Synthesis of Arborescent Polybutadiene

by

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Author’s Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

I understand that my thesis may be made electronically available to the public.

Abstract

Arborescent polymers are characterized by a tree-like architecture and a high branching functionality. This type of polymer can be synthesized by different techniques, but the 'grafting onto' method is attractive because it provides good control over the molecular weight of the graft polymer and the side-chains used as building blocks. This method was applied to the synthesis of arborescent polybutadiene, using cycles of epoxidation and anionic grafting reactions. The research focused on optimization of the grafting yield for the synthesis of the G0 polymers, obtained by grafting side-chains onto a linear epoxidized substrate, with the ultimate goal of synthesizing successive generations of graft polymers using these optimized conditions. Two additives potentially useful as reactivity modifiers, *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and lithium bromide (LiBr), were investigated to increase the grafting yield. The influence of solvent polarity was also examined, and the reaction time was varied from one day to one week while monitoring the grafting yield. Optimal results (with grafting yields reaching up to 85% in one week) were obtained in cyclohexane-tetrahydrofuran mixtures, in the presence of LiBr, with only small (2-3%) yield increases observed after 24 h of reaction. These optimal conditions, when applied to the synthesis of G1 and G2 polymers, led to grafting yields of 78-80% when using a 1:1 ratio of epoxide groups to living ends. The influence of excess substrate was also examined individually for each generation, and likewise led to small (2-4%) increases in grafting yield. The results obtained showed that the grafting reaction was successful on the basis of ^{1}H NMR spectroscopy and size exclusion chromatography analysis, and was sensitive to parameters such as the substitution level of the epoxidized substrate, the solvent composition, and the presence of additives.

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Dedication

I dedicate this work to my parents
and my family for their endless and consistent encouragement
and
to my beloved wife for her patience
“Welcome Aseel”

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List of Symbols and Acronyms

C_e	Coupling efficiency
DRI	Differential refractive index
f_n	Number-average branching functionality
G0, G1, G2…	Arborescent polymer generations
^{1}**H NMR**	Proton nuclear magnetic resonance
***m*-CPBA**	3-Chloroperoxybenzoic acid
MeOH	Methanol
M_n	Number-average molecular weight
M_w	Weight-average molecular weight
MWD	Molecular weight distribution
PBD	Polybutadiene
PDI	Polydispersity index
PIP	Polyisoprene
PS	Polystyrene
SEC	Size exclusion chromatography
THF	Tetrahydrofuran
TMEDA	*N,N,N',N'*-Tetramethylethylenediamine

Chapter 1 Introduction

1.1 Opening Remarks

Branched polymers have physical properties distinct from their linear counterparts due to their compact structure. Star-branched and arborescent (dendrigraft) polymers are particularly interesting among the branched polymer families, since their well-defined structure and uniform size make them useful as model branched macromolecules. In the synthesis of arborescent polymers, different parameters such as the side-chain molecular weight and the branching density can be varied and affect the physical properties of these materials. Various methods have been reported to synthesize this type of polymer with controllable side-chain molecular weight and composition, end groups, branching functionality, etc. Additionally, the living polymerization techniques used in their synthesis maintain a narrow molecular weight distribution.[1-3]

Arborescent polymers belong to the dendrigraft polymer family, most commonly synthesized through cycles of functionalization and grafting starting from a linear polymer substrate. Successive grafting reactions lead to generational growth. The key features of arborescent polymer syntheses are the use of building blocks (side-chains) of uniform size, and a random distribution of coupling sites within the grafting substrates. The second characteristic, in particular, leads to a random distribution of structural defects within the branched polymer structure, and a narrow molecular weight distribution is maintained from one generation to the next.[3] In the current investigation, the synthesis of arborescent polybutadiene started from linear polybutadiene building blocks. A linear substrate was functionalized with epoxide groups, to provide coupling sites for the grafting reaction of linear polybutadienyllithium. The epoxidation and grafting cycles were repeated to obtain the subsequent generations of arborescent polybutadiene. The main purpose of this study was to optimize the reaction conditions used, to ensure a high yield of graft polymer.

1.2 Thesis Outline

This thesis starts with a discussion of relevant background information and related studies on arborescent polymers derived from diene monomers in Chapter 2. The project objectives are explained in Chapter 3, while the detailed experimental procedures used in the work are provided in Chapter 4. This is followed, in Chapter 5, by the results obtained, and their analysis to provide explanations for the trends observed. Finally, the main conclusions drawn from the work are summarized in Chapter 6, and suggestions for future work are briefed discussed in Chapter 7.

Chapter 2 Literature Review

2.1 Dendrigraft Polymers

Synthetic polymers can be classified on the basis of their chain architecture as linear, cross-linked, star-branched, and dendritic structures.[4] Investigations have focused mainly on the first three architectural types in the past but over the last 20 years, dendritic polymers have led to remarkable achievements in the field of nanomaterials.[5]

Dendritic polymers, characterized by multi-level branching, can be further subdivided into three groups depending on their architecture: Dendrimers, hyperbranched polymers, and dendrigraft polymers, as shown in Figure 2-1.[2] Dendrimers have a strictly controlled structure arising from cycles of monomer protection, condensation, and deprotection, while similar polycondensation reactions are typically carried out without protecting groups in the synthesis of hyperbranched polymers, which leads to a large number of structural defects.[6]

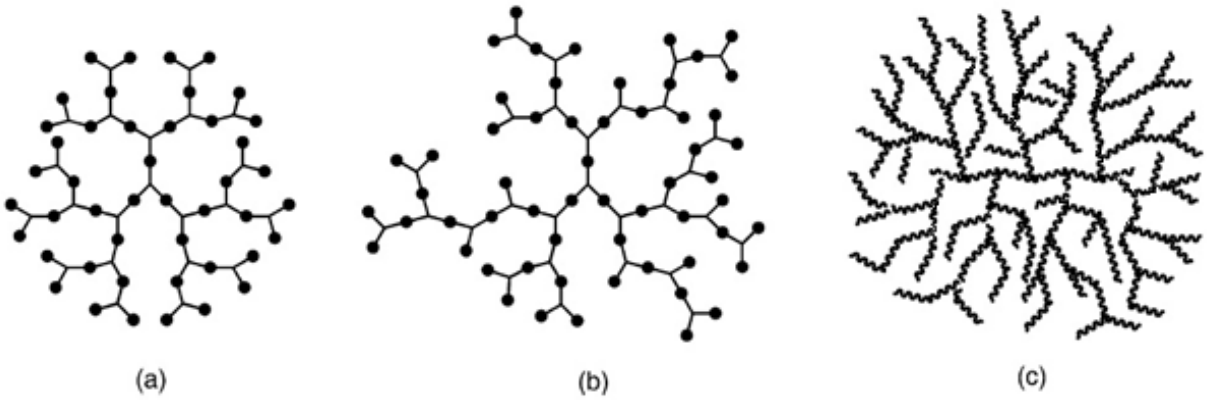


Figure 2-1. Dendritic polymers: (a) dendrimers, (b) hyperbranched polymers, and (c) dendrigraft polymers.[2]

Dendrigraft polymers (Figure 2-1c) were introduced in 1991 simultaneously by Tomalia et al. (under the trade name Comb-burst® polymers), and by Gauthier and Möller as the arborescent polymers.[3,7,8] The term 'arborescent' refers to the tree-like architecture of these molecules, resulting from successive grafting reactions. Dendrigraft polymers are

generally synthesized by ionic polymerization and grafting reactions. This approach determines the main features of dendrigraft polymers. In analogy to dendrimer syntheses, the preparation of dendrigraft polymers is generation-based, but starts from polymer chain building blocks rather than small molecule monomers. The generation-based growth typically leads to a geometric increase in molecular weight and branching functionality for successive generations. The structure of dendrigraft polymers is not as well controlled as for dendrimers however; the grafting reaction takes place randomly on the substrate rather than strictly at the chain ends of the previous generation. It should be pointed out that this characteristic of dendrigraft polymer syntheses is generally viewed as an advantage rather than a disadvantage: While the branching points are randomly distributed on the substrate, any structural defects are also randomly distributed. Consequently, the molecular weight distribution (MWD) obtained for dendrigraft polymers remains narrow ($M_w/M_n \approx 1.1$) over successive generations.[3,8,9]

2.2 Synthetic Methods

Dendrigraft polymers can be synthesized by three distinct techniques, namely 'grafting from', 'grafting onto', and 'grafting through' methods. The first two approaches are analogous to the 'core-first' or divergent techniques common in dendrimer syntheses, in that growth of the molecules takes place from the center outwards, while the third method is more closely related to the synthesis of hyperbranched polymers.[10,11]

The 'grafting from' and 'grafting onto' methods are closely related: Side-chains are added in successive grafting reactions (generations) starting from a linear substrate in both cases. The 'grafting from' technique is distinguished by the presence of initiating sites on the substrate, from which side-chains are grown by the addition of monomer, while the 'grafting onto' method relies on the presence of coupling sites on the substrate that are reacted with

preformed side-chains. The first approach makes it difficult to fully characterize the products, because it is impossible to determine the exact number and the molecular weight of the added side-chains unless they can be cleaved cleanly from the substrate after the reaction. Moreover, increasing the number of initiating sites present on the substrate increases its charge density. This may affect its solubility and lead to heterogeneous reactions that are difficult to control and/or give broad molecular weight distributions.[12]

A wide range of dendrigraft polymers have been synthesized by the 'grafting onto' method, which involves the introduction of coupling sites onto a substrate polymer, the preparation of living ionic polymer chains in a separate reaction, and coupling of the substrate polymer with the living polymer by combining the two components. The distinct steps involved in the preparation of the substrate and the side-chains facilitate the detailed characterization of the components serving for each grafting cycle (generation) in terms of molecular weight and average spacing between the branching points (branching density).[13]

While the 'grafting onto' and 'grafting from' methods rely on similar concepts, 'grafting through' involves a very different synthetic procedure for the preparation of dendrigraft polymers. These syntheses are typically carried out as one-pot reactions where living polymer chains are reacted with bifunctional monomers, having a vinyl group and another chemical functionality, able to extend the chain and to terminate the living ends by coupling, respectively. Each coupling reaction takes place randomly, gradually increasing the branching functionality and the molecular weight of the polymers.[14]

The current investigation focuses on the preparation of arborescent homopolymers from polybutadiene segments by applying the 'grafting onto' method. Consequently, this grafting technique will be discussed in more detail subsequently.

2.3 Arborescent Polymers by the 'Grafting Onto' Method

Comb-burst® and arborescent polymers were first synthesized using 'grafting onto' methods. This scheme starts from a linear polymer substrate that is functionalized with coupling sites. These functional groups are reacted with living ionic polymer chains to yield a comb-branched polymer, also called a generation zero (G0) arborescent polymer structure, as represented in Figure 2-2. In the next step, the G0 polymer is functionalized with coupling sites to serve as grafting substrate for the preparation of a G1 arborescent polymer. This represents the first generation of arborescent polymer, having by definition a dendritic (multi-level) branched architecture. Subsequent coupling reactions lead to arborescent polymers of generations G2, G3, etc.[15,16]

This method does not provide very strict control over the polymer architecture, because the coupling sites are randomly distributed on the substrate. However, ionic polymerization techniques still provide control over the MWD of the side-chains and lead to arborescent polymer structures of uniform size. The multi-step sequence of Figure 2-2 is best achieved if the grafting reaction proceeds in high yield and is not susceptible to cross-linking reactions. This requires minimizing side reactions in the functionalization and coupling processes.[15-17]

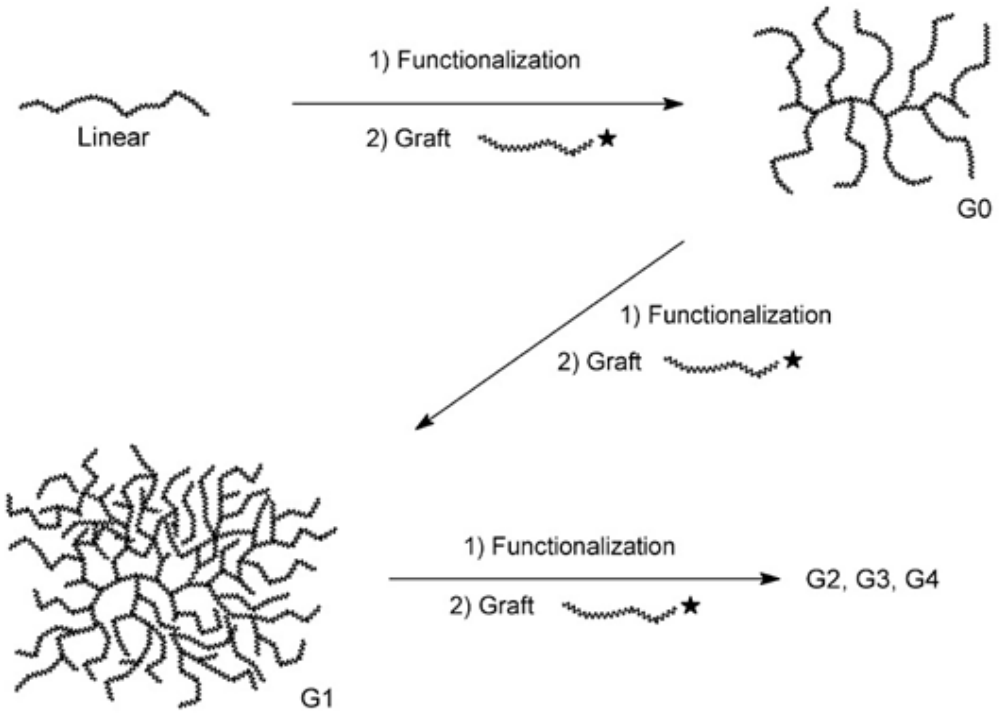
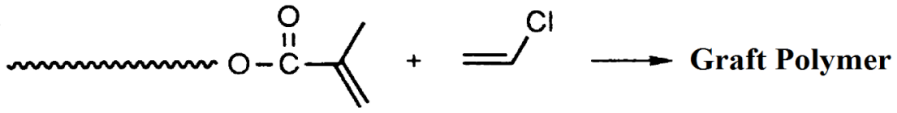


Figure 2-2. General 'grafting onto' scheme for the synthesis of dendrigraft polymers.[2]

2.4 Living Anionic Polymerization

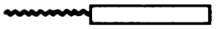
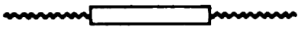
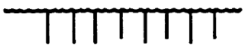
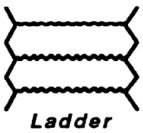
Living anionic polymerization is a chain reaction that occurs with neither termination nor chain transfer. This technique is a great synthetic tool to design macromolecular constructs. For example, it provides control over the composition of block copolymers by sequential addition of different monomers. Moreover, different electrophilic terminating reagents allow the introduction of chemical functionalities selectively at the chain ends (Figure 2-3). Combinations of these techniques applied to different types of monomers can yield a variety of polymer architectures (Table 2-1). For example, the simple copolymerization of macromonomer **1** in Figure 2-3 with vinyl chloride yields a graft polymer.[18,19]



1

Figure 2-3. Macromonomer (1), obtained from a hydroxyl-terminated polymer and methacryloyl chloride, and its copolymerization with vinyl chloride.[18]

Table 2-1. Polymer architectures obtained from living anionic polymerization.[18]

	Polymer	Application
1	OH *Functional ended*	Dispersing agents Synthesis of macromonomers
2	HO OH *α,ω-difunctional*	Elastomers synthesis Chain extension Cross-linking agents
3	 *AB Block*	Dispersing agents Compatibilizers for polymer blending
4	 *ABA Block*	Thermoplastic elastomers
5	 *Graft*	Elastomers Adhesives
6	 *Comb*	Elastomers Adhesives
7	 *Star*	Rheology control Strengthening agents
8	 *Ladder*	High-temperature plastics Membranes Elastomers
9	 *Cyclic*	Rheology control
10	 *Amphiphilic network*	Biocompatible polymers

The monomers most commonly employed in living anionic polymerization techniques are styrene, butadiene, methacrylic acid esters, acrylic acid esters, ethylene oxide, hexamethylcyclotrisiloxane, and lactones, but styrene is by far the most studied monomer. Butyllithium and sodium naphthalenide are commonly used initiators in anionic polymerization.[18] Butyllithium generates one active chain end, while sodium naphthalenide generates two active ends (Figure 2-4). Thus an AB block copolymer can be obtained when compound **2** is used as initiator for a monomer, while compound **3** produces an ABA block copolymer.[20] Star-branched polymers can be produced, for example, by reacting a substrate containing chlorosilane functionalities with **2**.[21] Furthermore, cyclic polymers can be synthesized through the addition of a coupling agent such as dibromo-*p*-xylene to a highly diluted solution of **3**.[22] Block copolymers of styrene/butadiene/styrene are an example of an A-B-A triblock copolymer structure commercially used as thermoplastic elastomers: Upon cooling of the copolymer melt, elastomeric properties are obtained due to physical cross-linking of the polystyrene blocks immobilized within the glassy domains (Figure 2-5).[18,23]

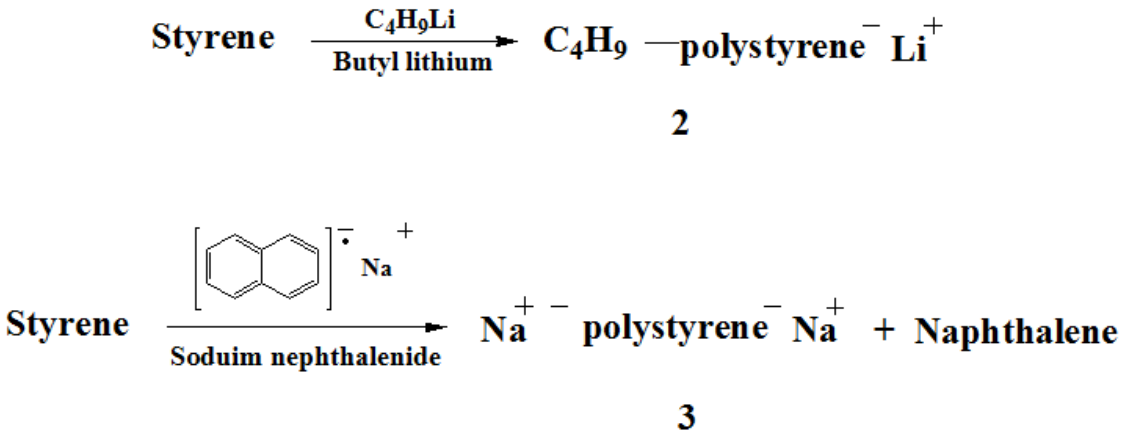


Figure 2-4. Active ends generated in the living anionic polymerization of styrene.[18]

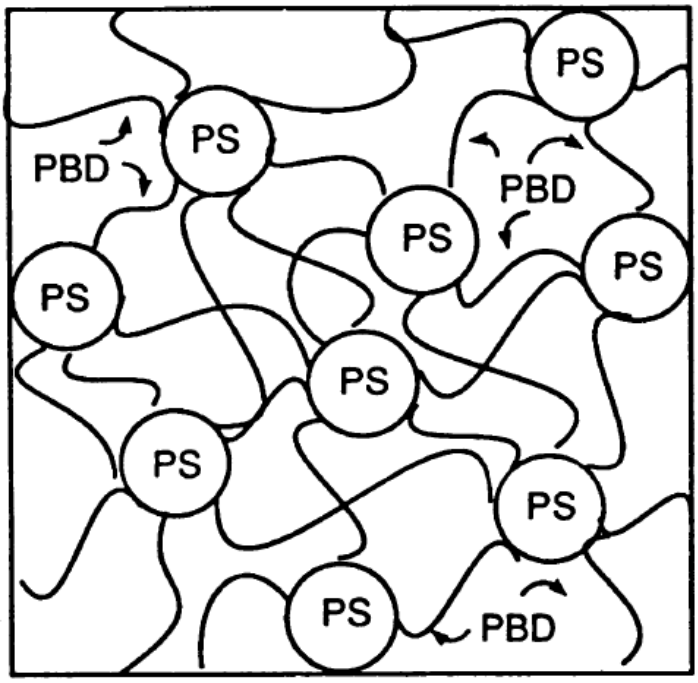


Figure 2-5. Thermoplastic elastomer from ABA styrene/butadiene block copolymer (PS: polystyrene, PBD: polybutadiene).[18]

The acrylic and methacrylic ester monomer families suffer from specific difficulties in anionic polymerization, due to their structure making them sensitive to side reactions. This includes proton abstraction in the acrylate monomers under the strongly basic conditions used in the polymerization reactions, and cyclization of the chain ends through backbiting. These reactions lead mainly to termination of the living chains, and thereby to an increase in the breadth of the molecular weight distribution (MWD) obtained. Methacrylate monomers can nevertheless polymerize anionically under strictly controlled conditions, including the use of a hindered initiator such as 1,1-diphenylhexyllithium, and reaction temperatures of -70^{o}C or lower, but the polymerization of acrylate monomers remains problematic under these conditions.[24-26]

Some strained heterocyclic compounds may also be polymerized anionically. Sodium and potassium alkoxide initiators thus promote the ring-opening polymerization of ethylene

oxide. The product obtained is water-soluble and has been employed as a component in non-ionic surfactants. However propylene oxide is not able to polymerize as well anionically, nor do other substituted oxides, due to chain transfer reactions.[18] On the other hand, ethylene sulfide and its substituted analogues can be polymerized when sulfide anion initiators are used.[27] Ring-opening anionic polymerization has likewise been observed for strained lactones[28] and for hexamethylcyclotrisiloxane.[29,30]

These examples represent relatively recent developments in living anionic polymerization. In addition, an impressive number of examples reported in the scientific literature reflect the importance of the anionic polymerization techniques and their promise for applications. Dendrigraft polymers prepared from diene monomers are also an area of great interest. Since elastomeric diene polymers are analogous to natural rubber, the synthesis of these materials is quite attractive. Dendrigraft architectures are interesting to enhance the physical properties of these materials.[31]

2.5 Anionic Polymerization of Dienes

Isoprene (also known as 2-methyl-1,3-butadiene) and 1,3-butadiene belong to the diene monomer family. Both monomers also have a similar structure and molecular weight (isoprene M_o = 68.1, butadiene M_o = 54.09). Polyisoprene and polybutadiene have comparable properties as elastomers, and can produce different chain microstructures depending on the polymerization conditions used (Figure 2-6).[32] Consequently, many of the results obtained in studies on polyisoprene also apply to investigations on polybutadiene.

