Synthesis and Characterization of Arborescent Graft Copolymers

by

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Abstract

Synthetic techniques are presented for the preparation of novel arborescent copolymers containing either polyisoprene, poly(2-vinylpyridine), poly(*tert*-butyl methacrylate), or poly(methyl methacrylate) side chains grafted onto polystyrene substrates of different architectures. Polyisoprene and poly(2-vinylpyridine) macroanions can be reacted directly with chloromethylated polystyrene substrates for this purpose. A convenient method for converting chloromethylated polystyrenes to their bromomethylated analogues is described. The more reactive bromomethyl sites are necessary for the synthesis of arborescent copolymers with either poly(*tert*-butyl methacrylate) or poly(methyl methacrylate) side chains. In each example provided, the *graft-on-graft* approach used provides control over the side chain molecular weight and the branching density, while a low apparent polydispersity is maintained for all copolymers ($M_w/M_n < 1.2$).

The arborescent copolymers are characterized by a compact, highly branched structure leading to interesting physical properties that are strongly influenced by the chemical composition of the side chains. For example, scanning force microscopy measurements in the phase contrast mode show that the isoprene copolymers display phase-separated morphologies (glassy core surrounded by a rubbery shell) to different extents, depending on their structure. Arborescent poly(2-vinylpyridine) molecules expand considerably more than their linear homologues when protonated with HCl. This enhanced polyelectrolyte effect is attributed to the higher charge density attained for the branched copolymers. This effect is even more noticeable for the arborescent poly(*tert*-butyl methacrylate) copolymers after hydrolysis and neutralization with NaOH.

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"If I have seen farther than others, it is because I was standing on the shoulders of giants."

Sir Isaac Newton

I dedicate this work to

Mary Lou and Dielle for their boundless patience,

and

my entire family for their constant encouragement.

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List of Abbreviations and Symbols

2VP	2-vinylpyridine
AIBN	azobisisobutyronitrile
CDMSS	4-(chlorodimethylsilyl)styrene
CMME	chloromethyl methyl ether
D_3	hexamethylcyclotrisiloxane
DIBAH	diisobutylaluminum hydride
DLS	dynamic light scattering
DMF	N,N-dimethylformamide
DMSO	dimethylsulfoxide
DPE	1,1-diphenylethylene
DRI	differential refractive index
DVB	divinylbenzene
FT-IR	fourier transform infrared
f_w	branching functionality
G0	generation 0
G1	generation 1
G2	generation 2
HPLC	high performance liquid chromatography
LHAA	6-lithiohexylacetaldehyde acetal
LS	light scattering
M_c	core molecular weight
M_b	branch molecular weight
M_{RU}	repeat unit molecular weight
MMA	methyl methacrylate
M_n	number-average molecular weight
M_w	weight-average molecular weight
MW	molecular weight
MWD	molecular weight distribution
N_b	branching multiplicity

N_c	core multiplicity
N_{RU}	number of repeat units
NMR	nuclear magnetic resonance
P2VP	poly(2-vinylpyridine)
P4VP	poly(4-vinylpyridine)
PA	polyacetylene
PB	polybutadiene
PCEVE	poly(chloroethyl vinyl ether)
PDI	polydispersity index (PDI = M_w/M_n)
PDMS	polydimethylsiloxane
PEI	poly(ethylenimine)
PEO	poly(ethylene oxide)
PEOX	poly(2-ethyl-2-oxazoline)
PIP	polyisoprene
PMAA	poly(methacrylic acid)
PMMA	poly(methyl methacrylate)
PPVS	poly(phenyl vinyl sulfoxide)
PS	polystyrene
PtBuMA	poly(*tert*-butyl methacrylate)
PTFE	polytetrafluoroethylene
PVS	phenyl vinyl sulfoxide
R_g	radius of gyration
R_h	hydrodynamic radius
SEC	size exclusion chromatography
tBuMA	*tert*-butyl methacrylate
TEA	triethylaluminum
THF	tetrahydrofuran
TMEDA	N,N,N',N'-tetramethylethylenediamine
TMSI	trimethylsilyl iodide
UV	ultraviolet
V_h	hydrodynamic volume

Chapter 1

Foreword

1.1 Introduction

Arborescent polymers are highly branched molecules prepared using anionic polymerization and grafting techniques.[1,2] The general synthetic route to arborescent polymers is shown in Figure 1.1. Successive functionalization and anionic grafting cycles yields comb-branched (generation 0 or G0), generation 1 (G1) polymers, and so on. The synthetic methods provide precise control over the size and topology of these molecules.[3] Unusual physical properties, consistent with a compact structure and rigid sphere topology, have been observed for these materials.[3-6]

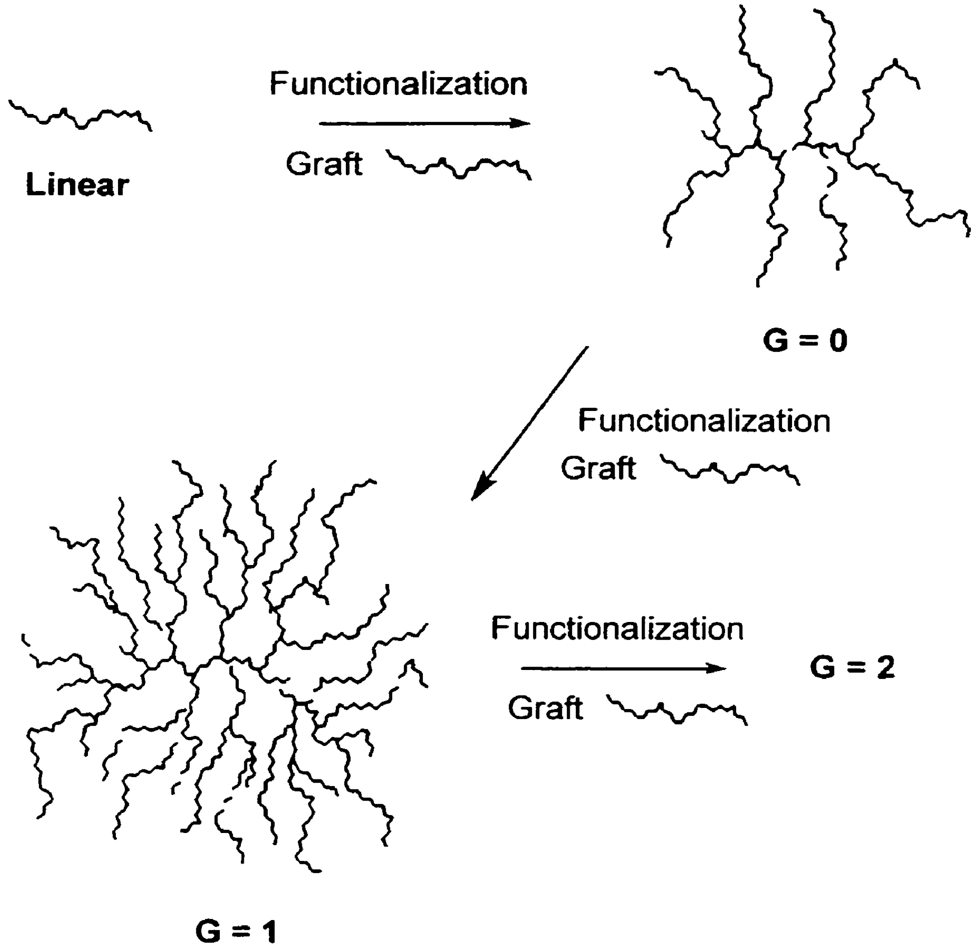

Figure 1.1 General synthetic route to arborescent polymers.

Since anionic polymerization techniques are used to prepare the polymeric segments serving as building blocks for arborescent polymers, control over the chemical composition of the molecules should also be possible. A wide range of monomers can be polymerized using anionic techniques. The incorporation of selected monomers in the synthetic scheme to obtain arborescent copolymers is of considerable interest.

1.2 Research Objectives

The incorporation of different monomers (other than styrene) in the synthesis of arborescent polymers is the focus of the research described herein. More specifically, the aim is to demonstrate that the synthetic methods available can be generalized to include a wide range of monomers to yield arborescent copolymers with different chemical compositions. Successive functionalization and anionic grafting cycles allow for precise control over the size of the polystyrene core, the number of grafting sites, the side chain molecular weight, and the chemical composition of the side chains. The strategy selected consists of preparing randomly functionalized linear or arborescent (G0, G1 and G2) polystyrene substrates onto which linear side chains derived from other monomers are grafted. These monomers are selected because they can be readily polymerized using conventional anionic techniques, and are expected to impart interesting physical properties to the highly branched copolymers. Unique characteristics such as core-shell molecular morphologies or interesting solution properties are expected for these graft copolymers, depending on the composition of the grafted side chains. Preliminary characterization results will be presented, in order to demonstrate the novelty of these materials.

1.3 Outline

Since arborescent polymers are a sub-class of dendritic polymers, the background information provided in this thesis first identifies the different families of polymers that have a dendritic structure (Chapter 2). The synthesis and some of the unique physical characteristics exhibited by these materials are highlighted. Many of the methods used to prepare polymers with dendritic structures have been derived from methods developed for the synthesis of comb-branched and star-branched polymers. A summary of these methods is also provided, including some important experimental considerations and limitations. Finally, the synthesis and key features of arborescent polymers are described in detail.

Chapters 3, 4 and 5 describe discrete projects concerning the synthesis and preliminary physical characterization of novel arborescent copolymers incorporating polyisoprene (Chapter 3), poly(2-vinylpyridine) (Chapter 4), or poly(*tert*-butyl methacrylate) (Chapter 5) side chains. Each chapter is organized in manuscript format: A separate introduction is provided to summarize background information pertinent to each project, as well as an abstract, experimental methods, results and discussion, and conclusions sections. Chapter 3 consists of a published manuscript,[7] while Chapters 4 and 5 were written in the same format and will submitted for publication.

Chapter 6 describes preliminary results on the attempted synthesis of arborescent copolymers incorporating poly(methyl methacrylate) side chains. The conclusions drawn from this exploratory work are also discussed, including suggestions to improve the synthetic methods. The overall conclusions from the thesis and suggestions for future work are provided in Chapter 7.

1.4 References

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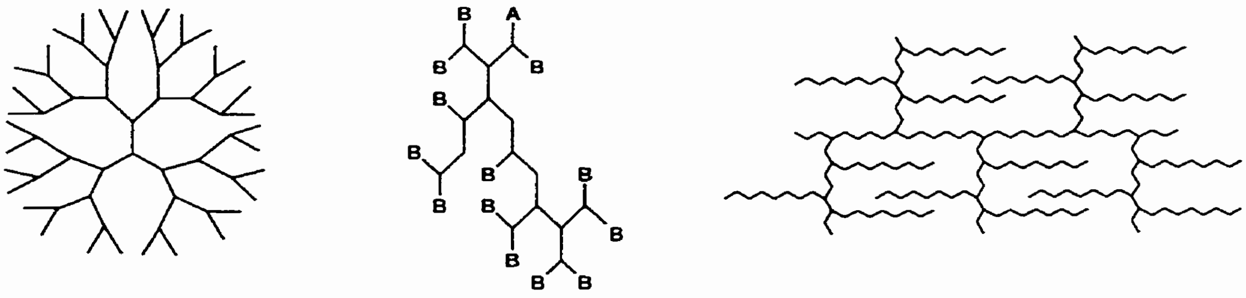
Chapter 2

Introduction

2.1 Dendritic Polymers

There has been considerable interest recently in macromolecules with a highly branched architecture. These molecules comprise a new class of macromolecules known as dendritic polymers. A wide range of synthetic methods has been developed for the synthesis of dendritic polymers of different structures. Dendritic polymers can be divided into three sub-classes according to the degree of structural perfection attained: *i*) dendrimers, *ii*) hyperbranched polymers, and *iii*) dendrigrafts. The architecture of each is compared in Figure 2.1.



(a) **(b)** **(c)**

Figure 2.1 Representative structures of dendritic macromolecules: (a) dendrimer, (b) hyperbranched polymer, and (c) dendrigraft polymer.

The different synthetic methods used to prepare each type of dendritic macromolecules will be compared in this Chapter. Anionic polymerization and grafting techniques, which have been adapted for the synthesis of some dendritic polymers, will also be described. The novelty of selected well-defined, well-characterized dendritic macromolecules with tailored architectures will be emphasized. Emphasis will be placed upon synthetic strategies that incorporate living anionic polymerization techniques.

