ANIONIC SYNTHESIS OF WELL-DEFINED FUNCTIONALIZED AND STAR-BRANCHED POLYMERS

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Manuela Ocampo
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ANIONIC SYNTHESIS OF WELL-DEFINED FUNCTIONALIZED AND STAR-BRANCHED POLYMERS

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Dissertation

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ABSTRACT

Novel methods for the synthesis of chain-end and in-chain functionalized polymers, as well as star polymers, were developed using anionic polymerization techniques. A new mechanism for the reaction of polymeric organolithium compounds with thiiranes has been found. The reaction of poly(styryl)lithium and poly(butadienyl)lithium with propylene sulfide and ethylene sulfide was investigated in hydrocarbon solution for the preparation of thiol-functional polymers. It was found by MALDI-TOF mass spectral analysis of the reaction products that the reaction proceeded by attack of the anion on the methylene carbon atom of the thiirane ring followed by ring opening to form the thiol-functionalized polymer. The reaction of poly(styryl)lithium with trimethylene sulfide did not produce the corresponding thiol-functionalized polymer; the resulting methyl-terminated polymer was formed by attack of the anion on the sulfur atom followed by ring opening to form a primary carbamion.

A new method for synthesis of alkoxy-silyl-functionalized polymers was developed. Using a general functionalization methodology based on the hydrosilation of vinyltrimethoxysilane with $ω$-silyl hydride-functionalized polystyrene, alkoxy-silyl-functionalized polystyrene was obtained in high yield (83 %). The main side product was vinylsilane-functionalized polymer. A small amount of dimer (approximately 2 %) was formed from the hydrosilation reaction of silyl hydride-functionalized polymer and vinylsilane-functionalized polymer.
Star polymers with an average number of 6.8 arms were obtained by reacting poly(styryl)lithium with 6.6 equivalents of vinyl(dimethyl)chlorosilane in benzene at 30 °C. It was found that, in benzene at 30 °C, vinyl(dimethyl)chlorosilane is an efficient linking agent for the preparation of well-defined star-branched polymers. In contrast, the reaction of poly(styryl)lithium with 5 equivalents of vinyl(dimethyl)chlorosilane in THF at -78 °C produced vinylsilane-functionalized polymer in high yield (> 93 %). Poly(styryl)lithium was reacted with 2.5 equivalents of vinyl(dimethyl)ethoxysilane; reaction occurred exclusively by the addition of the living anion to the vinyl group.

In-chain, dihydroxy-functionalized polystyrene was prepared by reaction of poly(styryl)lithium and 1,3-butadiene diepoxide. The hydroxyl functionalities were activated with potassium naphthalenide. Addition of ethylene oxide monomer yielded the corresponding heteroarm polystyrene/poly(ethylene oxide) stars.

Two commercially available triepoxides, N,N-diglycidyl-4-glycidyloxyaniline and Tactix 742, were used to prepare the corresponding 3-armed stars in high yield.
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1.1. Living anionic polymerization

The living nature of anionic polymerization was first recognized by Szwarc in 1956.\textsuperscript{1,2} The term living denotes the absence of termination and chain transfer reactions during chain-growth polymerization. Alkylolithium-initiated, living anionic polymerization has been demonstrated to be a convenient method to make well-defined polymers with control of molecular weight and molecular weight distribution.\textsuperscript{3} Since the product after all monomer has been consumed is a reactive polymeric organolithium compound, this provides versatile methods for the preparation of block copolymers by sequential monomer addition,\textsuperscript{4} chain-end functionalized polymers by reaction of the living chain ends with appropriate monomers and/or electrophilic terminating agents\textsuperscript{5,6} and star-branched polymers by linking reactions with multi-functional linking agents.\textsuperscript{7} It is possible to control the molecular weight of the final polymer by manipulating the stoichiometry of the reaction; from one initiator molecule, one polymer molecule is obtained. Hence, based on the ratio of the amount of monomer to the moles of initiator, the desired number average molecular weight ($M_n$) after complete monomer consumption can be calculated with equation 1.

\[
M_n = \frac{\text{grams of monomer}}{\text{moles of initiator}} \quad (1)
\]
A narrow molecular weight distribution polymer \((M_w/M_n \leq 1.1)\) can be obtained by living anionic polymerization given a comparable or faster rate of initiation \((R_i)\) relative to propagation \((R_p)\); this will ensure that all polymer chains grow for the same period of time. The molecular weight distribution is related to the degree of polymerization by the following equation:

\[
\frac{X_w}{X_n} = 1 + \frac{X_n}{(X_n + 1)^2} \approx 1 + \frac{1}{X_n}
\]  

(2)

The second approximation is valid for high molecular weights. It is noteworthy that since the relative breath of the distribution decreases as the degree of polymerization increases, it is easier to obtain narrow molecular weight distribution polymers of higher molecular weights. For instance, a polystyrene of \(M_n = 20000\) g/mol has a degree of polymerization \(X_n = 20000/104 = 192\). If we assume that the polymer has a Poisson distribution, the calculated molecular weight distribution for this polymer is \(X_w/X_n = 1.00\). In contrast, a polystyrene of \(M_n = 2000\) g/mol has a degree of polymerization \(X_n = 19.2\), and \(X_w/X_n = 1.05\). The values reported in the present document are the actual values obtained from the size exclusion chromatographic analyses. It is recognized that in some cases this number can be lower than the calculated value for a Poisson distribution polymer with that degree of polymerization, possibly due to experimental errors in the measurement, but we consider that it is of utmost importance to report the actual values obtained.

Obtaining a narrow molecular weight distribution polymer is not an indication of the “livingness” of the reaction; it is possible to obtain narrow molecular weight distribution polymers in systems that are not living. Also, a living polymerization does not guarantee a narrow molecular weight distribution, since broad molecular weight
polymers can be prepared by living anionic polymerization by using a less reactive initiator (such as $n$-butyllithium), a mixture of initiators or adding initiator continuously during the polymerization. Quirk and Lee critically reviewed the experimental criteria for living polymerization and these can be summarized as follows:

1. Polymerization continues until all the monomer has been consumed. Further addition of monomer results in continued polymerization.

2. The molecular weight ($M_n$) increases linearly with conversion (linear plot of $M_n$ versus % conversion).

3. The number of active centers is constant and independent of conversion.

4. The molecular weight can be controlled by the stoichiometry of the reaction.

5. Narrow molecular weight distribution polymers are obtained.

6. Block copolymers can be formed quantitatively by sequential monomer addition.

7. Quantitative end-functionalization of polymers.

8. The plot of rate of propagation as a function of time (equation 3) must be linear.

\[
\ln \left( \frac{M_0}{M} \right) = k_{\text{obs}} t
\]  

(3)

9. From a combination of criteria 2 and 8, the plot of the left hand side of equation 4 versus time must be linear.

\[
\ln \left( 1 - \frac{[I]}{[M]} X_n \right) = -k_p [I]_0 \cdot t
\]  

(4)

In general, except for the last criterion which indicates the absence of both chain transfer and chain termination, none of the criteria by itself is adequate to determine the living nature of a polymerization reaction. These criteria must be used with care, taking
into account their limitations and sensitivity with respect to chain transfer and chain termination reactions.

1.1.1. Monomers

The monomers that can be polymerized anionically are classified in two categories: (1) unsaturated monomers with one or more double bonds such as vinyl, diene and carbonyl-type monomers; and (2) cyclic monomers which can undergo ring opening reactions with nucleophiles (for example epoxides, cyclic sulfides, cyclic siloxanes and lactones). In the case of vinyl monomers, the presence of electron-delocalizing or electron-withdrawing substituents (such as aromatic rings, double bonds, carbonyl, ester, cyano, sulfoxide, sulfone and nitro groups) in the double bond is necessary in order to stabilize the negative charge that develops in the transition state as shown in equation 5.

\[
\begin{array}{c}
\text{R}^\ominus \\
\text{H}_2\text{C} & \overset{X}{\overset{Y}{\bigg|}} \\
\text{RC} & \overset{\delta^-}{\overset{\delta^-}{\bigg|}} \\
\text{Y} & \text{X} \\
\end{array}
\]

\[
\begin{array}{c}
\text{R}^\ominus \\
\text{H}_2\text{C} & \overset{X}{\overset{Y}{\bigg|}} \\
\text{RC} & \overset{\delta^-}{\overset{\delta^-}{\bigg|}} \\
\text{Y} & \text{X} \\
\end{array} \rightarrow \begin{array}{c}
\text{RCH}_2 \\
\text{C} \ominus \\
\end{array}
\] (5)

These substituents must be stable to the reactive anionic chain ends; relatively acidic or proton donating groups such as amino, hydroxyl, phenol, carboxyl or acetylene must not be present or must be protected by conversion to suitable derivatives and deprotected after polymerization.\(^{21}\) For instance, hydroxyl, phenol and amine functional groups can be protected by conversion to the corresponding silyl derivatives and deprotected by a mild hydrolysis after polymerization.

The reactivity of the monomers is closely related to the stability of the corresponding propagating carbanionic species. The stability of an anion can be deduced
from the $pK_a$ of the corresponding conjugate acid. The least reactive monomers are the ones that form the least stable anions, i.e. have the highest $pK_a$ values for the corresponding conjugate acids. More reactive initiators are required to initiate polymerization of these monomers. In general, the monomer and initiator must have a similar reactivity. Initiators that are too reactive lead to undesired side reactions, while less reactive initiators will have an inefficient or slow initiation leading to broader molecular weight distributions. The stability of the chain end must also be taken into account in the synthesis of block copolymers by sequential monomer addition; only less reactive monomers (higher $pK_a$) can initiate polymerization of more reactive monomers with more stable propagating anions (lower $pK_a$). For example, poly(styryl)lithium ($pK_a \sim 43$) can initiate the polymerization of methyl methacrylate ($pK_a \sim 30-31$), but not vice versa. The $pK_a$ values for the conjugate acid of some common monomers are listed in Table 1.1.$^{22,23}$

Table 1.1. List of $pK_a$ values of the conjugate acids of the anionic propagating species for some common monomers in DMSO.

<table>
<thead>
<tr>
<th>Monomer</th>
<th>$pK_a$ of conjugate acid in DMSO</th>
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<td>Ethylene$^{22}$</td>
<td>56</td>
</tr>
<tr>
<td>Dienes$^{22}$</td>
<td>44</td>
</tr>
<tr>
<td>Styrene$^{22}$</td>
<td>43</td>
</tr>
<tr>
<td>Alkyl methacrylates$^{23}$</td>
<td>30-31</td>
</tr>
<tr>
<td>Oxiranes$^{22}$</td>
<td>29-32</td>
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<td>Thiiranes$^{22}$</td>
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1.1.2. Nature and stability of organolithium compounds

Of all alkali metals, lithium is unique in that it exhibits the highest electronegativity and the smallest covalent and ionic bond radii, along with low-lying, unoccupied p-orbitals available for bonding. In addition to these properties, organolithium compounds possess their distinctive characteristics because of the nature of the C-Li bond which exhibits dual properties of both covalent and ionic bonds; they are unique in that 1,3-dienes can be polymerized to polydienes with high 1,4 microstructure.

In general, organolithium compounds are stable in hydrocarbon solvent at room temperature in the absence of impurities such as oxygen, moisture or carbon dioxide. Poly(styryl)lithium reacts with molecular oxygen to produce a mixture of products as shown in equation 6, and with carbon dioxide to produce the carboxylated polymer, dimeric ketone and trimeric alcohol as shown in equation 7.

\[
\text{PLi} + \text{O}_2 \xrightarrow{\text{ROH}} \text{P-P} + \text{P-O-O-P} + \text{P-O-O-H} + \text{P-O-H} \quad (6)
\]

\[
\text{PLi} + \text{CO}_2 \xrightarrow{\text{H}_3\text{O}^+} \text{PCOOH} + \text{P}_2\text{CO} + \text{P}_3\text{COH} \quad (7)
\]

At high temperatures the decomposition of polymeric organolithium compounds has been observed. The principal mode of the decomposition is loss of lithium hydride to form a double bond at the chain end; in the case of poly(dienes), the macrodiene formed can react with active chains to form dimeric and trimeric species.

Alkylolithium initiators and polymeric organolithium compounds are not stable in the presence of ethers. Thus, \(n\)-butyllithium reacts with tetrahydrofuran (THF) producing ethylene and the lithium enolate of acetaldehyde. Likewise, poly(styryl)lithium decomposes in the presence of pure THF as shown in Scheme 1.1.
Scheme 1.1. Decomposition of poly(styryl)lithium in THF.

1.1.3. Initiation

As mentioned earlier, the reactivity of the initiator must be comparable to the reactivity of the monomer; this provides a fast rate of initiation \( (R_i) \) relative to the rate of propagation \( (R_p) \), which allows the possibility of obtaining narrow molecular weight distribution polymers \( (M_w/M_n \leq 1.1) \).\(^{39}\) In general, the initiation of anionic polymerization of styrene and diene monomers is effected with alkyl lithium compounds such as sec-butyllithium and \( n \)-butyllithium.

The rate of initiation of polymerization with alkyl lithium compounds depends on the initiator, solvent, monomer and temperature. Alkyl lithium compounds are aggregated in hydrocarbon solution and the degree of aggregation depends on the structure of the initiator.\(^{25}\) Initiators containing bulky alkyl groups (e.g. sec-butyllithium) are less aggregated and hence more reactive than their linear counterparts (\( n \)-butyllithium). In general, the reactivity of the organolithium varies inversely with its degree of aggregation. The relative reactivities of organolithium initiators in hydrocarbon
solution, with the average degree of aggregation indicated in parenthesis, are shown below:\(^3\)

For styrene polymerization:
menthyllithium (2) > sec-BuLi (4) > i-PrLi (4-6) > i-BuLi > n-BuLi (6) > t-BuLi (4)

For diene polymerization:
menthyllithium (2) > sec-BuLi (4) > i-PrLi (4-6) > t-BuLi (4) > i-BuLi > n-BuLi (6)

In aromatic solvents, the kinetics of the initiation reaction exhibit a first-order dependence on monomer concentration and a fraction-order dependence on the initiator concentration. This fractional-order (1/n) dependence was found to be inversely related to the degree of aggregation of the initiator (n). For example n-butyllithium, which is aggregated predominantly into hexamers in aromatic and aliphatic hydrocarbon solutions, exhibits a one-sixth-order dependence on the initiator concentration in benzene as shown in equation 8.\(^{40}\)

\[
R_i = k_{obs} [BuLi]^{\frac{1}{6}} [M] \tag{8}
\]

This has been rationalized as an indication that the species that reacts with the monomer must be in the unassociated form. In contrast, this inverse correspondence between the degree of aggregation and the reaction order dependence is not observed for aliphatic solvents,\(^{41}\) i.e. a first order dependence on initiator concentration is observed. It appears that in aliphatic solvents the initiation process involves direct reaction of the aggregated species with the monomer.

1.1.4. Propagation

The kinetics of propagation of polymeric organolithium compounds are complicated by the presence of different propagating species with diverse degrees of
aggregation. In non-polar solvents most species are aggregated or unassociated, whereas in polar solvents there are ion pairs, contact and solvent-separated, and free ions present. The different species exist in equilibrium and each of these species can react with monomer at its own rate as illustrated in the Winstein spectrum in Scheme 1.2 where Mt represents the metallic counterion and [M] is the concentration of monomer.

\[
\text{(RMt)}_n \quad \text{n RMt} \quad \text{R}^-\text{Mt}^+ \quad \text{R}^-\text{Mt}^+ \quad \text{R}^- + \text{Mt}^+
\]

Scheme 1.2. Winstein spectrum of ionic species.

The rate of propagation of styrene and dienes with lithium as counterion exhibits a first order dependence on monomer concentration. The total chain end concentration of poly(styryl)lithium, \([\text{PLi}]_0\), shows fractional order dependence related to the degree of aggregation of the chain ends. In hydrocarbon solvent poly(styryl)lithium is mostly aggregated in dimers; hence, the reaction order dependence on total chain end concentration is one-half as shown in equation 9.

\[
R_p = \frac{-d[S]}{dt} = k_{obs}[\text{PLi}]_0^{1/2}[S] \tag{9}
\]

Although fractional order dependencies on the concentration of active centers are observed in the polymerization of dienes, there has been controversy for many years with respect to the degree of aggregation of these species. Therefore, a general correlation between the kinetic order dependence and the degree of aggregation could
not be established for the polymerization of dienes. Recently, the degree of aggregation of poly(butadienyl)lithium has been reinvestigated. Fetters and coworkers,\textsuperscript{45,46} studied the degree of aggregation of poly(butadienyl)lithium (PBDLi) in benzene using small angle neutron scattering, as well as dynamic and static light scattering. They reported that the primary degree of association is dimeric, and that a small amount of the PBDLi chains are aggregated into higher order species \((n > 100)\). Sato and coworkers\textsuperscript{47,48} combined dynamic and static light scattering measurements with previous polymerization kinetics studies. The results were consistent with poly(butadienyl)lithium aggregated in tetramers, and a minor component \((< 1 \text{ wt } \%)\) corresponding to aggregates consisting of a large number of PBDLi chains was detected. Allgaier and coworkers\textsuperscript{49-51} studied the polymerization of butadiene initiated with \textit{tert}-butyllithium in \(d_{16}\)-heptane. By combining \textit{in situ} \(^1\text{H} \) NMR and small angle neutron scattering techniques, they were able to determine quantitatively the degree of aggregation during all stages of the polymerization. At early reaction stages, highly aggregated species were found \((n \approx 100)\). The degree of aggregation decreased with increasing chain size and as the polymerization proceeded, it leveled off to a value of 4. It was also shown that during the polymerization, these aggregates coexisted with small amounts of even larger aggregates.

In summary, the aggregation behavior of PBDLi chain ends during the polymerization is very complex and it depends on concentration and molecular weight (conversion). Most evidence indicates that tetramers are the predominant aggregates. It has been concluded that the degree of aggregation cannot be directly related to the kinetic order dependency on the concentration of active centers and that both aggregates and dissociated species participate in the propagation reaction.\textsuperscript{49}
1.1.5. Effect of Lewis bases

The addition of Lewis bases such as tetrahydrofuran, diethyl ether and triethylamine increases the rate of initiation and the rate of propagation\textsuperscript{52} in alkyllithium-initiated polymerizations because it promotes the dissociation of organolithium aggregates.\textsuperscript{53}

It is important to note that organolithium compounds decompose in the presence of THF, as explained Section 1.1.3; therefore, these additives must be used in small amounts. Also, the ability of organolithium compounds to yield polydienes with high 1,4 microstructures is lost in the presence of Lewis bases.\textsuperscript{3,54}

1.1.6. Effect of alkali metal alkoxides

It has been confirmed that, in general, lithium alkoxides decrease the rate of propagation for styrene\textsuperscript{55} and butadiene\textsuperscript{56} polymerization initiated by alkyllithium compounds in hydrocarbon solution. Addition of other alkali metal alkoxides, such as sodium, potassium, rubidium and cesium tert-butoxide, increase the rate of propagation in alkyllithium-initiated polymerizations of styrene and butadiene\textsuperscript{57} because there is an exchange of the counterion in the propagating species from lithium to another alkali metal (M) as shown in reaction 10. Consistently, this also results in an increase of the amount of polybutadiene with 1,2-microstructure.

\begin{equation}
\begin{align*}
P\text{-Li} + \text{RO-Mt} & \rightleftharpoons \text{P-Li} & \text{Mt-OR} & \rightleftharpoons \text{P-Mt} + \text{RO-Li} \\
P_1\text{-Li} + P_2\text{-Mt} & \rightleftharpoons \text{P}_1\text{-Li} & \text{Mt-P}_2 & \rightleftharpoons \text{P}_1\text{-Mt} + P_2\text{-Li}
\end{align*}
\end{equation}
1.1.7. Effect of lithium halides

The presence of lithium halides in the polymerization media reduces the reactivity of organolithium compounds and increases their selectivity.\textsuperscript{58-61} Van Beylen and coworkers\textsuperscript{62} reported that the addition of LiCl reduced the rate of propagation of PSLi in tetrahydropyran at low concentrations of PSLi, and accelerated it at higher PSLi concentrations. The most significant use of lithium chloride as an additive is in the anionic polymerization of polar monomers, such as alkyl methacrylates. In order to avoid side reactions and effect a controlled polymerization, these reactions must be carried out with a less reactive initiator like 1,1-diphenylhexyllithium in THF at -78 °C. The addition of lithium halides creates cross-associated species as shown in equation 11 and provides better control of the polymerization.\textsuperscript{63,64}

\begin{equation}
\text{RC}\underset{\text{Li}}{\cdots}\text{Li}\underset{\text{Br}}{\cdots}\text{C}
\end{equation}

(11)

1.2. End group functionalization

Due to the absence of chain termination and chain transfer steps, alkyllithium-initiated anionic polymerization provides an excellent methodology for the preparation of a variety of \(\omega\)-chain-end functionalized polymers by reaction of the living carbanionic chain ends with appropriate electrophilic functionalizing agents.\textsuperscript{3,5,6}

1.2.1. Thiol-functionalized polymers

Among the types of functional polymers of synthetic interest are polymers with end-functional thiol groups (P-SH). These have found a range of applications including
stabilization of gold nanoparticles,\textsuperscript{65,66} spontaneous chemisorption onto gold surfaces to form monolayers,\textsuperscript{67,68} preparation of semiconductor cadmium sulfide (CdS) nanocomposites,\textsuperscript{72} and functional group attachment by chemical ligation,\textsuperscript{70} as well as potential applications for chain extension, reversible dimerization,\textsuperscript{71} block copolymer formation by chain transfer,\textsuperscript{72} and cross-linking reactions.\textsuperscript{73}

Thiol end-functionalized polymers have been prepared indirectly by atom transfer radical polymerization (ATRP). Hilborn and coworkers\textsuperscript{74} prepared polystyrene by ATRP; the resulting bromine end-group was reacted with thiourea to prepare an isothiouronium salt. Treatment of this salt with a base effected cleavage to form the thiol. The polydispersity of the polymers obtained was not narrow ($M_n/M_w > 1.1$) and the degree of functionality calculated from the $^1\text{H}$ NMR spectrum was 95\%. Tsarevsky and Matyjaszewski\textsuperscript{75} used a difunctional initiator containing a disulfide bond to prepare disulfide-containing polystyrene by ATRP. The thiol-functionalized polymers were obtained by cleavage of the internal disulfide bond by reduction with 2,3-dihydroxy-1,4-butanethiol. Also, dibromo-terminated polystyrene was prepared using 2,6-dibromohexanediol as a difunctional initiator. The bromine end groups were converted to thiol functionality by reaction with thiodimethylformamide followed by methanalysis.

There are few reports describing the anionic synthesis of well-defined, $\omega$-thiol-functionalized polymers. Nakahama and coworkers\textsuperscript{71} prepared $\omega$-thiol-functionalized polystyrenes and polyisoprenes by termination of the corresponding anionic living polymers with tert-butylidimethylsilyl-3-chloropropyl sulfide. Although these functionalization reactions were reported to be quantitative, the polymers had to be deprotected under nitrogen to obtain the desired thiol functionality as shown in Scheme
1.3. The resulting deprotected \( \omega \)-thiol-functionalized polymers were reported to undergo oxidative dimerization upon SEC analysis. Furthermore, the reactions were carried out in the polar solvent tetrahydrofuran (THF) at -78 °C. As mentioned before, the use of THF as solvent for the reaction is undesirable since poly(styryl)lithium chains decompose in the presence of THF; in addition, the unique ability of alkyl lithium compounds to produce polydienes with high 1,4 microstructure is lost in the presence of THF. Quantitative functionalization was confirmed by reacting the thiol functionalized polymer with acrylonitrile in the presence of sodium methoxide immediately after deprotection. The product from the Michael addition reaction was characterized by \(^1\)H NMR spectroscopy and elemental analyses. The thiol-functionalized polymer was treated with iodine as an oxidizing agent and the corresponding dimer was obtained in ca. 95 % yield.

![Scheme 1.3. Reaction of living polymeric organolithium compound with tert-butyldimethylsilyl-3-chloropropyl sulfide, a substituted haloalkane with a protected thiol functionality, and subsequent deprotection to obtain thiol-functionalized polymer.](image)

The reaction of polymeric organolithium compounds with thiiranes (episulfides, alkylene sulfides) is reported to be a viable route for the preparation of thiol-functional polymers. Tung and co-workers described the preparation of \( \omega \)-thiol- and \( \alpha,\omega \)-

---

14
dithiol-functionalized polybutadienes by reaction of poly(butadienyl)lithium and \(\alpha,\omega\) dilitiumpolybutadiene, respectively, with excess propylene sulfide or ethylene sulfide in the presence of THF. The thiol end-functionalized polybutadienes were used as chain transfer agents in the free radical polymerizations of styrene, styrene/acrylonitrile, and methyl methacrylate. The efficiency of the functionalization reaction was determined indirectly by the amount of block copolymer produced in a thermally initiated free radical polymerization of styrene and the thiol-functionalized polymer.

Stouffer and McCarthy\(^6^7\) functionalized poly(styryl)lithium in benzene and THF by terminations with stoichiometric and excess amounts of propylene sulfide to prepare \(\omega\)-thiol-functionalized polystyrene and polystyrene-\textit{block}-poly(propylene sulfide), respectively. The resulting polymers were used to prepare polymer monolayers by spontaneous adsorption on gold surfaces.

Kim and coworkers\(^6^9\) prepared telechelic \(\alpha,\omega\)-dithiol functionalized polystyrene by reaction of an unspecified amount of ethylene sulfide with \(\alpha,\omega\)-dilithiopolystyrene synthesized with lithium naphthalenide in the presence of THF (95/5, vol/vol, benzene/THF). Thiol functionalization yields were reportedly > 98 % as determined by \(^{1}\text{H}\) NMR analyses. These authors stated that formation of poly(propylene sulfide) blocks was unavoidable under their conditions.

A number of research groups have utilized the reactions of polymeric organolithium compounds with excess propylene sulfide or ethylene sulfide to prepare the corresponding block copolymers. Nevin and Pearce\(^7^6\) polymerized styrene and \(\alpha\)-methylstyrene with \(\eta\)-butyllithium and sodium naphthalenide in THF at \(-78\) °C. Ethylene sulfide and propylene sulfide were added to the resulting poly(styryl)lithiums and \(\alpha,\omega\) disodiopolystyrene to prepare the diblocks and triblocks, respectively. Morton and
coworkers reacted poly(α-methylstyrene) with propylene sulfide, followed by coupling of the active lithium thiolate chain ends with phosgene to prepare a triblock copolymer poly(α-methylstyrene)-b-poly(propylene sulfide)-b-poly(α-methylstyrene). They also polymerized isoprene and butadiene with a soluble dilithium initiator followed by addition of ethylene sulfide to prepare the triblocks, poly(ethylene sulfide)-b-poly(diene)-b-poly(ethylene sulfide).

In all of this previous research on the functionalization of polymeric organolithium compounds with propylene sulfide and ethylene sulfide, the mechanisms of these functionalization reactions have not been elucidated. In addition, the efficiency of these functionalizations and the question of whether oligomerization occurs have not been determined, especially in hydrocarbon solution. The only mechanistic information on the reactions of organolithium compounds with thiiranes is derived from studies of the reactions with simple alkylithium and aryllithium compounds. The reaction of simple organolithium compounds with thiiranes was first studied by Bordwell and coworkers. The "sulfur extrusion" reaction was reported to proceed by attack of the anion on sulfur to form a trigonal-bipyramidal intermediate, ring-opening to form an intermediate primary carbanion, and finally 1,2-elimination of the alkyl or aryl thiolate to form an olefin corresponding to the thiirane, as shown in Scheme 1.4b. Schuetz and Jacobs isolated alkyl allyl ethers and lithium mercaptides from the reactions of butyllithium and phenyllithium with 2-alkoxymethylthiiranes. Morton and Kammereck confirmed the results of Bordwell et al. for the reaction of ethyllithium with 2-methylthiirane at -78 °C in THF by identifying ethanethiol and propylene as the exclusive products. Trost and Ziman as well as Bonini and coworkers have shown that the desulfurization reaction of episulfides with n-butyllithium forms the corresponding alkenes derived from the
episulfides with complete stereospecificity. On the basis of these results and experiments involving generation of the proposed intermediates, 1-lithio-2-alkylthioalkanes, Trost and Ziman\textsuperscript{83} concluded that the trigonal-bipyramidal intermediate fragments via a concerted (Scheme 1.4a) rather than stepwise process (Scheme 1.4b) to give the alkene and alkylthiolate directly. To date, the sulfur extrusion mechanism has been the accepted mechanism for the reaction of organolithium compounds with thiiranes irrespective of the structure of the carbanion. However, it is not obvious that this reaction pathway will apply, for example, when more stable organolithium compounds are reacted with episulfides.

![Scheme 1.4. Mechanisms for the reaction of alkyllithium compounds with propylene sulfide by sulfur extrusion: (a) direct fragmentation of the trigonal, bipyramidal sulfurane intermediate; and (b) ring-opening to form a 1-lithio-2-alkylthioalkane intermediate followed by elimination of the alkene and formation of the thiolate anion.](image)

With regard to thietanes (four-membered cyclic sulfides), Morton and Kammereck\textsuperscript{78,82} reported that ethyllithium reacts, in THF at -78 °C, with thiacyclobutane (trimethylene sulfide) and 2-methylthiacyclobutane by attack of the anion on sulfur followed by ring opening to form a carbanion as shown in Scheme 1.5. In contrast to the reaction of ethyllithium with propylene sulfide, no elimination products such as cyclopropane were observed and the resulting propagating species was a carbanion that reacted with excess trimethylene sulfide to form polymer. The reaction of trimethylene
sulfide with lithium ethanethiolate as initiator did not yield any polymer. Further evidence of the carbanionic nature of the product was its ability to initiate polymerization of vinyl monomers like styrene. It was concluded that the alkylolithium-initiated anionic polymerization of thietanes in ether medium proceeds exclusively by carbanions.

\[
\begin{align*}
R^+& \text{Li}^+ + \quad \begin{array}{c}
S \\
R-(SCH_2CH_2CH_2)_n\text{Li}
\end{array} \\
\rightarrow & \quad R-SCH_2CH_2CH_2\text{Li} \\
\rightarrow & \quad R-(SCH_2CH_2CH_2)_n\text{Li}
\end{align*}
\]

Scheme 1.5. Reaction of alkylolithium compounds with trimethylene sulfide.

1.2.2. Functionalization by hydrosilation

Hydrosilation is the addition reaction of silicon hydrides to multiple bonds, such as carbon-carbon double bonds, in the presence of a catalyst as shown in equation 12.

\[
R^+ + \text{HSIR}'_3 \xrightleftharpoons[catalyst]{\text{catalyst}} R-SiR'_3
\]

The most widely used catalysts are based on Group VIII transition metals such as platinum (Pt), rhodium (Rh), ruthenium (Ru), nickel (Ni) and palladium (Pd). In particular, platinum (Pt) catalysts have been demonstrated to be exceptionally efficient in hydrosilation reactions. Platinum-catalyzed hydrosilations are regiospecific and yield only the anti-Markovnikov addition product, meaning hydrogen adds to the most substituted carbon as shown in equation 12. The most common platinum catalysts used are hexachloroplatinic acid, \( \text{H}_2\text{Pt}_6\text{Cl}_6 \cdot 6\text{H}_2\text{O} \), referred to as Speier’s catalyst, and Karstedt’s catalyst, \( \text{Pt}_2\{[(\text{CH}_2= \text{CH})\text{Me}_2\text{Si}]_2\text{O}\}_3 \). The selectivity of the reaction towards
different alkenes is shown in equation 13, with less substituted alkenes being more reactive towards hydrosilation.\(^{85,86}\)

\[
\begin{align*}
H & \quad \begin{array}{c}
C \equiv C \\
\text{CH}_2
\end{array} & > & H \quad \begin{array}{c}
C \equiv C \\
\text{R}
\end{array} & > & \begin{array}{c}
R \quad \begin{array}{c}
C \equiv C \\
\text{R}
\end{array}
\end{array}
\end{align*}
\]

The first accepted general mechanism for transition metal-catalyzed hydrosilation was proposed in 1965 by Chalk and Harrod.\(^90\) This mechanism (see Scheme 1.6) consists of the coordination of the olefin to the metal centre, followed by oxidative addition of the hydrosilane and then alkene insertion into the metal-hydride bond. The complex then reacts with excess olefin, regenerating the catalyst and forming the organosilicon compound by Si-C reductive elimination. A modified Chalk-Harrod mechanism\(^91\) was later proposed, in which the metal coordination and oxidative addition proceeds the same way, but alkene insertion is into the metal-silyl bond followed by C-H reductive elimination as illustrated in Scheme 1.6.

Hydrosilation reactions have been used to prepare functionalized polymers. Riffle and coworkers\(^92\) prepared epoxy-functionalized oligomers by hydrosilation of silyl hydride-functionalized, hydrogenated polybutadiene with allyl glycidyl ether in the presence of chloroplatinic acid. Quantitative functionalization was determined by \(^1\)H NMR spectroscopy and titration of the epoxy groups with hydrobromic acid. No other functionalizations were reported, although they recognized the versatility of the hydrosilation reaction, given that the silyl hydride-functionalized polymers can react with a variety of allylic compounds containing different functional groups such as epoxy, cyano, ester and keto.
Loos and Müller\textsuperscript{93} prepared maltoheptaose-\textit{b}-polystyrene copolymers by hydrosilation of anionically synthesized, silyl-hydride terminated polystyrene with triecosaacetyl-\textit{N}-allylmaltoheptaonamide in the presence of different rhodium, cobalt and platinum catalysts. The reaction was taken to completion as verified by the disappearance of the SiH peak (2156 cm\textsuperscript{-1}) in the IR spectrum.

