School
in Partial Fulfillment of the Requirement
for the Degree of
Master of Science

Abdulrahman Saad Alhathir

Pittsburg State University

Pittsburg, Kansas

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SYNTHESIS AND ELECTROCHEMICAL STUDY OF COPOLYMERS CONTAINING FERROCENE AND IMIDAZOLE

An Abstract of the Thesis by
Abdulrahman Saad Alhathir

Ferrocene-based polymers have been used in various applications such as sensors, semiconductors, lasers, solar cells, batteries, and photo-oxidation of thin films. However, ferrocene copolymers with electronic interactions between the ferrocene and neighboring moieties have not been well studied. To this end, copolymers of vinylferrocene and vinylimidazole were prepared in various ratios. Imidazole is well known to coordinate to various transition metals which may promote interactions between the ferrocene and imidazole moieties; and impart interesting electronic properties to the copolymer. Copolymers between vinylferrocene and vinylimidazole were prepared by free radical initiation and characterized by FTIR, ^1H -NMR, ^{13}C -NMR, and GPC. Each copolymer was electrochemically characterized in solution (CH_2Cl_2) and as a thin film. In addition, the electrochemical response of each material was tested in the presence of various electrolytes such as NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and $\text{Pb}(\text{ClO}_4)_2$. In addition, each polymer was studied using UV-vis spectroscopy in solution (CH_2Cl_2) and as thin films.

TABLE OF CONTENTS

CHAPTER I.....	1
1.1. Ferrocene.....	1
1.2. Charge and electron mobility.....	3
1.3. Ferrocene-containing polymers	6
1.4. Project Rationale	7
CHAPTER II.....	9
2.1. Materials	9
2.2. Instrumentation	9
2.3. Synthesis of vinylferrocene copolymers.....	10
2.3.1. Synthesis of vinylferrocene.....	10
2.3.2. Polymerization of vinylferrocene with vinylimidazole 1: 3 (poly 1)	10
2.3.3. Polymerization of vinylferrocene with vinylimidazole 1:1 (poly 2)	11
2.3.4. Polymerization of vinylferrocene with vinylimidazole 3:1 (poly 3)	11
2.4. Preparation of electrodes.....	11
2.4.1. Polymer for testing in methylene chloride.....	11
2.4.2. Cast film method.....	12
CHAPTER III	13
3.1. Polymer Synthesis and Characterization	13
3.2. Electrochemistry	16
3.2.1. The solution electrochemistry of polymers in CH ₂ Cl ₂	16
3.2.2. Electrochemical behavior of chemically modified electrodes in aqueous electrolytes for 1:1 copolymer	17
3.3. UV-Vis spectroscopy	21
CHAPTER IV	23
REFERENCES	25
APPENDIX.....	29

LIST OF TABLES

TABLE	PAGE
Table 1: Redox potentials of copolymers with CH_2Cl_2 and Bu_4NPF_6	16
Table 2: Summary of electrochemical parameters obtained from cyclic voltammetry for all copolymers with aqueous electrolytes of NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and $\text{Pb}(\text{ClO}_4)_2$	18

LIST OF FIGURES

FIGURE	PAGE
Figure 1: FTIR of 1:1 Copolymer.....	14
Figure 2: ^1H -NMR of 1:3 Copolymer.....	15
Figure 3: ^{13}C -NMR of 3:1 Copolymer.....	15
Figure 4: CVs of 1:3 Copolymer with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and an Ag pseudo reference electrode.....	17
Figure 5: Current versus square root of scan rate for 1:3 Copolymer.....	17
Figure 6: CVs of chemical modified electrodes on cast films of 1:1 Copolymer on platinum electrode in various aqueous electrolytes (NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and $\text{Pb}(\text{ClO}_4)_2$) at scan rates of 100 mV/s.....	19
Figure 7: CVs of chemical modified electrodes with cast films of all copolymers on platinum electrode in aqueous $\text{Pb}(\text{ClO}_4)_2$ at scan rates of 100 mV/s.....	20
Figure 8: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Cd}(\text{ClO}_4)_2$ at scan rates of 100 mV/s.....	20
Figure 9: UV-Vis Spectrum for 1:1 Copolymer in solution.....	22
Figure 10: UV-Vis Spectra of 1:1 copolymer in various aqueous electrolytes: NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and $\text{Pb}(\text{ClO}_4)_2$	22

LIST OF SCHEMES

SCHEME	PAGE
Scheme 1: Structure of Ferrocene.....	2
Scheme 2: Ferrocene Eclipsed (D_{5h}).....	3
Scheme 3: Ferrocene Staggered (D_{5d}).....	3
Scheme 4: Copolymerization of vinylferrocene and vinylimidazole.....	13
Scheme 5: Interaction of various heavy metals with polymers.....	19

LIST OF ABBREVIATIONS

Fc – Ferrocenyl

VFc - vinylferrocene

AIBN - α , α -azobisisobutyronitrile

Bu₄NPF₆ - Tetrabutylammonium hexafluorophosphate

CME - Chemically modified electrodes

Cp - Cyclopentadienyl

CV - Cyclic Voltammetry

E_{ox} - Oxidation potential

E_{red} - Reduction potential

E_{1/2} -Redox Potential

EDG - Electron donating group

CT - Charge transfer

CTC - Charge transfer complexes

IVCT - Intervalence charge transfer

ICT - Intermolecular charge transfer

HOMO - Highest Occupied Molecular Orbital

LOMO - Lowest unoccupied molecular orbital

FRP - Free radical polymerization

LAP - Living anionic polymerization

I_{pa} -Peak Anodic Current

I_{pc} -Peak Cathodic Current

GPC -Gel permeation chromatography

CHAPTER I

INTRODUCTION

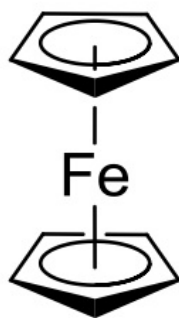
1.1. Ferrocene

Organometallic chemistry is a multidisciplinary science, and it has an important part in organic, inorganic, biochemistry, and materials science.¹ Since the discovery of ferrocene in the early 1950s, organometallic compounds have received an increased emphasis and acquired a different level of significance within the discipline of chemistry.¹ Woodward coined the name of ferrocene which is properly called bis(η^5 -cyclopentadienyl)iron(II) with the formula $[\text{Fe}(\text{C}_5\text{H}_5)_2]$.² The synthesis of ferrocene was unexpected and accidental in two independently different laboratories.³ In 1951, Kealy and Pauson's attempt to prepare fulvalene (C_{10}H_8) led to their synthesis of ferrocene instead.⁴ This reaction was performed by oxidation of cyclopentadienyl magnesium bromide (CpMgBr) with iron (II) chloride in ether. At roughly the same time, Miller and his co-workers Tebbboth and Tremaine isolated ferrocene. Their idea was to obtain amines by reacting cyclopentadiene and N_2 at 300°C under atmospheric pressure.⁵

Ferrocene has unpredicted physical properties such as diamagnetic, orange solid, relatively low melting (m.p. $173\text{-}174^\circ\text{C}$) without decomposition, insoluble in water, but readily soluble in organic solvents.^{1,3} The structural discovery of ferrocene was elucidated by two independent groups again. Wilkinson concluded there was only one C-

H stretching frequency observed in the 3300-2500 cm^{-1} in the I.R. spectrum⁶.

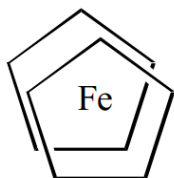
Additionally, since all the carbons were electronically similar, they must contribute equally in bonding to the iron atom. Shortly after the sandwich structure of ferrocene was proposed, it was rapidly verified using x-ray crystallography by Fischer and Pfab independently.^{7, 8}



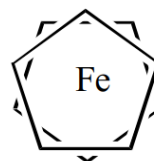
Scheme 1: Structure of Ferrocene

As shown in Scheme 1, ferrocene is a sandwich-structured compound containing an iron atom sandwiched between two planar π -bonded cyclopentadienyls (CP) anions.¹ Ferrocene is symmetrical, and its two cyclopentadienyl (CP) rings can be orientated in two extreme conformations.⁹ They are either an eclipsed parallel (D_{5h}) or staggered (D_{5d}), as illustrated in Scheme 2 and 3. Based on a gas phase study of ferrocene, the rotational energy of the eclipsed form about the Fe-CP axis is 4 kJ/mol. This eclipsed ferrocene is found to be slightly more stable than the staggered.⁹

Interesting inherent properties of ferrocene include high thermal stability, low toxicity, and possession of aromaticity and photochemical properties, as proven by Woodward.^{2, 10, 11, 12} Due to these properties, ferrocene and its derivatives can be used in



Scheme 2: Ferrocene Eclipsed (D_{5h})



Scheme 3: Ferrocene Staggered (D_{5d})

a myriad of applications and harsh reaction conditions without the concern of decomposition of the parent molecule. The ferrocenyl group is known as one of the strongest electron donating groups (EDG).¹³ Also, ferrocene is much more prone to electrophilic substitution than benzene, since 6 electrons are shared over five carbons. The resonance is responsible for the strong stability of the cyclopentadienyl ions.^{14, 15} As a result of the aromatic nature of ferrocene, this compound shows an ability to readily undergo Friedel-Crafts acylation.¹⁶ Many ferrocene derivatives can be prepared by using Friedel-Crafts reaction where one or both of cyclopentadienyl rings can be acylated. In addition, ferrocenophane, reported by Watts, is the first type of oligomeric ferrocene containing a bridge of carbon atoms between the two cyclopentadienyl ions.^{17, 18, 19} It was prepared and investigated intensively after the discovery of ferrocene due to the increase in strain that was present. The rings in this oligomeric ferrocene system may be connected by one or more bridges. Because of the well-defined and aforementioned properties, the applications of ferrocene are seen in various scientific fields. They are used as sensors, asymmetric catalysis, a mediator between redox enzymes and electrodes, and as liquid crystalline materials. The ability of large variety of derivatives that can be incorporated into biomolecules has made ferrocene very active for biological research.²⁰⁻

21

1.2. Charge and electron mobility

The study of ultrafast molecular processes has received great interest in modern years.²²⁻²³ Separation of electrical charges is an important process and regarded as the basis for many recent and promising developments. These developments include organic conductors and superconductors, as well as the production and storage of electricity. The photosynthesis in green plants and solar energy conversion are natural processes involving charge transfer.²⁴ Understanding the process of electron transport is essential and needed for future growth in many fields such as molecular electronics and biological enzymes.²⁵⁻²⁷ However, the study of charge transfer may be considered from different points of view and purpose.²⁷ A UV-Visible absorption spectrum is caused by the promotion of an electron in one orbital, usually a ground state orbital, to a higher energy orbital. The amount of energy needed to transfer the electron depends mostly on the nature of the two orbitals involved. A group that is responsible for the absorption and the color in a molecule is known as a chromophore. A system of extensively conjugated π -electrons have paid a special attention because they are energetically and kinetically preferred for typical excited state geometry.²⁸⁻²⁹

An exciton, which is a bound electron-hole pair, results from excitations in the molecular crystal. An exciton can be classified as a charge transfer (CT) exciton, Frenkel, or Wannier-Mott.³⁰ The concept of charge transfer (CT) can be defined as the excitations into a state that involves a complete convey of an electron from a donor to an acceptor or between them in the excited state of either species.³¹⁻³² Thus, in donor-acceptor molecules, when the electron is promoted from the ground state to the excited state, charge migrates to or towards the acceptor resulting a charge separated zwitterion or a highly polar state.³² Charge transfer events show an effect on the emission spectra by

developing a new structure-less band at a longer wavelength region.³¹ This donor-acceptor system is associated with several physical phenomena being optical CT electronic transitions, highly directional dipole moments, long-range electron transfer, twisted intermediate states, magnetic ordering, and solvatochromism.³³ The reaction of charge transport may be categorized as an intermolecular charge transfer and intramolecular charge transfer.

