ANIONIC SYNTHESIS OF FUNCTIONALIZED POLYMERS

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ABSTRACT

The synthesis of well-defined functionalized polymers is an important area of research due to their wide array of applications. The work presented herein can be divided into three categories: a) functional initiator synthesis; b) chain-end and in-chain functionalization and c) functional monomer synthesis and polymerization. All three methods involve both anionic polymerization and hydrosilation. In this work, all anionic polymerizations were performed at room temperature in hydrocarbon solvent with an alkyl lithium initiator.

A functional 4-pentenyllithium initiator was prepared in 70% yield and was used for the synthesis of α and α,ω-functionalized polystyrene. 4-Pentenyllithium was used to initiate styrene polymerization in benzene in the presence of 5 equivalents of tetrahydrofuran. Narrow polydispersity indices and good agreement between calculated and observed molecular weights were observed for the methanol-terminated product. α-Triethoxysilyl-functionalized polystyrene was quantitatively prepared by hydrosilation with triethoxysilane and α-4-pentenylpolystyrene. α-4-Pentenyl-ω-silyl hydride-functionalized polystyrene and α-4-pentenyl-ω-thiol hydride functionalized polystyrene were quantitatively prepared by terminating α-4-pentenylpoly(styrlyl)lithium with chlorodimethylsilane and ethylene sulfide, respectively. The α-4-pentenyl-ω-silyl hydride-functionalized polystyrene showed good agreement between calculated and observed molecular weights and a narrow polydispersity. α-4-Pentenyl-ω-thiol-functionalized polystyrene showed a dimer peak due to oxidative coupling when
quenched with methanol. Triethoxysilyl-functionalized, high-1,4-polybutadiene was prepared by reacting the pendant double bonds of the 1,2-units with triethoxysilane via hydrosilation.

High-yielding reactions between the polymeric organolithium chain-ends and silyl chlorides were used to obtain the desired polymeric silyl hydrides for further functionalization. In-chain and chain-end cyano-functionalized polystyrenes were prepared. Chain-end, silyl hydride-functionalized polystyrene was prepared quantitatively. Hydrosilation of chain-end, silyl hydride-functionalized polystyrene with allyl cyanide resulted in ω-cyano-functionalized polystyrene, which was prepared in 87% yield. In-chain, silyl hydride-functionalized polystyrene was prepared by terminating excess poly(styryl)lithium with dichloromethylsilane. The remaining poly(styryl)lithium was terminated with ethylene oxide to aid in chromatographic separation to yield the pure in-chain, silyl hydride-functionalized polystyrene in 96% yield. Hydrosilation of in-chain, silyl hydride-functionalized polystyrene with allyl cyanide resulted in cyano in-chain functionalized polystyrene in 58% yield after 2 weeks of reaction time at elevated temperature. ω-Silyl dihydride-functionalized polystyrene was prepared in 92% yield by inverse addition of poly(styryl)lithium to dichloromethylsilane then reduction with lithium aluminum hydride. Functionalization with allyl cyanide yielded ω-dicyano-functionalized polystyrene quantitatively.

Synthesis of functionalized polymers from silyl hydride-substituted monomers was also investigated. para-Dimethylsilylstyrene was prepared from 4-chlorostyrene in 84% yield. Homopolymerization, copolymerization, and end-capping of poly(styryl)lithium in cyclohexane with this monomer was investigated, and it was
found that a linking reaction is occurring. *meta*-Dimethylsilylstyrene was prepared from 3-bromostyrene in 75% yield. Anionic homopolymerization, and copolymerization of this monomer were investigated, and it was found that a more vigorous linking reaction was taking place compared to the *para*-substituted analog.
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1.1 Living Anionic Polymerization

In 1936 Karl Ziegler\textsuperscript{1} first proposed that anionic polymerization of styrene and butadiene occurred with consecutive addition of a monomer unit to an alkyllithium initiator and proceeded in the absence of chain transfer as well as chain termination. Later, in 1956, Szwarc and coworkers\textsuperscript{2,3} coined the term “living polymerization” to describe a type of polymerization in which the chain-end remained active until terminated. Szwarc and coworkers were the first to rigorously identify living anionic polymerization along with the potential advantages of this methodology. Anionic polymerization is an academically and industrially useful tool for producing polymers with unprecedented control of molecular structure and properties. The absence of chain termination and chain transfer steps in a chain growth polymerization (i.e. living polymerization) provides the ability to make polymers with predictable number average molecular weights and to prepare chain-end functional polymers as well as block copolymers with low degrees of compositional heterogeneity. Another advantage of living anionic polymerization is the ability to obtain materials with narrow molecular weight distributions. Narrow molecular weight distributions are those which have a value of $M_n/M_w \leq 1.1$.\textsuperscript{4}
Prior to the work of Szwarc and coworkers, Flory\textsuperscript{5, 6} had shown that the number average molecular weight could be predicted by the grams of monomer divided by the moles of initiator (Equation 1).

\[ M_n = \frac{\text{grams monomer consumed}}{\text{moles initiator}} \]  

(1)

Flory’s prediction also extended to the molecular weight distribution of polymers formed where the rate of initiation is comparable to or faster than the rate of propagation. The conclusion was that for a living polymerization the molecular weight distribution will decrease with increasing molecular weight according to equation 2.

\[ \frac{X_w}{X_n} = 1 + \left[ \frac{X_n}{(X_n + 1)^2} \right] \cong 1 + \frac{1}{X_n} \]  

(2)

There are five requirements that must be met in order to obtain a Poisson molecular weight distribution. Only one of these is that the polymerization is living.\textsuperscript{7}

1.) The growth of each polymer must proceed by addition of monomer only to an active terminal group.

2.) All active termini must be equally susceptible to reaction with monomer.

3.) All active centers must be introduced at the beginning of the polymerization.

4.) No chain transfer. No termination.

5.) Irreversible propagation.

To prepare a polymer with a narrow molecular weight distribution (low polydispersity), the rate of initiation must be competitive with or faster than the rate of polymerization.\textsuperscript{8} Initiator choice and reaction conditions which affect the rate of initiation are critical factors for controlling polydispersity.
The high reactivity of alkyllithium compounds necessitates the use of an inert atmosphere or high vacuum techniques to prevent reaction with oxygen, water, and carbon dioxide. A dimeric peak present in the GPC trace is an indication of reaction of a polymeric organolithium with air.\textsuperscript{9,10}

Anionic polymerization also provides control over the stereochemistry and microstructure. This aspect of anionic polymerization is particularly useful in the polymerization of 1,3-butadiene. The properties of the resulting polybutadiene can be tuned using experimental variables, providing different products from the same monomer. The amount of 1,4 enchainment can be tailored by changing the counterion, solvent, concentration, temperature, or polar additive.\textsuperscript{11} The glass transition temperature of polybutadiene can be tuned from -94 °C (11% 1,2) to -4 °C (pure 1,2) simply by changing reaction conditions.\textsuperscript{12-15} Anionic polymerization is also known to be one of the most effective ways of synthesizing polyisoprene with high \textit{cis}-1,4-content, with the goal of emulating the properties of natural rubber(100% \textit{cis}-1,4-polyisoprene).\textsuperscript{16} Preparation of polyisoprene with lithium as counterion in hydrocarbon solvent can provide >95% \textit{cis}-1,4 isoprene.\textsuperscript{7,17}

Another useful example of tunable stereochemistry by way of anionic polymerization is the case of methacrylate polymerization.\textsuperscript{18-20} In the case of lithium counterion in toluene, highly isotactic poly(methyl methacrylate) can be obtained. When using tetrahydrofuran as solvent and lithium as counterion, highly syndiotactic poly(methyl methacrylate) can be obtained. For methacrylate polymers the glass transition can be tuned from 50 °C (isotactic) to 135 °C (syndiotactic) by changing the solvent.\textsuperscript{20}
A consequence of living polymerization is that after complete consumption of monomer, all chain-ends remain active.\textsuperscript{3} This is advantageous for performing chemistry on the chain-end with electrophillic reagents.\textsuperscript{21} Reaction of the living, carbanionic chain-end with a multifunctional linking reagent will produce star, branched, or comb polymers.\textsuperscript{22} Reaction with an electrophile containing the appropriate protected functional group can provide chain-end functionalized polymers.\textsuperscript{23-26} A special type of chain-end functional polymers, having a functional group that can be polymerized, is referred to as a macromonomer.\textsuperscript{27-36} Thus, anionic polymerization can be used to synthesize well-defined polymers with unparalleled control over molecular weight, molecular weight distribution, polymer microstructure and architecture, as well as chain-end functional groups.\textsuperscript{7}

1.1.1 Monomers

The range of monomers that can be polymerized by anionic polymerization is dictated by the stability and reactivity of the organoalkali chain-end.\textsuperscript{37} Monomers that can be polymerized anionically fall into two categories; heterocyclic and those with one or more double bonds.\textsuperscript{38} This discussion will focus on the latter. Monomers with one or more double bonds include styrenes, dienes, and carbonyl-type structures. In general, a monomer which undergoes anionic polymerization must have a substituent on the double bond which stabilizes the negative charge. The caveat to this requirement is that the monomer must not terminate the propagating anion, on the time scale of monomer addition/polymerization.\textsuperscript{39} Thus, hydroxyl, amine, carboxyl, acetylene, and other electrophillic functional groups must either not be present or be protected.\textsuperscript{39, 40}
Monomers amenable to anionic polymerization include styrenes, dienes, methacrylates, epoxides, episulfides, cyclic siloxanes, and lactones.\textsuperscript{22, 41-45}

Initiator selection is also important for successful anionic polymerization. The reactivity of a given monomer is closely related to the stability of the propagating anion. The pK\textsubscript{a} of the conjugate acid of an anion can be used as an indication of the stability of the propagating anion. A higher pK\textsubscript{a} denotes a less stable anion, which is related to a more reactive monomer. The opposite is also true. An initiator should be chosen which exhibits reactivity similar to that of the propagating species in order to obtain a controlled polymerization. If the reactivity of the initiator is too high (base is too strong), undesirable side reactions can occur. If the reactivity of the initiator is too low (base is too weak), the efficiency will be low and the polydispersity will be high, if the initiator reacts with the monomer. The reactivity of an alkyl chain-end can be attenuated by using 1,1-diphenylethylene. Combination of \textit{n}-butyllithium with 1,1-diphenylethylene produces sterically hindered 1,1-diphenylhexyllithium, reducing the pK\textsubscript{a} from 56 to 32.\textsuperscript{46} This method is particularly useful for controlled polymerization of methacrylate and cyclic dialkylsiloxane monomers. The pK\textsubscript{a} values for corresponding conjugate acids of anionic chain-ends for selected monomers are provided below in Table 1.1.

Table 1.1. Selected pK\textsubscript{a} values of corresponding conjugate acids for the propagating carbanions of common monomers.\textsuperscript{46-48}

<table>
<thead>
<tr>
<th>Monomer</th>
<th>pK\textsubscript{a}(DMSO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>56</td>
</tr>
<tr>
<td>Styrene</td>
<td>44</td>
</tr>
<tr>
<td>Butadiene</td>
<td>43</td>
</tr>
<tr>
<td>Methacrylate</td>
<td>30-31</td>
</tr>
<tr>
<td>Oxirane</td>
<td>29-32</td>
</tr>
<tr>
<td>Diphenylethylene</td>
<td>32</td>
</tr>
</tbody>
</table>
1.1.2 Structure and Stability of Organolithium Compounds

Organolithium compounds offer unique properties compared to other organoalkali compounds. The small size, high electronegativity, and high charge density of lithium lead to both covalent and ionic characters of the carbon-lithium bond.\(^49,50\) Of specific interest for anionic polymerization is the observation that organolithium compounds are the only alkali metal derivatives that polymerize 1,3-dienes to high 1,4 microstructures.\(^7\)

Organolithium compounds do not simply exist in solution as individual entities, but rather they exist as aggregates.\(^7\) Aggregation affects many aspects of the polymerization, from side reactions to kinetics to microstructure, and therefore aggregation must be taken into account when considering any reaction which involves organolithium compounds. A unique balance to this aggregation phenomenon that is unique to organolithium compounds is that they are soluble in hydrocarbon solvents.\(^39\)

The high reactivity of organolithium compounds leads to special concerns related to the stability of these compounds under higher temperatures and atmospheric conditions. Under inert conditions, the main pathway for decomposition consists of elimination of lithium hydride.\(^39,51,52\) While organolithium compounds are typically stable (for a time-scale long enough to allow for synthetic manipulations) at room temperature, loss of lithium hydride occurs when they are heated. The presence of polar and protic impurities is detrimental to the stability of organolithium compounds. When exposed to oxygen, carbon dioxide, or water, organolithium compounds rapidly and exothermically react, sometimes resulting in combustion.\(^39\) Reaction with water simply results in deprotonation.\(^39\) If an organolithium compound reacts with oxygen, four products are observed as shown below in Scheme 1.1.\(^9,53\)
The combination of an organolithium compound with carbon dioxide results in three products as shown in Scheme 1.2.\textsuperscript{10,54-57} The resultant mixture is from an organolithium compound adding once, twice, or three times to the carbonyl group. Controlled polymerization requires the absence of water, oxygen, and carbon dioxide. This is usually accomplished through the use of high vacuum techniques or an inert atmosphere.\textsuperscript{58}

![Scheme 1.1. Reaction of polymeric organolithium and oxygen.](image)

1.1.3 Solvent

Propagating polymeric organolithium compounds exhibit a high reactivity; therefore, solvent choice is limited to alkanes, cycloalkanes, aromatic hydrocarbons, and ethers.\textsuperscript{8,22,59} The combination of ionic and covalent character of the carbon-lithium bond\textsuperscript{49,50} causes solvent choice to be imperative for control of the desired polymer properties. A more polar solvent will cause the carbon-lithium bond to exhibit more ionic character, while a non-polar solvent will cause the bond to exhibit more covalent character. When present in hydrocarbon solutions, organolithium compounds exist mostly as aggregates, in equilibrium with unassociated species. When present in more polar ethereal solvents, the nature of the organolithium compounds shifts towards ion pairs and free ions. The choice of solvent has a significant effect on the rates of
initiation, propagation, transfer, and termination reactions; therefore, the solvent must be carefully selected. These equilibria are represented by the Winstead spectrum in Figure 1.1.\textsuperscript{7,60}

\[
\begin{array}{cccccc}
\text{Aggregated} & \text{Unaggregated} & \text{Contact ion pairs} & \text{Solvent separated ion pairs} & \text{Free ions} \\
(RLi)_n & nRLi & R^{\ominus}Li^{\oplus} & R^{\ominus}/Li^{\oplus} & R^{\ominus}+Li^{\oplus} \\
\downarrow k_1[M] & \downarrow k_2[M] & \downarrow k_3[M] & \downarrow k_4[M] & \downarrow k_5[M]
\end{array}
\]

Figure 1.1. Winstead spectrum.

Solvent choice also plays in important role in the determination of the microstructure of polydienes and stereochemistry of poly(methyl methacrylate). High 1,4 enchainment of butadiene and isoprene can be obtained in non-polar solvent with lithium as counterion.\textsuperscript{61-63} Changing the solvent to a polar solvent, such as tetrahydrofuran, will result in formation of a polymer with high vinyl content (1,2-enchainment for butadiene and 4,3-enchainment for isoprene).\textsuperscript{64-66} With lithium as counterion a highly syndiotactic poly(alkyl methacrylate) will be obtained when THF is used as a solvent, while a highly isotactic polymer will be obtained in toluene.\textsuperscript{19,20,66}

Copolymerization can also be tuned with solvent choice. In the case of styrene-butadiene copolymers, the reactivity ratios are strongly dependent on solvent choice. In non-polar solvents, such as cyclohexane, a tapered block copolymer will form, with butadiene polymerizing first followed by styrene.\textsuperscript{67,68} With a polar solvent, like THF, the styrene will polymerize first and then butadiene will be added.\textsuperscript{67,69} The properties of these copolymers will be different due to 1,2- vs. 1,4-enchainment as discussed previously.\textsuperscript{12-14}
1.1.4 Initiation

A requirement for preparation of polymers with a narrow polydispersity (M_w/M_n ≤ 1.1)⁴ is that the rate of initiation must be faster or competitive with the rate of propagation. Alkylolithium initiators are commonly used in anionic polymerization and their reactivity depends on aggregation effects. Less aggregated species are more reactive. Steric effects at the alkyl group carbanion cause sec-butyllithium to aggregate into tetramers while n-butyllithium is hexameric in non-polar, hydrocarbon solvents.³⁹,⁷⁰

The aggregation of organolithium compounds is common for hydrocarbon solutions. The degree of aggregation is strongly dependent on the steric environment near the carbon-lithium bond. The greater the steric crowding, the less aggregated (more reactive) a given compound will be. A table of common initiators and their corresponding degrees of aggregation is presented below in Table 1.2. An example of this phenomenon is that n-butyllithium is aggregated into hexamers in benzene while sec-butyllithium is aggregated into tetramers. The difference between these two initiators is that the carbon-lithium bond is primary in the case of n-butyllithium while it is secondary in the case of sec-butyllithium. The consequence of this is that if n-butyllithium is used to initiate styrene polymerization in benzene, the resulting polymer will have a broad polydispersity. Under the same circumstances, if sec-butyllithium is used as an initiator the resulting polymer will have a narrow polydispersity.⁷
Table 1.2. Degrees of aggregation for initiators in hydrocarbon solvents.  

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Benzene</th>
<th>Cyclohexane</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyllithium</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>n-butyllithium</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>sec-butyllithium</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>tert-butyllithium</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>benzyllithium</td>
<td>2</td>
<td>-</td>
</tr>
</tbody>
</table>

Aggregation can be affected by polar solvents or polar additives. In general, organolithium compounds are less aggregated in polar media or in the presence of a Lewis base. It has been shown that addition of a Lewis base (such as THF) to a system with hydrocarbon solvent and n-butyllithium as initiator will decrease the polydispersity index.

Table 1.3. Degrees of aggregation for initiators in polar solvents.

<table>
<thead>
<tr>
<th>Initiator</th>
<th>Degree of Aggregation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>THF</td>
</tr>
<tr>
<td>ethyllithium</td>
<td>4</td>
</tr>
<tr>
<td>n-butyllithium</td>
<td>4</td>
</tr>
<tr>
<td>sec-butyllithium</td>
<td>-</td>
</tr>
<tr>
<td>tert-butyllithium</td>
<td>1</td>
</tr>
<tr>
<td>benzyllithium</td>
<td>1</td>
</tr>
</tbody>
</table>

The kinetics of initiation reactions are affected by aggregation phenomena. For a system of n-butyllithium-initiated polymerization in benzene at room temperature, the kinetic expression for initiation (Scheme 1.3) was reported to be \( \frac{1}{6} \) order in initiator and first order in monomer. This is explained by the proposal that the unaggregated species (BuLi*) is responsible for initiation.
\[
RLi^* + M \rightarrow \text{BuM-Li}
\]

\[
R_{\text{initiation}} = k_i \left[ RLi^* \right][M],
\]

where \( RLi^* \) is the unaggregated species

**Determine \([RLi^*]\) and substitute**

\[
\frac{K_d}{(RLi)_6} \rightleftharpoons 6 RLi^*
\]

\[
[RLi^*] = \{K_d \cdot (RLi)_6\}^{(1/6)}
\]

\[
\frac{1}{6} [RLi]_{\text{injected}} = (RLi)_6 \text{ if } K_d << 1
\]

\[
R_{\text{initiation}} = k_i \left( \frac{1}{6} \right) K_d \left[ RLi \right]^{(1/6)}[M] = k_{\text{obs}}[RLi]^{(1/6)}[M]
\]

Scheme 1.3. Initiation kinetics in benzene.

The fractional order dependence on initiator is not present in the case of polymerizations initiated in cyclohexane (Scheme 1.4).\textsuperscript{75} The monomer reacts directly with the aggregate in this case, resulting in a reaction order dependence on \([RLi]\) of 1. Additionally the rate of initiation is several orders of magnitude smaller, indicating a different mechanism for initiation in cyclohexane (Scheme 1.4).

\[
\left( \text{R-Li} \right)_n + M \xrightarrow{k_i} \left[ \text{RM-Li} \left( \text{R-Li} \right)_{n-1} \right]
\]

\[
R_{\text{initiation}} = k_i \left( \frac{1}{6} \right) [RLi]_{\text{injected}}[M] = k_{\text{obs}}[RLi]_{\text{injected}}[M]
\]

Scheme 1.4. Initiation kinetics in cyclohexane.

1.1.5 Propagation

The kinetics of polymerization are, not surprisingly, complicated by association phenomena.\textsuperscript{7} This is analogous to the complications discussed for initiation kinetics. The rate of polymerization (\(R_p\)) is employed for the description of propagation kinetics to
Relate monomer consumption, time, and chain-end concentration. The formula is presented in equation 3. The rate of polymerization is expressed as monomer loss per unit time, where \([\text{PLi}^*]\) represents the concentration of propagating chain-ends and \([\text{M}]\) represents monomer concentration, and \(k_p\) is the rate constant for propagation.

\[
R_p = -\frac{d[\text{M}]}{dt} = k_p[\text{PLi}^*][\text{M}]
\]  

(3)

In the case of styrene polymerization in hydrocarbon solvent the expression is altered, in that the reaction generally exhibits one-half order dependence in PSLi concentration (Scheme 1.5). The reason for this kinetic order in chain-end concentration is that the PSLi chain-ends are aggregated into dimers, and chain growth (monomer addition) occurs after dissociation into the unaggregated species.  

\[
\begin{array}{c}
\text{PSLi}^* + \text{S} \rightarrow \text{PS-S-Li} \\
R_p = k_p [\text{PSLi}^*][\text{S}],
\end{array}
\]

where PSLi* is the unaggregated species

Determine \([\text{PSLi}^*]\) and substitute

\[
[\text{PSLi}^*] = \left(\frac{K_d [\text{PSLi}]_{\text{total}}}{2}\right)^{1/2}
\]

\[
R_p = k_p (1/2) K_d [\text{PSLi}]^{1/2}[\text{S}] = k_{\text{obs}}[\text{PSLi}]^{1/2}[\text{S}]
\]

Scheme 1.5. Propagation kinetics.

