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Synthesis of ferrocene copolymers and investigation of their electrochemical properties.

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SYNTHESIS OF FERROCENE COPOLYMERS AND INVESTIGATION OF THEIR ELECTROCHEMICAL PROPERTIES

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SYNTHESIS OF FERROCENE COPOLYMERS AND INVESTIGATION OF THEIR ELECTROCHEMICAL PROPERTIES

An Abstract of the Thesis By
Ahmed Alzharani

Ferrocene is an organometallic compound. It is a classical metallocene consisting of two cyclopentadienyl rings bound on opposite sides of a central iron atom. Such organometallic compounds are also called sandwich compounds. Ferrocene copolymers have well known electrochemical capabilities. The main objective of this thesis is to synthesize vinyl ferrocene copolymers and test their electrochemical properties in aqueous solutions with different electrolytes (sodium nitrate, sodium perchlorate, and phosphate buffered saline). Vinylferrocene and 3-phenyl[5]ferrocenophane-1,5-dimethylene were synthesized using a Wittig reaction. Both ferrocene monomers were copolymerized with N-ethylmaleimide and N-phenylmaleimide and the resulting polymers were analyzed by Gel Permeation chromatography, IR and NMR. Cyclic voltammetry was used to characterize electrochemical properties of the copolymers. Ferrocene copolymers were deposited on the working electrode and the performance of the modified electrode versus electrolyte solution was studied. The application of this research is to understand how organometallic compounds work with electrolyte solutions to produce sensors with potential use in biological systems.

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LIST OF ABBREVIATIONS

AIBN - α, α-azobisisobutyronitrile

Bu_4NPF_6 Tetrabutylammonium hexafluorophosphate

CA - Chronoamperometry

CME - Chemically modified electrodes

Cp - Cyclopentadienyl

CV - Cyclic Voltammetry

Fc - Ferrocenyl

M_n - The Number Average Molecular Weight

n-Bu - *n*-butyl

PBS - Phosphate Buffer Saline

PD - polydispersity

Poly1 - Polymer from vinylferrocene with N-ethylmaleimide

Poly2 - Polymer from vinylferrocene with N-phenylmaleimide

Poly3 - Polymer from 3-phenyl[5]ferrocenophane-1,5-dimethylene with N-ethylmaleimide

Poly4 - Polymer from 3-phenyl[5]ferrocenophane-1,5-dimethylene with N-phenylmaleimide

PPM - parts per million

t-Bu - tert-butyl

TMS - Tetramethylsilane

VFc - vinylferrocene

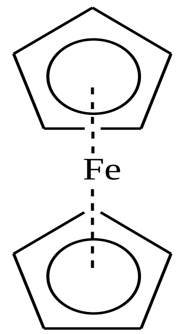
CHAPTER I

1. INTRODUCTION

1.1 Ferrocene

Ferrocene is an orange organometallic compound with formula $(C_5H_5)_2Fe$.[1] In 1951, Kealy and Pauson prepared ferrocene accidently when they were trying to synthesize fulvalene. It was prepared in diethyl ether by reacting cyclopentadienyl magnesium bromide and iron (III) chloride. Simultaneously, ferrocene was prepared by Miller, Tebboth, and Tremaine by a different method.[2] They reacted cyclopentadiene with iron as catalysts at 300ºC.[3]

The structure of ferrocene was determined by x-ray diffraction analysis.[4] The structure of ferrocene consists of two cyclopentadienyl anions $(C_5H_5)_2^-$ with each carbon atom interacting equally with the iron atom (Scheme 1). The rings are symmetric since no dipole moment is observed in solution. Ferrocene is a diamagnetic solid.[2] The protons of ferrocene are equivalent and show a sharp singlet in the ^{1}H-NMR spectrum.



Scheme 1. Structure of ferrocene

Since ferrocene was discovered, the field of organometallics has been an active area of research.[5,6] In 1952, Woodward showed that the rings of cyclopentadienyl ions were aromatic.[1] Therefore, the nomenclature of ferrocene was chosen due to the aromaticity which is similar to benzene.[1,4] Ferrocene is highly nucleophilic and readily undergoes electrophilic substitution. In Friedel-Crafts acetylation, ferrocene shows a higher reactivity than benzene and mesitylene. Numerous electrophilic reactions have been used to make derivatives of ferrocene.[7] Excellent thermal and photochemical stability are important characteristics of ferrocene for various applications.[8] The well-behaved redox properties of ferrocene polymers have also been used in electrochemical and catalytic applications.[9, 10] Electron donors such as nitrogen, sulfur, phosphorous, and oxygen have been used to change the oxidation potential of ferrocene and these materials are interesting for many applications.[4,11]

Ferrocene can be incorporated into polymer systems either into the backbone or on the side chains.[12] Properties of ferrocene such as electron donating ability, redox reversibility, and stability make the incorporation of ferrocene into polymers attractive.[11, 13] An example of incorporating ferrocene into the main chain of a polymer is polyferrocenylsilane (PFS). PFS was synthesized by ring opening polymerization.[14]

Ferrocene containing polymers exhibited semi-photoconductivity behavior, catalytic ability, and active redox reversibility.[12] In Schiff base polymers ferrocene was used to protect the hydrolysis of imines.[12]

1.2 Biosensors

Biosensors are important and are of interest to researchers in various fields such as medicine, biology, chemistry, physics, and engineering.[15] Biosensors have two main parts, analyte and transducer. The analyte is a material that interacts with a biological element and creates a recognition event. The second part, the transducer, is responsible to convert the biological response into an electronic signal.[15,16] The types of biosensors can be classified by mechanism of the transducers. For instance, biosensors are classified by detection mode to electrochemical, optical-detection, thermal-detection, resonant, and ion-sensitive field-effective transistor (ISFET) biosensors.[16]

Electrochemical biosensors are of particular interest in ferrocene containing polymers due to their low cost and ease of construction. Electrochemical biosensor categories are potentiometric, conductometric, and amperometric.[16] The conductometric biosensor measures change in conductivity and amperometric biosensor measures changes in the current. Potentiometric biosensors measure the changes in redox potential of an electrochemical reaction.[16]

1.3 Ferrocene Polymers

Organometallic compounds containing polymers have a wide range of applications such as sensor, semiconductor, laser, solar cell, batteries, biofuel cell, electrochemical devices, memory devices, or electrocatalysts.[12,17,18,19] In particular, ferrocene containing polymers have active redox properties suitable for use as electrocatalysts, modified electrode, and chemical sensor.[20,21,22] Ferrocene polymers have shown promise as electrochemical mediators in biosensor applications.[10, 23]

The use of redox active polymers to modify electrodes has shown promise for biosensor applications.[24] These materials facilitate electron transfer from the redox enzyme to the electrode surface. One example of a redox polymer for use in biosensor applications is ferrocene containing polymers. These materials have been shown to be effective in the detection of glucose or peroxides. In addition, ferrocene containing polymers offer the advantages of well understood chemistry and well behaved electrochemistry. Ferrocene can act as an electron mediator, to enhance the sensor signal.[25]

Although ferrocene polymers have been shown to be effective redox mediators, one of their limitations is low molecular weight, particularly in free radical polymerization. In addition to typical termination mechanisms, ferrocene monomers have an additional termination mechanism. Ferrocene can transfer an electron to the radical at the end of the growing chain, creating a zwitterion and stopping polymerization. To circumvent this problem, recently the synthesis of copolymers from 3-phenyl[5]ferrocenophane-1,5-dimethylene or vinylferrocene with various N-substituted maleimides was reported. These copolymers were high molecular weight and amorphous films could be solution cast from typical solvents such as THF or $CHCl_3$. Initial electrochemical studies on these materials revealed one oxidation potential, which was consistent with an alternating copolymer. The cyclic voltammograms in CH_2Cl_2 showed a greater I_{pc} than I_{pa} and I_{pa} scaled linearly with the scan rate which is characteristic of adsorption of the oxidized polymer to the electrode surface. In addition, oxidative electrodeposition from CH_2Cl_2 gave films with good redox activity in an aqueous NaCl solution making these materials good candidates as chemical modified electrodes (CMEs).[27,28,29]

1.4 Project rationale

In this research work, we focused on the electrochemical behavior of polymers synthesized from vinylferrocene or 3-phenyl-[5]-ferrocenophane-1,5-dimethylene with N-ethyl or N-phenylmaleimide. From the previous results, further characterization of these materials was warranted to determine their use in sensor or biofuel applications. The electrochemical behavior of electrodes modified with these copolymers with various electrolytes, as well as, their electrochemical stability will be presented.

CHAPTER II

2. EXPERIMENTAL

2.1 Materials

All starting materials were commercially available (purchased from Acros Organics) and used as received unless otherwise stated. Vinylferrocene and 3-phenyl[5]ferrocenophane-1,5-dimethylene were synthesized by a Wittig reaction according to a literature procedure.[26] Polymers were synthesized by known procedure.[26] N-Ethylmaleimide (Acros Organics) and N-phenylmaleimide (Acros Organics) were recrystallized using isopropanol then dried at room temperature under high vacuum. Column chromatography utilized silica gel (60 °A) (Acros Organics) as the stationary phase with chloroform or methylene chloride as the mobile phase.

2.2 Synthesis of vinylferrocene copolymers

2.2.1 Synthesis of vinylferrocene

To a 3-necked round bottom flask was added methyltriphenylphosphonium bromide (1.96 g, 5.5 mmol) under a N_2 atmosphere. Tetrahydrofuran (THF) (20 mL) was added and the mixture was stirred. *n*- Butyllithium (*n*-BuLi) (2.2 mL, 5.5 mmol) was added and stirring continued for 30 min. Ferrocenecarboxaldehyde (1.07 g, 5 mmol) was added and stirring continued. After 24 hours, water (0.5 mL) was added to the reaction, followed by removal of the solvent under reduced pressure. Purification by chromatography with silica gel and methylene chloride (CH_2Cl_2) gave 0.80 g (80%). IR (KBr, cm^{-1}) C=C-H: 3080, C=C: 1650. ^{1}H-NMR ($CDCl_3$, δ.ppm): 6.45 (1H.FeCH=C), 5.40 (1H.FeC=CH), 5.00 (1H.FeC=CH), 4.40(2H.CP-ring), 4.21(2H.CP-ring), 4.12 (5H.CP-ring).

2.2.2 Polymerization of vinylferrocene with N-ethylmaleimide and N-phenylmaleimide (Poly1)

To a round bottom flask was added vinyl ferrocene (0.212g, 1 mmol), N-ethylmaleimide (0.125g, 1 mmol), α,α-azobisisobutyronitrile (AIBN) (0.038g), and chlorobenzene (2 mL). A nitrogen atmosphere was established. The reaction mixture was heated at 70-80 ºC for 16 h. The reaction mixture was allowed to cool down to room temperature and then added dropwise into rapidly stirred methanol. The precipitate was collected by suction filtration and dried under reduced pressure to give 0.12g (82%) of the polymer. IR (KBr, cm^{-1}) C-H aromatic 3110, C-H aliphatic 2920, C=O 1740. ^{1}H-NMR ($CDCl_3$, δ.ppm): 3.42-4.55 (9H), 3.40-2.10 (7H), 0.75-1.35 (3H). GPC: M_n was 20,158 and polydispersity was 5.1

2.2.3 Polymerization of vinylferrocene with N-phenylmaleimide (Poly2)

The polymerization to give poly (vinylferrocene-co-N-phenylmaleimide) followed the procedure described for (2.3.2). The yield of the polymer was 0.14 g (86%). IR (KBr, cm^{-1}) C-H aromatic 3050, C-H aliphatic 2860, C=O 1742. ^{1}H-NMR ($CDCl_3$, δ.ppm): 7.40-6.50 (5H), 4.40-3.75 (9H), 3.75-1.40 (5H). GPC: M_n was 6,161 and polydispersity was 3.9.

2.3 Synthesis of 3-phenyl[5]ferrocenophane-1, 5-dimethylene copolymers

2.3.1 Synthesis of 1,1'-diacetylferrocene

Aluminum chloride (1.67g 12.5 mmol) and methylene chloride (35 mL) were added into a round bottom flask and a nitrogen atmosphere was established. Acetyl chloride (0.98 g 12.5 mmol) was then added and the reaction mixture was stirred for 0.5 h. Ferrocene (0.93g 5 mmol) was added and the reaction mixture was stirred overnight. The reaction mixture was poured into cold water to neutralize the $AlCl_3$. The layers were separated followed by removal of the methylene chloride under reduced pressure. Recrystallized from isopropanol gave 5.9 g (80%) of diacetyl ferrocene. IR (KBr, cm-1) C-H aromatic 3100, C-H aliphatic 2850, C=O 1675, C=C aromatic 1600. 1H-NMR (CDCl3, δ.ppm): 4.76 (4H.CP-ring), 4.49 (4H.CP-ring), 3.52 (6H. C-CH_3).

2.3.2 Synthesis of 3-phenyl[5]ferrocenophane-1, 5-dione

Diacetylferrocene (1g 3.7 mmol), benzaldehyde (0.3g 3.7 mmol), KOH (0.1g, 1.8 mmol), and 95% ethanol (25 mL) were added to a round bottom flask. The reaction mixture was stirred at room temperature for 16h. The precipitate was collected by filtration and dried under reduced pressure to give 0.9 g (68%) of 3-phenyl[5]ferrocenophane-1,5-dione. IR (KBr, cm^{-1}) C-H aromatic 3070, C=O 1720. ^{1}H-NMR ($CDCl_3$, δ.ppm): 7.42 (5H.phenyl), 4.91 (2H.CP-ring), 4.70, 4.61, 4.50, (6H. CP-ring), 4.28(1H.CH-Ph), 2.55(2H.CH-CH_2).

2.3.3 Synthesis of 3-phenyl[5]ferrocenophane-1, 5-dimethylene

To a 3 necked round bottom flask was added methyltriphenylphosphonium bromide (5.9 g, 5.5 mmol), and THF (50 mL) then a N_2 atmosphere was established. *n*-Butyllithium (5.9 mL) was added to the mixture and stirring continued for 30 min. 3-

phenyl[5]ferrocenophane-1,5-dione was added and stirred for 24 h. After 24 h, water (2 mL) was added to the reaction mixture, followed by removal of the solvent under reduced pressure. Purification by chromatography with silica gel and methylene chloride gave 2.75g (68%) of 3-phenyl[5]ferrocenophane-1,5-dimethylene. IR (KBr, cm^{-1}) C-H aromatic 3075, C-H aliphatic 2820, C=C at 1580 cm^{-1}. ^{1}H-NMR ($CDCl_3$, δ.ppm): 7.35 (5H.phenyl), 5.30 (2H.C=CH_2), 4.60(2H.C=CH_2), 4.60, 4.55, 4.30, 4.15 (8H. CP-ring), 4.16 (1H.CH-Ph), 2.60 (4H.CH-CH_2).

2.3.4 Polymerization of 3-phenyl[5]ferrocenophane-1, 5-dimethylene with N-ethylmaleimide (Poly3)

To a round bottom flask was added 3-phenyl[5] ferrocenophane-1,5-dimethylene (0.354g, 1 mmol), N-ethylmaleimide (0.125g, 1 mmol), AIBN (0.002g) and chlorobenzene (2 mL) under nitrogen atmosphere**.** The reaction was heated at 70-80 ºC for 16 h. After that, the reaction mixture was allowed to cool down to room temperature and then added dropwise into rapidly stirred methanol. The precipitate was collected by suction filtration and dried under reduced pressure to give 0.45g (82%) of the polymer. IR (KBr, cm^{-1}) C-H aromatic 3080, C-H aliphatic 2850, C=O 1735. ^{1}H-NMR ($CDCl_3$, δ.ppm): 7.85-6.50 (5H), 4.30-3.10 (9H), 2.80-0.60 (16H). GPC: M_n was 14,848 and polydispersity was 2.8.

2.3.5 Polymerization of 3-phenyl[5]ferrocenophane-1, 5-dimethylene with N-phenylmaleimide (Poly4)

The polymerization to give Poly4 followed the procedure described for (2.4.4) and the yield of the polymer was 0.5 g (80%). IR (KBr, cm^{-1}) C-H aromatic 3030, C-H aliphatic 2820, and C=O 1740. ^{1}H-NMR ($CDCl_3$, δ.ppm): 7. 50-6.50 (10H), 4.35-3.10 (9H), 2.90-0.80 (11H). GPC: M_n was 18,001 and polydispersity was 3.7.

2.4 Instrumentation

All NMR spectra were obtained using a Bruker DPX-300 spectrometer. Fourier-transform Infrared Spectra (FT-IR) were obtained using a Thermo Nicolet IR-300. Gel permeation chromatography (GPC) measurements were taken using a JMDG-4 Waters 515 HPLC pump, a 2410 differential refractometer (Waters), set of one 300x7.8 mm phennogel 5μ column. M_n, M_w, and polydispersity were calculated based on peaks present in chromatogram compared to polystyrene standard calibration. Cyclic voltammetry (CV) and chronoamperometry (CA) measurements were carried out using a Gamry Interface 1000 potentiostat with gold or platinum (2 mm OD), as working and counter electrodes with an Ag wire pseudo reference electrode. UV- visible spectra were obtained with a Shimadzu UV-1201.

