

**SYNTHESIS AND PROPERTIES OF
POLYSILANE-POLY(FERROCENYLSILANE)
RANDOM COPOLYMERS AND
OXIDIZED POLY(FERROCENYLSILANE)S**

by

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*A thesis submitted in conformity with the requirements
for the Degree of Master of Science,
Department of Chemistry
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*So I'm pickin' up the pieces,
And I'm puttin' them up for sale.
Throw your meal ticket out the window,
Put your skeletons in jail...*

"Synthesis and Properties of Polysilane-Poly(ferrocenylsilane)
Random Copolymers and Oxidized Poly(ferrocenylsilane)s"

Master of Science
1997

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ABSTRACT

Poly(ferrocenylsilane)s are polymers which feature alternating ferrocene and organosilane units. The synthesis of polymers that may have interesting electrical properties and which feature the ferrocenylsilane unit is herein outlined.

Polysilane-poly(ferrocenylsilane) copolymers are synthesized by the thermal ring-opening co-polymerization of a [1]silaferrocenophane and a cyclotetrasilane. These polymers were found to be random in nature, containing short silane and ferrocenylsilane segments.

Oxidized poly(ferrocenylsilane)s are synthesized by the reaction of poly(ferrocenylsilane)s with a number of one-electron oxidants. Molecular weight decline occurred throughout the course of the oxidation (and, in the case of one counterion, in the solid state afterward), but this decline could be minimized by the addition of methyl groups to the cyclopentadienyl rings of the ferrocenyl units, and the use of a mild one-electron oxidant ($[(p\text{-BrC}_6\text{H}_4)_3\text{N}][\text{PF}_6]$). Also, the crystal structure of an oxidized oligomer was determined.

ACKNOWLEDGEMENTS

First and foremost, I gratefully acknowledge Prof. Ian Manners for his supervision of this project, his guidance throughout the last year and a half, and the many X-Files / Simpsons / musicals discussions.

I also must specifically acknowledge Dr. Ron Rulkens for his help and advice in the lab, for taking the time to make sure that this guy with no experience in a synthetic lab knew what he was doing, and for being the finest synthetic chemist I know.

I must also thank the people with whom I have collaborated. With respect to Chapter Three, thanks to Ron Rulkens for assistance with the synthesis of the crystals, and Alan Lough for solving the crystal structure, and Prof. Geoff Ozin and Carol Bowes for the use of and assistance with the Mössbauer spectrometer. With respect to Chapter Two, I must acknowledge Prof. Krzysztof Matyjaszewski, the three gents who were responsible for much of the synthesis and characterization (Ron Rulkens, Eric Fossum, and Peter Miller) and, for the hole transport measurements, Rui Resendes and (at XRCC) Krish Murti.

To the rest of the gang in 327 (past and present)- Derek Gates, Dave "Giver of Life, Taker of Tapes" Balaishis, Mark MacLachlan, Prof. John Sheridan, Karen Temple, Andrew McWilliams, and Ben Langer - thanks for making 327 such a great working environment -- where else could I possibly play my PJ Harvey cds in a semi-public place? And to the rest of the guys in the lab (guys being used in the gender-neutral form connotating 'friends'), thanks for all your intelligence, your insights, and for making the "Manners Squad" a truly top-notch research group.

I also have to thank two special friends, Maggie Austen and Stephen Nicol, without whom the last year and a half would have been, at the very least, much less distracting.

And finally, I must thank Cliff and Nancy Currie for everything that they've done for me while I was in Toronto. I'll always think of you as family, no matter what the papers say.

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LIST OF ABBREVIATIONS

A	absorbance
AIBN	azobisisobutyronitrile
b	path length
c	concentration
Cp	cyclopentadienyl
CV	cyclic voltammetry
DDQ	2,3-dichloro-5,6-dicyanoquinone
DEPT	distortionless enhancement by polarization transfer
DSC	differential scanning calorimetry
EI	electron impact
Fc	ferrocenyl
fc	1,1'-ferrocenediyl
GC	gas chromatography
GPC	gel permeation chromatography
HPLC	high-performance liquid chromatography
M_n	number-average molecular weight
M_w	weight-average molecular weight
Me	methyl
MS	mass spectrometry
<i>o</i> -CA	<i>ortho</i> -chloranil
PDI	polydispersity index
RC	ring-centroid
ROP	ring-opening polymerization
TCNQ	tetracyanoquinodimethane
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	<i>N,N,N',N'</i> -tetramethylethylenediamine
TROP	thermal ring-opening polymerization
uv	ultraviolet
vis	visible
ϵ	molar absorptivity
λ_{\max}	wavelength of maximum absorbance

CHAPTER ONE

POLYMERS AND CONDUCTIVITY

Throughout most of this century, applications of polymers have taken advantage of their light weight, their processability, and their inertness. During this time, the idea that polymers could conduct electricity was never considered. The first report of a conducting polymer, an oxidized polyacetylene, appeared in 1977; in the two decades since that report, conducting polymers have progressed from novel curiosities to materials with applications. Also, polymers exhibiting semiconductivity and photoconductivity have been studied. (For the sake of this discussion, what will be discussed under the heading of "Conducting Polymers" will be those polymers featuring conjugated π -bonds; other types of polymers, such as polysilanes and polymers containing transition metals will be discussed as "Semiconducting Polymers".) The literature dealing with conducting polymers is quite extensive, and cannot be adequately summarized in such a limited space. The following chapter provides a broad overview of polymer systems that feature interesting conductive properties.

1.1 Conducting Polymers

1.1.1 Historical Background

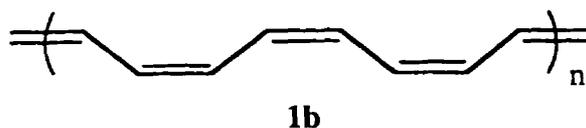
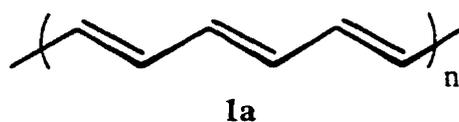
In 1964, Little¹ published a paper which speculated about the possible synthesis of an organic superconductor. His model compound was a substituted polyacetylene (shown in Figure 1), and he reasoned that, like the ring currents in benzene, the equivalence between the double and single bonds (*i.e.*, resonance) would lead to superconductivity along the polymer backbone, by means of a polarizability wave. It was proposed that as the electrons move along the polymer backbone, the side group (a diethyl-cyanine iodide dye), with its low-lying excited states, would become polarized and, by analogy to Cooper pairs of electrons, this polarization allows for a second electron to move along the polymer backbone. (This can be thought of as two 'motions': the electrons along the backbone, and the polarization wave along the side groups. That the polarization of the side groups is not immediately lost allows for superconductivity.) Using this model, Little speculated that superconducting polymers with very high superconducting transition temperatures (approx. 2200 K) could be expected for polyacetylene systems with a fully delocalized backbone. However, in polyacetylene, there are distinct double and single bonds; the lengths are different, the bonds are inequivalent. (Even so, in a polyacetylene with considerable localization, Little predicted a superconducting transition temperature of several hundred Kelvin.) Although his model could not be achieved in a real system, Little's theoretical superconductor did inspire many chemists and physicists to search for conducting polymers.

Another important system for the development of conducting polymers was poly(thiazyl), or $(\text{SN})_x$, which remains the only known polymer that, under the right conditions, exhibits superconductivity.² Synthesized from the cleavage of S_4N_4 when passed through silver gauze, $(\text{SN})_x$ has been known since early in this century.³ Pristine

poly(thiazyl) has a conductivity of 1000 S cm^{-1} at room temperature (and, at very low temperatures, $T < 0.26 \text{ K}$, it superconducts⁴); upon oxidation with bromine, the conductivity increases to $20,000 \text{ S cm}^{-1}$.⁵ This increase in conductivity after oxidation would be an important factor in the development of other conducting polymers. However, $(\text{SN})_x$ is not a true one-dimensional polymer. There are interactions between the unpaired electrons on the sulfur (III) atoms of adjacent chains that may be considered to be weak bonds; $(\text{SN})_x$ is really better described as a 3-dimensional solid state material. And it is this multi-dimensionality that gives rise to its most interesting properties.

1.1.2 Polyacetylene

Polyacetylene, which possesses the backbone structure in Little's model superconductor, is easily synthesized by Ziegler-Natta catalysis or a modification thereof, in which a mixture of a trialkylaluminum compound and a tetra-alkoxytitanium species polymerize acetylene. Polyacetylene exists in two forms, the *trans*- and *cis*- forms, shown below as **1a** and **1b**, respectively. In the pristine state, the *trans*- form has a conductivity of $10^{-5} \text{ S cm}^{-1}$, four orders of magnitude higher than that for the *cis*- form.

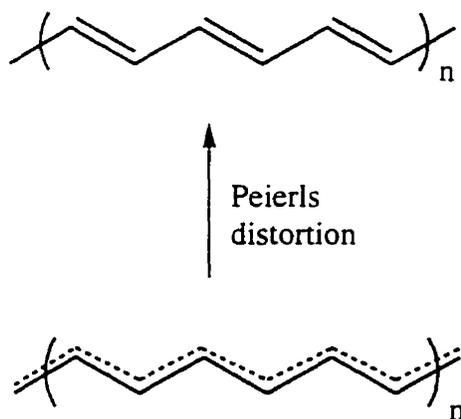


In 1977, MacDiarmid, Heeger, and their coworkers published that when *trans*-polyacetylene is oxidized, a substantial increase in electrical conductivity is observed;⁶ when oxidized with iodine vapour, a conductivity of 38 S cm^{-1} was reported. Interestingly,

about ten years prior to this,⁷ a report had appeared which discussed the effects of oxidation on the electrical properties of polyacetylene, using a number of oxidants, such as Lewis acids (BCl_3 and BF_3) or other electron acceptors (O_2 , Cl_2); the authors stated that conductivity increased, but they did not fully investigate the conductivity of the polymer.

Following the initial discovery of the conductivity of polyacetylene, the mechanism of the conductivity was studied in detail. If it was to follow Little's model of an organic superconductor, the conductivity would be metallic in nature, with a backbone of carbon atoms and a stream of electrons free to flow along it. Little's incorrect assumption that resonance along the polyacetylene backbone would make all the bonds equal in length and lead to superconductivity does not take into account the Peierls distortion; 'metallic' polyacetylene can be viewed as a chain of CH radicals, which is inherently unstable, and will undergo, at low temperatures, a metal-to-insulator transition, which results in the distinct double and single bonds observed in polyacetylene, as in Figure 1. The metallic state of poly(thiazyl), on the other hand, is stabilized by inter-chain interactions of the sulfur (III) atoms; it does not, therefore, undergo the Peierls distortion, and at low enough temperatures will superconduct.

Figure 1: The Peierls distortion in polyacetylene.

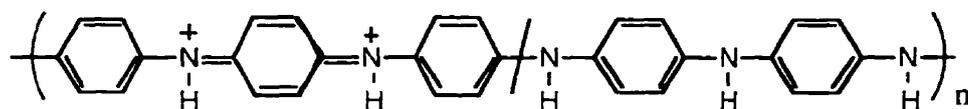
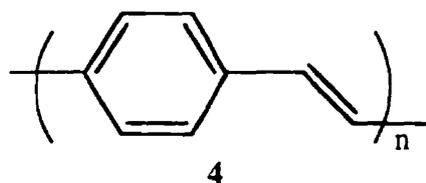
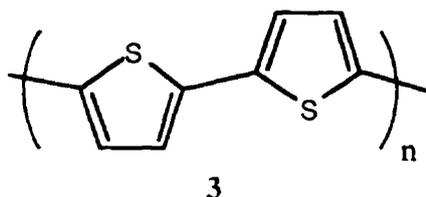
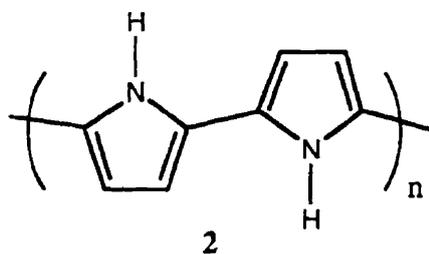


There appear to be two separate mechanisms for conductivity in polyacetylene samples. In highly ordered polyacetylene, for which conductivities of 10^5 S cm^{-1} have been reported, conduction is likely to be metallic in nature. However, these results have been irreproducible. In reproducible cases, for which conductivities of $1-3 \times 10^3 \text{ S cm}^{-1}$ have been reported, the conductivity is consistent with a hopping mechanism. Charges are isolated in positions along the backbone (no complete delocalization); an applied potential allows hopping to occur along chains, between chains, and between fibres.

Reports on polymers related to polyacetylene soon followed; the backbones of these systems all were conjugated π -systems.

1.1.3 Other Conjugated Polymers

A number of other conjugated polymers have been studied, including many featuring elements in the backbone other than carbon. The more important of these are shown below: polypyrrole (**2**), polythiophene (**3**), poly(phenylene vinylene) (**4**), and polyaniline (**5a**).

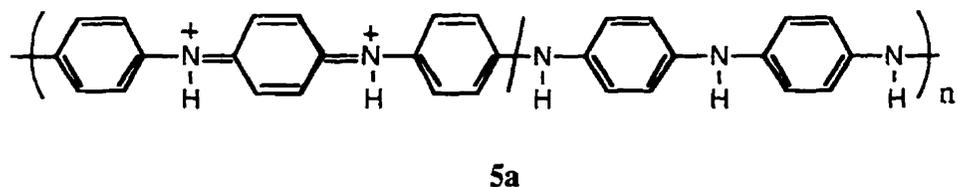


5a

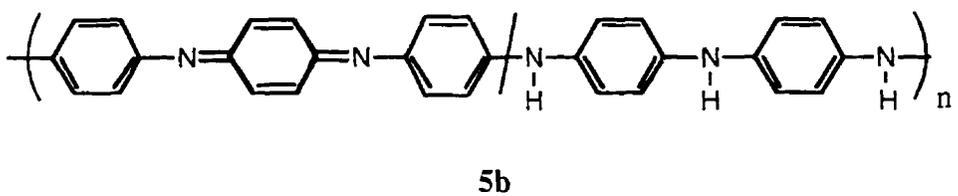
The major drawbacks concerning polyacetylene are its instability and insolubility; for commercial applications, the air-stable conducting polymers polypyrrole, polythiophene, and polyaniline are better suited, and have been studied. A primary problem in their processability has been their insolubility in the oxidized form. This has been an active area of research for polythiophene, and the solubility problem was overcome by the attachment of flexible alkyl groups (*e.g.*, *n*-butyl) to the thiophene ring.⁸

Polyaniline has some properties which make it unique among the conjugated polymers. Firstly, it is not synthesized like the others; polyaniline is prepared via the

oxidative polymerization reaction of aniline with $[\text{NH}_4]_2[\text{S}_2\text{O}_8]$ under acidic conditions;⁹ the resulting polymer salt is shown below:



Deprotonation of this salt leaves the emeraldine form of polyaniline, **5b**, shown below:



The emeraldine form is an insulator, and it becomes conductive when protonated, at lower pH. This high environmental stability (to air and water) allows polyaniline to be used in many applications for which other conducting polymers (such as polyacetylene) would be inappropriate. Polyaniline is soluble in N-methylpyrrolidone, which allows for the formation of films; manipulation of these films by stretch orientation results in anisotropic materials with conductivities of up to $10,000 \text{ S cm}^{-1}$.¹⁰

1.1.4 Uses of Conducting Polymers

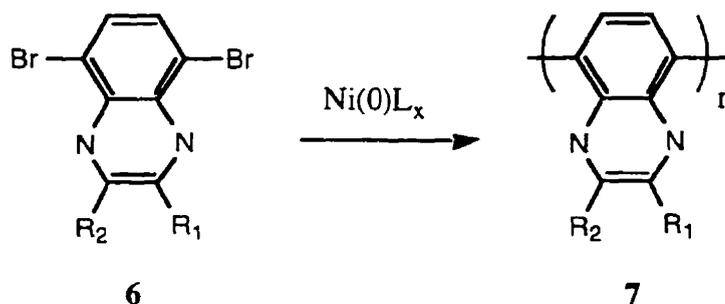
Given the ease of synthesis of conducting polymers, and their processability, it has been speculated that a conducting polymer revolution - in which conducting polymers

would, for the most part, replace metals - might occur. Such a revolution, however, is unlikely. As Miller pointed out in a recent review,¹¹ a number of factors upon which commercial success depends have been ignored: cost competitiveness, environmental compatibility, manufacturability, market acceptance, product longevity and reliability, return on investment, and safety. Conducting polymers will play an important role in the development of new materials, but it will most likely be due to the unique properties that they possess. Two areas which are receiving considerable attention are the development of conducting polymer-based sensors and conducting polymer-based light emitting diodes.

There are a number of characteristics unique to conducting polymers that make their potential use as sensors an attractive one.¹² A broad range of monomer types leads to a rich diversity of materials, each with their own unique properties; their electrochemical preparation can lead to easy mass production and miniaturization; the sensing characteristics of the polymer can be tailored after the film is prepared, by changing the oxidation state of the polymer; reversible responses are easily obtained at ambient temperatures. These properties can be applied to a number of types of sensors, such as biological, chemical, electrochemical, irradiation dosage, mechanical shock, and temperature sensors.¹¹

Conjugated polymers have also had success as materials for light emitting diodes, or LEDs. This use arises from the fact that many of the conjugated polymers (mainly those with aromatic systems) are fluorescent. In a polymer LED, a layer of conjugated polymer is sandwiched between a pair of electrodes.¹³ Upon application of a high electric field between the electrodes, holes and electrons are injected into the polymer layer from the anode and cathode respectively; these holes and electrons recombine radiatively if the polymer is fluorescent, and result in electroluminescence. Among those polymers that have been studied and used as materials in LEDs are such typical conjugated polymers as poly(*p*-phenylene),¹⁴ poly(*p*-phenylene vinylene),¹⁵ and poly(thiophene).¹⁶ Recently, a report appeared in the literature detailing the use of electron-accepting conjugated

polyquinoxalines in LEDs.¹⁷ These polymers, **7**, are synthesized via the dehalogenative polycondensation reaction of **6** using a nickel(0) complex, as shown below.



