SYNTHESIS OF FUNCTIONALIZED POLYCARBOSILANES VIA ACRYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION

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SYNTHESIS OF FUNCTIONALIZED POLYCARBOSILANES VIA ACYCLIC DIENE METATHESIS (ADMET) POLYMERIZATION

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A series of polycarbosilanes functionalized with both alkyl and alkoxy pendant groups were synthesized using a combination of nucleophilic substitution and acyclic diene metathesis (ADMET) polymerization. This polymerization is a step-growth polycondensation reaction consisting of the reaction of an α,ω-diene with a metal carbene catalyst and driven by the removal of ethylene. The parent α,ω-diene monomer used in this system contains two highly reactive silicon-chlorine bonds that can be substituted using a wide range of nucleophiles.

Two different pathways were employed to prepare these functionalized polycarbosilanes. The first route utilized involved the nucleophilic substitution of both silicon-chlorine bonds on the diene monomer with a variety of alcohols, creating a series of functionalized monomers. The substituted dienes then were polymerized via ADMET, producing a family of substituted poly(dialkoxycarbosilanes) that exhibit a wide range of
properties and variable hydrolytic stability, both of which are determined by the nature of the pendant group. This route ensures complete replacement of all silicon-chlorine bonds present, since substitution occurs on the monomer prior to polymerization.

The second synthetic route utilized involves functionalization of a polymer containing silicon-chlorine bonds in each repeat unit. This reactive poly(dichlorocarbosilane) is prepared by ADMET polymerization of the parent α,ω-diene, which is then modified via nucleophilic substitution, creating a family of derivative polymers. The macromolecular substitution reaction of the silicon-chlorine bonds in the polymer was achieved using a variety of alkyllithium reagents. Although this type of reaction is more difficult on polymers compared to monomers, quantitative substitution is effected using these potent nucleophiles, producing stable materials with varying properties.

The results presented demonstrate the dramatic effect that variation of the pendant group placed along the polymer backbone has on polymer properties. The combination nucleophilic substitution-ADMET polymerization is shown to be a highly versatile and flexible route for the synthesis of functionalized polymers, since substitution can be performed on the monomer or on the polymer. Using this strategy, polymer architectures can be realized that are difficult or impossible to synthesize by alternative methods.
CHAPTER 1
INTRODUCTION

Historical Perspective of Olefin Metathesis

In 1967, the expression "olefin metathesis" was first coined by Calderon\textsuperscript{1-5} and is defined in Ivin and Mol's seminal text \textit{Olefin Metathesis and Metathesis Polymerization} on page 1 as "the (apparent) interchange of carbon atoms between a pair of double bonds" (Figure 1-1).\textsuperscript{6}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{olefin_metathesis}
\caption{The olefin metathesis reaction.}
\end{figure}

The advent of olefin metathesis in the mid 1950s\textsuperscript{7} evolved from the development of transition metal based catalyst systems for the polymerization of $\alpha$-olefins and ethylene.\textsuperscript{8} Early metathesis catalyst systems were derived from the Phillips type (heterogeneous supported metal oxides at high temperature) or the Ziegler-Natta type (homogenous metal halide/alkyl aluminum mixtures at low temperature). These multi-component catalysts, formed \textit{in situ}, were ill-defined and difficult to understand. Because of this, the mechanism and nature of the active catalyst species were not known for some time. In an effort to study the mechanism of the olefin metathesis reaction,
the Dall’Asta group performed detailed labeling studies proving that olefin double bond cleavage and subsequent reformation occurred during the reaction.\textsuperscript{9-12} In 1970, Herrison and Chauvin discovered the mechanism of this double bond cleavage.\textsuperscript{13} They proposed that metathesis involved the formation of a metallacyclobutane intermediate, formed by the complexation of a metal carbene (the active catalyst) with an olefin. The formation of the four-membered ring is a critical step in metathesis chemistry, and it is common to all metathesis reactions. Although the existence of this species was questioned initially, the intermediate and the mechanism are now widely accepted by the scientific community.

The first polymers produced by metathesis involved the ring opening of strained cyclic olefins. For example, in 1963 the Dall’Asta laboratory produced high molecular weight polypentenamer (2) via the ring-opening metathesis polymerization (ROMP) of cyclopentene (1) using a catalyst system composed of a mixture of WCl\textsubscript{6} with Et\textsubscript{2}AlCl (Figure 1-2).\textsuperscript{9-12}

![Figure 1-2. Dall’Asta’s ROMP of cyclopentene.](image)

**The Four Types of Metathesis Reactions**

Today, olefin metathesis has become an extremely versatile tool for the formation of new carbon-carbon bonds in both small molecules and polymers. There are four main types of olefin metathesis reactions, and they are illustrated below in Figure 1-3.

Ring opening metathesis polymerization (ROMP) was the first olefin metathesis reaction discovered that produced high molecular weight polymers. This reaction is
driven by the thermodynamic release of ring strain present in the cyclic olefin monomer. Polymerization occurs due to a chain addition type propagation mechanism and is an exothermic reaction. The polymerization is usually terminated by the addition of a small amount of ethyl vinyl ether or a carbonyl-containing molecule, which reacts with the catalyst and destroys its activity.\(^6\) Ring opening metathesis polymerization has been shown to be quite useful for synthesizing a variety of different polymers and copolymers.\(^{14-16}\)

![Figure 1-3. The four main types of olefin metathesis reactions.](image)

In 1990, successful ADMET (acyclic diene metathesis) polymerization of \(\alpha,\omega\)-diienes was first performed by the Wagener group, which emerged as another important metathesis polymerization pathway.\(^{17,18}\) Acyclic diene metathesis is an example of step-growth polycondensation that involves the reaction of an \(\alpha,\omega\)-diene with an acid-free transition metal based alkylidene (or carbene) catalyst. As with any polycondensation reaction, high molecular weight material is produced by the release of a small molecule
during the reaction, driving the monomer↔polymer equilibrium towards polymer formation.\textsuperscript{19} In the case of ADMET, ethylene is the small condensate that is removed during the reaction under reduced pressure. Macrocycle formation occurs to a small extent in all polycondensation reactions. Therefore, ADMET polymerizations are typically performed in the bulk (neat) to minimize competing cyclization reactions, and since this reaction is thermally neutral, no heat sink is necessary. Polymerization of α,ω-dienes using ADMET is a useful method for synthesizing many unsaturated, linear polymers and copolymers with a variety of different functionalities that are inaccessible by other means.\textsuperscript{20}

The interest of olefin metathesis for synthesizing small molecules was limited in the early literature due to the incompatibility of many functional groups with the early catalysts. Ring closing metathesis (RCM) involves the intramolecular reaction of two olefin sites on the same molecule to form a new carbon-carbon bond, producing a cyclic olefin structure. Many difficult ring closures can be performed by this route due to the selectivity of metathesis catalysts for olefins over other functionalities present on the molecule. Ring closing metathesis is a useful tool for natural product synthesis because many different sizes of rings can be successfully synthesized. With the discovery of the latest generation metathesis catalysts that illustrate an increased tolerance to functional groups, interest in olefin metathesis for small molecule synthesis is increasing at a phenomenal rate.\textsuperscript{21-28}

Cross metathesis (CM) reactions are useful for the synthesis of small molecules as well. A cross metathesis reaction is different from RCM because it involves the intermolecular exchange of the olefinic carbons on two acyclic alkenes with no cyclization.
In CM, two olefins that possess in many cases different functional groups are reacted with a metathesis catalyst in order to produce a new olefin. This class of reactions has also found use in higher olefin, pheromone, and other natural products syntheses.29,30

**Acyclic Diene Metathesis Polymerization**

Acyclic diene metathesis is a step-growth polycondensation reaction that produces high molecular weight polymers by reacting an α,ω-diene with a metathesis catalyst and is driven forward by the removal of a small condensate, ethylene. The polymerization of acyclic olefins by this step-growth polymerization is a challenging endeavor because it is governed by the same rules as any polycondensation reaction, requiring high conversions (>99%) and no side reactions in order to produce high molecular weight materials.19 In the mid-1980s, the Wagener laboratory used styrene as a probe to determine whether vinyl addition or metathesis chemistry was occurring when using WCl₆/AlEtCl₂.17,31 If metathesis occurs, stilbene would be the product, and if vinyl addition is occurring, then polystyrene would be produced. Polystyrene was produced in this reaction, which was caused by the Lewis acid present in the catalyst system. Therefore, acid-free catalyst systems are necessary to promote metathesis chemistry and eliminate vinyl addition.

In 1986 the discovery of a well-defined, acid-free, single-site catalyst by the Schrock group enabled this polymerization to become a viable route for the synthesis of unsaturated linear polymers.32-36 These first catalysts discovered were based upon the early transition metals tungsten and molybdenum. Using these new catalyst complexes, the Wagener group was able to successfully polymerize 1,9-decadiene (3), producing polyoctenamer (4), by an ADMET polymerization (Figure 1-4).17,18
Since ADMET polymerizations are reversible, they are conducted in the bulk (neat) in order to maximize the molar concentration of monomer. This promotes a shift in the equilibrium of the reaction from monomer towards unsaturated polymer formation. Like many other polycondensation reactions, ADMET is performed under reduced pressure in order to remove the ethylene condensate. Removing the condensate irreversibly shifts the reaction equilibrium towards polymer formation and dramatically increases the molecular weight of the product polymer. The same kinetics (second order in monomer) and molecular weight distribution ($M_w/M_n \approx 2.0$) are observed for ADMET that are seen with other step-growth polycondensation reactions.$^{37}$

The clean mechanistic chemistry of ADMET is a direct result of the well-defined, single-site catalyst systems used. The only side reactions that occur during ADMET are cyclization and olefin interchange reactions. Cyclization is generally observed in polycondensation chemistry; therefore, an $\alpha,\omega$-diene monomer usually consists of a ten atom or longer chain in order to suppress the competing RCM cyclization reaction. Monomer chains shorter than ten have an increased propensity to form stable five, six, and seven-membered ring structures.$^{38-40}$ Internal interchange reactions occur, similar to that observed with polyester and polyamide condensation reactions.$^{19}$ In metathesis, these reactions involve an active catalytic species at the end of a polymer chain exchanging with an internal double bond on another chain (Figure 1-5). Two new polymer chains are the result.
Figure 1-5. Example of an olefin interchange reaction that can occur during ADMET.

The ADMET Reaction Mechanism

The catalytic cycle of ADMET is illustrated in Figure 1-6. A general reaction scheme involving an α,ω-diene with a metal alkylidene initiator is discussed for simplicity.

Each step in this catalytic cycle is a true chemical equilibrium, and the ultimate driving force for the reaction is the removal of ethylene. Initiation begins with the π-coordination [A] of a metal alkylidene with one olefin site of an α,ω-diene, forming B. An olefin exchange reaction through a retro [2+2] cycloaddition occurs, forming a new metal carbene C, the first intermediate in the catalytic cycle. The metal-carbene unit is now on the end of a monomer or growing polymer chain C, which then reacts with another monomer or polymer chain to form the first metallacyclobutane D. The distinguishing feature of the ADMET mechanism is the formation of two metallacyclobutane intermediates D, F, whereas the ROMP cycle only contains one. Cleavage of D through a retro [2+2] cycloaddition occurs, producing methylidene E (M=CH₂) and a dimer or polymer chain. The active catalyst E then reacts with another monomer or polymer terminus to form the second metallacyclobutane F in a [2+2] cycloaddition reaction. Upon productive ring cleavage of metallacyclobutane F, ethylene
is generated. A new alkylidene C is formed, bound to the growing polymer chain, which regenerates the initial intermediate discussed above. At this point, one catalytic cycle is completed, which is then repeated numerous times to generate high polymer.

![Diagram of catalytic cycle]

Figure 1-6. General ADMET catalytic cycle.

**Three Types of Catalyst Systems for ADMET**

Three distinct catalyst systems have been used for ADMET polymerization, ranging from the early, ill-defined catalyst mixtures to the recent early and late transition metal based well-defined systems.

"Classical" catalysts (5) are ill-defined systems consisting of a mixture of two or more components which form the active catalyst *in situ.* These systems are typically
composed of an early transition metal halide, such as WCl_6 or WOCl_4, with a main group alkylating agent, such as Bu_4Sn or EtAlCl_2, functioning as the activator (Figure 1-7).

![Diagram](image)

Figure 1-7. An example of an ill-defined metathesis catalyst (5).

These catalysts have limited utility because of the harsh reaction conditions they require. High temperatures (\(~100 ~\text{°C}\)) and the use of mild Lewis acids as activators make these systems incompatible with many functional groups. Nevertheless, these catalyst mixtures are cheap and easy to prepare, which makes them useful for some industrial applications and under certain conditions. These classical catalysts have limited utility because the active catalyst cannot be isolated, and consequently, catalyst concentration cannot be quantified or monitored during the reaction.

The discovery of well-defined, single-component alkylidene catalysts revolutionized the field of olefin metathesis. In the late 1980s, the Schrock laboratory synthesized a series of molybdenum (6)\(^\text{35,36}\) and tungsten (7)\(^\text{32-34}\) based alkylidenes which were found to be highly reactive catalysts for both ADMET and ROMP with no side reactions detectable (Figure 1-8). The preparation of these complexes provided an impetus for a significant research effort in metathesis chemistry.
Figure 1-8. The Schrock-type metathesis catalysts 6 and 7 used in ADMET.

Extensive study of these alkylidene complexes and their ligand set was completed in order to optimize their catalytic activity. The tungsten version of this catalyst (7) was the first catalyst utilized for ADMET.\textsuperscript{32-34} However, more emphasis on the molybdenum catalyst (6) is shown in the literature, and this is based upon several factors. The molybdenum catalyst (6) is more prevalent because it is easier to synthesize and more tolerant to functionalities such as carbonyl groups.\textsuperscript{43} The high reactivity observed from these Schrock alkylidene complexes is a result of the high oxidation state of the metal (+6) and the presence of electron-withdrawing fluorinated alkoxy ligands. The resulting highly electropositive metal center favors strong olefin-metal interaction, of critical importance if metathesis is to occur. The $\pi$-donor ability of the nitrogen and oxygen based ligands present stabilizes the metal center, and the high steric bulkiness of these ligands prevents decomposition through bimolecular reactions. The Schrock-type alkylidenes are highly active, allowing for metathesis of both terminal and internal olefins as well as ring-opening polymerization of low strain cyclic monomers.\textsuperscript{43} Even so, these catalysts are limited by the substantial oxophilicity of the metal center, requiring that all reactions performed use strict, anaerobic conditions involving Schlenk line or
glovebox manipulations. These catalysts are also intolerant to many different functional
groups, such as acids, alcohols, aldehydes, and ketones for the [W] version (7), and acids,
alcohols, and aldehydes for the [Mo] version (6).43

Researching more air, water, and functionality tolerant complexes, the Grubbs
group discovered a series of carbene complexes based on the late transition metal
ruthenium in the mid-1990s (Figure 1-9).44-50

![Figure 1-9. The first generation Grubbs’ ruthenium catalyst 8.](image)

Being less oxophilic, ruthenium carbene complexes are more tolerant to many functional
groups and preferentially react with olefins in the presence of acids, alcohols, aldehydes,
esters, and amides.50 The first generation Grubbs’ ruthenium catalysts all incorporate two
bulky, basic, and electron donating PCy3 ligands with large cone angles and two chlorine
ligands.46 This combination, in conjunction with the reactive benzylidene moiety bound
to the ruthenium metal center, produces catalyst 8 that is quite reactive in olefin
metathesis. On the other hand, the first generation Grubbs’ [Ru] catalyst (8) is slower
than the Schrock’s [Mo] catalyst (6) by an order of magnitude, but the advantage of its
functional group tolerance and the ease of handling eclipses this limitation. The
discovery of the ruthenium metathesis catalysts enables olefin metathesis to be a viable route for the synthesis of both functionalized small molecules and polymers of variable architectures.

Mechanistic studies of ruthenium catalyzed metathesis show a dissociative mechanism predominates which involves the dissociation of one PCy3 ligand followed by olefin coordination.\textsuperscript{48,50} The presence of a highly active monophosphine intermediate encouraged many research groups to evaluate other electron rich ligands in an attempt to further optimize and improve this catalyst system. In 1999, the Herrmann laboratory discovered a ruthenium catalyst based upon the first generation Grubbs’ catalyst (8), but the catalyst possessed two N-heterocyclic carbene (NHC) ligands instead of two PCy3 ligands (Figure 1-10).\textsuperscript{51,52} NHC-ligands are strong $\sigma$-donors and much less labile than the phosphine ligands.\textsuperscript{53-55} Replacement of both PCy3 ligands with NHC ligands produces catalyst 9 that is much more robust, but no increase in activity was observed.\textsuperscript{51,52}

Figure 1-10. The Herrmann catalyst (9) bearing two NHC-ligands.
Concurrently, the research groups of Grubbs and Nolan discovered in 1999 that using only one NHC-ligand and retaining one phosphine ligand produces a significantly improved metathesis catalyst 10 (Figure 1-11). \(^{52,56}\) Since the NHC-ligand is strongly electron donating and sterically demanding, the presence of only one of these ligands enhances the dissociation of the other phosphine ligand and also stabilizes the active catalytic species. Replacing the one phosphine with the NHC-ligand dramatically increases the reactivity and rate of the catalyst.

\[
\begin{align*}
\text{Mes} & \quad \text{NHC-ligand} \quad \text{Mes} \\
\text{Cl} & \quad \text{Ru} = \text{Mes} \\
& \quad \text{PCy}_3 \quad \text{PCy}_3
\end{align*}
\]

\(\text{Mes} = \text{mesityl (1,3,5-trimethylphenyl)}\)

Figure 1-11. The Grubbs second generation ruthenium catalysts 10 and 11.

In terms of activity, this second generation Grubbs catalyst (10) is more active than the first generation ruthenium catalyst (8), \(^{56}\) and the improved saturated NHC-ligand (11) is even more active than the unsaturated NHC-ligand (10). \(^{57-61}\) In fact, both of these second generation Grubbs catalysts (10, 11) match or exceed, in some cases, the activity of the Schrock alkylidene catalysts in both ADMET and ROMP reactions. \(^{62,63}\) In addition, the NHC-ligated Grubbs catalyst is even more tolerant to functionality, air, moisture, and temperature than the first generation catalyst. \(^{56-61}\) The discovery of this new series of catalysts has caused an explosion of interest in research involving olefin
metathesis, particularly in the ring closing metathesis of substituted olefins and the preparation of highly functionalized polymers.23,50

The discovery and use of both the Schrock and Grubbs metathesis catalysts has been instrumental in the synthesis of various polymer architectures and functionalities via ADMET.20 Once a desired $\alpha,\omega$-diene containing functionality or branching is prepared, ADMET polymerization can be performed, which retains the functionality and specific backbone sequence. Consequently, a broad range of polymers with designed architectures can be prepared that are difficult or impossible to synthesize via other routes.

