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ELECTROCHEMICAL STUDIES OF POLY 3-(4-METHOXYPHENYL)[5] FERROCENOPHANE-1,5-DIMETHYLENE AND COPOLYMERS WITH STYRENE AND N-PHENYLMALEIMIDE

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

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ELECTROCHEMICAL STUDIES OF POLY(3-(4-METHOXYPHENYL)[5] FERROCENOPHANE-1,5-DIMETHYLENE AND COPOLYMERS WITH STYRENE AND N-PHENYLMALEIMIDE

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ELECTROCHEMICAL STUDIES OF POLY(3-(4-METHOXYPHENYL)[5] FERROCENOPHANE-1,5-DIMETHYLENE AND COPOLYMERS WITH STYRENE AND N-PHENYLMALEIMIDE

An Abstract of Thesis by
Niyati Arora

Ferrocene is an organometallic compound in which an iron atom is sandwiched between two cyclopentadienyl rings. Ferrocene containing polymers receive a considerable amount of research because of their known chemistry, stable redox reactions and useful electrical systems. Noteworthy are their uses as electrode coatings, electro-catalysts and as an anode in battery applications. In this research, the synthesis and polymerization of a ferrocenophane diene is reported. Using a Wittig reaction 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene was synthesized from 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione. The homopolymer and copolymers with styrene and N-phenylmaleimide were synthesized via free radical polymerization from 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene using AIBN as the initiator. These polymers were characterized using ^{1}H-NMR, ^{13}C-NMR and FTIR spectroscopy and spectra for each polymer were consistent with the corresponding structure. UV-Vis spectra of each polymer showed an absorbance at 440nm which is consistent with a [3] ferrocenophane. Cyclic voltammetric studies revealed the chemical reversibility of the polymers. Thermogravimetric results showed their thermal stability to approximately 390°C.

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LIST OF ABBREVIATIONS

CP- Cyclopentadienyl
NMR-Nuclear Magnetic Resonance
UV-Vis- Ultraviolet-visible spectroscopy
IR-Infrared spectroscopy
CV- Cyclic Voltammetry
Ipa- Peak Anodic Current
Ipc- Peak Cathodic Current
HOMO- Highest Occupied Molecular Orbital
LUMO- Lowest Occupied Molecular Orbital
Mw-Weight Average Molecular weight
FT-IR- Fourier Transformed-Infrared Spectroscopy
Homo- Homopolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene
Ph-Ml- Copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with N-Phenylmaleimide
St- Copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with Styrene
Eox- Oxidation potential
Ered- Reduction potential
$E_{1/2}$- Redox potential
CH_2Cl_2- Dichloromethane
NBu_4PF_6- Tetrabutylammonium hexafluorophosphate
Bu_4NClO_4- Tetrabutylammonium Perchlorate
Bu_4NOTf- Tetrabutylammonium Triflate
AIBN- Azobisisobutylronitrile
NaCl- Sodium Chloride
$NaClO_4$- Sodium perchlorate

CHAPTER I

1. INTRODUCTION

1.1 Ferrocene

Ferrocene was accidently discovered in 1951 at Duquesne University in Pittsburgh, Pennsylvania by P.L. Paulson and T.J. Kealy during an attempt to synthesize fulvalene[1]. Cyclopentadienyl magnesium bromide was reacted with iron (II) chloride in diethyl ether and ferrocene was formed. During the same period ferrocene was synthesized by Treboth, Tremane and Miller by reacting cyclopentadiene with an iron catalyst at 300°C. The ferrocene structure is an iron atom “sandwiched” between cyclopentadiene anions, each giving 6π electrons to the Iron (II) cation[2] as shown in Figure 1. Ferrocene shows diamagnetic behavior and also possess nontoxicity, aromaticity and very interesting photochemical properties. Ferrocene behaves as a donor when present in the vicinity of an electron acceptor and thus can form charge transfer complex under photoexcitation phenomena. Ferrocene only shows one C-H stretch in the Infrared Spectrum which proves that all carbon atoms present in the molecule are equivalent[2]. The uniformity of the protons are also shown by the singlet shown in ^{1}H-NMR spectrum. It is an organometallic compound in which bonding occurs between the d-orbitals of the iron (II) metal center and p- orbitals of the cyclopentadienyl ligands $(C_5H_5)^-$. This type of bond is known as metal-ligand bond.

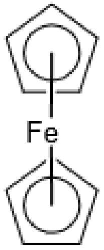


Figure 1. Ferrocene

The name ferrocene was given to this molecule because of its resemblance to the aromatic character of benzene[3]. It contains 6 delocalized electrons for each CP ring like benzene. When a strong base is used to deprotonate the cyclopentadiene ring the H^+ is expelled from the tetrahedral carbon in the structure. Then the lone pair of electrons resonates throughout the CP ring. The cyclopentadienyl rings are characterized by highly nucleophilic character and can undergo electrophilic substitution reactions, including Friedel-Crafts acylation, alkylation and sulfonation[4]. However, direct nitration and halogenation can disrupt the molecule by oxidizing the iron atom[4]. Moreover, the oxidizing potential of the molecules can be changed by adding functional groups which can be electron donating or withdrawing in character, which allow a diverse range of applications such as electrical conducting polymers and inclusion into solar cells[5],[6].

1.2 Electronic Properties of Ferrocene

Ferrocene is an electron rich and electrically active material which in turn possess electron rich aromatic behavior. The six d-electrons of the Fe^{2+} ion are bonded with the six π-electrons of the cyclopentadienyl anions which is in accordance to 18-electron stability rule for metals. The occupied bonding orbitals gives it the electronic stability[7]. The molecular orbitals diagram given below explains these phenomena. (Figure 2)

The symmetry of the ferrocene shows the overlapping molecular orbitals, between the central iron atoms (3d, 4s and 4p) along with the ligand orbitals.[8] The major aspects of the electronic structure of ferrocene are explained below:[7]

- Lowest energy ligand orbitals- a_{1g} and a_{2u}
- Highest energy metal orbitals- $3d_z{}^2/4s$, $4p_z$
- Essential metals orbitals- e_{2g}
- Two strong π-bonds are formed by overlapping of iron orbitals (dx_y & dy_z) with the ligands e_{2g} orbitals. These π-bonds are responsible for the stability of ferrocene.
- Unoccupied weak anti-bonding orbitals in- e'_{1g}
- Unoccupied non-bonding orbitals- a'_{1g}
- Unoccupied weakly bonding orbitals- e_{2g}
- HOMO for ferrocene- degenerate - e_{2g} or a'_{1g}[9]
- LUMO for ferrocene- out of phase dx_z/dy_z orbitals[10]

The electrochemical properties of the substituted ferrocene compounds such as ferrocene polymers are improved by the strong interaction between π-bonding of cyclopentadienyl rings and π-conjugated main chains.[11], [12], [13]

1.3 Ferrocene Polymers

Ferrocene when incorporated in polymers possess different and unique properties which include increase in redox stability, charge transfer complexes, reversible oxidation[14], [15], [16], electrocatalysis[17], battery applications[18], electrode coating[19], and resistance to thermal degradation. It has been successfully incorporated into polymers either pendant or within the polymer chain. Although the first polymer with ferrocene incorporated in side chain was developed in 1951, the first polymer having ferrocene within the main polymer backbone was developed in mid 1970's. Examples of ferrocene in the main chain polymer and pendant to the main polymer are shown in Figures 3 and 4, respectively.

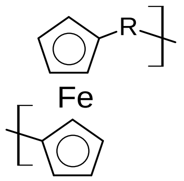


Figure 3. Ferrocene as the main chain polymer having 1,1' -substitution patterns of spacers about ferrocene unit.

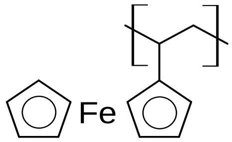


Figure 4. Ferrocene as the side chains of main polymer

Formation of ferrocene polymers have been limited by their difficulty to obtain high molecular weights, due to their ability to form zwitterion.[20] During free radical polymerization, the formation of zwitterion occurs due to transfer of electron from the ferrocene to the end of the growing polymer chain. This termination step increases polydispersity and lowers molecular weight.

1.4 New Polymerization Techniques

To circumvent polymerization difficulties with the polymerization of vinyl ferrocene, new techniques have been developed to obtain high molecular weight ferrocene polymers. Ring-opening polymerization of [1] or [2]ferrocenophanes has been reported by Manners.[21], [22] Ring opening polymerization of these monomers is a type of chain growth polymerization which can occur by free radical, anionic or cationic mechanism. This polymerization was first reported for the thermal ring-opening of silyl[1]ferrocenophane in 1992 as shown in Figure 5. An interesting property of this polymer was two oxidation waves in the cyclic voltammogram, indicating electronic communication between ferrocenyl moieties. These electronic communications arose from the d-p orbital overlap between the silyl moiety and the cyclopentadienyl rings which facilitated electronic communication between neighboring ferrocenes. Subsequent research extended this work to include additional functional groups such as sulfur, phosphorous, or ethylene.[23],[24]

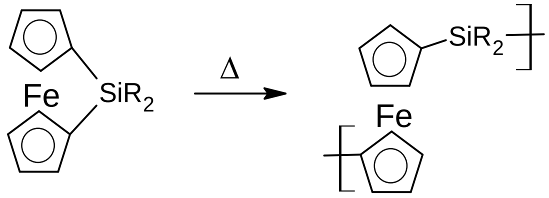


Figure 5. Thermal polymerization of silyl[1]ferrocenophane

Another method to facilitate polymerization of ferrocene monomers was accomplished by holding two vinyl moieties in close proximity within the ferrocenyl structure. The polymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene by radical polymerization was reported in 1996. [25] (Figure 6) The rigid structure of this monomer places the vinyl moieties in close proximity facilitating cyclopolymerization, producing a [3]ferrocenophane. In addition, upon cyclization, the resulting radical is much less sterically hindered than observed for the polymerization of vinylferrocene. Reducing steric hindrance facilitated polymerization and molecular weights up to ca. 20,000 were obtained. In addition, the resulting polyferrocenophane showed two oxidation potentials in the cyclic voltammograms, indicating electronic communication between ferrocenyl moieties. Since the ferrocenyl group is orthogonal to the polymer backbone, communications occur through cofacial stacking of the cyclopentadienyl rings through pi-pi interaction.

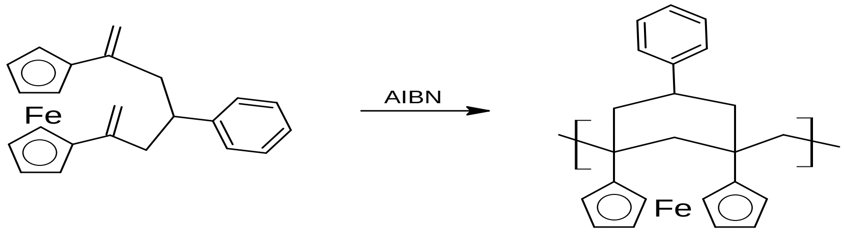


Figure 6. Cyclopolymerization of 3-Phenyl[5]ferrocenophane-1,5-dimethylene

Copolymerization of this ferrocenophane was performed with styrene to isolate the ferrocene moieties and produce a random copolymer as shown in Figure 7. As expected for copolymerization with styrene, the ferrocenyl moieties were isolated and thus the cyclic voltammogram only showed one oxidation wave. Copolymerization of this monomer with various N-substituted maleimides has also been reported.[26] as shown in Figure 8. These copolymers were synthesized to study donor-acceptor interactions between alternating electron rich ferrocenophane and electron deficient maleimide groups. Oxidation potentials of these polymers were higher than expected for a ferrocene containing polymer and UV spectrum showed absorbencies into the visible region. These results supported interactions between the ferrocenyl and maleimide moieties.

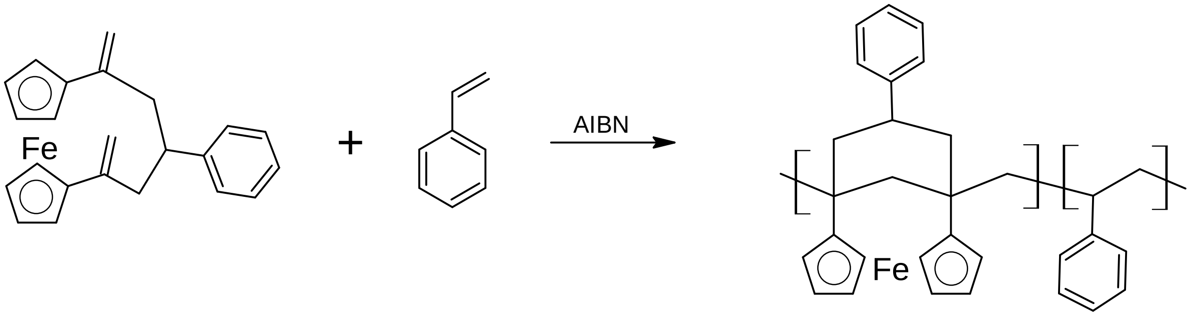


Figure 7. Copolymerization of 3-Phenyl[5]ferrocenophane-1,5-dimethylene with Styrene

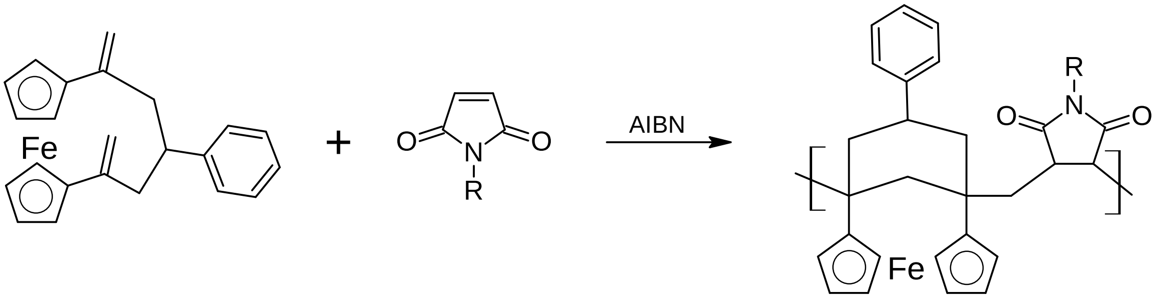


Figure 8. Copolymerization of 3-Phenyl[5]ferrocenophane-1,5-dimethylene with N-substituted Maleimide

1.5 Project Rationale

Poly(3-phenyl[5]ferrocenophane-1,5-dimethylene) exhibited interesting electronic properties and improved polymerizability compared to polyvinylferrocene. However, the molecular weight of this polymer was insufficient to cast films which limited its study. To improve film forming ability, side groups can be added to the phenyl moiety to improve entanglement of the polymer chains. To this end, this thesis reports the synthesis, polymerization and copolymerization of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene. The addition of a methoxy group to the phenyl moiety is the initial step for the inclusion of side groups to the polymer. In addition to the homopolymer, polymers with styrene and N-phenylmaelimide were synthesized to obtain random and alternating copolymers, respectively. To understand the effects of the methoxy group, the polymers were studied by UV-vis spectroscopy, cyclic voltammetry and TGA.

CHAPTER II

2. EXPERIMENTAL

2.1 Materials

All materials were purchased from Acros Organics and utilized as received unless otherwise stated. A Witting reaction was used to synthesize the 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene according to a literature procedure.[25] Chromatography was performed using silica gel (60 A) (Acros organic) as the stationary phase with dichloromethane as the mobile phase.