2.5 Preparation of electrodes

Electrodeposition method:

Electrochemical solutions were prepared by dissolving polymer (1mM) and tetrabutylammonium hexafluorophosphate (100mM) as supporting electrolyte, in methylene chloride (CH_2Cl_2) (10 mL). Chemical modified electrodes were prepared using chronoamperometry (CA) by stepping the potential from 0.0 to 1.0 V and holding at 1.0 V for 2 min. The electrodes were removed and air dried for 15 minutes prior to electrochemical experiments in aqueous solutions.

Cast film method:

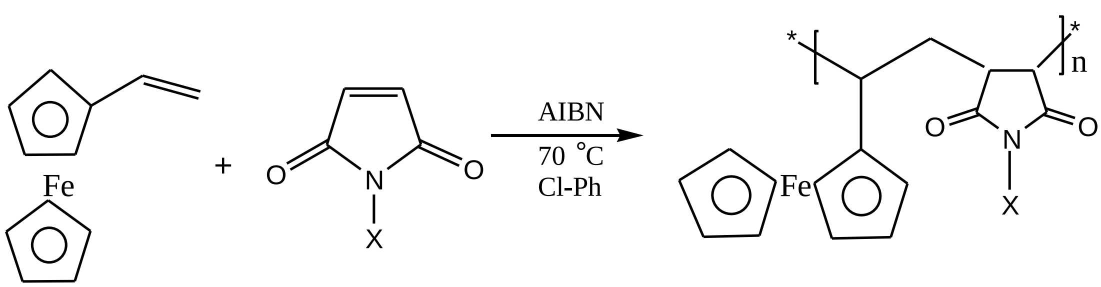
Chemical modified electrodes (CME) were also prepared by casting from polymer solutions directly on the electrode surface. CH_2Cl_2 solutions of Poly1-4 (1 mg/mL) were micropipetted (5µL) onto electrodes then allowed to air dry for 15-20 min. The electrodes were then placed into various aqueous electrolyte solutions for electrochemical analyses.

CHAPTER III

3. RESULTS AND DISCUSSION

3.1 Characterization of vinylferrocene copolymers

The synthesis and copolymerization of vinylferrocene with N-ethyl and N-phenylmaleimide were accomplished according to literature.[26] The Wittig synthesis of vinylferrocene was accomplished in 80% yield from ferrocene carboxaldehyde and methyltriphenyl-phosphonium bromide. Copolymerization of vinylferrocene with N-ethylmaleimide was performed in chlorobenzene with α,α-azobisisobutyronitrile (AIBN) as the initiator, giving good polymer yield (Scheme 2). The FTIR and ^{1}H-NMR spectra were consistent with the reported spectra in literature.[26]

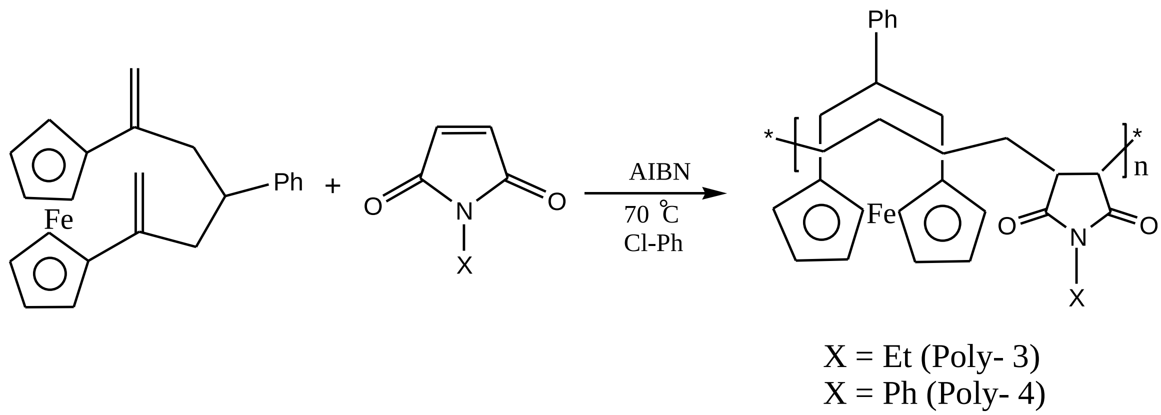


X = Et (Poly- 1)
X = Ph (Poly- 2)

Scheme 2. The reaction scheme of polymerization of vinylferrocene with N-ethyl and N-phenyl maleimide.

3.2 Characterization of 3-phenyl[5]ferrocenophane-1, 5-dimethylene copolymers

The synthesis and copolymerization of 3-phenyl[5]ferrocene-1,5-dimethylene with N-ethyl and N-phenylmaleimide were also accomplished according to literature.[26] Ferrocene was diacetylated under Friedal-Crafts conditions followed by conversion to 3-phenyl[5]ferrocenophane-1,5-dione by condensation with benzaldehyde. The dione was then converted to the diene using a Wittig reaction. Copolymerization was performed in chlorobenzene with α,α-azobisisobutyronitrile (AIBN) as the initiator, giving good polymer yields (Scheme 3). The FTIR and ^{1}H-NMR spectra were consistent with the reported spectra in literature.[26]



Scheme 3. Polymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene with N-ethyl and N-phenyl maleimide.

3.3 Electrochemical characterization

3.3.1 Electrochemical studies of chemically modified electrodes prepared by chronoamperometry on Au electrode

Cyclic Voltammetry (CV) for each polymer was performed from 0.0 V to 1.0 V and is shown in Table 1. For Poly1, E_{ox} and E_{red} were observed at 0.55 V and 0.51 V, respectively. In addition, greater current for E_{red} than for E_{ox} was observed which is consistent with polymer adsorption on the electrode surface. The electrochemical behavior exhibited reversible redox potential. Similar results were observed for polymers 2-4 and are consistent with previous reported data.[27,28,29]

Table 1. Redox potentials of Poly1-4

Polymer	E_{ox} (V)	E_{red} (V)	$E_{1/2}$ (V)
1	0.55	0.51	0.53
2	0.59	0.51	0.55
3	0.76	0.71	0.74
4	0.66	0.63	0.65

Chemical modified electrodes prepared by the chronoamperometry (CA) method were placed into 0.1M aqueous solutions of $NaNO_3$, $NaClO_4$, or PBS. CVs of Poly1 using $NaNO_3$, $NaClO_4$, or PBS on Au electrode are shown in Figure 1. Redox potentials ($E_{1/2}$) of Poly1 were observed using $NaNO_3$, $NaClO_4$, and NBS, at 0.31, 0.24, and 0.55V respectively (Table 2). Changes is oxidation potential versus electrolyte has been observed for poly(vinylferrocene) and may be a result of differences in ion pair stability or in solvation of the anion.[29] Poly2 exhibited similar electrochemical behavior compared to Poly1.

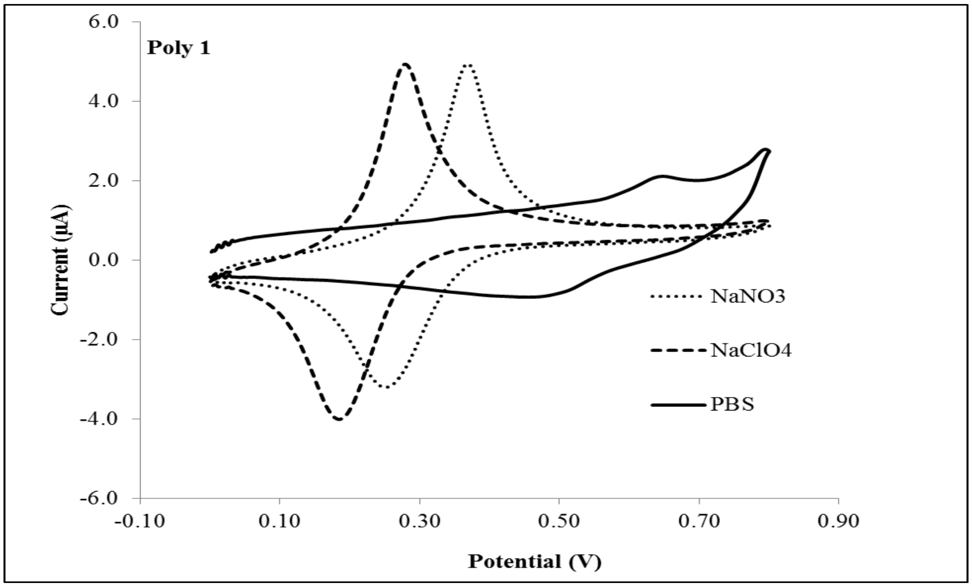


Figure 1. CVs of chemically modified electrode from Poly1 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

Redox potentials ($E_{1/2}$) of Poly3 were observed using $NaNO_3$, $NaClO_4$, and PBS, at 0.34, 0.25, and 0.30V, respectively (Table 2). This dependence of the potential on the electrolyte was consistent with Poly1 and Poly2 and may be a result of differences in ion pair stability or solvation of the anion. Poly4 exhibited similar electrochemical behavior to Poly3.

3.3.2 Electrochemical studies using cast films on Au electrode

CVs of Poly1 using $NaNO_3$, $NaClO_4$, or PBS as the supporting electrolyte are shown in Figure 2. The cyclic voltammograms with a Poly1 modified electrode showed greater current compared to electrodes prepared by electrochemical deposition. Redox potentials ($E_{1/2}$) of Poly1 were observed at 0.32, 0.14, and 0.54 V for $NaNO_3$, $NaClO_4$, and PBS respectively. These results are consistent with the results utilizing electrochemical deposition and similar results were observed for Poly2-4 (Table 3).

These data indicate that the electrochemical potentials of the polymers were not dependent on deposition technique.

Table 2. Redox potentials of chemically modified electrodes of Poly1-4 prepared by chronoamperometry with aqueous solutions of $NaNO_3$, $NaClO_4$, or PBS

Poly	Electrolyte	E_{ox} (V)	E_{red} (V)	$E_{1/2}$ (V)
1	$NaNO_3$	0.37	0.25	0.31
	$NaClO_4$	0.28	0.19	0.24
	PBS	0.64	0.45	0.55
2	$NaNO_3$	0.33	0.19	0.26
	$NaClO_4$	0.23	0.11	0.17
	PBS	0.61	0.44	0.53
3	$NaNO_3$	0.45	0.22	0.34
	$NaClO_4$	0.33	0.16	0.25
	PBS	0.32	0.28	0.30
4	$NaNO_3$	0.58	0.43	0.51
	$NaClO_4$	0.51	0.34	0.43
	PBS	0.34	0.30	0.32

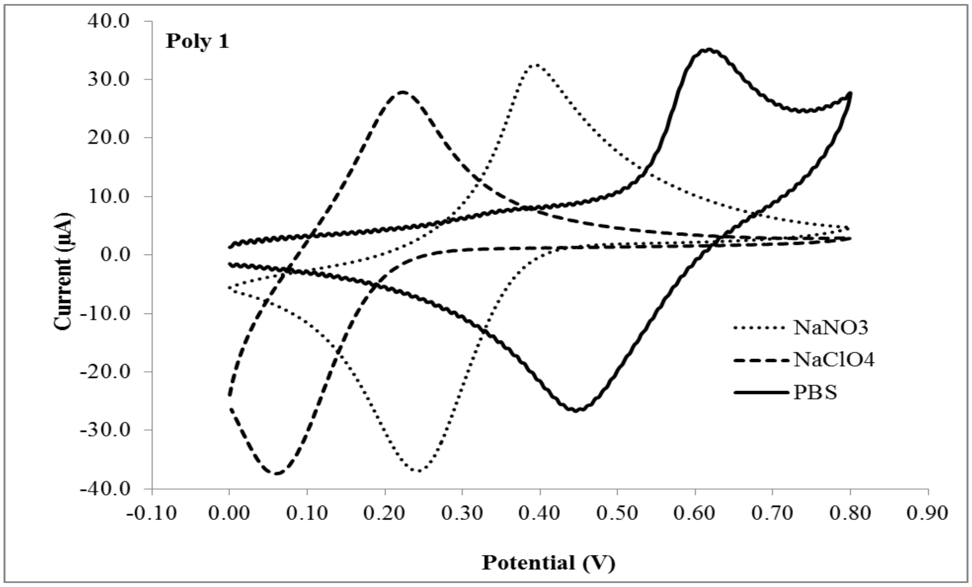


Figure 2. CVs of chemically modified electrode from Poly1 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

Table 3. Redox potentials of chemically modified electrodes of Poly1-4 prepared by solution cast films with aqueous solutions of $NaNO_3$, $NaClO_4$, and PBS

Poly	Electrolyte	E_{ox} (V)	E_{red} (V)	$E_{1/2}$ (V)
1	$NaNO_3$	0.38	0.25	0.32
	$NaClO_4$	0.21	0.07	0.14
	PBS	0.61	0.46	0.54
2	$NaNO_3$	0.43	0.25	0.34
	$NaClO_4$	0.31	0.12	0.22
	PBS	0.60	0.46	0.53
3	$NaNO_3$	0.41	0.29	0.35
	$NaClO_4$	0.30	0.12	0.21
	PBS	0.53	0.41	0.47
4	$NaNO_3$	0.46	0.28	0.37
	$NaClO_4$	0.29	0.10	0.20
	PBS	0.62	0.41	0.52

3.3.3 Electrochemical stability of Poly1-4 with PBS

Initial studies on the electrochemical stability of Poly1-4 were conducted with films prepared by electrochemical deposition onto a gold electrode. Chemical modified electrode was placed into PBS and cycled from 0.0 to 0.8 V for 100 scans. The CV scans for Poly1 are shown in Figure 3 and similar results were observed for Poly 2. Poly1 showed a consistent redox potential over 100 scans. However, a slight reduction in current was observed from 1.06 to 0.97 μA after 100 scans. A reduction in current may be due to loss of Poly1 from the electrode. For Poly3 (Figure 4), a consistent redox potential was observed for successive scans. In contrast to Poly1, Poly3 exhibited a complete loss in current within 25 scans, similar results were observed for Poly4. The results indicated complete loss of Poly3 from the electrode due to poor adhesion.

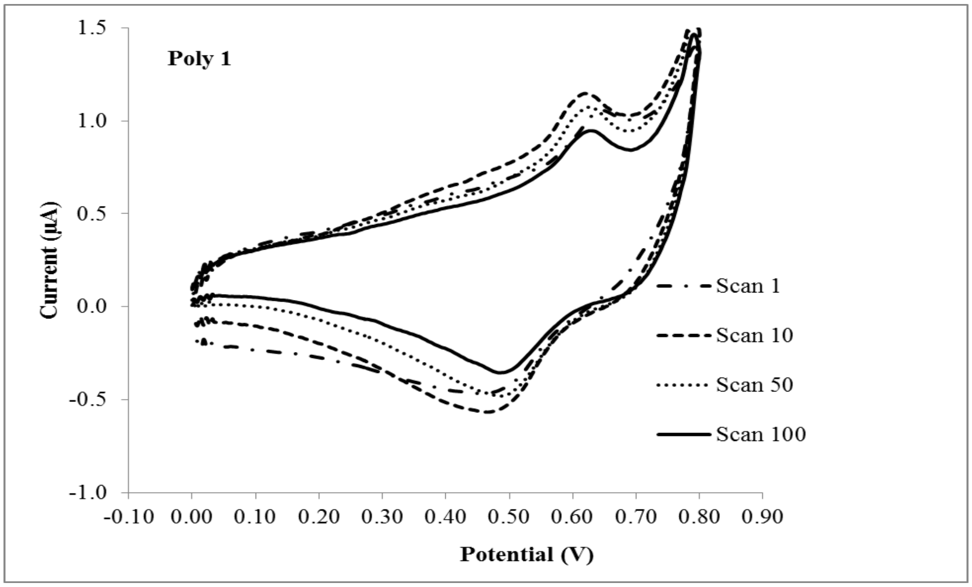


Figure 3. CVs of chemically modified electrode from Poly1 with PBS using Au working and counter electrodes and a Ag pseudo reference electrode: scans 1, 10, 50, and 100 are shown.