![Scheme 1.6. Chalk-Harrod and modified Chalk-Harrod mechanisms for hydrosilation of alkenes.](image)

In 2005, Quirk and coworkers\textsuperscript{94} proposed a new general functionalization method by the combination of anionic polymerization and hydrosilation chemistry. In the first step a \(\omega\)-silyl hydride functionalized polymer is prepared by termination of the living polymeric organolithium anion with dimethylchlorosilane. The silyl hydride-functionalized
polymer is then reacted with a substituted alkene compound by platinum catalyzed hydrosilation to yield the corresponding functionalized polymers as illustrated in Scheme 1.7.

The utility of this method was demonstrated by preparing amine-functionalized polystyrene by reaction of ω-silyl hydride functionalized polystyrene with allyl amine. In addition to the inherent advantages of a general functionalization method, which allows different substituted vinyl and allyl compounds to be introduced to the same polymer, the ω-silyl hydride functionalized polymer is stable towards diverse functional groups that are reactive with the anionic chain ends. Consequently, functional groups such as amino, carboxyl, phenol and nitro do not need to be protected during functionalizations by hydrosilation.

![Scheme 1.7. General functionalization methodology by the combination of living anionic polymerization and hydrosilation.](attachment:image)

In contrast to the hydrosilation of organic unsaturated compounds, the hydrosilation of unsaturated organosilicon compounds, such as vinylsilanes, has received very little attention. In general, vinyl-substituted compounds are less susceptible to
hydrosilation than allyl-substituted derivatives. On the contrary, vinyl silanes have been shown to be more reactive than allyl silanes. The reaction of vinyl silanes with silyl hydrides proceeds as shown in equation 14.

\[
R_3\text{SiH} + \text{SiR'}_3 \rightarrow R_3\text{Si} - \text{SiR'}_3 + \text{SiR}_3 \quad \alpha\text{-adduct} \quad \beta\text{-adduct} \quad (14)
\]

The regioselectivity of the reaction depends on the substituents on the silicon atoms as well as the catalyst used. In general, platinum-catalyzed hydrosilation of silyl hydrides with vinyl silanes takes place according to anti-Markovnikov addition giving \(\beta\)-adducts. A characteristic feature of the hydrosilation of vinyl silanes is substituent exchange at the silicon atom; the vinyl/H exchange shown in equation 15 leads to the formation of at least two and sometimes four products from hydrosilation.96,97

\[
R_3\text{SiH} + \text{SiR'}_3 \leftrightarrow \text{SiR}_3 + R'_3\text{SiH} \quad (15)
\]

1.2.3. Trialkoxysilane-functionalized polymers

There is interest in the use of silica as a reinforcing agent in rubbers due to the superior properties with silica compared to carbon black formulations; these improvements include lower rolling resistance and tread wear while maintaining comparable wet traction.98,99 However, lack of filler-polymer interaction for hydrocarbon elastomers leads to poor strength properties and strong particle-particle interactions resulting in formation of agglomerates in the polymer. This causes difficulties in filler dispersion and compound processability, which ultimately results in a detrimental effect on the properties of the filled rubber.100 In order to overcome these limitations, it is
necessary to increase the polymer-filler interaction and reduce the polarity of the silica surface. One way to achieve this is by addition of trialkoxysilane-functionalized polymers which can react with the surface of the silica reducing its polarity and promoting polymer-filler interaction.\textsuperscript{101,102} Besides the tire industry, there are other applications of trialkoxysilane-functionalized polymers such as the synthesis of hybrid glasses\textsuperscript{103} and star polymers by sol-gel reactions,\textsuperscript{104,105} star polymers by linking reactions\textsuperscript{106} and formation of two-dimensional polymeric nanomaterials crosslinked at the air/water interface.\textsuperscript{107,108}

There are few examples of well-defined, anionically synthesized trialkoxysilane-functionalized polymers. For example, Soutar and coworkers\textsuperscript{109} reacted poly(butadienyl)lithium (PBDLi) with a small molar excess of 3-chloropropyl(trimethoxy)silane in hexane/THF at low temperatures (-70 °C and -20°C) by normal and inverse addition, respectively. The main product (85 % yield) had a terminal -Si(OCH\textsubscript{3})\textsubscript{2}(CH\textsubscript{2})\textsubscript{3}Cl function, resulting from the displacement of one methoxy group (product 4 in Scheme 1.8). Polymer with double the molecular weight (dimer) was also formed by the displacement of two methoxy groups. Poly(butadienyl)lithium was also terminated with tetramethoxysilane, which resulted in a mixture of siloxy-functionalized polymers with -Si(OCH\textsubscript{3})\textsubscript{3}, bicoupled product with -Si(OCH\textsubscript{3})\textsubscript{2} links and products from further coupling as observed by polymodal GPC curves.

![Scheme 1.8. Products from the reaction of polymeric organolithium compounds with 3-chloropropylalkoxysilane.](image-url)
Derouet and coworkers\textsuperscript{110} reacted poly(isoprenyl)lithium (PILi) with various alkoxy silanes. For the reaction of PILi with tetramethoxysilane and tetraethoxysilane, the result was a mixture of products obtained from substitution of one, two or three methoxy or ethoxy groups with the poly(isoprenyl) chains. The composition of products was determined by \textsuperscript{1}H and \textsuperscript{29}Si NMR and was found to depend on the ratio of PILi to tetraalkoxysilane. The highest yield of trialkoxysilyl-functionalized polyisoprene (50 \%) was obtained from the reaction of stoichiometric amounts of PILi and tetramethoxysilane. It was not possible to prepare trialkoxysilyl-functionalized polyisoprene from the reaction of PILi with 3-chloropropyltrimethoxysilane; it was observed that the carbanion attack was exclusively on the silicon atom and not on the \(\alpha\)-chlorinated carbon. Polymer grafted silicas were synthesized by coupling the resulting functionalized polymers with silanol groups on a silica surface.

Long and coworkers\textsuperscript{104} prepared poly(styryl)lithium (PSLi) in THF at -78 °C and reacted it with 1.5 molar equivalents of \(p\)-(chloromethylphenyl)trimethoxysilane to form phenyltrimethoxysilyl-functionalized polystyrene as shown in equation 16. Although narrow molecular weight distribution polymers were not obtained (\(M_w/M_n = 1.13 - 1.22\)), high yields (> 99 \%) of the desired product were confirmed by \textsuperscript{1}H NMR spectroscopy and TLC. \textsuperscript{29}Si NMR results confirmed that displacement of the methoxy group by poly(styryl)lithium did not occur. The resulting polymers were used to prepare star polymers by a sol-gel process.\textsuperscript{105} Later, Long and coworkers\textsuperscript{111} reported that a larger excess of end-capping agent (10 molar equivalents) was needed to achieve quantitative functionalization of higher molecular weight polymers (10,000 g/mol). It is noteworthy that the reaction was carried out in THF at -78 °C; as noted earlier the use
of THF as polymerization media is not desirable because of the reactivity of the polymeric anionic chain ends towards THF.

![Equation 16]

Ohata and coworkers\(^{112}\) reacted living PSLi with different amounts of 4-triethoxysilyl-\(\alpha\)-methylstyrene (6.6 – 19.7 molar equivalents) in THF at -78 °C as shown in equation 17. Although no polystyrene homopolymer was detected by TLC, the resulting polymers did not exhibit narrow molecular weight distributions (\(M_w/M_n = 1.17 – 1.28\)) and oligomerization of the substituted \(\alpha\)-methylstyrene was observed (m = 3.3 – 6.6).

![Equation 17]

Quirk and coworkers\(^{113,114}\) added PSLi and PBDLi to benzene solutions of 3-chloropropyltriethoxysilane at room temperature. This resulted in formation of approximately 12 and 6 % dimer (product 2 in Scheme 1.8) respectively, as determined by SEC. Addition of lithium chloride did not improve the functionalization efficiency; however, when the PSLi chain end was end-capped with 1,1-diphenylethylene, no dimer was formed. The addition of PSLi and PBDLi to 3-glycidoxypropyltrimethoxysilane was also attempted and this resulted in formation of 48 and 56 % dimer, respectively. End-capping of the PSLi chains with 1,1-diphenylethylene decreased the dimer yield to 20 %. Again the addition of lithium chloride did not reduce the amount of dimer formed.
However, in the functionalization of PSLi in the presence of 5 equivalents of lithium 2,3-dimethyl-3-pentoxide, the amount of dimer was only 3%.

Oku and coworkers added a PSLi solution dropwise to a solution of 3-chloropropyltriethoxysilane. When the reaction was effected in benzene at room temperature, the main product (75%) was from the displacement of an ethoxy group by the PSLi anion (product 4 in Scheme 1.8). The reaction at 0 °C in benzene/THF (3/1) yielded 94% triethoxy-functionalized polystyrene (product 1 in Scheme 1.8).

Lutz and coworkers studied the effects of the following parameters on the functionalization of PSLi, PBDLi and SBRLi (living styrene/butadiene copolymer) with different trialkoxysilyl compounds: nature of the chain end, temperature, effect of additives such as lithium chloride and potassium alcoxides. They confirmed the results obtained by Quirk for the quantitative functionalization of diphenylethylene end-capped PSLi with 3-chloropropyltriethoxysilane. The functionalization of PSLi and PBDLi with 3-chloropropyltriethoxysilane in the presence of ether produced high amounts of coupled products and when LiCl was added no reaction at the chlorine was observed. When other functionalizing agents were used, 3-bromopropyltriethoxysilane or 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane, quantitative functionalization was not achieved and the amount of coupled products was higher. Quantitative substitution of only one ethoxy group to form triethoxysilyl-functionalized polyisoprene was only achieved when PILi was reacted with a large excess (5 molar equivalents) of tetraethoxysilane between 0 and 10 °C.

In summary, due to the reactivity of the propagating polymeric organolithium anion towards the alkoxy group, there has not been much success in the preparation
of well-defined, $\omega$-trialkoxyisilyl-functionalized polymers by living anionic polymerization. There is clearly a need for a method to effect this functionalization reaction.

Recently, Duran and coworkers$^{107,108}$ reported the synthesis of two-dimensional polymeric nanomaterials by crosslinking of triethoxysilane-functionalized polybutadiene-$b$-poly(ethylene oxide), three-armed, star copolymers [(PBD-$b$-PEO)$_3$] and polybutadiene homopolymers (PBD), at the air/water interface. The triethoxysilane-functionalized polymers were obtained by hydrosilation of the pendant double bonds on the polybutadiene block with triethoxysilane in the presence of Karstedt’s catalyst. As mentioned earlier, less substituted alkenes (as in 1,2-polybutadiene) are more reactive towards hydrosilation than more substituted alkenes (as in 1,4-polybutadiene). Therefore, in order to obtain high triethoxysilane functionality, polymers with high 1,2 content (vinyl) were used (76 mol % 1,2-PB in the star, (PBD-$b$-PEO)$_3$, and 89 mol % 1,2-PBD in homopolymer PBD). A conversion of 75 – 85 % of the 1,2-PBD pendant double bonds was reported. Analogous reactions with high 1,4-polybutadiene have not been investigated.

1.2.4. Hydroxyl-functionalized polymers

Hydroxyl-functionalized polymers can be readily prepared by reaction of the living polymeric organolithium anions with ethylene oxide.$^{117,118}$ It has been shown that the reaction of poly(styryl)lithium with excess ethylene oxide in benzene at 25 °C produces $\omega$-hydroxyl-functionalized polystyrene quantitatively without oligomerization of the ethylene oxide.$^{119}$
The lack of oligomerization was determined by the absence of resonance peaks at δ 69-70 and 72-73 ppm in the $^{13}$C NMR spectrum which would be expected for the product from the addition of two units of ethylene oxide (P-CH$_2$CH$_2$O-CH$_2$CH$_2$OH). These results were later confirmed by effecting the functionalization of poly(styryl)lithium in benzene with 3.3 equivalents of $^{13}$C-labeled ethylene oxide. The $^{13}$C NMR of the product showed no resonances corresponding to a second ethylene oxide unit at the chain end; furthermore, MALDI-TOF mass spectrometric analysis of the products showed only one distribution corresponding to the functionalized polystyrene with one unit of ethylene oxide. It was concluded that under these conditions no oligomerization of the ethylene oxide occurred. However, when 10 equivalents of ethylene oxide were added to poly(styryl)lithium, a small peak (ca. 3 %) was observed at 44 m/z units above the main distribution in the mass spectrum of the product corresponding to addition of two ethylene oxide units. This result prompted the reexamination of the oligomerization of ethylene oxide in the functionalization of poly(styryl)lithium in benzene using different amounts of ethylene oxide and longer reaction times. The products were analyzed quantitatively by MALDI-TOF mass spectrometry and $^1$H NMR spectroscopy. No oligomerization was observed using 4 equivalents of ethylene oxide for 12 hours. When 10 equivalents of ethylene oxide were added a small amount (4 %) of oligomerization was detected after 12 hours. After 1 week 5 % of functionalized polymer with two ethylene oxide units was detected. As the reaction time increased, the amount of

$$\text{PSLi} + \overset{\text{12 h}}{\text{C}_6\text{H}_6} \rightarrow \text{PSC}_2\text{H}_2\text{OH}$$

$\text{C}_6\text{H}_6$  $\text{CH}_3\text{OH}$

3-4 eq  25°C

(18)
oligomerization also increased; after 4 weeks, 35% of dimeric oligomer was found and even a small amount of product (5%) corresponding to addition of three ethylene oxide units was detected.

The inability of lithium alkoxides to polymerize ethylene oxide has been explained by their high degree of aggregation (see Table 1.2).\textsuperscript{122,123} However, other alkali metal alkoxides such as sodium and potassium are also aggregated in solution but can effect the polymerization of ethylene oxide.\textsuperscript{124} It was concluded that the degree of aggregation along with the strength of this association impedes the formation of reactive, unassociated species.\textsuperscript{118,121}

Table 1.2 Degree of aggregation of alkali metal alkoxides\textsuperscript{122}

<table>
<thead>
<tr>
<th></th>
<th>cyclohexane</th>
<th>benzene</th>
<th>diethyl ether</th>
<th>THF</th>
<th>Pyridine</th>
</tr>
</thead>
<tbody>
<tr>
<td>lithium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert-butoxide</td>
<td>5.8</td>
<td>6.2, 6.06</td>
<td>5.9</td>
<td>4.1</td>
<td>4.0</td>
</tr>
<tr>
<td>sodium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert-butoxide</td>
<td>8.2</td>
<td>8.3</td>
<td>4.3</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>potassium</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>tert-butoxide</td>
<td>3.9</td>
<td></td>
<td>3.9</td>
<td>4.0</td>
<td></td>
</tr>
</tbody>
</table>

Mays and coworkers\textsuperscript{125} reacted poly(styryl)lithium and poly(butadienyl)lithium with ethylene oxide in benzene. For poly(styryl)lithium reactions no oligomerization was observed after 24 hours of reaction time and addition of two ethylene oxide units was detected for longer reaction times (1 month). These findings confirmed the previous results reported by Quirk et. al.\textsuperscript{119-121} However, for the reaction of poly(butadienyl)lithium with 4 equivalents of ethylene oxide, after 24 hours products with one and two units of ethylene oxide were detected by MALDI-TOF mass spectrometry. These results suggested that the degree of ethylene oxide oligomerization depends on the nature of
the backbone chain. To confirm these results, Quirk et. al.\textsuperscript{126} reinvestigated the reaction of poly(butadienyl)lithium with ethylene oxide. Approximately 12 \% of dimeric ethylene oxide oligomerization was detected by MALDI-TOF mass spectrometry and \textsuperscript{1}H NMR spectroscopy for the functionalization of poly(butadienyl)lithium in benzene with 4 equivalents of ethylene oxide after 12 hours of reaction time. In order to eliminate the oligomerization of ethylene oxide, the reaction was monitored by UV-vis spectroscopy and terminated by addition of degassed methanol immediately after the disappearance of the UV absorption of poly(butadienyl)lithium ($\lambda_{\text{max}} = 284$ nm).

The reaction of poly(styryl)lithium with propylene oxide also yields a hydroxyl-functionalized polymer as shown in equation 19. However, this reaction is complicated by the acidity of the protons on the methyl substituent of the epoxide ring\textsuperscript{127} and the asymmetry of the propylene oxide ring. Regarding the latter, it has been shown that in the polymerization of propylene oxide attack on the least substituted carbon is the preferred reaction pathway.\textsuperscript{128} Quirk and Lizarraga\textsuperscript{129} studied the reaction of poly(styryl)lithium with propylene oxide in benzene. Hydroxyl-functionalized polymer was obtained in 93 \% yield; the non-functional polymer resulted from proton-transfer from the methyl group of propylene oxide. It is noteworthy that no oligomerization was observed and the regiochemistry of the chain end showed 97 \% addition of the poly(styryl)lithium to the least substituted carbon of the propylene oxide ring.

In continuation of these studies, the reaction of poly(styryl)lithium with 1-butene oxide was investigated.\textsuperscript{130} Due to the steric and electronic effects of the methyl group, it...
was expected that the methylene group adjacent to the ring would be less reactive to proton-transfer to poly(styryl)lithium, compared to propylene oxide. Accordingly, hydroxyl functionalized polystyrene was obtained in 99 % yield with no oligomerization of the 1-butene oxide. It was concluded that the efficiency of the functionalization of poly(styryl)lithium with epoxides is in the order: ethylene oxide > 1-butene oxide > propylene oxide.

\[
\text{PSLi} + 10 \text{ CH}_2\text{CH}_3 \xrightarrow{2 \text{ days} \atop \text{C}_6\text{H}_6 \atop 25^\circ\text{C}} \text{CH}_3\text{OH} \rightarrow \text{PSCH}_2\text{CHOH} + \text{PS-H} >99% \quad <1% \quad (20)
\]

The efficiency of the reactions of polymeric organolithium compounds with epoxides\textsuperscript{118-121,125,126,128,129} suggested that polyeopoxides could be used as linking agents. Thus, Quirk et al.\textsuperscript{131} investigated the reaction of excess poly(styryl)lithium with 1,3-butadiene diepoxide. It was shown that poly(styryl)lithium adds to the less substituted carbons of the diepoxide to form a coupled, in-chain, dihydroxyl-functionalized polymer. The use of these in-chain hydroxyl groups as initiation sites for ethylene oxide polymerization has been studied and results are reported in the present document. In addition, two commercially available triepoxides have been investigated as precursors for well-defined, in-chain functionalized, star-branched polymers.

1.3. In-chain functionalization

There are different types of in-chain functionalized polymers. The most common have a functional group on each repeat unit of the polymer by polymerization of functional monomers. A variety of in-chain functional polymers have been prepared by polymerization of functionalized styrene derivatives. However, the reactivity of the living
propagating anion towards functional groups containing reactive, polar groups and acidic hydrogens limits the number of polymerizable functional monomers. It is possible to polymerize monomers containing these reactive functionalities provided that they are protected before polymerization; the functional groups may be deprotected post-polymerization. Nakahama and coworkers\textsuperscript{132} developed a strategy for polymerization of styrene derivatives containing protected functional groups as shown in Scheme 1.9.

\begin{center}
\includegraphics[width=\textwidth]{scheme19.png}
\end{center}


This method presents several disadvantages; the most clear is that it involves at least two extra steps, the protection and subsequent deprotection of the functional group. Also different functional groups require different reaction conditions and protecting groups, thus requiring reaction schemes tailored according to the functionality. In addition, these polymerizations were generally performed in THF at -78 °C. The disadvantages of tetrahydrofuran as a polymerization solvent have already been discussed.

Recently, a new general functionalization methodology for in-chain functionalized polymers has been proposed.\textsuperscript{133} Analogous to the chain-end general functionalization methodology described in Section 1.2.2, it is a combination of anionic polymerization and hydrosilation reactions. Poly(4-vinylphenyldimethylsilane) was synthesized by
anionic polymerization using sec-butyllithium as initiator in benzene at room temperature. The resulting polymer has the silyl hydride functionality in every repeat unit. The later functionality can be further reacted with an allyl compound by hydrosilation to make in-chain functional polymers. Since the functionalization reaction is post-polymerization, there is no need to protect the functional groups. Another advantage is that the same polymer can be used to introduce a variety of functionalities by hydrosilation reactions, without the need of specific reaction conditions in the polymerization step. As an example, epoxide in-chain functionalized polymers were prepared by hydrosilation of poly(4-vinylphenyldimethylsilane) with allyl glycidyl ether. Hydroxyl in-chain functionalized polymers were obtained by hydrolysis of the epoxide groups.

In some cases having a functional group on every repeat unit is not desirable. Copolymerization with different monomers provides a method to randomly introduce a limited amount of functional groups in the chain and tailor the polymer properties. Thus, Quirk and Chowdury\textsuperscript{134} investigated the copolymerization behavior of styrene with (4-vinylphenyl)dimethylsilane (see Scheme 1.10). The monomer reactivity ratios were calculated by three methods: Fineman-Ross, Kelen-Tudos and error-in-variable (EVM). It was concluded that the (4-vinylphenyldimethylsilane) is preferentially incorporated and the copolymer tends to exhibit an alternating structure. The obtained in-chain functionalized copolymer was further reacted with allylamine to prepare amine functionalized copolymer which in turn was reacted with the free carboxyl moiety on (N-carbobenzyloxy)-L-phenylalanine to prepare amino acid-functionalized polymer.\textsuperscript{135}

Another general functionalization method involves the reaction of polymeric organolithium compounds with substituted 1,1-diphenylethylenes.\textsuperscript{136} It has proven to be
an excellent method for functionalization because the addition reaction is simple and quantitative, there is no oligomerization of the 1,1-diphenylethylene, the crossover reaction can be monitored by UV-vis spectroscopy and a variety of substituted 1,1-diphenylethylenes with functional groups on the aromatic ring can be prepared.\textsuperscript{3,5,136}

Moreover, the product of the addition reaction of the substituted 1,1-diphenylethylene to the living polymeric carbanion is also a carbanion (1,1-diphenylalkyllithium) that can initiate anionic polymerization of a monomer. Thus, this procedure has been described as a “living functionalization reaction” and provides methods to effect functionalization at the initiating (\(\alpha\)) end of the polymer chain, at the
terminating (ω) end of the chain and/or within the polymer chain. Quirk and Zhu\textsuperscript{137} used this methodology to prepare a dimethylamino-functionalized polystyrene-\textit{b}-polybutadiene diblock copolymer with the functional group at the interface between the two blocks. Poly(styrly)lithium was reacted with 1-(4-dimethylaminophenyl)-1-phenylethylene. After the addition reaction was complete, butadiene monomer was added to the living functionalized polymer as shown in Scheme 1.11. In the same manner, polystyrene-\textit{b}-poly(\textit{tert}-butyl acrylate),\textsuperscript{138} polystyrene-\textit{b}-poly(methyl methacrylate)\textsuperscript{139} and polystyrene-\textit{b}-poly(ethylene oxide)\textsuperscript{140} diblock copolymers with fluorescent groups at the block junctions have been prepared.

\[ \text{PSLi} + \text{CH}_3\text{OH} \rightarrow \text{PS-CH}_3\text{Li} \]

\[ \text{PS-CH}_3\text{Li} + \text{butadiene} \rightarrow \text{PS-PBD} \]

\[ \text{PS-PBD} + \text{H}_2\text{O} \rightarrow \text{PS-OH} \]

Although the functionalized polymers can be obtained in high yield, there are some limitations to this method. As already mentioned for other living functionalization methods, there is a need to use protecting groups for functionalities such as hydroxyl, carboxyl and amino. Also, the stoichiometry of the reaction must be strictly controlled. Although diphenylethylene does not oligomerize when a small molar excess is used,\textsuperscript{136} an excess of substituted diphenylethylene will result in polymer functionality that is
higher than one because it can copolymerize with the second monomer or add at the chain end when all the monomer has been consumed. A less than stoichiometric amount of substituted diphenylethylene will result in functionality lower than one. Since the copolymer is prepared by sequential monomer addition, the living functionalized polymer acts as initiator for the second block. Thus, the resulting diphenylalkyllithium must be able to initiate polymerization of the second monomer. As already discussed in Section 1.1.2, to have an effective initiation the reactivity of the initiator and monomer must be similar. In general, electron-donating substituents form very reactive initiators and the electron-withdrawing substituents stabilize the carbanion. For example, substituted diphenylethylenes with the diisopropylamide and oxazole groups, both carbonyl-protecting groups, form very stable carbanions to the point that they are not effective initiating species for styrene polymerization.\textsuperscript{141-143}

In-chain functionalized polymers with multiple functional groups along the polymer backbone can also be prepared by copolymerization of styrene or diene monomers with a substituted diphenylethylene derivative.\textsuperscript{141,144-148} The number of functional groups per polymer molecule can be controlled by the monomer feed ratio and the molecular weight. For example, copolymerization of styrene with 1.5 and 3.6 molar equivalents of 1-(4-dimethylaminophenyl)-1-phenylethylene produced copolymers with 24 and 36 amine groups per polymer chain, respectively.\textsuperscript{148}

Double diphenylethylene, 1,3-\textit{bis}(1-phenylethenyl)benzene (MDDPE), has been shown to react with sec-butyllithium to form a hydrocarbon-soluble, dilithium initiator.\textsuperscript{149,150} Analogously, the trifunctional diphenylethylene, 1,3,5-\textit{tris}(1-phenylethenyl)benzene, forms a trifunctional initiator.\textsuperscript{151} In a similar way, polymeric organolithium compounds react quantitatively with diphenylethylene derivatives to yield
living linking agents. There are different alternatives to treat the living linking agent; if the reaction is terminated with methanol the product is a coupled polymer (a in Scheme 1.12). If a different monomer is added and the polymerization is then terminated, the product is a heteroarm star-branched polymer (b in Scheme 1.12). The termination of these living anions with an electrophilic reagent (X-Y) will yield an in-chain difunctionalized polymer (c in Scheme 1.12).

Scheme 1.12. Reaction of polymeric organolithium compounds with 1,3-bis(1-phenylethenyl)benzene (MDDPE).

In order for these living linking agents to be useful to prepare in-chain functionalized polymers or star-branched polymers, they must react quantitatively with living carbanionic chains without oligomerization, the active centers must be retained stoichiometrically in the coupled product, and electrophiles must react quantitatively with the living linked product. Double diphenylethylene (MDDPE) is a very effective living linking agent. When the stoichiometry of the reaction is carefully controlled, the reaction of poly(styryl)lithium with MDDPE produces the coupled product in excellent yields (> 96 %). If the coupled product is terminated with an electrophilic reagent, the product is an in-chain functionalized polymer with two functional groups at the center of the chain.
Sen\textsuperscript{153} investigated the use of 1,4-\textit{bis}(1-phenylethenyl)benzene (PDDPE) to make a carboxyl-functional polymer with the carboxyl functionality in the middle of the chain. Poly(styryl)lithium was reacted with PDDPE ([PDDPE]/[Li]=1.2), and the resulting PDDPE-polystyrene macromonomer with terminal diphenylethylene functionality was reacted with poly(styryl)lithium followed by carbonation using gaseous carbon dioxide.

Triple diphenylethylene can also be used as living linking agent and terminated with an electrophilic reagent to produce a three-armed star polymer with three functional groups in the core of the star as shown in Scheme 1.13.

![Scheme 1.13. Reaction of polymeric organolithium compounds with 1,3,5-tris(1-phenylethenyl)benzene.](image)

Divinylbenzene (DVB) has also been used as a living linking agent to prepare star-branched polymers.\textsuperscript{154,155} After all monomer has been consumed in the polymerization, a living polymer can react with a controlled amount of divinylbenzene. The result has been described as a DVB nodule that serves as a branch point for the star polymer. Since it is a living linking reaction, after the polymerization/linking reaction has been completed there are a number of active anions in the core equal to the number of branches linked to the core. These active anions can be terminated with suitable electrophilic reagents to obtain in-chain, multi-functional, star-branched polymers with the functionalities in the core as shown in Scheme 1.14. The most significant limitation of this method is associated with the lack of control of the composition of the stars. Due
to the mechanism of the reaction, the number of arms per star varies from molecule to molecule. In general, the average number of arms in the star depends on the ratio of DVB to polymeric organolithium compound, molecular weight of the polymer precursor, polymer concentration, temperature and reaction time.\textsuperscript{156}

\begin{center}
\begin{tikzcd}
\text{Scheme 1.14. Reaction of polymeric organolithium compounds with divinylbenzene.}
\end{tikzcd}
\end{center}
CHAPTER II
EXPERIMENTAL

2.1. Inert atmosphere techniques

Due to the reactivity of organolithium compounds and other carbanionic species toward impurities such as oxygen, moisture or carbon dioxide,\textsuperscript{25} it is necessary to exclude these contaminants from the reaction environment by the use of an inert gas atmosphere\textsuperscript{157,158} or high vacuum techniques.\textsuperscript{8,159,160}

2.1.1. High vacuum techniques

The use of high vacuum techniques provides the most effective experimental method to exclude impurities from the reaction system\textsuperscript{8,159,160}. The vacuum line shown in Figure 2.1 was used to purify, dry, degas and transfer reactants and solvents into ampoules and reactors as needed. In order to attain high vacuum, the combination of a mechanical pump and an oil diffusion pump was used in conjunction with a two-stage Pyrex® glass manifold. A liquid nitrogen trap was used between the glass manifold and the diffusion pump in order to prevent solvents and reagents from entering the vacuum pump. The upper manifold was connected to the lower manifold by two Rotoflo® stopcock valves. The lower manifold consisted of one inner (A in Figure 2.1) and three outer (B in Figure 2.1) 24/40 ground glass joints used to attach flasks containing reactants, solvents and monomers. Two grease traps (C in Figure 2.1) were used to
attach reactors and ampoules by glass blowing directly to the vacuum line. Nitrogen gas (4.8 grade, Praxair) was introduced into the vacuum line through a Rotoflo® stopcock in the lower manifold, after passing through a U-tube bubbler to control the pressure.

![Diagram of a high vacuum line for anionic polymerizations](image)

Figure 2.1. Typical construction of a high vacuum line for anionic polymerizations.

The performance of the high vacuum line was evaluated using a Tesla coil. In the presence of air or gas flow in the vacuum line (e.g. from pinholes in the glassware), the Tesla coil creates a purple-colored electrical discharge along with noise when placed close to the glass surfaces. The absence of electrical discharge and noise indicates that the pressure in the system is less than approximately $10^{-3}$ torr.² The Tesla coil was also used to detect pinholes in the vacuum line, ampoules and reactors.
2.1.2. Schlenk line techniques

A two-manifold Schlenk line\textsuperscript{157} equipped with high vacuum stopcocks, inert gas inlets and a mechanical pump protected by a Dewar-cooled trap was used to perform hydrosilations and pull vacuum for sublimation of naphthalene. Successive evacuation and inert gas filling cycles were used to obtain a suitable atmosphere.

2.1.3. Glove box techniques

The glove box (VAC, Model \# HE-43-2) was used for initial transfers and weighing of air-sensitive compounds, dilutions or transfers of non- or low-volatility monomers or reactants, and transfer of metals (potassium, sodium) for the preparation of mirrors. The VAC purification system for the glove box consisted of a gas purifier with a copper catalyst for oxygen removal, molecular sieves for moisture removal, and a circulation blower. The regeneration of columns was done every 4 months or when needed to maintain the purifier’s ability to remove contaminants. The level of oxygen inside the dry box was tested by using a $(\text{Cp}_2\text{TiCl})_2\text{ZnCl}_2$ solution prepared by Sekutowski and Stucky’s method\textsuperscript{161}. A few drops of the solution were exposed to the atmosphere in the dry box; if the solution retained its green color as the solvent evaporated the oxygen content was less than 5 ppm; at higher concentrations of oxygen the solution turned yellow-orange. The level of moisture inside the dry box was tested qualitatively by cutting a small piece of sodium metal; a low level of moisture in the dry box was indicated by the sodium metal remaining shiny.

All glassware was stored in an oven at 140 °C overnight prior to transfer into the dry box. The antechamber was evacuated and purged with argon at least three times in a one hour span before transfer of the glassware and reactants into the dry box.
2.2. Purification of reagents

Due to the reactivity of anions towards moisture, oxygen and other impurities, it is necessary to purify solvents, monomers and other reagents.

2.2.1. Solvents

Most of the polymerization reactions were performed in benzene. Tetrahydrofuran was used as an additive in some cases.

2.2.1.1. Benzene

Benzene (ACS grade, EMD) was poured over freshly crushed calcium hydride (Acros Organics, ca. 93 %, 0-20 mm grain size), and stirred overnight under vacuum. The benzene was cooled with an isopropyl alcohol/dry ice bath (-78 °C), degassed three times by freeze-pump-thaw cycles and stirred in between cycles. Benzene was then vacuum distilled into an evacuated flask containing sodium dispersion (Hodgson Chemicals Inc., 40 % sodium dispersion in paraffin). It was stirred overnight and subjected to three intermittent freeze-pump-thaw cycles. The benzene was finally distilled into a storage flask equipped with a Rotoflo® stopcock containing an orange solution of poly(styryl)lithium; persistence of the characteristic orange color indicated the purity of the solvent. Benzene was distilled from poly(styryl)lithium into ampoules and reactors as needed.

2.2.1.2. Tetrahydrofuran

Tetrahydrofuran (THF, ACS grade, EMD) was stirred over freshly ground calcium hydride and degassed three times by freeze-pump-thaw cycles cooling with a isopropyl
alcohol/dry ice bath (-78 °C). THF was then vacuum distilled onto sodium dispersion and degassed three times by freeze-pump-thaw cycles. This step was repeated for additional drying. The THF was finally transferred via vacuum distillation onto a storage flask containing a sodium mirror. The preservation of the mirror indicated the purity of the solvent. The THF was distilled from the sodium mirror into ampoules and reactors as needed.

2.2.2. Monomers

The monomers used in the polymerization reactions described in this dissertation were styrene, butadiene and ethylene oxide.

2.2.2.1. Styrene

Styrene (Aldrich, 99 %) was stirred over freshly crushed calcium hydride overnight. It was cooled with liquid nitrogen and degassed by successive freeze-pump-thaw cycles. The styrene was transferred into an evacuated storage flask containing neat dibutylmagnesium (FMC Lithium Division, 17% in heptane). The styrene was stirred until a light yellow color appeared and then it was stored in the refrigerator until use. The monomer was transferred from dibutylmagnesium by vacuum distillation into calibrated ampoules as needed.