2.2 Synthesis of Poly 3-(4-Methoxyphenyl)[5]Ferrocenophane-1,5-Dimethylene and Copolymers with Styrene and N-Phenylmaleimide

2.2.1 Synthesis of 1,1-diacetylferrocene

Dichloromethane (150 mL) along with aluminum chloride (9.4 g, 0.071 mol) was added to a conical flask. After establishing a nitrogen atmosphere, acetyl chloride (5.5 g, 0.071 mol) was added and the solution was stirred for 30 minutes. Over a period of 15 minutes, ferrocene (5.07 g, 0.027 mol) was added to the solution, and then the reaction was stirred for 18 hours. The solution was poured over ice in a 500 mL beaker to neutralize the aluminum chloride. The organic phase was separated using a separatory funnel and the solvent was removed by rotary evaporator. The crude product was recrystallized using isopropyl alcohol. The crystals were collected by filtration and dried using a vacuum oven overnight. 1,1-diacetylferrocene (4.8 g) was recovered in a 64% yield. IR(cm^{-1}): 3100, 1680 and 1500. ^{1}H-NMR ($CDCl_3$, δ ppm): 4.67 (4H), 4.51 (4H), 2.5 (6H).

2.2.2 Synthesis of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione

1,1-diacetylferrocene (4.0 g, 0.015 mol), along with anisaldehyde (1.96 g, 0.01 mol) and 95% ethanol (150 mL) were added to 150 mL Erlenmeyer flask containing a stir bar and the mixture was stirred for 30 minutes. After 30 minutes, potassium hydroxide (0.48 g, 0.0086 mol) was added and the reaction was stirred for 18 hours at room temperature. Vacuum filtration was used to collect the product and then it was dried in a vacuum oven overnight. 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione (4.26 g) was recovered in a 74% yield. IR (cm^{-1}): 3000 and 1690. ^{1}H-NMR ($CDCl_3$, δ ppm) peaks at 7.27-6.89 (4H), 4.58-4.87 (8H), 4.30 (1H), 3.815 (3H) and 2.47-2.93 (4H).

2.2.3 Synthesis of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

Methyltriphenylphosphonium bromide (2.4 g, 0.011 mol) along with tetrahydrofuran (70 mL) was added to 2-necked round bottom flask. The mixture was stirred under nitrogen atmosphere. N-butyllithium was added (8.2 mL, 2.5 M) in THF and the solution was stirred for 30 minutes. 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione (2.4 g, 0.0068 mol) was added and the reaction was stirred for 24 hours. After completion of the reaction, distilled water (1.5 mL) was added to the solution and the solvent was removed with a rotary evaporator. Column chromatography was used to purify the product using silica gel with dichloromethane. The yield was 1.6 g (66%) of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene. IR (cm^{-1}): 3092, 3000, 2910 and 1670. ^{1}H-NMR ($CDCl_3$, δ ppm): 6.90 (4H), 5.25 (2H), 4.79 (2H), 4.45, 4.34, 4.30, 4.20, 4.1 (8H), 3.18 (3H) and 2.5 – 2.6 (4H). ^{13}C-NMR ($CDCl_3$, δ ppm): 158.1, 139.5, 127.7, 113.8, 108.7, 85.3, 70.8, 69.2, 64.2, 54.7, 43.9 and 38.5

2.2.4 Homo-polymerization of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

To a 15 mL 2-necked round bottom flask with a stir bar was added 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene (0.21g) and chlorobenzene (15 mL). A nitrogen atmosphere was established and AIBN (0.0040 g) was added. The mixture was stirred at 80°C for 18 hours. The reaction was precipitated after polymerization by dropwise addition into rapidly stirring petroleum ether. The solid was collected by vacuum filtration after precipitation. The homopolymer (0.20 g) was recovered in a 98% yield. IR (cm^{-1}) 3000, 2900 and 1610. ^{1}H-NMR ($CDCl_3$, δ ppm) 6.54-7.26 (4H), 4.34 (9H), 3.80 (3H) and 0.8-2.1 (8H).

2.2.5 Polymerization of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with N-Phenylmaleimide

In 15 mL 2-necked round bottom flask with a stir bar was added 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene (0.21 g), phenylmaleimide (0.04 g, 0.0015 mol) and chlorobenzene (15 mL). A nitrogen atmosphere was established and AIBN (0.0026 g) was added. The mixture was stirred at 80°C for 18 hours. The reaction was precipitated after polymerization by dropwise addition into rapidly stirring petroleum ether. The solid was collected by vacuum filtration after precipitation. The copolymer (0.19 g) was recovered in a 92% yield. IR (cm^{-1}): 3000, 2900 and 1700. ^{1}H-NMR ($CDCl_3$, δ ppm): 6.54-7.27 (9H), 4.34 (9H), 3.8 (3H) and 2.1 (4H).

2.2.6 Polymerization of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with Styrene.

In 15 mL 2-necked round bottom flask with a stir bar was added 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene (0.21 g), styrene (0.027 g, 0.0015 mol) and chlorobenzene (15 mL). A nitrogen atmosphere was established and AIBN (0.0026 g) was added. The mixture was stirred at 80°C for 18 hours. The reaction was precipitated after polymerization by drop wise addition into rapidly stirring petroleum ether. The solid was collected by vacuum filtration after precipitation. The copolymer (0.18 g) was recovered in a 93% yield. IR (cm^{-1}): 3000 and 2900. ^{1}H-NMR ($CDCl_3$, δ ppm): 6.54-7.27 (9H), 4.34 (9H), 3.8 (3H) and 2.1 (10H).

2.3 Instrumentation

Fourier Transform Infrared Spectroscopy (FT-IR) was done using a Perkin Elmer Spectrum 2 Spectrometer. All NMR spectra were obtained using a Bruker DPX-300 MHz spectrometer. Cyclic Voltammetry was performed using Gamry Interface 1000 potentiostat with a platinum working electrode and a carbon counter electrode, and an Ag/Ag^+ wire as a reference. Gel permeation chromatography (GPC) measurements were done using a JMDC-4 Waters 515 HPLC pump, 2410 differential refractometer, set of one 300×7.8 mm phennogel 5μ column. M_w, M_n and polydispersity were calculated based on peaks compared to a polystyrene standard calibration. UV-Vis spectroscopy was performed using a Genesys 150 UV-Visible Spectrophotometer.

2.4 Electrochemical Studies

For electrochemistry studies, solutions were prepared by dissolving each polymer (1 mM) with tetrabutylammonium hexafluorophosphate (100 mM), tetrabutylammonium perchlorate (100 mM) or tetrabutylammonium triflate (100 mM) as a supporting electrolyte, in dichloromethane.

The cyclic voltammetry of thin film materials was done by casting polymer films directly on the surface of an electrode. Thin films were prepared by casting 8 μL of the polymer solution of the polymer and air drying for about 10-15 minutes. Electrolyte solution were prepared by using sodium perchlorate (0.1 M) or sodium chloride (0.1 M) as the supporting electrolyte for the polymers.

CHAPTER Ⅲ

3. RESULTS & DISCUSSIONS

3.1 Synthesis and Characterization of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene.

The synthesis of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene was performed using a procedure in literature. Friedel-Crafts conditions were established for acylation of ferrocene. 1,1'-diacetylferrocene was condense with anisaldehyde to form 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione. 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione was recovered in a 74% yield. Figures 9 and 10 show the FT-IR and ^{1}H- NMR spectra for 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione, respectively. The FT-IR spectrum shows peaks at 3000 cm^{-1} for the aromatic C-H stretching and 1690 cm^{-1} for the carbonyl stretching. In the ^{1}H-NMR spectrum of the dione, signals were observed at 7.2 ppm and 6.8 ppm for the phenyl protons, 4.87 ppm, 4.61 ppm and 4.58 ppm for ferrocenyl protons, 4.30 ppm for the benzyl proton, 3.81 ppm for methoxy protons, and 2.93 ppm and 2.4 ppm for methylene protons.

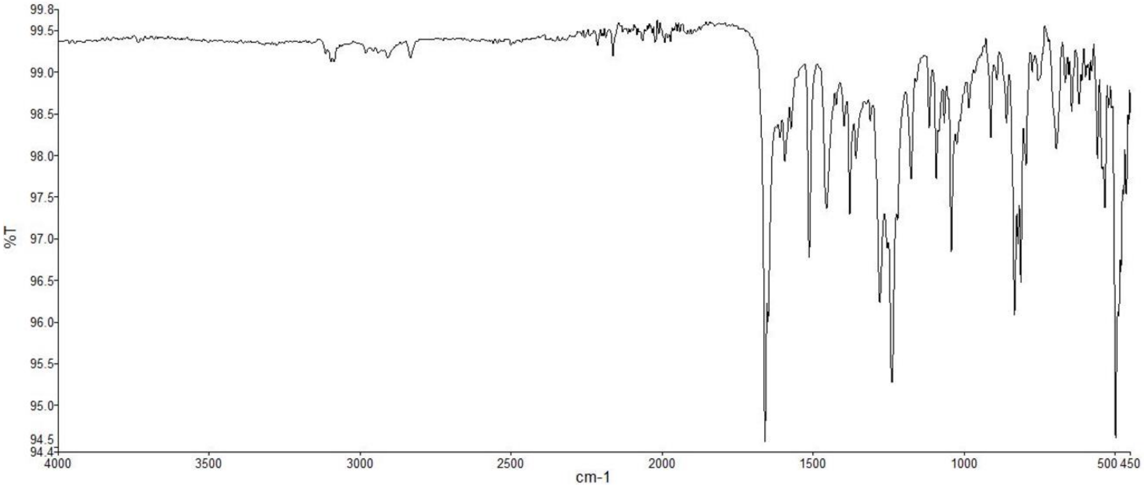
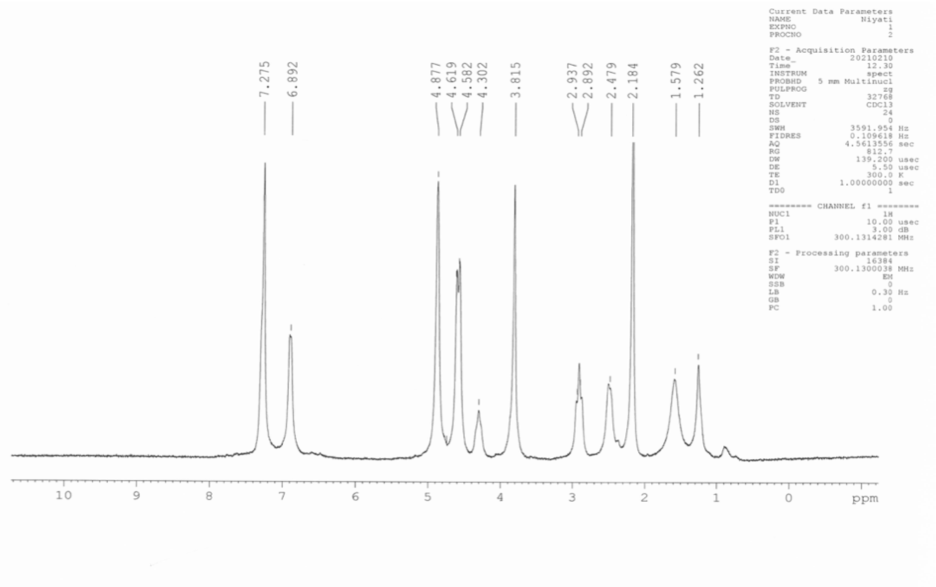


Figure 9: FT-IR spectrum for 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione



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LB                  0.30 Hz
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PC                  1.00
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Figure 10: ^{1}H-NMR spectrum for 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione

The monomer was formed using a Wittig reaction by converting 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dione to 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene as shown in Figure 11. The yield of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene was 66%. The FT-IR, ^{1}H-NMR and

^{13}C-NMR spectra are shown in Figures 12, 13 and 14, respectively. The FT-IR spectrum showed peaks at 3092 cm^{-1} for the =C-H stretching, 3000 cm^{-1} for the aromatic C-H stretching, 2910 cm^{-1} for the aliphatic C-H stretching and 1670 cm^{-1} for the C=C stretching In the ^{1}H-NMR spectrum, signals were observed at 7.2 ppm and 6.9 ppm for the phenyl protons, 5.2 ppm and 4.7 ppm for the vinylidene protons, 4.4 ppm, 4.3 ppm and 4.32 ppm for the ferrocenyl protons, 4.15 ppm for the benzyl proton, and 3.18 ppm for methoxy protons, and 2.51-2.6 ppm for methylene protons. The types of C atoms in the 3-(4-methoxyphenyl)[5]ferrocenophane-1,5 dimethylene were recognized by ^{13}C-NMR spectrum which showed signals at 158.1 ppm, 139.5 ppm, 127.7 ppm and 113.8 ppm for aromatic carbons, 140 ppm and 108.7 ppm for vinylidene carbons, 85.3 ppm for the substituted carbons of the CP rings, 70.8 ppm, 68 ppm, 69.2 ppm and 64.2 ppm for the unsubstituted ferrocenyl carbons, 54.7 ppm for the methoxy carbon, 43.9 for the methine carbon and 38.5 ppm for methylene carbons.

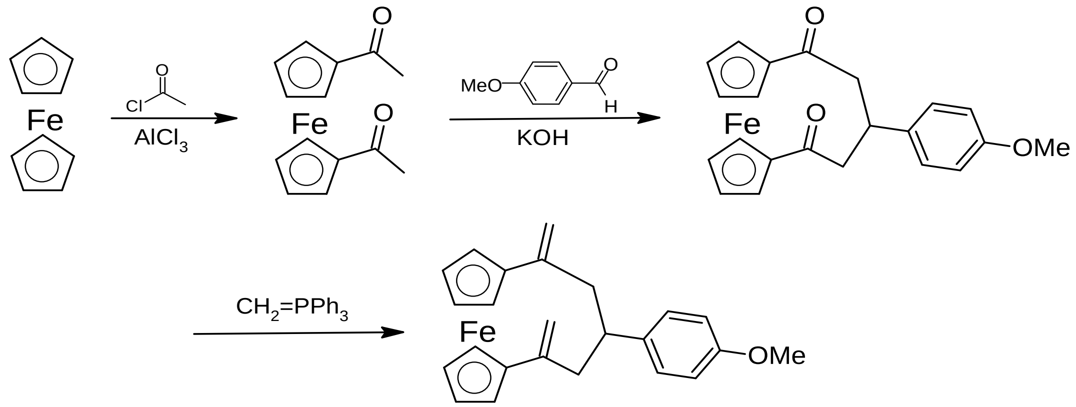

Figure 11: Synthesis of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

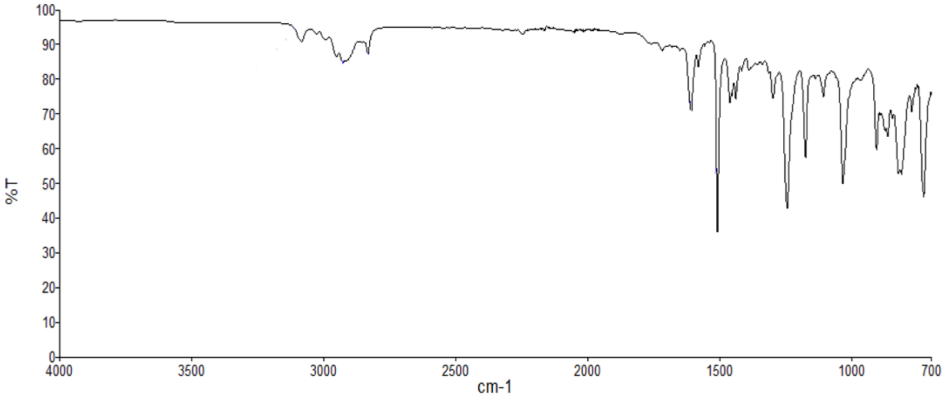

Figure 12: FT-IR spectrum for 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