When aromatic groups are introduced into the side chain, strongly fluorescent polymers result, which are useful in the development of LEDs.

As of 1993,¹⁸ there were approximately 20 commercially available products based on conducting polymers (mainly polypyrrole and polyaniline); it is an impressive beginning for materials that had been, not two decades earlier, unknown. There will, no doubt, continue to be more advancement in the application of conducting polymers as the properties become more fine-tuned.

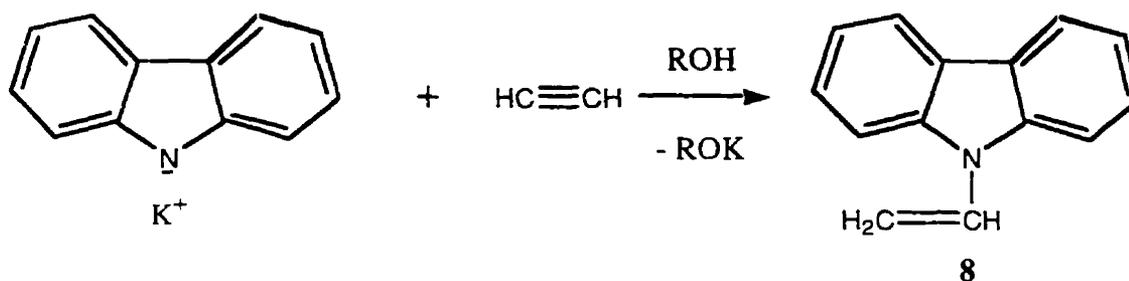
1.2 Photoconducting Polymers

1.2.1 Photoconductivity

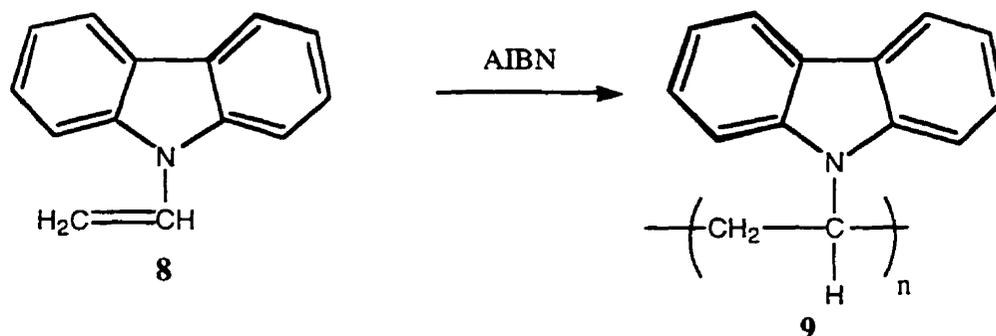
Photoconductivity is defined as the enhancement of conductivity upon illumination. A photoconductive polymer, therefore, is a polymer that is a poor conductor or insulator in the dark, yet a good conductor in the light.¹⁹ There are three main processes to be considered in photoconductivity: carrier generation, transport, and elimination of carriers.²⁰ Carriers are generated by the interaction of the system with light, and generally result in the excitation of an electron. Carriers are transported, in photoconducting polymers, by an electron hopping process, and are eliminated in an electron-hole recombination process. While a number of polymers exhibit some degree of photoconductivity, poly(*N*-vinyl carbazole) has achieved the most success, and it will be discussed in more detail.

1.2.2 Poly(*N*-vinyl carbazole)

Of all the photoconducting polymers, poly(*N*-vinyl carbazole) (PVK) is the most studied.²⁰ The precursor monomer, *N*-vinyl carbazole, (below), has been synthesized by various methods, the most straightforward of which involves the reaction of acetylene with the alkali metal salt of carbazole in polar solvents:



Various polymerization routes have been explored; the most commonly used is the free radical polymerization with various initiators, usually azobisisobutyronitrile (AIBN).



The photoconductivity process in PVK has been studied in detail.²⁰ Three types of carrier generation have been observed: intrinsic, generation by charge transfer complexes, and extrinsic. Intrinsic generation occurs when, simply, a photon excites an electron from a ground to an excited state, and instead of losing its energy by non-radiative dissipation, the electron enters a continuum state. While in this "thermal state", the coulombic interaction between the electron and the hole remains; the addition of an electric field will generate free carriers. In intrinsic carrier generation, only holes are generated for transport, and for PVK it requires uv light.

The photoconductivity of PVK has been dramatically enhanced by the addition of various dopants which form charge transfer complexes. The best example is 2,4,7-trinitrofluorenone, TNF. Its complex with PVK exhibits a photoresponse throughout the visible range, and has gained use as a photoreceptor in xerographic copiers. It is a unique system in that it transports both holes and electrons.

Extrinsic photogeneration is observed for a number of systems in which dyes form molecular dispersions in PVK. In this case, photoconductivity results from the electronic transitions in the dye molecules. There are many PVK/dye photoconductors in the patent

literature, and they exhibit photoresponse over the entire visible range and even the near IR region. Most systems, however, have a low photogeneration efficiency.

The carrier transport in PVK occurs by a thermally activated hopping process; in the direction of the electric field, positive holes hop between localized sites, which are viewed as carbazole cation radicals. (Electrons hop from neutral carbazole species to radicals, effectively moving the holes.) Transport is both field-dependent and thermally activated. In PVK/TNF, in which both holes and electrons are transported, the holes are transported via PVK while the electrons are transported via TNF (in both its free and its complexed forms). With increasing TNF content, hole transport decreases and electron transport increases.

The elimination of carriers occurs by the recombination of a hole and an electron, resulting in an electrically neutral species.

1.2.3 Other Photoconducting Polymers

Photoconductivity has been reported for a variety of polymers:¹⁹ in most cases, however, the reports only state that the material is photoconductive. Among these polymers are those with conjugated double bonds, those with large polynuclear aromatic groups, and those with aromatic amine groups. The carbazole group is a common feature of a number of photoconductive polymers. Also, a number of polymers doped with TNF (including polysilanes and polyphosphazenes) have been found to be photoconductive.

When injected with holes from photoelectrodes, poly(methylphenylsilane) conducts. An interesting property of this system is that its hole mobility is approximately four orders of magnitude higher than that of PVK.²¹ This large difference in mobility is attributable to the fact that conduction in polysilanes occurs due to σ -electron delocalization along the silicon backbone.²² Similarly, poly(methylphenylsilane) when doped with fullerenes photoconducts,²³ and has a higher charge-generation efficiency than fullerene-

doped PVK.²⁴ This is consistent with the different mechanisms of conductivity in the two systems. As well, fullerene-doped polysilane is a hole photoconductor, whereas pure solid fullerene films are electronic photoconductors.²⁵ Interestingly, polysilanes with alkyl substituents on silicon were not photoconductive, a result which suggests a specific interaction between the fullerene and the phenyl group.²³

1.2.4 Uses of Photoconducting Polymers

Of all polymers which possess interesting conduction properties, photoconductors (and specifically PVK) have had the greatest success as materials. Photoconductive polymers such as PVK/TNF have been used in xerographic copiers.²⁶ The basis of the xerographic process is the ability of a material to distinguish between dark area on a piece of paper (*e.g.*, the text) and the light areas (*e.g.*, the paper itself). Light is reflected from the paper, it is transported through a polymer transport layer, and it generates charge in the photoconductor. The charges migrate through the transport layer, and neutralize the previously charged surface, leaving the dark areas on the paper charged. From this, it is transferred to another sheet of paper, and then the system is cleaned and neutralized. Efficient polymeric photoconductors will improve the speed and quality of copies made.

1.3 Semiconducting Polymers

There have been many reports of polymers that exhibit semiconductivity, far too many to be summarized in a few pages. The discussion of semiconducting polymers that follows will be limited to some novel inorganic systems, the polysilanes and ferrocene-containing polymers.

1.3.1 Polysilanes

Polysilanes are polymers with backbones composed of silicon atoms.^{27,28} In addition to responding to light, the conductivity of polysilanes increases upon oxidation. There is not, however, a backbone of π -conjugated bonds to account for this, as in polyacetylene; the increase in conductivity is due to delocalization of the σ -electrons along the silicon backbone. The conductivity occurs by a hole transporting mechanism, and polysilanes have developed uses as hole transporting layers in LEDs.²⁹ Their use in LEDs is attributable to their high hole mobilities (which is due to strong interchain coupling of the σ -bonds), and to the ease of purifying samples with conventional techniques.

This phenomenon of σ -delocalization along the backbone is observed in polymers of the heavier group 14 elements as well. Tilley's pioneering work³⁰ on polystannanes has shown that the band gap decreases with a heavier element in the polymer backbone.

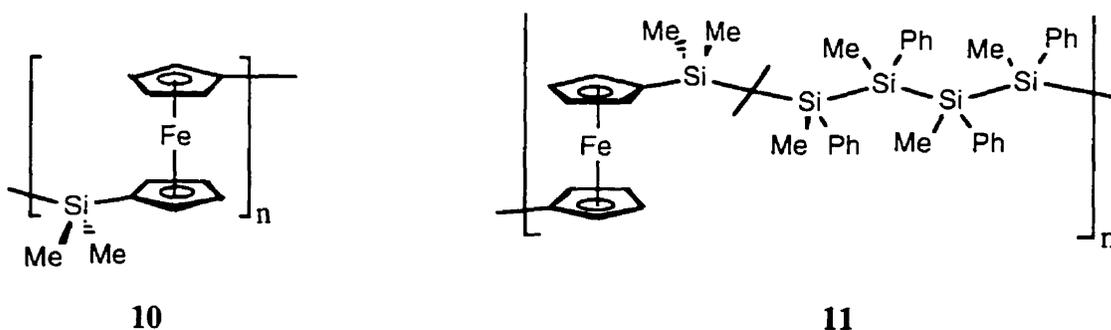
1.3.2 Ferrocene-Containing Polymers

Polymers containing ferrocene in the side group structure and in the backbone have been studied in detail. These polymers are easily oxidized, due to the reversibly oxidizable ferrocene unit. A variety of one-electron oxidants have been used with a variety of polymers; in all cases, conductivity has been a result of a hopping mechanism. Pittman

and his coworkers observed that, for a series of polymers with ferrocene in the backbone, conductivity was maximized between 35 and 65 %, and that it was independent (to a first approximation) of the counterion present. Yamamoto and his coworkers have reported a conductivity of $4.1 \times 10^{-2} \text{ S cm}^{-1}$ for a sample of crystalline 1,1'-polyferrocenylene, a substantially higher (approximately six orders of magnitude) conductivity than Pittman and his coworkers had reported on their amorphous sample. (The oxidation and conductivities of various ferrocene-containing polymers is covered in more detail in the Introduction to Chapter Three.)

1.4 Research Objectives

The goal of this project is the successful synthesis and study of polymers that may possess interesting electrical properties. These polymers contain a reversibly oxidizable iron (II) centre, as part of a ferrocene moiety. The polymers under investigation are the poly(ferrocenylsilane), **10**, and the polysilane-poly(ferrocenylsilane) random copolymer, **11**, shown below.



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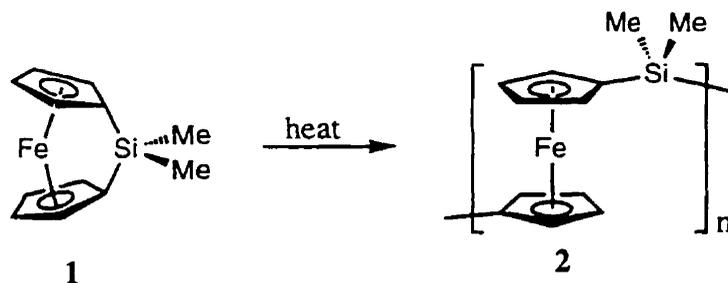
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CHAPTER TWO

POLYSILANE-POLY(FERROCENYLSILANE) RANDOM COPOLYMERS

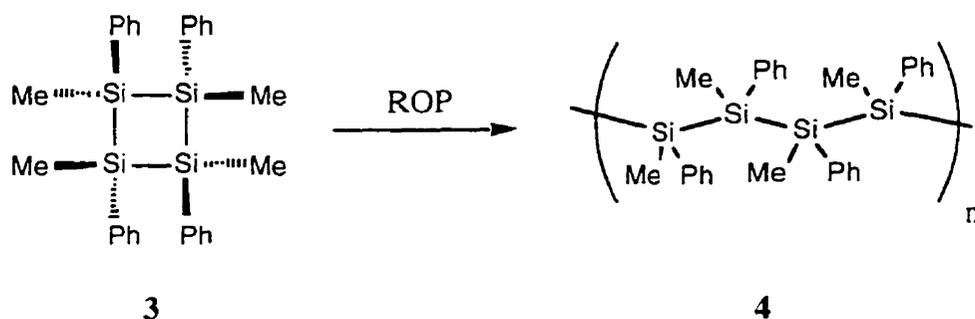
2.1 Introduction

The development of new polymer systems featuring transition metals in the polymer backbone is of interest, as these polymers may possess novel electrical, optical, or magnetic properties.^{1,2} Some important examples feature ferrocene units in the backbone, which have interesting properties due to the reversible oxidation of the iron centre. Poly(ferrocenylsilane)s possess alternating ferrocene and organosilane units in the backbone, and were first prepared by the condensation reaction of dilithioferrocene-TMEDA and dichlorosilanes; this reaction yields polymers of low molecular weight.³ In 1992, the synthesis of high molecular weight poly(ferrocenylsilanes), for example **2**, by the thermal ring-opening polymerization (TROP) of strained, silicon-bridged [1]ferrocenophanes, such as **1**, was reported.⁴ Subsequently, reports on the polymerization at room temperature by anionic methods⁵ and transition metal catalysis⁶ have appeared.

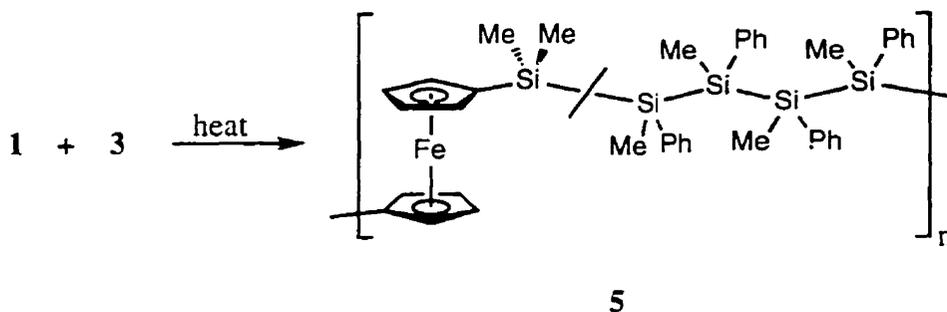


Polysilanes, with backbones composed of silicon atoms, have received considerable attention, for both their synthesis and their properties.⁷ A feature unique to

these systems, which leads to many of their interesting properties, is the delocalization of the σ -electrons along the silicon backbone. This is responsible for their electrical conductivity when doped. The primary method of producing polysilanes is Wurtz-type coupling of dichlorosilanes with sodium metal, the initial successful method for polysilane synthesis.⁷ Other methods have been used, such as dehydrogenative coupling of hydrosilanes,⁸ or anionic polymerization of masked disilenes,⁹ but the primary method still remains Wurtz coupling, or a modification thereof. In 1991, the anionic ring opening polymerization (ROP) of 1,2,3,4-tetramethyl-1,2,3,4-tetraphenyl-1,2,3,4-cyclotetrasilane, **3**, was reported, which yielded the polysilane, **4**.¹⁰



In 1995, it was reported in a communication that **3**, after melting, undergoes thermal ROP to yield high molecular weight polymer **4**, and that it thermally copolymerizes with the [1]silaferrocenophane **1** to yield the random copolymer **5**.¹¹ In this chapter, full details of the studies of both the synthesis and the characterization of the resulting copolymers are presented.



2.2 Experimental

2.2.1 Equipment and Chemicals

Equipment. Molecular weights (relative to linear polystyrene standards) were measured in THF using a Waters GPC equipped with linear, 10^2 , and 10^3 A Phenogel columns, a Waters 410 refractive index detector and a Waters 991 photodiode array. Spectra were analyzed at 338 and 450 nm, wavelengths specific for poly(methylphenylsilane) and poly(ferrocenylsilane) respectively.

Proton NMR spectra were recorded with a Varian Gemini 200 spectrometer. The 79.5-MHz ^{29}Si -NMR spectra were recorded on a Varian XL 400 spectrometer utilizing a DEPT pulse sequence (proton decoupled) with a $^2J_{\text{Si-H}}$ coupling of 6.7 Hz and were referenced externally to SiMe_4 . The solvent was C_6D_6 .

Mass spectra were obtained with a VG 70-250S mass spectrometer operating in electron impact mode. Pyrolysis mass spectrometry experiments were carried out by heating the sample probe up to 600 °C.

Thermogravimetric analyses were performed at a heating rate of $10\text{ °C}\cdot\text{min}^{-1}$ under prepurified N_2 using a Perkin Elmer TGA 7 Thermogravimetric Analyzer.