Diene polymerization yields a slightly different equation for the rate of polymerization, where the order with respect to chain-end concentration is approximately \(1/4\). This would be consistent with poly(butadienyl)lithium chain-ends being aggregated.
into mainly tetrameric species in hydrocarbon solution.\textsuperscript{83,84} The picture of chain-end aggregation for poly(butadienyl)lithium chain-ends is not as simple as poly(styryl)lithium. However, the actual structure has been controversial because of conflicting reports of the degree of aggregation,\textsuperscript{83,85} but the complex aggregation behavior of poly(butadienyl)lithium chain-ends has recently been elucidated.\textsuperscript{84,86} One conclusion from this work is that the main species of aggregate is tetrameric. However, small amounts of higher order aggregates are also seen with small angle neutron scattering techniques coupled with \textit{in-situ} \textsuperscript{1}H NMR spectroscopy.\textsuperscript{87,88}

1.1.6 Lewis Bases

A Lewis base acts as an electron pair donor, and its presence during anionic polymerization can dramatically affect polymer properties. The presence of a Lewis base can change microstructure, polydispersity, monomer reactivity ratios, and rates of initiation and propagation for alkyllithium initiated polymerizations of vinyl monomers in hydrocarbon solution.\textsuperscript{7} Common Lewis bases employed in anionic polymerization include ethers and amines. The presence of a Lewis base causes the average degree of aggregation to decrease, shifting the Winstein spectrum (see Figure 1.3) to the right, resulting in faster rates of initiation and polymerization.\textsuperscript{89,90} The most common instance where a Lewis base is employed is to decrease the polydispersity of polymers initiated with \textit{n}-butyllithium. Aggregation of \textit{n}-butyllithium into hexamers results in broad polydispersity when the initiator is used in hydrocarbon solvent. However, when as little as five equivalents of tetrahydrofuran are added, a polymer can be obtained with a narrow polydispersity index. This is particularly advantageous due to the lower cost and better thermal stability of \textit{n}-butyllithium relative to \textit{sec}-butyllithium.\textsuperscript{91}
Another example of the utility of addition of a Lewis base is in the copolymerization of butadiene and styrene. In the absence of a Lewis base, the reactivity ratios of styrene and butadiene are 15.5 and 0.04, respectively. The result of copolymerization is a tapered block copolymer, where butadiene is preferentially incorporated initially, and styrene is incorporated primarily after exhaustion of butadiene monomer. Addition of one equivalent of tetramethyleneethylenediamine (TMEDA) can shift the monomer reactivity ratios to 0.91 and 0.86, resulting in a random copolymer of styrene and butadiene.

The microstructure of polybutadiene can also be tuned with the aid of a Lewis base. For example, addition of 5 equivalents of THF can shift the percent of 1,2-enchainment from 10% to 44% in alkyllithium-initiated polymerization in cyclohexane.

The ability of a Lewis base to decrease the degree of aggregation can be important for the attenuation of undesired side reactions. When a side reaction is thought to take place in the aggregated structure, a Lewis base can be added to decrease the quantity of the undesired product. This is the case for functionalization of polystyrene with carbon dioxide. In the absence of a Lewis base, 60% of the carboxylate-functionalized polymer is can be obtained for polystyryl)lithium, with the remainder of the polymer chains forming the di-adduct and tri-adduct. When a 25/75 (v/v) THF/benzene solvent mixture is used to eliminate aggregation, a quantitative yield of the desired carboxy-functionalized polystyrene can be obtained.

1.1.7 Alkali Metal Alkoxides

Industrially, anionic polymerization is performed by first titrating impurities with excess initiator, then adding the prescribed quantity to reach the desired molecular
weight. Stoichiometry of monomer and initiator, however, is not the only variable in the reaction that is effected by this process. One product of reaction of excess initiator and impurities are alkali metal alkoxides. Lithium alkoxides cross-associate with organolithium compounds and have been shown to decrease the rate of propagation for styrene, butadiene, and isoprene.\textsuperscript{94, 95} Intentional addition of small amounts of potassium tert-butoxide, and other non-lithium alkali metal alkoxides, for butyllithium-initiated styrene/butadiene copolymerizations is one of the only ways to obtain a random copolymer of styrene and butadiene while retaining high 1,4-enchainment of butadiene.\textsuperscript{96, 97}

1.2 Chain-End Functionalization

One of the unique features of living polymerizations, in general, and alkyllithium-initiated polymerizations in particular, is the ability to prepare chain-end functionalized polymers.\textsuperscript{21} After complete monomer consumption, the resulting polymeric organolithiums can react with electrophiles to form ω-chain-end functionalized polymers (Scheme 1.6).\textsuperscript{7, 98, 99} Although many such reactions have been investigated, most of these functionalization reactions are not quantitative and each must be optimized.\textsuperscript{23}

\[
P–\text{Li} + X–Y \rightarrow P–X + LiY
\]

Scheme 1.6. Functionalization of P-Li with electrophiles.

A complication of functionalization with a variety of functional groups is the reactivity of these functional groups with the anionic chain-end. The majority of desirable functional groups will react with organolithium compounds either through unwanted electrophillic addition (e.g. carbonyls and amides) or through deprotonation
(e.g. amines and alcohols). As a result, most functional groups must be protected prior to exposure to the organolithium compound and deprotected post-polymerization. Well-defined, chain-end functionalized polymers have a wide array of useful applications. The functionality of the chain-end can be used to impart properties to the interfaces and surfaces of materials without affecting the bulk polymeric properties. A polymer or oligomer with functional groups reactive for polymerization (styryl, methacroyl, alcohol, or acids/esters/amides) is defined as a macromonomer. Macromonomers can be employed for polymerization systems where a low degree of polymerization is required to prepare a polymer with a high molecular weight. In addition, this type of system can be used to incorporate polymeric properties of one type of polymerization system (e.g. vinyl polymerization) into another type of polymerization system (e.g. condensation polymerization). This facet of chain-end functionalization is crucial for the design of polymer systems with goals for specific material properties, and limited polymerization efficiency.

1.2.1 General Functionalization Methods

General functionalization methods (GFM) are reactions that encompass reactions that efficiently introduce a variety of functional groups using the same chemistry for all groups. An example of a GFM is the addition of a polymeric organolithium to a substituted alkyl chloride as shown in Scheme 1.7.

Scheme 1.7. Functionalization of P-Li with alkyl chlorides.

This particular GFM is plagued with shortcomings and problematic inherent deficiencies. The functionalizing reagent must either be one of the few functional groups
stable to alkyllithium reagents, or protected. This limitation requires synthesis of a protected functional group, followed by deprotection post-polymerization.\textsuperscript{39} Another challenge is that reaction of an alkyl chloride with a polymeric organolithium is not simple or quantitative. As an example, Quirk and coworkers\textsuperscript{110} reported that functionalization of poly(styryl)lithium with 3-dimethylaminopropyl chloride proceeded in 67\% yield. Side reactions are numerous, and include elimination of hydrochloric acid from the functionalizing reagent, lithium halogen exchange, and Wurtz coupling.\textsuperscript{111} The undesired reactions can be attenuated through addition of lithium chloride, but this limits the scope of this GFM.\textsuperscript{108}

Another example of a GFM is employing substituted 1,1-diphenylethylene derivatives as functionalizing reagents (Scheme 1.8).\textsuperscript{112-114} This method offers distinct advantages over alkyl chloride functionalization, but protection/deprotection steps are essential to success. In addition, substituted diphenylethenes are not readily available; therefore, each must be synthesized from the corresponding benzophenone containing the appropriate protected functional group. Functionalization using diphenylethylene has clear advantages over all other available methods. Due to steric constraints, under most conditions diphenylethylene is only added once to a polymeric organolithium chain. Another significant advantage is that the product of addition is a living polymeric chain end (Scheme 1.8). This fact opens up an array of uses not present in other systems. The substituted DPE GFM offers the ability to place functional groups at the initiating end, in the center of the chain, at the interphase of between blocks, and at the chain-end.\textsuperscript{113}

Multiple functional groups can be incorporated, an important consequence of which is condensation-type macromonomers.\textsuperscript{114} Diphenylethylene chemistry has
recently been employed to prepare ring-opening metathesis macromers via norbornene-substituted diphenylethylene.\textsuperscript{115} Additionally, incorporation of a POSS group at the interface of a polystyrene-polydimethylsiloxane block copolymer was recently demonstrated using 1,1-diphenylethylene chemistry.\textsuperscript{116}

![Functionalization of P-Li with substituted diphenylethlenes.](image1)

Scheme 1.8. Functionalization of P-Li with substituted diphenylethlenes.

Yet another GFM was proposed by DeSimone and coworkers\textsuperscript{117, 118} in 1993, based on the high yielding reaction of polymeric organolithium compounds with silyl chlorides (Scheme 1.9). The side reactions of lithium halogen exchange and Wurtz coupling, analogous to those described for chloroalkanes, do not occur with chlorosilanes.\textsuperscript{110} This advantage is tempered by the fact that a reagent with a protected functional group must be synthesized, and post-polymerization deprotection must ensue. Nonetheless, this GFM provides chain-end functional polymers in high yield with few side reactions. Examples include alcohol and amine functional polystyrenes, prepared via the trimethylsilyl protected analogs.\textsuperscript{118}

![Functionalization of P-Li with chlorosilanes.](image2)

Scheme 1.9. Functionalization of P-Li with chlorosilanes.
The Quirk group has recently reported a new general functionalization method based on the combination of living anionic polymerization and hydrosilation chemistry as illustrated in Scheme 1.10. First, living poly(styryl)lithium is terminated with chlorodimethylsilane to prepare chain-end, silyl hydride-functionalized polystyrene. The resulting ω-silyl hydride-functionalized polymer can then react with a variety of readily available substituted alkenes to obtain the desired chain-end functionalized polymer. This methodology has been successfully applied to the synthesis of ether-, acetate, amine-, alcohol-, epoxy- and perfluoroalkyl-functionalized polymers.

\[
\text{PS-Li} + \text{Cl-Si-H} \rightarrow \text{PS-Si-H} + \text{LiCl}
\]

\[
\text{PS-Si-H} + \text{alkene} \rightarrow \text{PS-Si-alkyl}
\]

\[X = \text{NH}_2, \text{OH}, \text{CN}, \text{OEt}, \text{OAc}, \text{H}, (\text{CF}_2)_n\text{CF}_3, \text{CHCH}_2\]

Scheme 1.10. General functionalization.

Synthesis of polymers using the GFM described above has advantages over other methods because of the absence of protection/deprotection steps. With this new methodology the living anionic chain end is terminated prior to exposure to the functionalizing agent in a quantitative reaction. The resulting silyl hydride-functionalized polymer can then be used for a variety of functionalization reactions. This method, however, suffers from a limitation related to polybutadiene. Hydrosilation can be complicated by reaction between the chain-end and pendant vinyl groups of the
polymer chain. As of yet, functionalization of polybutadiene using this methodology has not been performed. Hydroxyl-functionalized polyisoprene was recently prepared by termination of poly(isoprenyl)lithium with chlorodimethylsilane, then hydrosilation with allyl alcohol using Karstedt’s catalyst.\textsuperscript{127}

Hydrosilation is a high yielding, regioselective reaction between a silyl-hydride species and an alkene, and it is tolerant to a variety of functional groups.\textsuperscript{128-130} A catalyst, typically platinum or rhodium, is required in parts per million concentrations for this transformation.\textsuperscript{131} The most effective catalyst is a hydrocarbon-soluble platinum(0) catalyst, called Karstedt’s catalyst (2.1-2.4 \% platinum divinyltetramethyldisiloxane in xylene).\textsuperscript{132, 133} The reactivity and utility of this catalyst is owed to the solubility and oxidation state, relative to other transition metal catalysts.\textsuperscript{134} Hydrosilation generally proceeds with addition of silicon to the least substituted end of the double bond. Three basic steps can be used to describe the mechanism of hydrosilation: 1) oxidative addition of the silyl-hydride to platinum; 2) migratory insertion, such that a hydrogen is added to the $\pi$-coordinated olefin which then becomes $\sigma$-coordinated to platinum; and 3) reductive elimination of the silicon-containing species and $\sigma$-coordinated aliphatic species.\textsuperscript{134} The steps are illustrated in Scheme 1.11. At the end of the reaction scheme depicted below, the platinum species can be reused indefinitely.

Scheme 1.11. Chalk-Harrod mechanism of hydrosilation.
Some debate over the mechanism above by Chalk and Harrod\textsuperscript{135,136} has occurred throughout the years.\textsuperscript{134,137-139} A modified mechanism was proposed in which the silicon species is transferred to the alkene, followed by elimination as shown in Scheme 1.12.\textsuperscript{137} This mechanistic approach aids in the explanation of an unsaturated side-product formed in hydrosilation reactions through simple $\beta$-hydride transfer to metal.\textsuperscript{139} It is likely the case that both mechanisms are occurring and that their relative importance is dependent on silyl hydride and alkene substituents as well as concentration.

Scheme 1.12. Modified Chalk-Harrod mechanism of hydrosilation.

Termination by an appropriate chlorosilane followed by hydrosilation with a functional alkene make it possible to prepare a variety of functionalized polymers. This technique has been used to chain-end functionalize polymers with a variety of different structures, such as fullerenes\textsuperscript{140}, amines\textsuperscript{119}, and isobutyl groups.\textsuperscript{36} In this research the scope of this GFM was expanded to include cyano functionalization, functionalization in the center of the chain, and placing two functional groups at the chain-end.

1.3 In-Chain Functionalization

In-chain functionalized polymers contain a functional group along the polymer chain. This designation of “in-chain functionalized” applies to polymers with one functional group in the middle of the chain, as well as to polymers with a functional
group in each repeat unit. In-chain functionalization is an important means of tuning the material properties of a polymer. Unlike typical chain-end functionalization, in-chain functionalization can have an effect on the bulk properties of a polymer. The nature of anionic polymerization limits the functionality of monomers severely for controlled polymerizations in hydrocarbon solution. There are a number of examples of controlled functional polymer preparation. However, the polymerizations were carried out in THF at -78°C. THF is industrially unattractive as a solvent, due to its high vapor pressure, flammability, ability to form peroxides, and harmful reaction with the eyes, skin, lungs, and gastrointestinal system. In addition, it is costly to maintain an industrial reaction at -78°C. A typical scheme for the preparation of an in-chain functionalized polymer is represented in Scheme 1.13.

![Scheme 1.13. In-chain functionalization](image)

A recent achievement for the preparation of functionalized polymers is the anionic polymerization of para-dimethylsilylstyrene. Polymerization of this monomer was reported previously in tetrahydrofuran at -78°C. This reaction was reported to also take place in benzene at room temperature without side reactions. Hydrosilation with a variety of readily available alkenes has afforded functional polymers as shown in Scheme 1.14. The monomer could also be copolymerized with styrene in an alternating fashion to afford a styrenic chain with the ability to tailor the amount of
functionality. The reactivity ratios for styrene and \( p \)-dimethylsilylstyrene are reported to be 0.17 and 1.9, respectively.\(^{120}\) An advantage of this method compared to other methods with substituted styrenes is that there is no need for protection and deprotection reactions. In this work, it was observed that polymerization of the \( p \)-dimethylsilylstyrene monomer in cyclohexane resulted in undesirable side reactions. These side reactions were investigated as described herein.

![Scheme 1.14. General in-chain functionalization.](image)

Another method for the inclusion of functional groups along the polymer chain is through use of substituted DPE’s. Diphenylethylene with a protected functional group can be added during polymerization to yield incorporation via copolymerization. This method also requires sequential addition of monomers as well as protection and deprotection steps.\(^{151, 152}\)

### 1.4 Functional Groups

#### 1.4.1 Alkenyllithium Initiators

The use of an unstaturated initiator for anionic polymerization was first reported by Waack and Doran\(^{153}\) in 1961. The initiator efficiency was less than 11% for both
allyllithium and vinyllithium. Later, in 1967, a more comprehensive study of the activity of allyllithium and vinyllithium compared to other alkyllithium initiators was completed.\textsuperscript{154} The resonance stability and hybridization of these initiators made them much less reactive than their aliphatic counterparts. In 1994, Takano et al.\textsuperscript{155} synthesized 4-pentenyllithium from 5-bromopentene and lithium. The polymerization of styrene in benzene was carried out at room temperature in the presence of a small amount of tetrahydrofuran. This procedure resulted in good agreement between calculated and observed molecular weights as well as a narrow polydispersity index.

Inclusion of an olefinic vinyl group in the polymer structure is advantageous for several reasons. The polymer can be used as a macromonomer for metallocene polymerization to make a comb-type, graft copolymer. In addition, the double bond can be modified in several ways, such as hydrosilation, hydroboration, hydration, and hydrohalogenation. Functionalization by hydrosilation will be shown.

1.4.2 Cyano Functionalization

Chain-end, cyano-functionalized polystyrene has been produced using ATRP.\textsuperscript{156, 157} 2-Bromopropionitrile and \textit{p}-cyanobenzyl bromide were used as ATRP initiators to produce polystyrenes with $M_n = 5,500$ and 5,100 Da and with $M_w/M_n = 1.10$ and 1.09, respectively. Although narrow molecular weight distributions were achieved with high efficiency of functionalization, monomer conversions were limited to less than 50%.

Synthesis of cyano-functionalized products from anionically synthesized materials in hydrocarbon solvent at room temperature or above has not yet been reported. DeSimone et al.\textsuperscript{118} proposed that termination of a polymeric organolithium compound
with a cyano-functionalized chlorosilane could be used to prepare the corresponding cyano-functionalized polymer, but no evidence for this reaction was presented. The acidity of the proton alpha to the cyano functionality (example: Ph-CH$_2$-CN, pK$_a$ = 21.9)$^{47}$ creates a unique challenge for the controlled anionic synthesis of a cyano-functionalized material. One would expect uncontrolled termination of poly(styryl)lithium (PSLi) (estimated pK$_a$ = 43 for the conjugate acid of PSLi based on toluene)$^{47}$ in the presence of an aliphatic cyano functionality.

Nakahama et al.$^{158}$ investigated the anionic polymerization of 2-, 3-, and 4-cyanostyrenes at -78 °C in THF. Although the polymerizations of 2-, and 3-cyanostyrenes were not controlled, anionic polymerization of 4-cyanostyrene with a variety of anionic initiators proceeded to form the corresponding polymers quantitatively with controlled molecular weights and narrow molecular weight distributions. Polymerization at higher temperatures resulted in loss of control and poor conversion even after long reaction times.

1.4.3 Triethoxysilane Functionalization

Polymers functionalized with triethoxysilane groups possess a wide variety of potential applications. The use of silica as a filler can be enhanced through use of a proper coupling agent. An addition of only 2 wt% of silica to an elastomer can increase the modulus nearly threefold.$^{159}$ Trialkoxysilane-functionalized polymers have been used to prepare organic-inorganic hybrid materials, which have a wide variety of applications from bone cements$^{160}$ to electrical applications.$^{161}$ Trimethoxysilane-functional polystyrene has been prepared by termination of poly(styryl)lithium with $p$-chloromethylphenyl trimethoxysilane at -78 °C in tetrahydrofuran.$^{162}$ Polymerization of
triethoxysilane-functionalized styrene was investigated by Hirao and coworkers\textsuperscript{145, 163} at -78°C in tetrahydrofuran. Synthesis of trimethoxysilane-functionalized polystyrene by termination of poly(styryl)lithium with chlorodimethylsilane followed by hydrosilation using vinyltrimethoxysilane was previously reported by our group.\textsuperscript{164} The yield of this reaction was limited to 80% due to dehydrosilation of trimethoxysilane and dimerization.

In this thesis the general functionalization method involving termination with a chlorosilane will be expanded to additional functional groups, as well as different chain architectures. Investigation of the utility of termination with chlorosilane then hydrosilation chemistry will be applied to preparing polymers with two functional groups at the chain-end as well as functionalization placing one functional group precisely in the center of the chain will be shown.
CHAPTER II
EXPERIMENTAL

2.1 Inert Atmosphere Techniques

The high reactivity of organolithium compounds towards water, oxygen, and carbon dioxide necessitates the implementation of an inert gas or high vacuum atmosphere. Air- and moisture-sensitive reagents as well as reagents coming in contact with these compounds must be purified and handled under an inert or high vacuum atmosphere.