Charge transfer complexes (CTC) are considered to be a significant application of intermolecular charge transfer (ICT), where an electron from a molecule with high charge density (donor) is transferred to a molecule with low charge density (acceptor).³⁴ In this case, the transition arises from the highest filled molecular orbital of the donor (HOMO) to the lowest empty molecular orbital of the acceptor (LUMO). The CTC could occur naturally (without any external action) if some requirements are satisfied. These requirements are the energetic position of the molecular orbitals, the difference between donor HOMO and acceptor LUMO, and spatial wave function overlap of the molecules such as no steric hindrance.³⁵ On the other hand, intramolecular charge transfer process is a process whereby the photoexcitation of D-A molecules is followed by an internal charge transfer (ICT) from donor (D) site to an acceptor (A) in the same molecule. Consequently, positive and negative charges are localized in two different and separated functional parts of the same molecule. Also, a new charge distribution generally leads to a large increase of the dipole moment, and it will cause a marked solvatochromic effect and a large Stokes shift. This kind of charge transfer process has obtained remarkable attention in photochemistry and biochemistry.³⁶ Ferrocene has the ability to undergo a one-electron oxidation behavior to give the ferrocenium cation. Additionally, ferrocene

shows a fast and reversible one-electron transfer on gold and other electrodes, and that makes ferrocene a good model for studying the electron transport phenomenon.³⁷ Due to the strong electron donation of ferrocene, various charge transfers were observed and measured in ferrocene containing organic dyads.³⁸ Finally, intervalence charge transfer (IVCT) was studied at conjugated ferrocenyl-containing oligomers.³⁹

1.3. Ferrocene-containing polymers

Organometallic polymeric compounds have attracted enormous attention in materials science because of their high thermal stability, fully reversible redox chemistry and unique sandwich structures.⁴⁰ Incorporation of ferrocene into polymers have been used to improve potential applications of organometallic polymer chemistry. The properties of ferrocene containing-polymers have been utilized for nanostructure applications and other material studies such as biodegradability, photoconductivity, and photo-oxidation of thin films.⁴¹⁻⁴² There are two general polymer architectures bearing the ferrocenyl moieties. Ferrocene can be an integral part of the polymer backbone or as pendant substituents bonded to the polymer main-chain.⁴³ An example of a ferrocene containing monomer is vinylferrocene reported by Arimoto and Haven in 1955.⁴⁴ Pyrolysis of 1-ferrocenylethanol under reduced pressure at 200°C in the presence of alumina gave a 21% yield of vinylferrocene.⁹ Afterward, vinylferrocene was produced by the dehydration of 1-ferrocenylethanol using acidic alumina in refluxing benzene resulting in a 75 % yield of the product. A Wittig reaction can also be used for the synthesis of vinylferrocene.⁴⁵ Subsequently, the reaction of a mixture of formylferrocene with methylenetriphenylphosphorane in dimethyl sulfoxide resulted in 81% yield of vinylferrocene.⁴⁶

Free radical polymerization (FRP) was successfully used to synthesize polyvinylferrocene, incorporating the ferrocene moiety pendant to the polymer chain chain. This polymerization was performed using azodiisobutyronitrile (AIBN) and potassium persulfate as initiators at 80°C.⁴⁴ Similarly, ferrocene-containing monomers such as ferrocenylmethyl acrylate (FMA) and ferrocenylmethyl methacrylate (FMMA) were polymerized by FRP, resulting in high molecular weight polymers. Living anionic polymerization (LAP) is a different approach of polymerization that can be utilized to prepare ferrocene-based polymers. Anionic polymerization gives a versatile route to produce polymers with controlled molecular weights, a low molecular weight distribution, or block polymer.⁴⁷ Well-controlled block copolymers with methyl methacrylate, acrylonitrile, and styrene were obtained via LAP. However, VFc and FMA were observed to be inactive towards anionic polymerization since only low molecular weight polymers were obtained.⁴⁷ In 2008, charge/discharge tests were conducted by Tamura and coworkers for polyvinylferrocene that showed the qualification for a rechargeable battery application.⁴⁸

1.4. Project Rationale

In this project, we focused on the structure and electrochemical properties of copolymers synthesized from vinylferrocene and vinylimidazole. By incorporating ferrocene into copolymers with imidazole, it was anticipated that enhanced electronic properties of polymers may result in an electrochemical communication that is not commonly observed in ferrocene containing polymers. In addition, the electronic properties of these copolymers will be studied in the presence of various metals. Imidazole is well known to coordinate to various metals and these interactions may

impart interesting electronic properties to the copolymer. The electronic interactions between the ferrocene and the imidazole will be studied by UV-Vis spectroscopy and by electrochemistry.

CHAPTER II

EXPERIMENTAL

2.1. Materials

All starting materials were commercially available and used as received unless noted otherwise. All reactions were performed under a dry nitrogen atmosphere unless mentioned otherwise. The Wittig reaction was used for the synthesis of vinylferrocene according to a literature procedure.⁴⁹ For purification and separation technique, column chromatography was done using silica gel (60°A) (Acros Organics) as the stationary phase with dichloromethane or chloroform as the mobile phase.

2.2. Instrumentation

All NMR spectra were taken using a Bruker DPX-300 spectrometer. Fourier transform Infrared Spectra (FT-IR) were recorded using a Thermo Nicolet IR-300. Cyclic voltammetry (CV) measurements were performed using a Gamry Interface 1000 potentiostat with platinum (2 mm OD) working and counter electrodes, and an Ag pseudo or Ag/AgCl reference electrode. UV- visible spectra were acquired utilizing a Gamry UV-Vis spectro-115u system.

2.3. Synthesis of vinylferrocene copolymers

2.3.1. Synthesis of vinylferrocene

Under a nitrogen atmosphere, methyltriphenylphosphonium bromide (1.96 g, 5.5 mmol) was placed into 3 round-necked bottom flask with a stir bar. Tetrahydrofuran (THF) (20 mL) was added, and the solution was stirred for 15 min. Then, n-butyllithium (n-BuLi) (2.2 mL, 5.5 mmol) was added and stirring continued for 25 min. After 25 min, ferrocenecarboxaldehyde (1.07 g, 5 mmol) was added and stirring continued. The mixture turned dark orange and was left to react for 16 hours. After 16 hours, water (0.5 mL) was added to the reaction mixture, followed by removal of the solvent under reduced pressure. Vinylferrocene was purified by column chromatography with silica gel and chloroform (CHCl_3) and yielded 0.81 g (81%). FTIR (cm^{-1}): =C-H : 3080, C=C : 1650. $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 6.45 (1H, FcCH=C), 5.40 (1H, FcC=CH), 5.00 (1H, FcC=CH), 4.40(2H, CP-ring), 4.21(2H, CP-ring), 4.12 (5H, CP-ring).

2.3.2. Polymerization of vinylferrocene with vinylimidazole 1: 3 (poly 1)

Vinylferrocene (0.215 g, 1 mmol), 1-vinylimidazole (0.282 g, 1 mmol), AIBN (0.0053 g, 1 wt %), and chlorobenzene (0.5 ml) were placed into 2 round-necked bottom flask with a stir bar. After establishing a nitrogen atmosphere, the reaction solution was heated at 70°C. Thereafter, the reaction mixture was allowed to react with constant stirring for 16 h. After cooling to room temperature, the solution was added to hexane (20 ml) to precipitate the copolymer. The resulting yellow solid was collected by suction filtration and dried at 70°C under reduced pressure in a vacuum oven to give 0.182 g (60.2 % yield) of the copolymer. FTIR (cm^{-1}): C-H aromatic 3110, C-H aliphatic 2920. $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 3.42-4.55 (9H), 7.20-6.42 (3H).

2.3.3. Polymerization of vinylferrocene with vinylimidazole 1:1 (poly 2)

In 15 ml 2 round-necked bottom flask with a stir bar, vinylferrocene (0.214 g , 1 mmol) and 1-vinylimidazole (0.092 g, 1 mmol) were dissolved in chlorobenzene (0.5 ml). AIBN (0.0036 g, 1 wt %) was used as an initiator for the polymerization. This polymerization was done under a nitrogen atmosphere, and the mixture was heated at 70°C. The stirred solution was left to react for 16 hours. After 16 hours, the solution was allowed to cool to room temperature and added to hexane to precipitation the copolymer. The resulting polymer was a yellow solid and gave (0.148 g, 57.2%). FTIR (cm^{-1}): C-H aromatic 3080, C-H aliphatic 2850. $^1\text{H-NMR}$ (CDCl_3 , δ ppm): 7.85-6.50 (3H), 4.30-3.10 (9H).

2.3.4. Polymerization of vinylferrocene with vinylimidazole 3:1 (poly 3)

To a round bottom flask was added vinylferrocene (0.211 g, 1 mmol), 1-vinylimidazole (0.034 g, 1 mmol), AIBN (0.0024 g, 1 wt %), and chlorobenzene (0.5 ml). A nitrogen atmosphere was established and the reaction mixture was heated at 70°C for 16 hours. After cooling to room temperature, the solution was added to hexane and the resulting precipitate was collected by suction filtration and dried at 70°C under reduced pressure. The product was a yellow solid (0.113 g, 55.2%). FTIR (cm^{-1}): C-H aromatic 3030, C-H 10 aliphatic 2820. $^1\text{H-NMR}$ (CDCl_3 , δ .ppm): 7.50-6.50 (9H), 7.72-6.45 (3H).

