ELECTRON DEFICIENT POLYARYLENESILOXANES

by

Dianne L. Braho

Submitted in Partial Fulfillment of the Requirements

for the Degree of

Master of Science

in the

Chemistry

Program

YOUNGSTOWN STATE UNIVERSITY

January, 1996

ELECTRON DEFICIENT POLYARYLENESILOXANES

Dianne L. Braho

I hereby release this thesis to the public. I understand this thesis will be housed at the Circulation Desk of the University library and will be available for public access. I also authorize the University or other individuals to make copies of this thesis as needed for scholarly research.

Signature:

1-11-96
Student, Dianne L. Braho Date

Approvals:

Jan 11/96
Thesis Advisor, Dr. Allen D. Hunter Date

1/11/96
Committee Member, Dr. Sherri Lovelace Date

Michael Serra 1/11/94
Committee Member, Dr. Michael Serra Date

1/11/96
Dean of Graduate Studies, Dr. Peter J. Kavinsky Date

ABSTRACT

The Synthesis and Characterization of Polyarylenesiloxanes and the related Electron Deficient Chromiumtricarbonyl Polyarylenesiloxanes

Dianne L. Braho

Master of Science

Youngstown State University, 1995

The syntheses and spectroscopic characterizations of a series of siloxane and siloxane chromiumtricarbonyl model complexes and polymers are reported. The siloxane model compound, $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzene-dimethanol, was prepared from $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-benzenedimethanol in methylene chloride by reaction with chlorotriisopropylsilane/pyridine. The siloxane polymers were prepared from $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-benzenedimethanol in methylene chloride by reaction with dichlorodimethylsilane/pyridine and were terminated with chlorotriethyl-silane and chlorotriisopropylsilane. The chromiumtricarbonyl starting material, (η^6-$\alpha,\alpha,$-α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl, was prepared via the reaction of $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-benzenedimethanol with chromiumhexacarbonyl in refluxing dibutylether/tetrahydrofuran under inert atmospheric conditions. The siloxane chromiumtricarbonyl complex, (η^6-$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl was prepared from (η^6-$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl by reaction with chlorotriisopropylsilane/-pyridine in methylene chloride. The siloxane chromiumtricarbonyl polymers were prepared from (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl in methylene chloride by reaction with dichlorodimethylsilane/pyridine and were terminated with chlorotriisopropylsilane. All of these compounds were characterized by IR and by ^{1}H and ^{13}C NMR spectroscopy. The molecular weights were estimated by NMR and viscosity measurements. The relative stabilities of the complexes are reported.

ACKNOWLEDGEMENTS

I would like to thank Dr. Hunter for his guidance during the research and help in preparing this thesis.

I would like to thank Dr. Sherri Lovelace for her help and ideas for the glovebag and her time and effort in reviewing this manuscript.

I would like to thank Dr. Michael Serra for his time and effort in reviewing this manuscript.

I would also like to thank the secretaries and stock room staff because their help made this manuscript possible.

TABLE OF CONTENTS

LIST OF FIGURES

FIGURE PAGE

LIST OF TABLES

LIST OF ABBREVIATIONS

R	alkyl
α	alpha, the Mark-Houwink exponent
α'	alpha prime, the Mark-Houwink exponent for a particular repeating unit
Å	angstroms
aq	aqueous
BO	bond order
br	broad (as in NMR)
Bu_2O	dibutylether
C	carbon
^{13}C	carbon-13 isotope (as in NMR)
CO	carbon monoxide
C-O	carbon-oxygen bond
cm^{-1}	reciprical centimeters
°	degree
δ	delta, chemical shift
$CDCl_3$	deuterated chloroform
DCD	Dewar-Chatt-Duncanson
Et	ethyl
FTIR	fourier transform infrared
g	gram
GPC	gel permeation chromatography
η^n	hapticity
HCl	hydrochloric acid
H	hydrogen
^1H	proton (as in NMR)

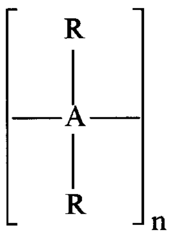
$\{^1H\}^{13}C$	broad band proton decoupled ^{13}C NMR
IR	infrared
K	the Mark-Houwink preexponential term
K'	the Mark-Houwink preexponential term for a particular repeating unit
$[\eta]$	intrinsic viscosity
η_{sp}	specific viscosity ($[(t-t_o)/t_o]$/concentration)
Pr^i	isopropyl
kcal	kilocalorie
L	ligand
MHz	megahertz
M	metal
M-C	metal-carbon bond
M-CO	metal-carbonyl linkage
Me	methyl
mL	milliliter
mmol	millimole
mol	mole
MW	molecular weight
M_i	molecular weight of the ith species
$\overline{M}_n$	number average molecular weight
$\overline{M}_w$	weight average molecular weight
$\overline{M}_v$	viscosity average molecular weight
m	multiplet (as in NMR)
n	number of moles
N_i	number of moles of the ith species
NMR	nuclear magnetic resonance

N	nitrogen
O	oxygen
ppm	parts per million
%	percent
P_2O_5	phosphorus pentoxide
π	pi (as in bonding)
q	quartet (as in NMR)
RB	round bottom
Si	silicon
s	singlet (as in NMR)
σ	sigma (as in bonding)
Σ	summation
T_{dec}	thermal decomposition temperature
T_g	glass transition temperature
T_m	melting point
THF	tetrahydrofuran
t	triplet (as in NMR)
t	seconds (as in viscosity measurement)
t_o	seconds for pure THF (as in viscosity measurement)
A	type of repeating unit
B	type of repeating unit
VBT	valence bond theory
H_2O	water

Part One
Introduction

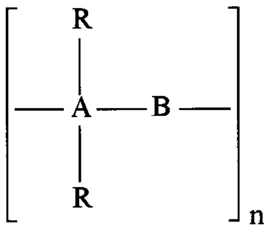
Chapter One
Polymers

Polymers are all around us. They are found in plants, animals, rubber, adhesives, fibers, and coatings.[1] They are composed of long chains of atoms linked together by covalent bonds. The repeating units of the resulting chains may also have side groups attached to their backbones. There may be one type of group in the repeating unit or there may be more than one type of group as depicted in **1.1.1** and **1.1.2,** respectively. Polymers may also have variations in their side chains (e.g. **1.1.3**).[2]



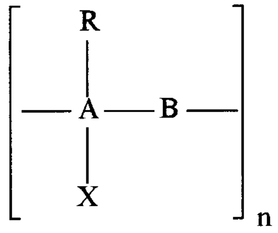
$$\left[-\overset{R}{\underset{R}{A}}- \right]_n$$

1.1.1



$$\left[-\overset{R}{\underset{R}{A}}-B- \right]_n$$

1.1.2



$$\left[-\overset{R}{\underset{X}{A}}-B- \right]_n$$

1.1.3

Polymers can have any number of repeating units in each chain and, as a result, a bulk sample will generally have a wide molecular weight distribution (Figure **1.1.1** on page 2). Properties vary with both average molecular weight and the width of the molecular weight distribution. In order to get optimum properties out of a polymer, the molecular weight range should generally be narrow. As shown in Figure **1.1.2** (page 2), there is a tradeoff between the physical properties of a polymer and its viscosity. The optimal molecular weight range, known as the working range, lies in the middle.[2]

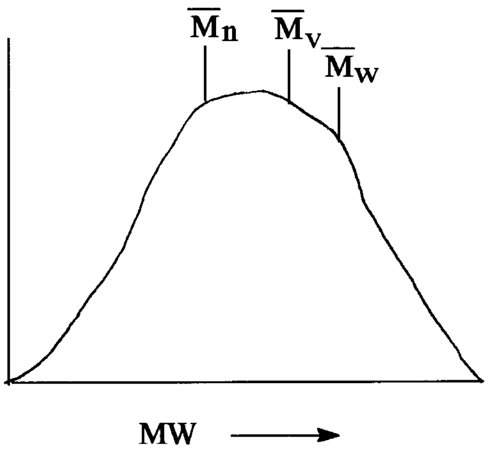


Figure 1.1.1. Molecular weight distribution

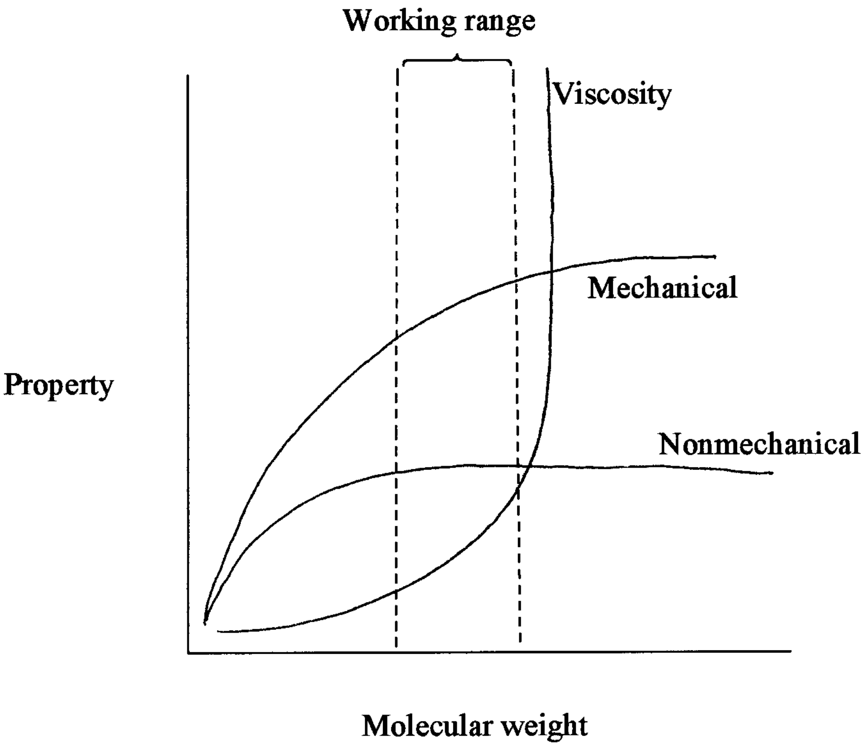


Figure 1.1.2. Dependence of polymer properties on molecular weight.

There are several ways of describing molecular weight distributions, three of the most common are the number average, weight average, and viscosity average molecular weights ($\overline{M}_n$, $\overline{M}_w$, and $\overline{M}_v$, respectively). The number average molecular weight is the summation of the number of moles in each fraction multiplied by the molecular weight of each fraction divided by the summation of the number of moles in each fraction.[1]

$$\overline{M}_n=\Sigma(N_iM_i)/\Sigma N_i \tag{1.1.4}$$

This average is commonly obtained by measuring colligative properties such as melting and boiling points or by end group analysis, all of which depend only on the number of particles present in solution.[2] Weight average molecular weight is the summation of the number of moles in each fraction multiplied by the square of the molecular weight of each fraction divided by the summation of the number of moles in each fraction multiplied by the molecular weight of each fraction.[2]

$$\overline{M}_w=\Sigma(N_iM_i^2)/\Sigma(N_iM_i) \tag{1.1.5}$$

The viscosity of a solution is related to the molecular weight of the polymer solutes by the Mark-Houwink-Sakurada equation.[1]

$$[\eta] = K\,\overline{M}_v^{\alpha} \tag{1.1.6}$$

where $[\eta]$ is the intrinsic viscosity of the solution (i.e. measured at infinite dilution), $\overline{M}_v$ is the viscosity average molecular weight, and K and α are the Mark-Houwink constants. These are a function of the temperature, the solvent, and the polymer's structure and do not vary with chain length for linear polymers except at low molecular weights where end effects become significant. The viscosity average molecular weight is defined as

$$\overline{M}_v=\Sigma(N_iM_i^{1+\alpha})/\Sigma(N_iM_i) \qquad (1.1.7)$$

The values of K vary widely (typically from 10^{-3} to 0.5) depending strongly on the strengths of the polymer-solvent interactions while the α values typically vary over a narrower range from 0.5 (for a randomly coiled polymer in a Theta solvent) to 0.8 with values over 1.0 for rod shaped polymers. These parameters are evalued from a plot of the log of $[\eta]$ versus log $\overline{M}$ ($\overline{M}_n$, or better $\overline{M}_w$, values are used for such studies) for a series of isostructural polymers differing only in molecular weight with α and log K being the measured slope and intercept, respectively.[1,2,3]

$$\log [\eta] = \log K + \alpha \log \overline{M} \qquad (1.1.8)$$

Inspection of equations 1.1.4, 1.1.5, and 1.1.7 indicates that $\overline{M}_w$ will always be greater than or equal to $\overline{M}_n$, that for non-rod like polymers $\overline{M}_n \leqslant \overline{M}_v \leqslant \overline{M}_w$, and that generally $\overline{M}_v$ will be closer to $\overline{M}_w$ than to $\overline{M}_n$.

Molecular weight distribution curves such as that shown in Figure 1.1.1 (page 2) are generally best obtained from and calibrated by gel permeation chromatography, GPC. GPC is a liquid chromatographic technique that separates solutes by molecular size. Materials having narrow molecular weight distributions have $\overline{M}_n \approx \overline{M}_v \approx \overline{M}_w$ and have polydispersity indicies (i.e. $\overline{M}_w / \overline{M}_n$) of close to one. Wider molecular weight distributions give larger $\overline{M}_w / \overline{M}_n$ values ranging up to ten or more. The value of $\overline{M}_n$ is more sensitive to the size of the low molecular weight fraction (i.e. due to their great N_i values per gram) while $\overline{M}_w$ is more sensitive to the size of the high molecular weight fraction.[4,5]

Two types of polymerization reactions are step-growth and chain-reaction polymerizations. Step-growth polymers grow by the sequential formation of bonds.[3] Often, step growth polymerizations are condensation reactions in which small molecules such as HCl or H_2O are lost in each bond forming step. For example, both reactive functional groups can be on one molecule.[1]

$$\text{n HO-A-B-OH} \rightarrow \text{-[A-B-O]}_n\text{-} + \text{n } H_2O \qquad (1.1.9)$$

Or the reaction can have two monomers which are each difunctional.[1]

$$\text{n HO-A-A-OH} + \text{n Cl-B-B-Cl} \rightarrow \text{-[A-A-O-B-B-O]}_n\text{-} + \text{2n HCl} \qquad (1.1.10)$$

Such reactions generally produce high $\overline{M}_w / \overline{M}_n$ values and broad molecular weight distributions. In contrast, chain-growth polymers are formed via the sequential addition of monomers to reactive chain ends.[4] The mechanism of such reactions consists of three steps: initiation, propagation, and termination. The initiation step starts the reaction (e. g. 1.1.11). It generally involves a highly reactive free radical, anion, or cation species known as the initiator. The propagation step(s) increases the molecular weight via the addition of monomers to the reactive end(s) of the chains. Finally, a termination step ends the chains growth (e. g. equations 1.1.12 and 1.1.13, respectively).[1]

Initiation:

$$R\bullet + CH_2{=}CH_2 \rightarrow RCH_2CH_2\bullet \qquad (1.1.11)$$

Propagation:

$$RCH_2CH_2\bullet + (CH_2{=}CH_2)_n \rightarrow RCH_2CH_2(CH_2CH_2)_{n-1}CH_2CH_2\bullet \qquad (1.1.12)$$

Termination:

$$RCH_2CH_2(CH_2CH_2)_{n-1}CH_2CH_2\bullet + R\bullet \rightarrow RCH_2CH_2(CH_2CH_2)_nR \qquad (1.1.13)$$

Such polymers generally have much narrower molecular weight distributions and their $\overline{M}_w / \overline{M}_n$ values approach one.[3]

Two distinct types of polymers are those with organic and inorganic backbones. Organic polymers have backbones comprised mainly of carbon atoms which may also be joined together with heteroatoms (typically oxygen and/or nitrogen). They are usually made from petroleum or natural gas derivatives and many are commercially prepared on very large scales as commodity materials. Inorganic polymers generally have backbones having inorganic elements (mainly from groups III, IV, V, VI including silicon, phosphorus, sulfur, germanium, and tin) alternating with O, N, and/or C containing functional groups. Inorganic polymers are produced on much smaller scales due to their higher costs but are useful for specialty applications due to the longer, stronger and more flexible bonds formed between these elements.[2]

Polymers which consist of a single repeating unit are known as homopolymers.

-A-A-A-A-A-A-A-A-A-A-A-A-A-A-A- (1.1.14)

Copolymers are polymers containing more than one monomer. Alternating copolymers have a regular alternating arrangement. Random copolymers have a random distribution. Block copolymers consist of blocks of linked monomers.[1]

Alternating

-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A-B-A- (1.1.15)

Random

-A-B-B-B-A-A-B-A-B-B-A-A-B-B-B-A-B-B-A-B-A- (1.1.16)

Block

-A-A-A-A-A-A-B-B-B-B-B-B-A-A-A-A-A-B-B-B-B- (1.1.17)

Due to their wide variety of backbones and side chains, polymers have unique and highly variable characteristics and properties. For polymers, the transition from solid to liquid occurs at two measurable temperatures known as the glass transition temperature, T_g, and the melting point, T_m. At T_g the polymer loses its glasslike properties and becomes flexible and assumes properties more commonly identified with rubber or plastic. There is greater rotational freedom and more segmental motion of the chains. At T_m, the polymer is in its liquid phase and the whole chain moves.[1,3]

Chapter Two

Polysiloxanes

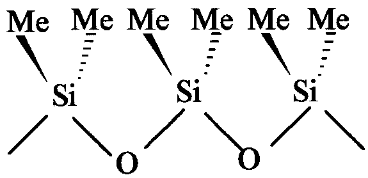
Polysiloxanes are inorganic polymers having alternating silicon and oxygen atoms in the backbone. The materials from which they are prepared, alkyl silicon chlorides, were first prepared in 1860 by reacting diethylzinc with silicon tetrachloride.[2,4,6]

$$Et_2Zn + SiCl_4 \rightarrow Et_2SiCl_2 + ZnCl_2 \qquad (1.2.1)$$

Due to the availability of the Grignard reaction in 1900, a wide variety of organosilanes R_nSiY_{4-n} were synthesized.

$$SiCl_4 + nRMgCl \rightarrow R_nSiCl_{4-n} + nMgCl_2 \qquad (1.2.2)$$

The first commercial products were based on polydimethylsiloxane. These "silicones" were commercialized in 1943.[2]



(1.2.3)

Silicone homopolymers are usually produced using acid or base-catalyzed equilibration of linear or cyclic intermediates. The fundamental starting materials for preparing siloxanes are silicon and tetrachlorosilane. The common way of producing elemental silicon is by reduction of silica (i. e. silicon dioxide) with carbon at high temperatures. The other major starting material, tetrachlorosilane, is prepared by chlorination of elemental silicon.[2]

$$SiO_2 + 2C \rightarrow Si + 2CO \qquad (1.2.4)$$

$$Si + 2Cl_2 \rightarrow SiCl_4 \qquad (1.2.5)$$

There are two routes for preparing the monomers. Kippling's preparation of the compounds uses the reaction of a Grignard reagent with tetrachlorosilane which produces dialkyldichlorosilanes as the major products.[2]

$$SiCl_4 + 2RMgCl \rightarrow R_2SiCl_2 + 2MgCl_2 \qquad 1.2.6)$$

The second and more direct route for preparing dichlorodimethylsilane is the Rochow process. This starts from elemental silicon which reacts with a methyl halide. The substantial quantities of mono and trimethyl silane biproducts are removed by distillation and recycled to produce additional dialkyldichlorosilane.[2]

$$3Si + 6RCl \rightarrow R_2SiCl_2 + RSiCl_3 + R_3SiCl \qquad (1.2.7)$$

Each of these processes is usefull under different conditions. Kippling's process is more appropriate in the lab since it does not require special equipment or facilities and is relatively selective. Rochow's process is more convenient on an industrial scale since the starting materials are inexpensive, the byproducts can be recycled, and purification can be easily carried out on a large scale.