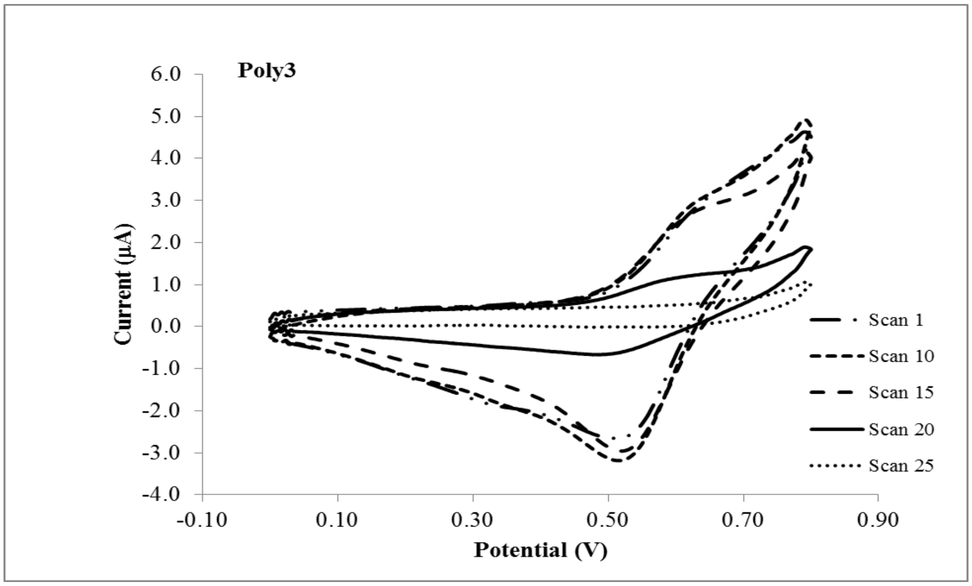


Figure 4. CVs of chemically modified electrode from Poly3 with using Au working and counter electrodes and a Ag pseudo reference electrode PBS: scans 1, 10, 15, 20, and 25 are shown.

Electrochemical stability studies were also conducted on cast films using a Au or Pt electrode. The CME was placed into PBS and cycled from 0.0 to 0.8 V for 100 scans. Figure 5 shows the CV for scans 1, 10, 20, 40, 60, 80, 100. Poly1 exhibited an initial shift in redox potential ($E_{1/2}$) from 0.58 to 0.43 V within the first 10 scans, indicating a morphology change with the polymer. Subsequent scans showed a consistent redox potential. However, a significant loss in current for oxidation was observed after 100 CV scans from 1.94 to 1.60 µA. These results indicate a loss in redox activity of the Poly1 or a loss of Poly1 from the electrode.

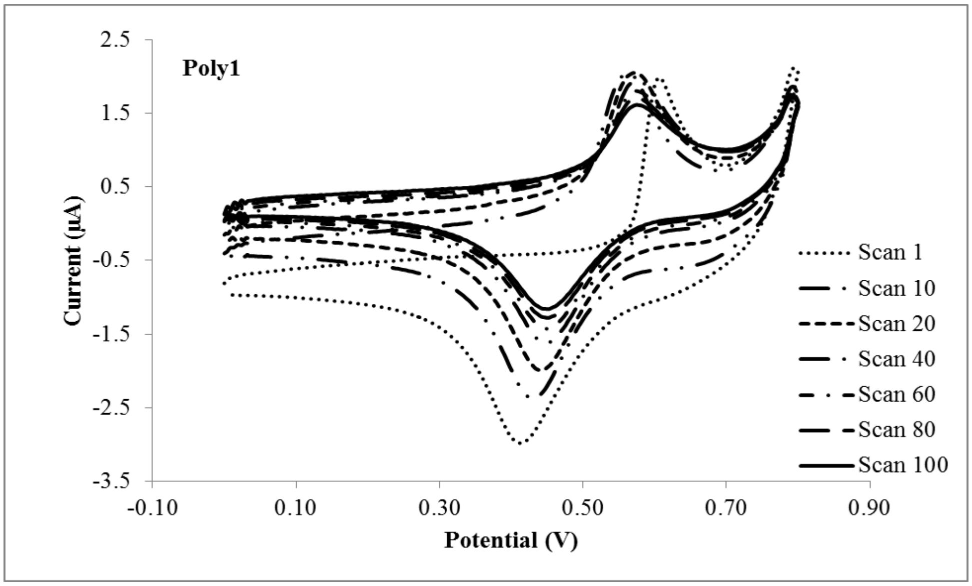


Figure 5. CVs of chemically modified electrode from Poly1 with PBS using Au working and counter electrodes and a Ag pseudo reference electrode: scans 1, 10, 20, 40, 60, 80, and 100 are shown.

Electrochemical studies of cast films of Poly3 on Au showed much different result compared to Poly1. Poly3 exhibited a consistent redox potential from 1 to 100 scans but a significant loss in current (Figure 6). CMEs from cast films of Poly3 were consistent with CMEs prepared by CA, indicating poor adhesion of the polymer to Au regardless of deposition technique.

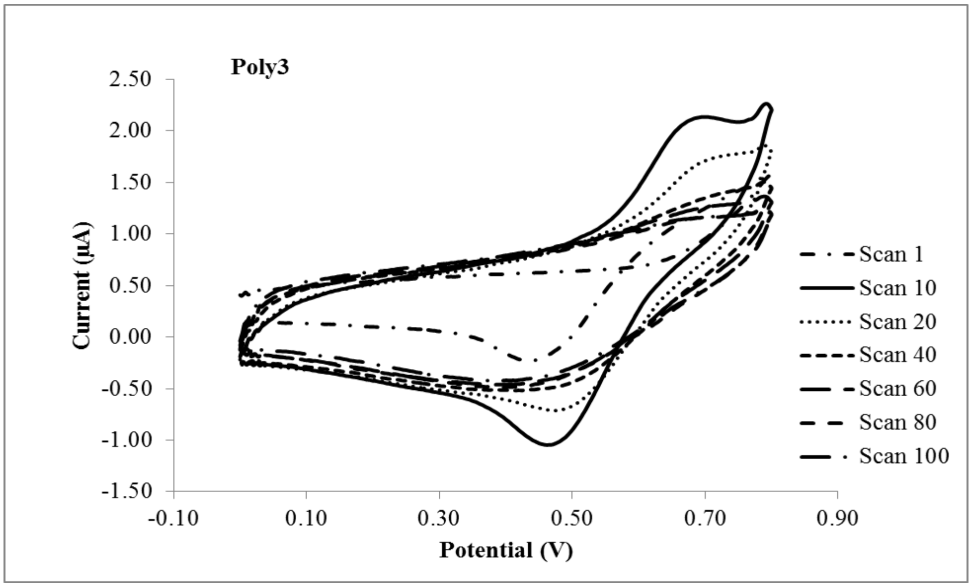


Figure 6. CVs of chemically modified electrode from Poly3 with PBS using Au working and counter electrodes and a Ag pseudo reference electrode: scans 1, 10, 20, 40, 60, 80, and 100 are shown.

The electrochemical stability of Poly1-4 was also tested with a Pt electrode by using casting films from methylene chloride. The CVs of Poly1 are shown in (Figure 7) and similar results were observed for Poly2-4. After 20 scans the reduction potential (E_{red}) shifted from 0.38 to 0.10 V. Although these results are not fully understood, they may indicate a change in morphology during the CV scans. When the polymer is in its neutral form, a weak charge transfer complex may increase the oxidation potential (E_{ox}). However, upon oxidation, the weak charge transfer complex dissipates and the reduction potential (E_{red}) returns to that expected for a ferroenyl moiety. In conjunction with the shift in redox potential, an increase in current was observed. These results suggest a change in morphology or increased hydration of the polymer which facilitates ion transport into and out of the film. Compared to films cast on Au electrodes, films cast on Pt electrodes showed excellent adhesion.

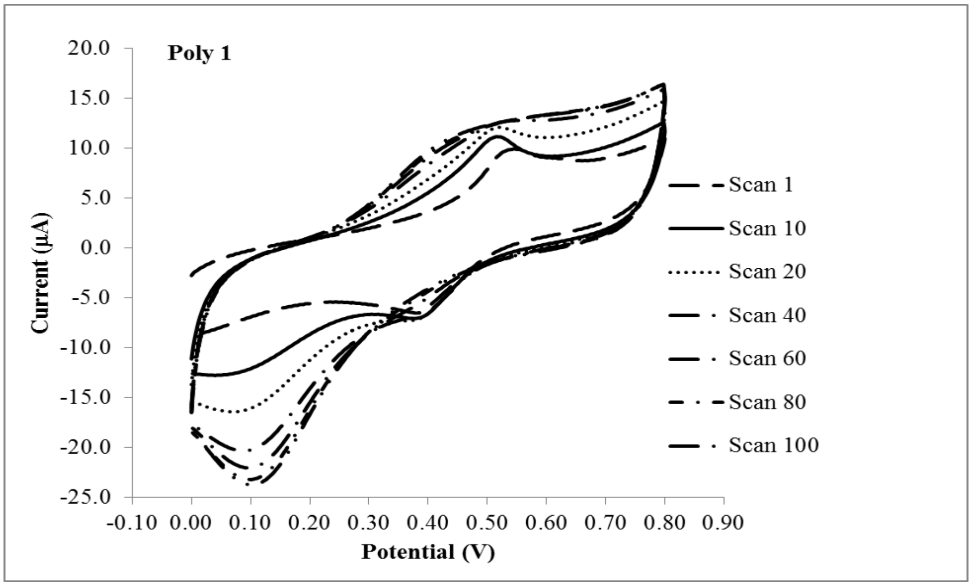


Figure 7. CVs of chemically modified electrode from Poly1 with PBS using Pt working and counter electrodes and a Ag pseudo reference electrode: scans 1, 10, 20, 40, 60, 80, and 100 are shown.

3.4 UV- visible studies

UV- visible spectroscopy can be used to characterize charge transfer complexes (CT). A new absorption is created from a weak resonance due to an electronic transition in the CT complex that formed from electron rich and electron poor groups. The UV spectrum of Poly4 in a solution of methylene chloride (Figure 8) showed an absorbance at 440 nm arising from electronic transitions in the ferrocene moiety. For thin films, the absorbance at 440 nm was also observed. However, a weak broad absorbance was observed extending well into the visible region. Similar behavior has been observed for solutions of ferrocene and bis(arene)iron(II) dications, previously in literature, and this broad absorbance has been attributed to a charge transfer complex.[30] By analogy, the weak, broad absorbance observed for Poly4 can be attributed to a charge transfer complex. Similar results were observed for Poly1-3. The absorption spectra for Poly1-4 thin films suggested a morphology, which places the ferrocenyl moiety in close proximity to the maleimide. Due to the close proximity of the electron rich ferrocene with the electron deficient maleimide, a weak charge transfer complex was formed.

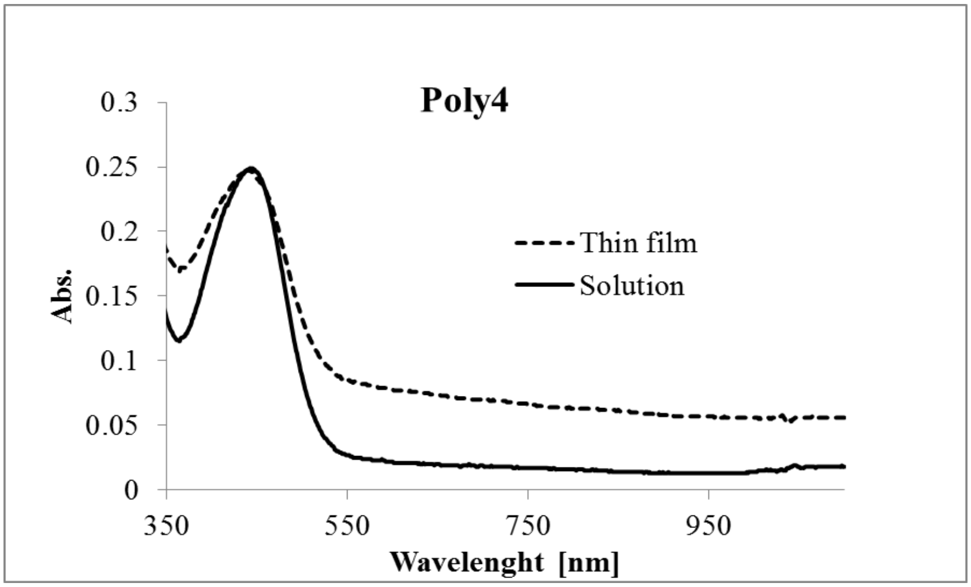


Figure 8. UV absorption spectra of Poly4 in solution and thin film

CHAPTER IV

4. CONCLUSIONS

Four polymers were synthesized according to a literature procedure.[26] The polymers were prepared by copolymerization of vinylferrocene or 3-phenyl[5]ferrocenphane-1,5-dimethylene with N-ethyl or N-phenylmaleimide using AIBN as the initiator. Characterization by FT-IR, ^{1}H-NMR, and GPC of all polymers were consistent with literature[26] and polymerization yields of 80-86% were obtained.

Chemically modified electrodes were prepared by depositing each polymer onto an electrode by CA or casting from solution. CV showed a dependency of redox potential versus electrolyte ($NaNO_3$, $NaClO_4$ or PBS), regardless of deposition technique. Electrochemical stability studies of polymers were performed by cycling the potential from 0.00 to 1.00 volts for 100 scans with PBS as the supporting electrolyte. Using an Au electrode, a loss in current was observed for the CMEs, indicating poor adhesion of the polymer to the electrode. However, using a Pt electrode, no loss in current was observed for Poly1-4, suggesting better adhesion of the polymers. In addition, electrochemical stability studies of all polymers showed a significant shift in the reduction potential and may indicate a charge transfer complex. In the UV visible spectra, all polymers showed a weak broad absorbance, extending well into the visible region. This absorbance was consistent with a charge transfer complex and has been observed previously in literature.[30]

4.1 Future Research

The promising results from this work indicated that continuing research with these materials is warranted. The good electrochemical response and stability suggest that these materials should be incorporated within a glucose sensor. Construction of these sensors can be performed by deposition of the polymer on to an electrode by electrodeposition or solution cast films. The next layer within a glucose sensor is the application of glucose oxidase onto the surface of the ferrocene polymer. The application of glucose oxidase can be accomplished by depositing from an aqueous solution with glutaraldehyde as a crosslinker for the enzyme. The glucose oxidase can also be applied to a surface electrostatically if the ferrocenyl moieties are oxidized to ferricinium.

The observed weak charge transfer complexes also warrant further characterization. To better understand these materials, a series of copolymers can be synthesized with various substituents on the phenyl moiety. The substituents can range from electron donating groups such as methyl or methoxy to electron withdrawing groups such as acetyl or cyano. By using a range of substituents, the strength of the complexes between the electron rich ferrocene and the electron poor maleimide can be analyzed. These charge transfer applications also give rise to the possibility of using these materials in photovoltaic applications.