2.2.2.2. Butadiene

Butadiene (Matheson, 99 %) was transferred through the vacuum line into an evacuated flask containing freshly crushed calcium hydride cooled with an isopropyl alcohol/dry ice bath. The butadiene was stirred for 4 h with periodic degassing. It was
then distilled into a flask containing neat $n$-butyllithium and stirred for 45 min while cooling with an isopropyl alcohol/dry ice bath. The butadiene was then distilled into an evacuated side arm ampoule attached to the corresponding reactor, sealed off the vacuum line with a flame and used immediately. The volume of butadiene was measured at -78 °C ($d = 0.731 \text{ g/cm}^3$)\textsuperscript{163}.

2.2.2.3. Ethylene oxide

Ethylene oxide (Aldrich, 99.5 +%) was transferred through the vacuum line to an evacuated flask containing freshly crushed calcium hydride, cooled with an isopropyl alcohol/dry ice bath and stirred with periodic degassing for 2 h. It was then distilled into a flask containing neat dibutylmagnesium with a pinch of 1,10-phenanthroline as an indicator, and stirred for 30 min. The permanent purple color of the ethylene oxide solution indicated the absence of impurities. The ethylene oxide was distilled from dibutylmagnesium into a calibrated ampoule, diluted to at least a 3:1 ratio of benzene/ethylene oxide, sealed off the line with a flame and stored in the freezer until used.

2.2.3. Initiators

For all styrene polymerizations, the initiator used was sec-butyllithium. Potassium naphthalenide was used in the activation of hydroxyl groups to initiate polymerization of ethylene oxide. Other initiators, such as $n$-butyllithium and dibutylmagnesium, were used in the purification of monomers.
2.2.3.1.  \textit{sec-Butyllithium}

\textit{sec-Butyllithium} (Chemetall Foote Corp. 12 \% in cyclohexane or FMC Lithium Division, 12 \% in cyclohexane/heptane) was used as received after transferring from the stock bottle to a 100 mL bottle in the dry box. The concentration of active carbon-bound lithium was determined by Gilman double titration with allyl bromide\textsuperscript{164}. To determine the total base, 3 aliquots of 1.1 mL of \textit{sec}-butyllithium were diluted with 10 mL of cyclohexane and sealed in crimp-top bottles in the dry box. The initiator solutions were quenched with 10 mL of distilled water. These solutions were titrated with standardized 0.1 N HCl using phenolphthalein as indicator. To determine the free base, that is lithium bonded to a non-carbon atom, 3 aliquots of 3 ml of \textit{sec}-butyllithium were quenched with 1 mL of allyl bromide (see 2.2.6.3) followed by 10 mL of distilled water. The solution was titrated with standardized 0.1 N HCl using phenolphthalein as indicator. The difference between the average of the two types of titration provided the concentration of \textit{sec}-butyllithium (carbon-bound lithium).

2.2.3.2.  \textit{n-Butyllithium}

\textit{n-Butyllithium} (FMC Lithium Division, 24 \% in heptane) was used as received after transferring from the stock bottle to a 100 mL bottle in the dry box.

2.2.3.3.  \textit{Dibutylmagnesium}

\textit{Dibutylmagnesium} (FMC Lithium Division, 17 \% in heptane) was used as received after transferring from the stock bottle into 100 mL bottle in the dry box.
2.2.3.4. **Potassium naphthalenide**

Naphthalene (Acros Organics, scintillation grade, 99 +%%) was transferred in the dry box into a 2-piece sublimator with an upper water-cooled condenser and a lower flat-bottom cylindrical sample container. The sealed apparatus was removed from the dry box and the naphthalene was sublimed under vacuum in the Schlenk line. The naphthalene (0.23 g) was removed from the apparatus in the dry box and placed into a graduated ampoule equipped with a Rotoflo® stopcock and a side-arm breakseal. The ampoule was attached to the vacuum line, evacuated, and then THF was distilled into the ampoule, with care to prevent the naphthalene from sublimating into the vacuum system. After all of the THF (approximately 25 mL) was distilled, the solution was frozen and degassed. The ampoule (C) was flame sealed and attached to the reactor, as shown in Figure 2.2. The reactor was attached to the vacuum line (through B) and evacuated. In the dry box, a weighed amount of potassium (0.051 g) was scraped on a small piece of a glass microscope slide and placed in the reactor. The slide with the potassium was positioned in the side arm (A), and the reactor was taken out of the dry box, attached to the vacuum line and evacuated. The potassium was heated slowly with a yellow flame while cooling the flask with an isopropyl alcohol/dry ice bath until a potassium mirror was formed. The reactor was then sealed off the line. The filter (E) and receiving ampoule (F) were attached to the reactor (part 2), evacuated in the vacuum line (through D) and sealed off with a flame. When the naphthalene solution was added to the potassium mirror, the solution turned dark green and was allowed to stir for 16 h in the dark. The breakseal connecting the two parts of the reactor was broken and the potassium naphthalenide was filtered through a coarse glass frit and transferred into ampoule F, with a Rotoflo® stopcock. The volume of the ampoule containing the
potassium naphthalenide was measured and then the ampoule was cooled, flame sealed and used immediately.

![Diagram of reactor set-up for preparation of potassium naphthalenide.](image)

Figure 2.2. Reactor set-up for preparation of potassium naphthalenide.

2.2.4. Functionalizing and terminating agents

Alkylolithium-initiated, living anionic polymerization is unique in that after all monomer is consumed the product is an active polymeric organolithium compound. This can be reacted with a variety of functionalizing and terminating agents to obtain chain-end functionalized polymers.

2.2.4.1. Cyclic sulfides

Propylene sulfide (Aldrich, > 96 %), ethylene sulfide (Aldrich, 98 %) and trimethylene sulfide (Aldrich, 97 %) were purified by stirring over freshly crushed calcium hydride with periodic degassing for 12 h, followed by distillation into calibrated ampoules, dilution with benzene (8 mL) and flame-sealing with a torch.
2.2.4.2. Chlorosilanes

Chlorodimethylsilane (Aldrich, 98 %) and vinylidimethylchlorosilane (Gelest, 97 %) were purified by stirring over freshly crushed calcium hydride with periodic degassing by freeze-pump-thaw cycles for 12 h, followed by distillation onto a second batch of calcium hydride, and finally distillation and collection of the middle fraction into calibrated ampoules. Benzene (8 mL) was used to dilute the terminating agents and the ampoules were flame-sealed. The $^1$H NMR spectra of chlorodimethylsilane and vinylidimethylchlorosilane are shown in Figures 1 and 2, Appendix B.

2.2.4.3. Vinlydimethylethoxysilane

Vinlydimethylethoxysilane (Gelest, 97 %) was transferred in the dry box into an evacuated flask with a Rotoflo® stopcock containing freshly crushed calcium hydride. It was then attached to the vacuum line and subjected to three freeze-pump-thaw cycles over a 12 h period followed by distillation into a flask with a second batch of calcium hydride. Finally the middle fraction was distilled into calibrated ampoules. Benzene (8 mL) was used to dilute the vinlydimethylethoxysilane and the ampoules were flame-sealed. The $^1$H NMR spectrum of vinlydimethylethoxysilane is shown in Figure 3, Appendix B.

2.2.4.4. Vinyltrimethoxysilane

Vinyltrimethoxysilane (Gelest, > 97 %) was purified by stirring over freshly crushed calcium hydride with periodic freeze-pump-thaw cycles for 12 h followed by distillation onto activated molecular sieves in a flask equipped with a Rotoflo® stopcock. The flask was stored in the freezer until use. The product was transferred in the dry box
into the reaction flask. The $^1$H NMR spectrum of vinyltrimethoxysilane is shown in Figure 4, Appendix B.

2.2.5. Linking agents

The living polymeric organolithium product can be reacted with substances with functionality greater than two to make star-branched polymers.

2.2.5.1. 1,3-Butadiene diepoxide

1,3-Butadiene diepoxide (Aldrich, 97 %) was purified by stirring over freshly crushed calcium hydride with periodic freeze-pump-thaw cycles for 12 h followed by short-path distillation into a calibrated ampoule. After dilution with benzene (8 mL), the ampoule was flame-sealed with a torch.

2.2.5.2. N,N-Diglycidyl-4-glycidyloxyaniline

N,N-Diglycidyl-4-glycidyloxyaniline (Aldrich, 97 %) was dissolved in benzene and stirred over freshly crushed calcium hydride with periodic freeze-pump-thaw cycles for 12 h. The solution was then filtered to remove CaH$_2$, and freeze-dried. The linking agent was stored in the freezer until needed. A weighed amount was transferred into an ampoule with a Rotoflo® stopcock in the dry box, then removed from the dry box and attached to the vacuum line, evacuated, diluted with benzene and flame-sealed.

2.2.5.3. Tactix 742

Tactix 742 (Huntsman) was dissolved in benzene and stirred over freshly crushed calcium hydride with periodic freeze-pump-thaw cycles for 12 h. The solution was then
filtered to remove CaH₂ and freeze-dried. After weighing, the Tactix was dissolved in benzene to a known concentration (0.32 M). The linking agent was stored in the freezer until needed. A measured amount was transferred into an ampoule with a Rotoflo® stopcock in the dry box, then removed from the dry box and attached to the vacuum line, evacuated, further diluted with benzene and flame-sealed.

2.2.6. Other reagents

The use of other terminating agents and additives is often necessary. These also have to be purified before use.

2.2.6.1. Methanol

Methanol (Fisher Scientific, reagent grade) was degassed on the vacuum line before distillation into ampoules and flame-sealed with a torch. Acidic methanol ampoules were prepared by adding 0.5 mL of glacial acetic acid (Fisher Scientific, 100%) into an ampoule with a Rotoflo® stopcock. The ampoule was attached to the vacuum line and the acetic acid was degassed. Methanol (0.5 mL) was distilled into the acid and the ampoule was flame sealed off the line.

2.2.6.2. Methyl iodide

Methyl iodide (Aldrich, < 96 %) was purified by stirring over phosphorus pentoxide with periodic degassing for 12 h in the dark, followed by vacuum distillation into calibrated ampoules and flame-sealing with a torch.
2.2.6.3. Allyl bromide

Allyl bromide (Aldrich, 97 %) was stirred over calcium chloride, activated in a vacuum oven at elevated temperature for 24 h, and subjected to intermittent freeze-pump-thaw cycles. Then it was vacuum transferred into a round-bottomed flask containing phosphorus pentoxide (Fisher Scientific, Certified ACS) that had been dried for 24 h on the vacuum line. The solution was stirred for an additional 24 h with intermittent degassing and vacuum distilled into a flask with a Rotoflo® stopcock. The allyl bromide was transferred into a brown amber bottle containing fleshly activated molecular sieves (4 Å) in the dry box where it was stored until used.

2.2.6.4. Lithium chloride

Lithium chloride (J. T. Baker, 99.7 %) was dried overnight in an oven at 140 °C, and used after allowing it to cool in a desiccator.

2.2.6.5. Potassium tert-amylate

Potassium tert-amylate (BASF Corp., 15 % in cyclohexane) was used as received. It was transferred into a calibrated ampoule with a Rotoflo® stopcock in the dry box, degassed in the vacuum line and sealed off with a flame.

2.2.6.6. 1,3-Divinyltetramethyldisiloxane-platinum

Karstedt’s catalyst, 1,3-divinyltetramethyldisiloxane-platinum (Gelest, 2.1-2.4 wt % Pt in xylene), was stored in the dry box and used without further purification.
2.2.6.7. Hydrogen hexachloroplatinate (IV) hydrate

Spier’s catalyst, hydrogen hexachloroplatinate (IV) hydrate (Aldrich, 99.9 %, Pt 38-40 wt %), was stored in the dry box and used as received.

2.3. Synthesis

Poly(styryl)lithiums (ca. 1,200–2,500 g/mol) were prepared under high vacuum conditions in sealed, all-glass reactors using breakseals. The reactor was built by glass blowing techniques and annealed to 650 °C overnight. All the glassware was rinsed with distilled water after annealing. Ampoules containing monomers, additives, and functionalizing, linking and/or terminating agents were attached to the reactor using glass-blowing techniques. A typical polymerization reactor is shown in Figure 2.3.

![Figure 2.3. Typical reactor for anionic polymerization.](image)

The reactor was attached to the vacuum line (via A), heated with a yellow flame and evacuated for at least 4 h with a septum covering the inlet G. The initiator, sec-butyllithium, was injected through the side arm (G) using a gas-tight syringe while maintaining a positive pressure of dry nitrogen through the reactor. After the addition, the side arm was sealed with a septum. The initiator was then frozen with an isopropyl
alcohol/dry ice bath and the side arm was sealed off with a flame. Benzene (approximately 10 vol % styrene) was then distilled into the reactor. When the required amount of benzene had been transferred, the solution was frozen and the reactor was sealed off the vacuum line with a flame. The reaction mixture was thawed at 30 °C. The polymerization was started by smashing the breakseal of the ampoule containing the styrene (B); the reactor was kept in a water bath at 30 °C, unless otherwise noted. Before addition of the additives, functionalizing and/or linking agent (in ampoules D and/or E), a 10 mL aliquot of the poly(styryl)lithium solution was transferred into an attached, empty ampoule (C) followed by removal by sealing with a hand torch. This base sample was then quenched with degassed methanol for characterization by SEC. After the reaction was finished, it was terminated by smashing the breakseal of the ampoule (F) containing the terminating agent (usually degassed methanol).

2.3.1. Functionalization with cyclic sulfides

In order to prepare thiol-functionalized polymers, poly(styryl)lithium was reacted with propylene sulfide, ethylene sulfide and trimethylene sulfide. Poly(butadienyl)lithium was also reacted with propylene sulfide.

2.3.1.1. Functionalization with 3.5 equivalents of propylene sulfide

Poly(styryl)lithium \([M_n (SEC) = 2.2 \times 10^3 \text{ g/mol}, M_n/M_w = 1.04]\) was prepared by adding 20 mL of styrene (18.03 g, 173 mmol) to a sec-butyllithium solution (5.9 mL, 1.46 M, 8.61 mmol) in benzene (150 mL) as described in Section 2.3.1. The functionalization was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing propylene sulfide (2.4 mL, 30.5 mmol). A change
of color from orange to light yellow was observed almost immediately. After 3 h, the reaction was quenched with acidic methanol. Solvent was removed from the resulting polymers using a rotary evaporator, followed by further drying on the high-vacuum line for 48 h.

2.3.1.2. Functionalization with propylene sulfide monitored by UV-vis spectroscopy

Poly(styryl)lithium \( [M_n (SEC) = 1.5 \times 10^3 \text{ g/mol}, M_n/M_w = 1.05] \) was prepared by adding 16 mL of styrene (14.42 g, 138 mmol) to a sec-butyllithium solution (8.0 mL, 1.46 M, 11.7 mmol) in benzene (150 mL) in a reactor equipped with a UV cell. A UV spectrum of the poly(styryl)lithium solution was taken prior to functionalization. The functionalization was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing 2.3 equivalents of propylene sulfide (2.1 mL, 26.6 mmol). A change of color from orange to light yellow was observed almost immediately. The reaction was followed by UV-vis spectroscopy taking a spectra after 5, 15, 30, 45, 60, 120, 240 and 270 min. The reaction was quenched with acidic methanol. Solvent was removed from the resulting polymers using a rotary evaporator, followed by further drying on the high-vacuum line for 48 h.

2.3.1.3. Functionalization with 1.3 equivalents of propylene sulfide

Poly(styryl)lithium \( [M_n (SEC) = 2.0 \times 10^3 \text{ g/mol}, M_n/M_w = 1.05] \) was prepared by adding 10 mL of styrene (9.016 g, 86.6 mmol) to a sec-butyllithium solution (3.4 mL, 1.49 M, 5.07 mmol) in benzene (100 mL) as described in Section 2.3.1. The functionalization was effected directly in the polymerization reactor by smashing the
breakseal for the ampoule containing propylene sulfide (0.5 mL, 6.34 mmol). A change of color from orange to light yellow was observed almost immediately. After 15 min, the contents were divided into two parts using an attached ampoule. The part remaining in the reactor was quenched with acidic methanol and the solution in the ampoule was quenched with methyl iodide (0.2 mL, 3.21 mmol). Solvent was removed from the resulting polymers using a rotary evaporator, followed by further drying on the high-vacuum line for 48 h. The same reaction was carried out in the presence of tetrahydrofuran; in this case 22 molar equivalents of tetrahydrofuran was added to the reaction mixture before adding the propylene sulfide.

2.3.1.4. Oxidation of thiol-functionalized polymer

Oxidation of the terminal thiol group with iodine was carried out in benzene under a dry nitrogen atmosphere in the dark. Thiol-functionalized polymer \( [M_n (SEC) = 2.1 \times 10^3 \text{ g/mol}; M_w/M_n = 1.06] \) from the reaction of poly(styryl)lithium and 1.3 equivalents of propylene sulfide was used. An excess amount of iodine (6.04 g, 47.6 mmol) was added to the functional polymer solution (1 g/250 mL of benzene) and stirred for 24 h. The resulting polymer was washed with a 10 % solution of sodium bisulfite (Fisher Scientific, Certified ACS) to remove excess iodine and analyzed by SEC.

2.3.1.5. Functionalization with 1.3 equivalents of ethylene sulfide

Poly(styryl)lithium \( [M_n (SEC) = 2.2 \times 10^3 \text{ g/mol}, M_n/M_w = 1.05] \) was prepared by adding 10.9 mL of styrene (9.83 g, 94.4 mmol) to a sec-butyllithium solution (3.4 mL, 1.49 M, 5.07 mmol) in benzene (100 mL). The functionalization was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing 1.3
molar equivalents of ethylene sulfide (0.4 mL, 6.72 mmol). A change of color from orange to light yellow was observed almost immediately. After 15 min, the contents were divided into two parts using an attached ampoule. The part remaining in the reactor was quenched with acidic methanol and the solution in the ampoule was quenched with methyl iodide (0.15 mL, 2.41 mmol). Solvent was removed from the resulting polymers using a rotary evaporator, followed by further drying on the high vacuum line for 48 h.

2.3.1.6. Functionalization with 1.3 equivalents of trimethylene sulfide

Poly(styryl)lithium [Mₙ (SEC) = 2.1 x 10³ g/mol, Mₙ/Mₘ = 1.02] was prepared by adding 12 mL of styrene (10.82 g, 103.9 mmol) to a sec-butyllithium solution (4.3 mL, 1.26 M, 5.42 mmol) in benzene (160 mL). The functionalization was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing 1.8 equivalents of trimethylene sulfide (0.7 mL, 9.63 mmol). A slow change of color from orange to light yellow was observed. After 15 min the contents were divided into two parts using an attached ampoule. The solution in the ampoule was quenched with acidic methanol. Styrene (11.4 mL, 10.28 g, 98.7 mmol) was added to the part that remained in the reactor, the reaction mixture changed slowly from light yellow to light orange. After 5 h at 30 °C the reaction mixture was completely orange. It was quenched with acidic methanol. Solvent was removed from the resulting polymers by freeze drying in the vacuum line.
2.3.2. Functionalization with chlorodimethylsilane

Poly(styryl)lithium \([M_n \ (SEC) = 2.0 \times 10^3 \ \text{g/mol}, \ M_n/M_w = 1.03]\) was prepared by adding 12.1 mL of styrene (10.91 g, 104.7 mmol) to a sec-butyllithium solution (3.8 mL, 1.44 M, 5.5 mmol) in benzene (120 mL). Functionalization of poly(styryl)lithium was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing 3.2 molar equivalents of chlorodimethylsilane (2.1 mL, 17.8 mmol) in benzene at room temperature. The disappearance of the characteristic orange color of the poly(styryl)lithium was observed immediately. After one day, the resulting polymers were precipitated into methanol, dried, redissolved in benzene and freeze dried, followed by further drying in an acetone-filled Abderhalden apparatus for 48 h at 56 °C.

2.3.3. Functionalization with vinyldimethylchlorosilane

Poly(styryl)lithium \([M_n \ (SEC) = 2.1 \times 10^3 \ \text{g/mol}, \ M_n/M_w = 1.03]\) was prepared by adding 13.3 mL of styrene (11.99 g, 115.1 mmol) to a sec-butyllithium solution (4.8 mL, 1.26 M, 6.05 mmol) in benzene (120 mL). Functionalization of poly(styryl)lithium was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing 6.6 molar equivalents of vinyldimethylchlorosilane (5.4 mL, 40.0 mmol) in benzene at 30 °C. The solution turned light orange immediately. After 12 h, the reaction was clear and a sample was removed from the reactor in an ampoule and quenched with methanol. After 3 days, the resulting polymer was removed from the reactor, precipitated into methanol, dried, redissolved in benzene and freeze dried.
2.3.4. Functionalization with vinyl(dimethyl)ethoxysilane

Poly(styryl)lithium \([M_n \text{ (SEC)} = 2.0 \times 10^3 \text{ g/mol}, M_n/M_w = 1.03]\) was prepared by adding 13.6 mL of styrene (12.26 g, 117.7 mmol) to a sec-butyllithium solution (4.8 mL, 1.26 M, 6.05 mmol) in benzene (130 mL). Functionalization of poly(styryl)lithium was effected directly in the polymerization reactor by smashing the breakseal for the ampoule containing 2.5 molar equivalents of vinyl(dimethyl)ethoxysilane (2.5 mL, 15.2 mmol) in benzene at 30 °C. The solution turned light orange immediately. After 12 h, a sample was removed from the clear solution in the reactor and quenched with methanol. After 3 days, the remaining polymer was quenched with methanol and removed from the reactor. Both samples were precipitated into methanol, dried, redissolved in benzene and freeze dried.

2.3.5. Functionalization by hydrosilation with vinyl(trimethoxysilane

A two-necked flask (25 mL) containing a mixture of silyl hydride-functional polystyrene (0.6 g, 0.3 mmol, M_n = 2100 g/mol), vinyl(trimethoxysilane) (0.1 mL, 0.1 g, 0.7 mmol), dry benzene (7 mL) and 2 drops of Karstedt’s or Speier’s catalyst was prepared in the dry box and sealed with a septum. The flask was then connected to an argon bubbler through the septum. Samples were taken periodically to follow the reaction by FTIR, NMR and/or MALDI-TOF mass spectrometry. The solution was stirred under an argon atmosphere at room temperature for 11 days. The resulting polymer was precipitated into a 7-fold excess of anhydrous methanol followed by filtration and freeze-drying from benzene.
2.3.6. Synthesis of heteroarm polystyrene/poly(ethylene oxide) stars

Poly(styryl)lithium was reacted with a commercial diepoxide, followed by termination with methanol. The resulting in-chain, dihydroxyl-functionalized coupled polymer was activated with potassium naphthalenide, followed by polymerization of ethylene oxide to prepare amphiphilic, heteroarm star polymers.

2.3.6.1. Coupling of poly(styryl)lithium with 1,3-butadiene diepoxide

Poly(styryl)lithium \([M_n\text{ (SEC)} = 1.2 \times 10^3 \text{ g/mol}, M_n/M_w = 1.04]\) was prepared by adding 17.9 mL of styrene (16.14 g, 155 mmol) to a sec-butyllithium solution (9.1 mL, 1.483 M, 13.5 mmol) in benzene (160 mL). The linking of poly(styryl)lithium was effected by adding 1,3-butadiene diepoxide (0.4 mL, 5.16 mmol). Since excess poly(styryl)lithium (2.6 molar equivalents) was used, there was no apparent change in the color of the reaction mixture after addition of the diepoxide. After 12 h the reaction was quenched with degassed methanol, dried using a rotary evaporator, redissolved in benzene and freeze dried. The linked product was separated from the excess non-functional polystyrene using a silica gel chromatography column with toluene as eluent for the non-functional polymer and tetrahydrofuran as eluent for the in-chain functionalized polymer. The in-chain functionalized polymer was dried in an Abderhalden apparatus for 48 h with dichloromethane under reflux at 40 °C.

2.3.6.2. Polymerization of ethylene oxide with in-chain dihydroxyl-functionalized polystyrene precursor

The dried in-chain dihydroxyl-functionalized polystyrene \([M_n\text{ (SEC)} = 2.2 \times 10^3 \text{ g/mol}, M_n/M_w = 1.02]\), from the reaction of poly(styryl)lithium and 1,3-butadiene
diepoxide (Section 2.3.4.1), was weighed (0.44 g) in the dry box and transferred into an
ampoule equipped with a Rotoflo® stopcock. The ampoule was attached to the vacuum
line and evacuated. After distillation of 7 mL of tetrahydrofuran into the ampoule, it was
sealed off from the vacuum line using a torch. The reactor was assembled with the
polymer solution, ethylene oxide (0.44 g) and acidic methanol ampoules; potassium
naphthalenide (0.05 M) was attached in a side ampoule with a Rotoflo® stopcock. The
assembled reactor was evacuated in the vacuum line and sealed off using a torch. After
the polymer solution was added to the reactor by smashing the breakseal, the reactor
was placed in a water bath at 50 °C and heated to reflux for 30 min. After cooling,
approximately 2 mL of potassium naphthalenide was added to the reactor and the color
changed from a light yellow to a dark yellow. Another 2 mL of potassium naphthalenide
was added and the color did not change. After an additional 4 mL potassium
naphthalenide were added, the color of the reaction mixture changed to green. The
reactor was placed in a water bath at 50 °C for 4 h and no change in color was
observed. The potassium naphthalenide ampoule was sealed off from the reactor.
Ethylene oxide was added to the reactor via a breakseal. After 2 weeks in a water bath
at 50 °C, the reaction was quenched with acidic methanol. The polymer was freeze dried
in the vacuum line.

2.3.7. Synthesis of 3-armed polystyrene stars using commercial triepoxides as
linking agents

Commercial triepoxides were investigated as precursors for preparation of three-
armed star polymers.
2.3.7.1. Without additives at 30 °C

Poly(styryl)lithium \([M_n (SEC) = 1.5 \times 10^3 \text{ g/mol}, M_n/M_w = 1.04]\) was prepared by adding 9.8 mL of styrene (8.84 g, 84.8 mmol) to a sec-butyllithium solution (4.9 mL, 1.483 M, 7.27 mmol) in benzene (160 mL) as described in Section 2.3.1. The linking of poly(styryl)lithium was effected by adding a commercial triepoxide, N,N-diglycidyl-4-glycidyloxyaniline (0.62 g, 2.24 mmol). Also, poly(styryl)lithium \((M_n = 1.5 \times 10^3, M_n/M_w = 1.04)\) was prepared by adding 11.6 mL of styrene (10.5 g, 100.4 mmol) to a sec-butyllithium solution (5.5 mL, 1.26 M, 6.97 mmol) in benzene (110 mL) as described in Section 2.3.1. The linking of poly(styryl)lithium was effected by adding a commercial triepoxide, Tactix 742 (3.5 mL, 0.32 M, 1.11 mmol). Since excess poly(styryl)lithium was used, there was no apparent change in the color of the reaction mixture after addition of the triepoxide (N,N-diglycidyl-4-glycidyloxyaniline or Tactix 742). After 12 h the reaction was quenched with degassed methanol, dried using a rotary evaporator, redissolved in benzene and freeze dried. The linked product was separated from the excess non-functional polystyrene using a silica gel chromatography column with toluene as eluent for the non-functional polymer and tetrahydrofuran as eluent for the in-chain functionalized polymer. The purified in-chain functionalized polymer was dried in an Abderhalden apparatus for 48 h with dichloromethane under reflux at 40 °C.

This reaction was repeated using poly(styryl)lithium prepared from 10.3 mL of styrene (9.29 g, 89.2 mmol) and a sec-butyllithium solution (5.4 mL, 1.483 M, 8.01 mmol) in benzene (100 mL). Poly(styryl)lithium \([M_n (SEC) = 1.7 \times 10^3 \text{ g/mol}, M_n/M_w = 1.04]\) was reacted with 0.29 equivalents of N,N-diglycidyl-4-glycidyloxyaniline (0.64 g, 2.29 mmol) and quenched with degassed methanol after 1 week. Another reaction was performed in the same way using 12.6 mL of styrene (11.36 g, 109.1 mmol) to a sec-
butyllithium solution (5.2 mL, 1.49 M, 7.75 mmol) in benzene (120 mL). Poly(styryl)lithium \( (M_n = 1.6 \times 10^3 \text{ g/mol}, M_n/M_w = 1.04) \) was reacted with 0.2 equivalents of N,N-diglycidyl-4-glycidyloxaniline (0.42 g, 1.51 mmol) and quenched with degassed methanol after 24 h.

2.3.7.2. In the presence of THF

Poly(styryl)lithium \( [M_n (SEC) = 1.6 \times 10^3 \text{ g/mol}, M_n/M_w = 1.04] \) was prepared by adding 10.2 mL of styrene (9.20 g, 88.3 mmol) to a sec-butyllithium solution (5.4 mL, 1.483 M, 8.01 mmol) in benzene (100 mL) as described in Section 2.3.1. After 12 h the polymerization was complete and 10 equivalents of THF (6.6 mL, 80.5 mmoles) was added to the reaction solution, followed by addition of 0.27 molar equivalents of N,N-diglycidyl-4-glycidyloxaniline (0.636 g, 2.29 mmol). After 12 h the reaction was quenched with methanol and worked up as described in Section 2.3.7.1.

2.3.7.3. In the presence of lithium chloride

Once the reactor was assembled and attached to the line, but before adding the initiator to make the poly(styryl)lithium, 10 equivalents of lithium chloride (LiCl, 3.1 g, 72 mmol) was introduced in the reactor through the initiator side arm with the aid of a glass funnel. The reactor was gently heated with a yellow flame and then the LiCl was heated to 150 °C while evacuating for 4 h. After cooling, poly(styryl)lithium \( [M_n (SEC) = 1.7 \times 10^3 \text{ g/mol}, M_n/M_w = 1.03] \) was prepared by adding 10.4 mL of styrene (9.38 g, 90.0 mmol) to a sec-butyllithium solution (5.0 mL, 1.49 M, 7.45 mmol) in benzene (100 mL) as described in Section 2.3.1. After 3 h, 0.19 equivalents of N,N-diglycidyl-4-
glycidyloxyaniline (0.4 g, 1.44 mmol) was added to the reaction. After 48 h, the reaction was quenched with methanol and worked-up as described in Section 2.3.7.1.

2.3.7.4. In the presence of potassium alkoxide

Poly(styryl)lithium \([M_n \ (SEC) = 1.5 \times 10^3 \ g/mol, \ M_n/M_w = 1.05]\) was prepared by adding 15 mL of styrene (13.5 g, 129.9 mmol) to a \textit{sec}-butyllithium solution (7.6 mL, 1.438 M, 10.93 mmol) in benzene (150 mL) as described in Section 2.3.1. After 2 h, 5.3 molar equivalents of potassium tert-amylate in cyclohexane (63 mL, 0.92 M, 58 mmol) was added into the solution. The characteristic orange color of the poly(styryl)lithium changed immediately to deep red. Next, 0.11 molar equivalents of N,N-diglycidyl-4-glycidyloxyaniline (0.34 g), was added. After 12 h at 30 °C, the reaction was quenched with methanol and worked-up as described in Section 2.3.7.1.

2.3.7.5. Linking/functionalization of poly(styrene-\textit{oligo}-butadienyl)lithium

Poly(styryl)lithium \([M_n \ (SEC) = 1.4 \times 10^3 \ g/mol, \ M_n/M_w = 1.04]\) was prepared by adding 10.2 mL of styrene (9.2 g, 88.3 mmol) to a \textit{sec}-butyllithium solution (5.2 mL, 1.494 M, 7.77 mmol) in benzene (100 mL) as described in Section 2.3.1. After removal of the base sample, 2.3 equivalents of butadiene (1.3 mL, 0.95 g, 17.6 mmol) was distilled from neat \(\alpha\)-butyllithium into a side ampoule connected to the reactor with a breakseal. The side ampoule was sealed off from the vacuum line and the butadiene was added to the reaction. After 2 h, 0.29 molar equivalents of N,N-diglycidyl-4-glycidyloxyaniline (0.616 g, 2.22 mmol) was added to the reaction. After 12 h at 30 °C, the reaction was quenched with methanol and worked-up as described in Section 2.3.7.1.
2.3.7.6. Without additives at 10 °C

Poly(styryl)lithium \[M_n \text{ (SEC)} = 1.3 \times 10^3 \text{ g/mol}, M_n/M_w = 1.05\] was prepared by adding 15 mL of styrene (13.5 g, 129.9 mmol) to a sec-butyllithium solution (7.6 mL, 1.39 M, 10.56 mmol) in benzene (150 mL) as described in Section 2.3.1. After 2 h at 30 °C, the reaction was cooled to 10 °C in a cyclohexane/dry ice bath and 0.11 molar equivalents of N,N-diglycidyl-4-glycidyloxylaniline (0.33 g, 1.19 mmol) was added. After 24 h, the reaction was quenched with methanol and worked-up as described in Section 2.3.7.1.

2.4. Characterization

All of the prepared polymers were thoroughly characterized. The characterization techniques used were size exclusion chromatography, \(^1\text{H}\) and \(^{13}\text{C}\) NMR spectroscopy, MALDI-TOF mass spectrometry, thin layer and column chromatography, FT-IR spectroscopy, UV-vis spectroscopy and elemental analysis.

2.4.1. Size exclusion chromatography

Size-exclusion chromatographic analyses (SEC) for the prepared polymers were performed using a Waters 150-C Plus instrument equipped with three HR-Styragel columns [100Å, mixed bed (50/500/10^3/10^4 Å), mixed bed (10^3/10^4/10^6 Å)] and a triple detector system with THF as eluent at a flow rate of 1.0 mL/min at 30 °C. The detector system consisted of a differential refractometer (Waters 410), a differential viscometer (Viscotek 100) and a laser light scattering detector (Wyatt Technology, DAWN EOS, \(\lambda = 670\) nm). Regular SEC calibrations were conducted with polystyrene standards (Polymer
Laboratories). The values of $M_n$ and $M_w$ are calculated with the light scattering detector results.