Cyclic voltammograms were recorded with a PAR model 273 potentiostat. A Pt working electrode and a Ag wire reference electrode in a Luggin capillary. All potentials are relative to the ferrocene/ferrocenium ion couple at 0.00 V, which was used as an internal reference. CH_2Cl_2 and MeCN solvents were freshly distilled from P_2O_5 , anhydrous grade $[\text{Bu}_4\text{N}][\text{PF}_6]$ (Aldrich) was used as supporting electrolyte (0.100 M), and the analyses were carried out under prepurified N_2 .

Hole mobility was determined by conventional time-of-flight techniques.¹² In this technique, the drift of a sheet of holes injected from the charge generating layer (CGL) is time-resolved and the transit time was determined in order to calculate the hole mobility at

an applied electric field. An electric field was applied across the device (featuring the copolymer as a charge transport layer) with a negative bias voltage (DC power supply) at the top electrode and an incident light (about 5 μ sec pulse) from a strobe was used to generate a sheet of charge carriers in the CGL. The duration of the light pulse was chosen to be much smaller than the typical transit time (about 1 msec in many organic and polymeric materials) so that the transport process does not interfere with the generation process.

Chemicals. Solvents were dried using standard methods, and were distilled under dinitrogen before use. All chemicals were purchased from Aldrich.

The ferrocenophane **1** was synthesized according to the literature reaction of dilithioferrocene-TMEDA with dichlorodimethylsilane;¹³ the tetrasilane **3** was synthesized via the literature reaction of octaphenylcyclotetrasilane with triflic acid, followed by methylation with methylmagnesium bromide.¹⁰

2.2.2 Synthesis of Materials

Synthesis of polymers 5a-c by thermal ROP. The same procedure was used for the synthesis of the three copolymer samples; what follows is the procedure for the synthesis of polymer **5a**. The ferrocenophane **1** (86 mg, 0.36 mmol) and the cyclotetrasilane **3** (75 mg, 0.18 mmol) were dissolved in hexanes, and the two solutions were mixed, and transferred to a Pyrex tube. The hexanes was pumped off slowly, leaving the mixture of the two compounds. The tube was evacuated, sealed, and heated at 150°C for two hours. The polymer was isolated by precipitation from THF into hexanes. Yield: 118 mg (74%).

Attempted transition metal-catalyzed ROP. These experiments were monitored by ¹H NMR. The two monomers (40 mg or 1.66×10^{-4} mol **1**, 20 mg or 4.16×10^{-5} mol **3**) were mixed with PtCl₂ (6 mg, 2.0×10^{-5} mol) in a NMR tube, with deuterated benzene as

solvent, and sealed. For the experiment at room temperature, the reaction was monitored by NMR daily; for the experiment at 60°C, the tube was heated in an oil bath for two hours, precipitated into methanol, and the ^1H NMR spectrum (in C_6D_6) was obtained; the spectrum showed large peaks corresponding to the ferrocenylsilane segments, and small peaks due to the silane units. (From integration, the polymer was 96% ferrocenylsilane.)

Anionic ROP attempts. As a general procedure for the attempted anionic ring-opening copolymerizations, 200 mg (0.415 mmol) **3** and 50 mg (0.20 mmol) **1** were dissolved in 1 mL THF, and initiator (10 μL of a 1.6 M solution of *n*-butyllithium) was added via syringe. This was left stirring for 30 minutes. was quenched with water, and the polymer that formed was precipitated in hexanes. GPC analysis (with the simultaneous collection of uv/vis spectra at 338 and 450 nm) showed that two homopolymers formed with M_n values of 13,300 for **2** and 17,700 for **4** (PDIs were approximately 1.8 in both cases).

Attempted synthesis of block copolymers. Two attempts to prepare block copolymers were made using anionic initiators. To a solution of 65 mg (0.135 mmol) **3** in 2 mL THF was added 5 μL of a 1.6 M solution of *n*-butyllithium. This solution rapidly (20 sec) polymerized, and to it was added a solution of 65 mg (0.27 mmol) **1** in 1 mL THF. No further reaction occurred; GPC showed just homopolymer **4** ($M_n = 10,000$). Similarly, to a solution of 130 mg (0.537 mmol) **1** in 2 mL THF was added 0.013 mmol ferrocenyllithium (produced *in situ* by the reaction of 5.5 mg FcHgCl and 16.25 mL of the *n*-butyllithium solution), and this was left stirring (and polymerizing) for 30 minutes. To this solution was added 130 mg (0.27 mmol) **3**. No further reaction occurred; GPC analysis (while simultaneously monitoring the uv/vis spectra at 338 and 450 nm) of the reaction mixture showed that only homopolymer **2** had formed ($M_n = 10,000$).

2.3 Results and Discussion

2.3.1 Copolymer Synthesis

Attempted anionic and transition metal-catalyzed ROP. That both monomers **1** and **3** polymerize by anionic initiation suggested that the synthesis of copolymers **5** might be achieved by anionic methods. The tetrasilane **3** undergoes ROP in the presence of *n*-butyllithium and 1,4-dipotassiooctaphenyltetrasilane;¹⁰ the ferrocenophane **1** undergoes ROP in the presence of a variety of anionic initiators, such as ferrocenyllithium, butyllithium, and phenyllithium.⁵ Copolymerization reactions were attempted with ferrocenyllithium, for which there was no observable reaction, and with butyllithium, in which the two homopolymers **2** and **4** formed (with incomplete conversion of **1** to **2**). Also, the synthesis of block copolymers (by the addition of the second monomer to a solution of the first monomer that had been anionically polymerized using *n*-butyllithium) was attempted; in each case, the only polymer observed was the homopolymer corresponding to the monomer that was initially ring opened.

Also, polymerization by transition metal catalysis was attempted. Various transition metal complexes, such as PtCl₂ or PdCl₂, polymerize the ferrocenophane **1**.⁶ Transition metal-catalyzed ring-opening of **3** has also been studied;¹⁴ the main product of this reaction is the cyclic dimer, the cyclooctasilane, which was generally formed in greater than 50% yield. Some higher molecular weight material was observed with less sterically hindering catalysts, but just as a tail on the GPC traces; number average molecular weights, M_n s, were all under 1000 (or, just slightly greater than two repeat units of **3**).

Bearing this in mind, copolymerization was attempted, using PtCl₂ as a catalyst. Experiments were attempted at both room temperature and 60°C. With a 4:1 ratio of **1** : **3**, polymerization occurred at room temperature over a four day period, with incomplete conversion of **3**; the resulting copolymer was comprised 96% of **1** (by ¹H NMR). As

expected, the polymerization occurred more easily for the ferrocenophane **1**; as well, the presence of **3** inhibited the polymerization, since homopolymerization of **1** occurs within a few hours. At 60°C, the reaction of a similar mixture of **1** and **3** was complete in two hours, and the polymer had the same composition as the product of the room temperature copolymerization, with incomplete conversion of **3**. Therefore, although **1** and **3** can copolymerize in the presence of a transition metal catalyst, the homopolymerization of **1** is much faster.

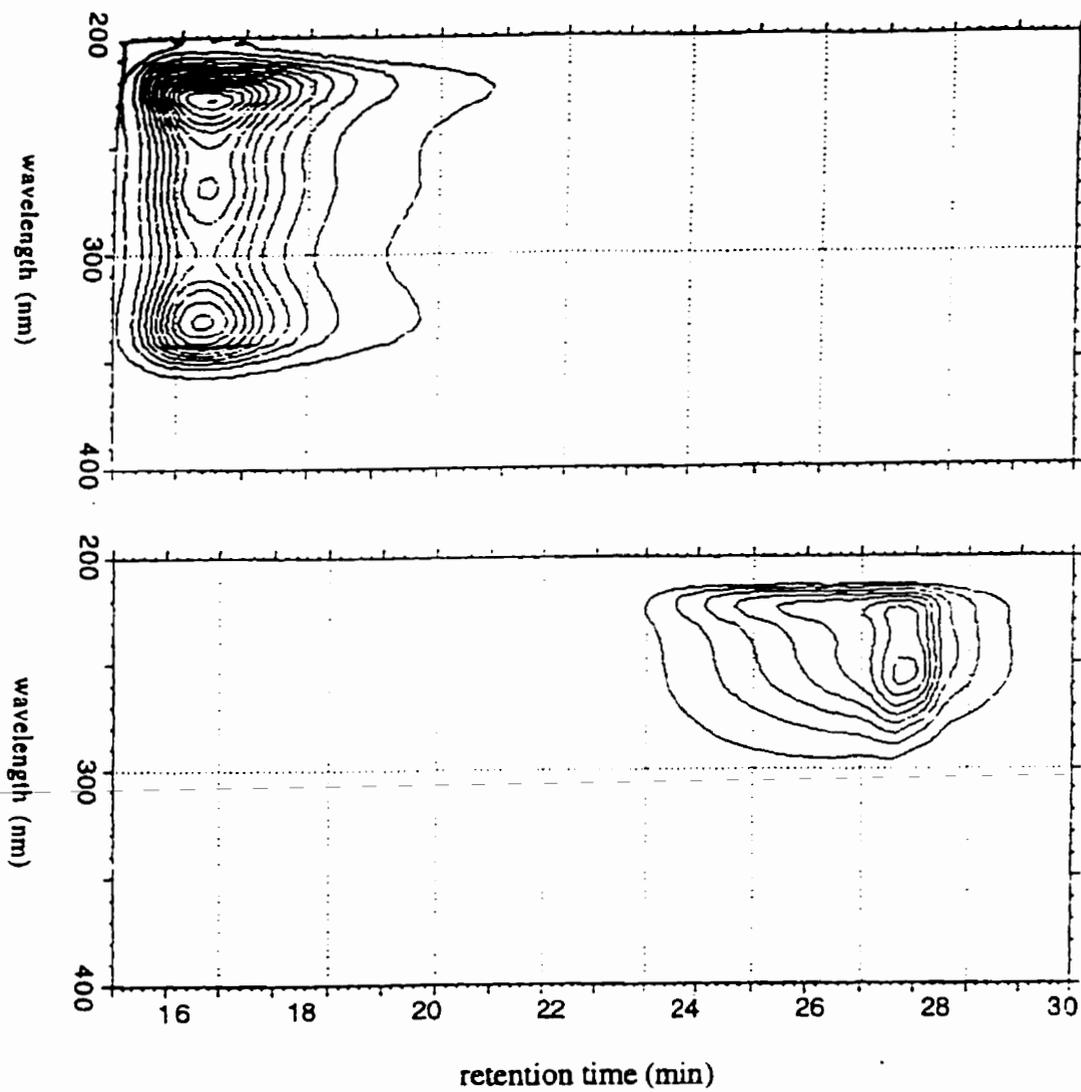
Synthesis of copolymers by thermal ROP. Upon discovery that **3** undergoes thermal ROP, thermal copolymerization was attempted by heating mixtures of **1** and **3**. This resulted in the formation of random copolymers **5**. By varying the ratio of **1** and **3**, a series of copolymers with varying composition was obtained. Analysis by ¹H-NMR confirmed that no unreacted monomer remained. The polymeric products were isolated as pale, amber powders by precipitation from THF into hexanes, and possessed number-average molecular weights (M_n) of 67 000–89 000 versus polystyrene standards, with polydispersities ranging from 2.4 to 3.5.

2.3.2 Characterization of Copolymers

The copolymers were characterized by a number of techniques. Polymer molecular weights were determined by gel permeation chromatography (GPC), with an online photodiode array detector, for the simultaneous monitoring of multiple wavelengths. The GPC results are summarized in Table 1; these results conclusively show that the copolymers are random in nature. Molecular weights are given for the polymers before and after exposure to UV light. It is well known that polysilanes undergo photodegradation upon exposure to UV light to give small cyclic species, while experiments with **2** show that poly(ferrocenylsilanes) do not degrade; in a copolymer system, the polysilane segments should degrade, while the ferrocenylsilane segments

should remain intact. Photodegradation experiments of **5** in THF were carried out using 340 nm uv light for 18h; the GPC trace of the product showed no absorption at 330 nm, indicating the absence of polysilane segments (Figure 1). For the three copolymers, this is observed; the molecular weights observed after photolysis (indicated by * in Table 1) correspond to oligomeric ferrocenylsilane segments ($n = 4 - 6$), and are proportional to the initial relative stoichiometries of the copolymers. This implies that, in the copolymers **5a-c**, the ferrocenylsilane segments are short chains.

Figure 1 Three dimensional GPC (wavelength x retention time x absorption) of polymer **5c** before (top) and after (bottom) photolysis by 340 nm uv light.



As well, it is easily shown that the silane segments are small, oligosilane units. The delocalization of the σ -electrons within the polysilane backbone causes a shift to higher wavelength of λ_{\max} with increasing chain length; this reaches a maximum of 338 nm at a chain length of approximately 30 silicon atoms (or, 7 or 8 units of y).⁷ The λ_{\max} values show that the silane segments are very short oligomeric units: as the quantity of the silane increases, λ_{\max} increases as well, but does not reach its maximum value, even in copolymer studied with the highest silane content. The data of Table 1 indicate that the copolymers **5a-c** contain short segments of silane and ferrocenylsilane repeat units.

Table 1 GPC data for polymers **5a-c**.

	3 : 1 mol : mol	M_n (PDI)	λ_{\max} (nm) (polysilane)	M_n (PDI)*
2	0 : 1	250,000 (1.6)	-	230,000 (1.9)
5a	1 : 2.2	89,000 (3.5)	325	1,730 (1.4)
5b	1 : 1	75,000 (3.1)	330	1,410 (1.2)
5c	2 : 1	67,000 (2.4)	333	1,050 (1.4)
4	1 : 0	91,000 (3.0)	338	-

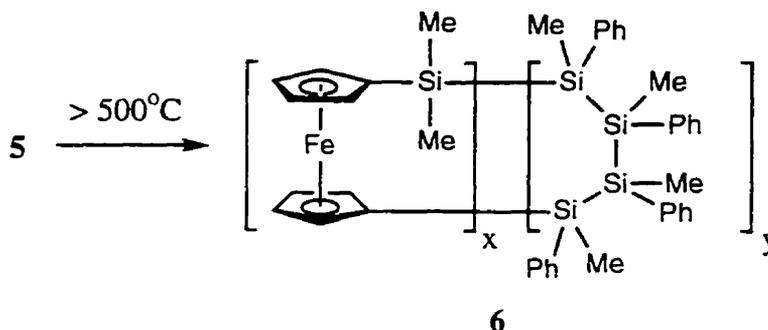
*: M_n of the remaining oligo(ferrocenylsilane) segments after irradiation with uv light (340 nm) in THF for 18 h.

Further structural characterization of the copolymers was provided by ^1H and ^{29}Si NMR spectroscopy. The ^1H NMR spectra of the copolymers (in C_6D_6) showed sharp signals for the ferrocenyldimethylsilane segments at 0.51 ppm (SiMe_2) and at 4.08 and 4.48 ppm ($\eta\text{-C}_5\text{H}_4$) and two broad signals for methylphenylsilane segments at -0.5 to +0.5 ppm (Me) and 6.5 to 7.5 ppm (Ph). The integration ratio of the phenyl and cyclopentadienyl regions of the ^1H NMR spectra of the copolymers confirmed that the relative amounts of **2** and **4** in the copolymers **5** were equal to the relative amounts of the two monomers **1** and **3** in the initial mixture prior to polymerization. Smaller, unresolved cyclopentadienyl resonances between 3.5 and 4.4 ppm were assigned to the ferrocenylsilane units near a juncture to a methylphenylsilane segment. Analysis of **5a-c** by ^{29}Si NMR (in C_6D_6) showed resonances for ferrocenyldimethylsilane units at -6.4 ppm and a broad resonance for atactic methylphenylsilane segments from -37 to -40 ppm and also revealed small peaks for SiMe_2 crossover groups between the ferrocenylsilane and methylphenylsilane segments at -17.3 and -6.6 ppm. The peaks are particularly apparent in the ^{29}Si NMR spectrum of polymer **5c** which possessed relatively short ferrocenylsilane blocks; in contrast, the resonances in the corresponding spectrum of **5a** are less intense as the ferrocenyl blocks are longer.

2.3.3 Thermal Stability

When poly(ferrocenylsilanes) are heated to high temperatures under vacuum, cyclic oligomeric depolymerization products can be detected by pyrolysis mass spectrometry.¹⁵ In the case of a copolymer, depolymerization fragments would represent parts of the initial copolymer chain; having established that the copolymer chain is random in nature, one would expect to observe cyclic depolymerization fragments containing both repeat units, as shown below. (Whereas in a block copolymer, depolymerization products would consist mainly of one of the repeat units.) Pyrolysis mass spectrometry was performed on the

polymers in Table 1, and gives an indication of the effects of varying ratios of the monomers in the polymer.



Pyrolysis mass spectrometry was also performed on the homopolymers **2** and **4**. The mass spectrum of **2** shows oligomeric ferrocenylsilane units of up to $x = 7$, while the mass spectrum of **4** showed no oligomeric silane units larger than $y = 2$, a result indicative of the lower thermal stability of the Si-Si bond. In sample **5a**, the copolymer rich in ferrocenylsilane repeat unit, the main depolymerization products are the cyclic ferrocenylsilane oligomers ($x = 2-7$, $y = 0$), with the dimer ($x = 2$, $y = 0$) being the major product. This corresponds well with the results obtained in the GPC experiments: following photolysis, the remaining segments (corresponding to ferrocenylsilane units) had $M_n = 1730$, which corresponds to approximately seven repeat units. There is essentially no evidence in the mass spectrum for the existence of oligosilane units after pyrolysis. However, there is evidence for some mixed oligomers: there are small peaks at $m/e = 722$ ($x = 1$, $y = 1$), $m/e = 602$ ($x = 1$, $y = 3/4$), $m/e = 482$ ($x = 1$, $y = 2/4$), and $m/e = 363$ ($x = 1$, $y = 1/4$). Fractional values for y are a result of Si-Si cleavage not occurring preferentially at every fourth silicon, and are as expected. As the silane content is increased in polymers **5b** and **5c**, cyclic ferrocenylsilanes ($x = 2-7$, $y = 0$) are again observed, but in smaller proportions. As well, more mixed oligomers are observed, up to $m/e = 1202$ ($x = 1$, $y = 2$). These mixed oligomers provided additional evidence regarding the random

nature of the copolymers.