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APPENDIX

SUPPLEMENTAL LISTS

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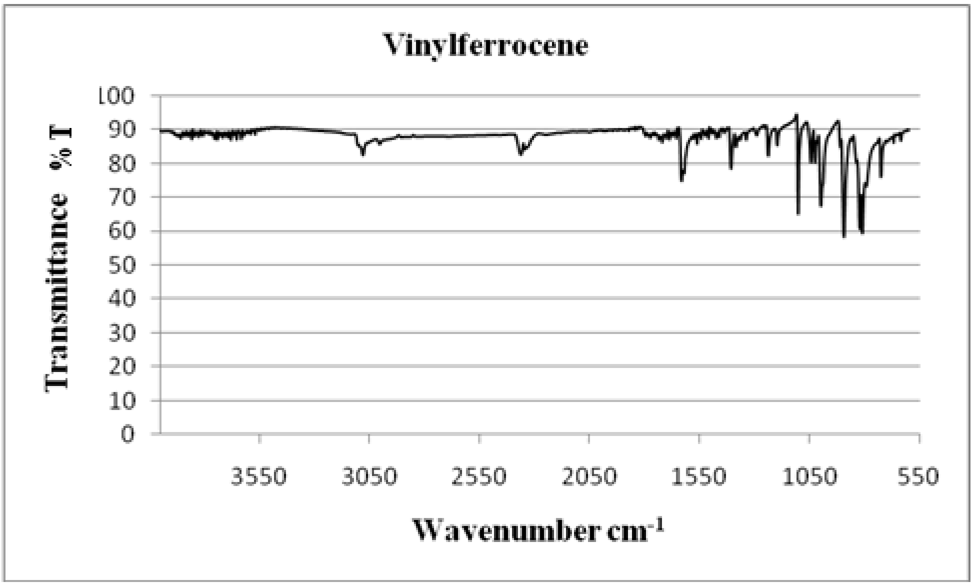


Figure S1. FTIR spectrum of vinylferrocene

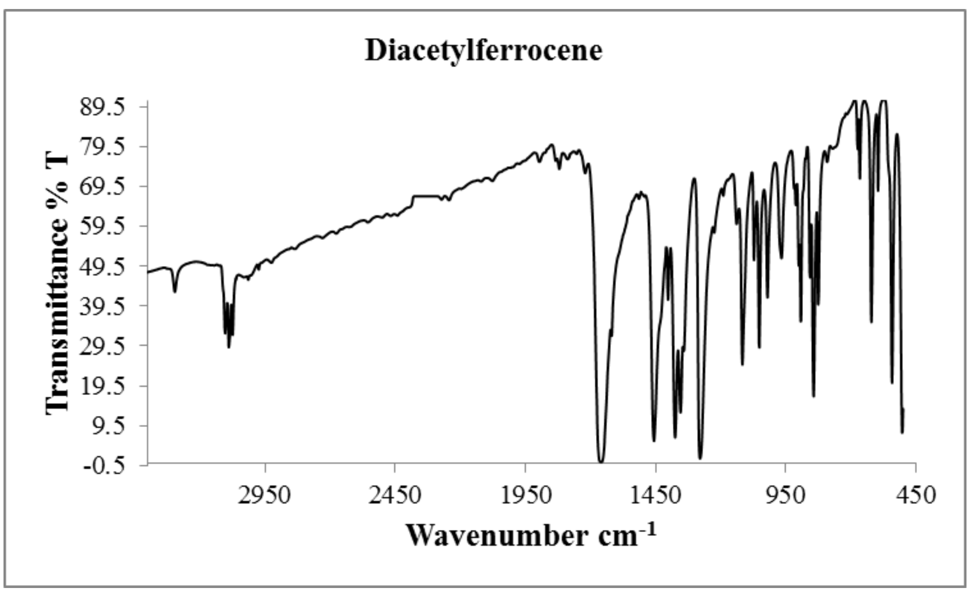


Figure S2. FTIR spectrum of 1, 1'-diacetylferrocene

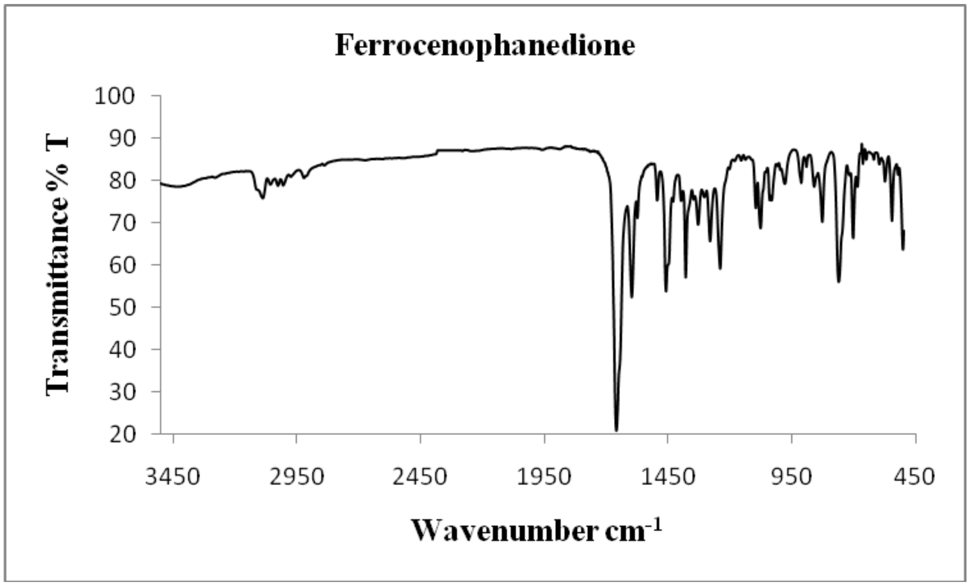


Figure S3. FTIR spectrum of 3- phenyl[5]ferrocenophane-1,5-dione

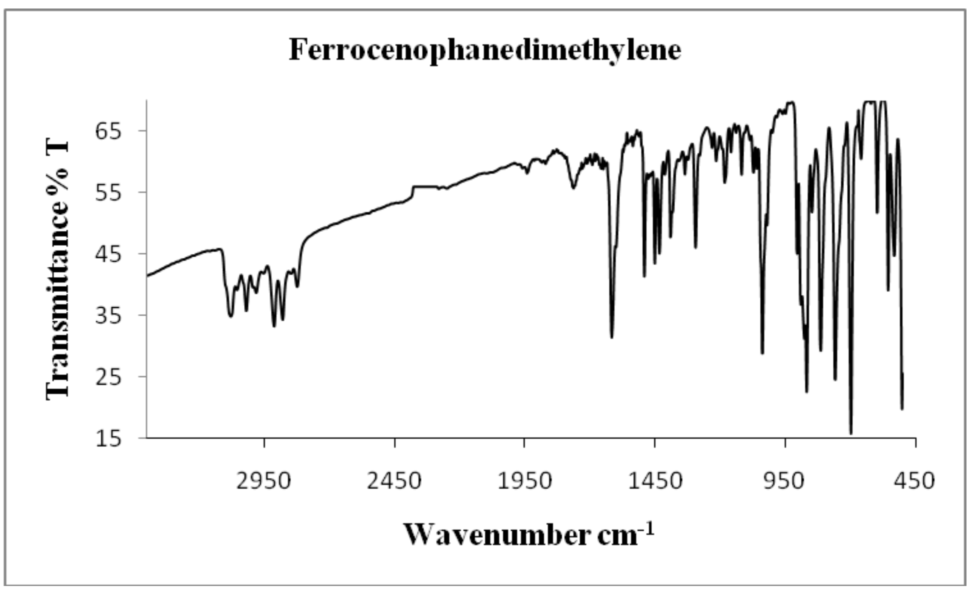


Figure S4. FTIR spectrum of 3- phenyl[5]ferrocenophane-1,5-dimethylene

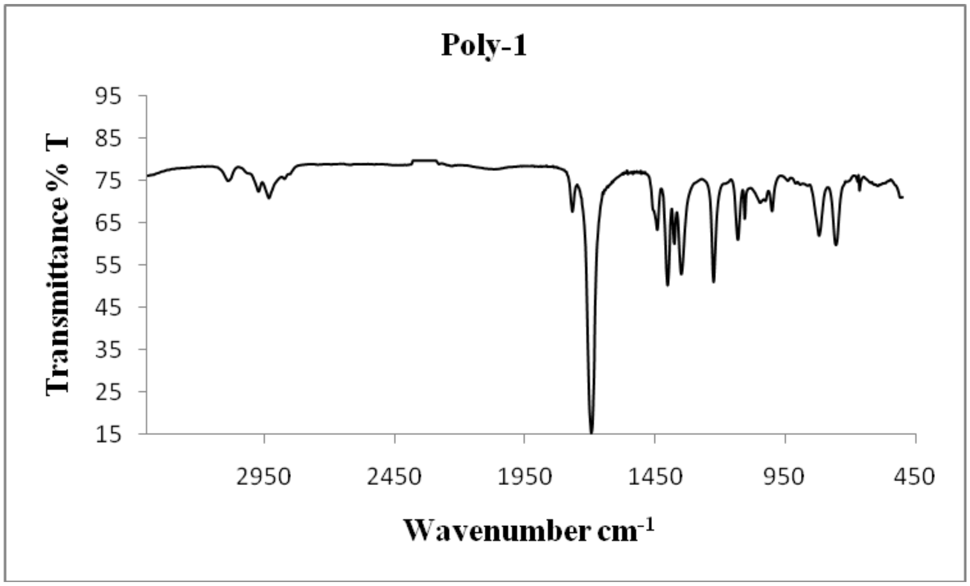


Figure S5. FTIR spectrum of Poly1

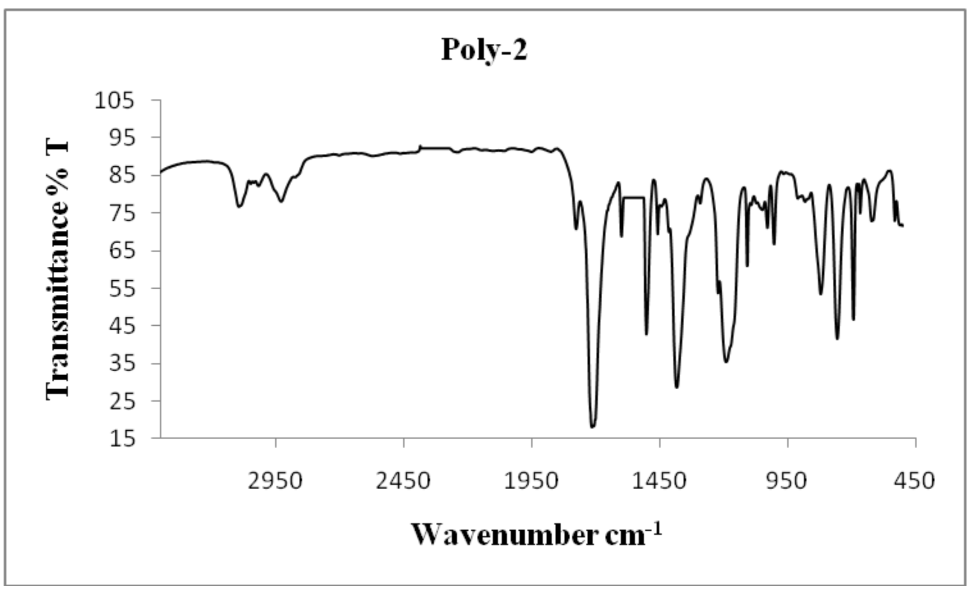


Figure S6. FTIR spectrum of Poly2

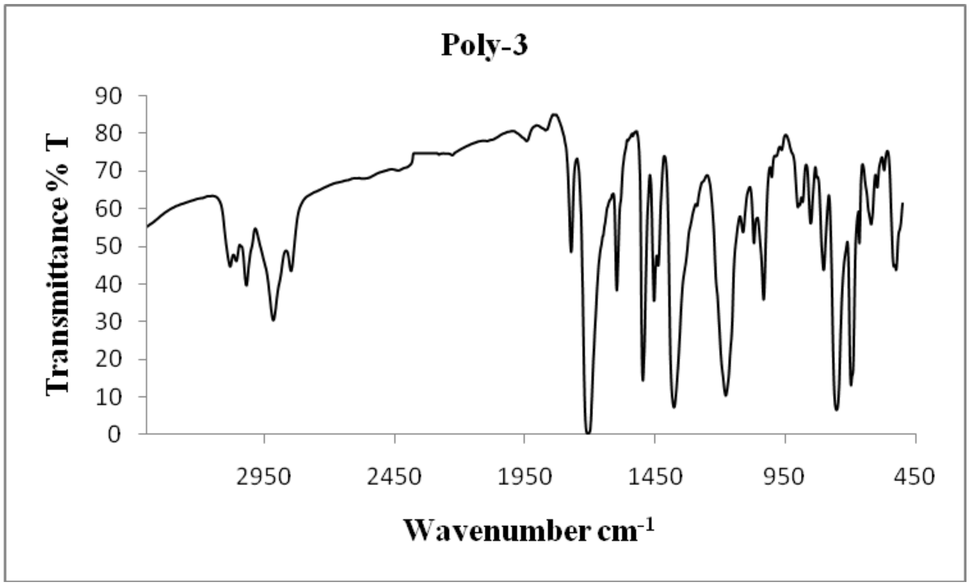


Figure S7. FTIR spectrum of Poly 3

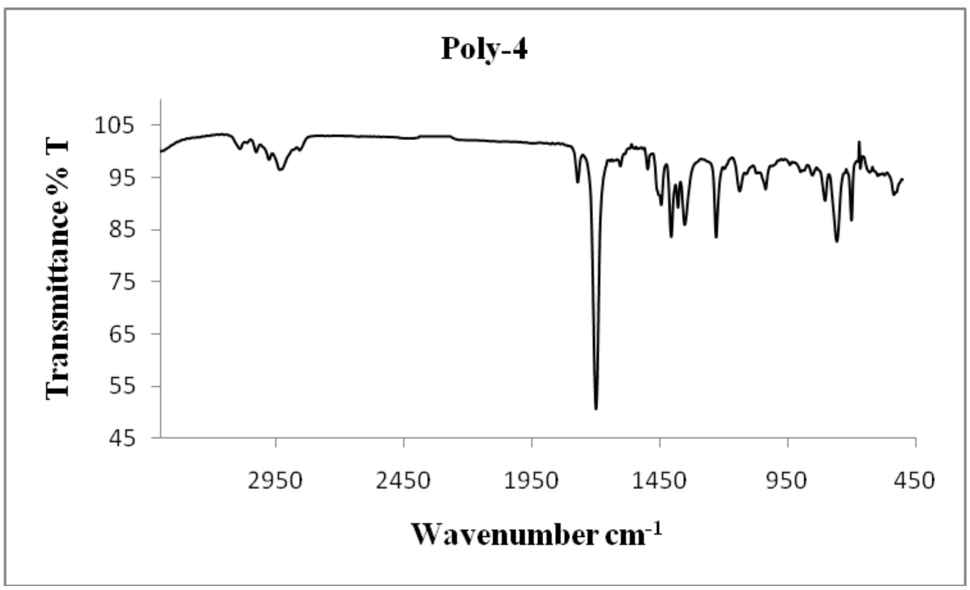
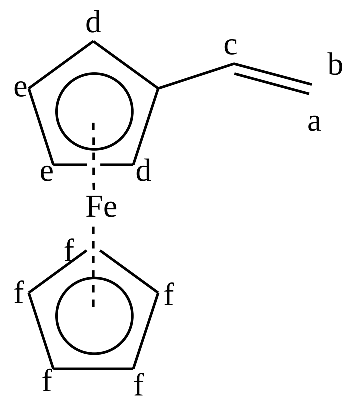


