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ELECTROCHEMICAL STUDIES OF COPOLYMERS OF 3-PHENYL[5]FERROCENOPHANE-1,5-DIMETHYLENE AND VARIOUS PARA-SUBSTITUTED N-PHENYLMALEIMIDES

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ELECTROCHEMICAL STUDIES OF COPOLYMERS OF 3-PHENYL[5]FERROCENOPHANE-1,5-DIMETHYLENE AND VARIOUS PARA-SUSTITUTED N-PHENYLMALEIMIDES

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 COPOLYMERS OF 3-PHENYL[5]FERROCENOPHANE-1,5-DIMETHYLENE AND VARIOUS PARA-SUSTITUTED N-PHENYLMALEIMIDES

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An Abstract of Thesis by
Henry Marshall Thomas

Ferrocene is an organometallic compound that consists of an iron atom sandwiched between two cyclopentadienyl rings. It has well understood redox properties and has been extensively studied making it useful in electrical systems. In this research alternating copolymers were synthesized via free radical polymerization from 3-phenyl[5]ferrocenophane-1,5-dimethylene and various para-substituted N-phenylmaleimides. Copolymers between this ferrocenophane and N-substituted maleimides have shown interesting electrical properties and the potential for charge transfer interactions between ferrocene and maleimide moieties. In this work, four new polymers were synthesized with differing electron withdrawing or donating groups on the para-position of the N-phenylmaleimide in order to influence potential for charge transfer complex formation. These polymers were characterized using ^{1}H-NMR, ^{13}C-NMR and FTIR spectroscopy. Thermogravimetric analysis of polymers showed them to be thermostable to approximately 380°C. Cyclic voltammetry of polymer solutions and thin films revealed electrochemical reversibility of the materials. UV-vis spectroscopy was used to study charge transfer complex formation. Weak absorbencies in the visible spectrum by polymer thin films suggest electrostatic interactions between ferrocenyl and maleimide moieties.

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LIST OF ABBREVIATIONS

CP-Cyclopentadienyl
NMR-Nuclear Magnetic Resonance
NIR-Near Infrared Spectroscopy
UV-Vis-Ultraviolet-visible spectroscopy
IR-Infrared spectroscopy
DFT-Density functional theory
Ipa-Peak Anodic Current
Ipc-Peak Cathodic Current
Mw- Weight Average Molecular weight
FT-IR-Fourier Transformed-Infrared spectroscopy
Eox = Oxidation potential
Ered = Reduction potential
E1/2-Redox Potential
CH_2Cl_2-Dichloromethane
AIBN-Azobisisobutyronitrile
NBu_4PF_6-Tetrabutylammounium hexaflourophophate
$NaClO_4$- Sodium Perchlorate

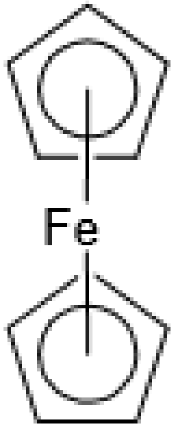
CHAPTER I.

1. INTRODUCTION

1.1 Ferrocene

Ferrocene was discovered in 1951 during an attempt by Kealy and Paulson to synthesize fulvalene[1] This was done by reacting cyclopentadienyl magnesium bromide with Iron (II) chloride in diethyl ether. Miller, Treboth, and Tremane synthesized ferrocene by reacting cyclopentadiene with Iron catalysts at 300° C during the same period. In 1952, the structure of ferrocene was first published consisting of on an iron atom “sandwiched” between two cyclopentadienyl (CP) anions [2]. Ferrocene is diamagnetic, and shows only one C-H stretch in the Infrared Spectrum, indicating that all carbon atoms in the molecule are equal. The ^{1}H-NMR spectrum of ferrocene shows one singlet, confirming the uniformity of the protons present in the cyclopentadienyl anions[2].

Scheme 1: Structure of Ferrocene



The name ferrocene was chosen for the molecule after it was discovered that the molecule was aromatic to reflect its similarity to benzene [3]. After this character was discovered, multiple metallic sandwich compounds have been prepared and researched [3], [4], [5]. Chromium dibenzene was synthesized and characterized after ferrocene's discovery. This material was found to undergo electronic transition when exposed to UV light[4]. The discovery of ferrocene is often credited with an increased interest of the field of organometallics [6]. The CP rings of the molecule are highly nucleophilic, and readily undergo electrophilic substitution reactions, including Friedel-Crafts acylation, alkylation, sulfonation, and metalation [6]. However, direct halogenation or nitration destroys the molecule, possibly as a result of oxidation of the iron atom in these reactions [6]. These ferrocene derivatives have proven useful for a variety of applications, including potential for intramolecular electron transfer [7]. Addition of functional groups of electron donating or withdrawing character has been proven to change the oxidation potential of the molecules, allowing for an even more diverse range of applications including as electrical conducting polymers and incorporation into solar cells[8],[9].

1.2 Charge Transfer Complexes

Charge transfer complexes can occur when an electron rich molecule with a low ionization potential experiences weak orbital interactions with an electron deficient molecule with high electron affinity. These complexes, known to be weak, are a result of electrostatic interactions between two molecular moieties and are often brightly colored[17]. Polymer blends of electron rich polymers with low molecular weight electron acceptors have been extensively studied due to their potential for use as thin film photovoltaics and in solar applications[18]. In polymer blends, excitation of these materials in the red portion of the visible spectra as well as into the infrared region can result in charge transfer complex excitation[19]. It has been shown that physical proximity and orientation of donors and acceptors are important in the formation of a charge transfer complex[20]. Although polymer blends have been extensively studied, little research has been reported on charge transfer complexation within polymer chains. Ferrocene has been shown to be a donor molecule when placed in close proximity to an electron acceptor and has demonstrated potential to form charge transfer complexes as a result of photoexcitation[23].

1.3 Ferrocene Polymers

Ferrocene has been successfully incorporated into both polymer backbones and polymer side chains[9], [10]. Ferrocene has unique properties that when incorporated into polymers can increase the redox potential, thermal degradation resistance, and mechanical integrity of polymer chains[10], [11]. The electronic properties of ferrocene have been proven useful for applications such as energy storage and electrocatalysis[16], [19].

The highly nucleophilic nature the CP rings possess further interesting characteristics. Because of the high electron density associated with these rings, they show potential to facilitate electron transfer to areas of low electron density within polymer chains[10]. Incorporation of ferrocene and resulting electron transfer mechanisms into polymer systems have proven useful in the development of enzymatic biosensor technology[12]. Ferrocene polymers have the added advantages of increased chemical stability and well understood redox properties. Polymeric thin films with ferrocene have also been shown to be useful in memory device applications and as thin film transistors[13], [14].

Ferrocene polymers have been studied extensively for their electronic applications as semi-conductors and for interactions between neighboring ferrocene moieties[14]. However, ferrocene polymers have been limited by their difficulty to synthesize them to high molecular weights, due to the potential for zwitterion formation[23]. Particularly in free radical polymerization, zwitterion formation by transfer of an electron from the ferrocene to the end of the growing polymer chain results in an additional termination step, lowering molecular weight and increasing polydispersity. Recent research has presented a new method of incorporating and protecting electronic interactions through the use of polymerization via cyclophanes[21], [22]. Use of ferrocenophanes has resulted in ferrocene incorporation pendant to the main polymer chains. High molecular weight polymers of 3-phenyl[5]ferrocenophane-1,5-dimethylene have been produced via free radical polymerization[21]. This cyclophane chemistry results in the CP rings of ferrocene stacking in close proximity to one another, and cyclic voltammetry of these polymers shows two oxidation potentials, indicative of electron interactions between ferrocenyl groups.

Polymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene with various N-substituted maleimides to high molecular weight copolymers have also been reported [21][22]. The maleimide comonomers were substituted with a methyl, ethyl, or phenyl at the nitrogen. Cyclic voltammetry of these polymers showed one oxidation potential, which is consistent with exactly alternating copolymers. ^{13}C-NMR was also consistent with an alternating monomer distribution. These results are expected by analogy to the exactly alternating distribution in the polymerization of vinylferrocene and maleic anhydride [15]. Cyclic voltammetry showed these polymers to be redox stable and electrochemically reversible. Cyclic voltammetry also revealed that I_{pa} scaled linearly with scan rate, indicating a high degree of adsorption to the electrode surface when oxidized, making these attractive as chemically modified electrodes. These polymers were also useful in forming amorphous films when solution cast. They were shown to be highly thermostable, with 15% mass loss at 385ºC. UV-vis studies of these polymers in solution show broad absorptions extending well into the Near IR region, indicating potential weak charge transfer complex formation.

1.4 Project Rationale

This work focuses on the effect of substitution of the N-phenylmaleimide on the electrochemical properties of the ferrocene-N-phenylmaleimide interactions. By polymerizing 3-phenyl[5]ferrocenophane-1,5-dimethylene with various para-substituted N-phenylmaelimides, it was possible to alter the electron deficiency of the maleimide group. Addition of an electron withdrawing substituent to the phenyl ring decreased the electron density of the maleimide group and was expected to result in an increase in the strength of a charge transfer complex. Charge transfer complexes are frequently observed in UV-vis spectroscopy and peaks in the visible region are indicative of this electrostatic interaction. Charge transfer interactions result in low energy thresholds to energy transfer between donor and acceptor excited states, resulting in absorbance of the energy of light in the UV-visible range. Secondary redox waves in thin films can also reveal partial charge transfer interactions. Charge transfer complexes in the polymer stabilize the electrons in the system, which results in higher applied voltage required for oxidation of the material, resulting in a second wave in Cyclic Voltammetry. In addition, these polymers were fully characterized electrochemically and thermally.

CHAPTER II.

2. EXPERIMENTAL

2.1 Materials

All materials were purchased from Acros Organics and used as received unless otherwise mentioned here. Maleimides were synthesized according to a commonly used synthetic procedure[24]. Equimolar concentrations of maleic anhydride and para-substituted anilines were refluxed in acetic acid for 16 hours followed by recrystallization from isopropanol.

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

2.2.1 Synthesis of 1,1-diacetylferrocene[21]

To a dry round bottom flask was added dichloromethane (150 mL) and aluminum chloride (9.4 g, 0.071 mol). After establishing a nitrogen atmosphere, acetyl chloride (5.5g, 0.071 mol) was added and the solution was stirred for 30 minutes. ferrocene (5.07g, 0.027mol) was then added over a period of 15 minutes, and the system was allowed to react for 16 hours. After 16 hours, the solution was poured over ice in a 500 mL beaker to neutralize remaining aluminum chloride. The organic phase was removed and the solvent was removed with a rotary evaporator. The solid was then collected and recrystallized from isopropyl alcohol. The solid was collected by vacuum filtration and dried under heat and vacuum overnight. 4.5g (63%) of 1,1-diacetylferrocene was recovered. ^{1}H-NMR ($CDCl_3$, δ ppm): (4.77, 4 H, CP-ring), (4.52, 4 H, CP-ring) (2.36, 6H, C-CH_3). IR (cm^{-1}): (3100, C-H aromatic), (1680, C=O, carbonyl), (1500 C=C, aromatic).

2.2.2 Synthesis of 3-phenyl[5]ferrocenophane-1,5-dione[21]

To a 150 mL Erlenmeyer flask with a stir bar was added 1,1'-diacetylferrocene (4.0 g, 0.015mol), Benzaldehyde (1.90 g, 0.018 mol) and 95% ethanol (150 mL).The reaction was stirred for 30 minutes. Potassium hydroxide (0.48g .0086 mol) was then added, and the reaction was stirred for 16 hours at room temperature. The product was collected by vacuum filtration and dried under heat and vacuum overnight. 4.28 g (75%) of the 3-phenylferrocenophane-1,5-dione was recovered. ^{1}H-NMR ($CDCl_3$, δ ppm): (7.20, 5H, phenyl protons), (4.89, 4.78, 4.62, 4.52, 8H, CP protons), (4.35, 1H, benzyl proton), (2.95, 2.51 4H, methylene protons). IR (cm^{-1}): (3000, C-H aromatics), (1690, carbonyl).

2.2.3 Synthesis of 3-phenyl[5]ferrocenophane-1,5-dimethylene[21]

To a round bottom flask was added methyltriphenylphosphonium bromide (2.4g, 0.011 mol) and tetrahydrofuran (70mL). The solution was stirred and a nitrogen atmosphere was established. After the nitrogen atmosphere was established, n-butyllithium was added (8.2 mL, 2.5 M), and the solution continued to stir for 30 minutes. Then 3-phenyl[5]ferrocenophane-1,5-dione was added (2.4g, 0.0068 mol). The reaction was stirred for 20 hours. After the reaction was complete, distilled water (1.5 mL) was added to the solution and then the solvent was removed using a rotary evaporator. The reaction mixture was purified by column chromatography using silica gel with chloroform as the mobile phase. The column yielded 1.4 g (58%) of 3-phenyl[5]ferrocenophane-1,5-dimethylene. ^{1}H-NMR ($CDCl_3$, δ ppm): (7.26, 5 H, phenyl protons), (5.26, 2H, vinylidene protons), (4.78, 2H, vinylidene protons), (4.47, 4.34, 4.30, 4.24, 8 H, CP-protons), (4.16, 1H, benzyl proton), (2.63, 4 H, C-CH_2). IR (cm^{-1}): (3093, =C-H stretch), (3000, C-H aromatic), (2915, C-H aliphatic), (1680, C=C stretch).

2.2.4 Polymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene with N-(4-acetylphenyl)maleimide

To a small round bottom flask was added 3-phenyl[5]ferrocenophane-1,5-dimethylene (0.21 g, $5.7x10^{-4}$ mol), N-(4-acetylphenyl)maleimide (0.063 g, $2.9x10^{-4}$ mol), and chlorobenzene (2 mL). A nitrogen atmosphere was established and AIBN was added (0.0026g). The reaction was stirred at 70ºC for 16 hours. After polymerization, the reaction mixture was precipitated by drop wise addition into rapidly stirring methanol. Upon precipitation, the solid was collected by vacuum filtration and dried under heat and vacuum overnight. 0.14g (90%) of polymer were recovered. ^{1}H-NMR ($CDCl_3$, δ ppm): (7.27, 9 H, phenyl protons), (4.34, 8H, CP protons), (2.7-0.8, 14 H, aliphatic protons). IR (cm^{-1}): (3100, C-H aromatic), (2885, C-H aliphatic), (1700, C=O). GPC (M_w:3700, PD: 5.2).

2.2.5 Polymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene with N-(4-cyanophenyl)maleimide

The synthetic procedure was as in 2.2.4. 3-Phenyl[5]ferrocenophane-1,5-dimethylene (0.20g, $5.0x10^{-4}$ mol), and N-(4-cyanophenyl)maleimide (0.065g, $3.2x10^{-4}$ mol) were polymerized using AIBN (0.0050g) as an initiator. The yield of polymer was 0.13 g (75%). ^{1}H-NMR ($CDCl_3$, δ ppm): (7.37, 9H phenyl protons), (4.34-3.54, 8 H, CP protons), (2.7-0.8, 11 H, aliphatic protons). IR (cm^{-1}): (3100, C-H aromatics), (2900, C-H aliphatics), (2280, C≡N), (1760, C=O). GPC (M_w: 11200, PD: 11.2)

2.2.6 Polymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene with N-(4-methoxyphenyl)maleimide

The synthetic procedure was as in 2.2.4. 3-Phenyl[5]ferrocenophane-1,5-dimethylene (0.20 g, 5.6x10^{-4} mol), and N-(4-methoxyphenyl)maleimide (0.059g, 2.9x10^{-4} mol) were polymerized using AIBN (0.0046g) as an initiator. The yield of copolymer was 0.11g (71%). ^{1}H-NMR ($CDCl_3$, δ ppm): (7.26, 9H, phenyl protons), (4.38-3.8, 8H, CP protons), (3.7, 3H, O-CH), (2.4-1.4, 11H, aliphatic protons). IR (cm^{-1}): (3000, C-H aromatics), (2800, C-H aliphatics), (1700, C=O), (1270, C-O). GPC (Mw: 7700, PD:10.3)

2.2.7 Polymerization of 3-phenyl[5]ferrocenophane-1,5-dimethylene with N-(4-methylphenyl)maleimide

The synthetic procedure was as in 2.2.4. 3-Phenyl[5]ferrocenophane-1,5-dimethylene (0.20g, 5.6x10^{-4} mol), and N-(4-methylphenyl)maleimide (0.058g, 3.1x10^{-4} mol) were polymerized using AIBN (0.0024g) as an initiator. The yield of polymer was 0.12g (70%). ^{1}H-NMR ($CDCl_3$, δ ppm): (7.24, 9H, phenyl protons), (4.34-3.7, 8H CP protons), (2.4-1.2, 14 H, aliphatic protons). IR (cm^{-1}): (3000, C-H aromatics), (2900, C-H aliphatics), (1700, C=O), (1550, C=C, aromatics). GPC (M_w: 15200, PD: 10.4)

2.3 Instrumentation

All NMR spectra were taken using a Bruker DPX-300 MHz spectrometer. Fourier Transform Infrared Spectroscopy (FT-IR) was performed using a Perkin Elmer Spectrum 2 Spectrometer. Cyclic Voltammetry and Chronoamperometry were carried out using a

Gamry Interface 1000 potentiostat with a platinum working electrode, a platinum counter electrode, and an Ag/Ag^+ counter electrode. UV-vis spectroscopy was performed using a Gamry UV-Vis spectro-115u system. Gel permeation chromatography (GPC) measurements were taken using a JMDG-4 Waters 515 HPLC pump, a 2410 differential refractometer (Waters), set of one 300x7.8 mm phennogel 5μ column. Mn, Mw, and polydispersity were calculated based on peaks compared to a polystyrene standard calibration.