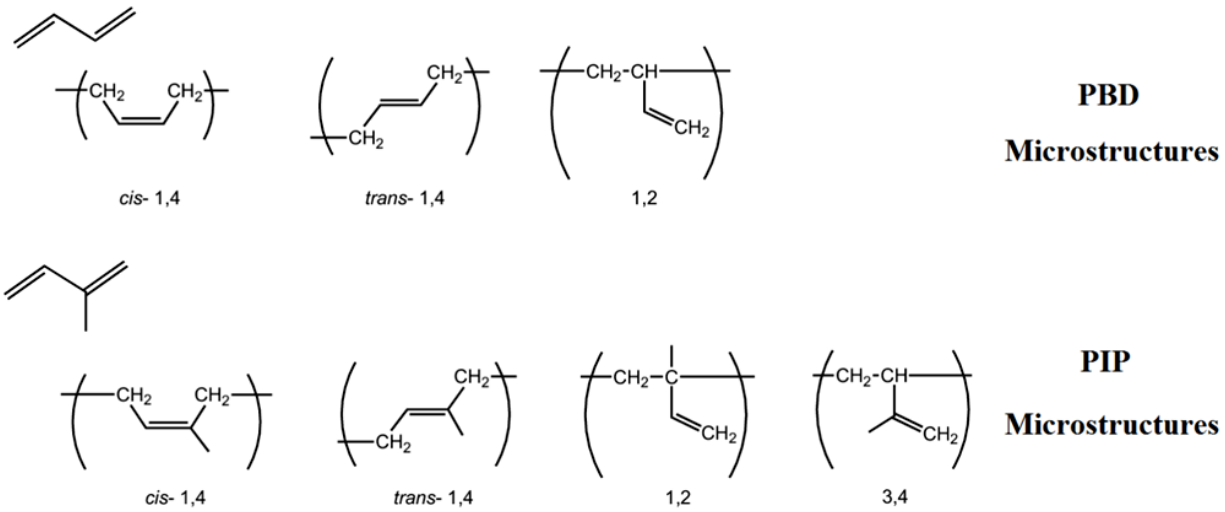


Figure 2-6. Possible microstructures for PBD and PIP.

In the anionic polymerization of diene monomers (e.g. 1,3-butadiene and isoprene), alkyllithium initiators are commonly used. The unique feature of organolithium compounds in comparison with the other alkali metal derivatives lies in their dual characteristic of ionic and covalent compounds. These molecules aggregate in the solid, solution, and gas phases.[33] Each compound has a different degree of dissociation, which influences its relative reactivity as initiator. In general, the relative reactivity of alkyllithium initiators in hydrocarbon solutions varies in the following order, with the degree of association (aggregation number) given between parentheses: menthyllithium (2) > *sec*-BuLi (4) > *i*-PrLi (4-6) > *t*-BuLi (4) > *i*-BuLi > *n*-BuLi (6).[34] The extent of aggregation therefore clearly influences the rate of initiation. The initiation step can be represented by Equation (2-1),[33]

$$\mathbf{I} + \mathbf{M} \xrightarrow{k_i} \mathbf{I\text{-}M^*} \qquad (2\text{-}1)$$

where **I** represents the initiator, **M** the monomer, and **I-M*** the initiated species; k_i is the rate constant for the initiation process. Therefore, the rate of initiation can be defined as the rate of monomer consumption over time:

$$R_i = -d[M]/dt = k_i[I].[M] \quad (2\text{-}2)$$

The equilibrium constant K_d for the dissociation of *sec*-BuLi in hydrocarbon solutions can be described as:

$$(sec\text{-BuLi}) \underset{}{\overset{K_d}{\rightleftharpoons}} 4\ sec\text{-BuLi} \quad (2\text{-}3)$$

As a result, the experimentally observed initiation rate is:

$$R_i = k_i K_d^{1/4} ([I]_o/4)^{1/4} .[M] \quad (2\text{-}4)$$

Aggregation of the polydienyllithium species formed after further monomer additions to the **I-M*** species obtained in the initiation step is also observed. The exact degree of association of polydienyllithium is controversial, as both dimeric and tetrameric species have been reported.[33] In addition, studies have shown that the dissociation equilibrium for both the initiator and the polydienyllithium species is influenced by the presence of THF. This is because THF, as a Lewis base, interacts with the counterions and enhances their dissociation. This was found to increase the reactivity of the initiator as well as the polybutadienyllithium species, by promoting the formation of dimeric species (Equation 2-5).[33]

$$1/2\ (PBDLi)_4 + THF \longrightarrow (PBDLi)_2 \cdot THF \quad (2\text{-}5)$$

While the degree of association of (polybutadienyllithium)$_2$ is lower than (polybutadienyllithium)$_4$, this has no influence on the dissociation process in itself (Equation 2-6). However the presence of THF also enhances the formation of free ions in the polymerization of dienes[33] (this will be discussed further in Chapter 3).

$$(PILi)_2 + THF \longrightarrow (PILi)_2 \cdot THF \quad (2\text{-}6)$$

Bidentate ligands, such as TMEDA, can further increase the reactivity of organolithium compounds (see Chapter 3). This interaction decreases the concentration of unassociated species for both of the initiator and polydienyllithium.[35]

The conditions used for the anionic polymerization of dienes are known to have a strong influence on the chain microstructure obtained. The polymerization temperature, solvent, and additives influence the relative amounts of *cis*- and *trans*-microstructures of the polymer chain.[33] The anionic polymerization of butadiene using sodium and lithium counterions has been compared by Garton and Bywater. The study confirmed the existence of *cis*- and *trans*-microstructure for the polybutadiene propagating center, but *cis*-microstructure were favored by decreasing the temperature.[36] Bywater also reported that the mole fraction of *trans*-units of polybutadienyllithium in THF decreased from 0.34 at 0 ^{o}C to 0.17 at -40 ^{o}C.[37]

Furthermore, four addition modes are possible for diene monomers: *cis*-1,4-, *trans*-1,4, 1,2- and 3,4-additions, albeit 3,4-addition can only be distinguished from 1,2-addition for isoprene and not for butadiene. The solvent polarity was found to have more influence on the chain microstructure of polyisoprene as compared to polybutadiene:[33] The absence of *trans*-units was reported when carrying out the polymerization of isoprene in THF. Changing the solvent from benzene to diethyl ether also led to a decrease in *trans*-units content from 65% to 25%. Anionic polymerization in THF at -20 ^{o}C using sodium and potassium counterions yielded exclusively *cis*-units for polyisoprene, while 22% *trans*-units formed with sodium and 10% *trans*-units with potassium for polybutadiene.[38,33] The polymerization of isoprene by organolithium initiators promotes a high content of *cis*-1,4-microstructures. Studies have shown that the absence of solvent or a lower organolithium compound concentration led to

higher content of *cis*-1,4 units. A ratio of *trans:cis* 1,4-structures of about 65:35 was reported in aromatic solvents, however the relation between the stereochemistry of the chains obtained and that of the propagating centers was not so clear.[39] The conformation adopted by the propagating center was studied by Worsfold and Bywater, who showed that the isomerization between *cis*- and *trans*-conformations could occur until it was locked by further monomer addition (Figure 2-7).[40]

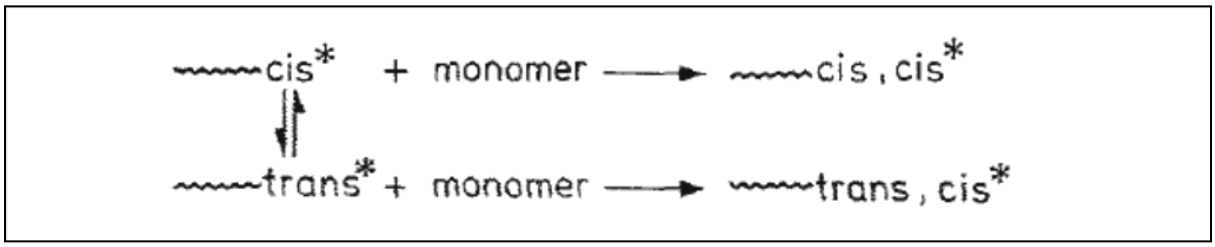


Figure 2-7. Isomerization of *cis*- and *trans*- propagating centers.[40]

For polybutadiene and polyisoprene, Morton et al. proposed different conformations for the propagating end of polybutadiene and polyisoprene in hydrocarbon solutions, with the lithium counterion σ-bonded to the terminal carbon atom (Figure 2-8). The equilibrium between the 4,1 and 4,3 isomers in (**a**) could produce around 10% of 3,4-microstructures, due to the unfavorable isomerization process. The equilibrium between covalent σ- and ionic π-species in (**b**) can lead to 1,4- and 3,4-microstructures, respectively. However the availability of *cis*- and *trans*-1,4 species depends on (**a**), but not on (**b**).[41,42] A number of studies have reported the formation of *cis*-1,4-polydiene microstructures to be favoured in hydrocarbon media. The polymerization in hydrocarbon with a lithium counterion of 1-phenylbutadiene, a strongly hindered diene, resulted in 50-60% *trans*-1,4-, 25% *cis*-1,4-, and 10-25% 3,4-units, but in THF the corresponding values were 80%, 10% and 10%.[43] Moreover, a high content of 1,4-microstructures was reported for 2,3-dimethylbutadiene polymerized in hydrocarbon media, while in THF at 0 ^{o}C equal amounts of 1,2- and 1,4-units were obtained.[44] These

studies indicate that in hydrocarbon solvents, the formation of the *cis*-microstructure is generally favored.

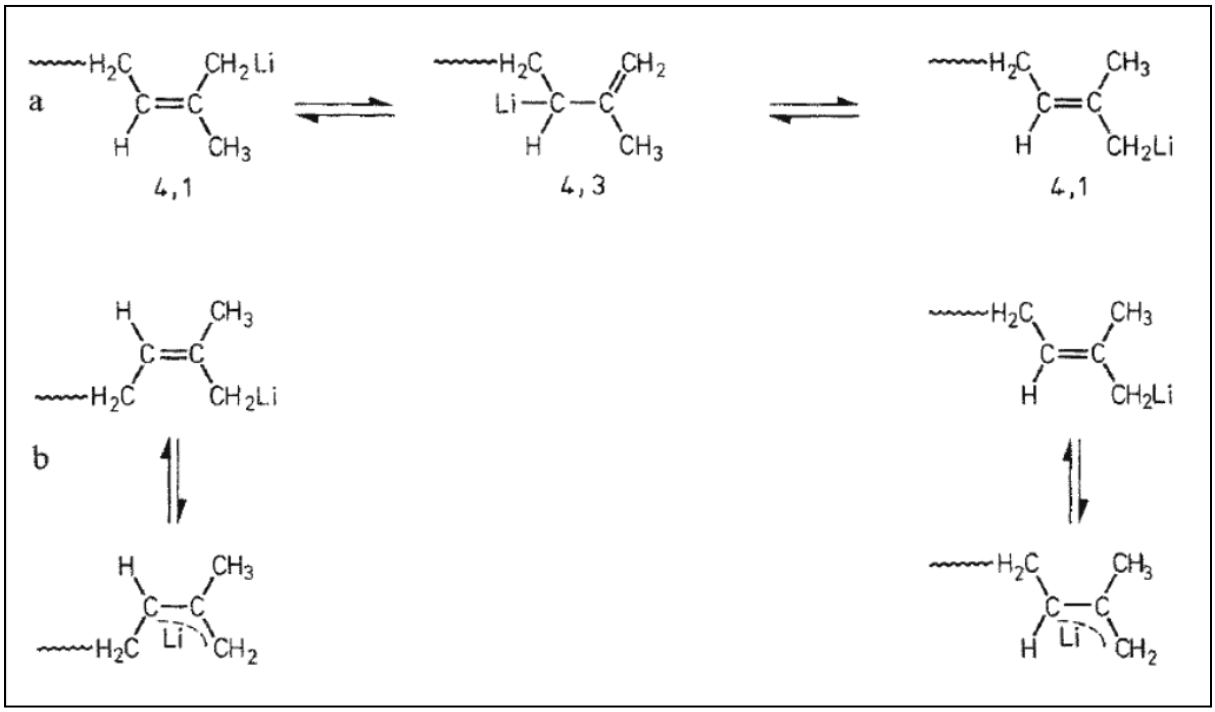


Figure 2-8. Conformation of the propagating center in hydrocarbon solutions.[33]

2.6 Diene Dendrigraft Polymers

Polymers derived from conjugated 1,3-diene monomers are technologically very important because of their elastomeric properties. These products generally have a high content of *cis*-1,4-microstructure, which provides them with superior elastomeric properties, high resilience, and low glass transition temperature, comparable in many cases to natural rubber. The architecture of these polymers also has an influence on their physical properties. For example, increasing the molecular weight of a linear polymer leads to a rapid increase in its melt viscosity. Thus it becomes difficult to process. On the other hand branched polymer architectures, such as the dendrigraft polymers, can have a viscosity comparable to or lower than the linear ones in spite of their very high molecular weight. The synthesis of these

polymer types is therefore significant from a technological viewpoint.[45] Following are some examples of studies on the synthesis of polybutadiene and polyisoprene with controlled, branched polymer architectures. These will be presented first for chlorosilane coupling substrates, in order of increasing branching functionalities achieved in the reactions, and then for epoxidized coupling substrates, more closely related to the current investigation.

2.6.1 Star-like Polydienes

In 1974, Hadjichristidis and Roovers studied the synthesis of star-like polyisoprene, by focusing on 4- and 6-arm branched polymers. The anionic polymerization of isoprene was initiated by *sec*-BuLi in benzene at 30 ^{o}C for 24 h. The star-like polymers were synthesized using a 20% excess of linear polyisoprenyllithium with respect to the chlorosilane coupling agents. For the synthesis of 4-arm stars the coupling agent 1,2-bis(dichloromethylsilyl)ethane was used, while the 6-arm polymer was obtained with 1,2-bis(trichlorosilyl)ethane. The prepared polymers under these conditions had a microstructure with 70% *cis*-1,4-, 23% *trans*-1,4-, and 7% 3,4-units and narrow molecular weight distributions.[46]

Another interesting study by Toporowski and Roovers concerned the synthesis of 18-arm star polybutadiene. The linear polybutadiene was prepared in benzene with *sec*-BuLi, and the coupling reaction was performed with a 30% excess of linear polymer with $[(Cl_3Si\text{-}CH_2\text{-}CH_2)_3Si\text{-}CH_2\text{-}]_2$. After 72 h, a tenfold amount of Et_3N was added with respect to the living ends. The reaction was allowed to proceed for three days before termination with methanol.[47] Due to the variations observed in the physical properties of these materials, scientists ultimately became interested in synthesizing star-branched polymers with even higher branching functionalities.

2.6.2 Dendrimer-star Polybutadiene

Using multifunctional coupling agents such as chloromethylated benzene derivatives or chlorosilane compounds, it was quickly realized that exceeding branching functionalities (*f*) of 6 was difficult.[48] It was found that even for the more reactive chlorosilane coupling agents, it was preferable to decrease the number of chlorine atoms per silicon to two or three and to include ethylene spacers between the silicon atoms. This is the main reason why more complex coupling agents were used in the synthesis of 8-, 12- and 18-arm polyisoprene.[49]

In 1993, an interesting study was published by Roovers et al. on the synthesis of high branching functionality polybutadiene stars containing up to 128 arms. The coupling agents used were polyfunctional chlorosilanes derived from carbosilane dendrimers. Substrates containing 32 vinyl end-groups were derivatized via hydrosilylation with methyldichlorosilane to obtain a coupling agent with 64 chlorosilane functional groups (Figure 2-9). A carbosilane substrate with 64 vinyl groups likewise produced 128 chlorosilane groups, ultimately yielding a 128-arm star. The anionic polymerization of 1,3-butadiene was initiated by *sec*-BuLi in benzene at room temperature, and the coupling agent was introduced. The reaction was allowed to proceed for 8 weeks, using 200% excess of living ends vs. Si-Cl to ensure the preparation of well-defined 128-arm star polybutadiene.[50]

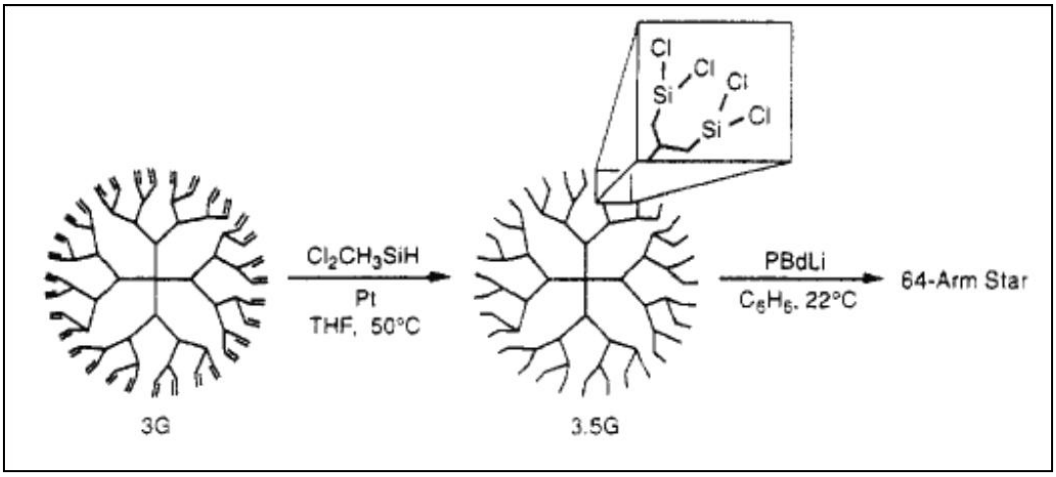


Figure 2-9. The synthesis of 64-arm star polybutadiene.[50]

The following discussion provides examples for the synthesis of branched architecture polydienes with branching functionalities even higher than the star-branched systems above.