Figure S8. FTIR spectrum of Poly4



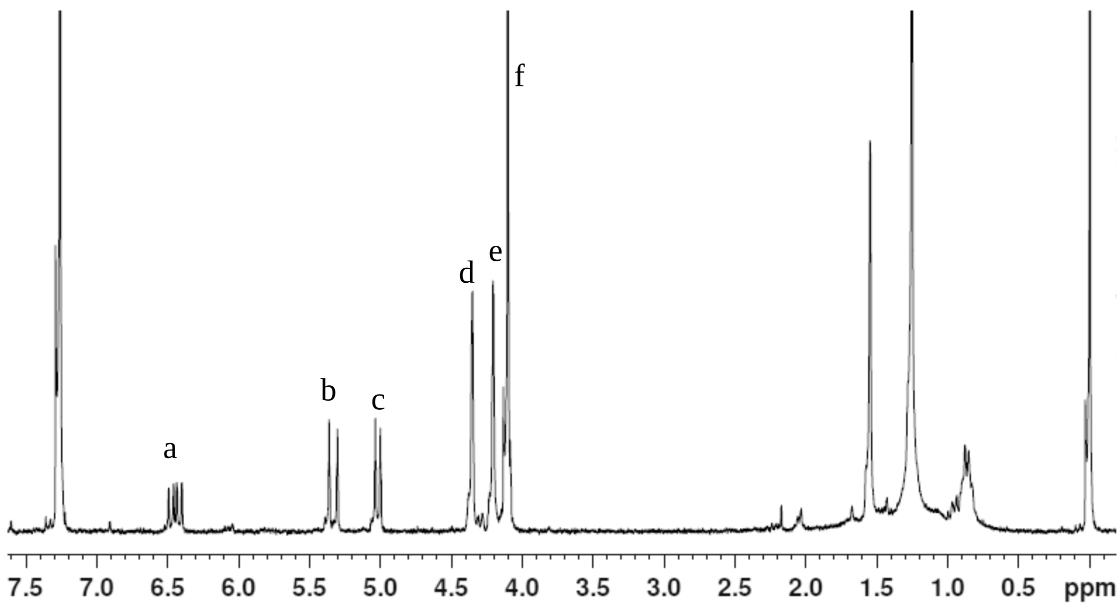


Figure S9. ^{1}H-NMR spectrum of Vinylferrocene

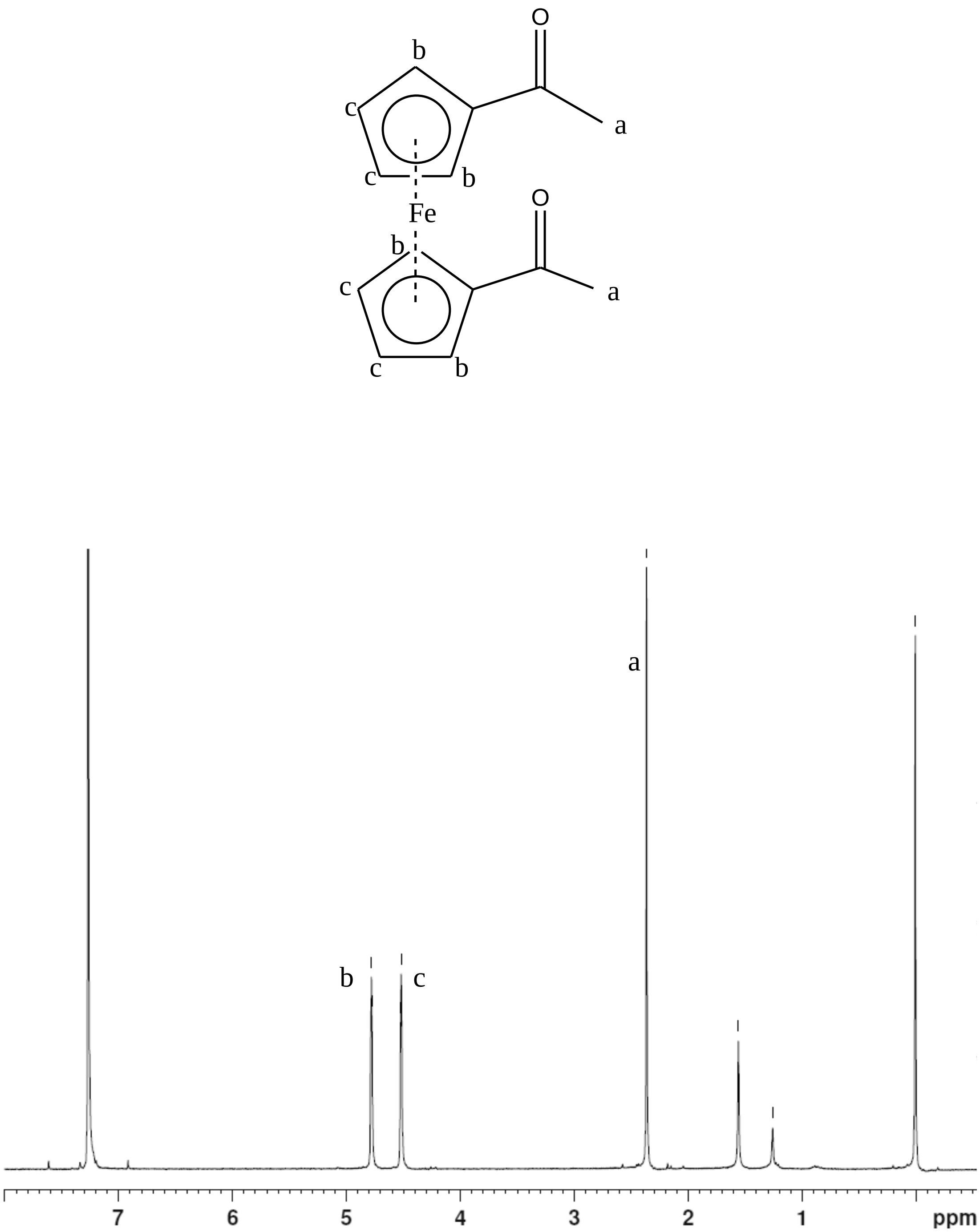
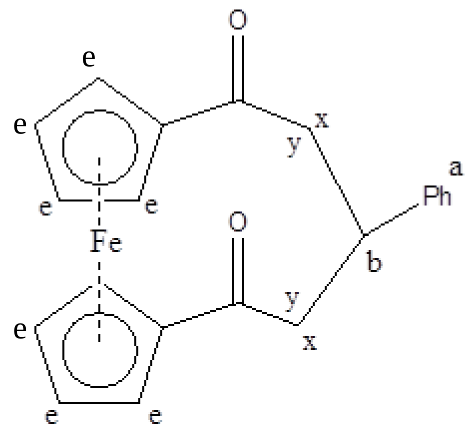


Figure S10. ¹H-NMR spectrum of 1,1'-diacetylferrocene



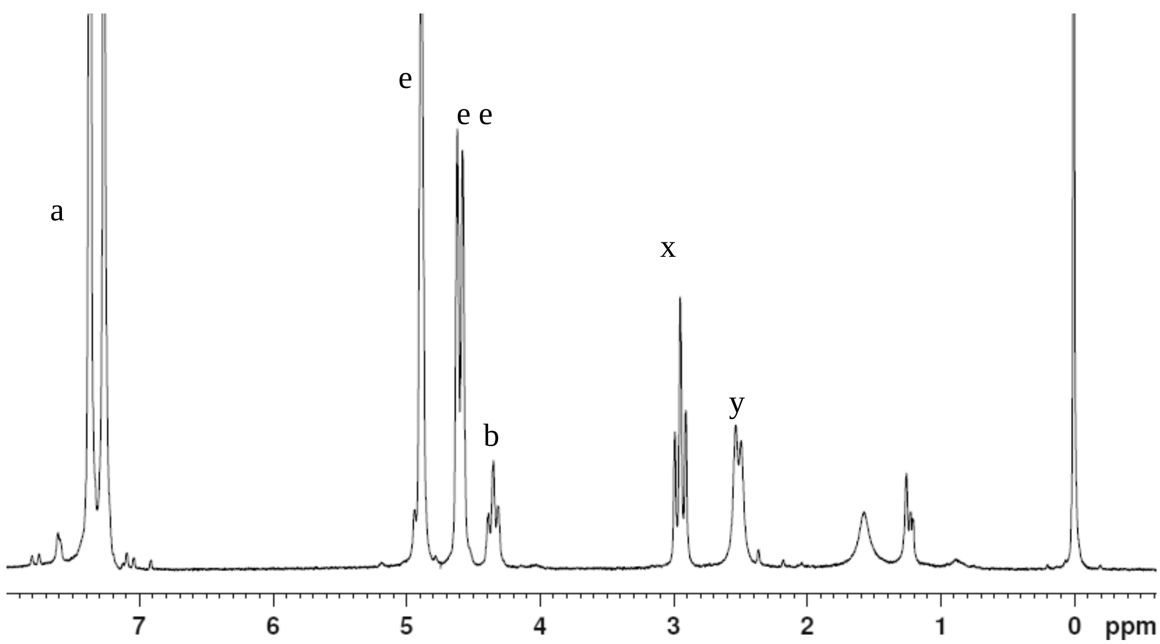
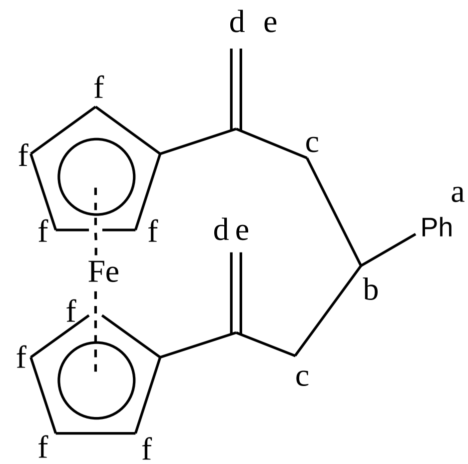


Figure S11. [1]H-NMR spectrum of 3- phenyl[5]ferrocenophane-1,5-dione



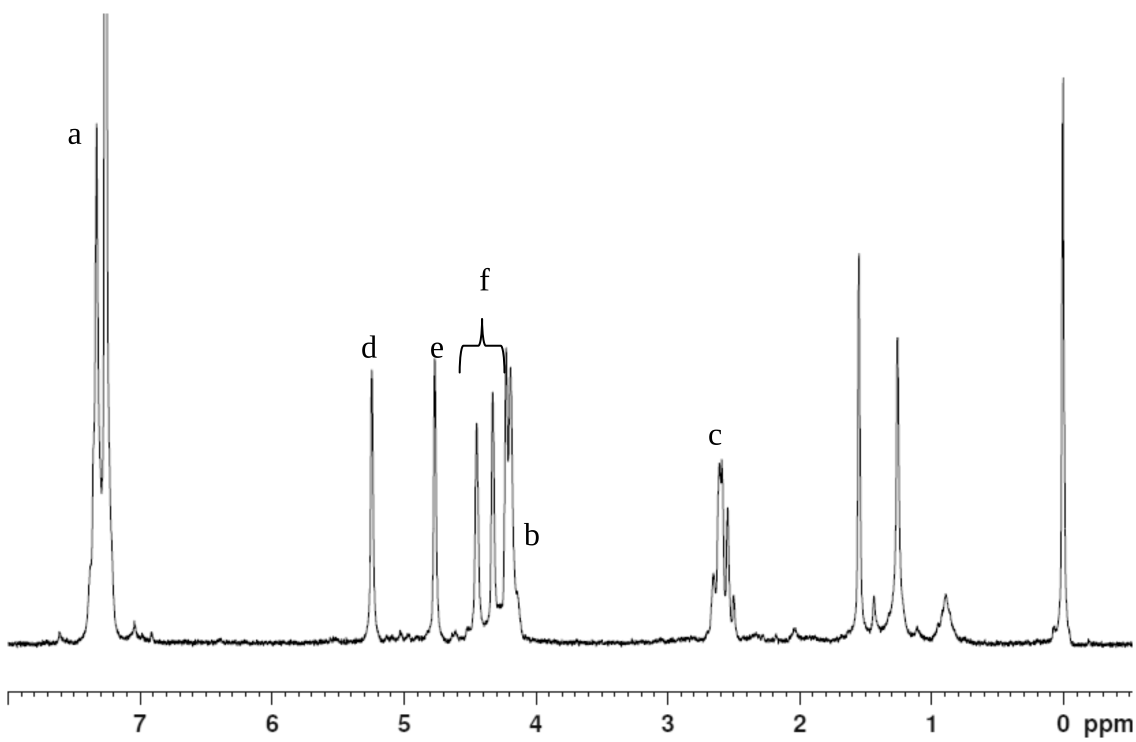


Figure S12. [1]H-NMR spectrum of 3- phenyl[5]ferrocenophane-1,5-dimethylene.

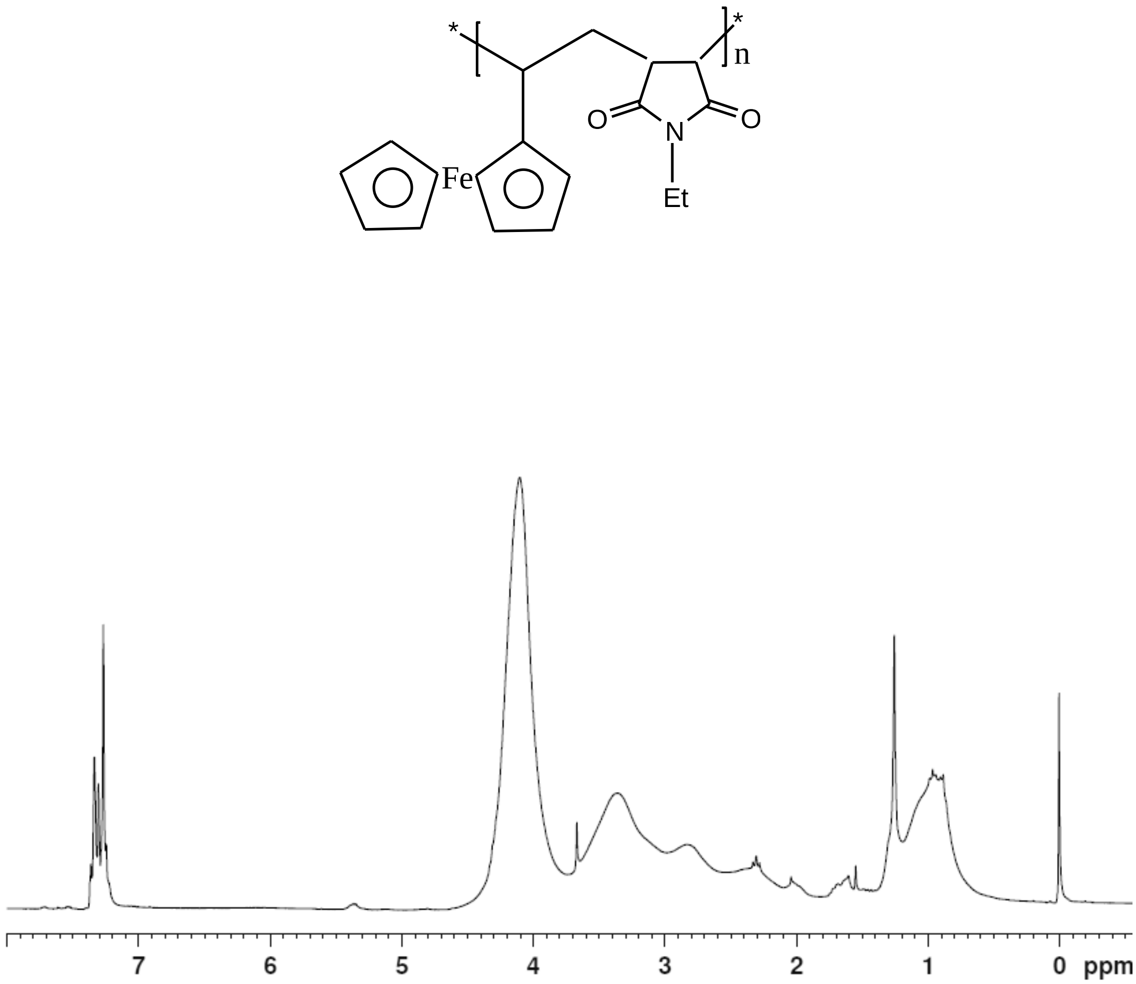
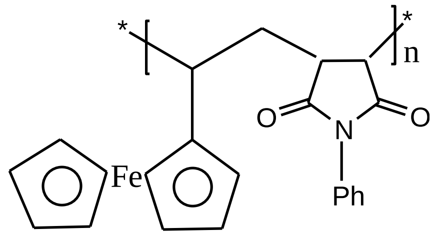


Figure S13. ^{1}H-NMR spectrum of Poly1



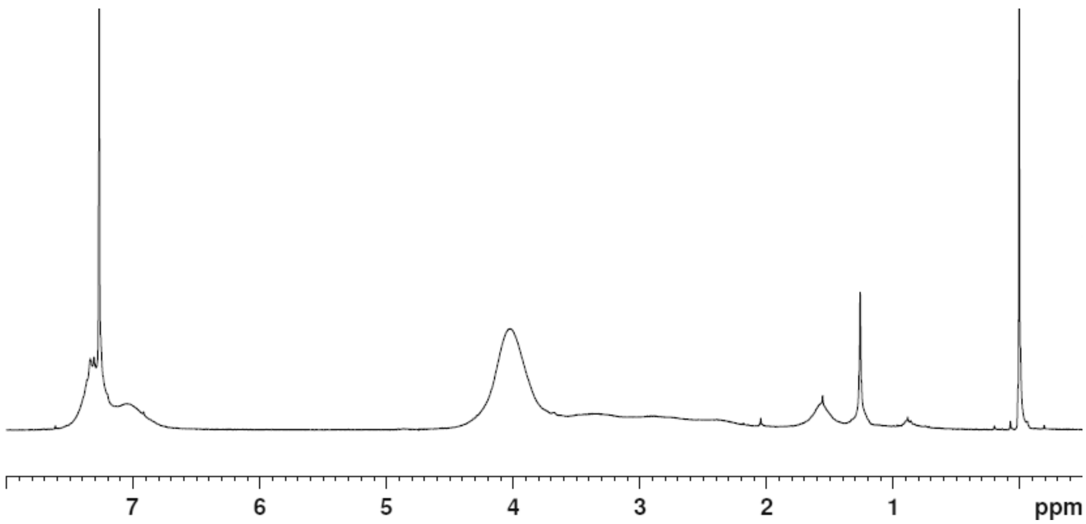
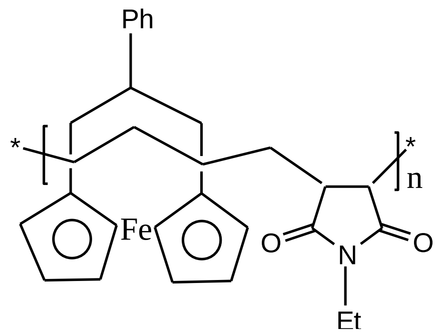