**Silicon Polymers and ADMET Polymerization**

Polycarbosilanes, polymers with a backbone composed of both silicon and carbon, do not exist in nature. Linear carbosilane polymers are useful materials due to their thermal, electronic, and optical properties but are difficult to prepare.64-66 The discovery of the Schrock and Grubbs metathesis catalysts has allowed the silicon functionality to be incorporated into polymer backbones quite easily. The Wagener group has demonstrated that ADMET is a viable route for the synthesis of polycarbosilanes, siloxanes, and other silicon containing polymers.67-69 Utilization of metathesis polymerization opens up a new route for the synthesis of these polymers that avoids many of the limitations found in earlier synthetic methods.

The first linear unsaturated polycarbosilanes synthesized using ADMET involved a polydimethylcarbosilane backbone.67 During this work, it was discovered that methylene spacer groups are necessary between the silicon atom and the double bond moiety in order for polymerization to occur. Divinyl substituted silanes would not
condense because of unfavorable steric interactions between the dimethylsilyl group adjacent to the double bond, and the catalyst.\textsuperscript{67} These steric interactions inhibit formation of the critical metallacyclobutane intermediate, thereby preventing metathesis from occurring. Further, vinyltrimethylsilanes will not self-metathesize and produce a dimer, as illustrated by Schrock.\textsuperscript{70} The addition of another methylene spacer group between the silicon atom and the olefin site was required to produce linear, silicon containing polymers (13) via ADMET polymerization (Figure 1-12).\textsuperscript{67}

![Chemical structure](image)

Figure 1-12. The synthesis of polydimethylcarbosilane (13) via ADMET.

Organofunctionalized polysiloxanes are another important class of silicon containing polymers, possessing a unique combination of properties ranging from hydrophobicity, low-temperature flexibility, and thermal stability.\textsuperscript{71-74} The presence of siloxane linkages in polymer chains as well as copolymers containing siloxane and olefin units enables useful materials to be synthesized because they combine the advantages of the hydrocarbon segment (increased mechanical properties of the polymer) with the flexibility and hydrophobicity of the siloxane segment.\textsuperscript{71-74} A series of this type of polymer (15) was synthesized using ADMET by altering both the number of methylene spacer groups between the double bond and the silicon atom and the length of the siloxane segment (Figure 1-13), demonstrating the compatibility of metathesis chemistry with these functionalities.\textsuperscript{68}
Reactive Polycarbosilanes and ADMET

An intriguing aspect of metathesis polymerization is that many reactive functional groups are inert to the catalysts used and remain intact after the reaction. The catalysts used in ADMET polymerization, the Schrock and Grubbs families of single-site catalysts, are the reason behind this behavior, for without the discovery of these well-defined selective catalysts, the synthesis of functionalized polymers via ADMET could not be a reality.

A class of polymers currently under investigation are recognized as latent reactive polymers, which possess silicon-methoxy groups. The Si-OCH₃ bond is inert to both the [Ru] (8, 10, 11) and [Mo] (6) metathesis catalysts, but this bond is hydrolytically unstable and reacts slowly over time with atmospheric moisture, crosslinking and releasing methanol. In order to produce a material that is both flexible and has good mechanical strength, a monomer containing hydrolytically reactive Si-OCH₃ groups (16) was copolymerized with a hydrolytically stable α,ω-diene monomer containing a flexible siloxane segment (17) (Figure 1-14).

Since each monomer has equal reactivity, a statistical copolymer (18) was synthesized composed of a “soft” siloxane segment with a “hard” segment containing the crosslinkable Si-OCH₃ groups. Further research effort in order to improve the
mechanical properties of these copolymers is ongoing, and the synthesis of these polymers via metathesis demonstrates the viability of employing reactive groups on polymer backbones.

![Chemical structures](image)

Figure 1-14. ADMET copolymerization of a "hard" and "soft" monomer.

**Reactive Si-Cl Bonds and ADMET**

Even more advantageous is the inherent compatibility of metathesis catalysts with the highly reactive Si-Cl bond. The Si-Cl bond is highly reactive to nucleophiles and is easily substituted, and this chemistry is widely utilized in industry to prepare large quantities of functionalized silanes. Incorporation of reactive Si-Cl bonds along a polymer backbone would serve as "handles" for further functionalization, producing materials with a wide range of applicability and properties. Previous work by the Wagener group involving the synthesis of chlorosilane oligomers, has proven that the Si-
Cl bond is inert to Schrock's [Mo] catalyst (6) under ADMET conditions. Linear, unsaturated, reactive polydichlorocarbosilanes can be designed and synthesized using this knowledge.

A suitable α,ω-diene monomer containing reactive Si-Cl bonds was necessary in order to synthesize dichlorocarbosilane polymers. Molecules of this type are not commercially available, so several pathways were evaluated to enable the synthesis of a parent α,ω-diene containing the appropriate dichlorosilane moiety. Ultimately, Grignard chemistry was successfully utilized to produce the parent monomer. After successful synthesis of this monomer, ADMET polymerization was performed, producing a poly(dichlorocarbosilane). This reactive polymer is not useful by itself without further modification because rapid hydrolysis of the Si-Cl bonds occurs, producing corrosive HCl gas and forming a crosslinked siloxane network polymer (Figure 1-15). However, the reactive polymer is useful as a precursor polymer backbone.

Figure 1-15. Hydrolysis of the reactive poly(dichlorocarbosilane), producing a crosslinked siloxane network polymer.
Obtaining an understanding of the substitution chemistry of the Si-Cl bonds is the first step in the preparation of functionalized polymers. A model study was performed on a substrate that would mimic a polymer repeat unit, where various nucleophilic reagents were reacted with a long chain dialkyldichlorosilane in order to evaluate the nucleophilic substitution reaction on a $R_2SiCl_2$ site. The second substitution of the Si-Cl bond is kinetically much slower than the first Si-Cl substitution. Additionally, both steric and electronic factors play a significant factor in the substitution reaction and determine whether mono or disubstitution is observed. Small, sterically undemanding nucleophiles such as methanol and ethanol are able to be disubstituted, whereas bulky nucleophiles such as $t$-butanol only allow one Si-Cl bond to be substituted. In the case of weaker phenolic nucleophiles, the presence of electron-donating groups allows disubstitution to occur, while electron-withdrawing groups promote only monosubstitution. A detailed study of this nucleophilic substitution reaction and the chemistry entailed has been discussed elsewhere.

Knowledge of the nucleophilic substitution chemistry of Si-Cl bonds learned during the model study was instrumental in the synthesis of substituted polycarbosilanes. The goal of this research was to produce a series of polycarbosilanes with differing pendant groups by exploiting the reactivity of Si-Cl bonds in nucleophilic substitution reactions. By replacing the chlorine atom with different groups, both the stability and the overall properties of the final functionalized polymer will be altered, but the parent polymer backbone remains the same.
The initial route studied to produce substituted polycarbosilanes involved the nucleophilic functionalization of the monomer, followed by ADMET polymerization (Figure 1-16).

![Diagram](image)

**Figure 1-16.** Two routes to produce substituted polycarbosilanes using both nucleophilic substitution and ADMET polymerization.

The advantage of this route is that quantitative substitution of each Si-Cl bond is not necessary because the monomer is purified prior to polymerization. This step ensures complete replacement of all Si-Cl bonds. Using this strategy, alcohol nucleophiles were first employed to replace the Si-Cl bonds with Si-OR bonds, and then reactive polymers containing Si-OR bonds were synthesized by ADMET polymerization of the functionalized diene monomer. The rate of hydrolysis of the resulting polymer pendant groups is governed by the identity of the OR group chosen.

Such materials would be useful for a variety of applications. For example, use of a reactive alkoxy group would enable slower hydrolysis to occur, producing a stable crosslinked network material after polymer shaping and processing. This process, known
as room temperature vulcanization (RTV), is widely used to produce a variety of industrially important materials.\textsuperscript{81}

Functionalization of the dichlorosilyl group was first performed on the parent \(\alpha,\omega\)-diene monomer using several different alcohols. Since the ruthenium metathesis catalysts are inert to and compatible with the functional groups substituted on the diene, ADMET polymerization was utilized in the preparation of these substituted polymers. The details are discussed in Chapter 2. A series of polymers with designed architectures was produced with very different properties and resulting hydrolytic stabilities.

The second route utilized for producing substituted polycarbosilanes was macromolecular substitution of a preformed, reactive polymer backbone containing two Si-Cl bonds per repeat unit (\textit{vide supra}). The advantage of this route is that an entire series of polymers can be synthesized from the exact same parent polymer backbone, creating a family of polymers with different properties. A parent dichlorocarbosilane polymer backbone was first synthesized, and then substitution reactions upon the polymer backbone were performed. Macromolecular substitution reactions can often be quite difficult because of limited accessibility of the Si-Cl bonds present in the polymer. It is critical to substitute each and every Si-Cl bond on the polymer backbone in order to produce a soluble, useful material. Any residual Si-Cl bonds left on the polymer backbone will hydrolyze upon exposure to the atmosphere, causing crosslinking of the polymer to occur, and an insoluble network will be formed. Using alkyllithium reagents as nucleophiles, successful comprehensive macromolecular substitution was performed, producing a series of stable, linear, unsaturated polycarbosilanes by a combination ADMET-macromolecular substitution route. These studies are detailed in Chapter 3.
The materials produced are hydrolytically stable because carbanion nucleophiles were utilized, replacing Si-Cl bonds with stable Si-C bonds.

As discussed above, impeding the hydrolysis of alkoxy functionalized polymers would allow for useful polymers as-is, as well as providing more time to process these materials before any crosslinking could occur. Hydrolysis could still be beneficial; however, the rate of which would be slowed considerably. Chapter 4 details the synthesis of model compounds with improved hydrolytic stability versus the substituted monomers employed in Chapter 2. These model compounds utilize nucleophiles that are sterically bulky or form stable rings, producing Si-OR bonds that more resistant to hydrolysis (Figure 1-17).

Alcohols such as isopropanol, phenol, and benzyl alcohol, as well as certain diols, were shown to effectively react with both Si-Cl bonds of a dichlorosilyl group. Certain reagents containing two OH groups per molecule were able to react with both Si-Cl bonds on the same silicon atom, producing stable cyclic structures.

All of the nucleophilic systems studied produce products with improved stability and consequently, can be worked up in the atmosphere. Utilization of these functional groups as pendant groups would presumably produce polymers with increased stability and considerably different properties than the polymers synthesized in this work.
Summary

A series of unsaturated, functionalized polycarbosilanes were synthesized using ADMET polymerization. The flexibility of this synthetic route demonstrates not only the inherent compatibility of modern metathesis catalysts used in the polymerization, but the ability of ADMET to prepare polymers with designed architectures and functionalities that are difficult or impossible to prepare by other means. Tolerance of the molybdenum (6) and ruthenium (8, 10, 11) catalysts to both silicon-chlorine and silicon-alkoxy bonds respectively, allow the utilization of both of these groups in ADMET. Exploitation of known chlorosilane substitution chemistry enabled successful, quantitative substitution to be realized, producing fully substituted polymers. Two different routes were successfully employed to produce these functionalized materials: polymerization followed by functionalization and functionalization prior to polymerization. Few other polymer synthesis routes are described in the literature that approach the same level of flexibility. The results described in this work demonstrate that ADMET polymerization is not only an extremely versatile route to functionalized polycarbosilanes, but polymer properties can be significantly modified by the nature of the polymer pendant group.
CHAPTER 2
NUCLEOPHILIC SUBSTITUTION AND ADMET POLYMERIZATION OF DIALKYOXYSILYLDIENES

Introduction

Alkoxysilanes are a class of compounds that enjoy a wide variety of applications ranging from biomedicine to lubricants and coatings.\(^82\)\(^{-89}\) Even so, their applications are dependent on the hydrolytic stability of the alkoxy group incorporated. For example, materials such as thin shell casings, resins, coatings, and low heat glasses require hydrolysis of the alkoxysilane incorporated in the final processing step.\(^90\) Other materials require the alkoxysilane groups to remain intact, and these alkoxysilanes are useful for materials such as lubricants, hydraulic fluids, and diffusion-pump oils.\(^90\)

Polymer Properties vs. Pendant Groups

The relationship between pendant group and product application can also be correlated in polymeric systems. The best example of this in the literature involves the Allcock group, who have studied a family of polymers based upon a reactive phosphazene backbone (20) (Figure 2-1).\(^94\)\(^{-100}\)

![Figure 2-1. Macromolecular substitution of poly(phosphazene).](image)
The parent poly(phosphazene) (20) contains two P-Cl bonds per repeat unit, and the resulting dichloropolymer is hydrolytically unstable. However, once functionalized, poly(phosphazenes) (21) become stable materials that can be useful for a wide variety of applications. The pendant group utilized governs the application of the resulting material. A myriad of pendant groups and combinations of different pendant groups have been successfully attached to this polymer backbone, forming a series of materials with a wide range of properties. In this system, functionalization via macromolecular substitution must occur after the ring opening polymerization of the parent monomer has been complete. The reason for this is that substitution of the cyclic hexachlorophosphazene trimer (19) prior to polymerization prevents ring opening from occurring and no high polymer forms.

Table 2-1 illustrates that by changing the pendant group of the polymer, the properties of the polymer produced can be vastly different. Many other pendant groups have been studied as well.

Table 2-1. Relationship of polymer properties vs. pendant group in poly(phosphazenes).

<table>
<thead>
<tr>
<th>Pendant Group</th>
<th>Properties</th>
<th>T_g/T_m (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OCH_2CH_3</td>
<td>elastomer</td>
<td>-84 / a</td>
</tr>
<tr>
<td>OC_6H_5</td>
<td>hydrophobic, microcrystalline thermoplastic</td>
<td>-8 / +390</td>
</tr>
<tr>
<td>OCH_2CF_3</td>
<td>hydrophobic, microcrystalline thermoplastic</td>
<td>-66 / +242</td>
</tr>
<tr>
<td>O(CH_2)_2O(CH_2)_2OCH_3</td>
<td>water-soluble elastomer</td>
<td>-84 / a</td>
</tr>
<tr>
<td>NHCH_3</td>
<td>glass, water-soluble</td>
<td>+14 / a</td>
</tr>
</tbody>
</table>

a) no T_m observed
For both of these reasons, an effort was directed towards the synthesis of a series of analogous alkoxy-substituted polycarbosilanes in order to study the effects the variation of a particular pendant group would have on the properties of this type of polymer. Each material synthesized would contain the exact same backbone but with different reactive alkoxy pendant groups. The polymer properties and atmospheric stability will be strongly influenced by the individual pendant group chosen. Such a series of polymers would have potential uses for a variety of applications such as hoses, belts, and conformable seals for gas masks (Figure 2-2).

![General structure of a functionalized polycarbosilane.](image)

Figure 2-2. General structure of a functionalized polycarbosilane.

The degree of hydrolytic stability of the polymer is completely dependent upon the pendant group. The parent silane monomer that is used contains two highly reactive Si-Cl bonds. After polymerization, the material produced is not very useful because rapid crosslinking of the hydrolytically sensitive Si-Cl bonds present in each repeat unit occurs. This hydrolysis reaction produces a siloxane polymer network which is insoluble and cannot be shaped or processed. In addition, corrosive HCl gas is liberated, which is highly undesirable. Because of this phenomenon, functionalization of the Si-Cl bonds with stable alkoxy or alkyl groups is necessary in order to produce a useful material.
As seen in previous model studies,\textsuperscript{79,80} small, sterically unhindered alkoxy groups such as methoxy and ethoxy, undergo facile substitution of Si-Cl bonds. These groups are commonly used in a variety of alkoxy silane polymers. The 2,2,2-trifluoroethoxy group was evaluated because fluorinated alkoxy groups have been shown to produce materials that are highly water-repellent and resist swelling by petroleum fluids.\textsuperscript{92-94} Further, phenoxy groups attached to silicon also tend to be more resistant to hydrolysis as well. This phenomenon has been discussed in the literature, but no one has offered a reasonable explanation based on either steric or electronic effects.\textsuperscript{101} These pendant groups were chosen for this study because of the differences in polymer properties they would impart, but also they would produce polymers with different hydrolytic stabilities.

After substitution of the Si-Cl bonds of the parent diene with the appropriate nucleophile, the functionalized monomers were polymerized using ADMET to produce high molecular weight materials of increased stability. Depending upon its ultimate use and choice of pendant group, the resulting polymer could be hydrolytically stable or crosslink slowly. By synthesizing completely substituted monomers prior to polymerization, all the reactive Si-Cl bonds have been functionalized, eliminating incomplete substitution of the polymer backbone. Incomplete substitution would be detrimental to the material because any residual Si-Cl bonds would crosslink when exposed to the atmosphere, producing an insoluble, intractable, brittle material. Metathesis catalysts such as Grubbs' ruthenium catalysts (8, 11) are not affected by the functionalities present on these pendant groups, thus allowing the functionalized
monomers to be easily polymerized. This inherent flexibility is a significant advantage to ADMET polymerization, since functionalization is not limited to macromolecular substitution reactions.

**Synthesis of the Parent Monomer**

In order to produce functionalized monomers, a synthetic route to an ADMET-capable \( \alpha, \omega \)-diene containing highly reactive Si-Cl bond(s) was desired. Therefore, the synthesis of this type of monomer was undertaken. There are two practical routes to produce new Si-C bonds: hydrosilation and Grignard chemistry. Initial attempts to synthesize the parent monomer 23 involved hydrosilation chemistry. Dichlorosilane gas was condensed and reacted with excess 1,5-hexadiene (22) in the presence of Speier’s catalyst (\( \text{H}_2\text{SiCl}_6 \)) (Figure 2-3).  

\[
\begin{align*}
\text{Si-H} + \text{H}_2\text{SiCl}_2 \xrightarrow{\text{H}_2\text{PtCl}_6} & \quad \text{Cl-Si} \quad \text{Cl} \\
\text{22} & \quad \text{23} \\
+ \text{cyclics and internal isomers formed}
\end{align*}
\]

Figure 2-3. Hydrosilation of a chlorosilane and a diene.

Although platinum catalysts are well known for their efficiency in hydrosilation chemistry, it is not a route without complications when using dienes. The hydrosilation reaction can produce cyclic species from an intramolecular reaction as well as low molecular weight polymers from intermolecular addition. In addition, internal olefin bond formation is facile, a direct consequence of using a late transition metal catalyst,
which is known to promote olefin migration via $\beta$-hydride elimination.\textsuperscript{103} All of these side reactions were observed in the reaction of 1,5-hexadiene (22) with $\text{H}_2\text{SiCl}_2$.\textsuperscript{79} A mixture of dialkenyldichlorosilane isomers were separated from the cyclics and polymer by distillation. Due to the trivial differences in their boiling points, the desired $\alpha,\omega$-diene (23), which was produced in approximately 10\% selectivity, could not be isolated from the other isomers. Varying reaction conditions and using alternative platinum hydrosilation catalysts such as Kardstedt’s, Pt(divinyltetramethylidisiloxane) in xylenes, were ineffective at completely suppressing this isomerization reaction. Therefore, this synthetic route was abandoned as being impractical.