2.1.1 High Vacuum Techniques

A high vacuum line, shown in Figure 2.1, provides the most effective experimental method to exclude impurities from the reaction system. The high vacuum line was used to dry, degas, purify, and transfer solvents and reagents into reactors and ampoules. High vacuum ($10^{-4}$ torr) was obtained with an Edwards RV-8 direct drive pump coupled with a silicone oil diffusion pump. Vacuum pressure was qualitatively measured using a Tesla coil. When the pressure is greater than $\sim 10^{-4}$ torr, the Tesla coil produces a bluish discharge along with noise, due to ionization/excitation of gaseous nitrogen. The qualitative measurement of a quiet line was a requirement to confirm the absence of leaks in the reactors, ampoules, and other apparatus connected to the vacuum line.
The vacuum line was constructed with an upper and lower manifold, made from Pyrex (borosilicate) glass, with airtight control of flow via Rotaflo® stopcocks. The vacuum line contained an inlet for nitrogen gas, used to provide a positive nitrogen atmosphere for injection of reactive chemicals into a flask or reactor connected to the vacuum line. Two connections with thick-wall glass and grease traps were used for attachment of ampoules and reactors directly via hand-blown, all-glass connections. Four connections with standard-taper, 24/40 ground-glass joints were used for attachment of flasks to the vacuum line.

![Diagram of vacuum line](image)

Figure 2.1. High vacuum line.

2.1.2 Schlenk Line Techniques

A Schlenk line was used for air- and moisture-sensitive reactions that were not carried out under vacuum, in the dry box, or using a nitrogen-filled balloon. A standard two-manifold system, with one manifold under positive nitrogen pressure and one under vacuum, was used in this case. With this system, reactions could be placed under
vacuum, then purged with nitrogen by simply changing the position of the Schlenk line valve. This is advantageous for reactions where control of the atmosphere is important, but not as critical as in anionic polymerization.

2.1.3 Glove Box Techniques

The transfer and handling of air/moisture sensitive material was performed in a Vacuum Atmospheres dry box (Model HE-193). An inert atmosphere was maintained by recirculation of argon via a Vacuum Atmospheres Omni Train inert gas purification system. This system maintained equilibrium oxygen and water concentrations below 1 ppm, and the atmosphere was tested prior to use by placing a few drops of a \((\text{Cp}_2\text{TiCl}_2)_2\text{ZnCl}_2\) complex dissolved in toluene onto weighing paper. Upon exposure to oxygen or water (>5 ppm), the complex changes from green to yellow as described by Sidutowski and Stucky.\(^{168}\)

2.2 Reagents

Reagents were used as received unless purity or reactive impurities presented complications in achieving the desired results were anticipated or observed. Oxygen and water must be removed from solvents used in anionic polymerization and Grignard reactions.

2.2.1 Reagents Used as Received

\textit{sec}-Butyllithium (FMC, ~1.5M in cyclohexane, after double titration).\(^{169}\)

\textit{n}-Butyllithium (FMC, ~1.5M in cyclohexane, after double titration).\(^{169}\)

2,6-Di-\textit{tert}-butyl-4-methylphenol (BHT) (Aldrich, > 99%).

Calcium hydride (Alfa, 95%).
Dibutylmagnesium (FMC Lithium Division, 15 wt% in heptane).

Sodium dispersion (Alfa, 50 wt% in paraffin oil).

4-Bromostyrene (Aldrich, 98%).

4-Chlorostyrene (Synquest Labs, 99%).

1,2-Dibromoethane (Aldrich, 99%).

Iodine (Fisher Scientific, 99.8%).

Magnesium turnings (Aldrich, 98%).

Karstedt’s catalyst (Platinum divinyltetramethylidisiloxane complex, Gelest, 2.1-2.4% Pt concentration in xylene).

Triethoxysilane (Aldrich, 98%).

Lithium metal (FMC, 98% stabilized with Na).

Lithium Aluminum Hydride (Aldrich, 95%).

2.2.2 Purification of Solvents.

2.2.2.1 Purification of Hydrocarbon Solvents

Benzene (EMD, ACS grade), cyclohexane (EMD, ACS grade), toluene (EMD, ACS grade), pentane (EMD, ACS grade) and heptane (EMD, 99%) were stirred over freshly-crushed calcium hydride (Acros Organics, 93%, 0-20 mm grain size) in a flask on the vacuum line overnight. The solvents were cooled to -78 °C in an isopropyl alcohol (IPA)/dry ice bath, degassed, and warmed repeatedly to remove air and hydrogen gas generated during the drying process. In order to further dry the solvents, the resulting solutions were vacuum transferred into a second flask containing sodium dispersion (Hodgson Chemicals Inc., 40% sodium dispersion in paraffin). The solvents were again subjected to several freeze, degas, thaw cycles before final distillation into flasks.
containing poly(styryl)lithium and equipped with Rotaflo® stopcocks. The orange color of the poly(styryl)lithium was used as an indication of purity. Solvents were distilled directly from these flasks, as needed, through the high vacuum line.\textsuperscript{56}

2.2.2.2 Tetrahydrofuran and Diethyl Ether

Tetrahydrofuran (EMD, ACS grade) and diethyl ether (EMD, ACS grade) were stirred over freshly-ground calcium hydride for 24 h with frequent degassing on the high vacuum line using a dry ice/isopropyl alcohol bath for cooling. They were vacuum transferred onto sodium mirrors\textsuperscript{166} in a 2-L flask equipped with a Rotaflo® stopcock. This step was repeated until the sodium mirror maintained its integrity. The purified THF and diethyl ether were distilled directly from the sodium mirror into ampoules and reactors, as needed.

2.2.3 Monomers

Monomers were purified to remove trace quantities of water, oxygen, and other alkyllithium-reactive impurities

2.2.3.1 Styrene

Styrene was stirred over freshly ground calcium hydride with periodic degassing using liquid nitrogen. A Rotaflo®-equipped flask was evacuated, tested for leaks, and then filled with a positive nitrogen atmosphere. 1,10-Phenanthroline (~100mg) and 2 mL of dibutylmagnesium were added and the flask was evacuated. The dried, degassed styrene was distilled into the Rotaflo®-equipped flask. A bright purple color served as an indication of active butylmagnesium complexed with phenanthroline. Purified styrene
was stored in the refrigerator and transferred into ampoules via short-path vacuum distillation as needed.  

2.2.3.2 Butadiene

1,3-Butadiene (Matheson, 99%) was transferred using the vacuum line from a gas cylinder into a flask containing freshly-ground calcium hydride and cooled with dry ice/isopropyl alcohol. The pressure was carefully monitored and the butadiene cylinder regulator was adjusted to avoid pressurizing the line. It was stirred for 5 h at -78 °C with periodic degassing before being transferred into a flask containing neat \( n \)-butyllithium, where it was stirred for another 30 minutes at -78 °C. The butadiene was then transferred into an evacuated ampoule connected to the reactor. After the correct volume was distilled (\( \delta = 0.731 \) g/mL at -78 °C)\(^{170} \), the ampoule was flame-sealed from the line and the butadiene was added to the reaction by smashing the breakseal.

2.2.3.3 4-Dimethylsilylstyrene

4-Dimethylsilylstyrene was synthesized as described below (see section 2.3.13), placed in a flask containing calcium hydride and then degassed several times using liquid nitrogen. The monomer was then vacuum distilled into a Rotoflo\textsuperscript{®}-equipped, round-bottomed flask containing dibutylmagnesium and 1,10-phenanthroline. A bright purple color served as an indication of the absence of organometallic-reactive impurities.

2.2.3.4 3-Dimethylsilylstyrene

3-Dimethylsilylstyrene was synthesized as described below (see section 2.3.17), placed in a flask containing calcium hydride then degassed several times using liquid nitrogen. The monomer was then vacuum distilled into a Rotoflo\textsuperscript{®}-equipped, round-
bottomed flask containing dibutylmagnesium and 1,10-phenanthroline. A bright purple color served as an indication of the absence of organometallic-reactive impurities.

2.2.4 Initiators

The polymerizations of styrene and diene monomers were initiated with sec-butyl lithium or 4-pentenyllithium. Other initiators, such as n-butyl lithium and dibutylmagnesium, were used for purification purposes.

2.2.4.1 sec-Butyllithium

sec-Butyllithium (FMC Lithium Division, ~1.5M in cyclohexane/heptane) was used, as received, after Gilman double titration with allyl bromide to determine the concentration of carbon-bound lithium.\(^{169}\) The amount of total base (carbanionic and non-carbanionic lithium species) was determined by injecting 1.0 mL of sec-butyl lithium solution into three crimp-cap bottles, each containing 10 mL of freshly distilled cyclohexane in the dry box. The bottles were sealed, removed from the dry box, quenched with 10 mL of distilled water, and titrated with standardized 0.1 N HCl solution using phenolphthalein as indicator. The amount of free base (non-carbanionic lithium species) was determined by quenching 3.0 mL of sec-butyl lithium in each of three crimp-cap bottles with 1 mL of allyl bromide and then adding 10 mL of distilled water. These solutions were then titrated with 0.1 N HCl using phenolphthalein as indicator. Subtracting the averaged amount of free base (allyl bromide quench) from the averaged amount of total base (water quench) gave the concentration of alkyl lithium. The sec-butyl lithium solution received was separated into 100-mL crimp-cap bottles with ca. 30 – 40 mL of solution per bottle to prevent contamination.
2.2.4.2 \textit{n}-Butyllithium

\textit{n}-Butyllithium (FMC Lithium Division, \(\sim1.5\text{M}\) in cyclohexane) was distributed into crimp-cap bottles in the glove box and used in excess, as needed, without further analysis or purification.

2.2.4.3 Dibutylmagnesium

Dibutylmagnesium (FMC Lithium Division, 17 wt\% in heptane) was distributed into crimp-cap bottles in the glove box and used without further analysis or purification.

2.2.3.4 4-Pentenyllithium

4-Pentenyllithium was synthesized as described herein (section 2.3.1) and divided into 15-20 mL portions and distributed into crimp-cap bottles and stored in the freezer. The initiator was used within one month of synthesis.

2.2.5 Functionalizing Reagents

The living nature of anionic polymerization affords advantages in the area of chain-end functionalization due to the lack of chain transfer and chain termination reactions. The active living chain-end can be quenched with a variety of reagents to quantitatively prepare functional polymers.

2.2.5.1 Chlorodimethylsilane\textsuperscript{119}

Chlordimethylsilane (Aldrich, 98\%) was quickly transferred into a long-necked, round-bottomed flask containing freshly-ground calcium hydride, in an ice bath in the fume hood. The flask was placed on the vacuum line and degassed several times using liquid nitrogen. A Rotoflo\textsuperscript{\textregistered}-equipped, round-bottomed flask containing freshly-ground calcium hydride was placed on the vacuum line and evacuated. Chlordimethylsilane
was distilled into the Rotoflo®-equipped, round-bottomed flask. Approximately 2 mL of the chlorodimethylsilane was distilled from the destination flask and discarded. The purified chlorodimethylsilane was stored in the freezer, and distilled as needed. When ~2 mL of the reagent remained, it was discarded.

2.2.5.2 Dichloromethylsilane\textsuperscript{171}

Dichloromethylsilane (Aldrich, 99%) was quickly transferred into a long-necked, round-bottomed flask containing freshly-ground calcium hydride, in an ice bath in the fume hood. The flask was placed on the vacuum line and degassed several times using liquid nitrogen. A Rotoflo®-equipped, round-bottomed flask containing freshly-ground calcium hydride was placed on the vacuum line and evacuated. Dichlorodimethylsilane was distilled into the Rotoflo®-equipped, round-bottomed flask. Approximately 2 mL of the dichlorodimethylsilane was distilled from the destination flask and discarded. The purified dichlorodimethylsilane was stored in the freezer, and distilled as needed. When ~5 mL of the reagent remained, it was discarded.

2.2.5.3 Ethylene oxide

Ethylene oxide (Aldrich, 99.5+%) was transferred through the vacuum line to an evacuated flask cooled to -78 °C and containing freshly-ground calcium hydride. It was stirred and degassed periodically over a period of 4 h. It was then transferred through the vacuum line to another flask containing neat dibutylmagnesium and a small amount of 1,10-phenanthroline as the indicator. The ethylene oxide was stirred at -78 °C for 30 min before being transferred to a calibrated ampoule, diluted with an equal amount of benzene, and flame-sealed from the vacuum line.
2.2.5.4 Ethylene sulfide

Ethylene sulfide (Aldrich, 96+%) was transferred to a long-necked, round-bottomed flask containing freshly-ground calcium hydride. It was stirred and degassed periodically over a period of 4 h. It was then transferred through the vacuum line to a Rotoflo®-equipped flask containing freshly-ground calcium hydride, stored in the freezer, and distilled into ampoules as needed.

2.2.5.5 Methyl Iodide

Methyl iodide (Aldrich, 99.5%) was transferred into a Rotoflo®-equipped, round-bottomed flask, then degassed via several freeze-pump-thaw cycles using a dry ice/isopropyl alcohol bath at -78 °C. The methyl iodide was then distilled into calibrated ampoules equipped with break seals. The desired quantity of methyl iodide was distilled, followed by benzene to ~ 10% by volume methyl iodide. The ampoule with diluted methyl iodide was heat-sealed and used within 48 hours.

2.2.6 Other reagents

2.2.6.1 5-Bromopentene

5-Bromopentene (Aldrich, 97%) was fractionally distilled in vacuo into an all-glass ampoule prior to use. The middle fraction was collected.

2.2.6.2 Allyl cyanide

Allyl cyanide (Aldrich, 98%) was purified by stirring over freshly-ground calcium hydride with periodic degassing for 12 h followed by distillation into an ampoule equipped with a Rotoflo® stopcock. The ampoule was stored in the freezer, and only opened in the dry box when needed for hydrosilation reactions.
2.3 Synthesis of Reagents, Monomers, and Polymers

The synthesis of reagents, monomers, and polymers was performed and optimized to prepare products in the highest yield with the best purity.

2.3.1 4-Pentenyllithium

To a 250-mL Morton, increased, glass reactor equipped with a diethyl ether ampoule (20 mL), 5-bromopentene ampoule (6.4 mL, 8.05 g, 0.0540 mol), Rotoflo® stopcock, and stir bar in the dry box was added lithium metal (FMC, 3.749g, 0.5402 mol). The reactor was removed from the dry box and placed under high vacuum. Heptane (50 mL) was distilled into the reactor and the reactor was separated from the vacuum line. Then, the 5-bromopentene ampoule was broken and the reaction was allowed to stir at room temperature for a period of 3 days. The reactor and diethyl ether ampoule was cooled to 0 °C and the contents of the ampoule were added. The reaction was stirred for a period of 24 h at 0 °C. Then, the reactor was again placed on the vacuum line and the solvent and volatile components were removed via high vacuum. The reactor was then placed in the dry box and the 4-pentenyllithium was taken up in heptane (50 mL) and filtered using a coarse glass frit. The product was characterized by double titration to yield 0.76 M 4-pentenyllithium (70%).

2.3.2 α-4-pentenylpolystyrene

4-Pentenyllithium (4.2 mL, 0.00319 mol) was added to an all-glass reactor equipped with a styrene ampoule (5.4 mL, 4.91 g, 0.047 mol), a tetrahydrofuran ampoule (1.09 mL, 0.9698 g, 0.0135 mol), and a methanol ampoule (~2 mL). The reactor was placed under high vacuum and then benzene (60 mL) was distilled in. Then the reactor
was separated from the line and the THF ampoule was broken followed by the styrene ampoule. The reaction was placed in a water bath at 30 °C. After a period of 6 h the methanol ampoule was broken. The reaction solution was precipitated into MeOH to yield the desired product ($M_n = 1600$, PDI = 1.06). Calculated $M_n = 1600$ g/mol.

2.3.3 α-Triethoxysilylpolystyrene

α-4-pentenylpolystyrene (0.0982 g), dry benzene (1 mL), triethoxysilane (0.0253 g) and Karstedt’s catalyst (2 drops) were added to a 5-mL, round-bottomed flask in the dry box. The reaction was stirred at room temperature for a period of 12 h until disappearance of the vinyl peaks in the $^1$H NMR spectrum. After freeze-drying to remove the solvent and excess triethoxysilane the desired α-triethoxysilyl-functionalized polystyrene was fully characterized to reveal quantitative conversion of the α-4-pentenylpolystyrene.

2.3.4 α-Pentenyl-ω-silyl hydride-functionalized polystyrene

4-Pentenyllithium (6.75 mL, 0.00317 mol) was added to an all-glass reactor equipped with a styrene ampoule (7.0 mL, 6.34 g, 0.0609 mol), a tetrahydrofuran ampoule (2.0 mL), and a chlorodimethylsilane ampoule (3.4 mL + 6.6 mL benzene, 0.0306 mol). The reactor was placed under high vacuum and benzene (~ 70 mL) was distilled in. Then the reactor was separated from the line and the THF ampoule was broken followed by the styrene ampoule. The reaction was placed in a water bath at 30 °C. After a period of 6 h the chlorodimethylsilane ampoule was broken. The reaction solution was precipitated into MeOH to yield the desired product. The calculated $M_n = 2000$ g/mol; $M_n$(GPC) = 2600 g/mol, PDI = 1.03.
2.3.5 α-Pentenyl-ω-thiol-functionalized polystyrene

4-Pentenyllithium (10.10 mL, 0.00313 mol) was added to an all-glass reactor equipped with a styrene ampoule (6.9 mL, 6.25 g, 0.0601 mol), a tetrahydrofuran ampoule (1.09 mL), and an ethylene sulfide ampoule (0.37 mL, 0.38 g, 0.00625 mol + 6.6 mL of benzene). The reactor was placed under high vacuum and then benzene (~ 70 mL) was distilled in. Then the reactor was separated from the line and the THF ampoule was broken followed by the styrene ampoule. The reaction was placed in a water bath at 30 °C. After a period of 2 h the contents of the ethylene sulfide ampoule were added. The reaction solution was precipitated into MeOH to yield the desired product. The calculated $M_n = 2,000$ g/mol; $M_n$(GPC) = 3,400 g/mol, PDI = 1.10.

2.3.6 Polybutadiene

Butadiene (20.0 mL, 14.6 g, 0.273 mol) was added to a solution of sec-butyllithium (5.85 mL, 1.25 M, 0.00731 mol) and cyclohexane (~ 200 mL) in an all-glass reactor. Polymerization proceeded at 30 °C for a period of 12 h. The reaction was terminated with degassed methanol, and then precipitated into a 10-fold excess of methanol. The methanol was decanted and the clear viscous liquid was collected and dried in vacuo. The calculated $M_n = 2,000$ g/mol; $M_n$(GPC) = 2,000 g/mol.

2.3.7 In-chain, triethoxysilane-functionalized polybutadiene

Polybutadiene (1.00 g, $M_n = 2,000$ g/mol, 0.5 mmol), triethoxysilane (0.434g, 2.64 mmol), benzene (c.a. 5 mL), and a few drops of Karstedt’s catalyst were added to a 20-mL, round-bottomed flask and allowed to stir for a period of 18 h. Disappearance of the vinyl $^1$H NMR peaks was noted, and the in-chain, triethoxysilane-functionalized polybutadiene was dried in vacuo.
2.3.9 ω-Silyl hydride-functionalized polystyrene\textsuperscript{119}

Chain-end, silyl hydride-functionalized polystyrene was prepared as previously reported by Quirk et al.\textsuperscript{119, 173} Poly(styryl)lithium (10.19 g, 0.00463 mol, $M_n = 2,200$ Da) was terminated with chlorodimethylsilane (1.00 g, 1.18 mL, 0.0107 mol) in benzene at room temperature followed by precipitation into methanol and drying.

2.3.10 ω-Cyanopolystyrene\textsuperscript{171}

Silyl-hydride, chain-end functionalized polystyrene (1.00 g, 0.45 mmol, $M_n = 2,200$ Da), dry benzene (10 mL), allyl cyanide (0.0610 g, 0.91 mmol), and Karstedt’s catalyst (0.10 mL) were added into a 25-mL, round-bottomed flask in the dry box. The flask was fitted with a reflux condenser and septum, then removed from the drybox and placed under positive argon pressure at room temperature for a period of 2 weeks. Silica gel was added, stirred overnight, and the mixture was separated via column chromatography using 3/1 (vol/vol) mixture of toluene/cyclohexane; the non-functional polystyrene was eluted, then the desired product was eluted using toluene. The product was extracted with water (3 x 10 mL), concentrated under reduced pressure, and freeze-dried from a benzene solution (0.87 g, 87%).

2.3.11 In-chain, silyl hydride-functionalized polystyrene\textsuperscript{171}

Functionalization of poly(styryl)lithium (16.4 g, 0.0137 mol, $M_n = 1,200$ Da) was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing the dichloromethylsilane (0.70 mL, 0.0067 mol; solution in 4.0 mL benzene) at room temperature. Since a slight excess of poly(styryl)lithium was used, the characteristic orange color of the poly(styryl)lithium remained. After one day, the resulting polymer was reacted with ethylene oxide (0.5 mL, 0.441 g, 0.01 mol; solution in
9.5 mL of benzene) to functionalize the unreacted poly(styryl)lithium with a polar end group (Scheme 3). After 1 h the colorless mixture was quenched with methanol. The product was removed from the reactor and precipitated into methanol; the resulting polymer was filtered and dried in a vacuum oven overnight. The silyl hydride, in-chain functionalized polymer was separated from the hydroxyl-functionalized polymer by silica gel column chromatography using a 3/1 (vol/vol) mixture of toluene/cyclohexane as eluent. The silyl hydride functionalized polymer eluted first from the mixture; these fractions were combined, concentrated under reduced pressure, and then freeze-dried from a benzene solution (14.8 g, 96%).