2.2 Dendrimers, Hyperbranched Polymers, and Dendrigrafts

2.2.1 Dendrimers

Dendrimers are prepared using iterative protection-condensation-deprotection reaction cycles that incorporate AB_n monomers into structural units referred to as dendrons. Assembly of these dendrons can proceed *via* a convergent[1] (core last) or a divergent[2] (core first) synthetic route (compared in Figure 2.2). The general structure of a dendron or dendrimer consists of a focal point (FP) or core, respectively, considered to be the generation zero. The core is the center of symmetry of the molecule and has a characteristic branching functionality. The focal point is a chemical functional group not found elsewhere in the molecule, and is part of a unit that has a characteristic branching functionality. The branching functionality is defined as the number of chemical bonds by which a repeat unit (monomer) is connected to the rest of the molecule. The first layer of multifunctional repeat units (monomers) attached to the focal point or core defines a generation 1 (G1) dendron (I) or dendrimer (II), respectively. When a convergent synthetic approach is used, reaction of G1 dendrons (I) with a multifunctional core yields a generation 2 (G2) dendrimer (III). Alternately, a second addition of branched repeat units (monomers) onto a G1 dendrimer (II) yields a G2 dendrimer (III) in a divergent approach.

The layered growth can continue over several generations where the number of repeat units incorporated for each generation increases exponentially. Likewise, there is an exponential increase in the number of terminal functional groups. The exponential increase in the number of repeat units is paralleled by an exponential increase in molecular weight for successive generations. Dendrimers are, in general, precisely defined molecules with a very low polydispersity index ($M_w/M_n < 1.01$) and an exactly predictable molecular weight. Since *small molecules* are used as building blocks for the construction of these macromolecules, many synthetic cycles (generations) must be completed to obtain macromolecules with a high molecular weight.

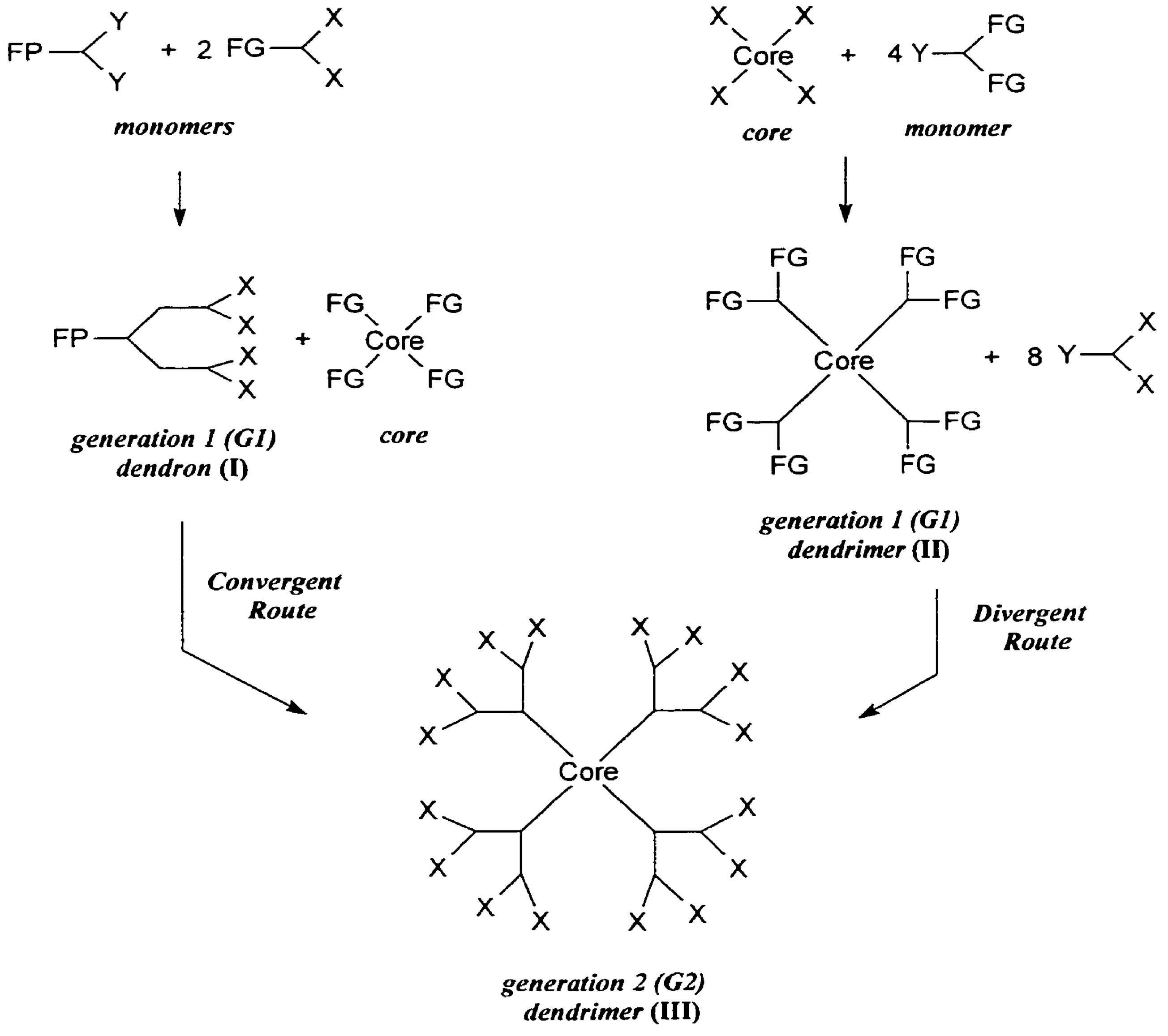


Figure 2.2 Convergent and divergent synthetic routes to dendrimers; FP, FG, X, Y are interconvertible reactive functional groups.

2.2.2 Hyperbranched Polymers

Hyperbranched polymers (Figure 2.1b) are typically derived from controlled one-pot condensation reactions of AB_n monomers to high molecular weights. When *n* is 2 or greater, polymerization of the monomers yields highly branched polymers. The synthesis of a hyperbranched polymer is represented in Figure 2.3. A monomer bearing three reactive (A and B) functional groups undergoes a self-condensation reaction. Functional groups of A-type react with the B-type functional groups, creating a branched structure. Each molecule consists of a single A-type reactive functional group and any number of type-B functional groups. Furthermore, branched molecules consisting of any number of monomer repeat units may react with another branched molecule, creating a much larger molecule.

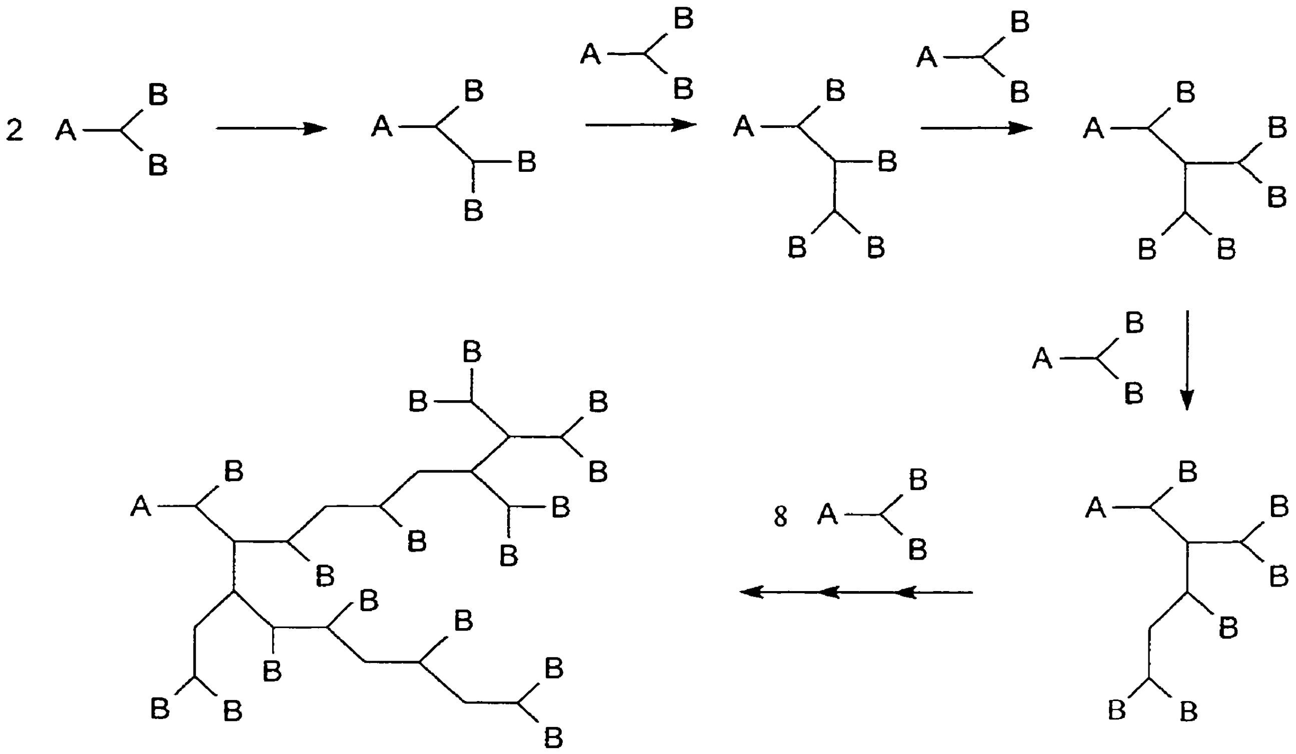


Figure 2.3 General synthetic route to a hyperbranched polymer.

Control over the branching process by this approach is limited, since molecular growth relies on random condensation reactions. Consequently, the molecular weight distribution of hyperbranched polymers tends to approach the Flory most probable distribution, with $M_w/M_n \approx 2$. In contrast to dendrimers, there is a considerable number of structural imperfections associated with hyperbranched polymers. Despite this, unique properties are observed for these molecules due to their compact, globular structure and the large number of terminal functional groups present. The synthesis and physical characteristics of hyperbranched polymers have been reviewed in considerable detail.[3]

2.2.3 Dendrigrafts

Dendrigrafts (or dendritic graft polymers; Figure 2.1c) are obtained from ionic polymerization and grafting schemes and combine features common to dendrimers and to hyperbranched polymers. Dendrigrafts are most commonly synthesized from polymeric chains that are assembled according to a dendrimer-like generation scheme, consisting of functionalization and grafting reaction cycles (Figure 2.4). Grafting polymer chains onto a linear (core) polymer functionalized with randomly distributed grafting sites yields a comb-branched (or generation G0) architecture. Repetition of the functionalization and grafting reactions subsequently leads to higher generation macromolecules (G1, G2, etc.). Since these materials are prepared by linking many *macromolecular* building blocks with the substrate, very high molecular weights can be attained in a few cycles. Different names have been suggested to describe graft polymers with a dendritic structure. The term *comb-burst polymer* was coined by Tomalia *et al.*, in reference to the analogous starburst polymers.[4] Gauthier and Möller used the designation *arborescent graft polymers*, to describe the tree-like architecture of the branched polystyrenes obtained.[5] More recently the terms *dendrigraft*[6] and *polymeric dendrimers*[7] have also been suggested to identify these materials.

