5-2016

BIOSENSORS DERIVED FROM COPOLYMERS OF VINYLFERROCENE WITH VARIOUS PARA SUBSTITUTED PHENYLMALEIMIDES

Nawrah Fahad Alghamdi
Pittsburg State University

Recommended Citation

Alghamdi, Nawrah Fahad, "BIOSENSORS DERIVED FROM COPOLYMERS OF VINYLFERROCENE WITH VARIOUS PARA SUBSTITUTED PHENYLMALEIMIDES" (2016). *Electronic Thesis Collection*. 93.
https://digitalcommons.pittstate.edu/etd/93

BIOSENSORS DERIVED FROM COPOLYMERS OF VINYLFERROCENE WITH VARIOUS PARA SUBSTITUTED PHENYLMALEIMIDES

A Thesis Submitted to the Graduate School
In Partial Fulfillment of the Requirements
For The Degree of Master of Science

Nawrah Fahad Alghamdi

Pittsburg State University

Pittsburg, Kansas

May, 2016

BIOSENSORS DERIVED FROM COPOLYMERS OF VINYLFERROCENE WITH VARIOUS PARA SUBSTITUTED PHENYLMALEIMIDES

Nawrah Fahad Alghamdi

APPROVED:

Thesis Advisor ____
Dr. Charles Neef, Chemistry Department

Committee Member ____
Dr. Khamis Siam, Chemistry Department

Committee Member ____
Dr. Ram Gupta, Chemistry Department

Committee Member ____
Dr. John T. Ikeda Franklin, English Department

ACKNOWLEDGEMENTS

At the outset, I would like to thank God for his blessings. Also, I would like to thank all the members and students of the Chemistry Department and those who helped me along the way. I would like to thank my adviser, Dr. Neef, especially, for his leadership and motivation to achieve this work. I would like to thank him for his teaching me and for his patience to improve my skills while supporting, and correcting my mistakes.

I would like to thank the members of my committee, Dr. Siam, Dr. Gupta, and Dr. Franklin of Pittsburg State University, for spending their time to read and correct my thesis. Also, I do not want to forget to thank Pittsburg State University for the materials, equipment, and very excellent services in laboratories, library, and online services.

I would like to thank the King Abdullah Scholarship for providing me with a full scholarship to complete my graduate studies in the United States of America.

I would like to thank my parents who are with me all the time, even though my father crossed over to the hereafter before I finished the master's degree but I really feel that he can see what I do. I am sure he would be proud of me. I would like to thank all my friends for spending wonderful time together.

Finally, I am very happy and I thank God for my small family, my husband (Nasser) and my children (Dayala, Abdullah), in particular. I really thank my husband for his support and encouragement to achieve this work. My small family gave me the motivation and the unlimited support that led me to become a successful student in my studies.

BIOSENSORS DERIVED FROM COPOLYMERS OF VINYLFERROCENE WITH VARIOUS PARA SUBSTITUTED PHENYLMALEIMIDES

An Abstract of the Thesis by
Nawrah Alghamdi

Five copolymers were synthesized from vinylferrocene with N-(4-methoxyphenyl)maleimide, N-(4-methylphenyl)maleimide, N-phenylmaleimide, N-(4-acetylphenyl)maleimide, and N-(4-cyanophenyl)maleimide. The resulting copolymers were characterized by gel permeation chromatography, IR spectroscopy and NMR spectroscopy. Thermal characterization of the copolymers included DSC and TGA. The copolymers were also characterized electrochemically by cyclic voltammetry in methylene chloride solutions and as a thin film in aqueous electrolytes. As a thin film, each copolymer showed changes in oxidation potential with different electrolytes (NaCl, $NaNO_3$, $NaClO_4$, and Na_2SO_4). These materials were also tested as biosensors for hydrogen peroxide and dopamine, and compared to polyvinyl ferrocene. Each material exhibited similar sensitivity to hydrogen peroxide. However, differences were observed when sensing dopamine with the methoxy and nitrile derivatives being the most sensitive.

TABLE OF CONTENTS

CHAPTER PAGE

LIST OF TABLES

LIST OF FIGURES

FIGURE PAGE

LIST OF SCHEMES

SCHEME PAGE

LIST OF ABBREVIATIONS

VFc – vinylferrocene

PVFc - polyvinylferrocene

AIBN - α, α-azobisisobutyronitrile

Bu_4NPF_6 Tetrabutylammonium hexafluorophosphate

CA - Chronoamperometry

CME - Chemically modified electrodes

CV - Cyclic Voltammetry

GPC -Gel permeation chromatography measurements

Fc - Ferrocenyl

Mw - Molecular Weight

Mn - Molecular Number

n-Bu - *n*-butyl

Poly1 - Polymer from vinylferrocene with N-(4-methoxyphenyl)maleimide

Poly2 - Polymer from vinylferrocene with N-(4-methylphenyl)maleimide

Poly3 - Polymer from vinylferrocene with N-(4-acetylphenyl)maleimide

Poly4 - Polymer from vinylferrocene with N-(4-cyanophenyl)maleimide

Poly5- Polymer from vinylferrocene with N-(4-phenyl)maleimide

TGA - Thermal Gravimetric Analysis

CHAPTER I

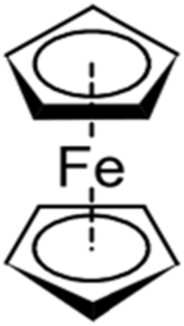
1. INTRODUCTION

1.1 Ferrocene

Scheme 1. The form of ferrocene

The structure of ferrocene was discovered and characterized in the early 1950's. In 1951, it was first prepared by the reaction of sodium cyclopentadienide with iron chloride. In 1954, the first predicted structure of ferrocene was as a sandwich shape in which two organic ring systems are coordinately bonded symmetrically to the metal atom. Ferrocene appears as orange crystals which are highly stable with a melting point of 174° C (Scheme 1.).[1] It was a successful and important example in the field of organometallic chemistry.[2]

Ferrocene was found to be an unusually stable compound. That was proved from its IR and NMR, and then confirmed by X-ray (Scheme 2).[2] Ferrocene is also called dicyclopentadienyliron. The molecular formula of ferrocene is $(C_5H_5)_2Fe$.[1]



Scheme 2. Structure of ferrocene

Ferrocene is a molecule which has a variety of important properties, such as high electron density, aromaticity, thermal stability and redox reversibility.[3] Many scientists and research groups around the world have shown interest in ferrocene studies because of its applications in material science.[4,5] Various ferrocene materials have been prepared in the past ten years.[6,7] For example, polymers containing ferrocene moieties have significant features, such as electrochemical, magnetic, catalytic, redox active and nonlinear optical properties.[8,9] Polymers which have ferrocene are very useful as redox catalysts in electrochemical reactions because of their high chemical stability and good characteristic electrochemical responses. Examples of these include electrochemical, chemiluminescent, fluorometric, piezoelectric and surface plasmon resonance immuno- sensors, impedance, biosensing chips and multi-channel microchips for multianalyte determination. [10, 11] Polymers which contain ferrocene have exhibited significant electrochemical behavior as catalytic ability, and active redox reversibility, high thermal stability good solubility in organic media, versatility in the synthesis of derivatives, and reversible redox ability. For instance, azo-bridged ferrocene oligomers and polymers have been shown to be efficient electron mediators between ferrocene moieties and other monomers. They have exhibited reversible oxidation waves in cyclic voltammetry in CH_2Cl_2 or THF.[12]

There are also many applications of ferrocene polymers. Electrode coatings, electro catalysts, and anodes in batteries are well known. To change the oxidation potential of ferrocene, electron donors such as nitrogen, sulfur, phosphorus, or oxygen have been used and these materials are interesting for many applications. Ferrocene units which are incorporated in the polymer main chain or pendant to the backbone are useful in electrochemical studies. For example, poly(ferrocenylsilane) polymers [13] and mixed valence ferrocene-ferricenium polymers[14] are two examples of polymers containing ferrocene which have been extensively studied. Additionally, strategies such as pendant to the polymer main chain or in hyper branched polymers have shown promise for a variety of applications such as batteries, electrode coatings, electrochemical sensors, and biosensors and bio-fuel cells.[15]

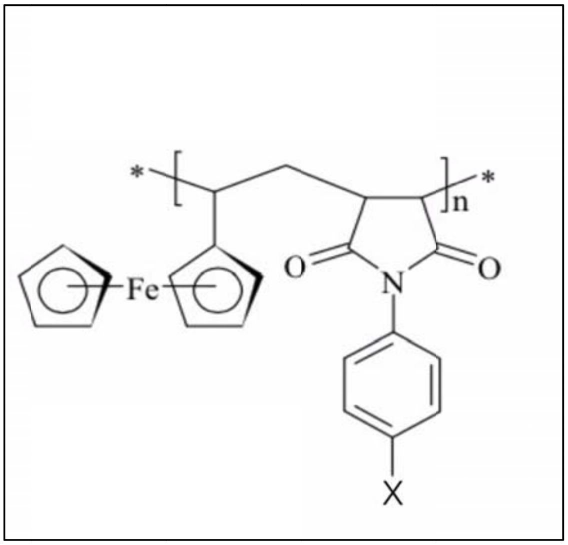
1.2 Ferrocene Biosensors

A biosensor is a device that measures the change in concentration of biomolecules such as glucose, hydrogen peroxide, serotonin, or dopamine. Biosensors are moveable, simple to use, and high specific analytical tools, which are compatible with data-processing technologies. Therefore, pharmacy, health care, pollution monitoring, and food industries have used biosensors.[16] There are many types of biosensors materials. In electrochemical anion sensors, ferrocene units were attached with secondary amides to the polymer. Glucose sensors have been fabricated using a screen-printing technique, which incorporates enzymes and ferrocene into the biosensors. [17, 18, 19] In addition, a new type of amperometric hydrogen peroxide biosensor was fabricated using poly(glycidyl methacrylate-co-vinylferrocene) to immobilize horseradish peroxidase on a glassy carbon electrode. The hydrogen peroxide biosensor showed a fast response and the biosensor was very sensitive for H_2O_2. [20] Also, using ferrocene encapsulated palladium (Pd)-linked organically-modified sol–gel glass (ormosil) has been shown to be an effective electro catalytic dopamine biosensor. The CV results of these biosensors showed good peak separation and a linear relation between peak current and square root of scan rate, which are suggesting well behaved reversible electrochemistry by the ormosil encapsulated ferrocene. [21]

In biosensor studies, redox active small ion molecules and redox active polymers have been used as well-known electron transfer mediators and electrochemical tags in biosensors. The polymers of these materials are also useful for mediator immobilization on an electrode surface. The most important materials of these are ferrocene and ferrocene polymers which are most commonly used in biosensors because of their high stability in redox reactions and easy derivative synthesis. Ferrocene derivatives are usually used on the electrode surface to build biosensors even though ferrocene derivatives can also work as media to transfer electrons. [22]

1.3 Project Rationale

In this research work, we focused on the structure/electrochemical property relationship and thermal stability of alternating copolymers of various para substituted phenylmaleimides with vinylferrocene. By changing substituents on the phenyl ring, it was anticipated that changes to the polymer surface may result in greater selectivity to biomolecules such as peroxide or dopamine. The electrochemical behavior of electrodes modified with these copolymers with various electrolytes, as well as their sensing ability, are reported.



Scheme 3. The structure of polymers, X= -OCH_3, -CH_3, -$COCH_3$, -CN, -H

CHAPTER II

2. EXPERIMENTAL

2.1 Materials

All starting materials were commercially available unless otherwise stated. Azobisisobutyronitrile (AIBN) was recrystallized from methanol and dried under reduced pressure prior to use. Vinylferocene was synthesized by a Wittig reaction according to a literature procedure.[12] Poly(vinylferrocene) was synthesized by free radical polymerization using AIBN as the initiator. Poly(vinylferrocene-co-N-phenylmaleimide) was synthesized accorded to the reported method.[23] Chloroform for GPC analysis were filtered/degassed through a 0.45 μm PTFE membrane.

2.2 Instrumentation

All NMR spectra were obtained using a Bruker DPX-300 spectrometer. Fourier transform infrared spectra (FT-IR) were obtained using a Perkin Elmer Spectrum 2 Spectrometer. Gel permeation chromatography (GPC) measurements were taken using a JMDG-4 Waters 515 HPLC pump, a 2410 differential refractometer (Waters), set of one 300*7.8 mm phennogel 5 m column. Cyclic Voltammetry (CV) and Chronoamperometry (CA) measurements were carried out using a Gamry Interface 1000 potentiostat with platinum (2 mm OD) working counter electrodes, and an Ag pseudo or Ag/AgCl reference electrode. Thermal stabilities of the copolymers were determined using TGA-Q50 and DSC-Q100, both made by TA instruments.

2.3 Synthesis of Copolymers

2.3.1 Polymerzition of vinylferrocene with N-(4-methoxyphenyl)maleimide (Poly1)

To a round bottom flask, vinylferrocene (0.212 g , 100 mmol), N-(4-methoxyphenyl)maleimide (0.20 g, 100 mmol), AIBN (0.0038 g, 1 wt %), and chlorobenzene (2 ml) were added. The flask was purged with nitrogen, and heated at 70ºC for 16 hours. The solution was allowed to cool to ambient temperature, diluted with $CHCl_3$ (1.5 mL), and then added drop by drop to rapidly stirred methanol. The resulting precipitate was collected by suction filtration and dried at 70ºC under reduced pressure in a vacuum oven to give 0.30 g (73.17 % yield) of the copolymer. IR (solid, cm^{-1}): 3050 (=C-H), 2950 (-C-H), 1750(C=O).^{1}H- NMR ($CDCl_3$, δ.ppm): 4.5-3.8 (9H) 3.7-2.1 (7H). ^{13}C -NMR ($CDCl_3$, δ.ppm): 68, 78, 115, 130, 159, 177,179.

2.3.2 Polymerzition of vinylferrocene with N-(4-methylphenyl)maleimide (Poly2)

The polymerization to give poly2 followed the procedure described for (2.3.1). The yield of the polymer was 0.28 g (71.79 %). IR (solid, cm^{-1}): 3050 (=C-H), 2950 (-C-H), 1750(C=O). ^{1}H-NMR ($CDCl_3$, δ.ppm): 4.6-3.8 (9H) 3.7-1.5 (9H). ^{13}C-NMR ($CDCl_3$, δ.ppm): 66, 68, 76, 126, 129, 131, 176, 177.

2.3. 3 Polymerzition of vinylferrocene with N-(4-acetylphenyl)maleimide (Poly3)

The polymerization to give poly3 followed the procedure described for (2.3.1). The yield of the polymer was 0.37g (87.70 %). IR (solid, cm^{-1}), 3050 (=C-H), 2950 (-

C-H), 1750(C=O), 1730 (C=O).^{1}H-NMR ($CDCl_3$, δ.ppm): 3.4-4.5 (9H) 3.4-2.1 (7H), 0.75-1.35 (3H). ^{13}C-NMR ($CDCl_3$, δ.ppm): 26, 37, 66, 77, 87, 112, 126, 128, 130, 136, 176, 177, 196.

2.3.4 Polymerzition of vinylferrocene with N-(4-cyanophenyl)maleimide (Poly4)

The polymerization to give poly4 followed the procedure described for (2.3.1). The yield of the polymer was 0.36 g (87.80 %). IR (Solid, cm^{-1}), 3050 (=C-H), 2950 (-C-H), 2250 (CN) 1750(C=O). ^{1}H-NMR ($CDCl_3$, δ.ppm): 3.4-4.5 (9H) 3.4-2.1 (7H), 0.75-1.35 (3H). ^{13}C-NMR ($CDCl_3$, δ.ppm): 25, 27, 39, 46, 54, 68, 78, 111, 118, 127, 172, 177.

2.3.5 Polymerzition of vinylferrocene with N-(4-phenyl)maleimide (Poly5)

The polymerization to give poly5 followed the procedure described for (2.3.1). The yield of the polymer was 0.36 g (86.71 %). IR (solid, cm^{-1}), 3050 (=C-H), 2950 (-C-H), 1750(C=O). ^{1}H-NMR ($CDCl_3$, δ.ppm): 3.4-4.5 (9H) 3.4-2.1 (7H), 0.75-1.35 (3H). ^{13}C-NMR ($CDCl_3$, δ.ppm): 25, 27, 39, 46, 54, 68, 78, 111, 118, 127, 172, 177.

2.4 Preparation of electrodes

For testing in methylene chloride:

Electrochemical solutions were prepared by dissolving each polymer (1mM) and tetrabutylammonium hexafluorophosphate (100mM) as supporting electrolyte, in methylene chloride (CH_2Cl_2) (10 mL).

Cast film method:

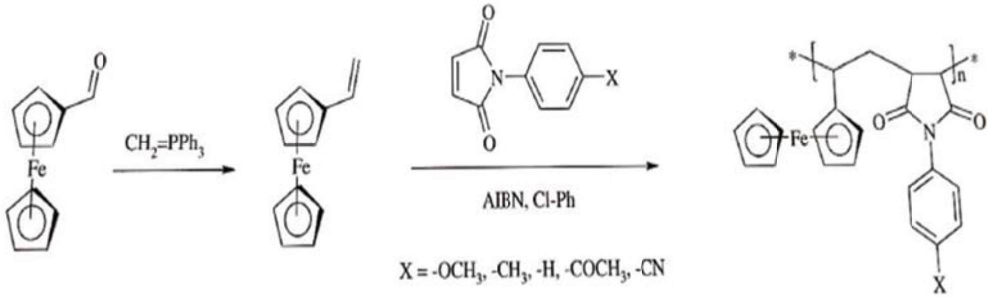
Chemical modified electrodes (CME) were prepared by casting from polymer solutions directly on the electrode surface. $CHCl_3$ solutions of Poly1-5 (3 mg/mL) were micropipetted (2μL) onto electrodes then allowed to air dry for 15-20 min. The electrodes were then placed into various aqueous electrolyte solutions for electrochemical analysis, using a Pt counter electrode and Ag/AgCl reference electrode.

CHAPTER III

3. RESULTS AND DISCUSSION

3.1 Synthesis and Characterization of Copolymers

The Wittig synthesis of vinylferrocene was accomplished in 70.5% yield from ferrocene carboxaldehyde and methyltriphenylphosphonium bromide. Copolymerization of vinylferrocene with N-(4-methoxyphenyl) maleimide, N-(4-methylphenyl) maleimide, N-phenylmaleimide, N-(4-acetylphenyl) maleimide, and N-(4-cyanophenyl) maleimide were accomplished using a literature procedure.[12] Copolymerization of vinylferrocene with each maleimide was performed in chlorobenzene with α,α-azobisisobutyronitrile (AIBN) as the initiator, giving good polymer yields (71.79 % - 87.8 %) (Schemes 3). GPC analysis of polymers 1-5 showed that the Mw ranged from 6,350-83,600 and polydispersities (PD) ranged from 3.9-24.2 (Table 1). For poly1 and poly2, Mws were somewhat low (6350 and 7295, respectively) suggesting that electron donating groups on the meleimide slows the propagation rate during the polymerization. In addition, PDs are relatively high but are not uncommon for vinylferrocene polymers.



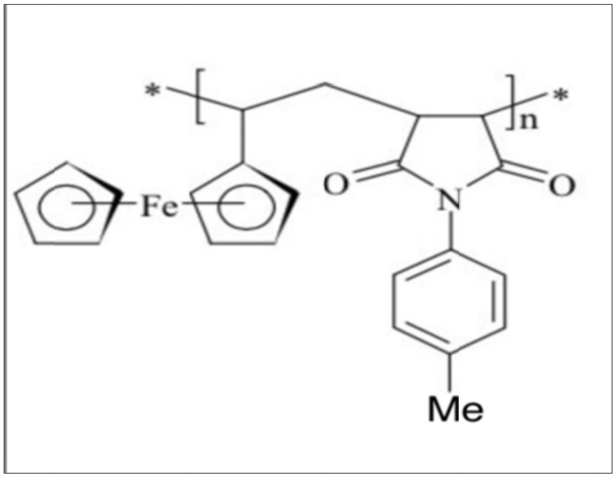
Scheme 4. Reaction scheme of polymerization of vinylferrocene with various N-substituted maleimides

Table 1. Gel permeation chromatography (GPC) measurements of copolymers

poly	X	Mw (g/mol)	Mn (g/mol)	Polydispersity (Mw/Mn)	%yield
1	-OCH3	6350	1478	4.30	73.17 %
2	-CH3	7295	1867	3.91	71.79 %
3	-COCH3	78829	3447	22.87	87.70 %
4	-CN	37796	3774	10.01	87.80 %
5	-H	83596	3454	24.20	86.71 %

3.1.1 Spectroscopy Analysis

The FTIR, ^{13}C-NMR, and ^{1}H-NMR spectra were consistent with structures of each copolymer. For poly2 (Scheme 5.), the FT-IR spectrum showed peaks at 3050, 2950, and 1750 for =C-H, -C-H, and C=O stretching, respectively (Figure 1.). In the ^{1}H-NMR spectrum of poly2, peaks were observed at 7.8-6.8 ppm for the phenyl proton, at 4.6-3.8ppm (9H) for the ferrocenyl protons, and at 3.7-1.5 ppm for the aliphatic protons (Figure 2.). In the ^{13}C-NMR spectrum of poly2, a fewer number of peaks were observed that expected probably due to coincidental overlap of signals (Figure 3.).



Scheme 5. The Structure of Poly2.