2.3.11 In-chain, cyano-functionalized polystyrene

Silyl-hydride, in-chain functionalized polystyrene (0.5154 g, 0.23 mmol, $M_n = 2200$ Da), dry toluene (10 mL), allyl cyanide (0.0365 g, 0.54 mmol), and 0.10 mL of Karstedt's catalyst were added into a 25-mL, round-bottomed flask in the dry box. The flask was fitted with a reflux condenser and a septum, removed from the dry box, and allowed to stir in an oil bath (90 °C) under pressure from a balloon filled with a 1/1 mixture of oxygen and argon for a period of 14 days. Incomplete reaction was observed by thin layer chromatography (TLC) after a period of 5 days, and additional catalyst (0.10 mL) and allyl cyanide (0.0355 g, 0.53 mmol) were added. After no further progress by TLC was observed, activated silica was added and stirred for 12 h. Then the non-polar product was separated via column chromatography using a 3/1 (vol/vol) mixture of toluene/cyclohexane. The desired product was eluted using a 3/1 (vol/vol) mixture of toluene/ethyl acetate, extracted with water (3 x 10 mL), concentrated under reduced pressure, and freeze-dried using benzene (yield: 0.30g, 58%).
2.3.12 PS-Si(CH$_3$)$_2$

An ampoule containing poly(styryl)lithium solution (100 mL, 0.034M in benzene, $M_n = 1,700$, PDI = 1.05) equipped with a Rotoflo® stopcock was attached to a reactor equipped with a stir bar and fitted with a dichloromethylsilane ampoule (27 mL, 0.26 mol, 76 equivalents). The reactor was placed under high vacuum, then benzene (50 mL) was distilled into the reactor and it was flame-sealed from the high vacuum line. The dichloromethylsilane ampoule was broken and the reaction was cooled to -5 °C using an ice bath. Poly(styryl)lithium was added to the solution dropwise. After complete addition the mixture was allowed to warm to room temperature; then the reactor was attached to the vacuum line and excess dichloromethylsilane/benzene was removed by freeze-drying from dry ice / isopropyl alcohol. The reactor was separated from the vacuum line and placed in the dry box where the polymerization product was dissolved in freshly distilled tetrahydrofuran (20 mL). The solution was transferred to a two-necked, round-bottomed flask, removed from the dry box, and placed under positive nitrogen pressure. The reaction was cooled to 0 °C and lithium aluminum hydride (0.0645 g, 0.0017 mol, 0.5 equivalents) was added to the solution in 3 portions over a period of 6 h. The reaction was allowed to warm to room temperature and stirred over a period of 12 h. The organic layer was extracted with water, then brine, and precipitated into methanol to yield the desired product (5.3 g, 92%). Calculated $M_n = 1,700$ g/mol; $M_n$(GPC) = 2,700 g/mol.

2.3.13 PS-Si(CH$_3$)(CH$_2$CH$_2$CH$_2$CN)$_2$

In the drybox PS-Si(CH$_3$)$_2$ (0.100 g, 0.037 mmol, $M_n = 2,700$ g/mol), allyl cyanide (0.00745g, 0.11 mmol), benzene (1 mL) and a few drops of Karstedt’s catalyst
were added to a 5 mL vial. The vial was capped and removed from the drybox. The reaction was monitored until disappearance of the Si-H band at 2,100 cm\(^{-1}\) was noted, after a period of 2 weeks. The reaction solution was then freeze-dried and characterized, revealing quantitative conversion of the starting material.

### 2.3.14 4-Dimethylsilylstyrene\(^{149,163}\) (p-DMSS)

A 3-necked, round-bottomed flask, equipped with a stir bar, reflux condenser, 3 septa, and containing magnesium (5.3 g, 0.22 mol) was placed on the high vacuum line and flame dried 4 times over a 12 h period. The flask was purged with positive nitrogen pressure and a few crystals of iodine (~50 mg) were added. The flask was evacuated and cooled using dry ice/isopropyl alcohol. THF (200 mL) was vacuum distilled into the flask. The reaction flask was then placed under positive nitrogen pressure using a balloon and needle (through the septum) and was removed from the vacuum line, fitted with an addition funnel, and then stirred for 30 minutes at room temperature. The reaction was cooled and maintained at 0 to 15 °C. 4-Chlorostyrene (20 mL, 23.1 g, 0.167 mol) was added via syringe pump at a rate of 10 mL/hour. After complete addition, the reaction was allowed to warm to room temperature over a period of 2 h.

Chlorodimethylsilane (18.5 mL, 15.77 g, 0.167 mol) was added to the addition funnel and then to the reaction over a period of 1 h. The reaction was allowed to stir overnight to yield a thick white paste. Toluene (200 mL) and water (200 mL) were added to extract the paste into a separatory funnel. The water was removed and extracted with toluene (2 x 50 mL) and the organic layer was collected in an Erlenmeyer flask. Anhydrous magnesium sulfate was added, the solution was filtered and then the solvent
was removed using a rotary evaporator (bath temp = 25 °C). The product, a clear oil with slight yellow tint, (22.75 g, 84%) was dried under high vacuum for 2h.

2.3.15 Poly(4-dimethysilylstyrene)

4-Dimethysilylstyrene (1.0 mL, 0.91 g, 0.00561 mol) was added to 0.75 mL of sec-butyllithium (0.267 M, 0.20 mmol) in 8 mL of cyclohexane in a 25-mL, round-bottomed flask equipped with a septum and nitrogen balloon. After a period of 1 h the polymerization was terminated with degassed methanol. The reaction mixture was precipitated into 100 mL of methanol and then dried in vacuo. Calculated $M_n = 4,500$ g/mol; $M_n$(GPC) = 6,300 g/mol.

2.3.16 Polystyrene end-capped with 4 equivalents of 4-dimethysilylstyrene

Styrene (1.60 mL, 1.54 g, 0.0147 mol) was added to sec-BuLi (0.99 mL, 0.0014 mol) in cyclohexane (~50 mL). Polymerization proceeded at 30 °C for 3 h, then an ampoule containing 4 equivalents $p$-DMSS (1.05 mL, 1 g, 0.0062 mol) was added. Polymerization continued for 2 h, and the solution was divided into two portions. Sample A was quenched with methyl iodide and Sample B was quenched with acidic methanol. Calculated $M_n = 1,700$ g/mol; sample A: $M_n$(GPC) = 3,400 g/mol; sample B: $M_n$(GPC) = 3,400 g/mol.

2.3.17 Poly(4-dimethysilylstyrene-co-styrene)

$sec$-BuLi (0.00454 mol) was added to a solution of $p$-DMSS (1.54 g 0.00953 mol), styrene (8.64 g, 0.083 mol), and cyclohexane (~100 mL) in an all-glass reactor. Polymerization proceeded at 30 °C. Sample A was terminated with acidic methanol after a period of 2 hours. Sample B was terminated with methanol after a period of 2 hours. The reaction mixtures were precipitated separately into methanol and dried at room
temperature in vacuo. Calculated $M_n = 1,800$ g/mol; sample A: $M_n$(GPC) = 2,900 g/mol; sample B: $M_n$(GPC) = 3,000 g/mol.

2.3.18 3-Dimethylsilylstyrene (m-DMSS)

A 3-necked, round-bottomed flask, equipped with a stir bar, reflux condenser, 3 septa, and containing magnesium (0.8632 g, 0.0355 mol) was placed on the high vacuum line and flame dried 4 times over a 12 hour period. The flask was purged with positive nitrogen pressure and a few crystals of iodine (~50 mg) were added. The flask was evacuated and cooled using dry ice/isopropyl alcohol. THF (75 mL) was vacuum distilled into the flask. The reaction flask was then placed under positive nitrogen pressure with using a balloon and needle (through the septum) and was removed from the vacuum line, fitted with an addition funnel, and then stirred for 30 minutes at room temperature. The reaction was cooled and maintained at 0 to 15 °C. 3-Bromostyrene (3.55 mL, 5 g, 0.0273 mol) was added via syringe pump at a rate of 10 mL/hour. After complete addition, the reaction was allowed to warm to room temperature overnight. Chlorodimethylsilane (3.03 mL, 2.58 g, 0.0273 mol) was added to the addition funnel and then to the reaction over a period of 2 h. The reaction was allowed to stir overnight to yield a mixture with a white precipitate. Diethyl ether (50 mL) and water (50 mL) were added to extract the mixture into a separatory funnel. The water was removed and extracted with diethyl ether (3 x 50 mL) and the organic layer was collected in an Erlenmeyer flask. Anhydrous sodium sulfate was added, the solution was filtered, and then the solvent was removed via a rotary evaporator (bath temp = 25 °C). The product, a clear oil with slight yellow tint, was dried under high vacuum for 2h (3.32 g, 75%).
2.3.19 Poly(3-dimethylsilylstyrene)

*m*-DMSS (2.38 g, 0.0147 mol) was added to *sec*-BuLi (0.0019 mol) in cyclohexane (70 mL) in an all-glass reactor. Polymerization proceeded at 30 °C. Sample A was terminated with methanol after a period of 30 minutes. Sample B was terminated with methanol after a period of 1 hour and 30 minutes. The reaction mixtures were separately precipitated into methanol and dried at room temperature in vacuo. Calculated $M_n = 2,000$ g/mol; sample A: $M_n$(GPC) = 5,200 g/mol; sample B: $M_n$(GPC) = 7,600 g/mol.

2.3.20 Poly(3-dimethylsilylstyrene-co-styrene)

*sec*-BuLi (0.00454 mol) was added to a solution of *m*-DMSS (0.73 g, 0.0055 mol), styrene (7.73 g, 0.074 mol), and cyclohexane (~100 mL) in an all-glass reactor. Polymerization proceeded at 30 °C. Sample A was terminated with methanol after a period of 45 minutes. Sample B was terminated with methanol after a period of 1 hour and 45 minutes. The reaction mixtures were separately precipitated into methanol and dried at room temperature in vacuo. Calculated $M_n = 1,860$ g/mol; sample A $M_n$(GPC) = 2,000 g/mol; sample B $M_n$(GPC) = 2,000 g/mol.

2.4 General Characterization

2.4.1 Fourier Transform Infrared Spectroscopy

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer (DIGILAB, Randolph, MA, USA) by casting polymer films on KBr plates from polymer solutions with subsequent drying at 40-50 °C to remove solvent. The data were processed using Win-IR software.
2.4.2 Nuclear Magnetic Resonance Spectroscopy

All $^1$H and $^{13}$C NMR spectra were acquired in CDCl$_3$ (Aldrich, 99.8 % D) as solvent using a Varian Mercury 300 or Varian 500 NMR spectrometer. The $^1$H NMR spectra were referenced to the residual proton impurities in the CDCl$_3$ at $\delta$7.26 ppm. $^{13}$C NMR spectra were referenced to $^{13}$CDCl$_3$ at $\delta$77.36 ppm. NMR samples were prepared in 5 mm NMR tubes with approximately 40 mg of polymer in 1.0 mL of CDCl$_3$.

2.4.3 Matrix Assisted Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA) or on a Bruker Ultraflex-III MALDI-TOF/TOF mass spectrometer (Bruker Daltonics, Inc., Billerica, MA) equipped with a nitrogen laser (337 nm) or a Nd:YAG laser (355 nm), respectively. Both instruments contain a single-stage pulsed ion extraction source and a two-stage gridless reflector. All spectra were measured in positive reflectron mode. Solutions of dithranol (20 mg/mL) (Alfa Aesar, 1,8,9-anthracenetriol, 97+%), or t-2-[3-(4-t-butyl-phenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) (Fluka, >99%), polymer sample (10 mg/mL), silver trifluoroacetate (10 mg/mL) (Aldrich, 98 %), sodium trifluoroacetate (NaTFA) (Fluka, >>99%), or sodium iodide (10 mg/mL) (MCD, 99%) were prepared in THF (Aldrich, 99.9 %). These solutions were mixed in the ratio of matrix:cationizing salt:polymer (10:1:2), and 0.5 µL of the mixture was applied to the MALDI sample target and allowed to dry. In order to minimize polymer fragmentation, the intensity of the laser pulses was frequently attenuated and adjusted to obtain the optimal signal intensity. The
mass scale was calibrated externally using the peaks of a polystyrene [or poly(methyl methacrylate)] standard at the molecular weight under consideration.

2.4.4 Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) analyses for the synthesized polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100 Å, mixed bed (50/500/10³/10⁴ Å), mixed bed (10⁴, 10⁵, 10⁶ Å)] and a triple detector system. The three detectors included a differential refractometer (Waters 410), a differential viscometer (Viscotek 100) and a laser light scattering detector (Wyatt Technology, DAWN EOS, $\lambda = 670$ nm). THF was used as eluent with a flow rate of 1.0 mL/min at 30 °C. The sample preparation ($M_n = 1,000 \sim 8,000$ Da) was performed with concentrations ranging from 0.5 to 13.0 mg/mL in THF. Prior to injection, the samples were filtered through a Teflon® filter with a 0.45 µm pore size.

2.4.5 Thin Layer Chromatography

Thin-layer chromatographic analyses (TLC) were performed by spotting and developing functionalized polymer samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with fluorescent indicator) using a mixture of toluene and cyclohexane as eluent.
CHAPTER III
RESULTS AND DISCUSSION

3.1 Synthesis of triethoxysilane-functionalized polymers

Triethoxysilane-functionalized polystyrene was synthesized using a combination of an unsaturated initiator and hydrosilation. This method combines the structural control of anionic polymerization with the functional group tolerance of hydrosilation chemistry. Triethoxysilane-functionalized polybutadiene was synthesized taking advantage of the pendant vinyl groups present in polybutadiene by hydrosilation with triethoxysilane.

Hydrosilation reactions were catalyzed using highly reactive, organic-soluble Karstedt’s catalyst [Pt₂(divinyltetramethyldisiloxane)₃ in xylene]. This high-yielding, functional group-tolerant, facile, hydrosilation reaction was used to prepare a variety of functionalized polymers.

3.1.1 Synthesis of 4-pentenyllithium

4-Pentenyllithium was synthesized as reported by Takano et al. from 5-bromopentene and lithium metal. The reagents were combined in an all-glass reactor and stirred in heptane for 3 days to activate the lithium metal. The reaction was cooled to 0 °C, diethyl ether was added, and the lithiation reaction proceeded rapidly (see Scheme 3.1). The solvent was removed via high vacuum, then the product was dissolved in heptane and the insoluble by-products were removed by filtration in the dry box. The initiator solution’s concentration was measured by Gilman double titration and found to be 0.76 M, corresponding to a yield of 70%.
3.1.2 Synthesis of α-4-pentenylpolystyrene

α-4-Pentenylpolystyrene was synthesized via 4-pentenyllithium-initiated anionic polymerization in benzene with 4.2 equivalents of tetrahydrofuran (THF) as shown in Scheme 3.2. THF was used in order to obtain a narrow polydispersity index. The primary nature of the alkyllithium bond in 4-pentenyllithium is analogous to that of n-butyllithium, which is highly aggregated in hydrocarbon solutions. The level of aggregation is decreased by addition of THF, therefore increasing the rate of initiation and decreasing the polydispersity index. Gel permeation chromatography (GPC) analysis revealed a narrow polydispersity index of 1.06 and $M_n = 1600$ g/mol as seen in Figure 3.1. This is in excellent agreement with the calculated molecular weight of 1,600 g/mol.
Figure 3.1. GPC curve of α-4-pentenylpolystyrene.

The structure of the α-4-pentenylpolystyrene was confirmed by proton nuclear magnetic resonance spectroscopy ($^1$H NMR) and matrix assisted laser desorption ionization – time of flight (MALDI-TOF) mass spectrometry. The $^1$H NMR spectrum (Figure 3.2) shows the vinyl protons from the initiator residue at δ 4.9 and 5.7 ppm with integrations as previously reported by Takano et al.\textsuperscript{155} Aliphatic methylene protons from the initiator residue are also visible at δ 1.0 and 1.4 ppm.

The MALDI-TOF mass spectrum clearly shows a clean and successful synthesis of the desired product. The peaks present in the low mass region of the spectrum are due to the matrix.\textsuperscript{174} Without fractional distillation of the 5-bromopentene prior to the synthesis, more than one product was observed in the mass spectrum.
However, when high purity reagents were used, one distribution was observed. The MALDI-TOF mass spectrum (Figures 3.3 and 3.4) showed the desired distribution with a representative monoisotopic mass peak at \( m/z = 1446.06 \) corresponding to the 13-mer, \( \alpha \)-4-pentenylpolystyrene, \( C_{5}H_{9}(C_{8}H_{8})_{13}-H\cdot Na^{+} \); calculated monoisotopic mass = 1445.94 Da. The calculated and observed masses are in excellent agreement, further documenting successful synthesis of pure \( \alpha \)-4-pentenylpolystyrene.

Figure 3.2. \(^1\)H NMR (CDCl\(_3\)) spectrum of \( \alpha \)-4-pentenylpolystyrene.
Figure 3.3. Full MALDI-TOF mass spectrum of $\alpha$-4-pentenylpolystyrene.

Figure 3.4. Expanded MALDI-TOF mass spectrum of $\alpha$-4-pentenylpolystyrene.
3.1.3 Synthesis of $\alpha$-triethoxysilylpolystyrene

Preparation of $\alpha$-triethoxysilylpolystyrene was accomplished by hydrosilation of $\alpha$-4-pentenylpolystyrene with triethoxysilane using Karstedt’s catalyst (Scheme 3.3).

This reaction was performed in the dry box at room temperature over a period of 12 hours, and proceeded to completion with no detectable side reactions.

Scheme 3.3. Synthesis of $\alpha$-triethoxysilylpolystyrene.

![Chemical Shift (ppm) vs Normalized Intensity](image)

No vinyl peaks at 4.9 and 5.7 ppm

Figure 3.5. $^1$H NMR spectrum (CDCl$_3$) of triethoxysilyl-functionalized polystyrene.

The $^1$H NMR spectrum (Figure 3.5) revealed the absence of vinyl protons at $\delta$ 4.9 and 5.7 ppm. In addition, the methylene protons adjacent to oxygen are apparent at $\delta$ 3.9
The full MALDI-TOF mass spectrum (Figure 3.6) showed one main distribution with good agreement between calculated and observed monoisotopic masses. The expanded trace of this spectrum (Figure 3.7) showed the desired distribution with a representative monoisotopic mass peak at $m/z = 1506.4$ corresponding to the 12-mer, triethoxysilyl-functionalized polystyrene, $(\text{CH}_3\text{CH}_2\text{O})_3\text{Si-C}_5\text{H}_{10}-(\text{C}_8\text{H}_8)_{12}-\text{Na}^+$; calculated monoisotopic mass = 1505.91 Da. A peak corresponding to the 13-mer $\alpha$-4-pentenylpolystyrene, $\text{C}_5\text{H}_9-(\text{C}_8\text{H}_8)_{13}-\text{H}·\text{Na}^+$ was not observed; calculated monoisotopic mass = 1445.94 Da. There was a small peak present at $m/z = 1448$ corresponding to the 13-mer hydrogenated starting material, $\text{C}_5\text{H}_{11}-(\text{C}_8\text{H}_8)_{13}-\text{H}·\text{Na}^+$; calculated monoisotopic mass = 1447.96 Da. This peak can arise from either an impurity of bromopentane in the initial material, or a side reaction of hydrogenation during hydrosilation, a commonly observed side reaction for hydrosilation reactions. \cite{128, 130, 134, 139}

![Figure 3.6. Full MALDI-TOF mass spectrum of triethoxysilyl-functionalized polystyrene.](image)
Figure 3.7 Expanded MALDI-TOF mass spectrum of triethoxysilyl-functionalized polystyrene.

3.1.4 Synthesis of α-4-pentenyl-ω-silyl hydride-functionalized polystyrene

Scheme 3.4. Synthesis of α-4-pentenyl-ω-silyl hydride-functionalized polystyrene.

Building on the synthetic procedure for the synthesis of α-4-pentenylpolystyrene, an α-4-pentenyl-ω-silyl hydride functionalized polystyrene was prepared by terminating α-4-pentenylpoly(styryl)lithium with chlorodimethylsilane (Scheme 3.4). This new methodology provides a platform for the synthesis of a wide array of polymer systems. There are numerous synthetic transformations that can take place on the double bond in
the alpha position. The terminal silyl-hydride is amenable to reaction with a variety of alkenes to provide a general functionality at the chain-end.\textsuperscript{119, 120, 127, 173} This polymer could be particularly useful for the synthesis of a functional polymer which has an affinity for glass. As shown above, the pentenyl group can be readily transformed into a triethoxysilyl group. Separately the silyl-hydride chain-end can be transformed into a variety of functional groups using established hydrosilation chemistry. This can be achieved by the drastically different activity of a trialkoxysilyl-hydride compared to a trialkylsilyl-hydride. The difference in activity for these silyl-hydrides is on the order of 700 to 1,000, with the more electron deficient silyl hydride being more reactive.\textsuperscript{128}

![Figure 3.8. GPC chromatogram of $\alpha$-4-pentenyl-$\omega$-silyl hydride-functionalized polystyrene.](image)

The $\alpha,\omega$-functional polystyrene was prepared in high yield. The GPC chromatogram (Figure 3.8) shows a narrow monomodal distribution. The observed molecular weight was 2,300 g/mol and the polydispersity was 1.03. This value was slightly higher than the calculated molecular weight of 2,000 g/mol. This could be
because of a lower initiator concentration than was determined by titration. The FTIR spectrum (Figure 3.9) shows a clear peak for the silyl-hydride band at 2113 cm$^{-1}$, which is close to the reported value of 2111 cm$^{-1}$ for silyl-hydride chain-end functionalized polystyrene.$^{119}$

![FTIR spectrum of α-4-pentenyl-ω-silyl hydride-functionalized polystyrene.](image)

Figure 3.9. FTIR spectrum of α-4-pentenyl-ω-silyl hydride-functionalized polystyrene.