2.4. Preparation of electrodes

2.4.1. Polymer for testing in methylene chloride

For electrochemical testing, solutions were prepared by dissolving each polymer (1mM) and tetrabutylammonium hexafluorophosphate (100mM), as supporting electrolyte, in methylene chloride (CH_2Cl_2).

2.4.2. Cast film method

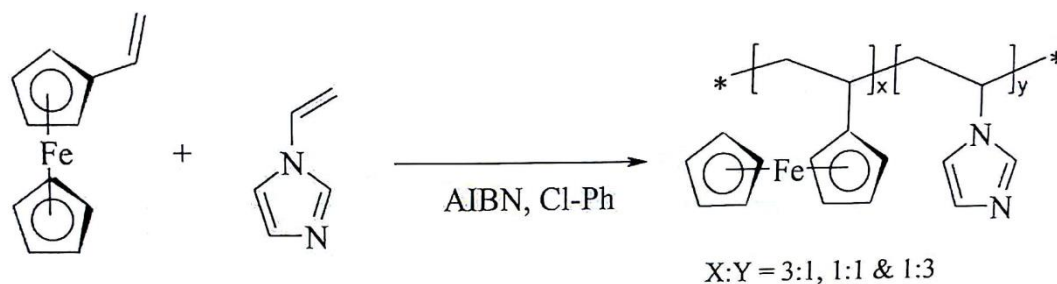
The preparation of chemically modified electrodes (CME) was done by casting from polymer solutions directly on the electrode surface. CHCl_3 solutions of Poly1-3 (2 mg/mL) were micropipetted (2 μL) onto electrodes and then allowed to air dry for 10-15 min. After that, the electrodes were placed into various aqueous electrolyte solutions for electrochemical analyses.

CHAPTER III

RESULT AND DISCUSSION

3.1. Polymer Synthesis and Characterization

The Wittig synthesis of vinylferrocene was achieved in 80% yield from ferrocene carboxaldehyde and methyltriphenylphosphonium bromide. Using a literature procedure, vinylferrocene with vinylimidazole were copolymerized with α,α -azobisisobutyronitrile (AIBN) as the initiator in chlorobenzene as illustrated in (Scheme 4).⁴⁹ The copolymerization of vinylferrocene with vinylimidazole resulted in good polymer yields (69 % - 88 %).



Scheme 4: Copolymerization of vinylferrocene and vinylimidazole

The infrared spectrum of polymers from a 1:1 ratio of vinylferrocene to vinyl imidazole is shown in Figure 1. The FTIR spectrum of 1:1 copolymer showed absorptions of C-H aromatic and, C-H aliphatic stretches at 3080 and 2850 cm^{-1} , respectively. The ^1H -NMR spectrum of the 1:3 copolymer displayed significant broad

peaks that were consistent with the structure of the copolymer (Figure 2). In addition, the ^1H NMR spectrum did not show signals at 5-6.5 ppm which indicating no residual monomers. The 9 protons for ferrocenyl moiety were seen at 4 ppm while the 3 protons of the imidazole were at 7 ppm. The aliphatic protons of the same polymer were observed at 0.8-2.7 ppm. In the ^{13}C -NMR spectra of a ratio of 3:1 copolymer (Figure 3), fewer signals appeared which was contrary to the 10 expected peaks. The disappearance of consistent signals may be caused by coincidental overlap of carbon signals or weakness in the signal due to difficulties associated with NMR spectroscopy of polymers.

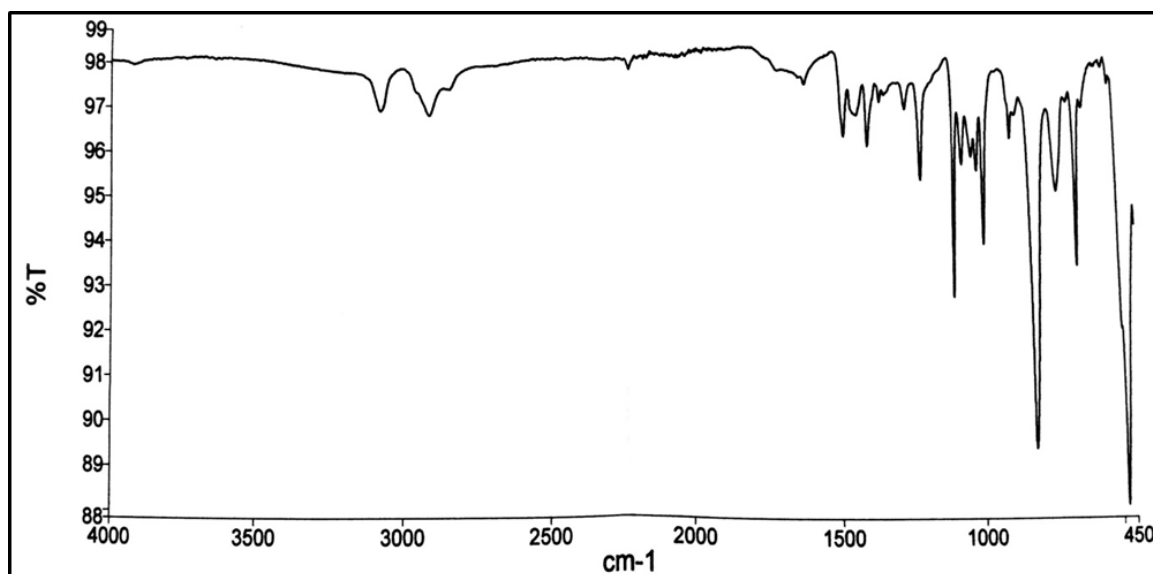


Figure 1: FTIR of 1:1 Copolymer

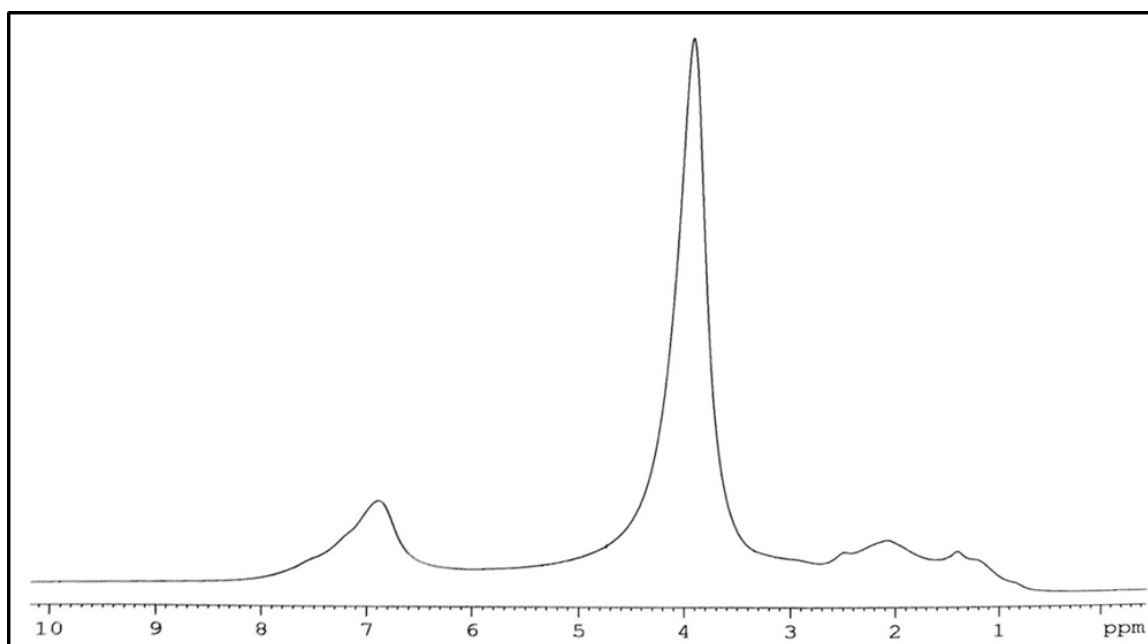


Figure 2: ^1H -NMR of 1:3 Copolymer

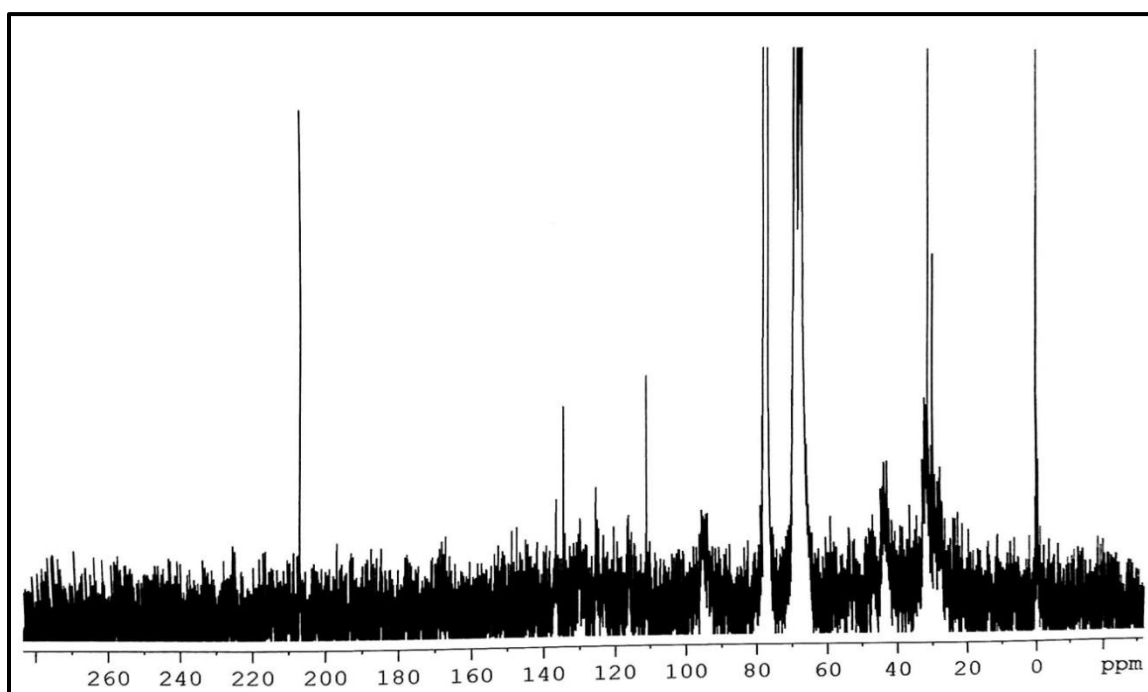


Figure 3: ^{13}C -NMR of 3:1 Copolymer

3.2. Electrochemistry

3.2.1. The solution electrochemistry of polymers in CH₂Cl₂

Cyclic voltammetry of polymers using a platinum electrode was performed to provide information on the electrochemistry of each polymer. All polymers were analyzed in CH₂Cl₂ solutions containing Bu₄NPF₆ as supporting electrolyte. CV measurements were carried out from 0.0 V to 1.0 V at scan rates of 20, 40, 60, 80 and 100 mV/s⁻¹. All copolymers exhibit a reversible, one-electron oxidation as evidenced by single oxidation and reduction peaks. The electrochemical data of each polymer are shown in Table 1. For the 1:1 copolymer, E_{ox} and E_{red} were observed at 0.55 V and 0.42 V, respectively. In cyclic voltammetry, redox potential (E_{1/2}) for a reversible redox process can be determined as the average value of the anodic and cathodic peaks: E_{1/2} = (E_{ox} + E_{red})/2.⁵⁰ The redox potential (E_{1/2}) of copolymer 1:3 was seen at 0.46 V. Figure 4 shows the CV of 1:3 copolymer in dichloromethane at various scan rates. In the CVs of copolymer 1:3, I_{pa} scaled linearly with the square root of the scan rate which was consistent with electrochemical reversibility (See Figure 5.).