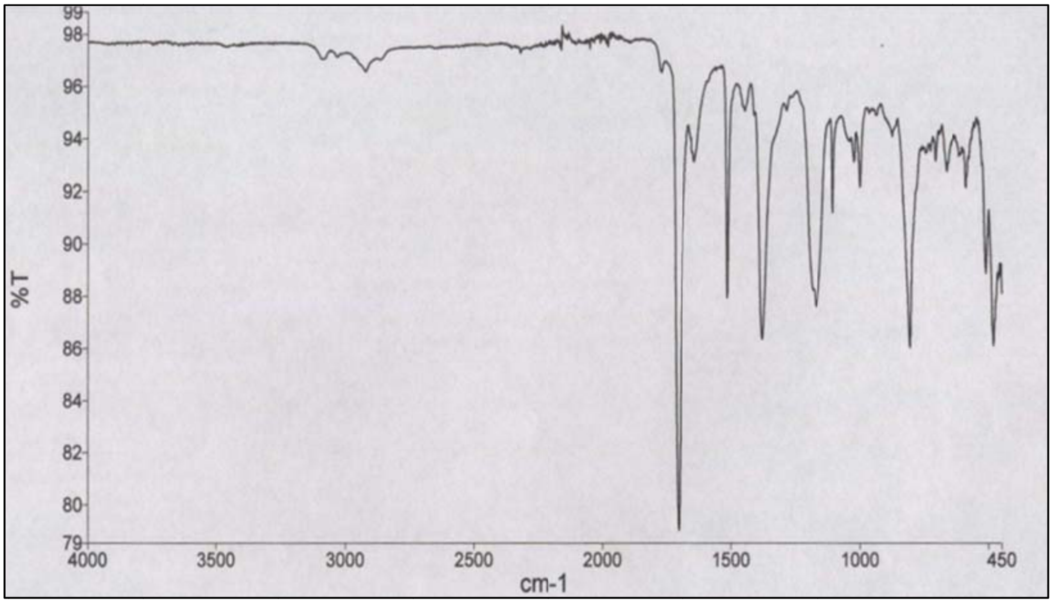


Figure 1. FTIR spectrum of Poly2

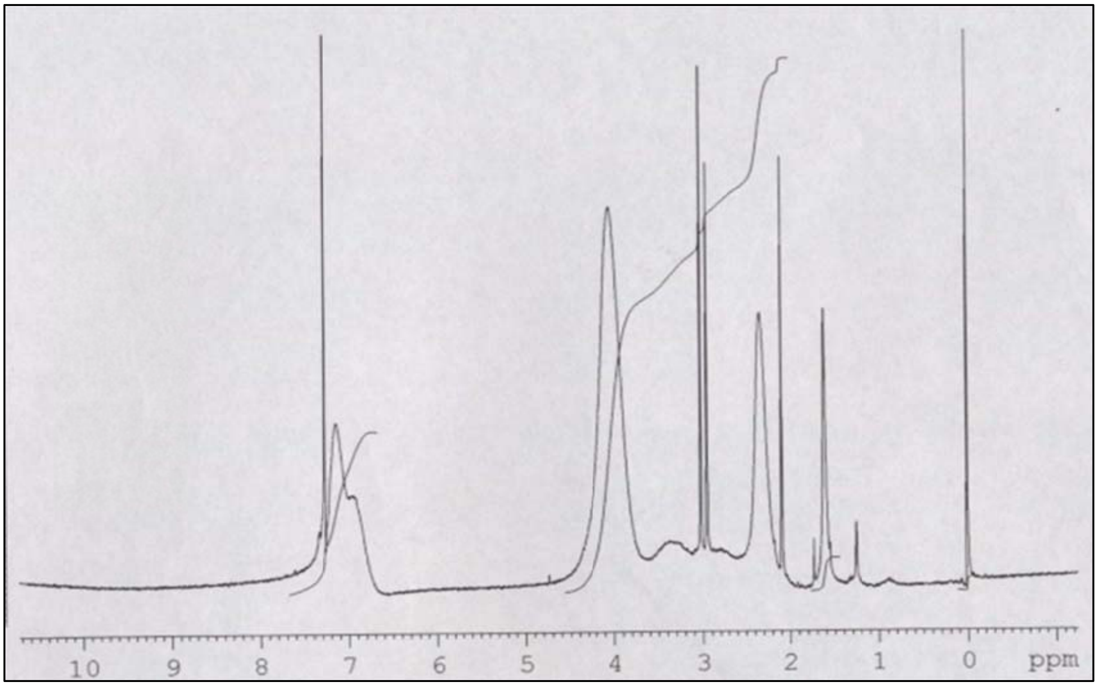


Figure 2. ^{1}H-NMR spectrum of Poly2

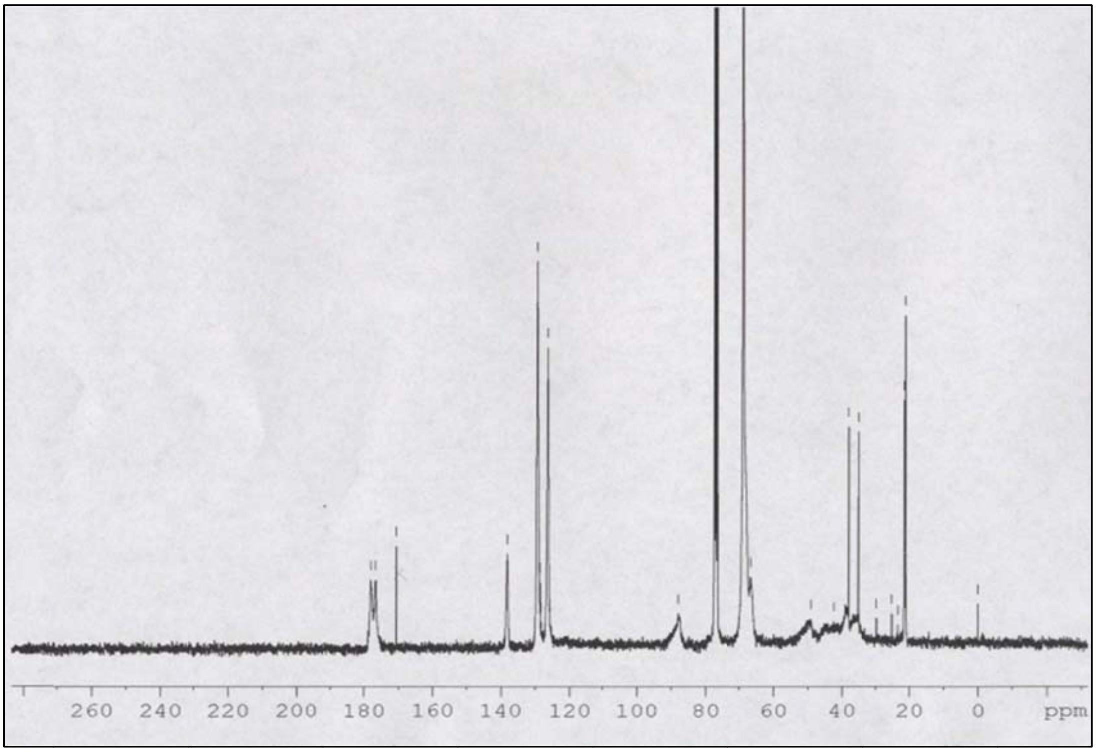


Figure 3. ^{13}C-NMR spectrum of Poly2

3.2 Electrochemical Studies

3.2.1 CVs of polymers in CH_2Cl_2

Cyclic voltammetry (CV) for each polymer was performed in CH_2Cl_2 with tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) as supporting electrolyte. CV of each polymer was performed from -0.20 V to 0.60V at scan rates of 20, 40, 60, 80, and 100 mV/s. For each polymer, a greater current for reduction than for oxidation was observed which was consistent with polymer adsorption on the electrode surface. Redox potentials of each polymer where referenced to 1,1'-diaceetylFerrocene (0.54V vs. Fc/Fc^+) the range of redox potentials of the polymers ranged from 0.45 to 0.49 V. (Table 1). The redox potentials were close in values, suggesting that the various substituent on the phenyl moiety had little or no effect on the oxidation potential of the ferrocenyl moiety. However, the current scaled linearly with the square root of the scan rate according to Randles Sevcik equation. These results suggest that the electrochemical process was diffusion controlled and the polymer does not completely adsorb on the electrode surface (Figure 4.). In addition, each of the polymers, showed a good current response, indicating that anions could flow freely into and out of the films (Figure 5.).

Table 2. Redox potentials of Poly1-5 with CH_2Cl_2 and p-tetrabutylammonium hexafluorophsphate:

X	Poly E1/2
-OCH_3	-0.47
-CH_3	-0.47
-H	-0.48
-$COCH_3$	-0.46
-CN	-0.44

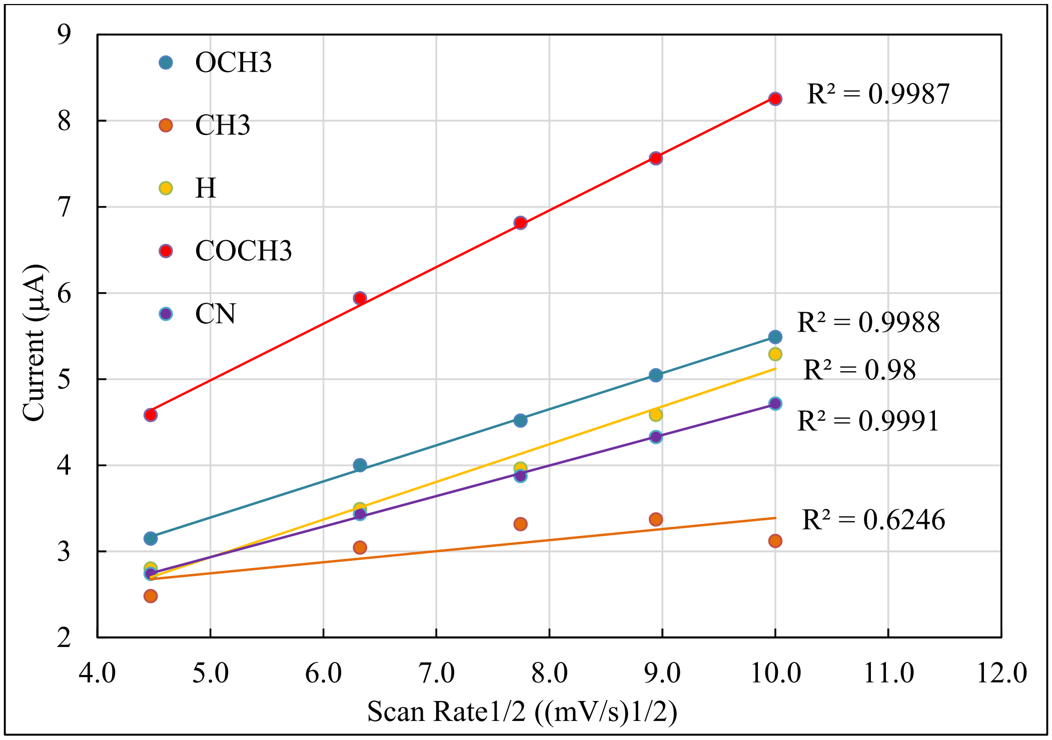


Figure 4. Current versus square root of scan rate for CV of Poly 1-5.

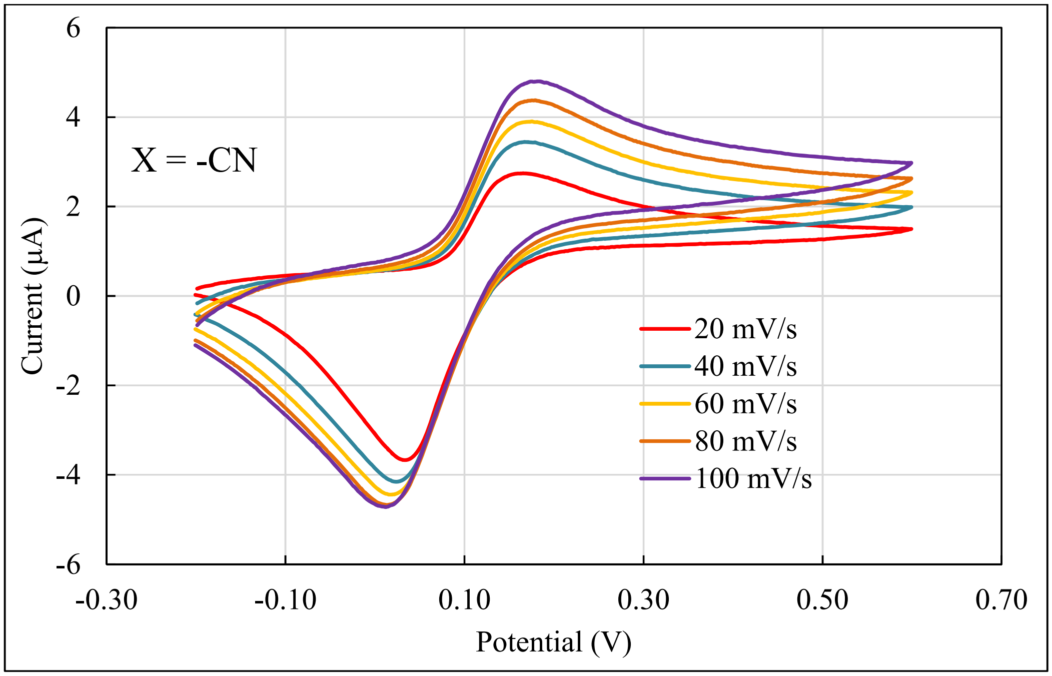


Figure 5. CVs of Poly4 with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and an Ag pseudo reference electrode

3.3.1. Electrochemistry of chemically modified electrodes in aqueous electrolytes

Chemically modified electrods (CMEs) were prepared by casting from a $CHCl_3$ solution and air-drying for 15 min. CMEs were then placed in various aqueous electrolytes. CVs were then taken to determine the electrochemical response for each electrolyte. The CVs of a CME with poly1 are shown in Figure 6 and similar results were observed for poly2-5. Oxidation potentials ($E_{1/2}$) ranged from 0.42 – 0.51 V (Table 2.). This type of behavior has been observed for other ferrocene containing polymers and is due to solvation of the anion. As an anion becomes more solvated, it is essentially larger and a greater potential is needed to force transport of the anion into the film upon oxidation. The lowest oxidation potential of the polymers was observed with $NaClO_4$ indicating that it migrates into and out of the film easiest. Therefore, subsequent electrochemistry was performed using $NaClO_4$ as the supporting electrolyte.

Table 3.Redox potentials of chemically modified electrodes of Polymers prepared by solution cast films in various aqueous electrolytes (Na_2SO_4, NaCl, NaClO4, and $NaNO_3$)

Electrolyte	OCH3 - E1/2	CH3 - E1/2	COCH3 - E1/2	CN - E1/2	H - E1/2
Na_2SO_4	0.48	0.48	0.47	0.46	0.47
NaCl	0.51	0.52	0.51	0.50	0.49
$NaClO_4$	0.42	0.42	0.43	0.41	0.42
$NaNO_3$	0.46	0.45	0.45	0.44	0.45

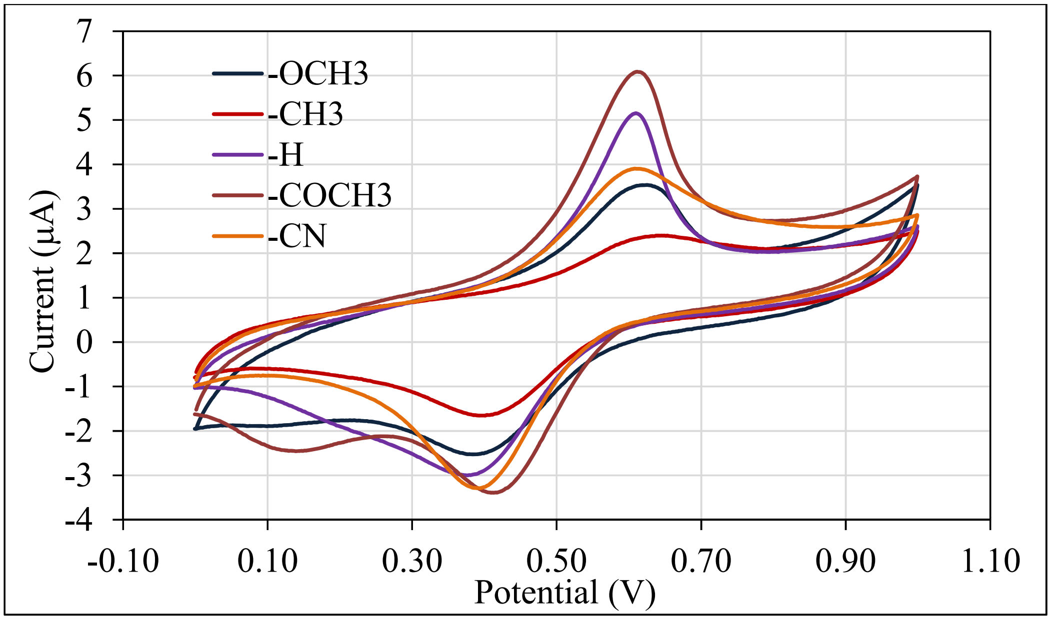


Figure 6. CVs of chemical modified electrodes on cast films of copolymers on platinum electrode in aqueous $NaClO_4$

3.3. Biosensor Studies

3.3.1 H_2O_2 Testing with Chemically Modified Electrodes (CMEs)

In this study, chemically modified electrodes (CMEs) were tested with various amount of H_2O_2 and compared to polyvinyleferrocene (PVFc) to determine their potential as a H_2O_2 biosensor. CMEs were prepared by casting films onto a Pt electrode and placed in aqueous H_2O_2 at concentrations of 0, 0.25, 0.50, 0.75, or 1.0 mM. The CVs of poly1 in the presence of H_2O_2 are shown in Figure 7. As the concentration of H_2O_2 was increased, an increase in the electrochemical response was observed. Similar behavior was observed for poly2-5. An increase in current with H_2O_2 concentration is consistent with other ferrocene containing polymers. However, when compared to PVFc, poly1-5 exhibited less current (Figure 8.).

These results indicate that poly1-5 were less sensitive than PVFc suggesting that the ferrocene amount was the primary factor to sensitivity.

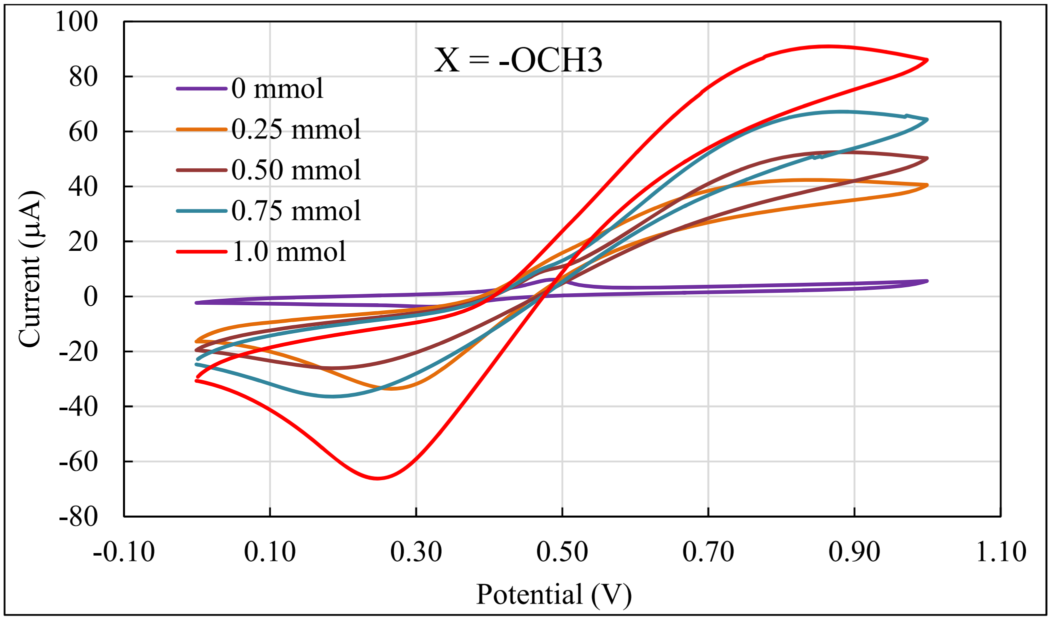


Figure 7. CVs of chemical modified electrodes with cast films of Poly1 on Pt electrode in aqueous solution ($NaClO_4$) with various concentrations of H_2O_2

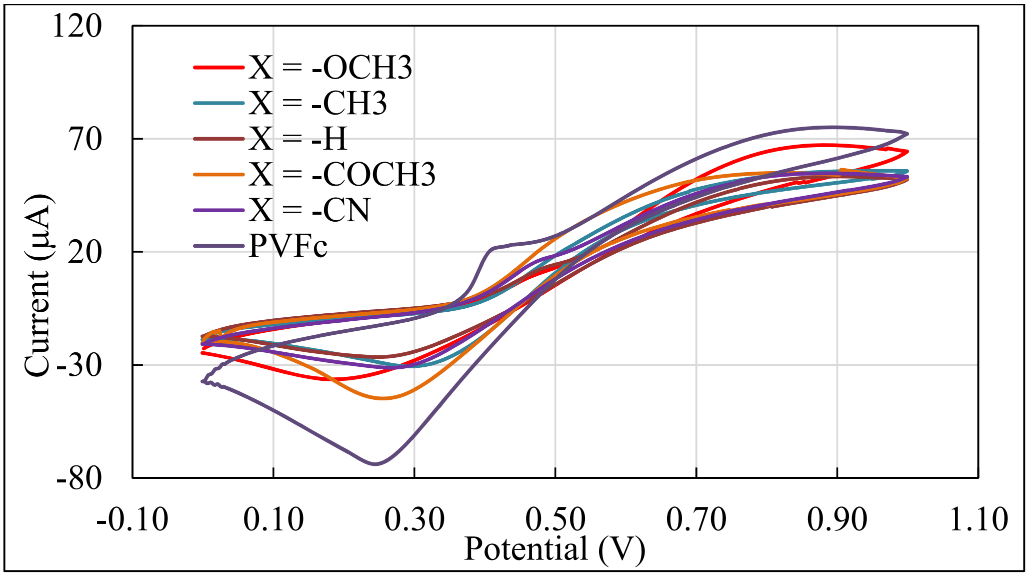


Figure 8. CVs of chemical modified electrodes with cast films of all copolymers on platinum electrode into aqueous solution ($NaClO_4$) with 0.75 mM H_2O_2

3.3.2 Dopamine Biosensors with Chemically Modified Electrodes (CMEs):

Biosensor studies with CMEs were also performed for the electrochemical sensing of dopamine. Initial studies focused on the CV response to various amounts of dopamine: 0, 10, 20, and 30 mM. CVs of poly1 versus dopamine concentration are shown in Figure 9. As dopamine concentration increased, an increase in current was observed indicating good sensitivity to dopamine. For comparison, the CV of each polymer and PVFc in the presence of dopamine (30 mM) is shown in Figure 10. In general, a greater amount of current was observed for each of the copolymers compared to PVFc. These results indicate that the amount of ferrocene is not the dominant factor. Even though the factors affecting dopamine sensitivity are not well understood, the maleimide moiety may change the morphology of the polymer or interact with dopamine to enhance sensitivity.