The $^1$H NMR spectrum (Figure 3.10) shows peaks with chemical shifts and integrations that are in good agreement with the proposed structure. The vinyl peaks are present at δ 4.9 and 5.7 ppm with integration values of 2 and 1, respectively. A broad peak is present for the silyl-hydride proton at δ 3.7 ppm with an integration value of 0.7, close to the expected value.$^{119, 171}$ The methyl protons adjacent to silicon are observed at 0.0 ppm with an integration value of 6 as expected. The $^{13}$C NMR spectrum (Figure 3.11) contains peaks that further confirm the structure of the functionalized polymer. The
vinyl carbons are observed at $\delta$ 139 and 114 ppm. The shifts for the methyl carbons adjacent to silicon at $\delta$ 6 ppm are in good agreement with the reported value.

Figure 3.10. $^1$H NMR spectrum (CDCl$_3$) of $\alpha$-4-pentenyl-ω-silyl hydride-functionalized polystyrene.

MALDI-TOF mass spectrometry confirmed successful synthesis of the $\alpha,\omega$-functionalized polymer. The MALDI-TOF mass spectrum (Figures 3.12 and 3.13) showed the desired distribution with a representative monoisotopic mass peak at $m/z = 2128.3$ correspoding to the 19-mer, $\alpha$-4-pentenyl-ω-silyl hydride functionalized polystyrene, $C_{5}H_{9}-(C_{8}H_{8})_{19}-Si(CH_{3})_{2}H\cdot Na^{+}$; calculated monoisotopic mass = 2128.36 Da. The calculated and observed masses are in excellent agreement, further documenting successful synthesis of pure $\alpha$-4-pentenyl-ω-silyl hydride functionalized polystyrene.
Figure 3.11. $^{13}$C NMR spectrum (CDCl$_3$) of α-4-pentenyl-ω-silyl hydride-functionalized polystyrene.

In addition to the main distribution, a minor distribution was also observed. This corresponded the α-4-pentenylpolystyrene, arising from termination with a proton instead of chlorodimethylsilane. The monoisotopic mass peak was observed at $m/z = 2070.2$ corresponding to the 19-mer, α-4-pentenyl functionalized polystyrene, C$_5$H$_9$-(C$_8$H$_8$)$_{19}$-H·Na$^+$; calculated monoisotopic mass = 2070.31 Da.
Figure 3.12 Full MALDI-TOF mass spectrum of α-4-pentenyl-ω-silyl hydride-functionalized polystyrene.

Figure 3.13. Expanded MALDI-TOF mass spectrum of α-4-pentenyl-ω-silyl hydride-functionalized polystyrene.
3.1.5 Synthesis of α-4-pentenyl-ω-thiol functionalized polystyrene

4-Pentenyllithium was used to initiate styrene polymerization in benzene in the presence of 5 equivalents of THF in an all-glass reactor. The poly(styryl)lithium was then terminated with 2 equivalents of ethylene sulfide and then quenched with methanol as shown in Scheme 3.5. The GPC chromatogram (Figure 3.14) shows the 2 traces. The curve in red corresponds to the desired α-4-pentenyl-ω-thiol-functionalized polystyrene, and the curve in blue corresponds to the methanol-terminated base sample. There is clearly a high molecular weight shoulder present for the ethylene sulfide-terminated polymer. This product has been observed in the past for thiol-functionalized polystyrenes after exposure to air, especially under basic conditions.\textsuperscript{176-178} The use of an acidic methanol quench is known to prevent dimerization.\textsuperscript{176}

Scheme 3.5. Synthesis of α-4-pentenyl-ω-thiol-functionalized polystyrene.
Figure 3.14. GPC chromatogram of α-4-pentenyl-ω-thiol-functionalized polystyrene (red) and α-4-pentenyl-functionalized polystyrene (blue).

The $^1$H NMR spectrum (Figure 3.15) shows the expected vinyl peaks for the 4-pentenyl initiator fragment at $\delta$ 4.9 and 5.7 ppm with integration ratio values of 2 and 1, respectively. The methylene protons adjacent to sulfur at $\delta$ 2.6 ppm are barely separated from the backbone protons, but still show good agreement for the desired product with an integration value of 2.\textsuperscript{173,176} The $^{13}$C NMR spectrum (Figure 3.16) shows the characteristic vinyl carbons $\delta$ 139 and 114 ppm.\textsuperscript{155} In addition, the shifts for the carbons adjacent to sulfur could be observed at $\delta$ 25 and 36 ppm as reported for poly(styryl)lithium terminated with ethylene sulfide.\textsuperscript{176}
Figure 3.15. $^1$H NMR spectrum (CDCl$_3$) of $\alpha$-4-pentenyl-$\omega$-thiol-functionalized polystyrene.

Figure 3.16. $^{13}$C NMR spectrum (CDCl$_3$) of $\alpha$-4-pentenyl-$\omega$-thiol-functionalized polystyrene.
The main distribution in the MALDI-TOF mass spectrum (Figures 3.17 and 3.18) has a representative monoisotopic mass peak at \( m/z = 1401.9 \) corresponding to the 12-mer, \( \alpha-4\)-pentenyl-\( \omega \)-thiol functionalized polystyrene, \( C_5H_9-(C_8H_8)_{12}-(CH_2)_2SH\cdot Na^+; \) calculated monoisotopic mass = 1401.82 Da. The calculated and observed masses are in excellent agreement. In addition to the main distribution, a minor distribution is also observed corresponding to the 11-mer, \( \alpha-4\)-pentenyl-\( \omega \)-oligo-ethylene sulfide-functionalized polystyrene, \( C_5H_9-(C_8H_8)_{11}-(CH_2)_2S(CH_2)_2S \cdot Na^+; \) calculated monoisotopic mass = 1357.76 Da. Traces of polymer with three and four \( C_2H_4S \) units at the \( \omega \)-chain end are also observed at \( m/z = 1314 \) and 1374, respectively; calculated monoisotopic masses for the corresponding 10-mer, \( C_5H_9-(C_8H_8)_{10}-(CH_2)_2S(CH_2)_nS \cdot Na^+ = 1313.70 \) and 1373.71 for \( n = 3 \) and 4, respectively. The distribution corresponding to the \( \alpha-4\)-pentenylpolystyrene, arising from termination with a proton instead of ethylene sulfide, may be present near the baseline corresponding to the 12-mer, \( \alpha-4\)-pentenyl-functionalized polystyrene, \( C_5H_9-(C_8H_8)_{12}-H\cdot Na^+; \) calculated monoisotopic mass = 1341.82 Da. The MALDI-TOF mass spectrum presents clear evidence for synthesis of the desired thiol-functionalized macromonomer product.
Figure 3.17. Full MALDI-TOF mass spectrum of α-4-pentenyl-ω-thiol-functionalized polystyrene.

Figure 3.18. Expanded MALDI-TOF mass spectrum of α-4-pentenyl-ω-thiol-functionalized polystyrene.
3.1.6 Synthesis of triethoxysilyl-functionalized polybutadiene

Triethoxysilyl-functionalized polybutadiene was prepared by hydrosilation of 91% (by $^1$H NMR) 1,4 polybutadiene with triethoxysilane, as shown in Scheme 3.6. Hydrosilation of the majority of the pendant vinyl groups was observed, while there was no detectable loss of the 1,4 double bonds. This observation is owed to the fact that hydrosilation reactions are selective towards the least-substituted double bonds.$^{128, 130}$ The hydrosilation of 1-hexene with triethoxysilane occurs at room temperature in one day, while hydrosilation of 3-hexene only proceeded to 36% after 24 days.$^{138}$

\[
\begin{align*}
\text{Karstedt's Catalyst} \\
\text{Benzene, r.t., 18h}
\end{align*}
\]


The $^1$H NMR spectra of polybutadiene (Figure 3.19) and the triethoxysilyl-functionalized product (Figure 3.20) show the selectivity of the hydrosilation towards the vinyl units. There is no loss of the protons for the 1,4 polybutadiene units ($\delta$ 5.4 ppm) compared to the initiator. The relative integration value for the 1,4-alkenyl protons at $\delta$ 5.4 ppm is 77 before hydrosilation and 74 after hydrosilation, as compared to the initiator protons at $\delta$ 0.7 ppm (integration value fixed at 6). However, complete
disappearance of the terminal vinyl protons (δ 4.9 ppm) is observed.\textsuperscript{179,180} The polybutadiene $^1$H NMR spectrum shows approximately 3.5 vinyl groups per polymer chain by the integration value of 7 for the terminal vinyl protons (δ 4.9 ppm) compared to the initiator methyl protons (δ 0.7 ppm, integration value = 6). The internal vinyl proton of the 1,2-polybutadiene is located at δ 5.6 ppm, and this peak decreases substantially after hydrosilation. In addition, the triethoxysilyl-functionalized polybutadiene $^1$H NMR spectrum shows the 6 methylene protons adjacent to oxygen in the triethoxysilyl group (δ 3.7 ppm)\textsuperscript{181} and the integration value indicates nearly quantitative conversion of the vinyl units. The integration value of 18 (δ 3.7 ppm), shows approximately that there are 3 triethoxysilyl groups per polymer chain by comparison to the initiator methyl protons, with a relative integration value of 6.

The MALDI-TOF mass spectra of the polybutadiene (Figures 3.21 and 3.23) and triethoxysilyl-functionalized material (Figures 3.22 and 3.24) appear surprisingly similar; that of the functionalized polymer is, however, complicated by overlap between the peaks for the starting material and the product. The polybutadiene starting material shows one clear distribution with a representative monoisotopic mass peak at $m/z = 2326.8$ for the 40-mer, polybutadiene, $C_9H_9-(C_6H_6)_{47}-H \cdot Ag^+$; calculated monoisotopic mass = 2326.86 Da. For the functionalized polymer, a challenge arises because the mass of one triethoxysilane unit is 164.27 Da, which is similar to the mass of 3 butadiene units, 162.14 Da. Despite this complication, there is no peak observed for the 47-mer, non-functionalized polybutadiene, $C_9H_9-(C_6H_6)_{47}-H \cdot Ag^+$;
Figure 3.19. $^1$H NMR spectrum (CDCl$_3$) of polybutadiene.

Figure 3.20. $^1$H NMR spectrum (CDCl$_3$) of triethoxysilyl-functionalized polybutadiene.
calculated monoisotopic mass = 2705.19 Da in the triethoxysilyl-functionalized polybutadiene mass spectrum. There is a distribution of the functionalized product with peaks for one, two, and three triethoxysilyl groups present per polymer chain. The width of the distribution, relative to that of the polybutadiene distribution, is indicative of overlapping products. It is clear that there is a distribution for a polybutadiene chain with one triethoxysilyl group, with a representative observed monoisotopic mass at $m/z = 2707.4$ for the 44-mer, polybutadiene with one triethoxysilane group, $C_4H_9-(C_4H_6)_{33}(C_4H_7Si(OCH_2CH_3)_3)_1-H \cdot Ag^+; \text{ calculated monoisotopic mass} = 2707.14 \text{ Da}$. It is also clear that there is a distribution for a polybutadiene chain with two triethoxysilyl groups, with a representative observed monoisotopic mass at $m/z = 2709.4$ for the 41-mer, polybutadiene with two triethoxysilane groups, $C_4H_9-(C_4H_6)_{39}(C_4H_7Si(OCH_2CH_3)_3)_2-H \cdot Ag^+; \text{ calculated monoisotopic mass} = 2709.08 \text{ Da}$. Additionally there is a distribution for a polybutadiene chain with three triethoxysilyl groups, with a representative observed monoisotopic mass at $m/z = 2657.3$ for the 37-mer, polybutadiene with three triethoxysilane groups, $C_4H_9-(C_4H_6)_{34}(C_4H_7Si(OCH_2CH_3)_3)_3-H \cdot Ag^+; \text{ calculated monoisotopic mass} = 2656.98 \text{ Da}$.

The presence of polybutadiene chains with more than 3 triethoxysilyl groups is statistically likely, however the peaks corresponding to these distributions are not conclusively evident via mass spectrometry.
Figure 3.21. Full MALDI-TOF mass spectrum of polybutadiene.

Figure 3.22. Full MALDI-TOF mass spectrum of triethoxysilyl-functionalized polybutadiene.
Figure 3.23. Expanded MALDI-TOF mass spectrum of polybutadiene.

Figure 3.24. Expanded MALDI-TOF mass spectrum of triethoxysilyl-functionalized polybutadiene.
3.2 Synthesis of cyano-functionalized polymers

The synthesis of well-defined, cyano-functionalized polystyrene was completed by anionic polymerization of styrene and termination with the appropriate silyl chloride followed by hydrosilation. Termination of polymeric organolithium compounds with silyl-halides is a quantitative reaction that proceeds in the absence of side-reactions.\textsuperscript{117-119} Hydrosilation is a high-yielding reaction which is tolerant to a wide array of functional groups.\textsuperscript{128, 130} The combination of these two chemistries for the efficient synthesis of functional polymers in hydrocarbon solvent at room temperature is one of the best methods available.\textsuperscript{119}

![Scheme 3.7. General functionalization.](image)

3.2.1 Synthesis of ω-silyl hydride-functionalized polystyrene

In order to investigate the versatility of the previously reported\textsuperscript{119} general functionalization method using anionic polymerization, silyl chloride linking, and hydrosilation chemistry (Scheme 3.7), the synthesis of cyano-functionalized polymers was investigated. The first step in this methodology involves preparation of a silyl hydride-functionalized polymer. Chain-end silyl hydride-functionalized polystyrene was
prepared as previously reported (Scheme 3.8).\textsuperscript{119} The GPC chromatogram (Figure 3.25) showed a narrow, monomodal curve with \(M_n = 2,200\) Da and \(M_w/M_n = 1.05\). For MALDI-TOF analysis of the silyl-hydride functionalized polymers, sodium iodide was used as the cationizing agent to prevent oxidation of the Si-H group to Si-OH as observed previously when silver trifluoracetate was used as the cationizing agent.\textsuperscript{119} The MALDI-TOF mass spectrum (Figure 3.26) showed only one distribution with a representative monoisotopic mass peak at \(m/z = 2012.4\) corresponding to the 18-mer, silyl hydride-functionalized polystyrene, \(C_4H_9-(C_8H_8)_{18}-SiH(CH_3)_2\cdot Na^+\); calculated monoisotopic mass = 2012.22 Da. The \(^1\)H NMR spectrum (Figure 3.27) showed the characteristic peaks for the -SiH proton at \(\delta \geq 3.5 - 3.8\) ppm and the characteristic resonance peaks for the methyl protons on the carbon bonded to silicon at \(\delta -0.1\) to \(-0.4\) ppm.\textsuperscript{119} The ratio of the integration of the 6 methyl initiator protons to the 6 methyl protons bonded to silicon is 1 : 1, as expected. The SiH resonance was broad due to the diverse diastereomeric structures, which arise due to the tacticity of the final styryl and penultimate styryl stereogenic centers. The pure \(\omega\)-silyl-hydride functionalized polystyrene was synthesized quantitatively with no detectable side products, as described previously in the literature.\textsuperscript{119,173}

![Scheme 3.8. Synthesis of \(\omega\)-silyl hydride-functionalized polystyrene.](image-url)
Figure 3.25. GPC chromatogram of ω-silyl hydride-functionalized polystyrene.

Figure 3.26. MALTI-TOF mass spectrum of ω-silyl hydride-functionalized polystyrene.
3.2.2 Synthesis of ω-cyano-functionalized polystyrene

The chain-end, silyl hydride-functionalized polystyrene (Mₙ = 2,200 Da) was reacted with 2 equivalents of allyl cyanide in the presence of a few drops of Karstedt’s catalyst (platinum 1,3-divinyltetramethyldisiloxane complex in xylene) at room temperature in benzene solution (Scheme 3.9). The reaction was monitored by thin layer chromatography using toluene as eluent. The silyl hydride functionalized polystyrene moved to the top of the TLC plate, while the cyanide chain-end functionalized polymer remained near the bottom of the plate. After two weeks when only one spot was detected, silica gel was added and stirred for 12 hours to effect catalyst separation. The functionalized polymer was purified by column chromatography using a mixture of toluene and cyclohexane as eluent for the non-functional polymer and toluene as eluent for the cyano-functionalized polymer. One spot on the TLC plate was observed for the
purified product. The cyano, chain-end functionalized polymer was isolated in 87% yield. The GPC trace (Figure 3.28) shows that a narrow monomodal distribution is maintained after functionalization.


Figure 3.28. GPC Trace of ω-cyano-functionalized polystyrene.

The $^1$H NMR spectrum of the purified product (Figure 3.29) shows that the characteristic peaks for the –SiH proton at $\delta$ 3.5 - 3.8 ppm have disappeared. The characteristic peaks for the new methylene protons on the carbon bonded to silicon are observed at $\delta$ 0.3 - 0.7 ppm. The integration ratios of the initiator methyl proton
resonances from the sec-butyl initiator fragment/ methylene protons bonded to the carbon adjacent to silicon/methyl protons bonded to carbon adjacent to silicon were 6/2/6, as expected for the cyano chain-end functionalized polystyrene. The $^{13}$C NMR spectrum of the purified product (Figure 3.30) shows the characteristic resonance peak for the carbon in the cyano functional group at δ 119.5 ppm. The characteristic resonance peak for the methyl carbons bonded to silicon is observed at δ -5 ppm. The methylene protons adjacent to silicon were also noted to be at δ 14 ppm. The characteristic resonance at 2110 cm$^{-1}$ for the –SiH group stretching band is missing from the FTIR spectrum in Figure 3.31 and a new resonance at 2249 cm$^{-1}$ that corresponds to the weak nitrile stretching band is present. These results are consistent with the formation of chain-end, cyano-functionalized polystyrene.

Figure 3.29. $^1$H NMR spectrum (CDCl$_3$) of purified ω-cyano-functionalized polystyrene.
Figure 3.30. $^{13}$C NMR spectrum (CDCl$_3$) of purified $\omega$-cyano-functionalized polystyrene.

Figure 3.31. FTIR spectrum of purified $\omega$-cyano functionalized polystyrene.
The MALDI-TOF mass spectrum of the purified product (Figure 3.32) shows one distribution. A representative monoisotopic mass peak at \( m/z = 2079.2 \) corresponds to the 18-mer, chain-end, cyano-functionalized polystyrene \( \text{C}_4\text{H}_9-\text{(C}_8\text{H}_8)_{18^-} \text{Si(CH}_3)_2\text{(CH}_2\text{CH}_2\text{CH}_2\text{CN})\cdot\text{Na}^+; \) calculated monoisotopic mass = 2079.26 Da. It is worth noting that there are no peaks corresponding to the 18-mer silyl hydride-functionalized polystyrene, \( \text{C}_4\text{H}_9-\text{(C}_8\text{H}_8)_{18^-}\text{SiH(CH}_3)_2\cdot\text{Na}^+; \) calculated monoisotopic mass = 2012.22 Da.

There is some evidence that suggests the formation of an unsaturated side-product. This product can arise from a hydrosilation occurring by the modified Chalk-Harrod mechanism of hydrosilation (Scheme 1.12), where instead of reductive elimination, \( \beta \)-hydride transfer to metal is observed. This is a well-known side reaction of hydrosilation reactions.\(^{128,138}\) The occurrence of this product is confirmed by a peak at -2 \( m/z \) from the main distribution in the MALDI-TOF mass spectrum (Figure 3.32). This distribution is consistent with the structure drawn in Figure 3.33. The \( ^1\text{H} \) NMR spectrum (Figure 3.29) also provides evidence for the presence of unsaturated product by showing a peak at \( \delta \) 3.2 ppm, which corresponds to the methylene protons adjacent to the unsaturation. The quantity of this side-product is estimated to be less than 5% of the total isolated yield.
3.2.3 Synthesis of in-chain silyl-hydride functionalized polystyrene

The living functionalization reactions of polymeric organolithium compounds with substituted 1,1-diphenylethylenes is one of the few general functionalization reactions that can be used to prepare in-chain functionalized polymers since this is a living functionalization reaction and the product is a substituted, polymeric 1,1-diphenylalkyllithium that can be used to initiate polymerization of a second monomer.113,
This method suffers from the limitation of most anionic functionalization reactions that protecting groups must be used for many functional groups of interest, e.g., 1° and 2° amine, hydroxyl, carboxyl and thiol. Therefore, it was of interest to investigate the utility of the GFM method based on the hydrosilation of silyl hydride-functionalized polystyrenes for the preparation of in-chain functionalized polymers as illustrated in Scheme 3.10.