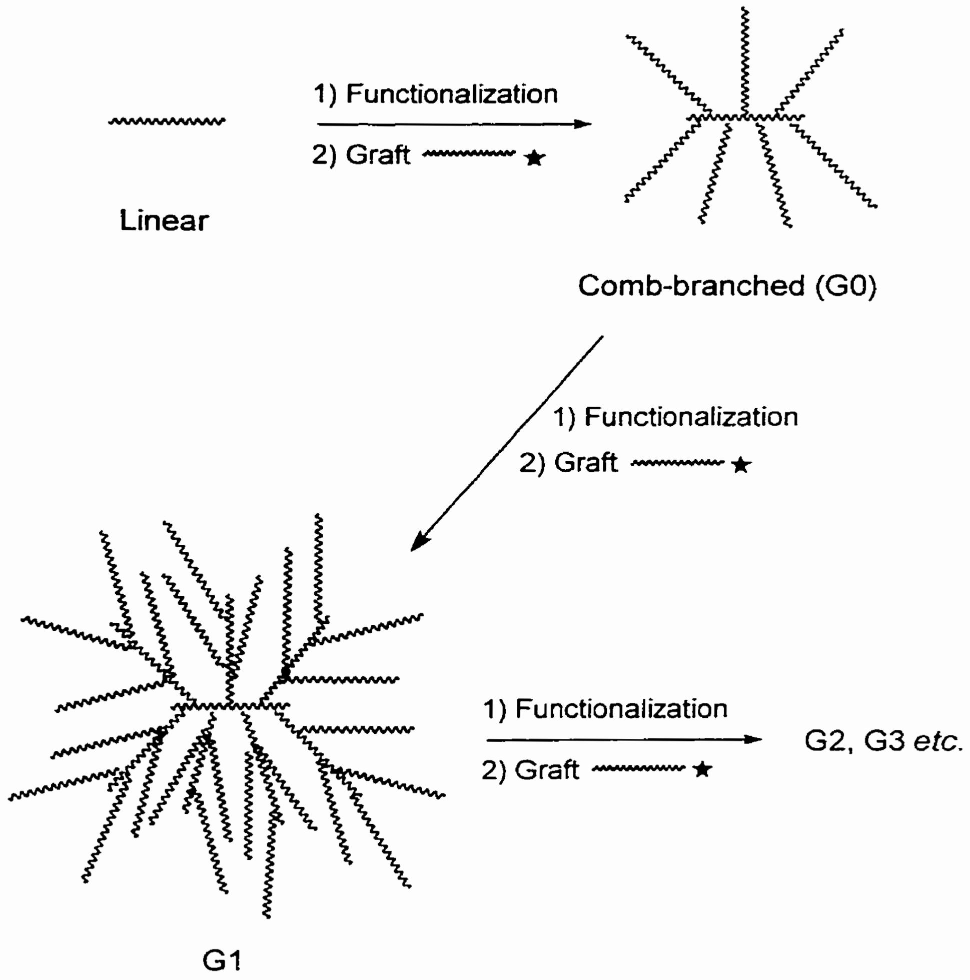


Figure 2.4 Generic synthetic route to comb-burst and arborescent polymers.

The architecture of dendrigraft polymers resembles that of dendrimers, since both systems consist of a core, cascade-branched units forming the interior of the molecule, and multiple chain termini. In dendrimers, the branching process leading to the next generation occurs strictly at the periphery (chain ends) of the molecule. In dendrigraft polymers, the grafting sites are distributed randomly along the chains of the substrate. This variation in the position of the branching points on the backbone leads to a 'diffuse layer growth' mechanism.[8] Nevertheless, the method still provides extensive control over the size, shape, flexibility, and chemical functionality (critical molecular design parameters) of the molecules.[1]

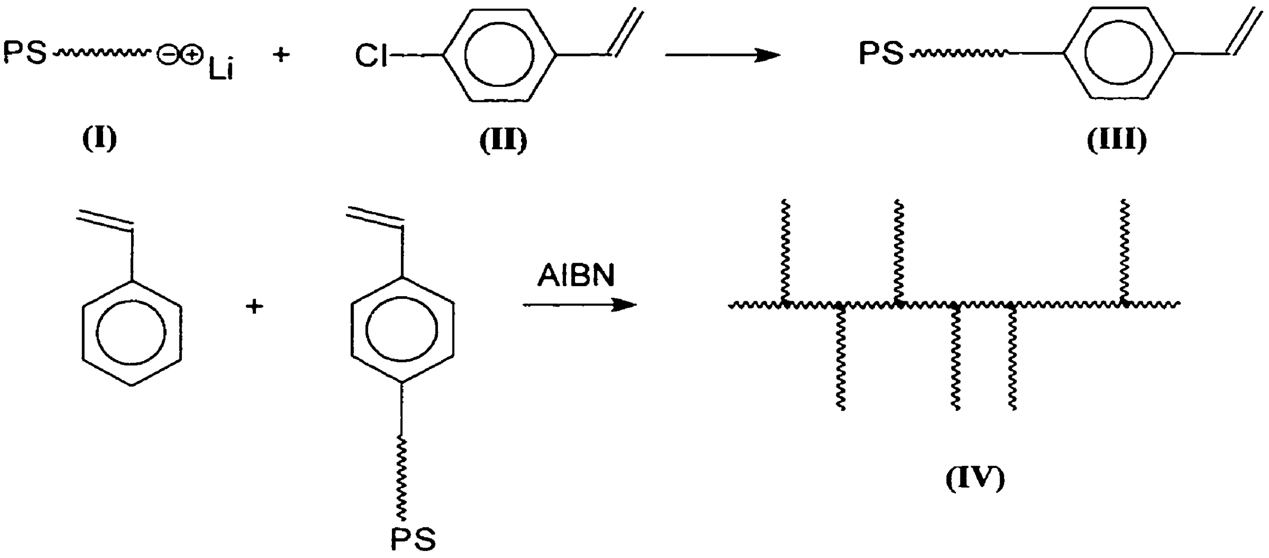
Many branched polymers with structures analogous to dendrimers or hyperbranched polymers have been prepared. In these cases, the molecules are assembled from polymer chains rather than small molecules, yielding macromolecules with a larger overall size and significantly higher molecular weights than dendrimers or hyperbranched polymers. The grafting techniques and some important considerations in the preparation of these materials are reviewed in the following section, followed by specific examples of synthetic methods.

2.3 Synthetic Routes to Graft Polymers

The preparation of graft polymers with a dendritic structure has been achieved by three different methods, generally described as *grafting through*, *grafting from*, and *grafting onto*. These synthetic routes have been adapted from techniques mostly reported to prepare comb-branched polymers. Since the basic synthetic approach and experimental considerations for conventional graft polymers also apply to the synthesis of dendritic graft polymers, a brief discussion of these methods is warranted.

2.3.1 *Grafting Through*

A *grafting through* approach to the preparation of graft polymers consists of two steps: Firstly, a linear polymer bearing a terminal vinyl group is prepared. This species is referred to as a macromonomer. The second step consists of the copolymerization of the macromonomer with a suitable comonomer, generally by radical polymerization. Numerous examples of comb-branched graft polymers prepared by this approach have been reported.[9] For example, the synthesis of comb-branched polystyrenes[10] can be achieved by first preparing polystyrene macromonomers (III) by deactivation of polystyryllithium (I) with *p*-chlorovinylbenzene (II) as shown in Scheme 2.1. The subsequent free-radical copolymerization of the macromonomer with styrene yields the comb-branched graft polymer (IV).

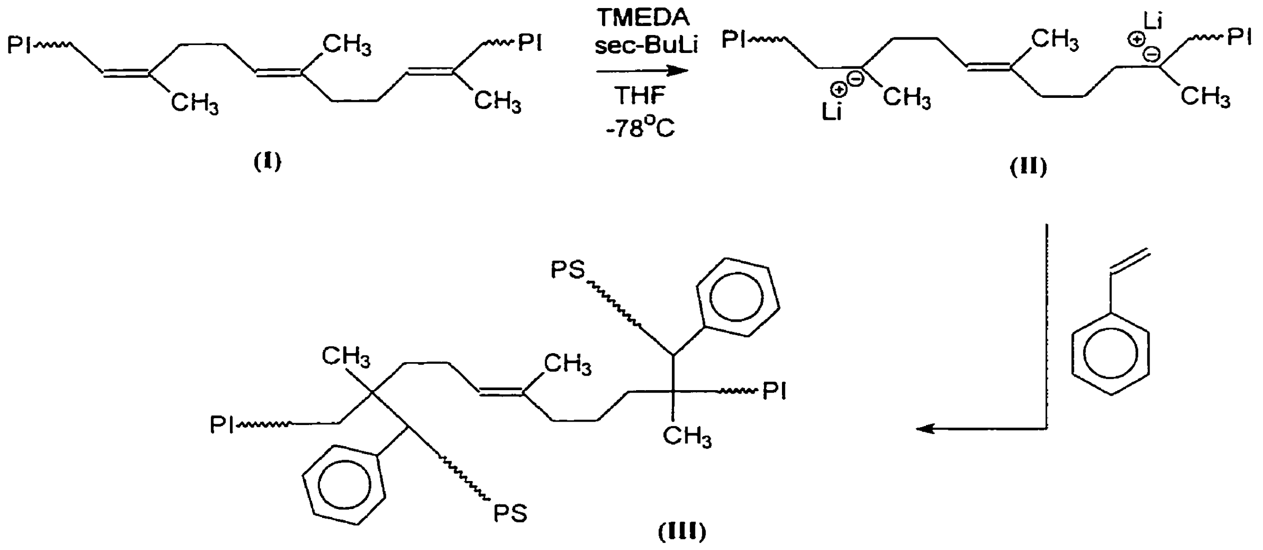


Scheme 2.1 Synthesis of comb-branched polystyrenes using a *grafting through* route.

Living polymerization techniques are ideally suited to the preparation of well-defined macromonomers, since they allow precise control over the molecular weight and chain-end functionality. The most common methods to incorporate a polymerizable moiety at the chain end are functional initiation or reactive termination. Since the macromonomer is prepared separately, it can be fully characterized. However, radical copolymerization of the macromonomer leading to the formation of the backbone results in a random distribution of the grafts.

2.3.2 *Grafting From*

In a *grafting from* scheme, a polymeric substrate is first functionalized to bear a number of accessible reactive groups. Activation of these groups to provide initiating sites, followed by addition of a monomer, results in the growth of side chains from the backbone polymer. For example, the synthesis of polyisoprene-*graft*-polystyrene[11] (PI-*g*-PS) is outlined in Scheme 2.2. Anionic centers are generated along a polyisoprene backbone (I) using *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and *sec*-butyllithium (sBuLi). From these reactive sites, the polymerization of styrene monomer may be initiated, yielding a graft copolymer (III).

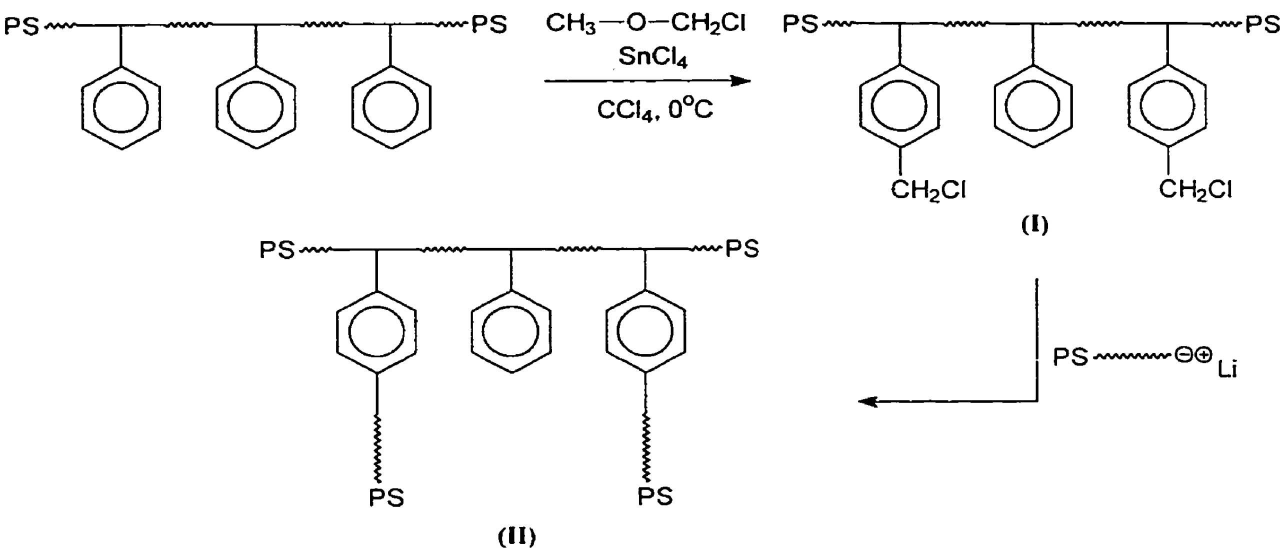


Scheme 2.2 Synthesis of polyisoprene-*graft*-polystyrene using a *grafting from* method

A number of synthetic limitations may be encountered when using a *grafting from* technique. Commonly, the grafted side chains are generated by ionic polymerization of a suitable monomer. However, it may be difficult to obtain a macromolecule with randomly distributed reactive sites. Solubility is also limited for polymeric substrates bearing multiple charges, leading to heterogeneous reaction conditions and a broad molecular weight distribution. In spite of these problems, many comb-branched polymers have been prepared by this approach.[12]

2.3.3 *Grafting Onto*

The *grafting onto* method is particularly well-suited (and most commonly used) for the preparation of graft polymers with a tailored structure and topology. It relies on the introduction of reactive (grafting) sites on a polymeric substrate, followed by coupling with 'living' polymer chains. For example, comb-branched polystyrenes[13] (II) have been prepared by first introducing chloromethyl groups along a polystyrene backbone (I) followed by coupling with polystyryllithium (Scheme 2.3). Using this approach the grafted polymer chains are, in general, randomly distributed along the backbone of the substrate polymer. The side chains and graft polymer can be characterized independently. By determining the molecular weight of the substrate, the side chains, and the graft polymer, the number of grafts introduced is easily calculated. This enables full characterization of the structure of the polymers obtained.