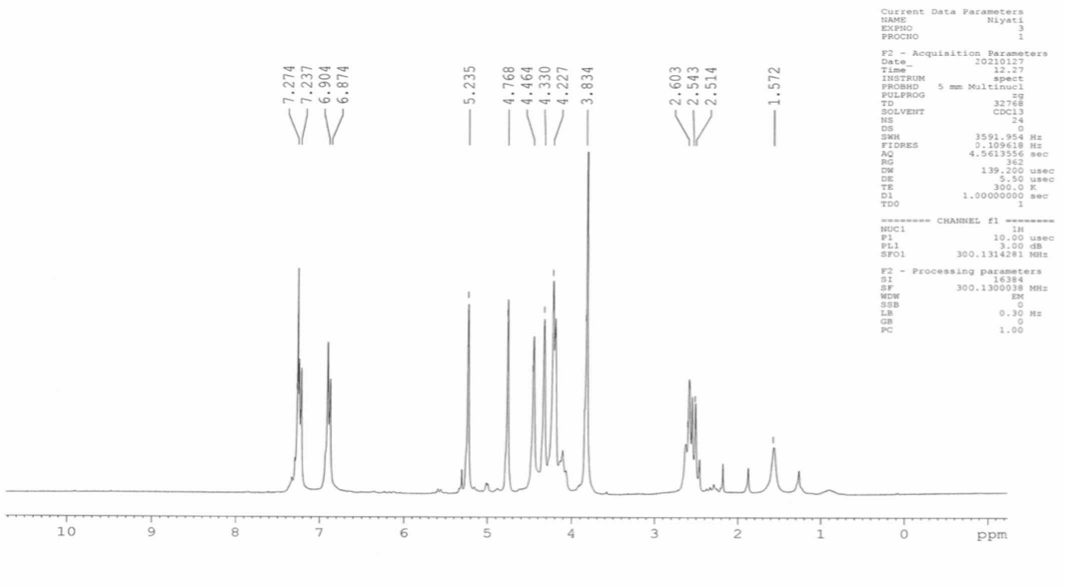

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Figure 13: ^{1}H-NMR spectrum for 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

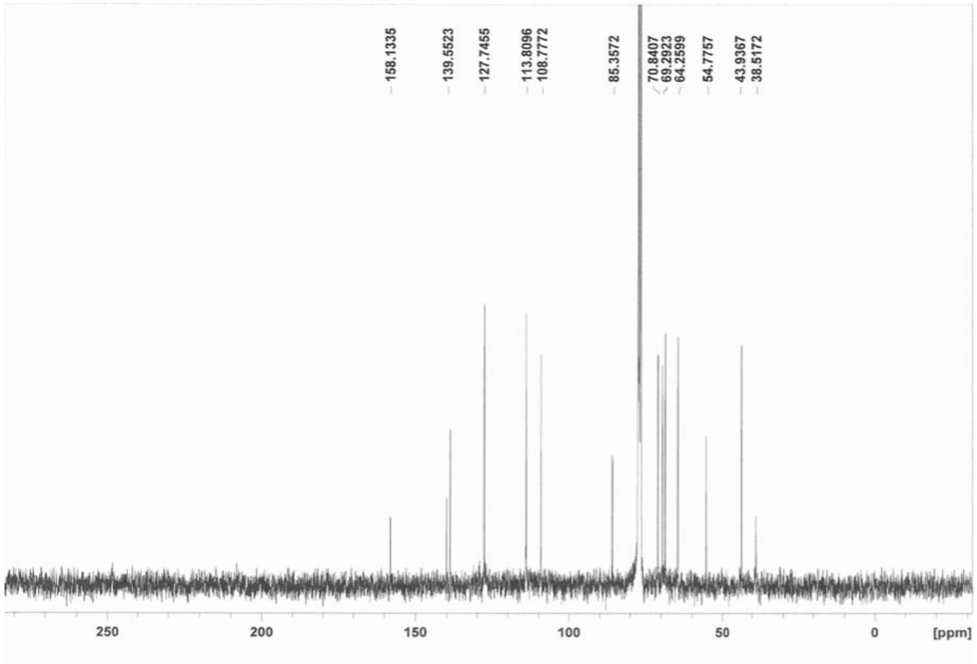


Figure 14: ^{13}C-NMR spectrum for 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

3.2 Homopolymerization and Copolymerization of 3-(4-methoxyphenyl) [5]ferrocenophane-1,5-dimethylene with N-Phenylmaleimide and Styrene

3.2.1 Synthesis and Characterization of homopolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

The monomer was homopolymerized (Homo) using AIBN as a free radical initiator as shown in Figure 15. The homopolymer was recovered in a 98% yield. The characterization of this polymer was done using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy shown in Figures 16, 17 and 18 respectively. The FT-IR spectrum showed peaks at 3000 cm^{-1} for the aromatic C-H stretching, 2900 cm^{-1} for aliphatic C-H stretching. The absence of band near 1670 cm^{-1} corresponding to C=C was absent, suggesting that residual monomer has either been reacted or removed during precipitation. Signals were observed at 6.54-7.26 ppm for phenyl protons, 4.34 ppm for ferrocenyl and benzyl proton, 3.80 ppm for methoxy protons, and 0.8-2.1 ppm for aliphatic protons. The absence of vinylidene proton signals at 4.74 and 5.20 was consistent with the FTIR spectrum and indicated the absence of residual monomer. The ^{13}C-NMR showed more peaks than expected because of the possibility of more than one conformation or due to different orientations of monomer addition. The homopolymer showed a M_w of 5,751, M_n of 3,034 and a polydispersity of 1.8. Polydispersity was greater than 1 and is typical of a radical polymerization.

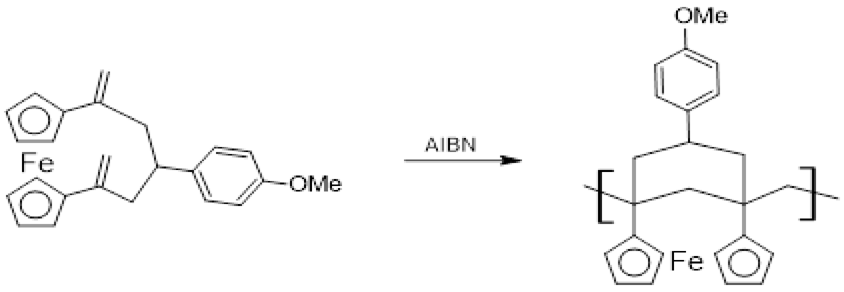


Figure 15: Homopolymerization of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene

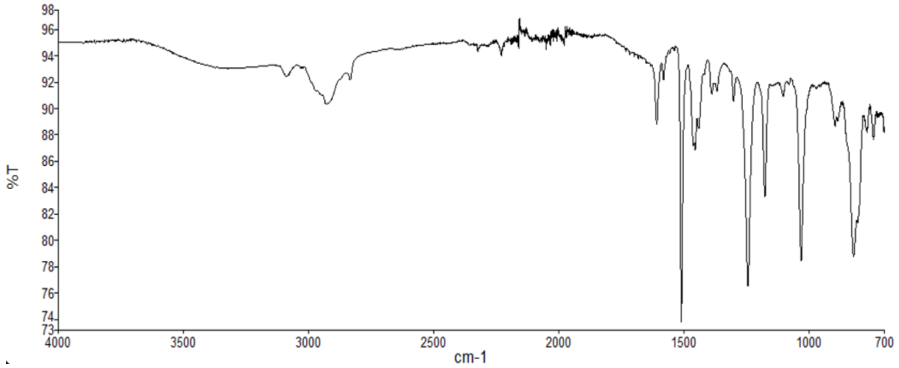
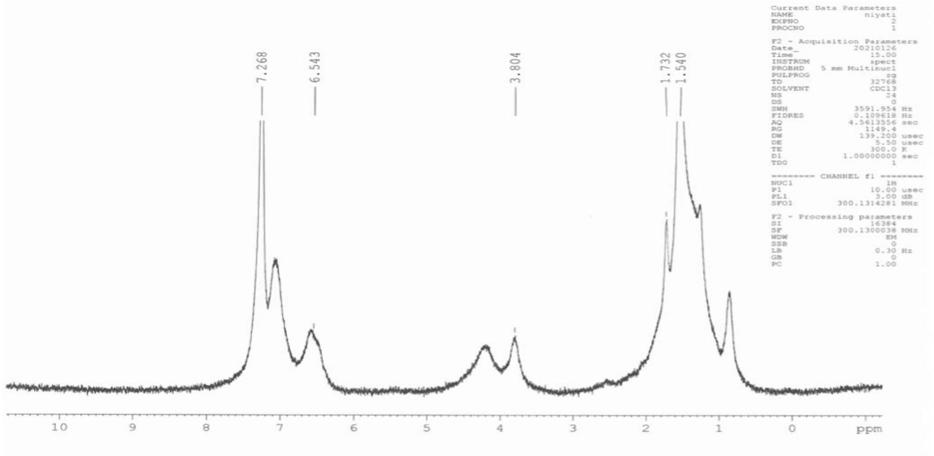


Figure 16: FT-IR of homopolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene



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D1            1.00000000 sec
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P1                 10.00 usec
PL1                 3.00 dB
SFO1         300.1314281 MHz

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Figure 17: ^{1}H-NMR spectrum of homopolymer of 3-(4-methoxyphenyl)[5] ferrocenophane-1,5-dimethylene

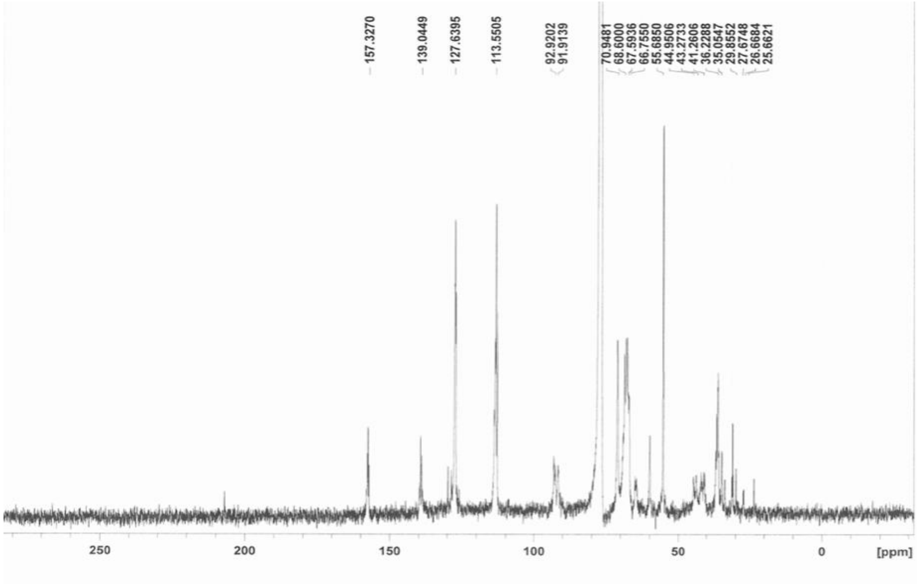

Figure 18: ^{13}C-NMR spectrum of homopolymer of 3-(4-methoxyphenyl)[5] ferrocenophane-1,5-dimethylene

3.2.2 Synthesis and characterization of copolymer of 3-(4-methoxyphenyl)[5] ferrocenophane-1,5-dimethylene with N-Phenylmaleimide

The ferrocenophane monomer was copolymerized with N-phenylmaleimide (Ph-Ml) using AIBN as a free radical initiator shown in Figure 19. The copolymer was recovered in a 92% yield. The characterization of this polymer was done using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy shown in Figures 20, 21 and 22, respectively. The FT-IR spectrum showed peaks at 3000 cm^{-1} for aromatic C-H stretching, 2900 cm^{-1} for aliphatic C-H stretching and 1700 cm^{-1} for carbonyl stretching. The ^{1}H-NMR spectrum exhibited signals at 6.54-7.27 ppm for phenyl protons, 4.0-4.8 for ferrocenyl protons, 3.8 ppm for methoxy protons and 1.0-2.1 ppm for aliphatic protons. The absence of vinylidene proton signals at 4.74 and 5.20 indicated the absence of residual monomer. The ^{13}C-NMR showed more peaks than expected because of the possibility of more than one conformation or due to different orientations of the monomer upon addition. The N-phenylmaleimide copolymer showed a M_w of 6,062 , M_n of 1,833 and a polydispersity of 3.3.

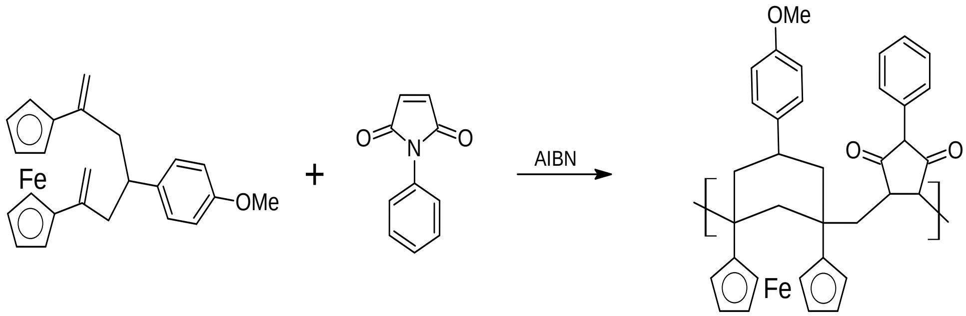

Figure 19: Copolymerization of 3-(4-methoxyphenyl)[5] ferrocenophane-1,5-dimethylene with N-phenylmaleimide

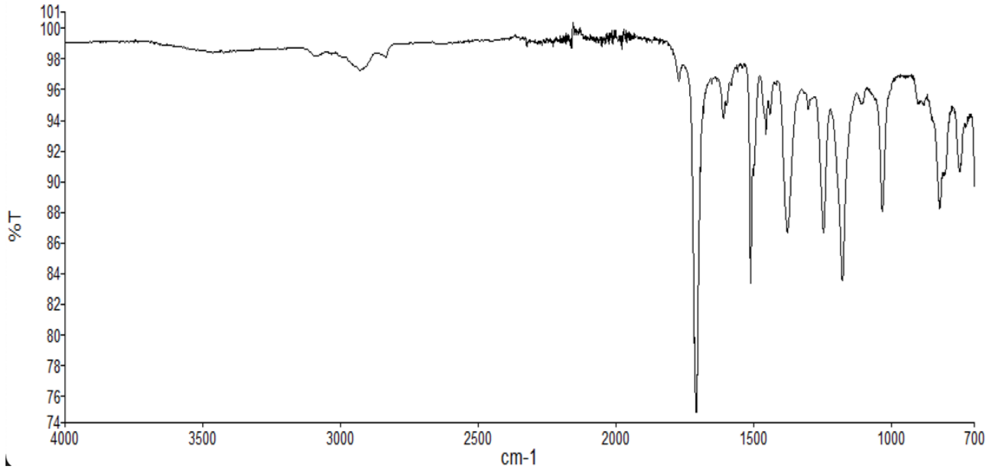

Figure 20: FT-IR Spectrum of copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with N-phenylmaleimide