To quantify the polymer’s sensitivity, chronoamperometry was performed for each of the copolymers at various dopamine concentrations and the responses of poly1 to dopamine are shown in Figure 11. The CA curves were then integrated to obtain the amount of charge and the change plotted versus dopamine concentration (Figure 12). For each copolymer, a linear response of charge versus dopamine concentration was observed, indicating good electrochemical response. The polymers that showed the greatest sensitivity to dopamine were poly1 and poly4. Since poly1 contains an electron rich methoxy moiety and poly4 contains an electron deficient nitrile, these results are not well understood. However, they may suggest that interactions with dopamine in its neutral form by poly1 or in its oxidized form by poly4 may facilitate sensitivity.

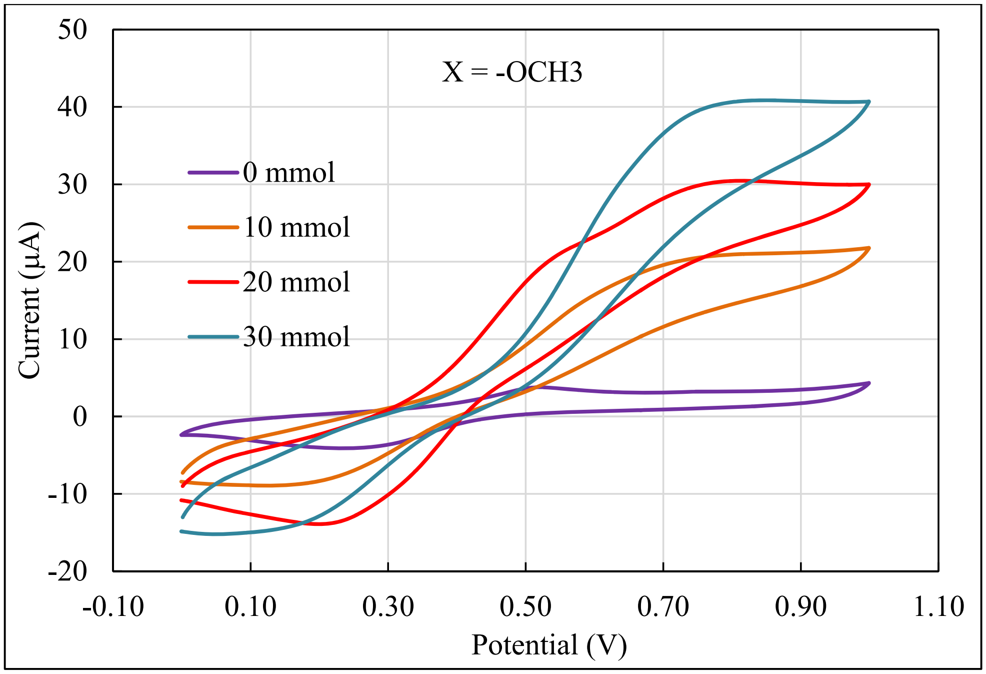


Figure 9. CVs of chemical modified electrodes on cast films of Poly1 on Pt electrode into aqueous solution ($NaClO_4$) with Dopamine at various scans.

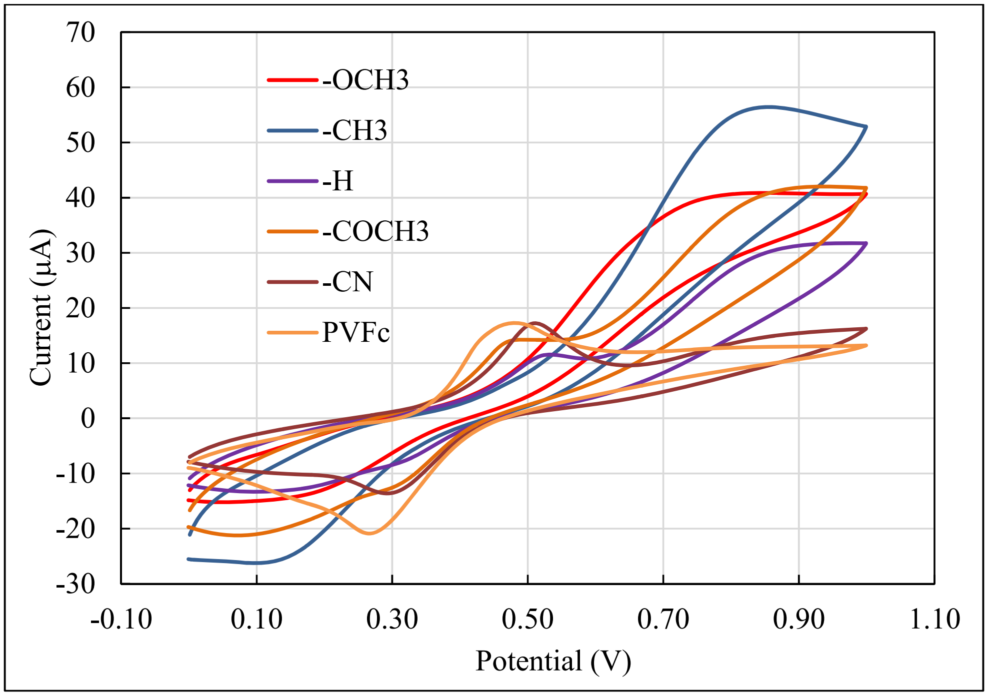


Figure 10. CVs of chemical modified electrodes on cast films of all copolymers on Pt electrode into aqueous solutions of Dopamine (40 mM).

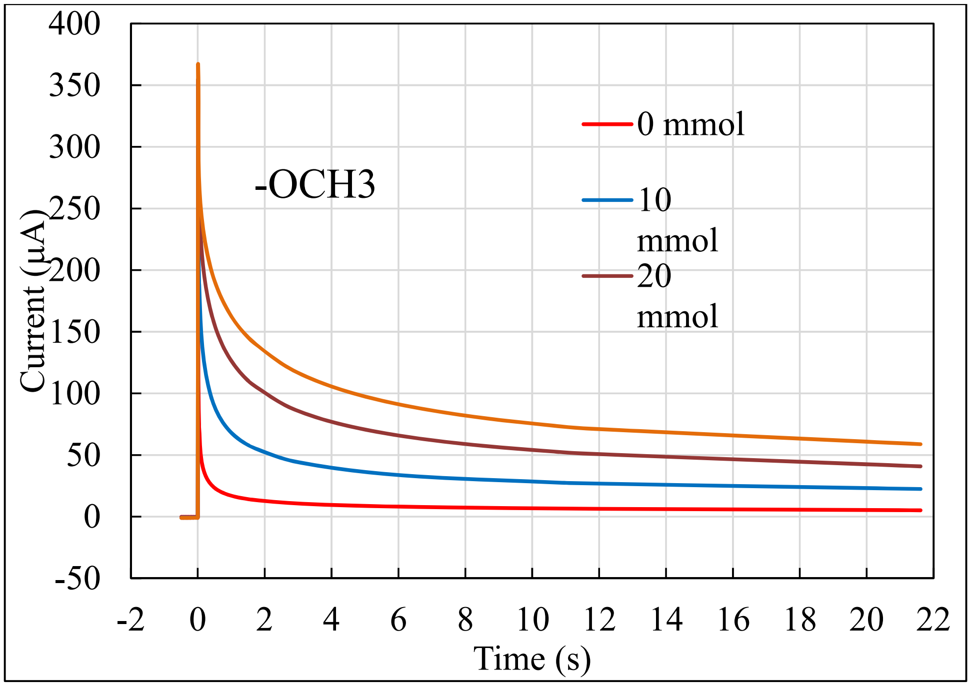


Figure 11. Poly1 (X= -OCH$_3$) with Dopamine

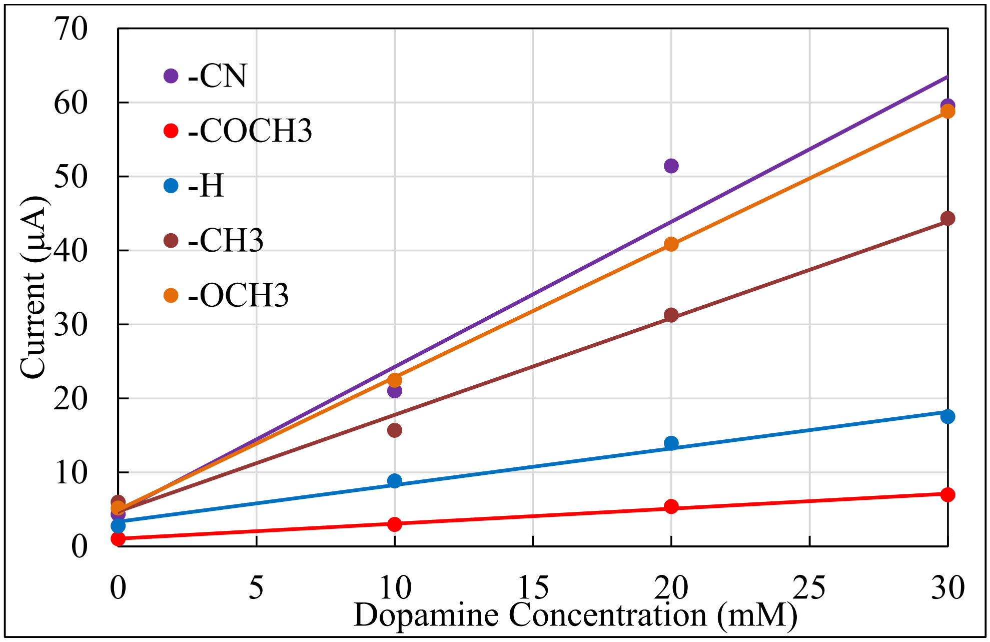


Figure 12. Integration CAs versus dopamine concentration for Poly1-5.

3.4 Thermal Gravimetric Analysis

Thermal Gravimetric Analysis of copolymers (TGAs) were recorded from room temperature to 700 °C at a temperature ramp of 10°C/min under nitrogen atmosphere (Figure 13). Thermal stability of each copolymer was determined at 10 % weight loss and ranged from 320 – 370°C. These stabilities were typical for ferrocene containing polymers. Char yields for the copolymers ranged from 22 to 38 % that was also typical for ferrocene polymers.

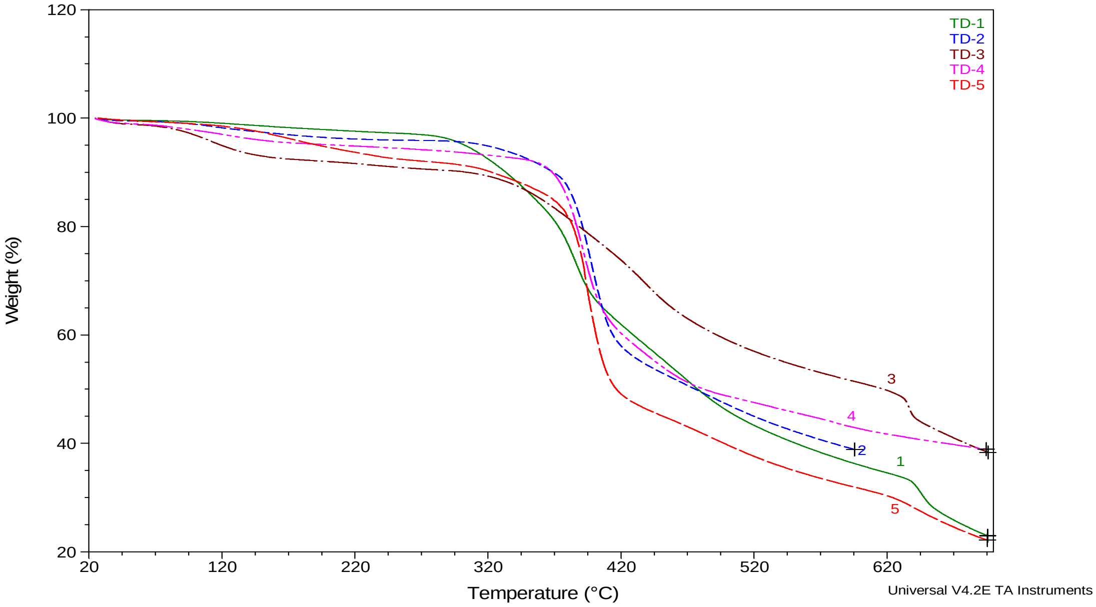


Figure 13. Overlay Graph of all TGA polymers

(TD-1= Poly1, TD-2= Poly2, TD-3= Poly3, TD-4= Poly4, TD-5= Poly5)

CHAPTER IV

4. CONCLUSIONS

Five copolymers were synthesized according to a literature procedure.[12] The polymers were prepared by copolymerization of vinylferrocene with various para substituted phenylmaleimides using AIBN as the initiator. Characterization by FT-IR, ^{1}H-NMR spectroscopy, and ^{13}C-NMR spectroscopy of all polymers were consistent with the anticipated structures and polymerization yields of 70-80% were obtained.

Chemically modified electrodes were prepared by depositing each polymer onto an electrode by casting from solution. CVs showed a dependency of redox potential versus electrolyte: NaCl, $NaNO_3$, $NaClO_4$, and Na_2SO_4. Cyclic voltametry (CV) for each polymer was performed in CH_2Cl_2 with tetrabutylammonium hexafluorophosphate as supporting electrolyte. The redox potentials were close in values, suggesting that substituents have little to no effect on the oxidation potential of the ferrocene. The electrochemistry of copolymer thin films showed good current response indicating that anions could flow freely into and out of the films. CMEs were tested with various amounts of H_2O_2 and compared to polyvinyleferrocene. As the concentration of H_2O_2 increased, an increase in electrochemical response was observed for each polymer. However, Poly1-5 were less sensitive than PVFc, suggesting that the ferrocene amount is the primary factor to sensitivity.

Biosensor studies using CMEs were also performed with dopamine. As dopamine concentration increased, an increase in current was observed, indicating good sensitivity to dopamine. A greater charge was observed for each of the copolymers compared to PVFc, suggesting that the amount of ferrocene is not the dominant factor. The maleimide moiety may change the morphology of the polymer or interact with dopamine to enhance sensitivity. The polymers that showed the greatest sensitivity to dopamine were Poly1 and Poly4. These results suggest that interactions with the maleimide moiety may facilitate sensitivity. For TGA, thermal stability of each copolymer was determined at 10 % weight loss and ranged from 320 – 370 °C. These stabilities were typical for ferrocene containing polymers. Char yields for the copolymers ranged from 22 to 38 % that was also typical for ferrocene polymers.

REFERENCES

(1) Jianping Yong, Xiaoyu Jiang, Xiaoyuan Wu, Shuijin Huang, Qikai Zhang, andCanzhong Lu, Synthesis and Characterization of Ferrocene Derivatives and Preliminarily Electrocatalytic Oxidation of L-Cysteine at Nafion-Ferrocene Derivatives Modified Glassy Carbon Electrode, Vol. **(2014),** 7 pages.

(2) G. Wilkinson *J. Organometal. Chem.* **(1975)**, 100, 273-276.

(3) Getautis, V.; Daskeviciene, M.; Malinauskas, T.; Jankauskas, V.Monatsh. *Organometal.* Chem. **(2007)**, 138, 277–283.

(4) Hudson, R. D. A J. Organomet. Chem. **(2001)**, 637, 47–69.

(5) Balavoine, G. G. A.; Daran, J. C.; Iftime, G.; Lacrolx, P. G.;Manoury, E.; Delaire, J. A.; Maltey-Fanton, I.; Natatani, K.; Bella, S. D. Organometallics **(1999),** 18, 21–29.

(6) Zhu, Y.; Wolf, M. O. Chem. Mater. **(1999),** 11, 2995–3001.

(7) Yang, Y. L.; Xie, Z. W.; Wu, C. Macromolecules **(2002),** 35, 3426–3432.

(8) Lin, Z. Adv. Mater. **(1999),** 11, 1153–1154.

(9) Baldoli, C.; Oldani, C.; Licandro; Ramani, E. P.; Valerio, A.; Ferruti, P.; Falciola, L.; Mussini, P. J. Organomet. Chem. **(2007),** 692: 1363-1371.

(10) Akram, M.; Stuart, M. C.; Wong, D. K. Y. Electroanalysis **(2006),** 18, 237–246.

(11) Qiu, J.; Zhou, W.; Guo, J.; Wang, R.; Liang, R. Anal. Biochem. **(2009),** 385, 264–269.

(12) Abd-El-Aziz, A.; Manners, I. Frontiers in transition metal-containing polymers, John Wiley and Sons, Inc. **(2007),** 18, 185-188.

(13) Ron Rulkens, Alan J. Lough, Ian Manners, Sherri R. Lovelace, Casey Grant, and William E. Geiger, J. Am. Chem. Soc. **(1996),** 118, 12683-12695

(14) Gilbert Stork, R. *J. Am. Chem. Soc.*, (**1972)**, *94* (14), pp 5110–5112.

(15) Jamie Carberry, Jennifer A. Irvin, Daniel T. Glatzhofer , Kenneth M. Nicholas , Charles J. Neef, High molecular weight copolymers of vinylferrocene and 3-phenyl[5]ferrocenophane-1,5-dimethylene with various N-substituted maleimides, **(2013)** ,73, 730–736.

(16) Chem. Anal. (Warsaw), **(2006),** 51, 839.

(17) Ryohei N., Kenji Y., Susan A., Isao K., A glucose sensor fabricated by the screen printing technique, Biosensors and Bioelectronics, **(1995)** Vol. 261–267.

(18) (a) Keefe, M. H.; Benkstein, K. D.; Hupp, J. T. Coord. Chem. Rev. 2000, 205, 201-228. (b) Martı´nez-Ma´n˜ez, R.; Sanceno´n, F. Chem. Rev. **(2003),** 103, 4419-4476.

(19) (a) Gale, P. A. Coord. Chem. Rev. **(2000),** 199, 181-233. (b) Gale, P. A. Coord. Chem. Rev. **(2001),** 213, 79- 128.

(20) Mehmet Ş, Emre Ç, Fatih A, Amperometric hydrogen peroxide biosensor based on covalent immobilization of horseradish peroxidase on ferrocene containing polymeric mediator, Sensors and Actuators B: **(2010)** ,Vol. 444–450.

(21) P.C. Pandey, S. Upadhyay, Tiwari, G. Singh, V.S. Tripathi A novel ferrocene encapsulated palladium-linked ormosil-based electrocatalytic dopamine biosensor, Sensors and Actuators B: **(2001),**Vol. 48–55.

(22) Shigehiro T, and Jun-ichi A. , Recent Progress in Ferrocene-Modified Thin Films and Nanoparticles for Biosensors **(2013),** 6, 5742-5762.

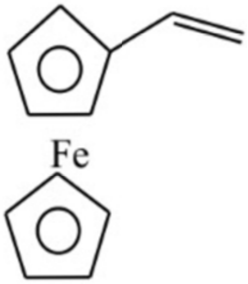
(23) Charles J. Neef, Danial T. Glatzhofer, Kenneth M. Nichols, Journal of Polymer Science: Part A: Polymer Chemistry, **(1997),** Vol. 35, 3365–3376.

(24) Graziella S, Antonella A, Carmine C, and Gaetano S, Sensors, **(2013),** Vol, 3878-3888.

APPENDIX

SUPPLEMENTAL LISTS

Vinylferrocene



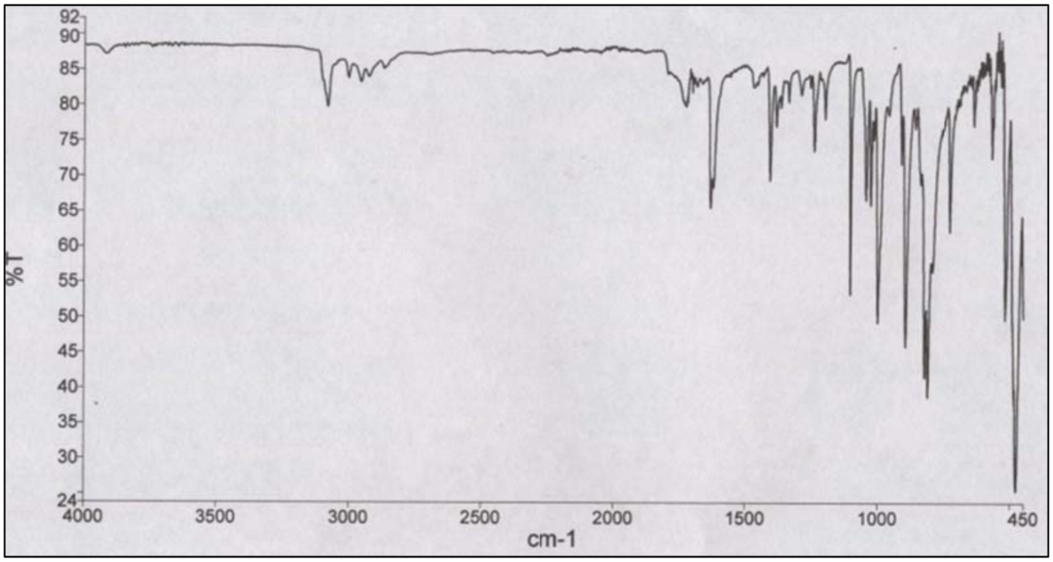
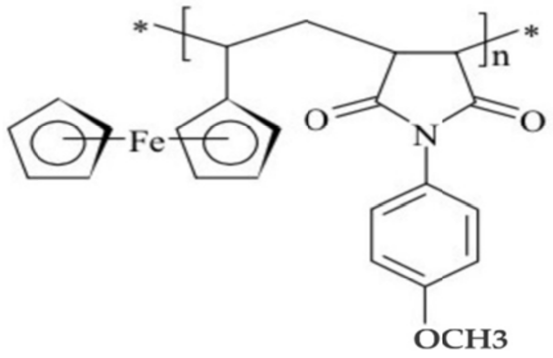