These monomers are made into polymers either by acid or base catalysts. The first step is hydrolysis of chlorosilanes which yields silanols and hydrochloric acid. Under acidic conditions, the silanols condense rapidly to produce siloxanes and water.

$$-\underset{|}{\overset{|}{\mathrm{Si}}}\mathrm{Cl} + \mathrm{H_2O} \rightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HCl} \qquad (1.2.8)$$

$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{HO}-\underset{|}{\overset{|}{\mathrm{Si}}}- \rightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}- + \mathrm{H_2O} \qquad (1.2.9)$$

$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{OH} + \mathrm{Cl}\underset{|}{\overset{|}{\mathrm{Si}}}- \rightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}- + \mathrm{HCl} \qquad (1.2.10)$$

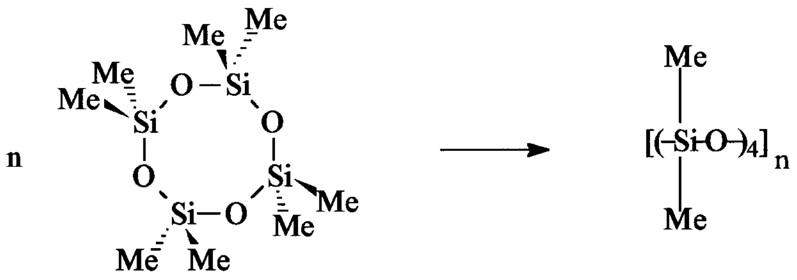
When dimethyldichlorosilane is hydrolyzed with excess water, linear and cyclic polydimethylsiloxanes are formed. The hydrogen chloride is partially or completely dissolved in the aqueous phase which results in a light, colorless siloxane oil as the second phase.[7]

$$\begin{gathered} \mathrm{Me_2SiCl_2} + \text{excess } \mathrm{H_2O} \rightarrow \\ \mathrm{HO(Me_2SiO)_mH} + \text{-}\mathrm{(Me_2SiO)_n}\text{-} + \mathrm{HCl} \end{gathered} \qquad (1.2.11)$$

About half of this siloxane oil consists of a mixture of cyclic species, with the majority being tetramers. There is a small amount of trimers present as well as cyclic polymers with as many as several hundred repeating units.[7] As expected for a condensation reaction, there is a gradual increase in molecular weight and a broad molecular weight distribution of products is observed. Since the end groups of each linear chain remain reactive, even the finished product will show changes in molecular weight with time. This is an undesirable property, since the physical characteristics will therefore change with time. To overcome this problem, one can include a small quantity of a monofunctional reagent since this will terminate the polymer with unreactive end groups and; therefore, inhibit further molecular weight changes. Typically, trimethylsilylchloride is used.[1]

$$\begin{gathered} n\mathrm{Me_2SiCl_2} + 2\mathrm{Me_3SiCl} + (n+1)\mathrm{H_2O} \rightarrow \\ \mathrm{Me_3SiO(Me_2SiO)_nSiMe_3} + (2n+2)\,\mathrm{HCl} \end{gathered} \tag{1.2.12}$$

An alternative way to prepare siloxane polymers is to use ring opening polymerization in which cyclic siloxanes are catalytically converted into polysiloxanes using Lewis acid catalysts.



(1.2.13)

Because this reaction procedes via an addition polymerization, one has much greater control over the polymerization process. This enables one to produce a much narrower molecular weight distribution.[4,8]

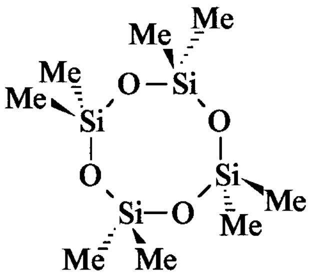
Bulk siloxane polymers can be quite flexible due to the extreme flexibility of the individual Si-O-Si linkages. Since the Si-O bond has a bond length (1.64 Å) which is greater than the C-C bond length (1.53 Å), steric interferences or intramolecular congestion is decreased.[2,9] In addition, the oxygen atoms are unhindered by side groups and the lone pairs are sterically undemanding. Finally, the bond angle for the Si-O-Si linkage is appoximately 143° which is more open than a tetrahedral angle of approximately 110°.[2] A combination of these three features gives materials having this silicone structure exceptional backbone flexibility compared to alkane polymers, especially at low temperatures. The Si-O bonds are also stronger than C-C bonds (106 vs. 82.6 kcal/mol, respectively) and are less prone to homolytic cleavage giving these materials better thermal stabilities as well.[2,8]

The primary limitation to the thermal stability of siloxane polymers is depolymerization reactions. Thermal degradation of any bond (1.2.14) not only fragments the molecule, but creates very reactive charged sites (1.2.15). These sites backbite down the chain recreating cyclic monomers and creating new reactive end groups which can continue this process to unzip the whole chain (1.2.16).[1,2,4]

$$\text{-SiMe}_2\text{-O-SiMe}_2\text{-O-SiMe}_2\text{-O-SiMe}_2\text{-O-}\downarrow\text{-SiMe}_2\text{-O-} \qquad (1.2.14)$$

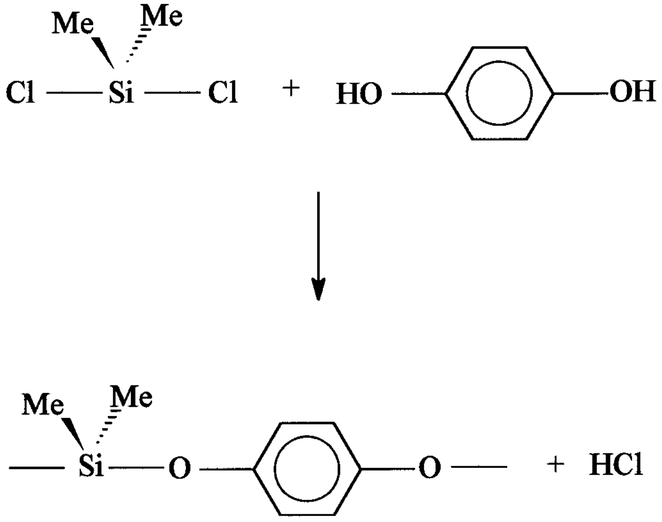
$$\text{-SiMe}_2\text{-O-SiMe}_2\text{-O-SiMe}_2\text{-O-SiMe}_2\text{-O-}^{-} \quad {}^{+}\text{-SiMe}_2\text{-O-} \qquad (1.2.15)$$

$$\text{-SiMe}_2\text{-O-SiMe}_2\text{-O-}^{-} \; +$$



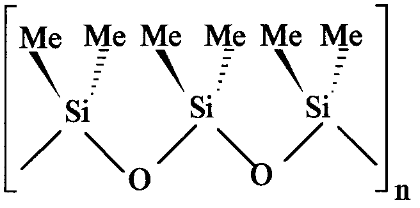
(1.2.16)

One of the more successful strategies for inhibiting the unzipping is to put rigid groups in the backbone, since these can prevent the backbiting. These structures can be prepared by reacting a small percentage of rigid monomers with the conventional siloxane starting materials.[9,10] For example, hydrolysis of dimethyldichlorosilane with 1,4-benzenediol produces a polymer with rigid as well as flexible properties and increased thermal stabilities (**1.2.17**).[2]

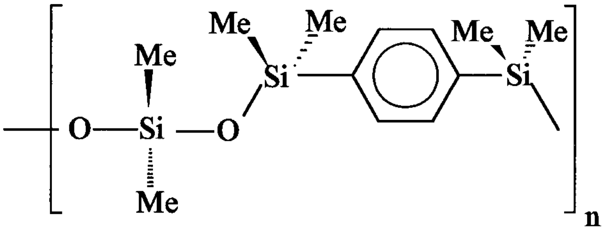


(1.2.17)

Previous studies comparing polydimethylsiloxane (PDMS) (1.2.18) to Poly(p-phenylene tetramethyldisiloxane) (1.2.19) resulted in the observation that the later had a higher T_g and T_m. Due to its extreme flexibility, PDMS has a T_g=–125°C [2] and T_m=–40 °C [2], whereas, poly(p-phenylene tetramethyldisiloxane) has a T_g=–61°C [11] and T_m=148° C [2]. As reported, this was due to the decreased flexibility and increased stability associated with addition of arene groups to the siloxane backbone.[11]



(1.2.18)



(1.2.19)

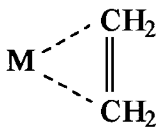
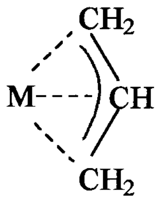
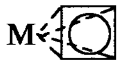
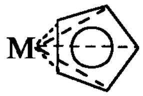
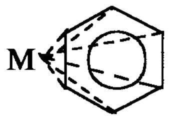
Chapter Three
Organometallic Compounds

In thermodynamic terms, transition metal organometallic compounds are generally thermally unstable and air sensitive. They were not well understood or widely studied from their first preparation in 1827 to about 1950. Due to the synthesis and characterization of the unusually stable and structurally novel ferrocene complex; however, organometallic chemistry was energized in 1951. From 1951 to the 1970's, many complexes which were kinetically stable were successfully prepared and characterized. Presently, the focus of organometallic chemistry is on the applications of organometallics to other fields.[12]

Organometallic chemistry is at the interface between inorganic and organic chemistry.[13] Transition metal organometallic complexes consist of one or more transition metals bonded to one or more ligands via at least one metal-carbon bond.[12] Acting as Lewis bases, the ligands can be considered to donate electrons to the transition metal centers which are acting as Lewis acids.[14] The kinetic stability of these organometallic complexes is related to the valence electron count around the metal center. As with noble gases, stability of the transition metal organometallic complexes is often observed when all of the valence orbitals are filled (i. e. corresponding to 18 valence electrons around the metal center).[12] When this "18-electron" rule is obeyed, (especially for low oxidation state complexes of the mid transition elements), the once inherently electron deficient transition metal has its bonding requirements satisfied resulting in increased stability for the organometallic complex.[15]

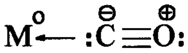
Ligands may bond to transition elements in more than one way. For example, π-hydrocarbon ligands can donate electrons from one or more of their multiple bonds to the metal. The hapticity (η^n) is defined as the number of ligand atoms within bonding distance of the metal (Table 1.3.1).[14,15,16] For unsaturated hydrocarbons, the maximum

Table 1.3.1. Hapticity table[9]

Symbol	Number of ligand atoms attached to metal	Examples
η^1-L	1	**M-CO**
η^2-L	2	
η^3-L	3	
η^4-L	4	
η^5-L	5	
η^6-L	6	

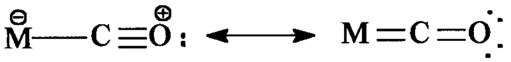
hapticity is the number of carbon atoms in the unsaturated system.[15] For example, benzene is normally observed as an eta six (η^6) complex in which all six ring carbons are within covalent bonding distance of the metal and it donates six electrons to the metal. A variety of organometallic complexes can be prepared by varying the type and number of ligands as well as the kind of metal used.[17]

A commonly used ligand in organometallic chemistry is carbon monoxide. Even though CO is an extremely weak Lewis base, it forms very strong metal-ligand bonds. This is because it has π^* orbitals which can function as π-symmetry electron acceptors.[15,18] Valence bond theory (VBT) and Dewar-Chatt-Duncanson (DCD) theory are two approaches to describing the bonding of the metal to the carbonyl ligands. According to VBT, the bonding of the carbonyl ligand to the metal (1.3.1) can be thought of as arising from two metal-carbonyl (M-CO) resonance structures (1.3.2 and 1.3.3).[13,14,16]



$$\overset{0}{M}\leftarrow :\overset{\ominus}{C}\equiv\overset{\oplus}{O}:$$

1.3.1



$$\overset{\ominus}{M}-C\equiv\overset{\oplus}{O}: \longleftrightarrow M=C=\ddot{O}:$$

1.3.2 **1.3.3**

The relative contributions of the two resonance structures depend on the electron richness of the metal. Resonance structure **1.3.2** makes a larger contribution to the resonance hybrid as the metal becomes more electron poor, which results in a lower M-C bond order (BO) and a higher C-O BO. Conversly, as the metal becomes more electron rich, resonance structure **1.3.3** makes a larger contribution to the resonance hybrid, resulting in a higher M-C BO and a lower C-O BO.[16]

According to DCD theory, the metal-carbonyl linkage can be understood in terms of synergic σ donation and π back donation of the electron density between the metal and the ligand (Figure 1.3.1). There is σ donation from the filled carbonyl σ-symmetry orbital localized on carbon (i.e. $\approx$ sp in character) to the empty metal σ-symmetry orbital ($\approx d^2sp^3$ for octahedral complexes) to form a sigma bond. There is also π back donation from filled π symmetry metal orbitals ($\approx d_{xy}$, d_{xz}, or d_{yz} for octahedral complexes) to empty π^* carbonyl orbitals to give the π back-bonds (there are two for each M-CO linkage).[13,15,16] For carbonyls, these two interactions are synergic and result in net electron transfer from the metal to the carbonyl ligand(s). Again, the electron richness of the metal affects the degree of π back donation. As the metal becomes more electron poor, there is less back donation and the M-C BO decreases while the C-O BO increases. Conversely, as the metal becomes more electron rich, more back donation occurs and the M-C BO increases while the C-O BO decreases.[16]

The overall electron richness can be measured using infrared spectroscopy. As the metal center becomes more electron rich and the amount of backbonding therefore increases, the IR stretching frequencies of the C-O bonds decrease. Net electron donating substituents (i.e. arenes) stabilize the metal carbonyl complexes by increasing the electron richness of the metal and consequently increasing the Cr-CO's bond strengths.[16]

Benzenechromiumtricarbonyl $(\eta^6\text{-}C_6H_6)CrCO_3$ and its derivatives were one of the first classes of organometallics to be studied and remain under active investigation. Benzenechromiumtricarbonyl was prepared by heating chromiumhexacarbonyl with benzene under reflux by Nicholls and Whiting in 1958.[15]

$$C_6H_6 + Cr(CO)_6 \rightarrow (\eta^6\text{-}C_6H_6)Cr(CO)_3 + 3CO \qquad (1.3.4)$$

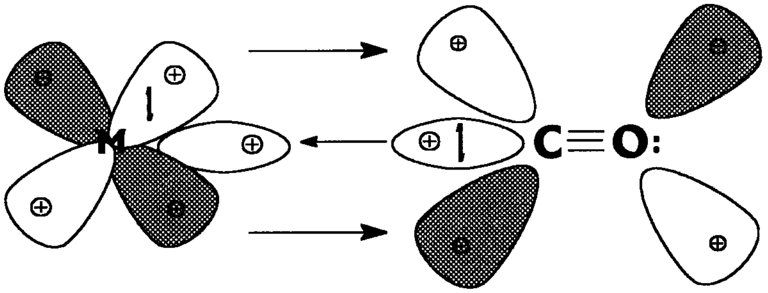
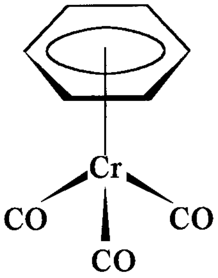


Figure 1.3.1. The DCD model of metal carbonyl bonding.[16]

A problem of hexacarbonyl subliming out of the mixture was overcome when Strohmeier invented an apparatus that washes the sublimed carbonyl back into the reaction vessel using solvent. Benzenechromiumtricarbonyl forms air stable yellow crystals, but when in solution it is oxidized by air. In benzenechromiumtricarbonyl, the benzene ring is planar and the chromiumtricarbonyl center is π-bonded the the benzene ring to give a 3-D tripod.[15,19]



(1.3.5)

The benzenechromiumtricarbonyl complex has been reported to have a dipole moment from the benzene ring to the carbonyl tripod. The chromium has a partial positive charge due to the carbonyl's electron-withdrawing effect. As a result, the arene ligand donates its electrons to chromium. The arene-chromium bond has a net electron transfer from the arene to the metal making the metal electron rich and the arene electron poor (i.e. comparable to nitrobenzene).[13,15,19]

By incorporating organometallic fragments into polymers, we hope to prepare polymeric materials with some novel characteristics. In this thesis, polymers are prepared having chromium tricarbonyl complexed groups to arylene siloxanes giving electron deficient polyarylenes.

Part Two

Experimental

Chapter One

Synthesis and Characterization of the Model Siloxanes and Polysiloxanes

Reagents and Reaction Conditions

Solvents and reagents were purchased from the Aldrich Chemical Company. Methylene chloride was dried over and distilled from P_2O_5. Tetrahydrofuran was predried over KOH and distilled from Na/benzophenone under argon (99.999 %, <3 ppm H_2O, <1 ppm O_2). Bu_2O was dried over and distilled from calcium hydride. Pyridine was dried over and distilled from potassium hydroxide and stored over 5Å molecular sieves under argon.[21]

All glassware and stirbars were dried at one hundred and ten degrees Celsius in an oven overnight to remove adsorbed water. The glassware and stirbars were removed from the oven and cooled under nitrogen gas. The 24/40 joints on the glassware were lubricated with silicone grease. Unless otherwise indicated, all reactions were performed under ultra high purity grade nitrogen gas (99.999 %, <3 ppm H_2O, <1 ppm O_2). The solids and solvents were added under a positive flow of nitrogen gas as seen through the mineral oil bubbler. All suba seals® were removed under positive flow of nitrogen gas and replaced with glass stoppers lubricated with silicone grease after the addition of reactants.[20,22]

Carbon and proton NMR analysis was performed on a Varian Gemini 2000, 400 MHz spectrometer. The carbon spectra were referenced to the chloroform peak defined as δ 77.0 ppm (t, $\underline{C}DCl_3$). The proton spectra were referenced to residual $CHCl_3$ in $CDCl_3$ defined as δ 7.27 ppm (s, $C\underline{H}Cl_3$).[23] Infrared spectroscopy was performed on a

Perkin Elmer 1600 Series FTIR instrument using THF as the solvent which was subtracted out as background. In addition, viscosity measurements of dilute solutions using THF as the solvent were performed using a Cannon-Fenske® viscometer in a glove bag.[1,22] A 30.0°C constant temperature bath was used. Plots of time $[(t-t_0)/t_0]$/conc. versus concentration (g/100mL) gave intrinsic viscosities. Using the Mark-Houwink-Sakurada relationship, the molecular weights were obtained.[1]

Spectroscopic data for α,α,α',α'-tetramethyl-1,4-benzenedimethanol (1)

The following data was obtained on compound **1**: ^{1}H NMR ($CDCl_3$); δ 1.59 ppm (s, 12H, $C(C\underline{H}_3)_2$), 1.72 ppm (s, br, 2H, O$\underline{H}$), 7.48 ppm (s, 4H, ArC$\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 31.53 ppm ($C(\underline{C}H_3)_2$), 72.36 ppm ($\underline{C}(CH_3)_2$), 124.81 ppm (Ar$\underline{C}$H), 148.25 ppm (Ar$\underline{C}$).