Table 1: Redox potentials of copolymers with CH₂Cl₂ and Bu₄NPF₆.

Polymer	E _{ox} (V)	E _{red} (V)	E _{1/2} (V)
1:3	0.55	0.37	0.46
1:1	0.55	0.42	0.48
3:1	0.57	0.21	0.39

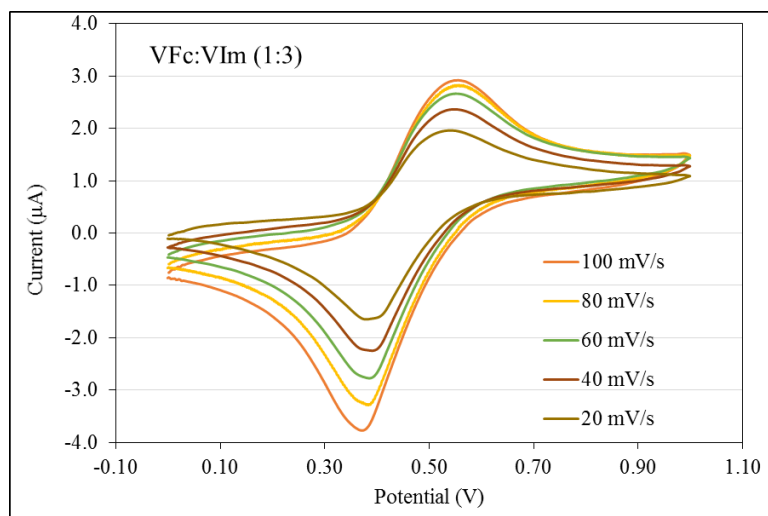


Figure 4. CVs of 1:3 Copolymer with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and an Ag pseudo reference electrode

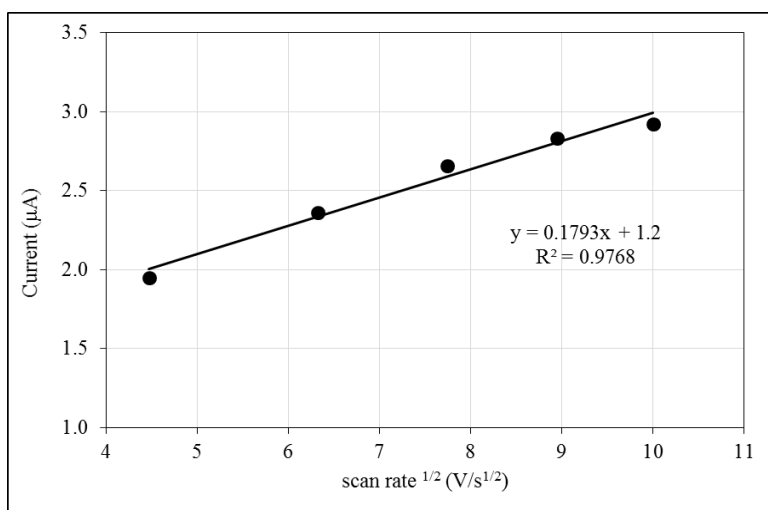


Figure 5. Current versus square root of scan rate for 1:3 Copolymer

3.2.2. Electrochemical behavior of chemically modified electrodes in aqueous electrolytes for 1:1 copolymer

Chemically modified electrodes (CMEs) were prepared by casting 2 μL of a CHCl_3 solution of the copolymer (2 mg/mL) and air-drying for 10 min. CMEs were then placed in various aqueous solutions of electrolytes (100 mM): NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$,

Zn(ClO₄)₂, Cd(ClO₄)₂, or Pb(ClO₄)₂. CVs were then performed to determine the electrochemical response of the polymer. The cyclic voltammetry (See Figure 6.) showed variations of the cathodic and anodic peak potentials for 1:1 copolymer in various aqueous solutions. The oxidation potentials of each polymer are summarized in Table 2. The major redox potentials ($E_{1/2}$) of 1:3 polymer were observed using NaClO₄, Mg(ClO₄)₂, Zn(ClO₄)₂, Cd(ClO₄)₂, Pb(ClO₄)₂ at 0.409, 0.424, 0.28, 0.405, and 0.32V respectively. The changes of oxidation potential versus electrolyte has been seen for poly(vinylferrocene) and may be due to the differences in ion pair stability or in solvation of the ion.

Table 2: Summary of electrochemical parameters obtained from Cyclic voltammetry for all copolymers with aqueous electrolytes of NaClO₄, Mg(ClO₄)₂, Zn(ClO₄)₂, Cd(ClO₄)₂, and Pb(ClO₄)₂

Polymer	Electrolyte	E_{ox} (V)	E_{red} (V)	$E_{1/2}$ (V)
1:3	NaClO ₄	0.47	0.33	0.40
	Mg(ClO ₄) ₂	0.49	0.35	0.42
	Zn(ClO ₄) ₂	0.36	0.20	0.31
	Cd(ClO ₄) ₂	0.48	0.33	0.40
	Pb(ClO ₄) ₂	0.75	---	---
		0.43	0.21	0.32
1:1	NaClO ₄	0.49	0.32	0.40
	Mg(ClO ₄) ₂	0.49	0.35	0.42
	Zn(ClO ₄) ₂	0.39	0.28	0.33
	Cd(ClO ₄) ₂	0.42	0.30	0.36
	Pb(ClO ₄) ₂	0.66	---	---
		0.37	0.25	0.31
3:1	NaClO ₄	0.48	0.32	0.40
	Mg(ClO ₄) ₂	0.48	0.36	0.42
	Zn(ClO ₄) ₂	0.38	0.27	0.32
	Cd(ClO ₄) ₂	0.49	0.35	0.42
	Pb(ClO ₄) ₂	0.40	0.25	0.34
		0.57	---	---

A single redox wave was observed with NaClO₄, Mg(ClO₄)₂ or Zn(ClO₄)₂ as the supporting electrolyte. However, two oxidation potentials were observed in the cyclic

voltammetry with $\text{Cd}(\text{ClO}_4)_2$ or $\text{Pb}(\text{ClO}_4)_2$ as the supporting electrolyte. This may be caused by the ability of these metals to coordinate to the imidazole which increases the electron deficiency of the imidazole. If this electron deficient imidazole is in close proximity to the ferrocene, then interactions resulted in a higher oxidation of the neighboring ferrocene (See Scheme 5.).

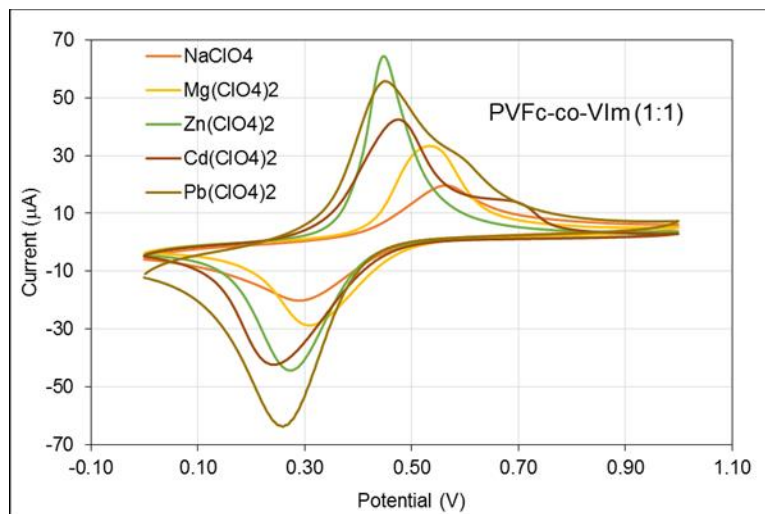
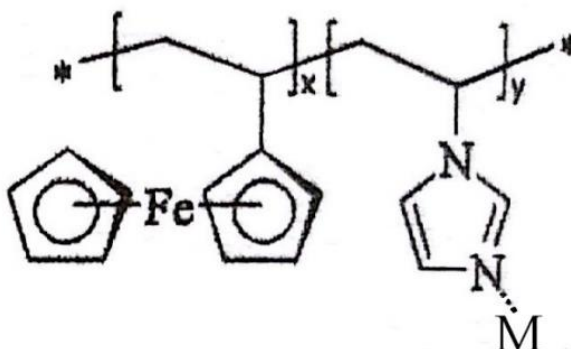


Figure 6. CVs of chemical modified electrodes on cast films of 1:1 Copolymer on platinum electrode in various aqueous electrolytes (NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and $\text{Pb}(\text{ClO}_4)_2$) at scan rates of 100 mV/s.