2.4 Electrochemical Studies

Polymer solutions for electrochemistry were prepared in dichloromethane at concentrations of 1mM with tetrabutylammounium hexaflourophophate (0.1 M) as the supporting electrolyte.

Electrochemistry in aqueous solutions were performed on cast films of the polymer using sodium perchlorate (0.1 M) as the supporting electrolyte. Thin films of the polymer were prepared by casting 2 μL of a dichloromethane solution of the polymer (1 mM) and air drying for about 15 minutes.

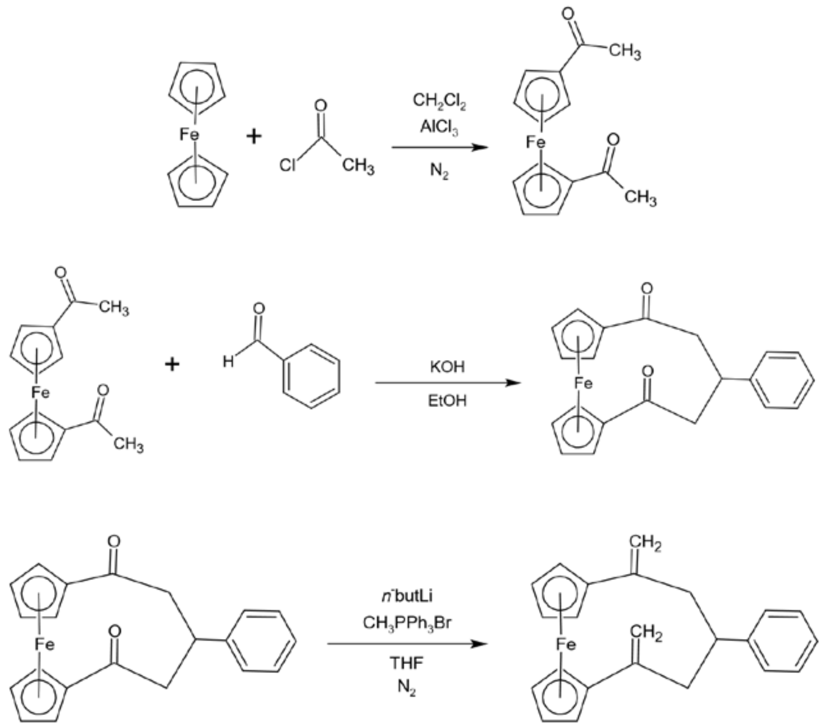
CHAPTER III.

3. RESULTS

3.1 Characterization of Copolymers of 3-phenyl[5]ferrocenophane-1,5-dimethylene and various para substituted N-phenylmaleimides.

The synthesis of 3-phenyl[5]ferrocenophane-1,5- dimethylene was accomplished according to literature procedure[21].

Scheme 2: Synthesis of 3-Phenyl[5]ferrocenophane-1,5-dimethylene



Ferrocene was acetylated under Friedel-Crafts conditions. A subsequent condensation reaction was used to react benzaldehyde with the 1,1’-diacetylferrocene to form 3-phenyl[5]ferroceneophane-1,5-dione. A Wittig reaction was then used to produce the monomer 3-phenyl[5]ferroceneophane-1,5-dimethylene. This monomer was then polymerized with para-substituted N-phenylmaleimides using AIBN as a free radical initiator as shown in Scheme 1. Good polymer yields were obtained, ranging from 70-90%. ^{1}H-NMR spectra of the copolymers showed very broad peaks that were consistent with similar spectra reported in literature[21]. Broadening of ^{1}H-NMR peaks as seen in the phenyl, ferrocenyl and aliphatic regions of the spectra is consistent with high molecular weight polymers. Broadening of spectra is expected, particularly in free radical polymerization of these substituents, as chiral centers are created when the maleimide is incorporated into the polymer. Also, the absence of the vinylidene proton peaks at 4.78 and 5.26 ppm are consistent with complete reaction of the methylene groups of the ferrocenophane monomer. In the ^{13}C-NMR of polymer 1, the presence of 7 aliphatic carbon resonances, as opposed to the expected 11 was likely a result of coincidental overlap of peaks. This number of prevalent carbon resonances in ^{13}C-NMR suggests that polymers are alternating with respect to monomer distribution. Random monomer distribution would result in a greater number of aliphatic carbon resonances. Alternation of monomer units is expected due to the electronic character of the monomers. The carbon-carbon double bond of the N-phenylmaleimide is electron deficient as a result of the electronegativity of the atoms in conjugation with this double bond. When a free radical is formed on this bond, the electron deficient radical will seek to react with an electron rich double bond, in this case, the methylene double bond of 3-

phenyl[5]ferrocenophane-1,5-dimethylene. When a radical attacks the first methylene double bond of the ferrocenophane, steric hindrance will drive the radical towards the center of the molecule. This molecule is stiff, and steric hindrance prevents attack of the radical until the second methylene of the ferrocenophane reacts with the radical center, completing cyclization of the ferrocenophane. The newly formed radical will have high electron density due to the multiple aromatic rings and aliphatics, and will show a higher affinity towards polymerization with the electron deficient phenylmaleimide. This should result in alternation of monomer units. FT-IR spectrum of polymer 1 does not show a band at 1680 corresponding to C=C double bonds. This indicates that all monomer has either been reacted or removed during precipitation. Polymer 1 showed a M_w of 3700 and a polydispersity of 5.2. The molecular weight was particularly low and the polydispersity was high. While these results are undesirable, they are consistent with ferrocene polymers as a result of termination due to zwitterion formation[21]. Characterization data for polymers 2-4 were similar to polymer 1.

Scheme 3: Copolymerization of 3-phenyl[5]phenylferrocenophane-1,5-dimethylene with parasusbtituted N-phenylmaleimides

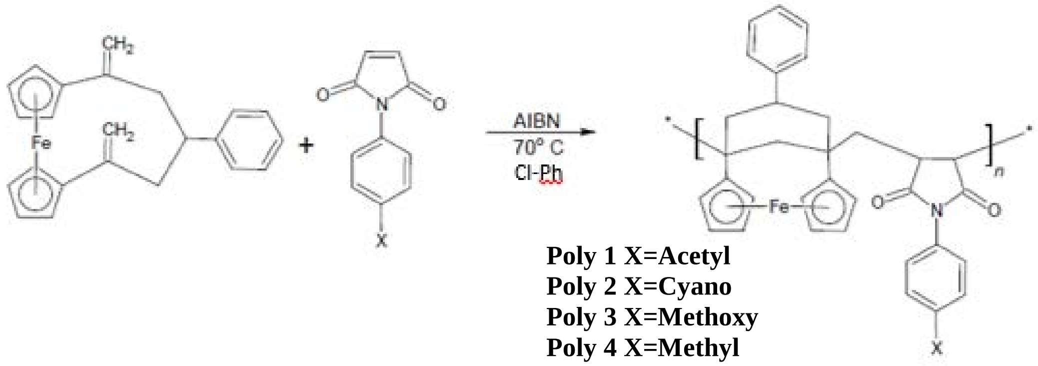


Table 1: Polymerization Results

Polymer	M_w	PDI	% Yield
Polymer 1 (X=Acetyl)	3700	5.2	90%
Polymer 2 (X=Cyano)	11200	11.2	75%
Polymer 3 (X=Methoxy)	7700	10.3	71%
Polymer 4 (X=Methyl)	15200	10.4	70%

3.2 DFT studies of Copolymers

Density Functional Theory (DFT) modeling of the optimum structure of the polymer backbone by Dr. Ben Tayo of Pittsburg State University produced the structures shown in Figures 1 and 2. Modeling was conducted using Gaussian 09 software to determine the lowest energy three dimensional orientation of the monomer units in space. No longer than a trimer model was produced due to the complexity of modeling a polymer with a large number of atoms. This model gave a single low energy conformation and showed the CP-ring of the ferrocene moiety in close proximity to the N-phenylmaleimide, with the smallest distance between ferrocenyl and maleimide moieties calculated to be 3.2Ǻ as shown by arrow A in Figure 1. The physical proximity of these moieties was a good indication of the potential for electronic interaction between π orbitals of electron rich ferrocene and electron deficient N-phenylmaleimide groups. Complete co-facial stacking of the maleimide and ferrocenyl moieties is impossible due to inability of the maleimide to rotate orthogonal to the polymer backbone. Steric hindrance is likely one reason why these molecules assort in this fashion. In the opposite configuration, bulky carbon and phenyl rings would be in very close proximity resulting in a high energy conformation.

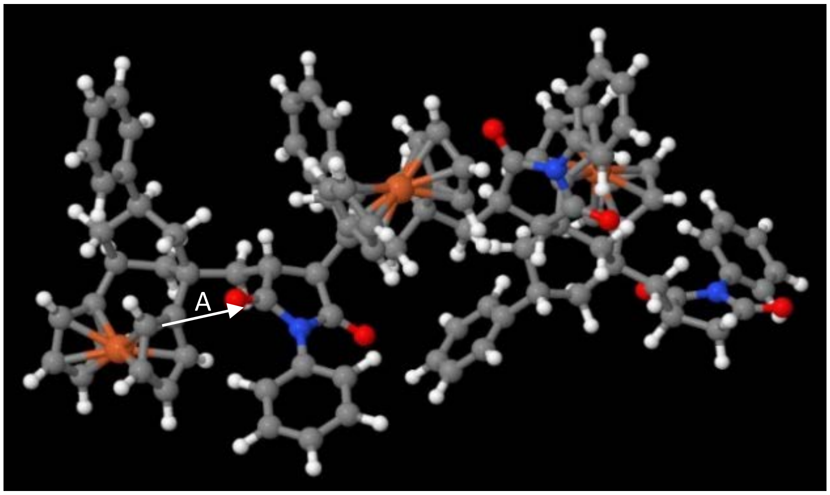


Figure 1: Ball and Stick model of Poly-3-phenylferrocenophane-1,5-dimethylene-co-N-Phenylmaleimide

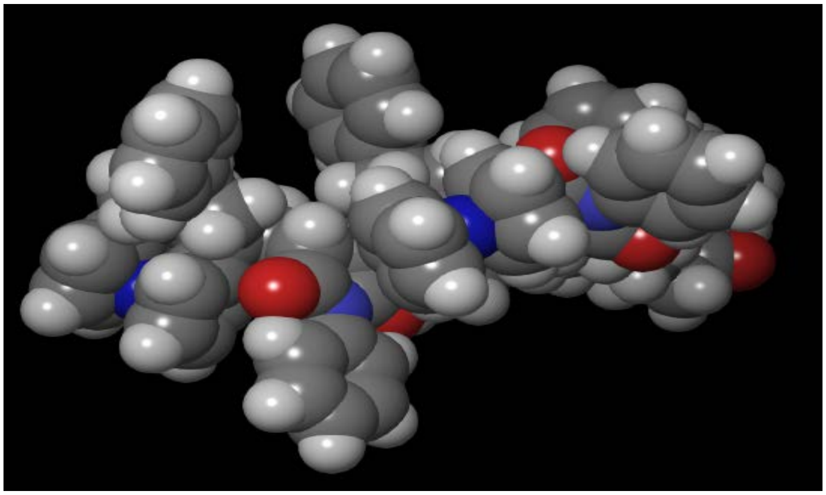


Figure 2: Space Filling model of Poly-3-phenylferrocenophane-1,5-dimethylene-co-N-phenylmaleimide

3.3 Thermogravimetric Analysis of Copolymers

Ferrocene has been proven to be useful as for its flame retardant properties and thermostability. Thermogravimetric analysis of the copolymers was conducted from room temperature to 600ºC. Polymers showed excellent thermostability to 380ºC. Polymer 1 (X=Acetyl) showed only 20% mass loss at 390ºC, and did not reach its first derivative peak until heated to 400 ºC. Over 45% of the mass was retained as char after reaching 600ºC as well. Similar results were observed for polymers 2-4. High char yields for all four polymers were observed ranging from 34-49%. Polymer 1 showed moderate char yield (42%) at 600ºC but was also the polymer to reach its maximum decomposition rate at the lowest temperature. This is indicative that the char yield and thermostability are not directly related. This lowest decomposition temperature is likely a function of the low molecular weight, leading to the earliest point of degradation. Polymer 2 (X=Cyano) showed the lowest char yield at 34%. Char yield appears to loosely increase with increasing electron donating character of the substituent of the N-phenylmaleimide, but further studies of these materials would be required to confirm this relationship. Polymer 4 showed both the highest thermostability and the highest char yield as shown in Table 1. This data suggests that while all polymers showed thermostability, polymer 4 (X=Methyl) would be the best candidate for use in high temperature applications.

Table 2: Thermostability and Char of Polymers 1-4

Polymer	**Peak Decomposition Rate Temperature (°C)**	**Char at 600°C (%)**
Polymer 1 (X=Acetyl)	400	42
Polymer 2 (X=Cyano)	461	34
Polymer 3 (X=Methoxy)	474	47
Polymer 4 (X=Methyl)	482	49

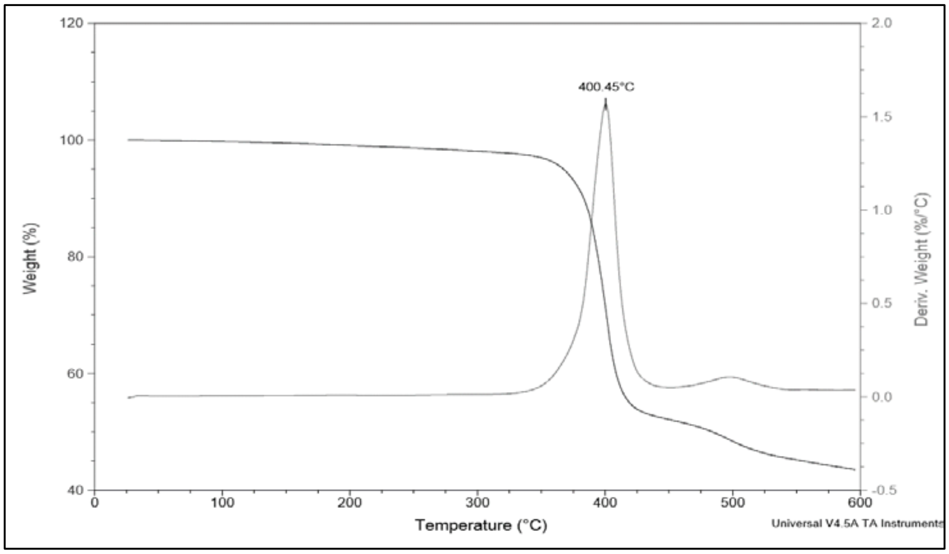


Figure 3:TGA plot of Polymer 1 (X=Acetyl)

3.4 Electrochemical Studies of Polymers

3.4.1 Electrochemical Studies of polymers in CH$_2$Cl$_2$

Solutions of polymers for electrochemistry were prepared in dichloromethane (5mg/mL) using 0.1M tetrabutylammounium hexaflourophophate (NBu$_4$PF$_6$) as supporting electrolyte. Cyclic voltammetry was run at scan rates of 20, 40, 60, 80 and 100 mV/s. The redox potentials of each polymer are shown in Table 3. Single redox waves in polymer solutions were consistent with exactly alternating polymers[21]. In previous studies of the homopolymer of 3-phenyl[5]ferrocenophane-1,5-dimethylene, ferrocene moieties were able to align with one another closely enough to interact with one another. These interactions resulted in stabilization of the electrons, resulting in two oxidation potentials, one corresponding to ferrocenes that experienced interaction, and one corresponding to moieties that did not experience interaction. Polymer 1 (X=Acetyl) showed an I_{pc}/I_{pa} ratio that was approximately 1 and gave E_{ox} and E_{red} values of 0.51 and 0.29 respectively. Cyclic voltammetry of Polymer 1 also showed I_{pa} to be directly proportional to the square root of the scan rate which was consistent with electrochemical reversibility. This electrochemical behavior was also observed with Polymers 2 and 4 (X=Cyano, Methyl, respectively). These results suggest that these polymers are both chemically and electrochemically reversible in polymer solutions. Chemical reversibility indicates that oxidation and reduction can both occur and return the material to the same composition before the reaction. Electrochemical reversibility refers to the kinetics of the reaction, and shows that the reaction can occur quickly enough to be diffusion controlled within the electrochemical system.