Scheme 2.3 Synthesis of comb-branched polystyrene using a *grafting onto* method

A synthetic method based on coupling reactions must meet a number of requirements to yield well-defined graft polymers. Ideally, both the grafted polymer chains and substrate polymer must have a narrow molecular weight distribution. If living polymerization techniques are employed, precise control over the molecular weight and the molecular weight distribution is possible. The living (cationic or anionic) polymeric ions must possess sufficient reactivity for the grafting reaction to proceed in high yield but without side reactions. It may be necessary to incorporate reactive functional (grafting) sites along the backbone of the substrate polymer by chemical modification. The modification must proceed without inducing cross-link formation, and is often accomplished using an addition reaction or by conversion of existing functional sites into reactive moieties.

There are numerous examples of comb-branched polymers prepared using a *grafting onto* approach. The most commonly used procedure involves the partial, random chloromethylation of polystyrene and subsequent reaction with living polymeric anions.

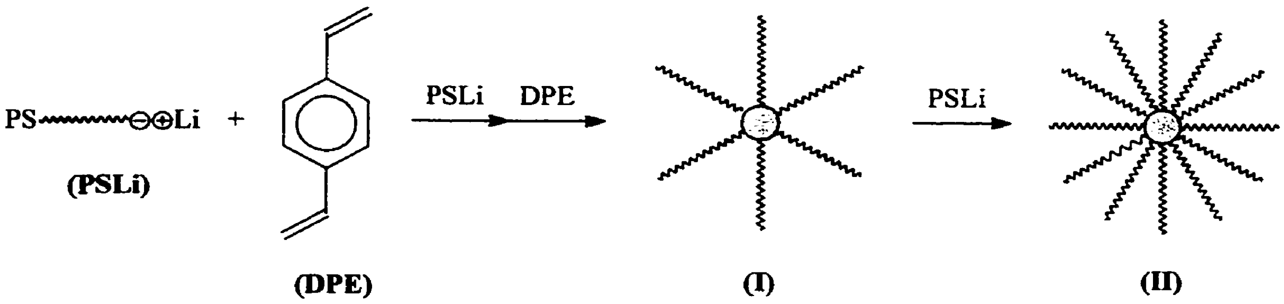
Comb-branched polystyrenes[13,14] and graft copolymers derived from a randomly chloromethylated polystyrene backbone grafted with polyethylene oxide,[15,16] polyisoprene,[17] poly(2-vinylpyridine),[18] and poly(4-vinylpyridine)[19] side chains have been prepared by this method. In these examples, the chloromethyl functionality has sufficient electron affinity to favour the coupling reaction with the macroanions over side reactions. When less nucleophilic macroanions are considered, more reactive functional groups must be introduced along the substrate polymer backbone. Comb-branched graft polymers derived from a randomly bromomethylated polystyrene substrate grafted with poly(2-vinylpyridine), poly(*tert*-butyl acrylate) and poly(*tert*-butyl methacrylate) side chains have been reported.[20] Although the grafted chains are randomly distributed along the polystyrene backbone in all cases, these graft copolymers are well defined with respect to the molecular weight of the backbone, the branches, and the average number of grafted side chains. Consequently, a narrow molecular weight distribution is obtained for the graft polymers. Other examples of reactive functional groups suitable for ionic grafting include chlorosilanes, esters, nitriles, pyridines, and anhydrides.[21]

2.4 Synthetic Routes to Star-branched Polymers

Star-branched polymers, defined as branched macromolecules with three or more chain termini and a single branching point, represent the simplest example of a well-defined branched structure. Since each molecule consists of more than two terminal groups and in some cases a large number of terminal groups, star-branched polymers are related to dendritic polymers. The synthetic routes to star-branched polymers resemble the methods used for the synthesis of both dendrimers and graft polymers. For example, the synthesis of star-branched polymers can be achieved using a 'core-first' synthetic route analogous to a *grafting from* approach, by an 'arm-first' route analogous to a *grafting onto* approach, or a *grafting through* approach consisting of block copolymerization of pre-formed 'arms' and a bifunctional monomer. Similarly, the 'core-first' and 'arm-first' methods are analogous to the divergent and convergent methods, respectively used for preparing dendrimers.

2.4.1 *Grafting Through*

Using a *grafting through* approach shown in Scheme 2.4, the copolymerization of polystyryllithium macroanions with a suitable divinyl monomer such as divinylbenzene (DVB) or ethylene dimethacrylate has been reported for the preparation of highly branched polymers with a structure most closely resembling star-branched polymers.[22] The rate of reaction of polystyryllithium with DVB and the rate of homopolymerization of DVB are comparable. However, the rate of addition of polystyryllithium to the residual double bond of DVB is one-tenth of the rate of addition to the first double bond. Consequently, polystyrylithium macroanions initiate the formation of small, tightly cross-linked nodules consisting of a homopolymerized core of DVB from which polystyrene arms emanate (I) (Scheme 2.4). As the DVB is consumed in the reaction, additional arms are then formed through the reaction of polystyrylithium with accessible double bonds within the DVB core (II). Since anionic polymerization techniques are used to generate the polystyrene arms, the arm length can be pre-determined. The average number of arms and the size of the DVB nodules can be varied by adjusting the quantity of DVB used relative to the amount of polystyryllithium macroanions and the overall concentration of both species, respectively.[23] This technique has also been applied to the synthesis of star-branched polybutadienes. The reaction of polybutadienyllithium with DVB is slow relative to polystyryllithium, and accordingly the size of the nodules and the number of arms are more difficult to control.[24] Most recently, this approach has been used to prepare a variety of multi-arm star copolymers with chemically different arms, which are designated as *miktoarm* star polymers.[25]



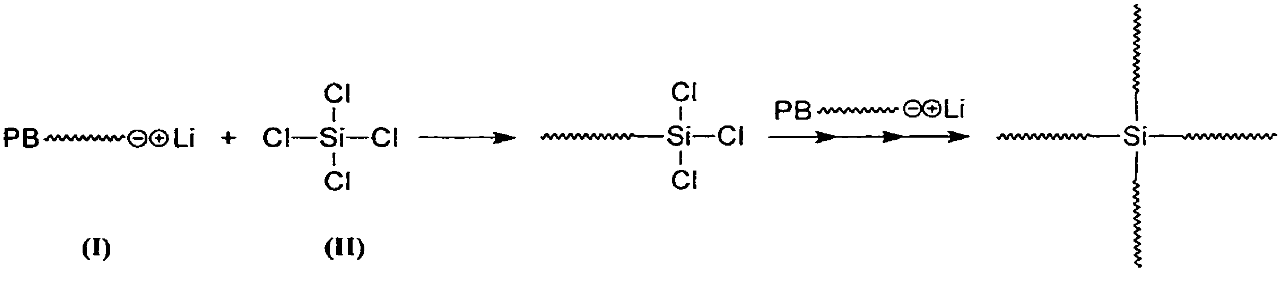
Scheme 2.4 Synthesis of star-branched polystyrene using a *grafting through* approach

2.4.2 "Core-first" Approach

The synthesis of star-branched polymers using a *grafting from* approach requires a multifunctional initiator that simultaneously initiates the polymerization of three or more arms. However, the same limitations encountered for the syntheses of graft polymers are also encountered for star-branched polymers: Multifunctional anionic initiators have limited solubility in solvents suitable for anionic polymerization. This technique is further limited by the inability to precisely control and independently measure the molecular weight of the arms.

2.4.3 "Arms-first" Approach

The most effective and widely used route to well-defined star-branched polymers is based on the 'arms-first' *grafting onto* approach. Similarly to graft polymers, the *grafting onto* route provides the ability to pre-determine the arm length and number of arms. Star-branched polymers are readily prepared from the reaction of living polymeric macroanions (the "arms") and a multifunctional linking agent serving as the "core". The synthesis of a four-armed star polybutadiene[26] is represented in Scheme 2.5. Polybutadienyllithium (I) is coupled to tetrachlorosilane (II), which serves as a tetrafunctional linking agent. Repeated coupling of polybutadienyllithium yields the four-arm star product (III). Well-defined star-branched polymers with up to 128 arms have been prepared using an 'arm-first' approach.[27]



(I) (II) (III)

Scheme 2.5 Synthesis of star-branched polybutadiene using a *grafting onto* approach

The majority of star-branched polymers reported in the literature have been prepared using ionic polymerization techniques. The highly reactive "arms" can be reacted almost quantitatively with the multifunctional core, leading to well-defined star-branched macromolecules with a completely characterized structure. The pioneering synthetic work of Bywater[28] and more recent examples including star-branched polymers with arms of chemically different compositions have been extensively reviewed.[29]

2.5 Synthesis and Properties of Dendritic Graft Polymers with Tailored Structures

There are numerous examples of dendritic graft polymers that have been prepared using adaptations of the classical *grafting through*, *grafting from*, and *grafting onto* methodologies developed to prepare randomly grafted and star-branched polymers. Certain methods are analogous to the divergent and convergent approaches to the synthesis of dendrimers, while others resemble the synthesis of hyperbranched polymers. In all cases, macromolecules rather than small molecules serve as structural units. Because of this approach, dendritic graft polymers comprise a unique class of materials. Since different methodologies can be adapted to prepare macromolecules with similar structures, the examples discussed in the following sections are classified according to the location of the branching points within the molecule. Specifically, the branching junctions can be located at terminal sites on the penultimate generation, or at sites randomly distributed throughout the molecule.