Thermogravimetric analysis (TGA) was also performed to obtain information regarding the thermal stability of the copolymers. The polymer studied, **5d**, contained approximately 60% ferrocenylsilane. The TGA scan (obtained under an atmosphere of N₂ at a scan rate of 10°C/min) is shown in Figure 2. The polymer is stable to weight loss to approximately 300°C, and 40% of the polymer remained following weight loss. Most of the weight loss occurs between 400 and 600°C, and possibly by two different mechanisms (indicated by the change in slope). The thermal degradation behaviour was quite similar to that observed in ferrocenylsilane homopolymer **2**.¹⁶ The copolymer **5d** had a slightly lower temperature at which 10% weight loss occurred (approximately 400°C, compared to approximately 430°C for the homopolymer **2**). This is consistent with the lower thermal stability of the polysilane segments.

2.3.4 Electrical Properties

Cyclic voltammetric studies of **5a-c** in CH₂Cl₂ showed the presence of two reversible oxidations at $E_{1/2} = 0.00$ and 0.23 V (relative to ferrocene/ferrocenium couple at $E_{1/2} = 0.00$ V) arising from the oligoferrocenylsilane segments, which was found previously for poly(ferrocenylsilane) homopolymers.^{17,18} An irreversible oxidation with $E_p(\text{ox}) = 0.39$ V was also detected, and corresponds to oxidative cleavage of the polysilane segments.¹⁹ The cyclic voltammogram of **5a** is shown in Figure 3.

The hole transporting capability of the copolymer **5d** was also investigated. The mobility of a charge carrier is the velocity per unit electric field; copolymer **5d** had a mobility of 4.0×10^{-6} cm²/V·s, at an electric field of 50,000 V/cm. There was, unfortunately, significant trapping of positive charge.

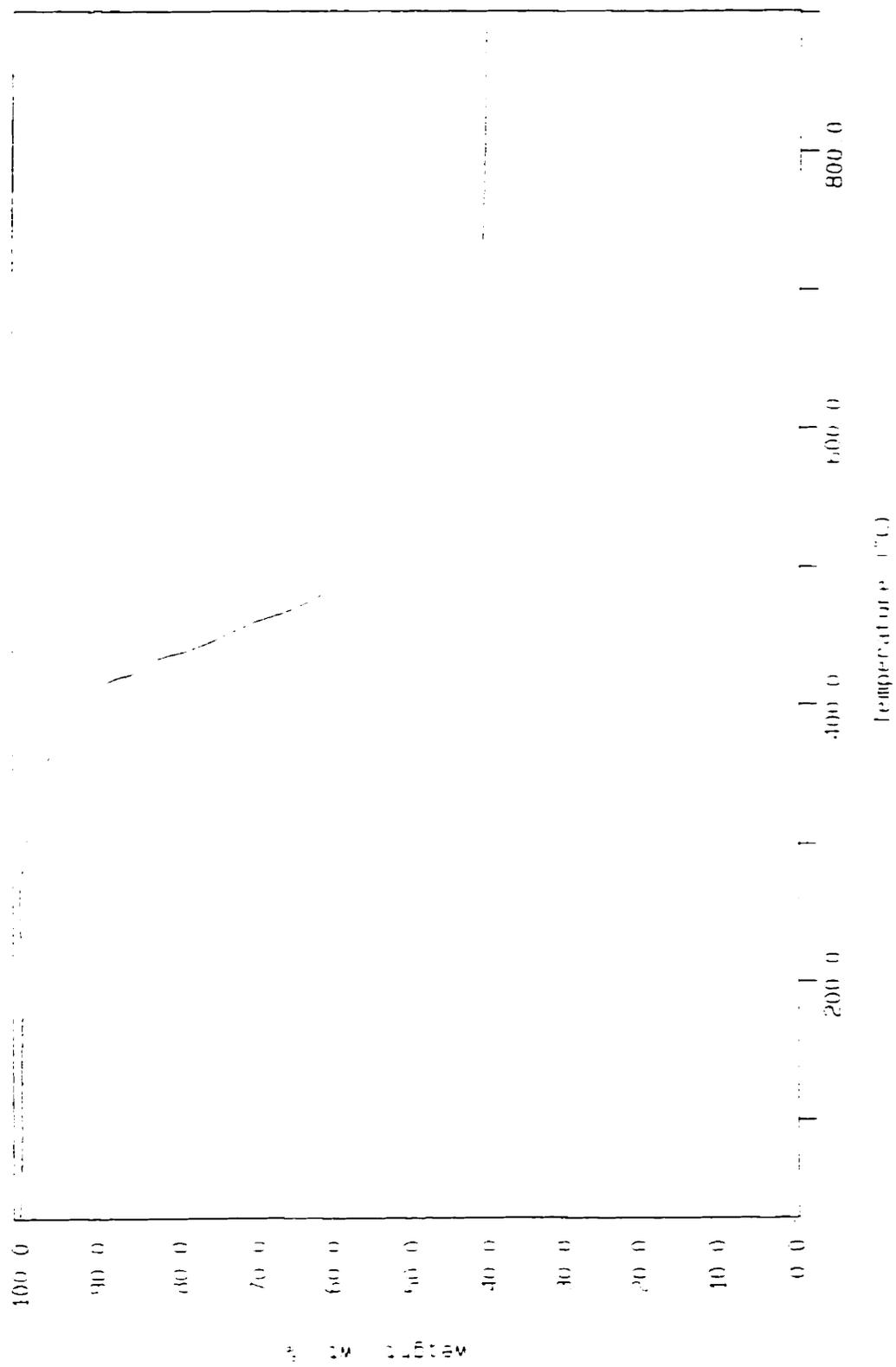
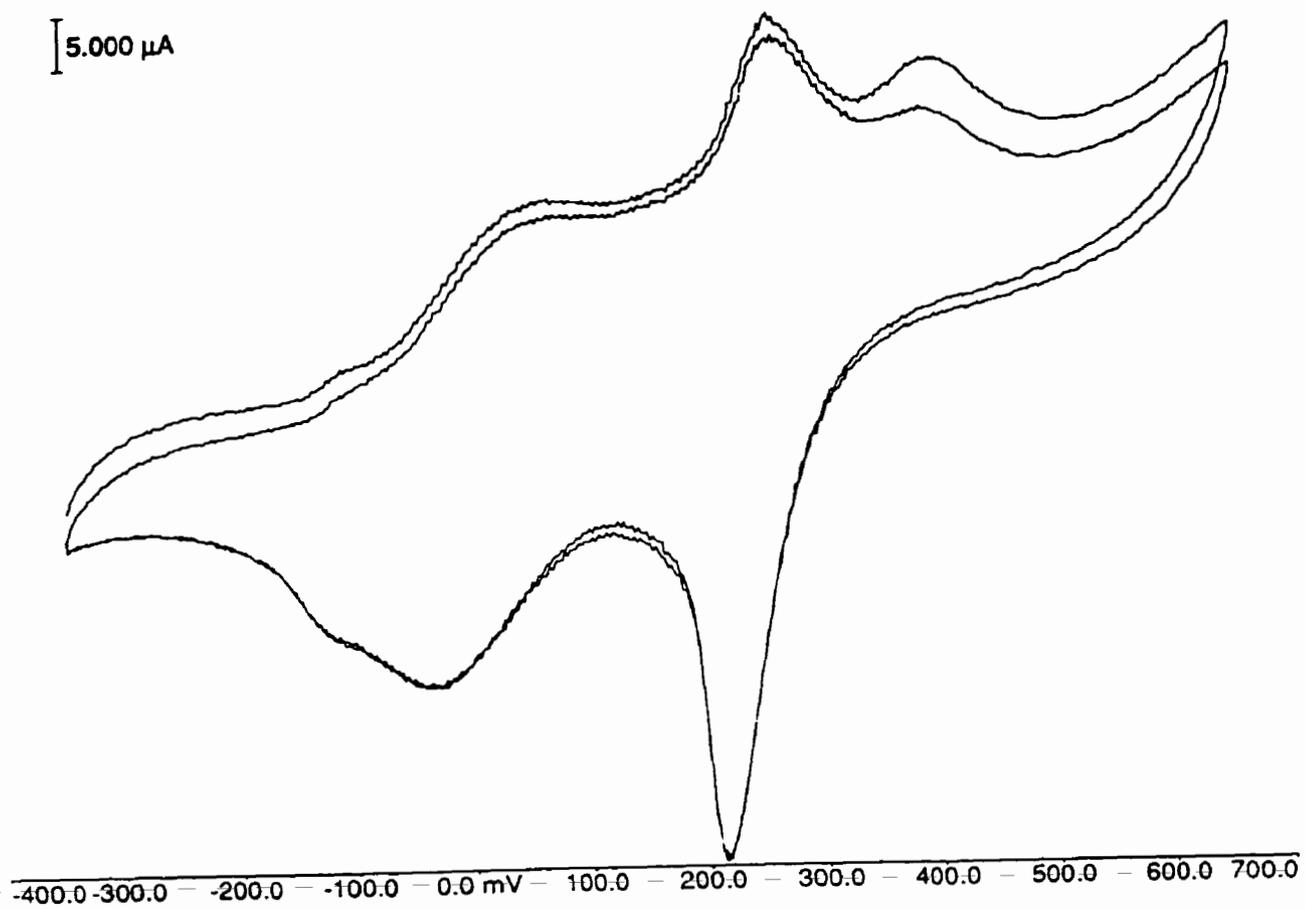
Figure 2 TGA scan of polymer 5d.

Figure 3 Cyclic voltammogram of polymer 5a.

2.4 Summary

Attempts to synthesize polysilane-poly(ferrocenylsilane) copolymers, via the ring-opening copolymerization of the ferrocenylsilane **1** and the cyclotetrasilane **3**, have been described; thermal ring-opening polymerization provided copolymers that have been shown, through various characterization techniques (gel permeation chromatography, NMR spectroscopy, mass spectrometry), to be random in nature, featuring alternating short chains of each monomer. Thermal stability of these polymers (by thermogravimetric analysis and pyrolysis mass spectrometry) was studied, and showed that the ferrocenylsilane segments are thermally more stable than the silane segments. As well, the hole transporting capability of the copolymer was measured.

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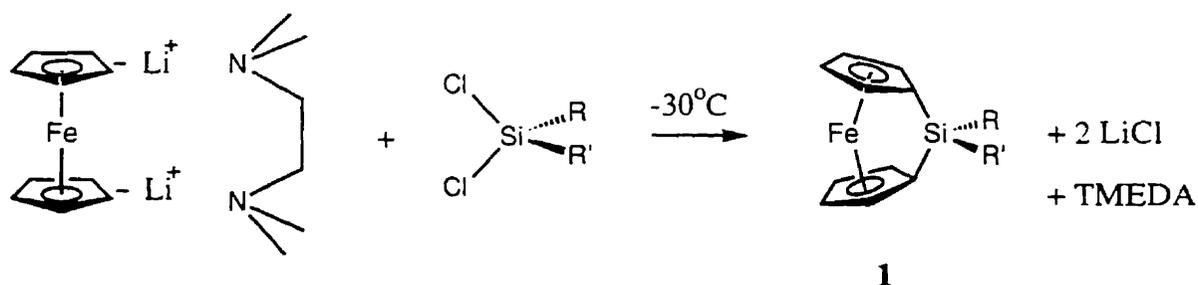
CHAPTER THREE

OXIDATION STUDIES OF POLY(FERROCENYLSILANE)S

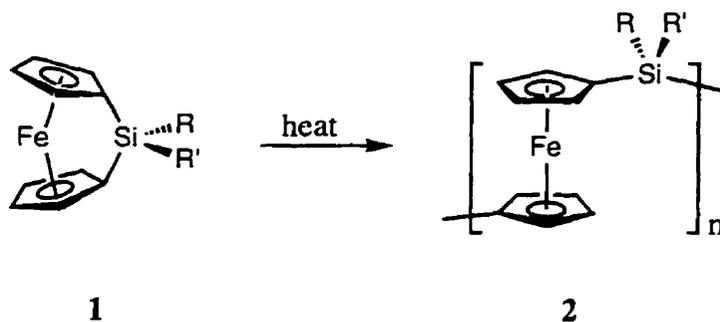
3.1 Introduction

3.1.1 Poly(ferrocenylsilane)s

Poly(ferrocenylsilane)s are polymers which possess alternating ferrocene and organosilane units. The synthesis of low molecular weight oligomers was reported in the late 1960s via the reaction of dichlorodialkylsilanes with dilithioferrocene-TMEDA.¹ High molecular weight poly(ferrocenylsilane)s were first reported in 1992, and were prepared by the thermal ring-opening polymerization of silicon-bridged [1]ferrocenophanes.² These ferrocenophanes, **1**, are synthesized by reacting the appropriate dichlorosilane with dilithioferrocene-TMEDA at temperatures around -30°C :



The ring strain introduced by having the cyclopentadienyl rings bent from the ideal parallel structure of ferrocene, and by the deviation from planarity of the sp^2 -hybridized *ipso*-carbon, provides the driving force for thermal ring-opening polymerization (TROP), at temperatures of about 150°C :

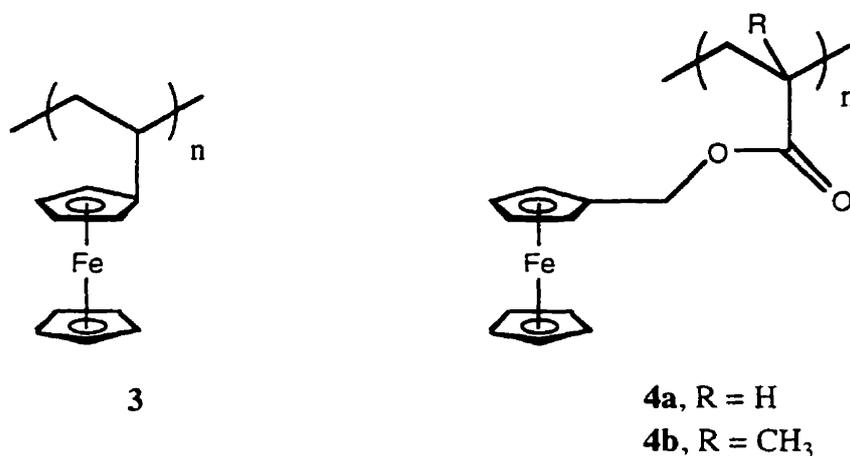


Since the initial report in 1992, much work has been done to advance the science of these novel polymers: the introduction of new bridging elements, metals, and groups attached to bridging elements in the metallocenophanes;³ new routes to their ring-opening polymerization, such as anionic initiation^{4,5} and catalysis by transition metal complexes,⁶ and copolymerization with other systems;⁷ the potential use of the polymers as ceramic precursors.⁸

The goals of the project described in this chapter are the investigation of the oxidation behavior of selected poly(ferrocenylsilane)s using a number of oxidants, the isolation of a stable oxidized poly(ferrocenylsilane), and the investigation of the properties of this system.

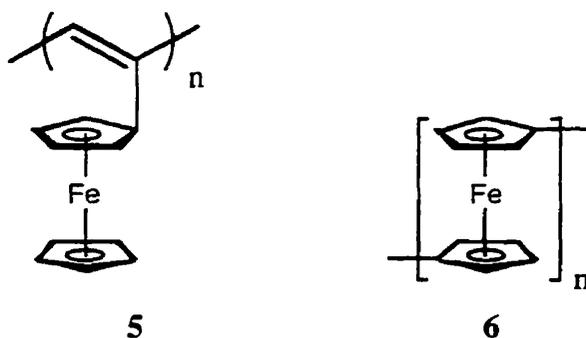
3.1.2 Previous Work on the Oxidation of Poly(ferrocene)s

In 1970, Pittman and his coworkers reported the synthesis, characterization, and oxidation of polymers containing ferrocene in the side group structure.⁹ The monomers vinylferrocene, ferrocenylmethyl acrylate, and ferrocenylmethyl methacrylate were polymerized by free radical initiation using azobisisobutyronitrile (AIBN). The resulting polymers (shown below respectively as **3**, **4a**, and **4b**) were treated with the one-electron oxidants 2,3-dichloro-5,6-dicyano-1,4-quinone (DDQ) and *o*-chloranil (*o*-CA), and the properties of the oxidized polymers were investigated.



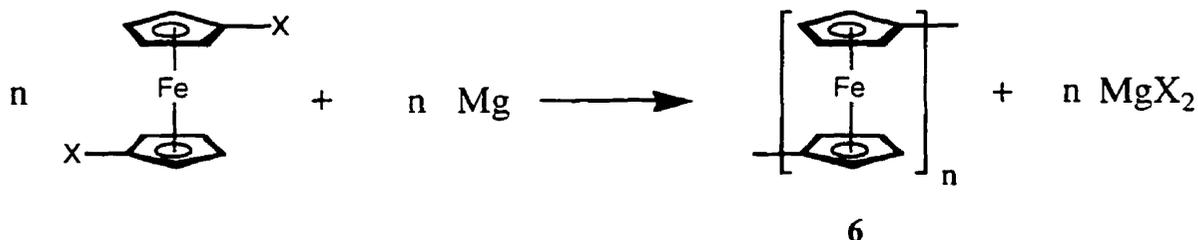
Infrared spectroscopy showed that both DDQ and *o*-CA acted as one-electron acceptors; one electron was transferred from a ferrocene for each acceptor molecule present. The researchers attempted to record the uv spectra of these polysalts, but found only insolubility in most solvents, and only partial solubility in *N,N*-dimethylformamide. Mössbauer spectroscopy proved to be a valuable characterization technique: iron (II) (i.e., ferrocene iron) has a much larger quadrupolar splitting than iron (III) (i.e., ferrocenium iron). (Generally, iron (II) has a splitting of about 2.4 mm/s, and iron (III) a splitting of about 0.4 mm/s, in a ferrocene environment.) This clear distinction allows Mössbauer spectroscopy to provide an indication of the percentage of iron sites that have been oxidized in a given sample. The Mössbauer spectrum of poly(ferrocenylmethyl acrylate), oxidized with *o*-CA showed, from integration of the peaks, that approximately 60% of the iron sites are oxidized.