Figure S1. FTIR spectrum of Vinylferrocene

Poly1



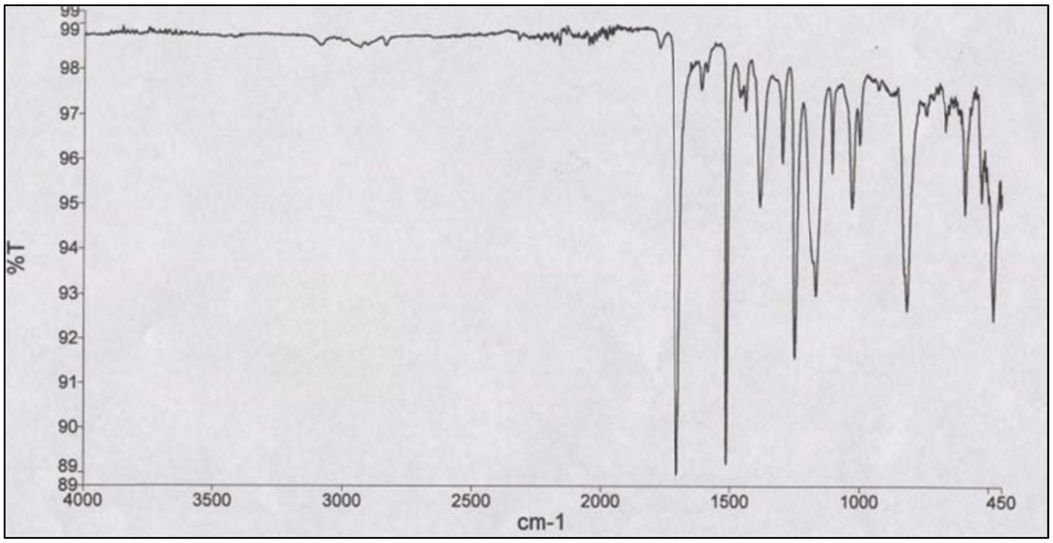
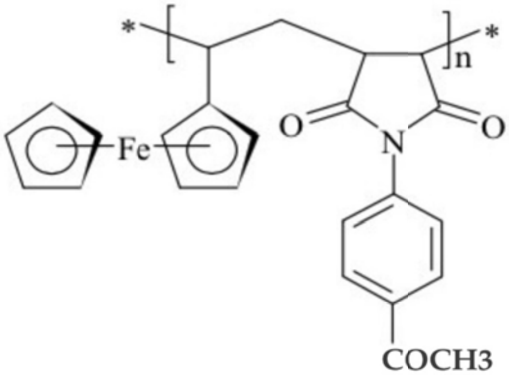


Figure S2. **FTIR spectrum of Poly1**

Poly3



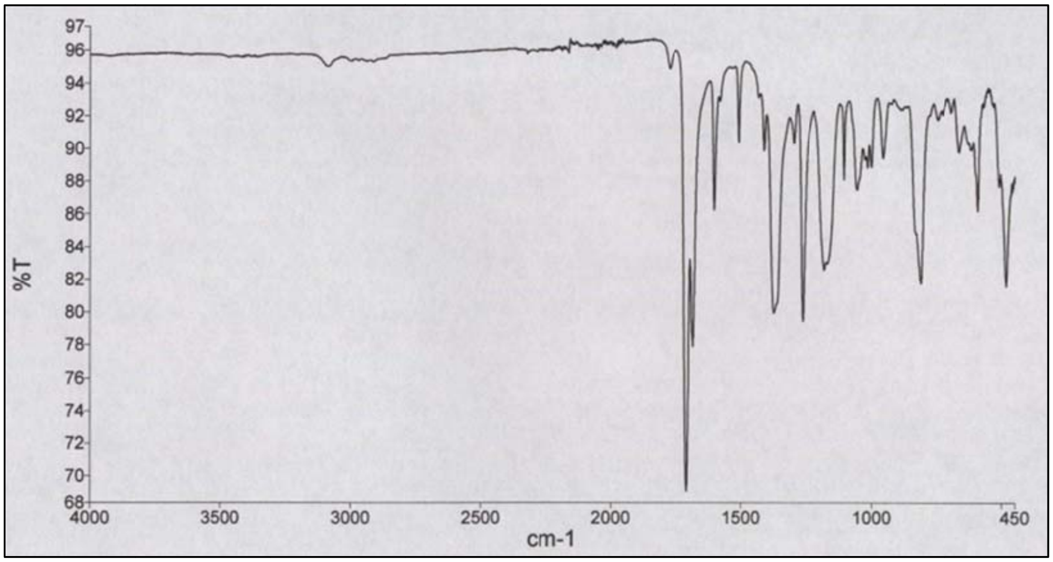
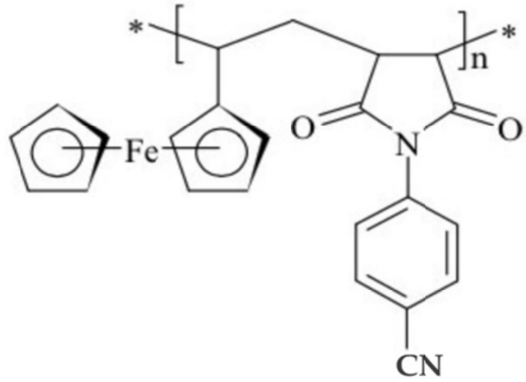


Figure S3. FTIR spectrum of Poly3

Poly4



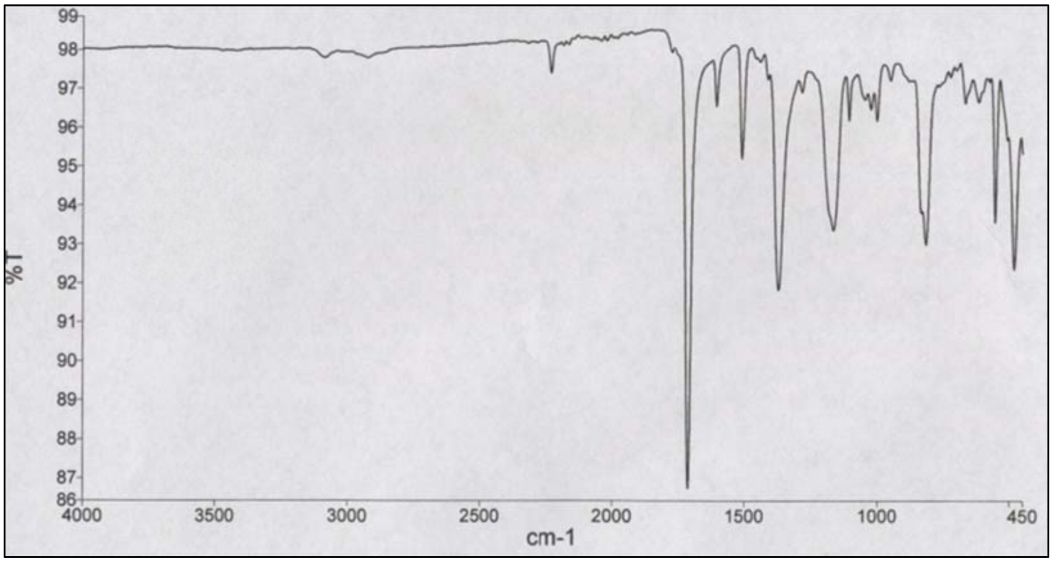
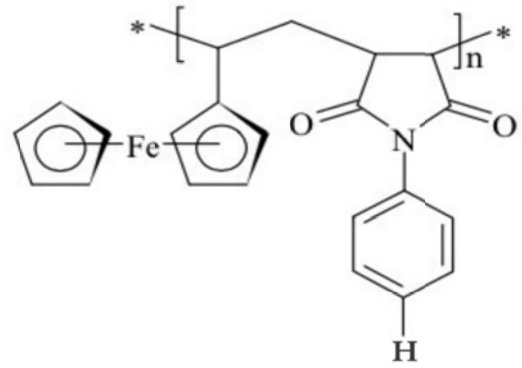