Table 3: Redox Potentials of Polymers 1-4 in CH_2Cl_2

Polymer	**E_{ox} (V)**	**E_{red} (V)**	**$E_{1/2}$ (V)**
Polymer 1 (X=Acetyl)	0.48	0.42	0.45
Polymer 2 (X=Cyano)	0.51	0.29	0.40
Polymer 3 (X=Methoxy)	0.09	-0.02	0.04
Polymer 4 (X=Methyl)	0.39	0.27	0.33

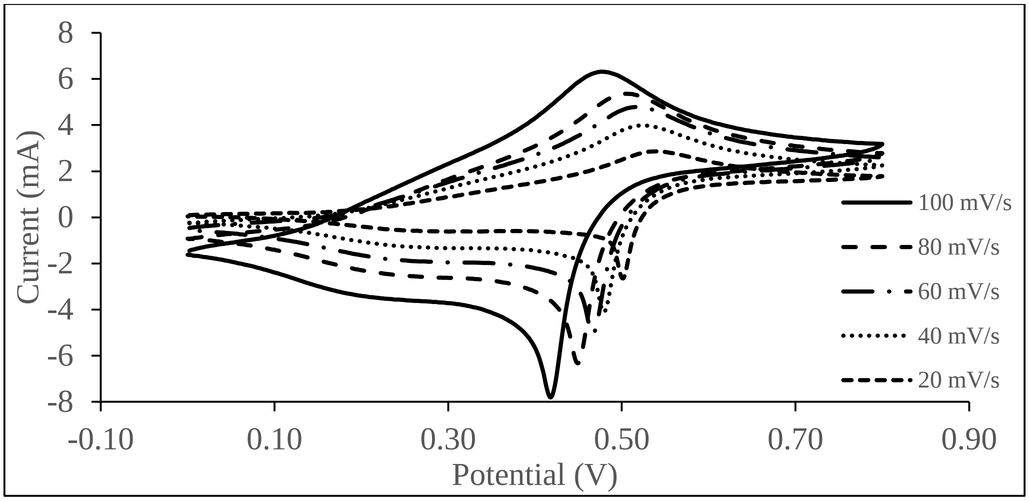


Figure 4. CV of Polymer 1 (X=Acetyl) in CH_2Cl_2 with NBu_4PF_6 as supporting electrolyte.

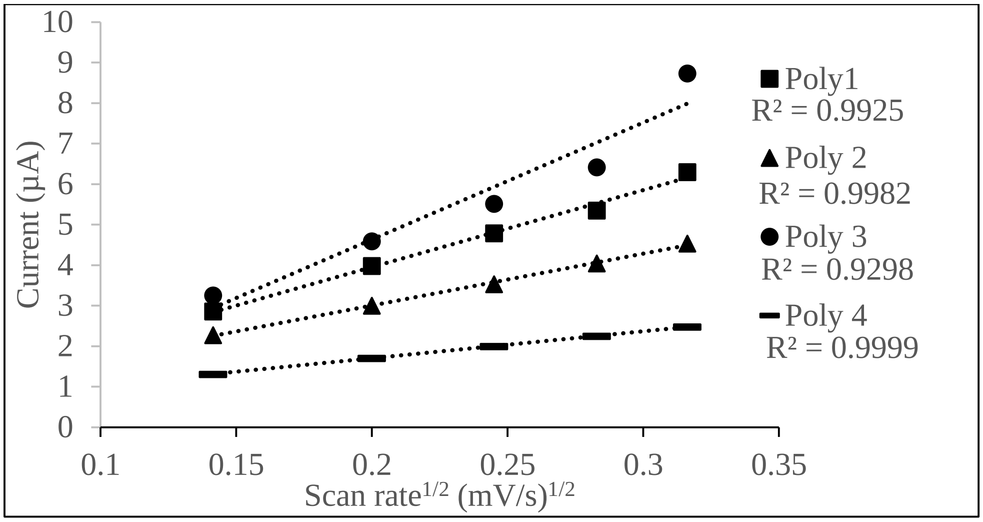


Figure 5. Plot of Current vs Scan Rate$^{1/2}$ for Polymer 1-4 solutions in CH_2Cl_2

Cyclic Voltammetry of Polymer 3 (X=Methoxy) in CH_2Cl_2 revealed I_{pc} to be significantly higher than I_{pa} as shown in Figure 6. At a 100 mV/s scan rate, the ratio between these two values was 2.51, showing electrochemical irreversibility and a complication in the reaction kinetics. In addition to the significantly higher current during the reduction event than the oxidation event, the cyclic voltammetry of this polymer solution did not show a direct relationship between the current and the square root of the scan rate as shown in Figure 5. Peak current was determined to correlate directly with scan rate, which is consistent with adsorption to the electrode (Figure 7). This affinity to bind to the electrode makes this polymer potentially viable as a chemically modified electrode that can be prepared using amperometry.

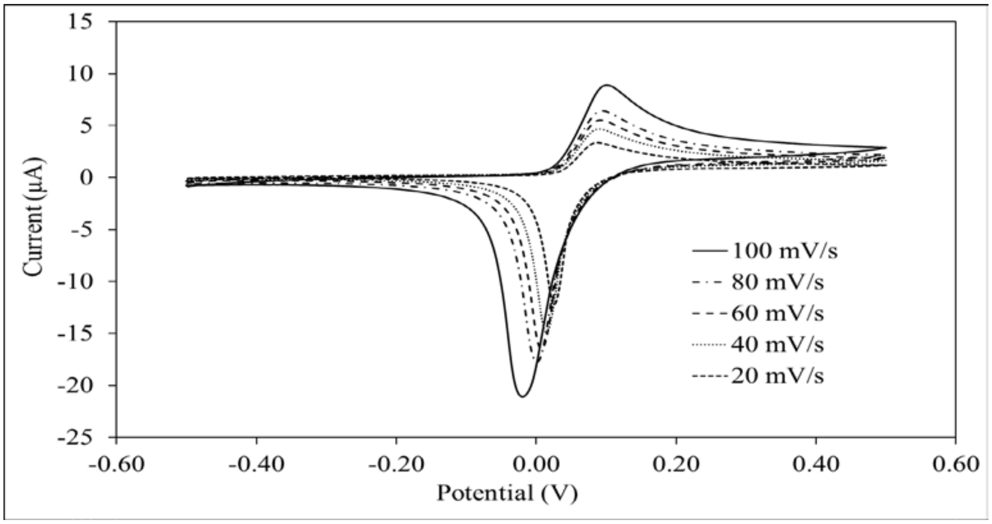


Figure 6. CV of Polymer 3 (X=Methoxy) in CH_2Cl_2 with NBu_4PF_6 as supporting electrolyte

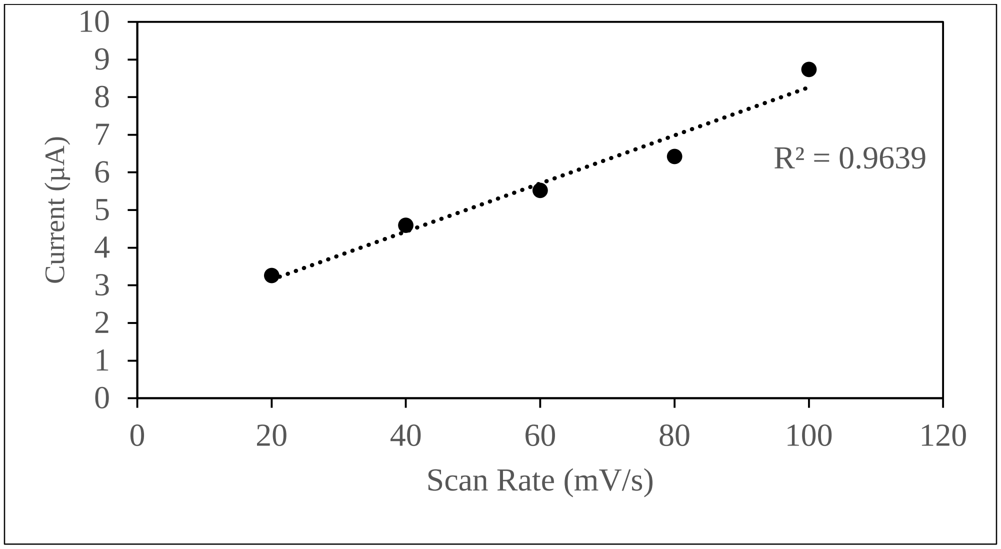


Figure 7. Plot of Current vs Scan rate for Polymer 3 (X=Methoxy) solution in CH_2Cl_2

3.4.2 Electrochemical Studies of Polymer Thin Films in 0.1 M $NaClO_4$ solutions

Thin films of polymers were cast on platinum electrodes from CH_2Cl_2 solutions and air dried prior to electrochemistry in aqueous solutions. Cyclic voltammetry was conducted in aqueous sodium perchlorate (0.1M) as supporting electrolyte. The redox potentials of the polymers can be seen in Table 4. The polymers showed a shift in oxidation potentials when solution cast as thin films relative to the polymer solutions. This is likely a result of a change in polymer morphology from solution to thin films. These thin films showed linear responses when plots of Current vs. Scan Rate$^{1/2}$ were generated, indicating electrochemical reversibility. These polymers showed greater current during at E_{red} than E_{ox} which is consistent with polymer films that are immobilized to an electrode. These data suggest that these polymers could be potentially useful for solution cast chemically modified electrodes. Secondary redox events, particularly as seen in the methyl-substituted polymer 4 around 0.66 volts, suggest weak charge transfer. In the polymer thin film, it is likely that there are a range of electronic environments. A weak charge transfer complex in the films would lead to differences in oxidation potentials between regions of the polymer as a result of charge stabilization of the ferrocenyl and maleimide moieties, potentially resulting in multiple redox waves.

Table 4: Redox Potentials of Polymer 1-4 Thin Films in Aqueous Solutions

Polymer	**E_{ox} (V)**	**E_{red} (V)**	**$E_{1/2}$ (V)**
Polymer 1 (X=Acetyl)	0.27	0.22	0.25
Polymer 2 (X=Cyano)	0.35	0.26	0.31
Polymer 3 (X=Methoxy)	0.35	0.24	0.29
Polymer 4 (X=Methyl)	0.30	0.20	0.25

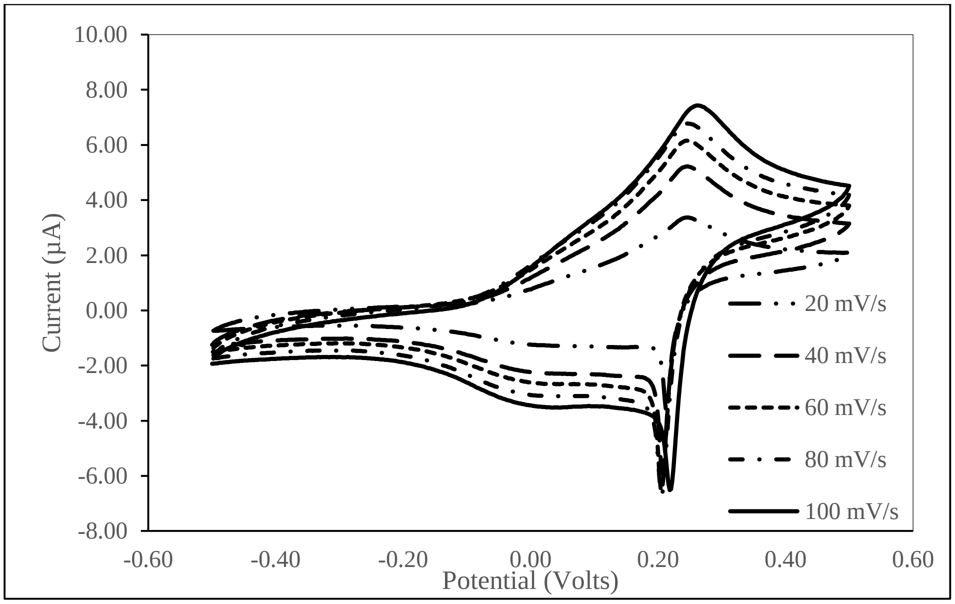


Figure 8: Cyclic voltammetry of Polymer 1 (X=Acetyl) in 0.1 M Aqueous $NaClO_4$ Solution

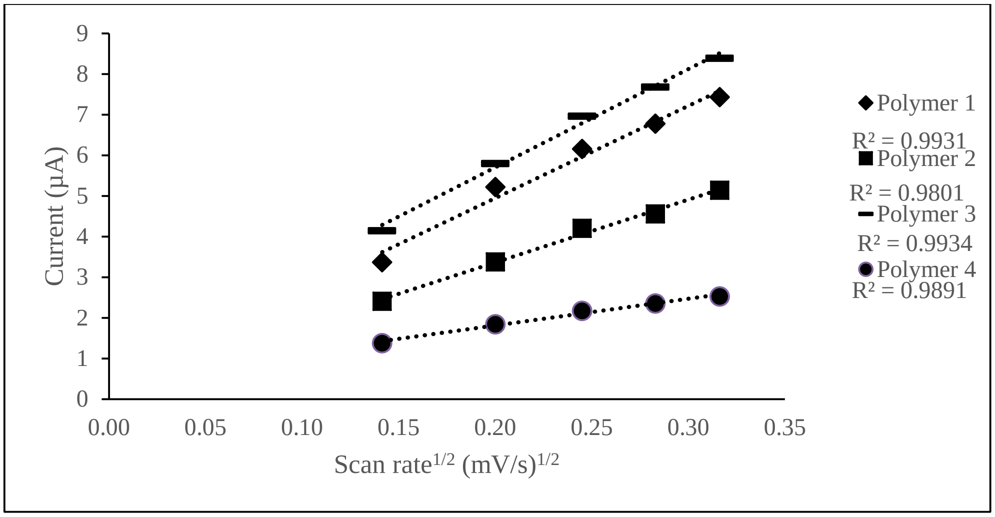


Figure 9: Current vs Scan Rate$^{1/2}$ of Polymer thin films in Aqueous 0.1M $NaClO_4$

3.5 UV-vis absorption studies of Copolymers

UV-vis spectroscopy is useful for characterizing charge transfer complex formation, as these interactions can often be excited in this range of the electromagnetic spectrum. Energy from light is absorbed and used to excite electronic interactions between electron rich and electron poor moieties. If the HOMO of the electron rich group is similar in energy level to the LUMO in the electron deficient group, an electronic transition can occur resulting in partial transfer of electron charge from the HOMO of the donor to the LUMO of the acceptor[23]. Polymer solutions were prepared in dichloromethane (10mg/mL) and were tested from 200-900nm. Polymer thin films were cast from dichloromethane (15 µL at a concentration of 5 mg/mL) on to Indium Tin Oxide (ITO) plates prior to testing.

Polymer 1 (X=Acetyl) in solution reached absorbance maxima but showed the typical ferroceneophane absorbance at 440 nm[21]. This solution also showed weak absorbance bands extending into the visible region of the spectrum. UV-vis spectroscopy of polymer 1 thin films also showed absorbance at 440 nm, as well as the weak absorbance bands extending into the visible spectrum. However, this film also showed a broad absorbance peak at 653 nm in the visible spectrum. Absorbance values in this region between ferrocene and bis(arene)iron(II) have been seen and attributed to charge transfer complexes previously in literature[23]. By analogy, the peak at 653 nm can be attributed to interactions caused by a charge transfer complex. Likewise, the absorbance values extending the length of the visible spectra can be attributed to similar interactions. The peak at 653 nm appears to indicate increased strength of the electrostatic interaction, and appears to show that the electron withdrawing acetyl substituent stabilizes the interaction between the two moieties. Polymer 2 (X=Cyano) also shows a slight peak around 570 nm which may be indicative of electrostatic interaction. This peak was too weak to definitively state that electrostatic interaction was responsible for this peak, but Polymer 2 still shows absorbance values in the higher wavelength range of the visible spectra. These data suggest that the electron withdrawing effect of the para-substituted phenyl ring on the maleimide influences the strength and stability of charge transfer complex formation in these polymers. Methoxyl-substituted polymer 3 and Methyl-substituted polymer 4 show absorbance values in the visible region but do not show a distinct peak absorbance. This is to be expected as the electron donating character of the substituent on the maleimide should increase electron density around the maleimide, increasing the energy level of the LUMO, limiting interaction. The breadth of the absorbance spectra in the visible region for all four materials is to be expected in polymer thin films due to the large number of environments in which the potential electrostatic interaction is expected to occur. Peaks extending into the NIR region also show potential for the formation of a charge transfer complex.