Figure S14. ^{1}H-NMR spectrum of Poly2



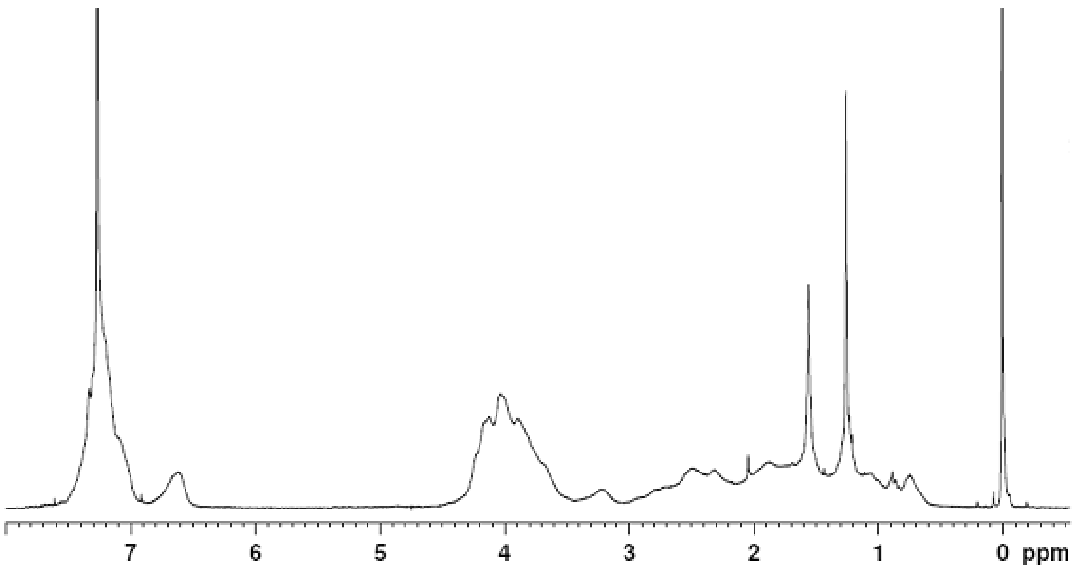
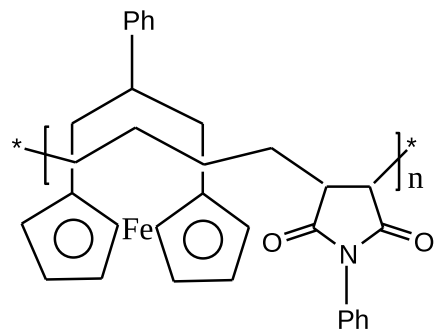


Figure S15. ^{1}H-NMR spectrum of Poly3



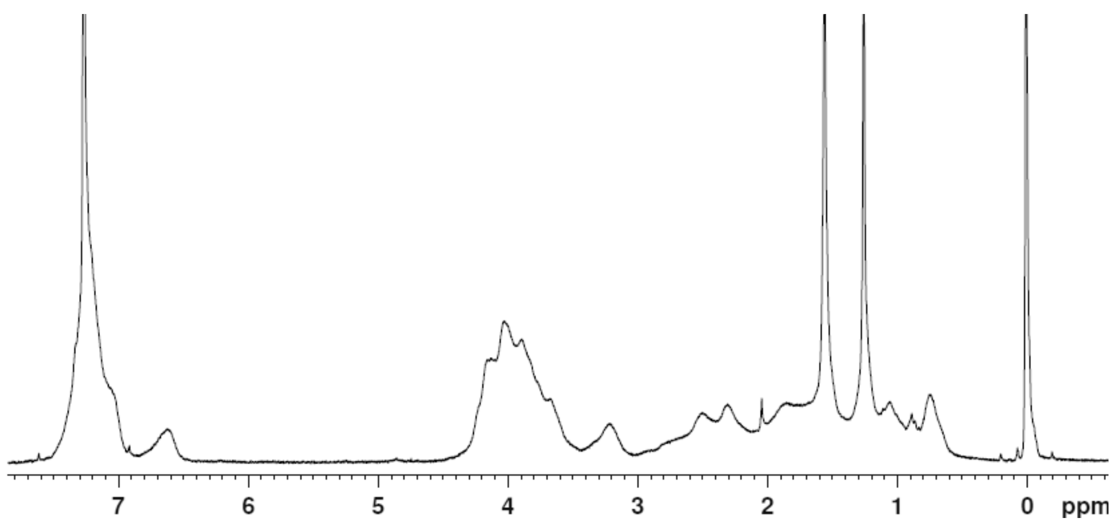


Figure S16. ^{1}H-NMR spectrum of Poly4

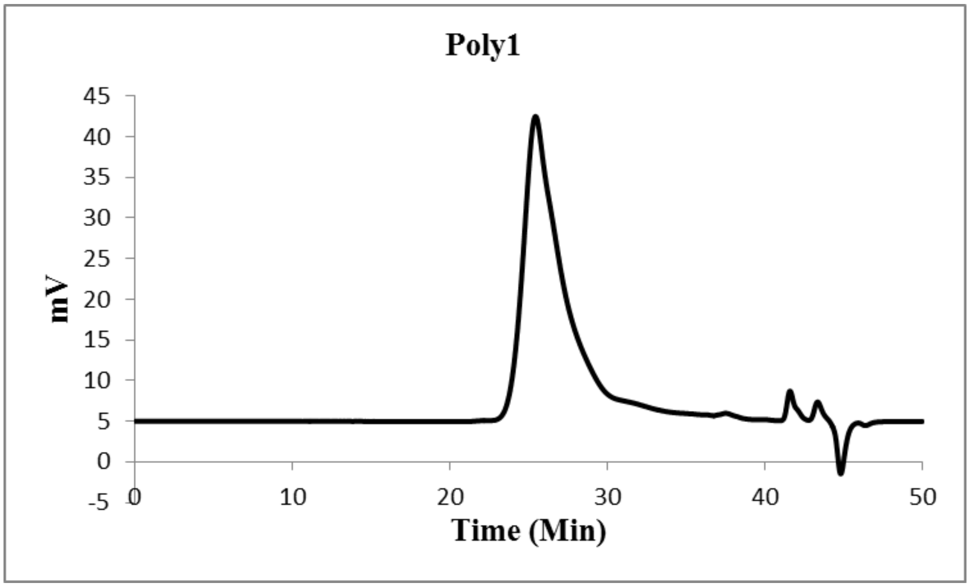


Figure S17. GPC trace of polymerized vinylferrocene with N-ethylmaleimide

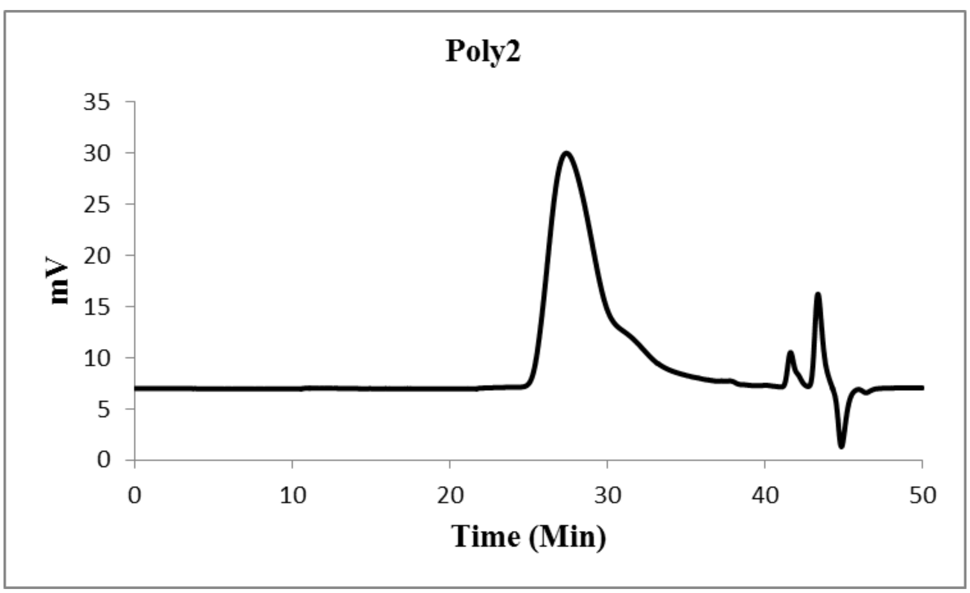


Figure S18. GPC trace of polymerized vinylferrocene with N-phenylmaleimide

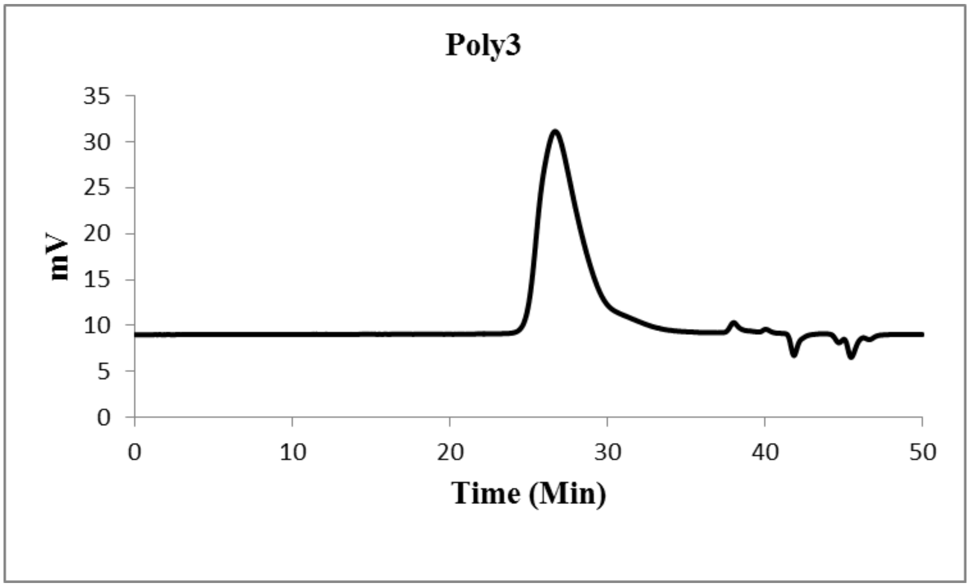


Figure S19. GPC trace of polymerized phenyl [5] ferrocenophane-1, 5- dimethylene with N-ethylmaleimide

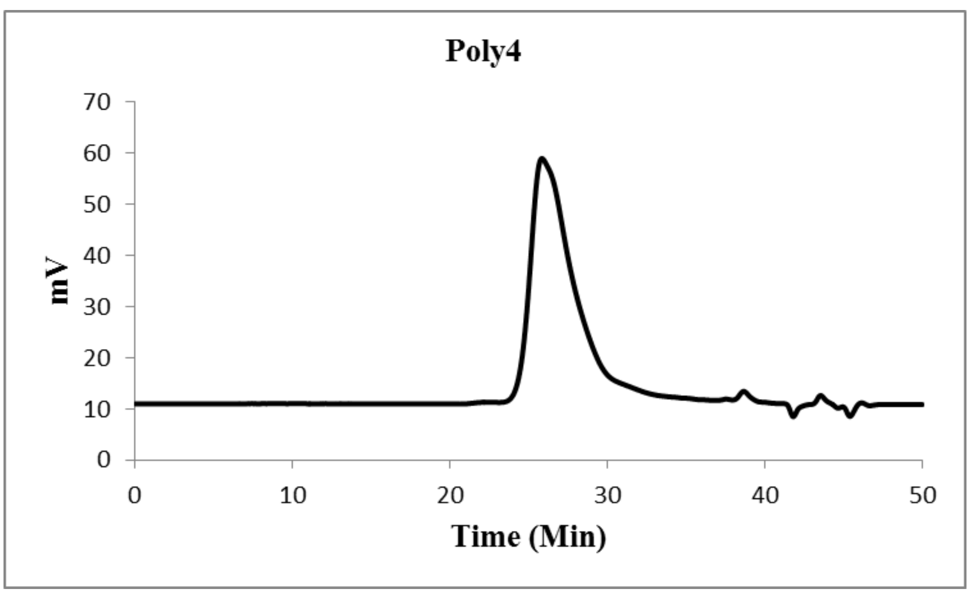


Figure S20. GPC trace of polymerized phenyl [5] ferrocenophane-1, 5- dimethylene with N-phenylmaleimide