2.6.3 Arborescent Polybutadiene

The synthesis of arborescent polybutadiene by a "grafting onto" approach was first reported by Hempenius in 1997 (Figure 2-10). Linear polybutadiene with $M_n \approx 10^4$ was synthesized through anionic polymerization with *sec*-BuLi in *n*-hexane at 17 ^{o}C for 48 h, to obtain a microstructure with ~ 6% 1,2-units. The hydrosilylation of polybutadiene with chlorodimethylsilane was performed to introduce chlorosilane coupling sites (Figure 2-11). Grafting of the functionalized linear polybutadiene substrate with $M_n \approx 10^4$ polybutadienyllithium produced generation 10-0, with about 10 side-chains. These hydrosilylation and grafting cycles were repeated to synthesize generation 10-1 and 10-2 arborescent polybutadiene. A 20% excess of living polybutadiene to chlorosilane groups was used in the grafting reactions. The arborescent polymers obtained by this technique contained up to 1160 arms for the generation 2 (10-2) polymer.[51]

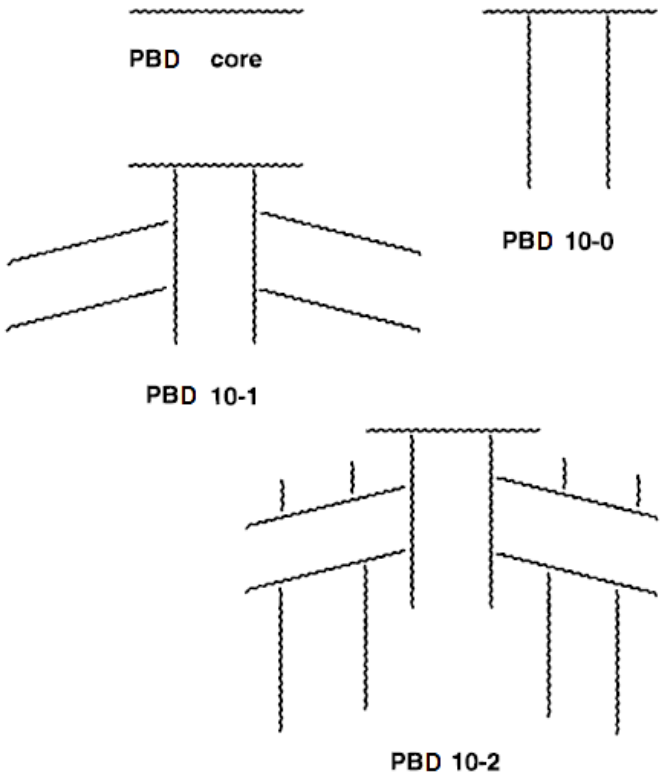


Figure 2-10. Cascade-branched polybutadienes with 10 branches per side-chain.[51]

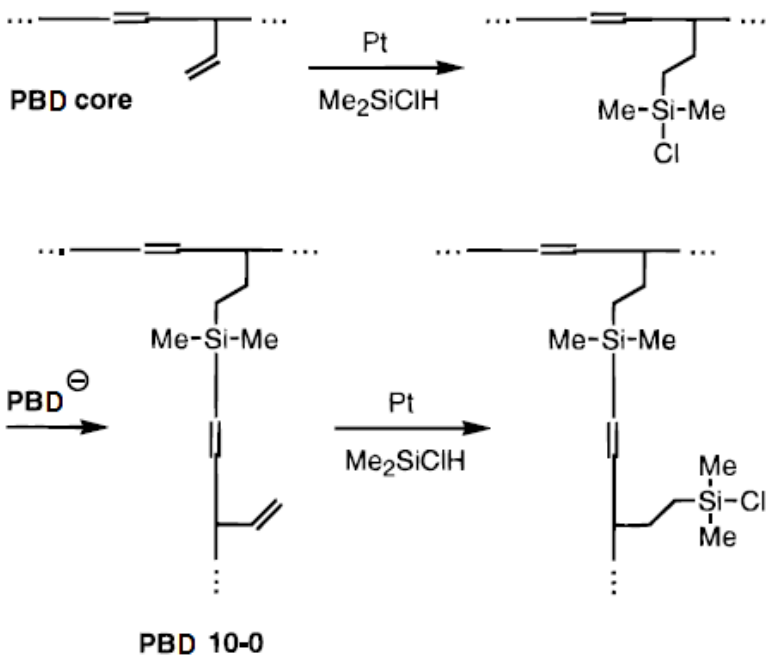


Figure 2-11. Hydrosilylation and grafting cycles of polybutadiene.[51]

2.6.4 Dendrimer-arborescent Hybrids of 1,4-Polybutadiene

A study published by Munam and Gauthier[52] in 2010 focused on the synthesis of hybrid polymers with high branching functionalities, by combining the carbosilane dendrimer substrates introduced by Roovers at al.[50] with the polybutadiene hydrosilylation and grafting techniques developed by Hempenius et al.[51] Carbosilane substrates were prepared containing 32, 64, or 128 Si—Cl functional groups and first coupled with 1,2-polybutadiene chains having a number-average molecular weight $M_n \approx 1000$ (Figure 2-12). These substrates were then further hydrosilylated with dichloromethylsilane and coupled with 1,4-polybutadiene side-chains, to obtain hybrid dendrimer-arborescent polymers with high branching functionalities (Figure 2-13). The hybrid polymers were synthesized with different lengths of 1,4-PBD side-chains ($M_n \approx 1500$, 5000 and 30,000), and up to 2830 side-chains. The branching functionality of the products was observed to vary not only when different substrates were used, but also as a function of the molecular weight of the side-chains, due to increased steric hindrance associated with longer chains.[52]

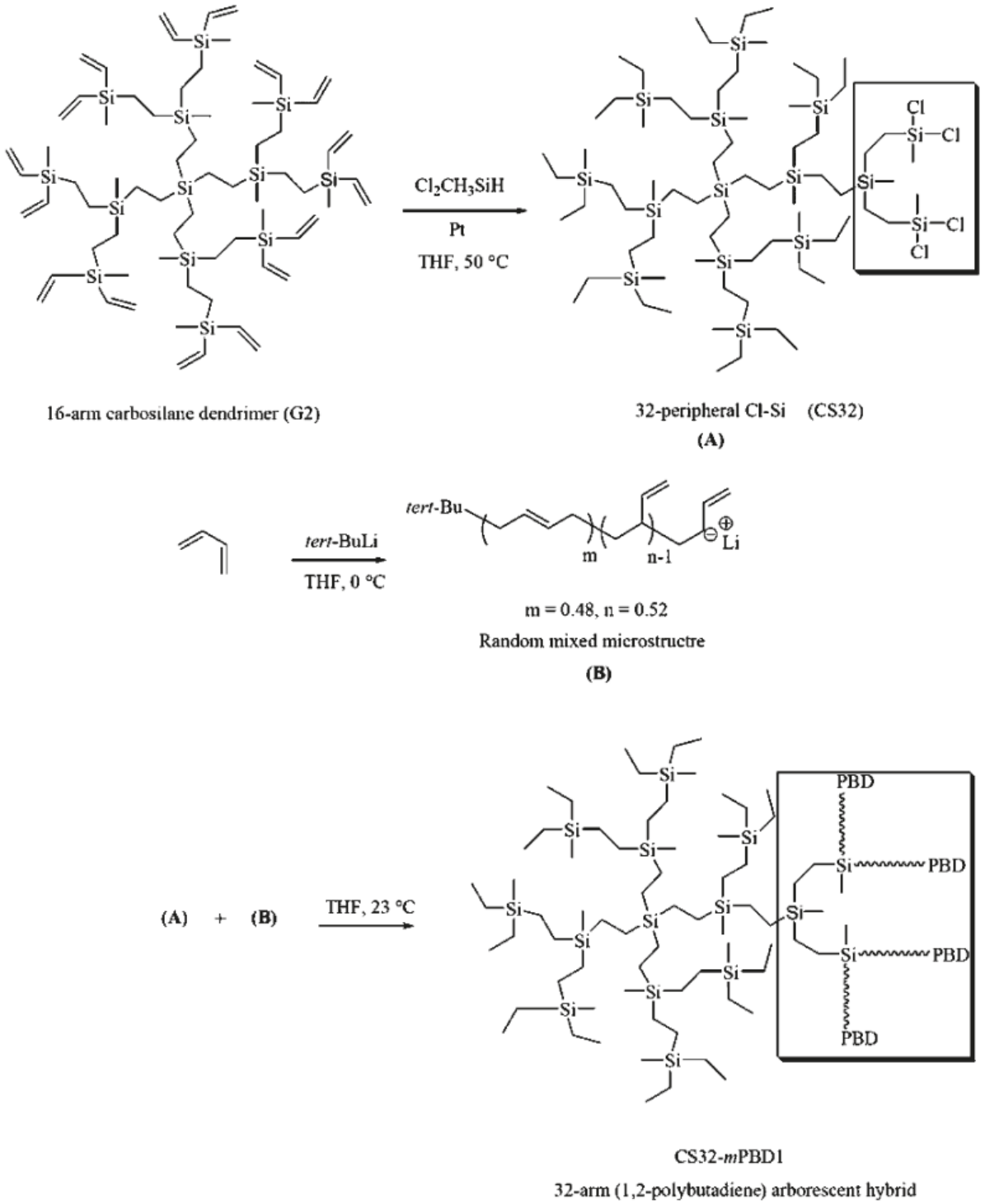


Figure 2-12. Synthesis of 32-arm star-like arborescent 1,2-PBD hybrid.[52]

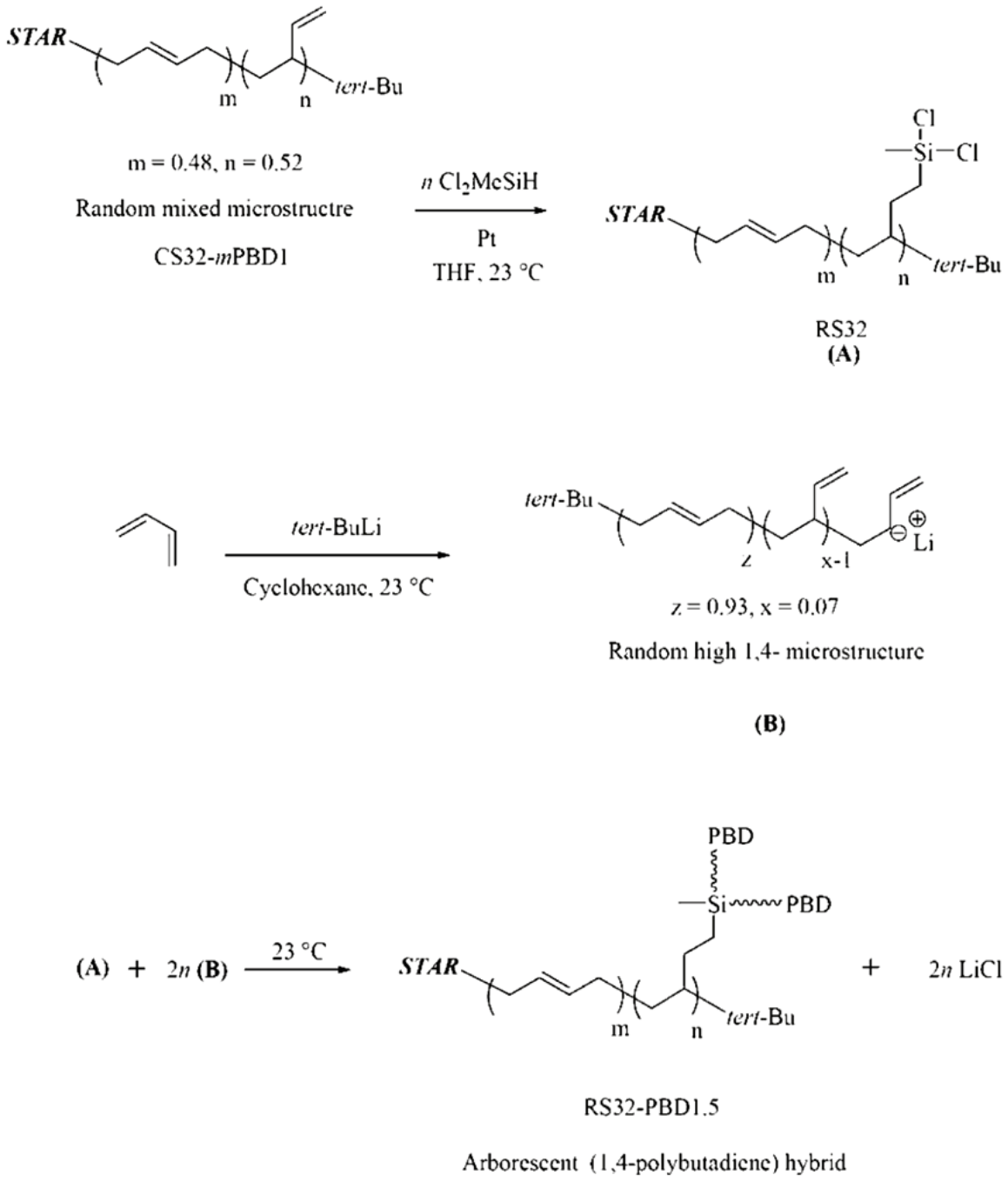


Figure 2-13. Synthesis of dendrimer-arborescent 1,4-PBD hybrid.[52]

2.6.5 Arborescent Polyisoprene

The synthesis of arborescent isoprene homopolymers based on epoxide coupling sites was first reported by Yuan and Gauthier in 2005. The anionic polymerization of isoprene was initiated by *tert*-butyllithium in non-polar solvent (hexane), to yield a high content of 1,4-

microstructures, with a weight-average molecular weight M_w = 5400. Partial epoxidation of the 1,4-units led to a random distribution of coupling sites along the chains. The linear substrate was then subjected to a grafting reaction with living polyisoprene chains to yield a comb-like arborescent polyisoprene G0 (Figure 2-14).[53]

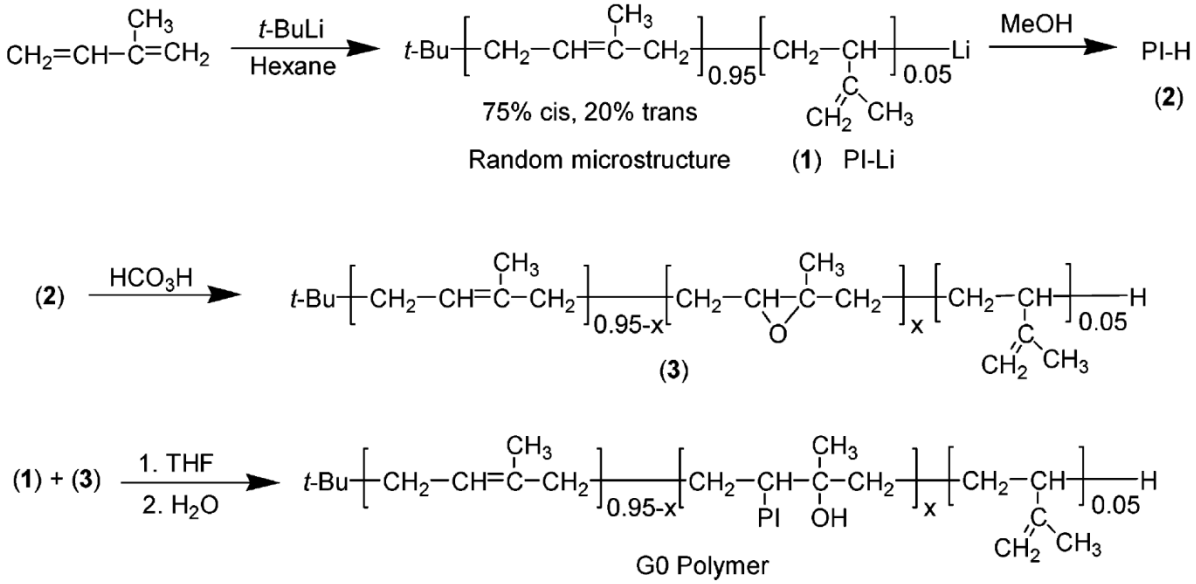


Figure 2-14. Synthesis of comb-like arborescent G0 PIP.[53]

The functionalization and grafting cycles were repeated to obtain arborescent polymers of generations G1 and G2. Unfortunately the synthesis of G3 arborescent molecules failed, possibly due to the observed poor solubility of the G2 substrate in the reaction medium.[53] The molecular weight of the polyisoprene side-chains used in the synthesis of the different generations was maintained around 5000, and is comparable to the current investigation, as is the grafting technique using epoxide functionalities.

Information on the grafting yield was collected for each generation, by removing sample aliquots for analysis as a function of time in the grafting reaction. The conditions used in terms of temperature and coupling site:living end ratio were also optimized to maximize the grafting yield.[53] Several additives were also investigated as reactivity modifiers to

increase the grafting yield. This included *N,N,N',N'*-tetramethylethylenediamine (TMEDA), BF_3, Me_3Al, LiCl, and LiBr under different conditions. The influence of solvent polarity was examined by introducing tetrahydrofuran (THF) in the reactions. These parameters are of particular interest for the current investigation, as their influence will also be examined in the synthesis of arborescent polybutadiene from epoxidized substrates. Consequently they are outlined in greater detail here, as they will be useful for the discussion of the results obtained. Lithium salts had the most significant influence among the different additives investigated. While both the chloride and bromide salts were effective, LiBr rather than LiCl was preferred as a reactivity modifier in the synthesis of the G0-G3 polymers. This choice was mainly based on the greater solubility of the bromide salt as compared to the chloride in the reaction medium, however.[53]

2.6.6 Dendrigraft Star-comb Polybutadiene

This study, most directly related to the current investigation, was published in 2009 by Zhang et al.[54] It used living anionic polymerization techniques in combination with a "grafting onto" method to synthesize so-called star-comb polymers, in a generation-based approach completely analogous to the arborescent polyisoprene syntheses (Figure 2-15). The synthesis started from a 4-arm star-like polymer substrate (identified as generation G0), functionalized by epoxidation to provide coupling sites, and grafted with living polybutadienyllithium side-chains to produce a G1 star-comb polymer. Repetition of the functionalization and grafting cycles resulted in generational growth (G2 – G4).[54]

The synthesis of star-comb polybutadiene started with the living anionic polymerization of butadiene initiated by *n*-butyllithium in cyclohexane, to produce a high content of 1,4-butadiene units. The 4-arm star-like polymer (G0) was obtained by adding $SiCl_4$ as a coupling agent for the polybutadienyllithium chains. The 1,4-units of the

polybutadiene side-chains were then partially epoxidized to serve as substrate in the subsequent grafting reaction. This epoxidation is therefore characterized by a random distribution of coupling sites along the substrate, in analogy to the other arborescent polymer syntheses. A dendrigraft star-comb polymer (G1) was obtained by further coupling polybutadienyllithium with the functionalized G0 substrate (Figure 2-16).