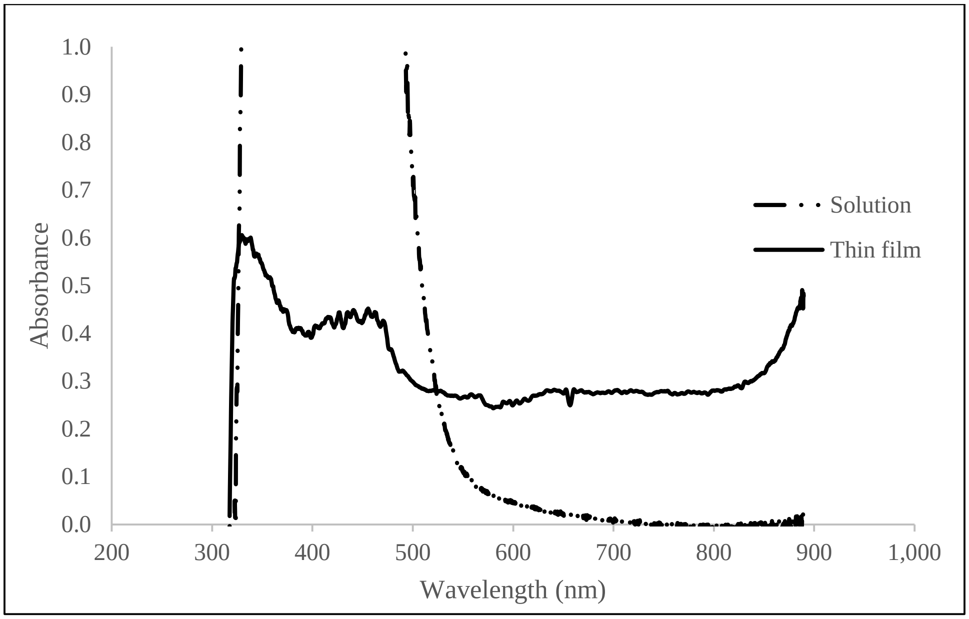


Figure 10: UV-vis Spectroscopy Data for Polymer 1 (X=Acetyl)

CHAPTER IV

4. CONCLUSIONS

4.1 Summary of results

Four new polymers were synthesized using free radical polymerization. These polymers were polymerized from 3-phenyl[5]ferrocenophane-1,5-dimethylene and N-phenylmaleimides substituted at the para position with an acetyl group, a cyano group, a methoxy group, or a methyl group respectively. Polymer yields ranged from 70-90% and these polymers were characterized using ^{13}C-NMR, ^{1}H-NMR, and FTIR. These spectra were consistent with the anticipated structure of an alternating copolymer[21]. TGA data of these polymers showed them to be thermostable to nearly 400ºC.

Cyclic voltammetry of polymers in CH_2Cl_2 gave a single redox wave, consistent with alternating monomer units[21]. The acetyl, cyano and methyl substituted polymers showed linear plots of Current vs. Scan Rate$^{1/2}$ and current values that were near equal during the oxidation and reduction events. Polymer 3, the methoxy substituted polymer, however, showed a significantly higher current during the reduction event than the oxidation event, and showed it’s current to be directly proportional to the scan rate, which was indicative of polymer adsorption to the electrode. Electrochemistry of polymer thin films in aqueous 0.1M $NaClO_4$ revealed polymers to be redox stable and electrochemically reversible. UV-vis spectra of the polymers as thin films or in solution showed weak absorbance values in the visible spectra, consistent with charge transfer formation. Polymer 1 and 2, with electron withdrawing substituents on the N-phenylmaleimide seemed to have stronger interactions in these ranges resulting in apparent secondary peaks in the visible spectra consistent with electrostatic interactions

4.2 Future Research

These polymers show potential for use in solar cell applications as a result of their ability to absorb visible light. New polymers with stronger electron withdrawing groups on the phenylmaleimide should be synthesized, and their electrochemistry should be examined. Also, these polymers should be examined in the NIR region in order to examine the potential for the charge transfer complex interactions to take place in this range. NIR spectroscopy will likely reveal peaks that would further clarify the interaction between the two moieties. Use of stronger electron acceptors other than phenylmaleimides could also prove useful in creating stronger charge transfer complexes with better defined interactions. DFT studies of copolymers of 3-phenyl[5]ferrocenophane-1,5-dimethylene with different acceptor substituents could provide direction as to what monomers may be most viable in producing close molecular geometries.

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APPENDIX

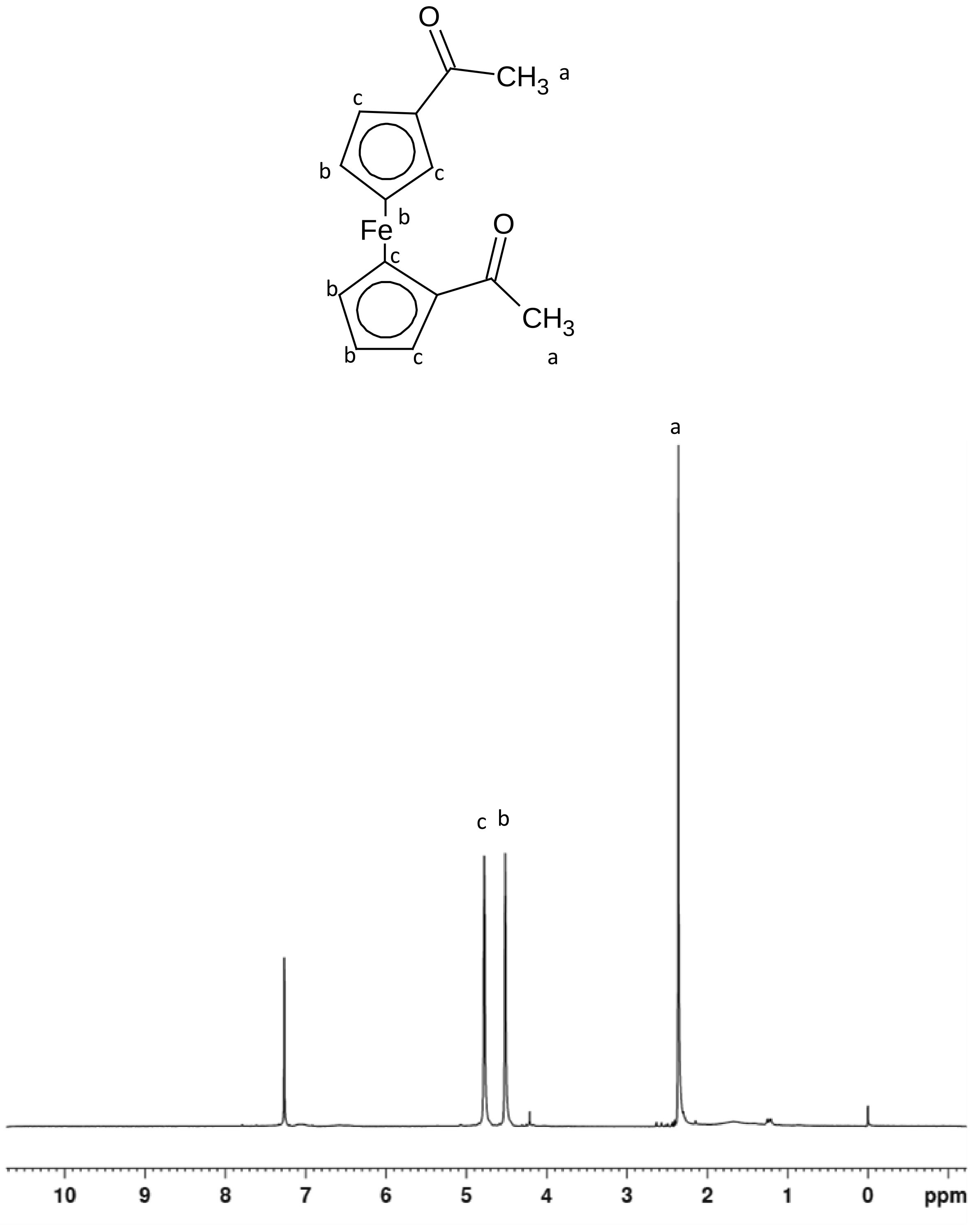


Figure S1: H-NMR of 1,1-diacetylferrocene

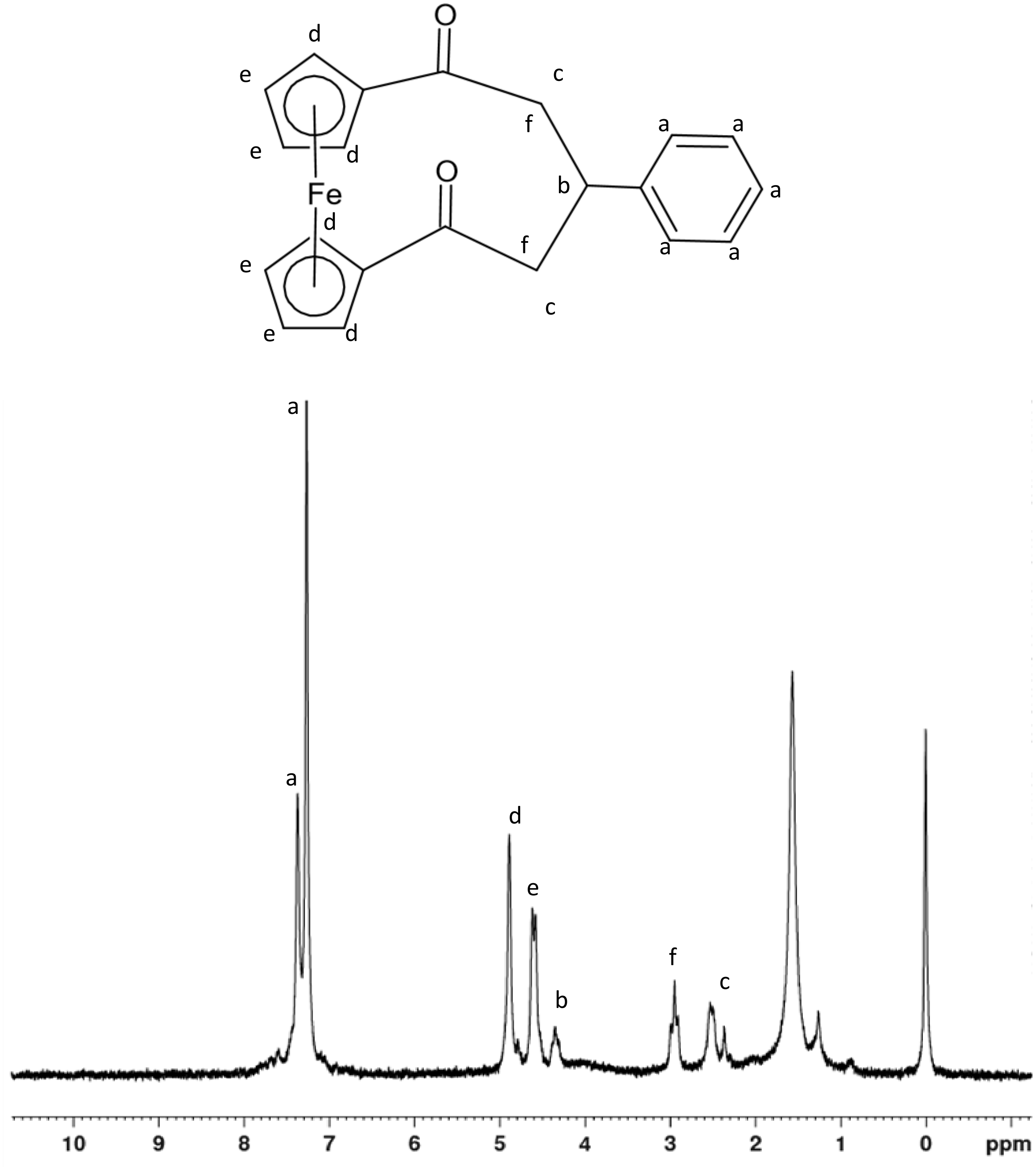


Figure S2: ^{1}**H-NMR of 3-phenyl[5]ferrocenophane-1,5-dione**

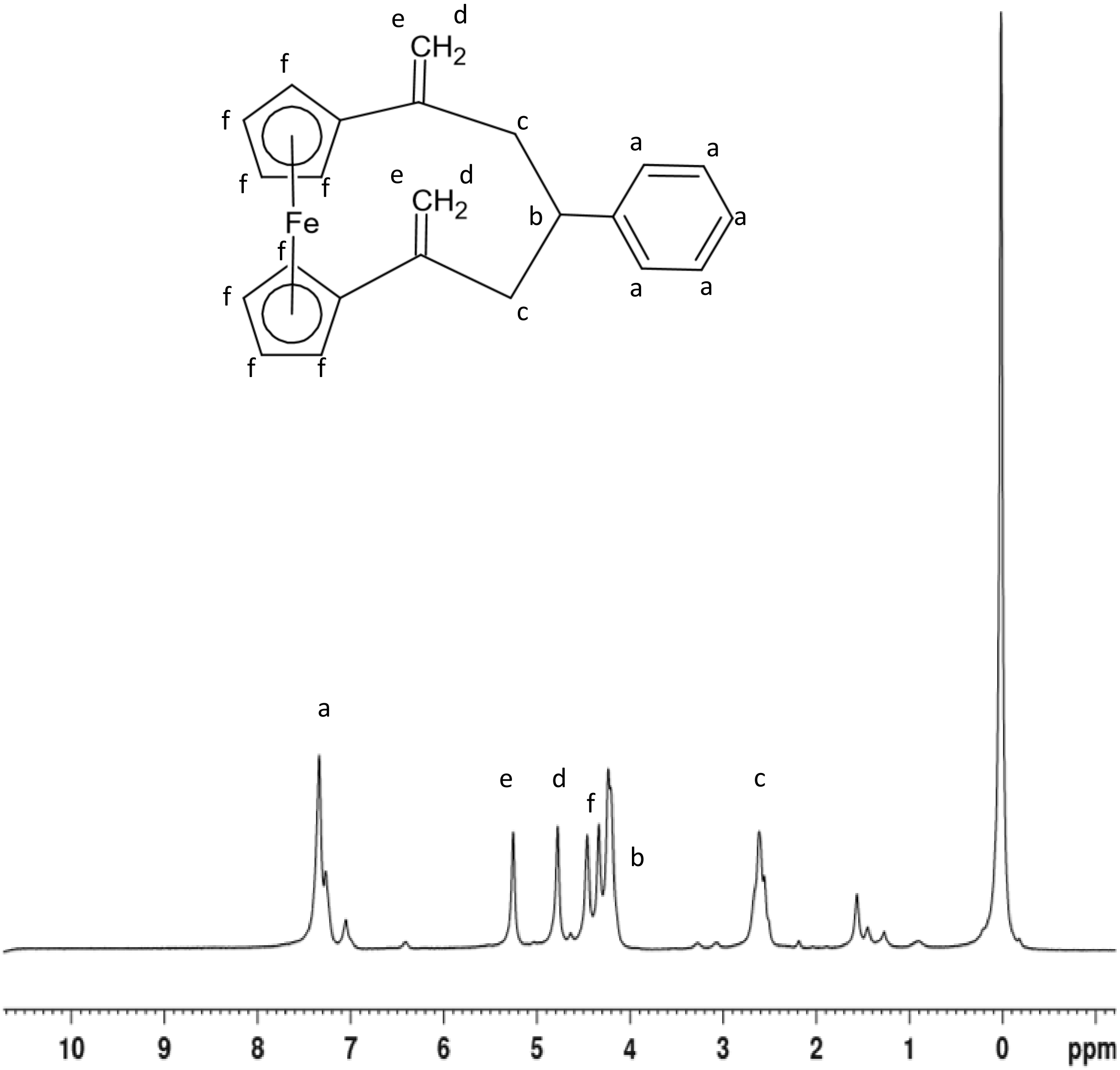
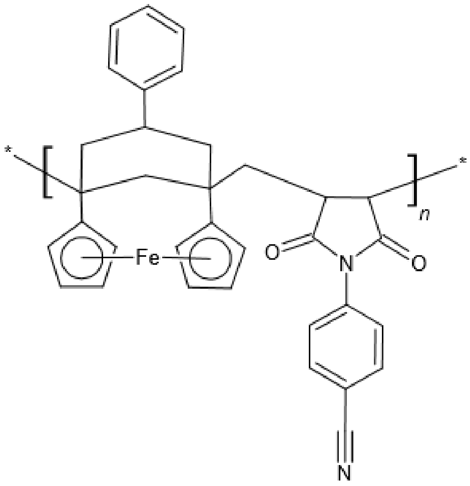