Size-exclusion chromatographic analyses (SEC) for fractionation were performed in the mass spectrometry laboratory using a Waters Breeze system equipped with a Waters 1515 Isocratic HPLC pump, three HR Styragel columns (100Å, 500 Å and $10^3$ Å) and a Waters 2414 refractive index detector detector with THF as eluent at a flow rate of 1.0 mL/min at 30 °C.

2.4.2. $^1$H and $^{13}$C NMR spectroscopy

All $^1$H (300 MHz), $^{13}$C (75 MHz, quantitative reverse-gate decoupled spectra with $\delta_1 = 6$ s), and DEPT ($\theta = 135^\circ$) NMR spectra were acquired in CDCl$_3$ [Aldrich (99.8 % D) or Alfa Aesar (99.8 % D) with 1 % vol/vol TMS] using a Varian Mercury 300 spectrometer. The NMR spectra were referenced to tetramethylsilane (TMS, 0 ppm) when present or to the residual proton impurities of the deuterated solvent for $^1$H NMR (CHCl$_3$, 7.27 ppm) or the carbon in the deuterated solvent for $^{13}$C NMR (CDCl$_3$, 77.0 ppm).

2.4.3. MALDI-TOF mass spectrometry

Matrix-assisted laser desorption-ionization time-of-flight mass spectra (MALDI-TOF) were recorded on a Bruker Reflex-III TOF mass spectrometer (Bruker Daltonics, Billerica, MA). The instrument was equipped with an LSI model VSL-337ND pulsed 337 nm nitrogen laser (3 nm pulse width), a single-stage pulsed ion extraction source, and a two-stage gridless reflector. Solutions of dithranol (20 mg/mL) (Alfa Aesar, 1,8,9-anthracenetrioil, 97+%), polymer sample (10 mg/mL), and silver trifluoroacetate (10
mg/mL) (Aldrich, 98%) 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 \( \mu \)L of the mixture was applied to the MALDI sample target and allowed to dry. The intensity of the laser pulses was adjusted to minimize undesirable polymer fragmentation and to achieve optimal signal intensity. Mass spectra were measured in the linear and reflectron modes, and the mass scale was calibrated externally using the peaks of a polystyrene standard at the molecular weight under consideration. The mass spectra were recorded in the laboratory of Professor Chrys Wesdemiotis by Dr. Michael J. Polce and David Dabney in the Department of Chemistry at The University of Akron.

2.4.4. Thin layer chromatography

Thin-layer chromatographic analyses (TLC) were carried out on the functionalized polymers by spotting and developing polymer samples on flexible silica gel plates (Selecto Scientific, Silica Gel 60, F-254 with fluorescent indicator), using toluene or a 50/50 (vol/vol) mixture of toluene/cyclohexane as eluents.

2.4.5. Column chromatography

Silica gel (EM Science, Silica Gel 60) was activated in an oven at 140 °C overnight before use and allowed to cool in a desiccator. Silica was mixed with toluene to prepare a slurry which was poured into the column. The silica was allowed to settle while gently tapping on the column to eliminate bubbles. Excess solvent was allowed to drain and a small layer of sand was added at the top of the column. The dissolved polymer was added slowly and uniformly to the sand using a pipette. The excess solvent
was allowed to drain. Toluene was used as eluent for the non-functional polymer and
tetrahydrofuran was used for the remaining functional polymer. The products eluting
from the column were analyzed by TLC.

2.4.6. FT-IR spectroscopy

Infrared spectra were recorded on an Excalibur Series FT-IR spectrometer
(DIGILAB, Randolph, MA, USA) by casting polymer films on KBr plates from THF
solutions. The data was processed using Win-IR Pro software after 16 scans.

2.4.7. UV-vis spectroscopy

UV-vis spectra were obtained using a Hewlett Packard 8452A diode-array
spectrophotometer. A quartz UV-vis cell (1 mm thickness) was attached directly to the
polymerization reactor and pure solvent was distilled into the cell for the background
reference prior to obtaining data for the polymer solution.

2.4.8. Elemental analysis

Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O
analyzer in the laboratory of Professor C. Pugh at The University of Akron.
CHAPTER III
RESULTS AND DISCUSSION

3.1. Synthesis of thiol-functionalized polymers

Thiol-functionalized polymers were prepared by reaction of poly(styryl)lithium and poly(butadienyl)lithium with thiiranes (propylene sulfide and ethylene sulfide).

3.1.1. Functionalization of poly(styryl)lithium with 3.5 equivalents of propylene sulfide

For the initial experiments, poly(styryl)lithium (PSLi, \( M_n = 2.2 \times 10^3 \) g/mol, \( M_w/M_n = 1.04 \)) was functionalized with 3.5 molar equivalents of propylene sulfide in benzene at 30 °C to investigate the questions regarding the mechanism of the reaction and the extent of oligomerization. The characteristic orange color of poly(styryl)lithium disappeared within minutes and turned light yellow. The reaction was allowed to proceed for 1 h. Since the base-catalyzed oxidation of thiols to disulfides in the presence of oxygen is well-known, the reaction was quenched with acidic methanol (methanol/acetic acid, 1/1, vol/vol). The SEC chromatogram for the resulting thiol-functionalized polystyrene (\( M_n = 2.5 \times 10^3 \) g/mol; \( M_w/M_n = 1.04 \)), shown in Figure 3.1, exhibits a narrow, monomodal curve. The stability of the prepared thiol-functional polymer toward oxidation was further confirmed by performing another SEC chromatogram after 3 months, resulting again in a narrow, monomodal curve (\( M_n = 2.4 \times 10^3 \) g/mol; \( M_w/M_n = 1.04 \)). These results stand in sharp contrast to the report of
Nakahama and coworkers\textsuperscript{71} that thiol-functionalized polystyrenes and polyisoprenes underwent oxygen-catalyzed dimerization reactions during SEC analysis in THF.

![Figure 3.1. SEC chromatogram of the acidic methanol quenched products from the functionalization of poly(styryl)lithium (M\textsubscript{n} = 2,200 g/mol) with 3.5 equivalents of propylene sulfide in benzene at 30 °C (A) 1 day and (B) 1 month after work-up.](image)

In order to investigate the mechanism of the functionalization reaction of poly(styryl)lithium with propylene sulfide, i.e., ring opening vs sulfur extrusion (see Scheme 3.1), precise information on the nature of the end groups was required. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) has been shown to be one of the most useful tools for the characterization of chain-end-functionalized polymers.\textsuperscript{120,121,130,166-168} The MALDI-TOF mass spectrum for the thiol-functionalized polymer (Figure 3.2) obtained using silver as cationizing agent showed five series of peaks. Within each series, the peaks were separated by $m/z$ 104, corresponding to a styrene repeat unit. The $m/z$ difference between each series was 74
corresponding to a propylene sulfide unit, which indicates that oligomerization was occurring during this functionalization.

Scheme 3.1 Mechanisms for the reaction of poly(styryl)lithium and propylene sulfide (A) with sulfur extrusion and (B) by ring opening.

Figure 3.2. MALDI-TOF mass spectrum of the product from the reaction of poly(styryl)lithium ($M_n = 2,200$ g/mol) and 3.5 equivalents of propylene sulfide in benzene at 30 °C using silver as cationizing agent.
The analysis of the mass spectral results was further complicated by the recognition that there was ambiguity in the assignment of structures to the peaks because of isobaric structures corresponding to either sulfur extrusion and propylene sulfide oligomerization or ring-opened structures with oligomerization and exchange of the thiol proton with a silver ion. For example, the peak at m/z 1979.6 could correspond to \([C_4H_9-(C_8H_8)_{15}-S-(C_3H_6S)_3-H\cdot Ag^+]\), i.e., the silver complex of the 15-mer of polystyrene, with a sulfur from sulfur extrusion, three units of propylene sulfide, and a terminal proton; the calculated monoisotopic mass \(\{57.07 \ (C_4H_9) + 15 \times 104.06 \ [(C_8H_8)_{15}] + 31.97 \ (S) + 3 \times 74.02 \ [(C_3H_6S)_{3}] + 1.008 \ (H) + 106.90 \ (Ag^+)\}\ = 1979.91\ Da. However, the peak at m/z 1979.6 could also correspond to \([C_4H_9-(C_8H_8)_{15}-(C_3H_6S)_2-Ag\cdot Ag^+]\), i.e., the silver complex of the 15-mer of polystyrene, two units of propylene sulfide, and a terminal silver; the calculated monoisotopic mass \(\{57.07 \ (C_4H_9) + 15 \times 104.06 \ [(C_8H_8)_{15}] + 2 \times 74.02 \ [(C_3H_6S)_{3}] + 2 \times 106.90 \ (Ag^+)\}\ = 1979.81\ Da. Thus, the calculated monoisotopic masses cannot distinguish between these two isobaric structures. In order to distinguish between these two structures, the experimental isotopic distribution (Figure 3.3) was compared with the theoretical isotopic distributions (Figure 3.4) calculated using Bruker XTOF 5.0.2 software. The experimental isotopic distribution (Figure 3.3) shows nine peaks, the first two peaks are small and the next four peaks have similar higher intensity. This number and shape of peaks matches to the theoretical isotopic pattern shown in Figure 3.4B which is composed of nine peaks and shows the small first two peaks followed by four peaks of similar higher intensity. In contrast, Figure 3.4A shows a theoretical isotopic distribution with eight peaks and only the third and fourth peaks peaks have similar intensity. It is clear from this comparison
that the correct structure corresponds to the disilver structure without sulfur extrusion (Figure 3.4B).

![Figure 3.3. Expanded region of the experimental MALDI-TOF mass spectrum corresponding to the isotopic peaks at m/z 1979.6.](image)

Figure 3.3. Expanded region of the experimental MALDI-TOF mass spectrum corresponding to the isotopic peaks at m/z 1979.6.

![Figure 3.4. Expanded region of the theoretical isotopic distributions for (A) the silver complex of the fifteen-mer of polystyrene, with sulfur from sulfur extrusion, three units of propylene sulfide and a terminal proton \([C_4H_9-(C_8H_8)_{15}-S-(C_3H_6S)_{3}-H\cdot Ag^+]\) and (B) the silver complex of the fifteen-mer of polystyrene, with two units of propylene sulfide and a terminal silver \([C_4H_9-(C_8H_8)_{15}-(C_3H_6S)_{2}-Ag\cdot Ag^+]\).](image)

Figure 3.4. Expanded region of the theoretical isotopic distributions for (A) the silver complex of the fifteen-mer of polystyrene, with sulfur from sulfur extrusion, three units of propylene sulfide and a terminal proton \([C_4H_9-(C_8H_8)_{15}-S-(C_3H_6S)_{3}-H\cdot Ag^+]\) and (B) the silver complex of the fifteen-mer of polystyrene, with two units of propylene sulfide and a terminal silver \([C_4H_9-(C_8H_8)_{15}-(C_3H_6S)_{2}-Ag\cdot Ag^+]\).

This assignment was confirmed by measuring the MALDI-TOF mass spectrum using sodium as the cationizing agent (Figure 3.5). Although the whole mass spectrum appears to be complicated, the expanded spectrum between \(m/z\) 1860 and 1970 can be readily assigned to series of polystyrene oligomers with 1-5 mers of propylene sulfide. For example, the peak at \(m/z\) 1864.3 corresponds to \([C_4H_9-(C_8H_8)_{15}-S-(C_3H_6S)_{3}-H\cdot Na^+]\); the calculated monoisotopic mass \(\{57.07 \cdot (C_4H_9) + 15 \times 104.06 \cdot [(C_8H_8)_{15}] + 3 \times 74.02\)
\[ [(C_3H_6S)_3] + 1.008 (H) + 22.99 (Na^+) \} = 1864.03 \text{ Da}. \]

The structural information from MALDI-TOF mass spectral analysis of the products of the reaction of poly(styryl)lithium with propylene sulfide (3.5 equivalents) unambiguously shows that the functionalization reaction occurs by direct ring-opening to form the corresponding 1-methylethenylthiolate end group. This result is rather surprising, especially since previous reports on the mechanisms of reactions of organolithium compounds with propylene sulfide found evidence only for attack on the sulfur with elimination of propylene, i.e., no functionalization by direct ring-opening occurred for simple alkyl- and aryllithium compounds. For the reactions of polymeric organolithium compounds with propylene sulfide, researchers have implicitly ignored the question of the nature of the end groups beyond the fact that a lithium thiolate end group was formed. The observation of significant amounts of oligomerization of propylene sulfide during

Figure 3.5. MALDI-TOF mass spectrum of the product from the reaction of poly(styryl)lithium (M_n = 2,200 g/mol) and 3.5 equivalents of propylene sulfide in benzene at 30 °C using sodium as cationizing agent.
Functionalization of poly(styryl)lithium with propylene sulfide also stands in sharp contrast to the analogous functionalization reactions with ethylene oxide.\textsuperscript{120,121} For room temperature functionalizations of poly(styryl)lithium using 3-5 equivalents of ethylene oxide in benzene for 12 h, no oligomerization was observed by MALDI-TOF mass spectral analysis.\textsuperscript{120,121} Although lithium thiolate end groups would be expected to be aggregated analogous to lithium alkoxides,\textsuperscript{169} a weaker interaction between the hard lithium cation and the softer thiolate anion compared to the hard alkoxide anion would be expected.\textsuperscript{170,171} This would tend to result in more dissociation of the lithium thiolate aggregates to more reactive, unassociated species that could participate in oligomerization. Because of the discrepancy found between our results and the previous literature, it was decided to further investigate the mechanism of this reaction, especially the effects of stoichiometry and the presence of Lewis base additives such as THF, since many of the previous functionalizations were carried out in the presence of ethyl ether or THF.\textsuperscript{67-69,72,80-84}

3.1.2. Functionalization of poly(styryl)lithium with 2.2 equivalents of propylene sulfide followed by UV-visible spectroscopy

In order to better control the structure of the resulting functionalized polymers and to simplify the analysis of the functionalization products, it was desirable to attempt to eliminate the oligomerization of the propylene sulfide. To achieve this objective, the effects of both the reaction time and the amount of propylene sulfide relative to chain ends were investigated. Poly(styryl)lithium (PSLi, $M_n = 1.5 \times 10^3$ g/mol, $M_w/M_n = 1.05$) was reacted with 2.2 molar equivalents of propylene sulfide in benzene at 30 °C while monitoring the reaction by UV-vis spectroscopy. Prior to the addition of the propylene
sulfide to the PSLi, the $\lambda_{\text{max}}$ was observed at 334 nm. After the addition of propylene sulfide, the color of the solution changed from bright orange to light yellow, and the $\lambda_{\text{max}}$ shifted to 280 nm (Figure 3.6). The reaction was followed for a few hours but it was noted that after 15 minutes there were no further changes in the UV-vis spectrum. From this experiment it was determined that 15 minutes was sufficient time for the poly(styryllithium) to crossover to propylene sulfide.

![Figure 3.6. UV-vis spectra of poly(styryl)lithium in benzene (A) prior to addition of 2.2 molar equivalents of propylene sulfide; (B) 5 minutes after addition of propylene sulfide; and (C) 15 minutes after addition of propylene sulfide.](image)

3.1.3. Functionalization of poly(styryl)lithium with 1.3 equivalents of propylene sulfide

In order to minimize oligomerization of propylene sulfide during functionalization, poly(styryl)lithium (PSLi, $M_n = 2.0 \times 10^3$ g/mol, $M_w/M_n = 1.05$) was reacted with 1.3 molar equivalents of propylene sulfide in benzene at 30 °C for 15 minutes, at which time the solution was divided into two parts. The two living polymer aliquots were quenched with acidic methanol and methyl iodide, respectively. The SEC chromatograms
for the thiol- and methylthio-functionalized polystyrenes ($M_n = 2.1 \times 10^3$ g/mol; $M_w/M_n = 1.06$) both showed narrow, monomodal curves (Figure 3.7).

Figure 3.7. SEC chromatograms of the reaction products from the functionalization of poly(styryl)lithium ($M_n = 2,000$ g/mol) with 1.3 equivalents of propylene sulfide in benzene at 30 °C after quenching with (A) acidic methanol and (B) methyl iodide.

The characteristic peak expected for the -SH proton in the $^1$H NMR spectrum at δ 1.2 - 1.6 ppm$^{166}$ could not be identified because it overlapped with the methylene protons in the polystyrene backbone and the methyl protons in the propylene sulfide unit. If there were sulfur extrusion, the methine proton of the terminal polystyrene unit would exhibit a resonance peak at δ 3.8 ppm as estimated by ChemNMR prediction software (CambridgeSoft). The $^1$H NMR spectrum in Figure 3.8 shows that there are no resonance peaks between δ 3 and 4 ppm. This confirms the results obtained by MALDI-TOF mass spectrometry, i.e. the mechanism of addition of propylene sulfide to poly(styryl)lithium is by ring opening and not by sulfur extrusion.
Figure 3.8. $^1$H NMR spectrum (CDCl$_3$) of thiol-functional polystyrene from functionalization of poly(styryl)lithium ($M_n = 2,000$ g/mol) with 1.3 equivalents of propylene sulfide in benzene at 30 °C.

The $^{13}$C NMR spectrum of the thiol-functionalized polystyrene (Figure 3.9) shows characteristic peaks at $\delta$ 24.6 and 32.8-33.8 ppm corresponding to the methyl (k) and methine (g) carbons of the functional group, respectively. It is noteworthy that there are no resonance peaks at $\delta$ 33.8 or 142.7 ppm arising from the terminal methylene carbon and terminal ipso carbon in non-functional polystyrene, respectively. These assignments were confirmed by a $^{13}$C DEPT-135 spectrum which showed positive peaks for both the $\delta$ 24.6 and 32.8-33.8 ppm peaks which establishes that they correspond to -CH$_3$ and -CH carbons (Figure 3.10). From a quantitative $^{13}$C NMR spectrum (12500 scans; Figure 5, Appendix B), an integration ratio of 1.06 was obtained for the area of the resonance corresponding to the methine carbon in the propylene sulfide unit at $\delta$ 32.8 - 33.8 ppm relative to the area corresponding to the initiator methyl carbon at $\delta$ 11.0 - 11.4 ppm. This result is consistent with quantitative functionalization of poly(styryl)lithium and 6 % of oligomerization of propylene sulfide.
Figure 3.9. $^{13}$C NMR spectrum (CDCl$_3$) of thiol-functional polystyrene from functionalization of poly(styryl)lithium ($M_n = 2,000$ g/mol) with 1.3 equivalents of propylene sulfide in benzene at 30 °C.

Figure 3.10. 135 DEPT spectrum (CDCl$_3$) of thiol-functional polystyrene from functionalization of poly(styryl)lithium ($M_n = 2,000$ g/mol) with 1.3 equivalents of propylene sulfide in benzene at 30 °C.

Thin layer chromatographic (TLC) analysis using a toluene:cyclohexane mixture (50/50, vol/vol) as eluent, which is capable of separating the non-functionalized polystyrene from the thiol-functionalized polystyrene, resulted in observation of only one spot ($R_f = 0.6$); i.e., no spot corresponding to non-functional polymer was observed.
This is consistent with the quantitative nature of the functionalization of PSLi with propylene sulfide.\textsuperscript{175}

The calculated elemental compositions for polymer with 18 polystyrene repeat units and one propylene sulfide repeat unit \([C_9H_7(C_8H_8)_{18}CH_2CH(CH_3)SH]\) are: C, 90.36; H, 8.04, S 1.60. The calculated elemental compositions for a polymer with 2 propylene sulfide units \([C_9H_7(C_8H_8)_{18}[CH_2CH(CH_3)S]_2H]\) are: C, 88.89; H, 8.04, S, 3.07. The elemental analysis reported C, 89.84; H, 0.74; S, 2.42 (by difference). These results are consistent with a product mixture consisting of 45\% of the product corresponding to monoaddition of propylene sulfide \([P-CH_2CH(CH_3)SH]\) and 55\% of the product corresponding to diaddition of propylene sulfide \([P-[CH_2CH(CH_3)S]_2H]\).

To facilitate analysis by MALDI-TOF mass spectrometry, the methyl iodide-quenched sample was investigated. The -SCH\textsubscript{3} end group is stable in the presence of silver, thus avoiding the complication from the silver-hydrogen exchange observed previously for the -SH group. Two distributions can be observed in the mass spectrum of this sample (Figure 3.11).

![Figure 3.11. MALDI-TOF MS of the product from methyl iodide-quenched, thiol-functionalization of poly(styryl)lithium (\(M_n = 2,100\) g/mol) with 1.3 equivalents of propylene sulfide in benzene at 30 °C.](image)
A representative peak in the major distribution at \( m/z \) 1814.0 corresponds to the methylthio-functionalized polystyrene 15-mer with one propylene sulfide unit \([\text{C}_4\text{H}_9-\text{(C}_8\text{H}_8)_{15}-\text{CH}_2\text{CH(\text{CH}_3)S-\text{CH}_3}\cdot\text{Ag}^+]\); the calculated monoisotopic mass \( \{57.07 \text{ (C}_4\text{H}_9) + 15 \times 104.06 [(\text{C}_8\text{H}_8)_{15}] + 74.02 \text{ (C}_3\text{H}_6\text{S}) + 15.02 \text{ (CH}_3) + 106.90 \text{ (Ag}^+))\} = 1813.91 \text{ Da}. \) The peaks in the minor distribution are observed \( m/z \) 74 above the corresponding peaks in the main distribution. A representative peak at \( m/z \) 1888.0 corresponds to the methylthio-functionalized polystyrene 15-mer with two propylene sulfide units \([\text{C}_4\text{H}_9-\text{(C}_8\text{H}_8)_{15}-[\text{CH}_2\text{CH(\text{CH}_3)S}]_2-\text{CH}_3\cdot\text{Ag}^+]\); the calculated monoisotopic mass \( \{57.07 \text{ (C}_4\text{H}_9) + 15 \times 104.06 [(\text{C}_8\text{H}_8)_{15}] + 2 \times 74.02 \text{ (C}_3\text{H}_6\text{S})_2 + 15.02 \text{ (CH}_3) + 106.90 \text{ (Ag}^+))\} = 1887.93 \text{ Da}. \) From the relative peak sizes it is evident that oligomerization only occurred to a small extent \((3.8 \pm 0.5\%)\). Thus, once again it is concluded that the structure of the thiol-functionalized polymer corresponds to the product arising from a ring-opening mechanism and not a sulfur extrusion mechanism (see Scheme 3.1).

All of this evidence indicates that poly(styryl)lithium attacks a ring carbon (presumably the less hindered methylene carbon) in propylene sulfide followed by ring opening and the formation of a thiolate anion. This result was rather surprising, especially since the previous mechanistic studies on the reactions of organolithium compounds with propylene sulfide were consistent with attack on the sulfur with elimination of propylene.\(^{67,69,80-84}\) A possible explanation for the differences in the mechanisms of these reactions can be deduced by considering the energetics of the reaction. For the reactions of propylene sulfide with primary alkylolithium compounds (RLi) reported by Bordwell et al.\(^{80}\) as well as Morton and Kammereck,\(^{82}\) the results were interpreted in terms of a mechanism involving attack of RLi on sulfur, opening of the ring to form another primary carbanion, and then elimination of the stable thiolate to
form propene (see Scheme 1.4b). In contrast, for the reaction of PSLi with propylene sulfide (see Scheme 3.1), attack at sulfur followed by ring-opening via the stepwise mechanism would form a less stable primary carbanion intermediate (estimated conjugate acid $pK_a > 56$)\textsuperscript{176} from a much more stable benzylic carbanion (estimated conjugate acid $pK_a = 43$).\textsuperscript{176} This step would be expected to be very unfavorable energetically in spite of the exothermic ring-opening contribution and the ultimate formation of a stable thiolate anion. Another possible explanation for the different mechanisms of these reactions is based on the chemoselectivity of the organolithium compound. A more stable benzylic carbanion is expected to be more chemoselective than a more reactive, less stable alkylithium such as ethyl- and phenylolithium. It is worth noting that if this were the case, the less stable more reactive ethyllithium would probably react with propylene sulfide to give a combination of products. This is not observed, i.e. attack of ethyllithium on sulfur with elimination of propylene is exclusively observed. It is worth noting that McDonald and Chowdury\textsuperscript{177} reported the allyllithium-initiated ring opening oligomerization of ethylene sulfide to form thiolates in the gas-phase where solvent and counter-ion effects are absent. The composition of the products was determined with a quadrupole mass spectrometer. They identified products ranging from monoaddition to tetraaddition of ethylene sulfide, i.e. compositions corresponding to those expected from a ring-opening mechanism. No compositions were observed that would result from the sulfur extrusion mechanism.
3.1.4. Effect of tetrahydrofuran on the functionalization of poly(styryl)lithium with 1.3 equivalents of propylene sulfide

Since the previous investigations\textsuperscript{67-69,72,80,82-84} of organolithium compounds with propylene sulfide were all carried out in ethyl ether or THF at low temperatures, it was important to investigate the effect of Lewis base additives such as THF on the course of the reaction of poly(styryl)lithium with propylene sulfide. It was considered that the mechanistic course of this reaction could be altered by the presence of Lewis bases which are known to promote dissociation of the organolithium aggregates and increase their reactivity.\textsuperscript{3,25} Thus, Morton and coworkers\textsuperscript{53} reported that poly(styryl)lithium, which is associated into dimers in benzene, is completely converted to the unassociated organolithium chain ends in the presence of 10 equiv of THF ([THF]/[PSLi] = 10). Therefore, poly(styryl)lithium (PSLi, $M_n = 2.2 \times 10^3$ g/mol, $M_w/M_n = 1.05$) was reacted with 1.3 molar equivalents of propylene sulfide in benzene at 30 °C, in the presence of 22 molar equivalents of tetrahydrofuran (THF). The MALDI-TOF mass spectrum of the methyl iodide-quenched sample showed two distributions (Figure 3.12). A representative peak in the major distribution at $m/z$ 1813.9 corresponds to the methylthio-functionalized polystyrene 15-mer with one propylene sulfide unit $[\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{15}-\text{CH}_2\text{CH}(\text{CH}_3)\text{S-CH}_3\cdot\text{Ag}^+]$; the calculated monoisotopic mass $\{57.07 (\text{C}_4\text{H}_9) + 15 \times 104.06 [((\text{C}_8\text{H}_8)_{15}] + 74.02 (\text{C}_3\text{H}_6\text{S}) + 15.02 (\text{CH}_3) + 106.90 (\text{Ag}^+)\} = 1813.91$ Da. The peaks in the minor distribution are observed at $m/z$ 74 above the main distribution. A representative peak at $m/z$ 1888.0 corresponds to the methylthio-functionalized polystyrene 15-mer with two propylene sulfide units $\{\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{15}[-\text{CH}_2\text{CH}(\text{CH}_3)\text{S}]_2-\text{CH}_3\cdot\text{Ag}^+]$; the calculated monoisotopic mass $\{57.07 (\text{C}_4\text{H}_9) + 15 \times 104.06 [((\text{C}_8\text{H}_8)_{15}] + 2 \times 74.02 [(\text{C}_3\text{H}_6\text{S})_2] + 15.02 (\text{CH}_3) + 106.90 (\text{Ag}^+)\} = 1887.93$ Da. The relative abundance
of the minor distribution with respect to the major propylene sulfide monoaddition
distribution was calculated to be $26.4 \pm 1.4\%$. From the comparisons of the abundance
for the oligomerized chain ends relative to the major propylene sulfide monoaddition
distributions in Figures 3.11 and 3.12 ($3.8 \pm 0.5\%$ and $26.4 \pm 1.4\%$, respectively), it is
evident that the oligomerization is promoted by the presence of THF. This is possibly
due to the lower degree of aggregation and higher reactivity of the lithium thiolate chain
ends in the presence of a Lewis base, THF\textsuperscript{25,169} It is noteworthy that the structure of the
resulting polymer is the same as that obtained in the absence of THF, which indicates
that the mechanism of reaction of PSLi with propylene sulfide in hydrocarbon solution
does not change in the presence of THF.

3.1.5. Oxidation of thiol-functionalized polymers

The thiol-functionalized polymer, from the reaction of poly(styryl)lithium and 1.3
molar equivalents of propylene sulfide, was oxidized under a nitrogen atmosphere in the
presence of excess iodine. The reaction was followed by SEC, and the appearance of a
different peak at double the molecular weight of the original polymer evidenced the formation of dimer as expected (see Figure 3.13). These results corroborate the presence of the -SH end group which is known to dimerize to the disulfide linkage (-SS-) in the presence of an oxidizing agent.71,165

![Figure 3.13. SEC chromatograms for the thiol-functional polystyrene (A) before addition of iodine; (B) 10 minutes after addition of iodine; and (C) 6 hours after addition of iodine.](image)

3.1.6. Functionalization of poly(butadienyl)lithium with propylene sulfide

In order to investigate the effect of the organolithium chain end structure on the mechanism of the functionalization with propylene sulfide, poly(butadienyl)lithium was reacted with 1.3 equivalents of propylene sulfide in benzene at 30 °C for 15 minutes. The SEC chromatogram for the thiol-functionalized polybutadiene (Mn = 2.0 x 10³ g/mol; Mw/Mn = 1.06) showed a narrow, monomodal curve (Figure 3.14).

The MALDI-TOF mass spectrum of the acidic methanol quenched sample with silver as cationizing agent showed one major distribution (Figure 3.15). A representative peak in the major distribution at m/z 1482.1 corresponds to the silverated (Ag⁺) thiol-functionalized polybutadiene 23-mer with one propylene sulfide unit [C₄H₉-(C₄H₆)₂₃-CH₂CH(CH₃)S·H·Ag⁺]; the calculated monoisotopic mass {57.07 (C₄H₉) + 23 x 54.05 [(C₄H₆)₂₃] + 74.02 (C₃H₆S) +1.008 (H) + 106.90 (Ag⁺)} = 1482.13 Da.

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Figure 3.14. SEC chromatograms of (A) base sample and (B) acidic methanol quenched product of the reaction of poly(butadienyl)lithium (Mₙ = 2,000 g/mol) with 1.3 equivalents of propylene sulfide in cyclohexane at 30 °C.

Figure 3.15. MALDI-TOF MS of the product from methanol–quenched, thiol functionalization of poly(butadienyl)lithium (Mₙ = 2,000 g/mol) with propylene sulfide in cyclohexane at 30 °C.
It is concluded that the structure of the thiol-functionalized polymer corresponds to the product arising from a ring-opening mechanism and not a sulfur extrusion mechanism (see Scheme 3.1). This indicates that poly(butadienyl)lithium attacks a ring carbon (presumably the less hindered methylene carbon) in propylene sulfide followed by ring opening and the formation of a thiolate anion, analogous to the reaction of poly(styryl)lithium with propylene sulfide. It is noteworthy, that there are no resolved peaks corresponding to non-functional polybutadiene, e.g. the 25-mer \([\text{C}_4\text{H}_9-(\text{C}_4\text{H}_6)_{25}-\text{H}\cdot\text{Ag}^+]\); calculated monoisotopic mass \{57.07 (\text{C}_4\text{H}_9) + 23 \times 54.05 [(\text{C}_4\text{H}_6)_{25}] +1.008 (\text{H}) + 106.90 (\text{Ag}^+)\} = 1516.21 \text{ Da}. This result is consistent with quantitative functionalization of poly(butadienyl)lithium with propylene sulfide without oligomerization. The lack of oligomerization for the poly(butadienyl)lithium reaction in contrast to the analogous reaction for poly(styryl)lithium may be due to the use of cyclohexane versus benzene as solvent. Benzene would be expected to promote more dissociation of the thiolate aggregates to form more reactive, unaggregated chain ends.²⁵,¹⁶⁹

The \(^1\text{H} \text{NMR}\) spectrum (Figure 3.16) shows resonance peaks in the region \(\delta \) 2.8 – 3.2 ppm that correspond to the methine protons (k) in the propylene sulfide unit. The new peak at \(\delta 1.42 \text{ ppm}\) corresponds to the methyl protons (m) in the propylene sulfide repeat unit.

The \(^{13}\text{C} \text{NMR}\) spectrum of the product from propylene sulfide functionalization of poly(butadienyl)lithium (Figure 3.17) shows new resonance peaks in the region \(\delta 24.9 – 47 \text{ ppm}\) that correspond to the propylene sulfide repeat unit. The methyl carbon in the propylene sulfide unit has a characteristic resonance at \(\delta 24.9 \text{ ppm}\). The resonance peaks at \(\delta 41.5 – 42.5 \) and \(46 – 47 \text{ ppm}\), correspond to the methylene carbon in the
propylene sulfide unit adjacent to a terminal 1,4-butadiene unit and a 1,2-butadiene unit, respectively. In the same manner, the peaks at δ 34.9 and 33.8 ppm correspond to the methine carbon in the propylene sulfide unit adjacent to a terminal 1,4-butadiene unit and a 1,2-butadiene unit, respectively.

Figure 3.16. $^1$H NMR spectrum (CDCl$_3$) of thiol-functional polybutadiene from the reaction of poly(butadienyl)lithium ($M_n = 2,000$ g/mol) with propylene sulfide in cyclohexane at 30 °C.

Figure 3.17. $^{13}$C NMR spectrum (CDCl$_3$) of thiol-functional polybutadiene from the reaction of poly(butadienyl)lithium ($M_n = 2,000$ g/mol) with propylene sulfide in cyclohexane at 30 °C.
3.1.7. Functionalization of poly(styryl)lithium with ethylene sulfide

In order to study the generality of the mechanism of the reaction of PSLi with thiiranes, poly(phenyl)lithium \( (M_n = 2.7 \times 10^3 \text{ g/mol}, M_w/M_n = 1.08) \) was reacted with 1.3 molar equivalents of ethylene sulfide at 30 °C in benzene for 15 minutes. The SEC chromatogram for the thiol-functionalized polystyrene \( (M_n = 2.1 \times 10^3 \text{ g/mol}; M_w/M_n = 1.06) \) showed a narrow, monomodal curve (Figure 3.18).