![Scheme 3.10. Synthesis of in-chain, silyl-hydride, functionalized polystyrene.](image)

In order to prepare pure, silyl hydride, in-chain functionalized polymers, an excess of poly(styryl)lithium (Mₙ = 1.2 x 10³ g/mol, Mₘ/Mₙ = 1.1) was reacted with dichloromethylsilane as shown in Scheme 3.10. After the linking reaction, the excess poly(styryl)lithium was functionalized with ethylene oxide, a very efficient hydroxyl-functionalizing agent. Then, after methanol termination, the hydroxyl-functionalized polystyrene could be easily removed from the desired in-chain functionalized product by simple silica gel column chromatography rather than by fractionation, as is common for silyl chloride linking reactions. The polar hydroxyl-functionalized polystyrene remains at the baseline of the TLC plate, while the desired product migrates with the solvent front. The GPC chromatogram (Figure 3.34) of the
crude reaction products shows a slightly broadened peak corresponding to the desired
coupled product plus some low molecular weight hydroxyl-functionalized polymer. After
silica gel column chromatography, the chromatogram of the purified product (Figure
3.34) shows a narrower, monomodal curve without the low molecular weight shoulder
(from the hydroxyl-functionalized polymer); the molecular weight of the product $M_n =
2.2 \times 10^3$ g/mol is roughly double the molecular weight of the precursor ($M_n = 1.2 \times 10^3$
g/mol) and the molecular weight distribution is narrow ($M_w/M_n = 1.06$), as expected.

![Figure 3.34. GPC trace of in-chain, silyl hydride-functionalized polystyrene; (A)
purified product, (B) crude product, (C) base sample.](image)

The $^1$H NMR spectra for the crude and the purified products are shown in Figure
3.35. The characteristic resonance for the $-\text{SiH}$ proton is observed at $\delta$ 3.2 - 3.8 ppm. It
overlaps with the resonance peak for the methylene hydrogens bonded to the carbon
adjacent to the hydroxyl group in the hydroxyethyl end group at $\delta$ 3.2 ppm in the $^1$H
NMR spectrum of the crude product.\textsuperscript{182,183} After purification by column
chromatography, this resonance peak corresponding to the hydroxyl-functionalized
polystyrene is not observed. The methyl protons bonded to the carbon adjacent to silicon have characteristic resonance peaks observed at $\delta -0.6 - 0$ ppm.\textsuperscript{119} The $^{13}$C NMR of the purified product (Figure 3.36) shows the characteristic resonance peaks for the methyl carbon attached to the silicon at $\delta -0.9$ ppm in addition to the peaks from the sec-butyllithium initiated polystyrene.\textsuperscript{182} The FTIR spectrum (Figure 3.37) showed the characteristic $\text{–SiH}$ group stretching band at 2116 cm\textsuperscript{-1}.\textsuperscript{119}

Figure 3.35. $^1$H NMR spectra (CDCl\textsubscript{3}) of the in-chain, silyl hydride-functionalized polystyrene; (A) before purification, (B) after purification.
Figure 3.36. $^{13}$C NMR spectrum (CDCl$_3$) of purified in-chain, silyl hydride-functionalized polystyrene.

Figure 3.37. FTIR spectrum of purified in-chain, silyl hydride-functionalized polystyrene.

The MALDI-TOF mass spectrum (Figure 3.38) of the purified product shows one distribution. A representative monoisotopic mass peak at $m/z = 1742.1$ corresponds to
the 15-mer, in-chain, silyl hydride-functionalized polystyrene, C_{4}H_{9}-(C_{8}H_{8})_{n}\text{SiH(CH}_{3})-(C_{8}H_{8})_{15-n}\text{-C}_{4}H_{9}\cdot \text{Na}^{+}; \text{calculated monoisotopic mass} = 1742.08 \text{ Da}. \text{ This result is consistent with quantitative in-chain, silyl hydride functionalization of poly(styryl)lithium using dichloromethylsilane.}

3.2.4 Synthesis of in-chain, cyano-functionalized polystyrene

The in-chain, silyl hydride-functionalized polymer (M_{n} = 2.2 \times 10^{3} \text{ Da}) was reacted with 2 equivalents of allyl cyanide in the presence of Karstedt’s catalyst in toluene (Scheme 3.11). After two weeks, no change in the yield of product was observed by TLC analysis; therefore, silica gel was added and stirred for 12 hours to aid in catalyst
The functionalized polymer was purified by silica gel column chromatography using 3:1 (vol:vol) toluene:cyclohexane as eluent for the non-functional polymer and 3:1 toluene:ethyl acetate (vol:vol) as eluent for the cyano-functionalized polymer. The cyano, in-chain functionalized polymer was isolated in 58% yield. The lower yield obtained compared to the chain-end, cyano-functionalized polymer (87%) is probably due to steric crowding around the –Si-H group from the two styryl units and one methyl group bonded to this silicon. It is known that inefficient linking reactions can occur when excess poly(styryl)lithium is reacted with silicon tetrachloride. Steric effects have also been shown to be important in hydrosilation reactions.

![Scheme 3.11. Synthesis of in-chain cyano-functionalized polystyrene.](image)

The $^1$H NMR spectrum of the purified product (Figure 3.39) shows the disappearance of the characteristic peak for the –SiH proton at $\delta$ 3.2 - 3.8 ppm. The characteristic peaks for the methylene protons on the carbon bonded to silicon are observed at $\delta$ 0 - 0.3 ppm. The peaks are broad due to the fact that the silicon is chiral, and diastereomeric based on the configuration of the chain-end, which gives rise to at least 6 diastereomeric peaks, ignoring penultimate effects. The $^{13}$C NMR spectrum of the purified product (Figure 3.40) shows the characteristic resonance peak for the carbon in the cyanoclyano-functional group at $\delta$ 119.35 ppm, almost identical to the analogous cyano chain-end functionalized polymer (δ 119.5 ppm; Section 3.2.2). The characteristic resonance peak for the methyl carbon bonded to silicon is observed at $\delta$ -0.9 ppm. The
FTIR spectrum (Figure 3.41) shows the disappearance of the characteristic absorption peak for the –SiH group at 2116 cm\(^{-1}\) and a new absorption peak at 2247 cm\(^{-1}\) that corresponds to the weak nitrile stretching band\(^{157,158}\). These results are consistent with the formation of the expected in-chain, cyano-functionalized polystyrene.

Figure 3.39. \(^1\)H NMR spectra (CDCl\(_3\)) of (A) in-chain, silyl-hydride functionalized polystyrene and (B) purified in-chain, cyano-functionalized polystyrene.
Figure 3.40. $^{13}$C NMR spectrum (CDCl$_3$) of purified in-chain, cyano functionalized polystyrene.

Figure 3.41. FTIR spectrum of purified in-chain, cyano functionalized polystyrene.
The MALDI-TOF mass spectrum of the purified product (Figure 3.42) exhibits one distribution. A representative monoisotopic mass peak at $m/z = 1601.1$ corresponds to the 13-mer, in-chain, cyano-functionalized polystyrene, $C_4H_9-(C_8H_8)_n$-$Si(CH_3)(CH_2CH_2CH_2CN)-(C_8H_8)_{13-n}-C_4H_9\cdot Na^+$; calculated monoisotopic mass = 1600.09 Da. It is worth noting that there are no peaks corresponding to the 13-mer silyl hydride-functionalized polystyrene, $C_4H_9-(C_8H_8)_n$-$SiH(CH_3)-(C_8H_8)_{13-n}-C_4H_9\cdot Na^+$; calculated monoisotopic mass = 1533.96 Da. Thus, it is concluded that in-chain, cyano-functionalized polystyrene was successfully prepared in high purity but the yield was limited to 58%.

Figure 3.42. MALDI-TOF mass spectrum of purified in-chain, cyano-functionalized, polystyrene.
3.2.5 Synthesis of $\omega$-silyl dihydride-functionalized polystyrene

The synthesis of polymers with more than one functional group at the chain end is an important synthetic challenge that can yield polymers with a wide array of desirable properties.\textsuperscript{114, 187, 188} Synthesis of polystyrene with two functional groups at the chain-end via the general functionalization method that has been the focus of this work is not straight-forward. Termination of poly(styryl)lithium with chloromethylsilane to prepare the PS-$\text{SiCH}_3\text{H}_2$ precursor would be the most simple approach to this route, but chloromethylsilane is not available due to the toxicity of this molecule.\textsuperscript{189} An approach was devised for the synthesis of PS-$\text{SiCH}_3\text{H}_2$ which utilized a different chlorosilane-termination. First, poly(styryl)lithium was added dropwise to a solution of 100 equivalents of dichloromethylsilane. This reaction resulted in preparation of mostly PS-$\text{SiCH}_3\text{HCl}$, which was then reduced using lithium aluminum hydride to yield the desired PS-$\text{SiCH}_3\text{H}_2$ in two steps without purification, as shown in Scheme 3.12.

![Scheme 3.12. Preparation of PS-$\text{SiCH}_3\text{H}_2$.](image)

The synthesis of PS-$\text{SiCH}_3\text{H}_2$ was complicated by the undesirable side reaction where two poly(styryl)lithium chains added to dichloromethylsilane. Dimer was observed because of this expected side reaction despite dropwise addition of diluted poly(styryl)lithium to a solution of a 100-fold excess of dichloromethylsilane. In addition, the hydrolytic stability of the silicon-chlorine bond required inert atmosphere techniques and prohibited characterization of the PS-$\text{SiCH}_3\text{HCl}$ intermediate. The
intermediate was isolated in the dry box and the lithium aluminum hydride reduction was performed under an inert atmosphere. After the reduction was complete the reaction mixture was extracted with water, filtered, dried with magnesium sulfate, and then characterized. The GPC trace (Figure 3.43) shows a higher average molecular weight and dimer formation compared to the methanol-terminated, base sample. The polydispersity remained narrow at 1.09. The infrared spectrum (Figure 3.44) indicates the presence of a silicon-hydrogen stretching band at 2130 cm\(^{-1}\).

![Figure 3.43. GPC Trace of the base sample (black) and PS-SiCH\(_3\)H\(_2\) (red).](image-url)

Reduced Product:
\[ M_n = 1,900 \text{ g/mol} \]
\[ \text{PDI} = 1.09 \]

Base Sample:
\[ M_n = 1,400 \text{ g/mol} \]
\[ \text{PDI} = 1.05 \]

\[ M_n (\text{calculated}) = 1,900 \text{ g/mol} \]
The $^1$H NMR spectrum (Figure 3.45) shows the peaks responsible for the Si-H$_2$ resonance at $\delta$ 3.8 ppm as well as the Si-CH$_3$ resonance at $\delta$ 0.0 ppm, in good agreement with the chain-end, silyl hydride-functionalized polystyrene.$^{119}$ The ratio of the integration of the peaks was lower than the desired product, but in accordance with some formation of dimer. The ratio of initiator methyl protons to the Si-CH$_3$ resonance should be 6 : 3 but was 6 : 2. In addition, the ratio of initiator methyl protons to the Si-H$_2$ resonance should be 6 : 2, but was 6 : 1.3. Additionally, sharp peaks at $\delta$ 5.2 ppm, $\delta$ 2.5 ppm, and $\delta$ 0.3 ppm were observed presumably due to small molecule impurities. These peaks have chemical shifts similar to the peaks of dichloromethylsilane ($\delta$ 5.5 ppm and $\delta$ 0.9 ppm)$^{190}$. These peaks likely arise from a condensation product of dichloromethylsilane and methanol.
The MALDI-TOF mass spectrum of the reduced product showed clear evidence that the desired product was obtained. The MALDI-TOF mass spectrum (Figure 3.46) shows one major distribution with a representative monoisotopic mass peak at $m/z = 1582.0$ corresponding to the 14-mer, $\omega$-silyl dihydride functionalized polystyrene, $\text{C}_4\text{H}_9$-$(\text{C}_8\text{H}_8)_{14}\text{SiH}_2(\text{CH}_3)\cdot\text{Na}^+$; calculated monoisotopic mass = 1581.95 Da. There was a minor distribution of a second product with a representative monoisotopic mass peak at $m/z = 1640.0$ corresponding to the 15-mer, polystyrene with an unsaturated chain-end, $\text{C}_4\text{H}_9$-$(\text{C}_8\text{H}_8)_{14}\text{C}_8\text{H}_6\cdot\text{Na}^+$; calculated monoisotopic mass = 1539.99 Da. This product is most likely formed by an elimination reaction at the chain-end during the reduction with lithium aluminum hydride. It is also possible that this product was formed during ionization. The $^1\text{H}$ NMR spectrum showed no evidence for formation of the unsaturated product, but $^1\text{H}$ NMR spectroscopy is not as sensitive to low-level impurities as is
MALDI-TOF mass spectrometry. The 14-mer dimeric product \([\text{C}_4\text{H}_9\text{-}(\text{C}_8\text{H}_8)_n\text{-SiH(CH}_3\text{-}(\text{C}_8\text{H}_8)_14\text{-C}_4\text{H}_9\cdot\text{Na}^+]\), which has a calculated monoisotopic mass of 1638.01 Da, was not observed.

![Figure 3.46. MALDI-TOF mass spectrum of PS-SiCH\(_3\)H\(_2\).](image)

### 3.2.6 Synthesis of \(\omega\)-dicyano-functionalized polystyrene

![Scheme 3.13. Synthesis of \(\omega\)-dicyano-functionalized polystyrene.](image)

The \(\omega\)-dicyano functionalized polystyrene was prepared by hydrosilation of allyl cyanide and the \(\omega\)-silyl dihydride functionalized polystyrene (Scheme 3.13).
reaction was monitored via IR spectroscopy. The Si-H stretching band is apparent at 2130 cm\(^{-1}\) in the starting material and the reaction solution\(^{119}\). After 2 weeks at room temperature, the band at 2130 cm\(^{-1}\) was no longer detectable, and a new absorption band at 2249 cm\(^{-1}\) was observed as shown in Figure 3.47. The signal at 2246 cm\(^{-1}\) is in good agreement with other cyano-functionalized polymers prepared in this research\(^{119, 171}\). The reaction went to completion, without the need for further purification. The product produced one spot by TLC in toluene. From the GPC data (Figure 3.48), it appears as though there is a branching reaction occurring during the hydrosilation. The high molecular weight shoulder increases in intensity, and another higher molecular weight shoulder appears. This reaction could be related to hydrosilation of an unsaturated product, analogous to the one formed in the chain-end, cyano-functionalized polystyrene synthesis.

![FTIR spectrum](image)

Figure 3.47. FTIR spectrum of \(\omega\)-dicyano-functionalized polystyrene.
Figure 3.48. GPC trace of ω-dicyano-functionalized polystyrene (red) and PS-SiCH$_3$H$_2$ (blue).

The $^1$H NMR spectrum (Figure 3.49) shows the disappearance of the Si-H resonance at 3.7 ppm; however, no other diagnostic peaks were observed. The MALDI-TOF mass spectrum in Figure 3.50 provided the most convincing evidence for quantitative hydrosilation to yield the ω-dicyano-functionalized polystyrene. The MALDI-TOF mass spectrum (Figures 3.50 and 3.51) shows only one distribution with a representative monoisotopic mass peak at $m/z = 1820.1$ corresponding to the 15-mer, ω-silyl dihydride functionalized polystyrene, C$_4$H$_9$-(C$_8$H$_8$)$_{14}$-Si(CH$_3$)(CH$_2$CH$_2$CH$_2$CN)$_2$·Na$^+$; calculated monoisotopic mass = 1820.24 Da. A peak corresponding to the mass of the 17-mer starting material, C$_4$H$_9$-(C$_8$H$_8$)$_{17}$-SiH$_2$(CH$_3$)·Na$^+$; calculated monoisotopic mass = at 1894.14 Da, is not observed in the spectrum of the
unpurified material. A small noise-level peak is observed at 1848 m/z, corresponding to the 16-mer styrene chain with an unsaturated terminal chain-end. Overall, the ω-dicyano functionalized polystyrene was prepared in high yield without the need for purification.

Figure 3.49. $^1$H NMR spectrum (CDCl$_3$) of ω-dicyano functionalized polystyrene.
Figure 3.50. Full MALDI-TOF mass spectrum of ω-dicyano-functionalized polystyrene.

Figure 3.51. Expanded MALDI-TOF mass spectrum of ω-dicyano-functionalized polystyrene.
3.3 Synthesis and polymerization of silyl-hydride functional monomers

The preparation and polymerization of functional monomers is an important method for tailoring the physical properties of a polymeric system. There are challenges for preparing polymers from functional monomers, mainly reaction of the active chain-end with a functional group. The synthesis and polymerization of \( p \)-dimethylsilylstyrene (\( p \)-DMSS) and \( m \)-dimethylsilylstyrene (\( m \)-DMSS) was investigated. Polymerizations were carried out at room temperature or above in hydrocarbon solvent.

3.3.1 Synthesis of \( p \)-DMSS

\[
\begin{align*}
\text{THF} & \quad 1) \text{Mg, I}_2 \\
\text{Cl} & \quad 2) \text{ClSiMe}_2\text{H} \\
\end{align*}
\]

Scheme 3.14. Synthesis of \( p \)-DMSS.

\( para \)-Dimethylsilylstyrene was synthesized from 4-chlorostyrene using a Grignard reaction followed by condensation with chlorodimethylsilane.\(^{148, 149, 192}\) Special care was taken to not allow the exothermic reactions to initiate polymerization. The chlorostyrene was added dropwise to activated magnesium in tetrahydrofuran, in an ice bath at 0 °C. After complete addition the reaction mixture was allowed to slowly warm to room temperature until most of the magnesium was consumed as determined by visual inspection. At this point, the reaction was again cooled to 0 °C, and the chlorodimethylsilane was added dropwise. The reaction mixture was allowed to stir overnight and by observation of the white solid it was clear that magnesium chloride was formed. The reaction products were partitioned between diethyl ether and water in order
to remove any water-soluble products and by-products. The organic layer was reduced, dried, and distilled into flame-sealed ampoules from calcium hydride immediately prior to use. Extraction and distillation produced a high-purity monomer with no detectable impurities.

The $^1$H NMR spectrum (Figure 3.52) shows peaks and integrations in good agreement with previously reported data.$^{148,149}$ The methyl protons bonded to silicon were present at $\delta$ 0.0 ppm, with an integral value of 6. The Si-H proton is located at $\delta$ 4.1 ppm with an integration of 1. Vinyl protons were apparent at $\delta$ 4.9, 5.5, and 6.4 ppm with integral values of 1. The aromatic protons at $\delta$ 7.1 and 7.2 ppm were observed and had a total integration value of 4. In addition to the NMR data, the monomer purity was tested by GC (Figure 3.53) and HPLC (Figure 3.54) to ensure the absence of impurities, which would complicate polymerization.

Figure 3.52. $^1$H NMR spectrum (CDCl$_3$) of $p$-DMSS.
Through gas chromatographic analysis (Figure 3.53), the purity of the monomer was found to be in excess of 97%. In addition, high pressure liquid chromatography (Figure 5.54) was performed to further characterize the purity of the silyl substituted monomer. The result of HPLC analysis was that the purity was in excess of 96%. With these results in hand, the polymerization was carefully investigated.
3.3.2 Polymerization of \( p \)-DMSS

![Scheme 3.15. Polymerization of \( p \)-DMSS.](image)

Careful analysis of polymerization of \( p \)-DMSS at room temperature in non-aromatic solvent was not performed until this work. The initial work was focused on
polymerization in tetrahydrofuran at -78 °C\textsuperscript{148,149} or in benzene at 20 °C\textsuperscript{120} In some cases, the result was a monomodal narrow distribution,\textsuperscript{120,148} while in other cases a high molecular weight shoulder was observed.\textsuperscript{149} Previous polymerization of \(p\)-DMSS in our group was performed in benzene, and resulted in a narrow monomodal distribution.\textsuperscript{120} It was of interest to investigate the polymerization in cyclohexane for practical applications.

\(p\)-DMSS was polymerized in cyclohexane using standard anionic polymerization techniques, under a nitrogen atmosphere with freshly distilled reagents as shown in Scheme 3.15. Polymerization was allowed to proceed for a period of one hour. In this case, a high molecular weight shoulder was observed. GPC analysis (Figure 3.55) showed \(M_n = 6,300\) g/mol and a polydispersity index of 2.42, while the calculated molecular weight was 5,000 g/mol. The main distribution is, in-fact, centered near 5,000 g/mol. There is a clear dimer shoulder present in the chromatogram. The molecular weight of the dimer peak roughly corresponds to 13,000 g/mol.

![Figure 3.55. GPC trace of poly(\(p\)-DMSS).](image-url)
The combination of the $^1$H NMR spectrum and the MALDI-TOF mass spectrum indicates that a side reaction was taking place. The $^1$H NMR spectrum (Figure 3.56) shows an unexpected peak at $\delta$ 3.1 ppm. This peak is, in itself, not conclusive with respect to the structure. The peak has the chemical shift similar to that for O-CH$_3$ of methanol at 3.49 ppm. The MALDI-TOF mass spectrum (Figure 3.57) revealed more clues about the structure of the side-product. The main distribution is in good agreement with calculated mass. The MALDI-TOF mass spectrum shows one major distribution with a representative monoisotopic mass peak at $m/z = 4295.5$ corresponding to the 26-mer, poly($p$-dimethylsilylstyrene), C$_4$H$_9$-(C$_{10}$H$_{14}$Si)$_{26}$-H·Na$^+$; calculated monoisotopic mass = 4295.41 Da. In addition to the main distribution there are two minor distributions at + 30 $m/z$ and + 60 $m/z$. These masses could correspond to structures with one or two methoxy groups substituted for a proton in the polymeric structure. The second most prevalent distribution in the MALDI-TOF mass spectrum has a representative monoisotopic mass peak at $m/z = 4163.4$ corresponding to the 24-mer, poly($p$-dimethylsilylstyrene) with one unit of $p$-dimethylmethoxysilylstyrene, C$_4$H$_9$-(C$_{10}$H$_{14}$Si)$_{24}$-(C$_{10}$H$_{16}$SiO)-H·Na$^+$; calculated monoisotopic mass = 4163.33 Da. The third most prevalent distribution in the MALDI-TOF mass spectrum has a representative monoisotopic mass peak at $m/z = 4193.2$ corresponding to the 23-mer, poly($p$-dimethylsilylstyrene) with two units of $p$-dimethylmethoxysilylstyrene, C$_4$H$_9$-(C$_{10}$H$_{14}$Si)$_{23}$-(C$_{10}$H$_{16}$SiO)$_2$-H·Na$^+$; calculated monoisotopic mass = 4193.35 Da. It is proposed that lithium methoxide displaces the Si-H proton, or adds to a 1,6 elimination product. Addition of P-Li to the elimination product is a possible linking mechanism as shown in Scheme 3.16.
Figure 3.56. $^1$H NMR spectrum of poly(p-DMSS).