In 1975, Pittman *et al.* extended their study of the oxidation properties of mixed valence ferrocene-containing polymers by reporting the conductivities of a variety of salts.¹⁰ Various polymers (polyvinylferrocene, **3**, polyethynylferrocene, **5**, and poly(1,1'-ferrocenylene), **6**) were oxidized with different one-electron oxidants (DDQ, iodine).



Of particular note is the conductivity of poly(1,1'-polyferrocenylene) oxidized with iodine, which was observed to be approximately $10^{-7} \text{ S cm}^{-1}$, or approximately eight orders of magnitude greater than the unoxidized polymers. The researchers also observed that the conductivity was maximized between 35 and 65% oxidation; that (to a first approximation) the conductivity was independent of anion present; and that increased conjugation of the polymer backbone (*i.e.*, from **3** to **5**) did not affect the conductivity. They conclude that the conductivity occurs electron-hopping (effectively, hole transport), in which each ferrocene centre is surrounded by a maximum number of ferrocenium centres.

In 1983, Yamamoto and his coworkers reported the synthesis of crystalline poly(1,1'-ferrocenylene), **6**, via the dehalogenative polycondensation reaction of 1,1'-dihaloferrocenes, and magnesium, shown below:¹¹

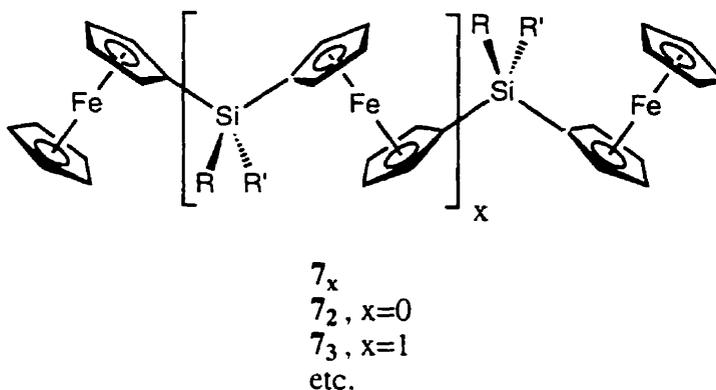


These polymers form adducts with a variety of electron acceptors, including iodine and TCNQ. The authors report that the oxidized crystalline polymers have substantially higher

electrical conductivities (by a factor of $10^2 - 10^6$) than the oxidized, amorphous poly(1,1'-ferrocenylene) salts reported by Pittman *et al.*;¹⁰ Yamamoto *et al.* reported a conductivity of $4.1 \times 10^{-2} \text{ S cm}^{-1}$ for **6** oxidized with 0.64 equivalents of TCNQ. As well, the Mössbauer spectrum of the TCNQ adduct at room temperature showed delocalization of the electrons on the Mössbauer timescale (10^{-7} s), indicating rapid electron exchange between the ferrocene and ferrocenium sites.

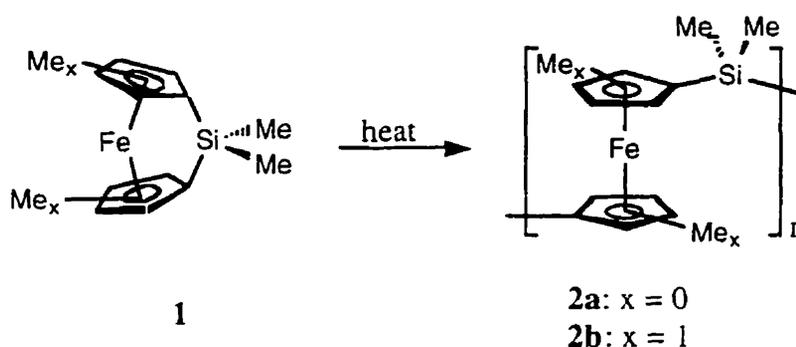
Although this is the first in-depth look at the synthesis and properties of oxidized poly(ferrocenylsilane)s, previous studies of these polymer systems have indicated that such a study would be interesting. Cyclic voltammetric studies of poly(ferrocenylsilane)s¹² show two reversible oxidations: the first is attributed to random oxidation of Fe(II) sites along the polymer backbone, while the second oxidation is due to the oxidation of those Fe(II) sites adjacent to previously oxidized Fe(III) sites. The second oxidation occurs at a potential between 0.2 and 0.3 V higher than the first potential, depending on the substituents on silicon. That two different oxidation potentials are observed indicates that there is a substantial interaction between adjacent iron sites in the polymers, and that alternating Fe(II) sites may be oxidized.

A series of model ferrocenylsilane oligomers, **7_x**, has been synthesized, and electrochemical studies on these systems have confirmed the alternating oxidation concept proposed for the high polymers.¹³



3.1.3 Research Objectives

Polymers studied. The focus of this project is the study of the oxidation behavior of poly(ferrocenylsilane)s. The two polymers chosen in this project were the poly(ferrocenylsilane)s, **2a** and **2b**, respectively. Polymer **2a** is the prototypical poly(ferrocenylsilane). The analogous dimethyl polymer with methyl groups on the cyclopentadienyl ring, **2b**, was studied; this polymer has a lower oxidation potential than the unmethylated system,¹⁴ and the methyl groups may stabilize the oxidized polymers.



Oxidants used. There are a variety of one-electron oxidants available;¹⁵ for this study, the ideal oxidant should have a number of characteristics. It should, of course, have an oxidation potential greater than that of the Fe(II) site in the polymer; the first oxidation occurs at -0.04 V (relative to the ferrocene-ferrocenium couple at 0.00 V;¹² all further potentials are relative to this). It should, in the ideal case, be an 'innocent' oxidant, and just function as a one-electron oxidant, not as a reactive electrophile or potential ligand. It would also be useful if the reduction product can be easily separated from the oxidized polymer.

The oxidants chosen for this project cover a range of strengths and reactivities, and will give a broad picture of the oxidation and reactivity of the poly(ferrocenylsilane)s. Nitrosonium hexafluorophosphate, [NO][PF₆], has a redox potential of 1.00 V, and is a clean oxidant; as it oxidizes the ferrocenylsilane, nitric oxide gas, NO(g), is evolved.¹⁵

Model Oligomers. Electrochemical studies of a series of oligomeric ferrocenylsilanes have shown these compounds to be useful models in describing the electrochemical behaviour of the poly(ferrocenylsilane)s.¹³ One of these oligomers, the trimer **7₃**, was used to obtain structural information on an oxidized system by single crystal X-ray diffraction. [As well, these oligomers were used to model decomposition of the poly(ferrocenylsilane)s upon oxidation.]

3.2 Experimental

3.2.1 Equipment and Chemicals

All reactions and manipulations were performed, except where indicated, under an inert atmosphere of prepurified dinitrogen (Canox) using standard Schlenk and vacuum line techniques. Solvents were distilled under dinitrogen using standard purification techniques.

Polymer molecular weights were estimated by gel permeation chromatography (GPC) using a Waters Associates liquid chromatograph equipped with a 510 HPLC pump, U6K injector, ultrastyrigel columns with a pore size between 10^3 - 10^5 Å, and a Waters 410 differential refractometer; the eluent used was a solution of 0.1% tetra-*n*-butylammonium bromide in THF, and the flow rate of was 1.0 mL/s.

Mössbauer spectra were obtained using a 6mCi ^{57}Co γ -ray source in a Rh matrix on a Ranger Scientific Inc. VT-1200 instrument equipped with a MS-1200 digital channel analyzer. Data were collected for a period of time sufficient to provide an adequate signal (generally 24 h to 1 week), were in the range of -15.8 to +15.8 mm/s, and were referenced to Fe powder.

For the uv/vis spectra, a Perkin-Elmer Lambda 12 UV/VIS Spectrometer was used.

3.2.2 Synthesis of Precursor Materials

The silicon-bridged [1]ferrocenophanes were synthesized by the literature reaction¹⁶ of the appropriate dialkyldichlorosilane with the dilithioferrocene-TMEDA (or, in the case of **1b**, dilithiated dimethylferrocene-TMEDA)¹⁷ complex in cold (approx. -30°C) ether, and were isolated by sublimation and/or recrystallization (or, for **1b**, vacuum distillation).

Poly(ferrocenylsilane)s were synthesized by the ring-opening polymerization of the silicon-bridged [1]ferrocenophanes;² polymerizations occurred either thermally by heating in an evacuated Pyrex tube or refluxing in xylenes, or at room temperature in toluene by using PtCl_2 as a catalyst.⁶ Polymers were isolated in air by dissolution in THF followed by precipitation into either hexanes or methanol.

Oligomeric ferrocenylsilanes were synthesized via the reaction of the ferrocenophane **1a** with dilithioferrocene·TMEDA in THF at 0°C (quenched with water), and were separated by column chromatography.¹³

In a separate reaction, the trimer **7₃** was synthesized as follows: to a solution of 0.869 g (3.59 mmol) of the [1]ferrocenophane **1a** in approximately 30 mL dried and freshly distilled hexanes was added 5.0 mL of a 1M solution of HCl (5.0 mmol) in diethyl ether; immediate formation of chloroferrocenyldimethylsilane indicated by a color change of the solution (red to orange), and verified as quantitative by GC-MS. Excess HCl was quenched with triethylamine, and the resultant white solid (triethylammonium chloride) was removed by filtration. The orange solution was added to a slurry of 0.535 g (1.71 mmol) dilithioferrocene·TMEDA in 50 mL hexanes. This was left stirring overnight, and the solution was filtered in air to remove LiCl. Thin-layer chromatography (eluent: 15% CH_2Cl_2 in cyclohexane) showed that the product was mainly a mixture of ferrocene, the dimer **7₂**, and the trimer **7₃**. The products were separated via column chromatography, using pretreated alumina. 0.15 g (14%) of the trimer **7₃** was isolated.

Tris-(*p*-bromophenyl)aminium hexafluorophosphate was synthesized by the literature reaction of *tris*-(*p*-bromophenyl)amine with nitrosonium hexafluorophosphate in dichloromethane; the aminium salt was isolated by precipitation into hexanes.^{18,19}

All other chemicals were purchased from Aldrich or Strem (1,1'-dimethylferrocene, nitrosonium hexafluorophosphate) and used without further purification.

3.2.3 Syntheses of Oxidized Polymers

Synthesis of 8a ($X^- = I_3^-$): Reaction with Iodine. Iodine (160 mg, 0.63 mmol) and the polymer **2a** (200 mg, 0.83 mmol repeat unit) were dissolved with stirring in approx. 20 mL and 30 mL freshly distilled dichloromethane, respectively. The iodine solution was added to the polymer solution via cannula, and left to stir for 2 hours. The reaction was immediate, with the formation of a green solution, and a green-black precipitate. The solid product was isolated by filtration, washed with dichloromethane, pumped dry, and collected. Yield: 283 mg (79 % based upon 50% oxidation).

Synthesis of 8a ($X^- = PF_6^-$): Reaction with [(*p*-Br-C₆H₄)₃N][PF₆]. *Tris*-(*p*-bromophenyl)aminium hexafluorophosphate (271 mg, 0.48 mmol) was dissolved, with stirring, in approximately 15 mL freshly distilled dichloromethane. This was added, with stirring, to a solution of 230 mg (0.95 mmol) polymer **2a** in 40 mL dichloromethane and left to stir for 2 hours. The light-green solution (containing *tris*-(*p*-bromophenyl)amine) was removed, the solid product was washed with dichloromethane, pumped dry, and isolated. Yield: 91 mg (34 % based upon 50% oxidation).

Synthesis of 8a ($X^- = PF_6^-$): Reaction with Iodine, Precipitation with [(*n*-Bu)₄N][PF₆]. Iodine (235 mg, 0.92 mmol) was dissolved in approximately 25 mL dichloromethane. This solution was added, with stirring, to a solution of polymer **2a** (300 mg, 1.24 mmol repeat unit) and tetrabutylammonium hexafluorophosphate (3.6 g, 9.3 mmol) in 100 mL dichloromethane, and left to stir for 2 hours. A reaction occurred, which yielded a black precipitate. This solid product was isolated by filtration with a filter frit, washed with dichloromethane, pumped dry, and isolated. Yield: 322 mg (83% based upon 50% oxidation, and full precipitation with [PF₆⁻]).

Synthesis of 8a ($X^- = PF_6^-$): Reaction with [NO][PF₆]. Polymer **2a** (200 mg, 0.83 mmol repeat unit) was dissolved in approximately 40 mL dichloromethane, with stirring. This solution was added, with stirring, to a suspension of [NO][PF₆] (73 mg, 0.42 mmol) in 10 mL dichloromethane. Reaction was immediate, and observed by the evolution of NO gas and the formation of a green/black precipitate. This was left stirring for two hours, filtered, washed with dichloromethane, pumped dry, and isolated. Yield: 85 mg (33% based upon 50% oxidation).

Synthesis of 8b ($X^- = PF_6^-$): Reaction with [NO][PF₆]. Polymer **2b** (200 mg, 0.74 mmol) was dissolved in approximately 40 mL dichloromethane, with stirring. This solution was added, with stirring, to a suspension of [NO][PF₆] (65 mg, 0.37 mmol) in 10 mL dichloromethane. Reaction was immediate, and observed by the evolution of NO gas and the formation of a green/black precipitate. This was left stirring for two hours, filtered, washed with dichloromethane, pumped dry, and isolated. Yield: 92 mg (36% based upon 50% oxidation).

Synthesis of 8b ($X^- = I_3^-$): Reaction with Iodine. Iodine (141 mg, 0.56 mmol) and the polymer **2b** (200 mg, 0.74 mmol repeat unit) were dissolved with stirring in approx. 20 mL and 30 mL freshly distilled dichloromethane, respectively. The iodine solution was added to the polymer solution via cannula, and left to stir for 2 hours. (The reaction was immediate, with the formation of a green solution, and a green-black precipitate.) Approximately 200 mL freshly distilled hexanes was added, to fully precipitate the product, which was isolated by filtration, washed with hexanes, pumped dry, and collected. Yield: 85 mg (25 % based upon 50% oxidation).

Synthesis of 8b ($X^- = PF_6^-$): Reaction with [(*p*-Br-C₆H₄)₃N][PF₆]. *Tris*-(*p*-bromophenyl)aminium hexafluorophosphate (232 mg, 0.37 mmol) was dissolved, with

stirring, in approximately 15 mL freshly distilled dichloromethane. This was added, with stirring, to a solution of 200 mg (0.74 mmol) polymer **2b** in 40 mL dichloromethane and left to stir for 2 hours. The light-green solution (containing the *tris*-(*p*-bromophenyl)amine) was removed by filtration, the solid product was washed with dichloromethane, pumped dry, and isolated. Yield: 100 mg (39 % based upon 50% oxidation).

Time-dependence of Oxidation. To determine whether there was an effect on the oxidation process due to the length of time in the reaction flask, oxidation reactions of polymer **2a** (23 mg, 0.095 mmol) with [(*p*-Br-C₆H₄)₃N][PF₆] (27 mg, 0.048 mmol) in CH₂Cl₂ were left stirring for periods of 1, 2, and 24 hours. At the given time, the solution was decanted, leaving the oxidized polymer; to this solid was added a solution of sodium naphthalide in THF to re-reduce the polymer, which was isolated by precipitation into hexanes, and the molecular weight was determined by GPC.

3.2.4 X-ray Structural Characterization of [7₃]²⁺[I₃]⁻₂ · 2 CH₂Cl₂

Crystals of [7₃]²⁺[I₃]⁻₂ · 2 CH₂Cl₂ were grown from CH₂Cl₂/cyclohexane by a diffusion controlled reaction of a solution of 7₃ with a solution of I₂ in a U-shaped tube. A suitable single crystal was mounted in epoxy under a flow of cold nitrogen. Summary of selected crystallographic data are given in Table 1 and selected bond length and angles are given in Table 3. Figure 1a shows the molecule and its labeling scheme. Data for the structure was collected on a Siemens P4 diffractometer using graphite monochromated MoK α radiation ($\lambda = 0.71073\text{\AA}$). The intensities of three standard reflections measured every 97 reflections, for each crystal, showed less than 4% variation. The data were corrected for Lorentz and polarization effects and for absorption (empirical corrections using SHELXA-90²⁰). The structure was solved and refined using the SHELXTLAPC²¹

package. Refinement was by full-matrix least-squares. The weighting schemes was $w = 1/[\sigma^2(F_o^2) + (0.0903P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$. Hydrogen atoms were included in calculated positions and treated as riding atoms. The central I atoms of the I_3^- anions lie on crystallographic inversion centers and there are two CH_2Cl_2 solvent molecules of crystallization for each cation molecule.