**Grignard Chemistry and Halosilanes**

Since ADMET polymerization is a step-growth polycondensation reaction, absolute monomer purity is required in order to achieve high molecular weight material.\textsuperscript{17-19} Because of the difficulty of purification of the desired $\alpha,\omega$-diene using hydrosilation chemistry, Grignard chemistry was evaluated in order to produce a useful monomer. The molecule targeted for synthesis via this route was a ten carbon, $\alpha,\omega$-diene containing a dichlorosilyl moiety in the center, di-4-pentenyldichlorosilane.

The Grignard reaction of a halosilane is quite different in reactivity than its carbon analog. It is well known that a Grignard reaction involving chlorosilanes is rarely stepwise and that multiple substitution of the substrate is favored in most instances.\textsuperscript{108} The reason for this increased reactivity is not based upon the differences in bond strengths, because a Si-Cl bond is stronger than a C-Cl bond as shown in Table 2-2. However, a significant difference lies the in length of both the Si-Cl and the Si-C bonds,
which are both longer than its carbon analog, causing the silicon atom to be more exposed to an attacking nucleophile.103

Table 2-2. Bond strengths and bond lengths for various silicon and carbon analogs.83,109

<table>
<thead>
<tr>
<th>Bond (Si-X or C-X)</th>
<th>Bond Strengths (kJ/mol)</th>
<th>Bond Lengths (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-Cl</td>
<td>472</td>
<td>2.05</td>
</tr>
<tr>
<td>C-Cl</td>
<td>335</td>
<td>1.78</td>
</tr>
<tr>
<td>Si-C</td>
<td>369</td>
<td>1.87</td>
</tr>
<tr>
<td>C-C</td>
<td>334</td>
<td>1.53</td>
</tr>
</tbody>
</table>

The two major disadvantages of this Grignard route are the general inability to produce clean, integral, partial substitution and that the removal of undesired corrosive, hydrolytically sensitive by-products is not trivial.108 The advantage of this route is that it produces silanes with the terminal olefins intact with absolutely no isomerization. Depending upon whether complete or partial substitution is desired, the sequence of addition of reagents becomes significant.108 If full substitution of a halosilane with a Grignard reagent is desired, a “normal” addition is advantageous. A “normal” addition involves addition of the halosilane directly to a solution of Grignard reagent. On the other hand, if partial substitution is necessary, then a “reverse” addition is utilized. This method involves the addition of a desired number of equivalents of Grignard reagent to a halosilane solution.

The other important factor of this reaction involves the miscibility of the Grignard reagent with the substrate solution. This is of critical importance because the reaction of the halosilane with the Grignard reagent must be slowed down in order to have a chance
of producing useful amounts of the desired partially substituted product. The less soluble the Grignard reagent is with respect to the solution of halosilane, the better the chance of partial substitution. Rosenberg et al. have demonstrated this by using heptane as the reaction solvent for the Grignard reaction involving arylichlorosilanes.\textsuperscript{110} In this work, they found that for the reaction of 2.1 equivalents of phenylmagnesiumbromide with SiCl\textsubscript{4}, 77% of disubstituted product was produced. The selectivity is the highest seen in the literature to date. This methodology was a key factor in the successful synthesis of di-4-pentenyldichlorosilane using Grignard chemistry.

**Synthetic Attempts**

Early attempts to synthesize this molecule used Et\textsubscript{2}O as the reaction solvent for both the formation of the Grignard reagent and for its reaction with the halosilane. The magnesium turnings used to form the Grignard reagent were kept free of oxide and moisture by storage in a vacuum oven before use. The magnesium was activated by a process called entrainment, involving the addition of a small amount of 1,2-dibromo-ethane.\textsuperscript{111,112} Apparently, this reactive organic halide cleans the surface of the magnesium metal and activates it, forming MgBr\textsubscript{2} (the activator) and ethylene, which is released in the process. After formation of the Grignard reagent, which involved the reaction of 5-bromo-1-pentene (24) with the Mg turnings, titration of RMgBr (25) was performed according to the method described in Vogel's to ensure the correct number of equivalents was added to the SiCl\textsubscript{4} (Figure 2-4).\textsuperscript{113} Typically, between 80-85% yield of Grignard reagent was formed in this reaction. In diethyl ether solvent, reacting SiCl\textsubscript{4} with the alkenyl Grignard reagent (25) using reverse addition produced about 50% selectivity for disubstitution.
Figure 2-4. Synthesis of di-4-pentenyldichlorosilane (26) via Grignard chemistry.

Gas chromatography of the reaction mixture illustrated a peak shoulder directly after the product peak. Carbon-13 NMR analysis of this species showed a resonance at 64.0 ppm, which is characteristic of a carbon atom bonded to an oxygen atom (Figure 2-5).

Figure 2-5. The $^{13}$C NMR spectrum of 26, when diethyl ether is used as the solvent (post-distillation).
The $^1$H NMR spectrum displayed a quartet at 3.87 ppm and a triplet at 1.65 ppm, which can be attributed to ethoxy group protons. Obviously, all of this evidence pointed to the formation of an undesirable by-product, an ethoxy-substituted silane.

Occurrence of by-product formation is attributed to diethyl ether reacting with SiCl$_4$ during the Grignard reaction. Literature precedence for this phenomenon is over 100 years old$^{114}$ and has been observed by others as well.$^{115-117}$ In addition to the Si-OEt bonds being formed, as proven by the NMR spectra discussed above, Si-Et bonds can also be produced. This can occur because EtCl by-product, created from the Si-OEt bond formation, can react with any residual magnesium.$^{117}$ This produces EtMgCl, which then reacts with the Si-Cl, forming new Si-Et bonds. Whitmarsh and Interrante have proven this phenomenon by preparing their chlorocarbosilane polymers in deuterated Et$_2$O and performing $^2$H NMR analysis.$^{117}$ Neither by-product, ethoxy nor ethyl substituted diene, can be effectively removed from its chloro analog by distillation. Hence, the use of ethereal solvent for this reaction is not desired.

Because side reactions occur when using Et$_2$O as the reaction solvent, it was necessary to replace Et$_2$O with heptane as the reaction solvent. Heptane does not react with Si-Cl bonds and form any undesirable products, and in addition, greater selectivities result when using this solvent. Using methodology modeled on Rosenburg’s system, excess (7.27 g, 0.30 mol) Mg turnings and 5-bromo-1-pentene (40.50 g, 0.27 mol) were reacted in 175 mL Et$_2$O, producing 82% yield of Grignard reagent (0.22 mol). Reverse addition of the Grignard reagent solution (2.1 equivalents) dropwise over 6 hours to SiCl$_4$ (16.86 g, 0.10 mol), dissolved in an excess of 500 mL heptane (2:1 heptane/ether), followed by refluxing overnight under Ar, produced the desired product. Complete
suppression of the formation of any Si-OEt and Si-Et bonds occurred, evidenced by GC, NMR, and elemental analyses. Using GC analysis, 73% selectivity towards di-4-pentenyldichlorosilane was observed, with 24% trisubstituted product and 3% monosubstituted product formed. No tetrasubstituted product was observed.

Purification and Spinning Band Distillation

Absolute isolation of the diene monomer from its reaction by-products is of critical importance if the synthesis of linear, soluble polymer is to be achieved. Any residual monoene, if reacted under ADMET conditions, would act as a chain termination agent in an ADMET polymerization, and any triene or tetraene present would react at every terminal olefin site, forming an insoluble network polymer (Figure 2-6).

During the dialkenyldichlorosilane monomer synthesis, three different alkylation products were produced (vide supra). Mono-, di-, and trisubstituted products were formed and separation of these compounds is not a trivial task.

![Diagram showing the outcome of mono and trisubstituted olefins in the reaction mixture.](image)
Chlorosilanes are corrosive and hydrolytically unstable materials, and in addition, vacuum distillation must be employed to distill these particular compounds due to their high boiling points. The boiling point of the monoene is around 220 °C at room temperature, the diene 260 °C, and the triene is slightly above 300 °C. As the distillation pressure is lowered, the efficiency of all columns, hence separation, is significantly reduced, often as much as 50-70%. Generally, the number of plates required to separate two different compounds is equal to 120/ΔT, where ΔT is the difference in boiling point between the two compounds. Since the difference at 4 Torr between mono-, di-, and trisubstituted dienes is approximately 15 °C per species, a minimum of eight distillation plates would be required to separate these components. Traditional laboratory Vigreux columns have three to six distillation plates, and it was not possible to separate the mixture. Therefore, a spinning band distillation column equipped with a Teflon band was employed in order to purify these materials. The Teflon band does not react with chlorosilanes, and the apparatus employed was rated at 30 distillation plates at ambient pressure. Even with reduced efficiency at lower pressures, the column is capable of separating this mixture. Since maintenance of pressure is crucial during vacuum distillation, a manostat containing dibutylphthlate was connected to the system in order to keep the pressure constant at 4 Torr during the entire distillation. Constant heating was controlled using a thermocouple monitored heating mantle connected to a Variac constant voltage regulator. Teflon boiling stones were used to order to prevent any superheating or “bumping” of the mixture.
After three hours of equilibration, consisting of constant reflux (30 drops/min) at the boiling point, the spinning band distillation column demonstrated its superior efficiency in purifying the monomer (Figure 2-7).

Figure 2-7. The $^{13}$C NMR spectrum of di-4-pentenyldichlorosilane (26).

Using a reflux ratio of 15:1, separation of the monomer, di-4-pentenyldichlorosilane (26), was achieved (BP: 90-92 °C/ 4 Torr), yielding 38% disubstituted product. Calculated yields by gas chromatography of the disubstituted product were much higher (73% selectivity), and the reduced yields obtained are attributed to distillation losses, hydrolysis polymerization of the chlorosilane from slight traces of moisture present, and
discarding of intermediate distillation fractions. The successful separation of the parent monomer is illustrated by the absence of any impurity peaks in the $^1$H, $^{13}$C, and $^{29}$Si NMR spectra and in the GC trace.

**Nucleophilic Substitution of the Parent Monomer**

After the di-4-pentenyldichlorosilane parent monomer (26) was successfully isolated, four functionalized monomers were synthesized via nucleophilic substitution of both Si-Cl bonds. The nucleophiles utilized were judiciously chosen based upon information discovered in a previous model study.$^{79,80}$ Four nucleophilic alcohols (MeOH, EtOH, CF$_3$CH$_2$OH, and PhOH) that would easily substitute both Si-Cl bonds and produce polymers that exhibit significantly different thermal properties and differences in hydrolytic stability were chosen. Based upon previous experience, the anticipated hydrolytic stability of the resulting products should range from dimethoxysilane (least stable) to diphenoxysilane (most stable). All four monomers were synthesized using two similar methodologies, by reaction of a dichlorosilane (26) with excess equivalents of an alcohol/amine or metal alkoxide nucleophile (Figure 2-8).

$$\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Si} & \quad \text{Si} \\
\text{Cl} & \quad \text{Cl} \\
\text{R} = \text{OCH}_3 & \quad 27 \\
\text{OCH}_2\text{CH}_3 & \quad 28 \\
\text{OCH}_2\text{CF}_3 & \quad 29 \\
\text{OC}_6\text{H}_5 & \quad 30 \\
\end{align*}$$

Figure 2-8. Functionalization of the dienes via nucleophilic substitution.
Synthesis of the Dimethoxy Functionalized Monomer

The dimethoxysilane containing α,ω-diene (27) was synthesized by a one-step reaction of di-4-pentenyldichlorosilane (26) with two equivalents of both MeOH and Et₃N per Si-Cl bond (Figure 2-9).

![NMR spectrum of di-4-pentenyldimethoxysilane (27).](image)

Triethylamine serves only as a proton acceptor, as it is sterically inhibited enough to be considered non-nucleophilic, and it is not a strong enough base to deprotonate the alcohol. Diethyl ether was used as the solvent because the triethylamine hydrochloride salts produced are reasonably insoluble in Et₂O, making purification by Schlenk filtration easier. After refluxing overnight under an inert atmosphere and subsequent work-up, the monomer was purified by vacuum distillation in 58% yield.
Using Metal Alkoxides as Nucleophiles

The diethoxysilane functionalized monomer (28) was synthesized by using KOEt as the nucleophile. Potassium ethoxide is a much stronger nucleophile than EtOH/NEt$_3$; however, either system is effective for this substitution reaction. The reason that KOEt was used in this reaction was to illustrate the versatility of the nucleophilic substitution reaction on these types of compounds and the viability of alternative reagents. The amount of KOEt utilized was two equivalents per Si-Cl bond, and this reaction required the use of THF as the solvent due to the solubility of the KOEt in this medium and its insolubility in Et$_2$O. The substitution of both Si-Cl bonds occurred readily, and this monomer was isolated after vacuum distillation at 0.005 Torr in 44% yield. Only one peak at -7.9 ppm was observed in the $^{29}$Si NMR spectrum, which verifies formation of a dialkoxydialkenyl silane and that complete substitution has occurred (Figure 2-10).$^{123,124}

![Figure 2-10. The $^{29}$Si NMR spectrum of di-4-pentenyldiethoxysilane (28).](image)

Incorporation of Fluorine Containing Nucleophiles

The di(2,2,2-trifluoroethoxysilyl) functionalized monomer (29) was synthesized because of the hydrophobicity of the 2,2,2-trifluoroethoxy entity. Further, this pendant
group has exhibited an increased resistance to hydrolysis in other reactive polymer systems.\textsuperscript{92-94} Although the nucleophilic strength of 2,2,2-trifluoroethanol is weaker than the other two nucleophiles discussed previously, substitution of both of the Si-Cl bonds in di-4-pentenyldichlorosilane still occurs. A fourfold excess of the 2,2,2-trifluoroethanol and Et\textsubscript{3}N in Et\textsubscript{2}O was reacted with di-4-pentenyldichlorosilane, and after reaction workup, the monomer was purified by vacuum distillation (57\% yield). Nuclear magnetic resonance spectroscopy, \textsuperscript{1}H, \textsuperscript{13}C, \textsuperscript{19}F, and \textsuperscript{29}Si, was completed, verifying the correct disubstituted product was synthesized. Figure 2-11 illustrates the \textsuperscript{13}C NMR spectrum of di-4-pentenyldi(2,2,2-trifluoroethoxy)silane. The presence of OCH\textsubscript{2}CF\textsubscript{3} groups in the product is confirmed by the two quartets in the \textsuperscript{13}C NMR spectrum due to \( \alpha \) one bond C-F coupling (\( ^{1}J = 280 \text{ Hz} \)) and \( \beta \) two bond C-F coupling (\( ^{2}J = 40 \text{ Hz} \)).

![Figure 2-11. \textsuperscript{13}C NMR spectrum of di-4-pentenyldi(trifluoroethoxy)silane (29).](image-url)
Phenolic Nucleophiles

The diphenoxysilyl functionalized monomer (30) was prepared in a similar fashion to the other monomers discussed; however, the substitution of the Si-Cl bonds did not occur without the addition of a small amount of DMAP (4-dimethylaminopyridine). It is likely that both the decreased nucleophilic strength of phenol and the increased steric bulk play a significant factor in its inability to effectively substitute two Si-Cl bonds. The use of DMAP and imidazole has been well established in the literature for assisting more difficult substitution reactions by acting as a good leaving group.\textsuperscript{125,126}

Di-4-pentenyldichlorosilane (26) was added to an ethereal solution of two equivalents of phenol and triethylamine per Si-Cl bond and a catalytic amount of DMAP. After reflux overnight under Ar and standard workup procedures, it was observed that the resulting diphenoxysubstituted monomer (30) exhibited an increased resistance to hydrolysis. This is clearly illustrated by the fact that the monomer was purified by silica gel column chromatography using hexanes/methylene chloride as the mobile phase (yield 53%). NMR analysis confirmed the correct product was isolated and purified. It is important to note that none of the other three substituted dialkoxyxsilyl monomers prepared could be exposed to the atmosphere, or especially an acidic silica gel column (pH ~ 5), for periods of time without significant degradation or hydrolysis to a siloxane.

Polymerization of the Substituted Monomers

After all four substituted monomers were synthesized, purified, and analyzed, the monomers were polymerized by standard ADMET methodology using the 2\textsuperscript{nd} generation Grubbs’ ruthenium metathesis catalyst (11) (Figure 2-12).
Polymerization of the 2,2,2-Trifluoroethoxysilyl Substituted Diene

Di-4-pentenyldi(2,2,2-trifluoroethoxy)silane (29) was chosen as an ADMET monomer because trifluoroethoxy pendant groups have been shown in the literature to resist swelling in petroleum fluids and to impart hydrophobicity to the resulting polymer.\textsuperscript{92-94} The best example of this lies in polyphosphazene systems, where a stable polymer was prepared containing two trifluoroethoxy groups bonded to a phosphorous atom per repeat unit. This functionalized polymer both repelled water and possessed a low T\textsubscript{g} and high a T\textsubscript{m}, which is characteristic of a microcrystalline thermoplastic material.\textsuperscript{92-94} It was hoped that similar stability and physical properties would result from a polycarbosilane analog.

The polymerization of di-4-pentenyldi(trifluoroethoxy)silane (29) was first attempted using Schrock’s molybdenum-based metathesis catalyst (6). This catalyst is highly active and well known for its utility in ADMET polymerization using low loadings. Under ADMET conditions, Si-Cl bonds were found to be inert to this metathesis catalyst.\textsuperscript{78,79} The monomer was carefully dried and degassed before combining with the [Mo] catalyst (6) in an Ar atmosphere glovebox in a 250:1
monomer:catalyst ratio (0.4% catalyst). No bubbling of ethylene was evident after the catalyst was mixed with the monomer, which is highly atypical. Usually, instantaneous reaction occurs when exposing a diene to Schrock's catalyst. The reaction tube was then sealed, removed from the glovebox, and placed on a high vacuum line. Under high vacuum (1 x 10⁻³ Torr), the evolution of ethylene was very slow and after 3 days, the reaction mixture had become viscous and gel-like. The polymerization procedure was terminated, and the solubility of the resulting product was tested. The polymer was determined to be insoluble in all solvents tested, including CHCl₃, THF, benzene, and boiling chlorobenzene. It is believed that some interaction between the trifluorosilyl groups and the catalyst produces a crosslinked gel.