Scheme 5: Interaction of various heavy metals with polymers

Comparison of copolymer 1:1 to copolymers 1:3 and 3:1 showed that copolymer 1:1 exhibited the strongest second oxidation wave (See Figures 7 and 8.). This was

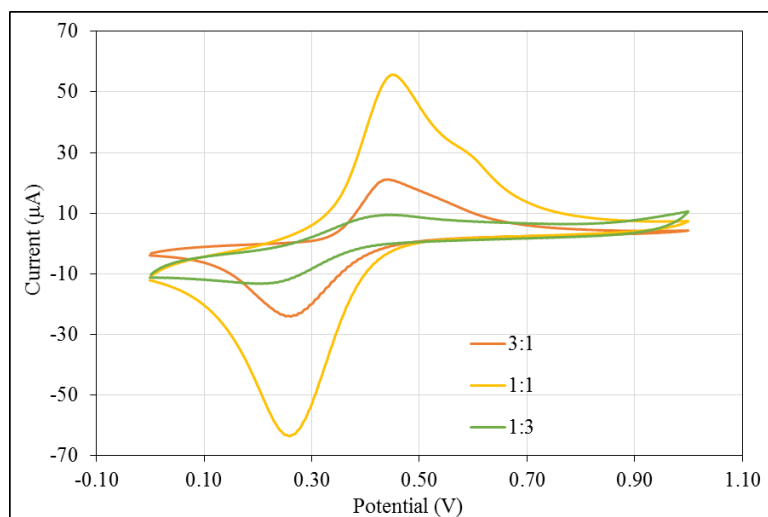


Figure 7. CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Pb}(\text{ClO}_4)_2$ at scan rates of 100 mV/s.

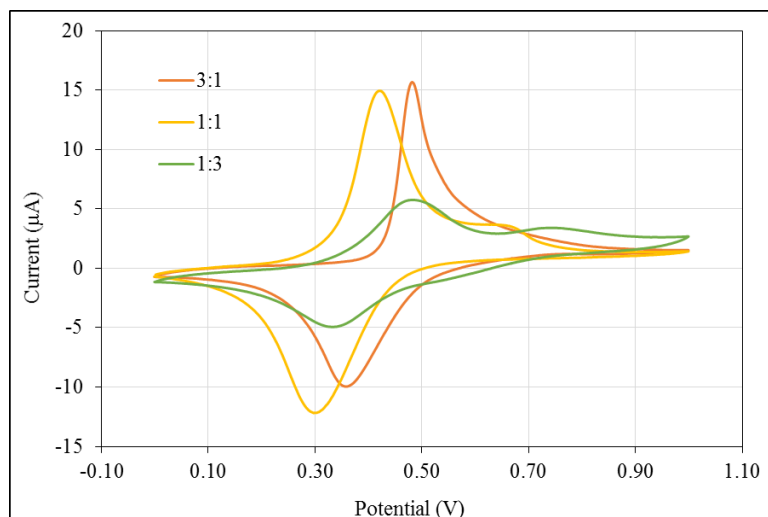


Figure 8. CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Cd}(\text{ClO}_4)_2$ at scan rates of 100 mV/s.

consistent with interactions between ferrocene and metal-coordinated imidazole, since a 1:1 copolymer would provide greater concentrations of these interactions.

3.3. UV-Vis spectroscopy

In the present work, the electronic communications of the ferrocene and imidazole moieties in the copolymers were investigated using UV–visible Spectroscopy. The ferrocenyl group is known as a strong electron donor while imidazole moiety is an electron acceptor. Charge transfer (CT) in donor-acceptor systems is associated with optical electronic transitions. The excitation of these copolymers in UV-Vis region may lead to the observation of the charge transfer interaction. Polymer thin films were prepared by casting from dichloromethane (10 μ L at a concentration of 5 mg/mL) on to Indium Tin Oxide (ITO) plates prior to testing. After the casting, polymer thin films were placed in each electrolytes: NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and $\text{Pb}(\text{ClO}_4)_2$ for UV-Vis measurements.

The UV-Vis spectrum of 1:1 copolymer in solution (Figure 9) showed an absorbance at 440 nm attributed to electronic transitions in the ferrocene moiety. Additionally, the UV-Vis spectra for 1:1 polymer thin films in water and in various aqueous electrolytes are shown in Figure 10. As was observed in solution, the polymer exhibited an absorption at 440 nm consistent with ferrocene. However, an additional absorption was observed at ca. 625 nm. This may be a result of an interaction between the ferrocene and imidazole moieties since these groups are in closer proximity in a thin film. In contrast, there was little to no change in the UV-Vis spectrum when it was placed into the various aqueous electrolytes. However, this testing was performed soon after placing the film into the aqueous electrolytes and an inadequate amount of time may not have been allowed for the system to come to equilibrium.

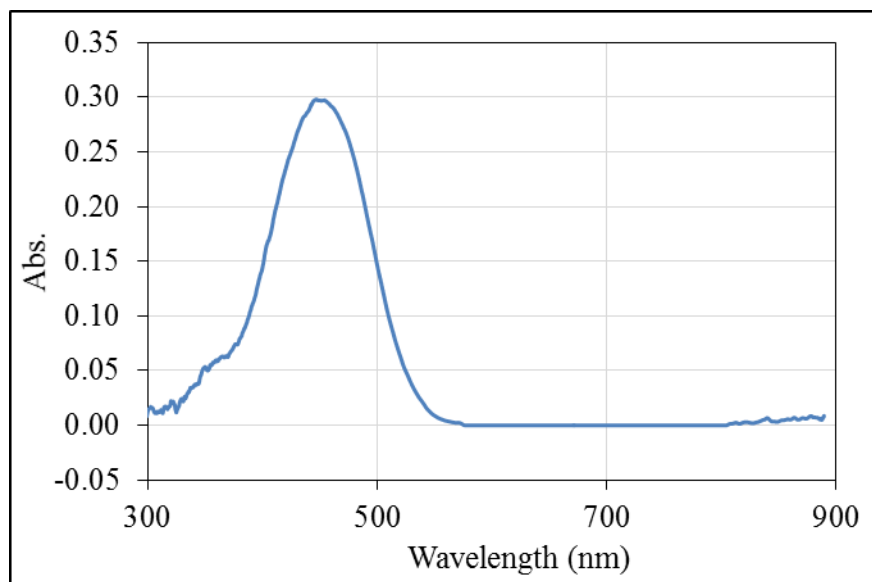


Figure 9: UV-Vis Spectrum for 1:1 Copolymer in solution

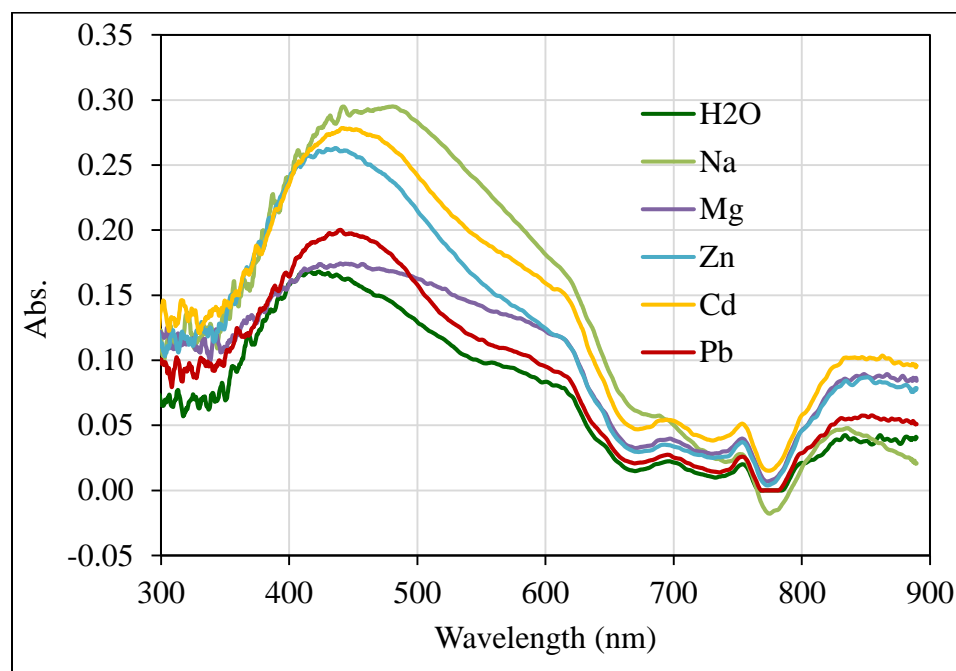


Figure 10. UV-Vis Spectra of 1:1 copolymer in various aqueous electrolytes:

NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$, $\text{Zn}(\text{ClO}_4)_2$, $\text{Cd}(\text{ClO}_4)_2$, and $\text{Pb}(\text{ClO}_4)_2$

CHAPTER IV

CONCLUSION

Using free radical initiation, three new copolymers with various ratios of co-monomers were synthesized using a literature procedure. The polymers were prepared by copolymerization of vinylferrocene with vinylimidazole using AIBN as the initiator. These reactions resulted in 69-88% yields of polymer. All polymers synthesized here were characterized by ^{13}C -NMR, ^1H -NMR, FTIR and GPC. The spectra of each copolymer were consistent with structures and polymerizations as illustrated in spectroscopy analysis.

The electrochemical behaviors of copolymers were tested in CH_2Cl_2 solutions of the copolymers, and cyclic voltammetry was carried out for each copolymer with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. All polymer solutions exhibited electrochemical reversibility which was consistent with the redox performance of ferrocene containing polymer. CMEs of polymer films were prepared by casting from CHCl_3 solutions and electrochemistry was performed in aqueous solutions of various supporting electrolytes: sodium perchlorate, cadmium perchlorate, zinc perchlorate, magnesium perchlorate, lead perchlorate. Cyclic voltammetry of 1:1 copolymer showed multiple oxidation waves with $\text{Cd}(\text{ClO}_4)_2$ and $\text{Pb}(\text{ClO}_4)_2$ compared to single oxidation potential with NaClO_4 , $\text{Mg}(\text{ClO}_4)_2$ or $\text{Zn}(\text{ClO}_4)_2$ as supporting

electrolytes. These significant multiple oxidation waves of 1:1 copolymer in the presence of $\text{Cd}(\text{ClO}_4)_2$ and $\text{Pb}(\text{ClO}_4)_2$ were consistent with interactions between the ferrocene and the metal-coordinated imidazole. In addition, the electronic communication in polymers was studied by UV-Vis spectroscopy. Comparing the solution versus thin film UV-Vis spectra of the 1:1 copolymer showed a significant increase in absorption at ca. 625 nm, suggesting interaction between the ferrocene and imidazole moieties. However, significant differences in the UV-Vis spectra of thin films of the 1:1 copolymer were not observed when the copolymer was exposed to different electrolytes.