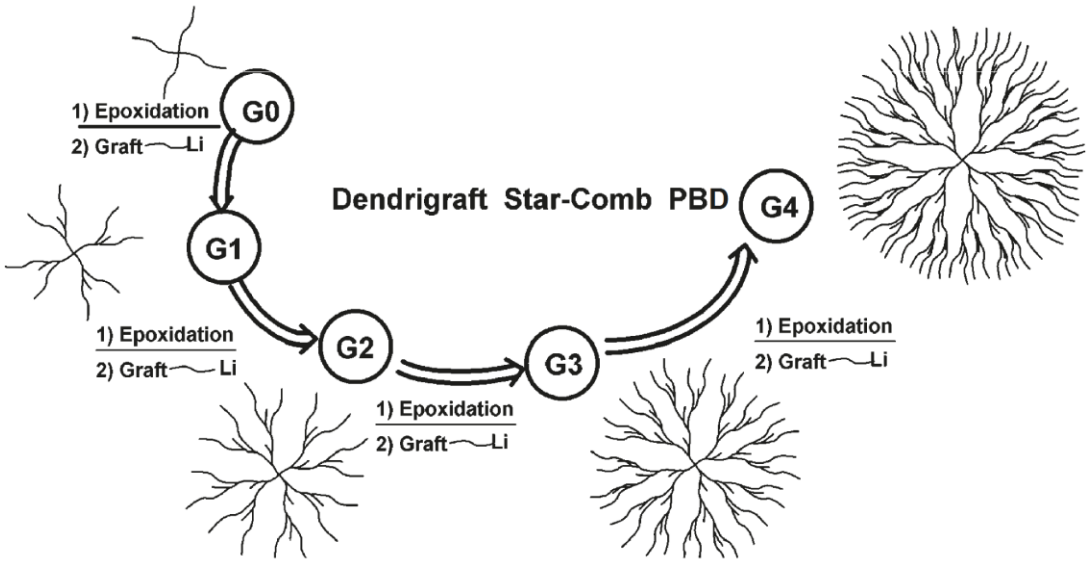


Figure 2-15. Generational growth in the synthesis of dendrigraft star-comb PBD.[54]

While the synthesis of dendrigraft star-comb polybutadienes of generations G0-G4 was reported, grafting yield data (66%) were only documented for the G1 polymer. Grafting yield information is therefore missing for all the other generations. Furthermore, the polybutadiene side-chains used in the reactions had a low molecular weight (M_n = 3000). The synthesis of such short polybutadiene chains is quite unchallenging, and grafting reactions typically proceed in high yield for such short chains. Yet the grafting yield achieved under these conditions was disappointingly low. It therefore appears that the conditions reported for these grafting reactions were far from optimal. These represent the main problems identified,

which we would like to address in a systematic fashion in the current investigation, by optimizing different parameters in the coupling reaction, and using side-chains with a higher molecular weight (M_n = 5000), comparable to the side-chains used in previous arborescent copolymer syntheses in our research group.

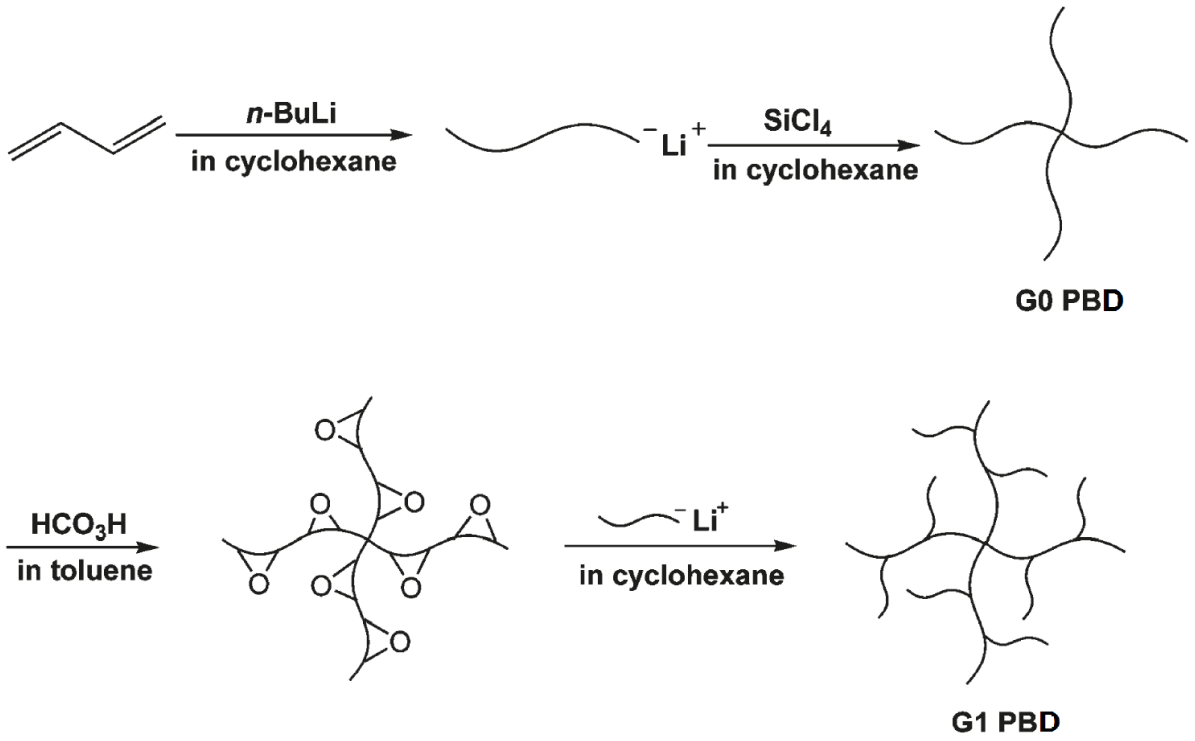


Figure 2-16. Synthetic scheme for dendrigraft star-comb PBD.[54]

2.7 Summary

The last two examples on the synthesis of arborescent polyisoprene and polybutadiene using epoxide coupling sites are directly related to the current project. Based on the information available, conditions providing the highest grafting yield will be determined and applied to the synthesis of arborescent polybutadiene. Thus LiBr was found to improve the grafting yield when used at a 6:1 ratio with respect to the living ends. The influence of

TMEDA, at a 6:1 molar ratio with respect to the living ends, was also examined. Based on the available literature, a substrate epoxidation level around 25% appears useful. These are some of the parameters that will be examined in the current study.

Chapter 3 Objectives

3.1 Overview

This project focused on the synthesis of arborescent polybutadiene by anionic polymerization and grafting. The grafting substrates were obtained by epoxidation of polybutadiene samples with a high 1,4-microstructure content. The conditions were adjusted to optimize the grafting reaction, first for the synthesis of the G0 polymer, and then for subsequent generations (G1 and G2) of arborescent polybutadiene. Key parameters such as the grafting yield (fraction of side-chains becoming attached to the substrate), and the molecular weight of the products were used to quantify the success of the coupling reaction. To that end, four specific topics had to be considered:

1- Synthesis of arborescent polybutadiene in cyclohexane according to a procedure reported in the literature,[54] through epoxidation and anionic grafting in cyclohexane.
2- Synthesis of the graft polymers in a mixed solvent system (cyclohexane-tetrahydrofuran) for comparison.
3- Investigation of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) as a reactivity modifier to increase the grafting yield.
4- Investigation of lithium bromide (LiBr) as a reactivity modifier to increase the grafting yield.

To provide a basis for comparison, all the grafting reactions were initially performed with a 1:1 molar ratio of living side-chains to coupling sites. Additionally, the influence of reaction time on the grafting yield was considered. This was achieved by monitoring the grafting yield attained in the reaction after one day and after one week. The optimized reaction conditions were then used to synthesize arborescent polymer samples of generations G1 and G2. Subsequently, the grafting reaction was examined further under modified conditions with an excess of coupling sites for each generation. The amount of excess

substrate used was determined in each case based on the yield obtained for the 1:1 grafting stoichiometry.

3.2 Linear Polybutadiene

The anionic polymerization technique was applied to the synthesis of linear polybutadiene serving as substrate for the preparation of the G0 polymer, as well as for the living side-chains used in the grafting reactions. In all cases the polymer chains had a target M_n of 5000, and the polymerization was performed in cyclohexane. Figure 3-1 describes the polymerization of 1,3-butadiene initiated by *sec*-butyllithium and terminated with acidified degassed methanol.

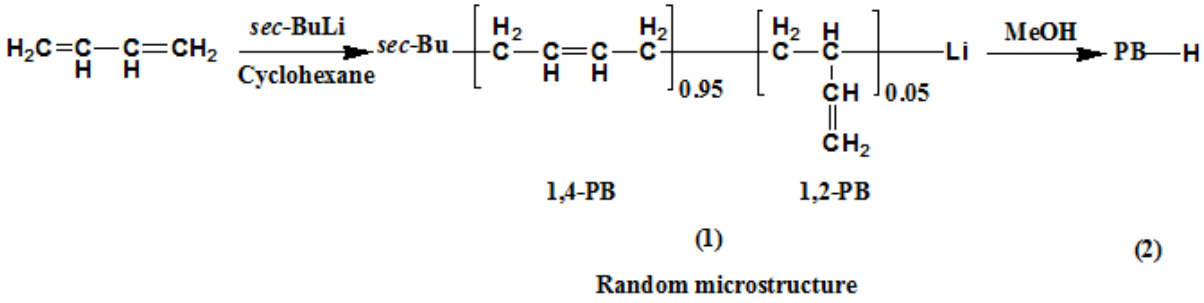


Figure 3-1. Synthesis of linear polybutadiene.

3.3 Polybutadiene Functionalization

Linear polybutadiene was functionalized to serve as substrate in the G0 polymer synthesis. Partial epoxidation was performed on the 1,4-butadiene structural units of the polymer, known to be more reactive than the 1,2-units in this reaction (Figure 3-2). The epoxide groups served as coupling sites for the grafting reaction. This functionalization reaction was also performed on the G0 and G1 arborescent polybutadiene substrates.

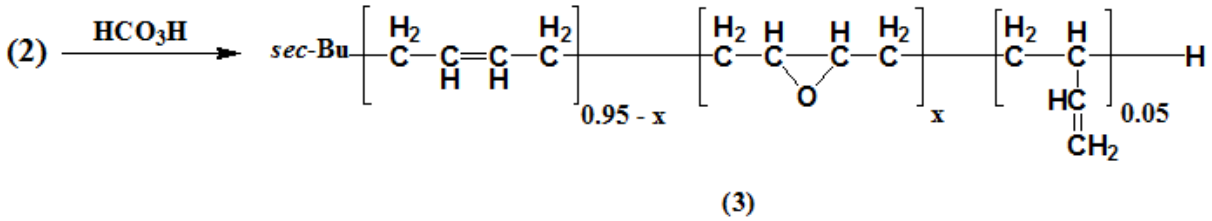


Figure 3-2. Epoxidation of linear polybutadiene.

3.4 Grafting reaction

The epoxidized linear polybutadiene substrate was used in the synthesis of the G0 polymer. The epoxidized G0 polymer likewise served as substrate for the G1 polymer synthesis, which was itself epoxidized to serve in the G2 polymer synthesis. In the grafting reaction, the living polybutadienyllithium chains attack the epoxide groups on the substrate. Consequently, each coupling reaction ultimately produces one hydroxyl (–OH) group. The grafting reaction illustrated in Figure 3-3 is shown as being carried out in cyclohexane and terminated with degassed acidic methanol, however as discussed below, tetrahydrofuran was also used as a co-solvent in most cases to promote the grafting reaction.

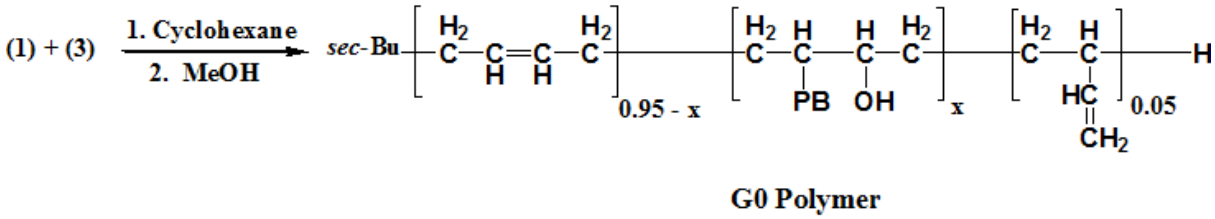


Figure 3-3. Grafting reaction for the synthesis of G0 arborescent polybutadiene.

3.5 Optimization of Grafting Reaction

As mentioned in Section 3.1, four variations of the grafting procedure were investigated and optimized, mainly for the synthesis of G0 polybutadiene. The G1 and G2 polymers were then synthesized based on the method producing the highest grafting yield in the G0 polymer

synthesis. Moreover, the optimal procedure was re-examined for the synthesis of G0, G1, and G2 polymers with an excess of substrate. Details on the four main procedures follow.

3.5.1 Synthesis of Arborescent Polybutadiene in Cyclohexane

Cyclohexane is a non-polar solvent yielding mainly a 1,4-polybutadiene chain microstructure. More detailed information on these reactions is needed beyond the data provided in Reference 54, since it serves as baseline for the modified conditions to be investigated.

3.5.2 Synthesis of Arborescent Polybutadiene in Cyclohexane/THF

Changing the polarity of the solvent used in the grafting reaction can have different effects. Anionic grafting in polar solvents typically proceeds in higher yield and at a faster rate than in non-polar solvents such as cyclohexane.[55] This is partly due to increased reactivity of the macroanions in the presence of solvents such as tetrahydrofuran (THF), since the lithium counterion is more efficiently solvated by polar solvents[56,57] (Figure 3-4). However living polybutadienyllithium is also subject to termination reactions in the presence of THF. Consequently, it remained to be determined whether the presence of THF in the grafting reaction would ultimately lead to an increase or a decrease in grafting yield. Another effect of THF is its influence on the microstructure of the polybutadiene chains: A predominantly 1,4-microstructure is obtained when 1,3-butadiene is polymerized in non-polar solvents such as cyclohexane, while a mixed microstructure with 1,2- and 1,4-butadiene units results in the presence of THF. Since the goal of the project was to generate graft polymers with a predominantly 1,4-microstructure, THF was only added in the grafting step of the procedure.

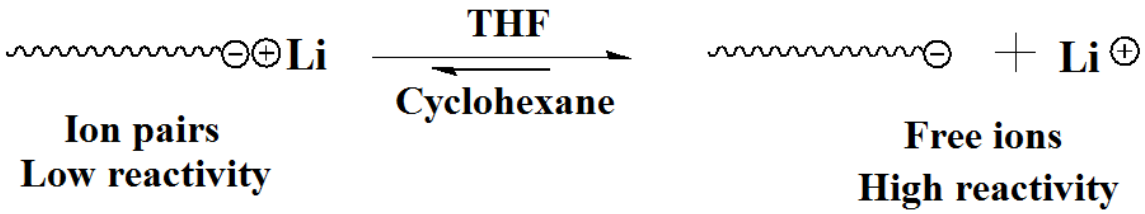


Figure 3-4. Ion pair–free ion equilibrium in solvents of different polarities.

3.5.3 Synthesis of Arborescent Polybutadiene with TMEDA

In this case the grafting reactions were performed in cyclohexane, but in the presence of TMEDA as a complexing agent for the counterions of the living polybutadienyllithium chains. This additive is known to be an efficient complexing agent for lithium cations. This should increase the reactivity (nucleophilicity) of the polybutadienyl macroanions similarly to THF, but without causing termination of the living chains (Figure 3-5).[58]

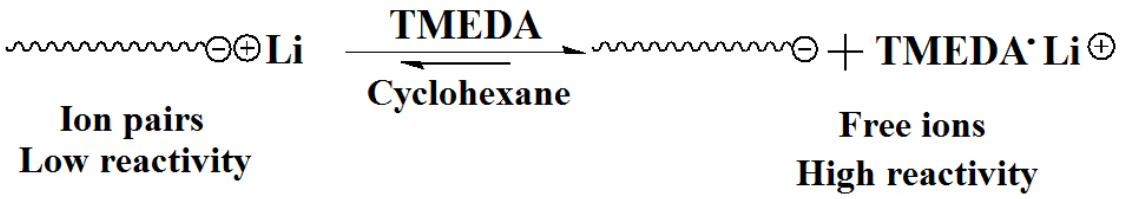


Figure 3-5. Ion pair – free ion equilibrium in the presence of TMEDA.

3.5.4 Synthesis of Arborescent Polybutadiene with LiBr

Certain salts such as LiBr have been shown to increase the grafting yield in the synthesis of arborescent polyisoprene when grafting polyisoprenyllithium side-chains onto epoxidized polyisoprene substrates. The increased yield was explained by the weak Lewis acid character of these salts, able to coordinate with the epoxide groups to increase their polarization and reactivity (Figure 3-6).[53]

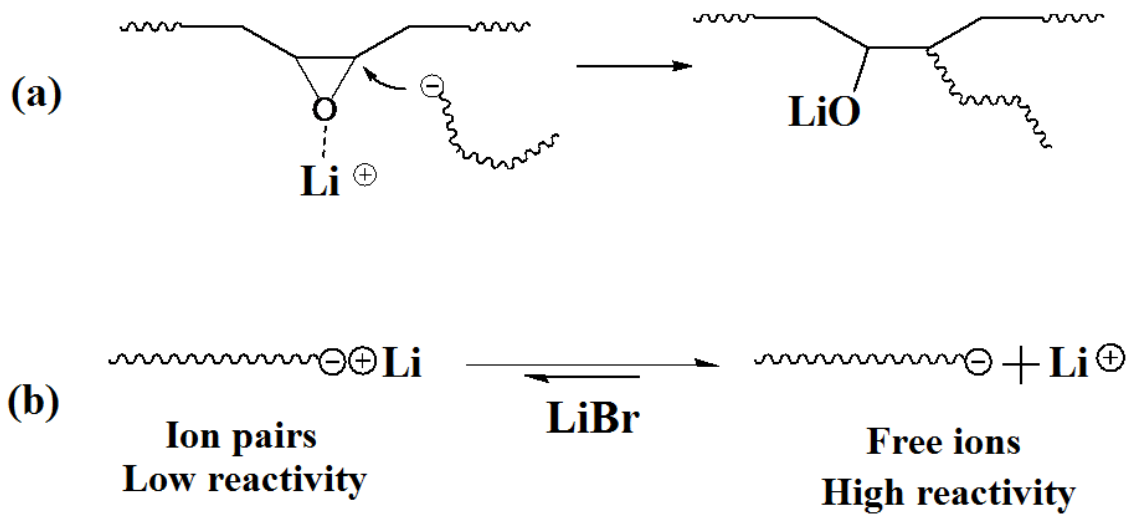


Figure 3-6. Influence of LiBr on (a) reactivity of epoxide groups, (b) ion pair–free ion equilibrium.

Chapter 4 Experimental Procedures

In this chapter the reagent purification, polymerization, and grafting procedures are described in detail. Throughout the project, some of the procedures used were modified as a consequence of the optimization process. For the sake of conciseness, each of the procedures used will be presented in their simplest form by avoiding the repetitive description of identical steps.