Figure S3: ^{1}H-NMR of 3-phenyl[5]ferroceneophane-1,5-dimethylene

Figure S4: ^{1}H-NMR of Polymer 1



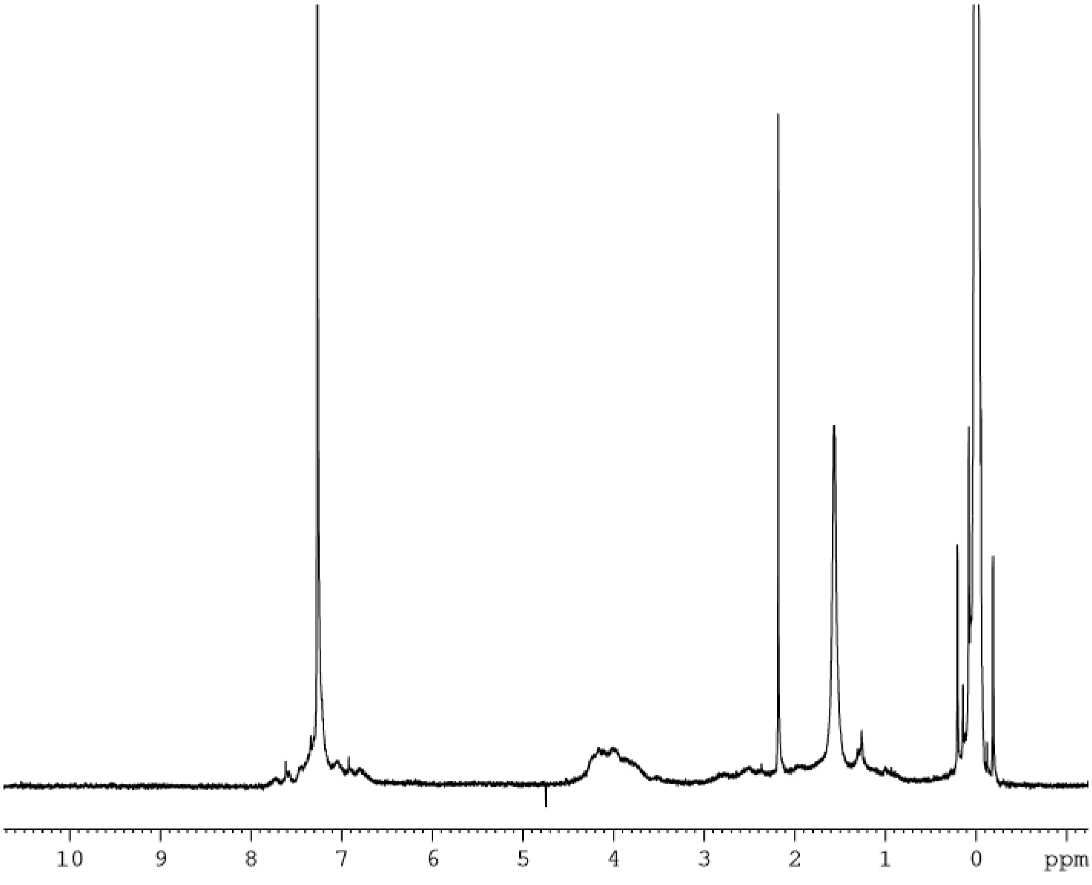


Figure S5: ^{1}H-NMR of Polymer 2

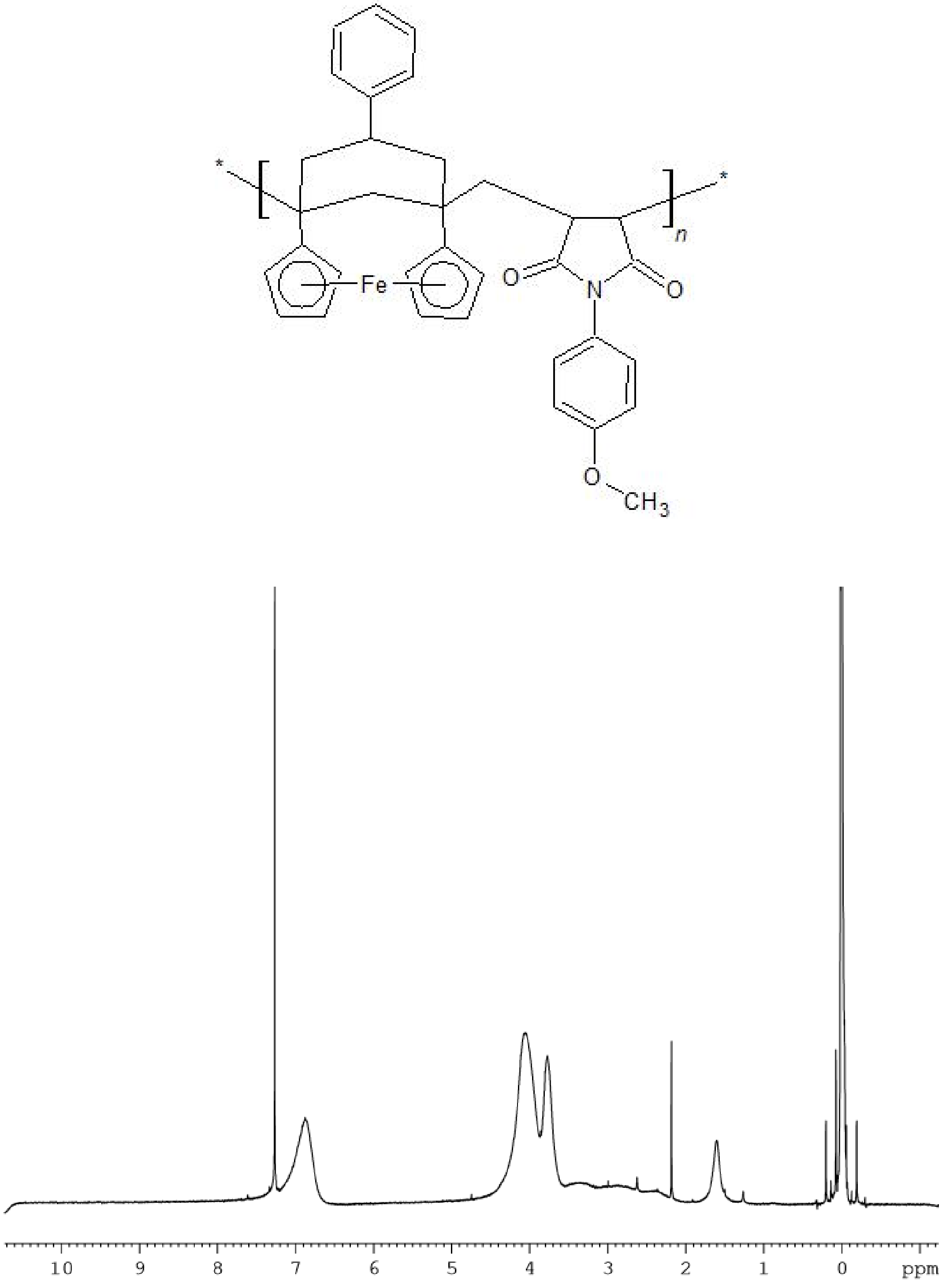


Figure S6: ^{1}H-NMR of Polymer 3

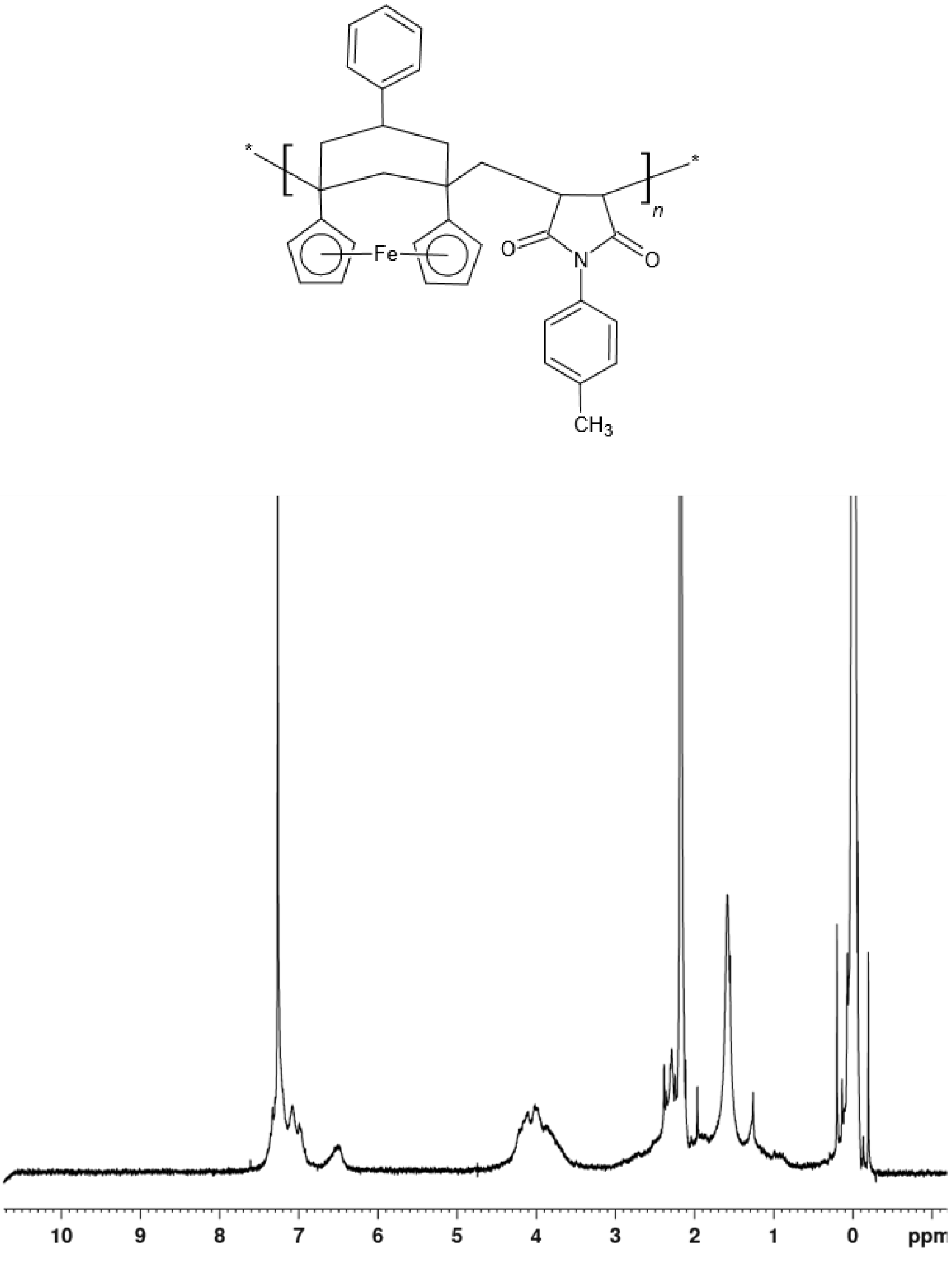


Figure S7: ^{1}H-NMR of Polymer 4

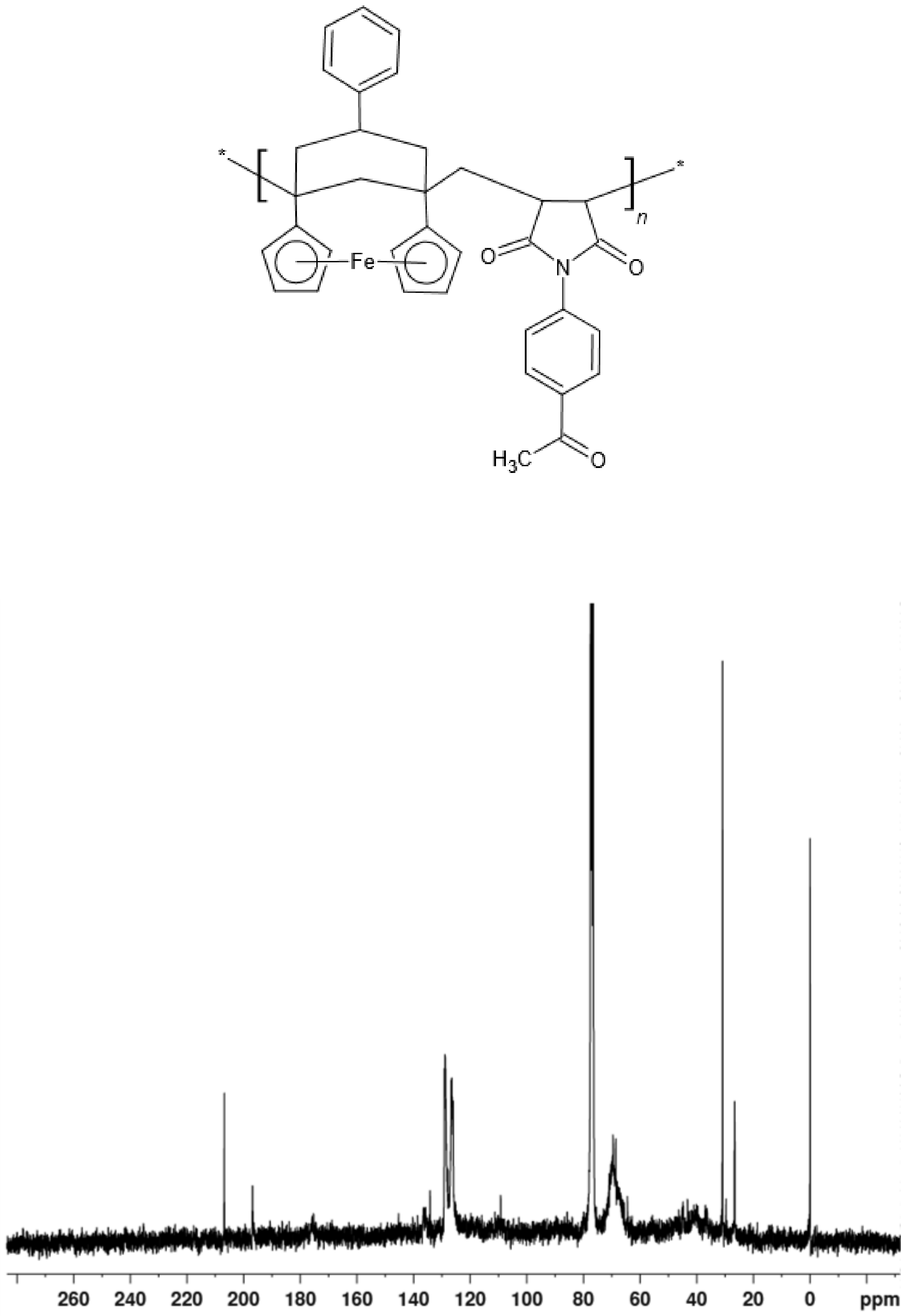


Figure S8: ^{13}C-NMR of Polymer 1

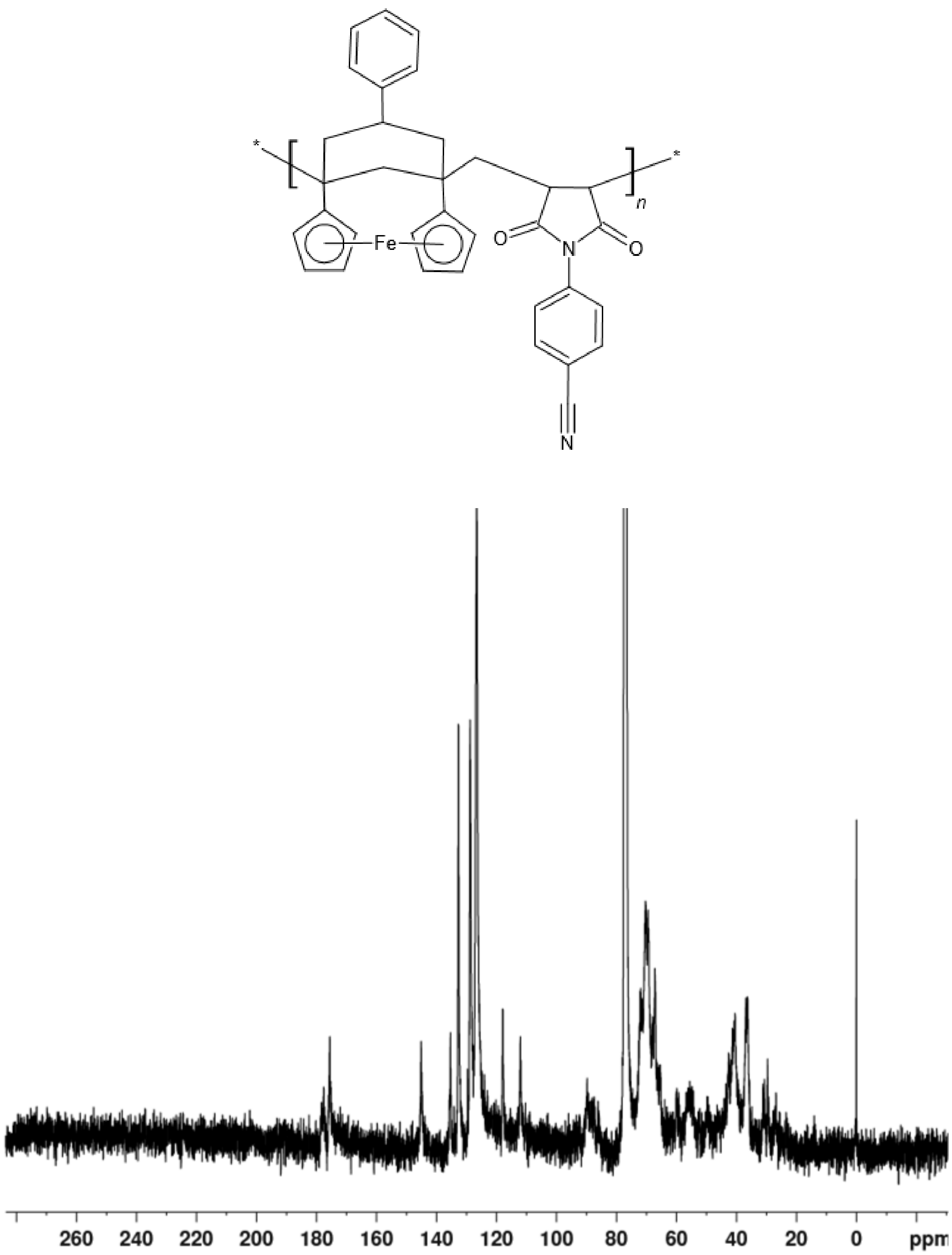


Figure S9: ^{13}C-NMR of Polymer 2