Preparation of α,α,α',α'-tetramethyl-O,O'-bistriethylsiloxy-1,4-benzenedimethanol (2)

The experimental apparatus, a three necked 100 mL RB flask was equipped with a gas inlet and a suba seal® (Figure 2.1.1) which was removed from the oven, assembled, and cooled using a drying tube containing anhydrous calcium sulfate to remove adsorbed water. A dried stir bar was added, the system was purged with nitrogen, and the joints were sealed with silicone grease. Methylene chloride (20 mL), pyridine (0.92 mL, 11.3 mmol), and α,α,α',α'-tetramethyl-1,4-benzenedimethanol (1.00 g, 5.15 mmol) were added under a positive nitrogen flow. A white suspension was visible in the flask. An ice water bath was placed under the flask and chlorotriethylsilane (1.90 mL, 11.3 mmol) was added dropwise over a 7 minute period via a syringe. The white solution was left to stir for 90 minutes. In air, the white solution was poured into a separatory funnel along with deionized water (15 mL). The aqueous and organic solvents formed two distinct layers. The separatory funnel was thoroughly shaken and vented and the organic layer, which was

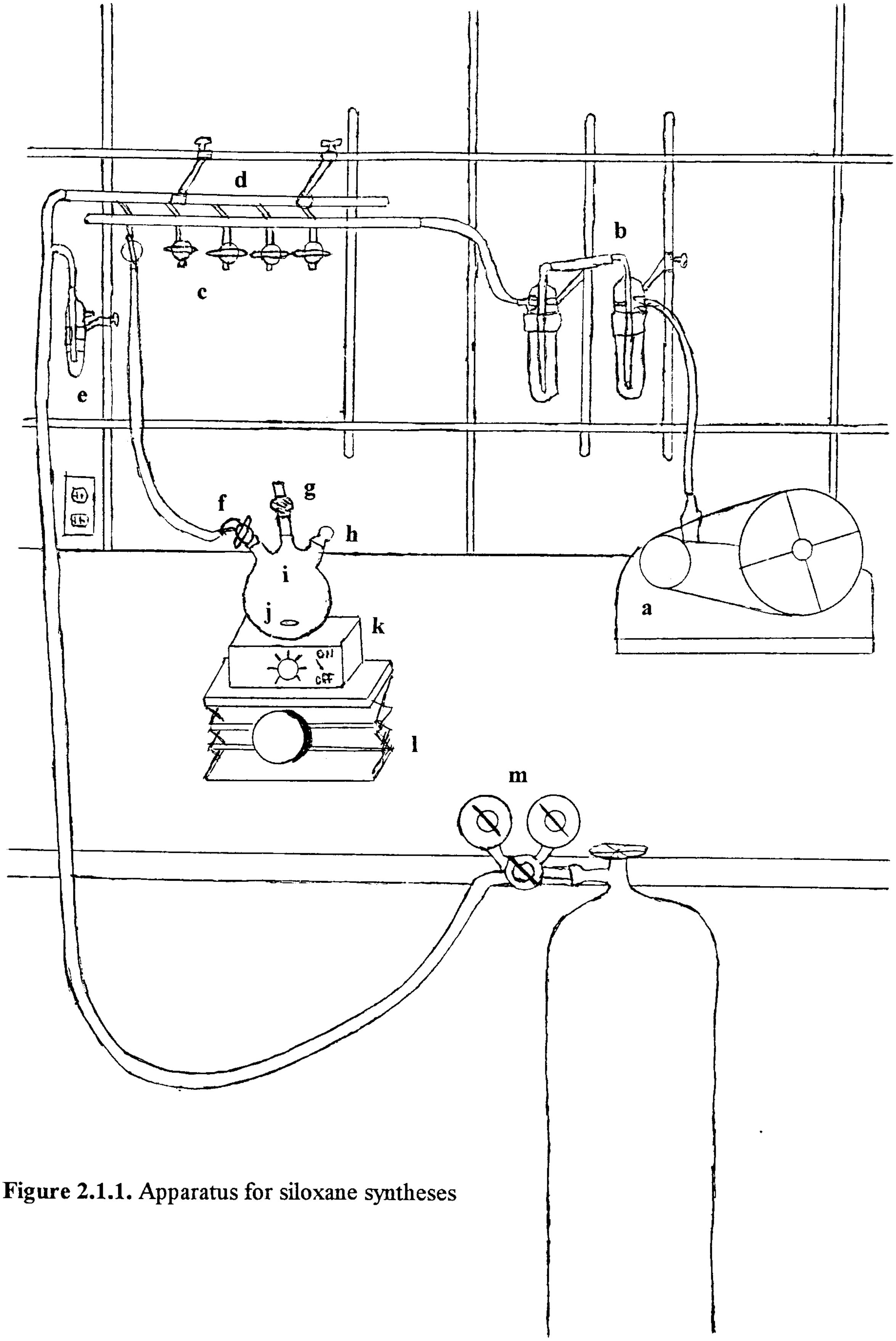


Figure 2.1.1. Apparatus for siloxane syntheses

Table 2.1.1. Parts of apparatus for siloxane synthesis

a	vacuum pump
b	cold traps
c	stopcock
d	manifold
e	mineral oil bubbler
f	stopcock
g	drying tube
h	stopper
i	3-necked RB
j	stir bar
k	stir plate
l	adjustable jack
m	regulator

the lower layer was removed and set aside. The aqueous layer was extracted with methylene chloride (3x5 mL). The organic layers were combined and back washed with deionized water (3x5 mL). The cloudy organic layer was dried over anhydrous sodium sulfate for one hour to remove any residual water that may have been present. The drying agent was removed by suction filtration. The residue was washed with methylene chloride (2x5 mL) and the methylene chloride was then removed by rotary evaporation. The product was a viscous liquid which was allowed to stand in air. The white crystals, α,α,α' ,α'-tetramethyl-O,O'-bistriethylsiloxy-1,4-benzenedimethanol, which resulted, weighed 0.30 g (13.5% yield, 0.693 mmol).

The following data was obtained on compound **2**: ^1H NMR ($CDCl_3$); δ 0.49 ppm (q, $C\underline{H}_2CH_3$), 0.51 ppm (q, $C\underline{H}_2CH_3$), 0.53 ppm (q, $C\underline{H}_2CH_3$), 0.55 ppm (q, $C\underline{H}_2CH_3$), another quartet at 0.58 ppm (q, $C\underline{H}_2CH_3$), 0.60 ppm (q, $C\underline{H}_2CH_3$), 0.62 ppm (q, $C\underline{H}_2CH_3$), 0.64 ppm (q, $C\underline{H}_2CH_3$), 0.92 ppm (t, $CH_2C\underline{H}_3$), 0.94 ppm (t, $CH_2C\underline{H}_3$), 0.96 ppm (t, $CH_2C\underline{H}_3$), another triplet at 0.96 ppm (t, $CH_2C\underline{H}_3$), 0.98 ppm (t, $CH_2C\underline{H}_3$), 1.03 ppm (t, $CH_2C\underline{H}_3$), 1.59 ppm (s, 13H, $C(C\underline{H}_3)_2$), 7.48 ppm (s, 4H, $ArC\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 5.74 ppm ($CH_2\underline{C}H_3$), 6.47 ($\underline{C}H_2CH_3$), 31.67 ppm ($C(\underline{C}H_3)_2$), 72.36 ppm ($\underline{C}(CH_3)_2$), 124.32 ppm ($Ar\underline{C}H$).

Preparation of α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol (3)

The experimental apparatus, a three necked 100 mL RB flask was equipped with a gas inlet and a suba seal® which was removed from the oven, assembled, and cooled using a drying tube containing anhydrous calcium sulfate to remove water adsorption. A dried stir bar was added, the system was purged with nitrogen, and the joints were sealed with silicone grease. Methylene chloride (40 mL), pyridine (1.83 mL, 22.7 mmol), and α, α,α',α'-tetramethyl-1,4-benzenedimethanol (2.00 g, 10.3 mmol) were added under a positive nitrogen flow. A white suspension was visible in the flask. An ice water bath was placed under the flask and chlorotriisopropylsilane (4.85 mL, 22.7 mmol) was added dropwise over a 5 minute period via a syringe. The solution appeared slightly tan. The solution was allowed to stir for ninety minutes. In air, the tan solution was poured into a separatory funnel along with deionized water (20 mL). The aqueous and organic layers were separated as previously described. The aqueous layer was extracted with methylene chloride (3x10 mL). The organic layers were combined and back washed with deionized water (3x10 mL). The cloudy organic layer was dried and the solvent was removed as previously described. The product was a very pale, tan, syrupy, liquid which was allowed to stand in air. The off-white crystals, α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol, which resulted, weighed 0.71 g (13.7% yield, 1.41 mmol).

The following data was obtained on compound **3**: ^{1}H NMR ($CDCl_3$); δ 1.06 ppm (s, [$CH(C\underline{H}_3)_2$]), 1.26 ppm (m, [$C\underline{H}(CH_3)_2$]), 1.60 ppm (s, 12H, $C(C\underline{H}_3)_2$), 7.48 ppm (s, 4H, ArC$\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 13.17 ppm ($\underline{C}H(CH_3)_2$), 31.29 ppm ($C(\underline{C}H_3)_2$), 72.36 ppm ($\underline{C}(CH_3)_2$), 124.78 ppm (Ar$\underline{C}$H), 148.55 ppm (Ar$\underline{C}$).

Preparation of Poly[dimethylsiloxane-co-(α,α,α',α'-tetramethyl-O,O'-1,4-benzenedimethanol)] triethylsiloxy terminated (4, 5, and 6)

The synthesis of compound **4** is used as the example for the preparation of the three polysiloxanes with varying molecular weights (compounds **4, 5, and 6**). The amount of reagents used for **4, 5,** and **6** are shown in Table 2.1.2. The experimental apparatus, a three necked 300 mL RB flask was equipped with a gas inlet and a suba seal® which was removed from the oven, assembled, and cooled using a drying tube containing anhydrous calcium sulfate to remove adsorbed water. A dried stir bar was added, the system was purged with nitrogen, and the joints were sealed with silicone grease. Methylene chloride (150 mL), pyridine (9.24 mL, 114. mmol), and α,α,α',α'-tetramethyl-1,4-benzenedimethanol (10.0 g, 51.5 mmol) were added under a positive flow of N_2 as

Table 2.1.2. Relative ratios of reactants for triethylsilyl terminated polysiloxanes

Compound	Dichlorodimethylsilane	Chlorotriethylsilane	Bifunctional alcohol
4	6.234 mL/51.40 mmol	0.0076 mL/0.045 mmol	10.0 g/51.50 mmol
5	6.238 mL/51.43 mmol	0.0051 mL/0.030 mmol	10.0 g/51.50 mmol
6	6.241 mL/51.45 mmol	0.0038 mL/0.023 mmol	10.0 g/51.50 mmol

seen through the mineral oil bubbler. A white suspension was visible as the solution was mechanically stirred. An ice water bath was placed under the flask. Dichlorodimethylsilane (6.23 mL, 51.4 mmol) was slowly added dropwise through the suba seal® via a syringe. During the addition, the formation of hydrogen chloride gas was visible and it was flushed from the reaction vessel with the flow of N_2. The solution was allowed to react for fortyfive minutes and appeared to have a slight pink tint. Chlorotriethylsilane (0.00759 mL, 0.0452 mmol) was added dropwise through the suba seal® with a syringe to terminate the polymerization. The solution now appeared tan in color, and was allowed to stir for two hours. In air, the tan solution was poured into a separatory funnel along with deionized water (100 mL). The aqueous and organic layers were separated as previously described. The aqueous layer was extracted with methylene chloride (3x50 mL). The organic layers were combined and back washed with deionized water (3x50 mL). The cloudy organic layer was dried and the solvent was removed as previously described. The product was a tan crystalline solid with traces of solvent remaining. The product was allowed to air dry. The resulting tan solid, poly[dimethylsiloxane-co-(α,α,α',α'-tetramethyl-O,O'-1,4-benzenedimethanol)], weighed 11.0 g (85.3% yield, 0.0876 mmol). The yields of compounds **4**, **5**, and **6** are found in Table 2.1.3. Refer to Table 2.1.4 for viscosity data.

The following data was obtained on compound **4**: ^{1}H NMR ($CDCl_3$); δ 0.073 ppm (s, 6H, $Si(C\underline{H}_3)_2$), 0.56 ppm (q, $CH_2C\underline{H}_3$), 0.58 ppm (q, $CH_2C\underline{H}_3$), 0.60 ppm (q, $CH_2C\underline{H}_3$), 0.62 ppm (q, $CH_2C\underline{H}_3$), 0.95 ppm (t, $C\underline{H}_2CH_3$), 0.97 ppm (t, $C\underline{H}_2CH_3$), 0.0988 ppm (t, $C\underline{H}_2CH_3$), 1.63 ppm (s, 12H, $C(C\underline{H}_3)_2$), 7.38 ppm (s, 4H, $ArC\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 2.48 ppm ($Si(\underline{C}H_3)_2$), 32.43 ppm ($C(\underline{C}H_3)_2$), 75.43 ppm ($\underline{C}(CH_3)_2$), 124.23 ppm ($Ar\underline{C}H$), 147.93 ppm ($Ar\underline{C}$). The integration ratio per hydrogen of the terminating triethylsilyl protons to the polymerizing dimethylsilyl protons was $1.3x10^{-2}$ to 5.0.

Table 2.1.3. Yields for the triethylsilyl terminated polysiloxanes, compounds **4-6**.

Compound	Weight (g)	mmol	% Yield
4	0.71	1.41	13.7
5	11.0	0.0876	85.3
6	12.5	0.0685	97.0

Table 2.1.4. Viscometry raw data for triethylsilyl terminated polysiloxanes (**4**, **5**, and **6**)

Time (seconds)

	Concentration (g/100mL)			
Compound	0.10	0.33	0.50	1.00
4	59.52	60.13	60.70	62.50
5	60.02	61.02	61.45	62.87
6	59.54	59.97	60.63	61.64

with t_0=58.80

The following data was obtained on compound **5**: ^1H NMR ($CDCl_3$); δ 0.074 ppm (s, 6H, $Si(C\underline{H}_3)_2$), 0.56 ppm (q, $CH_2C\underline{H}_3$), 0.58 ppm (q, $CH_2C\underline{H}_3$), 0.60 ppm (q, $CH_2C\underline{H}_3$), 0.62 ppm (q, $CH_2C\underline{H}_3$), 0.95 ppm (t, $CH_2C\underline{H}_3$), 0.97 ppm (t, $CH_2C\underline{H}_3$), 0.099 ppm (t, $CH_2C\underline{H}_3$), 1.63 ppm (s, 12H, $C(C\underline{H}_3)_2$), 7.38 ppm (s, 4H, $ArC\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 2.48 ppm ($Si(\underline{C}H_3)_2$), 32.43 ppm ($C(\underline{C}H_3)_2$), 75.43 ppm ($\underline{C}(CH_3)_2$), 124.23 ppm ($Ar\underline{C}H$), 147.94 ppm ($Ar\underline{C}$). The integration ratio per hydrogen of the terminating triethylsilyl protons to the polymerizing dimethylsilyl protons was 9.5×10^{-3} to 4.2.

The following data was obtained on compound **6**: ^1H NMR ($CDCl_3$); δ 0.075 ppm (s, 6H, $Si(C\underline{H}_3)_2$), 0.57 ppm (q, $C\underline{H}_2CH_3$), 0.59 ppm (q, $C\underline{H}_2CH_3$), 0.60 ppm (q, $C\underline{H}_2CH_3$), 0.63 ppm (q, $C\underline{H}_2CH_3$), 0.95 ppm (t, $CH_2C\underline{H}_3$), 0.97 ppm (t, $CH_2C\underline{H}_3$), 0.099 ppm (t, $CH_2C\underline{H}_3$), 1.63 ppm (s, 12H, $C(C\underline{H}_3)_2$), 7.38 ppm (s, 4H, $ArC\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 2.48 ppm ($Si(\underline{C}H_3)_2$), 32.42 ppm ($C(\underline{C}H_3)_2$), 75.43 ppm ($\underline{C}(CH_3)_2$), 124.23 ppm ($Ar\underline{C}H$), 147.93 ppm ($Ar\underline{C}$). The integration ratio per hydrogen of the terminating triethylsilyl protons to the polymerizing dimethylsilyl protons was 4.8×10^{-3} to 4.0.

Preparation of Poly[dimethylsiloxane-co-(α,α,α',α'-tetramethyl-O,O'-1,4-benzene-dimethanol)] triisopropylsiloxy terminated (7, 8, and 9)

The synthesis of compound **7** is used as the example for the preparation of the three polysiloxanes with varying molecular weight (compounds **7, 8,** and **9**). The amount of reagents used for **7, 8,** and **9** are shown in Table 2.1.5. The experimental apparatus, a three necked 100 mL RB flask was equipped with a gas inlet and a suba seal® which was removed from the oven, assembled, and cooled using a drying tube containing anhydrous calcium sulfate to remove adsorbed water. A dried stir bar was added, the system was purged with nitrogen, and the joints were sealed with silicone grease. Methylene chloride (50 mL), pyridine (9.25 mL, 0.0073 mmol), and α,α,α',α'-tetramethyl-1,4-benzene-

Table 2.1.5. Relative ratios of reactants for triisopropylsilyl terminated polysiloxanes

Compound	Dichlorodimethylsilane	Chlorotriisopropylsilane	Bifunctional alcohol
7	1.24 mL/10.26 mmol	1.9×10^{-3} mL/0.0090 mmol	2.00 g/10.28 mmol
8	1.25 mL/10.27 mmol	1.3×10^{-3} mL/0.0060 mmol	2.00 g/10.28 mmol
9	1.25 mL/10.27 mmol	9.7×10^{-4} mL/0.0045 mmol	2.00 g/10.28 mmol

dimethanol (2.00 g, 10.3 mmol) were added under a positive flow of N_2 as seen through the mineral oil bubbler. A white suspension was visible as the solution was mechanically stirred. An ice water bath was placed under the flask. Dichlorodimethylsilane (1.24 mL, 10.3 mmol) was slowly added dropwise through the suba seal® via a syringe. The solution was allowed to react for fortyfive minutes and appeared to have a slight tan tint. Chlorotriisopropylsilane (0.0019 mL, 0.0090 mmol) was added dropwise through the suba seal® with a syringe to terminate the polymerization. The solution now appeared tan in color, and was allowed to stir for two hours. In air, the tan solution was poured into a separatory funnel along with deionized water (20 mL). The aqueous and organic layers were separated as previously described. The aqueous layer was extracted with methylene chloride (3x10 mL). The organic layers were combined and back washed with deionized water (3x10 mL). The cloudy organic layer was dried and the solvent was removed as previously described. The tan product was rotary evaporated to remove the solvent, but as with the other compounds synthesized, some solvent remained. The products (**7, 8,** and **9**) were allowed to sit and air dry. Unlike compounds **4, 5,** and **6** and after more than 27 days, the final products were tan colored crystalline solids with traces of liquid still present. The product, poly[dimethylsiloxane-co-($\alpha,\alpha,\alpha',\alpha'$-tetramethyl-O,O'-1,4-benzenedimethanol)] weighed 0.80 g (31.0% yield, 0.00636 mmol). The yields of compounds **7, 8,** and **9** are found in Table 2.1.6. Refer to Table 2.1.7 for viscosity data.

The following data was obtained on compound **7**: ^{1}H NMR ($CDCl_3$); δ 0.081 ppm (s, 6H, $Si(C\underline{H}_3)_2$), 1.06 ppm (s, $[CH(C\underline{H}_3)_2]$), 1.24 ppm (m, $[C\underline{H}(CH_3)_2]$), 7.45 ppm (s, 4H, $ArC\underline{H}$). The integration ratio per hydrogen of the terminating triisopropylsilyl protons to the polymerizing dimethylsilyl protons was 5.2×10^{-2} to 2.0. ^{13}C NMR ($CDCl_3$); δ 28.22 ppm ($C(\underline{C}H_3)_2$), 125.81 ppm ($Ar\underline{C}H$), 143.51 ppm ($Ar\underline{C}$). The following are additional peaks obtained on compound **7**: ^{1}H NMR ($CDCl_3$); δ 2.17 ppm (8H), 5.10 ppm (2H), 5.40 ppm (2H). ^{13}C NMR ($CDCl_3$); δ 0.26 ppm, 21.18 ppm, 112.58 ppm, 140.89 ppm.

Table 2.1.6. Yields for triisopropylsilyl terminated polysiloxanes, compounds **7-9**.

Compound	Weight (g)	mmol	% Yield
7	0.80	0.00636	31.0
8	1.18	0.00627	45.7
9	1.30	0.00518	50.4

Table 2.1.7. Viscometry raw data for triisopropylsilyl terminated polysiloxanes (compounds **7-9**)

Time (seconds)

	Concentration (g/100mL)			
Compound	0.10	0.33	0.50	1.00
7	58.98	59.81	59.45	60.31
8	59.91	60.02	60.54	61.41
9	59.47	60.49	60.93	60.74

with t_o=58.80

The following data was obtained on compound **8**: ^{1}H NMR ($\mathrm{CDCl_3}$); δ 0.076 ppm (s, 4H, $\mathrm{Si(C\underline{H}_3)_2}$), 1.05 ppm (s, $\mathrm{[CH(C\underline{H}_3)_2]}$), 1.60 ppm (s, 3H, $\mathrm{C(C\underline{H}_3)_2}$), 7.45 ppm (s, 4H, $\mathrm{ArC\underline{H}}$). The integration ratio per hydrogen of the terminating triisopropylsilyl protons to the polymerizing dimethylsilyl protons was $5.0\mathrm{x}10^{-2}$ to 2.5. ^{13}C NMR ($\mathrm{CDCl_3}$); δ 33.78 ppm ($\mathrm{C(\underline{C}H_3)_2}$), 125.81 ppm ($\mathrm{Ar\underline{C}H}$), 143.50 ppm ($\mathrm{Ar\underline{C}}$). The following are additional peaks obtained on compound **8**: ^{1}H NMR ($\mathrm{CDCl_3}$); δ 2.01 ppm, 2.16 ppm (6H), 5.09 ppm (2H), and 5.40 ppm (2H). ^{13}C NMR ($\mathrm{CDCl_3}$); δ 0.26 ppm, 21.18 ppm, 112.59 ppm, and 140.89 ppm.