4.1 Reagent Purification

Anionic polymerization is highly sensitive to impurities such as moisture and oxygen. Consequently special purification techniques have been developed for the solvents, monomers, polymer substrates, and other additives prior to the reactions. All the glassware such as the ampoules, vacuum manifolds, and reactors were cleaned, and then dried in an oven at 120 ^{o}C overnight. The glassware was mounted on a high-vacuum line (Figure 4-1), evacuated, and flamed to remove moisture adsorbed on its surface, and purified nitrogen gas was used to purge all the glassware prior to the reactions.

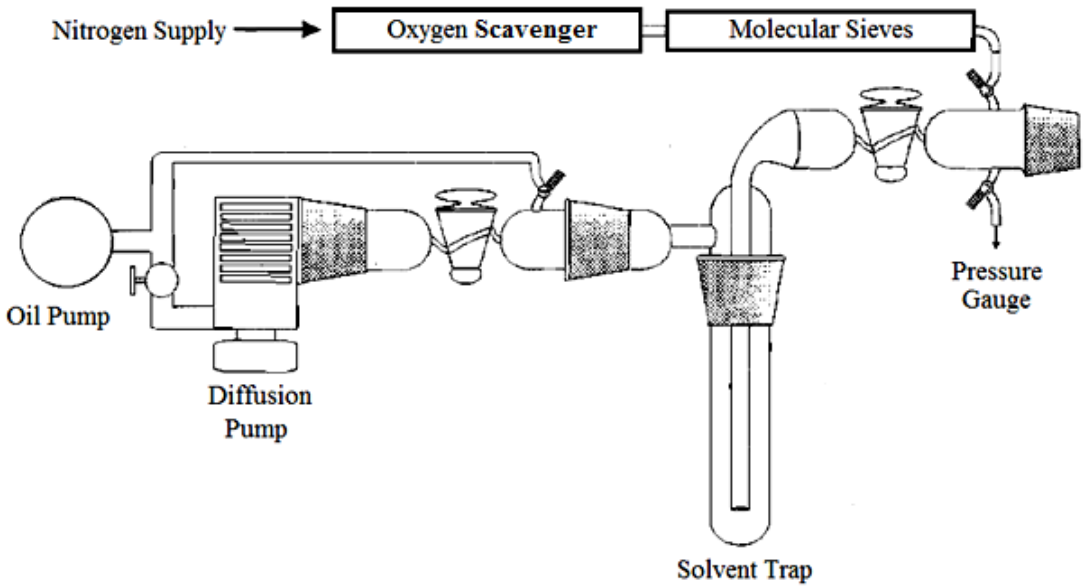


Figure 4-1. Vacuum line.[59]

Cyclohexane (BDH, HPLC grade) was purified over oligostyryllithium, generated *in situ* by adding styrene (6 mL) and *n*-butyllithium (*n*-BuLi, Aldrich, 2.5 M in hexane, 12 mL), and refluxing under nitrogen in the apparatus shown in Figure 4-2. The solvent was then collected by distillation and introduced directly into the polymerization reactor or the ampoule preparation manifolds through polytetrafluoroethylene (PTFE) tubing. Tetrahydrofuran (THF; Caledon, reagent grade) was purified using the same apparatus, by refluxing over sodium-benzophenone ketyl generated *in situ* from sodium metal (5 g) and benzophenone (Aldrich, 20 g) under dry nitrogen atmosphere.

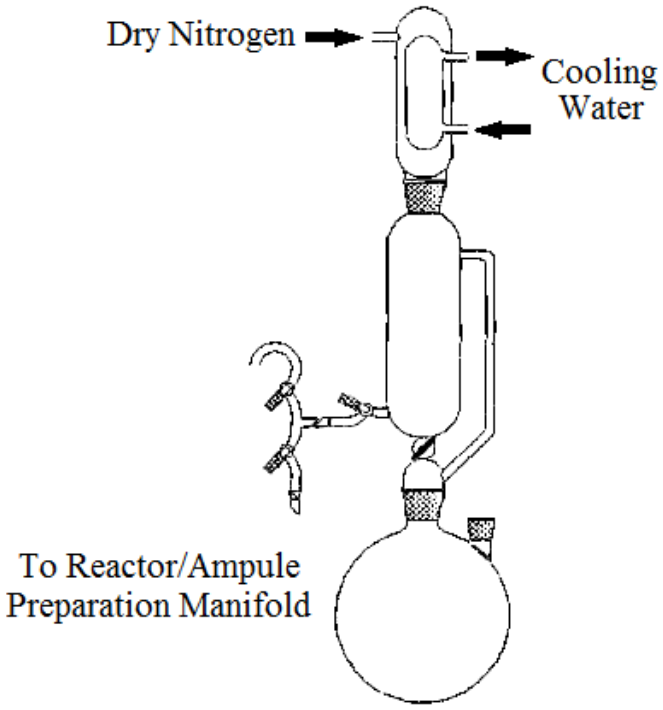


Figure 4-2. Apparatus for solvent distillation.[59]

N,N,N',N'-Tetramethylethylenediamine (TMEDA, 100 mL) was first purified by stirring with calcium hydride (~5 g) overnight, followed by distillation under nitrogen atmosphere. In a final purification step completed immediately before the grafting reaction, the TMEDA was diluted with dry cyclohexane (10 mL) in the round-bottomed flask of the

high-vacuum manifold shown in Figure 4-3, titrated with *tert*-butyllithium (*tert*-BuLi, Aldrich, 1.7 M in heptane) to a light yellow coloration, subjected to three freezing–evacuation–thawing cycles, and recondensed to the ampoule which was then filled with nitrogen for storage.

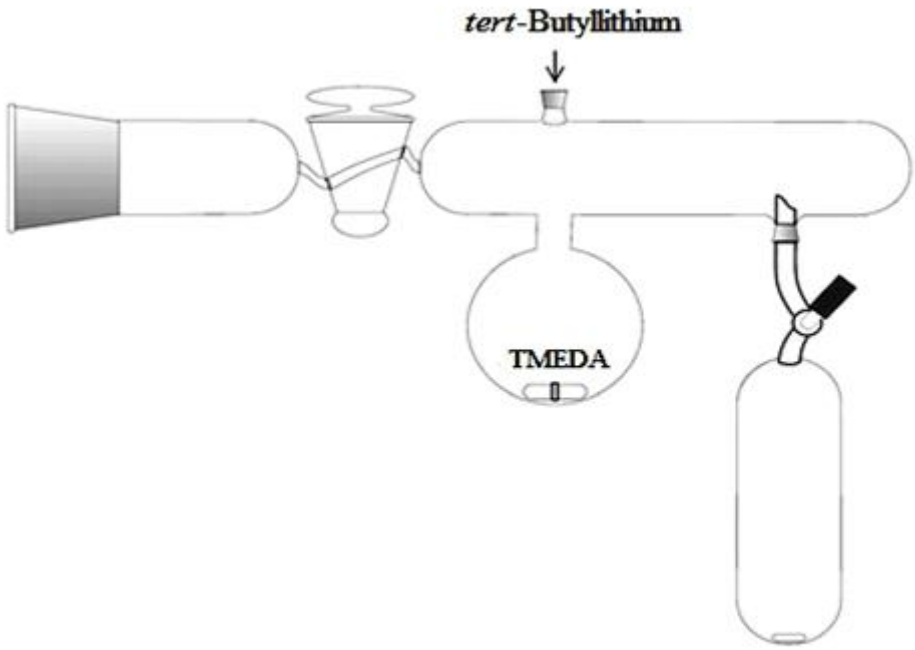


Figure 4-3. Apparatus for TMEDA purification.

1,3-Butadiene monomer (Praxair, 99 %) was purified using the high-vacuum manifold shown in Figure 4-4. **Warning:** Butadiene is a known carcinogen[60] and should be handled with great care in an efficient fume hood. The monomer was first condensed in the calibrated ampoule A immersed in liquid nitrogen, and *n*-BuLi (2.5 M in hexane, 1 mL per 10 g monomer) was added to flask C before applying vacuum for 30 min to remove the solvent. The monomer was then recondensed to flask C, stirred for 30 min at -10 ^{o}C (dry ice/2-propanol bath), and then subjected to three freezing–evacuation–thawing cycles before recondensation to the thick-wall ampoule B. The butadiene monomer was then diluted 1:1

with cyclohexane, filled with nitrogen, and stored over dry ice until used. In an alternate procedure, ampoule B was also used as a polymerization reactor to minimize contamination of the reaction.

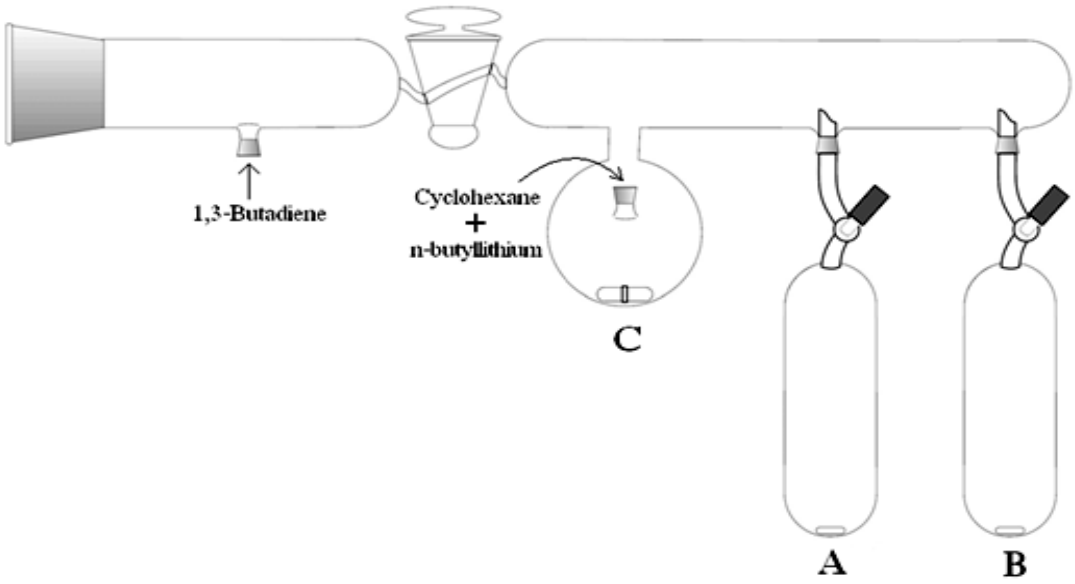


Figure 4-4. Apparatus for monomer purification.

The epoxidized polybutadiene samples serving as grafting substrates were purified by azeotropic drying using the apparatus shown in Figure 4-5. To this end the epoxidized polymer was loaded in the ampoule, the manifold was evacuated, and cyclohexane was condensed to the ampoule from the middle flask. The waste cyclohexane was then redistilled to the flask on the left. The azeotropic distillation procedure was repeated three times before dissolving the polymer in ca. 20 mL of dry cyclohexane and filling the ampoule with nitrogen. In an alternate procedure, the grafting substrate was purified using dry THF instead of cyclohexane. The additive LiBr was also purified by azeotropic drying using THF. In that case LiBr was loaded to the ampoule before mounting the system on the vacuum line. After evacuation, the ampoule was flamed to remove any moisture present in the LiBr. Three

cycles of azeotropic drying were then applied using THF. When LiBr was used in a cyclohexane:THF mixture, the epoxidized grafting substrate and LiBr were subjected to three cycles of azeotropic drying separately. The purified substrate was then dissolved in THF, transferred to the purified LiBr ampoule, and the mixture was subjected to one additional cycle of azeotropic drying. The substrate and LiBr were finally dissolved in THF and the ampoule was filled with nitrogen.

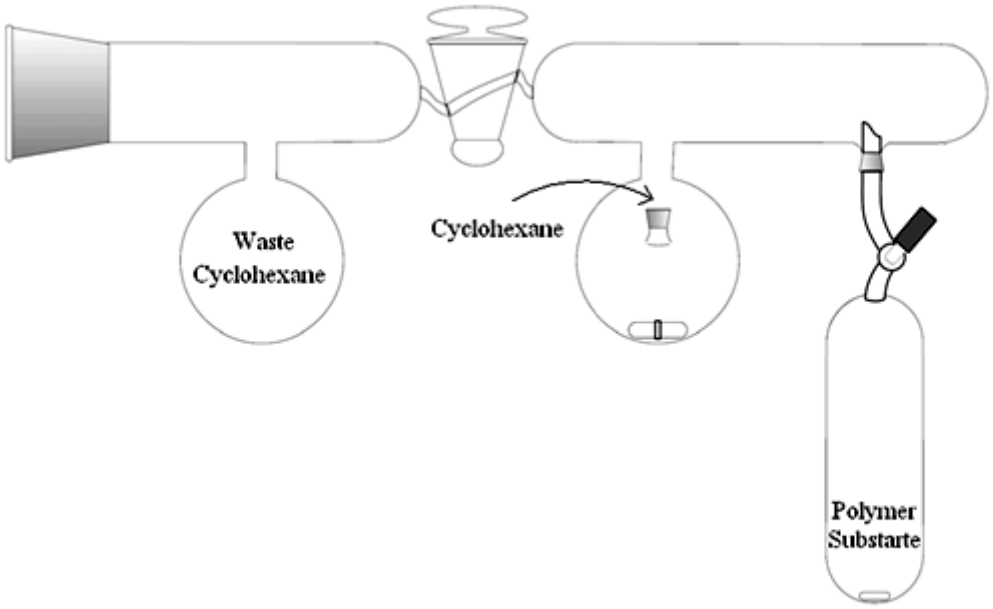


Figure 4-5. Apparatus for azeotropic purification of the grafting substrate.

The *sec*-butyllithium solution (*sec*-BuLi, Aldrich, 1.4 M in cyclohexane) serving as initiator for the polymerization reactions had to be titrated, as it is crucial to determine the exact amount needed for a specific target polybutadiene molecular weight. The titration method used was reported in the literature.[61] A 25 mL dry three-neck flask with a magnetic stirring bar was mounted on the vacuum line together with the dry THF inlet and a rubber septum, evacuated, and flamed. After purging the flask with nitrogen, 200 mg of *N*-

benzylbenzamide were loaded against nitrogen flow and dissolved in dry THF (10 mL). The solution was cooled to -40 ^{o}C in a dry ice/2-propanol bath. The *sec*-BuLi solution was added via syringe drop-wise to the benzamide solution until a persistent light blue color was reached, corresponding to the endpoint. As a confirmation, one extra drop of *sec*-BuLi led to an intense ink-blue color. The *sec*-BuLi solution concentration calculation was based on the volume added when the light blue color appeared.

4.2 Synthesis of Linear 1,4-Polybutadiene

Procedure L1: The polymerization reactor shown in Figure 4-6 was mounted on the high-vacuum line together with the dry cyclohexane inlet from the purification still, a purified monomer ampoule (25 g butadiene in 250 mL cyclohexane), and a rubber septum. The reactor was evacuated and flamed, filled with nitrogen, and 200 mL of dry cyclohexane were added. A solution of 2,2′-bipyridyl in cyclohexane (Aldrich, 99+%, 0.1 M, 0.5 mL) was prepared and added through the septum, and the solvent was titrated with *sec*-BuLi (Aldrich, 1.4 M in cyclohexane) to a stable reddish color. After 15 min the required amount of *sec*-BuLi initiator (3.5 mL, for a target M_n = 5000) was added, followed by the butadiene monomer. The reaction was allowed to proceed under nitrogen atmosphere for 24 h and terminated with degassed methanol acidified with HCl. The polybutadiene sample was recovered by evaporation to dryness inside a fume hood (to avoid potential exposure to residual butadiene monomer), dissolution in THF (40 mL), and precipitation by slow addition in ca. 400 mL of methanol with stirring. The polymer was dried under vacuum overnight, and analyzed by ^{1}H NMR spectroscopy and size exclusion chromatography (SEC). The sample was stored as a 50% cyclohexane solution in a freezer at -80 ^{o}C.[53]

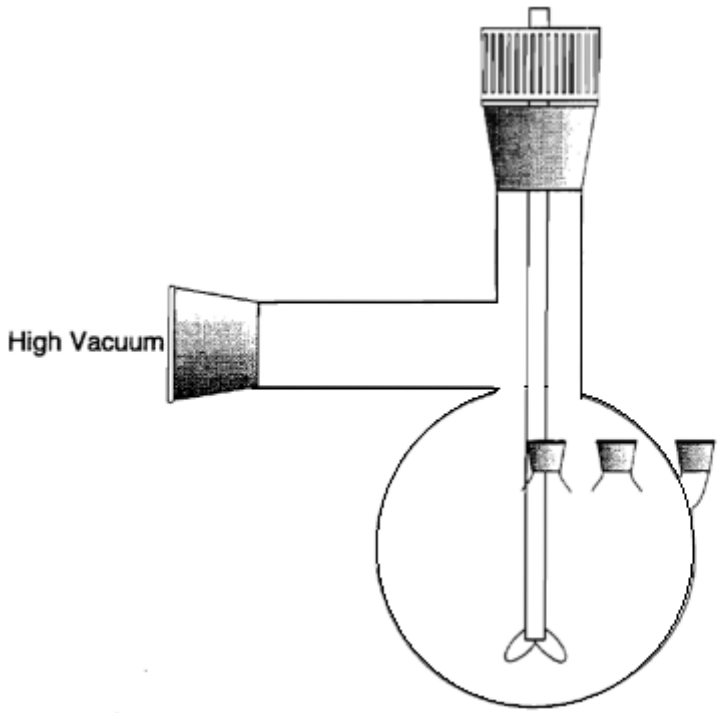


Figure 4-6. Anionic polymerization and grafting reactor.[59]

Procedure L2: In a different procedure, a double thickness wall ampoule (~1 L volume) served as polymerization reactor. In the last step of monomer purification, the purified monomer (10 g) was recondensed in the ampoule followed by dry cyclohexane (100 mL). In this procedure, the *sec*-BuLi initiator (1.4 mL, for a target M_n = 5000) was directly added to the monomer solution through the stopcock of the ampoule while purging with nitrogen. The solvent titration procedure with 2,2′-bipyridyl used in the previous procedure was skipped in this case, however. The ampoule was sealed and the polymerization was allowed to proceed for 24 h. Degassed acidified methanol was added through the stopcock opening to terminate the reaction. The product was recovered and analyzed as in procedure L1.

4.3 Epoxidation of Polybutadiene

Procedure E1: The grafting substrate was prepared by functionalization of the linear polybutadiene sample with epoxide groups using procedures adapted from the literature.[53]

Polybutadiene (5 g, 85.9 meq butadiene units) was dissolved in toluene (50 mL), and formic acid (1.5 mL) was added. Hydrogen peroxide (5.25 mL) was then added drop-wise with stirring over 15 min at 40 ^{o}C. The reaction was continued for 3 h at 40 ^{o}C with stirring, and the organic phase was collected and washed with distilled water until it reached pH 7. The product was recovered by evaporation to dryness, dissolution in THF (~100 mL), precipitation in methanol (~1 L), filtration, and drying under vacuum. The product was characterized by ^{1}H NMR spectroscopy and SEC analysis. The epoxidized polybutadiene substrate was further purified by the azeotropic drying procedure described in Section 4.1 before the grafting reaction.