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APPENDIX

SUPPLEMENTAL LISTS

FIGURE	PAGE
Figure S1: The structure of vinylferrocene.....	32
Figure S2: ¹ H-NMR of vinylferrocene.....	32
Figure S3: The structure of copolymer containing ferrocene with imidazole.....	33
Figure S4: ¹ H-NMR of 1:1 Copolymer.....	33
Figure S5: ¹ H-NMR of 3:1 Copolymer.....	33
Figure S6: FTIR of 1:3 Copolymer.....	34
Figure S7: FTIR of 3:1 Copolymer.....	34
Figure S8: ¹³ C-NMR of 1:3 Copolymer.....	34
Figure S9: ¹³ C-NMR of 1:1 Copolymer.....	35
Figure S10: CVs of Poly 2 with CH ₂ Cl ₂ and Bu ₄ NPF ₆ at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and an Ag pseudo reference electrode.....	35
Figure S11: CVs of Poly 3 with CH ₂ Cl ₂ and Bu ₄ NPF ₆ at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and an Ag pseudo reference electrode.....	36
Figure S12: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous Mg(ClO ₄) ₂ at scan rates of 100 mV/s.....	36
Figure S13: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous NaClO ₄ at scan rates of 100 mV/s.....	37
Figure S14: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous Pb(ClO ₄) ₂ at scan rates of 20 mV/s.....	37
Figure S15: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous NaClO ₄ at scan rates of 20 mV/s.....	38
Figure S16: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous Zn(ClO ₄) ₂ at scan rates of 20 mV/s.....	38
Figure S17: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous Mg(ClO ₄) ₂ at scan rates of 20 mV/s.....	39

Figure S18: CVs of chemical modified electrodes on cast films of all
copolymers on platinum electrode in aqueous $\text{Cd}(\text{ClO}_4)_2$ at scan rates of
20 mV/s.....39