Figure 3.57. MALDI-TOF mass spectrum of poly(p-DMSS).
Scheme 3.16. 1,6-Linking mechanism.
Scheme 3.17. Lithium methoxide-based linking mechanism.

The methoxide substitution could arise from addition of methanol to the 1,6-elimination product (Scheme 3.16), or from direct substitution of the polymeric product with lithium methoxide (Scheme 3.17). In both cases condensation in the presence of ambient humidity from the air can take place to form the dimeric species shown in Scheme 3.17. Since the linking mechanisms as shown in Schemes 3.16 and 3.17 yield dimers of different composition, MALDI-TOF mass spectrometry can be used to determine the prevailing reaction, as will be shown in the following section.
3.3.3 Synthesis of poly(styryl)lithium end-capped with 4 equivalents of \( p \)-DMSS

Scheme 3.18. Poly(styryl)lithium end-capped with 4 equivalents of \( p \)-DMSS.

Poly(styryl)lithium \( (M_n = 1,100) \) was end-capped with 4 equivalents of \( p \)-DMSS monomer in order to more clearly elucidate the mechanism of the linking reaction observed in hydrocarbon solvent (Scheme 3.18). Thirty minutes after addition of \( p \)-DMSS, the reaction was divided into two portions; portion A was quenched with methyl iodide and portion B was quenched with acidic methanol. The observed molecular weight was 3,400 g/mol (GPC) for both samples (See Figure 3.58), while the calculated molecular weight was 1,700 g/mol. The polydispersity of the methyl iodide terminated sample was 1.14, and the acetic acid/methanol terminated sample had a polydispersity of 1.09. It was concluded that the linking reaction was not eliminated with different terminating reagents. The acidic methanol quench revealed that the linking reaction is not due to the nucleophilicity of lithium methoxide. Quenching with methyl iodide further established this observation, as well as shifting the MALDI-TOF mass distribution of the intentionally terminated chains from the unintentionally terminated chains.
Figure 3.58. GPC trace of polystyrene end-capped with 4 equivalents of \textit{p}-DMSS quenched with methyl iodide (blue) acidic methanol (red).

The $^1$H NMR spectra (Figures 3.59 and 5.60) were also important in revealing the mechanism of chain-branching. The molecular weight calculated by NMR was much more similar to the molecular weight calculated from the ratio of grams monomer to moles of initiator than the GPC results. The molecular weight was calculated by comparing the backbone CH and CH$_2$ integration ($\delta$ 1.0 – 2.5 ppm) to the initiator CH$_3$ integration ($\delta$ 0.25 – 0.5 ppm; 6H).$^{120, 127, 173}$ The integration ratio was 36.1 backbone CH and CH$_2$ per chain. Divided by 3, this equates to 12 monomer units. Assuming that there are 4 units of DMSS and 8 units of styrene, the calculated molecular weight by NMR was 1,500 g/mol. This calculation reveals that, on average, more than one initiator unit is incorporated per polymer chain.
Figure 3.59. $^1$H NMR spectrum of polystyrene end-capped with 4 equivalents of $p$-DMSS and terminated with methyl iodide.

Figure 3.60. $^1$H NMR spectrum of polystyrene end-capped with 4 equivalents of $p$-DMSS and terminated with acidic methanol.
The MALDI-TOF mass spectral data further elucidated the chain branching mechanism of silyl hydride substitution. There was an overlap between the chain-end mass of the desired linear mass, and the proposed dimeric species. The addition of one initiator unit of 57 g/mol is nearly equivalent to the distribution with one DMSS unit replaced by a styrene unit (162.15 g/mol – 104.06 g/mol = 58 g/mol). For this reason, the methyl iodide-terminated sample was especially useful for the elucidation of the dimer structure (Figure 3.61). The peak of the dimer with two initiating chain ends was no longer overlapped with the desired distribution.

The methyl-iodide terminated sample has a separation of 4 Daltons between the dimeric and desired structure. The MALDI-TOF mass spectrum shows different distributions for the dimeric and desired products at low mass (Figure 3.62) and high mass (Figure 3.63). The distributions exhibit the spacing of a styrene unit (104.06 Da) between peaks, and correspond to a structure with the same number of $p$-DMSS units and the same end group mass. For example, a lower intensity distribution with monoisotopic peaks at $m/z = 1484.0$ and 1588.0 Da corresponds to butyl-initiated, 4(and 5) mers of styrene, 6 mers of $p$-DMSS, and terminated with a methyl group, $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)s_{(or 5,\text{C}_{10}\text{H}_{14}\text{Si})}_6\cdot\text{CH}_3\cdot\text{Na}^+$; calculated monoisotopic masses = 1483.96 Da (and 1588.02 Da). The distribution with the highest intensity exhibits a representative peak at $m/z = 1518.0$ corresponding to butyl-initiated, 9 mers of styrene, 3 mers of $p$-DMSS, and terminated with a methyl group, $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)9(\text{C}_{10}\text{H}_{14}\text{Si})3\cdot\text{CH}_3\cdot\text{Na}^+$; calculated monoisotopic mass = 1518.02 Da. The second most intense distribution exhibits a representative monoisotopic peak at $m/z = 1576.0$ corresponding to the butyl-initiated, 8 mers of styrene, 4 mers of $p$-DMSS, and terminated with a methyl group, $\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)8(\text{C}_{10}\text{H}_{14}\text{Si})4\cdot\text{CH}_3\cdot\text{Na}^+$;
calculated monoisotopic mass = 1576.05 Da, and this distribution is present across the low mass region of the spectrum corresponding to a different number of styrene units but the same end group mass and 4 units of p-DMSS. The next distribution exhibits a representative monoisotopic peak at \( m/z = 1530.0 \) corresponding to the butyl-initiated, 6 mers of styrene, 5 mers of p-DMSS, and terminated with a methyl group, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)\text{Si}(\text{C}_{10}\text{H}_{14})\text{CH}_3\cdot\text{Na}^+ \); calculated monoisotopic mass = 1530.01 Da. The next distribution exhibits a representative monoisotopic peak at \( m/z = 1564.1 \) corresponding to butyl-initiated, 11 mers of styrene, 2 mers of p-DMSS, and terminated with a methyl group, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{11}(\text{C}_{10}\text{H}_{14})\text{CH}_3\cdot\text{Na}^+ \); calculated monoisotopic mass = 1564.06 Da. There is a distribution that exhibits a representative monoisotopic peak at \( m/z = 1560.0 \) corresponding to the dimer with 2 butyl end groups, 9 mers of styrene and 3 mers of p-DMSS, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{9}(\text{C}_{10}\text{H}_{14})\text{Si}\cdot\text{Na}^+ \); calculated monoisotopic mass = 1559.93 Da. All of these distributions exhibit a variable quantity of styrene units (spacing = 104.1 Da); the end group masses are constant and the number of p-DMSS repeat units ranges between 1-6 for the monomeric and between 0-4 for the dimeric distribution. All other peaks are listed in the table in Figure 3.62.

In Figure 3.63, which displays the higher mass range, the linked product is more evident. The distributions with representative monoisotopic peaks at \( m/z = 2462.6 \) and 2566.7 (separated by 104.1 Da) are from polymer chains with the same end group mass and same number of p-DMSS repeat units, but a different number of styrene repeat units. The representative peak at \( m/z = 2566.7 \) corresponds to a dimer structure with two initiator residues, 14 mers of styrene, and 6 mers of p-DMSS, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{14}(\text{C}_{10}\text{H}_{14})\text{Si}\cdot\text{Na}^+ \); calculated monoisotopic mass = 2566.51 Da. Another major distribution with
a representative peak at \( m/z = 2520.7 \) corresponds to a dimer structure with two initiator residues, 12 mers of styrene, and 7 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_8)_{12}(C_{10}H_{14}Si)_7-C_4H_9\cdot Na^+ \); calculated monoisotopic mass = 2520.48 Da. The next most intense distribution with a representative at \( m/z = 2508.7 \) corresponds to a dimer structure with two initiator residues, 15 mers of styrene, and 5 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_8)_{15}(C_{10}H_{14}Si)_5-C_4H_9\cdot Na^+ \); calculated monoisotopic mass = 2508.48 Da. It should be noted that the distribution for the linear methyl-terminated polymer with 16 mers of styrene and 5 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_8)_{16}(C_{10}H_{14}Si)_5-CH_3\cdot Na^+ \) (calculated monoisotopic mass = 2570.54 Da) overlaps with the distribution at \( m/z = 2566.7 \). All distributions with the same end group mass and number of \( p \)-DMSS repeat units, but a varying amount of styrene repeat units, were observed across the high mass region of the MALDI-TOF mass spectrum.

![MALDI-TOF mass spectrum](image)

Figure 3.61. MALDI-TOF mass spectrum of polystyrene end-capped with 4 equivalents of \( p \)-DMSS and terminated with methyl iodide.
Methyl-Iodide Terminated
Calculated Masses 1470 to 1600 Da

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<td>I-S-12-Si-1-CH3</td>
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<td>D*S-7-Si-4</td>
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<tr>
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<td>I-S-9-Si-3-CH3</td>
</tr>
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Figure 3.62. Low mass region of the MALDI-TOF mass spectrum of polystyrene end-capped with 4 equivalents of $p$-DMSS terminated with methyl iodide.
Figure 3.63. High mass region of the MALDI-TOF mass spectrum of polystyrene end-capped with 4 equivalents of \( p \)-DMSS terminated with methyl iodide.
The MALDI-TOF mass spectrum for the acidic methanol terminated sample is shown in Figures 3.64 and 3.65. The acidic methanol terminated sample has a separation of 2 daltons between the dimeric and desired structure. The peaks at \( m/z = 1504.2 \) and 1608.3 belong to the same distribution, separated by a styrene unit (104.06 Da). The distribution has a representative peak at \( m/z = 1608.3 \) that corresponds to 10 mers of styrene, 3 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_5)_{10}(C_{10}H_{14}Si)_3-H\cdot Na^+ \); calculated monoisotopic mass = 1607.96 Da. Another major distribution has a representative monoisotopic mass peak at \( m/z = 1562.24 \), and corresponds to the 8 mers styrene, 4 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_5)_{8}(C_{10}H_{14}Si)_4-H\cdot Na^+ \); calculated monoisotopic mass = 1561.93 Da. There are other peaks (separated by 104.1 Da) corresponding to structures with the same number of \( p \)-
DMSS units and end group masses with a variable number of styrene units. The calculated monoisotopic mass of 1559.93 Da corresponds to the dimer with 2 initiator residues, 9 mers of styrene, and 3 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_{18})_9(C_{10}H_{14}Si)_3-C_4H_9 \cdot Na^+ \). The peak is present, but at low relative abundance. Additionally a small peak near the baseline at 1592.3 Da is visible, which corresponds to the methoxy-substituted structure with 8 mers of styrene, 3 mers of \( p \)-DMSS, and 1 mer of \( p \)-DMSS-\( OCH_3 \), \( C_4H_9-(C_8H_{18})_9(C_{10}H_{14}Si)_3(C_{11}H_{16}SiO)-C_4H_9 \cdot Na^+ \); calculated monoisotopic mass = 1591.93 Da.

The conclusion from these two experiments is that a linking reaction is taking place regardless of the quenching reagent. If a basic and nucleophilic lithium methoxide molecule were displacing the hydrogen of the Si-H bond, the problem would have likely been eliminated when using methyl iodide or a solution of methanol and acetic acid to quench the reaction. This is further evidence to support the linking mechanism proposed in Scheme 3.16.
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</tr>
</tbody>
</table>

Figure 3.65. Expanded MALDI-TOF mass spectrum of polystyrene end-capped with 4 equivalents of \( p \)-DMSS and terminated with acidic methanol.
3.3.4 Copolymerization of \( p \)-DMSS and styrene

A copolymerization reaction was also performed to further test the coupling reaction. The reaction was initiated by adding \textit{sec}-butyllithium to a mixture with a ratio of 10 moles of styrene to 1 mole of \( p \)-DMSS in cyclohexane (Scheme 3.19). This corresponds to 14.7 equivalents of styrene and 1.7 equivalents of \( p \)-DMSS per chain.

The copolymerization reaction was divided into two parts; one portion was terminated with methanol and the other sample was terminated with acidic methanol. The GPC traces (Figure 3.66) show a high molecular weight shoulder in both cases. In fact, it appears as though more dimer is formed for the sample quenched with acidic methanol. Analysis of the GPC chromatogram indicates a molecular weight of 3,000 g/mol for both samples and a molecular weight distribution of 1.15 for the methanol-quenched reaction and a polydispersity of 1.17 for the acidic methanol-quenched reaction. The calculated molecular weight was 1,800 g/mol. From this data it is clear that lithium methoxide does not play a pivotal role in the linking reaction. The \(^1\)H NMR spectrum (Figure 3.67) shows an approximate molecular weight of 1,200 g/mol (based on the ratio of backbone \( \text{CH} \) and \( \text{CH}_2 \) vs. initiator \( \text{CH}_3 \) (30.3 : 6), yielding 10 repeat units, one of which, on the average is \( p \)-DMSS.\(^{120,127,173} \) This NMR result shows a molecular weight slightly lower than the calculated molecular weight.
Figure 3.66. GPC trace of poly($p$-dimethylsilylstyrene-$co$-styrene) terminated with acidic methanol and methanol.

Figure 3.67. $^1$H NMR spectrum of the poly($p$-dimethylsilylstyrene-$co$-styrene) quenched with methanol.
The MALDI-TOF mass spectrum (Figures 3.68 – 3.70) showed the expected distributions in the low mass region. Different distributions for polymer chains with 0, 1, 2, and 3 p-DMSS units incorporated into the polystyrene chains were observed. The peaks at \( m/z = 1595.9 \) and 1700.0 belong to the same distribution, separated by a styrene repeat unit. The most prevalent distribution with a representative monoisotopic mass peak at \( m/z = 1700.0 \) corresponds to the 14 mer of styrene and 1 mer of p-DMSS, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{14}(\text{C}_{10}\text{H}_{14}\text{Si})-\text{H}·\text{Na}^+ \); calculated monoisotopic mass = 1700.03 Da. The second most prevalent distribution in the MALDI-TOF mass spectrum has a representative monoisotopic mass peak at \( m/z = 1653.9 \) and corresponds to 12 mers of styrene and 2 mers of p-DMSS, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{12}(\text{C}_{10}\text{H}_{14}\text{Si})_{2}-\text{H}·\text{Na}^+ \); calculated monoisotopic mass =
1654.00 Da. There is a distribution corresponding to the same end-group mass and 2
mers of \( p \)-DMSS, but a variable quantity of styrene repeat units. The third most
prevalent distribution in the MALDI-TOF mass spectrum has a representative
monoisotopic mass peak at \( m/z = 1642.0 \) and corresponds to 15-mer polystyrene, \( C_4H_9-(C_8H_{15})_{15}-H \cdot Na^+ \); calculated monoisotopic mass = 1642.01 Da. The distribution
corresponding to the butyl-initiated, proton-terminated, styrene homopolymer is visible
throughout the spectrum. The other distribution has a representative monoisotopic mass
peak at \( m/z = 1607.9 \) corresponding to 10 mers of styrene and 3 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_{10})_{10}(C_{10}H_{14}Si)_3-H \cdot Na^+ \); calculated monoisotopic mass = 1607.96 Da. Additionally, a
smaller peak near the baseline is observed at \( m/z = 1770.0 \) corresponding to 10 mers of
styrene and 4 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_{10})_{10}(C_{10}H_{14}Si)_4-H \cdot Na^+ \); calculated
monoisotopic mass = 1770.05 Da.

The higher mass region of the MALDI-TOF mass spectrum (Figure 3.70) showed
distributions corresponding to structures containing 2 initiator units per polymer chain.
The peaks at \( m/z = 3537.2 \) and 3641.3 belong to the same distribution, separated by a
styrene repeat unit. A representative monoisotopic mass peak at \( m/z = 3641.3 \)
corresponds to the 29 mers of styrene and 3 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_{20})(C_{10}H_{14}Si)_3-H \cdot Na^+ \); calculated monoisotopic mass = 3641.18 Da. These signals overlap with those
corresponding to the linear structure consisting of 28 mers of styrene and 4 mers of \( p \)-
DMSS, \( C_4H_9-(C_8H_{20})(C_{10}H_{14}Si)_4-H \cdot Na^+ \); calculated monoisotopic mass = 3643.18 Da.
The second most prevalent distribution in the higher mass region of the MALDI-TOF
mass spectrum has a representative monoisotopic mass peak at \( m/z = 3595.3 \) and
corresponds to 27 mers of styrene and 4 mers of \( p \)-DMSS, \( C_4H_9-(C_8H_{20})(C_{10}H_{14}Si)_4-H \cdot Na^+ \); calculated monoisotopic mass = 3595.18 Da.
$\text{C}_4\text{H}_9\cdot\text{Na}^+$; calculated monoisotopic mass = 3595.14 Da. The third major distribution in the high mass region has a representative monoisotopic mass peak at $m/z = 3583.3$ and corresponds to 27 mers of styrene and 4 mers of $p$-DMSS, $\text{C}_4\text{H}_9\cdot(\text{C}_8\text{H}_8)_{27}(\text{C}_{10}\text{H}_{14}\text{Si})_4\cdot\text{C}_4\text{H}_9\cdot\text{Na}^+$; calculated monoisotopic mass = 3595.14 Da. Other distributions are described in Figure 3.70. The peaks described above were present in the high mass region of the mass spectrum for distributions with the same end group masses and $p$-DMSS repeat units, but with variable amounts of styrene.

From the use of various quenching reagents and reaction times, it is apparent that the linking reaction is independent of the quenching reagent. Linking through 1,6-elimination of lithium hydride, followed by the addition of P-Li is unlikely (as proposed in Scheme 3.16). The methoxy-displaced distribution was also not observed for polymers containing styrene (Scheme 3.17). An additional mechanism of linking involving electron transfer and radical coupling cannot be dismissed (Scheme 3.20). This mechanism takes place by the polymeric organolithium transferring an electron to another polymer molecule, creating a radical chain-end (susceptible to coupling) and a polymeric radical anion. The radical anion can then lose a hydride to become a silyl radical, also susceptible to coupling reactions (Scheme 3.20). The products of linking by the proposed electron transfer mechanism have the same mass as those arising from the 1,6 lithium hydride elimination reaction. The fact that the proposed structures for the higher molecular weight species were not terminated by methyl-iodide (Scheme 3.20) is in support of the electron transfer mechanism, which produces an inactive polymer molecule.
<table>
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<th>Da</th>
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<td>1770.05</td>
<td>I-S-10-Si-4</td>
</tr>
</tbody>
</table>

Figure 3.69. Low mass region of the MALDI-TOF mass spectrum of poly(\textit{p-}
dimethylsilylstyrene-\textit{co}-styrene) quenched with methanol.
Figure 3.70. High mass region of the MALDI-TOF mass spectrum of poly(\textit{p-}dimethylsilylstyrene-\textit{co}-styrene) quenched with methanol.
Scheme 3.20. Electron transfer-based linking mechanism for \( p \)-DMSS.
3.3.5 Synthesis of $m$-DMSS


In order to remove the mechanistic pathway for 1,6-elimination of lithium hydride at the chain-end, a strategy was devised to incorporate the silyl hydride group through meta-substitution instead of para-substitution. Herein we report the first synthesis of meta-dimethylsilylstyrene ($m$-DMSS) from 3-bromostyrene via a Grignard reaction quenched with chlorodimethylsilane (Scheme 3.21).\textsuperscript{192} 3-Bromostyrene was used instead of 3-chlorostyrene because it was more readily available. In addition, 4-bromostyrene and 4-chlorostyrene were used to synthesize $p$-DMSS, and there were no detectable differences in the polymerization behavior. The reaction occurred in high yield with no detectable side-reactions. $m$-DMSS was obtained in 75% yield and purified to the standards necessary for anionic polymerization. The monomer was vacuum distilled from calcium hydride into an all-glass reactor immediately prior to use. The structure of the monomer was confirmed by $^1$H NMR spectroscopy (Figure 3.71). The shift in the vinyl peaks at 5.3 and 5.8 ppm for 3-bromostyrene to 4.8 and 5.4 ppm for the $m$-DMSS is evidence for complete consumption of the 3-bromostyrene starting material. It is also important to note that the integration ratio for the peaks of the product and starting material are as expected within an error of 10%. The peak assignments are shown in Figure 3.72.
Figure 3.71. $^1$H NMR spectra of $m$-DMSS and 3-bromostyrene.