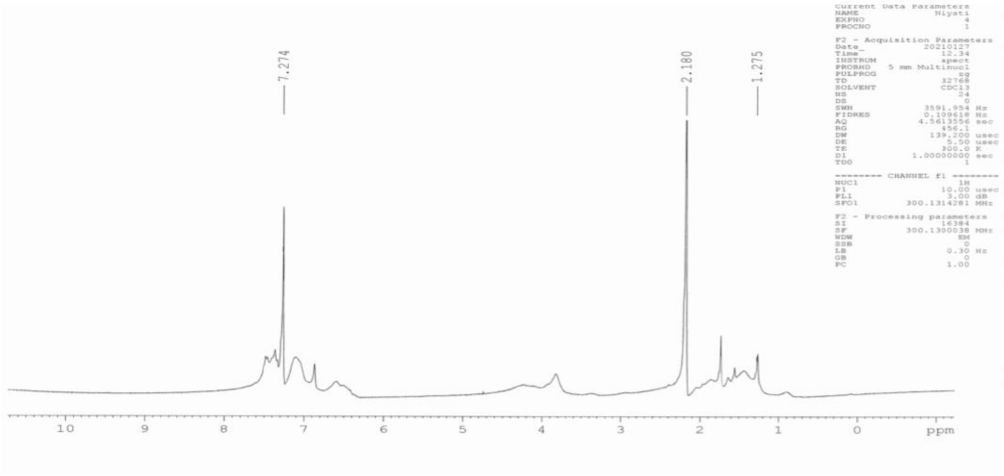

Figure 21: ^{1}H-NMR spectrum of copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with N-phenylmaleimide

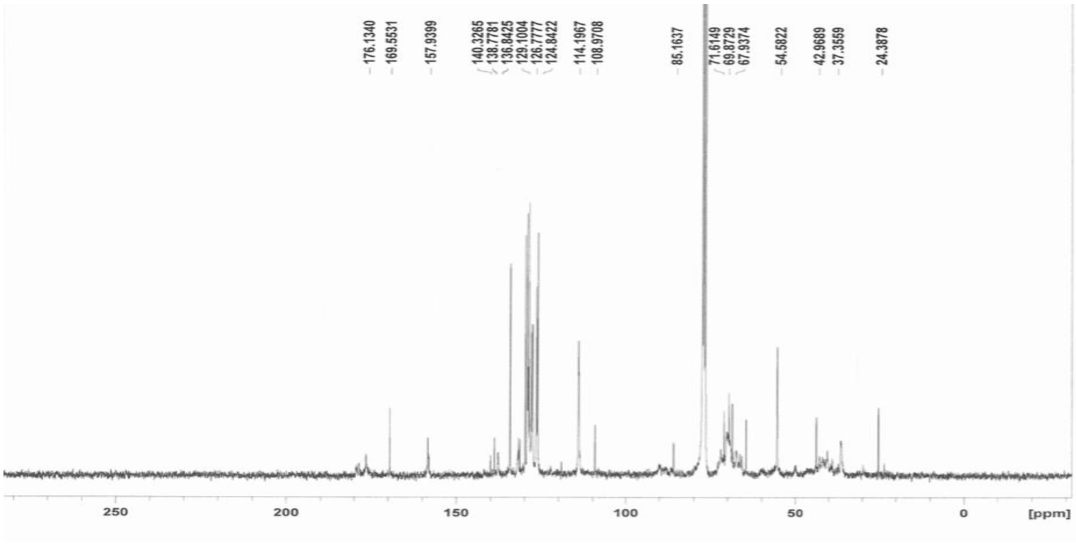

Figure 22: ^{13}C-NMR spectrum of copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with N-phenylmaleimide

3.2.3 Synthesis and Characterization of copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with Styrene.

The ferrocenophane monomer was copolymerized with styrene (St) using AIBN as a free radical initiator as shown in Figure 23. The copolymer was recovered in a 93% yield. The characterization of this polymer was done using FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy shown in Figures 24, 25 and 26, respectively. The FT-IR spectrum showed peaks at 3000 cm^{-1} for aromatic C-H stretching and 2900 cm^{-1} for aliphatic C-H stretching. The ^{1}H-NMR spectrum of the copolymer is shown in Figure 24. Signals were observed at 6.54-7.27 ppm for phenyl protons, 4.0-4.8 ppm for ferrocenyl protons, 3.8 ppm for methoxy protons and 2.1 ppm for aliphatic protons. The absence of vinylidene proton signals at 4.74 and 5.20 indicated the absence of residual monomer. The ^{13}C-NMR spectrum showed more peaks than expected as was observed for the previous polymers. The styrene copolymer showed a M_w of 10,740 , M_n of 9,000 and a polydispersity of 1.1.

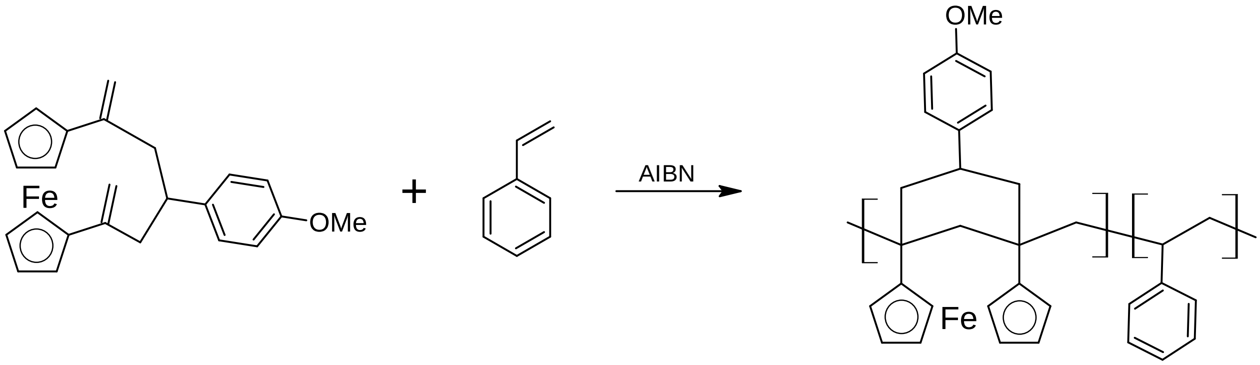

Figure 23: Copolymerization of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with Styrene

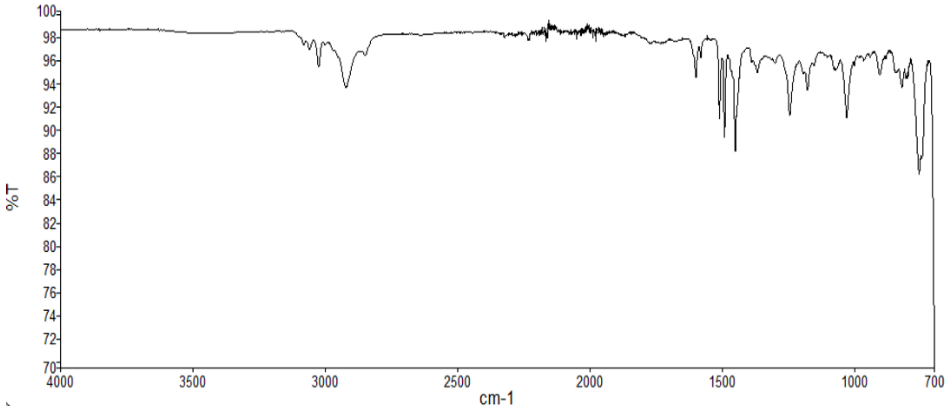

Figure 24: FT-IR spectrum of copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with Styrene

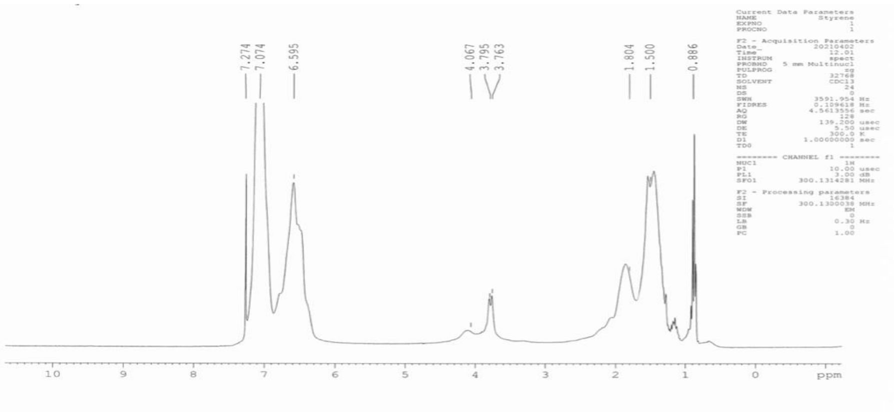

Figure 25: ^{1}H-NMR spectrum of copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with Styrene

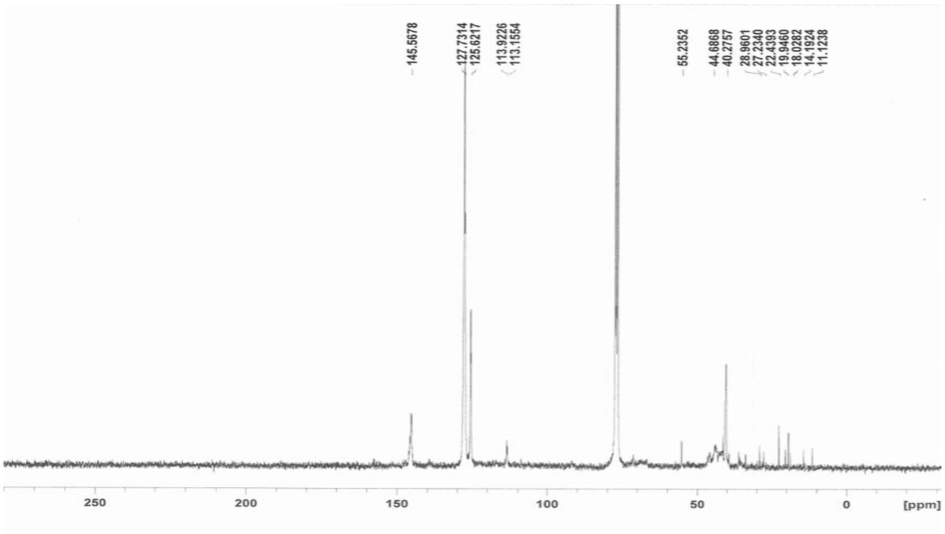

Figure 26: ^{13}C-NMR spectrum of copolymer of 3-(4-methoxyphenyl)[5]ferrocenophane-1,5-dimethylene with Styrene

3.3 Thermogravimetric Analysis of Polymers

Thermogravimetric analysis was carried out at temperatures ranging from room temperature to 800°C. Thermal stability was measured at the onset of decomposition temperature and char yield was determined at 800°C. In the TGA of Homopolymer there is a loss of weight around 100°C as shown in the TGA and derivative plot in Figure 27 since the polymer was stored on the bench top prior to TGA, this loss of weight was likely due to absorption of moisture by the polymer. The homopolymer showed thermostability to 387°C. Copolymers with N-phenylmaleimide and styrene showed thermostabilities of 349°C and 360°C respectively. Thermal stabilities depend on the structure of the polymer. The homopolymer showed highest degradation temperature amongst all because of its cage like structure.[26] The observed char yields for homopolymer, N-phenylmaleimide and styrene copolymer were 20.1, 11 and 2.5 respectively. As observed for thermal stability, the cage like structure of the homopolymer increased char yield

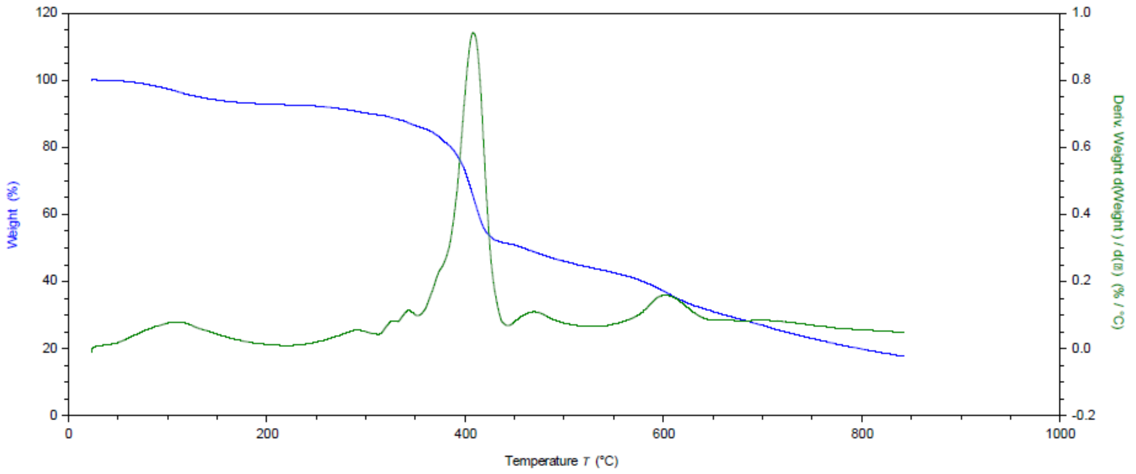

Figure 27: TGA and Derivative plot of Homo polymer

3.4 Electrochemical Studies of Polymers

3.4.1 Electrochemical Studies of polymers in CH_2Cl_2

Polymer solutions for electrochemistry were prepared in dichloromethane (5 mg/mL) using 0.1M tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), tetrabutylammonium perchlorate (Bu_4NClO_4) or tetrabutylammonium triflate as the supporting electrolyte. The cyclic voltammetry was performed in the range of 0.0 V to 0.80 V, with scan rates of 20, 40, 60, 80 and 100 mV/s. The redox potentials of each polymer with each salt are shown in Tables 1, 2 and 3. Initial electrochemical studies on these materials revealed one oxidation potential for each polymer. The CVs of the homopolymer with Bu_4NPF_6 as the supporting electrolyte is shown in Figure 28 and similar results were observed with each polymer and electrolyte combination. Cyclic voltammograms of the homopolymer showed the oxidation potentials ($E_{1/2}$) of 0.45, 0.44, 0.54 using Bu_4NPF_6, Bu_4NClO_4, or Bu_4NOTf, respectively. The cyclic voltammograms of homopolymer showed approximately equal I_{pc} and I_{pa} for each supporting electrolyte, suggesting that these polymers are chemically reversible. However, $E_{ox} – E_{red}$ was greater than 60 mV indicating a lack of electrochemical reversibility. In addition, the current scaled linearly with the square root of the scan rate indicating that the polymer remained soluble in both neutral and oxidized states, shown in Figure 29. Copolymers with maleimide showed similar $E_{1/2}$ potentials to the homopolymer but the copolymer with styrene exhibited lower $E_{1/2}$ potentials by ca. 0.1-0.15 V. An increase in $E_{1/2}$ using maleimide has been observed in previous research.[27] Since this copolymer was expected to be alternating, electron interactions occur between the electron-rich ferrocene and the electron-deficient of maleimide. A higher than expected $E_{1/2}$ of the homopolymer may suggest a step-wise oxidation of the polymer as shown in Figure 30. As one ferrocene moiety was oxidized to a ferrocenium ion, electronic interaction occurred between the ferrocenium ion with neighboring ferrocenyl groups. This interaction would result in an overall increase in $E_{1/2}$ and a significant difference in E_{ox} and E_{red} since various conformations within the polymer would result in different degrees of electronic communication. For the styrene copolymer, a lower $E_{1/2}$ would be consistent with isolation of the ferrocene moieties since this was expected to be a random copolymer. For the copolymers, the difference in E_{ox} and E_{red} were somewhat lower than the homopolymer but were consistent with chemical reversibility but not electrochemical reversibility.