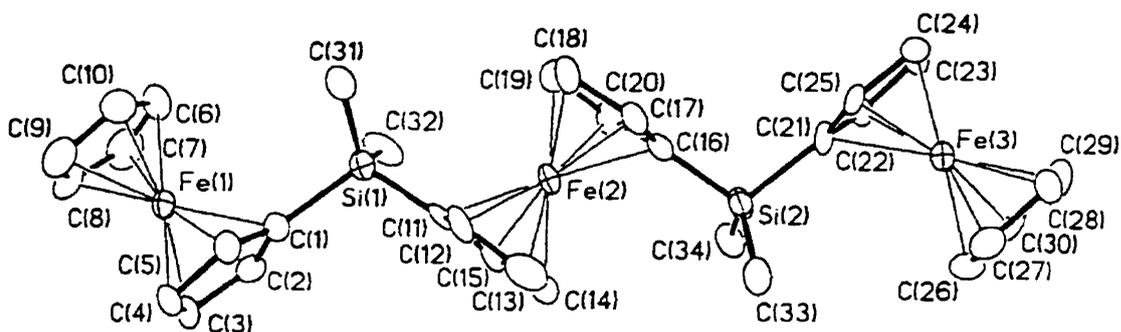
3.3 Results

3.3.1 Crystal Structure of an Oxidized Oligomer

In an attempt to model the oxidation behavior of poly(ferrocenylsilane)s, we attempted to obtain single crystals of a partially oxidized oligo(ferrocenylsilane). The diffusion-controlled reaction of **7₃** with three equivalents of iodine in CH₂Cl₂/cyclohexane (1:5) resulted in the direct formation of X-ray quality single crystals of mixed-valence triferrocenylsilane [**3₃**]²⁺ [I₃]⁻₂. A summary of selected crystallographic data is given in Table 1 and selected bond length and angles are given in Table 3. The molecular structure of [**7₃**]²⁺ [I₃]⁻₂ (Figure 1a) differs significantly from that of the neutral analog **7₃** in which the terminal ferrocene moieties are oriented in opposite directions and perpendicular to the central ferrocene unit.¹³ Thus the terminal ferrocenium groups of [**7₃**]²⁺ are positioned at a maximum separation, which is the lowest energy conformation due to the coulombic repulsion of the two positively charged centers. The molecular structure of [**7₃**]²⁺ confirms that the terminal ferrocene units are oxidized in the first oxidation process of **7₃**. This is shown by the average iron-cyclopentadienyl Ring Centroid distance, d(Fe-RC) which is an average of 1.692(10) Å for the terminal iron atoms, typical for that of ferrocenium species and larger than the average Fe-RC distance of the central iron atom of [**7₃**]²⁺ which is 1.630 (10) Å, typical for a pristine ferrocene center. (For comparison, d(Fe-RC) is 1.705(6) Å²² for [Fe(η-C₅H₄SiMe₃)₂]⁺ [AlCl₄]⁻ and 1.638(4) Å for the central fc unit of **7₃**.²³) The shortest iron-iodine distance, d(Fe-I), in [**7₃**]²⁺ [I₃]⁻ was found for the terminal iron atoms (d(Fe-I) = 4.634(2) and 4.513(2) Å for Fe(1) and Fe(3) versus 5.530(2) Å for d(Fe-I) of Fe(2)) showing a closer interaction of the terminal ferrocenium groups with the triiodide counter-ions. Figure 1b shows the interesting layered structure of [**7₃**]²⁺ [I₃]⁻₂ · 2 CH₂Cl₂ in which layers of the linear triiodide counter ions are in between layers of the mixed-valence dicationic tri(ferrocenylsilane).

A summary of selected crystallographic data is given in Table 1, atomic coordinates are given in Table 2 and selected bond angles and length are given in Table 3. Figure 1a shows the molecule and labeling scheme, and Figure 1b shows the packing.

Figure 1. a) Molecular structure of dicationic trimer, $[7_3]^{2+}$.



b) Packing diagram of $[7_3]^{2+} [I_3]^- \cdot 2 CH_2Cl_2$.

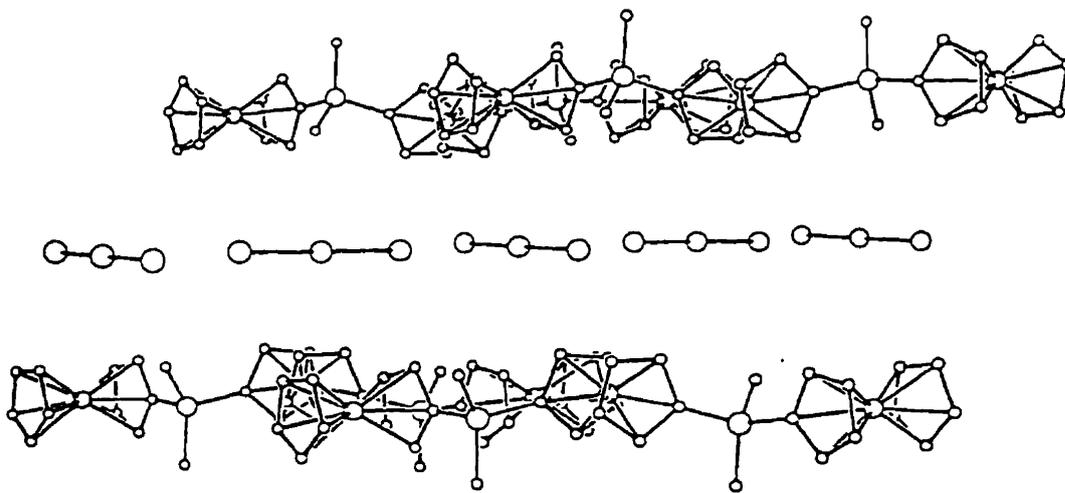


Table 1. Crystal Data and Structure Refinement for $[7_3]^{2+}[I_3]^-_2 \cdot 2 CH_2Cl_2$.

empirical formula	$C_{36}H_{42}Cl_4Fe_3I_6Si_2$
formula weight	1601.63
temperature	173(2) K
wavelength	0.71073 Å
crystal system / space group	triclinic / $P\bar{1}$
unit cell dimensions	$a = 11.578(3)$ Å $b = 13.381(2)$ Å $c = 16.245(3)$ Å $\alpha = 87.612(12)^\circ$ $\beta = 75.798(14)^\circ$ $\gamma = 80.222(12)^\circ$
volume, Z	$2404.3(8)$ Å ³ , 2
density (calculated)	2.212 kg/dm ³
absorption coefficient	5.043 mm ⁻¹
F(000)	1500
crystal size	0.32 x 0.42 x 0.5 mm
range θ collected	2.6 to 27.0°
limiting indices	$-12 \leq h \leq 14$, $-16 \leq k \leq 17$, $-20 \leq l \leq 20$
reflections measured	11040
independent reflections	10511 ($R_{int} = 9.06\%$)
refinement method	Full-matrix least-squares on F^2
restraints / parameters	0 / 470
goodness-of-fit on F^2	0.932
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0726$, $wR_2 = 0.2014$
extinction coefficient	0.0002 (2)
largest diff. peak and hole	2.106 and -1.650 eÅ ⁻³
Absorption Correction	min. max. 0.876, 0.797

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$] for $[\text{Zr}_3]^{2+} [\text{U}_3]^{2-} \cdot 2 \text{CH}_2\text{Cl}_2$. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
I(1)	5000	0	5000	43(1)
I(2)	5414(1)	-2202(1)	5025(1)	52(1)
I(3)	-5000	0	10000	50(1)
I(4)	0	-5000	10000	51(1)
I(5)	-6316(1)	-1662(1)	10605(1)	57(1)
I(6)	847(1)	-3342(1)	10650(1)	62(1)
I(7)	7538(2)	-5502(1)	4920(1)	134(1)
I(8)	5000	-5000	5000	117(1)
Fe(1)	2923(2)	80(1)	7852(1)	29(1)
Fe(2)	-1630(2)	-2530(1)	7580(1)	31(1)
Fe(3)	-6393(2)	-5012(1)	7850(1)	30(1)
Si(1)	204(3)	-867(3)	7967(3)	33(1)
Si(2)	-3766(3)	-4098(3)	8129(2)	32(1)
C(1)	1857(11)	-1025(9)	7874(8)	28(3)
C(2)	2437(12)	-1176(9)	8562(9)	33(3)
C(3)	3704(11)	-1337(9)	8211(9)	31(3)
C(4)	3950(11)	-1275(9)	7334(10)	36(3)
C(5)	2799(11)	-1109(9)	7123(10)	35(3)
C(6)	1873(14)	1490(10)	8043(13)	56(5)
C(7)	2650(16)	1339(11)	8606(11)	53(4)
C(8)	3792(15)	1191(9)	8126(10)	42(4)
C(9)	3782(15)	1259(10)	7274(10)	44(4)
C(10)	2582(15)	1428(10)	7217(12)	51(4)
C(11)	-66(10)	-2137(9)	7730(9)	31(3)
C(12)	84(11)	-2547(11)	6905(10)	40(3)
C(13)	-198(13)	-3542(12)	7010(11)	50(4)
C(14)	-528(13)	-3730(10)	7870(11)	45(4)
C(15)	-446(11)	-2875(10)	8329(10)	39(3)
C(16)	-3309(11)	-2884(9)	7792(9)	30(3)
C(17)	-2933(12)	-2520(10)	6960(11)	44(4)
C(18)	-2667(13)	-1530(12)	6969(12)	53(4)
C(19)	-2913(13)	-1236(10)	7829(10)	41(3)
C(20)	-3304(11)	-2046(10)	8335(10)	36(3)
C(21)	-5341(11)	-3918(9)	7994(8)	29(3)
C(22)	-6454(11)	-3801(8)	8637(9)	33(3)
C(23)	-7427(12)	-3611(9)	8236(10)	37(3)
C(24)	-6969(13)	-3622(9)	7376(11)	43(4)
C(25)	-5666(13)	-3797(8)	7219(10)	37(3)
C(26)	-5585(14)	-6456(10)	8077(11)	48(4)
C(27)	-5558(13)	-6364(9)	7218(10)	42(3)

C(28)	-6774(13)	-6142(10)	7137(10)	42(4)
C(29)	-7497(14)	-6086(10)	7953(10)	45(4)
C(30)	-6787(14)	-6283(8)	8552(9)	39(3)
C(31)	-161(12)	68(11)	7166(10)	44(4)
C(32)	-573(13)	-517(12)	9064(10)	54(4)
C(33)	-2841(12)	-5149(10)	7430(11)	47(4)
C(34)	-3767(13)	-4325(11)	9238(10)	45(4)
C(1S)	856(28)	3181(19)	5565(17)	118(10)
Cl(1)	843(6)	1963(5)	5327(4)	101(2)
Cl(2)	286(5)	3374(5)	6673(5)	105(2)
C(2S)	-2403(20)	1778(18)	5739(15)	96(7)
Cl(3)	-3010(5)	1581(4)	6818(4)	86(2)
Cl(4)	-1671(5)	665(4)	5206(4)	85(2)

Table 3. Selected bond lengths (Å) and angles (°) for $[7_3]^{2+} [I_3]^-_2 \cdot 2 CH_2Cl_2$.

Fe(1)-C(1)	2.074(12)	Fe(2)-C(11)	2.026(11)	Fe(3)-C(21)	2.112(11)
Fe(1)-C(2)	2.076(13)	Fe(2)-C(12)	2.010(14)	Fe(3)-C(22)	2.088(11)
Fe(1)-C(3)	2.082(13)	Fe(2)-C(13)	2.027(14)	Fe(3)-C(23)	2.076(12)
Fe(1)-C(4)	2.077(11)	Fe(2)-C(14)	2.016(14)	Fe(3)-C(24)	2.052(13)
Fe(1)-C(5)	2.066(11)	Fe(2)-C(15)	2.035(13)	Fe(3)-C(25)	2.075(13)
Fe(1)-C(6)	2.054(13)	Fe(2)-C(16)	2.038(13)	Fe(3)-C(26)	2.060(13)
Fe(1)-C(7)	2.059(13)	Fe(2)-C(17)	2.013(13)	Fe(3)-C(27)	2.081(13)
Fe(1)-C(8)	2.051(12)	Fe(2)-C(18)	2.020(20)	Fe(3)-C(28)	2.108(13)
Fe(1)-C(9)	2.076(14)	Fe(2)-C(19)	2.038(13)	Fe(3)-C(29)	2.055(14)
Fe(1)-C(10)	2.070(20)	Fe(2)-C(20)	2.032(13)	Fe(3)-C(30)	2.062(12)
Si(1)-C(1)	1.859(13)	Si(1)-C(31)	1.842(14)	I(1)-I(2)	2.9047(11)
Si(1)-C(11)	1.851(12)	Si(1)-C(32)	1.830(20)	I(3)-I(5)	2.9090(13)
Si(2)-C(16)	1.815(13)	Si(2)-C(33)	1.854(13)	I(4)-I(6)	2.9056(13)
Si(2)-C(21)	1.863(13)	Si(2)-C(34)	1.820(20)	I(7)-I(8)	2.873(3)
C(1)-Si(1)-C(11)	107.8(6)				
C(31)-Si(1)-C(32)	114.7(7)				
C(16)-Si(2)-C(21)	102.6(5)				
C(33)-Si(2)-C(34)	112.6(7)				

3.3.2 Degree of Oxidation of Polymers

Characterization techniques for the oxidized polymers are limited. As a means of quantifying the degree of oxidation of the polymers, uv/vis spectroscopy was used. Polymers **8a** and **8b** ($X = \text{PF}_6^-$) are soluble in acetonitrile, and degree of oxidation can be obtained directly. (When $X = \text{I}_3^-$, the polymers were insoluble in acetonitrile and soluble in dimethyl sulfoxide; however, in both cases, an orange precipitate, unoxidized polymer, formed within 30 minutes.) The orange colour of the ferrocenyl group is due to an absorption at approximately 440 nm, which has been assigned to the ${}^1A_{1g} \rightarrow a{}^1E_{1g}$ transition;²⁴ the green colour of the ferrocenium unit is due to an absorption at approximately 650 nm, corresponding to the ${}^2E_{2g} \rightarrow {}^2E_{1u}$ transition.¹⁰

Since the oxidized polymers contained both Fe(II) and Fe(III) sites, both peaks (at approximately 440 nm and 650 nm) will appear in the uv/vis spectra, and it is possible to obtain the ratio of sites (and thus the percent oxidation) from the Beer-Lambert absorption law:

$$A = \epsilon bc \quad (\text{Eq. 1})$$

in which A is the absorbance and ϵ the molar absorptivity at a given wavelength, b is the path length and c the concentration. This, of course, applies to both Fe(II) and Fe(III) sites. And since the path length b will be the same in both cases, the concentration ratio, $c_{\text{Fe(III)}}/c_{\text{Fe(II)}}$, can be written as:

$$\frac{c_{\text{Fe(III)}}}{c_{\text{Fe(II)}}} = \frac{\epsilon_{\text{Fe(II)}} A_{\text{Fe(III)}}}{\epsilon_{\text{Fe(III)}} A_{\text{Fe(II)}}} \quad (\text{Eq. 2})$$

The absorbances are measured directly in the experiment; values for the molar absorptivity are available for ferrocene and some of its derivatives. For the purpose of this project,

bis(trimethylsilyl)ferrocene and its ferrocenium salt formed from oxidation with [(*p*-BrC₆H₄)₃N][BF₄] were used as standards. This system was chosen due to its similarity to the repeat unit of the polymer. The uv/vis spectrum of a mixture of equal concentrations of these compounds was obtained, and the ratio of the molar absorptivities, $\epsilon_{\text{Fe(II)}}/\epsilon_{\text{Fe(III)}}$, was determined to be 0.79. Equation 2 can then be modified to give:

$$\frac{c_{\text{Fe(III)}}}{c_{\text{Fe(II)}}} = 0.79 \frac{A_{\text{Fe(III)}}}{A_{\text{Fe(II)}}} \quad (\text{Eq. 3})$$

Measurement of the uv/vis spectra of the oxidized polymer will immediately give the absorbance ratio, from which the concentration ratio and the degree of oxidation can be easily determined. In all cases examined (polymers **2a** and **2b** oxidized with the nitrosonium and aminium salts), the degree of oxidation was approximately 30%. (It was closer to 40% for polymer **2a** oxidized with iodine and precipitated with PF₆⁻.) All reactions had been done with the stoichiometry of 50% oxidation; perhaps once the oxidized polymer precipitates, no further oxidation takes place. It is important to note that the degree of oxidation was the same for oxidations with both polymers: the methyl groups on the cyclopentadienyl rings in polymer **2b** do not inhibit the oxidation. (This degree of oxidation based on the stoichiometry is consistent with what was previously reported for the oxidation of poly(ferrocenyldibutylsilane) with FeCl₃.²⁵)

As well, there was no significant dependence on either degree of oxidation or molecular weight decline when the reaction time is varied. Samples of polymer **2b** oxidized with the aminium salt and left reacting for 1, 2, and 24 hours showed no significant changes in the result. This suggests that, once the reaction occurs and the polymer precipitates, no further molecular weight decline will occur. As a standard, however, reaction times for oxidation were universally two hours.

3.3.3 Oxidation of poly(ferrocenyldimethylsilane), **2a**

Of the systems being studied, polymer **2a** is the prototypical ferrocenylsilane. Due to the relative ease of its synthesis, it was the main polymer studied, and provided an overview of the oxidation behavior of poly(ferrocenylsilane)s.