Figure S4. FTIR spectrum of Poly4

Poly5



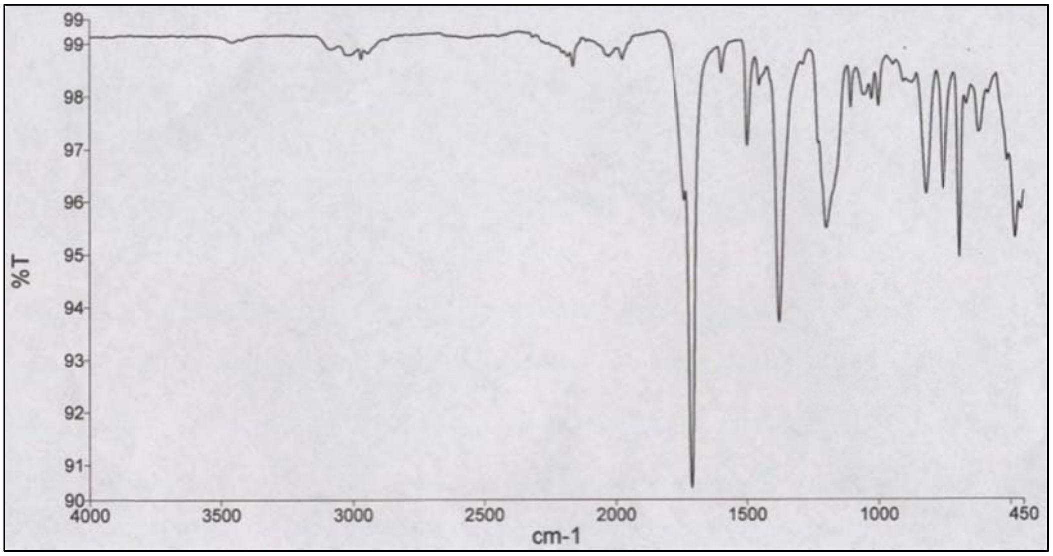


Figure S5. FTIR spectrum of Poly5

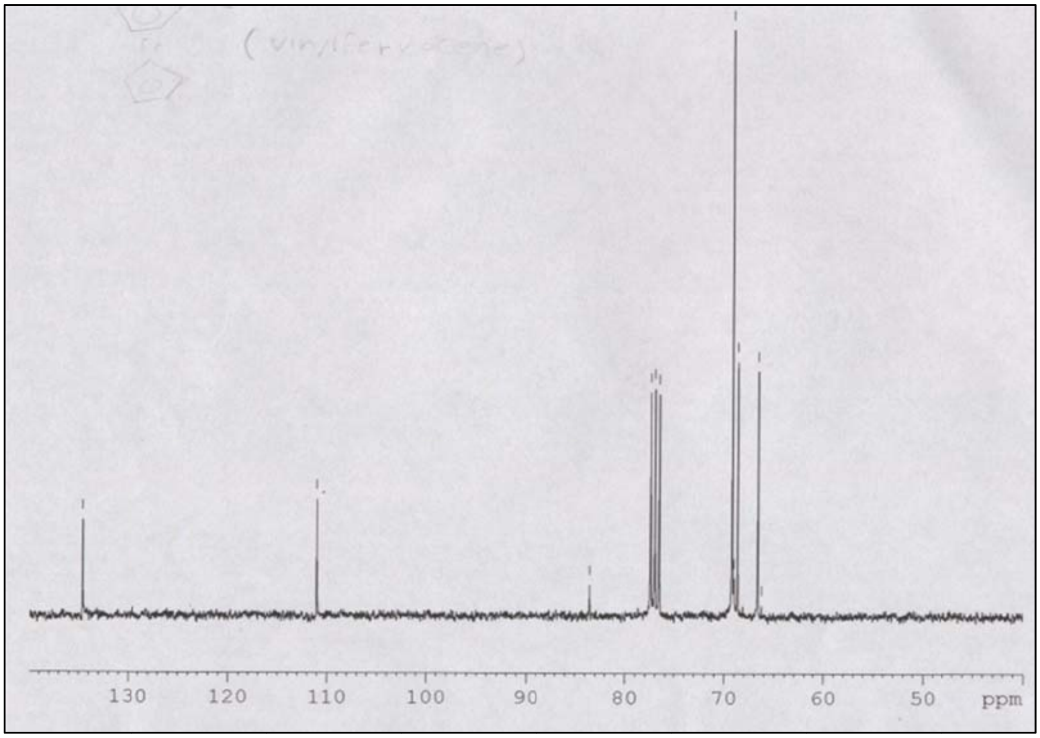


Figure S6. **^{13}C-NMR spectrum of Vinylferrocene**

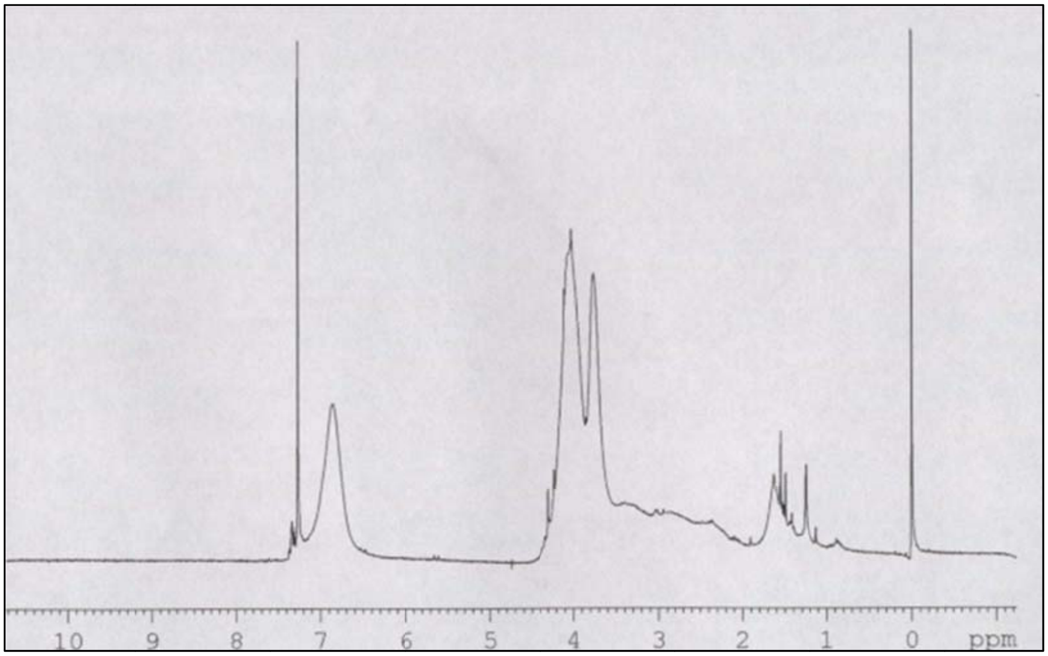


Figure S7. **^{1}H-NMR spectrum of Poly1**

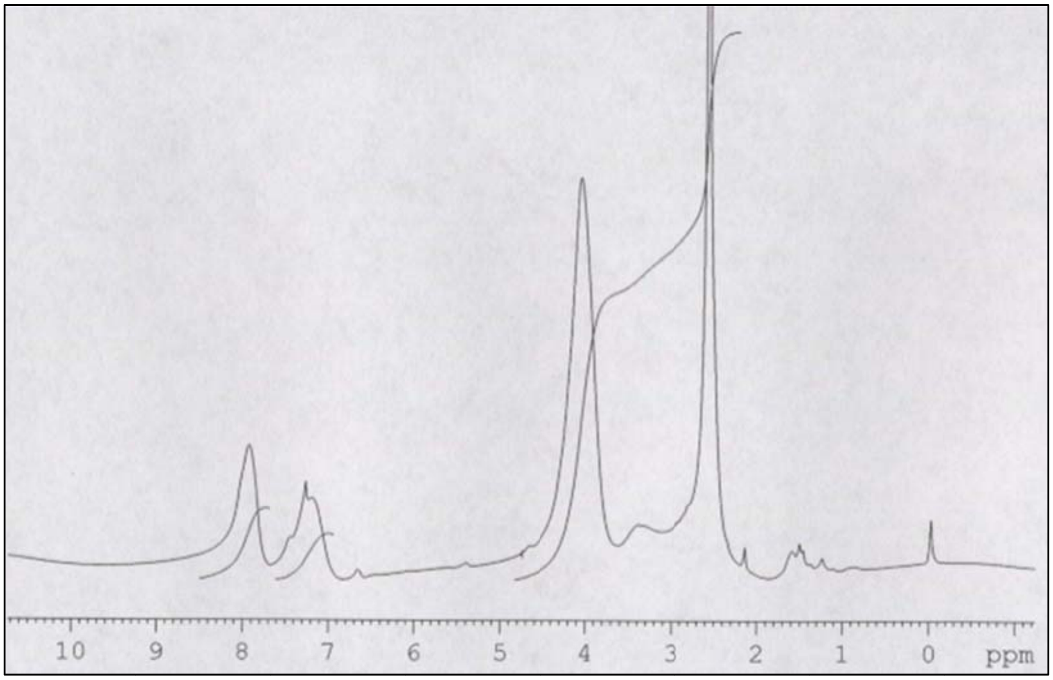


Figure S8. ^{1}H-NMR spectrum of Poly3

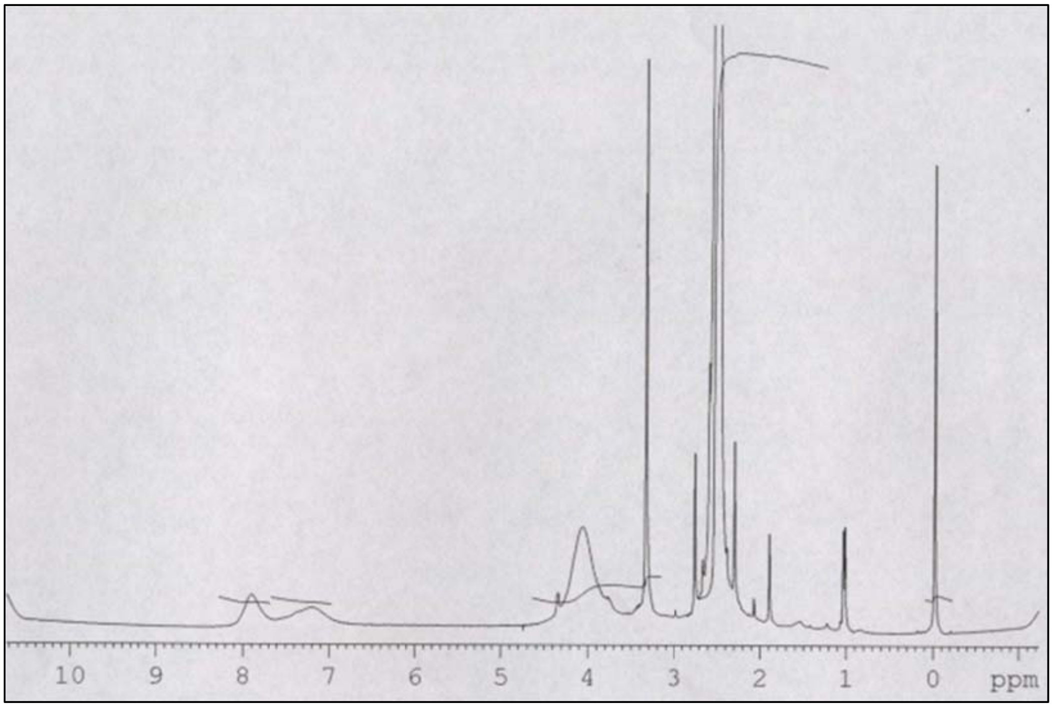


Figure S9. ^{1}H-NMR spectrum of Poly4

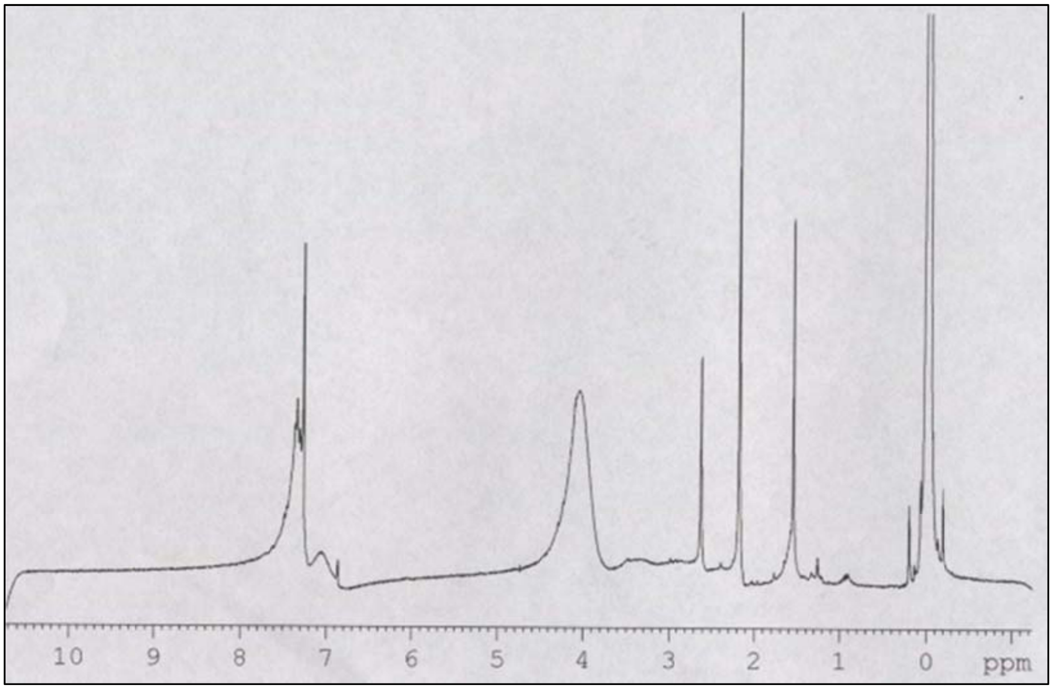


Figure S10. **^{1}H-NMR spectrum of Poly5**

Figure S

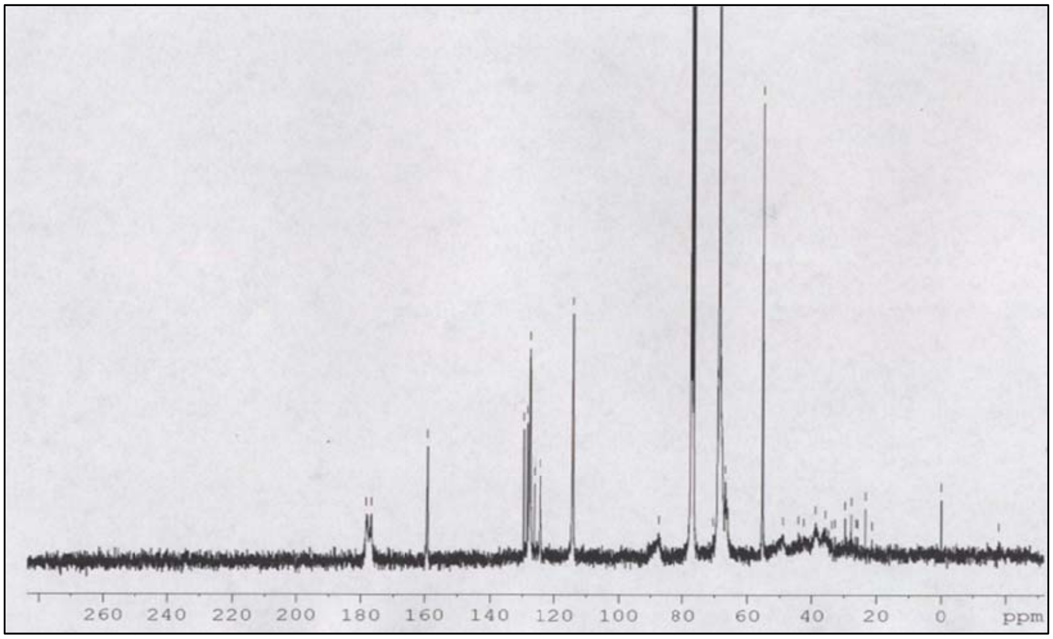


Figure S11.**^{13}C-NMR spectrum of Poly1**

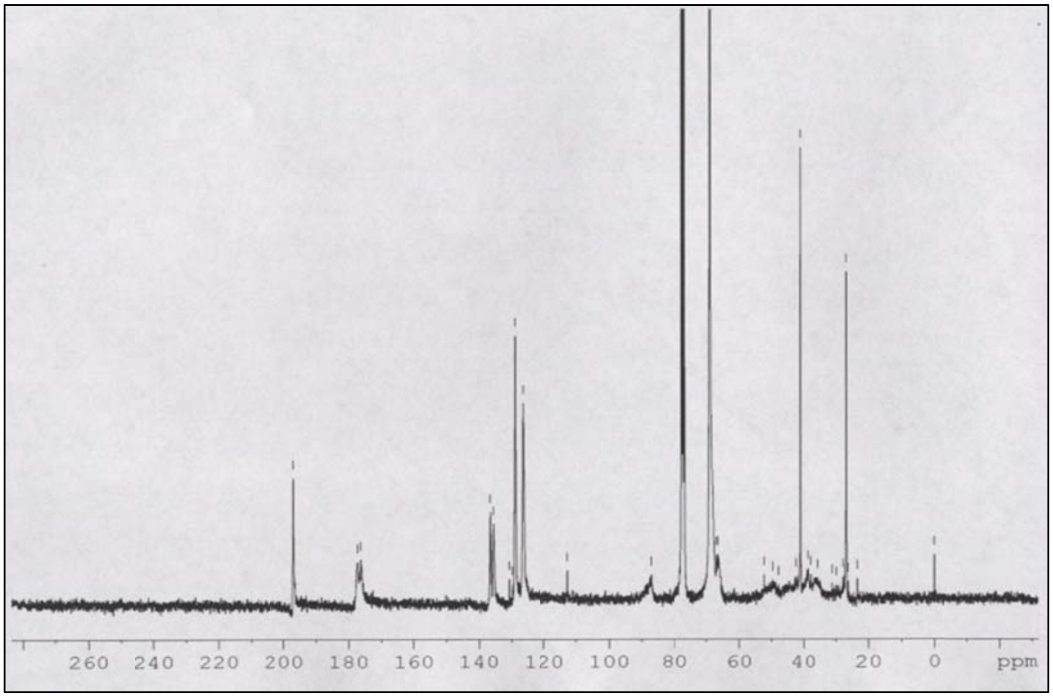


Figure S12. ^{13}C-NMR spectrum of Poly3

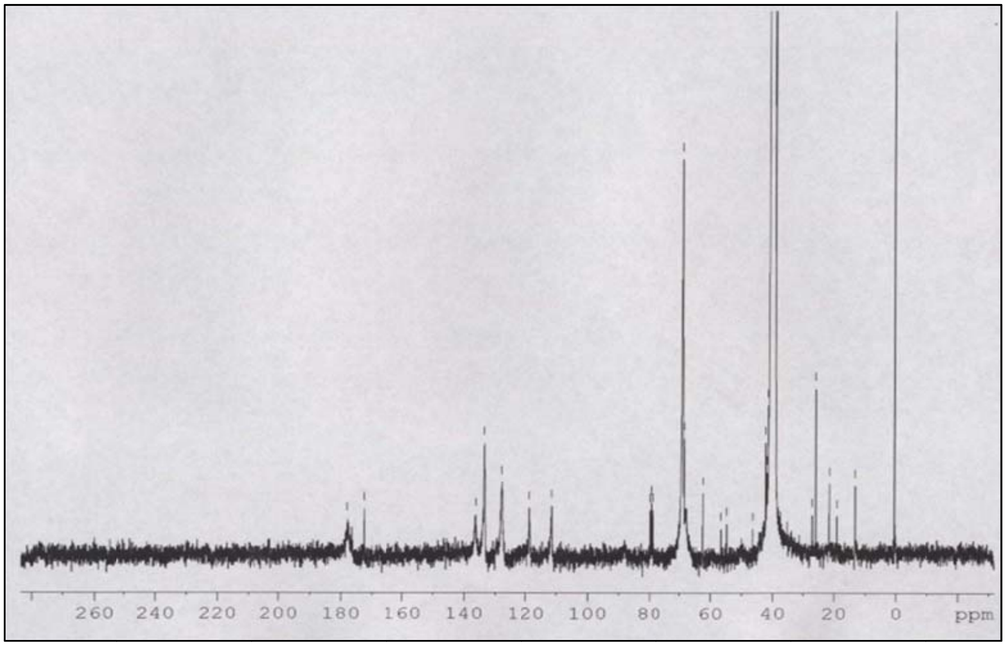


Figure S12. ^{13}C-NMR spectrum of Poly4

Gel permeation chromatography (GPC) measurements

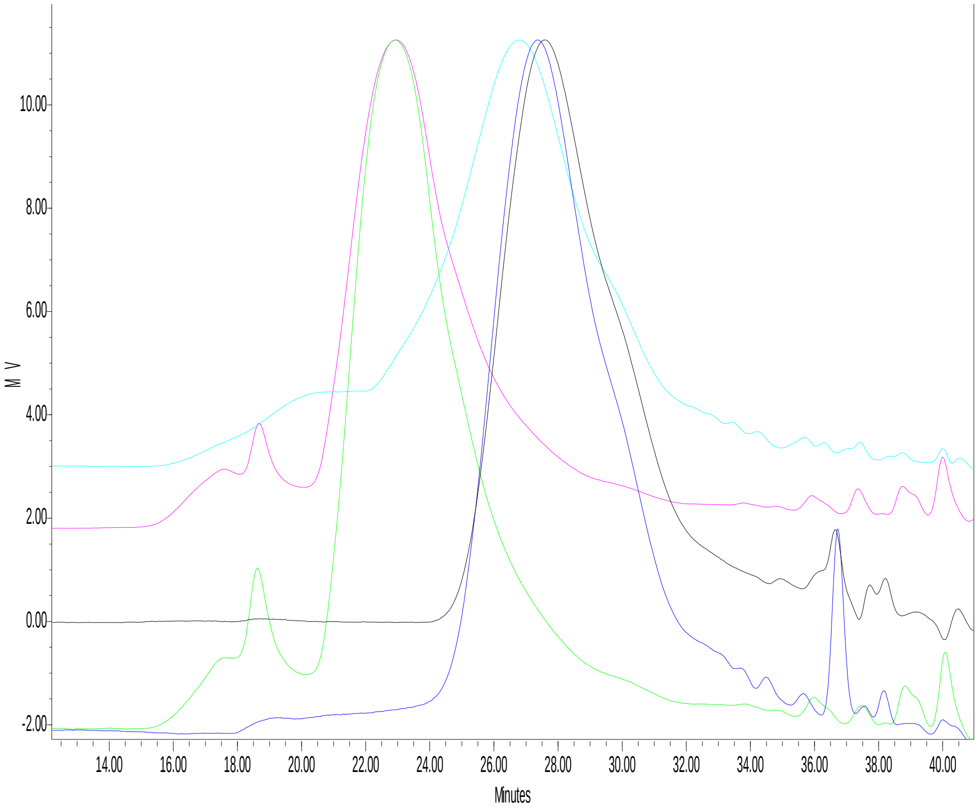


Figure S14. GPC graphs for all copolymers

{Poly1 (-OCH$_3$), Poly2 (-CH$_3$), Poly3 (-COCH$_3$), Poly4 (-CN), Poly5 (-H)}

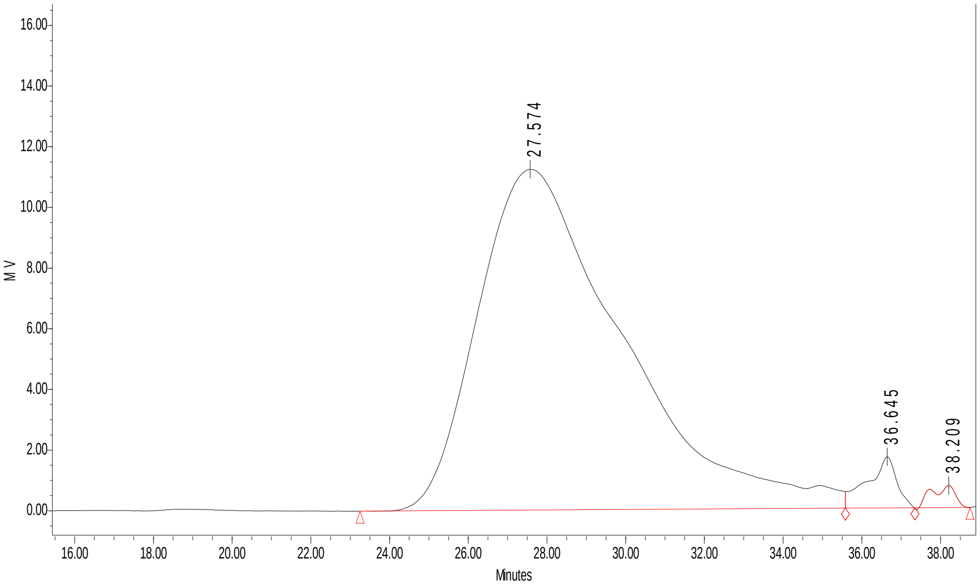


Figure S15. Poly1 GPC (Mn=1478 g/mol, Mw =6350 g/mol)

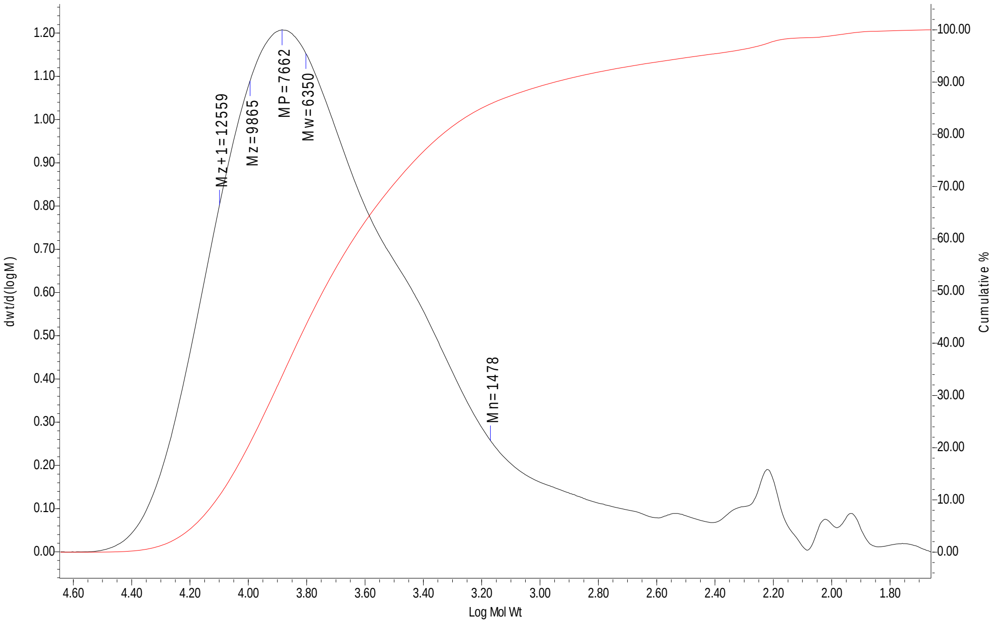


Figure S16. Poly1 Molecular weight distribution

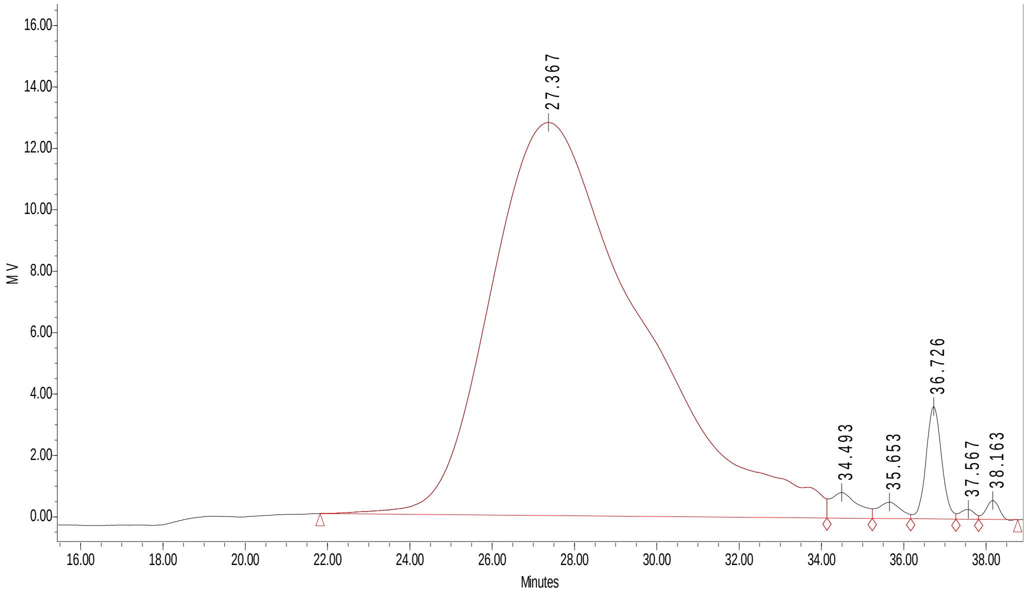


Figure S17. Poly2 GPC (Mn=1867 g/mol, Mw =7295 g/mol)

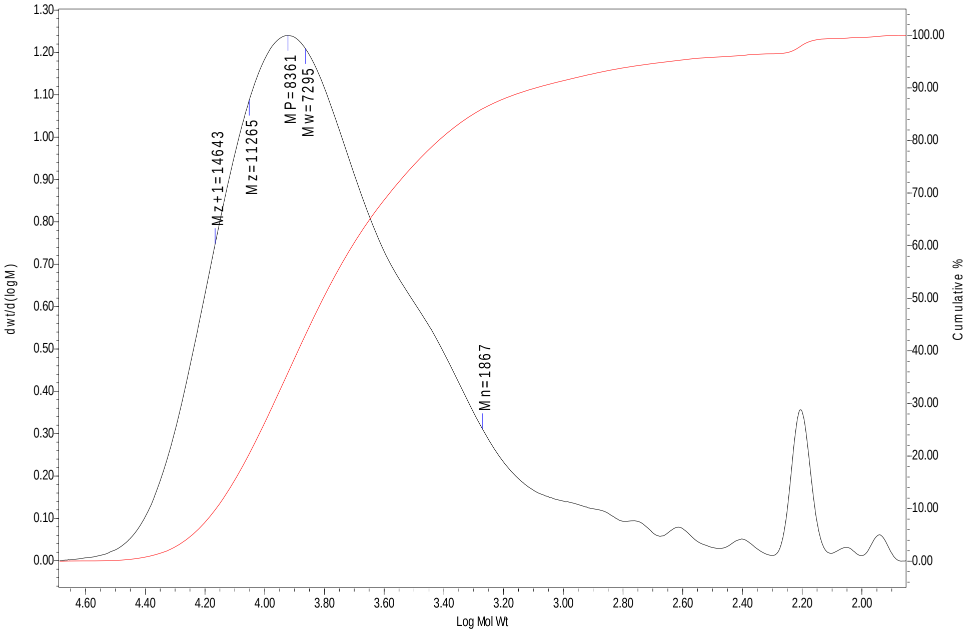


Figure S18. Poly2 Molecular weight distribution

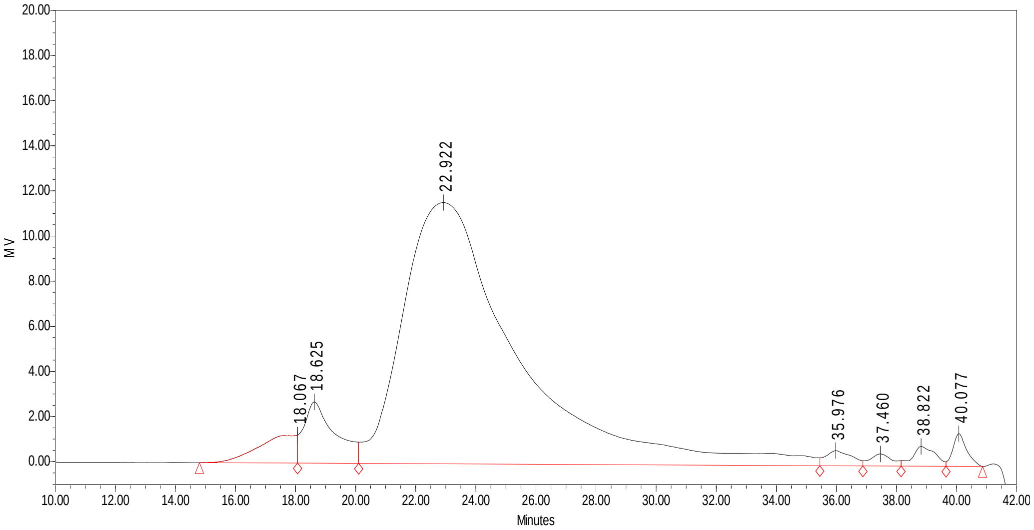


Figure S19. Poly3 GPC (Mn=3447 g/mol, Mw =78829 g/mol)

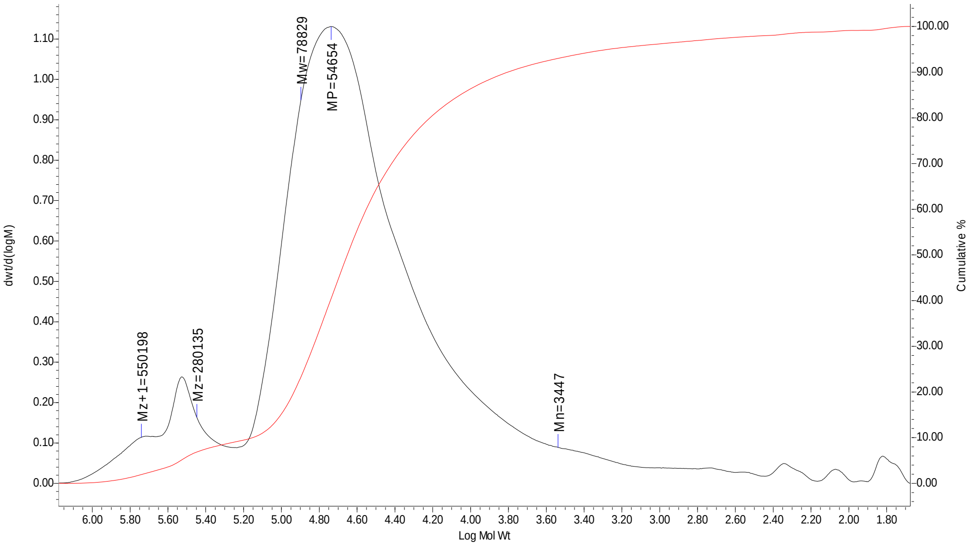


Figure S20. Poly3 Molecular weight distribution

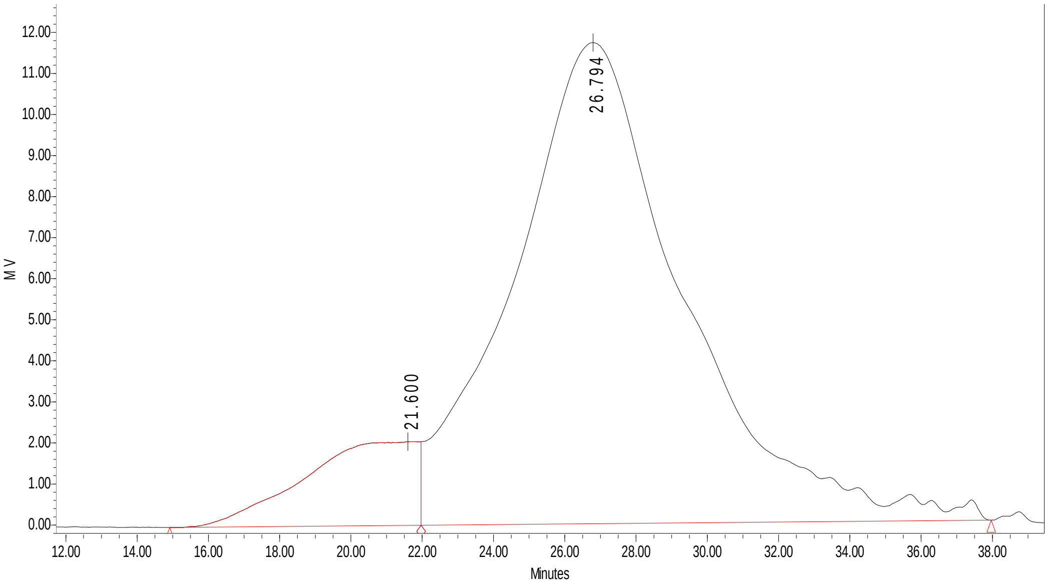


Figure S21. Poly4 GPC (Mn=3774 g/mol, Mw =37796 g/mol)