Table 1: Redox Potentials of Polymers in Tetrabutylammonium Hexafluorophosphate at 100 mV/s

Polymer	Salt	E_{ox}	E_{red}	$E_{1/2}$	E_{ox} - E_{red} (mV)
Homo	Bu_4NPF_6	0.54	0.36	0.45	180
Ph-ML	Bu_4NPF_6	0.51	0.38	0.44	130
St	Bu_4NPF_6	0.38	0.24	0.31	140

Table 2: Redox Potentials of Polymers in Tetrabutylammonium Perchlorate at 100 mV/s

Polymer	Salt	E_{ox}	E_{red}	$E_{1/2}$	E_{ox} - E_{red} (mV)
Homo	Bu_4NClO_4	0.52	0.37	0.44	150
Ph-ML	Bu_4NClO_4	0.53	0.44	0.48	90
St	Bu_4NClO_4	0.37	0.24	0.30	130

Table 3: Redox Potentials of Polymers in Tetrabutylammonium Triflate at 100 mV/s

Polymer	Salt	E_{ox}	E_{red}	$E_{1/2}$	E_{ox} - E_{red} (mV)
Homo	Bu_4NOTf	0.62	0.47	0.54	150
Ph-ML	Bu_4NOTf	0.60	0.52	0.56	80
St	Bu_4NOTf	0.55	0.39	0.47	160

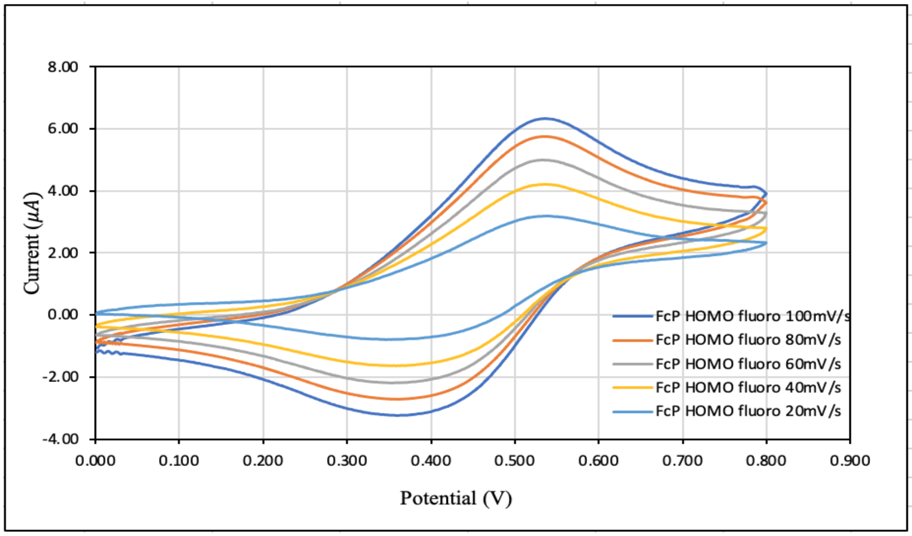

Figure 28: CV of Homopolymer in CH_2Cl_2 with Bu_4NPF_6 as supporting electrolyte.

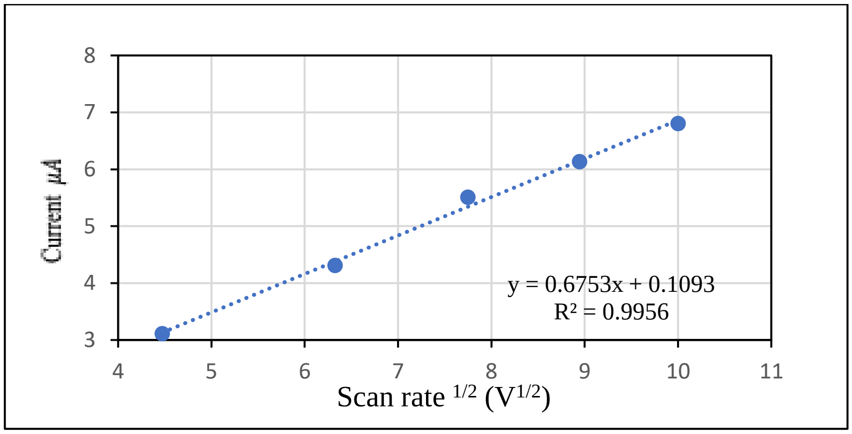

Figure 29: Current versus Scan Rate$^{1/2}$ for CVs of Homopolymer with Bu_4NPF_6 as supporting electrolyte.

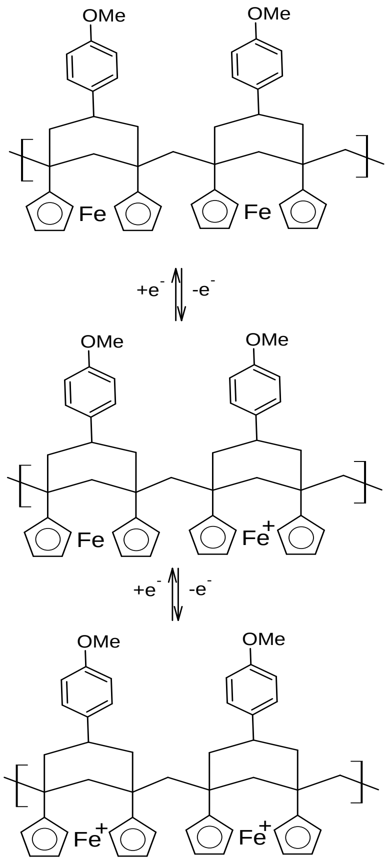

Figure 30: Oxidation Mechanism of Homopolymer

3.4.2 Electrochemical Studies of Polymer Thin Films in 0.1 M NaCl or $NaClO_4$ Solutions.

Thin films of polymers were casted on the platinum electrodes from dichloromethane solutions and then air dried. Cyclic voltammetry was conducted in aqueous solutions of sodium perchlorate (0.1 M, $NaClO_4$) or sodium chloride (0.1 M, NaCl) as a supporting electrolyte. CV using $NaClO_4$ as the electrolyte showed poor redox waves, suggesting poor ion transport into the film and could be due to poor hydration of the polymer as shown in Figure 31. The redox potentials of polymers using sodium chloride as a supporting electrolyte are shown in Table 4. The cyclic voltammograms showed greater I_{pc} than I_{pa} as shown in Figure 32 for homopolymer suggesting slow ion transfer into the film and similar results were observed for styrene. The phenylmaleimide copolymer showed very poor redox waves in the CV suggesting poor ion movement into and out of the polymer.

Table 4: Redox Potentials of Polymers Thin film in aqueous solutions at 100mV/s

Polymer	Electrolyte	E_{OX} (V)	E_{red} (V)	$E_{1/2}$ (V)
HOMO	NaCl	0.09	-0.18	-0.045
Ph-MI	NaCl	0.49	-0.11	0.19
St	NaCl	0.11	-0.18	-0.035

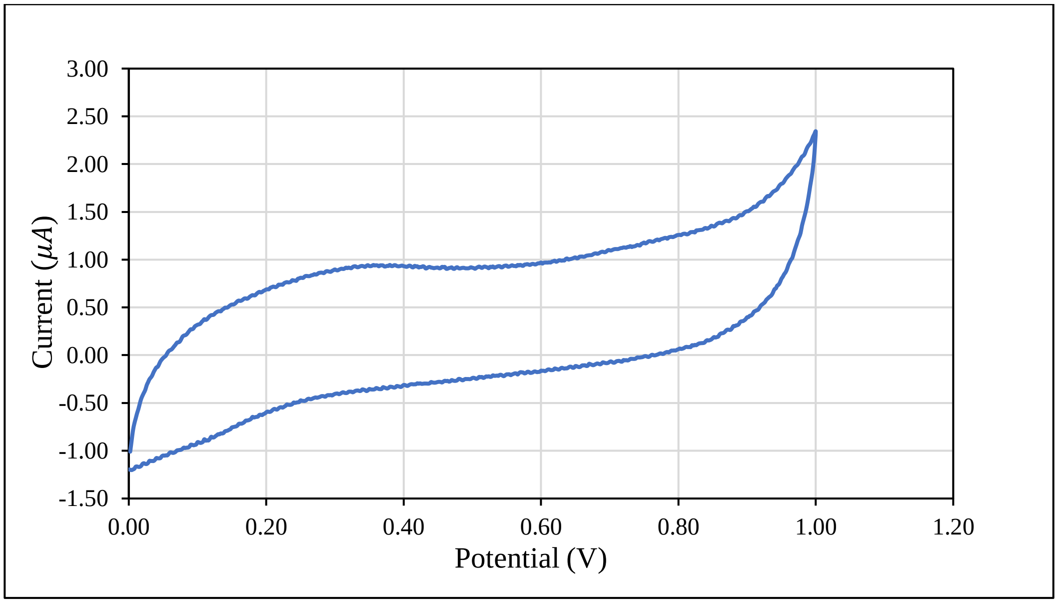

Figure 31: Cyclic Voltammetry (20 mV/S) of Homopolymer in 0.1M Aqueous $NaClO_4$ Solution

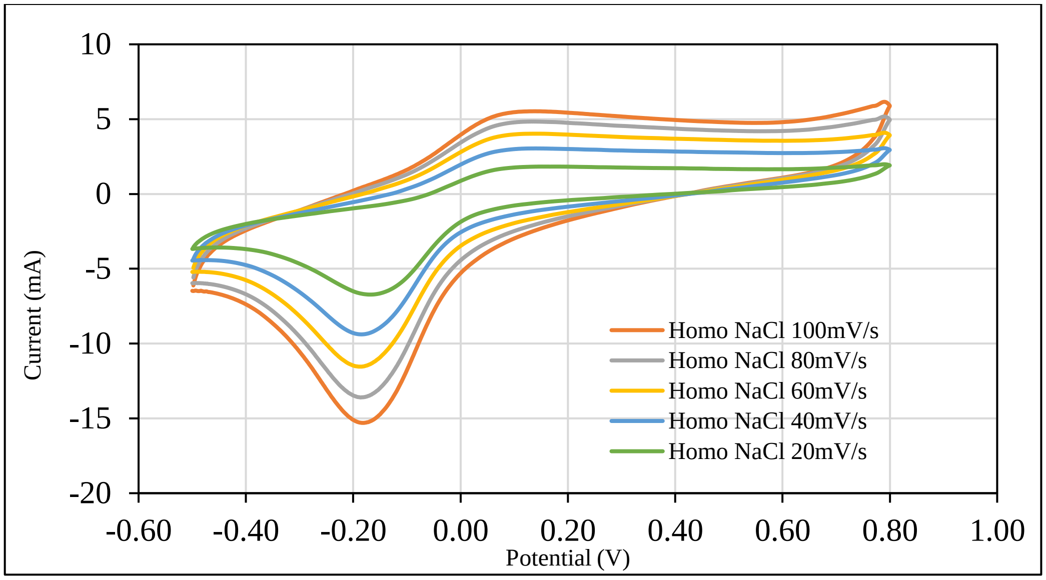

Figure 32: Cyclic Voltammetry of Homopolymer Thin Films in 0.1 M Aqueous NaCl Solution

3.5 UV-vis absorption studies of Copolymers

UV-vis spectroscopy is important for investigating electronic transitions of chromophores. Polymer solutions were prepared in chloroform (10 mg/mL) and were tested from 250-800 nm. The UV-Vis spectra of each polymer exhibited an absorbance at ca. 440 nm for the ferrocenyl moiety as shown in Figure 33. Ferrocenophanes are known to show a shift in their absorbency that is dependent on the length of the bridge, as shown in Table 5.[27] An absorbance of 440 nm was consistent with the formation of a [3]ferrocenophane during polymerization as expected for the cyclopolymerization.

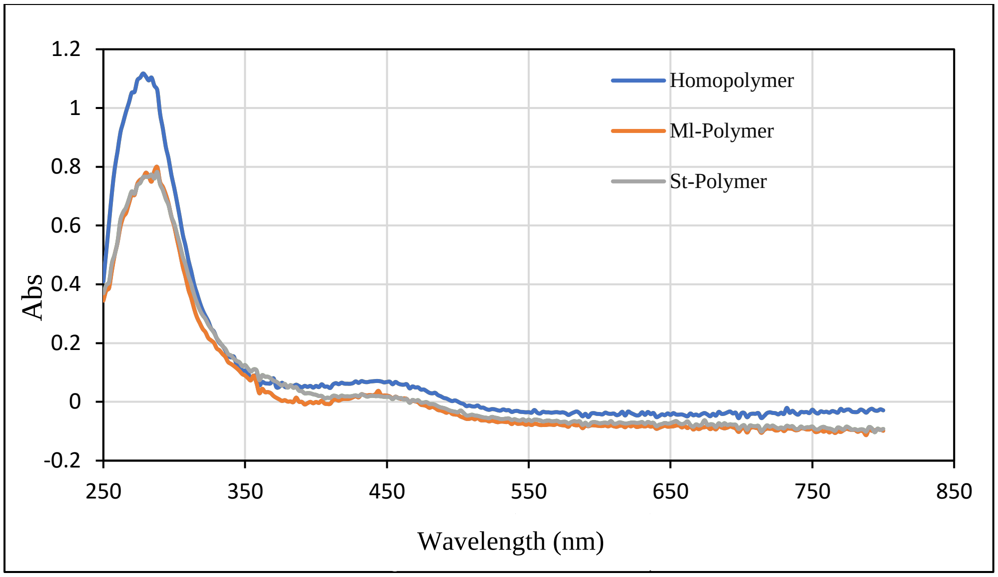

Figure 33: UV-vis spectrum of polymers

Table 5: UV data for Various Ferrocenophanes[19]

Compound	λ_{max} (nm)
1,1-dimethylferrocene	437
[2]ferrocenophane	472
[3]ferrocenophane	442
[4]ferrocenophane	433
[5]ferrocenophane	448

CHAPTER IV

4. CONCLUSIONS

4.1 Summary of results

A novel ferrocenophane diene monomer has been synthesized and free radically polymerized. Homopolymerization, as well as, copolymerization with styrene or N-phenylmaeimide was accomplished by free radical initiation in yields ranging from 92-98%. Characterization by ^{1}H-NMR, ^{13}C-NMR, and FTIR spectroscopy was consistent with the polymer or copolymer structures.

TGA data showed thermostability of the polymers ranging from 349 to 387°C. Cyclic voltammetry of polymers in CH_2Cl_2 gave a single redox wave and a linear relation between current vs. scan rate$^{1/2}$. However, the homopolymer showed a large difference between E_{ox} and E_{red}, suggesting various conformations within the polymer backbone causing different degrees of interaction between neighboring ferrocenyl moieties. CVs of thin films revealed polymers to be chemically reversible with slow ion transport within the film. In addition, UV-Vis spectra exhibited an absorbance at ca. 440 which was consistent with the formation of a [3]ferrocenophane during polymerization.