Figure S1: The structure of vinylferrocene

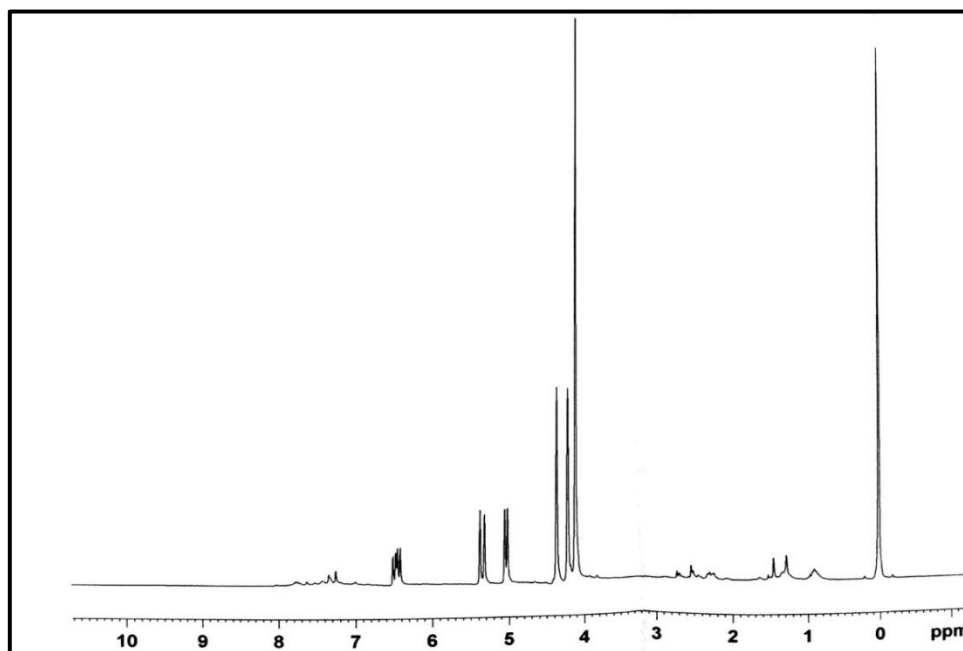


Figure S2: ¹H-NMR of vinylferrocene

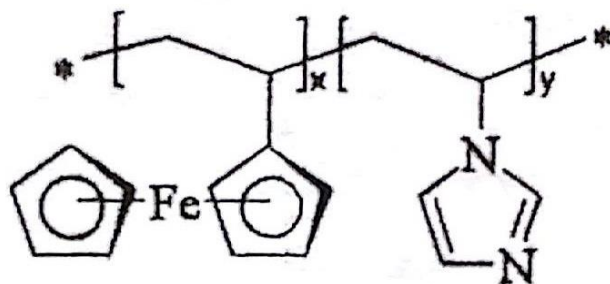


Figure S3: The structure of copolymer containing ferrocene with imidazole

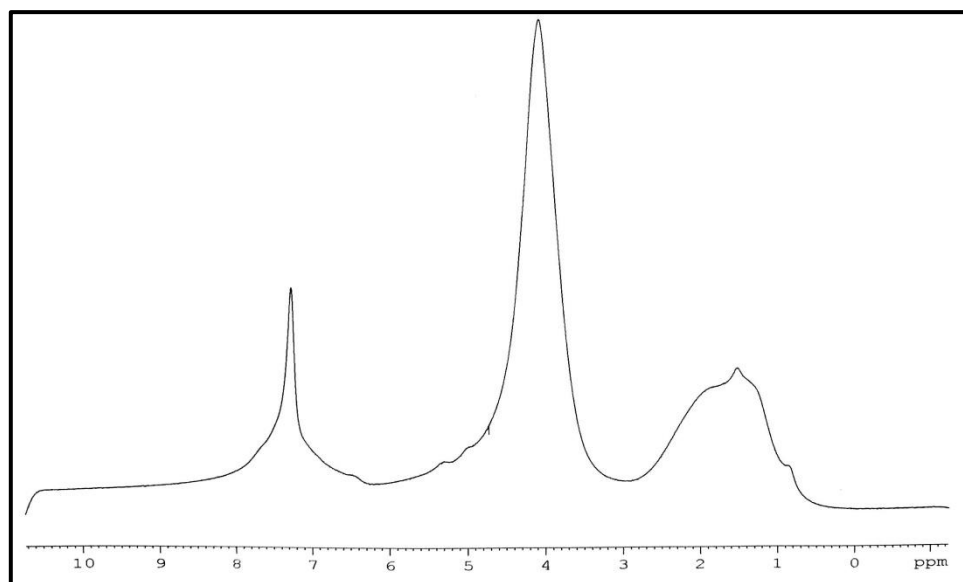


Figure S4: ^1H -NMR of 1:1 Copolymer

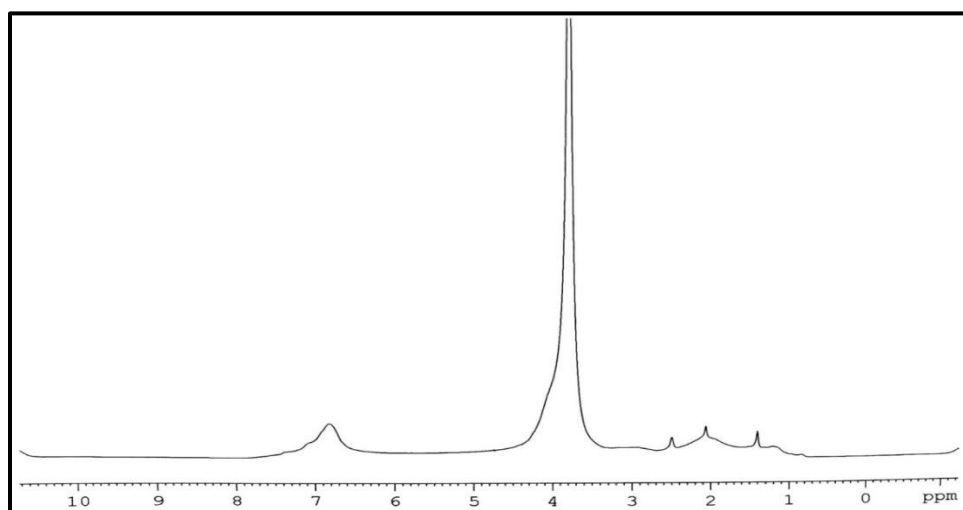


Figure S5: ^1H -NMR of 3:1 Copolymer

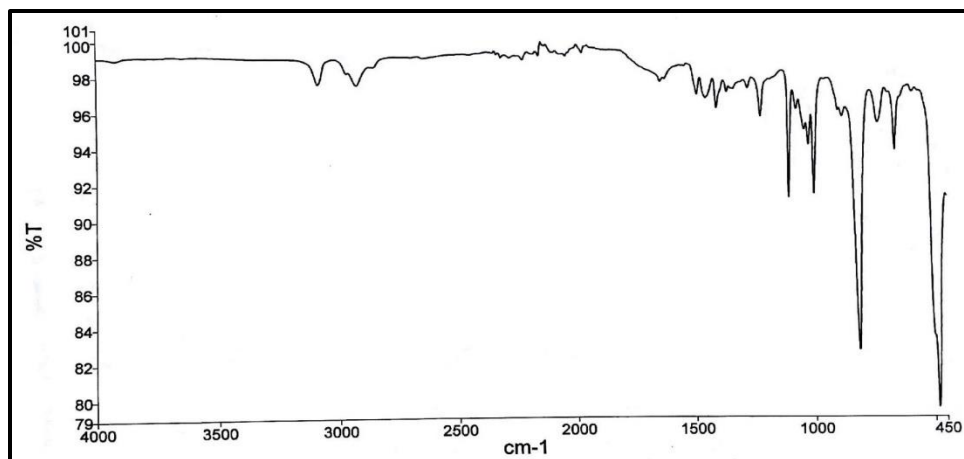


Figure S6: FTIR of 1:3 Copolymer

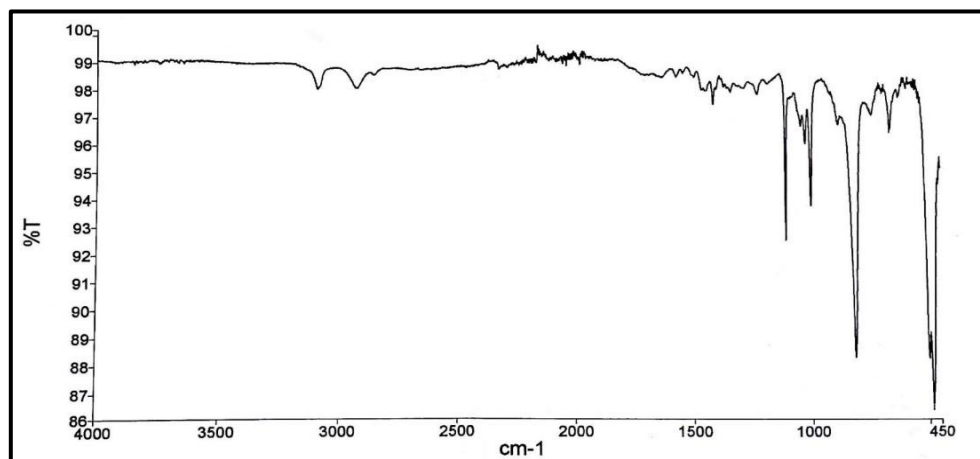


Figure S7: FTIR of 3:1 Copolymer

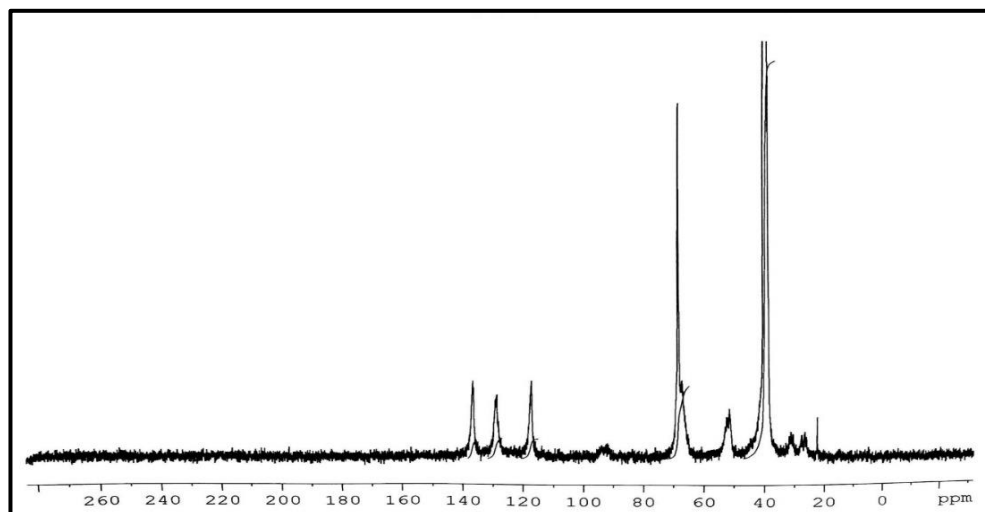


Figure S8: ¹³C-NMR of 1:3 Copolymer

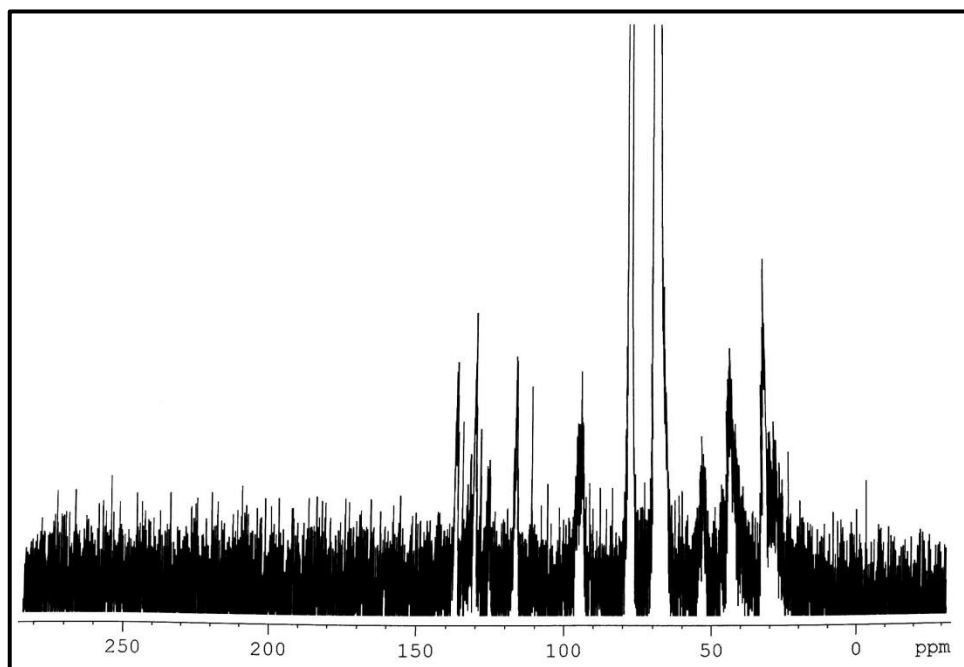


Figure S9: ^{13}C -NMR of 1:1 Copolymer

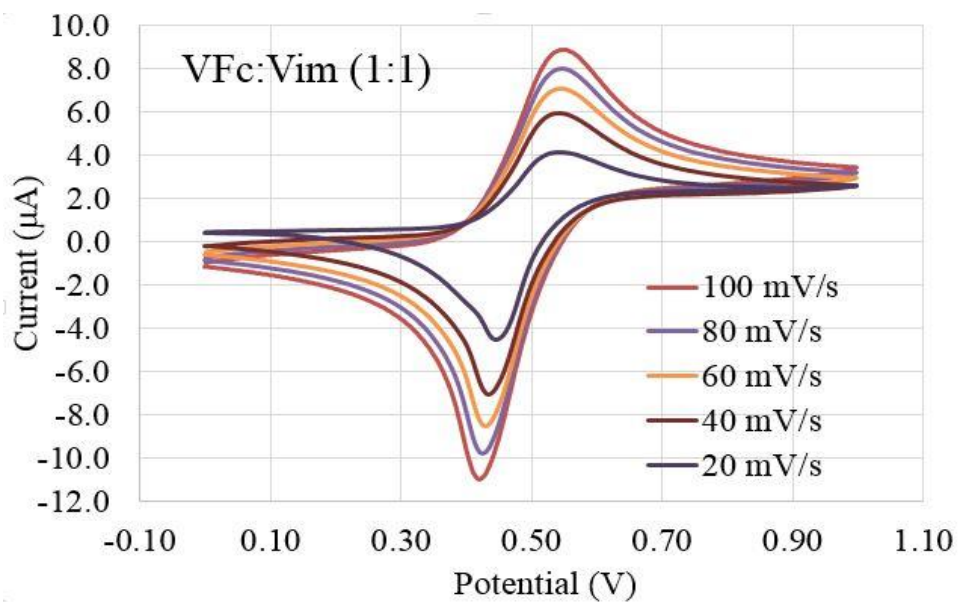


Figure S10. CVs of Poly 2 with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and an Ag pseudo reference electrode

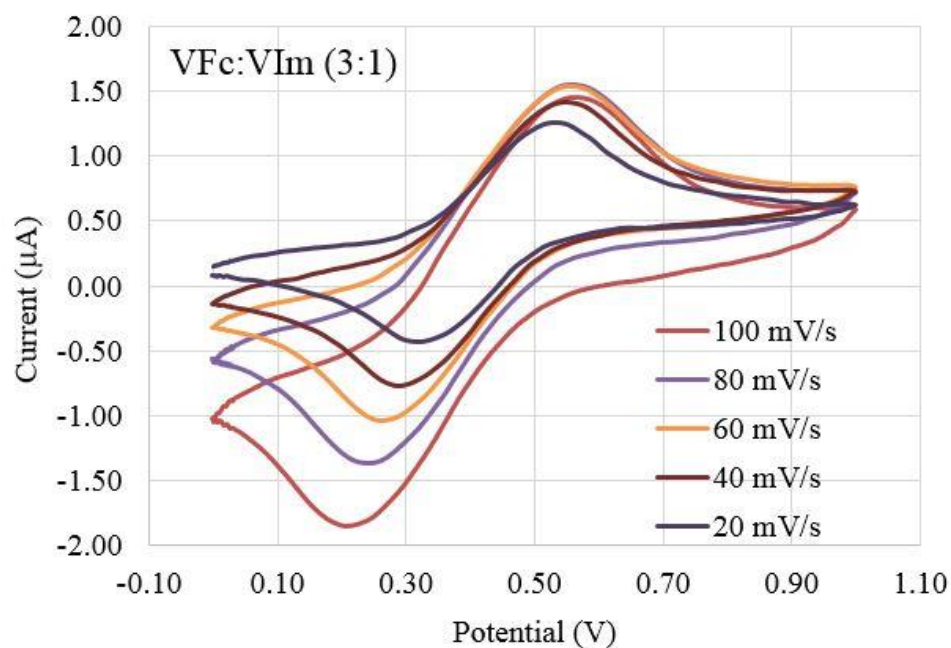


Figure S11. CVs of Poly 3 with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and an Ag pseudo reference electrode

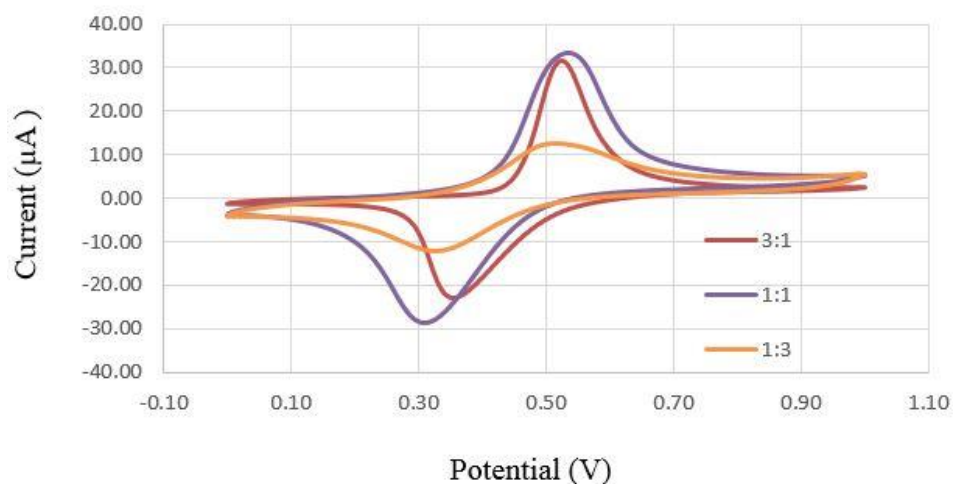


Figure S12: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Mg}(\text{ClO}_4)_2$ at scan rates of 100 mV/s

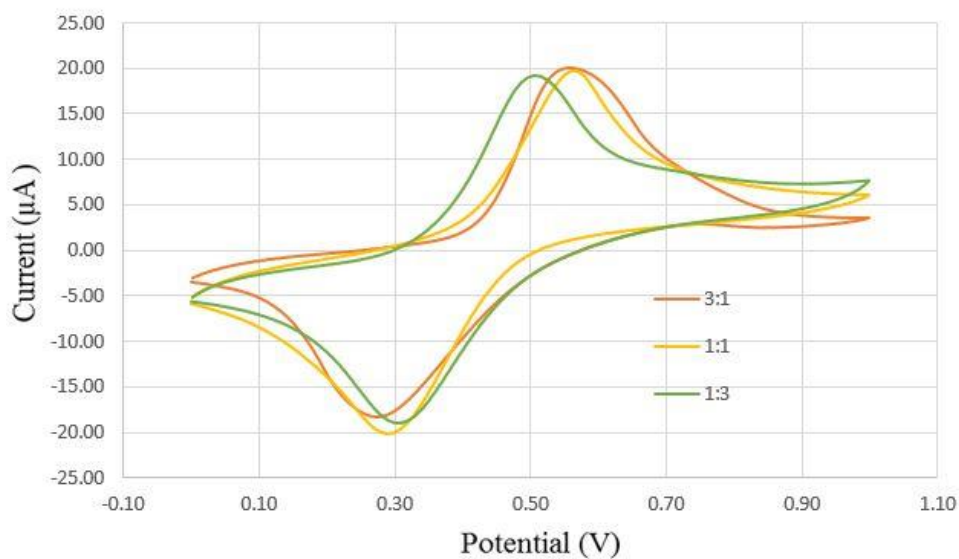


Figure S13. CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous NaClO_4 at scan rates of 100 mV/s.