The following data was obtained on compound **9**: ^{1}H NMR ($\mathrm{CDCl_3}$); δ 0.07 ppm (s, 2H, $\mathrm{Si(C\underline{H}_3)_2}$), 1.05 ppm (s, $\mathrm{[CH(C\underline{H}_3)_2]}$), 1.24 ppm (m, $\mathrm{[C\underline{H}(CH_3)_2]}$), 1.56 ppm (s, 2H, $\mathrm{C(C\underline{H}_3)_2}$), 7.45 ppm (s, 2H, $\mathrm{ArC\underline{H}}$). The integration ratio per hydrogen of the terminating triisopropylsilyl protons to the polymerizing dimethylsilyl protons was $6.2\mathrm{x}10^{-3}$ to 2.7. ^{13}C NMR ($\mathrm{CDCl_3}$); δ 33.78 ppm ($\mathrm{C(\underline{C}H_3)_2}$), 76.48 ppm ($\mathrm{\underline{C}(CH_3)_2}$), 125.81 ppm ($\mathrm{Ar\underline{C}H}$), 143.50 ppm ($\mathrm{Ar\underline{C}}$). The following are additional peaks obtained on compound **9**: ^{1}H NMR ($\mathrm{CDCl_3}$); δ 2.16 ppm (2H), 5.09 ppm (2H), and 5.40 ppm (2H). ^{13}C NMR ($\mathrm{CDCl_3}$); δ 21.18 ppm, 28.22 ppm, 112.59 ppm, and 140.89 ppm. ^{13}C NMR ($\mathrm{CDCl_3}$); δ 33.78 ppm ($\mathrm{C(\underline{C}H_3)_2}$), 125.81 ppm ($\mathrm{Ar\underline{C}H}$), 143.50 ppm ($\mathrm{Ar\underline{C}}$).

Chapter Two

Synthesis and Characterization of the Tricarbonylchromium Complexes and Model Compounds

Preparation of (η^6-α,α,α',α'-tetramethyl-1,4-benzene-dimethanol)chromium-tricarbonyl (10)

The experimental apparatus, a three necked 300 mL RB flask under nitrogen was equipped with a gas inlet, a stopper, and a suba seal® (Figure 2.2.1) which was removed from the oven, assembled, and cooled to remove water adsorption. A dried stir bar was added, the system was purged with nitrogen, and the joints were sealed with silicone grease. A heating mantle was attached to a variac and a stir plate was placed beneath the round bottom flask. Bu_2O (150 mL) and THF (17 mL) were added to the round bottom, then the solution was deaerated for 10 minutes with N_2 gas. The solids α,α,α',α'-tetramethyl-1,4-benzenedimethanol (5.00 g, 25.7 mmol) and chromium hexacarbonyl (6.00 g, 27.0 mmol) were added. The stopper was replaced with an air condenser and the suba seal® was replaced with the stopper under positive gas flow. The solution was heated with the variac set at 45% to produce a mild reflux. After 20 minutes the solution turned yellow and colorless crystals sublimed onto the side of the flask. After 26 hours, the heating mantle was removed and the solution was allowed to cool under nitrogen. The solution was brown-gold with no crystals on side. Two-thirds of the solvent was removed in vacuo which produced yellow crystals in the flask. The flask was placed under N_2 and placed in the freezer for 72 hours. The flask containing a green solution with yellow crystals was removed from the freezer. The crystals were collected by suction filtration in air. They were washed with cold hexanes (2x15 mL). The crude yellow product, (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl, 10, with a slight green tinge weighed 5.45 g (64.1% yield, 16.5 mmol).

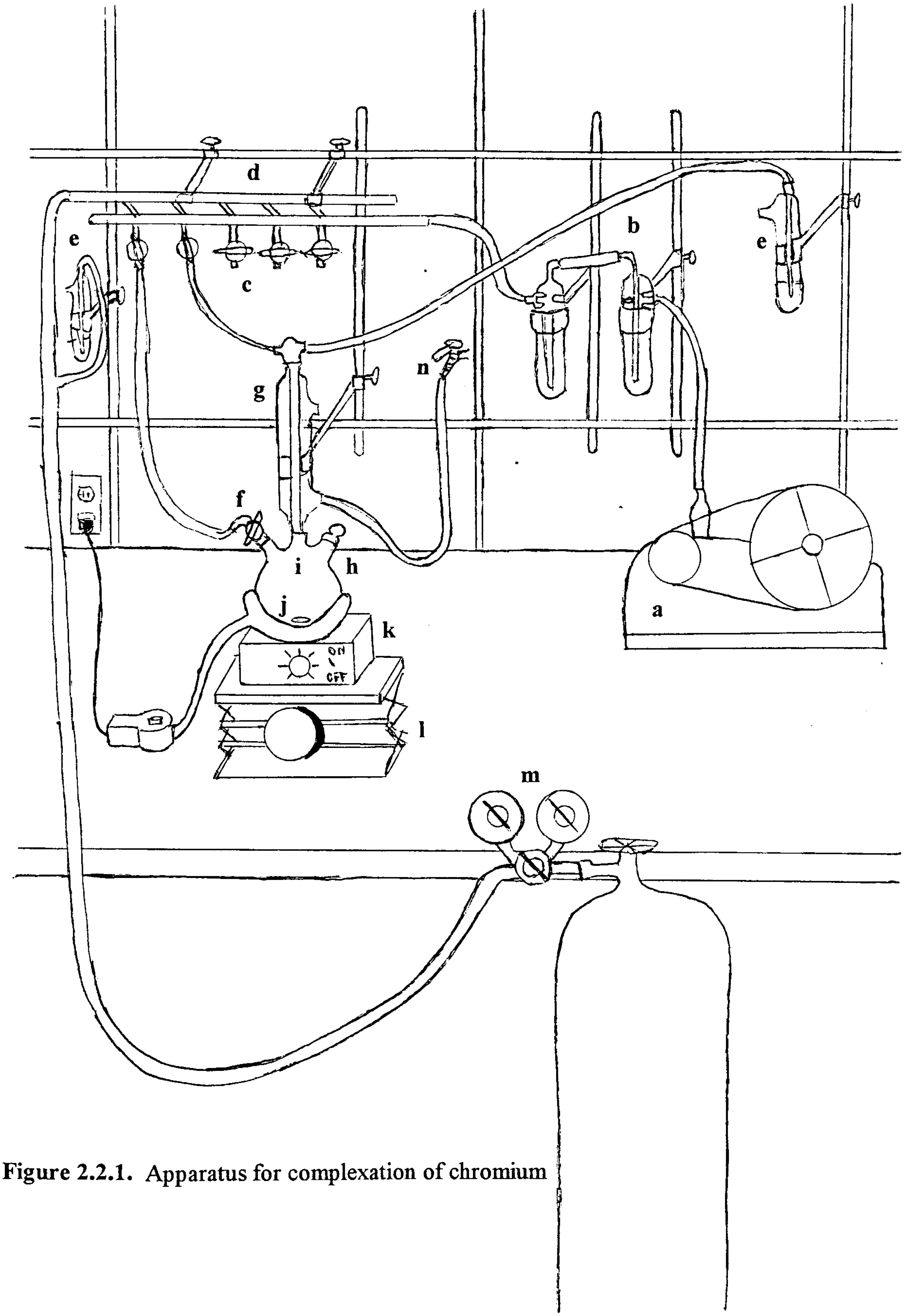


Figure 2.2.1. Apparatus for complexation of chromium

Table 2.2.1. Parts of apparatus for complexation of chromium

a	vacuum pump
b	cold traps
c	stopcock
d	manifold
e	mineral oil bubbler
f	stopcock
g	air condenser
h	stopper
i	3-necked RB
j	stir bar
k	stir plate
l	adjustable jack
m	regulator
n	air jet

The yellow-green crystals were recrystallized in a schlenk tube using deaerated CH_2Cl_2 (20 mL) to dissolve them. Deaerated hexanes (20 mL) were carefully dispensed down the side of the tube, thus forming two layers. The tube was put under N_2 and placed in the freezer for nine days. The yellow crystalline solid was suction filtered and washed with cold hexanes (2x15 mL).[19,24] The purified yellow crystalline solid of (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl were placed in clean schlenk tube under N_2. The crystals weighed 2.10 g (38.6% recovery, 6.36 mmol).

The following data was obtained on compound 10: ^1H NMR ($CDCl_3$); δ 1.57 ppm (s, 12H, C(C$\underline{H}_3$)$_2$), 1.83 ppm (s, 2H, O$\underline{H}$), 5.59 ppm (s, 4H, Cr-ArC$\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 31.38 ppm (C($\underline{C}H_3$)$_2$), 71.32 ppm ($\underline{C}$(CH_3)$_2$), 90.17 ppm (Cr-Ar$\underline{C}$H), 122.45 (Cr-Ar$\underline{C}$), 269.25 ppm ($\underline{C}$O). IR (THF, cm^{-1}) ν_{CO} = 1883, 1962.

Preparation of (η^6-α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl (11)

The experimental apparatus, a three necked 100 mL RB flask was equipped with a gas inlet and a suba seal® which was removed from the oven, assembled, and cooled using a drying tube containing anhydrous calcium sulfate to remove adsorbed water. A dried stir bar was added, the system was purged with nitrogen, and the joints were sealed with silicone grease. Methylene chloride (25 mL) and (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl (1.00 g, 0.30 mmol) were added to the flask under a positive flow of N_2. Dried pyridine (0.54 mL, 0.66 mmol) was added through the suba seal® using a syringe. An ice water bath was placed under the flask and chlorotriisopropylsilane (1.42 mL, 0.66 mmol) was added dropwise over an 8 minute period. The solution was allowed to stir for one hour. The solution was green with an apparent loss of volume. The green solution was poured into a separatory funnel with deionized water (15 mL). The aqueous layer was extracted with methylene chloride (3x5 mL) The organic layers were combined and back washed with deionized water (3x10 mL). The cloudy organic layer was dried over anhydrous sodium sulfate for one hour. The drying agent was removed by suction filtration and washed with methylene chloride (2x10 mL). The yellow solution was placed in a schlenk tube under N_2. The solvent was removed in vacuo which produced a golden-yellow slimy looking product and the tube was placed under N_2. The yellow product, (η^6-α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl, weighed 0.98 g (63.9% yield, 1.93 mmol).

The following data was obtained on compound **11**: ^{1}H NMR ($CDCl_3$); δ 1.09 ppm (d, [CH(C$\underline{H}_3$)$_2$]), 1.23 ppm (m, [C$\underline{H}$(CH$_3$)$_2$]), 1.57 ppm (s, 12H, C(C$\underline{H}_3$)$_2$), 5.57 ppm (s, Cr-ArC$\underline{H}$). ^{13}C NMR ($CDCl_3$); δ 13.05 ppm ($\underline{C}$H(CH$_3$)$_2$), 17.09 ppm (CH($\underline{C}$H$_3$)$_2$), 31.00 ppm (C($\underline{C}$H$_3$)$_2$), 70.79 ppm ($\underline{C}$(CH$_3$)$_2$), 90.06 ppm (Cr-Ar$\underline{C}$H), 124.26 ppm (Cr-Ar$\underline{C}$), 234.34 ppm ($\underline{C}$O). IR (THF, cm^{-1}) ν_{co} = 1892, 1964.

Preparation for Poly[dimethylsiloxane-co-((η^6-α,α,α',α'-tetramethyl-O,O'-1,4-benzenedimethanol)chromiumtricarbonyl)] triisopropylsilyl terminated (12, 13, and 14)

The synthesis of compound **12** is used as the example for the preparation of the three chromium complexed polysiloxanes with varying molecular weight (compounds **12, 13,** and **14**). The amount of reagents used for **12, 13,** and **14** are shown in Table 2.2.2. The experimental apparatus, a three necked 100 mL RB flask was equipped with a gas inlet and a suba seal® which was removed from the oven, assembled, and cooled using a drying tube containing anhydrous calcium sulfate to remove adsorbed water. A dried stir bar was added, the system was purged with nitrogen, and the joints were sealed with silicone grease. Methylene chloride (50 mL), pyridine (0.49 mL, 6.10 mmol), and (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl (2.00 g, 6.06 mmol) were added under a positive flow of N_2 as seen through the mineral oil bubbler. An ice water bath was placed under the flask. Dichlorodimethylsilane (0.73 mL, 6.04 mmol) was

Table 2.2.2. Relative ratios of reactants for chromium complexed polysiloxanes

Compound	Dichlorodimethylsilane	Chlorotriisopropylsilane	Bifunctional alcohol
12	0.733 mL/6.04 mmol	0.00114 mL/0.00532 mmol	2.00 g/6.06 mmol
13	0.734 mL/6.05 mmol	0.00759 mL/0.00355 mmol	2.00 g/6.06 mmol
14	0.734 mL/6.05 mmol	0.00570 mL/0.00266 mmol	2.00 g/6.06 mmol

slowly added dropwise through the suba seal® via a syringe. The yellow solution was allowed to react for fiftysix minutes. Chlorotriisopropylsilane (0.0011 mL, 0.0053 mmol) was added dropwise through the suba seal® with a syringe to terminate the polymerization. The solution was allowed to stir for ninetysix minutes. The yellow solution was poured into a separatory funnel with deionized water (15 mL). The aqueous layer was extracted with methylene chloride (3x5 mL) The organic layers were combined and back washed with deionized water (3x10 mL). The cloudy organic layer was dried over anhydrous sodium sulfate for one hour. The drying agent was removed by suction filtration and washed with methylene chloride (2x10 mL). The yellow solution was placed in schlenk tube under N_2. The solvent was removed in vacuo which produced a yellow product. The tube was placed under N_2. The product, poly[dimethylsiloxane-co-((η^6-α, α,α',α'-tetramethyl-O,O'-1,4-benzenedimethanol)-chromiumtricarbonyl)], weighed 1.73 g (73.6% yield). The yields of compounds **12-14** are found in Table 2.2.3. Refer to Table 2.2.4 for viscosity data.

The following data was obtained on compound **12**: ^{1}H NMR ($CDCl_3$); δ 0.08 ppm (s, 6H, Si(C$\underline{H}_3$)$_2$), 1.05 ppm (s, [CH(C$\underline{H}_3$)$_2$]), 1.25 ppm (m, [C$\underline{H}$(CH$_3$)$_2$]), 1.57 ppm (s, 12H, C(C$\underline{H}_3$)$_2$), 5.31 ppm (s, 1H, Cr-ArC$\underline{H}$), 5.59 ppm (s, 3H, Cr-ArC$\underline{H}$). The integration ratio per hydrogen of the terminating triisopropylsilyl protons to the polymerizing dimethylsilyl protons was $1.2x10^{-2}$ to 2.0. ^{13}C NMR ($CDCl_3$); δ 12.13 ppm ($\underline{C}$H(CH$_3$)$_2$), 16.72 ppm (CH($\underline{C}$H$_3$)$_2$), 30.92 ppm (C($\underline{C}$H$_3$)$_2$), 70.70 ppm ($\underline{C}$(CH$_3$)$_2$), 90.31 ppm (Cr-Ar$\underline{C}$H), 122.29 ppm (Cr-Ar$\underline{C}$), 235.18 ppm ($\underline{C}$O). IR (THF, cm^{-1}) ν_{co} = 1883, 1961.

The following data was obtained on compound **13**: ^{1}H NMR ($CDCl_3$); δ 0.07 ppm (s, 3H, Si(C$\underline{H}_3$)$_2$), 1.05 ppm (s, [CH(C$\underline{H}_3$)$_2$]), 1.25 ppm (m, [C$\underline{H}$(CH$_3$)$_2$]), 1.57 ppm (s, 12H, C(C$\underline{H}_3$)), 5.59 ppm (s, 4H, Cr-ArC$\underline{H}$). The integration ratio per hydrogen of the terminating triisopropylsilyl protons to the polymerizing dimethylsilyl protons was $4.8x10^{-3}$ to 5.0. ^{13}C NMR ($CDCl_3$); δ 12.40 ppm ($\underline{C}$H(CH$_3$)$_2$), 16.82 ppm

Table **2.2.3.** Yields for the chromium complexed siloxane compounds **12-14**.

Compound	Weight (g)	mmol	% Yield
12	1.73	0.00892	73.6
13	2.02	0.00695	86.0
14	2.12	0.00548	90.0

Table 2.2.4. Viscometry raw data for chromium complexed polysiloxanes

Time (seconds)(30.0°C)

	Concentration (g/100mL)			
Compound	0.10	0.33	0.50	1.00
12	56.92	56.98	57.16	58.63
13	57.44	57.24	58.16	59.73
14	57.53	58.01	58.08	59.08

with t_0=57.31

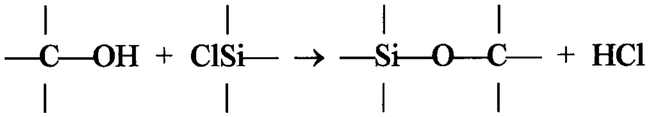
$(CH(\underline{C}H_3)_2)$, 30.92 ppm $(C(\underline{C}H_3)_2)$, 70.70 ppm $(\underline{C}(CH_3)_2)$, 90.31 ppm (Cr-Ar$\underline{C}$H), 122.80 ppm (Cr-Ar$\underline{C}$), 235.16 ppm ($\underline{C}$O). IR (THF, cm^{-1}) ν_{CO} = 1884, 1960.

The following data was obtained on compound **14**: ^1H NMR ($CDCl_3$); δ 0.07 ppm (s, 3H, $Si(C\underline{H}_3)_2$), 1.05 ppm (s, $[CH(C\underline{H}_3)_2]$), 1.25 ppm (m, $[C\underline{H}(CH_3)_2]$), 1.57 ppm (s, 12H, $C(C\underline{H}_3)_2$), 5.59 ppm (s, 4H, Cr-ArC$\underline{H}$). The integration ratio per hydrogen of the terminating triisopropylsilyl protons to the polymerizing dimethylsilyl protons was 4.8×10^{-3} to 6.0. ^{13}C NMR ($CDCl_3$); δ 7.88 ppm $(\underline{C}H(CH_3)_2)$, 10.03 ppm $(CH(\underline{C}H_3)_2)$, 30.94 ppm $(C(\underline{C}H_3)_2)$, 70.70 ppm $(\underline{C}(CH_3)_2)$, 90.31 ppm (Cr-Ar$\underline{C}$H), 122.29 ppm (Cr-Ar$\underline{C}$), 235.16 ppm ($\underline{C}$O). IR (THF, cm^{-1}) ν_{CO} = 1883, 1961.

Part Three
Results and Discussion

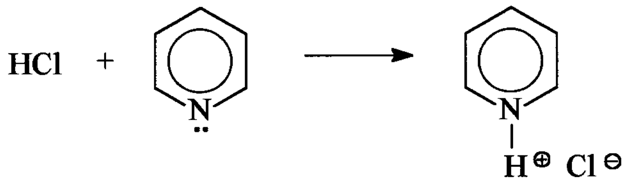
Chapter One
Synthesis and Characterization of the Polysiloxanes

The monoaromatic model compounds and the polyorganosiloxanes were prepared via condensation reactions.



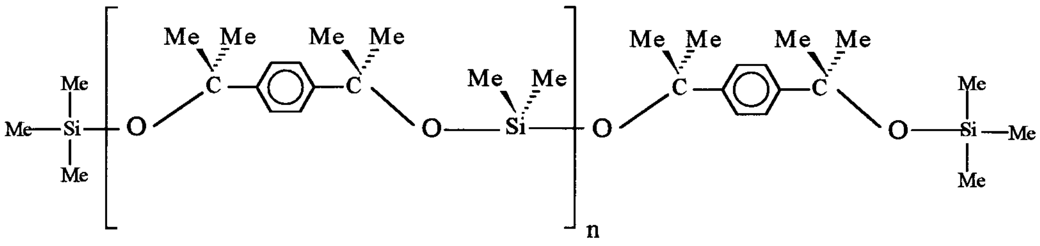
$$-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{OH} + \mathrm{Cl}\overset{|}{\underset{|}{\mathrm{Si}}}- \rightarrow -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{C}}}- + \mathrm{HCl} \qquad (3.1.1)$$

Hydrochloric acid is produced as a by product in these reactions. HCl can cleave Si-O bonds and can catalyze various siloxane rearrangement reactions.[12] A base such as pyridine is, therefore, added to capture free HCl.



(3.1.2)

Pilot syntheses using trimethylsilyl end groups resulted in products which displayed too much overlap between the methyl protons of the end groups and those on the repeating units in their ^{1}H NMR spectra.