4.2 Future Research

Subsequent research with these materials should focus on further characterization. From the large separation in E_{ox} and E_{red} in the homopolymer, it was surmised that there were various degrees of electronic interactions between neighboring ferrocenyl moieties. This could be characterized by studying partially oxidized samples of the polymer by UV-Vis-Near IR spectroscopy. An absorbance in the Vis-Near IR region would confirm these electronic interactions. Also, further electrochemical studies on thin films of these materials should be conducted. CV versus thickness of the film should be studied to determine if ion transport improves as film thickness decreases and better defined CV scans can be obtained.

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APPENDIX

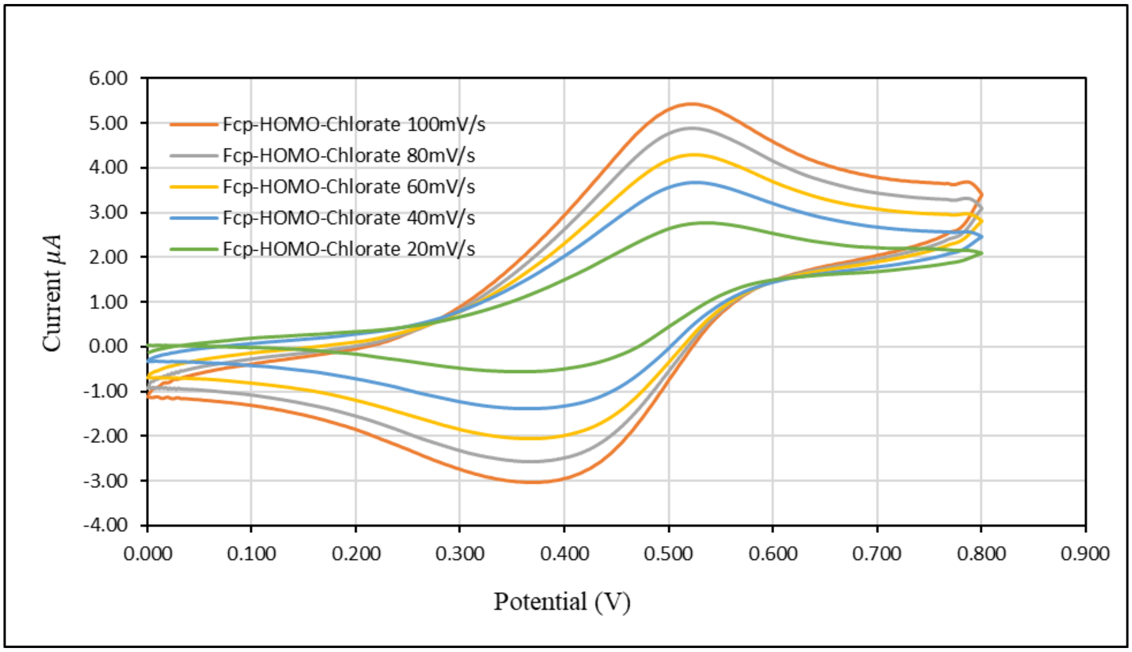

Figure S1: CV of homopolymer in CH_2Cl_2 with Bu_4NClO_4 as a supporting electrolyte.

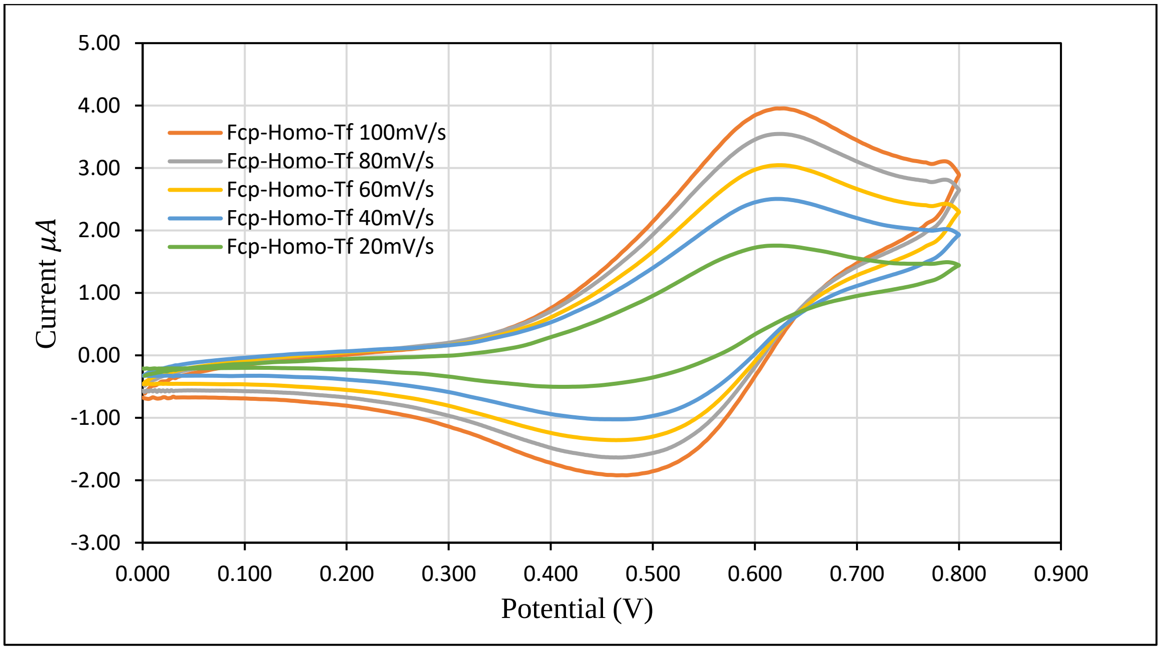

Figure S2: CV of homopolymer in CH_2Cl_2 with Bu_4NOTf as a supporting electrolyte.

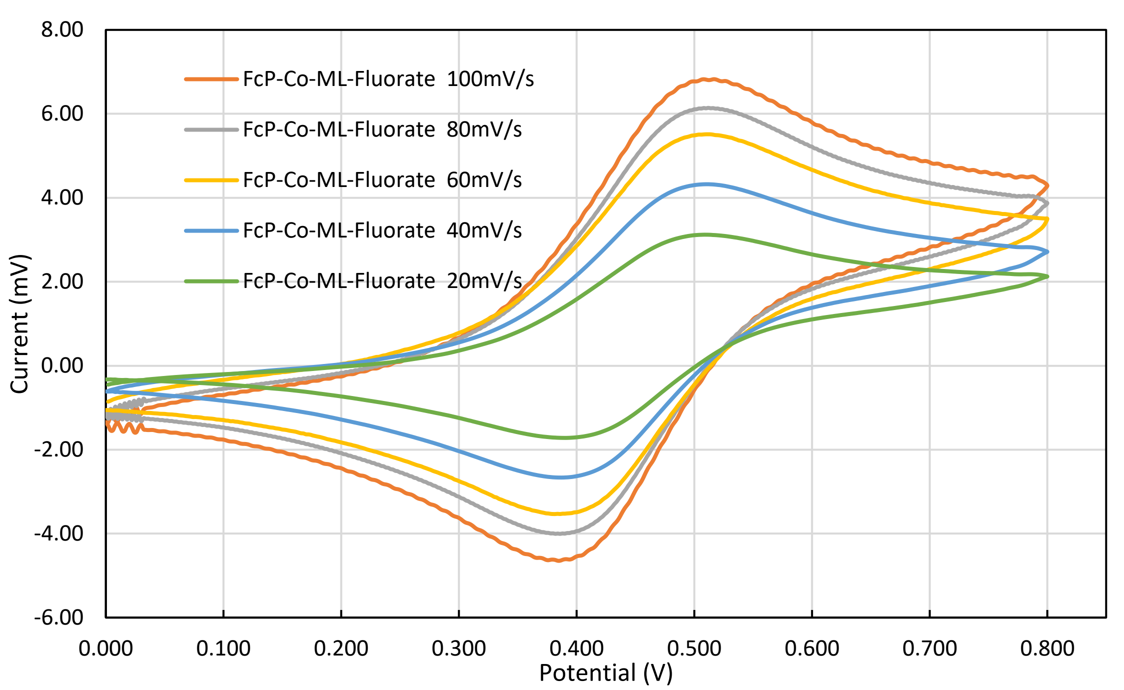

Figure S3: CV of N-Phenylmaleimide copolymer in CH_2Cl_2 with Bu_4NPF_6 as a supporting electrolyte.

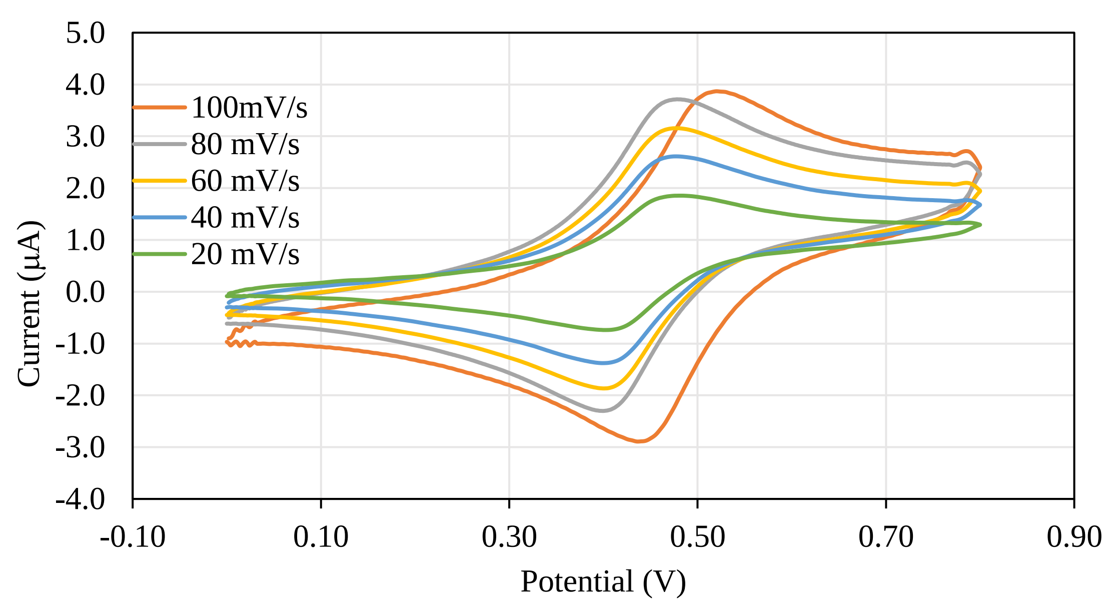

Figure S4: CV of Maleimide polymer in CH_2Cl_2 with Bu_4NClO_4 as a supporting electrolyte.

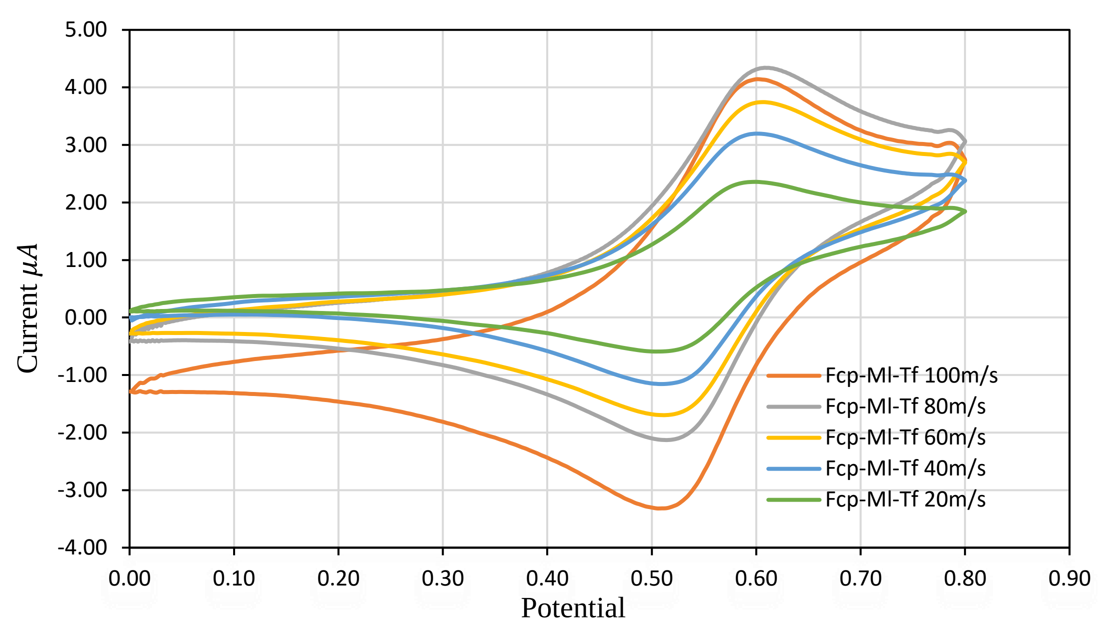

Figure S5: CV of Maleimide polymer in CH_2Cl_2 with Bu_4NOTf as a supporting electrolyte.

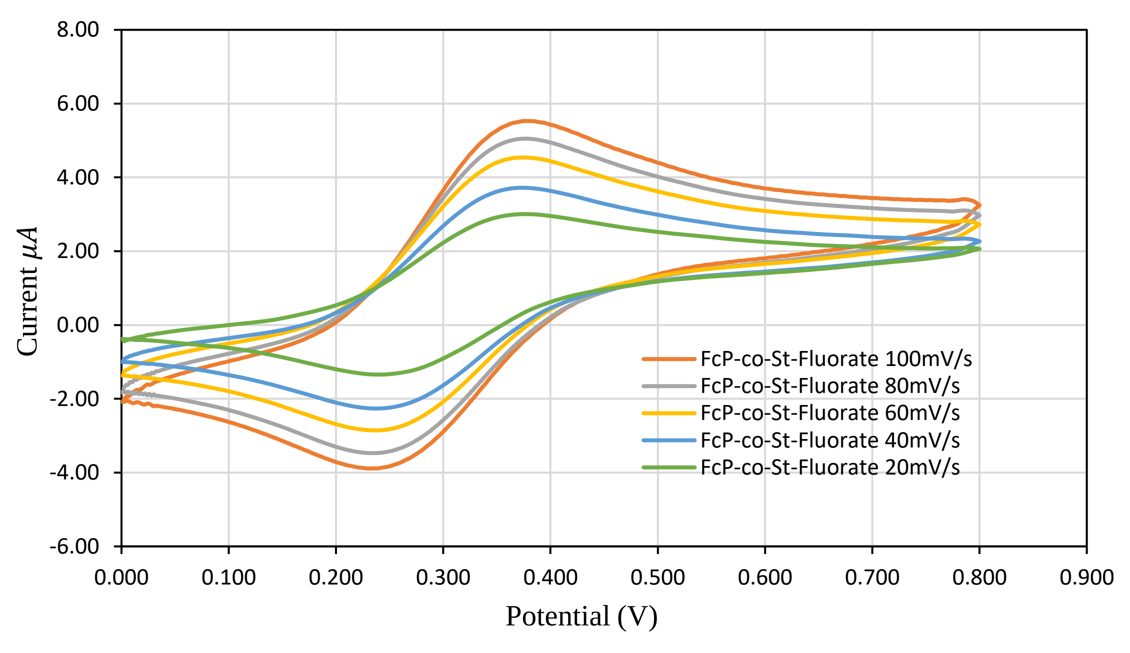

Figure S6: CV of Styrene polymer in CH_2Cl_2 with Bu_4NPF_6 as a supporting electrolyte.