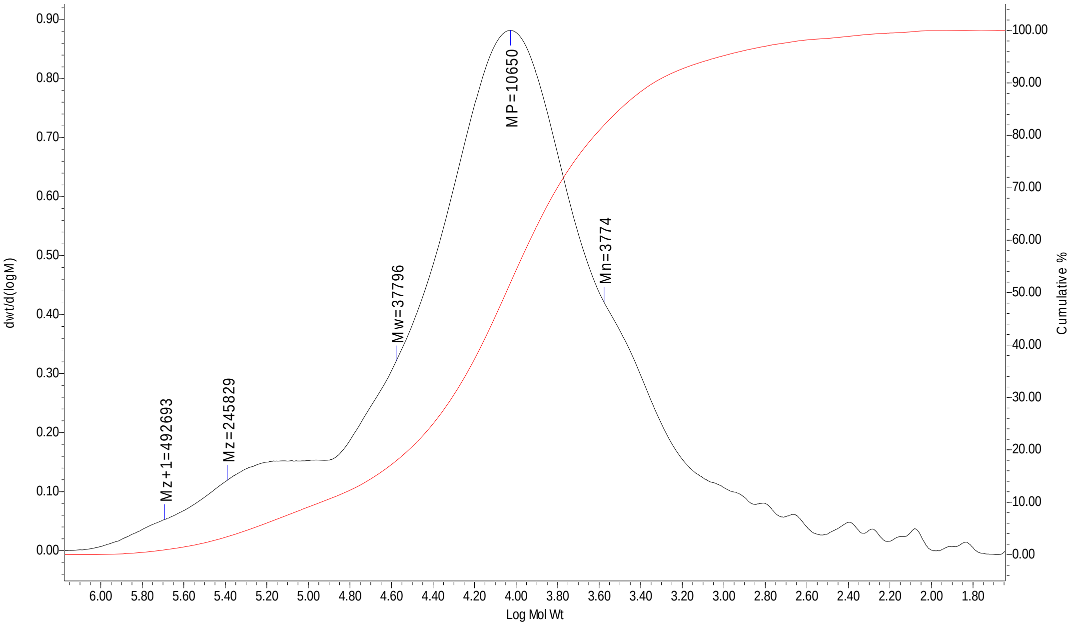


Figure S22. Poly4 Molecular weight distribution

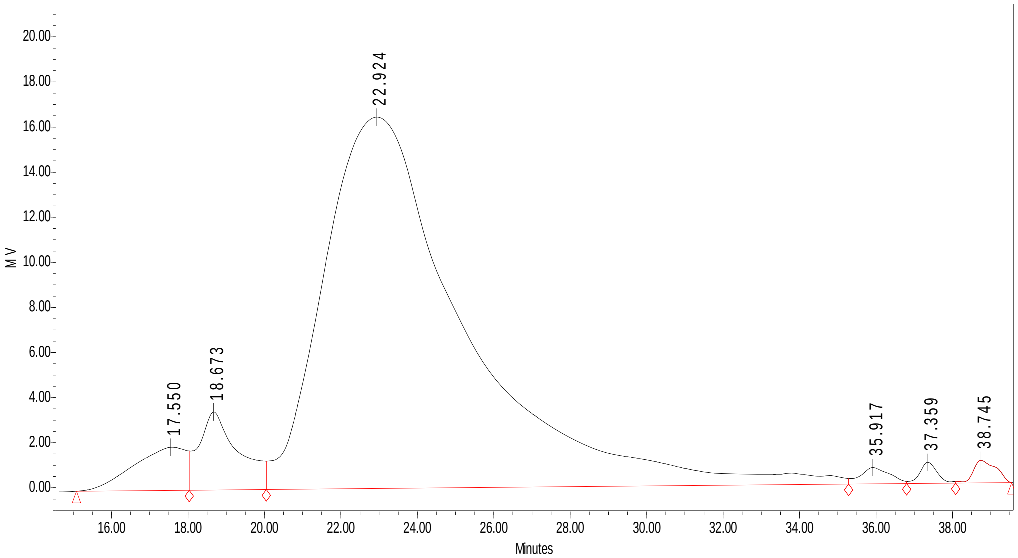


Figure S23. Poly5 GPC (Mn=3454 g/mol, Mw =83596 g/mol)

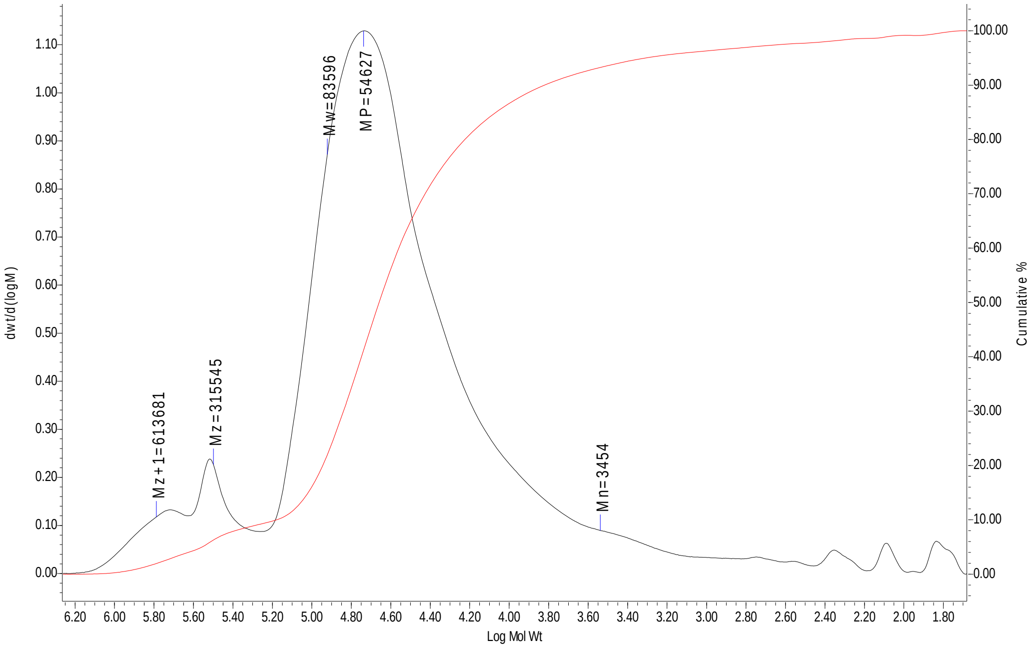


Figure S24. Poly5 Molecular weight distribution

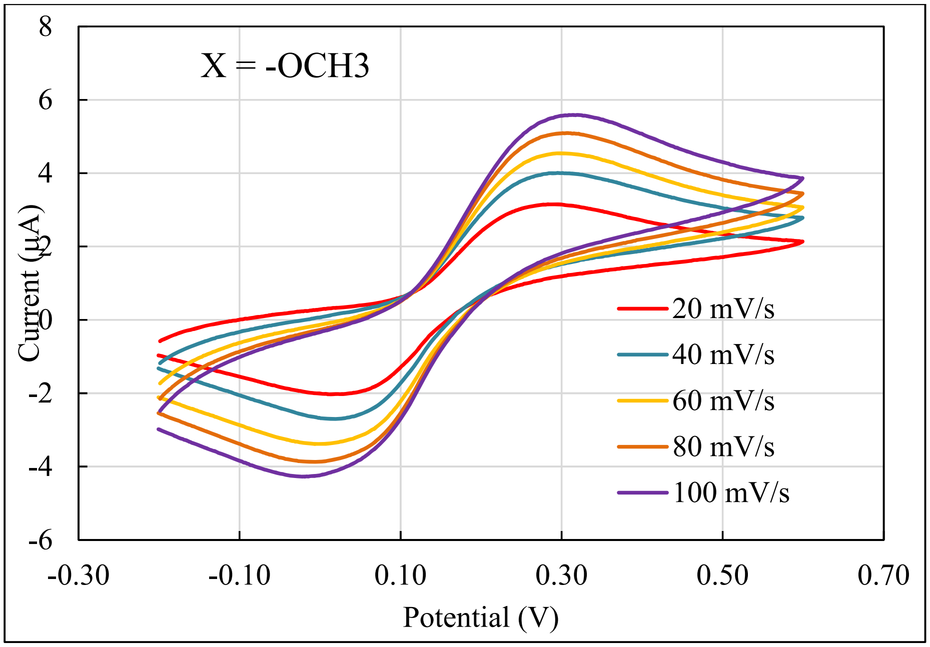


Figure S13. CVs of Poly1 with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and a Ag pseudo reference electrode

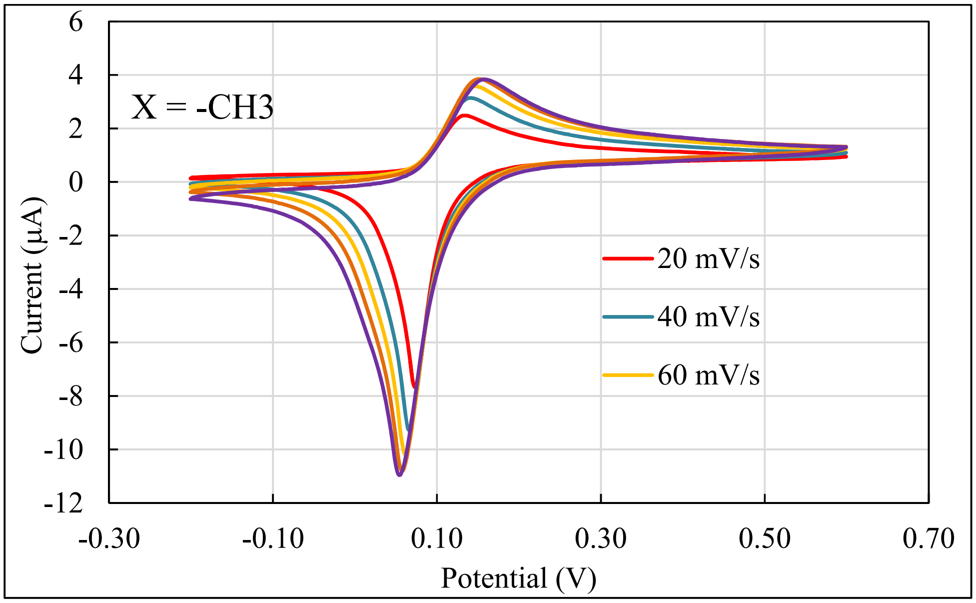


Figure S26. CVs of Poly2 with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and a Ag pseudo reference electrode

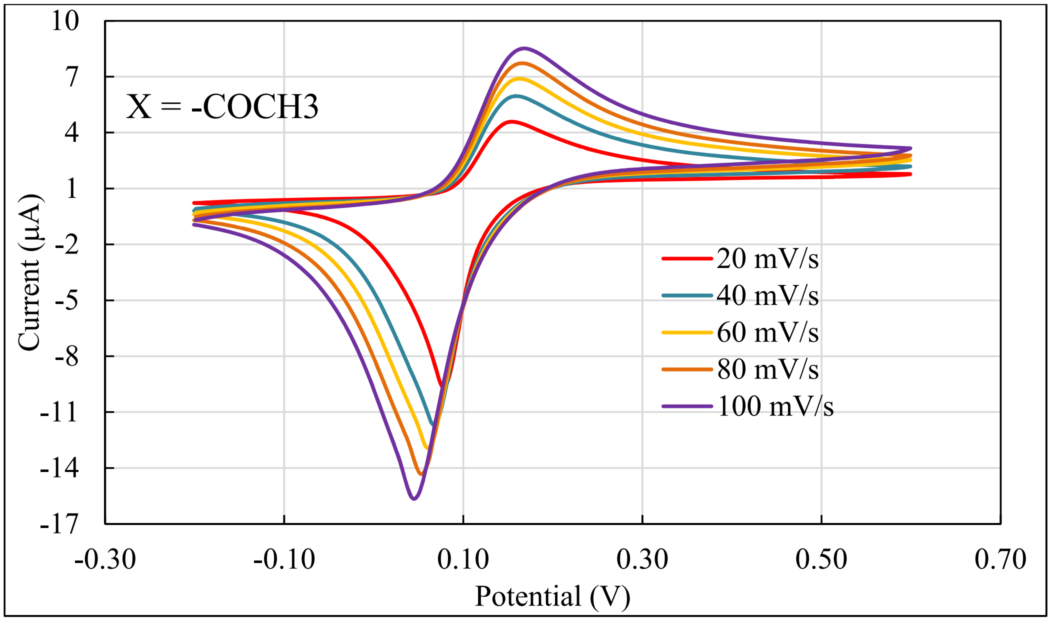


Figure S27. CVs of Poly 3 with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and a Ag pseudo reference electrode

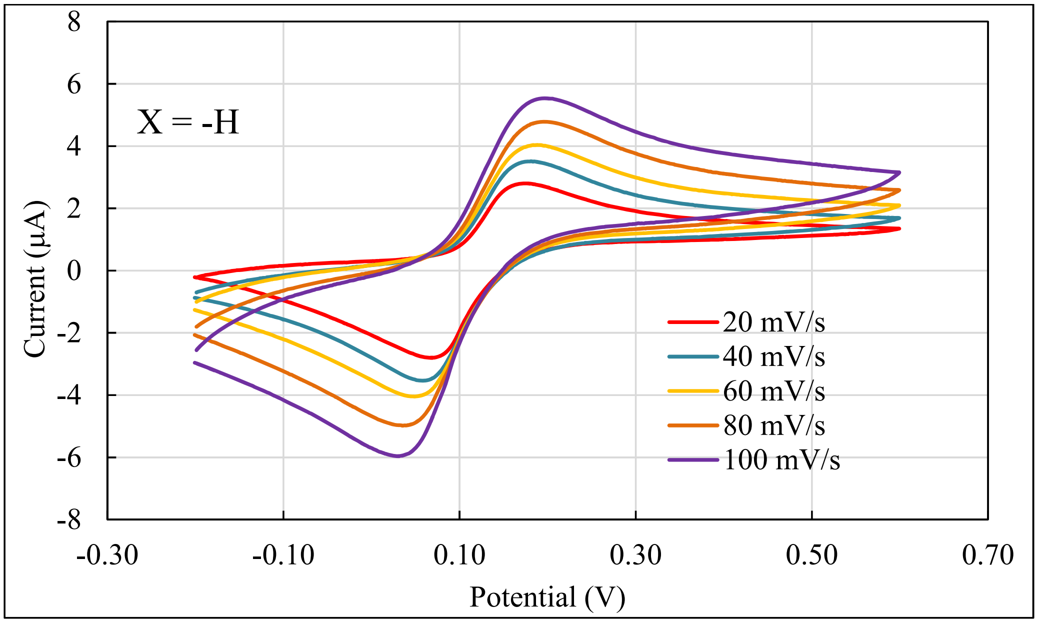


Figure S28. CVs of Poly5 with CH_2Cl_2 and Bu_4NPF_6 at scan rates of 20, 40, 60, 80, and 100 mV/S using Pt working and counter electrodes and a Ag pseudo reference electrode

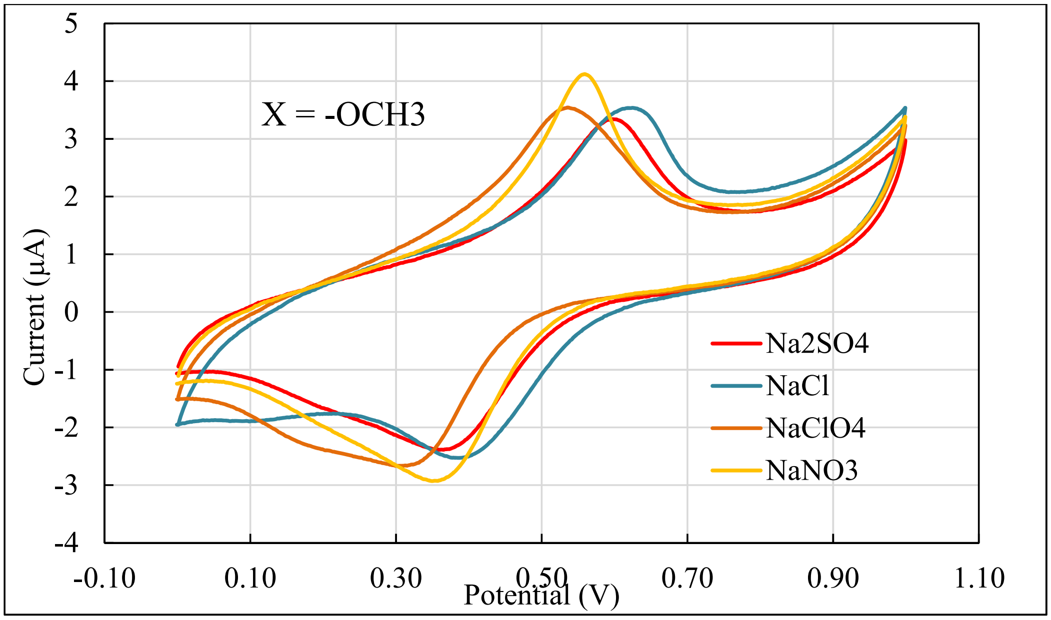


Figure S29. CVs of Poly1 in H_2O with various aqueous electrolytes (Na_2SO_4, NaCl, $NaClO_4$, $NaNO_3$)

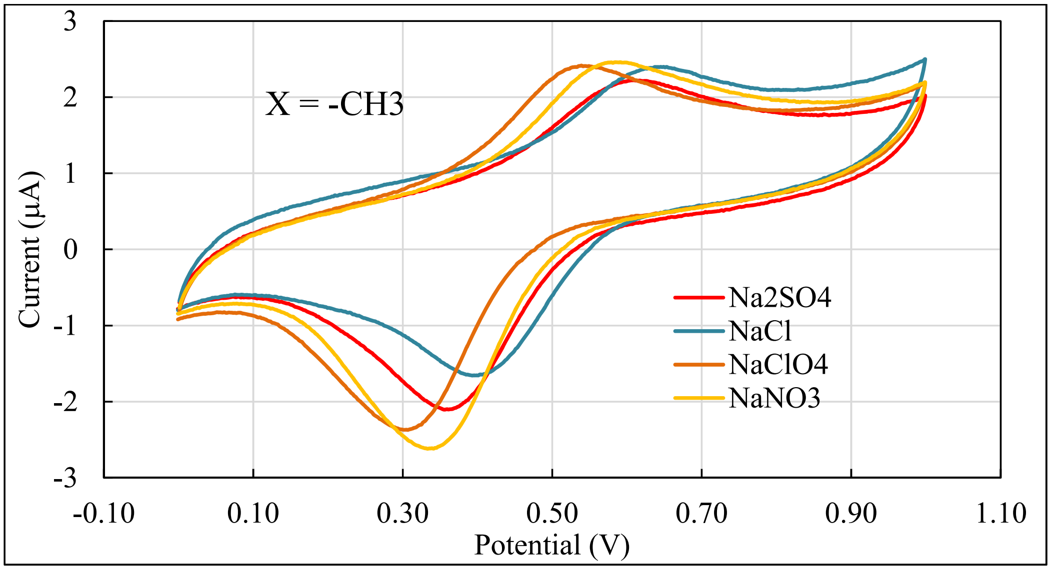


Figure S30. CVs of Poly2 in H_2O with various aqueous electrolytes (Na_2SO_4, NaCl, $NaClO_4$, $NaNO_3$)

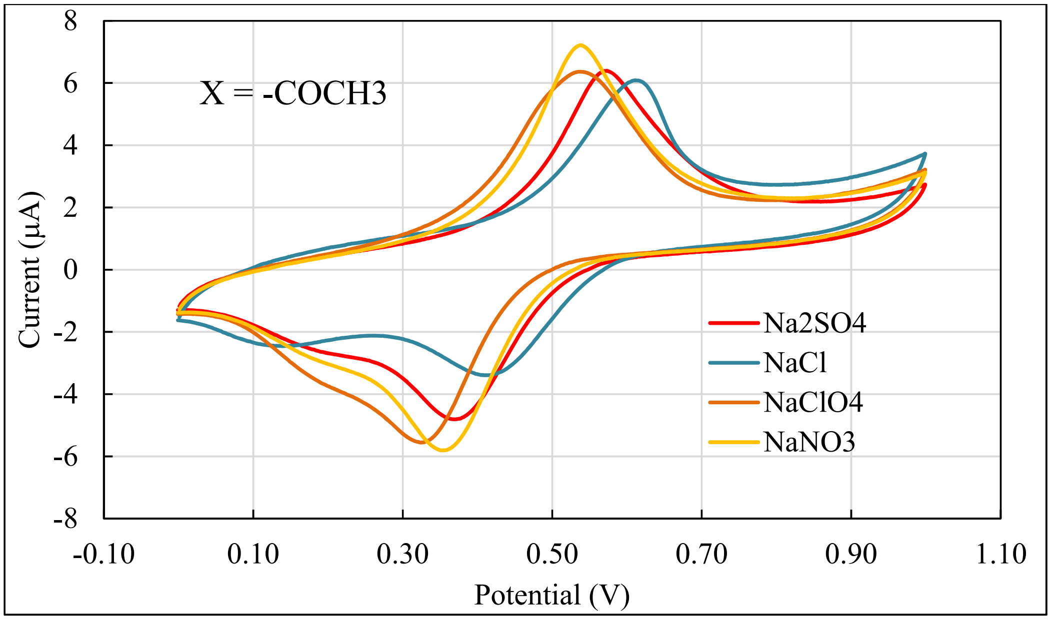


Figure S31. CVs of Poly3 in H_2O with various aqueous electrolytes (Na_2SO_4, NaCl, $NaClO_4$, $NaNO_3$)

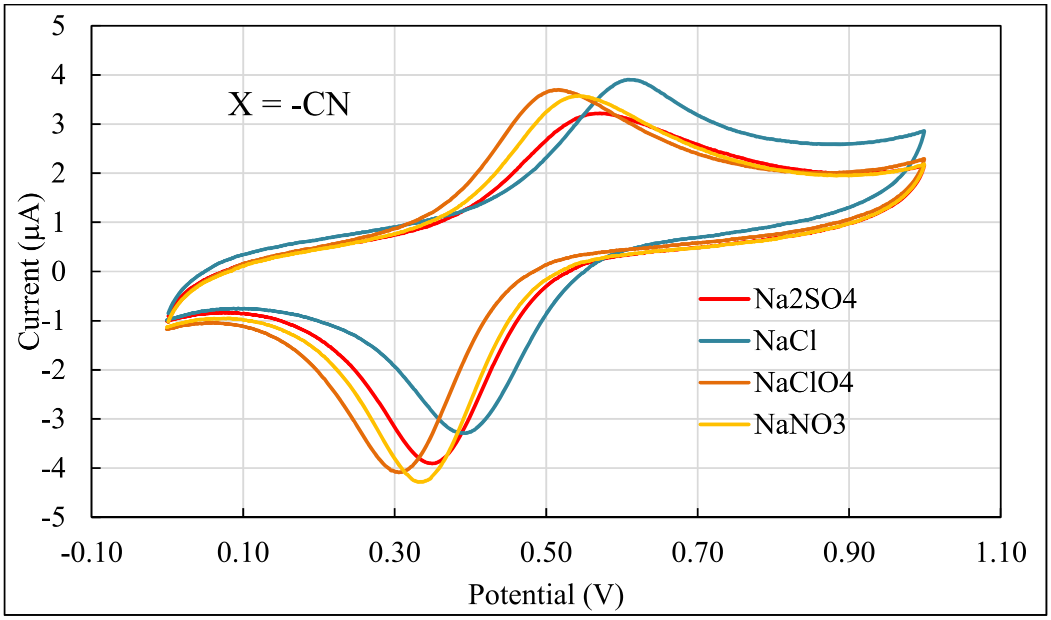


Figure S32. CVs of Poly4 in H_2O with various aqueous electrolytes (Na_2SO_4, NaCl, $NaClO_4$, $NaNO_3$)