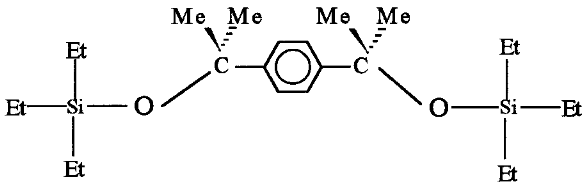
Chlorotriethylsilane was then examined as a terminating group. The ^1H NMR spectra of the triethylsilyl terminated polymers seemed to display appropriate spectra for the compounds. The ^1H NMR spectra of the hexaethyldisiloxane I prepared was used as a reference for the end groups of these polymers. This spectra, however, showed overlap of the methylene and methyl protons of the ethyl groups in different environments, implying a possible impurity. As a result, chlorotriisopropylsilane was chosen as the terminating group. The ^1H NMR spectra of the hexaisopropyldisiloxane I prepared were consistent with spectra in the *Aldrich Library of ^{13}C and ^1H FT NMR Spectra.*[18] The polymers prepared using chlorotrimethylsilane and chlorotriethylsilane were tan opaque solids, while the tan colored materials prepared using chlorotriisopropylsilane were more crystalline in appearance. Since the physical appearances were different, both the triisopropylsilyl terminated models and polymers and the triethylsilyl terminated models and polymers were characterized.

Synthesis and characterization of α,α,α',α'-tetramethyl-O,O'-bistriethylsiloxy-1,4-benzenedimethanol (2)

The siloxane model compound, α,α,α',α'-tetramethyl-O,O'-bistriethylsiloxy-1,4-benzenedimethanol, was prepared by adding pyridine and then chlorotriethylsilane to α,α, α',α'-tetramethyl-1,4-benzenedimethanol in methylene chloride.

$$1,4\text{-}C_6H_4(CMe_2OH)_2 + 2\,Et_3SiCl + 2\,\text{pyridine} \rightarrow$$

(3.1.3)

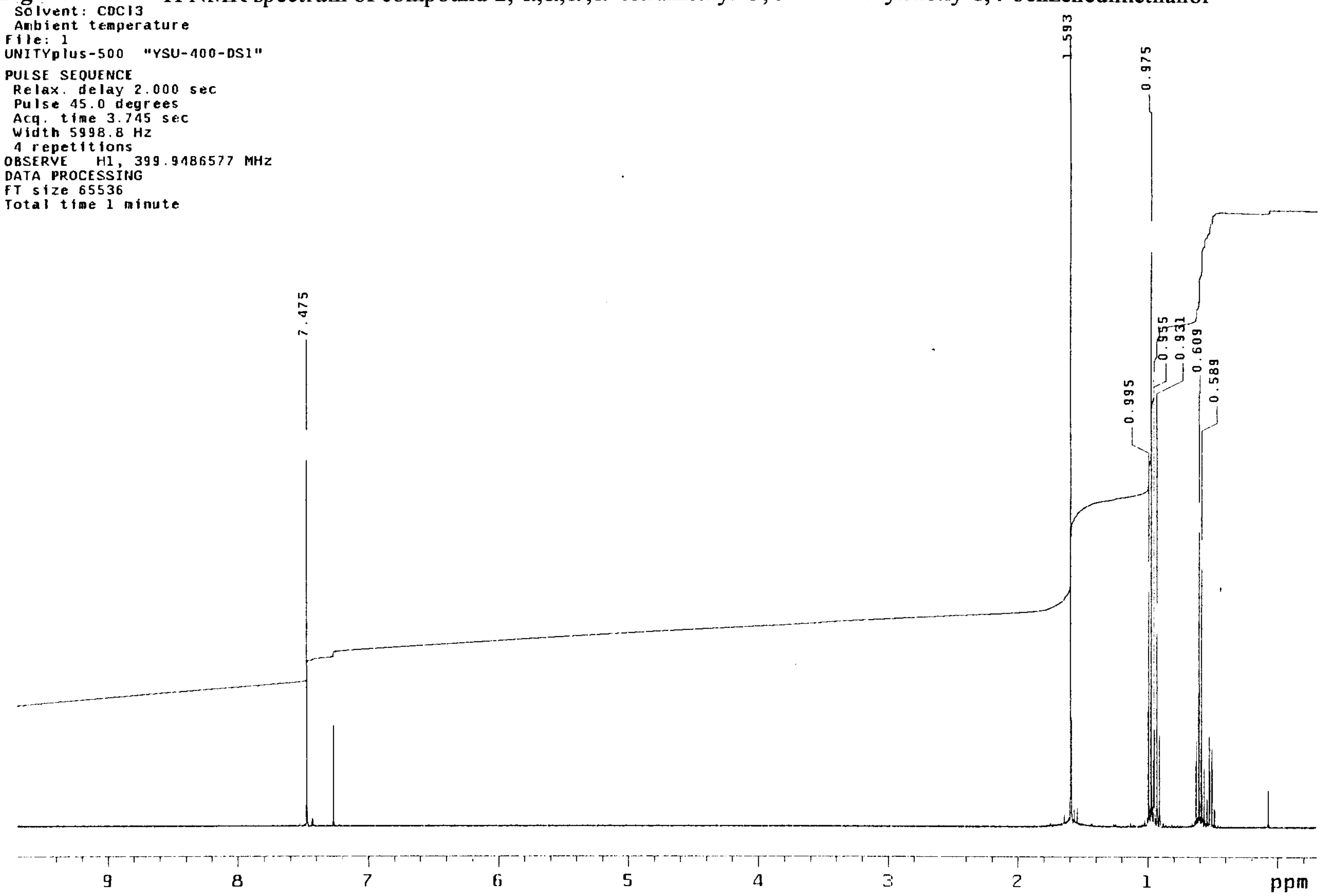


+ 2 pyridine·HCl

The presence of pyridine shifted reaction 3.1.1 to the right. A 10% excess of pyridine and chlorotriethylsilane were used to ensure conversion to the starting diol. In this and subsequent silicone syntheses, an ice water bath was placed under the flask to aid in the regulation of temperature since the reaction was exothermic. The resulting tan solution was allowed to react for thirty minutes. The organic and aqueous phases of the tan solution were separated and the organic phase was dried as described in the experimental section. The resulting organic solution was rotary evaporated to remove the solvent. The product, α,α,α',α'-tetramethyl-O,O'-bistriethylsiloxy-1,4-benzenedimethanol, was isolated as a waxy white solid.

The ^1H NMR ($CDCl_3$) spectrum of compound **2** (Figure 3.1.1) was assigned using the ^1H NMR spectra of the starting diol and hexaethyldisiloxane for comparison.[18] The quartet at 0.59 ppm was assigned to the methylene groups and the triplet at 0.98 ppm to the methyl groups of the triethyl end groups. The second quartet at 0.51 ppm and second triplet at 0.93 ppm is consistent with peaks of hexaethyldisiloxane. The singlet at 1.59 ppm was assigned to the benzylic carbon's methyl groups. The singlet at 7.48 ppm was assigned to the four equivalent aryl protons.

Figure 3.1.1. ^{1}H NMR spectrum of compound **2**, α,α,α',α'-tetramethyl-O,O'-bistriethylsiloxy-1,4-benzenedimethanol

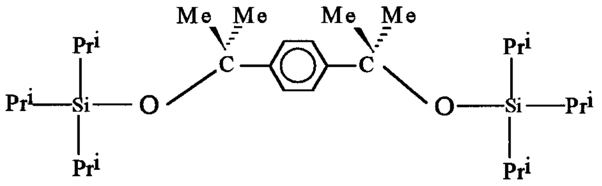


Synthesis and characterization of α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol (3)

The siloxane model compound, α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol, was prepared by adding pyridine and then chlorotriisopropylsilane to α,α,α',α'-tetramethyl-1,4-benzenedimethanol in methylene chloride. The solution reacted for thirty minutes.

$$1,4\text{-}C_6H_4(CMe_2OH)_2 + 2\ Pr^i{}_3SiCl + 2\ \text{pyridine} \rightarrow$$

(3.1.4)



$$+ \ 2\ \text{pyridine}\cdot HCl$$

The organic and aqueous phases of the tan solution were separated and the organic phase was dried as described in the experimental section. The resulting organic solution was rotary evaporated to remove most of the solvent, although traces of liquid were still present. The resulting product was then allowed to air dry. The final product, α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol, was needle-like tan crystals.

The ^1H NMR ($CDCl_3$) spectrum of compound **3** was assigned using the ^1H NMR spectra of the starting diol and hexaisopropyldisiloxane for comparison.[25] The singlet at 1.06 ppm was assigned to the methyl groups and the multiplet at 1.26 ppm to the methyne groups of the isopropyl fragments, the singlet at 1.60 ppm to the benzylic carbon's methyl groups, and the singlet at 7.48 ppm to the four equivalent aryl protons.

Synthesis and characterization for each reaction of Poly[dimethylsiloxane-co-(α,α,-α',α'-tetramethyl-O,O'-1,4-benzenedimethanol)] triethyl terminated (4, 5, and 6)

The three polysiloxanes varying in molecular weight were prepared by reacting α, α,α',α'-tetramethyl-1,4-benzenedimethanol and dichlorodimethylsilane in the appropriate ratios after the addition of pyridine in methylene chloride. The pale pink solutions reacted, with stirring, for thirty minutes.

$$\text{n}\,[1,4\text{-}C_6H_4(CMe_2OH)_2] + \text{n-1}\,[Cl_2SiMe_2] + 2(\text{n-1})\,\text{pyridine} \rightarrow \tag{3.1.5}$$

$$H\text{—}[OCMe_2\text{-}1,4\text{-}C_6H_4\text{-}CMe_2O\text{-}SiMe_2O\text{-}]_nCMe_2\text{-}1,4\text{-}C_6H_4\text{-}CMe_2O\text{—}H\ +$$

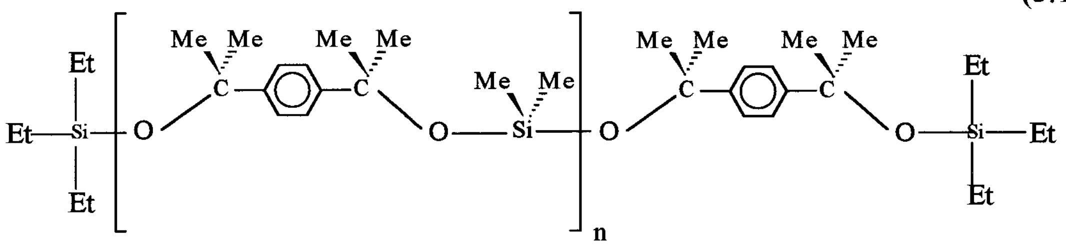
$$2(\text{n-1})\ \text{pyridine}\cdot HCl$$

Since by stoichiometry the end groups of each chain were reactive alcohols, chlorotriethylsilane was added to terminate the chain. The reagents in the reaction flask were stirred under nitrogen for sixty minutes.

$$H\text{—}[OCMe_2\text{-}1,4\text{-}C_6H_4\text{-}CMe_2O\text{-}SiMe_2O\text{-}]_nCMe_2\text{-}1,4\text{-}C_6H_4\text{-}CMe_2O\text{—}H\ + 2\ Et_3SiCl$$

$$+\ 2\ \text{pyridine} \rightarrow$$

(3.1.6)



$$+2n\ \text{pyridine}\cdot HCl$$

The overall reaction was therefore

$$n\,[1,4\text{-}C_6H_4(CMe_2OH)_2] + n\text{-}1\,[Cl_2SiMe_2] + 2n\text{ pyridine} + 2\,Et_3SiCl \rightarrow \tag{3.1.7}$$

$$Et_3Si\text{—}[OCMe_2\text{-}1,4\text{-}C_6H_4\text{-}CMe_2O\text{-}SiMe_2O\text{-}]_nCMe_2\text{-}1,4\text{-}C_6H_4\text{-}CMe_2O\text{—}SiEt_3$$
$$+\ 2n\text{ pyridine}\cdot HCl$$

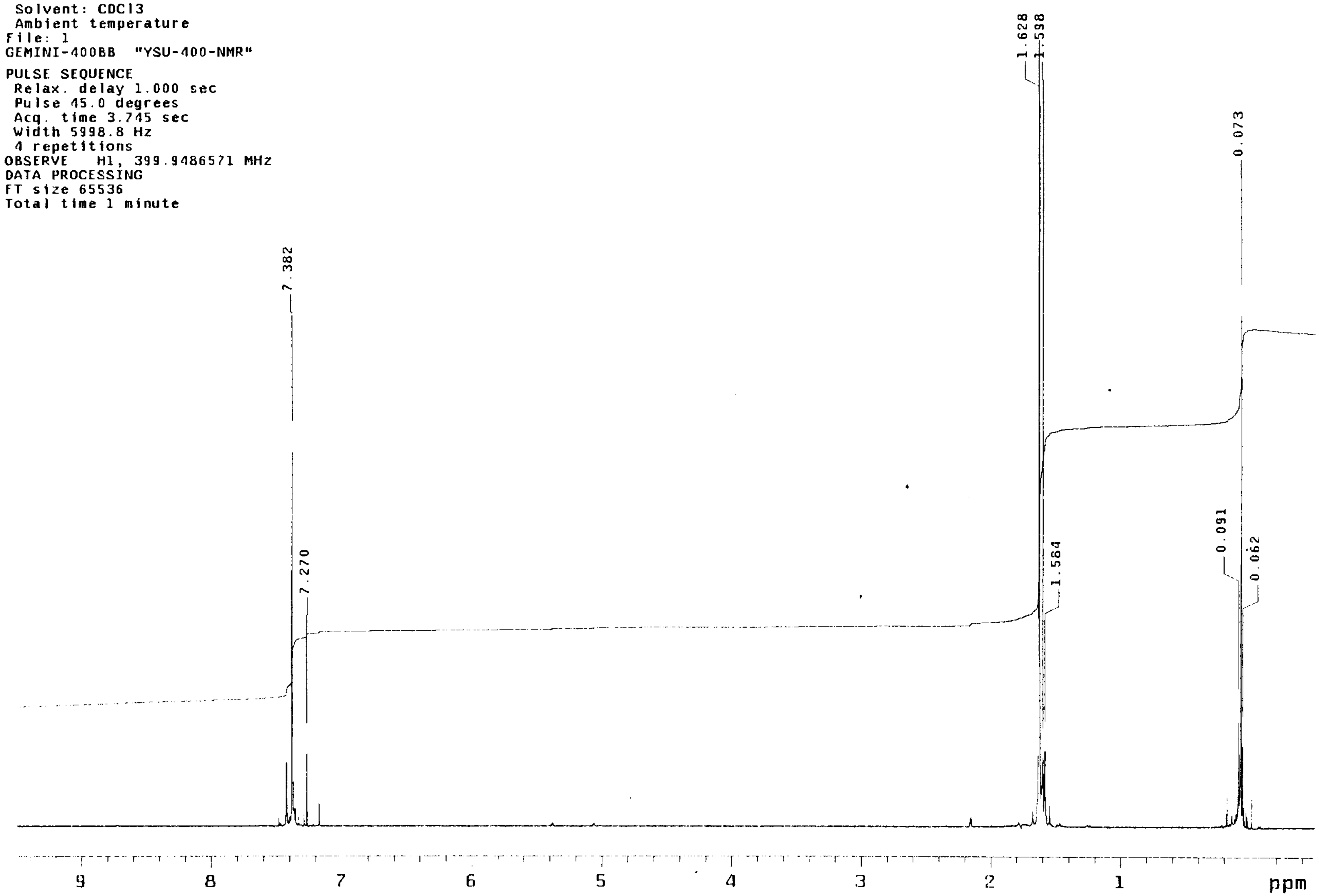
The organic and aqueous phases of the tan solution were separated and the organic phase was dried as previously described in the experimental section (i.e. H_2O/organic extraction). The resulting organic solution was rotary evaporated to remove the solvent, but as with compound **3,** not all of the solvent was removed. The products (**4, 5,** and **6**) were allowed to air dry for 7 days. The final products were tan solids which were air stable. The siloxane polymers are more air stable as solids than in solution.

The ^1H NMR ($CDCl_3$) spectra of compounds **4** (Figure 3.1.2), **5,** and **6** were assigned using the resonance frequencies of the starting diol, hexaethyldisiloxane, and compound **3** for comparison. The ^1H and ^{13}C NMR ($CDCl_3$) spectra of compounds **4, 5,** and **6** agree with the expected values from calculations based on their assigned molecular weights (Table 3.1.1). The number average molecular weights of compounds **4, 5,** and **6** were estimated from the integration ratios of the ^1H NMR spectra ($\overline{M}_{4n} \approx 9.4\times10^4$(g/mol), $\overline{M}_{5n} \approx 1.1\times10^5$(g/mol), and $\overline{M}_{6n} \approx 2.1\times10^5$(g/mol)). The viscosities of compounds **4, 5,** and **6** were determined using a Cannon-Fenske® viscometer in a 30.0°C constant temperature bath. The flow times of four dilutions with known volumes of THF were measured for each compound. Specific viscosities, η_{sp}, were plotted versus concentration to determine the intrinsic viscosities, $[\eta]$.

The estimated molecular weights of the linear polymers fall between 10^4 and 10^6. The linear relationship of the Mark-Houwink equation was assumed[28]

$$[\eta] = K\,\overline{M}_v^{\alpha} \tag{3.1.8}$$

Figure 3.1.2. ^{1}H NMR spectrum of compound 4, triethylsilyl terminated polysiloxane



```
 Solvent: CDCl3
 Ambient temperature
File: 1
GEMINI-400BB  "YSU-400-NMR"
PULSE SEQUENCE
 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 3.745 sec
 Width 5998.8 Hz
 4 repetitions
OBSERVE   H1, 399.9486571 MHz
DATA PROCESSING
FT size 65536
Total time 1 minute
```

Table 3.1.1. ^1H and ^{13}C NMR data for triethylsilyl terminated polysiloxanes (δ in ppm)

		COMPOUND		
^1H NMR Data	**Theoretical[23,28]**	**4**	**5**	**6**
$C(C\underline{H}_3)_2$	1.5	1.63(12H)	1.63(12H)	1.63(12H)
$ArC\underline{H}$	6.8-7.5	7.38(4H)	7.38(4H)	7.39((4H)
$Si(C\underline{H}_3)_2$	0.05-0.1	0.073(6H)	0.074(6H)	0.076(6H)
^{13}C NMR Data				
$Si(\underline{C}H_3)_2$	2.5	2.48	2.48	2.48
$C(\underline{C}H_3)_2$	4-40	32.43	32.43	32.42
$Ar\underline{C}H$	110-130	124.23	124.23	124.23
$\underline{C}(CH_3)_2$	55-85	75.43	75.43	75.43
$Ar\underline{C}$	120-150	147.93	147.94	147.93

where $[\eta]$ is the intrinsic viscosity, $\overline{M}_v$ is the viscosity average molecular weight, and K and α are the Mark-Houwink parameters. For each of the three samples, we can write a version of this equation.

$$[\eta_4] = K_4 \overline{M}_{v4}^{\alpha_4} \tag{3.1.9a}$$

$$[\eta_5] = K_5 \overline{M}_{v5}^{\alpha_5} \tag{3.1.9b}$$

$$[\eta_6] = K_6 \overline{M}_{v6}^{\alpha_6} \tag{3.1.9c}$$

Where $[\eta_4]$, $[\eta_5]$, and $[\eta_6]$ are the experimental intrinsic viscosities of the three polymers, $\overline{M}_{v4}$, $\overline{M}_{v5}$, and $\overline{M}_{v6}$ are their viscosity average molecular weights, and K_4, K_5, and K_6 and α_4, α_5, and α_6 are their Mark-Houwink parameters. However, since polymers **4**, **5**, and **6** are isostructural in their repeating units (i.e. only their molecular weight varies), we know that K_4, K_5, and K_6 must be equal as must α_4, α_5, and α_6:

$$K_4=K_5=K_6=K' \tag{3.1.10}$$

$$\alpha_4=\alpha_5=\alpha_6=\alpha' \tag{3.1.11}$$

where K' and α' are the Mark-Houwink parameters for this repeating unit. Equations 3.1.9a-c are therefore reduced to

$$[\eta_4] = K' \overline{M}_{v4}^{\alpha'} \tag{3.1.12a}$$

$$[\eta_5] = K' \overline{M}_{v5}^{\alpha'} \tag{3.1.12b}$$

$$[\eta_6] = K' \overline{M}_{v6}^{\alpha'} \tag{3.1.12c}$$

Since a plot of log $[\eta]$ versus log $\overline{M}_v$ is linear for linear polymers, constants K and α are the intercept and slope, respectively, as shown by equation 3.1.13.