Procedure E2: A sample of linear polybutadiene (5 g, 85.9 meq butadiene units) was dissolved in dichloromethane (100 mL) and epoxidized by adding *m*-chloroperoxybenzoic acid (*m*-CPBA, Aldrich, 77% max purity, 4.8 g, 21.4 mmol).[61] The flask was purged with nitrogen and the reaction was stirred for 3 h at 0 ^{o}C. The solution was collected, washed with an aqueous 1% NaOH solution (400 mL) once, and multiple times with distilled water (400 mL) until the aqueous phase became neutral. The polymer was precipitated in methanol, then purified again by dissolution in THF (~100 mL) and precipitation in methanol. The epoxidized polymer was collected by filtration and dried under vacuum, and analyzed by ^{1}H NMR spectroscopy and SEC. This epoxidized linear polymer served as substrate for the G0 polymer syntheses.[62]

The G0 polymer was likewise epoxidized, to serve as substrate for the G1 polymer synthesis, according to Procedure E2. In this case the G0 polybutadiene sample (3.3 g, 59.7 meq butadiene units) and *m*-CPBA (3.3 g, 14.9 mmol, 77%) were reacted in dichloromethane (68 mL) under the same conditions discussed previously. Epoxidation of the G1 polymer was also performed according to Procedure E2, with the polymer (2.6 g, 47 meq butadiene units) and *m*-CPBA (2.5 g, 11.2 mmol) dissolved in 60 mL of dichloromethane.[62]

4.4 Grafting Reaction

The experimental procedures described below refer to the synthesis of a G0 arborescent polybutadiene sample. This was investigated using eight different reaction conditions, four of which were carried out in the polymerization reactor of Figure 4-6, while the same reactions were also repeated in an ampoule reactor. Only the optimal procedures were applied to the synthesis of the higher generation G1 and G2 polymers. After each grafting reaction the crude arborescent polybutadiene samples were recovered by the same method described for the linear polymer, but they were also further purified to remove the linear polybutadiene contaminant from the graft polymer.[53] This was achieved by precipitation fractionation from mixtures of 2-propanol and hexane. While these two solvents are miscible, the less soluble graft polymer can be selectively precipitated while leaving the linear chains dissolved. After repetition of this purification step twice, the graft polymer was recovered and analyzed by SEC and ^{1}H NMR spectroscopy.

4.4.1 Synthesis of G0 Polybutadiene

The following polymerization reactions were all performed in the reactor flask. Each procedure represents a different grafting technique, while the side-chains were always synthesized by the same method, namely the polymerization of butadiene (20 g, 370 mmol), initiated by *sec*-BuLi (2.8 mL, target M_n = 5000) in 200 mL of cyclohexane. This corresponds to the method described for the preparation of linear polybutadiene (Procedure L1), without chain termination.

Procedure 1-1: A sample of the side-chains was removed and terminated with acidified methanol for characterization (M_n = 5200, PDI = 1.06). The epoxidized substrate (0.87 g in 10 mL of cyclohexane, 25 mol% epoxidation level, 3.7 meq epoxidized butadiene units, corresponding to a 1:1 molar ratio of epoxide groups vs. living ends) was added to the living

polybutadienyllithium after 24 h of polymerization. The grafting reaction was allowed to proceed overnight and then terminated with degassed acidified methanol.

Procedure 2-1: Characterization of a sample of the side-chains yielded M_n = 5400 and a PDI = 1.07. After 24 h of polymerization, the substrate and TMEDA (3.41 mL in 10 mL of cyclohexane, molar ratio 6:1 TMEDA vs. living ends) were added, and the reaction was allowed to proceed overnight. The reaction was then terminated with degassed acidified methanol.

Procedure 3-1: The side-chain sample removed prior to the grafting reaction had M_n = 5100 and a PDI= 1.07. In this procedure the substrate was purified with THF through azeotropic drying, and redissolved in 66 mL of THF (corresponding to a 1:3 ratio of THF:cyclohexane in the grafting reaction). After the side-chain polymerization was completed, the substrate was added and the grafting reaction was allowed to proceed overnight. The reaction was then terminated with degassed acidified methanol.

Procedure 4-1: The side-chain sample had M_n = 5100 and a PDI = 1.06. The substrate was purified as described in Procedure 3-1. LiBr (2.08 g, 6:1 ratio LiBr:living ends) was also subjected to three cycles of azeotropic drying using THF. The purified substrate was then transferred, via syringe, to the purified LiBr solution, and the mixture was subjected to a further cycle of azeotropic drying with THF. The mixture was finally redissolved in 66 mL of THF (corresponding to a 1:3 ratio of THF:cyclohexane in the grafting reaction) and added to the living polymer. The grafting reaction was allowed to proceed overnight and terminated with degassed acidified methanol.

In the previous procedures, longer (one week) reaction times were not investigated, due to the gradual disappearance of the color of the living polymer solution. In the following (alternate) procedures, however, all the polymerization and grafting reactions were performed

in sealed ampoules, which provided a cleaner environment for the reactions. This allowed extension of the grafting reaction to one week.

4.4.2 Synthesis of G0 Polybutadiene: Alternate Procedures

The alternate procedures were mainly based on performing the reactions in sealed ampoules. In this case the living polybutadienyllithium serving as side-chains was prepared according to the method described in Procedure L2, without the termination step. Butadiene monomer was collected (12.8 g, 237 mmol) and purified with 1 mL of *n*-BuLi 2.5 M solution. The solvent (cyclohexane, 130 mL) was recondensed directly to the ampoule through the vacuum manifold. After purging with nitrogen, the initiator (1.8 mL *sec*-BuLi, 2.52 mmol) was added against nitrogen flow via syringe after removing the stopcock of the ampoule, which was then sealed again. The reaction was allowed to proceed for 24 h and a sample was removed, terminated, and characterized by SEC to insure that the desired molecular weight was attained, without terminating the rest of the reaction. In the alternate procedures, the grafting reaction was allowed to proceed for up to one week but a sample was also removed after 24 h, terminated, and analyzed.

Procedure 1-2: Side-chain characterization yielded M_n = 5000 and a PDI= 1.04. The substrate (0.58 g, 25 mol% substitution level, 2.49 meq epoxide groups, 1:1 molar ratio of coupling sites to living ends) was purified by azeotropic drying with cyclohexane, redissolved in 50 mL of cyclohexane, and transferred against nitrogen flow to the ampoule containing the living polymer solution via syringe. After one week the reaction was terminated with degassed acidified methanol.

Procedure 2-2: The side-chains synthesized had M_n = 5100 and a PDI = 1.04. The substrate (0.57 g, 25 mol% substitution level, 2.45 meq epoxide groups, 1:1 molar ratio of coupling sites to living ends) was purified and redissolved in cyclohexane (50 mL), and TMEDA (2.18

mL, 6:1 molar ratio of TMEDA with living ends) was titrated and stored in a separate ampoule as outlined in Section 4.1. After the side-chain polymerization was completed, the substrate and TMEDA solutions were transferred from their respective ampoules to the ampoule containing polybutadienyllithium via syringe. The grafting reaction was allowed to proceed for up to one week before termination.

Procedure 3-2: The side-chains had M_n = 5200 and a PDI= 1.03. The substrate was purified azeotropically with THF and redissolved in 45 mL of THF (1:3 ratio of THF:cyclohexane in the grafting reaction). Upon completion of the side-chain polymerization, the substrate was transferred to the ampoule via syringe. The grafting reaction was terminated with degassed acidified methanol after one week.

Procedure 4-2: The side-chains had M_n = 5400 and a PDI = 1.03. As in Procedure 3-2, ampoules were prepared in THF for the substrate (0.56 g, 25 mol% substitution level, 2.4 meq epoxide groups, 1:1 molar ratio of coupling sites to living ends) and LiBr (1.3 g, 6:1 ratio LiBr:living ends). The purified substrate solution was transferred to the purified LiBr ampoule, and the mixture was subjected to one additional cycle of azeotropic drying before redissolution in 45 mL of THF and transfer to the living polymer solution. The grafting reaction was allowed to proceed for up to one week and terminated with degassed acidified methanol.

All the reactions described so far concerned the synthesis of comb-like (G0) polybutadiene with a 1:1 molar ratio of living ends to coupling sites. However, the method reported in Procedure 4-2 was also further investigated using 17% excess of substrate in the reaction. The rationale for this ratio lies in the grafting yield obtained in the unmodified Procedure 4-2, amounting to 85%. A 17% excess (1/0.85 = 1.17) of substrate could therefore potentially lead to full consumption of the living polymer in the grafting reaction, or 100%

grafting yield. In this case side-chains were prepared with M_n = 5100 and a PDI= 1.03. The substrate (0.69 g, 1:1.17 molar ratio of living ends to coupling sites) and LiBr were purified, diluted and introduced as explained in Procedure 4-2, and the grafting reaction was carried out and terminated as by the same method.

4.5 Synthesis of G1 and G2 Arborescent Polybutadiene

The synthesis of G1 and G2 arborescent polybutadiene was first carried out according to Procedure 4-2, using a 1:1 molar ratio of living ends to coupling sites. An excess of coupling sites was also used in a second series of reactions, in analogy to the G0 polymers. Living polybutadienyllithium was prepared according to Procedure L2 without termination from butadiene (19.2 g, 355 mmol) purified with *n*-BuLi (2 mL), diluted with 200 mL of cyclohexane, and initiated with 2.7 mL (3.78 mmol) of *sec*-BuLi. The polymerization time was 24 h, and a sample was removed for termination and analysis. A sample was also removed one day after the beginning of the grafting reaction, which was terminated after one week.

4.5.1 Arborescent G1 Polybutadiene

The side-chains had M_n = 5400 and a PDI = 1.03. The G0 epoxidized substrate (0.84 g, 26 mol% epoxidation level, 3.9 meq epoxide groups, 1:1 molar ratio of living ends to epoxide groups) was purified by azeotropic drying with THF. LiBr (2 g) was also subjected to azeotropic drying and redissolution in THF. The purified substrate was transferred to the LiBr ampoule and the mixture was subjected to an additional cycle of azeotropic drying before redissolution in ~ 66 mL of THF. After the preparation of polybutadienyllithium, the purified mixture in THF was transferred to the living polymer solution.

In a separate reaction, living polybutadiene was prepared with M_n = 5300 and a PDI = 1.03. LiBr (2 g) and epoxidized G0 (1.05 g, 26 mol% epoxidation level, 4.8 meq epoxide

groups, 1:1.17 molar ratio of living ends to epoxide) were purified and introduced as explained previously. A sample was removed after 24 h and the reaction was terminated with degassed methanol/HCl after one week.

4.5.2 Arborescent G2 Polybutadiene

The side-chains used had M_n = 5100 and a PDI = 1.04. The epoxidized G1 substrate (0.9 g, 24 mol% epoxidation level, 3.7 meq epoxide groups, 1:1 molar ratio living ends to epoxide) and LiBr (2 g) were purified and introduced according to Procedure 4-2. In another grafting reaction, side-chains with M_n = 5400 and a PDI = 1.03 were used. An ampoule containing LiBr (2 g) and the substrate (1.15 g, 24 mol% epoxidation level, 4.8 meq epoxide groups, 1:1.28 molar ratio of living ends to epoxide) were prepared as explained in Procedure 4-2.

The G0, G1, and G2 polymers were recovered by dissolution in a minimal amount (60-150 mL) of THF and precipitation in methanol, like the linear polymer. The graft polymers were purified from contaminants and residual linear polymer by precipitation fractionation from hexane/2-propanol mixtures, the less soluble graft polymer being selectively precipitated while the side-chains remained dissolved. The precipitation fractionation procedure was repeated three times for each sample on average, using SEC analysis to confirm complete purification of the samples.

4.5.3 Polymer Characterization

The polymer samples were analyzed by ^{1}H NMR spectroscopy, using samples dissolved in $CDCl_3$ (5% w/v), on a Bruker Avance 300 MHz NMR instrument. These analyses provided information about the polymer microstructure and epoxidation level.

The molecular weight and molecular weight distribution of the polymer samples, and the grafting yield were determined by size exclusion chromatography (SEC) analysis. The

instrument used was a Viscotek TDA-302 size exclusion chromatograph equipped with refractive index, UV, viscosity (VISC), and two-angle laser light scattering (7^o and 90^o, λ= 670 nm) detectors. The instrument was calibrated with a polystyrene standard (Viscotek, peak molecular weight M_p = 99 500 and M_w/M_n = 1.03). For analysis in THF, the reported refractive index increment of the standard was d*n*/d*c* = 0.185 mL/g. The instrument had three PolyAnalytik mixed bed columns PAS-103-L, PAS-104-L and PAS-105-L with dimensions of 8 mm (ID) × 300 mm (L) each, with overall range polystyrene molecular weight range capability from 10^3 to 10^7. The mobile phase used was THF, at a flow rate 1.0 mL/min and a column temperature of 30 ^{o}C. Samples were prepared, based on their molecular weight, at concentrations from 2–5 mg/mL in THF. The result analysis and instrument control were performed by the Viscotek OmniSEC software package.

Chapter 5 Results and Discussion

The synthesis of arborescent polybutadiene was described in Figure 2-2. The linear polybutadiene substrate was synthesized by two different methods, whereas the reaction was either carried out in a round bottom reactor attached to the vacuum line (Procedure L1) or in a sealed ampoule (Procedure L2). Functionalization of the polymers with epoxide coupling sites was also performed by different approaches identified as Procedures E1 and E2. The epoxidized polybutadiene was then reacted with living polybutadienyllithium to produce G0 (comb-branched) arborescent polybutadiene. The synthesis of the G0 samples was likewise investigated according to eight different procedures. The preferred/optimal methods for the functionalization (Procedure E2) and grafting (Procedure 4-2) reactions were then applied to synthesize the G1 and G2 polymers. The results obtained for each of the procedures investigated will be discussed in details below.

5.1 Linear Polybutadiene

The linear polybutadiene samples were synthesized in pure cyclohexane, to obtain chains with a high 1,4-microstructure content.[33,54] Because of the low polarity of cyclohexane, the polymerization reaction was slow and required 24 h for completion even though the target molecular weight (M_n = 5000) was relatively low. The molecular weight in anionic polymerization at full conversion is controlled by the amounts of monomer and initiator used. The number of moles of polybutadiene chains formed in the reaction at full monomer conversion can be calculated as the ratio of the monomer mass to target M_n according to Equation 5-1, and also corresponds to the number of moles of initiator required if 100% initiation efficiency is assumed. The initiator solution volume (V_i) needed was determined from the known initiator concentration (C_i = 1.4 mol/L) according to Equation 5-2.

$$\text{n (mol)} = \frac{\text{Mass (g)}}{\text{M}_\text{n}\ \text{(g/mol)}} \tag{5-1}$$

$$V_i(\text{ml}) = \frac{n\ (\text{mol})}{C_i\ (\text{mol/L})} * 1000 \qquad (5\text{-}2)$$

The polymerization was terminated with degassed acidified methanol, so as to minimize side reactions with impurities (e.g. CO_2, O_2) leading to dimerization of the chains, and the polymer was recovered by precipitation. ^{1}H NMR analysis was used to estimate the M_n of the linear polybutadiene samples based on end-group analysis (Figure 5-1). Using the ratio of the integrated signals for the methyl protons of the *sec*-butyl end groups (δ 0.8 ppm) and the unsaturated units (δ 4.9-5.4 ppm), a number-average degree of polymerization (DP_n) was obtained.[63] The M_n values were obtained by multiplying the DP_n by the molecular weight of the butadiene structural unit (54.09).

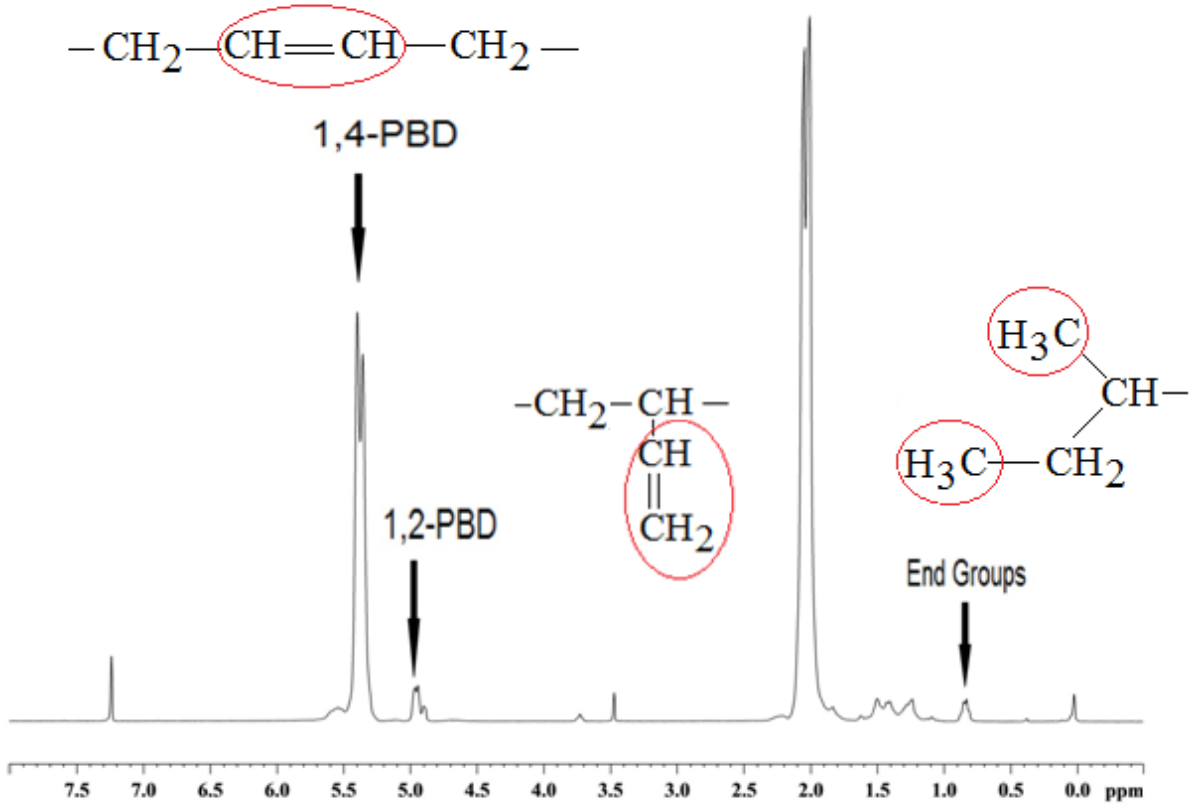


Figure 5-1. ^{1}H NMR spectrum for linear polybutadiene.

^{1}H NMR analysis shows that two types of structural units are present within the polybutadiene chains: 1,4-units as the major product (~95%), and 1,2-units as the minor product (~5%). The 1,4-units are preferred because of their better elastomeric properties, greater thermal stability, and higher reactivity in the epoxidation reaction.

Sample analysis by size exclusion chromatography (SEC) can also provide M_n, as well as M_w and the polydispersity index ($PDI = M_w/M_n$) for the products, but the M_n estimated by this method is considered less reliable than the value derived from NMR analysis. For example, M_n = 5670 was calculated from the NMR spectrum of the linear polybutadiene sample, while the value obtained from SEC analysis was M_n = 5500. This is because the absolute M_n determination by SEC relies on the light scattering detector, which is less sensitive in the low molecular weight range, so the signal is rather noisy (Figure 5-2). The SEC traces obtained for the linear polybutadiene samples derived from Procedures L1 and L2, using the differential refractive index (DRI) detector, are shown in Figure 5-3 for comparison. The noise level is negligible in both cases, but a small shoulder can be noticed on the left of the main peak in the elution curve (Figure 5-3 a). This shoulder likely corresponds to a small amount of dimerization of the primary chains, and could be due to impurities in the nitrogen gas, gradual contamination of the reactor due to the slow diffusion of air during the polymerization, or impurities in the methanol used to terminate the polymerization reaction.