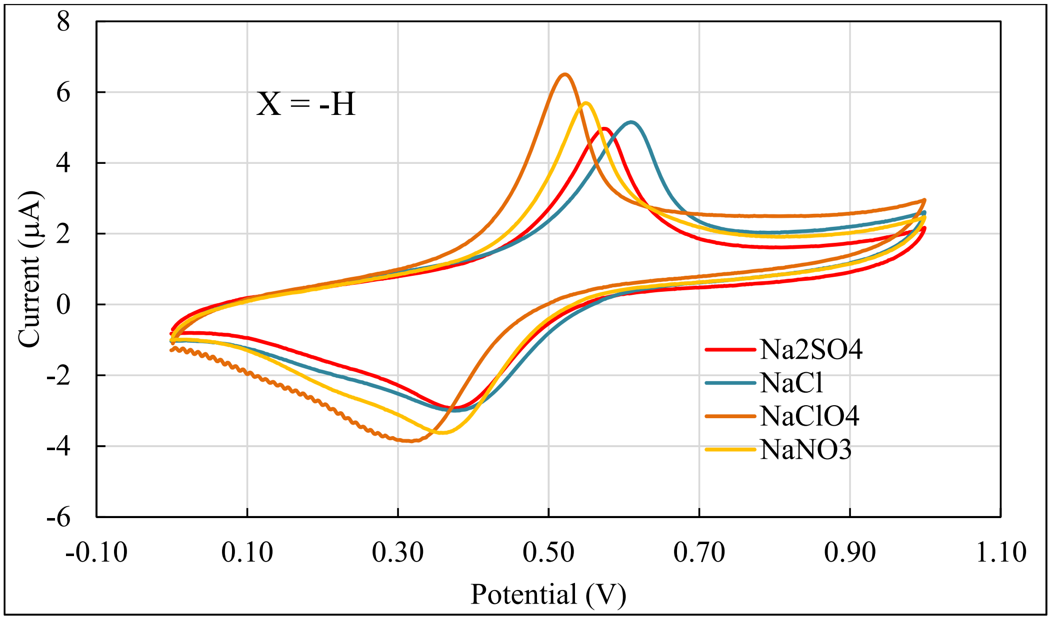


Figure S33. CVs of Poly5 in H_2O with various aqueous electrolytes (Na_2SO_4, NaCl, $NaClO_4$, $NaNO_3$)

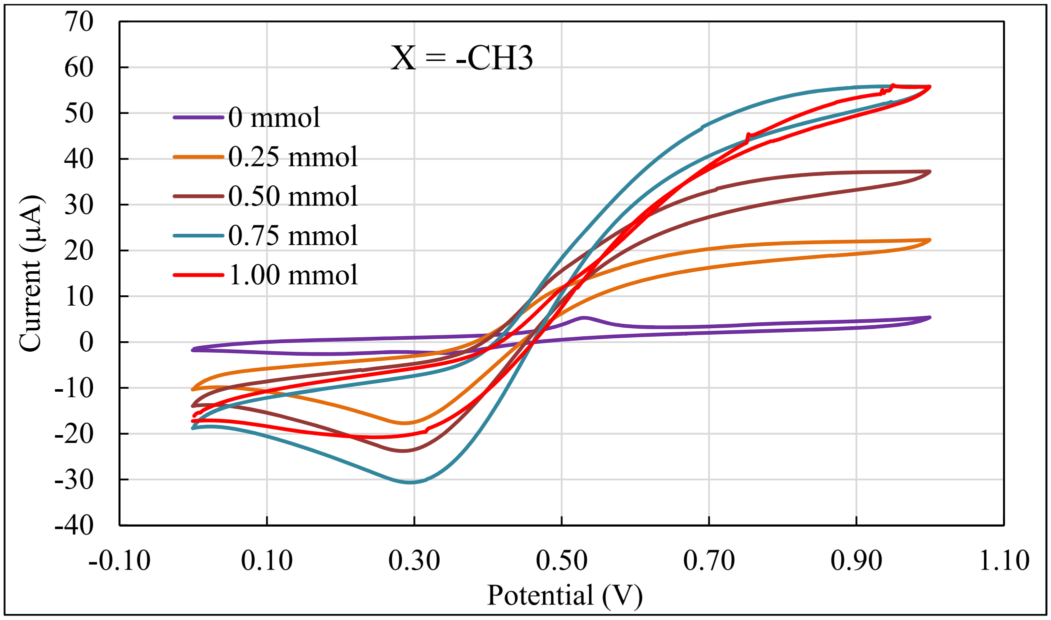


Figure S34. CVs of chemical modified electrodes on cast films of Poly2 on Pt electrode into aqueous solution ($NaClO_4$) with various concentrations of H_2O_2

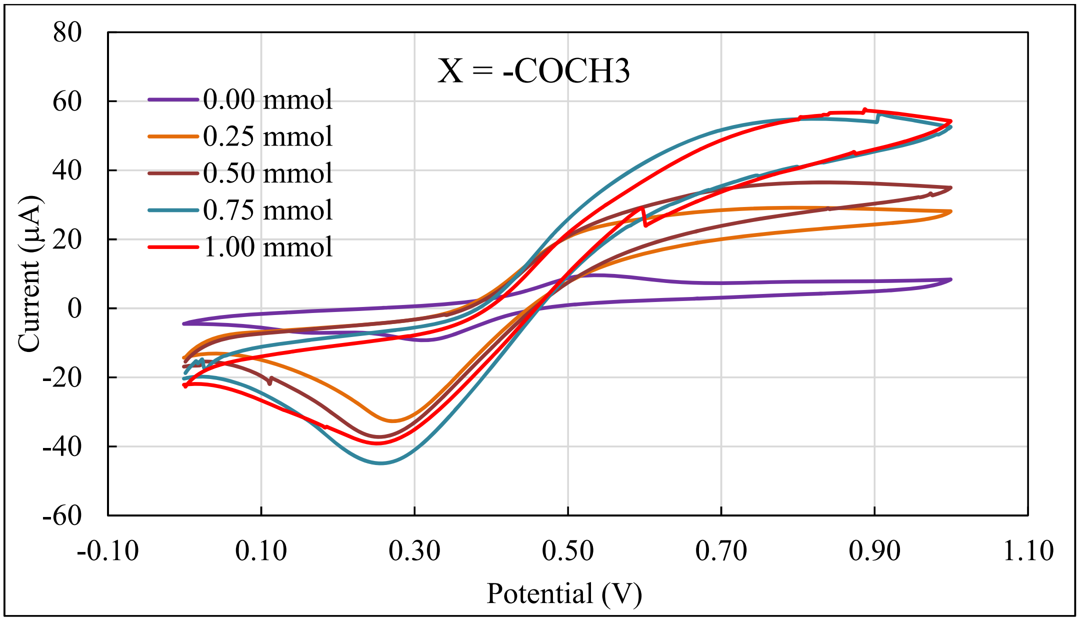


Figure S35. CVs of chemical modified electrodes on cast films of Poly3 on Pt electrode into aqueous solution ($NaClO_4$) with various concentrations of H_2O_2

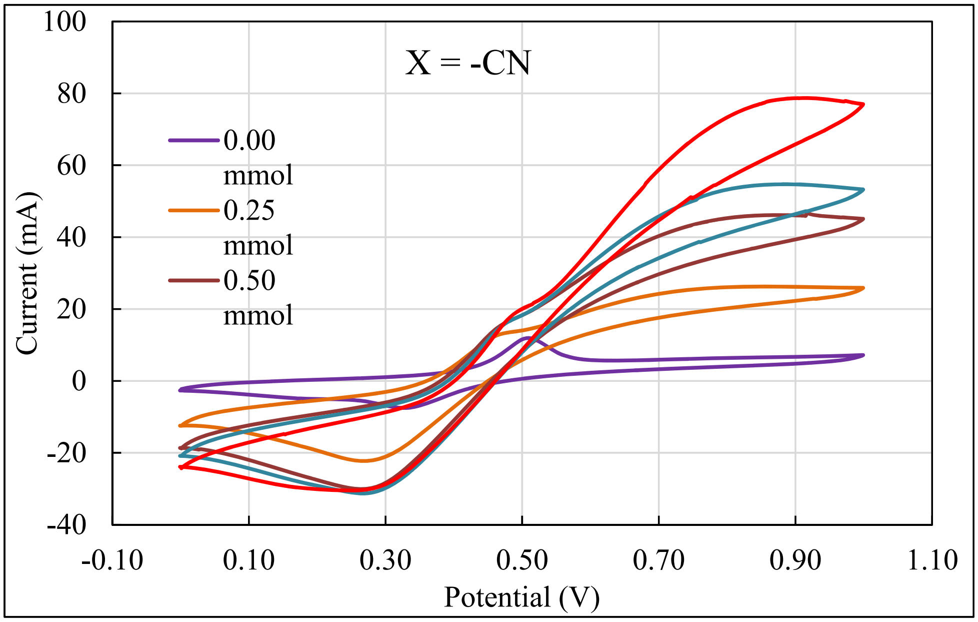


Figure S36. CVs of chemical modified electrodes on cast films of Poly4 on Pt electrode into aqueous solution ($NaClO_4$) with various concentrations of H_2O_2

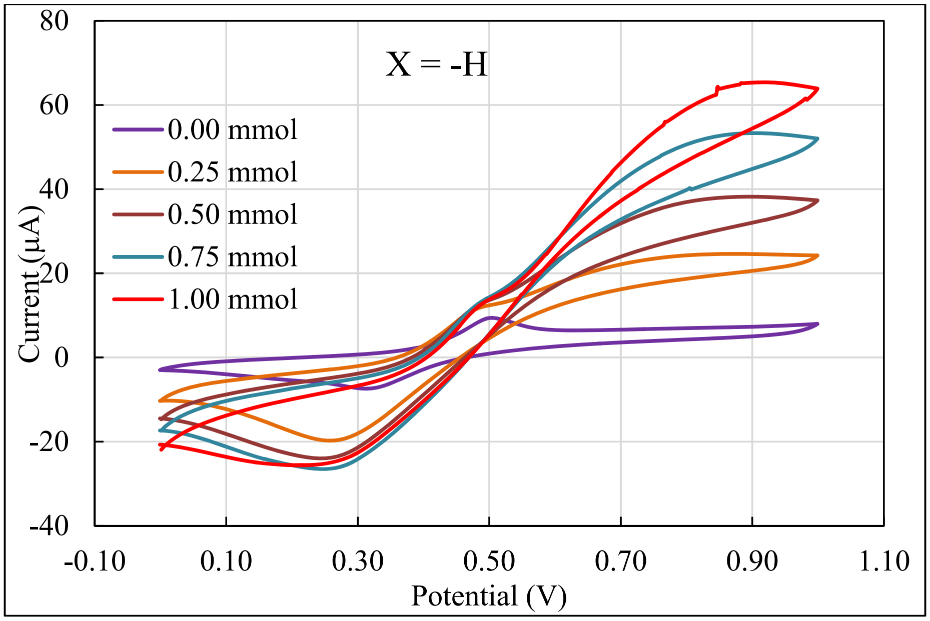


Figure S37. CVs of chemical modified electrodes on cast films of Poly5 on Pt electrode into aqueous solution ($NaClO_4$) with various concentrations of H_2O_2

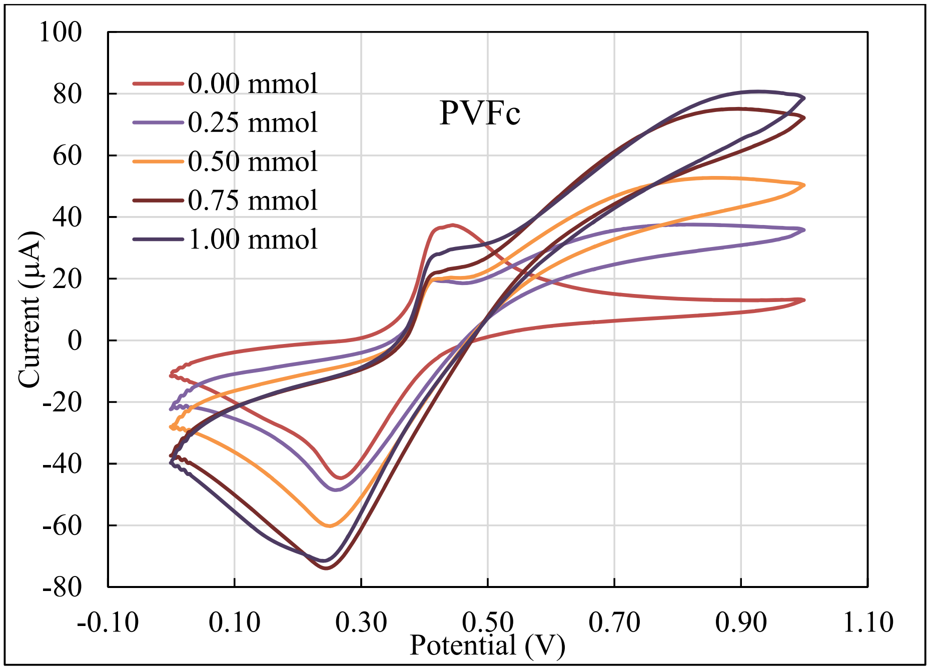


Figure S38. CVs of chemical modified electrodes on cast films of PVFc on Pt electrode into aqueous solution ($NaClO_4$) with various concentrations of H_2O_2

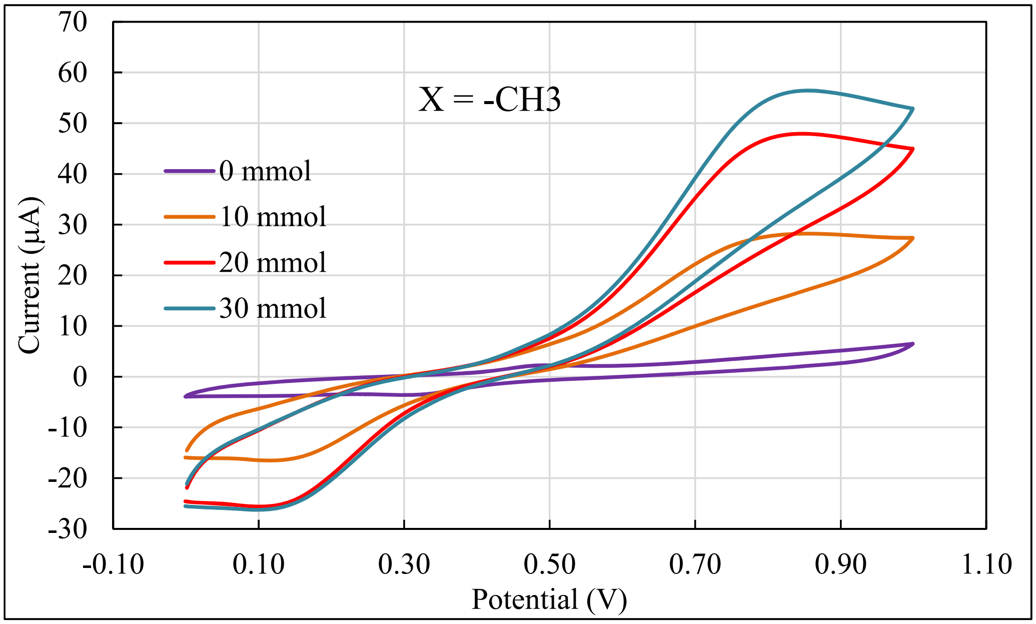


Figure S39. CVs of chemical modified electrodes on cast films of Poly2 on Pt electrode into aqueous solution ($NaClO_4$) with Dopamine at various scans.

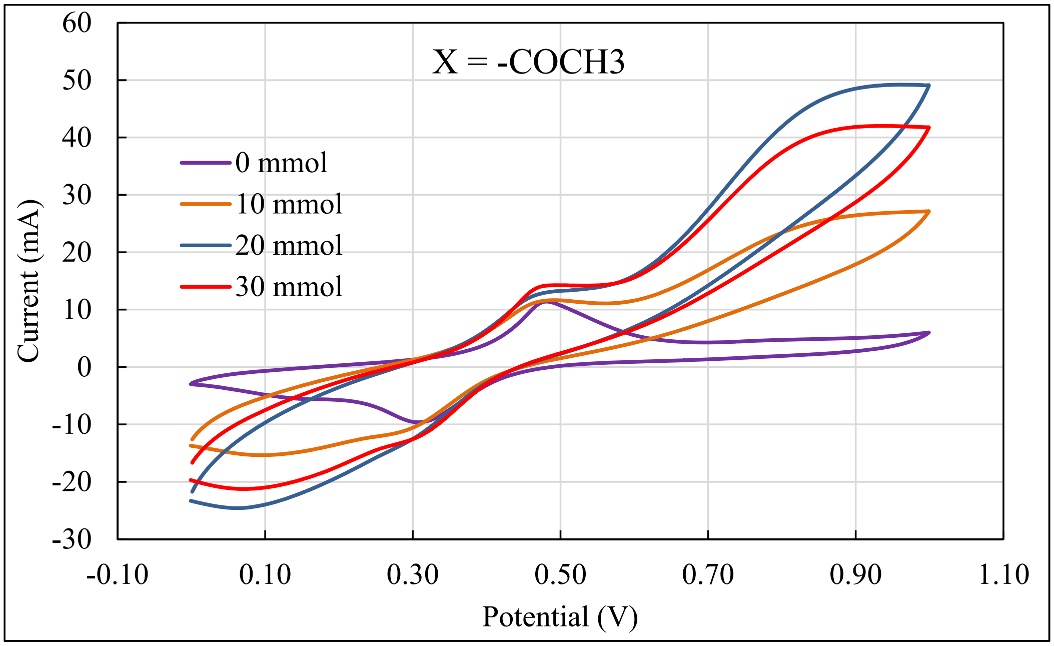


Figure S40. CVs of chemical modified electrodes on cast films of Poly3 on Pt electrode into aqueous solution ($NaClO_4$) with Dopamine at various scans.

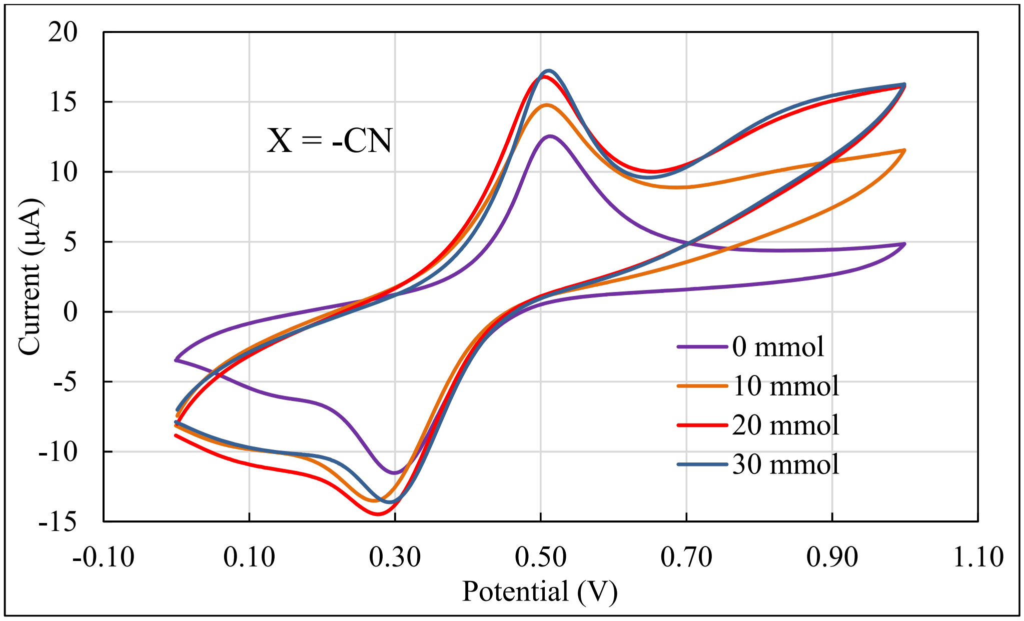


Figure S41. CVs of chemical modified electrodes on cast films of Poly4 on Pt electrode into aqueous solution ($NaClO_4$) with Dopamine at various scans.

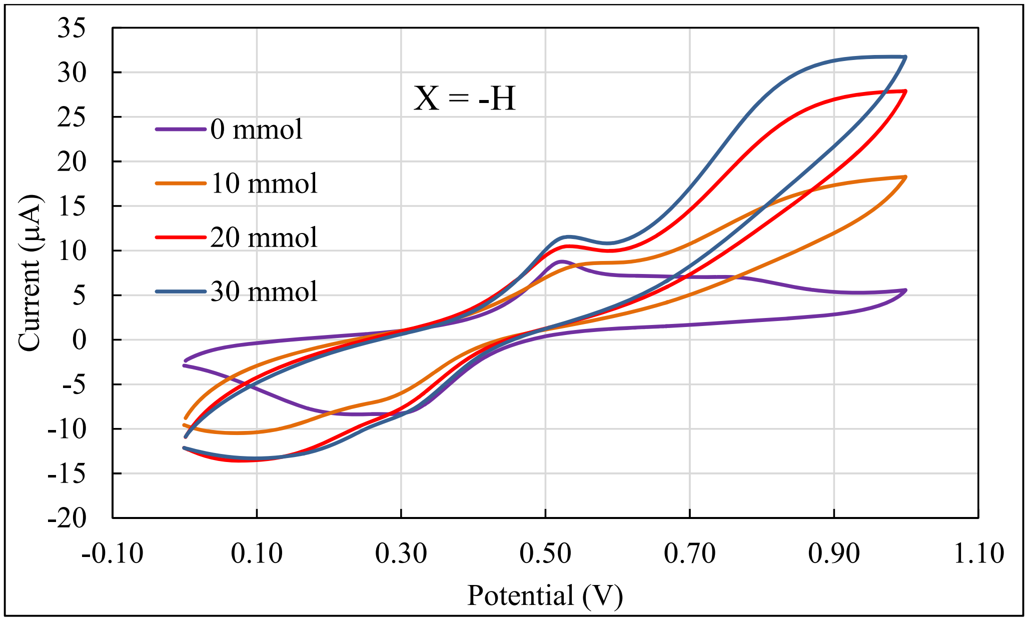


Figure S42. CVs of chemical modified electrodes on cast films of Poly5 on Pt electrode into aqueous solution ($NaClO_4$) with Dopamine at various scans.