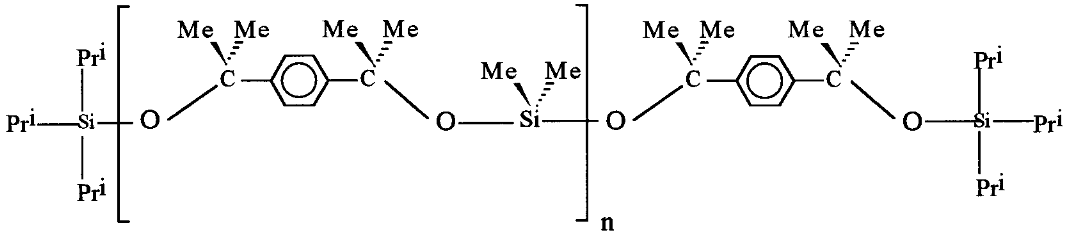
$$\log\,[\eta] = \log K + \alpha \log \overline{M}_V \qquad (3.1.13)$$

The values of K and α were initially estimated using the NMR determined values of $\overline{M}_n$ versus approximations for $\overline{M}_V$. These initial K and α values were put back into equations 3.1.12a-c with the experimental $[\eta]$ values to determine $\overline{M}_V$ for each of the three polymers. Subsequent plots of log $[\eta]$ versus these log $\overline{M}_V$ values determined new K and α values. Iterations of equations 3.1.12a-c were performed until the values went to consistancy (Figure 3.1.3). The iteratively estimated values of K and α are $2.3\text{x}10^{-5}$ and 0.76, respectively. The iteratively estimated viscosity average molecular weights are $\overline{M}_{V4}=1.0\text{x}10^5$(g/mol), $\overline{M}_{V5}=1.1\text{x}10^5$(g/mol), and $\overline{M}_{V6}=2.1\text{x}10^5$(g/mol). The NMR determined number average molecular weights are $\overline{M}_{n4}\approx 9.4\text{x}10^4$(g/mol), $\overline{M}_{n5}\approx 1.1\text{x}10^5$(g/mol), $\overline{M}_{n6}\approx 2.1\text{x}10^5$(g/mol). For compounds **5** and **6**, the $\overline{M}_n$ and $\overline{M}_V$ values are generally consistent, but for compound **4**, $\overline{M}_{n4} < \overline{M}_{V4}$.

Synthesis and characterization for each reaction of Poly[dimethylsiloxane-co-(α,α,-α',α'-tetramethyl-O,O'-1,4-benzenedimethanol)] (7, 8, and 9)

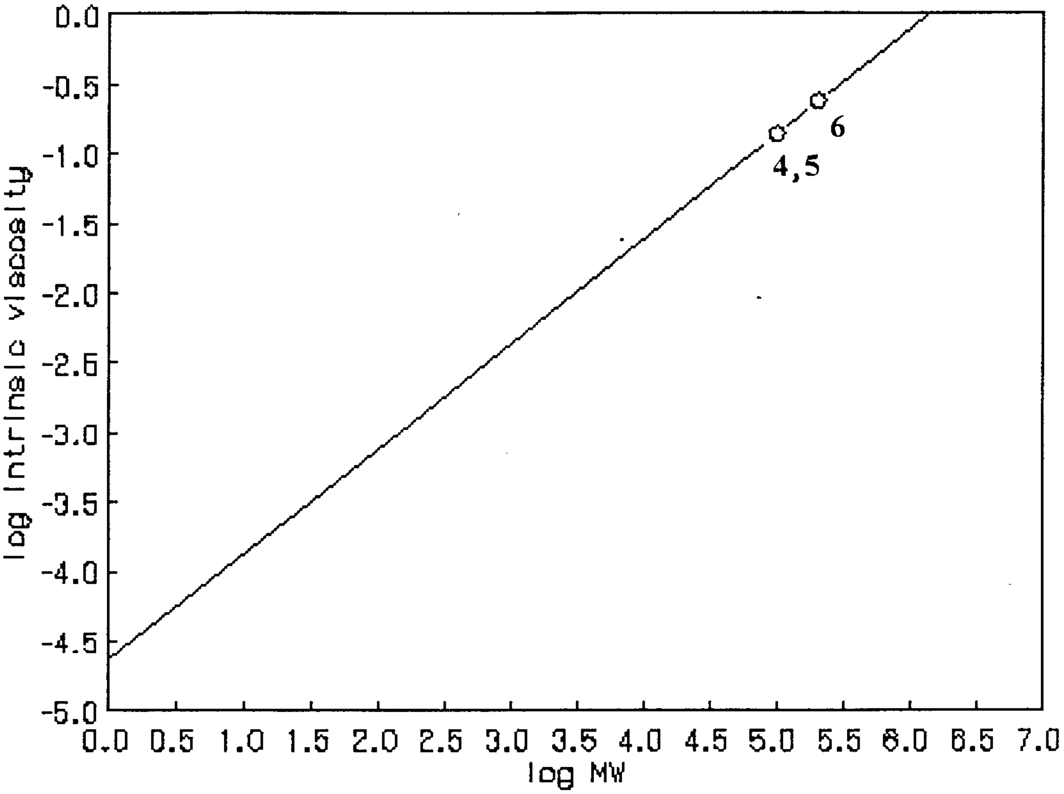
These polysiloxanes were prepared by reacting $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-benzenedimethanol and pyridine with dichlorodimethylsilane in methylene chloride. The polymers were terminated with chlorotriisopropylsilane.

$$n\,[1,4\text{-}C_6H_4(CMe_2OH)_2] + n\text{-}1\,[Me_2SiCl_2] + 2\,Pr^i_3SiCl + 2n\ \text{pyridine} \rightarrow \qquad (3.1.14)$$



+ 2n pyridine·HCl

Figure 3.1.3. Determination of α and K for compounds 4, 5, and 6



The organic and aqueous phases of the tan solution were separated and the organic phase was dried as described in the experimental section. The resulting tan organic solution was rotary evaporated to remove as much solvent as possible, but as with the other compounds synthesized, some solvent remained. The products (**7, 8,** and **9**) were allowed to air dry. However, after 15 days, the products still had traces of liquid possibly due to the presence of hexaisopropyldisiloxane as a byproduct. Vaporization of the liquid was attempted by exposing the products to a stream of nitrogen for five hours. After 27 days, however, the final products are tan colored crystalline materials with traces of liquid still present.

The ^{1}H NMR ($CDCl_3$) spectra (Figure 3.1.4 shows compound **8**) of compounds **7, 8,** and **9** were assigned using the resonance frequencies of the starting diol, hexaisopropyldisiloxane and compounds **3, 4, 5,** and **6** for comparison. Refer to Table 3.1.2 for ^{1}H NMR data. All three compounds (**7, 8,** and **9**) also had two additional peaks at 5.09 ± 0.00 ppm and 5.40 ± 0.00 ppm. The ^{13}C NMR ($CDCl_3$) spectra of compounds **7, 8** (Figure 3.1.5), and **9** do not agree with the expected values or the spectra of compounds **4, 5,** and **6** (Table 3.1.2). All three compounds (**7, 8,** and **9**) had peaks at 28.18 ± 0.00 ppm, and 112.84 ± 0.00 ppm. The viscosities of compounds **7, 8,** and **9** was determined using the Cannon-Fenske® viscometer as described for compounds **4, 5,** and **6**. Using the estimated $\overline{M}_n$ values from the integration ratios of the ^{1}H NMR ($\overline{M}_{n7}=1.0\times10^4$(g/mol), $\overline{M}_{n8}=1.3\times10^4$(g/mol), and $\overline{M}_{n9}=1.1\times10^5$(g/mol)), the relationship in equation 3.1.13 and $[\eta_7] = 0.034$, $[\eta_8] = 0.089$, and $[\eta_9] = 0.126$, the viscosity average molecular weights of compounds **7, 8,** and **9** were determined as $\overline{M}_{v7}=6.1\times10^3$(g/mol), $\overline{M}_{v8}=7.7\times10^4$(g/mol), and $\overline{M}_{v9}=1.9\times10^5$(g/mol). For compounds 7, **8**, and 9, $\overline{M}_v > \overline{M}_n$. The Mark-Houwink parameters were determined from the plot of log [η] versus log $\overline{M}_v$ as $K=1.24\times10^{-3}$ and $\alpha=0.38$ (Figure 3.1.6). The small alpha value implies randomly coiled polymers were synthesized.

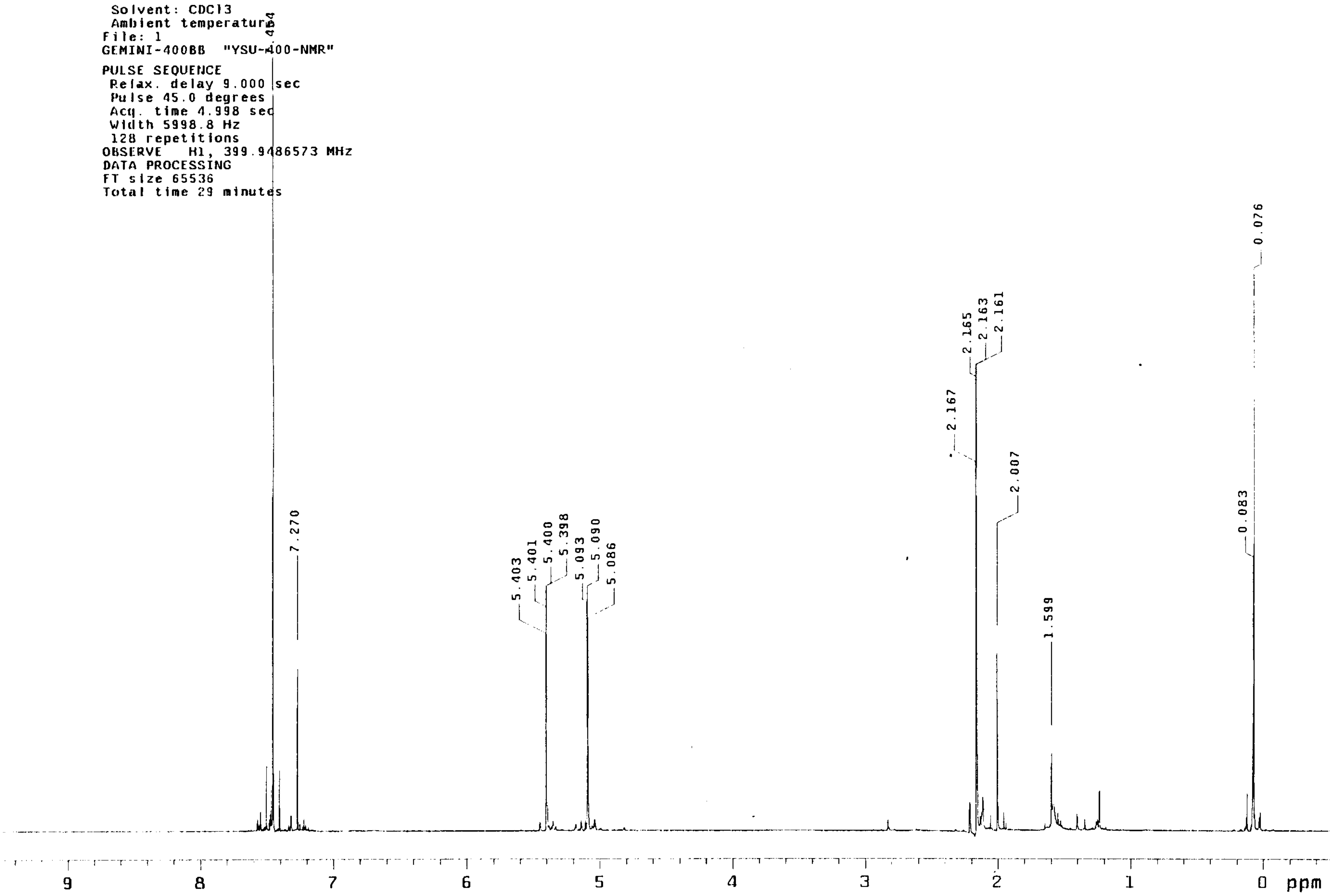


Figure 3.1.4. ^{1}H NMR spectrum of compound 8, triisopropylsilyl terminated polysiloxane

```
 Solvent: CDCl3
 Ambient temperature
File: 1
GEMINI-400BB  "YSU-400-NMR"

PULSE SEQUENCE
 Relax. delay 9.000 sec
 Pulse 45.0 degrees
 Acq. time 4.998 sec
 Width 5998.8 Hz
 128 repetitions
OBSERVE   H1, 399.9486573 MHz
DATA PROCESSING
FT size 65536
Total time 29 minutes
```

Figure 3.1.5. ^{13}C NMR spectrum of compound **8**, triisopropylsilyl terminated polysiloxane

```
STANDARD 13C
 Solvent: CDCl3
 Ambient temperature
File: 13
GEMINI-400BB  "YSU-400-NMR"
PULSE SEQUENCE
 Pulse 90.0 degrees
 Acq. time 0.640 sec
 Width 100.0 kHz
 40832 repetitions
OBSERVE  C13, 100.5671485 MHz
DECOUPLE  H1, 399.9510872 MHz
 Power 58 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
FT size 131072
Total time 7.3 hours
```

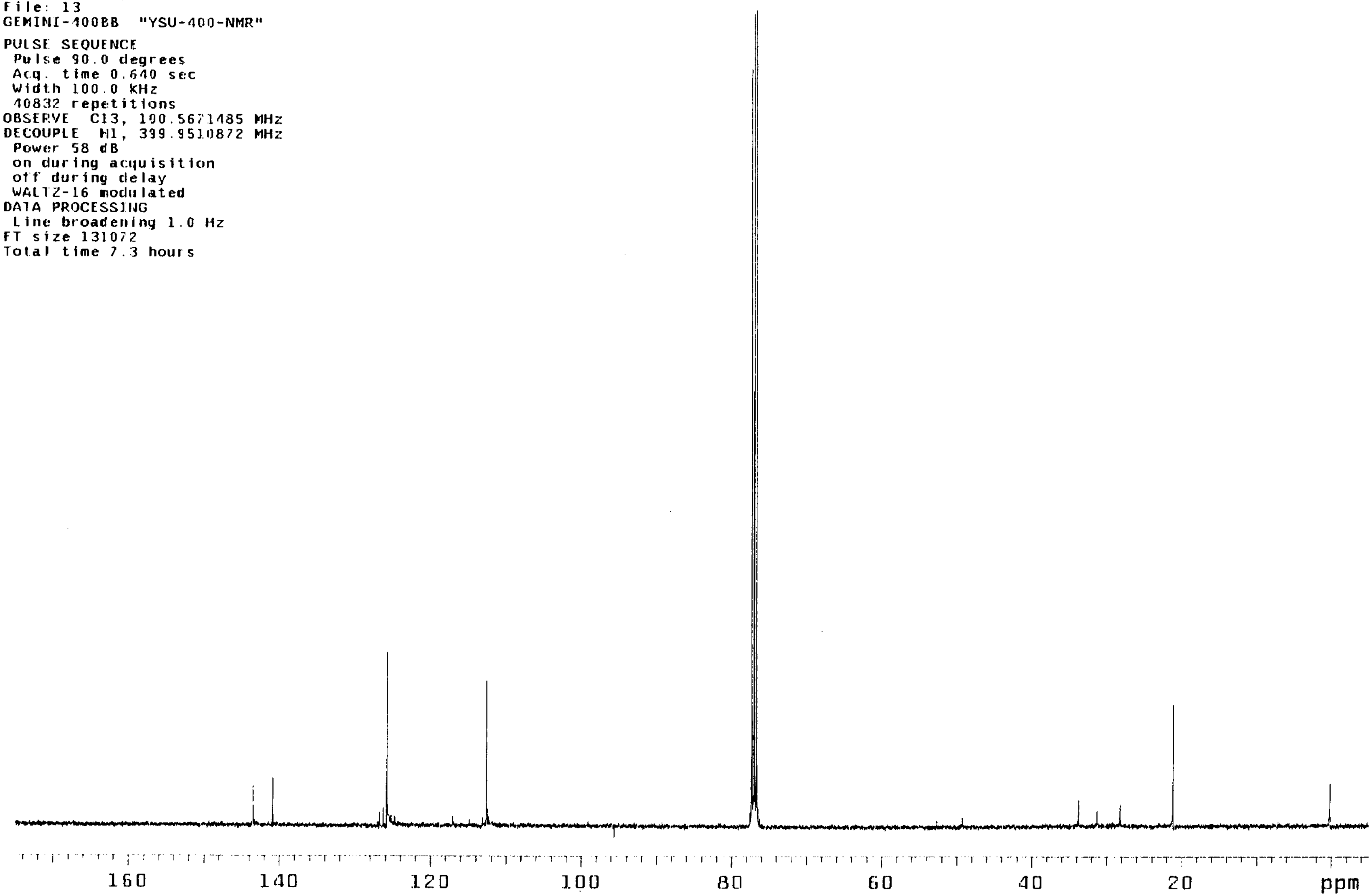
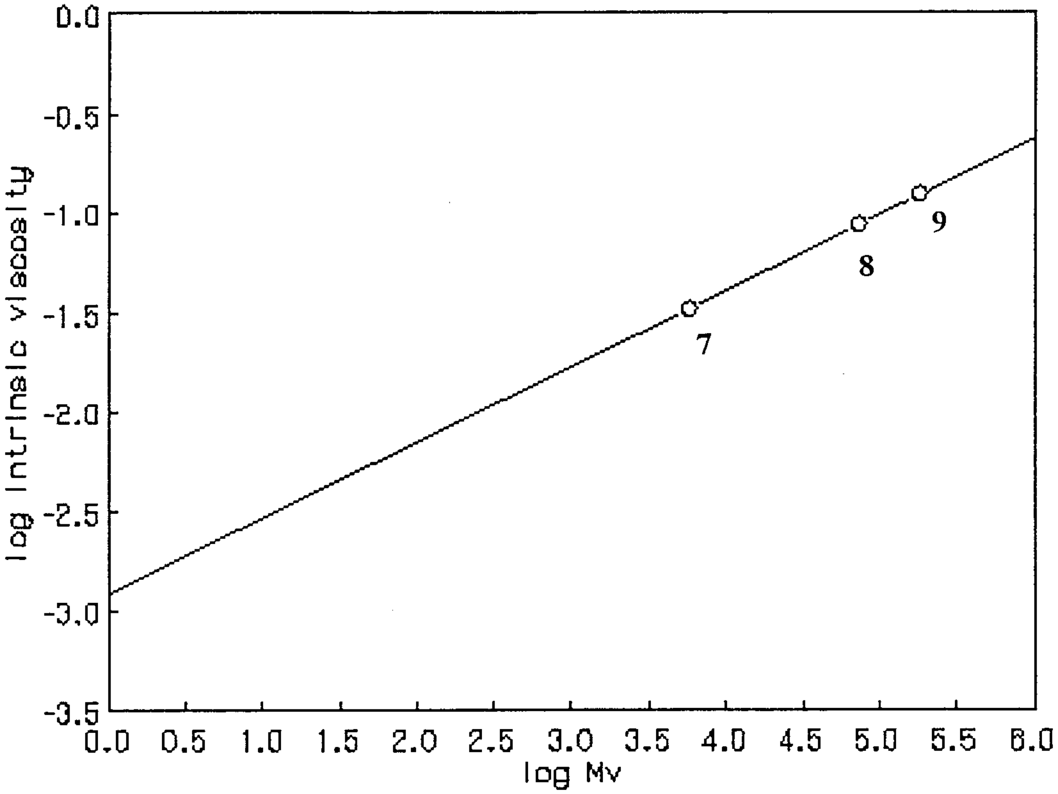


Table 3.1.2. ^1H and ^{13}C NMR data for triisopropylsilyl terminated polysiloxanes (δ in ppm)

		COMPOUND		
^1H NMR Data	**Theoretical[23,28]**	**7**	**8**	**9**
$C(C\underline{H}_3)_2$	1.5	2.17	2.16	2.16
$ArC\underline{H}$	6.8-7.5	7.45	7.45	7.45
$Si(C\underline{H}_3)_2$	0.05-0.1	0.081	0.076	0.081
^{13}C NMR Data				
$Si(\underline{C}H_3)_2$	2.5	0.26	na	na
$C(\underline{C}H_3)_2$	4-40	21.18	21.18	21.18
$Ar\underline{C}H$	110-130	125.81	125.81	125.81
$\underline{C}(CH_3)_2$	55-85	na	na	na
$Ar\underline{C}$	120-150	140.89 143.51	140.89 143.51	140.89 143.51

Figure 3.1.6. Determination of α and K for compounds **7**, **8**, and **9**



From the data, it must be concluded that compounds **7, 8,** and **9** were not the compounds whose synthesis were attempted. Numerous attempts at producing these polymers gave similar NMR spectra. Since the sensitivity of end groups decreases as MW increases, emphasis will be on compounds **4, 5,** and **6** with **12, 13,** and **14**.