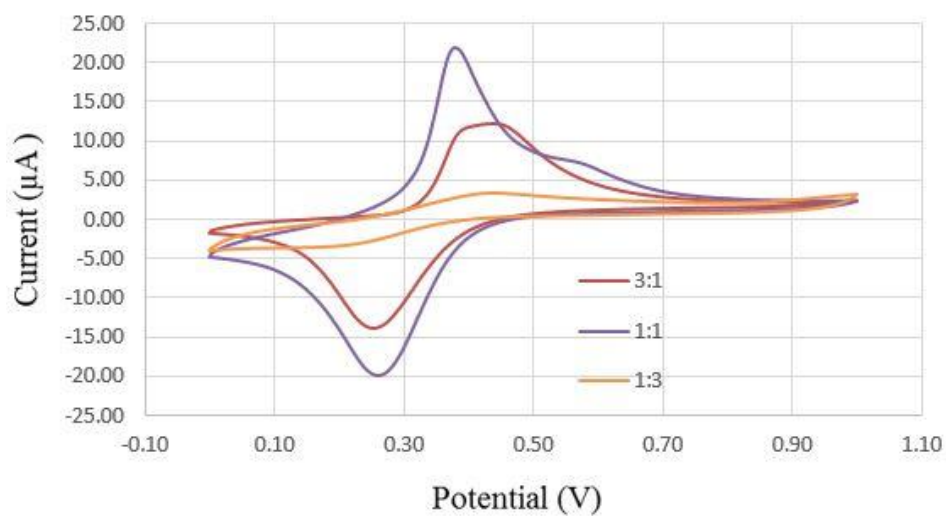


Figure S14. CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Pb}(\text{ClO}_4)_2$ at scan rates of 20 mV/s.

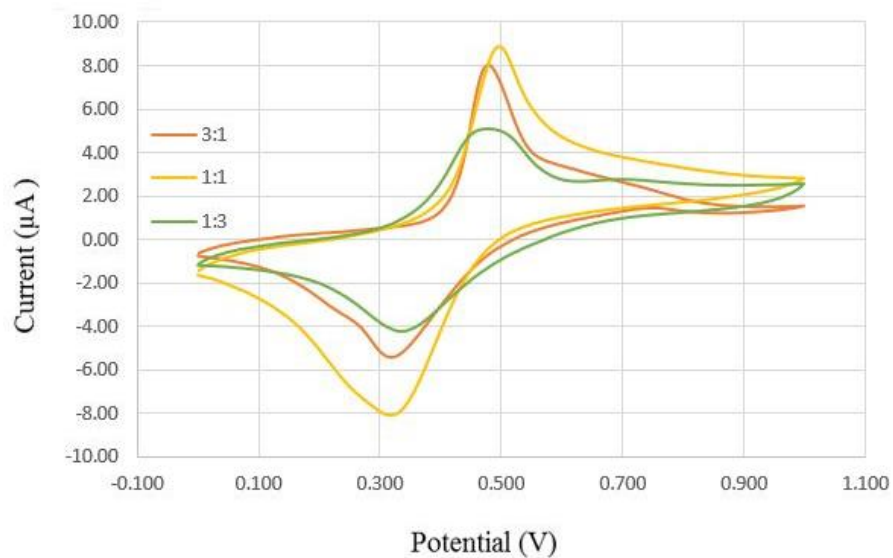


Figure S15: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous NaClO_4 at scan rates of 20 mV/s

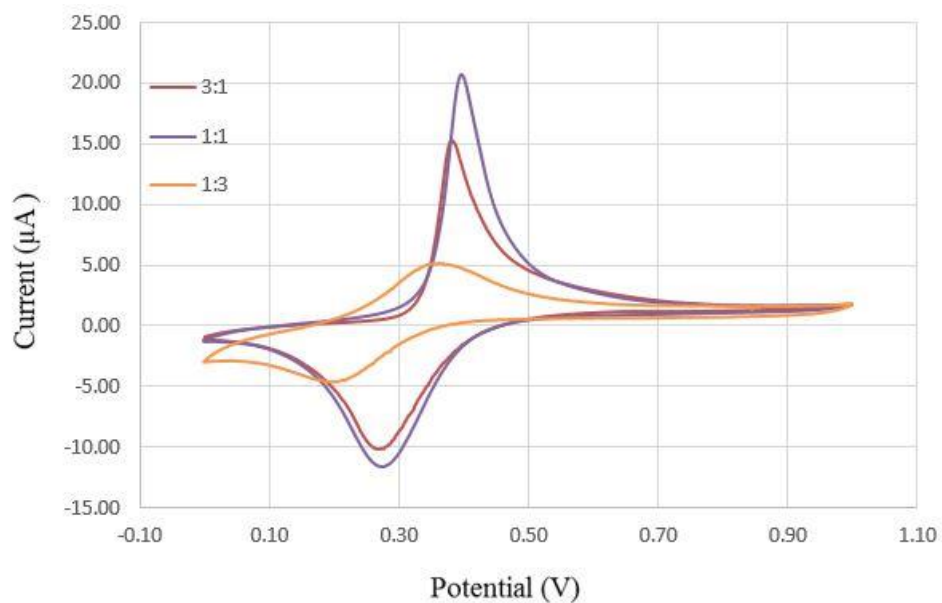


Figure S16: CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Zn}(\text{ClO}_4)_2$ at scan rates of 20 mV/s

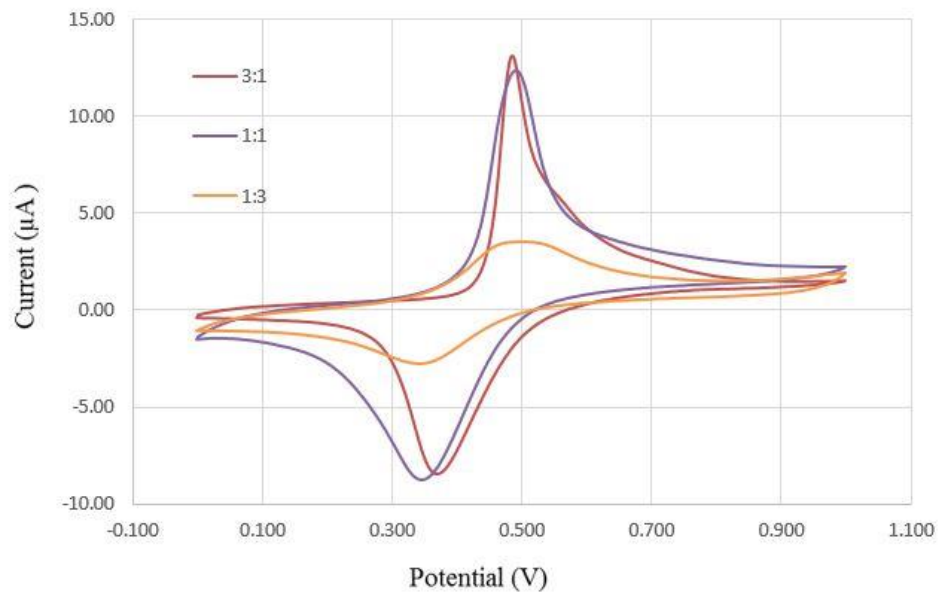


Figure S17. CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Mg}(\text{ClO}_4)_2$ at scan rates of 20 mV/s

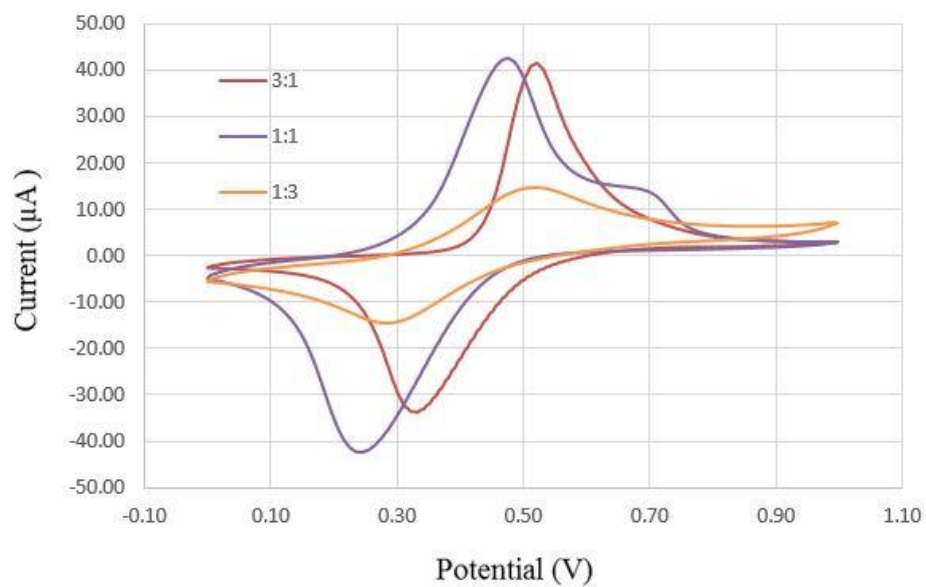


Figure S18. CVs of chemical modified electrodes on cast films of all copolymers on platinum electrode in aqueous $\text{Cd}(\text{ClO}_4)_2$ at scan rates of 20 mV/s