Since a crosslinked polymer was obtained when using Schrock's catalyst (6), polymerization using Grubbs' 2nd generation ruthenium catalyst (11) was attempted under identical conditions. The metathesis catalyst was added to a flask containing the monomer inside of an Ar atmosphere glovebox. The monomer to catalyst ratio used was 400:1 (0.25% catalyst), typical for ADMET polymerizations involving ruthenium catalysts. No bubbling was evident, which is normal using this catalyst system, as it is slower and usually has an induction period of several minutes. The reaction flask was sealed, removed from the glovebox, and placed under reduced pressure on a high vacuum line. As the temperature was raised slowly to 45 °C using an oil bath, bubbling (ethylene evolution) became evident. As the reaction mixture was stirred overnight at constant temperature and at 1 x 10⁻³ Torr, ethylene slowly evolved, concurrent with an increase in solution viscosity. After 24 hours, the reaction mixture became too viscous to stir and the oil bath temperature was slowly raised to 60 °C. Stirring and ethylene evolution
continued for another six hours, after which both ceased. At this point, the polymerization procedure was stopped and a sample was removed for NMR analysis. The resulting viscous polymer (33) was soluble in chloroform. Subsequent NMR analysis indicated that ADMET polymerization occurred with no detectable side reactions. Nevertheless, it was observed that rapid crosslinking occurs with this polymer even when stored under an Ar atmosphere. This infers that even trace quantities of moisture, from the initial aliquot being removed, are able to hydrolyze the Si-OCH$_2$CF$_3$ bonds. It appears that the presence of the trifluoro group weakens the silicon-alkoxy bond towards hydrolysis instead of promoting increased stability via a hydrophobic effect.

Because this polymer crosslinks rapidly, molecular weight analysis using gel permeation chromatography (GPC) was unable to be performed. The level of moisture present in GPC solvents such as THF and CHCl$_3$ is sufficient to form an insoluble network. Instead, end-group analysis of the $^1$H NMR spectrum was used to calculate the number average molecular weight ($M_n$) of the polymer (Figure 2-13).

Since the end groups of ADMET polymers are terminal olefins, integration of these resonances versus internal olefin resonances produced by metathesis enables the average degree of polymerization to be calculated. Multiplication of the average degree of polymerization by the molecular weight of the polymer repeat unit calculates the $M_n$. Using this method, the $M_n$ was determined to be 12,000 g/mol. Integration of the quantitative $^{13}$C NMR spectrum resonances indicated a trans olefin content of approximately 80%, which is typically observed in ADMET polymerizations using well-defined ruthenium or molybdenum-based metathesis catalysts.$^{17,18,31}$
Differential Scanning Calorimetry (DSC) was used to thermally analyze this polymer. The DSC analysis of polymer 33, which was most likely partially crosslinked, revealed a glass transition temperature \( T_g \) of \(-63 \, ^\circ C \) and no discernable melting temperature \( T_m \) when scanning from \(-95 \, ^\circ C \) to \( 70 \, ^\circ C \). These thermal analysis results are typically observed for amorphous elastomers.

**Polymerization of Di-4-pentenyldiethoxysilane**

The 2\textsuperscript{nd} generation Grubbs’ ruthenium catalyst (11) was used to polymerize di-4-pentenyldiethoxysilane (28). Monomer and catalyst were mixed together in a flask under an Ar atmosphere using a 200:1 monomer:catalyst ratio (0.5% catalyst). It is important to note that once again, evolution of ethylene did not occur until the reaction mixture was
placed under high vacuum (1 x 10⁻³ Torr) and the external oil bath temperature had reached at least 35 °C. This is in agreement with results observed by others when using this particular catalyst. Over the next 3 days, the temperature of the oil bath was slowly raised to 65 °C to facilitate stirring. Throughout this time period, slow evolution (bubbling) of ethylene was observed concurrently with an increase in the solution viscosity of the mixture. After stirring ceased, the polymerization procedure was terminated and the resulting polymer (32) was taken into an Ar atmosphere glovebox, where all further manipulations were performed. This included preparation of the sample for DSC analysis, thus minimizing the possibility of unintentional crosslinking. Polymer 32 was soluble in CHCl₃, and subsequent ¹H NMR analysis revealed ADMET polycondensation chemistry had occurred. The molecular weight characterization via end group analysis revealed a $M_n = 15,000$ g/mol (Figure 2-14).

![Figure 2-14](image_url)
Carbon-13 NMR analysis indicated a typical cis/trans olefin ratio of the product polymer. Molecular weight analysis was attempted using GPC, but the polymer crosslinked during sample preparation in the CHCl₃ solvent. Most likely the moisture levels present in standard chromatographic solvents are sufficient to promote hydrolysis of the ethoxysilyl group at a rate that prevents analysis by GPC.

Thermal analysis by DSC revealed a very low $T_g$ (-83 °C) for this polymer and no observed $T_m$ when scanning a temperature range from -95 °C to 70 °C. Multiple DSC scans of this polymer sample and quenching with liquid N₂ were utilized to eliminate any previous thermal history and for repetitive data verification. The temperature of analysis was purposely limited to 70 °C in order to avoid any thermal crosslinking of the polymer.

**Polymerization of Di-4-pentenyldimethoxysilane**

Di-4-pentenyldimethoxysilane (27) was polymerized in the same manner ($1 \times 10^{-3}$ Torr) as the diethoxy functionalized monomer, using the 2⁰ generation Grubbs’ catalyst (11) in a monomer to catalyst ratio of 200:1 (0.5% catalyst). Over 5 days, the oil bath temperature was slowly increased to 60 °C during the course of the polymerization. After this time period, the polymerization procedure was terminated and the product was taken into an Ar atmosphere glovebox. It is well known that methoxy substituted silanes hydrolyze rather quickly upon exposure to atmospheric moisture and this is accelerated by both acidic and basic media, making handling difficult due to the presence of reactive groups in each repeat unit of the polymer. Consequently, this methoxy functionalized polycarbosilane (31) had to be kept under an inert atmosphere to prevent hydrolysis and gelation. Like its diethoxysubstituted analog, polymer 31 was also too hydrolytically sensitive for GPC analysis to be performed. However, the polymer was soluble in CHCl₃
and $^1$H NMR end-group analysis indicated a $M_n$ of 11,000 g/mol. Typical ADMET condensation chemistry occurred, no side products or reactions were detected, and typical stereoselectivity was observed. Preparing the sample pan and performing the analysis under an inert nitrogen atmosphere enabled DSC analysis to be performed. The sample was cold-quenched prior to scanning, in a similar fashion to the other dialkoxy polymers. The scan rate and temperature range were also identical to that of the ethoxy-functionalized polymer. The $T_g$ of this methoxy-functionalized polymer (31) was $-80 \, ^\circ{C}$, and no $T_m$ was observed.

**Polymerization of Di-4-pentenyldiphenoxysilane**

The 2nd generation Grubbs’ catalyst (11) was also used for the ADMET polymerization of di-4-pentenyldiphenoxysilane in an analogous fashion to the previous examples, using a monomer to catalyst ratio of 200:1 (0.5% catalyst). During this reaction, ADMET polymerization occurred, producing a viscous, oily polymer (34). No side reactions were detected via NMR analyses, and the trans olefin content was determined to be approximately 80%. Since it was discovered during the synthesis and purification of the monomer that this molecule is resistant to hydrolysis, the analysis of polymer 34 was not performed under the same rigorous inert conditions that the previous three polymers required. The resulting unsaturated polymer was readily soluble in chloroform, and GPC analysis was performed in this solvent using dual UV/RI detectors. The molecular weight analysis indicated a $M_n$ of 18,000 g/mol and a polydispersity index ($M_w/M_n$) of 1.8, typical for step-growth ADMET polymers. The DSC sample was not prepared in an inert atmosphere; however, the sample was treated identically to that of the other samples in terms of temperatures scanned ($-95 \, ^\circ{C}$ to 70 °C), the number of
scans, and the initial cold-quench of the sample pan. Figure 2-15 illustrates the DSC scan of the phenoxy substituted polymer. This thermal analysis proved interesting; the glass transition temperature of the diphenoxy-substituted polymer was $-29^\circ C$, an increase of over 50 degrees compared to the other alkoxy-substituted analogs. No $T_m$ was observed for this polymer within the range of temperatures scanned.

![Graph](image)

Figure 2-15. DSC scan of the phenoxy-substituted polymer (34).

**Conclusions and Comparisons**

The goal of this study was to examine the effects of varying the pendant group on a common carbosilane backbone. Four derivative monomers were synthesized from the same parent monomer containing two highly reactive bonds. The ancestral $\alpha,\omega$-diene 26 is functionalized via substitution chemistry by reaction with excess nucleophile, in this case, an alcohol (or alkoxide). Complete substitution at both sites is controlled by careful product purification and isolation. All of these functionalized monomers were
polymerized using the same methodology, ADMET polycondensation, and four different polymers with well-defined microstructures and similar molecular weights were produced. Since the polymer backbone is stable, the atmospheric stability of these materials is directly determined by the identity of the alkoxy pendant group. The pendant group incorporated has also demonstrated an influence in the physical properties of the resulting polymer, particularly the glass transition temperature. A variation of 54 degrees is a result of simply changing the pendant group from ethoxy to phenoxy.

Interestingly, the glass transition temperatures of the substituted polycarbosilanes produced by ADMET polymerization are comparable to their poly(phosphazene) (21) and poly(silylenemethylene) analogs when the same pendant groups are used, in spite of having vastly different polymer backbones as illustrated in Table 2-3.

Table 2-3. Comparison of three different polymers with identical pendant groups.

<table>
<thead>
<tr>
<th>Pendant Group (OR)</th>
<th>Tgs of poly-carbosilanes via ADMET</th>
<th>Tgs of poly-phosphazenes [NP(OR)2]n</th>
<th>Tgs of polysilylene methylenes [Si(CH3)(OR)CH2]n</th>
</tr>
</thead>
<tbody>
<tr>
<td>OMe</td>
<td>-80 °C</td>
<td>-76 °C</td>
<td>a</td>
</tr>
<tr>
<td>OEt</td>
<td>-83 °C</td>
<td>-84 °C</td>
<td>-79 °C</td>
</tr>
<tr>
<td>OCH2CF3</td>
<td>-63 °C</td>
<td>-66 °C</td>
<td>-51 °C</td>
</tr>
<tr>
<td>OC6H5</td>
<td>-29 °C</td>
<td>-8 °C</td>
<td>-18 °C</td>
</tr>
</tbody>
</table>

a) not determined

The viability of substituting silicon-containing monomers prior to polymerization was evaluated in this chapter. The ADMET polymerization of substituted monomers using functionality tolerant metathesis catalysts has been shown to be an effective route
for producing functionalized polymers of this type. The advantage of this route is that all of the functionality is guaranteed to be in place prior to polymerization. This assures that quantitative functionalization of the backbone is a reality, since substituting a polymer backbone can be much more difficult and often leads to incomplete functionalization.

The ADMET polymerization route possesses a significant advantage compared to other systems, where prior monomer functionalization can lead to catalyst deactivation or thermodynamically unfavorable polymerization conditions. Further, this methodology is versatile and flexible, since one parent monomer can be substituted rather simply using various nucleophiles, creating a large family of derivative polymers with vastly different properties. The alternative route to polymer functionalization, macromolecular substitution, where a reactive polymer backbone is derivitized, will be discussed in Chapter 3.
CHAPTER 3
MACROMOLECULAR SUBSTITUTION USING ALKYLLITHIUM REAGENTS

Introduction

Macromolecular substitution is a synthetic approach that involves the functionalization of a pre-formed polymer backbone containing reactive groups with an appropriate reagent. Using this strategy, variation of the side chains or pendant groups can be accomplished. A related family of polymers could then be synthesized from the same parent polymer backbone using this methodology. Since polymer properties can be heavily influenced by the properties of its pendant group, a variety of different materials with a wide range of properties and applications can be synthesized from only one parent polymer.

Often, a significant drawback of this concept is the requirement that the functionalization reaction be quantitative. This can be difficult and challenging to accomplish, due to a variety of factors. Many chemical reactions are not quantitative and produce undesirable by-products. This severely limits the choice of synthetic tools available. In addition, the reactivity of functional groups on a polymer backbone is often reduced compared to small molecules due to limited accessibility and steric hindrance. In many instances, it is difficult for a reagent (nucleophile) to have enough encounters with the polymer backbone in order to quantitatively substitute all of the reactive groups along the backbone.
In spite of these limitations, there are several successful examples of macromolecular substitution in the literature involving polymers containing hydrolytically sensitive phosphorus-chlorine and silicon-chlorine bonds. The Allcock group has quantitatively substituted a poly(dichlorophosphazene) backbone containing two reactive P-Cl bonds per repeat unit with a myriad of different nucleophiles, producing a family of stable polymers with differing properties. A more detailed discussion of this polymer system is found in Chapter 2.

Another pertinent series of polymers prepared using macromolecular substitution are the poly(silylenemethylenes), studied by the Interrante laboratory. The parent polymer, poly(dichlorosilylenemethylene) (36) was synthesized by the ring opening polymerization of 1,3-dichloro-1,3-dimethyl-1,3-disilacyclobutane (35) using a platinum-based catalyst (H₂PtCl₆). A series of derivative polymers (37) were then produced through the nucleophilic substitution of the Si-Cl bonds present each repeat unit. Several different nucleophilic reagents were utilized, including alcohol/amine, an effective system discussed previously in Chapter 2 (Figure 3-1).

\[
\begin{align*}
&(\text{CH}_3)(\text{Cl})\text{Si} \xrightarrow{\text{H}_2\text{PtCl}_6} \left(\text{Si}-\text{CH}_2\right)_n \xrightarrow{\text{ROH/Et}_3\text{N or NaOR}} \left(\text{Si}-\text{OR}\right)_n
\end{align*}
\]

Figure 3-1. Ring opening polymerization of a silylenemethylene, followed by macromolecular substitution.

The West group has also successfully utilized macromolecular substitution in the preparation of completely functionalized polysilanes (40). The parent reactive
polymer was synthesized via a ring opening polymerization of 1,1,2,2,3,3,4,4-octachlorocyclotetrasilane (38). The resulting polysilane backbone (39) contained two Si-Cl bonds per repeat unit. Substitution was enabled using a variety of different alcohol nucleophiles in conjunction with an amine base as a proton acceptor. A series of functionalized polysilanes (40) with interesting electronic and physical properties were the result (Figure 3-2).

Figure 3-2. Ring opening polymerization of a cyclotetrasilane, followed by macromolecular substitution.

Polymerization of the Parent Monomer

To demonstrate the synthetic flexibility of the carbosilane backbone prepared via ADMET polymerization, macromolecular substitution of the reactive parent poly(dichlorocarbosilane) was performed. This polymer was synthesized by the ADMET condensation polymerization of the α,ω-diene monomer di-4-pentenyldichlorosilane (26); the preparation of which was discussed in Chapter 2. Since it has been established that Si-Cl bonds are inert to metathesis catalysts, two highly reactive bonds per repeat unit of the polymer remain available for further reaction after polymerization is complete. The parent polymer itself is not useful due to its extreme hydrolytic sensitivity, but the reactive functionalities present can be converted to more stable
moieties via simple nucleophilic substitution reactions. As a result, one basic polymer can be converted into a whole family of derivative polymers with identical molecular weight and molecular weight distribution.

Di-4-pentenyldichlorosilane (26) was polymerized using standard procedures for ADMET polymerization. The monomer was carefully degassed using three freeze-pump-thaw cycles and stored in an anhydrous environment before polymerization was attempted. These steps were performed because Schrock's [Mo] metathesis catalyst (6) was used to polymerize this monomer, and this early transition metal alkylidene is highly sensitive to both moisture and oxygen. In an Ar atmosphere glovebox, di-4-pentenyldichlorosilane was added to a reaction flask, followed by Schrock's [Mo] catalyst (6) with a monomer to catalyst ratio of 500:1 (0.25% catalyst) (Figure 3-3).

![](https://example.com/figure3_3.png)

**Figure 3-3.** ADMET polymerization of di-4-pentenyldichlorosilane (26) using Schrock's [Mo] catalyst (6).

Upon mixing catalyst and monomer, bubbling (ethylene evolution) occurred instantly, evidence of the high activity and high rate of reaction of this catalyst. The flask was sealed, removed from the glovebox, and attached to a high vacuum line. The contents of the reaction mixture were stirred at room temperature under intermittent vacuum, and after a few hours, stirring had ceased due to increased solution viscosity. The reaction flask was immersed in an oil bath, and the bath temperature was slowly increased to
40 °C over the course of a day, enabling stirring to continue. As the temperature was raised, full dynamic vacuum was applied. Slow bubbling of the contents continued, resulting in the gradual formation of a thick, viscous oil. The polymerization procedure was continued for another 48 hours, after which stirring ceased. The reaction flask was not opened to the atmosphere in order to terminate the polymerization and destroy the active catalytic species, which is common practice for ADMET polymerization using the [Mo] catalyst (6), but instead was taken into a glovebox.

Solubility tests of the resulting polymer 41 were then performed using carefully dried and degassed solvents. Only low molecular weight oligomers were soluble in polar solvents such as chloroform, but complete solubility of the polymer was observed in lower polarity hydrocarbon solvents such as benzene and toluene. Spectroscopic analysis by NMR was utilized to confirm that the desired polymer had formed and no side reactions were detected. Since polymer 41 is extremely moisture sensitive due to the presence of a large number of hydrolytically unstable groups along the backbone, molecular weight determination by GPC analysis could not be performed. This polymer crosslinks rapidly when exposed to the level of moisture present in chromatographic solvents. End-group analysis by integration of the $^1$H NMR resonance signals was not a viable method to determine the molecular weight either, as catalyst residue peaks were present in the same region of the vinylic end groups at 5.0 ppm and 5.8 ppm, thus preventing accurate integration of these resonances. However, after conversion of the Si-Cl bonds to more stable moieties, molecular weight data can be obtained. Thermal analysis using DSC of this parent polymer (41) was also performed. Careful arrangements were made to avoid exposure to any moisture, and the sample was prepared
in an inert atmosphere. The sample was scanned from -90 °C to 70 °C, revealing a T_g at -57 °C and no discernable T_m, indicative of an amorphous elastomer. Considering the differences between the phosphazene and carbosilane backbones, it is surprising that their glass transition temperatures are quite similar. Poly(dichlorophosphazene) exhibits a T_g of -66 °C, only a difference of 9 °C.\textsuperscript{92}

**Functionalization with Alkyllithium Reagents**

After the solubility of the parent dichlorocarbosilane polymer had been determined, it was functionalized with several different alkyl groups through nucleophilic substitution reactions using alkyllithium reagents (Figure 3-4).