Chapter Two

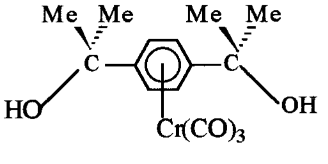
Synthesis and Characterization of the Chromiumtricarbonyl Complexed Monomers and Polyorganosiloxanes

Since the chromium complexed monoaromatic model compound and the chromium complexed polyorganosiloxanes were air sensitive, they were synthesized under anaerobic and anhydrous conditions as described in the experimental section. The chromium complexed polyorganosiloxanes were prepared via condensation reactions with hydrochloric acid as a by product. This necessitates the addition of pyridine, since it acts as a base to capture the HCl formed which would otherwise decompose the organometallic linkages.[20]

Synthesis and characterization of (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl (10)

The starting material, (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl, was prepared by reacting α,α,α',α'-tetramethyl-1,4-benzenedimethanol with chromium hexacarbonyl in dibutylether/tetrahydrofuran.

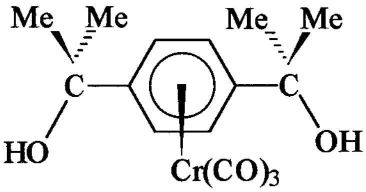
$$1{,}4\text{-}C_6H_4(CMe_2OH)_2 + Cr(CO)_6 \rightarrow \qquad (3.2.1)$$



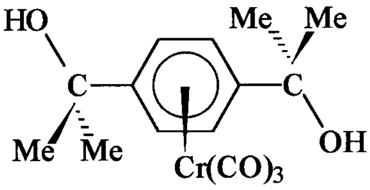
$+ \ 3CO$

These reactions were refluxed for 23-28 hours to ensure completion of the reaction. The yellow solution was extremely air sensitive and even minimal contact with air resulted in the product decomposing and turning green. Any unreacted $Cr(CO)_6$ was removed by sublimation during the solvent evaporation. The resulting yellow crystals had a green tint and had to be purified by recrystallization to produce bright yellow crystals of the product.

The ^1H NMR ($CDCl_3$) spectrum of compound **10** (Figure 3.2.1) was assigned using the resonance frequencies of the starting diol for comparison. The singlet at 1.57 ppm was assigned to the benzylic carbon's methyl groups, the singlet at 1.83 ppm to the hydroxyl protons, and the singlet at 5.59 ppm to the complexed aromatic ring hydrogens. The singlet at 7.45 ppm was due to about 3% of the arene in the NMR sample being uncomplexed (i.e. possibly there was some decomposition in the NMR tube). The observed singlet at 5.59 ppm results from the bonuation of only trans-type isomers or the free rotation of the $-CMe_2OH$ substituents which prevents the observation of isomerism,



cis-type isomer



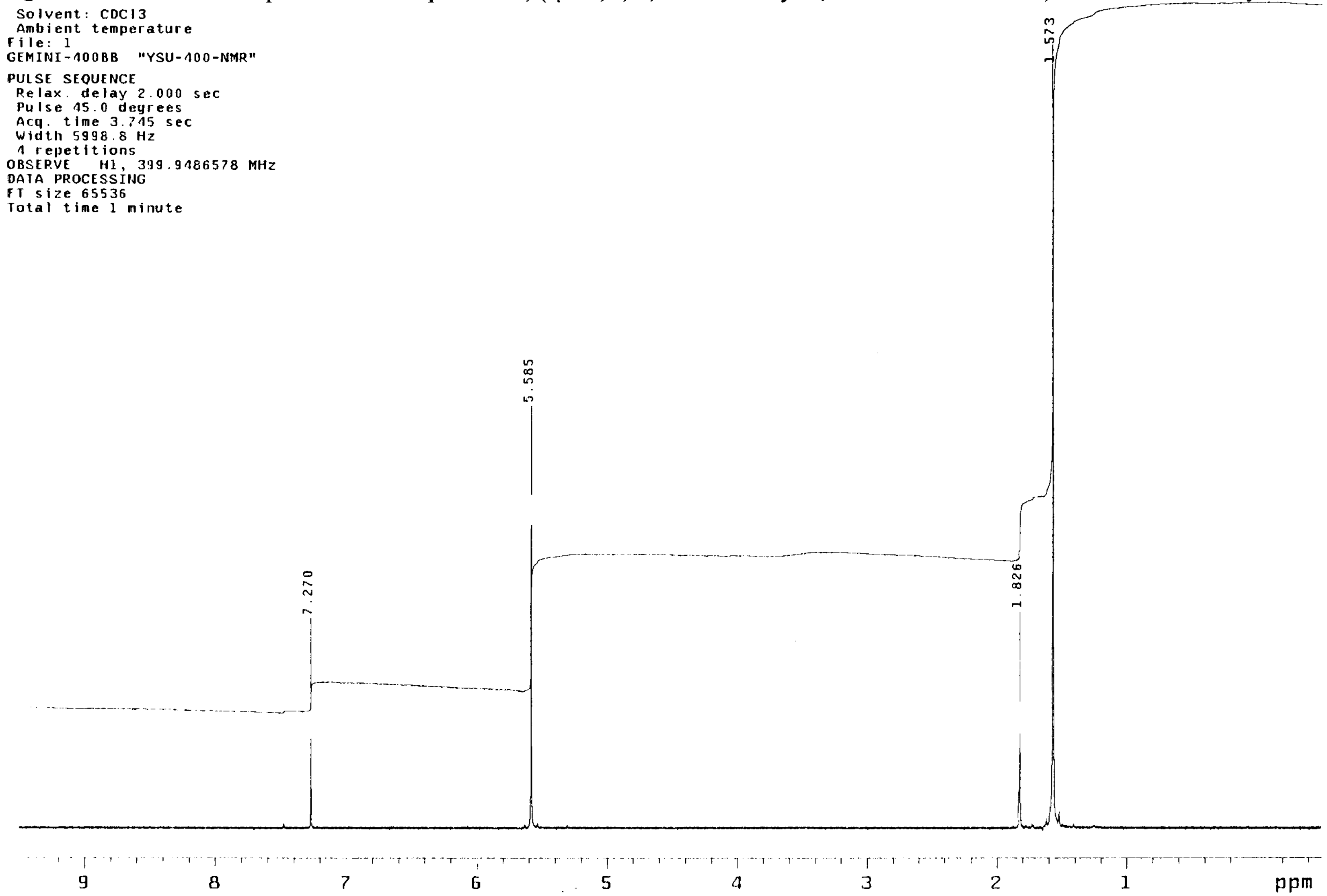
trans-type isomer

The Cr complexed aryl protons were shifted 1.89 ppm upfield from the starting benzylic alcohol. The infrared spectrum of compound **10** (Figure 3.2.2) showed CO stretching frequencies at 1883 cm^{-1} and 1962 cm^{-1} in THF, indicative of an (η^6-arene)$Cr(CO)_3$ complex. Compound **10** was stable under nitrogen if the crystals were completely dry.

Synthesis and characterization of (η^6-α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl (11)

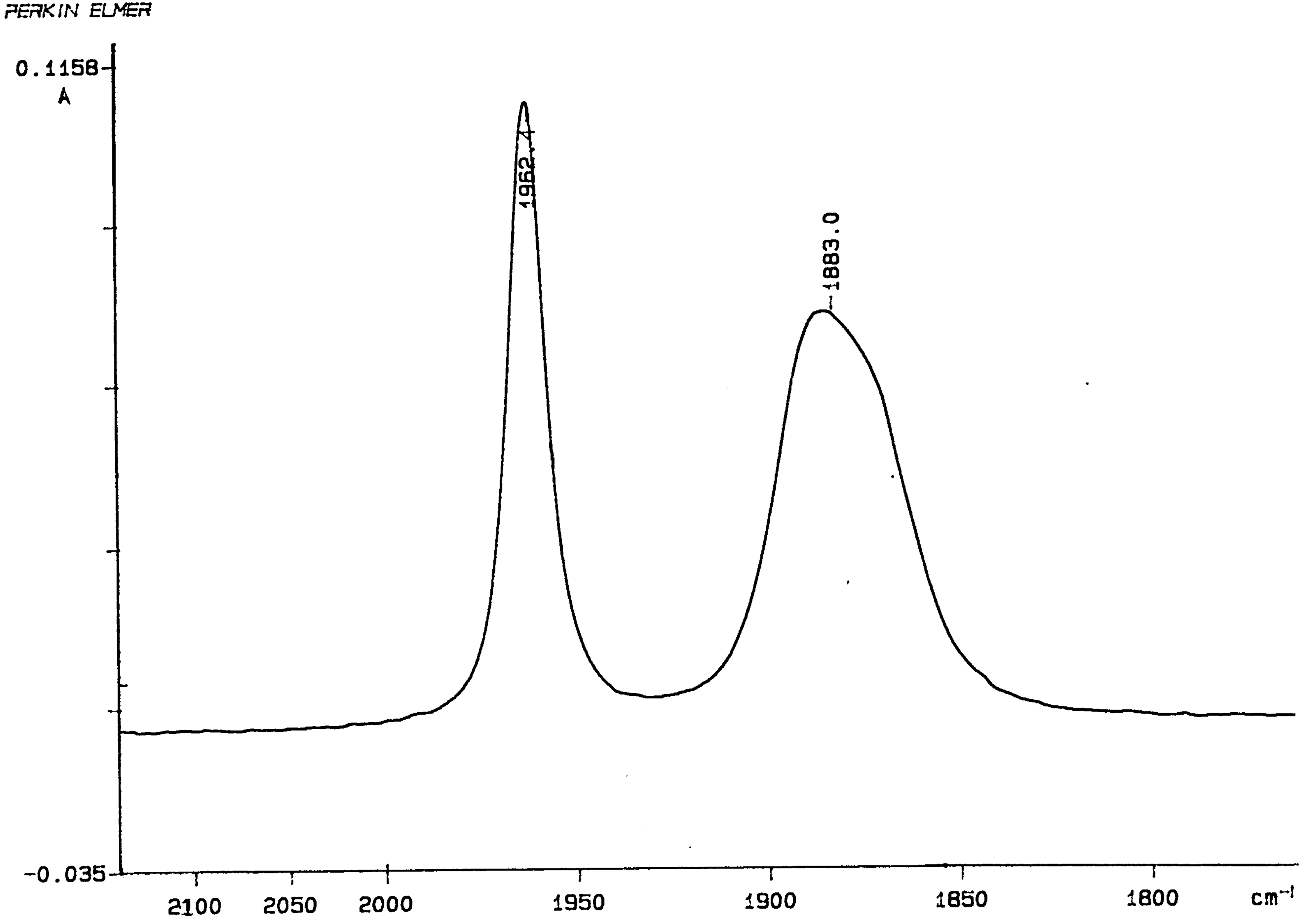
The model compound, (η^6-α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl, was prepared by reacting (η^6-α,α,α',α'-

Figure 3.2.1. ^{1}H NMR spectrum of compound 10, (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl



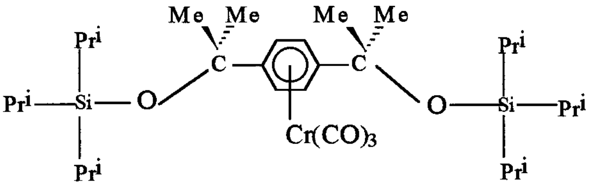
```
 Solvent: CDCl3
 Ambient temperature
File: 1
GEMINI-400BB  "YSU-400-NMR"

PULSE SEQUENCE
 Relax. delay 2.000 sec
 Pulse 45.0 degrees
 Acq. time 3.745 sec
 Width 5998.8 Hz
 4 repetitions
OBSERVE   H1, 399.9486578 MHz
DATA PROCESSING
FT size 65536
Total time 1 minute
```

Figure 3.2.2. IR spectrum of compound 10, (η^6-$\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,4-benzene-dimethanol)chromiumtricarbonyl



tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl and chlorotriisopropylsilane, after the addition of pyridine, in methylene chloride under a nitrogen atmosphere.

$$(\eta^6\text{-}1,4\text{-}(CMe_2OH)_2C_6H_4)Cr(CO)_3 + 2\ ClSiPr^i_3 + 2\ \text{pyridine} \rightarrow \tag{3.2.2}$$

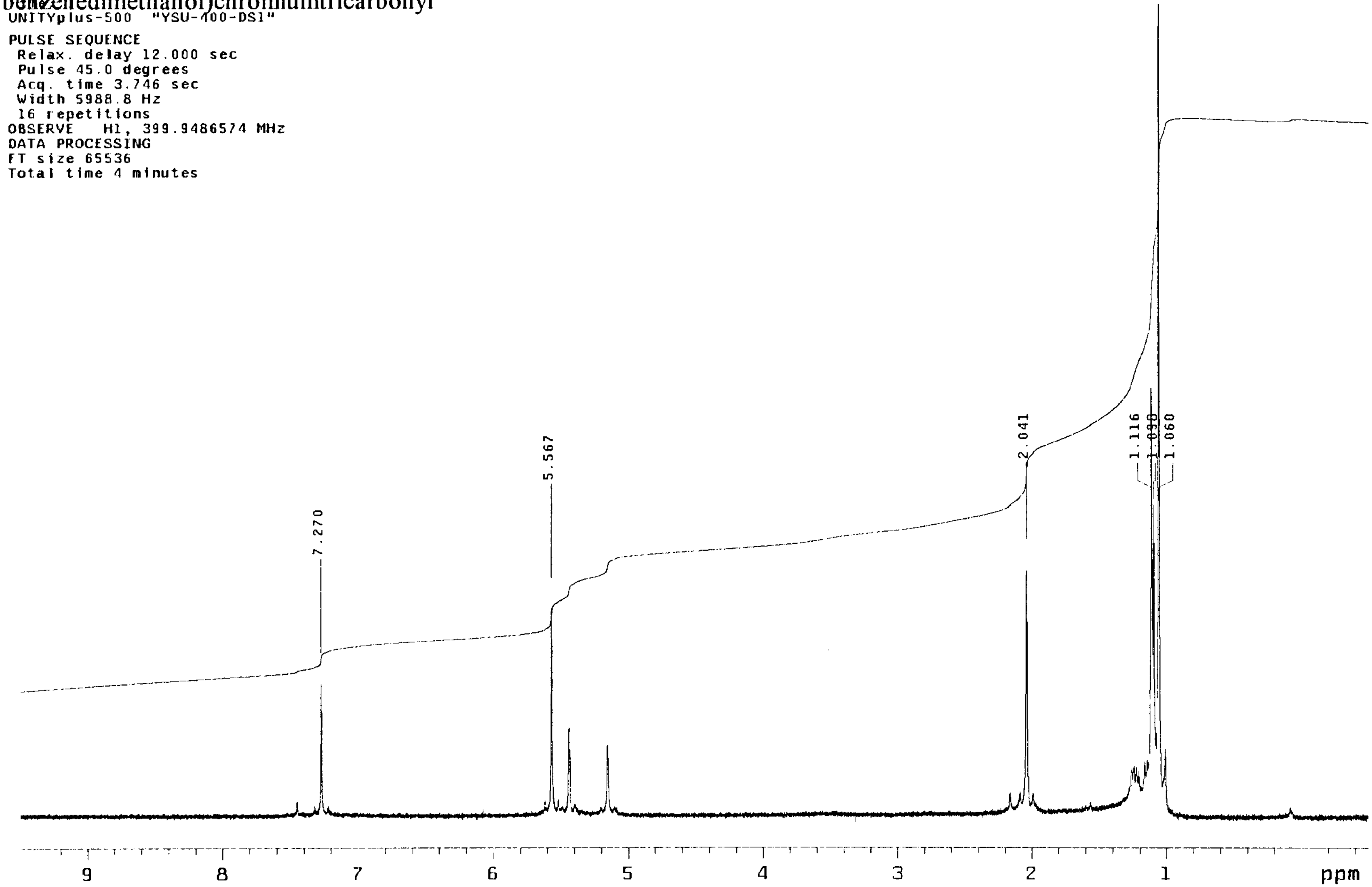


$+ \ 2n\ \text{pyridine}\cdot HCl$

The reaction was left for 18 hours. The resultant green-yellow solution was separated and dried as previously described in the experimental section (i.e. H_2O/organic extraction). The green-yellow solution appeared bright yellow once separation of the organic phase was complete. Upon removal of the solvent, the powdery product, (η^6-α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl, was orange-yellow in color.

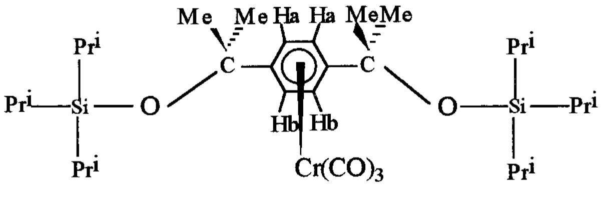
The ^1H NMR ($CDCl_3$) spectrum of compound **11** (Figure 3.2.3) was assigned using the resonance frequencies of the starting material, compound **10**, and hexaisopropyldisiloxane for comparison. The doublet at 1.09 ppm was assigned to the methyl groups of the triisopropyl end group, the multiplet at 1.23 ppm to the methyne groups of the triisopropyl end group, the singlet at 1.57 ppm to the benzylic carbon's methyl groups, the singlets (combined integration 4H) at 5.15, 5.44, and 5.57 ppm to the aromatic hydrogens of the Cr-arene complex. The singlet at 7.45 ppm was due to about 3% of the arene in the NMR tube being uncomplexed (i.e. possibly there was some decomposition in the NMR tube). Unlike compound **10** which has less bulky CMe_2OH substituents, compound **11** appears to have restricted rotation about the (aryl)-($CMe_2OSiPr^i_3$) group, probably due to the bulky siloxy end groups. The three signals

Figure 3.2.3. ^{1}H NMR spectrum of compound **11,** (η^6-α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl

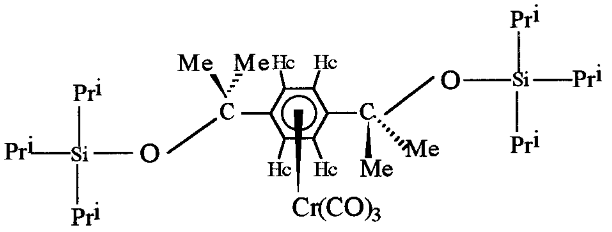


```
 Solvent: CDCl3
 Ambient temperature
 [illegible]
UNITYplus-500  "YSU-400-DS1"

PULSE SEQUENCE
 Relax. delay 12.000 sec
 Pulse 45.0 degrees
 Acq. time 3.746 sec
 Width 5988.8 Hz
 16 repetitions
OBSERVE   H1, 399.9486574 MHz
DATA PROCESSING
FT size 65536
Total time 4 minutes
```

assigned to aromatic hydrogens of the Cr-arene complex are likely due to a mixture of cis and trans isomers (3.2.3, 3.2.4, respectively). The singlet at 5.57 ppm (2H) was probably due to the trans-isomer while the singlets at 5.15 (1H) and 5.44 (1H) ppm were probably due to the cis-isomer. The cis/trans ratio of 1:1 implies equal amounts of each isomer are present.