The MALDI-TOF mass spectrum of the acidic methanol quenched sample with sodium as cationizing agent showed two major distributions (Figure 3.19). A representative peak in the major distribution at \( m/z \) 1702.1 corresponds to the sodiated \((\text{Na}^+)\) thiol-functionalized polystyrene 15-mer with one ethylene sulfide unit \([\text{C}_4\text{H}_9-\text{(C}_8\text{H}_8)_{15^-}\text{CH}_2\text{CH}_2\text{S-H}\cdot\text{Na}^+]\); the calculated monoisotopic mass \{57.07 \( \text{(C}_4\text{H}_9) + 15 \times 104.06 \text{[(C}_8\text{H}_8)_{15}] + 60.00 \text{(C}_2\text{H}_4\text{S}) +1.008 \text{(H)} + 22.99 \text{(Na}^+)\}\ = 1701.97 \text{ Da. The peaks in the minor distribution observed at } m/z 60 \text{ above the main distribution correspond to the products from oligomerization of ethylene sulfide at the chain end. Thus, the peak at } m/z 1762.1 \text{ corresponds to the thiol-functionalized polystyrene 15-mer with two ethylene sulfide units } [\text{C}_4\text{H}_9^-(\text{C}_8\text{H}_8)_{15^-}(\text{CH}_2\text{CH}_2\text{S})_2\text{-H}\cdot\text{Na}^+]\); the calculated monoisotopic
mass \{57.07 (C_4H_9) + 15 \times 104.06 [(C_8H_8)_{15}] + 2 \times 60.00 [(C_2H_4S)_{2}] + 1.008 (H) + 22.99 \ (Na^+)\} = 1761.97 \text{ Da}.

Figure 3.19. MALDI-TOF MS of product from methanol–quenched, thiol functionalization of poly(styryl)lithium \( (M_n = 2,700 \text{ g/mol}) \) with ethylene sulfide in benzene at 30 °C.

These results show that the mechanism of reaction between PSLi and ethylene sulfide is through ring opening by attack of the PSLi on one of the methylene carbons of ethylene sulfide, analogous to the reaction of poly(styryl)lithium and propylene sulfide. From the comparisons of the abundance for the oligomerized chain ends relative to the major propylene sulfide and ethylene sulfide monoaddition distributions in Figures 3.11 and 3.19 \( (3.8 \pm 0.5 \% \text{ and } 34.6 \pm 1.0 \%, \text{ respectively}) \), it is evident that significantly more oligomerization is occurring during the functionalization of ethylene sulfide \textit{versus} propylene sulfide. It has been shown that the attack of the poly(styryl)lithium anion is on the least substituted, methylene carbon of the propylene sulfide. Both carbons in ethylene sulfide are methylene carbons which makes ethylene sulfide more susceptible

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to attack by poly(styryl)lithium than propylene sulfide. In addition, the reduced steric congestion in the ethylene sulfide also promotes oligomerization. It is anticipated that lower extents of oligomerization would result from the use of a smaller excess of either thiirane. There are two minor distributions 16 \textit{m/z} units above the main distributions (peaks \textit{m/z} 1718.0 and 1778.0) which could represent two isobaric structures: (1) the corresponding potassiated (K$^+$) thiol-functionalized polystyrene 15-mer with 1 and 2 ethylene sulfide units, respectively; the calculated monoisotopic masses are {57.07 (C$_4$H$_9$) + 15 x 104.06 [(C$_8$H$_8$)$_{15}$] + 60.00 (C$_2$H$_4$S) +1.008 (H) + 38.96 (K$^+$)} = 1717.94 Da and \{57.07 (C$_4$H$_9$) + 15 x 104.06 [(C$_8$H$_8$)$_{15}$] + 2 x 60.00 [(C$_2$H$_4$S)$_2$] +1.008 (H) + 38.96 (K$^+$)} = 1777.94 Da, respectively; or (2) the sodiated (Na$^+$) thiol-functionalized polystyrene 14-mer with 3 and 4 ethylene sulfide units, respectively; the calculated monoisotopic masses are \{57.07 (C$_4$H$_9$) + 14 x 104.06 [(C$_8$H$_8$)$_{14}$] + 3 x 60.00 [(C$_2$H$_4$ S)$_3$] + 1.008 (H) + 22.99 (Na$^+$)} = 1717.91 Da and \{57.07 (C$_4$H$_9$) + 14 x 104.06 [(C$_8$H$_8$)$_{14}$] + 4 x 60.00 [(C$_2$H$_4$ S)$_4$] + 1.008 (H) + 22.99 (Na$^+$)} = 1777.91 Da. Although we cannot distinguish between these possibilities, a small amount of contamination by potassium ions is a reasonable possibility. The small distribution with a representative monoisotopic mass peak at \textit{m/z} 1772.0, corresponds to the loss of H$_2$S from the major distribution product [C$_4$H$_9$-(C$_8$H$_8$)$_{16}$-CH=CH$_2$.Na$^+$]; the calculated monoisotopic mass \{57.07 (C$_4$H$_9$) + 16 x 104.06 [(C$_8$H$_8$)$_{16}$] + 27.05 [(C$_2$H$_3$)] + 22.99 (Na$^+$)} = 1772.1 Da.

The $^{13}$C NMR spectrum of the product from ethylene sulfide functionalization of poly(styryl)lithium (Figure 3.20) shows characteristic peaks for the methylene carbons in the ethylenethiol chain-end unit at $\delta$ 36.1 and 24.8 ppm.\textsuperscript{178} Once more, it is noteworthy that there are no resonance peaks at $\delta$ 33.8 or 142.7 ppm arising from the terminal methylene carbon and terminal \textit{ipso} carbon in unfunctionalized polystyrene.\textsuperscript{119}
Figure 3.20. $^{13}$C NMR spectrum (CDCl$_3$) of thiol-functionalized polystyrene from reaction of poly(styryl)lithium ($M_n = 2,700$ g/mol) with 1.3 equivalents of ethylene sulfide in benzene at 30 °C.

Thin-layer chromatographic (TLC) analysis of the ethylene sulfide functionalization product using a toluene:cyclohexane mixture (50/50, vol/vol) as eluent resulted in observation of only one spot ($R_f = 0.6$); i.e., no spot corresponding to unfunctionalized polymer was observed. This is in accord with the quantitative nature of the functionalization of PS Li with ethylene sulfide. It is also noteworthy that no distribution corresponding to unfunctionalized polystyrene was detected in the MALDI-TOF mass spectrum. Thus, these results are consistent with quantitative functionalization of poly(styryl)lithium with ethylene sulfide analogous to the results for propylene sulfide functionalization.

3.1.8. Functionalization of poly(styryl)lithium with trimethylene sulfide

Morton and Kammereck reported that ethyllithium reacted with 2-methylthiacyclobutane and thiacyclobutane (trimethylene sulfide) by attack of the anion on sulfur followed by ring opening to form a primary carbanion. There are no reports of the reaction of polymeric organolithium compounds with four-membered cyclic sulfides.
There are two possible mechanisms by which the poly(styryl)lithium can react with trimethylene sulfide. The first mechanism is analogous to the reaction of ethyllithium with trimethylene sulfide, i.e. attack of the anion on sulfur followed by ring opening to form a carbanion. The second option is the attack of the anion on a carbon atom adjacent to sulfur followed by ring opening to form the thiolate anion. In order to investigate the mechanism of this reaction, poly(styryl)lithium ($M_n = 2.3 \times 10^3$ g/mol, $M_w/M_n = 1.05$) was reacted with 1.3 equivalents of trimethylene sulfide in benzene. Upon addition of the trimethylene sulfide, the reaction solution changed color from bright orange to light yellow. After 15 minutes at 30 °C, the reaction solution was divided into two parts. One part was terminated with acidic methanol. Additional styrene monomer was added to the second part and allowed to react for 20 hours; upon addition of the styrene the reaction solution slowly changed color from light yellow to orange. The color change is consistent with the formation of poly(styryl)lithium chain ends and hence that the added styrene added to the functionalization product. Since the thiolate anion cannot initiate the polymerization of styrene, this was the first evidence for the presence of carbanions in the reaction mixture. The SEC chromatogram for the acidic methanol quenched sample showed a narrow monomodal curve (Figure 3.21).

![Figure 3.21. SEC chromatogram of the acidic methanol quenched product of the reaction of poly(styryl)lithium ($M_n = 2,300$ g/mol) with 1.3 equivalents of trimethylene sulfide in benzene at 30 °C.](image-url)
The MALDI-TOF mass spectrum of the acidic methanol quenched sample with sodium as cationizing agent showed one major distribution (Figure 3.22). A representative peak in the major distribution at \( m/z \) 1716.4 corresponds to the sodiated \((Na^+)\) functionalized polystyrene 15-mer with one trimethylene sulfide unit. The MALDI-TOF analysis can determine the mass of the product but does not give any information regarding the structure of the product; hence the corresponding polymer can be \([C_4H_9-(C_8H_8)_{15}-CH_2CH_2CH_2S-H\cdot Na^+]\) or \([C_4H_9-(C_8H_8)_{15}-SCH_2CH_2CH_2-H\cdot Na^+]\); the calculated monoisotopic mass \{57.07 (C_4H_9) + 15 \times 104.06 [(C_8H_8)_{15}] + 74.02 (C_3H_6S) + 1.008 (H) + 22.99 (Na^+)\} = 1716.03 Da. There is a very small series of peaks observed at \( m/z \) 74 above the corresponding peaks in the main distribution. A representative peak at \( m/z \) 1790.6 corresponds to the functionalized polystyrene 15-mer with two trimethylene sulfide units \([C_4H_9-(C_8H_8)_{15}-[CH_2CH_2CH_2)S]_2-H\cdot Na^+]\); the calculated monoisotopic mass \{57.07 (C_4H_9) + 15 \times 104.06 [(C_8H_8)_{15}] + 2 \times 74.02 (C_3H_6S) + 1.008 (H) + 22.99 (Na^+)\} = 1790.05 Da. It is worth noting that no peaks corresponding to non-functional polystyrene can be observed, e.g. for the 16-mer \([C_4H_9-(C_8H_8)_{16}-H\cdot Na^+]\); calculated monoisotopic mass \{57.07 (C_4H_9) + 16 \times 104.06 [(C_8H_8)_{15}] + 1.008 (H) + 22.99 (Na^+)\} = 1746.07 Da. This result is consistent with quantitative functionalization of poly(styryl)lithium with trimethylene sulfide.

From the mass spectrometry results it was concluded that there was incorporation of at least one trimethylene sulfide into the polymer; however the structure cannot be determined from this analysis. The \(^1H\) NMR spectrum in Figure 3.23 shows new resonance peaks between \( \delta \) 3.2 and 3.5 ppm; these resonance peaks correspond to the methine proton in the terminal polystyrene repeat unit next to a sulfur atom, estimated \( \delta \) 3.8 ppm by ChemNMR prediction software (CambridgeSoft). Also, by
Figure 3.22. MALDI-TOF MS of product from methanol–quenched, thiol functionalization of poly(styryl)lithium ($M_n = 2.1 \times 10^3$ g/mol) with 1.3 equivalents of trimethylene sulfide in benzene at 30 °C, with sodium as cationizing agent.

Figure 3.23. $^1$H NMR spectrum (CDCl$_3$) of the acidic methanol quenched product of the reaction of poly(styryl)lithium ($M_n = 2,300$ g/mol) with 1.3 equivalents of trimethylene sulfide in benzene at 30 °C.
comparison with the initiator peaks in Figure 3.8 it is evident that there is a new peak at
$\delta$ 0.77 ppm which corresponds to the terminal methyl protons from the trimethylene
sulfide; the estimated chemical shift is $\delta$ 0.9 ppm by ChemNMR prediction software
(CambridgeSoft). The methylene protons in the trimethylene sulfide unit have an
expected chemical shift of $\delta$ 2.6 and 1.7 ppm, as estimated by ChemNMR prediction
software (CambridgeSoft). These peaks overlap with the methylene protons in the
polystyrene backbone and cannot be distinguished. Hence, from the $^1$H NMR results it is
tentatively concluded that there is formation of a product from the attack of
poly(styryl)lithium on the sulfur atom of trimethylene sulfide followed by ring opening.
The resonance peaks corresponding to the methylene protons in the thiol-functionalized
polymer, formed by attack of poly(styryl)lithium on the carbon atom of trimethylene
sulfide followed by ring opening, are expected at $\delta$ 1.5 – 2.5 ppm as estimated by
ChemNMR prediction software (CambridgeSoft). If present, these peaks overlap with the
methylene protons in the polystyrene backbone and cannot be distinguished; therefore
the possibility of this product being formed cannot be discarded from these results.

The estimated $^{13}$C NMR chemical shifts calculated with ChemNMR prediction
software (CambridgeSoft) for the possible ring opening products from the reaction of
poly(styryl)lithium and trimethylene sulfide are shown in Figure 3.24. The $^{13}$C NMR
spectrum shown in Figure 3.25 shows characteristic resonance peaks corresponding to
addition of poly(styryl)lithium to trimethylene sulfide from attack of the anion on the
sulfur followed by ring opening (A). The peak at $\delta$ 13.4 ppm corresponds to the terminal
methyl carbons of the trimethylene sulfide repeat unit (predicted 13.0 ppm). The
resonance peaks at $\delta$ 47.0 - 47.5 ppm corresponds to the methine carbon in the
terminal polystyrene repeat unit adjacent to sulfur (predicted 50.0). The methylene
carbons in the trimethylene sulfide repeat unit have resonance peaks at \( \delta \) 22.5 and 33.0 ppm (predicted 23.3 and 32.8 ppm). These later peaks can also correspond to the methylene carbons from the thiol-functionalized polymer formed by attack of poly(styryl)lithium on the carbon atom of trimethylene sulfide followed by ring opening (B), the predicted chemical shifts for these carbons are 24.9, 30.2 and 35.2 ppm. Once again, the possibility of this product being formed cannot be discarded from these results.

Figure 3.24. Predicted \(^{13}\)C NMR chemical shifts for the ring opening product of the reaction of poly(styryl)lithium with trimethylene sulfide (A) by attack on the sulfur atom and (B) by attack on a carbon atom.

Figure 3.25. \(^{12}\)C NMR spectrum (CDCl\(_3\)) of the acidic methanol quenched product of the reaction of poly(styryl)lithium (M\(_n\) = 2,300 g/mol) with 1.3 equivalents of trimethylene sulfide in benzene at 30 °C.

Since a thiolate anion does not initiate polymerization of styrene but a carbanion does, it was anticipated that if any attack of the poly(styryl)lithium occurred on the
sulfur of trimethylene sulfide, then a primary carbanion would be formed that would initiate styrene polymerization. Hence, additional styrene monomer was added to the reaction mixture 15 minutes after the addition of trimethylene sulfide to poly(styryl)lithium. The SEC chromatogram shown in Figure 3.26 shows a bimodal curve with a small low molecular weight peak. This indicates that most of the chain ends are carbanions since they polymerized styrene; this observation is consistent with the $^1$H and $^{13}$C NMR results. The low molecular weight product can be trimethylene sulfide-functionalized polystyrene (-CH$_3$ end group), thiol-functionalized polystyrene (-SH end group) or non-functional polystyrene. The trimethylene sulfide-functionalized polystyrene (-CH$_3$ end group) is expected to have initiated the polymerization of styrene and formed higher molecular weight products. The MALDI-TOF analysis of the polymer before addition of the additional styrene shows only functionalized polystyrene, no non-functional polystyrene was detected (see Figure 3.22). Hence, it is anticipated that the low molecular weight peak in the SEC chromatogram corresponds to thiol-functionalized polystyrene.

Figure 3.26. SEC chromatogram of (A) base sample and (B) acidic methanol quenched product of the reaction of PSLi ($M_n = 2,300$ g/mol) with 1.3 equivalents of trimethylene sulfide followed by addition of styrene monomer in benzene at 30 °C.
To confirm this conclusion, the product from the reaction of poly(styryl)lithium with 1.3 equivalents of trimethylene sulfide was oxidized under argon atmosphere in the presence of iodine. Thiol-functionalized polymer, if present, is known to dimerize to the disulfide linkage (-SS-) in the presence of an oxidizing agent. The reaction was followed by SEC for 4 days, the absence of a new peak at double the molecular weight of the original polymer is consistent with the lack of -SH end group in the product. From the oxidation experiment it was concluded that there was no thiol-functionalized polystyrene present. This result was rather surprising, as it was already mentioned there was no non-functional polystyrene detected in the mass spectrum of the functionalized product before the addition of styrene (see Figure 3.22) and trimethylene sulfide-functionalized polymer was expected to initiate the polymerization of styrene and form higher molecular weight products. From the SEC results, the low molecular weight product can be estimated as 5 % of the poly(styryl)lithium (see Appendix C). In order to investigate the nature of the low molecular weight products, the MALDI-TOF mass spectrum of the product after the addition of styrene was obtained. From these results, it was determined that the low molecular weight products are a combination of non-functional polystyrene and trimethylene sulfide-functionalized polymer. It is always possible to have some termination reactions due to impurities present when adding functionalizing agents and monomers to the reaction.

The $^1$H NMR spectrum of the crude product of the reaction of poly(styryl)lithium with trimethylene sulfide followed by additional styrene monomer is shown in Figure 3.27. The resonance peaks between $\delta$ 2.8 and 4.0 are characteristic of the methine proton in the terminal polystyrene repeat unit adjacent to a sulfur atom. This is
consistent with formation of a product from the attack of poly(styryl)lithium on the sulfur atom of trimethylene sulfide followed by ring opening.

In conclusion, the reaction of poly(styryl)lithium with trimethylene sulfide occurs exclusively by attack of the anion on the sulfur of trimethylene sulfide followed by ring opening to form a primary carbanion, analogous to the reaction of ethyllithium with trimethylene sulfide reported by Morton and Kammereck.\textsuperscript{82} Trimethylene sulfide-functionalized polystyrene (\(-\text{CH}_3\) end group) was obtained in a high yield (> 95 %). Thiol-functionalized polystyrene was not obtained by reaction of poly(styryl)lithium with trimethylene sulfide. These results are in contrast with the results obtained when poly(styryl)lithium was reacted with propylene sulfide. It has been proposed that the difference in the mechanisms for the reactions of ethyllithium and poly(styryl)lithium with propylene sulfide was due to the difference in pK\textsubscript{a} of the organolithium compound. It was observed that a more stable poly(styryl) anion attacked a ring carbon in propylene sulfide followed by ring opening and formation of a thiolate anion, while ethyllithium attacked on sulfur with elimination of propylene. Hence, it was expected that the reaction of poly(styryl)lithium with trimethylene sulfide would also occur by attack on the carbon to form a more stable thiolate anion. Since this was not the case, it is concluded that the pK\textsubscript{a} argument is not applicable for the reaction of poly(styryl)lithium with trimethylene sulfide. A plausible explanation is again chemoselectivity of the poly(styryl)lithium towards attack on the carbon of propylene and ethylene sulfide and attack on the sulfur in trimethylene sulfide.
3.2. Synthesis of trimethoxysilane-functionalized polymers

One of the unique features of living anionic polymerization is the ability to prepare a variety of chain-end functionalized polymers by post-polymerization reaction of the polymeric carbanionic chain ends with electrophilic reagents.\textsuperscript{3,5,6} One of the limitations of this method is that optimized experimental procedures must be investigated for each functionalization using a different electrophilic reagent.\textsuperscript{3,5} A second limitation is that many functional groups are not stable to anionic chain ends; therefore, the functional groups must be converted to anionically stable moieties using protecting groups and these protecting groups must be removed after the functionalization reaction to generate the desired functional group.\textsuperscript{21} A useful alternative is to develop general functionalization reactions in which one chemistry can be used to generate a wide
variety of different functional groups. One such general anionic functionalization methodology is the silyl hydride functionalization/hydrosilation procedure outlined in Section 1.2.2 and illustrated in Scheme 3.2. The advantages of this method include: (a) the silyl hydride-functionalized polymer can be isolated by precipitation into methanol and it is stable to water and air; (b) one silyl hydride-functionalized polymer can be used to generate a variety of different chain-end functional polymers using different substituted alkenes; (c) most functional groups of interest do not interfere with the hydrosilation reaction and thus protecting groups are not required. In order to investigate the applicability of this methodology for the preparation of trialkoxysilyl-functionalized polymers, it was first necessary to prepare a silyl hydride-functionalized polymer.

Scheme 3.2. General functionalization methodology by the combination of living anionic polymerization and hydrosilation.

3.2.1. Functionalization of poly(styryl)lithium with chlorodimethylsilane

Poly(styryl)lithium (PSLi, $M_n = 2.1 \times 10^3$ g/mol, $M_n/M_w = 1.02$) was reacted with 2.3 equivalents of chlorodimethylsilane in benzene at 30 °C as shown in Equation 21.
The SEC chromatogram for the silyl hydride-functionalized polystyrene \((M_n = 2.2 \times 10^3 \text{ g/mol}; M_w/M_n = 1.02)\) showed a narrow, monomodal curve (see Figure 3.28).

The \(^1\text{H}\) NMR spectrum showed the characteristic peaks corresponding to the -SiH proton at \(\delta \ 3.8 \text{ ppm}\) and for the silicon-bonded methyl groups at \(\delta \ -0.1 \text{ ppm}\) (see Figure 3.29). The integration ratio of the six methyl protons of the dimethylsilane unit to the six methyl protons from the sec-butyl end group (\(\delta \ 0.5 – 0.8 \text{ ppm}\)), was observed to be 1:1, indicating that the reaction was quantitative.

Figure 3.28. SEC chromatogram of silyl hydride-functionalized polystyrene \((M_n = 2.2 \times 10^3 \text{ g/mol}; M_w/M_n = 1.02)\).
The MALDI-TOF mass spectrum for the silyl hydride functionalized polymer obtained using sodium as cationizing agent showed only one distribution (see Figure 3.30). A representative peak at m/z 2012 corresponds to the silyl hydride-functionalized polystyrene 18-mer, C₄H₉-(C₈H₈)₁₈-Si(CH₃)₂H·Na⁺; calculated monoisotopic mass \{57.07 (C₄H₉) + 18 \times 104.06 [(C₈H₈)₁₈] + 27.98 + 2 \times 15.02 (CH₃) + 1.008 + 22.99 (Na⁺)\} = 2012.24 Da. No peaks corresponding to the unfunctionalized polystyrene homopolymer were observed, e.g. the polystyrene 19-mer, C₄H₉-(C₈H₈)₁₉-H·Na⁺; calculated monoisotopic mass \{57.07 (C₄H₉) + 19 \times 104.06 [(C₈H₈)₁₉] + 1.008 + 22.99 (Na⁺)\} = 2058.26 Da. These results confirm both the structure of the product and the quantitative nature of the reaction.
3.2.2. Hydrosilation of silyl hydride-functionalized polymer with vinyltrimethoxysilane

In order to prepare trimethoxysilyl-functionalized polystyrene, the silyl hydride functionalized polystyrene was reacted with vinyltrimethoxysilane in benzene at room temperature in the presence of Karstedt’s catalyst as shown in Equation 22. The SEC chromatogram for the trimethoxysilyl-functionalized polystyrene ($M_n = 2.5 \times 10^3$ g/mol; $M_w/M_n = 1.11$) showed a monomodal curve with a small high molecular weight shoulder which corresponds to double the molecular weight of the main peak (see Figure 3.31).

Figure 3.30. MALDI-TOF MS of silyl hydride-functionalized polystyrene ($M_n = 2,200$ g/mol), using sodium as cationizing agent.
Figure 3.31. SEC chromatogram of the products from the hydrosilation of vinyl trimethoxysilane with silyl hydride-functionalized polystyrene \((M_n = 2,500 \text{ g/mol}; \frac{M_w}{M_n} = 1.11)\) in benzene at room temperature.

The MALDI-TOF mass spectrum of the trimethoxysilyl-functionalized polymer (Figure 3.32 and 3.33) obtained using silver as cationizing agent showed two distributions centered at \(m/z\) 2000 and a third distribution centered at \(m/z\) 4000. A representative peak of the major distribution (1) at \(m/z\) 1827.9 corresponds to the trimethoxysilyl-functionalized polystyrene 14-mer, \(C_{4}H_{9}-(C_{8}H_{8})_{14}-\text{Si}(\text{CH}_{3})_{2}\text{CH}_{2}\text{Si}(\text{OCH}_{3})_{3}\cdot\text{Ag}^{+}\); calculated monoisotopic mass \(\{57.07 (C_{4}H_{9}) + 14 \times 104.06 [(C_{8}H_{8})_{14}] + 27.98 (\text{Si}) + 2 \times 15.02 (\text{CH}) + 2 \times 14.03 (\text{CH}_{2}) + 27.98 (\text{Si}) + 3 \times 31.03 (\text{OCH}_{3}) + 106.90 (\text{Ag}^{+})\} = 1827.93\) Da. A peak in the minor distribution (2) is observed at \(m/z\) 1809.9 and corresponds to the vinylsilane-functionalized polystyrene 15-mer, \(C_{4}H_{9}-(C_{8}H_{8})_{15}-\text{Si}(\text{CH}_{3})_{2}\text{CH=CH}_{2}\cdot\text{Ag}^{+}\); calculated monoisotopic mass \(\{57.07 (C_{4}H_{9}) + 15 \times 104.06 [(C_{8}H_{8})_{15}] + 27.98 (\text{Si}) + 2 \times 14.03 (\text{CH}) + 27.98 (\text{Si}) + 3 \times 31.03 (\text{OCH}_{3}) + 106.90 (\text{Ag}^{+})\} = 1809.93\) Da.
+ 15 x 104.06 [(C₆H₅)₁₅] + 27.98 (Si) + 2 x 15.02 (CH₃) + 13.02 (CH) + 14.03 (CH₂) +
106.90 (Ag⁺}} = 1809.96 Da. From the peak sizes, the side product is estimated to
correspond to 12 % of the low molecular weight product.

Figure 3.32. MALDI-TOF MS of the products of hydrosilation of vinyltrimethoxysilane
with silyl hydride-functionalized polystyrene (Mₙ = 2,200 g/mol) in benzene at room
temperature, using silver as cationizing agent.

Figure 3.33. Expanded MALDI-TOF MS in the range of m/z 1720 – 1830 of the products
of hydrosilation of vinyltrimethoxysilane with silyl hydride-functionalized polystyrene (Mₙ
= 2,200 g/mol) in benzene at room temperature, using silver as cationizing agent.
Thin layer chromatographic (TLC) analysis showed two spots; the majority of the product stayed at the bottom of the TLC plate and a small fraction displaced to the top (see Figure 3.34).

Each spot was scrapped off the TLC plate and the products were analyzed separately by MALDI-TOF mass spectrometry (Figures 3.35 and 3.36). The MALDI-TOF mass spectrum of the bottom fraction (Figure 3.35) shows only one distribution with a representative peak at \( m/z \) 1827.9 corresponding to the desired trimethoxysilane-functionalized polystyrene 14-mer (calculated monoisotopic mass = 1827.93 Da). The MALDI-TOF mass spectrum of the top fraction (Figure 3.36) shows 3 distributions centered at \( m/z \) 2000 and a high molecular weight distribution centered at \( m/z \) 4000. The latter corresponds to dimer presumably formed from the reaction of silyl hydride-functionalized polymer with the vinylsilane-functionalized polymer as shown in equation 23. Thus, a representative peak in the high molecular weight distribution at average mass \( m/z \) 3699 corresponds to the coupled product with 32 styrene units, \( \text{C}_4\text{H}_9\text{-(C}_8\text{H}_8\text{)}_n\text{-Si(CH}_3)_2\text{CH}_2\text{CH}_2\text{Si(CH}_3)_2\text{-(C}_8\text{H}_8\text{)}_{32-n}\text{-C}_4\text{H}_9\text{·Ag}^+ \); calculated average mass \{2 x 57.12 \( \text{(C}_4\text{H}_9 \text{)}\) + 32 x 104.15 \{\text{(C}_8\text{H}_8)_{32}\} + 2 x 28.08 \{\text{Si}\} + 4 x 15.02 \{\text{CH}_3\} + 2 x 14.03 \{\text{CH}_2\} + 107.87 \text{Da} \}.\)
Figure 3.35. MALDI-TOF MS of the bottom TLC fraction of the products of hydrosilation of vinyltrimethoxysilane with silyl hydride-functionalized polystyrene (M_n = 2,200 g/mol) in benzene at room temperature.

Figure 3.36. MALDI-TOF MS of the top TLC fraction of the products of hydrosilation of vinyltrimethoxysilane with silyl hydride-functionalized polystyrene (M_n = 2,200 g/mol) in benzene at room temperature.
(Ag⁺)) = 3699.4 Da. In the low molecular weight region, the major distribution (2) with a representative monoisotopic mass peak at m/z 1809.9 corresponds to the minor product observed in the crude mixture of products (Figure 3.28), i.e. the vinylsilane-functionalized polystyrene 15-mer. A representative peak in the minor distribution (4) at m/z 1829.9 corresponds to the 16-mer of non-functional polystyrene, C₄H₉-(C₈H₈)₁₆-H·Ag⁺; calculated monoisotopic mass \(57.07 \times 4\) + \(16 \times 104.06 \times [(C₈H₈)₁₆] + 1.008 (H) + 106.90 (Ag⁺)) = 1829.98 Da. The non-functional polystyrene corresponds to less than 2 % of the crude product; the distribution of non-functional polymer overlaps with peaks in the main product, e.g. at m/z 1827.9 in Figure 3.33. There is a very small third distribution (3) with a representative monoisotopic mass peak at m/z 1799.9, that corresponds to the 15-mer of oxidized silyl hydride-functionalized polystyrene, C₄H₉-(C₈H₈)₁₅-Si(CH₃)₂OH·Ag⁺; calculated monoisotopic mass = 1799.96 Da. This product represents less than 1 % of the crude product. From this mass spectrometric analysis it is estimated that the trimethoxysilane-functionalized polymer corresponds to 85 % of the low molecular weight product. From the SEC chromatogram the amount of dimer can be estimated as 2 %. Hence, from a combination of mass spectrometric and SEC analyses, the relative amounts of product can be calculated: trimethoxysilane-functionalized polymer 83 %, vinylsilane-functionalized polymer 12 %, dimeric product 2 %, non-functional polymer 2 % and unreacted silyl hydride-functionalized polymer 1 %.

\[
\text{Si} \quad \text{CH}_3
\]

\[
\text{CH}_3\quad \text{Si} \quad \text{H}_2\text{Si}\quad \text{CH}_3
\]

\[
\text{Pt} \quad \text{Si} \quad \text{CH}_3\quad \text{CH}_3\quad \text{Si} \quad \text{H}_2\text{Si}\quad \text{CH}_3
\]

(23)
The $^1$H NMR spectrum (Figure 3.37) showed the disappearance of the peak at $\delta$ 3.8 ppm corresponding to the $-\text{SiH}$ proton absorption and appearance of new resonance peaks at $\delta$ 3.5 ppm corresponding to the methoxy protons and between $\delta$ 0 and 0.6 ppm corresponding to the methylene protons between the silicon atoms $-\text{SiCH}_2\text{CH}_2\text{Si}-$. The expansion of the region between $\delta$ 5.3 and 6.1 ppm reveals two peaks that can be assigned to the protons in the vinyl group of the vinylsilane-functionalized polystyrene.

![Chemical structure of vinyltrimethoxysilane and silyl hydride-functionalized polystyrene](image)

Figure 3.37. $^1$H NMR spectrum (CDCl$_3$) of the crude products of hydrosilation of vinyltrimethoxysilane with silyl hydride-functionalized polystyrene ($M_n = 2,500$ g/mol) in benzene at room temperature.

The quantitative $^{13}$C NMR spectrum (12200 scans, Figure 3.38) showed the characteristic peak for the methoxy carbons (-OCH$_3$) at $\delta$ 50.8 ppm. The resonance peak for one of the methyl carbons on the initiator fragment can be observed at $\delta$ 11.3 ppm. The integration ratio of the three methoxy carbons of the trimethoxysilane unit to the carbon from the sec-butyl end group was observed to be 3:1.25 (theoretical 3:1). From these results the yield of trimethoxysilane-functionalized polymer can be calculated as

111
80 %. This result is in excellent agreement with the results from mass spectrometry and SEC analyses (83 % of the low molecular weight product).

The vinylsilane-functionalized polymer side product represents approximately 12 % of the low molecular weight product. The dimer side product, presumably formed from the hydrosilation of the vinylsilane-functionalized polymer with silyl hydride-functionalized polymer, corresponds to approximately 2 % of the total product. Therefore, it is important to consider the mechanism by which the vinylsilane-functionalized polymer is being formed.

A characteristic feature of the hydrosilation of vinylsilanes is substituent exchange at the silicon atom; the vinyl/H exchange as shown in equation 15 leads to the formation of at least two and sometimes four products from hydrosilation.96,97

\[
R_3SiH + SiR'3 \xrightarrow{\text{SiR}_3} R'_3SiH + SiR_3
\]  

(15)
Although this exchange is well-known and has been proven numerous times, the mechanism by which this exchange takes place has not been elucidated. The most accepted hydrosilation mechanism is that proposed by Chalk and Harrod.\textsuperscript{90} As shown in Scheme 3.3A, this mechanism consists of the coordination of the olefin to the metal centre (a), followed by oxidative addition of the hydrosilane (b) and then alkene insertion into the metal-hydride bond (c). After the alkene insertion there are two options, if hydrosilation continues its normal course, the complex reacts with excess olefin, regenerating the catalyst and forming the organosilicon compound, trimethoxysilane functionalized polymer in this case, by Si-C reductive elimination (d); or the silicon from the vinylsilane compound coordinates with the metal forming ethylene (e), which in turn can form the vinylsilane-functionalized polymer by Si-C reductive elimination between the polymer and ethylene (f). Based on the modified Chalk-Harrod mechanism, there is another possible mechanism that can be proposed for the formation of the vinyl silane side product as shown in Scheme 3.3B. Olefin coordination is followed by oxidative addition into the metal centre (b); then the alkene inserts into the metal-silyl bond in a Markovnikov fashion leading to a 2,2-disilylalkylPt species (g). This step is reversible and can go back to (b) or the platinum can coordinate with the silyltrimethoxy group, eliminating the vinyl silane side product. If this mechanism were taking place, other Markovnikov addition products should be observed. It is worth noting that in general platinum-catalized hydrosilation of silyl hydrides with vinyl silanes takes place according to anti-Markovnikov addition giving $\beta$-adducts.