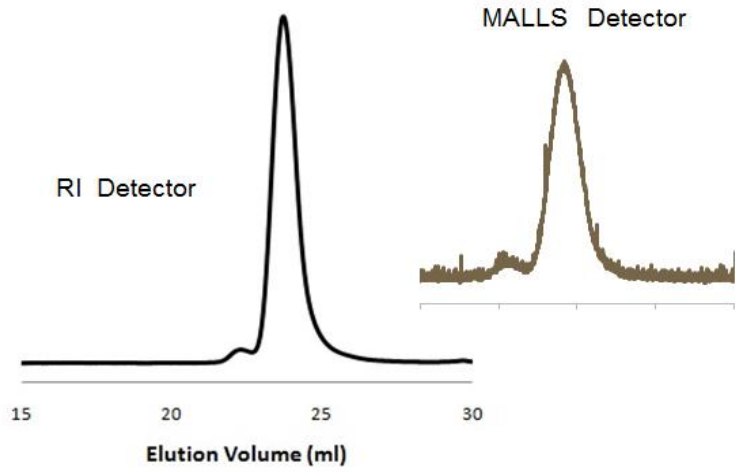


Figure 5-2. SEC analysis of linear polybutadiene with the DRI and MALLS detectors.

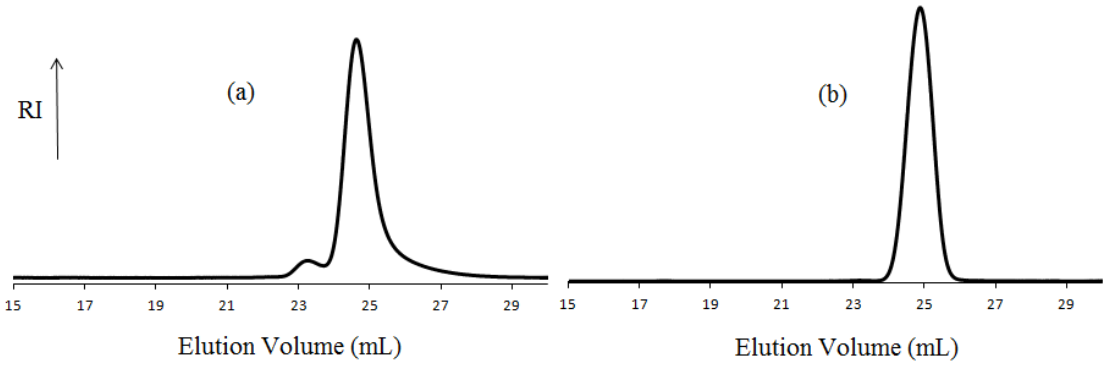


Figure 5-3. SEC analysis of linear polybutadiene, (a) sample L1, (b) sample L2.

The SEC trace for linear polybutadiene synthesized according to Procedure L2, represented in Figure 5-3 (b), shows that the polymer synthesized in a sealed ampoule has no shoulder. It therefore seems that the dimerization results mainly from gradual contamination of the reactor by air over the extended time period (24 h) required for polymerization. The reaction carried out in the round bottom reactor must be more exposed to atmospheric impurities since the reactor has multiple (leaky) ground glass joints, remains attached to the nitrogen-purged vacuum line during the whole reaction, and the rubber septum mounted on

the reactor is punctured from the moment that the polymerization reaction is initiated. In Procedure L2 the polymerization was performed in an ampoule sealed with a single high-vacuum PTFE stopcock, and therefore was much better isolated from the exterior environment. These polymerization conditions therefore appear optimal in a situation where extended reaction times are required such as in the present case.

5.2 Epoxidation of Polybutadiene

Coupling sites were randomly introduced on the substrates through epoxidation of a portion of the 1,4-butadiene structural units. The main motivation for controlling the epoxidation reaction was to provide substrates with optimal substitution levels for the grafting reactions (*vide infra*). The epoxidation reaction was initially performed with performic acid, generated *in situ* from formic acid and hydrogen peroxide (Procedure E1). Epoxidation is an electrophilic reaction, so it is sensitive to the electron density on the double bonds. Both the electron density and the reactivity of a double bond increase with the number of alkyl substituents, and therefore the reactivity of substituted alkenes toward epoxidation decreases in the order tetra → tri → di → mono → unsubstituted.[64,65] Epoxidation is relatively insensitive to steric effects, but the reaction with performic acid is heterogeneous and is therefore influenced by the stirring efficiency.[53,54] This led to difficulties in controlling the substitution level attained. For example, reproducing a certain epoxidation level required using the same amount of polymer, solvent volume, and stirring rate from one reaction to the next, which was difficult to achieve. The reaction time and the temperature obviously also had a strong influence on the results obtained, due to the presence of excess performic acid in the reaction. Furthermore, it was difficult to control the substitution level attained for the upper generation substrates due to their higher viscosity. Consequently, the epoxidation reaction had to be optimized for each generation and polymer concentration, leading to multiple failed reactions and product loss. To overcome these difficulties, a new approach

was examined (Procedure E2). The alternate functionalization reaction uses *m*-CPBA. The epoxidation level was easier to control in this procedure because the reactions were homogeneous.

To evaluate the epoxidation level attained, it was necessary to determine the fraction of 1,4-units by ^{1}H NMR analysis of the polymer samples according to Equation 5-7, where $I_{1,2\text{-PBD}}$ and $I_{1,4\text{-PBD}}$ represent the integrated intensities for the peaks at δ 4.9 ppm and 5.3 ppm, respectively.

$$\frac{3x}{(1-x)2} = \frac{I_{1,2-PBD}}{I_{1,4-PBD}} \tag{5-7}$$

As seen in Figure 5-1, the NMR spectrum of linear polybutadiene has three olefinic hydrogen atoms associated with each 1,2-butadiene unit, but only two hydrogen atoms for every 1,4-butadiene unit. By taking this into consideration in Equation 5-7, the molar fraction of 1,2-PBD units (*x*) can be determined, while the molar ratio of 1,4-butadiene units (*x'*) equals *1-x*.

The epoxidation level was controlled by adjusting the amount of *m*-CPBA used in the reaction, corresponding to the number of moles of *1,4*-butadiene units to be reacted. Figure 5-7 shows the ^{1}H NMR spectrum obtained for an epoxidized PBD sample, with a substitution level of 25 mole%. The substitution level was calculated using Equation 5-8.

$$\frac{2y}{2x'-2y} = \frac{I_{Epoxidized\ PBD}}{I_{1,4-PBD}} \tag{5-8}$$

The epoxide ring has two hydrogen atoms producing distinct signals at δ 2.7 and 2.9 ppm (Figure 5-4), and the factor (*y*) represents the molar ratio of epoxidized butadiene units. The

area (integrated intensity) of both peaks is represented in Equation 4 as $I_{Epoxidized\ PBD}$, while *x'* is the molar fraction of *1,4*-butadiene units.

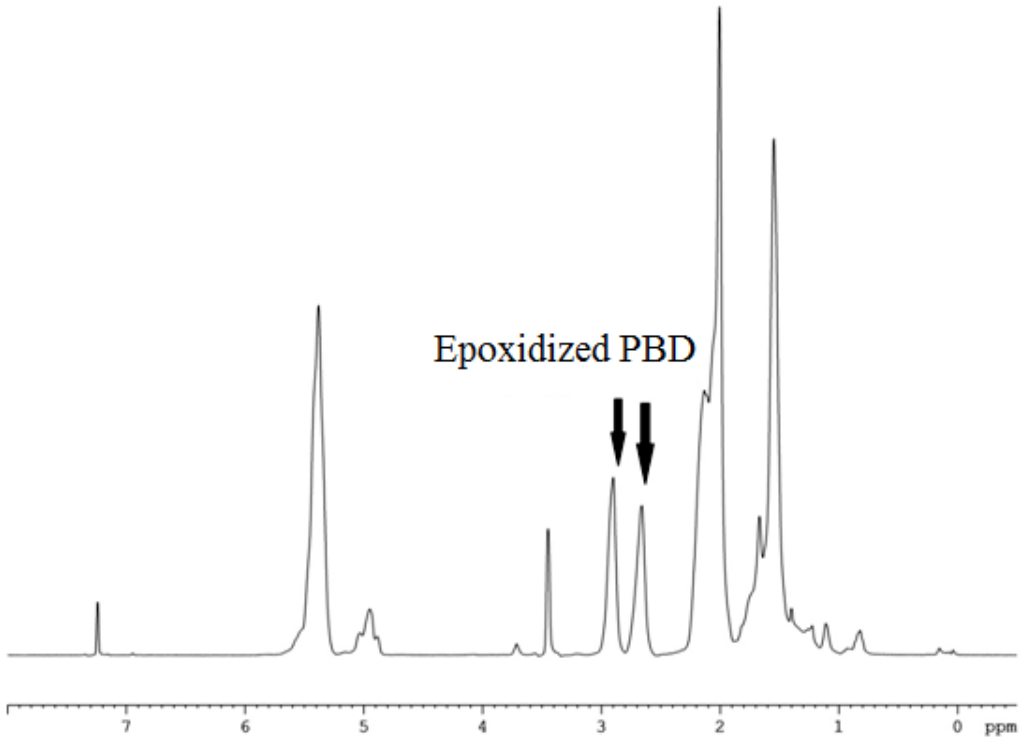


Figure 5-4. ^{1}H NMR spectrum for 25 mole% epoxidized polybutadiene.

5.3 Grafting Yield, Branching Functionality, and Coupling Efficiency

The use of SEC analysis was of fundamental importance in the current project because, beyond the characterization of the substrates and the side-chain samples, it was the primary tool to gage the success of the grafting reactions. This was achieved mainly on the basis of two parameters, namely the grafting yield and the coupling efficiency (the determination of latter requiring the determination of the branching functionality). Due to their significance, these parameters must be defined before any of the results for the grafting reactions are presented.

The grafting yield (G_y) represents the fraction of polybutadienyllithium chains becoming coupled with the substrate in a grafting reaction. It was determined using the

differential refractometer (DRI) detector trace obtained from the SEC instrument. If it is assumed that the refractive indices of the graft and the linear polymers are identical, then the response of the detector is directly proportional the concentration of each component. The grafting yield may then be calculated according to Equation 5-9, using the peak areas identified on Figure 5-5.

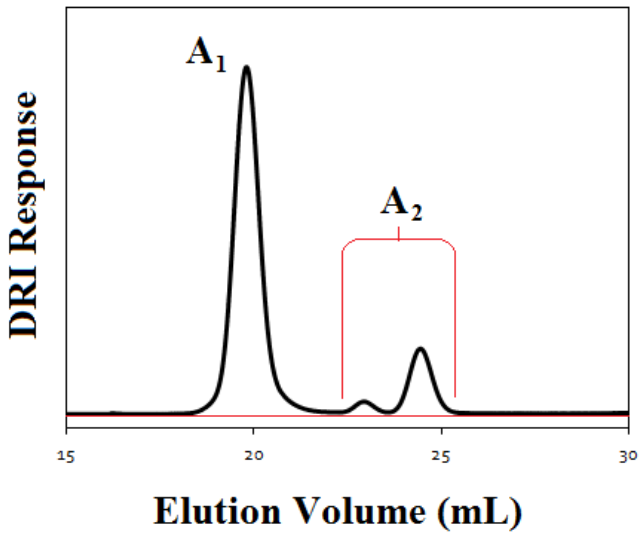


Figure 5-5. SEC determination of the grafting yield: (A_1) graft polymer, (A_2) main peak for side-chains with small amount of dimerization contamination.

$$G_y = \frac{A_1}{(A_1+A_2)} \times 100 \tag{5-9}$$

In Equation 5-9, A_1 represents the peak area for the graft polymer, while A_2 is defined as the total peak area for the linear chain contaminant (terminated and dimerized side-chains). Using this simplified calculation method, the grafting yield is slightly overestimated. This is because the peak area of A_1 incorporates the response for both the side-chains and the grafting substrate. To obtain a more accurate estimate of the grafting yield, the peak area A_1 must be corrected by subtracting the contribution from the substrate. The exact (corrected)

response for the graft polymer A_1' is obtained by multiplying A_1 by the weight fraction of the side-chains in the graft polymer sample as

$$A_1' = A_1 \frac{[M_n(G) - M_n(G-1)]}{M_n(G)} \tag{5-10}$$

where $M_n(G)$ is the number-average molecular weight of the graft polymer of generation G, while $M_n(G\text{-}1)$ represents the number-average molecular weight of the substrate of the previous generation.

The number-average branching functionality f_n, corresponding to the number of side-chains grafted in the last reaction cycle, is a useful parameter to describe the structure of arborescent polymers. It is estimated from Equation 5-11, where M_n^{br} is the number-average molecular weight of the side-chains grafted in the last reaction cycle.

$$f_n = \frac{M_n(G) - M_n(G-1)}{M_n^{br}} \tag{5-11}$$

Another useful quantity to quantify the success of a grafting reaction is the coupling efficiency C_e, defined as the fraction of epoxide coupling sites consumed. Its definition according to Equation 5-12 essentially corresponds to the ratio of the number of coupling sites on the substrate to the branching functionality, since M_o is the molecular weight of the butadiene units (54.09) and E is the mole% of epoxidized units in the substrate.

$$C_e = \frac{f_n M_o}{M_n(G-1)E} \times 100 \tag{5-12}$$

5.4 Influence of Substrate Epoxidation Level

In the early stage of the project, substrates were synthesized with three different epoxidation levels. Each substrate was subjected to a grafting reaction according to Procedure 1-1, in order to examine the influence of the epoxidation level on the grafting yield (Table 5-1). The SEC analysis results are also compared for the grafting reactions using the 25 and 30 mole% epoxidized substrates in Figure 5-6. All these reactions were performed in pure cyclohexane, using a 1:1 molar ratio of coupling sites to living ends, and $M_n \approx 5000$ side-chains.

At low substitution levels, the number of coupling sites on the substrate is decreased, as well as the grafting yield. This may be explained in part by the introduction of a larger amount of protic impurities in the grafting reaction, since a larger amount of substrate was required to achieve a 1:1 molar ratio of coupling sites to living ends in that case. On the other hand, increasing the substitution level of the substrate also increases its polarity, causing it to become much less soluble in cyclohexane (a non-polar solvent). The density of coupling sites along the substrate also increases with the epoxidation level, ultimately leading to steric overcrowding and the inaccessibility of a portion of the coupling sites. A substrate substitution level of ~25 mole% therefore seems to represent a reasonable compromise to limit the introduction of protic impurities in the reaction and making optimal use of the coupling sites.

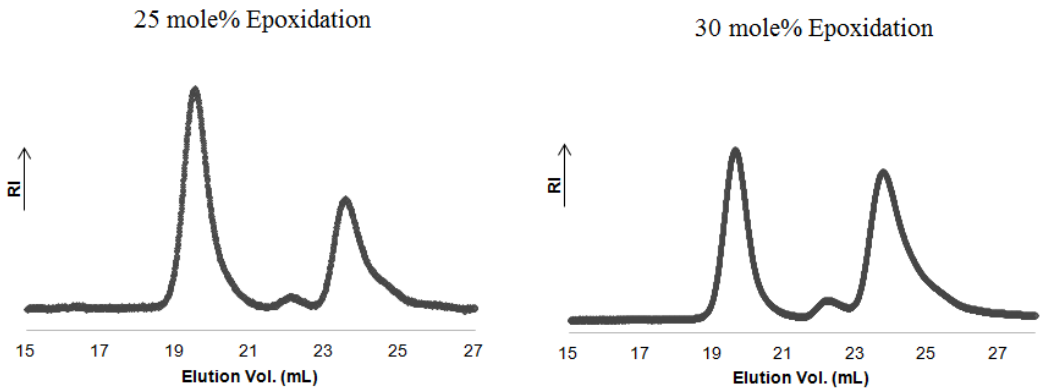


Figure 5-6. SEC analysis of G0 grafting reactions for two different epoxidized substrates.

Table 5-1. Grafting yield for substrates with different epoxidation levels.

Molar ratio of epoxidized PBD %	Grafting yield %
20	63
25	68
30	55

5.5 Optimization of the Grafting Reaction

Since the main goal of this research was to optimize the grafting reaction of polybutadienyllithium onto epoxidized polybutadiene, a series of reactions was planned in a logical fashion to be directly comparable. After determining that the optimal substitution level of the substrate was ~25 mole%, a series of reactions was planned using a 1:1 molar ratio of living ends to coupling sites to provide a common basis for comparison. It was initially planned to perform all the grafting reactions in the round bottom polymerization reactor. However due to multiple failed reactions, polymerization and grafting in a sealed ampoule was attempted and found to produce more consistent results. The results obtained for each of the reactions described in Chapter 3 are discussed below.

Procedure 1-1: This reaction was performed to serve as baseline for the other grafting reactions, since it corresponds to the method previously described in the literature.[54] This reaction was carried out in a non-polar solvent (cyclohexane) without reactivity modifiers. It was terminated after one day and had a grafting yield of 68%. After 24 h, noticeable fading of the living polymer solution coloration was observed from the beginning of the reaction. This coloration change could have been due to termination by impurities. The low grafting yield and non-uniform peaks observed in the SEC elution curve of the product (Figure 5-7) clearly indicate the occurrence of chain termination during the grafting reaction: Tailing on the rightmost peak (side-chains) corresponds to chain termination during polymerization of the monomer, and a small dimer peak with a molecular weight twice as large as the side-chains, presumably resulting from O_2 or CO_2 contamination of the reaction from the air, is also present.

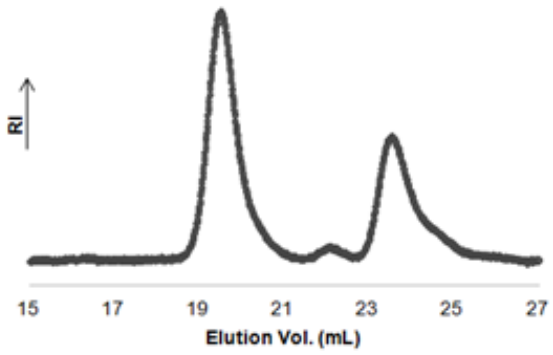


Figure 5-7. SEC analysis of G0 polybutadiene prepared according to Procedure 1-1.

Procedure 2-1: In this reaction TMEDA was investigated as a reactivity modifier to enhance the ionization and reactivity of the chain ends in cyclohexane. The amount of additive used, corresponding to a 6:1 molar ratio of TMEDA to living ends, corresponded to the conditions reported in the literature for the synthesis of arborescent polyisoprene.[53] This approach only

increased the grafting yield slightly (71% vs. 68% in pure cyclohexane). Upon addition of TMEDA to the reaction the color changed immediately from light yellow to orange, presumably due to the complexation of the lithium ions by TMEDA and delocalization of the negative charge at the chain end on the penultimate monomer unit. The same rapid color fading was observed as in Procedure 1-1, however. The slight increase in grafting yield observed was presumably due to enhanced chain end ionization, making the chains ends more nucleophilic.[53]

Procedures 3-1 and 4-1: The addition of THF to the grafting medium was investigated in Procedure 3-1, while the addition of LiBr/THF was examined in procedure 4-1. Both procedures were therefore carried out in the presence of THF, which is sensitive to proton abstraction leading to termination of the living polymer chains. The rate of side reactions involving contaminants such as protic impurities, O_2, and CO_2 is also expected to increase in the presence of a polar solvent like THF. Consequently, poor grafting yields of 10% and 12% were obtained for Procedures 3-1 and 4-1, respectively. As a result, all the procedures were modified to allow stricter control over the conditions used in the polymerization and grafting reactions, by using sealed ampoules as reactors.

Procedure 1-2: This procedure was based on Procedure 1-1, modified to provide baseline data comparable to Procedure 1-1 in a sealed reactor environment. In analogy to Procedure L2, SEC analysis of a side-chain sample removed prior to grafting yielded a well-defined and symmetrical peak, but without shoulder (Figure 5-3). The grafting yield improved slightly by this approach (from 68% to 70%), while the color of the solution was clearly more persistent and still very noticeable after 24 h. This improved color stability, and the absence of a dimer peak both suggest that atmospheric contamination of the reaction was at the origin of dimer formation as postulated earlier. This approach allowed the investigation of the influence of increased reaction time on the grafting yield from one day to one week, and led to a slight

improvement to 74%. Since the reaction was carried out in a non-polar solvent, the low grafting yield could be due to slow reaction kinetics. Longer reaction times could potentially improve the grafting yield further, albeit very long reaction times are not very practical.