![Figure 3-4. Macromolecular substitution using alkyllithium reagents.](image)

The rationale behind this approach is twofold. First, the parent polymer is soluble in non-polar solvents, which are compatible and miscible with alkyllithium reagents. Second, alkyllithium reagents are more nucleophilic than the alcohol systems discussed in Chapter 2, and are well known for their ability to react with Si-Cl bonds with high conversion.\textsuperscript{80} An additional advantage of utilizing carbanion nucleophiles lies in the stability of the resulting bonds formed. Silicon-carbon bonds are similar in bond strength to that of carbon-carbon bonds and most importantly, are stable to hydrolysis.\textsuperscript{82,83} After
functionalization of all of the silicon-chlorine bonds present, the polymer would be stable, with the exception of slow oxidation of the unsaturated internal double bonds on the polymer. This can be inhibited by integration of a small percentage of antioxidants within the polymer matrix.81

Macromolecular Substitution Using Methyllithium

After the parent dichlorosilane polymer (41) was prepared by ADMET polymerization (vide supra), methyllithium was employed for the macromolecular substitution reaction. The dichlorocarbosilane polymer (41) was dissolved in an excess of freshly distilled, rigorously dried benzene in a carefully dried and argon-purged Schlenk flask. The polymer solution was cooled to 0 °C using an ice bath, and a fourfold excess of 1.6M methyllithium in ether (2 equivalents per Si-Cl bond) was slowly added. Under a continuous argon stream, the reaction mixture was allowed to warm slowly to room temperature and stirred overnight. A cloudy white precipitate of LiCl was observed in the polymer solution, indicating that substitution of the Si-Cl bonds had occurred. After no additional precipitate formation was observed, the polymer solution was cannulated into a fivefold excess of rigorously dried, cold methanol, precipitating out a clear, viscous, oily material. This procedure also enabled the excess methyllithium to be destroyed by the protic non-solvent, as well as dissolving all of the LiCl precipitate. The product, poly(di-4-pentenyl)dimethylsilane (42) was then dried in vacuo overnight.

Polymer 42 was readily soluble in chloroform and no gel formation was observed. When the polymer was exposed to the atmosphere, it remained soluble without gelation. This evidence strongly suggests that quantitative substitution of the Si-Cl bonds occurred. Any residual Si-Cl bonds will react rapidly with atmospheric moisture, producing stable
Si-O-Si bonds and creating a crosslinked network polymer. An insoluble network will form with only a few crosslinks present. Since this did not occur, all of the chlorine atoms were replaced with methyl groups. This was corroborated by $^1$H, $^{13}$C, and $^{29}$Si NMR spectroscopic evidence. The $^{29}$Si NMR spectrum illustrated only one peak at 2.3 ppm, indicative of a silicon atom bonded to four alkyl groups, and the lack of a signal at 33 ppm from the parent dichlorocarbosilane polymer (41) (Figure 3-5).

![Figure 3-5. The $^{29}$Si NMR spectrum of the methyl functionalized polycarbosilane (42).](image)

The $^1$H NMR spectrum illustrated that no side-reactions, crosslinking, or alkylation of the polymer backbone occurred as a consequence of using the alkylolithium reagent. This is in contrast to results observed by Rushkin and Interrante in the poly(silylenemethylene) system. Vinylic end groups were not observed in the $^1$H NMR spectrum, evidence of the formation of a moderately high molecular weight polymer (Figure 3-6). The $^{13}$C NMR spectrum illustrated that the cis/trans olefin content (~80% trans) was not affected and in agreement with other ADMET polymers synthesized.
Molecular weight determination for polymer 42 was easily accomplished using GPC because it was hydrolytically stable. Using a refractive index (RI) detector, the number average molecular weight ($M_n$) was determined to be 16,000 g/mol with a ($M_n/M_w$) of 2.3, a range commonly observed for ADMET polymers. Thermal analysis by DSC was also performed, indicating a $T_g$ of $-89^\circ$C. This is the lowest $T_g$ observed for the whole series of polymers produced and illustrates a high degree of chain flexibility in the polymer backbone combined with a small pendant group.

**Synthesis of the Phenyl Substituted Polymer Using Phenyllithium**

Using the parent dichlorosilane polymer (41), a polycarbosilane substituted with two phenyl pendant groups per repeat unit was synthesized using analogous methodology to that of the dimethyl substituted polymer. Di-4-pentyldichlorosilane (26) was polymerized via ADMET using Schrock’s [Mo] catalyst (6) and dissolved in excess dry benzene. Four equivalents of phenyllithium (1.8M in cyclohexane-ether) per silicon
atom was added in a similar fashion to that discussed above, and after stirring overnight under argon, two equivalents of methyllithium was added to the reaction mixture. Methyllithium was added to the reaction mixture to assure that any residual Si-Cl bonds remaining on the polymer backbone would be substituted, since MeLi is sterically unencumbered and was shown to quantitatively substitute Si-Cl bonds. During the reaction, precipitation of LiCl salts was observed in this reaction as well, indicating that substitution chemistry was occurring. After the reaction was complete, the polymer was cannulated into an excess of carefully dried, cold methanol, precipitated out of solution, and dried in vacuo, giving an off-white, tacky, elastomeric solid.

Polymer 44 was readily soluble in chloroform and did not become insoluble upon exposure to atmospheric moisture, indicating complete substitution of the Si-Cl bonds occurred. Spectroscopy was used to monitor the percent of phenyl and methyl substitution of the backbone. Since silicon-methyl groups resonate at frequencies very close to the common NMR reference standard tetramethylsilane (TMS), deuterated solvents containing no TMS had to be employed for both $^1$H and $^{13}$C NMR analysis to ensure accurate quantification of the substitution. For this macromolecular substitution using sequential addition of phenyllithium and methyllithium, no Si-Me peaks were observed in either the $^1$H or $^{13}$C NMR spectra. Therefore, the substitution with phenyllithium was determined to be quantitative. The $^{29}$Si NMR spectrum illustrated only one peak at -6.6 ppm, confirming a R$_2$SiPh$_2$ backbone structure.

The $^{13}$C NMR of the phenyl substituted derivative polymer (44) is illustrated in Figure 3-7, showing typical cis/trans olefin stereochemistry and providing evidence for a well-defined polymer microstructure.
This spectrum shows an additional peak at 32 ppm, which was suspected to be the adjacent allylic carbon present as a cis olefin linkage on the polymer backbone. In order to prove the type of carbon that was present, both APT (Attached Proton Test) and DEPT (Distortionless Enhancement by Polarization Transfer) NMR experiments were performed. Both experiments concluded that the peak in question was from a CH₂ carbon. The APT test separates the types of carbons present in a structure by showing CH and CH₃ peaks pointing downward and CH₂ peaks pointing upward. As seen in Figure 3-8, the APT experiment shows the peak at 32 ppm pointing upward.

The DEPT analysis separates all the carbons on the basis of the number of protons attached, giving four separate spectra, one for each type of carbon: quaternary, CH, CH₂, and CH₃. The peak at 32 ppm shows up as a CH₂ peak in the DEPT analysis as well. In addition, the fact that there is a resonance at 130 ppm, attributed to the cis internal olefin
upfield from the *trans* internal olefin resonance, which is also pointed downward, confirms the supposition that the peak at 32 ppm is a result of roughly 20% *cis* olefin present in the resulting polymer backbone and is not due to main chain alkylation or proton abstraction by the alkyllithium reagent.

Figure 3-8. APT NMR spectrum of poly(di-4-pentenyl)diphenylsilane (44).

Since polymer 44 was readily soluble in chloroform and was not prone to crosslinking, molecular weight determination was conducted using GPC analysis. The molecular weight was found to be 22,000 g/mol with a polydispersity index (M<sub>w</sub>/M<sub>n</sub>) of 2.3 using tandem RI and UV detectors (λ=254 nm). The DSC analysis illustrated a much higher T<sub>G</sub> than that observed for all the other functionalized polymers, most likely due to
rigid, more bulky phenyl substituents directly bonded to the silicon atom. The polymer possessed a $T_g = -2 \, ^\circ\text{C}$ and no $T_m$, demonstrated in Figure 3-9.

![DSC scan of the phenyl substituted polycarbosilane (44).](image)

**Using Butyllithium as a Nucleophile**

Macromolecular substitution chemistry was employed to functionalize the dichlorosilane polymer (41) using $n$-butyllithium. Poly(di-4-pentenyl)dichlorosilane (41) was once again synthesized using Schrock’s [Mo] catalyst (6) using the method discussed previously. Polymer 41 was dissolved in freshly distilled, dry benzene and the solution was chilled to 0 °C with an ice bath. Under argon with vigorous stirring, two equivalents of 1.6M $n$-BuLi in hexanes per Si-Cl bond was slowly added, and the precipitation of LiCl salts began immediately. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Excess methyllithium was then added in order to react with any residual Si-Cl bonds present and stirred overnight. After this time period, the
polymer was precipitated by cannulation of the reaction mixture into a large excess of ice-cold, freshly distilled, dry methanol. The solvent was removed by filter cannulation, and the polymer was dried at room temperature under vacuum for 24 hours. The resulting polymer (43) was a clear, viscous oil which was readily soluble in chloroform.

Using NMR analysis, it was discovered that butyl group incorporation was not quantitative in this case. The presence of methyl groups on the polymer was observed in both the $^1$H and $^{13}$C NMR spectra. Additional resonance peaks at $-0.10$ ppm in $^1$H NMR and at $-5.1$ ppm in the $^{13}$C NMR are indicative of silicon-methyl groups. Figure 3-10 shows the $^1$H NMR spectrum possessing a Si-CH$_3$ peak.

![Figure 3-10. $^1$H NMR spectrum of the butyl-methyl functionalized polycarbosilane (43).](image)

After it was confirmed that methyl groups were attached to the polymer backbone, quantification of the methyl incorporation was determined. Quantitative $^{13}$C
NMR integration, performed by using a pulse sequence that allows complete $^{13}$C nuclear relaxation, determined the amount of methyl content in the polymer to be 18%. In addition to the amount of methyl groups present, the substitution pattern at each silicon atom of the polymer needed to be determined. There are three possibilities for the nucleophilic substitution: butyl-Si-butyl, butyl-Si-methyl, and methyl-Si-methyl. The percentage of methyl-Si-methyl formation was assumed to be trivial since the overall percent of methyl group substitution was not large. The $^{29}$Si NMR spectra for this polymer illustrated two peaks at 3.0 and 3.1 ppm, illustrated in Figure 3-11.

![Figure 3-11](image)

Figure 3-11. $^{29}$Si NMR analysis of the resulting polymer (43) from the butyl and methyllithium substitution.

Since there are only two types of silicon environments present, one of the three possibilities outlined above did not occur. In order to distinguish between the methyl-Si-methyl and butyl-Si-methyl substitution pattern possibilities for the second peak, this peak was compared to the resonances observed for the fully methyl substituted polymer. The completely methyl functionalized polymer contains a peak at 2.3 ppm in the $^{29}$Si
NMR, whereas both the peaks present for the butyl polymer were around 3.0 ppm. In addition, the methyl-Si-methyl possibility should also be ruled out because of the large percentage of butyl groups that were on the polymer backbone. Further, it would appear logical that excess n-BuLi would easily be able to substitute at sites containing two Si-Cl bonds. Therefore, it is believed that the NMR evidence, along with the order of reagent addition and the low amount of methyl substitution observed, rules out the methyl-Si-methyl possibility for the substitution pattern observed.

The butyl functionalized polycarbosilane (43) was also stable in the atmosphere, allowing for molecular weight determination by GPC analysis. Using this technique, the polymer $M_n$ was determined to be 12,000 g/mol with a $M_w/M_n$ of 1.9. The polydispersity index observed for this sample is characteristic of polymers produced by step-growth polymerization. Although the molecular weights of the series of polymers produced by macromolecular substitution are not identical, it is not a function of pendant group variation. Each macromolecular substitution reaction was performed on a different batch of parent dichlorocarbosilane polymer (41). The molecular weight discrepancies observed are attributed to variations of experimental conditions encountered during each polymerization of parent polymer, particularly the difficulties of stirring the polymer solution as its viscosity increases. Thermal analysis of this amorphous elastomer (43) illustrated a low $T_g$ of −76 °C with no observed $T_m$, when scanning the sample from −95 °C to 70 °C (Figure 3-12). The low $T_g$ is attributed to both the flexibility of the butyl side groups and the resulting irregular polymer structure, which is due to the presence of a small amount of methyl groups placed randomly along the polymer backbone.
Substitution Reactions of Comparative Polymer Systems

Comparisons of ADMET unsaturated polycarbosilanes with Interrante’s substituted poly(silylenemethylenes) (37) are interesting. The glass transition temperature of ADMET polymer 43 is -76 °C, comparable to the poly(silylene-methylene) containing both butyl and methyl pendant groups prepared by ring-opening polymerization. In spite of significant differences between the polymer backbones and method of preparation, the $T_g$ of the latter polymer is -63 °C, only a 13 °C difference.$^{130}$

At the beginning of this chapter, it was discussed that macromolecular substitution was quantitative on the silylenemethylene polymers when utilizing an alcohol/amine nucleophilic system, which reacted readily with the one Si-Cl present in each repeat unit.$^{101,129}$ However, when substituting with alkyl groups (carbanions) on this backbone, a quantitative reaction did not occur. A methylene group flanked by two silicon atoms in the $\alpha$-position is more acidic and shows a greater propensity for proton
abstraction by alkyllithiums or other strong bases. Proton abstraction on the bridgehead carbon was indeed observed by Rushkin and Interrante using alkyllithium reagents, producing an insoluble, crosslinked polymer. This crosslinking reaction was attributed to carbanion formation on the polymer backbone, which then reacts further with Si-Cl bonds present in other polymer chains (Figure 3-13). This reaction forms new stable Si-C bonds between two or more polymer chains, producing an irreversible crosslink site.

![Figure 3-13. Proton abstraction of the bridgehead carbon, producing a crosslinked polymer.](image)

Consequently, the strongest nucleophiles able to used in the poly(silylenemethylene) system were Grignard reagents. These are several orders of magnitude weaker in nucleophilic strength than alkyllithium reagents. Butylmagnesium chloride was reacted with poly(chloromethylsilylenemethylene) and incomplete substitution occurred. Only about 70% of the sites available were substituted with butyl groups. Earlier reports in the literature show that when using Grignard reagents, substitution of a fourth group to a sterically hindered chlorotrialkylsilane is difficult.
Conclusions

Three functionalized polycarbosilanes were produced from the same parent dichlorocarbosilane polymer, synthesized by metathesis polycondensation. All of these alkylated polymers were tacky, elastic materials that were stable under atmospheric conditions (Table 3-1). This stability is a result of the complete replacement of hydrolytically sensitive Si-Cl bonds with stable Si-C bonds during the macromolecular substitution reaction. Phenyl and methyl group disubstitution of the polymers proved to be quantitative, whereas butyl group substitution was only 82%, and exhaustive substitution completed using methyllithium. The inability of n-BuLi to quantitatively substitute all of the Si-Cl bonds present along the polymer backbone may be the result of aggregation of the nucleophile (n-BuLi) with benzene.

Table 3-1. Molecular weight and thermal data for the three polymers synthesized via ADMET-macromolecular substitution.

<table>
<thead>
<tr>
<th>Pendant Group</th>
<th>$M_n$ (g/mol)</th>
<th>$M_w/M_n$</th>
<th>$T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>16000</td>
<td>2.3</td>
<td>-89</td>
</tr>
<tr>
<td>CH$_3$(CH$_2$)$_3$ / CH$_3$</td>
<td>12000</td>
<td>1.9</td>
<td>-76</td>
</tr>
<tr>
<td>C$_6$H$_5$</td>
<td>22000</td>
<td>2.3</td>
<td>-2</td>
</tr>
</tbody>
</table>

In contrast with polymers containing alternating [-Si-CH$_2$-] backbones, proton abstraction on the main chain was not observed during the substitution reactions performed on this series of polymers. Since these polymers are not susceptible to crosslinking when exposed to alkyllithium reagents as nucleophiles, a great deal of flexibility in the choice of macromolecular substitution reagents is permitted. This opens
the potential to synthesize a whole series of polymers using either alkylithium or Grignard reagents, leading to a wide range of stable polymers with the incorporation of various functionalities.
CHAPTER 4
HYDROLYTICALLY RESISTANT SILYL ETHERS

Introduction

Nucleophilic substitution has long been exploited as a flexible route of modifying the properties of reactive silanes. Highly reactive silicon-halide bonds are readily attacked by a variety of nucleophiles, producing compounds that can be utilized as protecting groups and reagents in organic synthesis\textsuperscript{82-86} or as pendant groups on inorganic polymers.\textsuperscript{65,66} Silyl ethers, molecules containing a reactive silicon-alkoxy bond, are susceptible to hydrolysis, a reaction that is kinetically dependent upon the nature of the substituents adjacent to this bond, chemistry which is quite old and useful.\textsuperscript{85} If hydrolysis is not desired in the product, then an alternative route of functionalization of the reactive silicon-chlorine bonds is through alkylation reactions. Formation of a silicon-carbon bond via Grignard or alkyllithium substitution chemistry has been shown to be quite straightforward due to both the high reactivity of both reagent and substrate, and the thermodynamic stability of the resulting product.\textsuperscript{103}

The substitution reaction of Si-Cl bonds has been determined to proceed in a S\textsubscript{N}2-like fashion by mechanistic studies.\textsuperscript{142-144} Therefore, the limitations of S\textsubscript{N}2 reactions still apply, particularly sterics, to the substitution of chlorosilanes. In the case of dialkyl-dichlorosilanes, the substitution of the first Si-Cl bond is quite facile. The second Si-Cl bond is more difficult to substitute, and the rate of reaction is considerably slower.
Previous studies show that small, linear alcohol nucleophiles react with both Si-Cl bonds adequately. On the other hand, as the steric bulk of the nucleophile is increased, substitution at the second Si-Cl bond becomes considerably more difficult and is often completely inhibited. If two chlorine atoms can be replaced with bulky substituents, significant improvements to hydrolytic stability can be achieved, especially in the case of dialkoxy silanes. An in-depth study of the nucleophilic substitution reaction on dialkyldichlorosilanes using sterically unencumbered nucleophiles has been discussed elsewhere.79,80

Different methods of synthesizing substituted carbosilane polymers containing various pendant groups via ADMET polymerization have been discussed in Chapters 2 and 3. Several of the polymers discussed in Chapter 2 were shown to be hydrolytically unstable, with the chemistry and rate of hydrolysis determined by the identity of the pendant group. Slowing or preventing the hydrolysis of the pendant groups of these polymers would be advantageous, allowing for characterization or processing before any crosslinking begins, as well as providing easier handling. This chapter will focus on the synthesis of compounds that both model the carbosilane polymer repeat unit and are hydrolytically stable or undergo slow hydrolysis. Since the carbon-silicon backbone is of a set architecture, this goal can be accomplished by either increasing the steric bulk of the nucleophiles or by producing cyclic structures using chelating nucleophiles. Both routes were explored in this work. A logical extension of these studies would be to produce ADMET polymers of increased stability using the knowledge acquired from these approaches.
Di-\textit{n}-hexyldichlorosilane was chosen as a model substrate to study the nucleophilic substitution reaction on two Si-Cl bonds that would produce more hydrolytically stable products. This silane contains two linear alkyl chains and two chlorine groups bound to a central silicon atom. It serves as a plausible model because of the similarities to the repeat unit of the polymers synthesized in Chapters 2 and 3. The environment around the silicon atom is virtually identical to the analogous ADMET capable \(\alpha,\omega\)-diene, which should allow the results of this model study to be easily applied to polymers.