In order to attempt to eliminate or reduce the amount of vinylsilane-functionalized polymer, the effect of reaction time was studied. Hence, a sample was taken after one hour for the hydrosilation reaction of 2.3 equivalents of
Scheme 3.3. (a) Chalk-Harrod mechanism for hydrosilation and proposed mechanism for the formation of vinylsilane-functionalized polymer by vinyl/H exchange during hydrosilation of silyl hydride-functionalized polystyrene with vinyltrimethoxysilane (b) Proposed mechanism for the formation of vinylsilane-functionalized polymer by vinyl/H exchange during hydrosilation of silyl hydride-functionalized polystyrene with vinyltrimethoxysilane based on the modified Chalk-Harrod mechanism.
vinyltrimethoxysilane with silyl hydride-functionalized polystyrene in benzene at room temperature in the presence of Karstedt’s catalyst. MALDI-TOF mass spectrometric analysis was performed on the sample, and the resulting spectrum is shown in Figure 3.39. A representative monoisotopic mass peak of the main distribution is observed at $m/z$ 1699.8 corresponds to the 15-mer of the starting material, silyl hydride-functionalized polystyrene; $C_4H_9-(C_8H_8)_{15}-Si(CH_3)2H\cdot Na^+$; calculated monoisotopic mass \{57.07 (C_4H_9) + 15 x 104.06 [(C_8H_8)_{15}] + 27.98 + 2 x 15.02 (CH_3) + 1.008 + 22.99 (Na^+))\} = 1700.05 Da. There is a minor distribution (1) with a representative monoisotopic mass peak at $m/z$ 1639.8 that corresponds to the desired product, trimethoxysilane-functionalized polystyrene 13-mer, $C_4H_9-(C_8H_8)_{13}-Si(CH_3)2CH_2CH_2Si(OCH_3)3\cdot Na^+$; calculated monoisotopic mass \{57.07 (C_4H_9) + 13 x 104.06 [(C_8H_8)_{13}] + 27.98 (Si) + 2 x 15.02 (CH_3) + 2 x 14.03 (CH_2) + 27.98 (Si) + 3 x 31.03 (OCH_3) + 22.99 (Na^+))\} = 1640.04 Da. It is worth noting that even after only one hour of reaction time there is a small peak (2) at $m/z$ 1725.9 which indicates the presence of the undesired side product, the 15-mer of vinylsilane-functionalized polystyrene; $C_4H_9-(C_8H_8)_{15}-Si(CH_3)2CH=CH2\cdot Na^+$; calculated monoisotopic mass \{57.07 (C_4H_9) + 15 x 104.06 [(C_8H_8)_{15}] + 27.98 (Si) + 2 x 15.02 (CH_3) + 13.02 (CH) + 14.03 (CH_2) + 22.99 (Na^+))\} = 1726.09 Da. It was concluded that the formation of the side product occurred from the beginning of the reaction and that reducing the reaction time did not eliminate the formation of the undesired side product.
The hydrosilation reaction was performed in the presence of a different catalyst to attempt to eliminate the formation of the vinylsilane-functionalized polystyrene. Hence, 2.3 equivalents of vinyltrimethoxysilane was reacted with silyl hydride-functionalized polystyrene in benzene at room temperature in the presence of Speier’s catalyst ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$). The reaction was slower than in the presence of Karstedt’s catalyst. A sample was removed from the reaction after 1 hour and analyzed by MALDI-TOF mass spectroscopy. The spectrum showed only one distribution corresponding to the starting silyl hydride-functionalized polystyrene. Another sample was removed and analyzed after 24 hours; the resulting spectrum is shown in Figure 3.40. At least four distributions can be identified in the mass spectrum. The main distribution has a representative monoisotopic mass peak at $m/z$ 1700.0, which corresponds to unreacted...
silyl hydride-functionalized polystyrene 15-mer, as detailed in the previous discussion. The second highest distribution (1) with a representative monoisotopic mass peak at \( m/z \) 1639.9 corresponds to the desired trimethoxysilane-functionalized polystyrene, as detailed in the previous discussion. There are two distributions (5) and (6) with representative monoisotopic mass peaks at \( m/z \) 1730.0 and \( m/z \) 1716.0, respectively. These products have not been observed before and these are placed 14 and 28 \( m/z \) units below the distribution of the desired product (1), respectively. It is well known that methoxy groups are easily hydrolyzed to form hydroxyl groups in the presence of water. Hydrolysis of one of the methoxy groups in the trimethoxysilane unit will result in the loss of the mass corresponding to \( \text{CH}_2 \) (14 mass units). Hydrolysis of two methoxy groups, means a loss of two \( \text{CH}_2 \) units and a mass loss of 28. Hence, the distributions (5) and (6) are assigned to the partially hydrolyzed trimethoxysilane-functionalized products from the hydrolysis of one and two methoxy groups, respectively. The calculated monoisotopic mass for the 14-mer of the partially hydrolyzed trimethoxysilane-functionalized polystyrene with two methoxy groups \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{14}-\text{Si(CH}_3)_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)_2\text{OH}^+\cdot\text{Na}^+ \), is 1730.07 Da; and the calculated monoisotopic mass for the 14-mer of the partially hydrolyzed trimethoxysilane-functionalized polystyrene with one methoxy group, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{14}-\text{Si(CH}_3)_2\text{CH}_2\text{CH}_2\text{Si(OCH}_3)(\text{OH})_2^+\cdot\text{Na}^+ \), is 1716.05 Da. The calculated monoisotopic mass for the 14-mer of trihydroxysilane-functionalized polystyrene, i.e. the completely hydrolyzed trimethoxysilane-functionalized polymer, \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{14}-\text{Si(CH}_3)_2\text{CH}_2\text{CH}_2\text{Si(OH)}_3^+\cdot\text{Na}^+ \), is 1702.02 Da. Since the main distribution lies at \( m/z \) 1700.0, it is evident that the completely hydrolyzed product, if present, would overlap with the starting material and hence it cannot be observed in the present spectrum. It is worth noting that, although
the reaction was performed under an inert atmosphere and all reactants were dried prior to use, the catalyst used was Speier’s catalyst, chloroplatinic acid hexahydrate H₂PtCl₆·6H₂O. Hence, the water present in the catalyst effected the hydrolysis of the methoxy groups that gave rise to the range of products observed.

In any case, the purpose of the experiment was to determine if the use of a different catalyst would avoid the formation of the vinylsilane side product. Once again, a very small distribution (2) with a representative monoisotopic mass peak at $m/z$ 1726.0 corresponding to the vinylsilane-functionalized polystyrene 15-mer, was observed. It was concluded that in the presence of Speier’s catalyst the hydrosilation reaction is slower, gives a range of products from hydrolysis of the methoxy groups and also forms vinylsilane-functionalized product at early stages of the reaction.

![Figure 3.40. MALDI-TOF MS of the products of hydrosilation of vinyltrimethoxysilane with silyl hydride-functionalized polystyrene (Mₓ = 2,200 g/mol) after 24 hours of reaction time using Speier’s catalyst in benzene at room temperature.](image-url)
3.2.3. Functionalization of poly(styryl)lithium with vinlyldimethylchlorosilane in benzene at 30 °C

In order to obtain more information and improve the characterization of the product from the hydrosilation reaction of poly(styryl)lithium with vinyltrimethoxysilane, it was desired to prepare the side product, vinylsilane-functionalized polymer. It was anticipated that the vinylsilane-functionalized polymer could be synthesized by reaction of poly(styryl)lithium with vinlyldimethylchlorosilane.

The reaction of vinlyldimethylchlorosilane with tert-butyllithium at low temperatures in hydrocarbon solvent has been investigated by Jones and coworkers.\textsuperscript{181,182} The major products were the cis- and trans- 1,3-disilacyclobutanes as shown in equation 24.

\[
\text{SiCl} + \text{Li} \rightarrow \text{SiSi} \quad (24)
\]

Based on trapping and competition experiments with various chlorosilanes and 1,3-butadiene, a mechanism was proposed. This mechanism suggests that the reaction starts by addition of tert-butyllithium to vinylsilane to form an $\alpha$-lithiochlorosilane. The $\alpha$-lithiochlorosilane eliminates lithium chloride to form a silaethylene intermediate which dimerizes to form the 1,3-disilacyclobutane product. In the presence of THF, products from the coupling of intermediate lithium compounds with chlorosilanes were obtained in addition to the 1,3-disilacyclobutanes. In contrast to these results, the anionic polymerization of trimethylvinylsilane has been reported. Nametkin and coworkers\textsuperscript{183} first reported the anionic polymerization of trimethylvinylsilane using ethyllithium as initiator in heptane; the polymerization was reportedly living although a slow
termination and chain transfer to monomer at high temperature occurred. The propagation was reported to take place by attack of an $\alpha$-methine anion to the vinyl group in the vinyltrimethylsilane. Later, Asami and coworkers reported that an isomerization reaction occurs in the anionic polymerization of vinyltrimethylsilane with $n$-butyllithium in hexane and is enhanced in the presence of TMEDA. This isomerization occurs by abstraction of a silylmethyl proton by the propagating silylmethine anion. This results in the incorporation of $-\text{CH}_2\text{CH}_2\text{Si(CH}_3)_2\text{CH}_2-$ units in the polymer backbone. Rickle reported the anionic synthesis of polystyrene-$b$-poly(trimethylvinylsilane) copolymer by sequential monomer addition. Rempp and coworkers reported the preparation of vinylsilane-functionalized polystyrene by reaction of poly(styryl)lithium with vinyltrimethylchlorosilane and vinyl(chloromethyl)dimethylsilane in THF at -70 °C. They reported the occurrence of coupling side reactions observed by SEC. The side reactions were reported to be unavoidable even when end-capping the poly(styryl)lithium with diphenylethylene or ethylene oxide. Later Tezuka and Araki reported the synthesis of vinylsilane-functionalized polystyrene in high yields (91 – 98 %) by reaction of poly(styryl)lithium with 5 equivalents of vinyltrimethylchlorosilane in a THF/benzene (2/1, vol/vol) solution at -50 °C. The products were analyzed by SEC and $^1$H NMR spectroscopy. Recently, Wilczek reported a one-pot synthesis of polymers containing branches upon branches by continuous addition of vinylchlorosilane and styrene monomer to a poly(styryl)lithium solution. The results are consistent with a mechanism in which the poly(styryl)lithium is terminated with vinylchlorosilane to form vinylsilane-functionalized macromonomer.
Based on this background, poly(styryl)lithium (Mₙ = 2.1 x 10³ g/mol, Mₙ/Mₚ = 1.03) was reacted with 6.6 equivalents of vinyl(dimethyl)chlorosilane in benzene at 30 °C. The reaction was expected to proceed according to equation 25.

\[
\text{Si} \quad \text{CH}_3 \quad \text{CH}_3 \\
\text{Li} \quad \text{Si} \quad \text{CH}_3 \quad \text{CH}_3
\]

(25)

Immediately after the vinyl(dimethyl)chlorosilane was added, the reaction mixture changed from bright orange to yellow. After 12 hours the reaction mixture was clear and a sample was removed from the reactor with a side ampoule. The reaction was terminated with methanol after 3 days. The products were precipitated into methanol and freeze-dried. The SEC chromatogram (Figure 3.41) showed a trimodal curve with a higher molecular weight and broad molecular weight distribution (Mₙ = 1.4 x 10⁴ g/mol, Mₙ/Mₚ = 1.2). There is a small peak at low molecular weight (higher elution volume); the vinylsilane-functionalized polymer, if formed, should have the same molecular weight as the base polymer. From the SEC results it is possible that vinylsilane-functionalized polymer was prepared but it is evident that there were side reactions occurring.

Poly(styryl)lithium can react with vinyl(dimethyl)chlorosilane in two ways (i) it can displace the chlorine and add to the silicon deactivating the chain end (A in Scheme 3.4) or (ii) it can add to the double bond (B in Scheme 3.4); if more than one equivalent is added, the resulting carbanion can oligomerize to form the dimethylchlorosilyl ethyl anion (D in Scheme 3.4). In case (i) the product A is a vinylsilane-functionalized polymer; this
Figure 3.41. SEC chromatograms of the products of the reaction of poly(styryl)lithium ($M_n = 2,100 \text{ g/mol}$) with 6.6 equivalents of vinyldimethylchlorosilane in benzene at 30 °C (A) after 12 h (B) after 3 days and (C) base sample.

Scheme 3.4. Products from the reaction of poly(styryl)lithium with vinyldimethylchlorosilane in benzene at 30 °C.
is a macromonomer and the double bond can further react to add to a living chain, either a poly(styryl)lithium chain end (to form F in Scheme 3.4) or dimethylchlorosilylethyllithium chain end (such as D in Scheme 3.4), in the reaction mixture. When vinylidimethylchlorosilane oligomerizes (to form D in Scheme 3.4), each repeat unit has a chloride that can be displaced by other living carbanionic chain end. Again this living carbanionic chain can be either a poly(styryl)lithium chain end (to form E in Scheme 3.4) or a dimethylchlorosilylethyllithium chain end (such as D in Scheme 3.4). These reactions can occur repeatedly to form star branched polymers. From the molecular weight of the resulting polymer (M_n = 1.4 x 10^4 g/mol, M_w = 1.6 x 10^4 g/mol) and the precursor (M_n = 2.08 x 10^3 g/mol, M_w = 2.14 x 10^3 g/mol), the average number of arms can be calculated to be 6.8.

The intrinsic viscosity for the high molecular weight peak, 0.046 dL/g, was obtained from the SEC results. This result can be compared with the intrinsic viscosity for the linear polystyrene analogue (M_w = 1.6 x 10^4 g/mol), 0.111 dL/g, calculated with the Mark-Howkink-Sakurada equation, \( \eta = K M^a \), with \( K = 12.3 \times 10^{-5} \) dL/g and \( a = 0.703 \) in THF solvent at 35 °C. A commonly used parameter to evaluate branching is the ratio of intrinsic viscosities of the branched polymer and a linear analogue of the same chemical composition and molecular weight \( g' = \frac{[\eta]_{\text{branched}}}{[\eta]_{\text{linear}}} \). The relationship between the g’ value and the number of arms has been previously reported and the theoretical g’ values for different numbers of arms have been calculated. The experimental g’ value is calculated to be 0.42. The calculated g’ value for a six-armed star is 0.56 and for a nine-armed star is 0.42. These results are consistent with formation of a star-branched polymer with the average number of arms > 6.8 obtained from the SEC results.
The $^1$H NMR spectrum of the crude product is shown in Figure 3.42. The characteristic peaks for the methyl protons on a carbon attached to silicon are observed at $\delta$ -1.0 – 0.5 ppm. There are peaks observed in the region $\delta$ 5.5 - 6.05 ppm which correspond to vinyl protons. This is an indication that some of the chains are terminated with a vinyl group. It is probable that the vinylsilane-functionalized product was obtained from the attack of poly(styryl)lithium on the silicon of vinyltrimethylsilane (A in Scheme 3.4), but also higher molecular weight living chains can react with vinyltrimethylchlorosilane in the same manner to give vinylsilane-functionalized coupled or star products (e.g. H in Scheme 3.4).

![Figure 3.42. $^1$H NMR spectrum (CDCl$_3$) of the product of the reaction of poly(styryl)lithium ($M_n = 2,100$ g/mol) with 6.6 equivalents of vinyltrimethylchlorosilane in benzene at 30 °C after 3 days.](image)

In order to acquire more information about the composition of the product, the MALDI-TOF mass spectrum of the polymer was obtained (Figure 3.43). Due to the high
Figure 3.43. MALDI-TOF mass spectrum of the product of the reaction of poly(styryl)lithium ($M_n = 2,100$ g/mol) with 6.6 equivalents of vinyldimethylchlorosilane in benzene at 30 °C after 3 days.
molecular weight of the polymer, it was very difficult to obtain a good spectrum. It is only possible to observe more easily ionizable, low molecular weight products. Two distributions are observed, a low molecular weight distribution centered at m/z 1700 and a higher molecular weight distribution centered at m/z 3500. In the lower molecular weight region there are 4 distributions observed. The main distribution with a representative peak at m/z 1725.7 corresponds to the 15-mer of the vinylsilane-functionalized polymer (A in Scheme 3.4), \( C_4H_9-(C_8H_8)_{15}-\text{Si(CH}_3)_2\text{CH}=\text{CH}_2·\text{Na}^+ \); calculated monoisotopic mass \( \{57.07 \times C_4H_9 + 15 \times 104.06 \times (C_8H_8)_{15} + 27.98 \times \text{Si} + 2 \times 15.02 \times \text{CH}_3 + 13.02 \times \text{CH} + 14.03 \times \text{CH}_2 + 22.99 \times \text{Na}^+ \} = 1726.09 \text{ Da} \). This distribution is evidence for the occurrence of path A in Scheme 3.4. A minor distribution with a representative peak at m/z 1777.7 corresponds to the proton terminated polystyrene 13-mer with 2 vinyldimethylchlorosilane repeat units, \( C_4H_9-(C_8H_8)_{14}-(\text{CH}_2\text{CH}[\text{Si(CH}_3)_2\text{Cl}])_2\text{H}·\text{Na}^+ \); calculated monoisotopic mass \( \{57.07 \times C_4H_9 + 14 \times 104.06 \times (C_8H_8)_{14} + 2 \times \{14.03 \times \text{CH}_2 + 13.02 \times \text{CH} + 27.98 \times \text{Si} + 2 \times 15.02 \times \text{CH}_3 + 34.97 \times \text{Cl} \} + 1.008 \times \text{H} + 22.99 \times \text{Na}^+ \} = 1778.06 \text{ Da} \). This distribution provides evidence for the occurrence of path B in Scheme 3.4. A small distribution at m/z 1745.7 corresponds to non-functional polystyrene 16-mer, \( C_4H_9-(C_8H_8)_{16}-\text{H}·\text{Na}^+ \); calculated monoisotopic mass \( \{57.07 \times C_4H_9 + 16 \times 104.06 \times (C_8H_8)_{16} + 1.008 \times \text{H} + 22.99 \times \text{Na}^+ \} = 1746.07 \text{ Da} \). The higher molecular weight products are anticipated to be consistent with the corresponding coupled products.

A representative peak at m/z 3221.6 corresponds to vinylsilane-functionalized polystyrene dimer with 28 styrene repeat units and one vinyldimethylchlorosilane repeat unit (C in Scheme 3.4), \( C_4H_9(C_8H_8)_{28-n}-(\text{CH}_2\text{CH}[\text{Si(CH}_3)_2\text{C}_8\text{H}_{8-n}·\text{C}_4\text{H}_9])_2\text{Si(CH}_3)_2\text{CH}=\text{CH}_2·\text{Na}^+ \); calculated monoisotopic mass \( \{2 \times 57.07 \times C_4H_9 + 28 \times 104.06 \times \text{C}_8\text{H}_{8-n} · 1.008 \times \text{H} + 22.99 \times \text{Na}^+ \} = 3221.6 \text{ Da} \).
\[(C_8H_8)_{28} + [14.03 \text{ (CH}_2) + 13.02 \text{ (CH)} + 27.98 \text{ (Si)} + 2 \times 15.02 \text{ (CH}_3)] + 27.98 \text{ (Si)} + 2 \times 15.02 \text{ (CH}_3) + 13.02 \text{ (CH)} + 14.03 \text{ (CH}_2) + 22.99 \text{ (Na}^+)\} = 3220.98 \text{ Da. This distribution provides evidence for the occurrence of path C in Scheme 3.4. A representative peak at m/z 3239.8 corresponds to proton terminated polystyrene dimer with 29 styrene repeat units and one vinylidimethylchlorosilane repeat unit (proton terminated E in Scheme 3.4 with n = 0), } C_9H_{38}(C_8H_{16})_{29-n}(CH_2CH[Si(CH_3)_{2-n}C_4H_9])H\cdot\text{Na}^+; \text{ calculated monoisotopic mass } \{2 \times 57.07 \text{ (C}_4H_9) + 29 \times 104.06 \text{ [(C}_8H_8)_{28} + \text{ [14.03 \text{ (CH}_2) + 13.02 \text{ (CH)} + 27.98 \text{ (Si)} + 2 \times 15.02 \text{ (CH}_3)] + 1.008 + 22.99 \text{ (Na}^+)\} = 3241.00 \text{ Da. Although the difference between calculated and observed monoisotopic mass for this product is 1.2 Da, this is a reasonable structure assignment and the mass difference can be due to the calibration having been performed in the low mass region, where the signal to noise ratio is substantially larger.}

In conclusion, vinylidimethylchlorosilane is a difunctional molecule that can react in different ways with poly(styryl)lithium in benzene at 30 °C to give a mixture of products. The products range from vinylsilane-functionalized polymer, to dimeric products and to higher order stars. Vinylidimethylchlorosilane acts as a monomer/functionializing/linking agent to form star-branched polymers with an average of 6.8 arms per molecule in an analogous way as the reaction of poly(styryl)lithium with divinylbenzene as described in the Introduction.\textsuperscript{154,155} From the SEC results it was noted that the low molecular weight peak, presumably vinylsilane-functionalized polymer, decreased in intensity between 12 hours and 3 days sample. This indicates that there can be further coupling of the polymer chains with longer reaction times.
3.2.4. Functionalization of poly(styryl)lithium with vinylidimethylchlorosilane in THF at -78 °C

Based on the previous results from Rempp and coworkers\textsuperscript{188} and Tezuka and Araki,\textsuperscript{189} an attempt was made to prepare vinylsilane-functionalized polystyrene by reacting poly(styryl)lithium with 5 equivalents of vinylidimethylchlorosilane in THF at -78 °C. Poly(styryl)lithium was prepared in benzene to effect a controlled polymerization and to obtain a polymer with narrow molecular weight distribution. After the polymerization was completed, the reactor was reattached to the vacuum line and evacuated. The solvent was removed by freeze-drying and approximately 100 mL of THF was distilled into the reactor; it was then sealed-off the vacuum line with a torch. The characteristic bright red color of the poly(styryl)lithium in THF disappeared immediately after addition of the vinylidimethylchlorosilane at -78 °C. The SEC chromatogram of the resulting product in Figure 3.44 exhibits a narrow molecular weight distribution peak with a small high molecular weight shoulder ($M_n = 2.0 \times 10^3$ g/mol, $M_n/M_w = 1.04$).

![Figure 3.44. SEC chromatograms of (A) base sample and (B) the products of the reaction of poly(styryl)lithium ($M_n = 1,800$ g/mol) with 5 equivalents of vinylidimethylchlorosilane in THF at -78 °C.](image)

The $^1$H NMR spectrum of the crude products is shown in Figure 3.45. The expansion of the region between $\delta$ 5.3 and 6.0 reveals two peaks that can be assigned
to the protons in the vinyl group of the vinylsilane-functionalized polystyrene. The characteristic peaks for the six methyl protons on a carbon attached to silicon are observed at $\delta \ -0.1$ to -0.4 ppm. The integration ratio of these peaks and the peaks corresponding to the six methyl protons in the initiator ($\delta \ 0.43 - 0.68$ ppm) is $5.6 : 6$ (theoretical 6:6). This corresponds to a 93% yield of vinylsilane-functionalized polymer. This result corroborates the results from the SEC analysis where a high molecular weight shoulder was observed indicating that the reaction was not quantitative and that there is a side reaction occurring.

**Figure 3.45.** $^1$H NMR spectrum (CDCl$_3$) of the products from the reaction of poly(styryl)lithium ($M_n = 1,800$ g/mol) with 5 equivalents of vinyldimethylchlorosilane in THF at -78 °C.

The MALDI-TOF mass spectrum of the polymer products is shown in Figure 3.46. There is only one distribution in the lower $m/z$ range with a representative peak at $m/z$ 1725.4 that corresponds to the 15-mer of the vinylsilane-functionalized polymer, $C_4H_9-(C_8H_8)_{15}^\cdot Si(CH_3)2CH=CH_{2}\cdot Na^+$; calculated monoisotopic mass $\{57.07 \ (C_4H_9) + 15 \times 104.06 \ [(C_8H_8)_{15}] + 27.98 \ (Si) + 2 \times 15.02 \ (CH_3) + 13.02 \ (CH) + 14.03 \ (CH_2) + 22.99 \ (Na^+)) = 1726.09 \ Da$. It is worth noting that there are no peaks observed for non-
functional polystyrene, e.g. the 16-mer of non-functional polystyrene, \(\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{16}\text{H}^+\cdot\text{Na}^+\); calculated monoisotopic mass \(\{57.07\ (\text{C}_4\text{H}_9) + 16 \times 104.06\ [(\text{C}_8\text{H}_8)_{16}] + 1.0089\ (\text{H}) + 22.99\ (\text{Na}^+)\} = 1746.07\ \text{Da}\). There is a small high molecular weight distribution with a representative average mass peak at \(m/z\ 3222.0\). This distribution most likely corresponds to a dimeric product. The possible structures of the polymer have been considered but the peak could not be assigned to any of them. Thus it can be concluded that in THF at \(-78\ °C\), poly(styryl)lithium reacts predominantly with the silyl chloride functionality to form vinylsilane-functionalized polymer as expected. The formation of stars in benzene at \(30\ °C\) may be due to the reactivity of the double bond in both the vinylidimethylchlorosilane repeat unit and the vinylsilane-functionalized polymer toward further reactions with poly(styryl)lithium. Thus, vinylidimethylchlorosilane is an ambident electrophile which can react competitively at one or both sites depending on the reaction conditions.

![Figure 3.46. MALDI-TOF mass spectrum of the product of the reaction of poly(styryl)lithium (\(M_n = 1,800\ \text{g/mol}\)) with 5 equivalents of vinylidimethylchlorosilane in THF at \(-78\ °C\).](image-url)
3.2.5. Functionalization of poly(styryl)lithium with vinylidimethylethoxysilane

Since the reaction of poly(styryl)lithium with 6.6 equivalents of vinylidimethylchlorosilane in benzene at 30 °C proved to be an efficient means for the preparation of higher order stars, it was desired to investigate the efficiency of analogous, non-chlorine containing compounds. Therefore, the reaction of poly(styryl)lithium (M_n = 2.0 x 10^3 g/mol, M_n/M_w = 1.04) with 2.5 equivalents of vinylidimethylethoxysilane in benzene at 30 °C was investigated. The SEC chromatograms of the products (Figure 3.47) after 12 hours and 3 days of reaction time showed narrow monomodal curves and no significant increase in molecular weight of the polymer (M_n = 2.3 x 10^3 g/mol, M_n/M_w = 1.1 and M_n = 2.0 x 10^3 g/mol, M_n/M_w = 1.03, respectively).

![SEC chromatograms](image)

Figure 3.47. SEC chromatograms of the products of the reaction of poly(styryl)lithium (M_n = 1,800 g/mol) with 2.5 equivalents of vinylidimethylethoxysilane in benzene at 30 °C (A) after 12 h, (B) after 3 days and (C) base sample.

The ^1H NMR spectrum of the polymer shown in Figure 3.48 shows characteristic resonance peaks at δ -0.2 - 0.6 ppm corresponding to the protons on the methyl groups.
attached to silicon, at $\delta$ 3.2 – 3.5 ppm corresponding to the methyl protons in the methoxy group and at $\delta$ 3.5 – 3.8 ppm corresponding to the methylene protons in the ethoxy group. It is worth noting that there are no resonances between $\delta$ 5 and 6.5 ppm indicating that there is no detectable amount of vinyl groups in the product. The negligible increase in the molecular weight of the polymer along with the results from the $^1$H NMR (presence of ethoxy and methoxy groups and absence of vinyl groups) indicate that the poly(styryl)lithium exclusively attacked the vinyl group on the vinyltriethoxysilane and perhaps oligomerized and did not attack the silicon to displace the ethoxy group.

Figure 3.48. $^1$H NMR spectrum (CDCl$_3$) of the product of the reaction of PSLi ($M_n = 2,000$ g/mol) with 2.5 equivalents of vinyltrimethylethoxysilane in benzene at 30 °C after 3 days with work-up by precipitation into methanol.

The integration ratios of the six methyl protons in the initiator ($\delta$ 0.6 - 0.95 ppm) to the three methyl protons in the methoxy group and the two methylene protons in the
ethoxy group was observed to be 6 : 0.76 : 1.33. From these results it can be calculated that there is an average of 0.25 methoxy and 0.66 ethoxy groups per polymer chain. Taking into account that 2.5 equivalents of vinyldimethylethoxysilane were added and that the reaction proceeded for 3 days, 0.91 ethoxy and methoxy repeat units per polymer chain is lower than expected. Since the resulting product was precipitated into methanol, the presence of methoxy groups in the polymer can be explained by exchange of ethoxy groups with methanol. Partial hydrolysis of methoxy or ethoxy groups during the precipitation process is anticipated; hence there may be some hydroxyl groups in the repeat units. This can explain the low number of ethoxy and methoxy repeat units per polymer chain.

The polymer can consist of four different repeat units: n repeat units of styrene, x repeat units of vinyldimethylethoxysilane, y repeat units of vinyldimethylmethoxysilane and z repeat units of vinyldimethylhydroxysilane. A representation of the possible polymer structure is shown in Scheme 3.5. The composition of the vinylsilane block can be a random combination of the three different repeat units (ethoxy, methoxy and hydroxyl). It is worth noting that the scheme is a tool to simplify the interpretation of the mass spectrometric results and does not imply the exact structure of the vinyldimethylalkoxysilane block. The subscripts n, x, y and z are used to illustrate the number of repeat units in the polymer and do not represent the length of a block.

Scheme 3.5. Representation of the possible structure of the polymer product from the reaction of poly(styryl)lithium (M_n = 2,000 g/mol) with 2.5 equivalents of vinyldimethylethoxysilane after 3 days.
To confirm the structures of the end groups of the products, the MALDI-TOF mass spectrum of the polymer products using silver as cationizing agent was obtained (Figure 3.49). The MALDI-TOF mass spectrum of the polymer products shows 6 distributions. The peaks within each distribution are separated by \( m/z \) 104, consistent with a styrene repeat unit. The separation within some of the distributions (e.g. C, D and E) is \( m/z \) 14 that corresponds to a methylene (\( CH_2 \)) unit; this corresponds to the differences between an ethoxy and a methoxy group and also between a methoxy and a hydroxyl group. A representative peak E at \( m/z \) 1881.9 corresponds to the polystyrene 14-mer with 2 units of vinylidimethylethoxysilane (from Scheme 3.4, \( n = 14 \), \( x = 2 \), \( y = 0 \) and \( z = 0 \)) \( C_4H_9-(C_8H_8)_{14-}\{CH_2CH[Si(CH_3)_2(OCH_2CH_3)]\}_2-H\cdotAg^+; \) calculated monoisotopic mass = 1882.02 Da. The distribution D with a representative peak at \( m/z \) 1867.9 is 14 \( m/z \) units lower than for the E distribution and corresponds to the product from exchange of one ethoxy group for a methoxy group; i.e. the polystyrene 14-mer with 1 unit of vinylidimethylethoxysilane and 1 vinylidimethylmethoxysilane (from Scheme 3.5, \( n = 14 \), \( x = 1 \), \( y = 1 \) and \( z = 0 \)); calculated monoisotopic mass = 1868.01 Da. Accordingly, distribution C with a representative peak at \( m/z \) 1853.8 is at 28 \( m/z \) units less than distribution E and 14 \( m/z \) units less than distribution D and corresponds to the product from exchange of the remaining ethoxy group of distribution D for a methoxy group; i.e. the polystyrene 14-mer with 2 units of vinylidimethylmethoxysilane (from Scheme 3.5, \( n = 14 \), \( x = 0 \), \( y = 2 \) and \( z = 0 \)); calculated monoisotopic mass = 1853.99 Da. An isomeric composition with \( n = 14 \), \( x = 1 \), \( y = 0 \) and \( z = 1 \) is also possible. The most abundant distribution is B. A representative peak at \( m/z \) 1835.9 corresponds to the polystyrene 12-mer with 3 units of vinylidimethylhydroxysilane and 1 unit of
vinyldimethylmethoxysilane (from Scheme 3.5, \( n = 12, x = 0, y = 1 \) and \( z = 3 \)); calculated monoisotopic mass = 1835.95 Da.

There are two possible distributions overlapping distribution B. Distribution B’ that corresponds to the polystyrene 13-mer with 2 units of vinyldimethylhydroxysilane and 1 unit of vinyldimethylmethoxysilane (from Scheme 3.5, \( n = 13, x = 0, y = 1 \) and \( z = 2 \)); calculated monoisotopic mass = 1837.96 Da. The second possible distribution is B” that corresponds to the polystyrene 14-mer with 1 unit of vinyldimethylhydroxysilane and 1 unit of vinyldimethylmethoxysilane (from Scheme 3.5, \( n = 14, x = 0, y = 1 \) and \( z = 1 \)); calculated monoisotopic mass = 1839.98 Da. After comparing the experimental isotopic pattern with the theoretical isotopic pattern for product B (Figure 6, Appendix B), it is concluded that the overlapping products B’ and B” have minor yields.