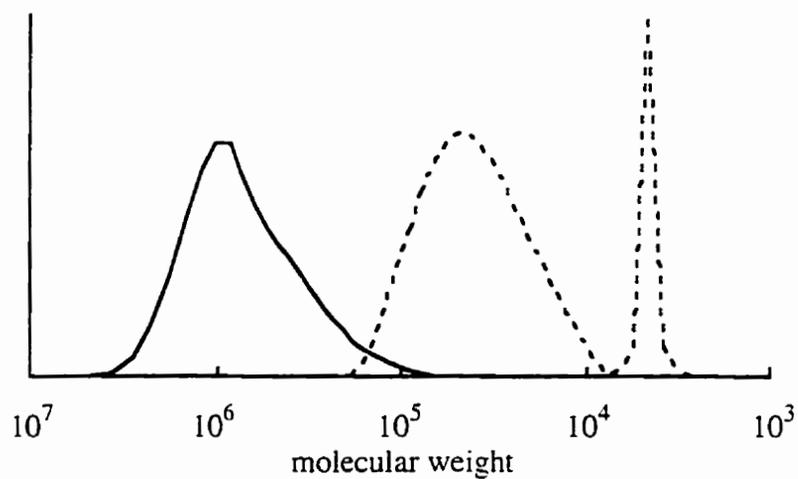
Oxidation with Iodine. As an oxidant, iodine has the advantage of leaving no reduction products which need to be removed; iodine in the reduced form will exist as the triiodide counterion, I_3^- . In this reaction, substantial molecular weight decline occurred during oxidation, and afterward in the solid state as well (Figure 2). This suggests that neither iodine nor the counterion I_3^- is an innocent species. Throughout the oxidation, and in the solid state afterward, this species may be cleaving a C(aryl)-Si bond. As an attempt to prove this hypothesis, iodine was reacted with the ferrocenylsilane dimer **7₂**, left in the oxidized state for a period of time, re-reduced with sodium naphthalide, and studied by GC-MS. Unfortunately, there appeared to be no fragmentation occurring.

If the oxidation with iodine is done in the presence of an excess of PF_6^- , the molecular weight decline is much less, and there is no further decline in the solid state, further supporting the notion that the oxidized polymer is reacting with the triiodide counterion. (See Figure 3.) The degradation that is observed (in the case where PF_6^- is the counterion) is likely a result of the presence of triiodide in both the solution and the solid sample. However, this shows quite clearly that (at least over the span of two weeks) the oxidized polymer, when precipitated with PF_6^- as a counterion, is stable in the solid state.

A ^{57}Fe Mössbauer spectrum of polymer **2a** oxidized with iodine, precipitated with PF_6^- is shown in Figure 4. The doublets for Fe(II) and Fe(III) are clearly separated, indicating electron localization on the Mössbauer timescale.

Figure 2. Molecular weight of **2a**, oxidized with iodine. a) GPC traces of the unoxidized polymer (solid line, $M_n = 500,000$, PDI = 2.0) and the re-reduced sample (dashed line, $M_n = 50,000$ (PDI = 2.0); 6000). b) Molecular weight of re-reduced samples (higher molecular weight fractions) as a function of time.

a)



b)

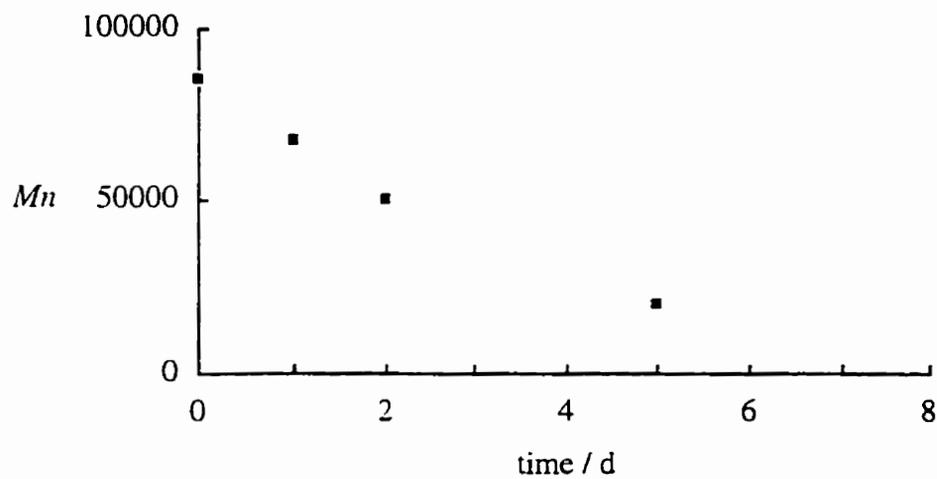
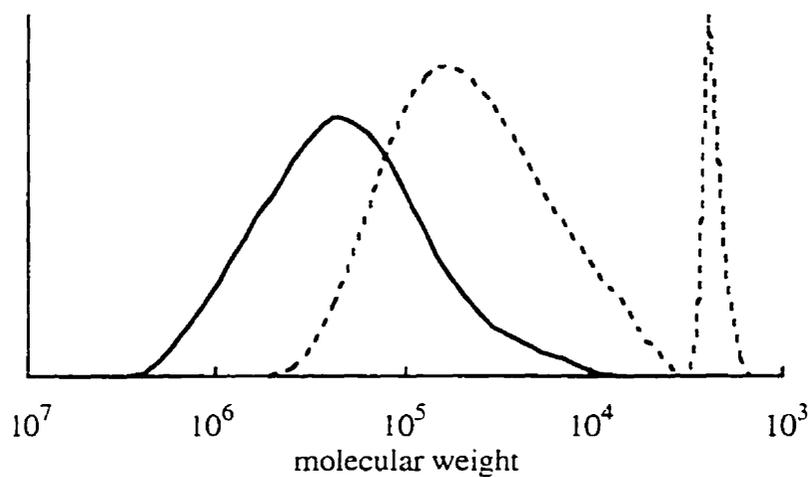


Figure 3. Molecular weight of **2a**, oxidized with iodine, precipitated with PF_6^- . a) GPC traces of the unoxidized polymer (solid line, $M_n = 130,000$, PDI = 2.0) and the re-reduced sample (dashed line, $M_n = 40,000$ (PDI = 2.3); 3000). b) Molecular weight of re-reduced samples (higher molecular weight fractions) as a function of time.

a)



b)

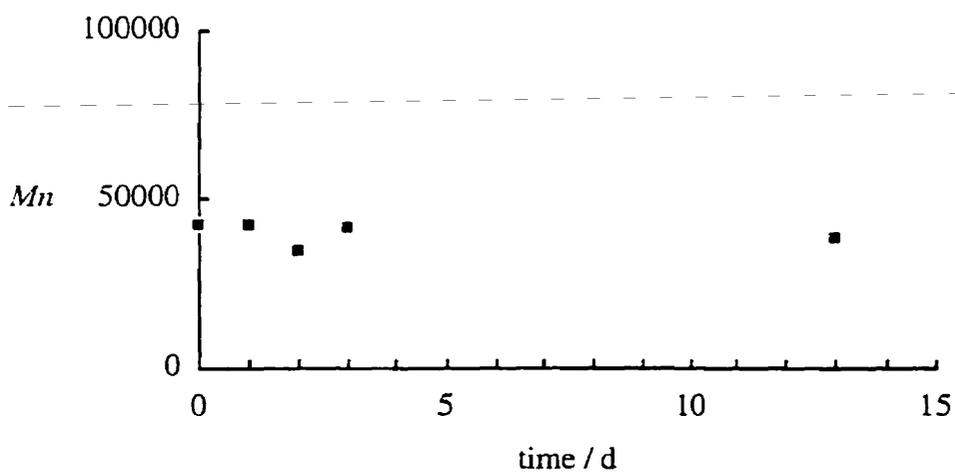
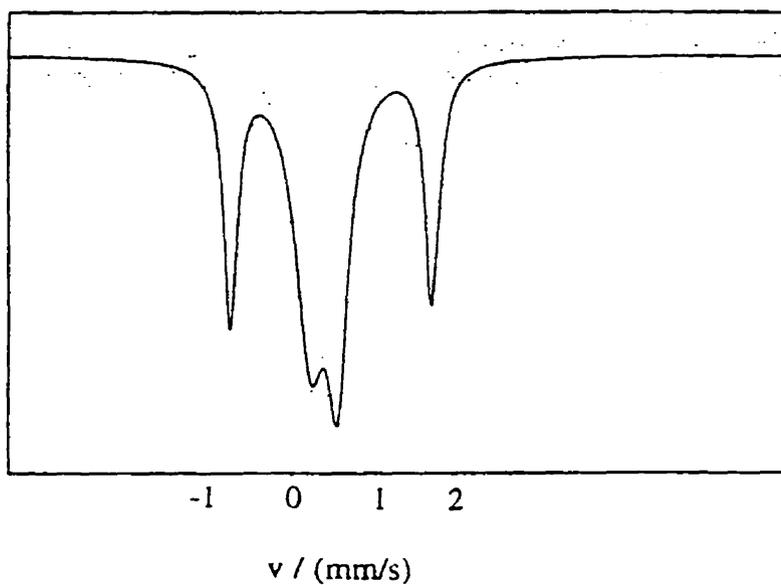


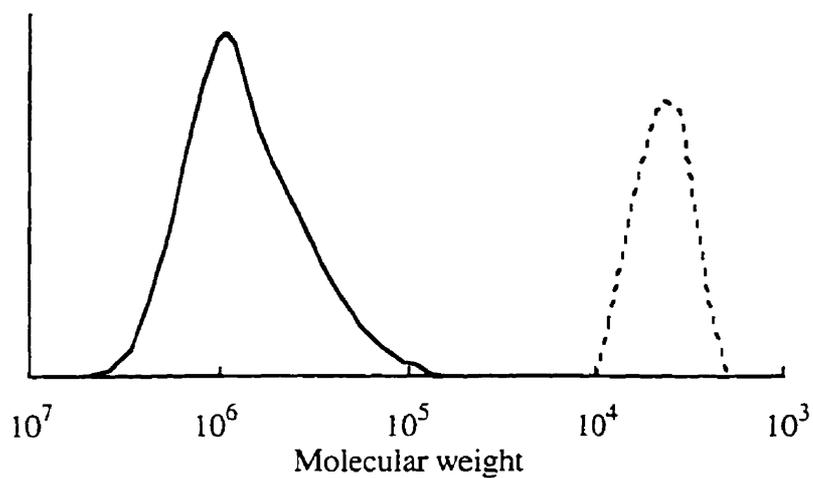
Figure 4. ^{57}Fe Mössbauer spectrum of polymer **2a** oxidized with iodine, precipitated with PF_6^- . Doublets for both Fe(II) and Fe(III) sites are distinguishable. The isomer shifts are 0.492 and 0.397 mm/s and the quadrupolar splittings are 2.36 and 0.313 mm/s, for Fe(II) and Fe(III), respectively. (Referenced to iron powder.)



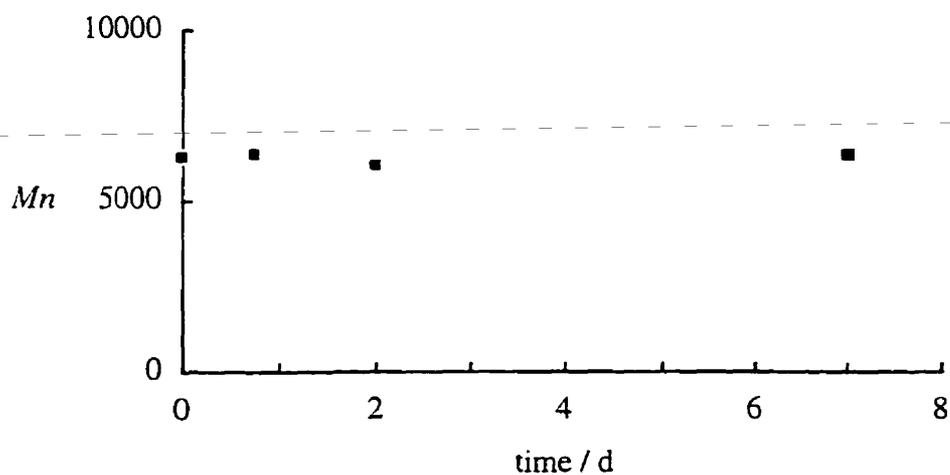
Oxidation with a Nitrosonium Salt, [NO][PF₆]. Nitrosonium salts are desirable oxidants in this study because upon oxidation, nitric oxide gas, NO(g), is given off, giving cleanly the oxidized polymer and counterion. However, as Connelly and Geiger point out in a recent review,¹⁵ these salts are non-innocent; a number of alternate reactions can occur. Re-reduction of the polymer samples after a few hours in the oxidized form yielded a polymer with a number average molecular weight, M_n , substantially lower than that of the pristine polymer (degradation from $M_n = 500,000$ to $M_n = 6,000$; see figure 5a). Clearly, either the nitrosonium salts are not innocent one-electron oxidants in this reaction or the oxidized polymer is not stable. Re-reduction of samples at later times showed no further molecular weight reduction (Figure 5b); this indicates that the molecular weight decline occurred during the initial oxidation process. A milder and more innocent oxidant should provide better results.

Figure 5. Molecular weight of **2a**, oxidized with $[\text{NO}][\text{PF}_6]$. a) GPC traces of the unoxidized polymer (solid line, $M_n = 500,000$, PDI = 1.6) and the re-reduced sample (dashed line, $M_n = 6000$, PDI = 1.3). b) Molecular weight of re-reduced samples as a function of time in the solid state.

a)



b)

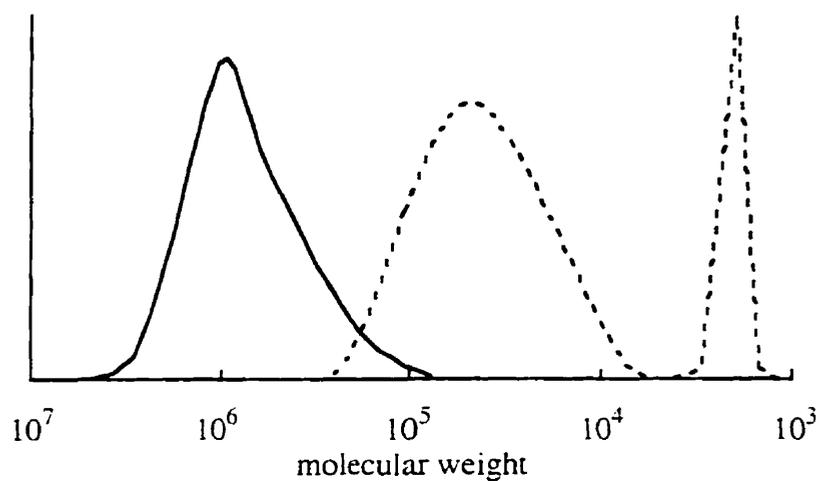


Oxidation with *tris*-(*p*-bromophenyl)aminium cation. This cation, due to its intense blue color, is colloquially known as "Magic Blue".¹⁵ It functions almost exclusively as a one-electron oxidant (*i.e.*, it is much less "non-innocent" than either nitrosonium salts or iodine).

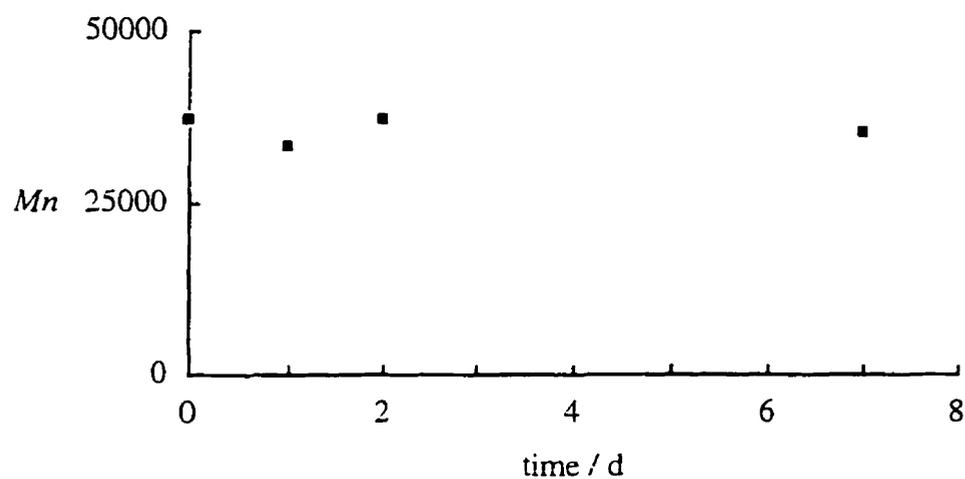
As with both iodine and [NO][PF₆], there is substantial molecular weight decline throughout the oxidation; but there is no further decline in the solid state afterward (as in the [NO][PF₆] case). (See Figure 6.) This evidence suggests a number of conclusions. Firstly, that there is no molecular weight decline in the solid state in the cases with a PF₆⁻ counterion suggests that the oxidized polymer, once formed, is stable. Also, that degradation is seen in the solid state for the polymer with the triiodide counterion suggests that the oxidized polymer reacts with the triiodide. That the initial molecular weight decline is less in the reaction with iodine than in the other cases suggests that there is a dependence on the oxidation strength of the oxidant: that substantial molecular weight decline is observed in both the nitrosonium (in which a number of alternate reactions can occur) and the aminium (in which, usually, only one-electron oxidation can occur) cases suggests that the stability of the polymer backbone to oxidation is, at least in the case of polymer **2a**, not directly related to the reactivity of the oxidant (*i.e.*, reactivity other than one-electron oxidation). Polymer **2a** may be prone to backbone cleavage through oxidation. In an attempt to determine this, and in an attempt to synthesize oxidized polymers in which molecular weight decline is minimized, the oxidation behavior of polymer **2b** (in which methyl groups are randomly substituted on the cyclopentadienyl rings) was studied.