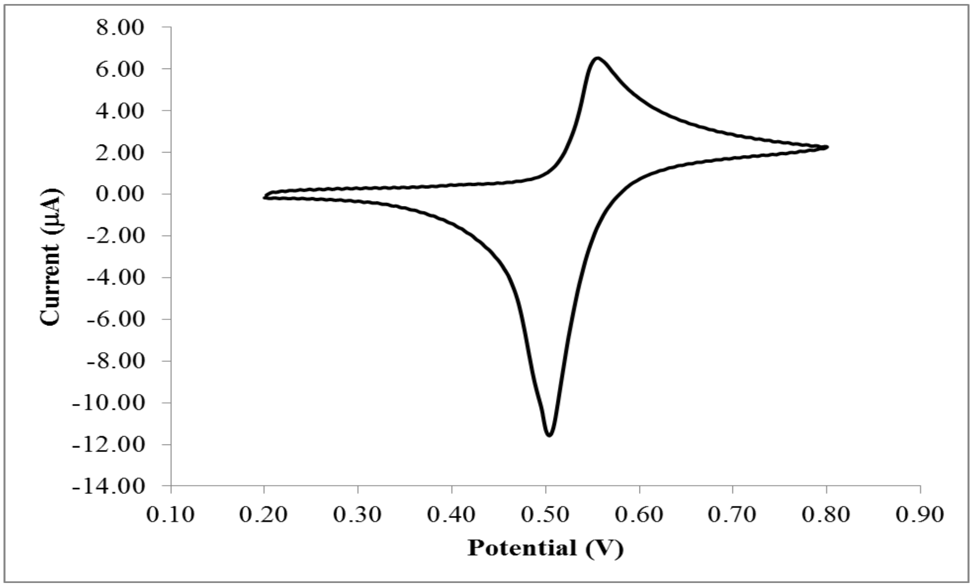


Figure S21. CV of Poly1 on Au electrode

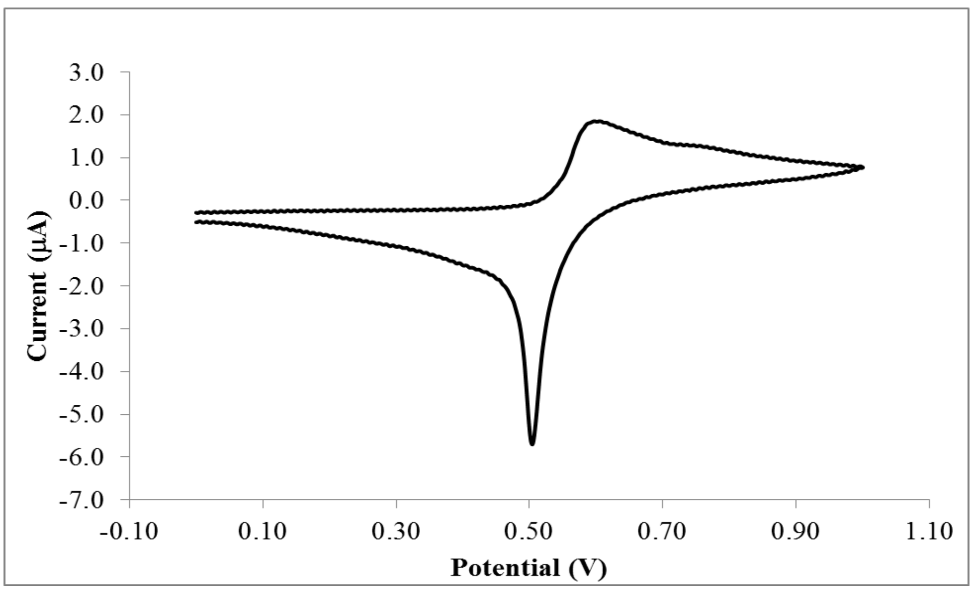


Figure S22. CV of Poly2 on Au electrode

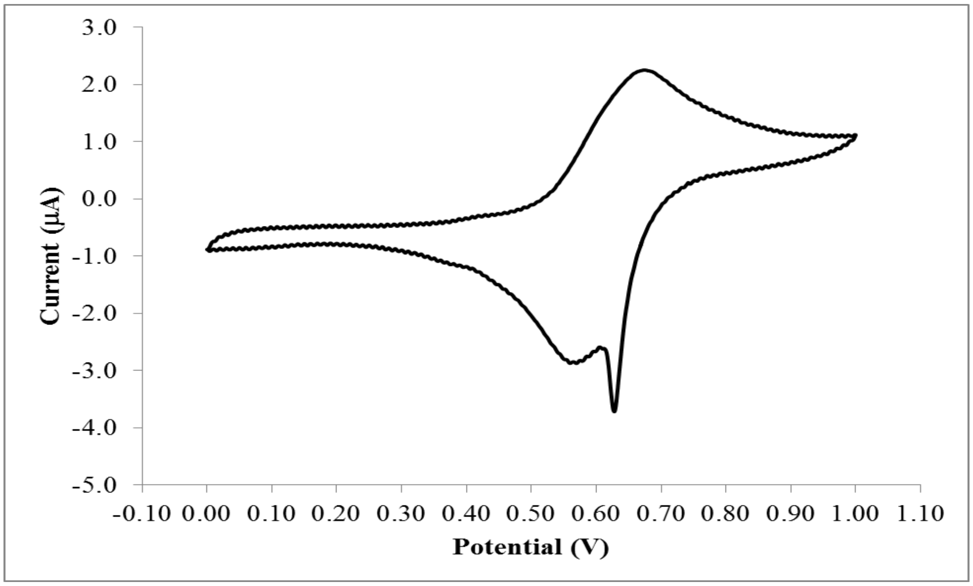


Figure S23. CV of Poly3 on Au electrode

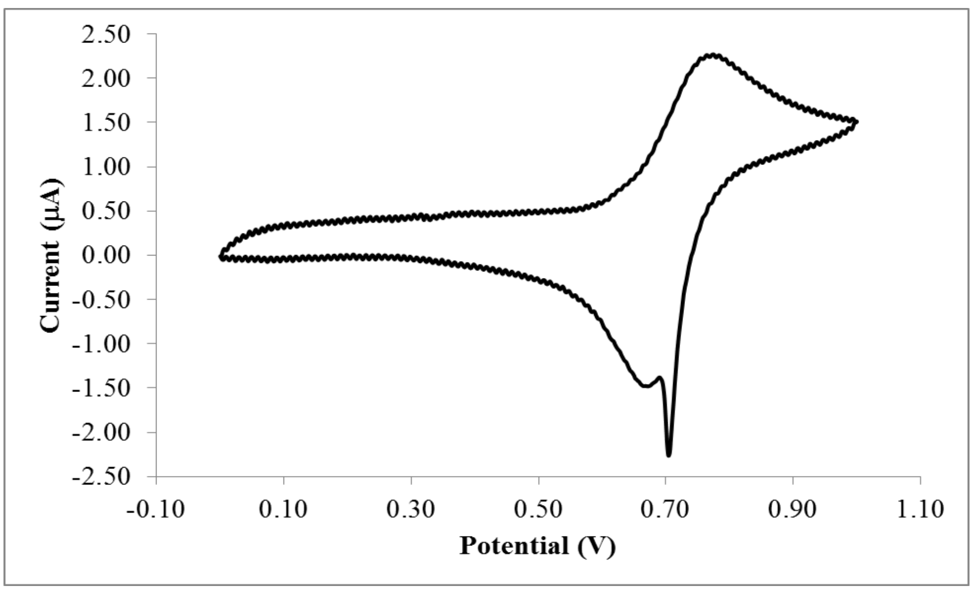


Figure S24. CV of Poly4 on Au electrode

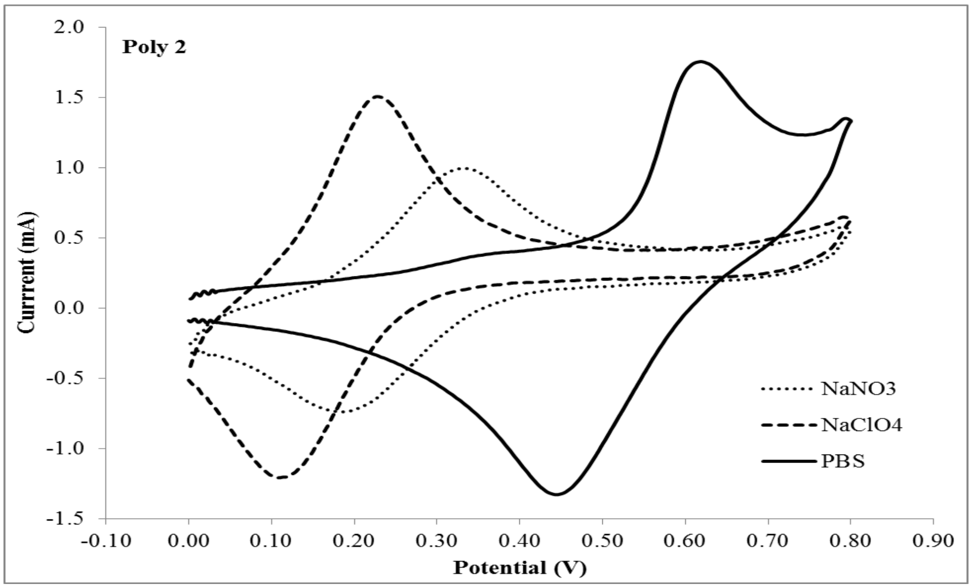


Figure S25. CVs of chemically modified electrode (CA) from Poly2 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

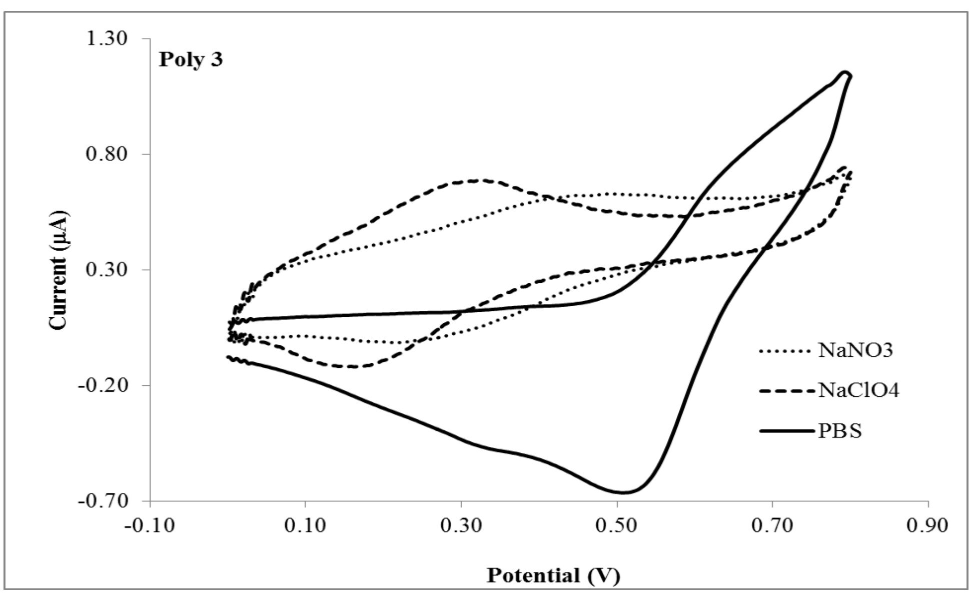


Figure S26. CVs of chemically modified electrode (CA) from Poly3 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

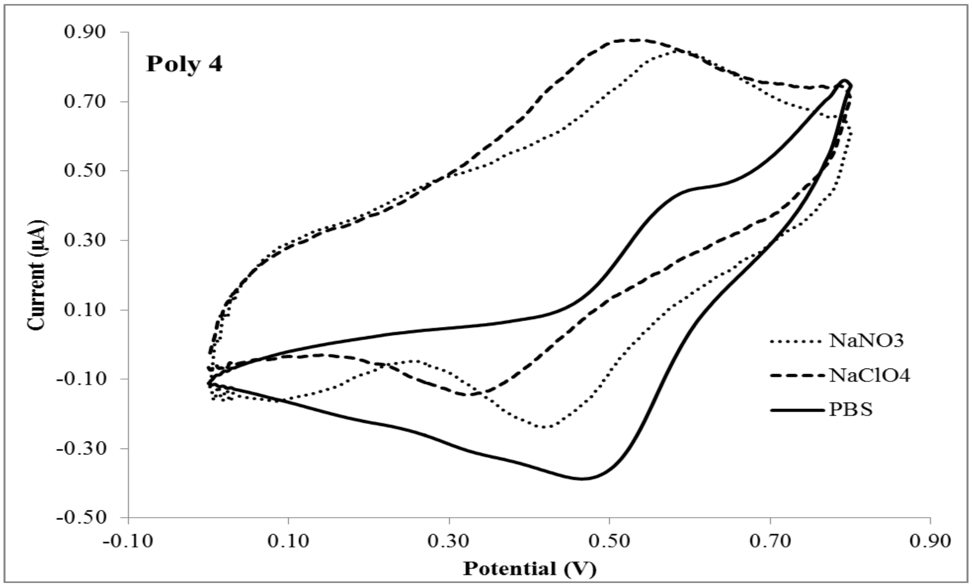


Figure S27. CVs of chemically modified electrode (CA) from Poly4 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

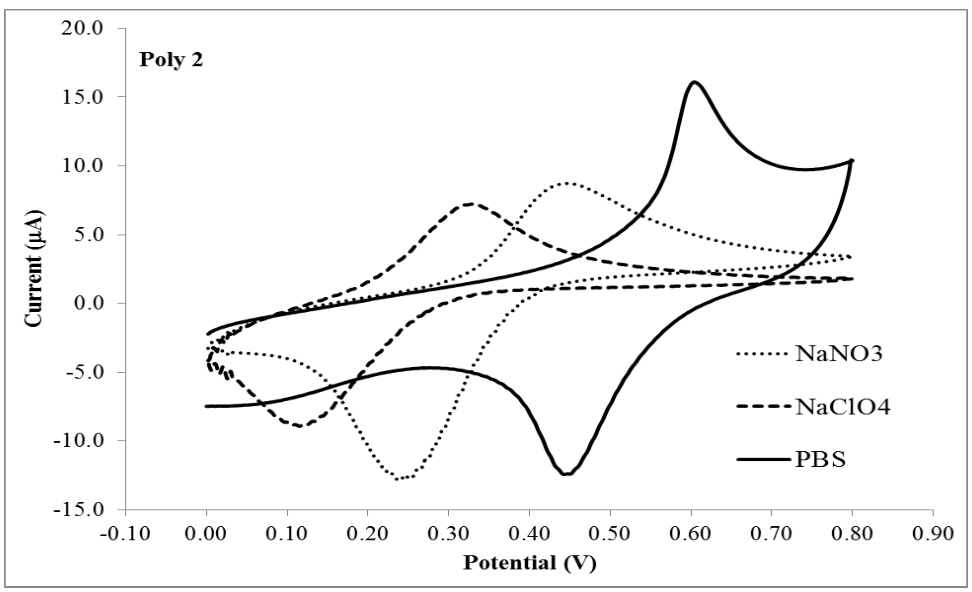


Figure S28. CVs of chemically modified electrode (cast films) from Poly2 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

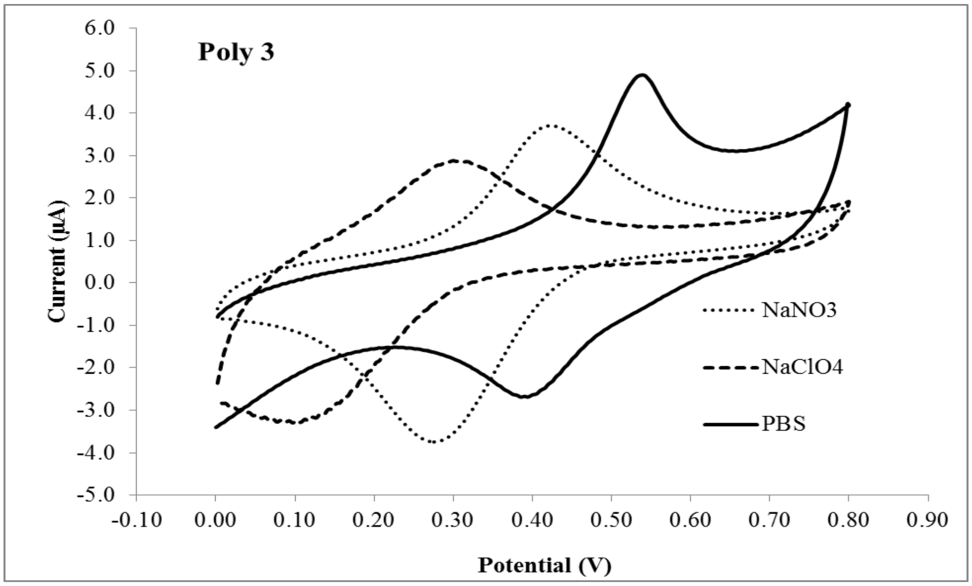


Figure S29. CVs of chemically modified electrode (cast films) from Poly3 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

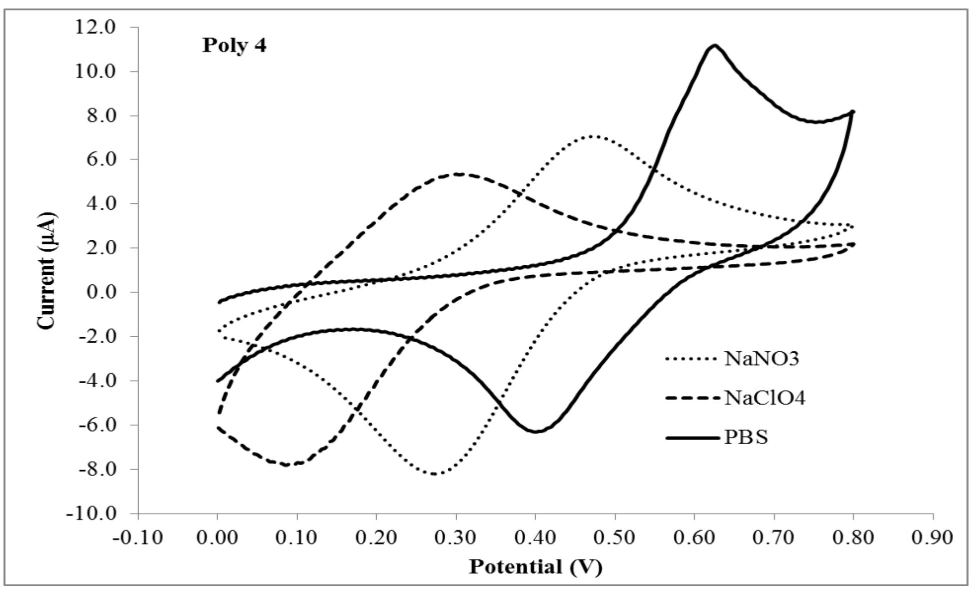


Figure S30. CVs of chemically modified electrode (cast films) from Poly4 with aqueous solutions on Au electrode 0.1M of $NaNO_3$, $NaClO_4$, and PBS

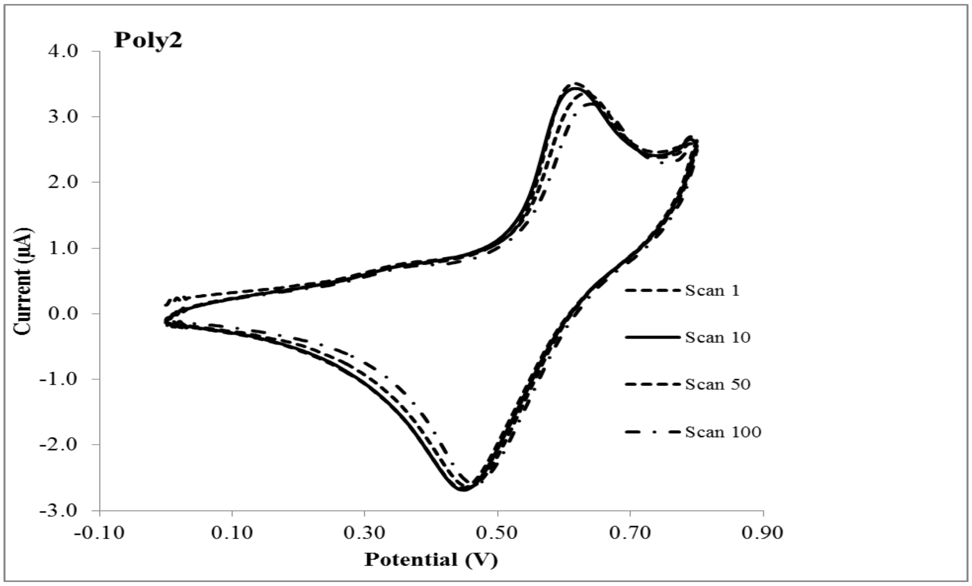


Figure S31. CVs of chemically modified electrode (CA) from Poly2 with PBS using Au working and counter electrodes and a Ag pseudo reference electrode scans 1, 10, 50, and 100 are shown.

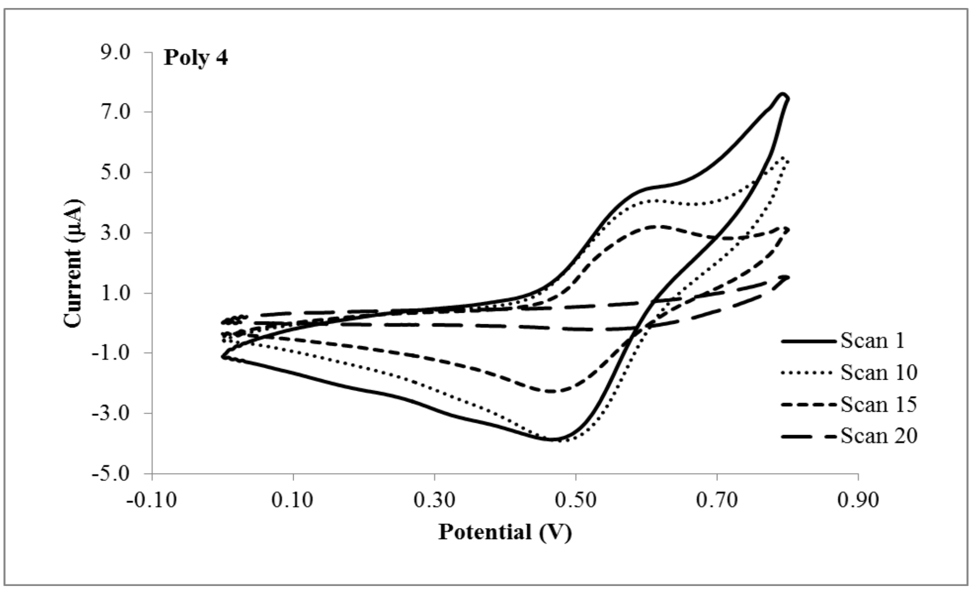


Figure S32. CVs of chemically modified electrode (CA) from Poly4 with PBS using Au working and counter electrodes and a Ag pseudo reference electrode scans 1, 10, 50, and 100 are shown.