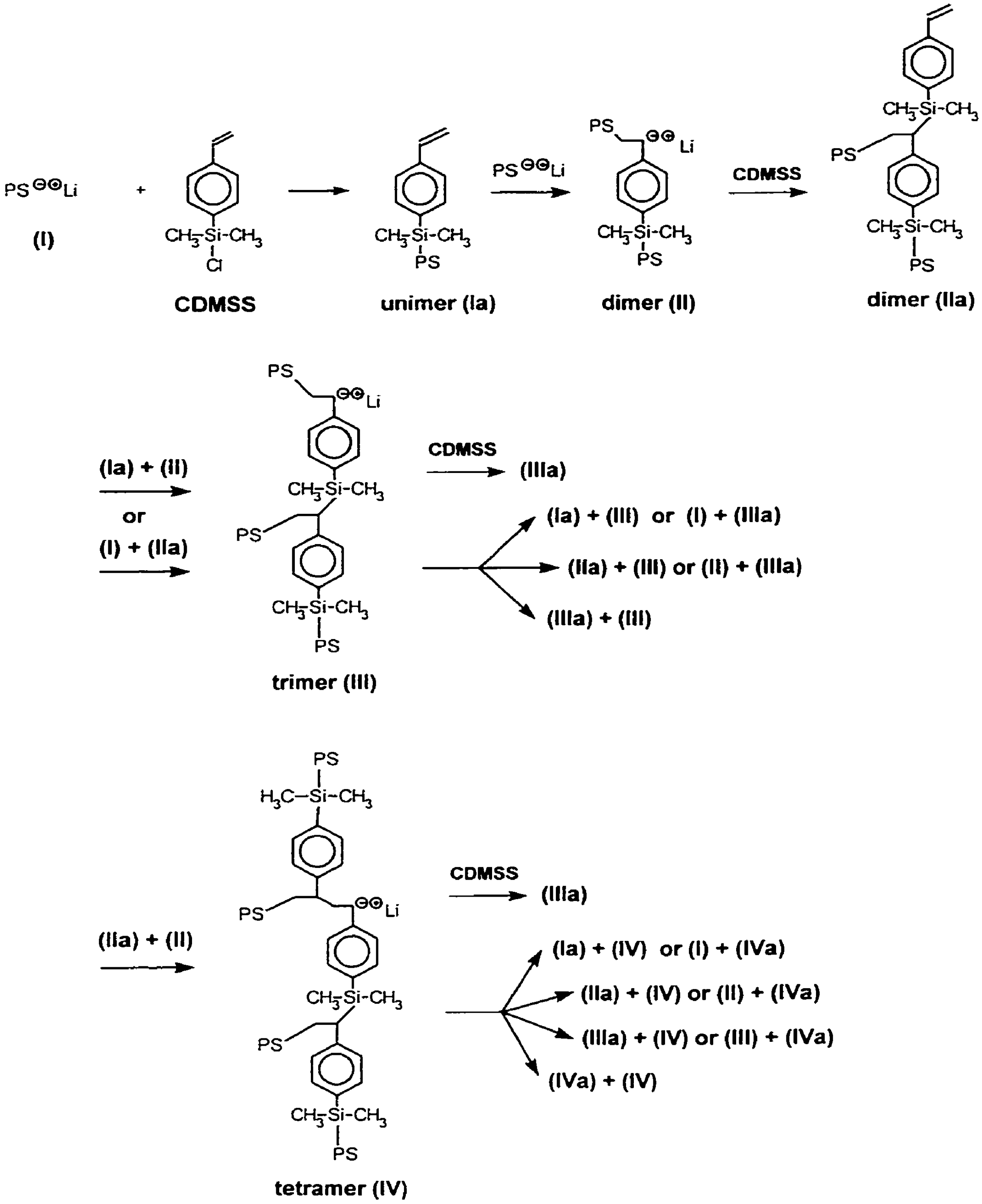
2.5.1 Convergent (Self-Branching) Anionic Polymerization

An interesting approach to the synthesis of highly branched polymers, analogous to the convergent hyperbranched polymer syntheses, uses self-branching condensation reactions of macroanions in a *grafting through* scheme. The method has been suggested by Knauss *et al.* for the synthesis of dendritic polystyrenes[30,31] and polyisoprenes[32] of high molecular weight. An interesting feature of self-branching anionic polymerization is that it is a one-pot reaction that yields graft polymers with narrow molecular weight distributions in some cases.

A procedure used in the self-branching polymerization reaction for the preparation of dendritic polystyrenes is outlined in Scheme 2.6. Oligomeric polystyryllithium (PS) chains are reacted with a small molecule coupling agent such as 4-(chlorodimethylsilyl)styrene

(CDMSS), containing a polymerizable double bond as well as a reactive moiety that preferentially reacts with the oligomer. Slow addition of the coupling agent to a solution of living PS oligomers (unimer I) leads to the formation of some CDMSS-capped chains (unimer Ia), that subsequently react again with the PS oligomers to give living dimers (II, living dendrons composed of two PS oligomers). Continued addition of the coupling agent results in capping of a portion of the living dimers with CDMSS (dimer IIa). Capped (unsaturated) and uncapped (living) species may subsequently react with each other and with CDMSS to give higher generation products of increasing branching functionatities.

At each step of the reaction, every molecule carries either a single anionic reactive site or a vinyl group at the focal point. After a few coupling cycles or generations, the accessibility of that reactive site is expected to decrease, ultimately limiting the growth of the molecules. This problem can be minimized by adding styrene monomer along with the coupling agent, to increase spacing between coupling points within the structure. This modified approach enables the formation of dendritic molecules up to the sixth (average) generation, using a CDMSS to styrene ratio of 1:10 in the coupling reaction (Table 2.1).[33] The average generation attained in a reaction is determined by the amount of coupling agent used, as well as by the amount of styrene monomer spacer added. The apparent molecular weight distribution obtained in these reactions remains relatively narrow ($M_w/M_n = 1.14\text{-}1.66$), presumably because of the role of steric crowding in limiting the growth of the molecules. The narrow molecular weight distributions obtained were rationalized in terms of a kinetic model relating steric crowding effects to the individual rate constants of the coupling reactions involved.[30]



Scheme 2.6 Convergent self-branching anionic polymerization method for the preparation of dendritic polystyrenes.

The variation in intrinsic viscosity with molecular weight was examined for a series of dendrigraft polystyrenes obtained by varying the ratio of styrene monomer to coupling agent in the grafting reaction.[30] The polymers are characterized by lower intrinsic viscosity values relative to linear polystyrenes of comparable molecular weight.

Table 2.1 Characteristics of Dendritic Polystyrenes Obtained by the Self-Convergent Grafting Method (Adapted from Reference 33)

Initial Chain M_n $^{a)}$	$M_w^{LS\ a)}/10^3$	M_w/M_n $^{a)}$	Average Generation
620	117	1.24	5.8
950	106	1.22	5.4
4 779	131	1.21	4.1
9 114	222	2.15	3.3
17 570	225	1.16	3.3
35 490	282	1.25	2.6
57 660	433	1.18	2.6

a) Determined by SEC analysis using a multi-angle laser light scattering detector

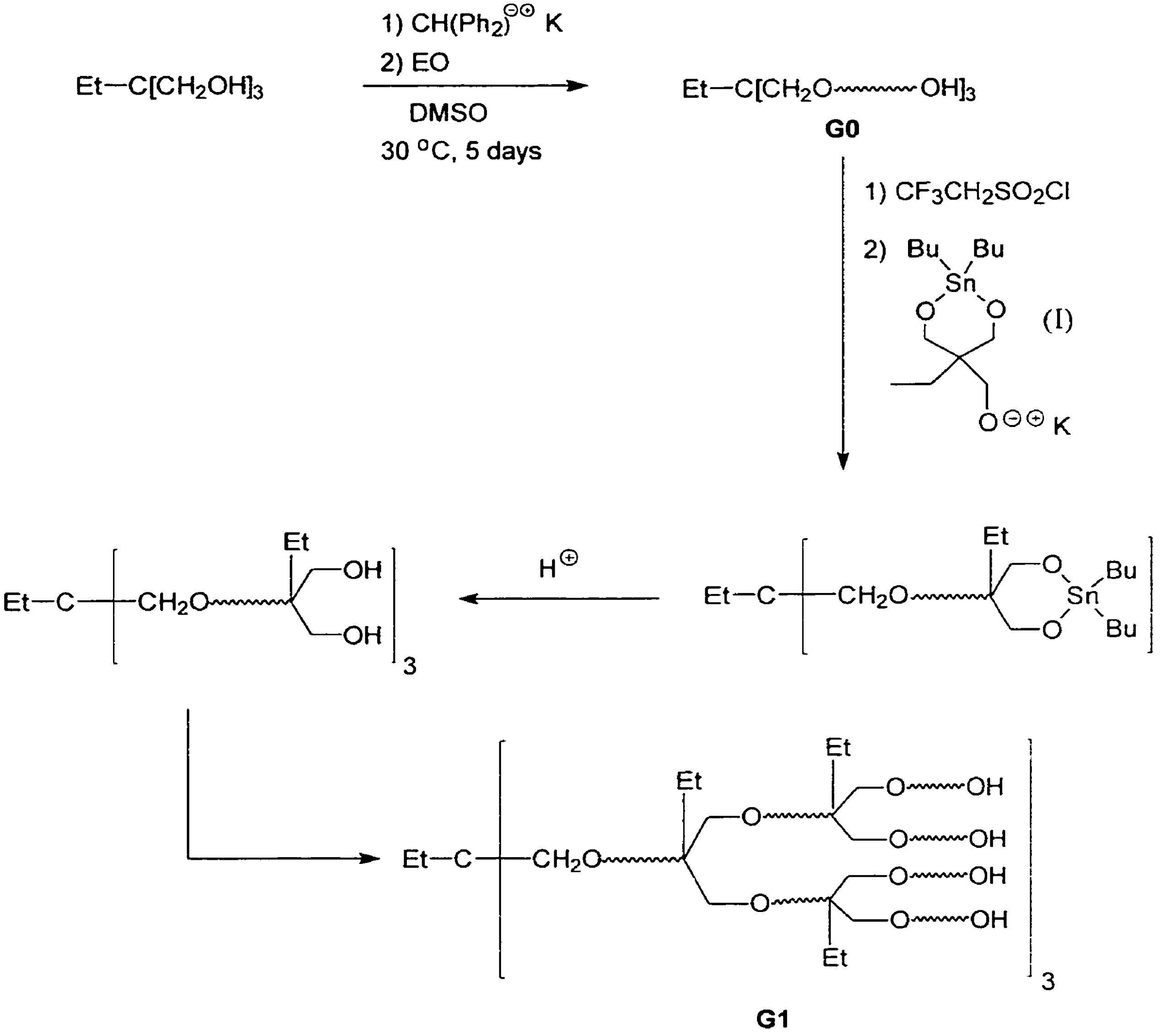
The approach outlined in Scheme 2.6 was also directly applied to the synthesis of dendritic polyisoprenes, by substitution of isoprene for the styrene monomer.[31] Two coupling agents were examined in this case, namely CDMSS and 2-chlorodimethylsilyl-1,3-butadiene. Other interesting architectures have been prepared based on these reactive dendron structures. For example, the focal anion present on the molecules (after full consumption of the coupling agent) can be used to initiate the polymerization of monomers such as styrene. The synthesis of more complex structures such as linear-dendritic hybrids, or polystyrene stars with dendritic polystyrene end blocks should, therefore, also be possible.

2.5.2 Dendritic Polymers Prepared Using a Terminal Grafting Approach

2.5.2.1 Dendritic Poly(ethylene oxide) by Terminal Grafting

A *grafting from* approach has been developed for the generation of poly(ethylene oxide)-based graft polymers with a dendritic structure.[34] New polymer chains of increasing branching functionality are successively generated from the previous generation. For example, a triarm star-branched polymer with living (PEO) arms is first prepared from a trifunctional alcohol initiator, by titration with diphenylmethylpotassium and addition of purified ethylene oxide (EO), as shown in Scheme 2.7. The polymer is then 'arborized' to a hexafunctional substrate by treatment with trifluoroethanesulfonyl chloride and a cyclic tin-based ketal derivative (I), bearing two protected hydroxyl groups in a six-membered ring. After hydrolysis under mildly acidic conditions, the hexafunctional triarm polymer is again used to initiate the polymerization of ethylene oxide. Repetition of the arborization and ethylene oxide polymerization reactions can be used to synthesize dendritic PEO structures containing up to 12 PEO chains (generation G2).

Characterization results have been reported for different dendritic poly(ethylene oxide)s of generation G1, prepared by adding various amounts of ethylene oxide to the initiator core in the side chain growth reaction (Table 2.2). Because of the *grafting from* method used for their synthesis, the molecular weight of the PEO branches cannot be accurately determined, and hence it is impossible to confirm that the branches grown during each cycle are of uniform length. Nonetheless, the apparent molecular weight distribution (based on linear PEO calibration standards) is relatively narrow for the generations characterized ($M_w/M_n = 1.1-1.3$). Comparison of the molecular weight data obtained from light scattering and SEC indicates that the SEC values are significantly underestimated, as observed for other dendrigraft polymers. Comparison of the hydrodynamic volume ratio for the branched polymers and linear PEO samples of comparable molecular weight gives a ratio close to $V_{H,dend}/V_{H,lin} \approx 0.5$, indicative of the compact, highly branched structures expected for these materials.



Scheme 2.7 Synthesis of dendritic poly(ethylene oxide)s by terminal grafting.