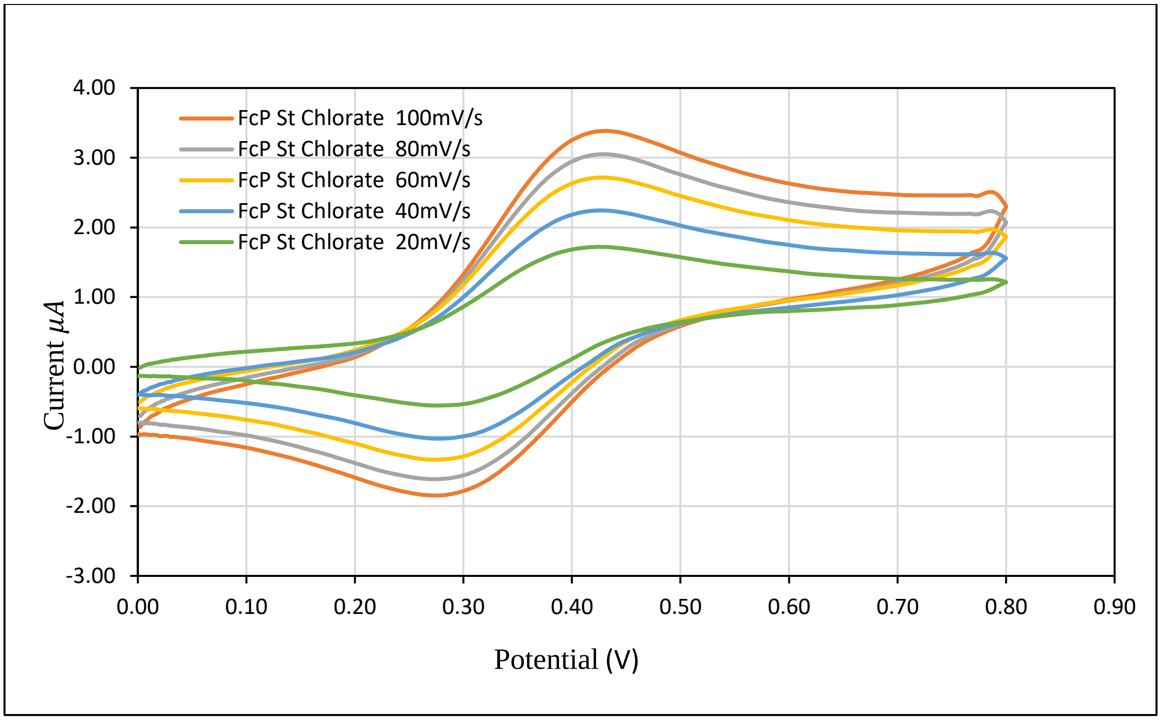

Figure S7: CV of Styrene polymer in CH_2Cl_2 with Bu_4NClO_4 as a supporting electrolyte.

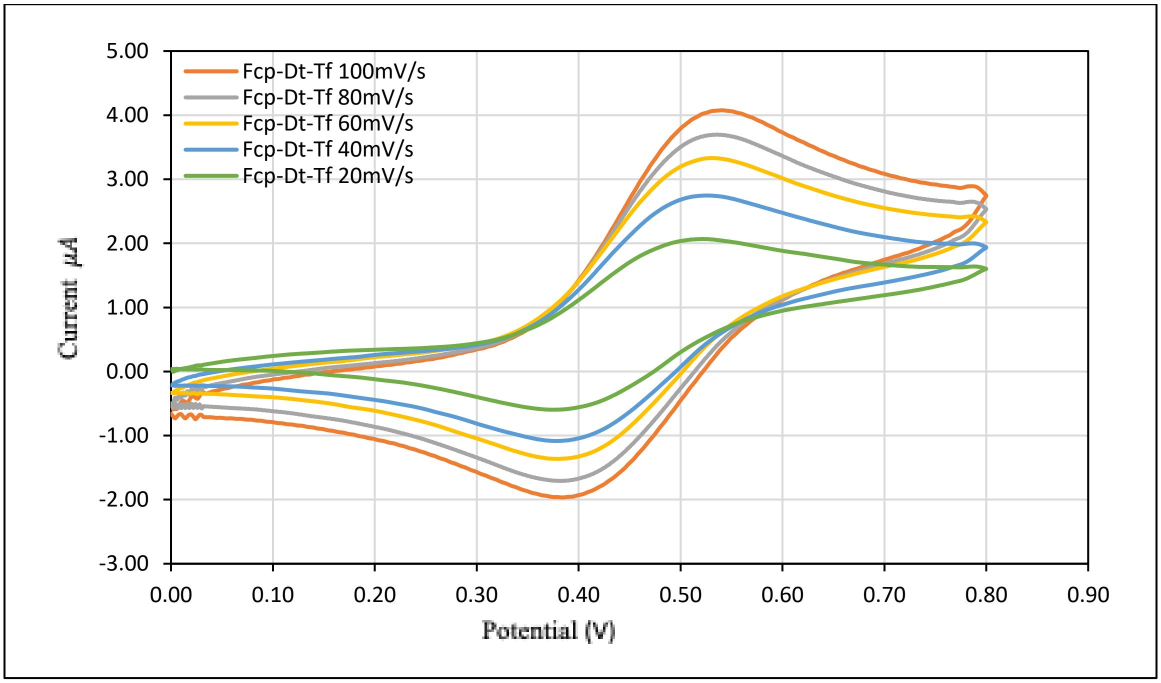

Figure S8: CV of Styrene polymer in CH_2Cl_2 with Bu_4NOTf as a supporting electrolyte.

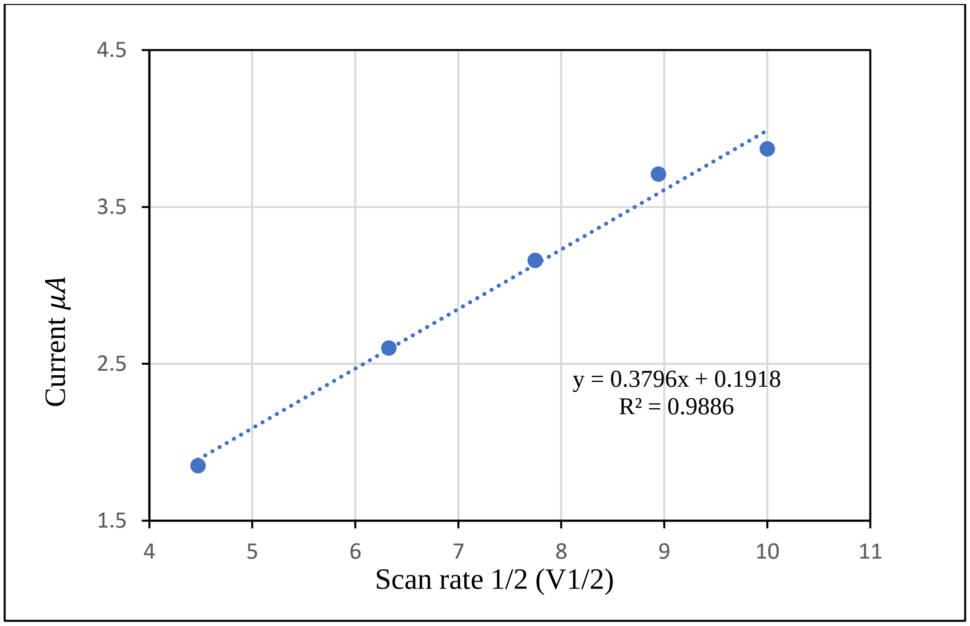

Figure S9: Current versus Scan Rate½ for CVs of Homopolymer with Bu_4NClO_4 as supporting electrolyte.

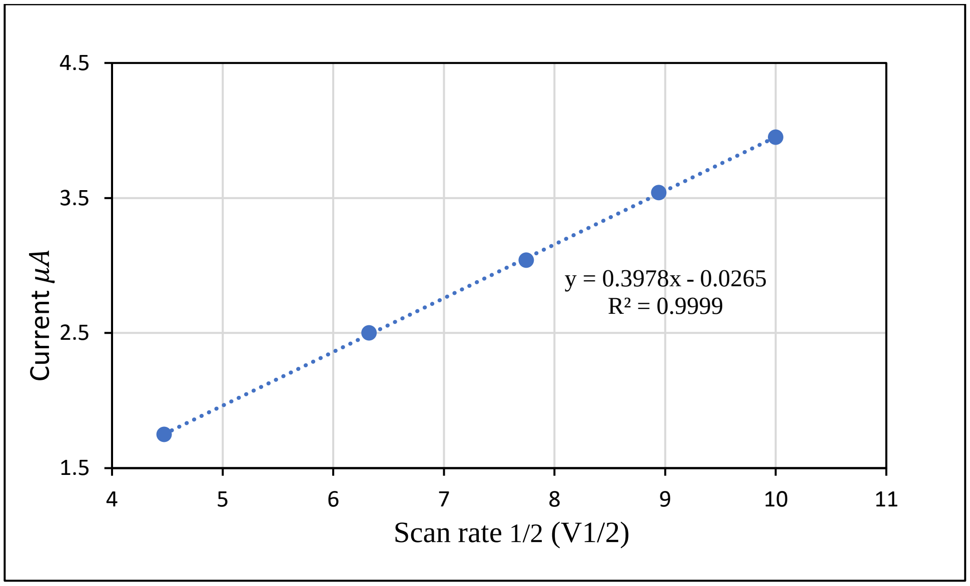

Figure S10: Current versus Scan Rate½ for CVs of Homopolymer with Bu_4NOTf as supporting electrolyte.

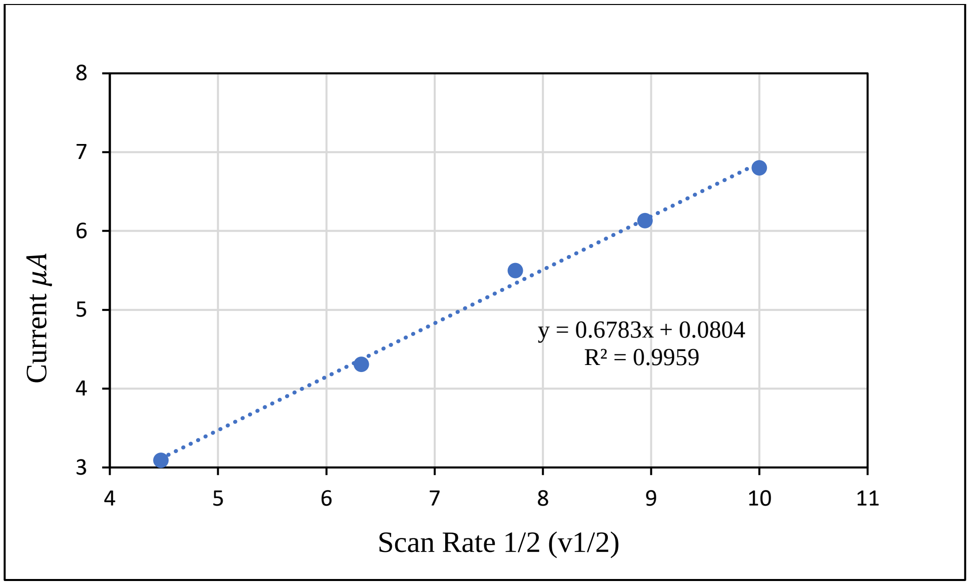

Figure S11: Current versus Scan Rate½ for CVs of Maleimide copolymer with Bu_4NPF_6 as supporting electrolyte.

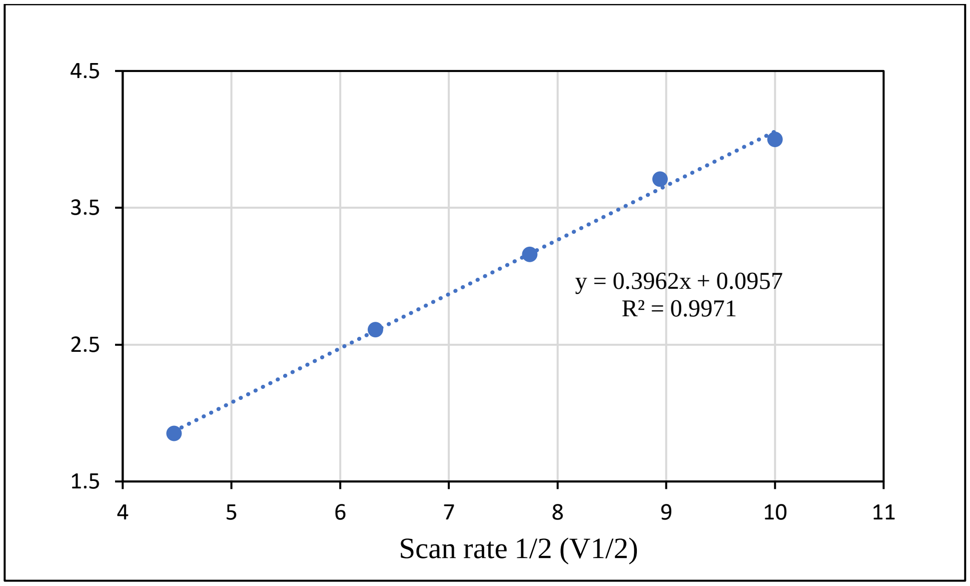

Figure S12: Current versus Scan Rate½ for CVs of Maleimide copolymer with Bu_4NClO_4 as supporting electrolyte.

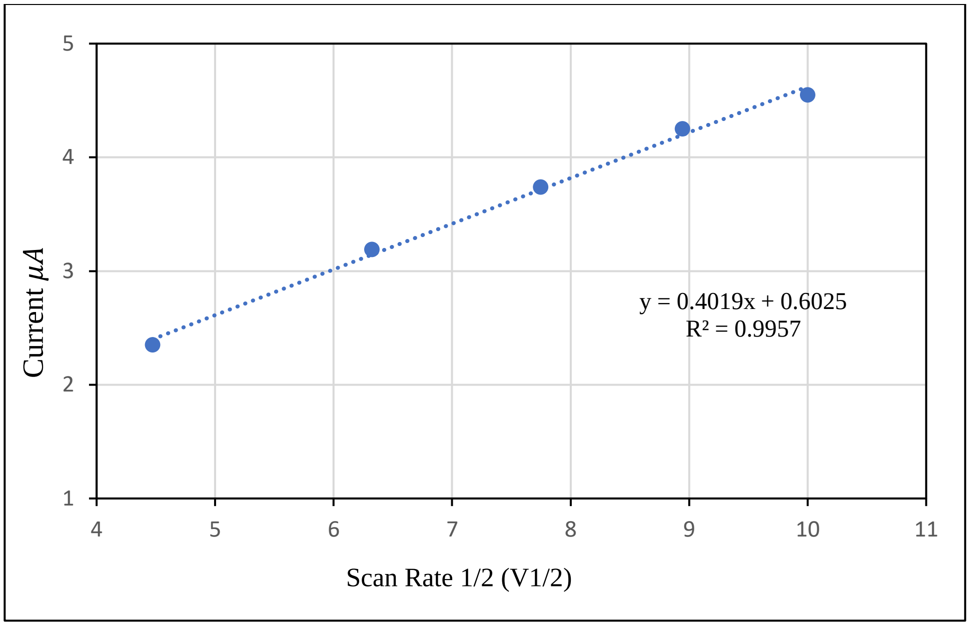

Figure S13: Current versus Scan Rate½ for CVs of Maleimide copolymer with Bu_4NOTf as supporting electrolyte.