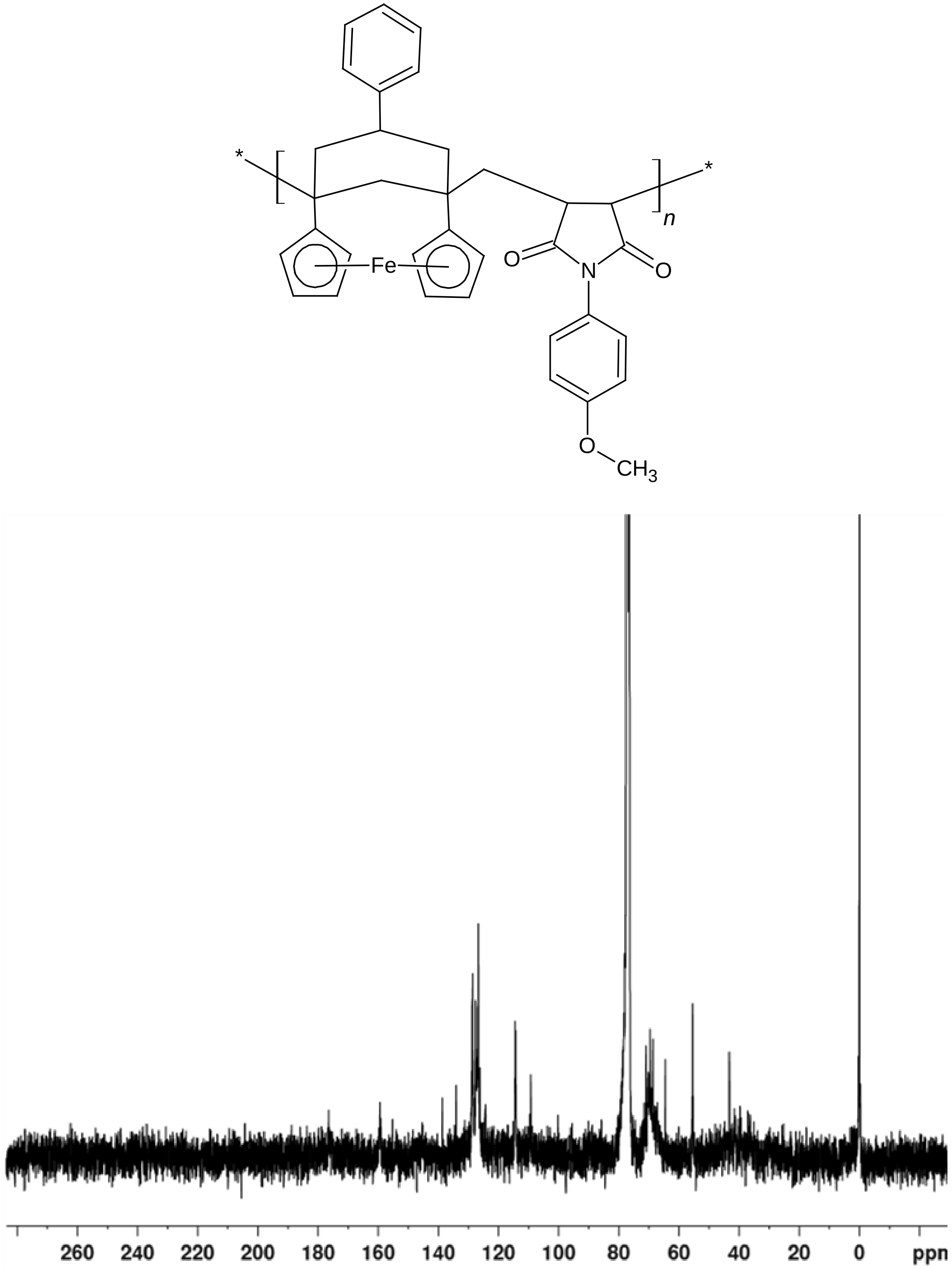


Figure S10: ^{13}C-NMR of Polymer 3

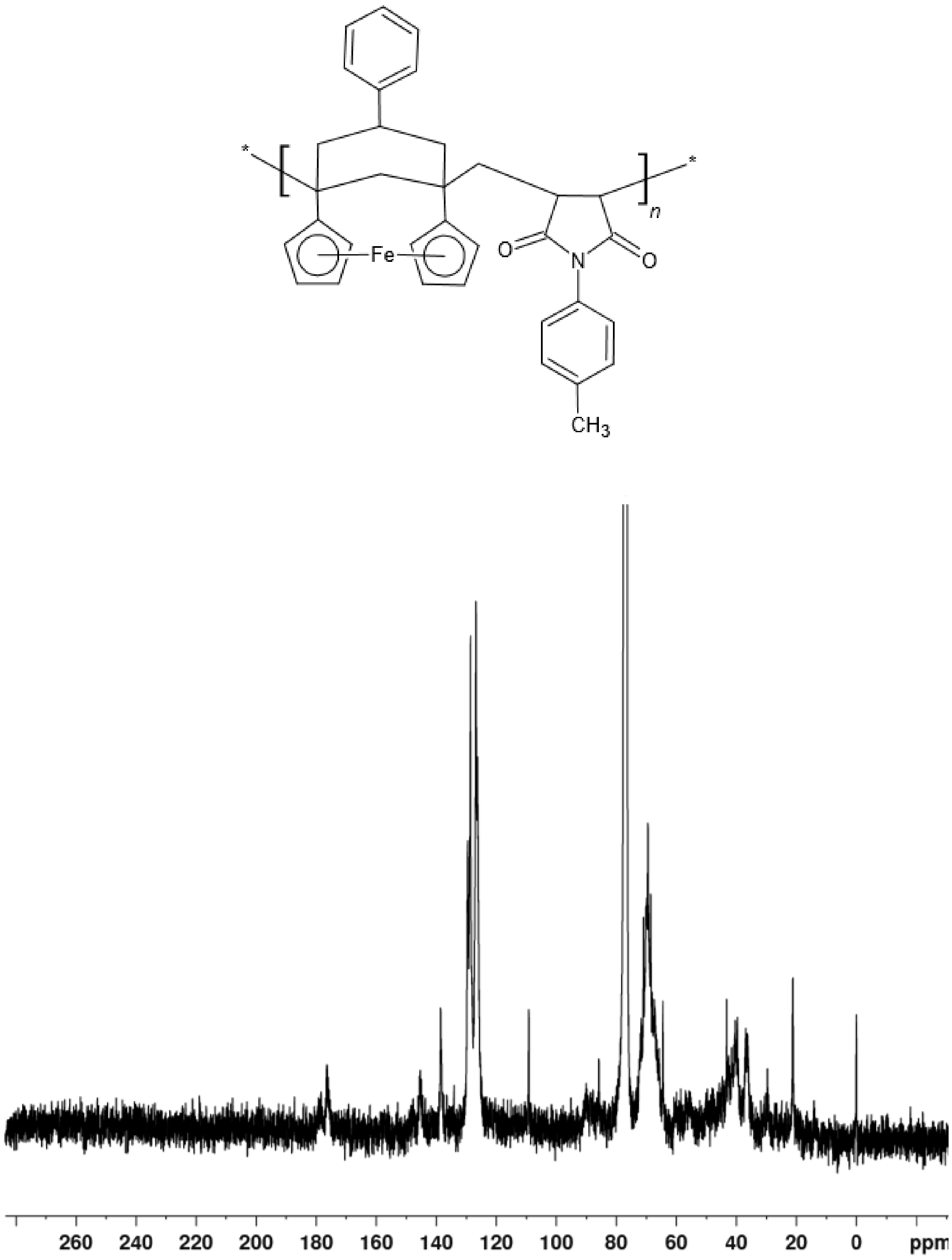


Figure S11: ^{13}C-NMR of Polymer 4

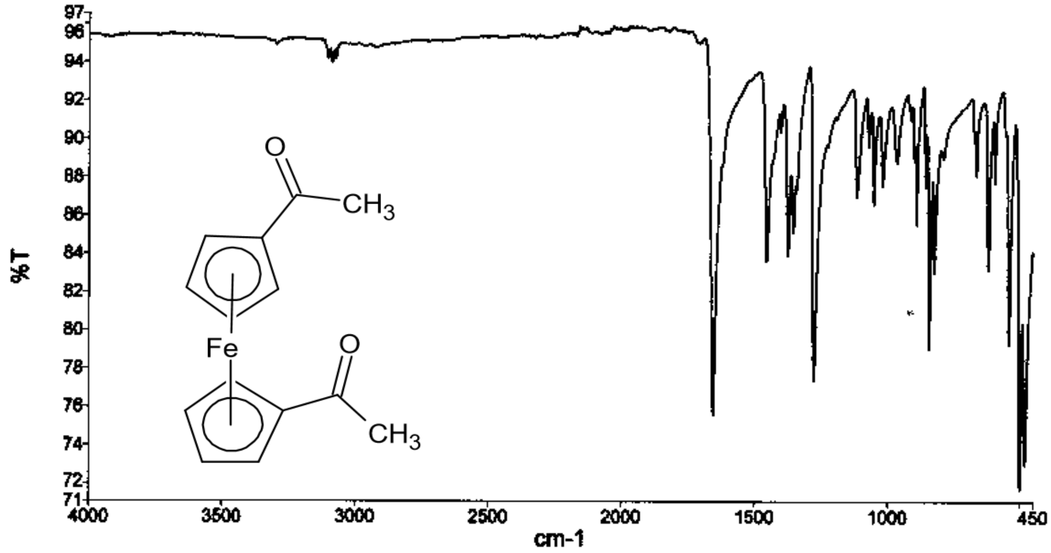


Figure S12: FTIR of 1,1-diacetylferrocene

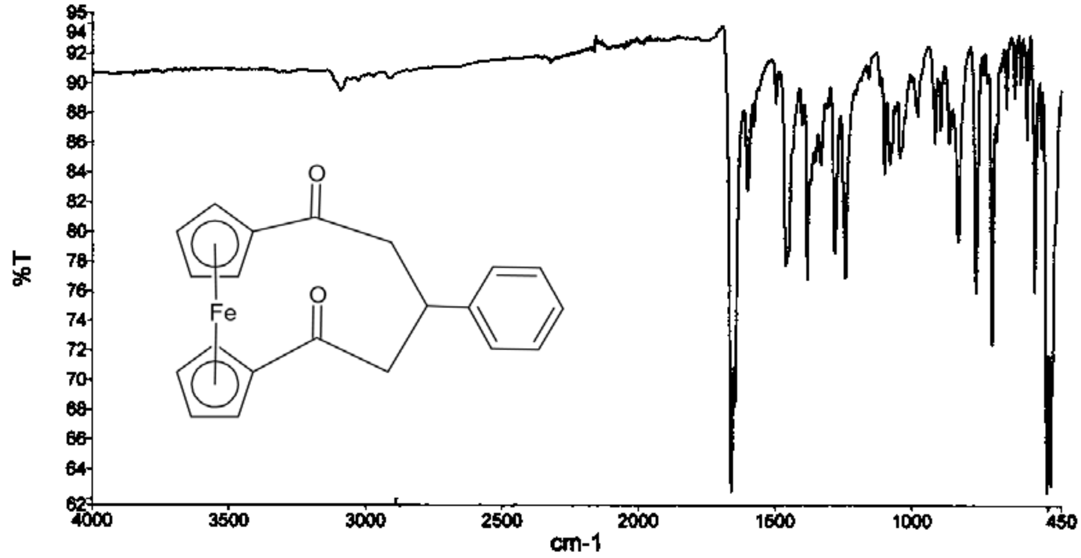


Figure S13: FTIR of 3-phenyl[5]ferrocenophane-1,5-dione

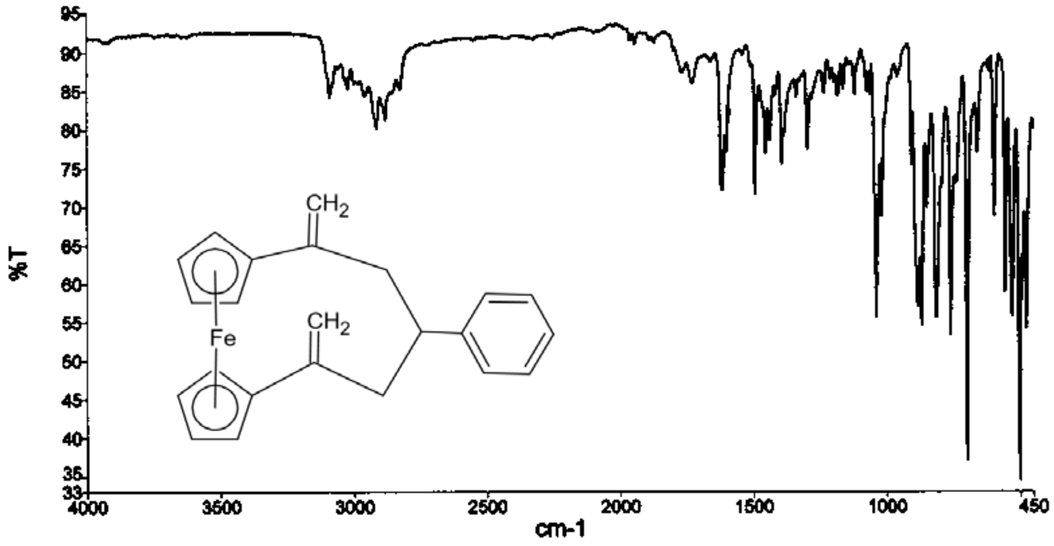


Figure S14: FTIR of 3-phenyl[5]ferrocenophane-1,5-dimethylene

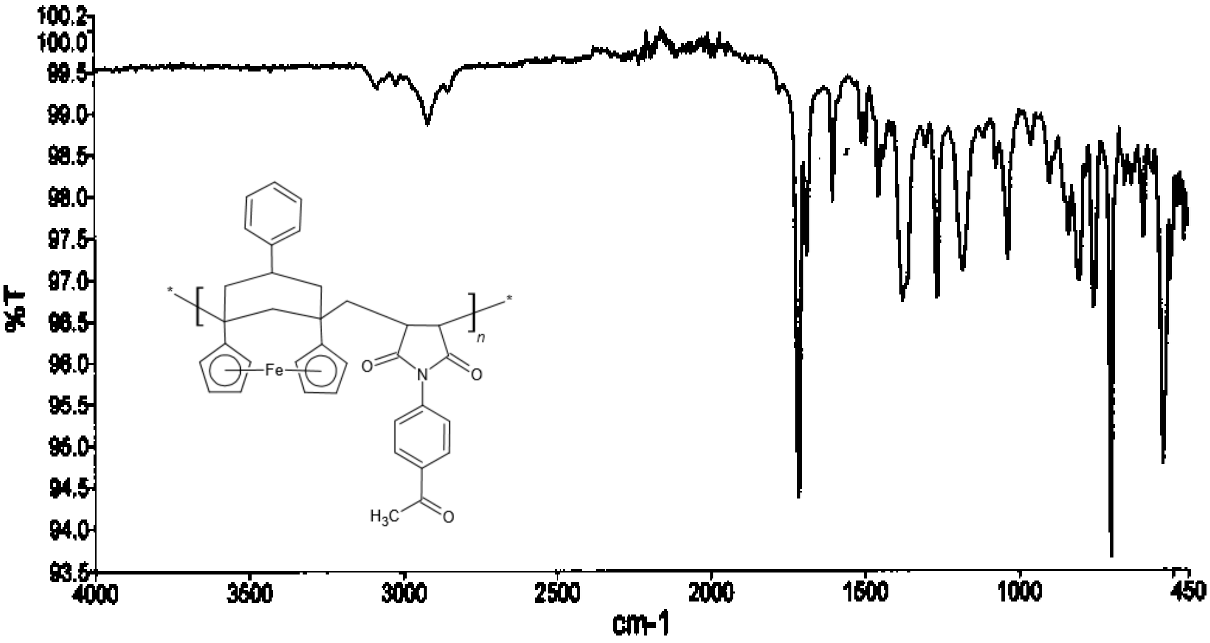