**Sterically Bulky Aliphatic Nucleophiles**

Increasing both the steric bulk of the substrate (groups bound to the silicon atom) as well as the attacking nucleophiles decreases the hydrolysis or degradation of the resulting silyl ether\textsuperscript{140,145}. To test this hypothesis in the case of dialkyldichlorosilanes, isopropyl alcohol and \(t\)-butyl alcohol were evaluated as nucleophiles by reacting them with di-\textit{n}-hexyldichlorosilane (45), using Et\textsubscript{3}N as the proton acceptor (Figure 4-1).

![Figure 4-1. Reacting di-\textit{n}-hexyldichlorosilane (45) with isopropanol.](image)

The reaction of isopropyl alcohol successfully leads to a disubstituted silane (46) in 32\% yield, which could be worked up in the atmosphere, and exposed to solvents that
were not anhydrous without significant hydrolysis. Elemental analysis and NMR confirmed the identity of di-\textit{n}-hexyldiisopropanoxysilane (46). The $^{13}$C NMR spectrum is shown below (Figure 4-2). Tertiary-butyl alcohol was reacted using similar conditions to that of the isopropyl alcohol, but only the monosubstituted product was produced. It is believed that the steric bulk of the \textit{t}-butyl group is too great to effect the second substitution.

![13C NMR spectrum of di-\textit{n}-hexyldiisopropanoxysilane (46).](image)

**Figure 4-2.** The $^{13}$C NMR spectrum of di-\textit{n}-hexyldiisopropanoxysilane (46).

**Lithium Reagents as Nucleophiles**

Since alcohols are comparatively weak nucleophiles, significantly stronger bulky alkyllithium reagents were studied. The rationale for using bulky alkyllithium reagents as nucleophiles was to determine if the inability of \textit{t}-butyl alcohol to substitute both Si-Cl bonds can be overcome with a stronger nucleophile of similar bulk. Additionally, any successful reaction would produce a product containing new Si-C bonds and be
completely stable to the atmosphere. However, steric hindrance still dominates the results of this reaction, as both tert-butyllithium and (trimethylsilylmethyl)lithium were not able to produce the desired disubstituted product. In addition, the reaction of tert-butyllithium created a product that was lithiated at the α carbon to the silicon atom. This lithiation reaction is a result of both steric hindrance and the presence of chlorine atoms bound to the silicon. Chlorine atoms increase the acidity of the methylene groups adjacent to the silicon atom, making them more susceptible to lithiation. There are competing reactions occurring when the lithium reagent is added to the chlorosilane: metalation versus coupling (Figure 4-3). Previous work shows that if the molecule is sterically bulky, making the substitution difficult, then lithiation predominates. Coupling (substitution) will occur at the less hindered sites. The reaction of tert-butyllithium produces a mixture of the lithiated and the substituted product, which is attributed to the differences in the environment around the silicon atom before and after the first Si-Cl bond is reacted.

\[
\text{Me}_3\text{SiCl} + t\text{-BuLi} \rightarrow \begin{array}{c}
\text{Me}_3\text{SiC(CH}_3)_3 \\
(\text{coupling})
\end{array}
\]

\[
\text{LiCH}_2\text{SiMe}_2\text{Cl} \rightarrow \begin{array}{c}
\text{Me}_3\text{SiCl} \\
(\text{metation})
\end{array}
\]

\[
\text{Me}_3\text{SiC} \rightarrow \text{Me}_3\text{SiCH}_2\text{SiMe}_2\text{Cl}
\]

Figure 4-3. Competition between metalation and coupling.

It is likely that the first Si-Cl bond is substituted in this reaction, and at the second Si-Cl bond, a mixture of substitution and metalation occurs. The steric bulk of both the trisubstituted silane substrate and the nucleophilic agent allow for lithiation to occur instead of quantitative nucleophilic substitution of the Si-Cl bond.
In contrast, α-metallation has not been observed when reacting \( n \)-butyllithium or phenyllithium with di-\( n \)-hexyldichlorosilane.\(^{150}\) These reagents act as nucleophiles and not as bases, and no α-lithiation of the C-H bond adjacent to silicon is observed. Disubstituted product is formed in 79% yield when reacting di-\( n \)-hexyldichlorosilane (45) with \( n \)-butyllithium, and in 68% yield using phenyllithium. Sec-butyllithium was not studied since it has been shown in the literature to pose an α-lithiation hazard similar to \( t \)-butyllithium.\(^{151}\)

**Nucleophiles Containing a Phenyl Group**

Phenyl group containing nucleophiles were studied to in order to produce materials that exhibit an increased resistance to hydrolysis. Although not considered to be extremely bulky groups, phenoxysilanes have been shown in the literature to be more hydrolytically stable.\(^{101}\) Initially, attempts to substitute both Si-Cl bonds in di-\( n \)-hexyldichlorosilane (45) with the nucleophilic systems phenol/Et\(_3\)N or sodium phenoxide failed. The addition of a small amount of DMAP (4-dimethylaminopyridine) as a substitution promoter enabled a diphenoxydialkylsilane to form, which was discussed earlier in Chapter 2. The phenoxy group significantly increased the hydrolytic stability of resulting polymer.

Benzyl alcohol would be an interesting probe to evaluate the effect of a methylene group between the phenyl group and the oxygen atom. Benzyl alcohol is not a phenol, and it would be interesting to examine if the resulting silyl ether linkage is susceptible to hydrolysis. Upon reaction with di-\( n \)-hexyldichlorosilane (45) in the presence of Et\(_3\)N, disubstitution occurred readily in a yield of 62%. This reaction does not require the
addition of DMAP like phenol, yet the resulting product was rather stable to hydrolysis, as it was purified on a silica gel column in the atmosphere without substantial decomposition.

**Diols as “Chelating” Nucleophiles**

After examining the possibility of increased hydrolytic resistance using bulky monoalcohol reagents, the effect dialcohols have on the substitution reaction and the stability of their resulting products was studied. Diols would be interesting to study because one molecule would react with both Si-Cl bonds present, forming a cyclic alkoxy silane structure under the right conditions (Figure 4-4). Depending on the size of the ring formed and the steric environment around the silicon atom, hydrolysis may be slowed considerably. This approach is used in the formation of silane protecting groups.\(^{82,84,152}\) Polymers with such pendant groups might have interesting properties and improved resistance to hydrolysis.

![Figure 4-4. Using chelating nucleophiles to produce more stable cyclic silicon containing structures.](image)

Several diols, including diphenylsilanediol, were employed as nucleophiles and reacted with di-\(n\)-hexyl dichlorosilane (45) under conditions identical to that used for linear alcohols. Although silicon and carbon are in the same group on the periodic table, the chemistry of the two elements is quite different, and the effect on the acidity of
hydroxyl groups is no exception. Silanol protons are considerably more acidic than alcohol carbon analogs. This increased acidity reduces the nucleophilic strength of its conjugate base, meaning that a silanol is a weaker nucleophile than an alcohol. In spite of this, the resulting siloxane (Si-O-Si) bond of a Si-Cl substitution reaction is thermodynamically favored and highly stable, which may allow dissubstitution to occur. Unfortunately, the reaction of diphenylsilanediol with di-n-hexyldichlorosilane (45) did not produce a cyclic monomer and instead produced a low molecular weight siloxane oligomer with a molecular weight of approximately 700 g/mol. This occurred presumably because the cyclic species that would have formed from an intramolecular reaction would have been a highly strained four-membered ring. Therefore, after the first Si-Cl bond is substituted, the other Si-OH bond of diphenylsilanediol undergoes an intermolecular reaction with another molecule of di-n-hexyldichlorosilane (Figure 4-5).

![Figure 4-5. Intermolecular reaction between the monosubstituted product with another di-n-hexyldichlorosilane.](image)

Aromatic based diols such as catechol (1,2-dihydroxybenzene) were also evaluated in this substitution study. If the desired product di-n-hexyl(1,2-phenylenedioxy)silane could be produced, it should have excellent stability to hydrolysis, and any polymer derivatives synthesized bearing these substituent groups should have
interesting physical properties. Nevertheless, dissubstitution did not occur when using this nucleophile. The reason behind this failure may be unfavorable ring strain. A five-membered ring would have been the result in this reaction, but this cyclic structure was most likely too strained to form. The substitution chemistry of both dimethyl-dichlorosilane and diphenyldichlorosilane has been evaluated with catechol.\textsuperscript{153,154} The requirement for any 1,3-dioxa-2-sila-substituted five-membered ring is that the average bond angles are $\leq 108^\circ$.\textsuperscript{153} This requirement cannot be met unless some of the bond angles in the cyclic structure are compressed below that of a tetrahedral bond angle of 109.5\textdegree. Since the bond angles between the aromatic carbon and hydroxyl group on catechol are typical of bond angles in aromatic compounds and are approximately 120\textdegree, this ring compression is magnified between the other bond angles in the ring. Therefore, the increased ring strain prevents the reaction from occurring. It has been shown in other systems that the addition of methylene spacers between the hydroxyl group and the aromatic ring is required for the dissubstituted cyclic monomers to form.\textsuperscript{154,155}

Since the aromatic diol, catechol, did not produce a cyclic monomer, aliphatic cyclic diols were evaluated as nucleophiles instead. The bond angles around the hydroxyl groups would not be as large and would be easier to compress, resulting in a less strained system. Two commercially available cyclohexanediols were studied, trans-1,2-cyclohexanediol and a mixture of cis- and trans-1,3-cyclohexanediol. Trans-1,2-cyclohexanediol was reacted with di-$n$-hexyl dichlorosilane (45) in the presence of Et\textsubscript{3}N and did not produce a dissubstituted product. A crystalline material was isolated from the reaction, which was believed to be a dimer or oligomer. A small amount of DMAP was added in an attempt to promote substitution of both of the Si-Cl bonds, but the results
were the same; dimer or oligomer formation had occurred. Five-membered cyclic alkoxy silanes were not able to be synthesized by this reaction. After the first substitution occurs, it is easier for the second -OH group present to react with another di-\textit{n}-hexyl dichlorosilane molecule, producing a linear species, instead of wrapping around the same molecule and forming a strained cyclic entity.

Since the formation of five-membered rings from the reaction of di-\textit{n}-hexyl dichlorosilane (45) with geminal and vicinal diols resulted in dimer and oligomer formation, diols containing an additional methylene spacer between the two hydroxy groups were studied. These diols would form six-membered rings upon disubstitution, which possess low ring strain and high stability. The first nucleophile chosen was 2,4-dimethyl-2,4-pentanediol. The interesting characteristic of this nucleophile is the fact that both hydroxyl groups are bonded to tertiary carbons, a similar steric environment to \textit{t}-butanol. These tertiary alcohol sites should increase the hydrolytic stability of the resulting compound and sterically protect both alkoxy silane bonds. As noted earlier, \textit{t}-butanol was unable to effectively dissubstitute di-\textit{n}-hexyl dichlorosilane. However, when di-\textit{n}-hexyl dichlorosilane (45) was reacted with 2,4-dimethyl-2,4-pentanediol in the presence of the proton acceptor \textit{Et}_3\text{N} and DMAP, both Si-Cl bonds were substituted by the same diol, forming a stable six-membered ring (47) (Figure 4-6).

![Figure 4-6. Reaction of di-\textit{n}-hexyl dichlorosilane (45) with 2,4-dimethyl-2,4-pentanediol.](image_url)
The resulting product was quite stable under atmospheric conditions and reaction workup. After purification by distillation, the product was isolated in 41% yield, and NMR analysis was used to confirm the structure of product 47. Figure 4-7 illustrates the $^{29}\text{Si}$ NMR spectrum with one peak at $-5.7$ ppm, indicative of a $\text{R}_2\text{SiOR}_2$ environment at the silicon atom.

![Structure of the product](image)

Figure 4-7. The $^{29}\text{Si}$ NMR spectrum of di-$n$-hexyl(di-2,4-dimethyl-2,4-pentanedioxy)silane (47).

A mixture of cis- and trans-1,3-cyclohexanediol was studied for several reasons. First, the cyclohexyl 1,3-diol groups should be more flexible than the analogous 1,2-diol groups, making it more likely to chelate around the two Si-Cl bonds and form a six-membered ring. In addition, this diol mixture would determine if one isomer would be conformationally preferred over the other, due to the different spatial orientation of the cis isomer versus the trans isomer. Di-$n$-hexyldichlorosilane (45) was reacted with a mixture of cis- and trans-1,3-cyclohexanediol under identical conditions as the 2,4-dimethyl-2,4-pentanediol (Figure 4-8). A disubstituted cyclic product (48) was observed
which was resistant to atmospheric hydrolysis during workup. Both a viscous oil and a
small amount of solid material were the result. The viscous liquid was purified by
vacuum distillation and isolated in 45% yield, but the solid material could not be distilled.

![Chemical structure](image)

Figure 4-8. Reaction of cis and trans 1,3-cyclohexanediol with di-n-hexyldichlorosilane.

Product 48 was analyzed by NMR spectroscopy and several interesting
observations were made. Most importantly, the $^{13}$C NMR spectrum of the product
elucidates pertinent structural information of the product because only one peak at 68.5
ppm is observed at the frequency where an oxygen atom is bonded to a carbon atom
(Figure 4-9). In the starting material, there are two peaks from both the cis and trans
isomers present at 69.0 ppm and 66.6 ppm. Therefore, since the product is
symmetrical, it is believed that only one of the isomers reacts to form the product.

The product observed in this reaction is likely due to the reaction of the cis
isomer; the trans isomer is effectively prevented from forming a cyclic species. This is
caused by the spatial conformation of the $-\text{OH}$ groups on the cyclohexane ring (Figure 4-
10). During the reaction, a cis or trans hydroxyl group has equal reactivity with one Si-
Cl bond. Once this bond is formed, the $-\text{OH}$ group on the cis isomer is able to reach
around for an intramolecular attack and form a six-membered ring. The trans isomer
-OH group is spatially inaccessible and therefore must initiate an intermolecular attack on another chlorosilane, forming an oligomeric species.

![Reaction structure](image)

Figure 4-9. The $^{13}$C NMR spectrum of the cis 1,3-cyclohexanediol chelated product (48).

![Conformations](image)

Figure 4-10. Conformations of the cis- and trans-1,3-cyclohexanediols.

**Hydrolytic Stability of Silacycloalkanes**

The hydrolytic stability of diisopropyl and di-$t$-butyl substituted dioxosilacycloalkanes has been evaluated in the literature. It was found that for the diisopropyl substituted silanes, five-membered ring species are easily cleaved during silica gel thin layer chromatography (mildly acidic environment, pH $\approx$ 5). Even when using bulky
substituents such as di-\(t\)-butyl groups, five-membered dioxosilacycloalkanes are rapidly hydrolyzed under basic conditions. In contrast, the six-membered ring analogs are hydrolytically stable for hours in environments with pH levels varying from 4-10.\(^{152}\) Similar stability is also observed on six-membered 1,3-dioxo-2-silacycloalkanes with smaller substituents bonded to the silicon atom, demonstrating the superior hydrolytic resistance of this ring structure.

**Conclusions**

Slowing or inhibiting hydrolysis of alkoxyisilane bonds on silicon-containing polymers can be beneficial because it allows for easier manipulation and processing of materials without significant hydrolytic crosslinking. It is well known that increasing the steric bulk of the substituents on the silicon atom slows or inhibits hydrolytic bond cleavage. On a linear polycarbosilane, the choice of substituents may be limited by the requirements of the polymer backbone. In an effort to improve the hydrolytic stability of the series of substituted carbosilane ADMET polymers prepared in this work, only two reactive sites on the silicon atom can be modified. Substitution of reactive Si-Cl bonds using alkyllithium reagents produces a stable alkylated material, but careful considerations must be made to avoid competing lithiation reactions. Use of phenoxy groups was found to increase hydrolytic stability. However, tertiary alcohols were unable to substitute both Si-Cl bonds; secondary alcohols such as isopropanol are the most sterically hindered nucleophiles able to substitute both sites. These show significant improvements in hydrolytic stability compared to primary alkoxyisilanes. Cyclic species were also evaluated in an effort to study the effect that a ring structure would have on moisture resistance. Four and five-membered rings from geminal and vicinal hydroxy
groups did not form, due to excessive ring strain of the potential product. Six-membered rings form readily and show good stability under atmospheric conditions.$^{152}$

It would be very interesting to apply the knowledge learned in the experiments described in this chapter for the preparation of new substituted polycarborasilanes via ADMET polymerization. Since these substituents all display reduced tendencies to be hydrolyzed under atmospheric conditions, the resulting polymers should show the same properties. Not only would these polymers possess interesting architectures and a broad range of physical properties, but also the rate of and ability to be crosslinked can be selectively chosen by judicious choice of the pendant group.
CHAPTER 5
EXPERIMENTAL

Materials

Di-\(n\)-hexyldichlorosilane was purchased from Gelest, distilled under reduced pressure (bp = 113 °C/6 mmHg), and stored over activated 4Å molecular sieves under argon. The 5-bromo-1-pentene was purchased from Aldrich and stored over activated 4Å molecular sieves. Silicon tetrachloride (Aldrich) was transferred to a dried Kontes flask via cannula and stored in an Ar atmosphere glovebox. The 1,2-dibromoethane (Aldrich) was distilled from CaH₂ and stored over activated 4Å sieves. Anhydrous methanol and 2-propanol were purchased from Aldrich, further dried over Mg/I₂, and stored over activated 3Å molecular sieves. Purification of 2,2,2-trifluoroethanol (Aldrich) was accomplished by distillation under Ar and was stored over activated 3Å sieves. Benzyl alcohol (anhydrous) and \(t\)-butyl alcohol (anhydrous) were purchased from Aldrich and stored over activated 4Å sieves. Phenol (Aldrich) was azeotropically distilled from benzene. A 50/50 mixture of \(cis\)- and \(trans\)-1,3-cyclohexanediol (Aldrich) and 2,4-dimethyl-2,4-pentanediol were used as received. Magnesium turnings (Aldrich) were dried in a vacuum oven at 100 °C before use. The lithium reagents CH₃Li [1.4M in Et₂O] (Acros) and [1.6M in ether] (Aldrich), C₆H₅Li [1.8M in cyclohexane-ether] (Aldrich), and \(n\)-BuLi [1.6 M in hexanes] (Aldrich) were used as received and titrated according to the method by Suffert.¹⁵⁷ Potassium ethoxide and 4-dimethylaminopyridine (DMAP)
(Aldrich) were used as received. Triethylamine was purchased from Aldrich and dried by distillation over CaH₂. N-phenyl-l-naphthylamine was dried at 56 °C under vacuum using an Abderhalden apparatus. Diethyl ether and pentane (Fisher) were dried and distilled over NaK-benzophenone ketyl. Benzene (Aldrich) and THF (Fisher) were dried and distilled over K-benzophenone ketyl. Heptane, toluene, and o-xylene (Aldrich) were dried by distillation over Na-benzophenone ketyl. Hexanes, chloroform, and CH₂Cl₂ (Fisher) were used as received. Deuterated solvents, C₆D₆ and CDCl₃, (Cambridge Isotope Laboratories) were stored over activated 4Å sieves. The NHC-ligated 2nd generation Grubbs’ [Ru] catalyst (11) Cl₂Ru(IMes)(PCy₃)[=CHPh] was synthesized by literature procedure. Schrock’s [Mo] catalyst (6), [Mo=CHCMe₂Ph(=N-C₆H₃-i-Pr₂-2,6)(OCMe(CF₃)₂)₂], was prepared using a literature procedure.