Table 2.2 Characteristics of G1 Dendritic Poly(ethylene oxides) Obtained by Terminal Grafting Method (Adapted from Reference 34)

$M_w^{LS\ a)}$	$M_w^{\ b)}$ (SEC)	$M_w/M_n^{\ b)}$	$V_{H,dend}/V_{H,lin}$
9 400	4 200	1.17	0.51
14 000	6 500	1.14	0.49
21 000	10 000	1.10	0.47
28 000	11 300	1.30	0.48

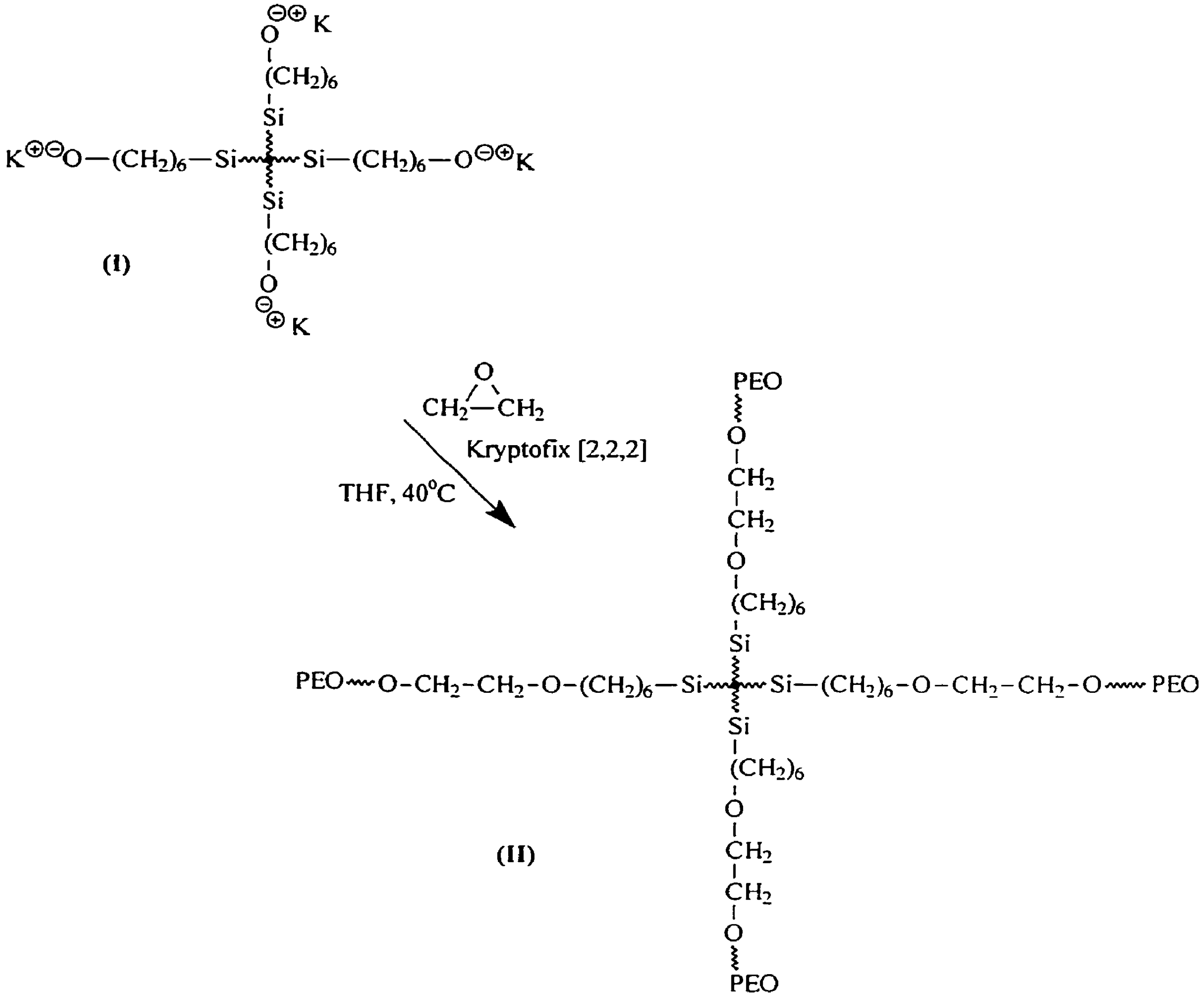
a) Absolute M_w for the graft polymers from light scattering
b) Apparent values for the graft polymers, from SEC analysis

2.5.2.2 Dendritic Polystyrene-*graft*-Poly(ethylene oxide) Copolymers by Terminal Grafting

Using a variation of the method described in Scheme 2.7, dendritic block copolymers consisting of PS and PEO blocks can also be prepared.[35] In this case a hexafunctional compound, hexa[4-(1-chloroethyl)phenethyl]benzene is activated with $SnCl_4$ to initiate the living cationic polymerization of styrene. Termination of the six PS chains using the cyclic tin-based ketal derivative of Scheme 2.7 (I), followed by hydrolysis under mildly acidic conditions, yields a six-arm star-branched PS with 12 reactive hydroxyl groups at the chain ends. Anionic polymerization of EO after titration of the hydroxyl groups with diphenylmethylpotassium yields a G1 dendritic PS-PEO copolymer with 12 PEO outer arms.

2.5.2.3 Star Poly(ethylene oxide)s by *Grafting From* Carbosilane Dendrimers

Star-branched poly(ethylene oxide)s with 4, 8, and 16 arms have been prepared from hydroxyl functionalized carbosilane dendrimers of generation zero (G0), one (G1), and two (G2), respectively.[36] Using a *grafting from* approach, poly(ethylene oxide) (PEO) arms are grown anionically from reactive multifunctional dendritic cores (I). The low inherent solubility of the multifunctional dendrimer cores in tetrahydrofuran (THF) is overcome by adding Kryptofix® [2,2,2], a cryptate that efficiently solvates the potassium counterions. Titration of the hydroxyl-functionalized dendritic core with potassium naphthalene followed by addition of ethylene oxide (EO) yields a 4-arm star PEO (II), as shown in Scheme 2.8.



Scheme 2.8 Synthesis of 4-arm star PEO using a *grafting from* approach

Characterization data have been reported for star PEO samples with 4, 8 and 16 arms and different PEO arm lengths (Table 2.3). In all cases, the apparent molecular weight distribution of the star polymers is narrow ($M_w/M_n \leq 1.09$). However, the *grafting from* method used prevents direct characterization of the arm molecular weight. The intrinsic viscosity of the various star polymers and linear PEO samples of comparable molecular weight was measured in water at 35°C. The data obtained are displayed in a double logarithmic plot of the intrinsic viscosity (η) vs. molecular weight (M_w) (Figure 2.5). The data is consistent with the compact, branched structure expected for these star polymers: The intrinsic viscosity of the star PEO samples is considerably lower than for linear PEO samples. Secondly, the intrinsic viscosity of the star polymers decreases as the number of arms increases. For star polymers of equivalent molecular weight, as the number of arms increases, the average molecular weight of the arms is proportionally lower and the overall structure is more compact.

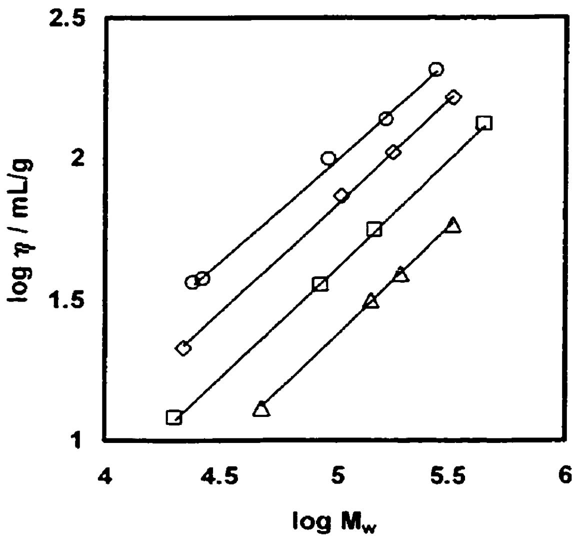


Figure 2.5 Intrinsic viscosity in water at 35°C of star PEO prepared by grafting from carbosilane dendrimers. Symbols: Linear, ○; 4-arm, ◇; 8-arm □; and 16-arm star PEO, △.

Table 2.3 Characteristics of Star Poly(ethylene oxides) Obtained by *Grafting From* Method (Adapted from Reference 36)

Sample Description	$M_w^{LS\ a)}$	$M_w/M_n^{\ b)}$
4-arm star PEO		
PEO14	21 900	1.06
PEO16	105 000	1.07
PEO17	178 000	1.06
PEO18	328 000	1.09
8-arm star PEO		
BC8PEO2k	20 400	1.08
BC8PEO8k	85 100	1.07
BC8PEO25k	150 000	1.06
BC8PEO60k	457 000	1.08
16-arm star PEO		
BC16PEO2kF1	48 000	1.06
BC16PEO2kF1	142 000	1.07
BC16PEO2kF1	192 000	1.09
BC16PEO2kF1	326 000	1.07

a) Absolute M_w for the graft polymers from static light scattering
b) Apparent values for the graft polymers, from SEC analysis

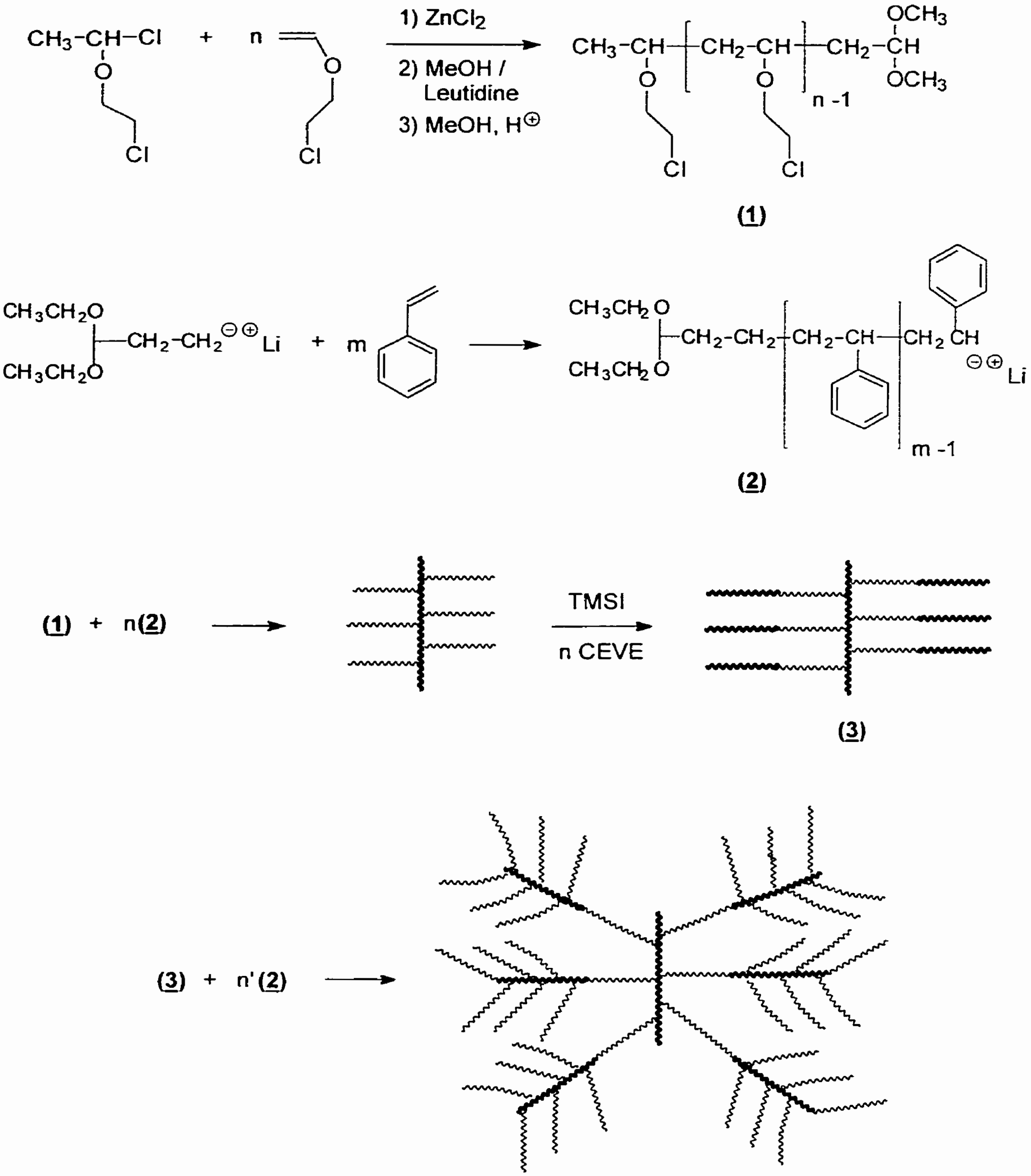
2.5.2.4 Dendritic Polystyrenes by *Grafting Onto* Poly(chloroethyl vinyl ether)

The synthesis of dendrigraft polymers based on poly(chloroethyl vinyl ether) (PCVE) and polystyrene macromolecular building blocks was recently reported by Deffieux and Schappacher.[37] The synthetic path used for the preparation of these compounds is shown in Scheme 2.9. Living cationic polymerization is first used to prepare a linear PCVE backbone. The anionic polymerization of styrene is then initiated with a lithioacetal compound, to generate polystyryllithium with a protected hydroxyl group at the chain end (RO-PSLi).