Figure S15: FTIR of Polymer 1

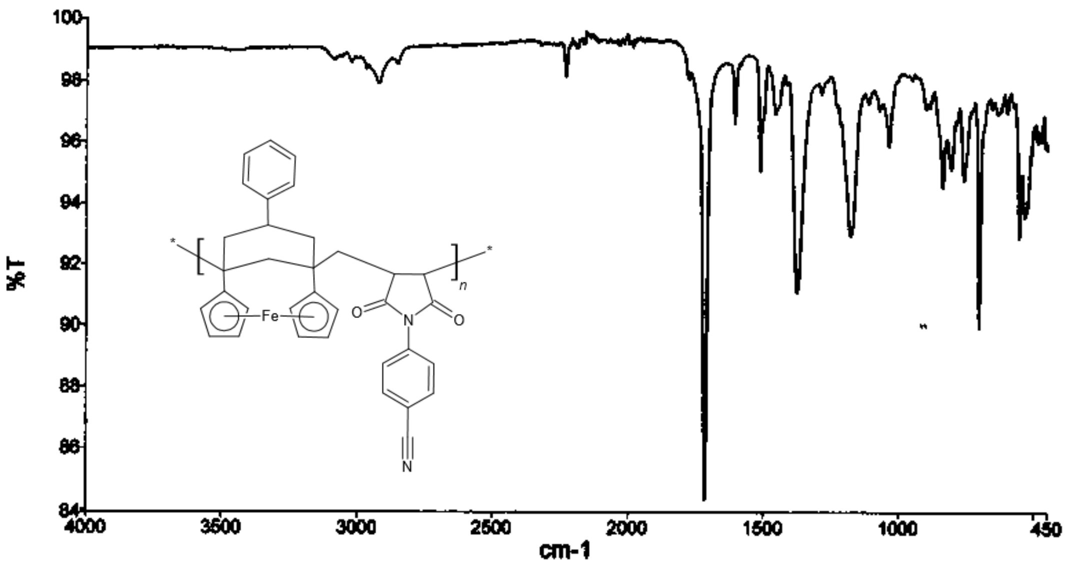


Figure S16: FTIR of Polymer 2

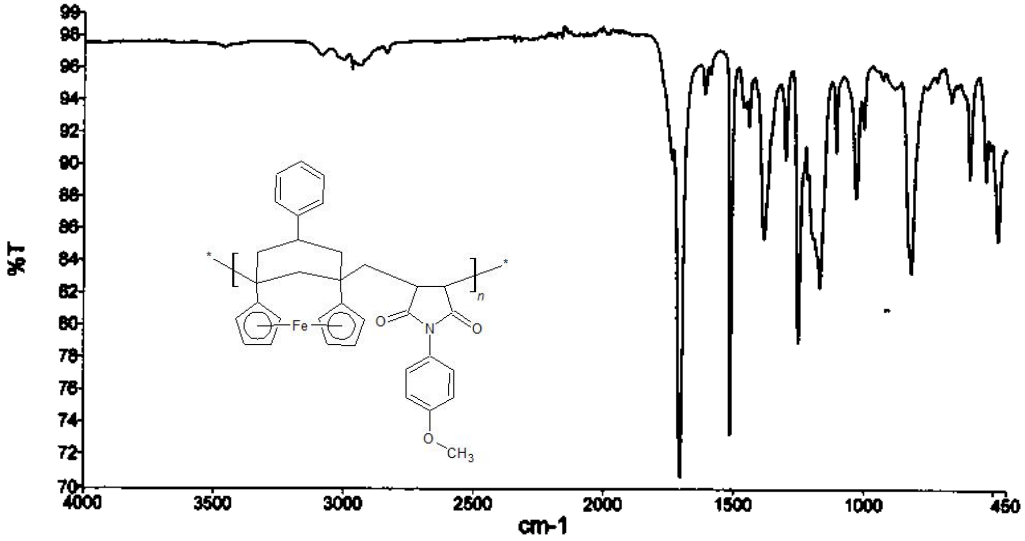


Figure S17: FTIR of Polymer 3

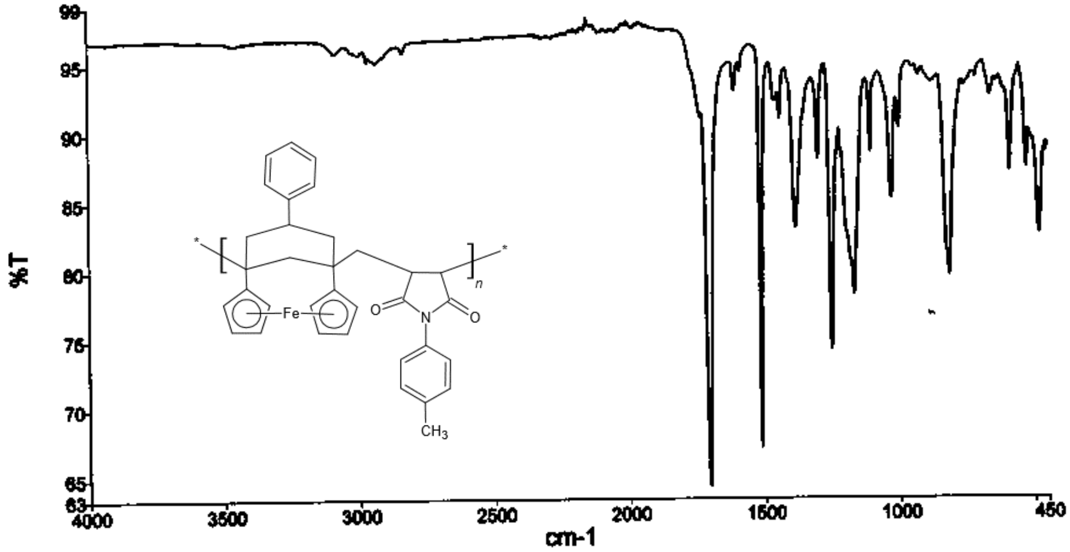


Figure S18: FTIR of Polymer 4

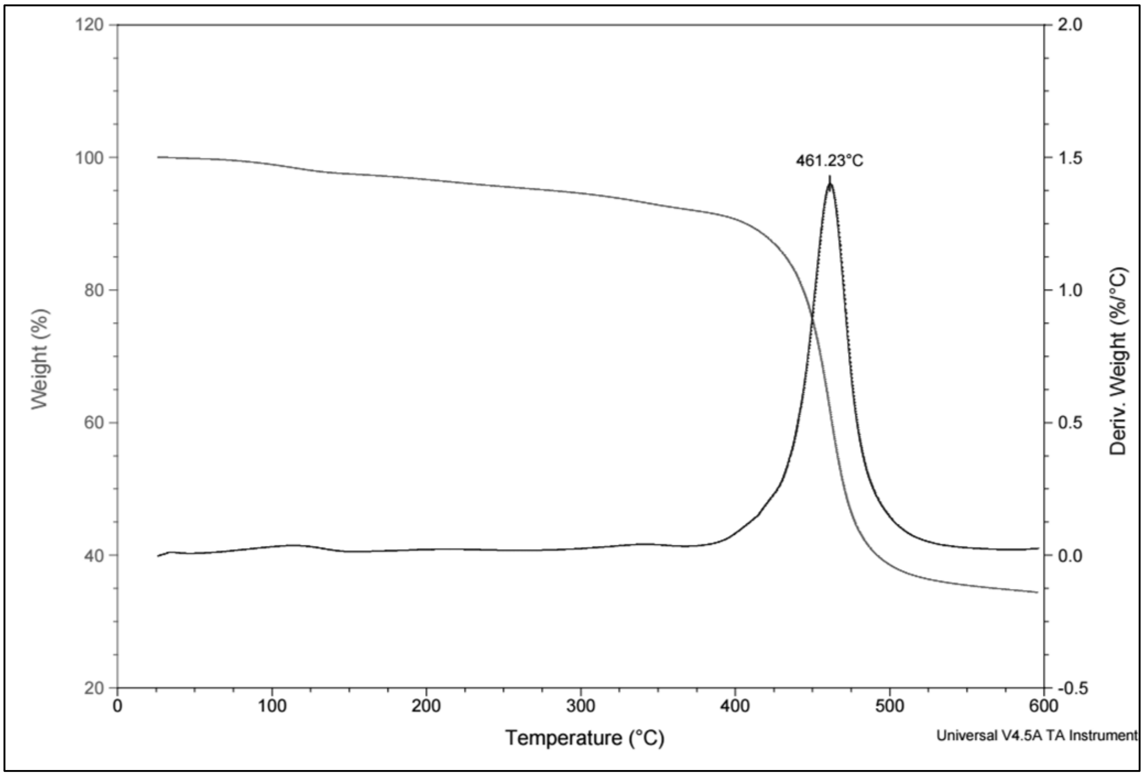


Figure S19 TGA of Polymer 2 (X=Cyano)

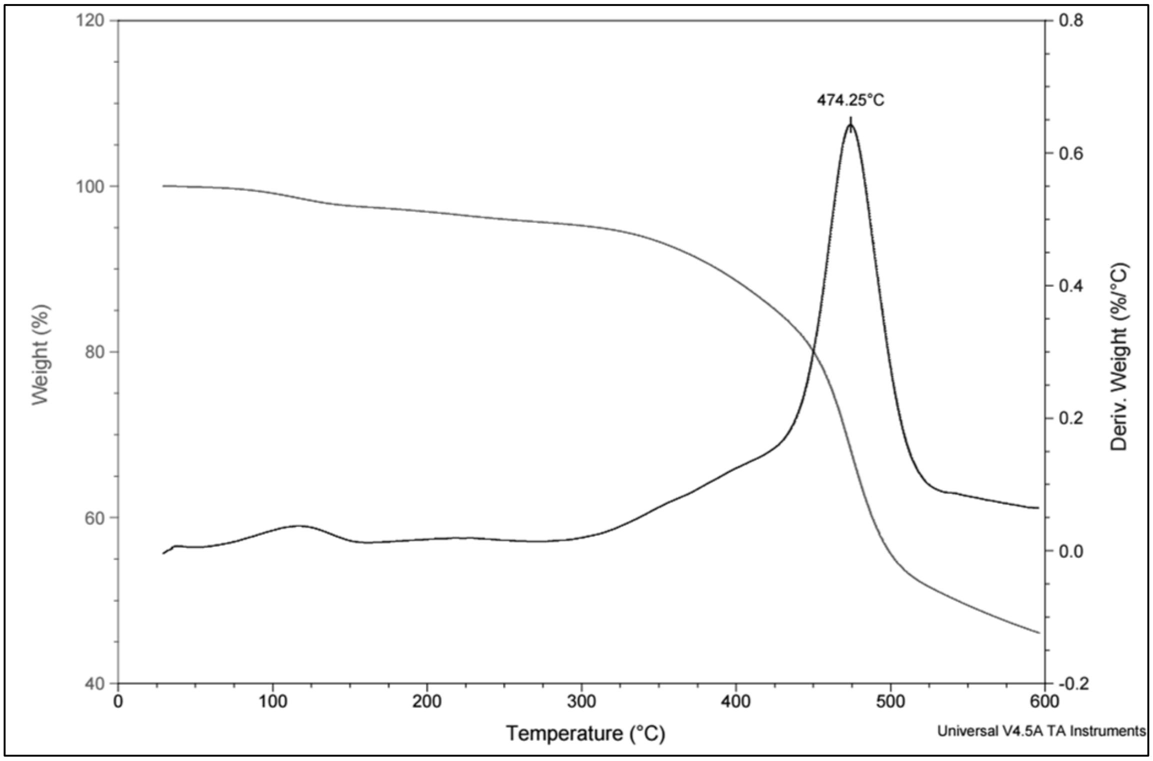


Figure S20: TGA of Polymer 3 (X=Methoxy)

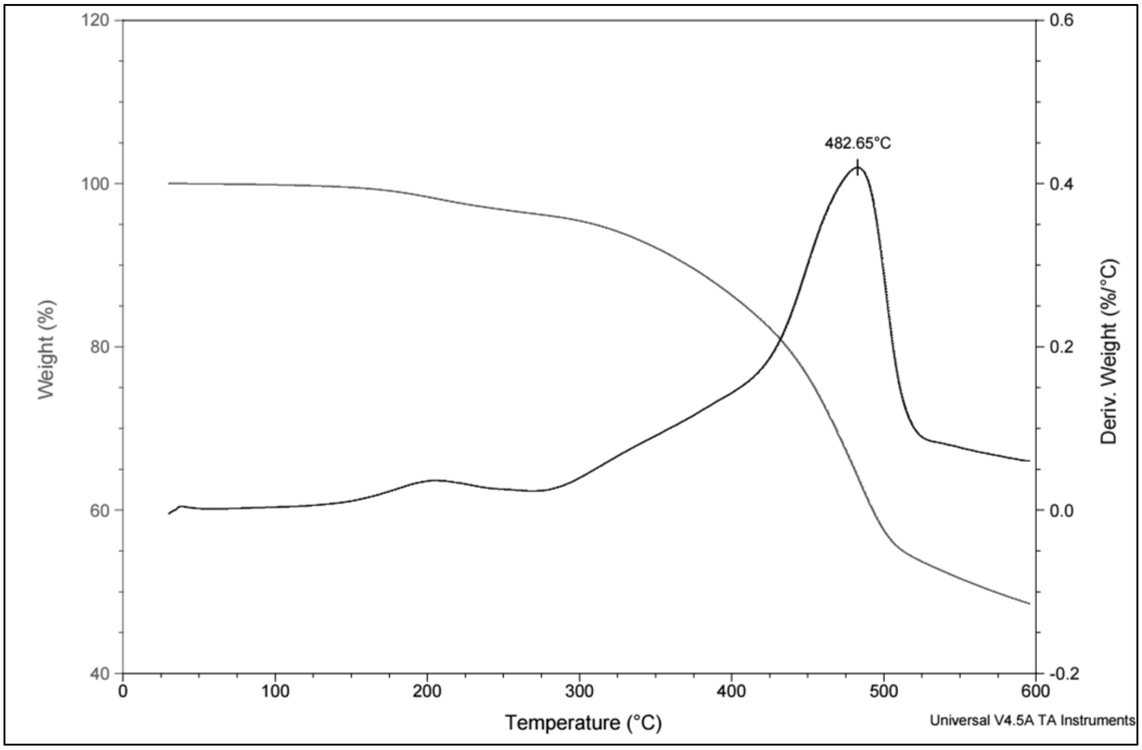


Figure S21: TGA of Polymer 4 (X=Methyl)