Instrumentation

All NMR spectra, ¹H (300 MHz), ¹³C (75 MHz), ¹⁹F (282 MHz), and ²⁹Si (60 MHz) were conducted on either a Varian VXR, Gemini, or Mercury series superconducting spectrometer system and referenced to residual C₆H₆ or CHCl₃ solvent signals. Fluorine-19 NMR spectra were internally referenced to CFCl₃. For the ²⁹Si NMR spectra, a heteronuclear gated decoupling pulse sequence with a pulse delay of 30 s was used, with a 1% internal TMS reference added. For quantitative ¹³C NMR experiments, a gated decoupling pulse sequence was used with a delay of 10 s. Gas chromatography was performed on a Shimadzu GC-17A gas chromatograph equipped with a 15m Restek RTX-5 crossbonded 5% diphenyl-95% dimethyl siloxane column using He as the carrier gas and a FID detector. Gel permeation chromatography was
performed using two 300mm Polymer Laboratories gel 5μm mixed-C columns. The GPC instrument consisted of a Rainin SD-300 pump, Hewlett-Packard 1047-A RI detector, Kratos Spectroflow 757 UV detector (254 nm), TC-45 Eppendorf column heater set to 30 °C, and a Waters U6K injector. The solvent used was CHCl₃ at a flow rate of 1.0 mL/min and the peaks were referenced to polystyrene standards from Polymer Laboratories (Amherst, MA). Differential scanning calorimetry measurements were taken using a Perkin Elmer DSC 7 instrument equipped with TAC 7/DX controller and a CCA7 cooling accessory. The samples were scanned from −95 °C to 70 °C at a heating rate of 10 °C per minute. Liquid N₂ was used as the coolant. Spinning band distillation was performed using a B&R Instruments Model 8T regulated with a dibutylphthlate-filled manostat. Elemental analyses were performed by Atlantic Microlab (Norcross, GA).

Synthesis of Substituted Dialkoxy silane Monomers

Synthesis of di(4-pentenyl)dichlorosilane (26)

A 500 mL three-necked flask equipped with an addition funnel, condenser, and stir bar was flame-dried under vacuum. The apparatus was then flushed with Ar and 7.27 g Mg turnings (0.30 mol) were weighed and added to the flask. Freshly distilled dry diethyl ether (175 mL) was added to the flask via cannula, followed by the addition of 0.2 mL of 1,2-dibromoethane. Bubbling ensued, the gray mixture was stirred at room temperature for 1 h, and 5-bromo-1-pentene (40.50 g, 0.27 mol) was added dropwise via addition funnel over 2 h. The reagent was refluxed overnight, followed by removal of insoluble material by filter cannulation into a 250 mL volumetric flask fitted with an air-
free adapter. This gray solution was filled to the volume mark with additional dry diethyl ether via cannula. The 4-pentenyl magnesium bromide formed was titrated by the method described in Vogel’s (0.22 mol, 81.5%). Following titration, a 1000 mL three-neck round bottom flask equipped with a condenser, addition funnel, and stir bar was flame dried under vacuum. After purging the flask with Ar, 500 mL of dry heptane was added via cannula. In a separate 25 mL pear-shaped flask and added to the round bottom flask, SiCl₄ (16.86 g, 0.10 mol) was diluted with 10 mL dry heptane via cannula. The Grignard solution was transferred to an addition funnel via cannula and added dropwise over 6 h. The solution was refluxed overnight, forming a white precipitate. The product was separated from magnesium salts by filter cannulation into a 1000 mL Schlenk flask; the residual salts were washed with 2 x 100 mL portions of pentane, and all organic solutions were combined. All solvent was removed in vacuo, giving a crude yellow liquid product. The product, a clear, colorless liquid, was purified by vacuum spinning band distillation.

Boiling point: 90-92 °C (4 mmHg), % yield (GC): 73%; isolated 8.80 g, 38%. ¹H NMR (δ, CDCl₃): 1.10 (Si-CH₂)(m, 4H), 1.59 (CH₂)(m, 4H), 2.10 (CH₂CH)(m, 4H), 4.98 (CH₂CH)(m, 4H), 5.74 (CHCH₂)(m, 2H). ¹³C NMR (δ, CDCl₃): 19.7 (Si-CH₂), 21.7 (CH₂), 36.2 (CH₂CH), 115.5 (CHCH₂), 137.7 (CHCH₂). ²⁹Si NMR (δ, C₆D₆): 33.3 (R₂SiCl₂). Elemental Anal. for C₁₀H₁₈SiCl₂: Calcd (Found) C 50.84 (50.79) H 7.68 (7.78).

Synthesis of di(4-pentenyl)dimethoxysilane (27)

Into a 250 mL three-necked round bottom flask equipped with a condenser and stir bar, 150 mL of dry diethyl ether was added via cannula. Using a syringe, 5.3 mL (0.038 mol) of dry Et₃N was added to the reaction flask, followed by 1.6 mL (0.038 mol)
of dry MeOH. Di(4-pentenyl)dichlorosilane, (2.26 g, 0.0095 mol), was diluted with 10 mL dry diethyl ether and added to the reaction flask via cannula. Precipitation of Et₃NH⁺Cl⁻ salts was immediate. The reaction mixture was refluxed overnight, followed by removal of all volatiles in vacuo. Dry pentane was used to wash the product mixture (3 x 75 mL) and to precipitate any dissolved salts. The crude product was isolated as a yellow liquid and then purified by vacuum distillation. The final product was a clear, colorless liquid. Boiling point: 50 °C (0.005 mmHg), % yield (GC) 98%; isolated 1.26 g, 58%. ¹H NMR (δ, CDCl₃): 0.62 (Si-CH₂)(m, 4H), 1.45 (CH₂)(m, 4H), 2.05 (CH₂CH)(m, 4H), 3.52 (OCH₃)(s, 6H), 4.98 (CHCH₂)(m, 4H), 5.81 (CHCH₂)(m, 2H). ¹³C NMR (δ, CDCl₃): 11.4 (Si-CH₂), 22.1 (CH₂), 37.3 (CHCH₂), 50.3 (OCH₃), 114.8 (CH₂CH), 138.5 (CHCH₂). ²⁹Si NMR (δ, C₆D₆): -4.2 (R₂SiOR₂). Elemental Anal. for C₁₂H₂₄SiO₂: Calcd (Found) C 63.12 (63.47), H 10.60 (10.65).

**Synthesis of di(4-pentenyl)diethoxyxilane (28)**

A 250 mL three-necked round bottom flask equipped with a stir bar was taken into a glovebox and charged with 1.57 g (0.019 mol) of KOEt. Di(4-pentenyl)-dichlorosilane, (2.00 g, 0.0084 mol), was weighed out in the glovebox into a separate 25 mL flask. Both flasks were removed from the glovebox and an addition funnel and condenser were attached. Dry THF was added to the three-necked flask using a cannula (150 mL); the chlorosilane was diluted with 10 mL dry THF. The chlorosilane solution was transferred to the addition funnel via cannula and added dropwise over 30 min. Precipitation of white salts occurred immediately and the reaction mixture was refluxed overnight under Ar. Residual THF was removed in vacuo, and the product was washed with 3 x 75 mL of dry pentane. Any remaining inorganic salts precipitated out by the
washes were removed via filter cannulation. All volatiles were removed under vacuum, giving a crude orange liquid product, which was subsequently purified by vacuum distillation. The distilled product was a clear, colorless liquid. Boiling point: 47-50 °C (0.005 mmHg), % yield (GC) 88%; isolated 0.95 g, 44%. $^1$H NMR (δ, CDCl₃): 0.65 (Si-CH₂)(m, 4H), 1.13 (CH₂CH₃)(t, 6H), 1.58 (CH₂)(m, 4H), 2.05 (CH₂CH)(m, 4H), 3.68 (OCH₂)(q, 4H), 5.07 (CHCH₂)(m, 4H), 5.78 (CHCH₂)(m, 2H). $^{13}$C NMR (δ, CDCl₃): 13.0 (Si-CH₂), 19.1 (OCH₂CH₃), 23.3 (CH₂), 38.1 (CHCH₂), 58.6 (OCH₂), 115.3 (CH₂CH), 139.3 (CHCH₂). $^{29}$Si NMR (δ, C₆D₆): -7.9 (R₂SiOR₂). Elemental Anal. for C₁₄H₂₈SiO₂: Calcd (Found) C 65.58 (65.92), H 11.02 (10.98).

Synthesis of di(4-pentenyl)di(trifluoroethoxy)silane (29)

Using an analogous procedure to that of 27, 4.7 mL (0.034 mol) of Et₃N and 2.5 mL (0.034 mol) of CF₃CH₂OH were added to the reaction flask containing diethyl ether. Addition of 2.00 g (0.0084 mol) of di(4-pentenyl)dichlorosilane to the reaction mixture was performed via cannula. Identical workup and reaction conditions were used as in the preparation of 27, and the isolated product was a cloudy, yellow suspension that was purified by vacuum distillation. The final isolated product was clear and colorless. Boiling point: 50-51 °C (0.005 mmHg), % yield (GC) 98%; isolated 1.76 g, 57%. $^1$H NMR (δ, CDCl₃): 0.71 (Si-CH₂)(m, 4H), 1.50 (CH₂)(m, 4H), 2.10 (CH₂CH)(m, 4H), 4.03 (OCH₂)(q, 4H), 5.03 (CHCH₂)(m, 4H), 5.78 (CHCH₂)(m, 2H). $^{13}$C NMR (δ, CDCl₃): 11.3 (Si-CH₂), 21.5 (CH₂), 36.9 (CHCH₂), 60.3, 60.8, 61.3, 61.8 (OCH₂), 115.3 (CH₂CH), 118.0, 122.0, 125.7, 129.5 (CF₃), 138.0 (CHCH₂). $^{29}$Si NMR (δ, C₆D₆): -7.7 (R₂SiOR₂). $^{19}$F NMR (δ, CFCl₃): -77.2 (t, CF₃). Elemental Anal. for C₁₄H₂₂SiO₂F₆: Calcd (Found) C 46.14 (46.41), H 6.09 (6.13).
Synthesis of di(4-pentenyl)diphenoxysilane (30)

In a glovebox, 1.85 g (0.020 mol) of phenol was weighed into a 250 mL three-necked round bottom flask. In a separate 25 mL flask, 1.17 g (0.0049 mol) of di(4-pentenyl)dichlorosilane was added. Both flasks were fitted with septa and removed from the glovebox. A condenser was attached and the phenol was dissolved in dry diethyl ether (150 mL) added via cannula, followed by the addition of 2.7 mL (0.020 mol) of Et3N by syringe. The di(4-pentenyl)dichlorosilane was diluted with 10 mL dry diethyl ether and added to the phenol solution via cannula. Precipitation of the Et3NH+Cl− salts occurred immediately upon addition. After one hour, a catalytic amount of DMAP (0.040 g, 4 x 10−4 mol) was added to the reaction, which was then refluxed overnight. After this period, insoluble salts were separated from the product via filter cannulation. All volatiles were removed by rotary evaporation. The product was purified by column chromatography (3:1 hexanes: methylene chloride). % yield (GC) 98%; isolated 0.91 g, 53%. 1H NMR (δ, CDCl3): 0.86 (Si-CH2)(m, 4H), 1.51 (CH2)(m, 4H), 2.04 (CH2CH)(m, 4H), 4.98 (CHCH2)(m, 4H), 5.72 (CHCH2)(m, 2H), 6.96 (aromatic CH)(m, 6H), 7.23 (aromatic CH)(m, 4H). 13C NMR (δ, CDCl3): 12.4 (Si-CH2), 21.8 (CH2), 36.9 (CHCH2), 114.9 (CH2CH), 119.7, 122.0, 129.6 (aromatic CH), 138.3 (CHCH2), 154.3 (aromatic C). 29Si NMR (δ, C6D6): -8.6 (R2SiOR2). Elemental Anal. for C22H28SiO2: Calcd (Found) C 74.96 (75.10), H 8.01 (8.00).
ADMET Polymerization of Substituted Dialkoxysilanes

Synthesis of Poly[(di-4-pentenyl)dimethoxysilane] (31)

A 10 mL round bottom flask equipped with stir bar and air-free adapter was taken into an inert atmosphere glovebox. Di(4-pentenyl)dimethoxysilane, (0.39 g, 0.0017 mol), was weighed and added to the round bottom flask. Second generation Grubbs’ catalyst, (7.4 mg, 8.7 x 10^-6 mol), was added to the monomer and stirred (monomer:catalyst ratio 200:1). The flask was sealed, removed from the glovebox, and placed on a high vacuum line. Ethylene evolution did not occur until the temperature of the oil bath reached 35 °C. Intermittent vacuum was applied for 24 h, and dynamic vacuum (1 x 10^-3 mmHg) was applied for another 24 h. At this point, the reaction mixture became viscous and stirring ceased. The temperature was then increased to 60 °C and slowly stirred under vacuum for 24 h. At this time, the polymerization was stopped, and the flask was taken into the glovebox for storage. The resulting polymer was soluble in CHCl₃. ¹H NMR (δ, CDCl₃): 0.62 (Si-CH₂)(br, 4H), 1.42 (CH₂)(br, 4H), 2.00 (CH₂CH)(br, 4H), 3.52 (OCH₃)(s, 6H), 5.38 (CH)(br, 2H). ¹³C NMR (δ, CDCl₃): 11.5 (Si-CH₂), 22.8 (CH₂), 36.2 (CHCH₂), 50.3 (OCH₃), 130.4 (CH). Elemental Anal. for C₁₀H₂₀Si₂O₂: Calcd (Found) C 59.96 (59.71), H 10.07 (10.06).

Synthesis of Poly[(di-4-pentenyl)diethoxysilane] (32)

The polymer was synthesized in an analogous manner to 31. Di(4-pentenyl)-diethoxysilane (0.50 g, 0.0020 mol) was added to a flask containing 8.3 mg (9.8 x 10^-6 mol) of the 2nd generation Grubbs’ [Ru] catalyst and polymerized in vacuo. ¹H NMR (δ, CDCl₃): 0.64 (Si-CH₂)(br, 4H), 1.21 (CH₃)(br, 6H), 1.42 (CH₂)(br, 4H), 2.00
(CH₂CH)(br, 4H), 3.76 (OCH₂)(q, 4H), 5.38 (CH)(br, 2H). ¹³C NMR (δ, CDCl₃): 12.2 (Si-CH₂), 18.5 (OCH₂CH₃), 23.0 (CH₂), 36.3 (CHCH₂), 58.1 (OCH₂), 130.4 (CH).

Elemental Anal. for C₁₂H₂₄SiO₂: Calcd (Found) C 63.12 (62.72), H 10.60 (10.62).

Synthesis of Poly[(di-4-pentenyl)di(trifluoroethoxy)silane] (33)

The polymer was synthesized in a manner analogous to 31. Di(4-pentenyl)-di(trifluoroethoxy)silane (0.50 g, 0.0014 mol) was mixed with (2.9 mg, 3.4 x 10⁻⁶ mol) 2nd generation Grubbs’ Ru catalyst in a flask under ADMET conditions. ¹H NMR (δ, CDCl₃): 0.70 (Si-CH₂)(br, 4H), 1.45 (CH₂)(br, 4H), 2.03 (CH₂CH)(br, 4H), 4.02 (OCH₂)(q, 4H), 5.37 (CH)(br, 2H). ¹³C NMR (δ, CDCl₃): 10.7 (Si-CH₂), 22.1 (CH₂), 35.3 (CHCH₂), 60.3, 60.8, 61.3, 61.8 (q, OCH₂), 122.1, 125.7, 127.5 (q, CF₃), 130.5 (CH). Elemental Anal. for C₁₂H₁₈SiO₂F₆: Calcd (Found) C 42.84 (43.57), H 5.40 (5.56).

Synthesis of Poly[(di-4-pentenyl)diphenoxysilane] (34)

The polymer was synthesized in a manner analogous to 31. The polymerization flask was charged with 0.45 g (0.0013 mol) of di(4-pentenyl)diphenoxysilane and 6.5 mg (7.7 x 10⁻⁶ mol) of the 2nd generation Grubbs’ [Ru] catalyst. ¹H NMR (δ, CDCl₃): 0.82 (Si-CH₂)(br, 4H), 1.44 (CH₂)(br, 4H), 1.93 (CH₂CH)(br, 4H), 5.23 (CH)(br, 2H), 6.97 (aromatic CH)(m, 6H), 7.22 (aromatic CH)(m, 4H). ¹³C NMR (δ, CDCl₃): 12.4 (Si-CH₂), 22.4 (CH₂), 35.8 (CHCH₂), 119.7, 121.9, 129.5 (aromatic CH), 130.3 (CH), 154.2 (aromatic C). Elemental Anal. for C₂₁H₂₆SiO₂: Calcd (Found) C 74.04 (73.34), H 7.46 (7.45).
Preparation of Substituted Polymers via a One-Pot, Two-Step ADMET Polymerization-Macromolecular Substitution

Synthesis of Poly[(di-4-pentenyl)dichlorosilane] (41)

A 25 mL round bottom flask containing a stir bar and equipped with an air-free adapter was taken into an inert atmosphere glovebox and 0.72 g (0.0030 mol) of di(4-pentenyl)dichlorosilane was added. Schrock’s catalyst was added (4.8 mg, 6.3 x 10^-6 mol) to the liquid monomer and the evolution of ethylene was immediate and vigorous. The monomer to catalyst ratio used was 500:1 (0.2%). The flask was closed, taken out of the glovebox, and placed on a high vacuum line and stirred with intermittent vacuum applied. Bubbling due to the evolution of ethylene continued, and after 5 h, stirring had ceased due to increased solution viscosity. The flask was then subjected to dynamic vacuum (1 x 10^-3 mmHg), temperature was increased to 40 °C, and the contents of the flask were stirred for 48 h. After this time period, stirring ceased and the polymerization was stopped. The flask was taken into the glovebox due to the high hydrolytic sensitivity of the polymer. The resulting poly(dichlorocarbosilane) was soluble in hydrocarbon solvents such as toluene and benzene, but insoluble in more polar media such as CHCl₃ and THF. ¹H NMR (δ, C₆D₆): 0.90 (Si-CH₂)(br, 4H), 1.45 (CH₂)(br, 4H), 1.90 (CH₂-CH)(br, 4H), 5.40 (CH)(br, 2H). ¹³C NMR (δ, C₆D₆): 20.0 (Si-CH₂), 22.6 (CH₂), 35.3 (CH₂-CH), 130.6 (CH). ²⁹Si NMR (δ, C₆D₆): 33.5 (R₂SiCl₂).