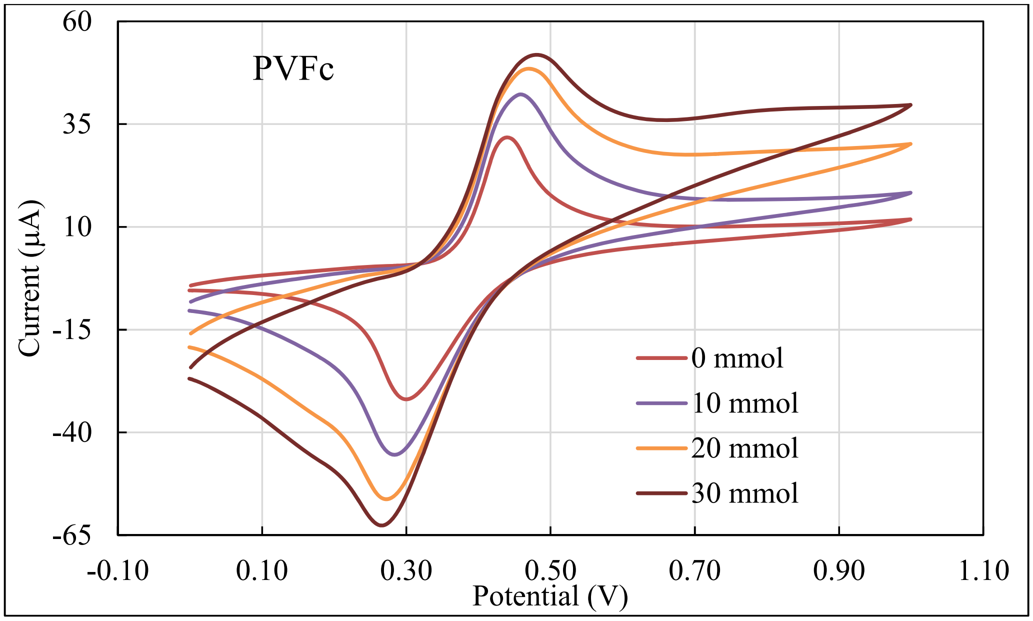


Figure S43. CVs of chemical modified electrodes on cast films of PVFc on Pt electrode into aqueous solution ($NaClO_4$) with Dopamine at various scans.

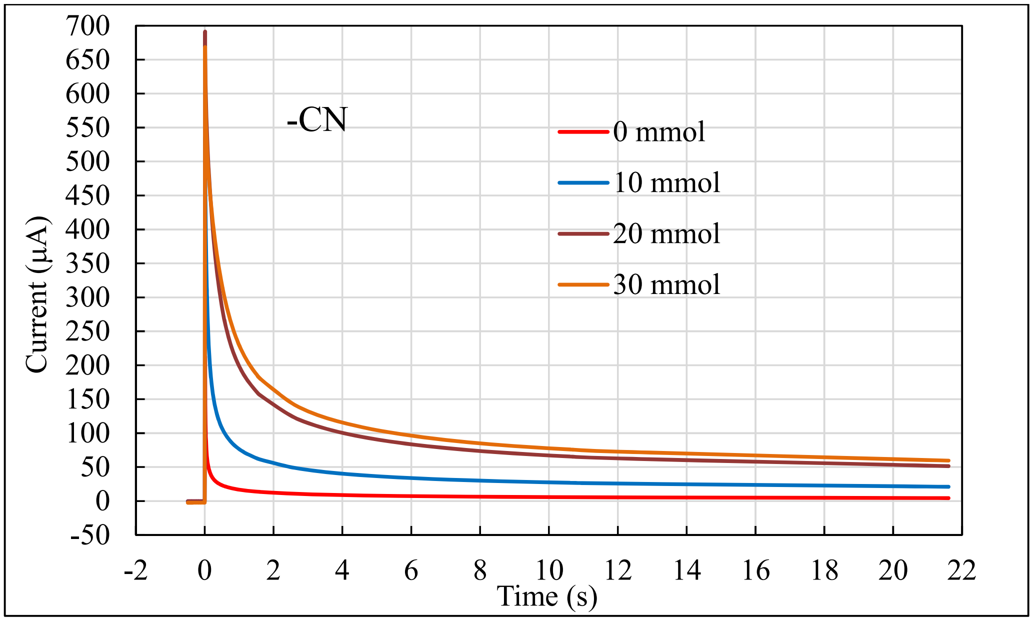


Figure S44. Poly4 (X= -CN) with Dopamine

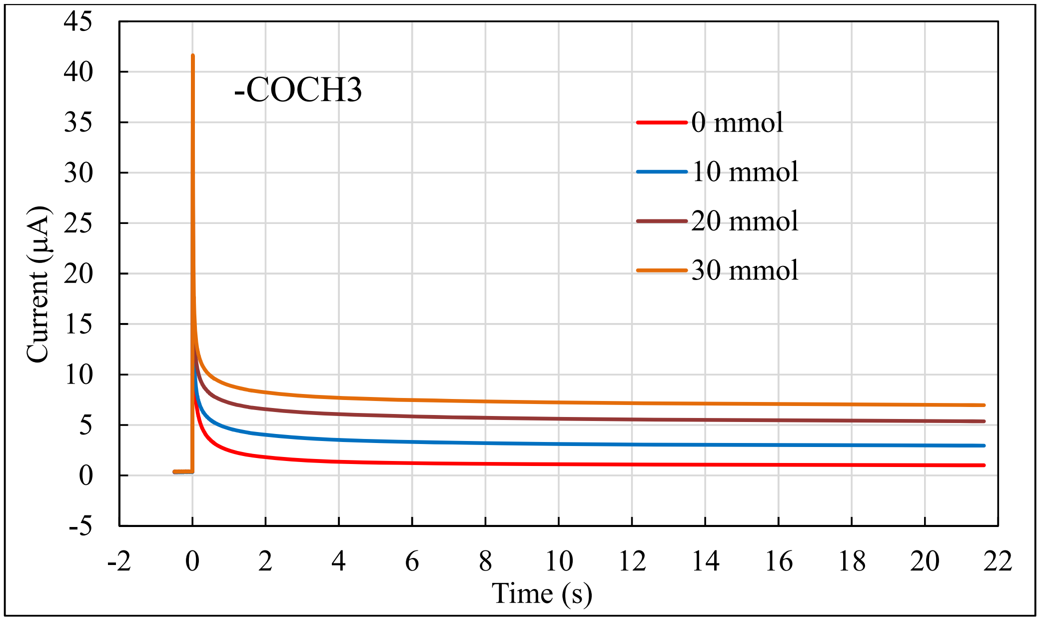


Figure S45. CA of Poly3 (X= -COCH$_3$) with Dopamine

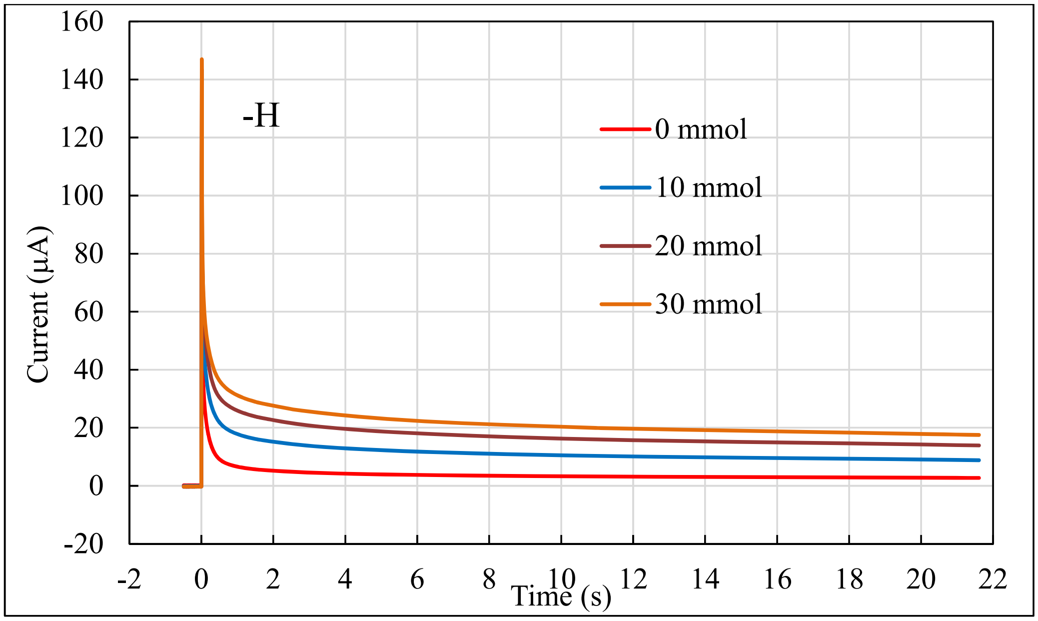


Figure S46. CA of Poly4 (X= -H) with Dopamine

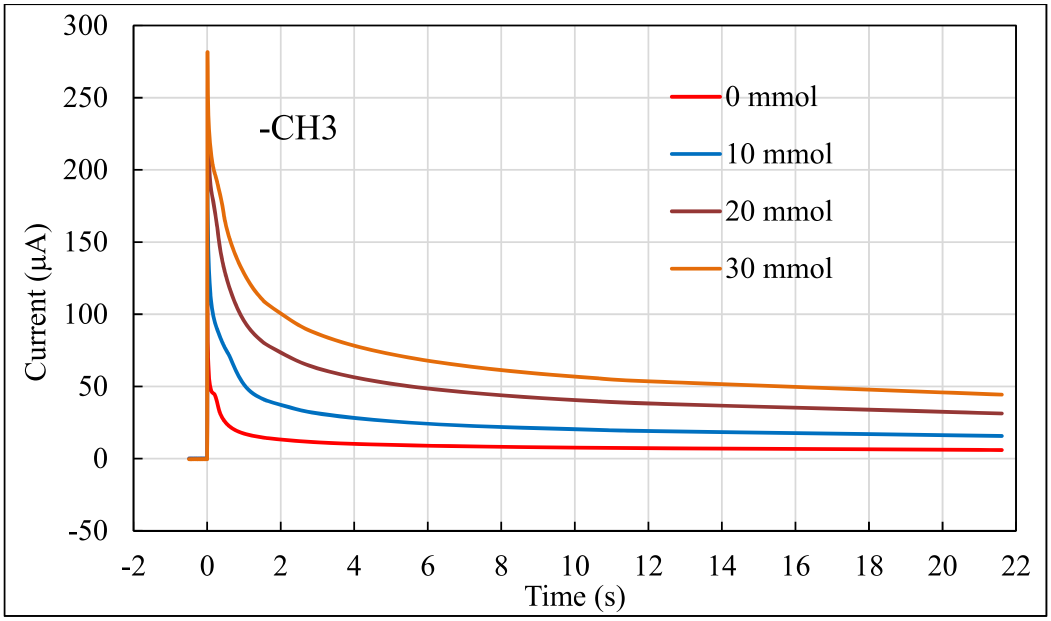
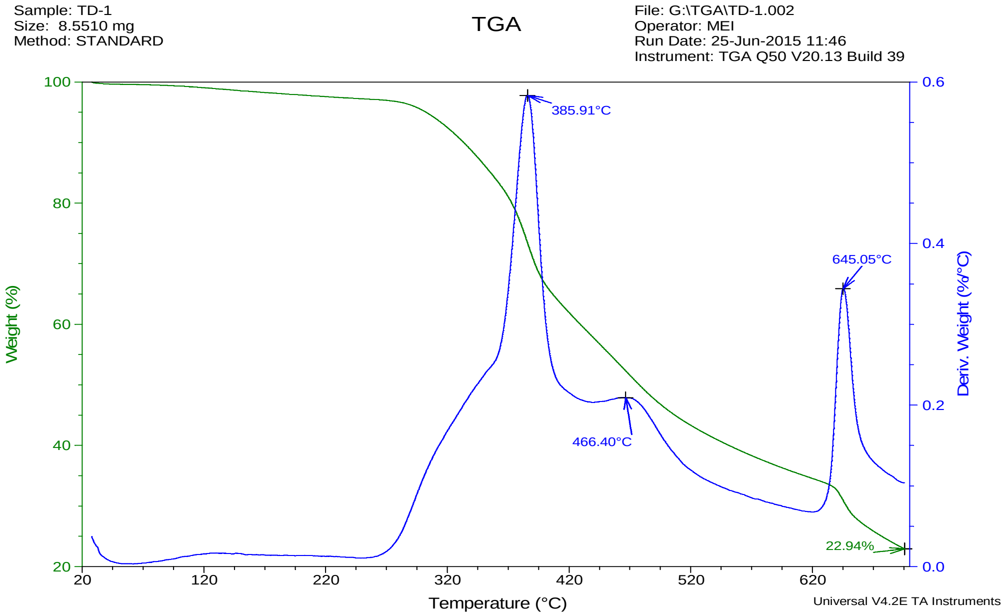


Figure S47. CA of Poly2 (X= -CH$_3$) with Dopamine



Sample: TD-1
Size: 8.5510 mg
Method: STANDARD

File: G:\TGA\TD-1.002
Operator: MEI
Run Date: 25-Jun-2015 11:46
Instrument: TGA Q50 V20.13 Build 39

Figure S48. TGA of Poly1: X=OCH_3

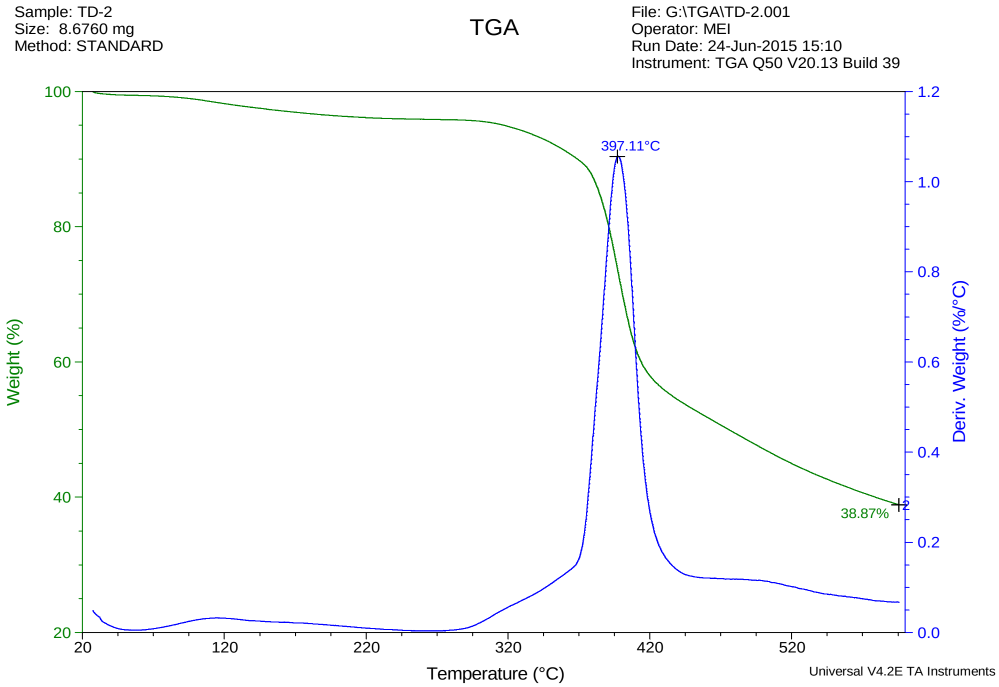


Figure S49. TGA of Poly2: X=CH_3

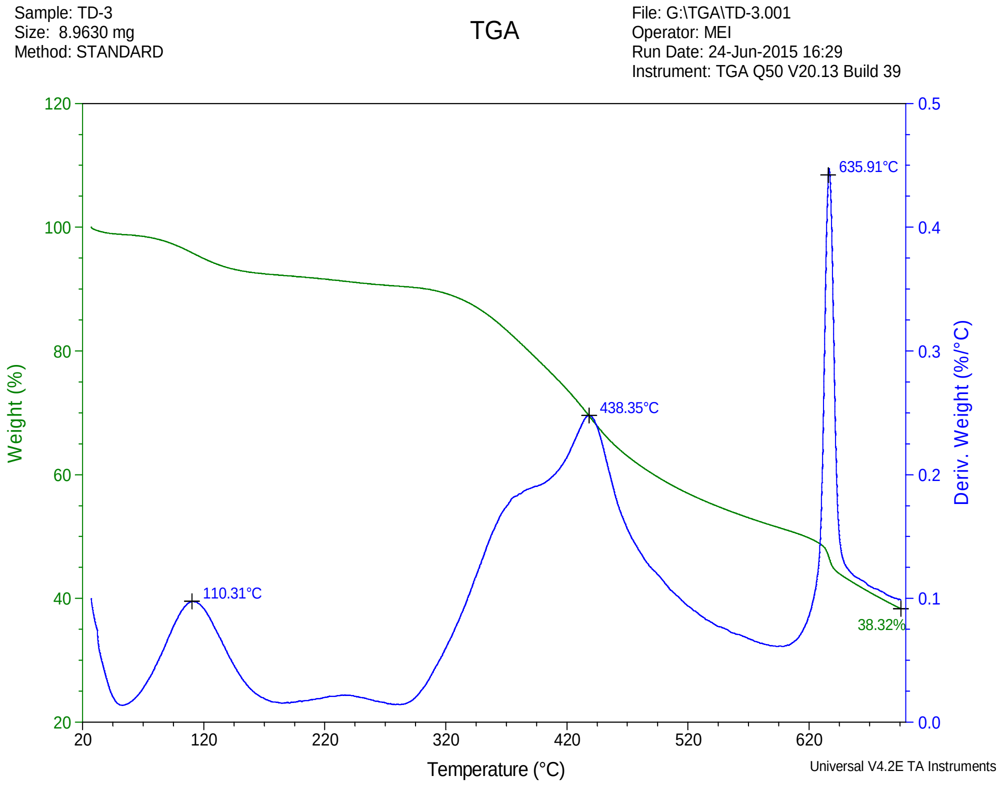


Figure S50. TGA of Poly3: X=$COCH_3$

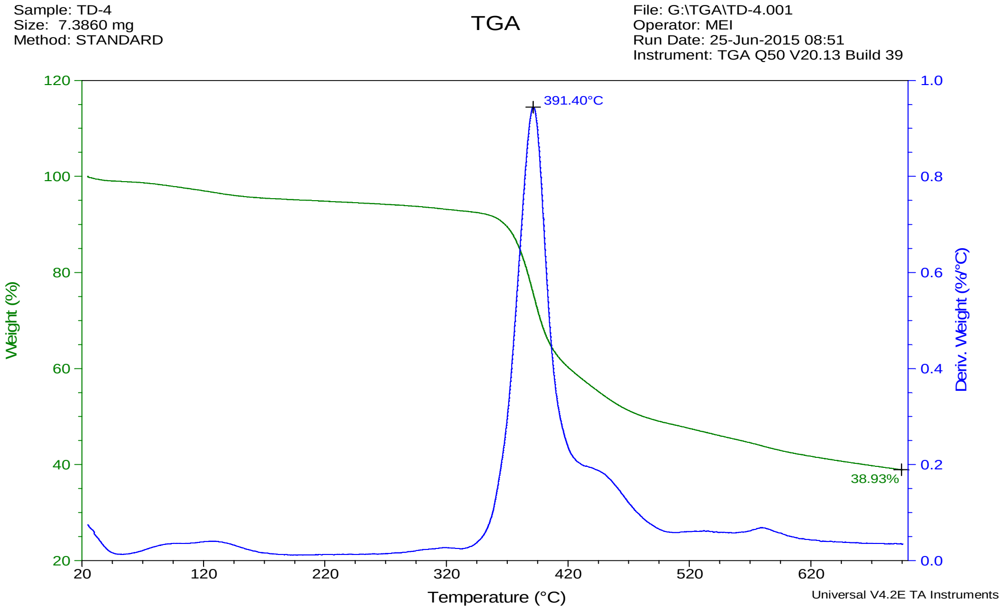


Figure S51. TGA of Poly4: X= CN

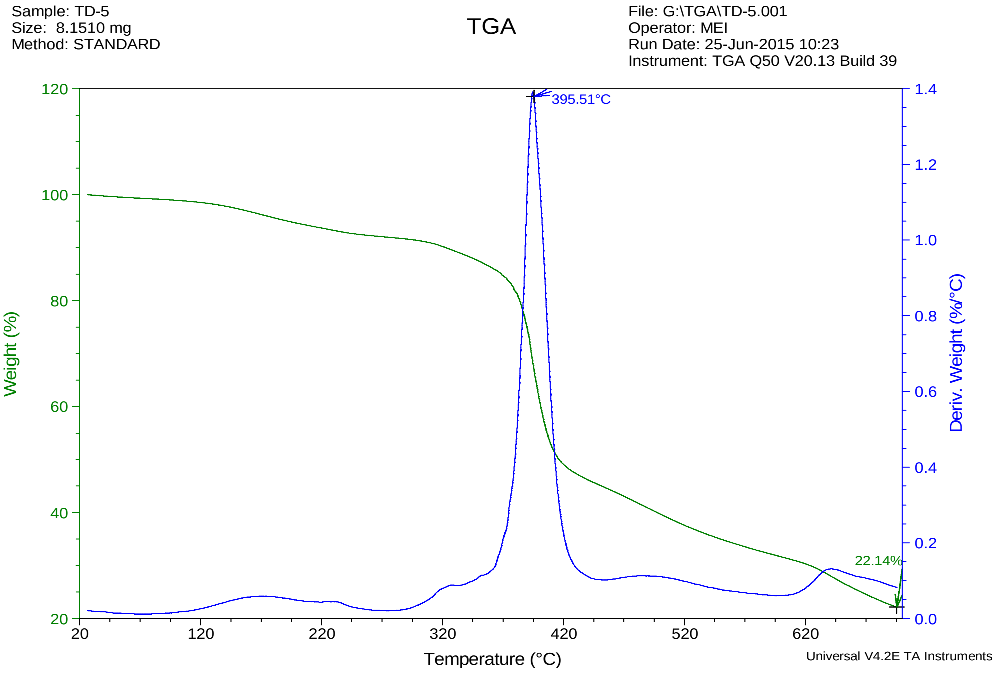


Figure S52. TGA of Poly5: X= H