Coupling of the RO-PSLi side chains with the PCVE backbone generates a comb-branched structure. Subsequent treatment of the acetal chain termini with trimethylsilyl iodide (TMSI) yields α-iodoether groups, that can be activated with zinc chloride to initiate the cationic polymerization of a new aliquot of chloroethyl vinyl ether. The resulting comb-branched (G0) structure with PS-*block*-PCVE side chains can be subjected to further grafting with RO-PSLi, and so on, to prepare the higher generation polymers.

The architecture obtained from the grafting process described has branching points located only in the terminal (outer) portion of the side chains on the substrate, rather than randomly distributed along the backbone polymer. While the layer structure obtained by this method is not expected to be as well defined as in the case of terminal grafting, the increase in molecular weight for each generation is higher, since a large number of chains can be grafted in a single reaction. Variations in the architecture of the graft polymers are possible by controlling the length of the PCEVE and PS blocks used in the synthesis. The length of the PS block influences the overall size of the molecules whereas the branching multiplicity of the side chains is primarily determined by the length of the PCEVE blocks.

The synthetic route described was used for the synthesis of three first-generation dendritic copolymers with a molecular weight reaching 10^7 and a narrow apparent molecular weight distribution (M_w/M_n = 1.05-1.33, Table 2.4). The branched polymers have a radius of gyration (R_g) 5-10 times smaller than linear polystyrene samples of comparable molecular weight. The molecular weight of the products determined by light scattering (M_w^{LS}) is in good agreement with the theoretical M_n calculated for complete consumption of the chloroethyl vinyl ether units in the grafting reaction.



Scheme 2.9 Synthesis of dendritic polystyrenes by grafting onto poly(chloroethyl vinyl ether)-*graft*-polystyrene.

Table 2.4 Characteristics of $PCEVE_1$-*g*-(PS_1-b-$PCEVE_2$-g-PS_2) Copolymers (Adapted from Reference 37)

$PCEVE_1$ DP_n [a]	PS_1 DP_n [a]	$PCEVE_2$ DP_n [a]	PS_2 DP_n [a]	M_n^{th} $/10^3$ [b]	M_n $/10^3$ [a]	M_w^{LS} $/10^3$	M_w/M_n [a]	R_g (nm)
26	51	82	52	11 606	460	9 500	1.06	25
26	146	50	52	7 300	----	5 700	1.33	30
60	30	55	37	13 250	500	10 350	1.05	28

a) From SEC analysis using linear PS calibration
b) Theoretical molecular weight based on the PS and PCEVE block lengths

2.5.3 Grafted Polymers with Randomly Distributed Branching Points

The examples discussed so far describe polymer architectures based on substrates with grafting sites located strictly at the end of the side chains (in analogy to dendrimer syntheses), or at least preferentially located towards the outer end of the side chains. Examples of systems that have randomly distributed grafting sites include comb-burst and arborescent graft polymers. The general synthetic route to comb-burst and arborescent polymers was described in Figure 2.4. Reactive sites are first randomly introduced along a linear polymer chain. Living polymeric chains are then coupled with the reactive sites, to give a comb-branched (G0) graft polymer. The introduction of functional groups on the comb-branched structure, followed by grafting, yields a G1 structure. Cycles of functional group introduction and grafting leads to G2 and higher generations. One consequence of this approach is that the position of the branching points in the molecule fluctuates, resulting in a 'diffuse layer growth' mechanism, or partial interpenetration of the layers added in each grafting reaction.[8] A number of examples of the synthesis of these types of dendritic polymers are described in the following sections.

2.5.3.1 Comb-burst Polymers

The synthesis of *comb-burst* poly(ethylenimine)-*graft*-poly(2-ethyl-2-oxazoline) (PEI-PEOX) copolymers and poly(ethylenimine) (PEI) homopolymers was reported by Tomalia *et al.* in 1991.[4] The synthetic scheme used involves successive grafting reactions of living poly(2-ethyl-2-oxazoline) (PEOX) oligomers onto PEI substrates. PEOX is prepared by cationic polymerization, to generate side chains with a narrow molecular weight distribution and reactive chain termini. A comb-branched or G0 PEI-PEOX graft copolymer is first prepared by grafting PEOX oligomers onto a linear PEI core (Scheme 2.10). Subsequent deprotection of the oxazoline groups under acidic conditions yields the G0 PEI homopolymer. The secondary amine functionalities generated along the side chains of the comb polymer can serve as coupling sites for further grafting of PEOX chains in the preparation of generation G1. The synthesis of PEI comb-burst polymers of higher generations is achieved by repetition of the deprotection and grafting cycles.

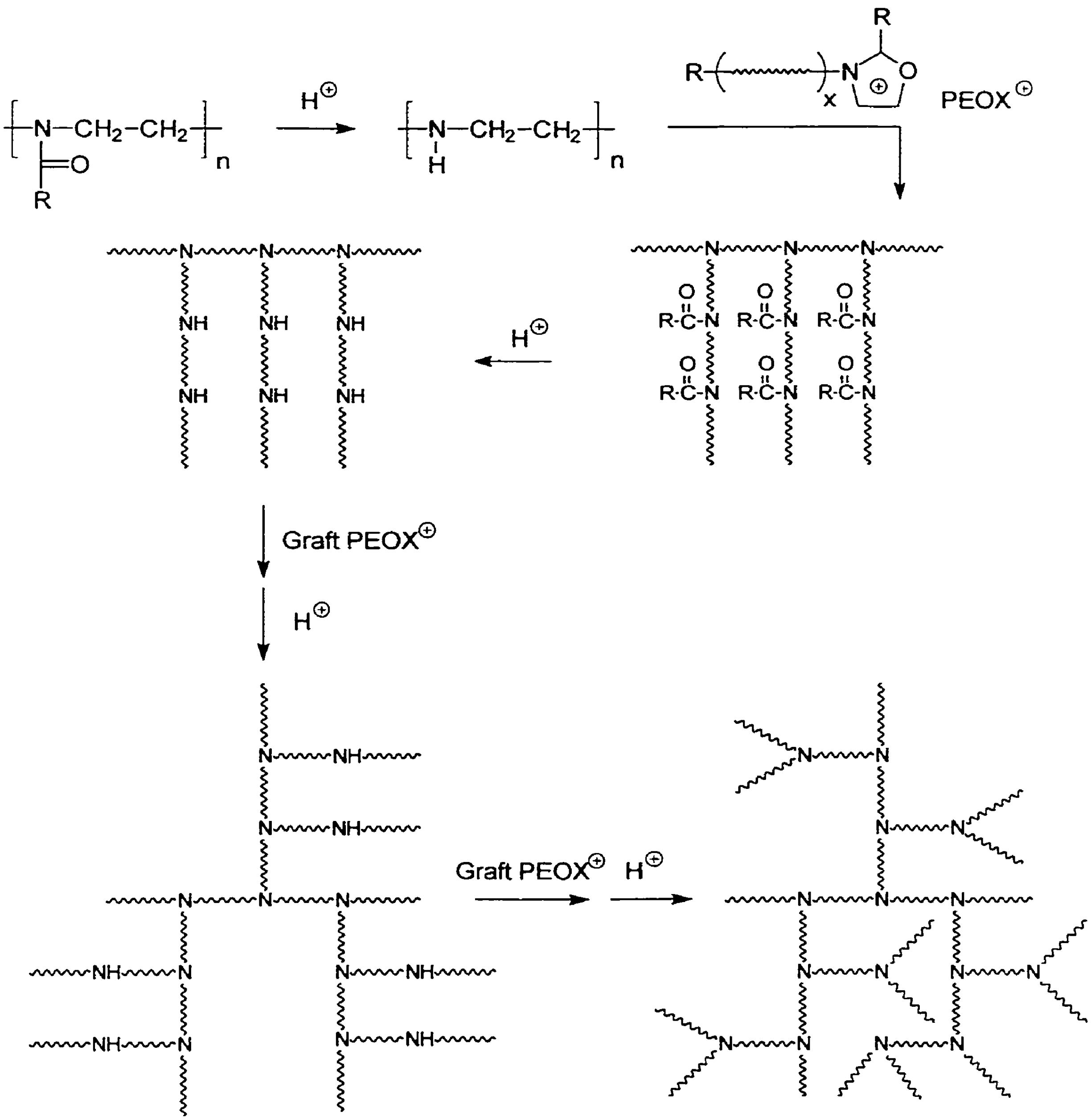
A geometric increase in the molecular weight of the polymers is observed for successive generations. The number of repeat units assembled (or overall degree of polymerization, N_{RU}) can be predicted from the number of reactive functional groups at the core (initiator core multiplicity, N_c), the number of reactive functional groups on each branch (branch cell multiplicity, N_b), and the generation G using Equation 2.1. Defining M_c, M_{RU} and M_t as the molecular weight of the core, the repeat units and the terminal units, respectively, the theoretical attainable molecular weight (MW) can be calculated from Equation 2.2. It should be noted that these equations assume that every repeat unit of the core and side chains can react to produce a branching point, and that therefore N_c and N_b also correspond to the degree of polymerization (DP) of the core and the branches, respectively.

$$N_{RU} = N_c \left[\frac{N_b^{G+1} - 1}{N_b - 1} \right] \tag{2.1}$$

$$MW = M_c + N_c \left[M_{RU} \left(\frac{N_b^{G+1} - 1}{N_b - 1} \right) + M_t N_b^{G+1} \right] \tag{2.2}$$

It is clear from Equations 2.1 and 2.2 that if high molecular weights are desired with a minimum number of reiterative grafting cycles, N_c and N_b must be large. When polymeric building blocks are used, N_c and N_b are much greater (5-100) than for dendrimers where values of 2-4 are normally encountered. In other words the number of repeat units N_{RU}, assembled as a function of generation G, is dependent upon *i*) the degree of polymerization of the grafted side chains, and *ii*) the number of chains grafted onto the substrate. Since living polymerization techniques are used to generate the PEOX side chains, varying the ratio of monomer to initiator controls the degree of polymerization. Variation in the degree of polymerization of the core determines the number of chains grafted onto the core polymer.[38]

Characterization data for comb-burst PEI samples have been reported for up to the third generation (G3) (Table 2.5). In this example short PEOX chains (with a degree of polymerization $N_b = 10$) were grafted onto a linear ($N_c = 20$) PEI core, in order to produce a G0 PEI graft polymer with a high branching density. The length of the PEOX chains was increased ($N_b = 100$) for subsequent generations. Comb-burst polymers with a weight-average molecular weight (from light scattering measurements) $M_w = 10^3$-10^7 are thus obtained, while maintaining a relatively narrow apparent [linear poly(ethylene oxide) equivalent] molecular weight distribution ($M_w/M_n = 1.1$-1.5). The M_w and branching functionality (f) of the polymers are seen to increase essentially geometrically for successive generations, as predicted by Equation 2.



Scheme 2.10 Synthesis of comb-burst poly(ethylene imine)s.