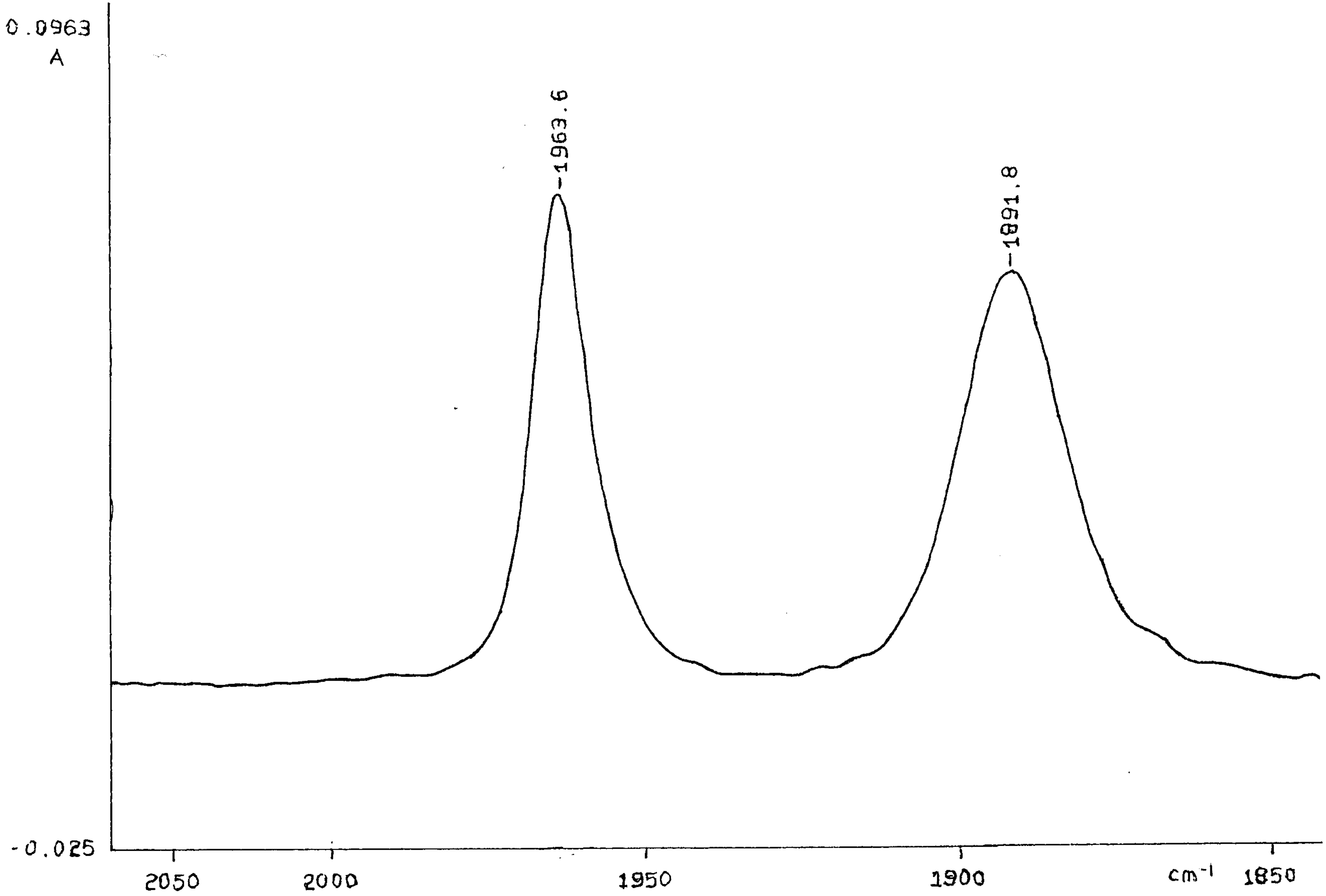
cis-isomer (3.2.3)



trans-isomer (3.2.4)

The Cr complexed aryl protons were shifted 2.32, 2.03, and 1.91 ppm upfield from the starting diol. The infrared spectrum of compound **11** in THF (Figure 3.2.4) showed stretching frequencies at 1892 and 1964 cm^{-1}, compared to compound **10** with frequencies at 1883 and 1962 cm^{-1}, indicative of an arene-$Cr(CO)_3$ complex. Since compound **11** had higher frequencies, Cr was less electron rich than compound **10**. Compound **11** was relatively stable under nitrogen and decomposes in air in solution or the solid state at RT in 5-10 minutes. The schlenk® tube with the solid product was kept in the freezer at 0°C to increase stability.

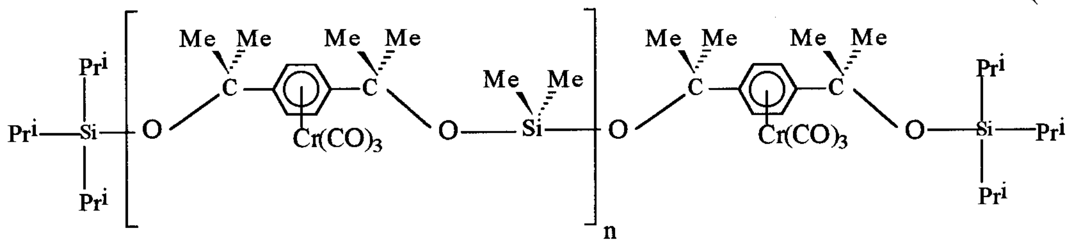
Figure 3.2.4. IR spectrum of compound **11**, (η^6-α,α,α',α'-tetramethyl-O,O'-bistriisopropylsiloxy-1,4-benzenedimethanol)chromiumtricarbonyl



Synthesis and characterization for each reaction of Poly[dimethylsiloxane-co-((η^6-α, α,α',α'-tetramethyl-O,O'-1,4-benzenedimethanol)-chromiumtricarbonyl)] (12, 13, and 14)

The three polysiloxanes containing complexed chromium were prepared by reacting (η^6-α,α,α',α'-tetramethyl-1,4-benzenedimethanol)chromiumtricarbonyl, pyridine, dichlorodimethylsilane and chlorotriisopropylsilane in methylene chloride.

$$n(\eta^6\text{-}1,4\text{-}(CMe_2OH)_2C_6H_4)Cr(CO)_3 + n\text{-}1Cl_2SiMe_2 + 2\ ClSiPr^i_3 + 2n\ \text{pyridine} \rightarrow \quad (3.2.3)$$



+ 2n pyridine·HCl

The ^1H NMR ($CDCl_3$) spectra of compounds **12, 13,** and **14** were compared to the frequencies of compounds **10** and **11**. The NMR data is presented in Table 3.2.1. The ^1H and ^{13}C NMR frequencies are only affected at the aromatic protons and carbons. Due to the net electron transfer of the arene electron density to Cr, the electron poor aromatic protons of the chromium complexed polymers were shifted up field and were shielded compared to those of the aromatic protons of the siloxanes, as expected. The chromium complexed model (compound **11**) and lower MW polymer had different environments for the Cr-Ar hydrogens, presumably due to restricted rotation about the aryl-CMe_2 bonds (see above).

The integration of the ^1H NMR spectra, the frequencies of the ^{13}C NMR spectra, and the IR frequencies confirming the presence of arene-$Cr(CO)_3$ units support the

Table 3.2.1. ^1H and ^{13}C NMR Data for Chromium Complexes (δ in ppm)

	COMPLEX		
^1H NMR Data	**12**	**13**	**14**
$CH(C\underline{H}_3)_2$	1.054	1.053	1.054
$C\underline{H}(CH_3)_2$	1.254	1.254	1.252
$C(C\underline{H}_3)_2$	1.573	1.572	1.573
$ArC\underline{H}$	5.586 5.309	5.585	5.585
$Si(C\underline{H}_3)_2$	0.075	0.071	0.073
^{13}C NMR Data			
$CH(\underline{C}H_3)_2$	16.724	16.815	7.88
$\underline{C}H(CH_3)_2$	12.129	12.400	10.033
$C(\underline{C}H_3)_2$	30.924	30.924	30.939
$Ar\underline{C}H$	90.305	90.305	90.305
$\underline{C}(CH_3)_2$	70.704	70.704	70.704
$Ar\underline{C}$	122.287	122.803	122.287
$\underline{C}O$	235.178	235.163	235.163

proposed structures. The singlet at 7.47 ± 0.02 ppm was due to about 6% of the arene being uncomplexed. The infrared spectra of compounds **12** (Figure 3.2.5), **13**, and **14** showed CO stretching frequencies at 1960 ± 0.5 $\mathrm{cm^{-1}}$ and 1883 ± 0.5 $\mathrm{cm^{-1}}$, confirming the presence of arene-$Cr(CO)_3$ units. The electron richness of Cr is similar for compounds **10**, **12**, **13** and **14** since the frequencies are within 2 $\mathrm{cm^{-1}}$. The stability and solubility are affected by chromium complexed to a ring. The chromium polymers are extremely unstable to air in solution and are stable only for minutes as solids in air. The chromium polymers are more soluble in THF, CH_2Cl_2 and $CDCl_3$ than are their siloxane counterparts. Due to their instability in air, the viscosities of compounds **12**, **13**, and **14** were determined using a Cannon-Fenske® viscometer connected to a glove bag under N_2. Using the estimated $\overline{M}_n$ values from the integration ratios of the ^1H NMR ($\overline{M}_{n12}=5.5\times10^4$(g/mol), $\overline{M}_{n13}=3.2\times10^5$(g/mol), and $\overline{M}_{n14}=3.8\times10^5$(g/mol)), the relationship in equation 3.1.13, and $[\eta_{12}] = 0.006$, $[\eta_{13}] = 0.021$, and $[\eta_{14}] = 0.023$, the viscosity average molecular weights of compounds **12**, **13**, and **14** were estimated as $\overline{M}_{v12}=5.8\times10^4$(g/mol), $\overline{M}_{v13}=3.5\times10^5$(g/mol), and $\overline{M}_{v14}=4.0\times10^5$(g/mol). For compounds **12**, **13**, and **14**, $\overline{M}_v > \overline{M}_n$ as expected. The Mark-Houwink parameters were estimated from the plot of log $[\eta]$ versus log $\overline{M}_v$ as $K=2.8\times10^{-6}$ and $\alpha=0.70$ (Figure 3.2.6). Compared to the triethylsilyl terminated polymers with an $\alpha=0.76$, compounds **12**, **13**, and **14** are less rigid.

Figure 3.2.5. IR spectrum of compound 12, chromium complexed polysiloxane

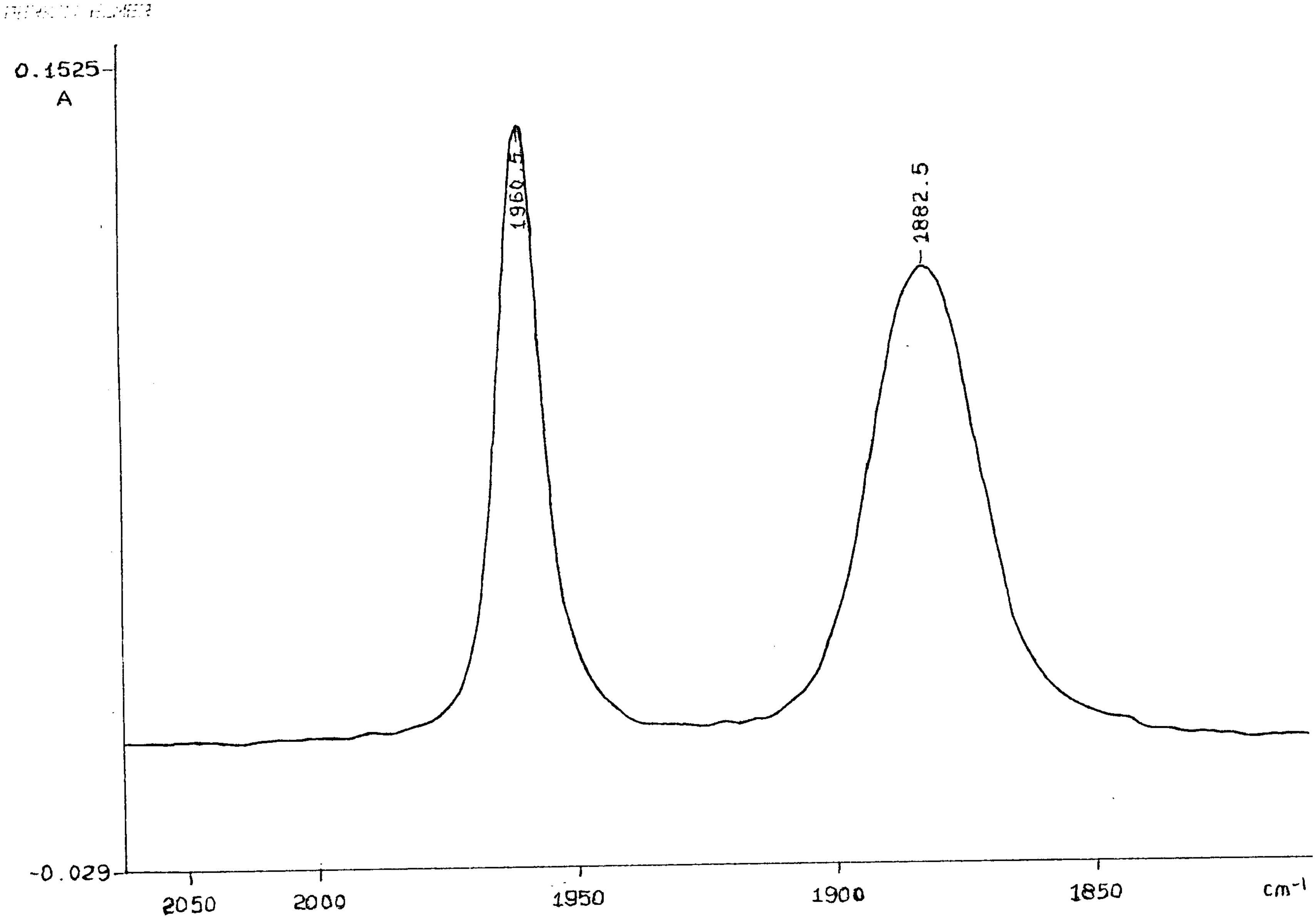
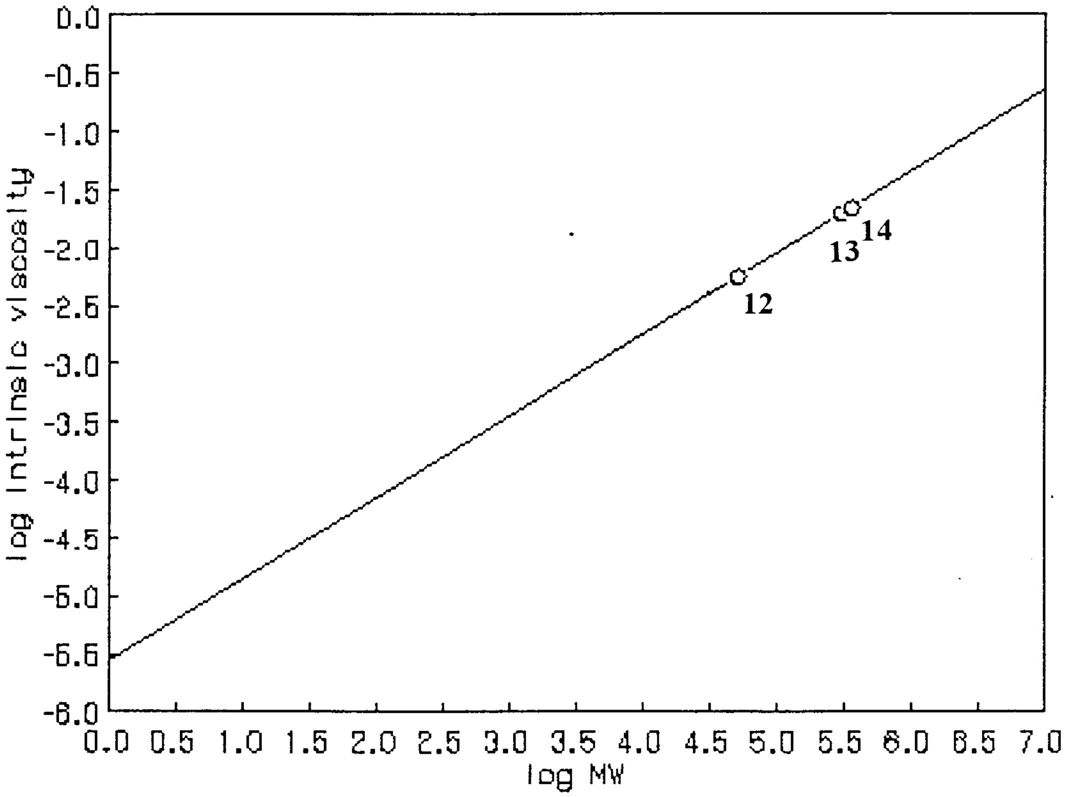


Figure 3.2.6. Determination of α and K for compounds **12**, **13**, and **14**



Part Four

Conclusion

The chromium complexed polymers were less air stable than their polysiloxane counterparts. The chromium polymers were unstable to air in solution and as solids and decomposed within minutes. The siloxane polymers were air stable in solution and as solids. The chromium polymers were more soluble in CH_2Cl_2, THF, and $CHCl_3$ than their siloxane counterparts. The molecular weights of both types of polymers are comparable even though the chromium complexed polysiloxanes had lower values for K and α.

In the future, a broader distribution of reactant ratios which would produce polymers with more varied molecular weights should be used. Better estimates of molecular weight are also needed, such as GPC or light scattering. The wider molecular weight distribution would be better for viscosity measurements. End groups that are simple, yet, have different chemical shifts than the polymers should be investigated such as acyl halides. End groups which consist of distinctive chemical groups such as amines or carbonyls could be studied.

References

1. Stevens, M. P., *Polymer Chemistry: An Introduction,* Oxford University Press, New York, **1990**.
2. Mark, J. E.; Allcock, H. E.; West, R., *Inorganic Polymers,* Prentice-Hall, Inc., Englewood Cliffs, **1992**.
3. Lecture Notes, Chemistry 824, Y.S.U., Hunter, A. D., *Polymers*, Fall **1994**.
4. Allcock, H. R.; Lampe, F. W., *Contemporary Polymer Chemistry,* Prentice-Hall, Inc., Englewood Cliffs, **1981**.
5. Campbell, D.; White, J. R., *Polymer Characterization,* Chapman and Hall, New York, **1991**, 13.
6. Wilkinson, G.; Stone, F. G. A.; Abel, E. W., *Comprehensive Organometallic Chemistry*, Pergamon Press, **1982**, Vol. 2, 306-307.
7. Stone, F. G. A.; Graham, W. A. G., *Inorganic Polymers*, Chapter 5, Academic Press, New York, **1962**.
8. Preston, J., *Encyclopedia of Polymer Science and Technology: Supplement Vol. 2,* Interscience Publishers, New York, **1977**.
9. Yilgör, I.; McGrath, J. E., *Advances in Polymer Science*, **1988**, *86.* 1-9.
10. Hani, R.; Lenz, R. W., In *Silicon-Based Polymer Science. A Comprehensive Resource;* Zeigler, J. M.; Fearon, F. W. G., Eds.; Advances in Chemistry Series; American Chemical Society: Washington, DC, **1990**; *Vol. 224.*
11. Koide, N.; Lenz, R. W., *J. Polym. Sci., Polym, Symp.* **1983**, *70*, 91-105.
12. Lukehart, C. M., *Fundamental Transition Metal Organometallic Chemistry,* Brooks/Cole Publishing Company, Monterey, California, **1985**.
13. Crabtree, R. H., *The Organometallic Chemistry of the Transition Metals,* John Wiley and Sons, New York, **1994**.
14. Wilkinson, G.; Stone, F. G. A.; Abel, E. W., *Comprehensive Organometallic Chemistry*, Pergamon Press, **1982**, Vol. 3.

15. Powell, P., *Principles of Organometallic Chemistry,* Chapman and Hall, NewYork, 1988.
16. Lecture Notes, Chemistry 993, Y.S.U., Special Topics in Inorganic Chemistry, Hunter, A. D., *Organometallics,* Spring 1994.
17. Ebbing, D. D., *General Chemistry*, 4th Ed., Houghton Mifflin Company, Boston, 1993.
18. Zeiss, H., *Organometallic Chemistry*, Reinhold Publishing Corporation, New York, 1960.
19. Thayer, J. S., *Organometallic Chemistry: An Overview,* VCH Publishers, Inc., New York, 1988.
20. Coyne, G. S., *The Laboratory Handbook of Materials, Equipment, and Technique,* Prentice-Hall, New Jersey, 1992.
21. Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R., *Purification of Laboratory Chemicals,* Pergamon Press, New York, **1980,** 205, 427.
22. Shriver, D. F.; Drezdzon, M. A., *The Manipulation of Air-Sensitive Compounds*, 2nd Ed., John Wiley and Sons, New York, 1986.
23. Fresenius, W.; Huber, J. F. K.; Pungor, E.; Rechnitz, G. A.; Simon, W.; West, Th. S., *Tables of Spectral Data for Structure Determination of Organic Compounds*, Springer-Verlag, New York, 1989.
24. Fessendon, R. J.; Fessendon, J. S., *Organic Laboratory Techniques*, 2nd Ed., Brooks/Cole Publishing Company, Pacific Grove, 1993.
25. Pouchert, C. J.; Behnke, J., *Aldrich Spectra of* ^{13}C *and* ^{1}H *NMR Spectra*, Aldrich Chemical Co., Milwaukee, **1993,** Vol. 3, 643c.
26. Clarson, S. J.; Semlyen, J. A., *Siloxane Polymers*, Prentice Hall, New Jersey, 1993.
27. Pearce, E. M.; Wright, C. E.; Bordoloi, B. K., *Laboratory Experiments in Polymer Synthesis and Characterization*, The Pennsylvania State University, University Park, 1982.

28. Merker, R. J.; Scott, M. J., *Journal of Polymer Science*, A, **2**, 15(1964).

29. Brandrup, J.; Immergut, E. H., *Polymer Handbook*, 3rd Ed., John Wiley and Sons, New York, **1989**.