Figure 3.72. Peak assignments for $^1$H NMR spectrum a→h, left→right.
3.3.6 Polymerization of \( m \)-DMSS

![Scheme 3.22. Polymerization of \( m \)-DMSS.](image)

After successful synthesis of pure \( m \)-DMSS, the homopolymerization was investigated in cyclohexane at 30 °C using sec-butyllithium as initiator (Scheme 3.22). During the polymerization one sample was removed after 30 minutes of reaction time, while another sample proceeded for a period of 1 hour and 30 minutes. The polymerization is complete after 15 minutes or less based on the rate constant for styrene.\(^{195}\) After a reaction time of 30 minutes GPC analysis indicated \( M_n = 5,200 \text{ g/mol, PDI} = 1.19 \), and at 1 hour and 30 minutes the GPC results were \( M_n = 7,600 \text{ g/mol, PDI} = 1.25 \) (Figure 3.73). The GPC curves of the polymerization showed a higher \( M_n \) than the calculated molecular weight (2,000 g/mol) and a wide molecular weight distribution. The polydispersity increased with polymerization time; this is evidence for a linking reaction instead of a living polymerization where the polydispersity decreases with increasing molecular weight.\(^5\) Thus, the GPC data in Figure 3.73 suggests that a linking reaction is taking place with this monomer also.
Figure 3.73. GPC traces of poly(m-DMSS) at 30 minutes (blue) and 1 hour and 30 minutes (red) polymerization time.

The $^1$H NMR spectra (Figure 3.74) also provided evidence for a linking reaction. A peak appears at $\delta = -0.1$ to -0.5 ppm corresponding to Si-CH$_3$ in which the silicon is also bonded to a species more electronegative than hydrogen.$^{175}$ The integration ratio of the Si-H peak also decreases (relative to that of initiator CH$_3$) with longer reaction time. It should also be noted that the calculated molecular weight based on the integration ratio of initiator CH$_3$ groups to backbone CH and CH$_2$ protons remains constant at near 1,400 g/mol, close to the calculated molecular weight of 2,000 g/mol.$^{120,127,173}$

Analysis of the MALDI-TOF mass spectrum (Figures 3.75-3.77) clearly shows the presence of a higher molecular weight polymer species. In Figure 3.75, a spectrum is presented which shows the entire mass range. It is clear that there are at least 4
distributions present at progressively larger masses. The center of mass of the lowest molecular weight distribution is around 1,700 g/mol, in good agreement with the desired polymer product. In addition, several distributions of higher molecular weight species can be observed at higher \( m/z \).

Figure 3.74. \(^1\)H NMR spectra of poly(\(m\)-dimethylsilylstyrene); 30 minute polymerization time (above), 1 hour 30 minutes polymerization time (below).
Upon careful inspection of the low mass distribution in the mass spectrum (Figure 3.76), it is clear that the most prevalent peaks are at $m/z = 1,701.9$ and $1,864.0$, separated by one $m$-DMSS repeat unit ($162.1$ Da). The representative monoisotopic mass peak at $m/z = 1,701.9$ corresponds to the 10-mer, poly($m$-dimethylsilylstyrene), $C_4H_9$-($C_{10}H_{14}Si$)$_{10}$H·$Na^+$; calculated monoisotopic mass = $1,701.97$ Da. The second most intense peak in Figure 3.76 is the shifted by $56.06$ g/mol (from $1,701.89$ to $1,757.95$ $m/z$). This mass corresponds to a 10-mer with an additional butyl group ($57.07$ g/mol) minus one proton. The second most prevalent distribution in the MALDI-TOF mass spectrum has a representative monoisotopic mass peak at $m/z = 1,758.0$, which corresponds to the 10-mer dimer of poly($m$-dimethylsilylstyrene), $C_4H_9$-($C_{10}H_{14}Si$)$_{10}$-$C_4H_9$·$Na^+$; calculated monoisotopic mass = $1,758.03$ Da. In addition, a distribution that corresponds to a 10-mer, 3-branched structure has a representative monoisotopic mass peak at $m/z = 1,814.0$ corresponding to the 10-mer, poly($m$-dimethylsilylstyrene), containing 3 initiator units $C_4H_9$-($C_{10}H_{14}Si$)$_{10}$-$C_4H_9$-$C_4H_8$·$Na^+$; calculated monoisotopic mass = $1,814.09$ Da. The
structure for the linked products are shown in Scheme 3.23. There are a few additional, minor distributions in Figure 3.76, which have not been identified.

Figure 3.76. Low mass region of the MALDI-TOF mass spectrum of poly(m-dimethylsilylstyrene).

At a higher mass range (3860-4040 m/z) the MALDI-TOF mass spectrum (Figure 3.77) shows the presence of higher molecular weight structures. The main distribution at m/z = 3865.2 and 4027.6 is separated by a m-DMSS repeat unit (162.15 Da). The distribution with a representative monoisotopic mass peak at m/z = 4027.6 corresponds to the 24-mer poly(m-DMSS) with two initiator fragments C_4H_9-(C_{10}H_{14}Si)_{24}-C_4H_9·Na^+; calculated monoisotopic mass = 4027.29 Da. The other major distribution with a representative monoisotopic mass peak at m/z = 3921.5 corresponds to the 23-mer poly(m-DMSS) with 3 initiator fragments, C_4H_9-(C_{10}H_{14}Si)_{23}-C_4H_9C_4H_8·Na^+; calculated
monoisotopic mass = 3921.26 Da. In addition to those two distributions a third cluster of peaks is evident. It is obvious from the width and peak-height pattern of isotopic distribution compared to the other distributions that two products are present. At the low-mass end of the grouping, the linear polymer which has a representative monoisotopic mass peak at \( m/z = 3971.5 \) corresponding to the 24-mer, poly\((m\text{-dimethylsilylstyrene})\), \( C_4H_9-(C_{10}H_{14}Si)_{24}-H\cdot Na^+ \); calculated monoisotopic mass = 3971.23 Da. The other distribution corresponds to the 23-mer, poly\((m\text{-DMSS})\), with 4 initiator fragments, \( C_4H_9-(C_{10}H_{14}Si)_{10}-C_4H_9C_4H_8C_4H_8\cdot Na^+ \); calculated monoisotopic mass = 3977.32 Da.

Desired Homopolymer

\[
\text{Desired Homopolymer}
\]

2-armed

3-armed

4-armed

Scheme 3.23. Proposed structures of higher molecular weight products.
Using evidence from a combination of $^1$H NMR spectroscopy and MALDI-TOF mass spectrometry, the linking reaction mechanism was proposed to be nucleophillic substitution of the silyl hydride with a polymeric organolithium in the case of $m$-DMSS polymerization. Execution of this reaction in ether at high temperatures with a variety of silanes and alkyllithiums$^{196-198}$ was reported previously, but in hydrocarbon solvent at room temperature it has not been reported. The mass spectral data showing additional initiator units in the place of a proton provided some confirmation of the linking reaction. The $^1$H NMR showed a decreasing integration for the Si-H proton (relative to initiator CH$_3$) with increasing reaction time as well as a signal for Si-CH$_3$ adjacent to a benzylic
carbon at δ -0.5 ppm. The facile formation of distributions containing many initiating units, as compared to the $p$-DMSS polymerization, points towards a different mechanism for each monomer.

3.3.7 Copolymerization of $m$-DMSS and styrene

Scheme 3.24. Copolymerization of $m$-DMSS and styrene.

The copolymerization of 10 weight percent $m$-DMSS (1 mole/chain) and styrene (16.4 moles/chain) was investigated to see if the undesirable side reactions were less prevalent when the $m$-DMSS monomer was present in a lower concentration (Scheme 3.24). In addition, the copolymerization is more likely of interest for industrial applications. The calculated molecular weight was 1,860 g/mol. The reaction was divided into two samples; portion A was quenched with methanol after a period of 45 minutes, portion B was quenched with methanol after 1h and 45 minutes. The molecular weight observed by GPC analysis (Figure 3.78) was 2,000 g/mol in both cases. On longer reaction time the polydispersity index increased from 1.10 to 1.11. The shape of the GPC trace indicates the presence of a high molecular weight shoulder, despite the relatively narrow polydispersity and good agreement between calculated and observed molecular weights. The dimer portion is estimated to be less than 5%, and is only evidenced by an unsymmetrical GPC curve. This was partially explained by the fact that there is only one equivalent of $m$-DMSS per polymer chain. The GPC results (see Figure
3.78) at different reaction times for the copolymerization showed that dimer was formed after 45 minutes, and the quantity increased after a period of one hour and 45 minutes. The polymerization is complete within 15 minutes, based on the rate constant for styrene.\textsuperscript{195} The GPC evidence, in itself, does not conclusively prove dimer formation.

![Figure 3.78. GPC trace of poly(m-dimethylsilylstyrene-co-styrene) at 45 minutes (blue) and 1 h 45 minutes (red) polymerization time.]

The \textsuperscript{1}H NMR spectra (Figure 3.79) provided insight into the nature of the linking reaction. The ratio of the integration for the Si-H resonance at 4.1 ppm\textsuperscript{120, 148, 149} with respect to the initiator methyl protons at 0.7 ppm was observed to decrease from 1.9 : 6 to 1.7 : 6 with increasing reaction time. In addition, a signal at -0.5 ppm increased with increasing reaction time. This signal is likely due to the H-Si-(CH\textsubscript{3})\textsubscript{2} shifting to R-Si-(CH\textsubscript{3})\textsubscript{2}, where R is a structure that donates electron density to the silicon atom.\textsuperscript{175} There have been no reports of silyl hydride substitution by a polymeric organolithium in
hydrocarbon solvent at room temperature. This reaction typically is observed at higher temperature in ethereal solvents.\textsuperscript{196-198}

Figure 3.79. \textsuperscript{1}H NMR spectra of poly(\textit{m}-dimethylsilylstyrene-co-styrene) at 45 minutes (above) and 1 h 45 minutes (below) polymerization time.
The MALDI-TOF mass spectrum was also used to confirm the occurrence of a linking reaction. The MALDI-TOF mass spectra corresponding to the two reaction times were nearly identical, in this case the 1 h 45 minute sample was investigated, because the high molecular weight peaks had a higher intensity. The peak values were identical. The full spectrum (Figure 3.80) clearly shows the existence of a dimer distribution as well as the expected main distribution.

![Figure 3.80. Full MALDI-TOF mass spectrum of poly(m-dimethylsilylstyrene-co-styrene) after 1 hour and 45 minutes.](image)

Upon more careful inspection of the main distribution, all of the structures for the expected copolymer can be observed in Figures 3.81 and 3.82. The main distribution in the low mass region of the mass spectrum has a spacing of $m/z = 104.1$, with a representative monoisotopic mass peak at $m/z = 1538.0$, which corresponds to 14-mer
polystyrene, C₄H₉-(C₈H₈)₁₄-H·Na⁺; calculated monoisotopic mass = 1537.94 Da. The second most prevalent distribution has a representative monoisotopic mass peak at \( m/z = 1596.0 \) corresponding to 13 mers of styrene, and 1 mer of \( m \)-DMSS, C₄H₉-(C₈H₈)₁₄(C₁₀H₁₄Si)₁-H·Na⁺; calculated monoisotopic mass = 1595.97 Da. The smallest distinguishable distribution has a representative monoisotopic mass peak at \( m/z = 1550.0 \) corresponding to 11 mers of styrene, 2 mers of \( m \)-DMSS, C₄H₉-(C₈H₈)₁₁(C₁₀H₁₄Si)₂-H·Na⁺; calculated monoisotopic mass = 1549.94 Da.

Figure 3.81. Low mass region of the MALDI-TOF mass spectrum of poly(\( m \)dimethylsilylstyrene-có-styrene).

The main distribution for the high mass region of the MALDI-TOF mass spectrum (Figure 3.82) has a representative monoisotopic mass peak at \( m/z = 3005.0 \)
corresponding to the 26 mers of styrene, 1 mer of \( m \)-DMSS, and two initiator fragments, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{26}(\text{C}_{10}\text{H}_{14}\text{Si})_1-\text{C}_4\text{H}_9-\text{Na}^+ \); calculated monoisotopic mass = 3004.81 Da. The spacing between peaks for this distribution was 104.1 \( m/z \), with the next peak at \( m/z = 3109.1 \) corresponding to a structure with the same end group masses and number of \( m \)-DMSS repeat units (one), but with an additional styrene repeat unit. The overlapping linear structures could also be present: the 25-mer styrene, 2-mer \( m \)-DMSS, \text{poly}(m-dimethylsilylstyrene-co-styrene), \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{25}(\text{C}_{10}\text{H}_{14}\text{Si})_2-\text{H-}\text{Na}^+ \); calculated monoisotopic mass = 3004.81 Da. The second most prevalent distribution has a representative monoisotopic mass peak at \( m/z = 3063.0 \) corresponding to the 25 mers of styrene, 2 mers of \( m \)-DMSS, and two initiator fragments, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{25}(\text{C}_{10}\text{H}_{14}\text{Si})_2-\text{C}_4\text{H}_9-\text{Na}^+ \); calculated monoisotopic mass = 3062.84 Da. Peaks for this distribution with a different number of styrene repeat units were observed. Overlapping with this peak is the linear polymer with calculated monoisotopic mass = 3064.84 Da., corresponding to the 24 mers of styrene, 3 mers of \( m \)-DMSS, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{24}(\text{C}_{10}\text{H}_{14}\text{Si})_3-\text{H-}\text{Na}^+ \).

A third distribution has a representative monoisotopic mass peak at \( m/z = 3017.0 \) corresponding to 23 mers of styrene, 3 mers of \( m \)-DMSS, and two initiator fragments, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{23}(\text{C}_{10}\text{H}_{14}\text{Si})_3-\text{C}_4\text{H}_9-\text{Na}^+ \); calculated monoisotopic mass = 3016.80 Da. The spacing for this distribution was equivalent to a styrene unit (104.1 Da). This peak also has an overlapping linear structure with a calculated monoisotopic mass = 3018.81 Da corresponding to the 22 mer of styrene, 4 mer of \( m \)-DMSS, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{22}(\text{C}_{10}\text{H}_{14}\text{Si})_4-\text{H-}\text{Na}^+ \). A low intensity distribution corresponding to the 3-armed structure with 24 mers of styrene, 2 mers of \( m \)-DMSS, and 3 initiator fragments, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{24}(\text{C}_{10}\text{H}_{14}\text{Si})_2-\text{H-}\text{Na}^+ \).
C₄H₉C₄H₈·Na⁺; calculated monoisotopic mass = 3014.84 Da may be observed near the baseline, but it is not entirely clear.

![MALDI-TOF mass spectrum](image)

Figure 3.82. High mass region of the MALDI-TOF mass spectrum of poly(m-dimethylsilylstyrene-co-styrene).

From the spectral and chromatographic evidence, it is clear that the m-DMSS monomer is also susceptible to an undesirable linking reaction. For this monomer, substitution could also occur via nucleophillic substitution of the silyl hydride with a polymeric organolithium chain-end (Scheme 3.25). It is also possible for electron transfer and radical coupling to take place (Scheme 3.26). The linking reaction for meta-dimethylsilylstyrene was faster than the para-substituted monomer. The linking
observed for the *para*-substituted analog was not eliminated by removing the pathway for 1,6-lithium hydride elimination. One can conclude that either a different linking mechanism is involved for the *meta*-substituted monomer, or that the proposed linking mechanism for the *para*-substituted monomer is not the exclusive pathway. The 1,6-lithium hydride elimination reaction proposed for the *para*-substituted analog could not take place for the *meta*-substituted derivative. However, linking reactions were also observed for the *meta*-substituted, therefore it is concluded that either the 1,6-elimination mechanism is not occurring, or another mechanism can also be operating competitively.

![Figure 3.85 Proposed structure of the dimer.](image)

![Scheme 3.25. Nucleophillic substitution.](image)
Scheme 3.26. Electron transfer mechanism of chain-branching for m-DMSS.
CHAPTER IV

CONCLUSION

Living anionic polymerization remains as the gold standard of living polymerization methodologies. Controlled radical polymerization has inherent reactions of disproportionation and radical coupling. Some carbocationic polymerizations suffer from β-hydride elimination and chain-transfer to monomer. Insertion polymerization with metallocene catalysts is limited generally by β-hydride transfer to the metal. All of these types of polymerizations can be performed under conditions where the side reactions are reduced and living conditions can exist. The lack of an inherent mode of termination sets anionic polymerization apart from all others. Limitation to only intentional termination of the polymeric product is an advantage which can be employed for the precise synthesis of chain-end functionalized polymers, block copolymers, and star-branched polymers. Despite this unprecedented ability to do precise chemistry on a polymer chain-end, anionic polymerization suffers from a lack of functional group tolerance due to the reactivity of the anionic chain-end. One method to circumvent this issue is through polymerization at low temperature in tetrahydrofuran. These conditions, however, are not industrially attractive and result in loss of the unique high 1,4 diene stereospecificity obtained for lithium as counterion in hydrocarbon solutions. In this work a combination of anionic polymerization and hydrosilation chemistry was used to prepare an array of functionalized polymers with well-defined
structures under industrially viable conditions. The work presented herein can be divided into three categories: a) functional initiator synthesis; b) chain-end and in-chain functionalization and c) functional monomer synthesis and polymerization.

Triethoxysilyl-functionalized polystyrene was prepared by synthesizing a functional initiator with an unsaturated group then hydrosilation. An alkyl-substituted double bond is not active towards anionic polymerization, therefore it remains intact for the length of the polymerization process. The initiator, 5-pentenyllithium, was prepared in 70% yield from 5-bromopentene, and then used to initiate styrene polymerization in the presence of ~5 equivalents of tetrahydrofuran. The α-functionalized polymer was simply terminated with methanol and was reacted with triethoxysilane in the presence of Karstedt’s catalyst to quantitatively prepare α-triethoxysilyl-functionalized polystyrene as determined by MALDI-TOF mass spectrometry and 1H NMR spectroscopy. Hydrosilation of a pendant vinyl group was then expanded to the 1,2 units of polybutadiene, where triethoxysilane was added quantitatively, while no addition to the 1,4 units was detected by 1H NMR spectroscopy.

Synthesis of an α,ω-difunctionalized polystyrene was also reported in this work. The unsaturated initiator was combined with termination by chlorodimethyl silane, resulting in a polymer with a mono-substituted double bond at the initiating chain end and a silyl hydride group at the terminal chain end. This polymer could be used to prepare a variety of α-triethoxy-ω-functionalized polystyrenes with a variety of functional groups at the ω chain-end by subsequent hydrosilation reactions.

A combination of anionic polymerization and hydrosilation chemistry was used to prepare chain-end functionalized polystyrene and polystyrene with one functional group.
placed precisely in the center of the chain. For the preparation of \( \omega \)-cyano-functionalized polystyrene, silyl hydride-functionalized polystyrene was prepared by anionic polymerization. The chain-end, silyl hydride-functionalized polystyrene was reacted with allyl cyanide in the presence of Karstedt’s catalyst to prepare \( \omega \)-cyano-functionalized polystyrene in 87% isolated yield. For the synthesis of a polymer with the functional group placed precisely in the center of the chain, a new methodology for the synthesis of in-chain, silyl hydride-functionalized polystyrene was developed. An excess of poly(styryl)lithium was reacted with dichloromethylsilane, resulting in formation of the in-chain, silyl hydride-functionalized polystyrene. The excess poly(styryl)lithium was reacted with ethylene oxide in order to obtain a pure in-chain, silyl hydride-functionalized polystyrene after column chromatography. The silyl hydride-functionalized polystyrene was reacted with allyl cyanide in the presence of Karstedt’s catalyst to prepare the in-chain, cyano-functionalized, polystyrene in 58% isolated yield. The yield was lower in this case due to steric hindrance around the substituted Si-H bond. These polymers have proven useful for the study of polymer dynamics.\(^{202,203}\)

The methodology of preparing chain-end functionalized polymers through a combination of living anionic polymerization and hydrosilation chemistry was expanded to include polymers with two functional groups at the \( \omega \)-chain end. First, polystyrene was prepared with a disilyl hydride group at the chain-end. This was achieved by terminating poly(styryl)lithium with a large excess of dichloromethylsilane, then reduction with lithium aluminum hydride. The silyl dihydride-functionalized polymer was reacted with allyl cyanide in the presence of Karstedt’s catalyst at room temperature for a period of 2 weeks. The difunctional chain-end functional polymer was prepared in
over 95% yield (as determined by MALDI-TOF mass spectrometry and \(^1\)H NMR spectroscopy) without the need for purification at any step.

Lastly, the polymerization of styrenic monomers containing a silyl hydride groups in cyclohexane with sec-butyllithium as initiator at room temperature was investigated. A high molecular weight product was observed and the structure was elucidated. A 1,6-elimination of lithium hydride followed by coupling with a polymeric organolithium compound was proposed to be occurring during polymerization of \(p\)-dimethylsilylstyrene. In an effort to remove this pathway of chain termination and linking, \(m\)-dimethylsilylstyrene was prepared. The new monomer was polymerized in cyclohexane with sec-butyllithium as initiator at room temperature. Polymerization and copolymerization of \(m\)-dimethylsilylstyrene resulted in high molecular weight shoulders, and observed molecular weights higher than the calculated \(M_n\). Linking by another mechanism is observed for the case of \(m\)-DMSS. Linking reactions took place in the case of both monomers for various reaction times with different terminating reagents. Further investigation is currently underway towards the identification and elimination of these undesirable side-reactions.
CHAPTER V

REFERENCES


189. ChemYQ Chloromethylsilane MSDS. http://www.chemyq.com/En/xz/xz3/26397cthsg.htm (May 4, 2010),

190. Sigma-Aldrich http://www.sigmaaldrich.com/spectra/fnmr/FNMR000119.PDF (May 4, 2010),