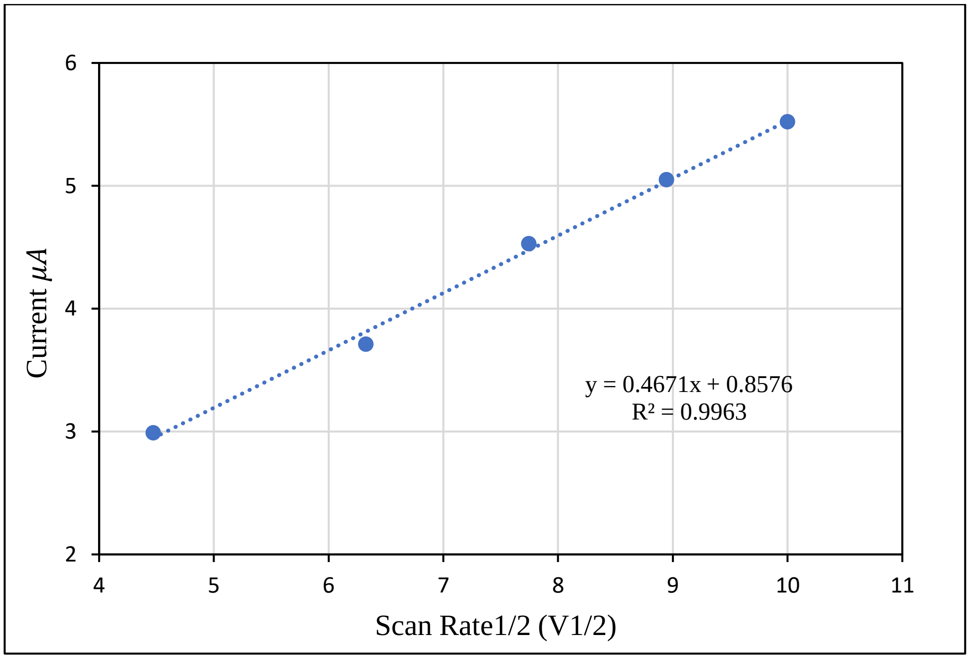

Figure S14: Current versus Scan Rate½ for CVs of Styrene copolymer with Bu_4NPF_6 as supporting electrolyte.

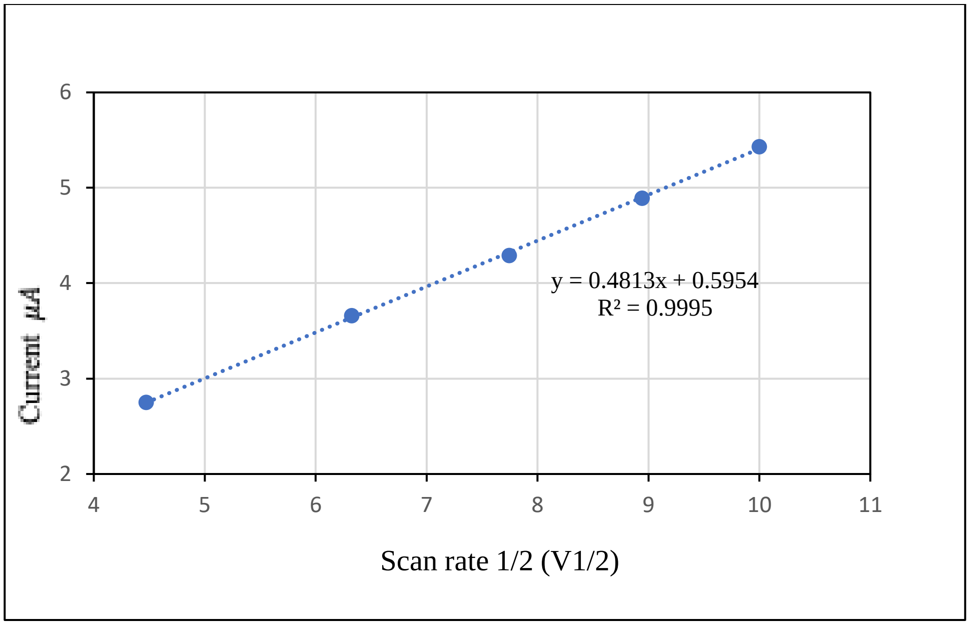

Figure S15: Current versus Scan Rate½ for CVs of Styrene copolymer with Bu_4NClO_4 as supporting electrolyte.

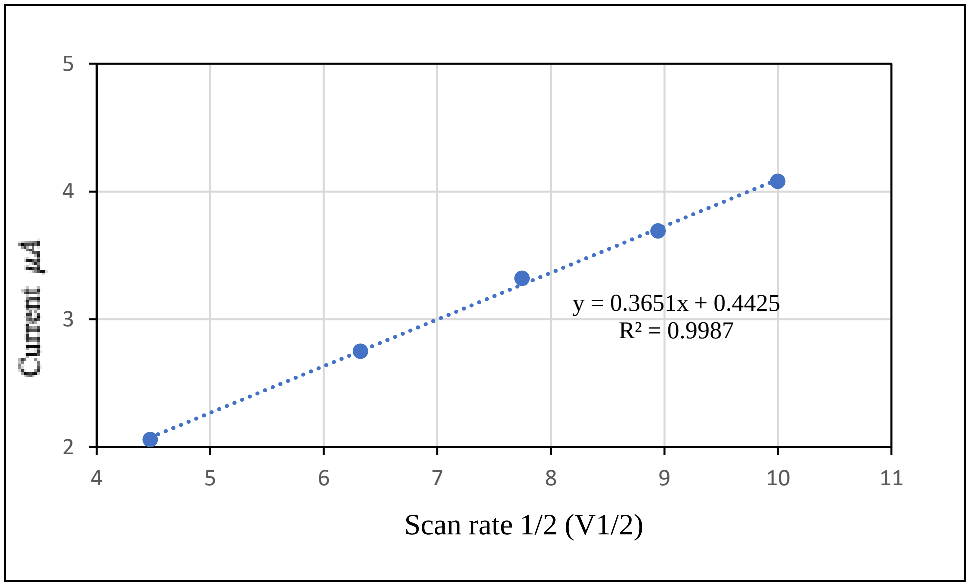

Figure S16: Current versus Scan Rate½ for CVs of Styrene copolymer with Bu_4NOTf as supporting electrolyte.

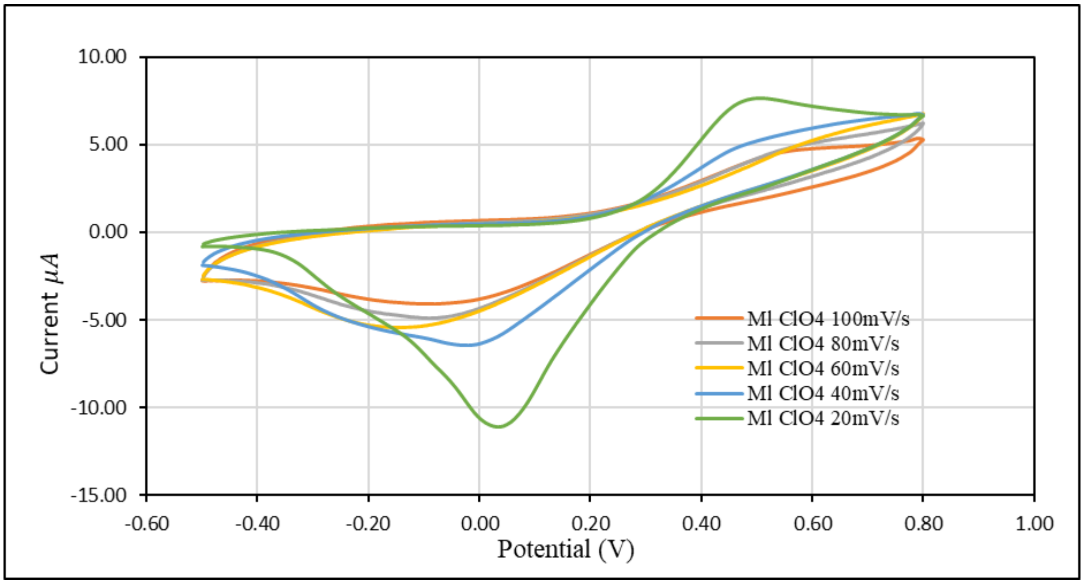

Figure S17: Cyclic Voltammetry of Maleimide copolymer Thin Films in 0.1M Aqueous NaCl Solution

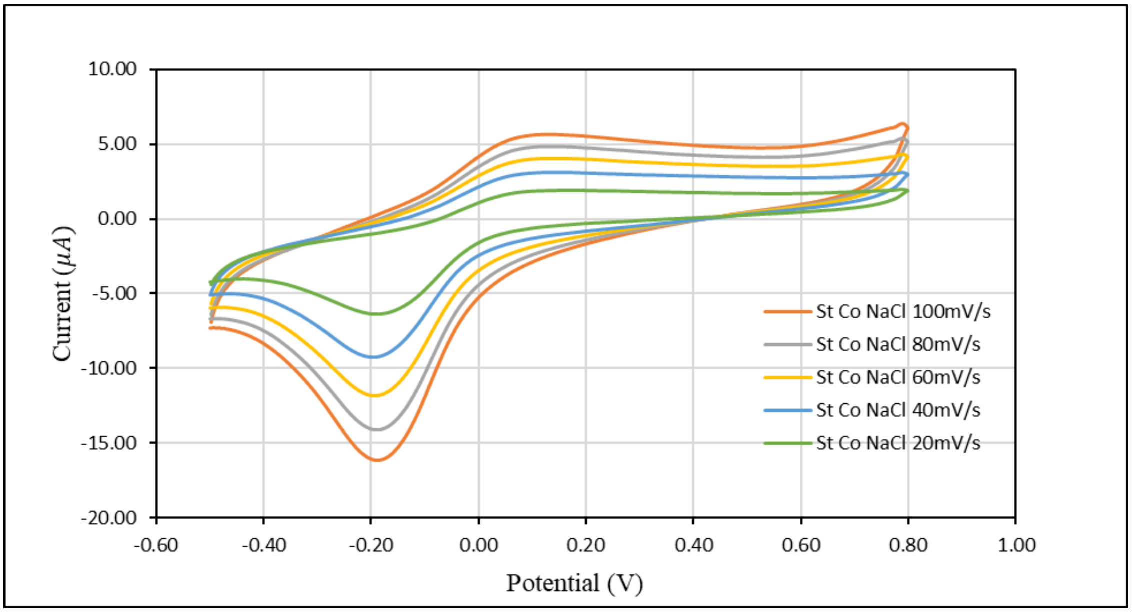

Figure S18: Cyclic Voltammetry of Styrene copolymer Thin Films in 0.1M Aqueous NaCl Solution

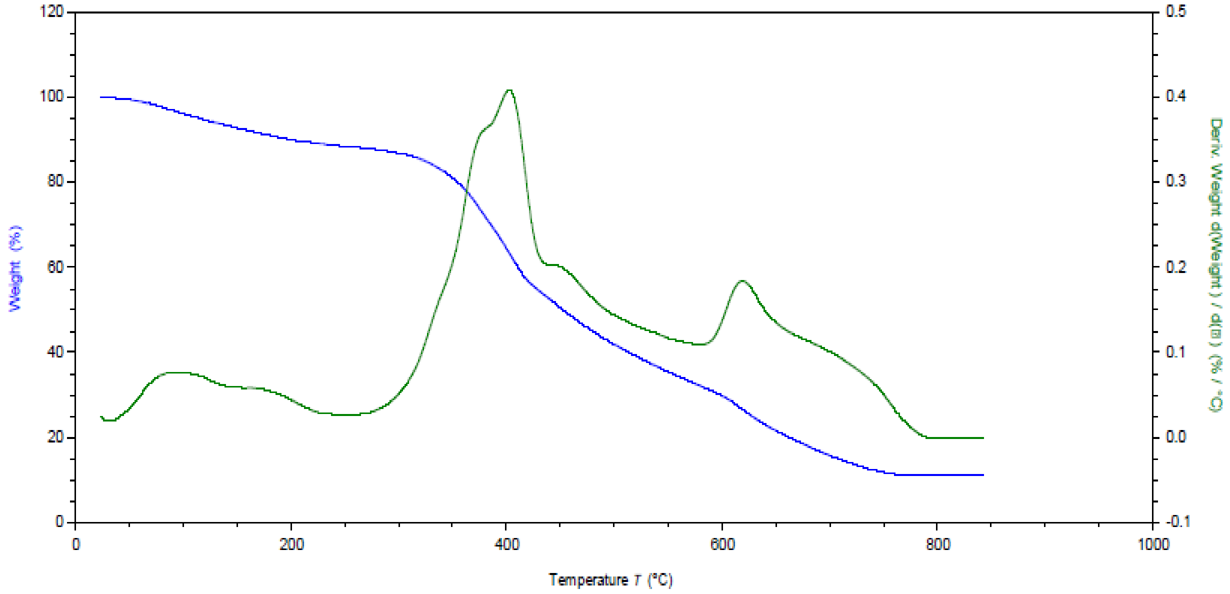

Figure S19: TGA and Derivative plot of Ph-Ml polymer

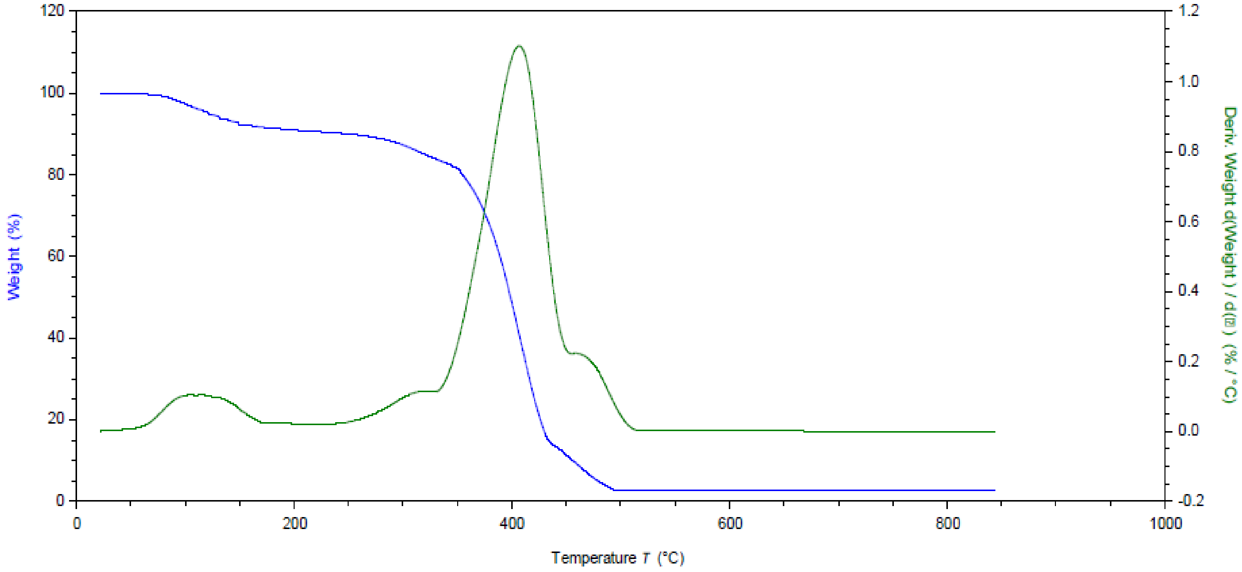

Figure S20: TGA and Derivative plot of Co-St polymer