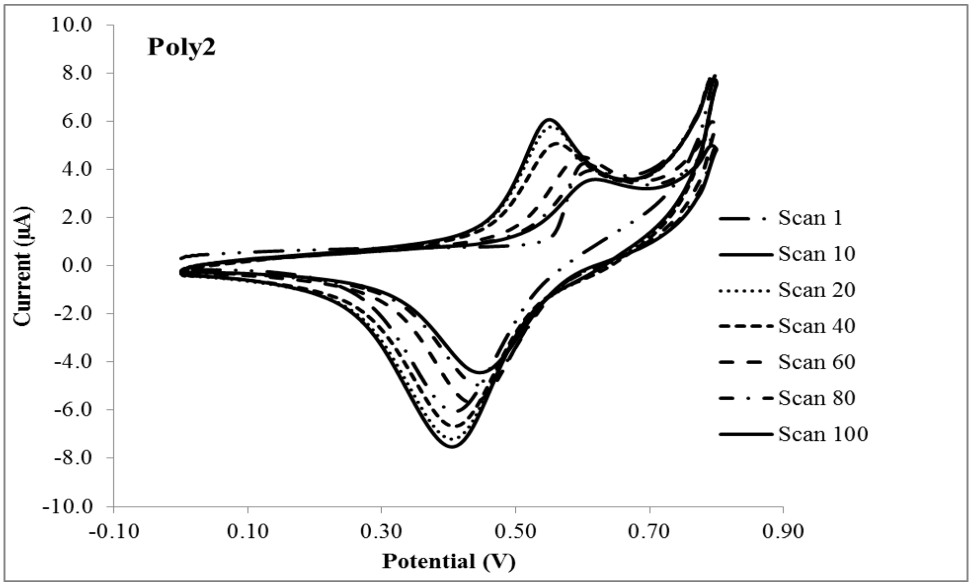


Figure S33. CVs of chemically modified electrode (cast films) from Poly2 with PBS using Au working and counter electrodes and a Ag pseudo reference electrode scans 1, 10, 20, 40, 60, 80, and 100 are shown.

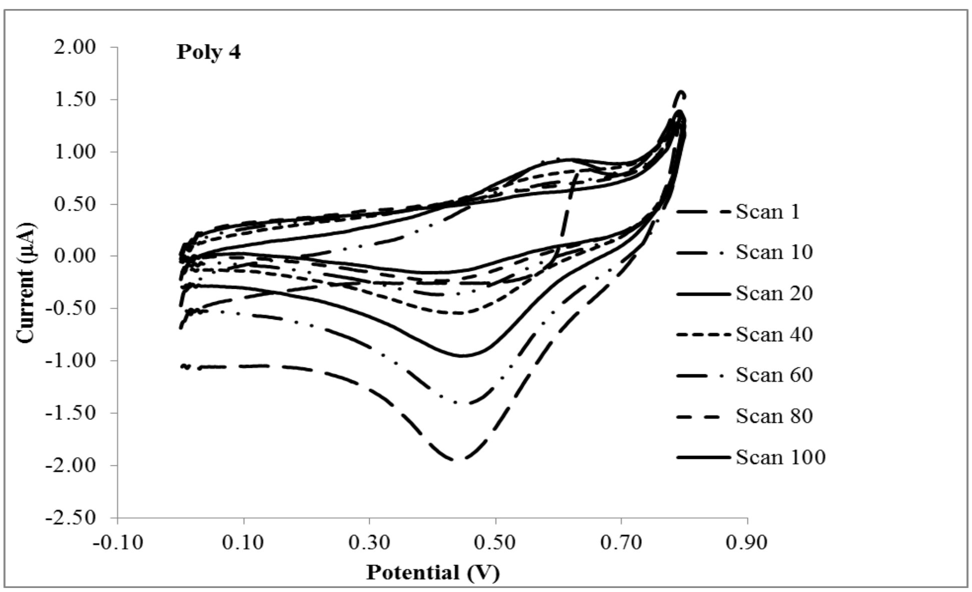


Figure S34. CVs of chemically modified electrode (cast films) from Poly4 with PBS scans using Au working and counter electrodes and a Ag pseudo reference electrode 1, 10, 20, 40, 60, 80, and 100 are shown.

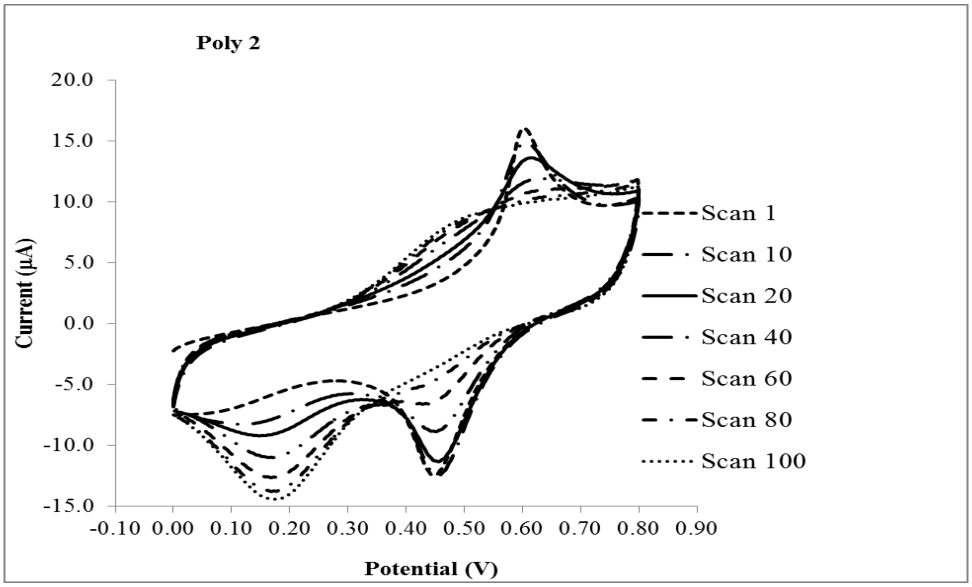


Figure S35. CVs of chemically modified electrode (fast films) from Poly2 with PBS using Pt working and counter electrodes and a Ag pseudo reference electrode scans 1, 10, 20, 40, 60, 80, and 100 are shown.

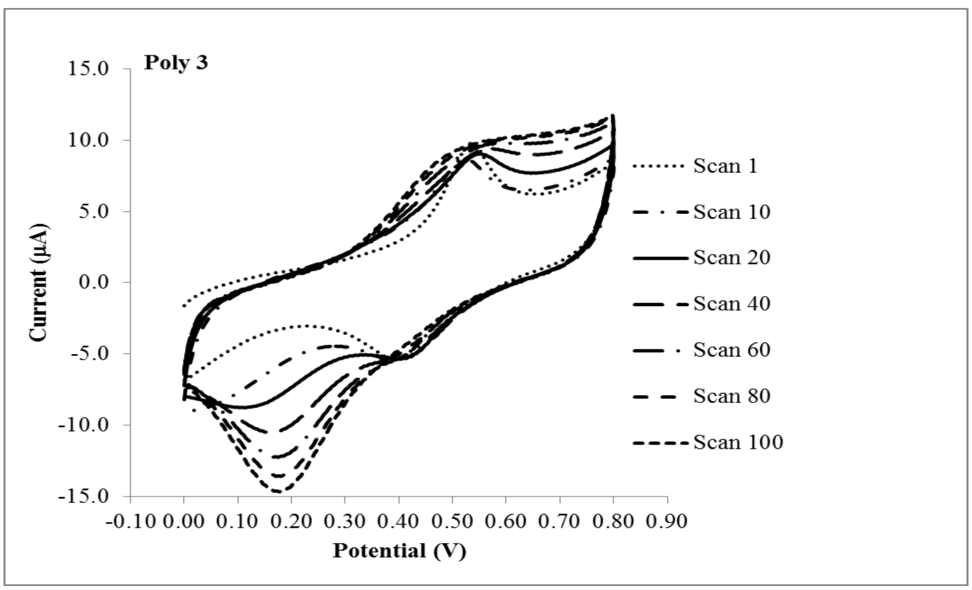


Figure S36. CVs of chemically modified electrode (cast films) from Poly3 with PBS using Pt working and counter electrodes and a Ag pseudo reference electrode scans 1, 10, 20, 40, 60, 80, and 100 are shown.

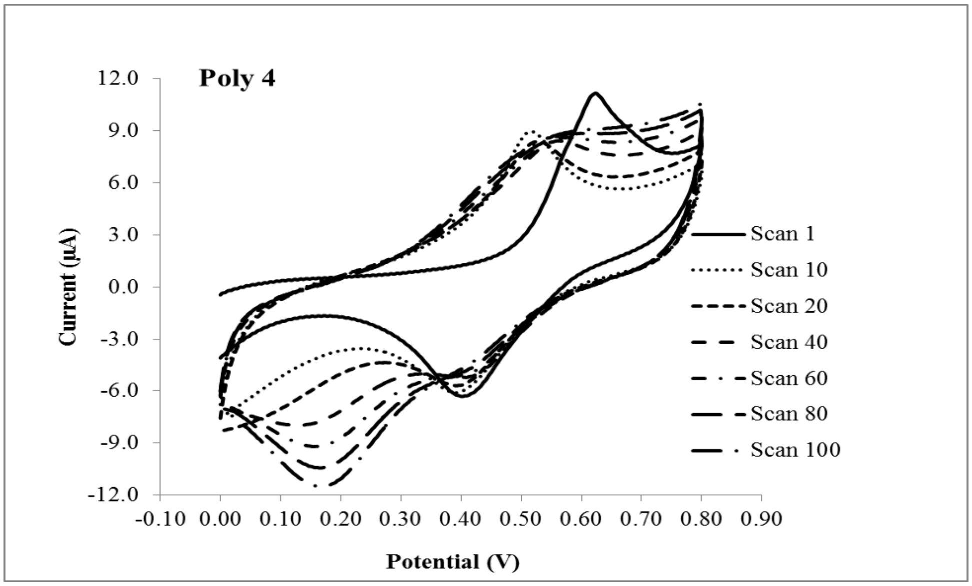


Figure S37. CVs of chemically modified electrode (cast films) from Poly4 with PBS using Pt working and counter electrodes and a Ag pseudo reference electrode scans 1, 10, 20, 40, 60, 80, and 100 are shown.

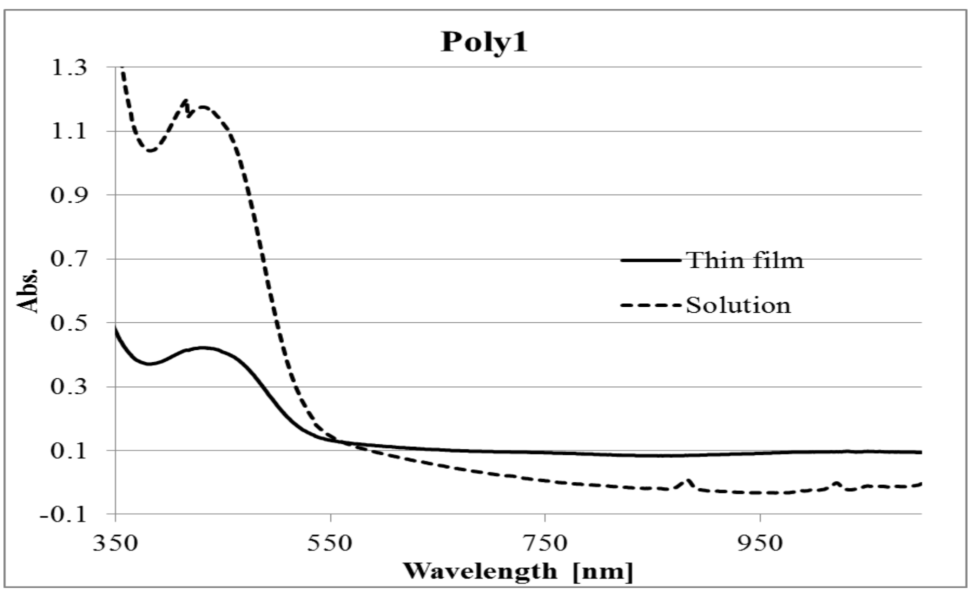


Figure S38. UV-visible spectrum absorption of Poly1

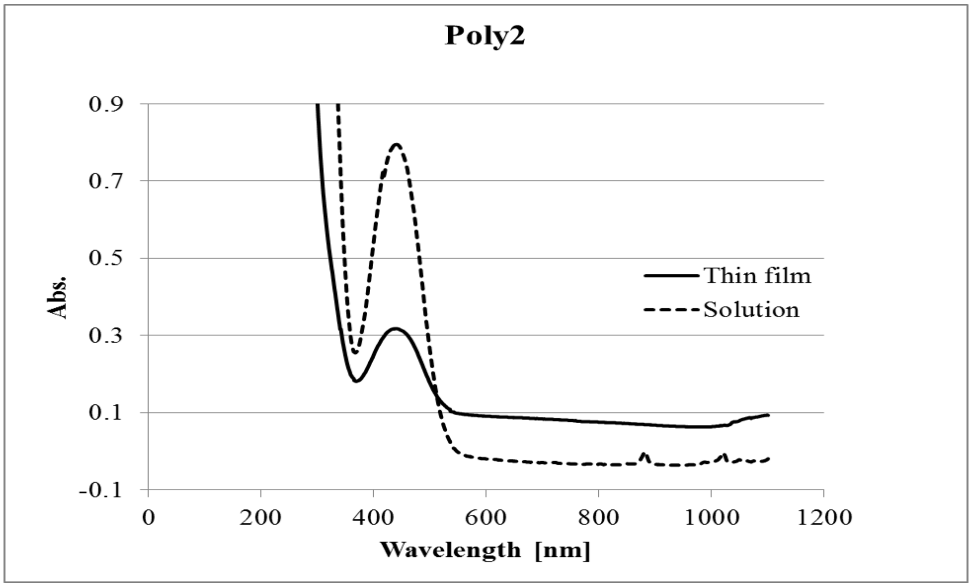


Figure S39. UV-visible spectrum absorption of Poly2

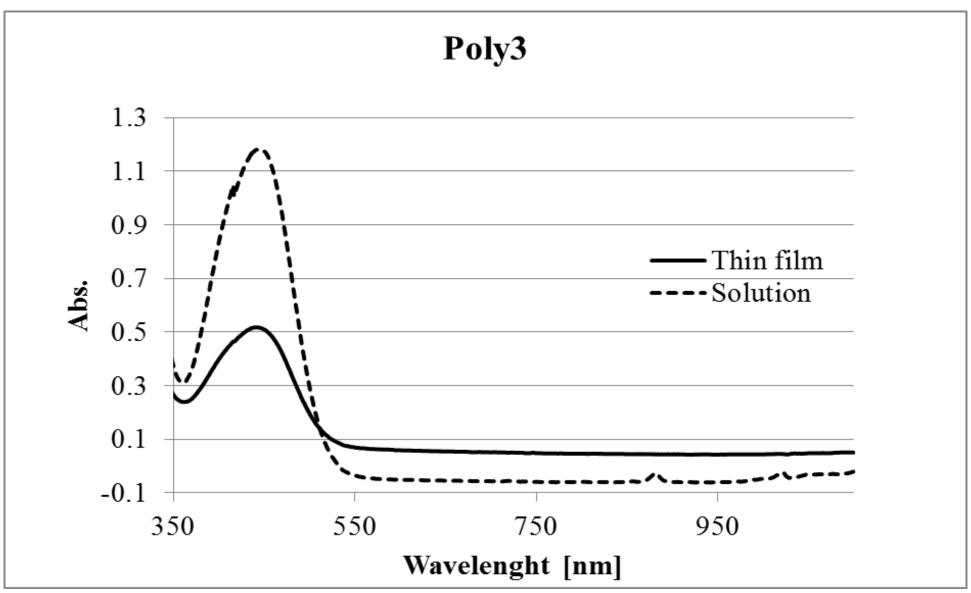


Figure S40. UV-visible spectrum absorption of Poly3