Figure 6. Molecular weight of **2a**, oxidized with $[(p\text{-BrC}_6\text{H}_4)_3\text{N}^+][\text{PF}_6^-]$. a) GPC traces of the unoxidized polymer (solid line, $M_n = 500,000$, PDI = 1.6) and the re-reduced sample (dashed line, $M_n = 38,000$ (PDI = 1.8); 3000). b) Molecular weight of re-reduced samples (higher molecular weight fractions) as a function of time.

a)



b)



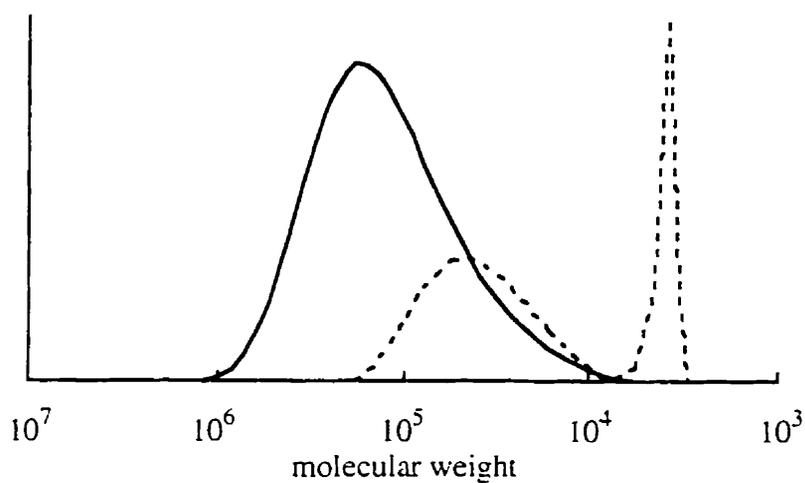
3.3.4 Oxidation of methylated polymer, 2b

Studies on the poly(ferrocenylsilane) **2a** show that oxidation results in molecular weight decline, either due to the inherent instability of the oxidized polymers, or due to some reaction with the oxidant (or, in the case of triiodide, counterion). As a further investigation of the stability of the oxidized polymers, the behavior of polymer **2b**, in which the cyclopentadienyl rings each contained one methyl group (at random positions). That the methyl groups can serve as electron donors may serve to stabilize the oxidized polymers. **8b**. For comparison with the oxidation of polymer **2a**, polymer **2b** was oxidized with iodine, [NO][PF₆], and [(*p*-BrC₆H₄)₃N][PF₆].

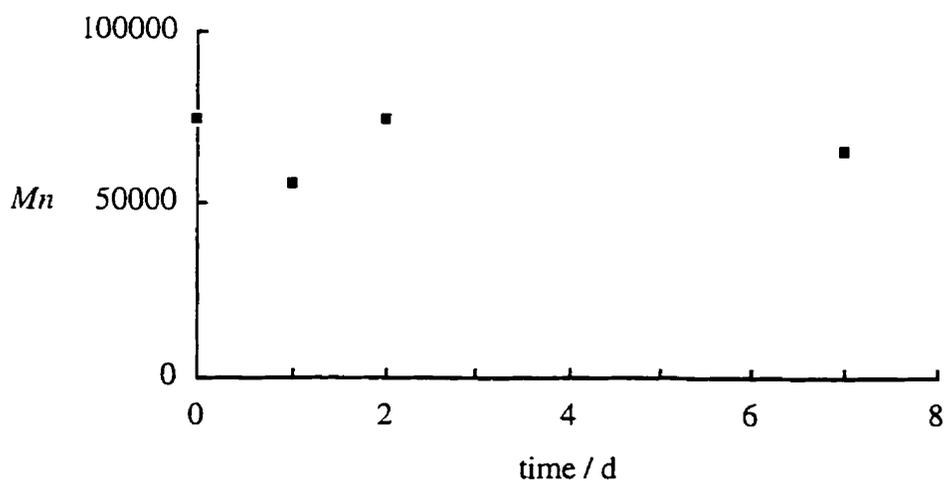
Oxidation with Iodine. When polymer **2b** was oxidized with iodine, there was, as in the other cases, substantial molecular weight decline and the appearance of a lower molecular weight peak. However, there was no further observed molecular weight decline in the solid state, unlike that for polymer **2a**. (See Figure 7.) This suggests that, as expected, the methyl groups on the cyclopentadienyl rings are contributing to the stability of the oxidized polymer: in this case, they may inhibit Si-C(aryl) cleavage that is most likely occurring in polymer **2a**.

Figure 7. Molecular weight of **2b**, oxidized with iodine. a) GPC traces of the unoxidized polymer (solid line, $M_n = 100,000$, PDI = 1.8) and the re-reduced sample (dashed line, $M_n = 40,000$, PDI = 2.0). b) Molecular weight of re-reduced samples (higher molecular weight fractions) as a function of time. (In b, the pristine polymer had a molecular weight of 220,000.)

a)



b)

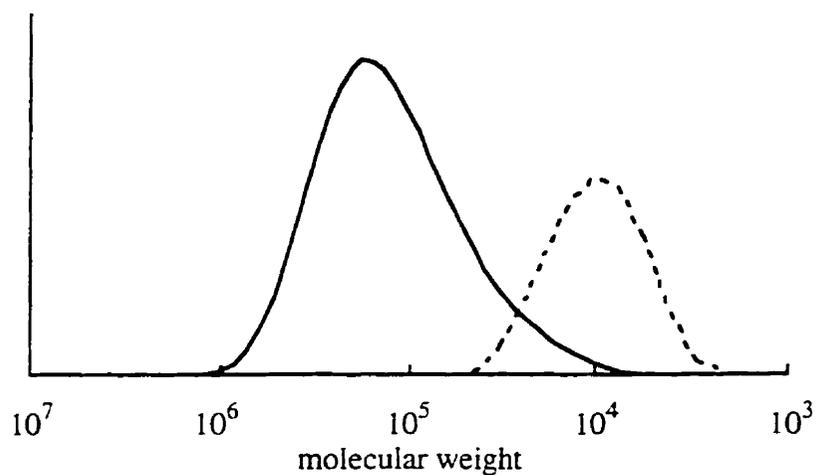


Oxidation with a Nitrosonium Salt, [NO][PF₆]. As observed for the oxidation of polymer **2a**, there is substantial molecular weight decline throughout the course of the oxidation, and then none further in the solid state. (See Figure 8.) The molecular weight of the polymer **2b** declined from 100,000 to 10,000; the decline is substantially less than what was observed for polymer **2a** (in which the molecular weight decreased from 500,000 to 6,000). This suggests, as above, that the methyl groups are contributing to the stability of the oxidized polymer, especially since the observed degree of oxidation was the same in both cases.

Oxidation with *tris*-(*p*-bromophenyl)aminium cation. Studies with the other oxidants have shown that the polymer **2b** shows less molecular weight decline during oxidation than polymer **2a**. Oxidation with the "Magic Blue" cation shows the least molecular weight decline: the molecular weight of polymer **2b** decreases from 100,000 to 70,000 throughout oxidation, and there is no further decline in the solid state afterward. (See Figure 9.)

Figure 8. Molecular weight of **2b**, oxidized with [NO][PF₆]. a) GPC traces of the unoxidized polymer (solid line, $M_n = 100,000$, PDI = 1.8) and the re-reduced sample (dashed line, $M_n = 10,000$, PDI = 1.5). b) Molecular weight of re-reduced samples (higher molecular weight fractions) as a function of time.

a)



b)

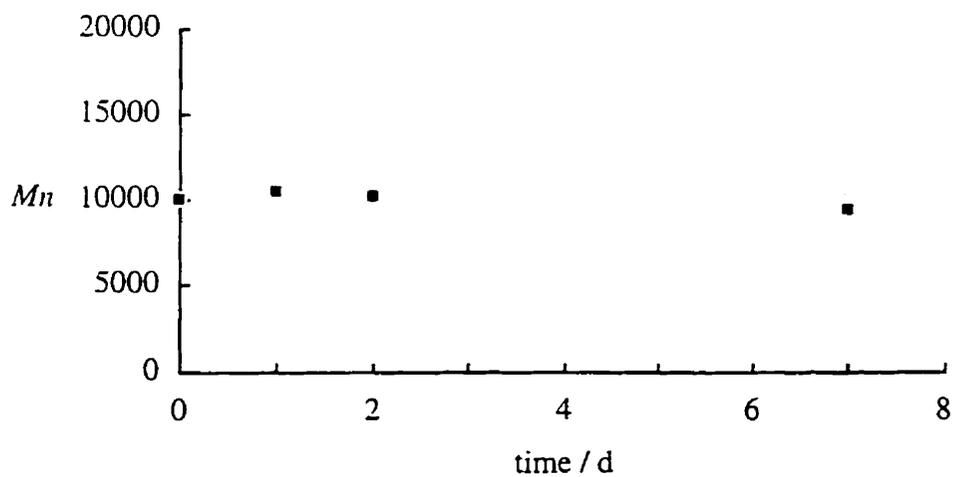
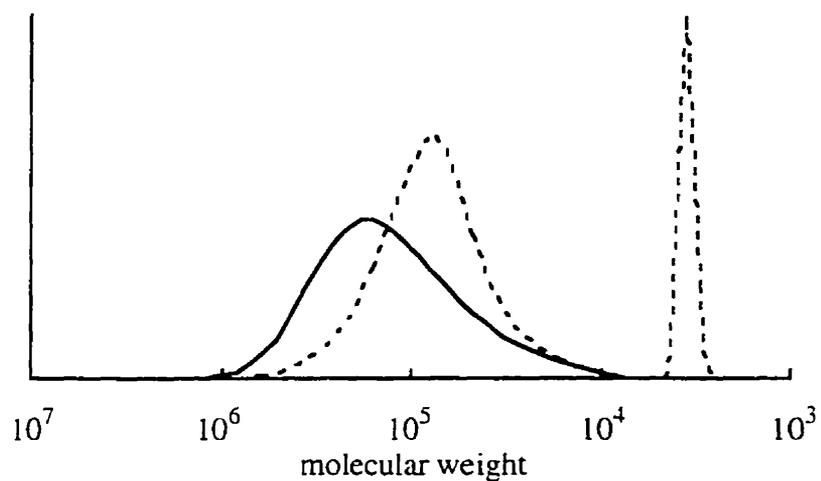
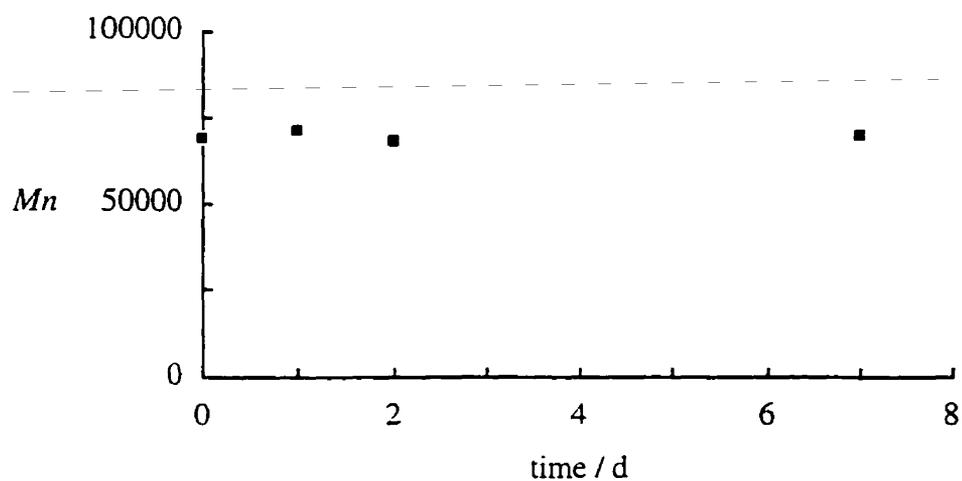


Figure 9. Molecular weight of **2b**, oxidized with $[(p\text{-BrC}_6\text{H}_4)_3\text{N}^+][\text{PF}_6^-]$. a) GPC traces of the unoxidized polymer (solid line, $M_n = 100,000$, PDI = 1.8) and the re-reduced sample (dashed line, $M_n = 70,000$ (PDI = 1.5); 3,000). b) Molecular weight of re-reduced samples (higher molecular weight fractions) as a function of time.

a)



b)



When these results are considered together, there are a number of conclusions that can be drawn about the oxidation behavior of these polymers:

1. The degree of oxidation is (for the nitrosonium and aminium salts, at least) independent of the oxidant used.
2. There is a molecular weight decline inherent to the oxidation process. While it is observed for all oxidants investigated, it is minimized for oxidants which are essentially only oxidants (*i.e.*, the aminium salt).
3. In the presence of an inert counterion (*e.g.*, PF_6^-), there is no further molecular weight decline in the solid state. With triiodide as counterion, there is further molecular weight decline following the reaction.
4. The presence of methyl groups on the cyclopentadienyl rings (polymer **2b**) does not hinder the oxidation process; it does, however, reduce the molecular weight decline through oxidation. Also, the methyl groups appear to stabilize the oxidized polymer to reaction with triiodide.

3.4 Summary

The oxidation behavior of two ferrocenylsilane polymers has been examined with a variety of oxidizing agents. A general characteristic of all oxidation reactions has been molecular weight decline of the polymer. This has been related to the strength and reactivity of the oxidant, the inertness of the counterion, and stability of the ferrocenium units within the polymer backbone. Molecular weight decline was minimized by using a mild oxidant (tris-*p*-bromophenylammonium hexafluorophosphate) and a polymer with methyl groups randomly substituted on the cyclopentadienyl ring.

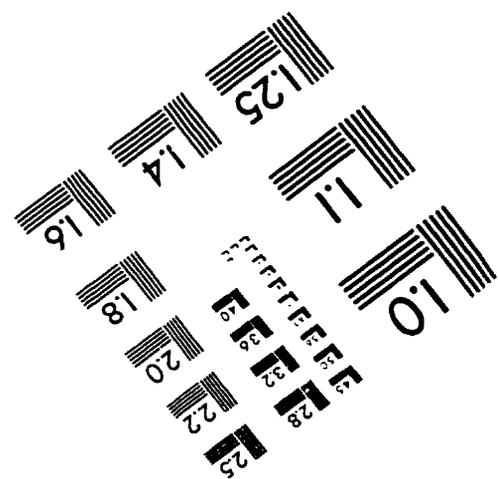
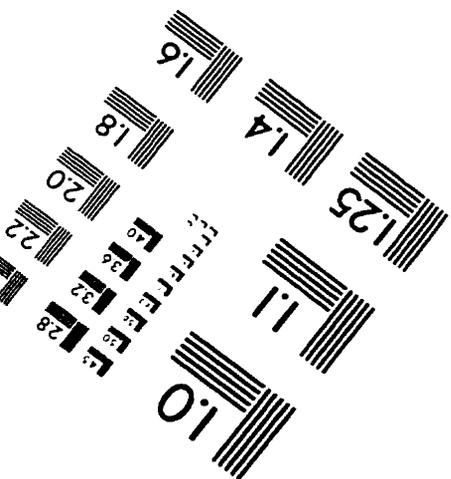
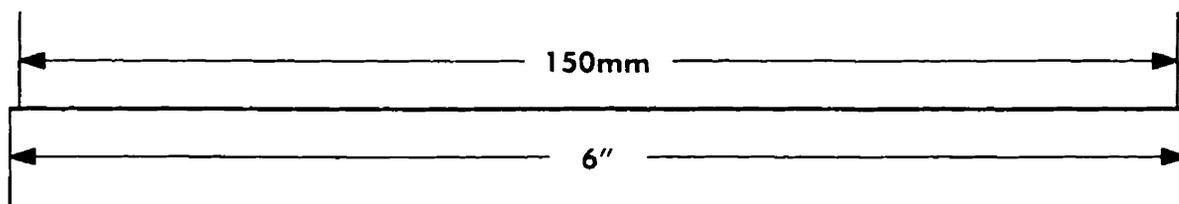
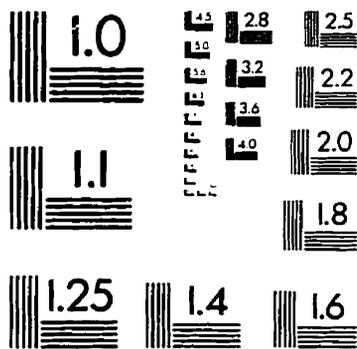
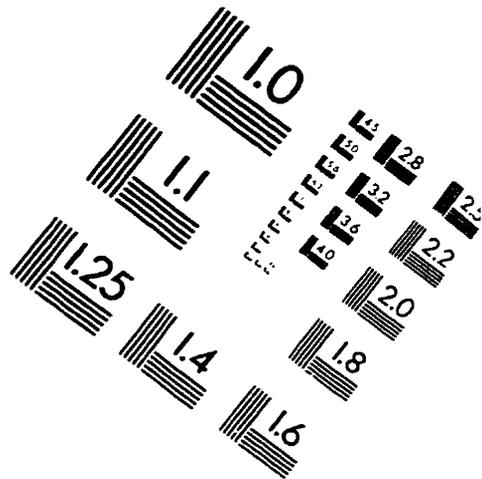
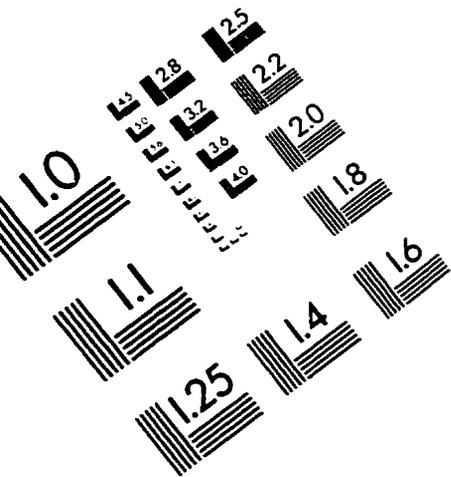
Also, the crystal structure of an oxidized oligomer (the dicationic trimer) was obtained, and the information provided by it - that the terminal ferrocene units were oxidized while the central one was not - was consistent with the electrochemical model previously determined.

3.5 References

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IMAGE EVALUATION TEST TARGET (QA-3)



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