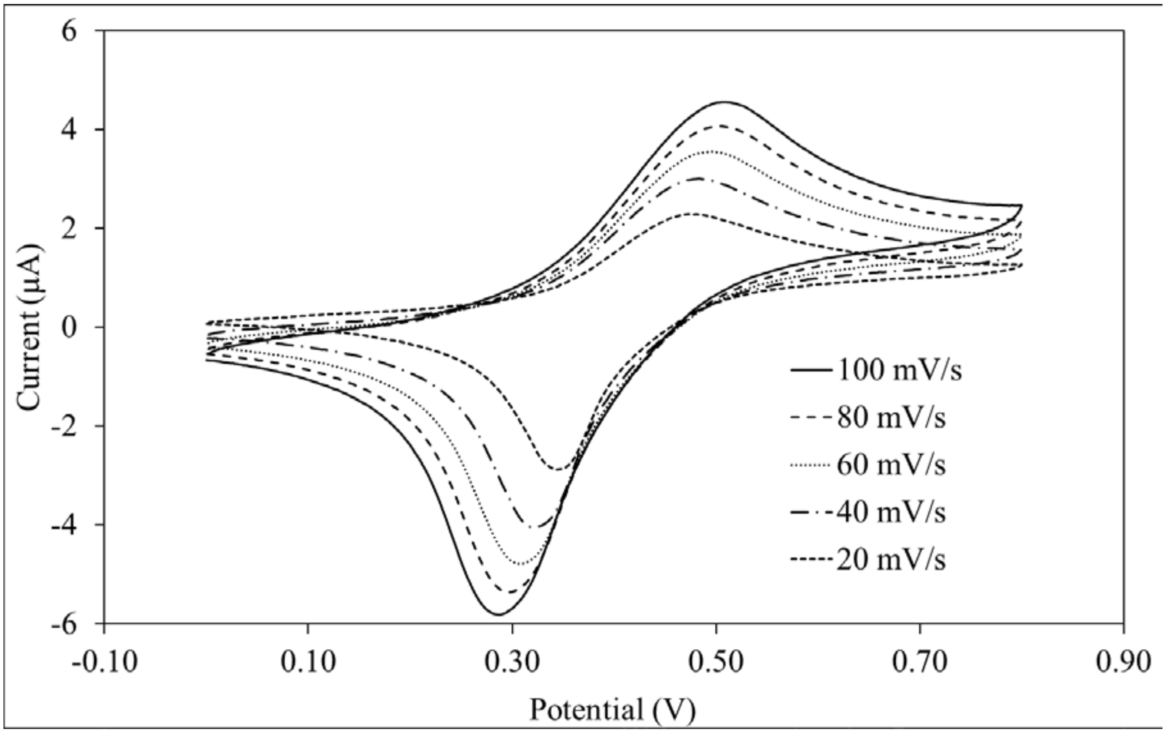


Figure S22: CV of Polymer 2 (X=Cyano) in CH_2Cl_2

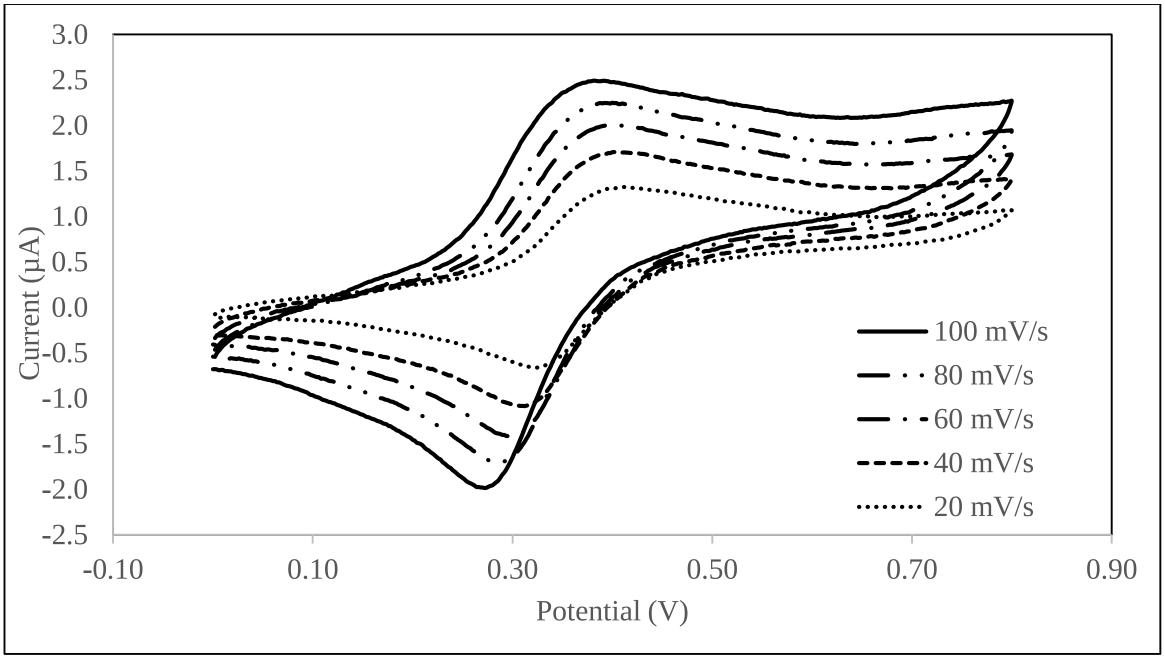


Figure S23: CV of Polymer 3 (X=Methoxy) in CH_2Cl_2

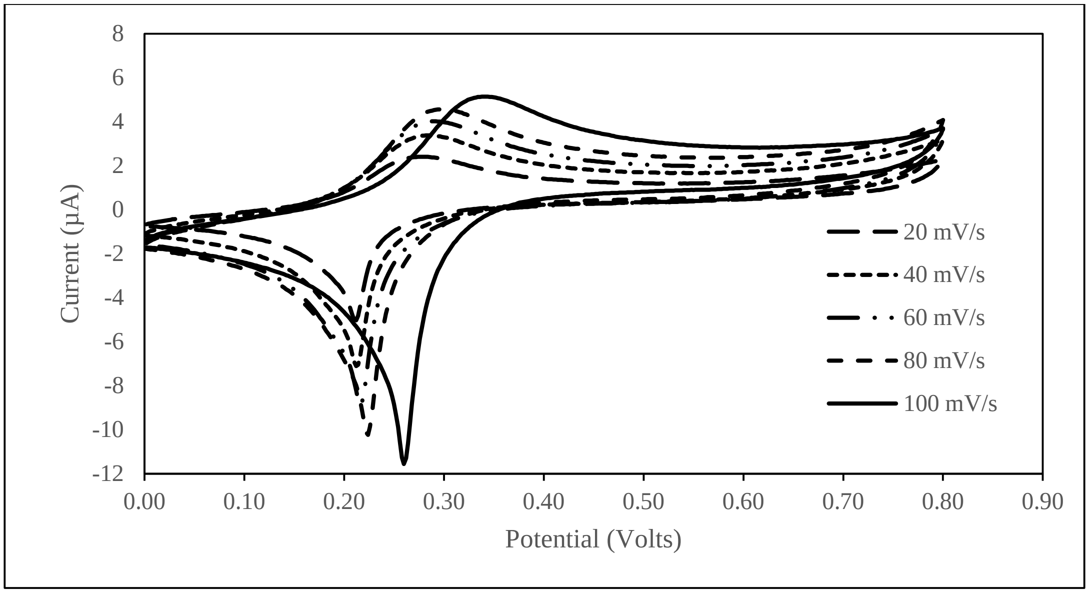


Figure 24: CV of Polymer 2 (X=Cyano) Thin Film in Aqueous .1 M $NaClO_4$

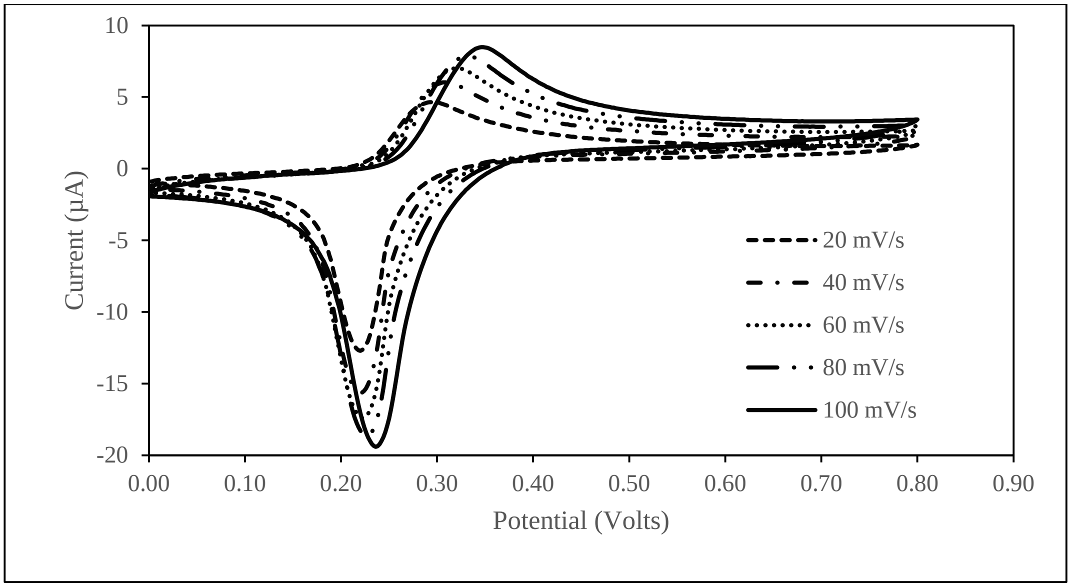


Figure 25: CV of Polymer 3 (X=Methoxy) Thin Film in Aqueous .1 M $NaClO_4$

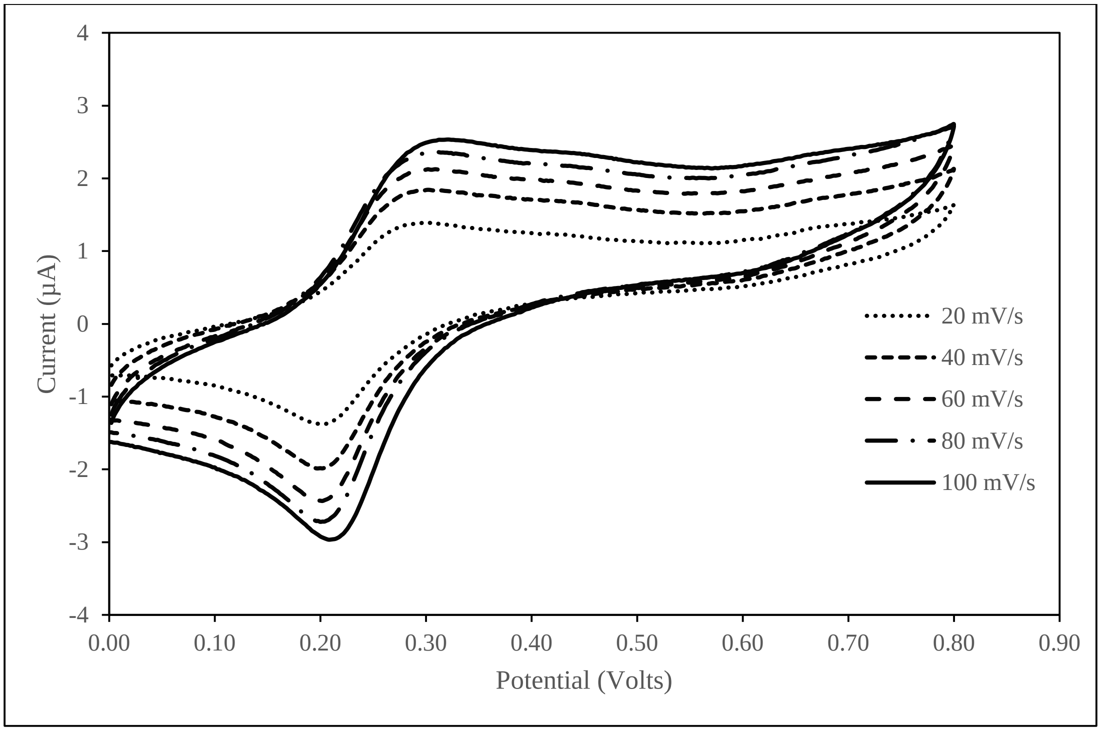


Figure S26: CV of Polymer 4 (X=Methyl) Thin Film in .1 M NaClO₄ Solution

Figure S27: UV-vis Absorbance Spectra of Polymer 2 (X=Cyano)

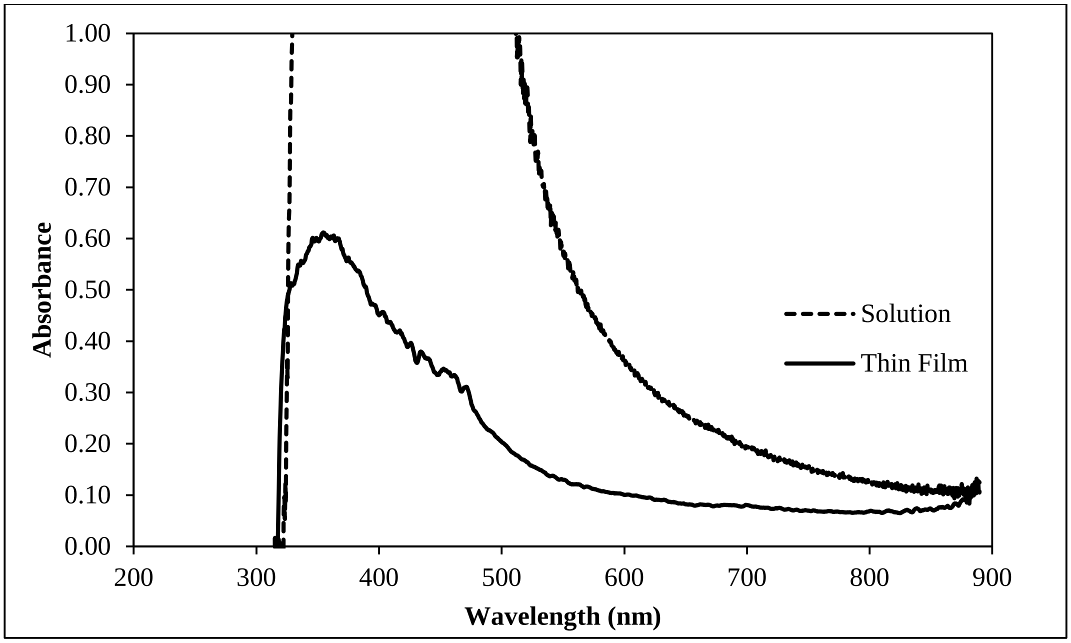


Figure S28: UV-vis Absorbance Spectra of Polymer 3 (X=Methoxy)

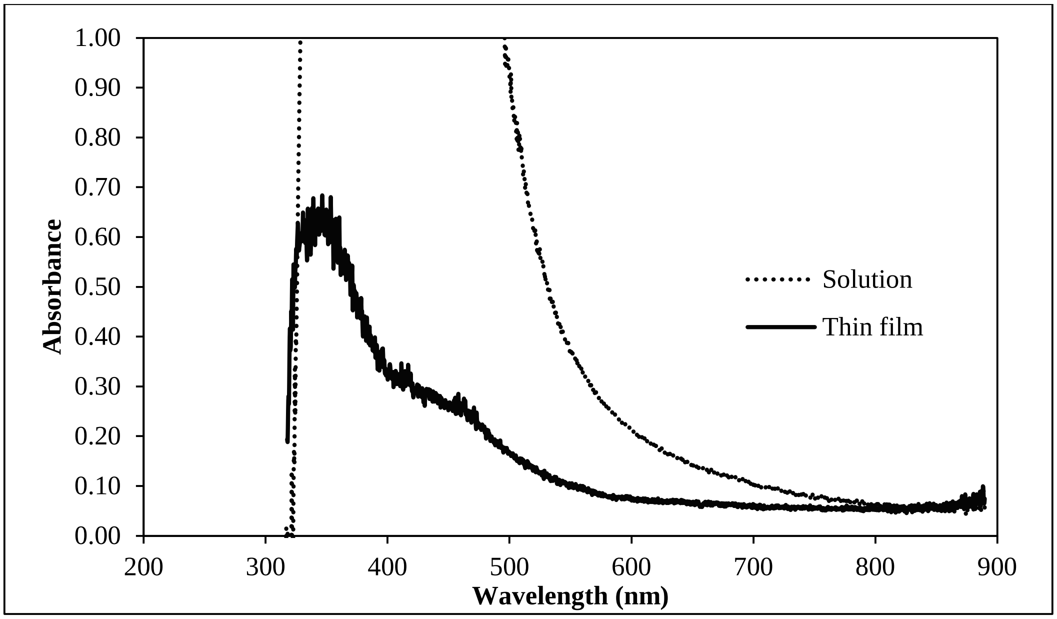


Figure S29: UV-vis Absorbance Spectra of Polymer 4 (X=Methyl)