Synthesis of Poly[(di-4-pentenyl)diphenylsilane] (44)

Di(4-pentenyl)dichlorosilane (0.72 g, 0.0030 mol) was polymerized using Schrock’s [Mo] catalyst (4.8 mg, 6.3 x 10^-6 mol) as discussed above in the preparation of
Once the polymerization was complete, the flask was removed from the vacuum line and filled with Ar. The polymer was dissolved in dried benzene (15 mL) added via cannula. The polymer solution was cooled to 0 °C using an ice bath. An excess of 1.8 M PhLi, 2 equivalents per silicon-chlorine bond, (6.7 mL, 0.012 mol) was added via syringe dropwise. The flask was allowed to slowly warm to room temperature overnight while maintaining stirring and an Ar atmosphere. To ensure that all Si-Cl bonds were reacted, 1.4M MeLi (5.0 mL, 0.0070 mol) was added to the flask via syringe slowly at room temperature and stirred for 24 h under Ar. The reaction mixture maintained a reddish-brown color. Using a cannula, the polymer solution was then added to 175 mL of cold, dry, freshly distilled CH₃OH. Upon addition, the reaction mixture turned clear and an off-white polymer precipitated out of solution. Solvents (CH₃OH and benzene) were removed by cannula filtration and the polymer was allowed to dry in vacuo at RT for 48 h. Yield after precipitation: 0.55 g, 63%. ¹H NMR (δ, CDCl₃): 1.04 (Si-CH₂)(br, 4H), 1.36 (CH₂)(br, 4H), 1.97 (CH₂CH)(br, 4H), 5.28 (CH)(br, 2H). ¹³C NMR (δ, CDCl₃): 12.1 (Si-CH₂), 23.7 (CH₂), 36.5 (CHCH₂), 130.4 (CH), 127.7, 129.0, 134.8, 136.3 (arom C). ²⁹Si NMR (δ, CDCl₃): -6.6 (R₂SiPh₂). Elemental Anal. for C₂₀H₂₄Si: Calcd (Found) C 82.15 (80.56) H 8.28 (8.19).

Synthesis of Poly[(di-4-pentenyl)-n-butylmethyilsilane] (43)

The synthesis of this polymer was performed using an analogous procedure to polymer (44). Di(4-pentenyl)dichlorosilane (0.72 g, 0.0030 mol) was polymerized using Schrock’s [Mo] catalyst (4.6 mg, 6.0 x 10⁻⁶ mol). The polymer was dissolved in dry benzene and 7.5 mL, (0.012 mol) 1.6M n-BuLi was added, followed by 5.7 mL (0.0080 mol) 1.4M MeLi. Typical polymer workup procedures were utilized. Yield after
precipitation: 0.79 g, 90%. $^1$H NMR ($\delta$, CDCl$_3$): -0.10 (Si-$CH_3$)(s, 3H), 0.50 (Si-$CH_2$)(br, 14H), 0.86 (CH$_3$)(br, 9H), 1.26 (CH$_2$)(br, 20H), 1.98 (CH$_2$CH)(br, 8H), 5.36 (CH)(br, 4H). $^{13}$C NMR ($\delta$, CDCl$_3$): -5.1 (Si-$CH_3$), 12.1, 13.5 (Si-$CH_2$), 13.8 (CH$_3$), 24.1, 26.2, 26.7, 26.9, 36.7, 36.8 (CH$_2$), 130.5 (CH). $^{29}$Si NMR ($\delta$, CDCl$_3$): 3.0, 3.1 (R$_4$Si). Elemental Anal. for C$_{13}$H$_{26}$Si: Calcd (Found) C 74.22 (74.69) H 12.47 (12.55).

Synthesis of Poly[(di-4-pentenyl)dimethylsilane] (42)

Di(4-pentenyl)dichlorosilane, (0.56 g, 0.0024 mol), was polymerized in a 25 mL flask using 5.3 mg (6.9 x 10$^{-6}$ mol) of Schrock’s [Mo] catalyst under typical ADMET conditions. After backfilling the flask with Ar, the polymer was dissolved in 15 mL of dry benzene and chilled to 0 °C using an ice bath. A two-fold excess of 1.6M MeLi was added (5.8 mL, 0.0093 mol) via syringe dropwise over 15 minutes. The flask was stirred overnight under Ar and slowly allowed to warm to room temperature. After 12 h, another 2 equivalents of 1.6M MeLi were added (3.0 mL), and the flask was stirred for an additional 6 h. The reaction mixture was then transferred via cannula into a Schlenk flask containing 200 mL of cold, dry MeOH. A white polymer precipitated from solution. Excess MeOH was then removed via cannula, and the resulting off-white polymer was dried for 48 h in vacuo at room temperature. Yield after precipitation: 0.31 g, 78%. $^1$H NMR ($\delta$, CDCl$_3$): -0.08 (Si-$CH_3$)(s, 6H), 0.46 (CH$_2$)(br, 4H), 1.31 (CH$_2$)(br, 4H), 1.97 (CH$_2$CH)(br, 4H), 5.36 (CH)(br, 2H). $^{13}$C NMR ($\delta$, CDCl$_3$): -3.4 (Si-$CH_3$), 14.9 (Si-$CH_2$), 24.1, 36.6 (CH$_2$), 130.5 (CH). $^{29}$Si NMR ($\delta$, CDCl$_3$): 2.3 (R$_4$Si). Elemental Anal. for C$_{10}$H$_{20}$Si: Calcd (Found) C 71.37 (69.94) H 11.99 (11.75).
Synthesis of Hydrolytically Resistant Substituted Silanes

Synthesis of di-n-hexyl(di-2-propoxy)silane (46)

In a 250 mL three-necked round bottom flask, flame-dried and equipped with a stir bar and reflux condenser, 75 mL of dry Et₂O was added via cannula under an inert atmosphere. Using a syringe, 5.9 mL (0.042 mol) of Et₃N was added, followed by 3.2 mL (0.042 mol) of 2-propanol. Using vigorous stirring, di-n-hexyldichlorosilane, (3.0 mL, 0.011 mol) was then added dropwise; a precipitate formed immediately from the generation of triethylamine hydrochloride salts. The reaction mixture was refluxed under Ar for 18 h, cooled to room temperature, and filtered through a Schlenk filter frit containing Celite to remove the organic salts. Volatiles were removed using vacuum rotary evaporation. Pentane (50 mL) was added to the product. The reaction mixture was then washed quickly with 2 x 50 mL of water, dried over MgSO₄, and filtered. Pentane was removed using vacuum rotary evaporation and the product isolated as a clear, light yellow liquid. Isolated yield: 1.09 g, 32%. ¹H NMR (δ, CDCl₃): 0.57 (Si-CH₃)(t, 4H), 0.87 (CH₃)(t, 6H), 1.15 (CH(CH₃)₂)(d, 12H), 1.27 (CH₂)(br, 16H), 4.10 (OCH)(m, 2H). ¹³C NMR (δ, CDCl₃): 13.5 (Si-CH₂), 14.1 (CH₃), 22.6, 27.0, 31.5, 33.2 (CH₂), 25.8 (CH(CH₃)₂), 64.5 (OCH). ²⁹Si NMR (δ, C₆D₆): -2.6 (R₂SiOR₂). Elemental Anal. for C₁₈H₄₀SiO₂: Calcd.(Found) C 68.29 (68.32), H 12.75 (12.68).

Synthesis of di-n-hexyl(dibenzoxy)silane (49)

Using an analogous procedure to that for the synthesis of (46), the three-necked flask was charged with 2.2 mL (0.021 mol) benzyl alcohol, 2.9 mL (0.021 mol) Et₃N, and 100 mL dry Et₂O. Di-n-hexyldichlorosilane (1.5 mL, 0.0055 mol) was added to the flask
slowly via syringe with vigorous stirring. A large quantity of white solid immediately precipitated out of solution. The reaction mixture was refluxed overnight under Ar. Filtration through a Schlenk filter frit containing a Celite layer was utilized to remove the organic salt precipitate. The ethereal solvent was removed by vacuum rotary evaporation, and the product was purified by column chromatography using 3:1 (hexanes: ethyl acetate) as the eluent. The product was isolated as a pale yellow liquid. Isolated yield: 1.41 g, 62%. \textsuperscript{1}H NMR (δ, CDCl\textsubscript{3}): 0.74 (Si-CH\textsubscript{2})(t, 4H), 0.87 (CH\textsubscript{3})(t, 6H), 1.23 (CH\textsubscript{2})(br, 16H), 4.83 (OCH\textsubscript{2})(s, 4H), 7.35 (aromatic CH)(m, 10H). \textsuperscript{13}C NMR (δ, CDCl\textsubscript{3}): 12.6 (Si-CH\textsubscript{2}), 14.1 (CH\textsubscript{3}), 22.6, 22.7, 31.5, 33.0 (CH\textsubscript{2}), 64.4 (OCH\textsubscript{2}), 126.3, 127.1, 128.2 (aromatic CH), 140.8 (aromatic C). \textsuperscript{29}Si NMR (δ, CDCl\textsubscript{3}): -3.6 (R\textsubscript{2}SiOR\textsubscript{2}). Elemental Anal. for C\textsubscript{26}H\textsubscript{40}SiO\textsubscript{2}: Calcd. (Found) C 75.68 (75.56), H 9.78 (9.97).

**Synthesis of di-\textit{n}-hexyl(diphenoxy)silane (50)**

Phenol was weighed, 2.69 g (0.029 mol), and added to a 250 mL three-necked round bottom flask in an Ar atmosphere glovebox. The flask was fitted with septa and removed from the glovebox. A condenser was attached, the flask placed under an Ar atmosphere, and approximately 75 mL of Et\textsubscript{2}O was added via cannula. By syringe addition, the reaction vessel was charged with 4.0 mL (0.029 mol) of Et\textsubscript{3}N and 2.0 mL (0.0070 mol) of di-\textit{n}-hexyldichlorosilane. Precipitation of organic salts occurred, and the reaction mixture was stirred for 1 h. At this point, a catalytic amount of 4-dimethylaminopyridine (DMAP), 0.020 g (1.6 x 10\textsuperscript{-4} mol), was added, and the reaction mixture was refluxed for 24 h under Ar. Diethyl ether was removed by rotary evaporation and the product was dissolved in 50 mL pentane. The pentane solution was quickly washed with 2 x 20 mL of H\textsubscript{2}O, followed by an additional wash of 2 x 20 mL of 1M NaOH. The
product solution was dried over MgSO₄, filtered, and all volatiles were removed by rotary evaporation. Purification of the product was achieved using silica gel column chromatography with a mobile phase consisting of 3:1 (hexanes:CH₂Cl₂) as the eluent. The product was isolated as a pale yellow liquid. Isolated yield: 1.44 g, 53%. ¹H NMR (δ, DMSO-d₆): 0.80 (Si-CH₃)(Si-CH₃)(m, 10H), 1.21 (CH₂)(br, 16H), 6.97 (aromatic CH)(dd, 6H), 7.27 (aromatic CH)(t, 4H). ¹³C NMR (δ, DMSO-d₆): 12.5 (Si-CH₂), 13.9 (CH₃), 21.7, 21.8, 30.7, 31.9 (CH₂), 119.4, 122.1, 129.8 (aromatic CH), 153.8 (aromatic C). ²⁹Si NMR (δ, CDCl₃): -8.1 (R₂SiOR₂). Elemental Anal. for C₂₆H₄₀SiO₄: Calcd.(Found) C 74.95 (74.57), H 9.44 (9.80).

Synthesis of di-n-hexyl(2,4-dimethyl-2,4-pentanedi oxy)silane (47)

Preparation of this compound was performed in a manner analogous to compound 50, requiring 150 mL of dry Et₂O, 3.3 mL (0.012 mol) Et₃N, 1.7 mL (0.012 mol) of 2,4-dimethyl-2,4-pentanediol, and 1.60 g (0.0059 mol) di-n-hexyldichlorosilane. The diethylether was removed by rotary evaporation and the product was washed with 50 mL of pentane and filtered. After the pentane was removed by rotary evaporation, the product was purified by vacuum distillation. Boiling point: 57-58 °C (0.005 mmHg), % yield (GC): 87%; isolated 0.80 g, 41%. ¹H NMR (δ, CDCl₃): 0.55 (Si-CH₂)(t, 4H), 0.85 (CH₃)(t, 6H), 1.32 (CH₂, CH₃)(br, 28H), 1.79 (CH₂)(s, 2H). ¹³C NMR (δ, CDCl₃): 14.4 (Si-CH₂), 16.9 (CH₃), 22.8, 22.9, 31.8, 33.2 (CH₂), 32.9 (CH₃), 51.9 (CCH₂C), 72.7 (C). ²⁹Si NMR (δ, CDCl₃): -5.7 (R₂SiOR₂). Elemental Anal. for C₁₉H₄₀SiO₂: Calcd. (Found) C 69.45 (69.47), H 12.28 (12.41).
Synthesis of di-\textit{n}-hexyl(1,3-cyclohexanedioxy)silane (48)

Preparation of this compound was performed in a manner analogous to compound 50, using 5.50 g (0.047 mol) of 1,3-cyclohexanediol dissolved in 175 mL of dry \textit{Et}_2\text{O}, 6.4 mL (0.046 mol) \textit{Et}_3\text{N}, and 4.00 g (0.015 mol) di-\textit{n}-hexyldichlorosilane. Work up was similar to that of 47, and the product was purified by vacuum distillation. Boiling point: 126-127 °C (1 mm Hg), % yield (GC): 96%; isolated 2.12 g, 45%. $^1$H NMR ($\delta$, CDCl$_3$): 0.66 (Si-CH$_2$)(t, 4H), 0.85 (CH$_3$)(t, 6H), 1.33 (CH$_2$)(br, 20H), 1.90 (CH$_2$)(br, 3H), 2.20 (CH$_2$)(d, 1H), 4.23 (OCH)(s, 2H). $^{13}$C NMR ($\delta$, CDCl$_3$): 14.1 (CH$_3$), 15.3, 16.0, 17.8, 22.5, 22.6, 23.1, 31.5, 31.6, 32.6, 33.0 (CH$_2$), 36.4 (CHCH$_2$CH), 68.5 (OCH). $^{29}$Si NMR ($\delta$, CDCl$_3$): -4.8 (R$_2$SiOR$_2$). Elemental Anal. for C$_{18}$H$_{36}$SiO$_2$: Calcd. (Found) C 69.18 (69.20), H 11.62 (11.77).

Synthesis of di-\textit{n}-hexyl(di-\textit{n}-butyl)silane (51)

Into a three-neck round bottom flask, 100 mL of \textit{Et}_2\text{O} was added by cannula, followed by 5.0 mL (0.018 mol) of di-\textit{n}-hexyldichlorosilane, added by syringe addition. The reaction vessel was cooled to 0 °C. An addition funnel was incorporated for the slow addition (dropwise over 15 min) of 28.1 mL (0.045 mol) 1.6M \textit{n}-BuLi to the solution. Upon addition, a white precipitate was produced, and the reaction mixture was stirred for 12 h, slowly warming to room temperature overnight. In order to quench any residual lithium reagent present, 10 mL of H$_2$O was added slowly under inert atmosphere, followed by an additional 100 mL of H$_2$O and \textit{Et}_2\text{O}. Two extractions with 100 mL of H$_2$O were completed, and the organic layer was dried over MgSO$_4$ and filtered. The solvent was removed by rotary evaporation and purified by column chromatography using silica gel as the stationary phase and 20:1 (hexanes: ethyl acetate) as the mobile
phase. The product was isolated as a pale yellow liquid and dried in vacuo. Isolated yield: 4.45 g, 79%. $^1$H NMR (δ, CDCl$_3$): 0.47 (Si-CH$_2$) (t, 8H), 0.87 (CH$_3$) (t, 12H), 1.26 (CH$_2$) (br, 24H). $^{13}$C NMR (δ, CDCl$_3$): 12.3, 12.5 (Si-CH$_2$), 13.8, 14.2 (CH$_3$), 22.7, 23.9, 26.3, 26.9, 31.6, 33.7 (CH$_2$). $^{29}$Si NMR (δ, CDCl$_3$): 1.1 (R$_4$Si). Elemental Anal. for C$_{20}$H$_{44}$Si: Calcd. (Found) C 76.84 (76.55), 14.20 (14.09).

Synthesis of di-$n$-hexyl(diphenyl)silane (52)

Preparation of this compound was performed in a manner analogous to compound 51, using 2.14 g (0.0080 mol) di-$n$-hexyl dichlorosilane, 11.1 mL (0.020 mol) PhLi, and 75 mL of Et$_2$O. Workup and purification were similar to that of 51. Isolated yield: 1.93 g, 68%. $^1$H NMR (δ, CDCl$_3$): 1.07 (Si-CH$_2$) (t, 4H), 0.86 (CH$_3$) (t, 6H), 1.24 (CH$_2$) (br, 16H), 7.36 (aromatic CH) (m, 10H). $^{13}$C NMR (δ, CDCl$_3$): 12.5 (Si-CH$_2$), 14.1 (CH$_3$), 22.6, 23.6, 31.4, 33.4 (CH$_2$), 127.7, 128.9, 134.8 (aromatic CH), 136.7 (aromatic C). $^{29}$Si NMR (δ, C$_6$D$_6$): -4.5 (R$_2$SiPh$_2$). Elemental Anal. for C$_{24}$H$_{36}$Si: Calcd. (Found) C 81.76 (81.28), H 10.30 (10.35).
REFERENCES


151. Magnus, P.; Roy, G. Organometallics 1982, 1, 553.


BIOGRAPHICAL SKETCH

Anne Cameron Church was born on August 23, 1974, in Florence, SC to Ann and Ernie Church. At age 3, the family moved to Asheville, NC, where her brother John Mason was born. Cameron spent her teen years in Raleigh, NC, after another relocation. As a junior in high school, she moved again, to Edgefield, SC. It was at Strom Thurmond High School that her instructor, Ms. Sandra Gladden, introduced chemistry to Cameron.

Two years later, in the fall of 1992, she left rural Edgefield to attend the College of Charleston in Charleston, SC. At college, Cameron continued to study chemistry and in her junior year began to do research in heterocycle synthesis with Professor Charles Beam. In 1996, after graduating cum laude with a BS in chemistry, she decided to continue pursuing her studies in graduate school. Cameron came to the University of Florida in the fall of 1996 and began her graduate career in the group of Professor Ken Wagener studying metathesis polymer chemistry. After completing her MS and PhD degrees in the fall of 2001, she moved to Edgefield, SC.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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George B. Butler Professor of Polymer Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

December 2001

Dean, Graduate School