Procedure 2-2: By carrying out the grafting reaction in an ampoule and in the presence of TMEDA the grafting yield reached 73% after one day, and 75% after one week. Slight fading of the color was observed, as in Procedure 2-1, but to a lesser extent. It therefore appears that in the presence of TMEDA the reactivity of chains ends is increased, even with a polar solvent like THF added. Unfortunately, the use of TMEDA in the reaction also increases the potential for contamination by protic impurities. This could also explain in part the modest increase in grafting yield observed in comparison to Procedure 1-2.

Procedure 3-2: Grafting was accomplished in the presence of a significant amount of THF (25% by volume) mixed with cyclohexane, and led to 78% yield after 24 h, reaching 80% after one week with slight color fading. Considering the relatively high grafting yield attained after one week, the observed color fading could simply be due to the coupling reaction. The improved grafting yield in the presence of THF can be explained by its Lewis base character (as discussed in Section 2-5 and 3-5-2), increasing the ionization level and the nucleophilicity of the chain ends in the grafting reaction.

Procedure 4-2: This procedure, using LiBr as a Lewis acid promoter to enhance the reactivity of the epoxide coupling sites in the presence of THF, led to the highest grafting yield of 82% after one day and 85% after one week. These are the best results obtained for the G0 arborescent polybutadiene synthesis using equimolar amounts of coupling sites and living ends. Correspondingly, Procedure 2-4 was considered optimal and was selected for the synthesis of the G1 and G2 arborescent polymers. The synthesis of a G0 arborescent polybutadiene sample under the optimal conditions can be described with a series of SEC

elution curves as shown in Figure 5-8. The side-chains (curve a), when coupled with the epoxidized substrate (curve b) yield the crude G0 graft polymer of curve c, corresponding to a grafting yield of 85%. The linear polymer contaminant was successfully separated from the graft polymer by precipitation fractionation to yield curve d.

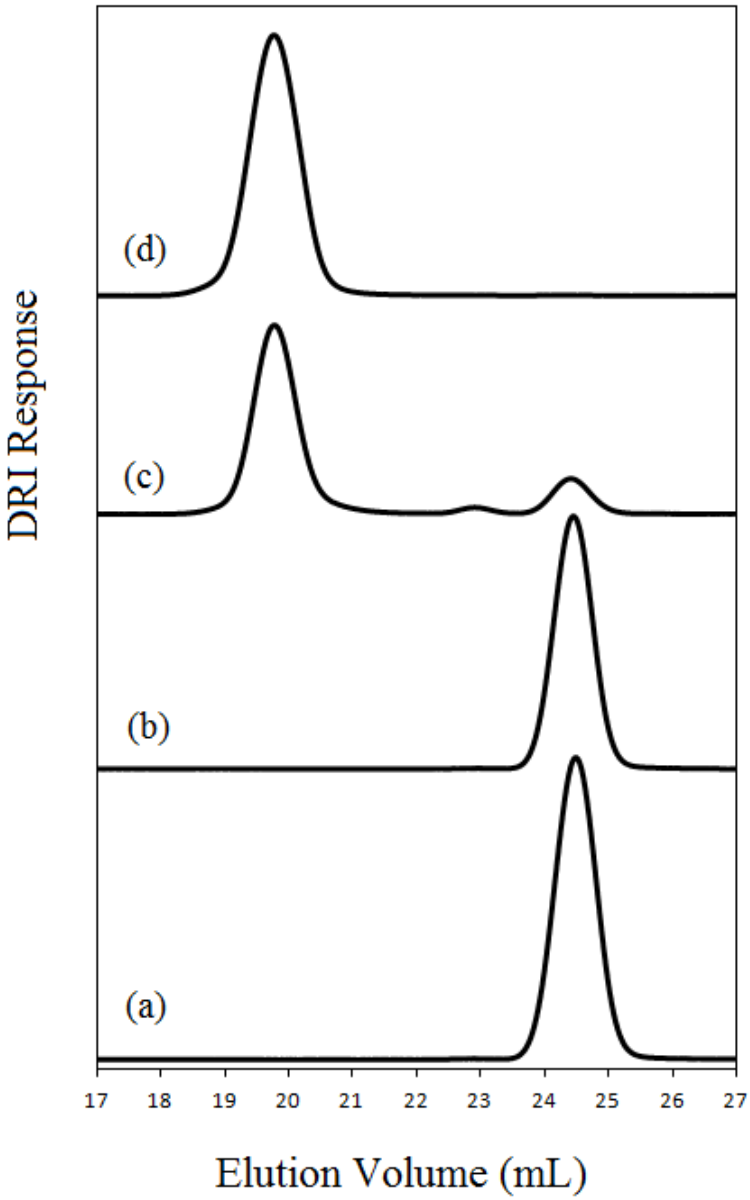


Figure 5-8. Synthesis of G0 arborescent polybutadiene under optimal conditions: (a) side-chains, (b) epoxidized substrate, (c) crude G0 graft polymer, (d) fractionated G0 sample.

5.6 Synthesis of G1 and G2 Arborescent Polybutadiene

The G0 and G1 substrates were successfully functionalized according to Procedure E2, described for the linear polybutadiene samples. The target functionalization levels for the G0 and G1 polymers was also 25 mole%, while the experimental epoxidation levels varied from 24 to 26 mole%, i.e. essentially 25 mole% within experimental error limits (Table 5-2). The epoxidation reaction had no effect on the molecular weight distribution of the substrates, as indicated by the essentially identical PDI values obtained before and after the functionalization (3rd and last columns of the table, respectively).

Table 5-2. Polybutadiene substrates prepared according to E2.

Polybutadiene substrate			**Product**	
Generation	M_n **/10^3**	M_w/M_n	***E*** **/mol%**	M_w/M_n
Linear	5.6	1.05	25	1.05
G0	140	1.04	26	1.04
G1	3400	1.05	24	1.06

Table 5-3 summarizes the results obtained when grafting $M_n \approx 5000$ polybutadiene side-chains on the epoxidized substrates described in Table 5-2 according to Procedure 2-4 (THF:cyclohexane ratio of 1:3, LiBr:living ends molar ratio of 6:1, and 1:1 molar ratio of coupling sites vs. living ends) one week reaction time. The data collected show that generational growth is associated with a decrease in grafting yield, in analogy to all other arborescent polymer systems previously investigated.[1,2,53] It is interesting to note that there is a significant decrease in grafting yield for the G1 and G2 polymer syntheses as compared to the G0 sample. This can be attributed in part to the –OH groups introduced at the branch

junctions of the G0 and G1 substrates during the coupling reaction (Figure 5-9), contributing to the deactivation of a portion of the living polybutadienyllithium chains in the next grafting cycle. For example, the G0 substrate (M_n= 140000) had an epoxidation level of 26% and f_n = 23 side-chains, and therefore 23 –OH groups located at the branch junctions. Since the molecular weight of a butadiene structural unit is M_o = 54.09, the overall degree of polymerization of the epoxidized G0 sample is 140000/54.09 = 2588. The number of coupling sites on the G0 substrate is 2588×0.26 = 672. The mole fraction of –OH groups within the substrate, that could potentially participate in living chain deactivation is therefore 23/(672 + 23) = 0.033 or 3.3%. Consequently, a decrease in grafting yield on the order of 3.3% could be expected in the synthesis of the G1 polymer as compared to the G0 sample, due to the presence of –OH groups at the branch junctions. Whether this contribution to living chain deactivation is significant remains questionable however, because of these hydroxyl groups are located closer to the center of the polymer substrate, and therefore less accessible to the living chains. This is particularly true for the upper generation, more crowded (e.g. G1) substrates.

Table 5-3. Synthesis of arborescent polybutadiene samples in mixed reaction medium (3:1 cyclohexane:THF) in presence of LiBr (6:1 molar ratio vs. living ends), using ~25 mol% epoxidized substrate with a 1:1 molar ratio of coupling sites vs. living ends and one week reaction time.

Gen	$M_n^{br}/10^3$	M_w/M_n	yield%	G_y%	$M_n/10^3$	f_n	E/mol%	C_e%
G0	5.4	1.03	85	84	135	23	25	92
G1	5.4	1.04	80	79	3050	539	26	80
G2	5.1	1.05	78	76	62050	11500	24	76

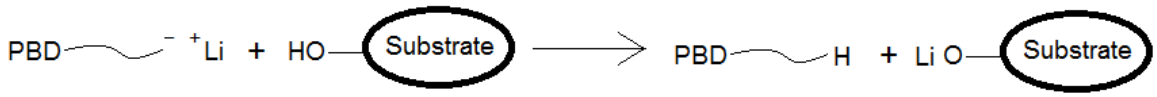


Figure 5-9. Living chains deactivation by –OH groups at the branch junctions of the substrate.

It can be noted from the last column of Table 5-3 that a decrease in coupling efficiency (C_e) was experienced in the synthesis of the upper generations, presumably because the coupling sites become less accessible as a consequence of increased steric congestion. In other words, some of the side-chains were either not able to access the coupling sites, or side reactions such as dimerization became more significant. A significant decrease in grafting yield could also be due to a greater tendency for protic impurities to become trapped in the denser, high molecular weight upper generation substrates. It is also interesting that in spite of the very high branching functionalities attained (f_n of up to 11500 for the G1 polymer) the rate of increase in f_n remains almost constant from one generation to the next, being 23-fold from G0 to G1, and 21-fold from G1 to G2.

The synthesis of successive generations of arborescent polybutadiene samples is illustrated in Figure 5-10, using SEC analysis traces starting from a linear polybutadiene substrate with $M_n \approx 5000$ (curve a). The traces for arborescent polybutadiene generations G0, G1 and G2 are respectively presented as curves b–d, after the graft polymers were purified from the linear side-chain contaminant by precipitation fractionation in mixtures of hexane and 2-propanol.

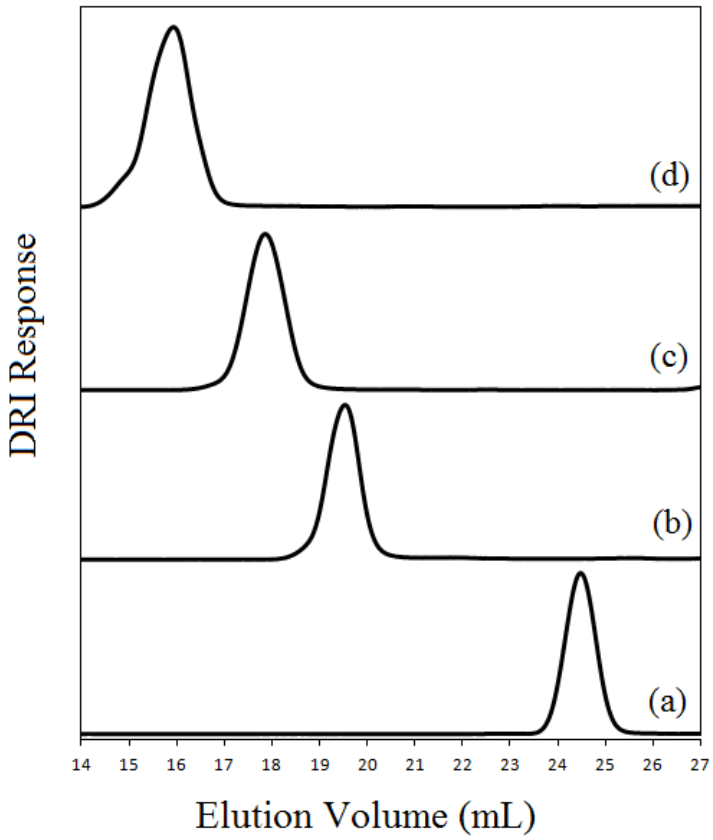


Figure 5-10. SEC traces for (a) side-chains, (b–d) arborescent G0, G1 and G2 PBD.

The influence of the reaction time on the grafting yield was also investigated for the arborescent polymer syntheses carried out in sealed ampoules using a ~25 mol% epoxidized substrate. The four grafting procedures examined are compared in Table 5-4, and the grafting yield achieved in each case is systematically slightly higher after one week than after one day.

Table 5-4. Grafting yield attained for different procedures and reaction times.

Reaction conditions	Grafting yield % 1 Day	Grafting yield % 1 Week
Pure cyclohexane	70	74
Cyclohexane in the presence of TMEDA 6:1 vs. living ends	73	75
Cyclohexane:THF, 3:1 mixture	78	80
Cyclohexane:THF, 3:1 mixture, with LiBr 6:1 vs. living ends	82	85

Optimization of the grafting yield for the G1 and G2 polymers was also attempted on the basis of the grafting yield achieved using a 1:1 molar ratio of coupling sites to living chains in one week, by increasing the amount of substrate in the reactions. The modified ratios were calculated theoretically to achieve 100% grafting yield, and thus depend on the generation number (Table 5-5).

Table 5-5. Influence of the molar ratio of coupling sites:living ends on the grafting yield after one week.

Ratio	G0	G1	G2
1:1	85	80	78
1.17:1	87	——	——
1.25:1	——	84	——
1.28:1	——	——	81

For example, the synthesis of the G0 polymer using a 1:1 ratio of epoxide groups to living ends proceeded with 85% grafting yield after one week. It was thus hypothesized that, if no living chains were deactivated during the grafting reaction, i.e. if the grafting yield

attained were only limited by steric crowding of the coupling sites as chains were added on the substrate, an excess of substrate could potentially increase the grafting yield to 100%. The additional amount of substrate required to achieve this can be calculated as $(1/G_y - 1) \times 100\%$, or 17% for the G0 polymer synthesis. This excess of substrate could therefore theoretically lead to the consumption of all the polybutadienyllithium chains present in the reaction. When attempted, this modified procedure only led to an insignificant increase in grafting yield from 85% to 87%, however. This clearly shows that the yield of the grafting reaction is limited by residual protic impurities and other deactivation reactions, rather than by steric crowding of the substrate.

The synthesis of the G1 and G2 arborescent polybutadiene samples was attempted with an excess of substrate, in analogy to the G0 sample. The living polymer serving as side-chains was likewise synthesized in cyclohexane, and the grafting reaction was carried out in the presence of THF (3:1 volume ratio of cyclohexane:THF) and LiBr (6:1 molar ratio LiBr vs. living ends) for one week. The G1 polymer was obtained in 80% yield. The conditions were modified using a 25% excess of epoxidized substrate, leading to a grafting yield slightly increased by 4%, to 84% after one week. The G2 polymer synthesis, again based on Procedure 2-4 (1:1 molar ratio of epoxide groups to living ends), had a grafting yield of 78%. An excess of epoxidized substrate (1.28:1 coupling sites vs. living ends) likewise increased the grafting yield by 3%, to 81% after one week. The results obtained with excess coupling substrate in the G1 and G2 polymer syntheses again both support the conclusions drawn from the analogous G0 reaction, namely that the grafting yield is limited by residual protic impurities and other side reactions rather than by steric hindrance of the substrate.

Chapter 6 Conclusions

The synthesis of arborescent polybutadiene samples of generations G0–G2 was successfully achieved. The anionic polymerization techniques used provided extensive control over the molecular weight of polybutadienyllithium serving as side-chains, while also producing narrow molecular weight distributions, and therefore side-chains of uniform size. The ability to analyze samples after each reaction step is a clear advantage when applying the 'grafting onto' method.

6.1 Functionalization

Substrate synthesis was achieved according to two procedures. The procedure identified as E1, based on the *in situ* generation of performic acid, is commercially relevant due to its low cost. Unfortunately it was difficult to achieve reproducible substitution levels by that method, due to the heterogeneity of the reaction medium and its ensuing sensitivity to the stirring efficiency. Following a number of failed reactions, epoxidation reaction Procedure E2 was developed. This method, using *m*-chloroperoxybenzoic acid under homogeneous conditions, provided much better control over the substitution level attained.

6.2 Grafting Yield Optimization

The synthetic procedures and the grafting conditions were optimized in the current project by focusing on polymers with side-chains having $M_n \approx 5000$. It is clearly preferable to perform the polymerization and grafting reactions in sealed ampoules. The substitution level selected for the substrate (~25 mol%) seems to represent a reasonable compromise to avoid excessive steric crowding limiting the grafting yield attained, while achieving dense arborescent structures with high branching functionalities. This substitution level also provided substrates soluble in all the solvent systems used in the investigation, including pure cyclohexane, a non-polar solvent. The grafting yield was maximized when the reactions were performed in the presence of LiBr (6:1 molar ratio vs. living ends) and THF (1:3 volume ratio

of THF vs. cyclohexane), reaching 85% for the G0 polymer. The influence of excess substrate on the grafting yield was not very significant, amounting to ~2%. Allowing the reactions to proceed for longer time (one week vs. one day) likewise led to a small (~2%) increase in grafting yield.

6.3 Graft Polymer Syntheses

All of the reactions were initially planned to be performed in a round bottom reactor attached to the vacuum line throughout the grafting process. Difficulties in reproducing the results were experienced in the initial portion of the work however, which led to the development of analogous reactions carried out in sealed ampoules. The synthesis of linear polybutadiene was thus achieved in the round bottom reactor according to Procedure L1, as well as in an ampoule (Procedure L2). The results obtained from both Procedures L1 and L2 were acceptable, but Procedure L2 was better in terms of avoiding small amounts of dimerization during the polymerization. Similarly to the synthesis of the linear polymer, the grafting reactions were carried out according to different procedures. Four grafting methods, identified as Procedures 1-1 through 1-4, were performed in the round bottom reactor using pure cyclohexane, cyclohexane with TMEDA, cyclohexane-THF, and cyclohexane-THF with LiBr, respectively. These represent the different grafting protocols discussed in the objectives of Chapter 3. Quite surprisingly, the reactions incorporating THF (Procedures 1-3 and 1-4) failed under these conditions. These reactions were adapted by carrying them out in sealed ampoules (Procedures 2-1 through 2-4). All these procedures provided higher grafting yields than the corresponding round bottom reactor techniques. Since Procedure 2-4 (incorporating THF and LiBr) had the highest yield among the different approaches examined, it was applied to the synthesis of the G1 and G2 arborescent polybutadiene samples. The influence of excess grafting substrate in the synthesis of the G0, G1, and G2 polymers was also investigated according to Procedure 2-4 but led to marginally improved results.

Chapter 7 Future Work

The synthesis of arborescent polybutadiene offers a number of interesting possibilities. The synthesis of a G3 arborescent polybutadiene sample has not been achieved in this project due to time limitations. Based on literature reports for the synthesis of arborescent polyisoprene,[53] the synthesis of a G3 sample could be quite challenging: Low solubility of the substrate and insignificant grafting yields were reported for these samples. The solubility of the epoxidized substrates was observed to increase at lower substitution levels, however, while the coupling efficiency decreased for the upper generation samples. It should therefore be possible to obtain G3 arborescent polybutadiene samples in good yield by decreasing the epoxidation level from 25 mole% to 10-15 mole%, for example, if necessary.

Another noteworthy point is that this investigation only considered relatively short polybutadiene side-chains. It would be very interesting to examine the influence of longer side-chains (e.g. with M_n = 30,000-80,000). The grafting conditions used may need to be re-examined for longer side-chains however, since their solubility characteristics are different. The rheological properties of these materials have not been investigated previously, but are expected to be very interesting in view of the enhanced entanglement effects reported for star-branched polymers, even for relatively low branching functionalities.[66]

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