Figure 3.49. MALDI-TOF mass spectrum of the products of the reaction of PSLi (\( M_n = 2,000 \) g/mol) with 2.5 equivalents of vinyldimethylethoxysilane in benzene at 30 °C after 3 days and work-up by precipitation into methanol, using silver as cationizing agent.
Distribution A with a representative peak at \( m/z \) 1827.9 corresponds to the polystyrene 15-mer with 1 unit of vinyltrimethylhydroxysilane (from Scheme 3.5, \( n = 15 \), \( x = 0 \), \( y = 0 \) and \( z = 1 \)); calculated monoisotopic mass = 1827.97 Da. The product corresponding to distribution F, with a representative peak at \( m/z \) 1911.9, contains a cyclic siloxane unit which could arise from the condensation (\( \mathrm{H_2O} \) loss) of two adjacent alkoxy- or hydroxysilane units. The calculated monoisotopic mass for the 15-mer of the product shown in Table 3.1 \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_{15}-\{\text{CH}_2\text{CH}[\text{Si}(\text{CH}_3)_2-\text{O}-(\text{CH}_3)_2\text{Si}]\text{CHCH}_2-\text{H}\text{Ag}^+ \), 1911.96 Da agrees well with the observed \( m/z \) 1911.9. Although the distribution is well resolved in the spectrum obtained with silver as cationizing agent, distribution F is not observed when using sodium, even though all other distributions (A - E) are detected (Figure 7, Appendix B). Hence it is possible that this product is formed during the MALDI-TOF analysis when using silver as cationizing agent. Alternatively, distribution F could be below noise level in the spectrum measured using sodium because it contains only one, relatively rigid oxygen atom, where \( \text{Na}^+ \) would preferentially bind. A summary of the interpretation of the results from the MALDI-TOF mass spectrometric analysis is shown in Table 3.1. The distribution corresponding to polystyrene homopolymer, calculated monoisotopic mass 1829.98 Da, overlaps with distribution A, hence the possible existence of polystyrene homopolymer in the product cannot be excluded from this results. A thin-layer chromatogram of the product showed only one spot (\( R_f = 0 \)) indicating the absence of non-functional polystyrene (< 2 %)\(^{175} \) and that the crossover to vinyltrimethylethoxysilane was fast and quantitative. It is not possible to obtain an accurate estimate of the composition of the products from the mass spectrometric results, because the main distribution peak is a combination of 3 products that could not be isolated to quantify them independently.
Table 3.1. Products of the reaction of poly(styryl)lithium ($M_n = 1,800$ g/mol) with 2.5 equivalents of vinyltrimethylethoxysilane after 3 days, identified from the MALDI-TOF mass spectrum obtained using silver as cationizing agent.

<table>
<thead>
<tr>
<th>DISTRIBUTION</th>
<th>REPRESENTATIVE $m/z$ OBSERVED</th>
<th>CALCULATED MONOISOTOPIC MASS (Da)</th>
<th>STRUCTURE $(Ag^+)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1827.9</td>
<td>1827.97</td>
<td><img src="image" alt="Structure A" /></td>
</tr>
<tr>
<td>B</td>
<td>1835.9</td>
<td>1835.95</td>
<td><img src="image" alt="Structure B" /></td>
</tr>
<tr>
<td>B'</td>
<td>1837.9</td>
<td>1837.96</td>
<td><img src="image" alt="Structure B'" /></td>
</tr>
<tr>
<td>B''</td>
<td>1839.9</td>
<td>1839.98</td>
<td><img src="image" alt="Structure B''" /></td>
</tr>
<tr>
<td>C</td>
<td>1853.8</td>
<td>1853.99</td>
<td><img src="image" alt="Structure C" /></td>
</tr>
<tr>
<td>D</td>
<td>1867.9</td>
<td>1868.01</td>
<td><img src="image" alt="Structure D" /></td>
</tr>
<tr>
<td>E</td>
<td>1881.9</td>
<td>1882.02</td>
<td><img src="image" alt="Structure E" /></td>
</tr>
<tr>
<td>F</td>
<td>1911.9</td>
<td>1911.96</td>
<td><img src="image" alt="Structure F" /></td>
</tr>
</tbody>
</table>
In conclusion, poly(styryl)lithium reacts with vinyltrimethylethoxysilane exclusively at the vinyl moiety to form the corresponding carbanion that oligomerizes. In contrast to the reaction of poly(styryl)lithium with vinyltrimethylchlorosilane, further reactions of living chain ends at the silicon to displace the ethoxy group were not observed and higher molecular weight products were not formed. This could be due to the lower reactivity of the ethoxy groups compared to the chloride. Some of the ethoxy groups from the vinyltrimethylethoxysilane oligomer have exchanged with methoxy from the methanol and some of the repeat units have been hydrolyzed. The polymers contain 1 to 4 repeat units of vinyltrimethylalkoxysilane (ethoxy, methoxy and/or hydroxyl). From the mass spectrometric results, it was observed that out of the seven products identified only two with small distributions (D and E) contain vinyltrimethylethoxysilane repeat units (one and two respectively); five products contain vinyltrimethylmethoxysilane repeat units and 6 out of 7 contain vinyltrimethylhydroxysilane repeat units. This result is consistent with the values obtained from the $^1$H NMR which indicate that the majority of the product is hydrolyzed: 0.66 ethoxy, 0.25 methoxy and 1.59 hydroxy (by difference assuming that all of the monomer reacted) groups per polymer chain. The differences between the vinyltrimethylchlorosilane and vinyltrimethylethoxysilane can be attributed to the lower reactivity of the ethoxysilane groups compared to chlorosilane groups in both competition with addition to the vinyl groups and in further linking reactions after oligomerization.
3.3. Synthesis of polystyrene/poly(ethylene oxide) stars

As discussed in the Introduction, there are not many examples of well-defined in-chain functionalized polymers. Previous work in our laboratories by Contractor,\textsuperscript{131} has demonstrated that the reaction of poly(styryl)lithium with 1,3-butadiene diepoxide is an efficient method for the preparation of in-chain, dihydroxyl-functionalized polystyrene. One of the many applications of hydroxyl-functionalized polymers is as initiator for the polymerization of ethylene oxide. Hence, it was of interest to investigate the use of this dihydroxyl-functionalized polymer to prepare heteroarm polystyrene/poly(ethylene oxide) stars. The first step was to replicate the previous work to prepare in-chain, dihydroxyl-functionalized polystyrene.

3.3.1. Coupling of poly(styryl)lithium with 1,3-butadiene diepoxide

Poly(styryl)lithium ($M_n = 1.2 \times 10^3$ g/mol, $M_n/M_w = 1.05$) was reacted in excess with 1,3-butadiene diepoxide as shown in equation 26. The regiochemistry of the reaction has been previously studied by $^{13}$C and 135 DEPT NMR and it was determined that attack of poly(styryl)lithium is on the least-substituted, methylene carbons of the 1,3-butadiene diepoxide as shown.\textsuperscript{131}

\[
2.6 \text{ PSLi} + \text{butadiene diepoxide} \rightarrow \text{PSCH}_2\text{CHCHCH}_2\text{PS} + \text{PS-H} \quad \text{OH}
\]

The SEC chromatogram of the crude product (Figure 3.50) shows a bimodal curve ($M_n = 2.0 \times 10^3$ g/mol, $M_n/M_w = 1.09$). The non-functional polystyrene was separated from the in-chain functionalized polymer by column chromatography using toluene as eluent for the non-functional polymer and THF for the functional material.
The TLC chromatogram of the purified product showed only one spot \((R_f = 0)\) corresponding to the functionalized polymer. The SEC chromatogram of the purified in-chain functionalized polystyrene (Figure 3.50) showed a narrow monomodal curve \(\left( M_n = 2.7 \times 10^3 \text{ g/mol}, \frac{M_n}{M_w} = 1.02 \right)\).

![SEC chromatograms of (A) base sample, (B) crude product and (C) purified product from the coupling reaction of PSLi with 1,3-butadiene diepoxide in benzene at 30 °C.](image)

The MALDI-TOF mass spectrum of the purified product (Figure 3.51) shows one distribution with a representative peak at 1994.3 Da that corresponds to the in-chain, dihydroxyl functionalized polymer with 17 polystyrene repeat units \(\text{C}_4\text{H}_9\cdot\text{C}_8\text{H}_8\cdot\text{CH}_2\cdot\text{CH(OH)}\cdot\text{CH(OH)}\cdot\text{CH}_2\cdot\text{C}_8\text{H}_8\cdot\text{Na}^+\); calculated monoisotopic mass \(\{2 \times 57.07 (\text{C}_4\text{H}_9) + 17 \times 104.06 [(\text{C}_8\text{H}_8)_{17-n}] + 2 \times 14.03 (\text{CH}_2) + 2 \times 13.02 (\text{CH}) + 2 \times 17.00 (\text{OH}) + 22.99 (\text{Na}^+)\} = 1994.25 \text{ Da}\). There are no peaks observed for non-functional polystyrene, e.g. the 19-mer \(\text{C}_4\text{H}_9\cdot\text{C}_8\text{H}_8_{19-H}\cdot\text{Na}^+\); calculated monoisotopic mass = 2058.26 Da.
Figure 3.51. MALDI-TOF MS of the purified product from the reaction of poly(styryl)lithium and 1,3-butadiene diepoxide in benzene at 30 °C.

The $^1$H NMR spectrum of the in-chain, dihydroxyl functionalized polymer in Figure 3.52 shows the characteristic peaks for the methine protons on the carbon bonded to the hydroxyl group between $\delta$ 2.5 and 3.1 ppm.

Figure 3.52. $^1$H NMR spectrum (CDCl$_3$) of the purified product from the reaction of poly(styryl)lithium and 1,3-butadiene diepoxide in benzene at 30 °C.
3.3.2. Polymerization of ethylene oxide with in-chain dihydroxyl-functionalized polystyrene precursor

In order to make the polystyrene/poly(ethylene oxide) hetero-arm star, the in-chain, dihydroxy-functionalized polymer ($M_n = 2.7 \times 10^3$ g/mol, $M_n/M_w = 1.02$) was titrated with potassium naphthalenide to generate the corresponding potassium alkoxide. It was desirable to add stoichiometric amounts of potassium naphthalenide to react with the hydroxyl groups, because an excess of potassium naphthalenide would initiate polymerization of the ethylene oxide and the product would be contaminated with poly(ethylene oxide) homopolymer. The reaction is shown in Scheme 3.6.


The SEC chromatogram of the star product in Figure 3.53 shows a narrow monomodal curve with a low molecular weight tail ($M_n = 5.2 \times 10^3$ g/mol, $M_w = 5.4 \times 10^3$ g/mol, $M_w/M_n = 1.05$). The low molecular weight tail in the SEC chromatogram could have corresponded to either poly(ethylene oxide) homopolymer or starting material. In
order to remove the poly(ethylene oxide) homopolymer, the polymer was dissolved in benzene and washed three times with water in a separation funnel. The SEC chromatogram of the purified product in Figure 3.53 shows a narrow monomodal curve with a low molecular weight tail ($M_n = 5.1 \times 10^3$ g/mol, $M_w = 5.6 \times 10^3$ g/mol, $M_w/M_n = 1.05$). The theoretical molecular weight of the poly(ethylene oxide) arms was calculated to be the same as the molecular weight of the polystyrene starting material, i.e. approximately 1200 g/mol for each arm, 2400 g/mol total. The molecular weight of the polymer obtained increased from 2700 g/mol to 5100 g/mol as determined by SEC which is approximately double; this indicates that the ethylene oxide was incorporated into the polymer as expected.

The intrinsic viscosity of the polystyrene/poly(ethylene oxide) heteroarm star was calculated from the SEC results as 0.067 dL/g. This result can be compared with the intrinsic viscosity for the linear polystyrene analogue ($M = 5.1 \times 10^3$ g/mol), 0.050 dL/g calculated with the Mark-Howkink-Sakurada equation $[\eta] = K M^a$ with $K = 12.3 \times 10^{-5}$ dL/g and $a = 0.703$ in THF solvent at 35 °C. The resulting $g'$ value is 1.3. Since the $g'$ value
for a star polymer should be less than one, it is obvious that this system has some
different behavior which is probably due to the fact that it is not a homopolymer star but
a heteroarm star of polystyrene and poly(ethylene oxide).

The $^1$H NMR spectrum of the purified product is shown in Figure 3.54. The
characteristic peaks for the four methylene protons in the poly(ethylene oxide) backbone
are observed between $\delta$ 3.3 - 4.0 ppm.

![Figure 3.54. $^1$H NMR spectrum (CDCl$_3$) of the purified polystyrene/poly(ethylene oxide)
hetero-arm star.](image)

The molecular weight of the ethylene oxide arms can be calculated from the ratio
of the area of the peaks for the four methylene protons in the poly(ethylene oxide)
backbone with respect to the area of the peaks from the six methyl protons of the
initiator $\delta$ 0.5 – 0.8 ppm. The ratio is 105 : 6; this indicates that there is an average of
26.3 ethylene oxide repeat units per initiator fragment. The molecular weight of the
ethylen oxide repeat unit is 44.05 g/mol; hence, the average molecular weight of each poly(ethylene oxide) arm is 1160 g/mol. The total molecular weight of poly(ethylene oxide) is approximately 2300 g/mol; these values are in good agreement with the calculated molecular weight of 2400 g/mol based on complete incorporation of ethylene oxide into the polymer. The molecular weight of the polystyrene arms can also be calculated from the ratio of the five aromatic protons δ 6.3 - 7.6 ppm, with respect to the six methyl protons of the initiator as 51.5 : 6.0. The average number of styrene repeat units is 10.3 and the molecular weight of the styrene repeat unit is 104.15 g/mol; hence the average molecular weight of each polystyrene arm is calculated as 1070 g/mol. Adding the molecular weight of two initiator fragments (57.1 g/mol) and the linking agent (86.0 g/mol), the total molecular weight of the polystyrene precursor calculated by 1H NMR spectroscopy is 2350 g/mol. This result is in excellent agreement with the calculated molecular weight and the results obtained from the SEC analysis of the polymer.

The MALDI-TOF mass spectrometric analysis of the purified star using sodium as cationizing agent is shown in Figure 3.55. There are 3 distributions observed. The distribution at lower m/z 800 - 1500 has an m/z 44 difference between peaks which indicates an ethylene oxide repeat unit. A representative peak at m/z 1079.5 corresponds to the 24-mer poly(ethylene oxide) with no end groups, (CH₂CH₂O)₂₄·Na⁺; calculated monoisotopic mass \(24 \times \left[2 \times 14.03 \text{(CH₂)} + 15.99 \text{(O)}\right] + 22.99 \text{(Na⁺)}\) = 1079.62 Da. Szwarc and Richards⁹⁵ reported that the mechanism of homopolymerization of ethylene oxide initiated with sodium naphthalenide proceeds by addition of the ethylene oxide to the naphthalene ring as shown in Scheme 3.6. Although this would be the expected product, it is worth noting that there are no peaks
at δ 5.3 – 5.5 ppm corresponding to the naphthalene in the ¹H NMR spectrum of the polymer after purification. However, these peaks were observed in the ¹H NMR spectrum of the water soluble fraction from the purification step. The other possible mechanism is through an electron transfer process to ethylene oxide which would produce an ethylene oxide radical anion and consequently the –OCH₂CH₂-CH₂CH₂O– dianion by dimerization. In the latter case after quenching the reaction with methanol, the product would have 2 hydrogens as end groups and molecular weight 2 mass units higher than observed. A reasonable explanation for the formation of this product is the intramolecular attack of the alkoxide anion to an internal carbon α to oxygen (backbiting) to form cyclic polymers. The peaks in the range m/z 1300 and 3000 differ by m/z 104 which indicates that the repeat unit is polystyrene.

Figure 3.55. MALDI-TOF MS of the purified polystyrene/poly(ethylene oxide) hetero-arm star.

PEO 1079.5
PS 1994.3
PS/PEO star copolymer
A representative peak at \( m/z \) 1994.13 corresponds to the in-chain, dihydroxyl functionalized polystyrene precursor with 17 polystyrene repeat units \( \text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_n-\text{CH}_2\text{CH(OH)CH(OH)CH}_2-(\text{C}_8\text{H}_8)_{17-n}\cdot\text{C}_4\text{H}_9\cdot\text{Na}^+ \); calculated monoisotopic mass \( \{2 \times 57.07 \text{(C}_4\text{H}_9) + 17 \times 104.06 \text{[(C}_8\text{H}_8)_{17}]+2 \times 14.03 \text{(CH)} + 2 \times 13.02 \text{(CH)} + 2 \times 17.00 \text{(OH)} + 22.99 \text{(Na}^+)\} = 1994.24 \text{Da} \). The presence of this product indicates that the formation of alkoxide anions from the in-chain, dihydroxyl functionalized polystyrene precursor was not quantitative, presumably due to reduced accessibility to the hydroxyl groups due to steric hinderance.

There is a high molecular weight distribution between \( m/z \) 2500 and 4500 which is not resolved. It is worth noting that although the low molecular weight poly(ethylene oxide) and polystyrene products appear to be highly abundant this is due to the higher ionization efficiency of these products relative to the higher molecular weight product. The observed abundance does not correlate to the actual quantity of each component in the product. This is also confirmed by the SEC results which show a narrow, monomodal curve. The lower mass poly(ethylene oxide) and polystyrene products have a higher ionization efficiency versus the higher molecular weight polystyrene/poly(ethylene oxide) heteroarm star and suppress its detection. In an attempt to obtain resolved isotope clusters for the high molecular weight product it was necessary to remove the low molecular weight products. This was achieved by a fractionation of the product in the SEC. Fractions were collected every minute by using the SEC in the mass spectrometry laboratory. The SEC chromatogram is shown in Figure 3.56.
Figure 3.56. SEC chromatogram of purified polystyrene/poly(ethylene oxide) heteroarm star and the elution ranges for fractionation.

The MALDI-TOF mass spectrum of the high molecular weight product (fractions 4 and 5, retention volume = 21 – 23 minutes) is shown in Figure 3.57. The molecular weight of the polystyrene and poly(ethylene oxide) repeat units is 104 and 44, respectively. Since the product is a copolymer of these two monomers, the possible composition combinations are immense. The expanded spectrum shows almost a peak at each mass. To facilitate the data analysis, the MALDI-TOF mass spectrum for the in-chain, dihydroxyl-functionalized starting material in Figure 3.51 was examined. This spectrum shows the distribution of the precursor between $m/z$ 1200 and 3400, indicating that the polymer contains from 11 to 31 styrene units and the most abundant peaks between $m/z$ 1900 and 2400 contain from 18 to 22 styrene repeat units. Having determined the reasonable combinations of styrene and ethylene oxide units, it is possible to assign some of the distributions in the spectrum. The peaks have been labeled according to the number of styrene (M) and ethylene oxide (N) repeat units. For example, the peak at $m/z$ 3078.9 labeled as $M_{16}N_{27}$, corresponds to the
polystyrene/poly(ethylene oxide) hetero-arm star with 16 styrene repeat units and 27 ethylene oxide repeat units, \( \text{C}_{4}H_{9}-(\text{C}_{8}H_{8})_{n} \cdot \text{CH}_{2}\text{CH}[\text{O-(CH}_{2}\text{CH}_{2}O]_{m}\text{H}]\text{CH}[\text{O-(CH}_{2}\text{CH}_{2}O]_{27}\cdot \text{CH}_{2}\cdot \text{C}_{4}H_{9}\cdot \text{Na}^{+} \); calculated monoisotopic mass \( \{2 \times 57.07 \cdot \text{(C}_{4}H_{9}) + 16 \times 104.06 \cdot \ [(\text{C}_{8}H_{8})_{16}] + 2 \times 14.03 \cdot \text{(CH}_{2}) + 2 \times 13.02 \cdot \text{(CH)} + 27 \times 44.05 \cdot \ [(\text{CH}_{2}\text{CH}_{2}O)_{27}] + 2 \times 17.00 \cdot \text{(OH)} + 22.99 \cdot \text{(Na}^{+})\} = 3078.89 \text{ Da} \). It is also possible to identify peak differences that correspond to polystyrene or ethylene oxide repeat units. Therefore, a polymer with an additional styrene unit \( (\text{M}_{17}N_{27} \ m/z \ 3182.9) \) is observed at \( m/z \) 104 higher. Polymers with one \( (\text{M}_{16}N_{28} \ m/z \ 3122.9) \) and two \( (\text{M}_{16}N_{29} \ m/z \ 3166.9) \) ethylene oxide units more are observed at \( m/z \) 44 and 88 higher, respectively.

![Figure 3.57. MALDI-TOF MS of the high molecular weight fraction of the purified polystyrene/poly(ethylene oxide) hetero-arm star, M = styrene, N = ethylene oxide.](image)

### 3.4. Synthesis of 3-armed polystyrene stars using triepoxides as linking agents

The reaction of poly(styryl)lithium with 1,3-butadiene diepoxide proved that epoxides are efficient functionalizing/linking agents, and it was desired to investigate a trifunctional triepoxide as means to prepare higher order stars.
3.4.1. Synthesis of polystyrene stars using N,N-diglycidyl-4-glycidyloxyaniline as linking agent

The reaction of 5 equivalents of poly(styryl)lithium ($M_n = 1.6 \times 10^3$ g/mol, $M_n/M_w = 1.04$) with N,N-diglycidyl-4-glycidyloxyaniline, a commercial triepoxide, was studied to synthesize three-armed polystyrene stars as shown in equation 28.

$$
\text{PSLi} \quad + \quad \text{excess) + } \text{PS} \quad - \quad \text{H} \quad + \quad \text{PS-H}
$$

The SEC chromatogram of the product exhibits a bimodal curve as shown in Figure 3.58. Since an excess of poly(styryl)lithium was used, the product was a mixture of functionalized/linked higher molecular weight polymer and non-functional polystyrene. The star product was easily isolated by column chromatography using toluene as eluent for the non-functional polystyrene and THF as eluent for the functionalized/linked product. The SEC chromatogram of the purified product exhibited a narrow monomodal curve ($M_n = 4.4 \times 10^3$ g/mol, $M_w = 4.5 \times 10^3$ g/mol, $M_w/M_n = 1.03$). The intrinsic viscosity of the polymer determined from the SEC analysis with a viscosity detector was 0.049 dL/g. The intrinsic viscosity of a linear polystyrene analogue ($M_w = 4.5 \times 10^3$ g/mol) is 0.045 dL/g calculated using the Kuhn-Mark-Howkink-Sakurada equation $[\eta]=K'M^a$ with $K= 12.3 \times 10^{-5}$ dL/g $\text{cm}^3$ and $a = 0.703$ in THF solvent at 35 °C. The calculated $g'$ value for a three-armed star is 0.83, the resulting $g'$ value is larger than 1. This difference can be due to the complexity of the linking agent which can affect the overall behavior of the polymer in the solvent THF. Also it is worth noting
that the values of $K$ and $a$ were determined using polystyrene samples with molecular weights between $5.0 \times 10^4$ and $1.8 \times 10^7$ g/mol. Hence, it is possible that these values are not applicable at the low molecular weights of the polymers analyzed ($5.0 \times 10^3$ g/mol).

![Elution Volume (ml) diagram]

Figure 3.58. SEC chromatograms of (A) crude product, (B) purified product and (C) base sample of the reaction of 5 equivalents of PSLi ($M_n = 1.6 \times 10^3$ g/mol) with $N,N$-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.

The MALDI-TOF mass spectrum of the crude product was obtained without cationizing agent. Since the linking agent contains a nitrogen atom in its structure, the product that contains linking agent easily ionizes with a proton from the slightly acidic, phenol-type matrix, dithranol (Figure 3.59). Non-nitrogen containing species would not be expected to ionize without a cationizing agent. When a cationizing agent, e.g. silver, is used, the species that do not contain linking agent, such as non-functional polystyrene, also ionize. The complication is that in most cases both protonated and silverated clusters are observed, i.e. every distribution is doubled. A further complication is that the molecular weight of a polystyrene repeat unit is 104.06 g/mol and the mass of silver is 106.9 g/mol. This leads to overlapping of protonated and silverated clusters complicating the analysis of the data. Obtaining the spectrum without a cationizing
agent facilitates its interpretation. In order to confirm the correctness of the spectrum obtained from the crude product without cationizing agent, a spectrum of the purified product was obtained with and without cationizing agent. The latter results corroborate the initial interpretation of the spectrum obtained from the crude product without cationizing agent.

![Figure 3.59 Structure of dithranol.](image)

The mass spectrum (Figure 3.60) shows two distributions: a lower molecular weight distribution centered at \( m/z \) 2800 and a higher molecular weight distribution centered at \( m/z \) 4200. It is anticipated that the distribution at lower molecular weight, expanded region \( m/z \) 2000 – 2130, corresponds to the linked product of two PSLi chains. The structures of the expected products are shown in Scheme 3.7.

![Scheme 3.7. Expected products from the linking of two PSLi to N,N-diglycidyl-4-glycidyloxyaniline.](image)

The calculated monoisotopic mass for the two products in Scheme 3.7 with 16 styrene repeat units \( \{[\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_n-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2]_2(\text{CH}_2\text{CHCH}_2\text{O})\}(-\text{OC}_{6}\text{H}_4\text{N})\cdot\text{H}^+; \)
calculated monoisotopic mass \( \{2 \times 57.07 \ (\text{C}_4\text{H}_9) + 16 \times 104.06 \ (\text{C}_8\text{H}_8)_{16} + 2 \times 58.08 \ [\text{CH}_2\text{CH}(\text{OH})\text{CH}_2] + 57.07 \ (\text{CH}_2\text{CHCH}_2\text{O}) + 106.10 \ (-\text{OC}_{6}\text{H}_4\text{N}) + 1.008 \ (\text{H}^+)\} = 2059.29 \) Da. As observed in the expanded spectrum there are no peaks at this \( m/z \).
Figure 3.60. MALDI-TOF MS of the purified product of the reaction of 5 equivalents of PSLi ($M_n = 1,600$ g/mol) with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C. A possible side product is shown in the mass spectrum (B in Figure 3.60).
A representative peak in the major distribution at \( m/z \) 2015.3 is \( m/z \) 44 lower than the mass corresponding to the expected product (A in Figure 3.60). The calculated monoisotopic mass of an epoxide group (\( \text{CH}_2\text{CH}_2\text{O} \)) is 44.03 Da; hence the product observed in the mass spectrum could correspond to the loss of an epoxide group, e.g. structure B in Figure 3.60. The calculated monoisotopic mass for the proposed product with 16 styrene repeat units \{\([\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_n-\text{CH}_2\text{CH(OH)}\text{CH}_2]-\text{OC}_6\text{H}_4\text{N-CH}_2\text{OCH}[\text{CH}_2(\text{C}_8\text{H}_8)_{16-n}\text{C}_4\text{H}_9]\text{CH}_2]^{-}\text{H}^+; \{2 \times 57.07 \ (\text{C}_4\text{H}_9) + 16 \times 104.06 \ (\text{C}_8\text{H}_8)_8 + 58.08 \ (\text{CH}_2\text{CH(OH)}\text{CH}_2) + 106.10 \ (-\text{OC}_6\text{H}_4\text{N}) + 43.04 \ (\text{CH}_2\text{OCH}) + 2 \times 14.03 \ (\text{CH}_2) + 1.008 \ (\text{H}^+)) \} = 2015.26 \text{ Da}, which is in excellent agreement with the observed \( m/z \) 2015.3. The main distribution at higher molecular weight (see Figure 3.60), expanded region \( m/z \) 3960 – 4210, has a representative average peak at \( m/z \) 3994; this corresponds to the linked product of three PSLi chains with 34 styrene repeat units; \{\([\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_3-\text{CH}_2\text{CH(OH)}\text{CH}_2]_3(-\text{OC}_6\text{H}_4\text{N})^{-}\text{H}^+; \ \text{calculated average mass} \{3 \times 57.12 \ (\text{C}_4\text{H}_9) + 34 \times 104.15 \ (\text{C}_8\text{H}_8)_34 + 3 \times 58.08 \ [\text{CH}_2\text{CH(OH)}\text{CH}_2] + 106.10 \ (-\text{OC}_6\text{H}_4\text{N}) + 1.008 \ (\text{H}^+)) \} = 3993.9 \text{ Da.}

The \(^1\text{H} \) NMR spectrum of the purified polymer is shown in Figure 3.61. The characteristic peaks for the methine protons in the carbon adjacent to oxygen are at \( \delta \) 3.1 – 3.8 ppm. There is also a new peak at \( \delta \) 5.7 - 6.1 ppm which could correspond to the methylene protons between the oxygen and nitrogen atoms in the five-membered ring of the proposed product (see structure B in Figure 3.60). The chemical shift for these methylene protons was predicted to be \( \delta \) 5.43 ppm by ChemNMR software (CambridgeSoft). Heaney and coworkers\(^{197} \) reported a chemical shift of \( \delta \) 4.82 ppm for the methylene protons between oxygen and nitrogen in N-phenyl-3-oxazoline (Figure 3.62).
Figure 3.61. $^1$H NMR spectrum (CDCl$_3$) of the purified product of the reaction of 5 equivalents of PSLi ($M_n = 1,600$ g/mol) with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.

![Figure 3.61. 1H NMR spectrum (CDCl3) of the purified product of the reaction of 5 equivalents of PSLi (Mn = 1,600 g/mol) with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.](image)

Figure 3.62. Structure of N-phenyl-3-oxazoline

To support the purified product was obtained. The $^{13}$C NMR spectrum shown in Figure 3.63 shows a series of peaks at $\delta$ 65 – 69 ppm that correspond to the carbon bonded to the hydroxyl group (a). There is a peak at $\delta$ 72 – 74 ppm; according to NMR shift predictions with ChemNMR software (CambridgeSoft), this peak can correspond to the methylene carbon next to the oxygen in the linking agent (predicted $\delta$ 80.2 ppm) or to the methine carbon in the ring of the proposed product (predicted $\delta$ 81.6 ppm). The correct assignment could be determined by $^{135}$DEPT NMR analysis; if it is a methylene carbon it will yield a negative peak in the DEPT spectrum, while a methine carbon will yield a positive peak. The $^{135}$DEPT NMR of the polymer is shown in Figure 3.64. The peaks at $\delta$ 65 – 69 are positive confirming their assignment to the methine carbon adjacent to the hydroxyl group. The peak at $\delta$
72 – 74 ppm is negative indicating that it is a methylene carbon and hence it can be assigned to the methylene carbon next to the oxygen in the linking agent (see b in Figure 3.64). The predicted $^{13}$C NMR shift (ChemNMR software [CambridgeSoft]) for the methylene carbon between the oxygen and nitrogen atoms in the five-membered oxazoline ring of the proposed product is $\delta$ 88.4 ppm. Heaney and coworkers reported a $\delta$ 81.1 ppm chemical shift for this methylene carbon. This is peak is not observed in the $^{13}$C NMR spectrum (see Figure 3.63).

![Figure 3.63](image)

**Figure 3.63.** $^{13}$C NMR spectrum (CDCl$_3$) of the purified product of the reaction of 5 equivalents of PSLi ($M_n = 1,600$ g/mol) with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.

![Figure 3.64](image)

**Figure 3.64.** 135 DEPT NMR (CDCl$_3$) spectrum of the purified of the reaction of PSLi ($M_n = 1,600$ g/mol) with 5 equivalents of N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.
Since there are no peaks in the $^{13}$C NMR that can correspond to the chemical shift expected for the methylene carbon between the oxygen and nitrogen of the proposed oxazoline product, it was necessary to determine if the absence of a resonance peak is due to the low sensitivity of the analysis. Hence, an HMQC (Heteronuclear Multiple Quantum Correlation) experiment was performed. The results are shown in Figure 3.65. The spectrum shows that the protons that have a resonance peak at $\delta$ 5.8 - 6.0 ppm are attached to a carbon with a resonance peak at $\delta$ 114 ppm. This indicates that this protons do not correspond to the methylene unit between nitrogen and oxygen in the proposed structure (expected chemical shift $\delta$ 81 - 88 ppm), and the correlation of these peaks with a carbon resonance at $\delta$ 114 ppm suggests that there might be an aromatic methine carbon (positive peaks in the DEPT NMR) in the side product. In conclusion, the structure of the side product cannot be elucidated at this point. It is worth noting that the HMQC analysis is also helpful in confirming the assignments in the regions $\delta$ 3.2 – 3.8 ppm of the $^1$H NMR and $\delta$ 66 – 70 ppm and $\delta$ 72 – 74 ppm of the $^{13}$C NMR spectra. The peaks at $\delta$ 66 – 70 ppm correspond to the carbon bonded to the hydroxyl group, i.e. they correlate to the CH$_2$O protons in the region $\delta$ 3.2 – 3.8 ppm. Furthermore, the two peaks at higher field, $\delta$ 66 - 68 ppm, correspond to the methine carbon $\beta$ to the oxygen in the linking agent (a' in Figure 3.65C), i.e. they correlate with the proton peaks at $\delta$ 3.2 – 3.6 ppm. The peaks at $\delta$ 68 - 70 ppm correspond to the methine carbons $\beta$ to the nitrogen in the linking agent (a in Figure 3.65C), i.e. they correlate with the proton peaks at $\delta$ 3.3 – 3.8. The peak at $\delta$ 72 – 74 ppm has two small peaks overlapping. The assignment of the main peak is confirmed to correspond to the methylene carbon next to the oxygen in the linking agent (c in Figure
3.65C) since this peak correlates with the proton signal at 3.4 – 3.6 ppm. The two small overlapping peaks could correspond to a signal from the side product.

Figure 3.65. HMQC (CDCl₃) spectrum of the purified of the reaction of PSLi (Mₙ = 1,600 g/mol) with 5 equivalents of N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.
From these results it can be concluded that the formation of three-armed star occurs in competition with a side reaction that forms coupled product. From the MALDI-TOF results it can be concluded that the side product may correspond to either the proposed structure (B in Figure 3.60) or an isomeric product, the structure of which cannot be elucidated with the current information. In order to increase the yield of three-armed star with respect to the two-armed side product several approaches were attempted: variation of reaction conditions, modification the chain end of the polymer and the use of additives.

3.4.1.1. Effect of tetrahydrofuran on the linking reaction

Addition of Lewis bases such as tetrahydrofuran promotes the dissociation of organolithium aggregates and increases the reactivity of the chain ends. It was anticipated that the presence of THF would increase the reactivity of the chain ends and promote addition of poly(styryl)lithium to the epoxide moiety versus the undesired side reaction. The linking reaction was carried out with 3.6 equivalents of poly(styryl)lithium \((M_n = 1.6 \times 10^3 \text{ g/mol}, M_n/M_w = 1.04)\) in the presence of 10 equivalents of THF. The SEC chromatogram of the purified product (Figure 8 Appendix B) showed a narrow monomodal curve \((M_n = 4.7 \times 10^3 \text{ g/mol}, M_n/M_w = 1.02)\). The average number of arms calculated from the SEC results was 2.94 and the amount of 3-armed star was 94% (see Appendix D). The MALDI-TOF mass spectrum (Figure 9, Appendix B) of the purified product showed 4 distributions corresponding to 1-armed polystyrene linked product with two unreacted epoxides, 2-armed polystyrene linked product with one unreacted epoxide, 2-armed polystyrene linked product without unreacted epoxide functionalities and the five-membered ring and three-armed polystyrene star.
3.4.1.2. Effect of lithium chloride on the linking reaction

Lithium chloride has been shown to be an efficient additive in the polymerization of methyl methacrylates; it reduces the reactivity of the chain ends and increases their selectivity.\textsuperscript{58-61} In order to evaluate the effect of lithium chloride in the linking reaction, 5 equivalents of poly(styryl)Lithium ($M_n = 1.7 \times 10^3$ g/mol, $M_n/M_w = 1.03$) was reacted with N,N-diglycidyl-4-glycidyloxyaniline in the presence of 10 equivalents of lithium chloride. The SEC of the purified product (Figure 10, Appendix B) showed a narrow monomodal curve ($M_n = 4.9 \times 10^3$ g/mol, $M_n/M_w = 1.02$). The average number of arms calculated from the SEC results was 2.88 and the amount of 3-armed star was calculated to be 88%. Once again, the MALDI-TOF mass spectrum (Figure 11, Appendix B) of the purified product showed a mixture of products consisting mainly of 2-armed polystyrene linked product without unreacted epoxide functionalities and three-armed polystyrene star.

3.4.1.3. Effect of potassium alkoxide on the linking reaction

In general alkali metal alkoxides (other than lithium) increase the rate of propagation of poly(styryl)lithium.\textsuperscript{57} It was anticipated that the potassium alkoxide would form cross-associated species with both the poly(styryl)lithium chain ends and the alkoxide anions resulting from the reaction of poly(styryl)lithium with an epoxide in the linking agent. In order to evaluate the effect of added potassium alkoxide in the linking reaction, 9 equivalents of poly(styryl)lithium ($M_n = 1.5 \times 10^3$ g/mol, $M_n/M_w = 1.05$) were reacted with the linking agent in the presence of 5.3 molar equivalents of potassium tert-amylate. The SEC chromatogram of the purified product (Figure 12 Appendix B) showed a narrow monomodal curve ($M_n = 4.4 \times 10^3$ g/mol, $M_n/M_w = 1.05$). The average
number of arms calculated from the SEC results was 2.87 and the amount of 3-armed star was calculated to be 87%. The crude product showed 2 distributions in the MALDI-TOF mass spectrum (Figure 13, Appendix B) corresponding to 2-armed polystyrene linked product without unreacted epoxide functionalities and three-armed polystyrene star.

3.4.1.4. Effect of organolithium chain end structure on the linking reaction

Poly(styryl)lithium chain ends are highly sterically hindered. Thus, it was anticipated that reducing the steric congestion of the chain ends would facilitate the reaction of the polymeric chain ends with the epoxide ring and hence increase the yield of the three-armed product from addition of poly(styryl)lithium to the epoxide moiety relative to the undesired coupled product. Poly(styryl)lithium (M<sub>n</sub> = 1.4 x 10<sup>3</sup>, M<sub>n</sub>/M<sub>w</sub> = 1.04) was end-capped with 2.3 equivalents of butadiene. The linking agent was reacted with 3.4 equivalents of poly(styrene-oligo-butadienyl)lithium. The SEC chromatogram of the purified product (Figure 14, Appendix B) showed a narrow monomodal curve (M<sub>n</sub> = 3.8 x 10<sup>3</sup>, M<sub>n</sub>/M<sub>w</sub> = 1.02). The average number of arms calculated from the SEC results was 2.71 and the amount of 3-armed star was calculated to be 71%. The MALDI-TOF mass spectrum of the crude product (Figure 15, Appendix B) showed 2 distributions corresponding to 2-armed polystyrene linked product without unreacted epoxide and three-armed polystyrene star.

3.4.1.5. Effect of temperature on the linking reaction

It was anticipated that reducing the temperature of the reaction would change the relative reaction rates for the addition of poly(styryl)lithium to the epoxides and the side
reaction. Hence, the reaction of 9 equivalents of poly(styryl)lithium ($M_n = 1.3 \times 10^3$, $M_n/M_w = 1.05$) with the linking agent at 10 °C was investigated. The SEC chromatogram of the purified product (Figure 16, Appendix B) showed a narrow monomodal curve ($M_n = 3.6 \times 10^3$, $M_n/M_w = 1.02$). The average number of arms calculated from the SEC results was 2.77 and the amount of 3-armed star was calculated to be 77%. The MALDI-TOF mass spectrum (Figure 17, Appendix B) of the purified product showed two distributions corresponding to 2-armed polystyrene linked product without unreacted epoxide and three-armed polystyrene star.

Table 3.2. Summary of the results of the reactions of poly(styryl)lithium with N,N-diglycidyl-4-glycidyloxyaniline

<table>
<thead>
<tr>
<th>EXPERIMENT</th>
<th>ADDITIVE</th>
<th>$M_n$ base (g/mol)</th>
<th>$M_n$ product (g/mol)</th>
<th>Average number of arms</th>
<th>3-armed star (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 eq. PSLi @ 30°C</td>
<td>---</td>
<td>$1.5 \times 10^3$</td>
<td>$4.4 \times 10^3$</td>
<td>2.93</td>
<td>93</td>
</tr>
<tr>
<td>3.6 eq. PSLi @ 30°C</td>
<td>10 eq. THF</td>
<td>$1.6 \times 10^3$</td>
<td>$4.7 \times 10^3$</td>
<td>2.94</td>
<td>94</td>
</tr>
<tr>
<td>5 eq. PSLi @ 30°C</td>
<td>10 eq. LiCl</td>
<td>$1.7 \times 10^3$</td>
<td>$4.9 \times 10^3$</td>
<td>2.88</td>
<td>88</td>
</tr>
<tr>
<td>9 eq. PSLi @ 30°C</td>
<td>5.3 eq. KOR</td>
<td>$1.5 \times 10^3$</td>
<td>$4.4 \times 10^3$</td>
<td>2.93</td>
<td>93</td>
</tr>
<tr>
<td>3.4 eq. P(S-ω-BD)Li @ 30°C</td>
<td>---</td>
<td>$1.4 \times 10^3$</td>
<td>$3.8 \times 10^3$</td>
<td>2.71</td>
<td>71</td>
</tr>
<tr>
<td>9 eq. PSLi @ 10 °C</td>
<td>---</td>
<td>$1.3 \times 10^3$</td>
<td>$3.6 \times 10^3$</td>
<td>2.77</td>
<td>77</td>
</tr>
</tbody>
</table>

In conclusion, the reaction of poly(styryl)lithium with the commercially available N,N-diglycidyl-4-glycidyloxyaniline forms the three-armed functionalized polystyrene star as the main product and a two-armed linked side product. Attempts were made to increase the yield of the desired three-armed functionalized polystyrene star by increasing the amount of excess polystyrene, modification of the structure of the chain end to the less sterically hindered butadienyllithium, using additives such as THF, lithium.
chloride and potassium alkoxides and reducing the reaction temperature. The average number of arms in each star can be estimated from the ratio of the average number molecular weight of the product relative to the average number molecular weight of the corresponding precursor obtained from the SEC analyses. The summary of the results is shown in Table 3.2. Under all of these reaction conditions, the formation of the two-armed product could not be avoided.

3.4.2. Synthesis of polystyrene stars using Tactix 742 as linking agent

In view of the difficulties in eliminating the side reaction to form coupled product in the preparation of three-armed polystyrene stars with N,N-diglycidyl-4-glycidyloxyaniline as linking agent, it was desired to try a different commercially available triepoxide as linking agent. Tactix 742 is a commercially available triepoxide with a reported structure as shown in Scheme 3.8. The HPLC and MALDI-TOF analyses of Tactix 742 (Figures 18 and 19, Appendix B) showed that it actually contained a mixture of compounds including di- and penta-functional analogs. The $^1$H NMR spectrum (Figure 3.66) shows the characteristic peaks for the protons on the epoxide functionality at $\delta$ 2.5 – 3.2 ppm, as well as the methylene protons adjacent to the oxygen at $\delta$ 3.6 – 4.4 ppm. The aromatic protons are observed at $\delta$ 6.6 – 7.3 ppm. The peaks at $\delta$ 5.4 – 6.2 ppm are assigned to the triarylmethyl proton a; the estimated chemical shift using ChemNMR software (CambridgeSoft) is 5.34 ppm.

Immediately after the addition of Tactix 742 to 5 equivalents of poly(styryl)lithium ($M_n = 1.4 \times 10^3$ g/mol, $M_w = 1.5 \times 10^3$ g/mol, $M_w/M_n = 1.07$) in benzene at 30 °C, the reaction solution changed from bright orange to dark red. After 24 hours the reaction was quenched with methanol.
The SEC chromatogram of the crude product (Figure 3.67) showed a bimodal curve. The lower molecular weight curve corresponds to the excess poly(styryl)lithium and the higher molecular weight product is anticipated to correspond to the star product. The TLC chromatogram showed two spots: a polar spot ($R_f = 0$) corresponding to the functionalized star product and a non-polar spot ($R_f = 1$) corresponding to the excess non-functional polystyrene. The products were separated by column chromatography using toluene as eluent for the non-functional polymer and
tetrahydrofuran for the functionalized star product. The SEC chromatogram (Figure 3.66) of the purified product shows a monomodal curve ($M_n = 4.7 \times 10^3$ g/mol, $M_w = 5.3 \times 10^3$ g/mol, $M_w/M_n = 1.14$). From the SEC results the average number of arms was calculated to be 3.4.

![SEC Chromatogram](image)

Figure 3.67. SEC chromatogram of (A) base sample, (B) crude product and (C) purified product of the reaction of 5 equivalents of PSLi with Tactix 742 in benzene at 30 °C.

The MALDI-TOF mass spectrum of the purified product (Figure 3.68) shows three distributions. The main distribution is centered at $m/z$ 3800. A representative monoisotopic mass peak at $m/z$ 3363.9 corresponds to three-armed polystyrene star with 26 styrene repeat units, $[\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_n-\text{CH}_2\text{CH(OH)CH}_2\text{O(C}_6\text{H}_4)]_3-\text{CH·Na}^+$; calculated monoisotopic mass $\{[57.07 \times (\text{C}_4\text{H}_9) + 2 \times 14.03 \times (\text{CH}_2) + 13.02 \times (\text{CH}) + 17.00 \times (\text{OH}) + 15.99 \times (\text{O}) + 76.10 \times (\text{C}_6\text{H}_4)] \times 3 + 26 \times 104.06 [(\text{C}_8\text{H}_8)_{26}] + 13.02 \times (\text{CH}) + 22.99 \times (\text{Na}^+)] = 3363.04$ Da. These results are consistent with the average number of arms of 3.4 obtained by SEC. The lower molecular weight distribution centered at $m/z$ 2500 would correspond to two-armed product. Four distributions can be observed in this $m/z$ range. Distribution D with a representative monoisotopic mass peak at $m/z$ 2427.1 corresponds
Figure 3.68. MALDI-TOF mass spectrum of the product of the reaction of 5 equivalents of PSLi ($M_n = 1,600$ g/mol) with Tactix 742 in benzene at 30 °C.
to the low molecular mass tail of the main distribution, i.e. three-armed polystyrene star with 17 styrene repeat units, $[\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_n-\text{CH}_2\text{CH(OH)CH}_2\text{O(C}_6\text{H}_4)]_3^-\cdot\text{Na}^+$; calculated monoisotopic mass \{57.07 (\text{C}_4\text{H}_9) + 2 \times 14.03 (\text{CH}_2) + 13.02 (\text{CH}) + 17.00 (\text{OH}) + 15.99 (\text{O}) + 76.10 (\text{C}_6\text{H}_4)\} \times 3 + 17 \times 104.06 \{[(\text{C}_6\text{H}_4)_{17}] + 13.02 (\text{CH}) + 22.99 (\text{Na}^+)\} = 2426.48 \text{ Da}. The 2-armed product from partial reaction of the linking agent (Scheme 3.9) with 18 styrene repeat units, $\{[(\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_n-\text{CH}_2\text{CH(OH)CH}_2\text{O-(C}_6\text{H}_4)]_2[(\text{C}_6\text{H}_4)\text{-OCH}_2(\text{CH}_2\text{CHO})]\}-\cdot\text{Na}^+$; \{57.07 (\text{C}_4\text{H}_9) + 2 \times 14.03 (\text{CH}_2) + 13.02 (\text{CH}) + 17.00 (\text{OH}) + 15.99 (\text{O}) + 76.10 (\text{C}_6\text{H}_4)\} \times 2 + [76.10 (\text{C}_6\text{H}_4) + 2 \times 14.03 (\text{CH}_2) + 13.02 (\text{CH}) + 2 \times 15.99 (\text{O}) + 18 \times 104.06 \{[(\text{C}_6\text{H}_4)_{26}] + 13.02 (\text{CH}) + 22.99 (\text{Na}^+)\}$ has a calculated monoisotopic mass = 2472.46 Da. No peaks can be observed at this $m/z$, this is an indication of the high efficiency of the linking agent. Tactix 742 is a commercially available triepoxide; it was used as received except for drying over calcium hydride and degassing (basic purification steps for use in anionic polymerization). In order to explain the other distributions, the presence of impurities in the linking agent must be considered. The synthesis of the triglycidyl ether of tri(hydroxyphenyl)methane (Tactix 742) has been reported by reaction of tri(hydroxyphenyl)methane with 3 equivalents of epichlorohydrin. The tri(hydroxyphenyl)methane was prepared by reaction of 4-hydroxybenzaldehyde with excess phenol in the presence of p-toluenesulfonylic acid. The structures of possible bifunctional by-products of this synthesis, arising from incomplete reaction of the triphenol with epichlorohydrin are shown in Scheme 3.9. The calculated monoisotopic mass for the 2-armed product with 18 styrene repeat units, from the linking reaction of 2 poly(styryl)lithium chains with product A in Scheme 3.10; $\{[(\text{C}_4\text{H}_9-(\text{C}_8\text{H}_8)_n-\text{CH}_2\text{CH(OH)CH}_2\text{O(C}_6\text{H}_4)]_2[(\text{C}_6\text{H}_4)\text{OH}]\}-\cdot\text{Na}^+$, \{57.07 (\text{C}_4\text{H}_9) + 2 \times 14.03 (\text{CH}_2) + 13.02 (\text{CH}) + 17.00 (\text{OH}) + 15.99 (\text{O}) + 76.10 (\text{C}_6\text{H}_4)\} \times 2 + [76.10 (\text{C}_6\text{H}_4) + 17.00
This is in excellent agreement with an observed representative monoisotopic mass peak of the major distribution (C in Figure 3.68) in the low molecular weight region at \( m/z \) 2417.0.

Scheme 3.9. Possible structures of bifunctional by-products in Tactix 742.

A representative monoisotopic mass peak of distribution B is 16 \( m/z \) units below distribution C at \( m/z \) 2400.9. The calculated monoisotopic mass for the 2-armed product with 18 styrene repeat units, from the linking reaction of two poly(styryl)lithium chains with product B in Scheme 3.9; \{[(C_4H_9-(C_8H_8)_n-CH_2CH(OH)CH_2O(C_6H_4)]_2(C_6H_5)}-CH\cdot Na^+; 
\{(57.07 (C_4H_9) + 2 \times 14.03 (CH_2) + 13.02 (CH) + 17.00 (OH) + 15.99 (O) + 76.10 (C_6H_4)) \times 2 + 77.11 (C_6H_5) + 18 \times 104.06 [(C_8H_8)_18] + 13.02 (CH) + 22.99 (Na^+)\} = 2400.44 Da. The formation of product B cannot be easily deduced from the synthesis of the linking agent; it is not clear at the moment if this product is an impurity in the linking agent or it was formed during the synthesis or MALDI-TOF analysis of the product. A representative monoisotopic mass peak in Distribution A appears 36 mass units below distribution C at \( m/z \) 2381.1, and thus could be the dehydration product from the 2-armed product (- 2 x H_2O). A third distribution in the high molecular weight region is centered at \( m/z \) 6400; it is anticipated that this product corresponds to a 5-armed star. During the condensation reaction of acetone and phenol to form bisphenol-
A there is a preference for the \textit{para}- position\textsuperscript{199} but attack on the \textit{ortho}- position is possible. This is also a possibility in the synthesis described for Tactix 742. After attack of 4-hydroxybenzaldehyde on the \textit{ortho}- position of phenol, attack of another 4-hydroxybenzaldehyde molecule on the \textit{para}- position would result in a penta-functional linking agent as shown in Scheme 3.10. A representative average mass peak in the higher molecular weight distribution at \textit{m/z} 6292.2 corresponds to the 5-armed star with 50 styrene repeat units, from the reaction of poly(styryl)lithium and the linking agent shown in Scheme 3.10; 

\[
\text{[C}_4\text{H}_9\text{-(C}_8\text{H}_8)_n\text{-CH}_2\text{CH(OH)CH}_2\text{O(C}_6\text{H}_4\text{)]}_2\text{-CH-[}}\text{((C}_6\text{H}_3\text{-OCH}_2\text{CH(OH)CH}_2\text{O(C}_8\text{H}_8)_n\text{-C}_9\text{H}_9\text{)]}_2\text{Na}^+;}
\]

calculated average mass \([57.12 (\text{C}_4\text{H}_9) + 2 \times 14.03 (\text{CH}_2) + 13.02 (\text{CH}) + 17.00 (\text{OH}) + 15.99 (\text{O}) + 76.10 (\text{C}_6\text{H}_4)] \times 4 + [57.12 (\text{C}_4\text{H}_9) + 2 \times 14.03 (\text{CH}_2) + 13.02 (\text{CH}) + 17.00 (\text{OH}) + 15.99 (\text{O}) + 75.09 (\text{C}_9\text{H}_9)] + 50 \times 104.15 [(\text{C}_8\text{H}_8)_{50}] + 2 \times 13.02 (\text{CH}) + 22.99 (\text{Na}^+)\) = 6291.84 Da.


The $^1$H NMR spectrum (Figure 3.69) of the purified product shows the disappearance of all the resonance peaks corresponding to the protons on the epoxide functionality in the Tactix 742 at $\delta$ 2.5 – 3.2 ppm, as well as the methylene protons.
adjacent to the oxygen at $\delta$ 3.6 – 4.4 ppm (see figure 3.64). The characteristic resonance peaks for the methine protons adjacent to an hydroxyl group are observed at $\delta$ 2.4 – 3.0 ppm and new peaks for the methylene protons adjacent to the oxygen are observed at $\delta$ 3.0 – 3.8 ppm.

![Figure 3.69. $^1$H NMR spectrum (CDCl$_3$) of the purified product of the reaction of 5 equivalents of PSLi ($M_n = 1,600$ g/mol) with Tactix 742.](image)

The intrinsic viscosity for the purified functionalized star polymer, 0.041 dL/g, was obtained from the SEC results. This result can be compared with the intrinsic viscosity for the linear polystyrene analogue ($M_w = 5.3 \times 10^3$ g/mol), 0.051 dL/g, calculated with the Mark-Howkink-Sakurada equation,$^9$ $[\eta] = K M_a^a$, with $K = 12.3 \times 10^{-5}$ dL/g and $a = 0.703$ in THF solvent at 35 °C.$^{192}$ The experimental $g'$ value is calculated to be 0.80. The relationship between the $g'$ value and the number of arms has been previously reported and the theoretical $g'$ values for different number of arms have been calculated.$^{193,194}$ The calculated $g'$ value for a three-armed star is 0.83 and for a five-armed star is 0.63. These results are consistent with average number of arms = 3.4 obtained from the SEC results.
FTIR spectroscopic analysis provided further evidence of the efficiency of the linking agent. The spectrum of the purified functionalized star polymer shows the disappearance of the characteristic absorption bands for the epoxide rings at 833 cm\(^{-1}\) and 970 cm\(^{-1}\) and the appearance of the characteristic broad absorption at 3550 cm\(^{-1}\) corresponding to the O-H stretch.\(^{173}\)

In summary, the reaction of excess poly(styryl)lithium with Tactix 742 in benzene at 30 °C produces three-armed functionalized polystyrene star as the main product. Two-armed functionalized linked polystyrene and five-armed functionalized polystyrene star are minor products. The minor products are formed from reaction of poly(styryl)lithium with impurities in the linking agent, not from side reactions during the linking reaction. It is concluded that this is a very efficient and useful linking agent for preparation of functionalized polystyrene stars.
CHAPTER IV

SUMMARY

A new mechanism for the reaction of polymeric organolithium compounds with thiiranes has been found. The reaction of poly(styryl)lithium and poly(butadienyl)lithium with propylene sulfide and ethylene sulfide was investigated in hydrocarbon solution at 30 °C for the preparation of thiol-functional polymers. It was found by MALDI-TOF mass spectral analysis of the reaction products that the reaction proceeded by attack of the anion on the methylene carbon atom of the thiirane ring followed by ring opening to form the thiol-functionalized polymer. This is in contrast with the previously reported “sulfur extrusion” mechanism for the reaction of simple alkyllithium and aryllithium compounds with thiiranes. Addition of a Lewis base, such as tetrahydrofuran, increased the amount of oligomerization of propylene sulfide from 4% to 26 % but did not change the mechanism of the reaction.

The reaction of poly(styryl)lithium with trimethylene sulfide was also investigated. In this case, the product was formed by attack of the anion on the sulfur atom followed by ring opening mechanism in an analogous way as the reaction of ethyllithium with trimethylene sulfide as reported by Morton and Kammereck. The resulting polymer was methyl-terminated; thiol-functionalized polymer was not obtained.

A new method for synthesis of alkoxysilyl-functionalized polymers was developed. Using a general functionalization methodology based on the hydrosilation of vinyltrimethoxysilane with ω-silyl hydride-functionalized polystyrene, alkoxysilyl-
functionalized polystyrene was obtained in high yield (83 %). The main side product was the vinylsilane-functionalized polymer. A small amount of dimer (approximately 2 %) was formed, presumably from the hydrosilation reaction of silyl hydride-functionalized polymer and vinylsilane-functionalized polymer.

In an attempt to prepare vinylsilane-functionalized polymer, poly(styryl)lithium was reacted with 6.6 equivalents of vinyltrimethylchlorosilane in benzene at 30 °C. Star polymers with an average of 6.8 arms per star were obtained. It was found that, in benzene at 30 °C, vinyltrimethylchlorosilane is an efficient linking agent for the preparation of well-defined, star-branched polymers. In contrast, the reaction of poly(styryl)lithium with 5 equivalents of vinyltrimethylchlorosilane in THF at -78 °C produced the macromonomer, vinylsilane-functionalized polymer, in high yield (> 93 %).

It was desired to use an analogous non-chlorine containing compound for the preparation of well-defined star-branched polymers. Hence, poly(styryl)lithium was reacted with vinyltrimethylmethoxysilane; the product obtained resulted exclusively from the addition of the living anion to the vinyl group. The reaction did not yield any higher molecular weight products from the displacement of ethoxy groups by the living chains as observed for chloride groups in vinyltrimethylchlorosilane.

In-chain, dihydroxyl-functionalized polystyrene was prepared by the reaction of poly(styryl)lithium and 1,3-butadiene diepoxide. The hydroxyl functionalities were activated by titration with potassium naphthalenide. Polymerization of ethylene oxide yielded heteroarm polystyrene/poly(ethylene oxide) stars.

Polyepoxides have been found to be efficient linking agents. Hence, poly(styryl)lithium was reacted with a commercially available triepoxide, N,N-diglycidyl-
4-glycidyloxyaniline, to prepare three-armed stars. The resulting product was a combination of three-armed star and coupled product as determined by MALDI-TOF MS. There were two competing reactions: addition of a poly(styryl)lithium to the epoxide functionality and the side reaction that leads to coupled product. Attempts to increase the amount of three-armed star product by varying reaction conditions; decreasing the steric requirements of the chain end and the use of additives, such as lithium chloride, potassium alkoxides and Lewis base, were all unsuccessful.

A second approach for the synthesis of three-armed stars was to use a different linking agent, Tactix 742, a commercially available triepoxide. Star polymers with an average of 3.4 arms per star were obtained. The product from the reaction of poly(styryl)lithium with Tactix 742 consisted of mainly the three-armed, star product. The side products were coupled product and five-armed star, resulting from impurities in the linking agent. The high efficiency of the linking agent was demonstrated by the absence of unreacted epoxide functionalities as determined by $^1$H NMR and FTIR analyses.
REFERENCES


APPENDIX A

TITRATION CALCULATIONS

The concentration of active carbon-bound lithium in the sec-butyllithium initiator was determined by Gilman double titration with allyl bromide. An ordinary titration determines the total base, which includes LiH, LiOH, ROLi and RLi. To determine the total base, 3 aliquots of 1.1 mL of sec-butyllithium initiator solution were diluted with 10 mL of cyclohexane and quenched with 10 mL of distilled water. The solutions were titrated with standardized 0.1 N HCl using phenolphthalein as indicator. The free base is composed by the lithium bonded to non-carbon atom, such as lithium alkoxides. To determine the free base, 3 aliquots of 3 mL of sec-butyllithium initiator solution were diluted with 10 mL of cyclohexane quenched with 1 mL of allyl bromide, and then treated with 10 mL of distilled water. Allyl bromide reacts with the carbon-bound lithium compounds without producing LiOH. Sample data for the titrations is given in Table 1.

Table 1. Data for the determination of sec-butyllithium concentration.

<table>
<thead>
<tr>
<th>Sample</th>
<th>sec-Butyllithium (mL)</th>
<th>Allyl bromide (mL)</th>
<th>0.1 N HCl (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.1</td>
<td>0</td>
<td>16.9</td>
</tr>
<tr>
<td>2</td>
<td>1.1</td>
<td>0</td>
<td>16.5</td>
</tr>
<tr>
<td>3</td>
<td>1.1</td>
<td>0</td>
<td>16.3</td>
</tr>
<tr>
<td>4</td>
<td>3</td>
<td>1</td>
<td>0.8</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>1</td>
<td>0.7</td>
</tr>
<tr>
<td>6</td>
<td>3</td>
<td>1</td>
<td>0.8</td>
</tr>
</tbody>
</table>
The average of the three repetitions was calculated. For the total base, the average was 16.6 mL. For the free base, the average is 0.77 mL.

The base is calculated using the following equation:

\[ \text{Base} = mL \text{ HCl} \times \frac{\text{conc. HCl mol}}{1 L} \times \frac{1}{\text{aliquot in mL}} \]

hence, the total base is:

\[ \text{Total base} = 16.6 \text{ mL} \times \frac{0.1 \text{ mol}}{1 L} \times \frac{1}{1.1 \text{ mL}} = 1.509 M \]

and the free base is:

\[ \text{Free base} = 0.77 \text{ mL} \times \frac{0.1 \text{ mol}}{1 L} \times \frac{1}{1.1 \text{ mL}} = 0.026 M \]

The concentration of sec-butyllithium is determined by the difference between total base and free base as follows:

\[ \text{sec-butyllithium concentration} = \text{total base} - \text{free base} \]

\[ \text{sec-butyllithium concentration} = 1.51 \text{ M} - 0.03 \text{ M} = 1.48 \text{ M} \]
Figure 1. $^1$H NMR spectrum (CDCl$_3$) of chlorodimethylsilane.
Figure 2. $^1$H NMR spectrum (CDCl$_3$) of vinyldimethylchlorosilane.
Figure 3. $^1$H NMR spectrum (CDCl$_3$) of vinyldimethylethoxysilane
Figure 4. $^1$H NMR spectrum (CDCl$_3$) of vinyltrimethoxysilane.
Figure 5. Quantitative $^{13}$C NMR spectrum (CDCl$_3$) of thiol-functional polystyrene from functionalization of poly(styryl)lithium ($M_n = 2,100$ g/mol) with 1.3 equivalents of propylene sulfide in benzene at 30 °C.
Figure 6. Theoretical isotopic distributions for the silver complex of the 12-mer of polystyrene with 3 units of vinyldimethylhydroxysilane and 1 unit of vinyldimethylmethoxysilane.
Figure 7. MALDI-TOF mass spectrum of the products of the reaction of PSLi ($M_n = 2,000$ g/mol) with 2.5 equivalents of vinyl(dimethylethoxysilane in benzene at 30 °C after 3 days and work-up by precipitation into methanol, using sodium as cationizing agent.
Figure 8. SEC chromatograms of (A) base sample, (B) crude product and (C) purified product of the reaction of 3.6 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C in the presence of 10 equivalents of THF.
Figure 9. MALDI-TOF MS of the purified product of the reaction of 3.6 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C in the presence of 10 equivalents of THF.
Figure 10. SEC chromatograms of (A) base sample, (B) crude product and (C) purified product of the reaction of 5 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxanilines in benzene at 30 °C in the presence of 10 equivalents of lithium chloride.
Figure 11. MALDI-TOF MS of the purified product of the reaction of 3.6 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C in the presence of 10 equivalents of lithium chloride.
Figure 12. SEC chromatograms of (A) crude product (B) purified product and (C) base sample, of the reaction of 9 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C in the presence of 5.3 equivalents of potassium tert-amylate.
Figure 13. MALDI-TOF MS of the crude product of the reaction of 9 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C in the presence of 10 equivalents of potassium tert-amylate.
Figure 14. SEC chromatograms of (A) crude product, (B) purified product and (C) base sample of the reaction of 3.4 equivalents of poly(styrene-oligo-butadienyl)lithium with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.
Figure 15. MALDI-TOF MS of the crude product of the reaction of 3.4 equivalents of poly(styrene-oligo-butadienyl)lithium with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 30 °C.
Figure 16. SEC chromatograms of (A) base sample, (B) crude product and (C) purified product of the reaction of 9 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 10 °C.
Figure 17. MALDI-TOF MS of the purified product of the reaction of 9 equivalents of PSLi with N,N-diglycidyl-4-glycidyloxyaniline in benzene at 10 °C.
Figure 18. HPLC of Tactix 742.
Figure 42. MALDI-TOF MS of Tactix 742.

<table>
<thead>
<tr>
<th>Experimental m/z</th>
<th>PRODUCT</th>
<th>Calculated monoisotopic mass (Da)</th>
</tr>
</thead>
<tbody>
<tr>
<td>483.2</td>
<td>[M + Na]⁺</td>
<td>483.18</td>
</tr>
<tr>
<td>793.3</td>
<td>[N + Na]⁺</td>
<td>793.82</td>
</tr>
<tr>
<td>887.4</td>
<td>[M + O + Na]⁺</td>
<td>887.34</td>
</tr>
<tr>
<td>943.4</td>
<td>[2M + Na]⁺</td>
<td>943.37</td>
</tr>
<tr>
<td>1197.5</td>
<td>[N + O + Na]⁺</td>
<td>1197.98</td>
</tr>
<tr>
<td>1253.5</td>
<td>[M + N + Na]⁺</td>
<td>1254.00</td>
</tr>
</tbody>
</table>
APPENDIX C

CALCULATIONS FOR TRIMETHYLENE SULFIDE EXPERIMENT

In order to determine the nature of the chain ends after the reaction of poly(styryl)Lithium with trimethylene sulfide, additional styrene monomer was added to the reaction mixture. The SEC results show a bimodal curve with a small low molecular weight peak (see Figure 3.26). This indicates that the majority of the chains extended but there was a small percentage that did not react further. Below are the calculations for the amount of chain extended polymer:

Styrene 1 = 10.5 mL x 0.9016 g/mL = 9.47 g

3.8 mL sec-butyllithium x 1.26 M = 4.79 mmol

Calculated M_n base = 9.47 g / 4.79 x 10^{-3} mol = 2.0 x 10^3 g/mol

Obtained M_n base = 2.4 x 10^3 g/mol

Effective moles of sec-butyllithium = 9.47 g / 2.4 x 10^3 g/mol = 3.95 mmol

Base sample = 4.33 g of polystyrene

Moles removed in base sample = 4.33 g / 2.4 x 10^3 g/mol = 1.80 mmol

Remaining moles in reaction mixture = 3.95 mmol - 1.80 mmol = 2.15 mmol

M_n of chain extended product = 1.5 x 10^4 g/mol

Molecular weight increase = 1.5 x 10^4 g/mol - 2.4 x 10^3 g/mol = 1.26 x 10^4 g/mol

Styrene 2 = 27.4 ml x 0.9016 g/mL = 24.7 g

Moles of polymer that chain extended = 24.7 g / 1.26 x 10^4 g/mol = 1.96 mmol
Moles of non-functional polymer = 2.15 – 1.96 = 0.19 moles

% of functionalized moles = 0.19 mmol / 3.95 mmol = 95 %

The percentage of trimethylene sulfide functionalized polymer was estimated as 95%.
APPENDIX D
THREE-ARMED STAR YIELD CALCULATIONS

From the SEC results:
If \( X \) = percentage of three-armed star polymer then,
\[
M_{\text{star}} = 2M_{\text{base}} (1 - X) + 3M_{\text{base}}X
\]

Rearranging the formula the percentage of 3-armed star from the SEC results can be calculated
\[
X = \frac{M_{\text{star}} - 2M_{\text{base}}}{M_{\text{base}}}
\]

For example for the reaction of 3.6 equivalents of poly(styryl)lithium with N,N-diglycidyl-4-glycidyloxyaniline in the presence of THF (Section 3.4.1.1).

\( M_{\text{base}} = 1.6 \times 10^3 \) g/mol

\( M_{\text{star}} = 4.7 \times 10^3 \) g/mol

\[
X = \frac{4.7 \times 10^3 - 2 \times 1.6 \times 10^3}{1.6 \times 10^3} \times 100 = 94\%
\]