The efficiency of the grafting reaction is reported to range between 65-80%, and to be sensitive to a number of factors. The grafting efficiency thus decreases as the PEOX chain length is increased, or as the size of the PEI core increases. This effect is attributed to steric congestion resulting from a high segmental density within the core. in particular for higher generations. As the structure fills in, the number of readily accessible sites decreases at the expense of the grafting efficiency. Other parameters like the reaction time, the presence of additives such as diisopropylethylamine (a proton trap), and the ratio of PEOX chains to grafting sites also influence the grafting efficiency.[38]

Table 2.5 Characterization Data for PEI Comb-Burst Polymers (Adapted from Reference 4)

Sample	$M_w^{LS\ a)}$	$M_w/M_n^{b)}$	$f^{c)}$
Core	1 000	1.05	----
G0	2 500	1.22	5
G1	138 000	1.34	26
G2	1 080 000	1.47	176
G3	10 400 000	1.20	745

a) Weight-average molecular weight from light scattering measurements
c) Apparent polydispersity index for the graft polymers, from SEC analysis
d) Number of branches added, based on M_w (N_b)

A range of molecular topologies is accessible using comb-burst branching strategies. It was mentioned that the number of coupling sites available on the core polymer chain (N_c) and the multiplicity of the grafted branches (N_b) can be varied independently, but the molecular topology also varies with the ratio N_c / N_b. For example, the synthesis of rod-shaped comb-burst PEI can be achieved by successive grafting reactions of PEOX side chains with $N_b = 5$ onto a linear PEI core with $N_c = 200$.[39] When $N_c >> N_b$ a rod-like topology is expected. Conversely, if $N_c << N_b$, a spherical topology is obtained. Another way to control the topology is by varying the branching density as a function of polymer generation. It was thus postulated that comb-burst polymers with hollow interiors could be synthesized if low graft densities were used for the early generations, and high graft densities for the latter.

The intrinsic viscosity of PEI comb-burst polymers increases non-linearly for successive generations up to G2, and then decreases slightly for the G3 polymer, in analogy to many dendritic polymers.[40]

2.5.3.2 Arborescent Polystyrenes

Gauthier and Möller[5] described in 1991 the use of anionic polymerization and grafting to prepare polystyrenes with a dendritic structure. Styrene is well-suited to be incorporated into a synthetic scheme aimed at producing multiply grafted polymers. The anionic polymerization of styrene yields reactive macroanions with exceptional living characteristics. A wide range of reactive, electrophilic functional groups can be introduced onto polystyrene substrates by electrophilic substitution. The synthetic steps leading to the preparation of arborescent polystyrenes[5] are summarized in Scheme 2.11. Partial chloromethylation of a linear polystyrene, under conditions selected to minimize the occurrence of cross-linking reactions, serves to introduce coupling sites on the backbone polymer. The substrate is then reacted with polystyryllithium, after capping of the chains with a 1,1-diphenylethylene (DPE) unit. Subsequent chloromethylation and grafting cycles lead to higher generation arborescent polystyrenes.

The use of DPE as a reactivity modifier for the polystyryl anions constitutes a key step to avoiding side reactions in the coupling process: The direct reaction of uncapped polystyryl anions with chloromethylated polystyrene only proceeds with a yield around 50%, due to a competing metal-halogen exchange reaction (Figure 2.6a). In contrast, the grafting efficiency is increased to over 96% after capping with DPE (Figure 2.6b). The deep red coloration of the capped macroanions facilitates monitoring of the stoichiometry of the coupling reaction, by slowly adding a solution of the chloromethylated substrate to the macroanion solution until the coloration fades.

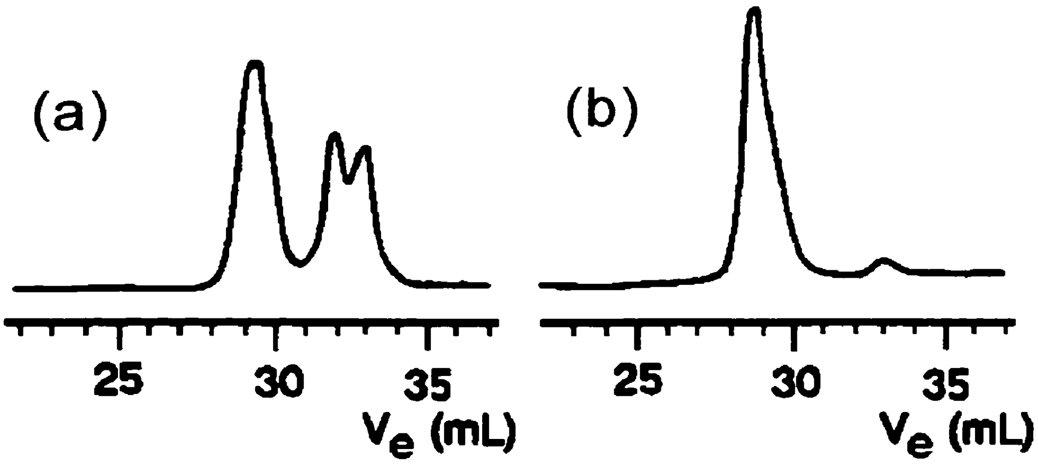
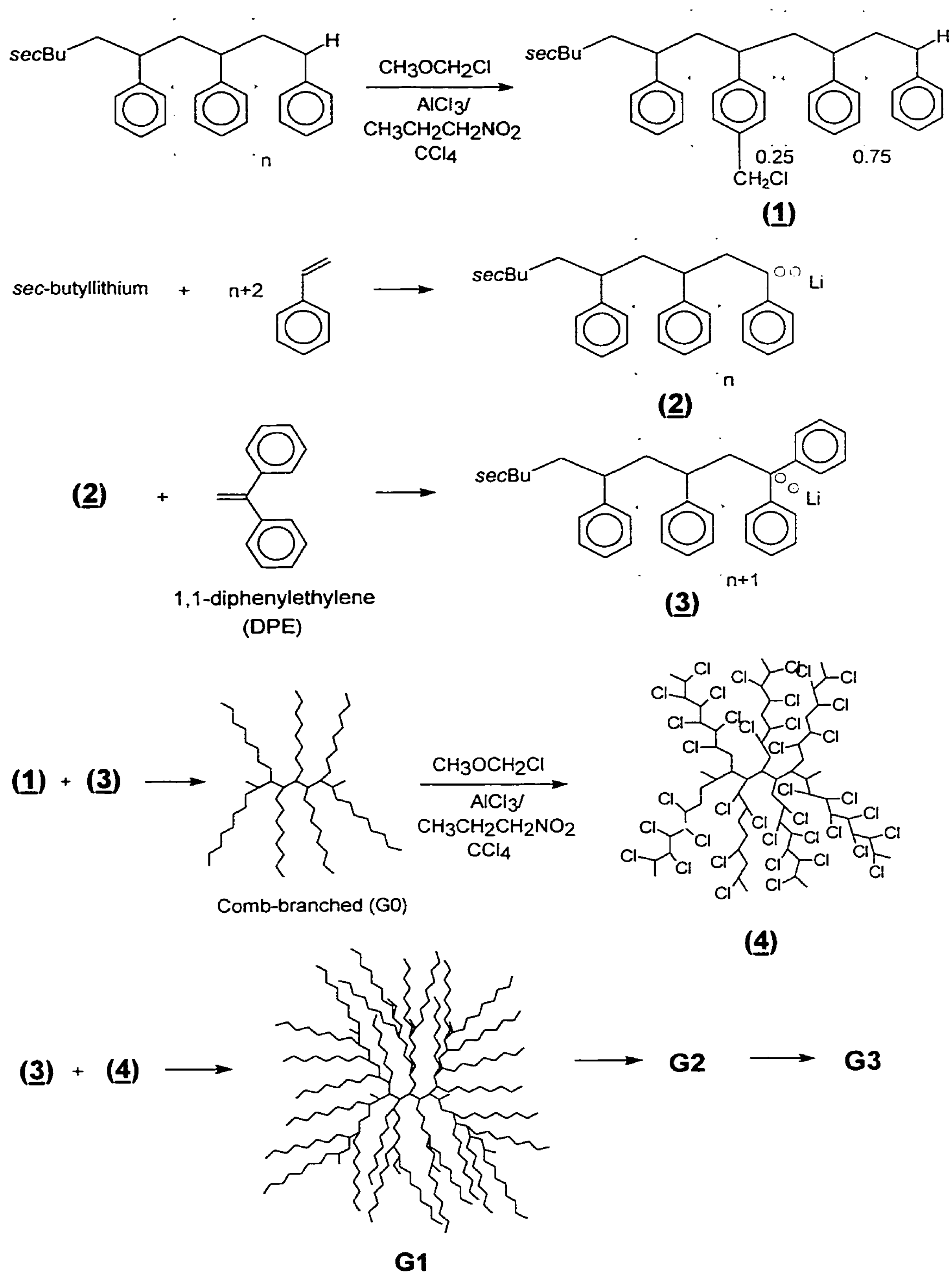


Figure 2.6 SEC traces for raw grafting products formed in the coupling reaction of chloromethylated polystyrene with polystyryllithium (a) without DPE capping, and (b) with DPE capping of the polystyryl macroanions (Adapted from Reference 5)

For a series of reactions where the molecular weight of the branches (M_b) and the number of grafting sites per backbone chain (branching functionality, f) remain constant for each generation, the molecular weight of a generation G polymer can be predicted using Equation 2.3.

$$M = M_b + M_b f + M_b f^2 + M_b f^3 + \ldots = \sum_{x=0}^{G+1} M_b f^x \qquad (2.3)$$

A geometric increase in the branching functionality and overall molecular weight is thus expected, if all the coupling sites on the grafting substrate are consumed in the reaction.



Scheme 2.11 Synthesis of arborescent polystyrenes.

Since anionic polymerization techniques are used, polymeric building blocks with a controllable molecular weight and a narrow molecular weight distribution can be generated. The number of functional groups on the grafting substrate can be likewise varied, which provides control over the branching density for each generation. Consequently the side chain molecular weight and branching density can be determined independently for each generation, in analogy to comb-burst polymers.

Characterization data for two series of arborescent polystyrenes prepared from either $M_w \approx 5\,000$ (S05) or $M_w \approx 30\,000$ (S30) polystyrene (PS) side chains[41] are compared in Table 2.6. The molecular weight (M_w) and branching functionality (f_w) increase in an approximately geometric fashion for each generation up to G2, as predicted by Equation 2.3. The smaller increases observed for the G3 polymers, and for the G4 polymer in the S05 series, can be explained in terms of steric overcrowding effects limiting the accessibility of grafting sites on the substrate. A broad range of molecular weights ($M_w^{LS} \approx 6\times10^4$-$5\times10^8$) and branching functionalities ($f_w = 14$-$22\,000$) can be achieved while maintaining a low apparent (linear polystyrene equivalent) polydispersity ($M_w/M_n \leq 1.22$). Comparison of the apparent molecular weights M_w from SEC analysis to the absolute molecular weights determined from light scattering measurements (M_w^{LS}) shows that SEC analysis strongly underestimates the molecular weight, due to the very compact structure of the molecules.[41]

The influence of branching functionality and side chain molecular weight on the physical properties of arborescent polystyrenes has been demonstrated in a number of studies.[41-44] For example, arborescent polystyrenes with short ($M_w \approx 5\,000$) side chains show almost no swelling in a good solvent (toluene) relative to a poor solvent (cyclohexane). In contrast, molecules with larger ($M_w \approx 30\,000$) side chains swell considerably.

Table 2.6 Characterization Results for Two Series of Arborescent Polystyrenes with Different Side Chain Molecular Weights (Adapted from Reference 5)

			S05 Series			
G	$M_w^{br}/10^{3\ a)}$	M_w^{br}/M_n^{br}	M_w^{LS}	$M_w^{\ b)}$	$M_w/M_n^{\ b)}$	$f_w^{\ c)}$
0	4.3	1.03	6.7×10^4	4.0×10^4	1.07	14
1	4.6	1.03	8.7×10^5	1.3×10^5	1.07	170
2	4.2	1.04	1.3×10^7	3.0×10^5	1.20	2 900
3	4.4	1.05	9×10^7	4.5×10^5	1.15	17 500
4	4.9	1.08	2×10^8	----	----	22 000
			S30 Series			
G	$M_w^{br}/10^4$	M_w^{br}/M_n^{br}	M_w^{LS}	M_w	M_w/M_n	f_w
0	2.8	1.15	5.1×10^5	2.1×10^5	1.12	18
1	2.7	1.09	9.0×10^6	5.9×10^5	1.22	310
2	2.7	1.09	1×10^8	----	----	3 400
3	2.8	1.09	5×10^8	----	----	14 300

a) The subscript *br* refers to the branches (or side chains)
b) Apparent values for the graft polymers, from SEC analysis
c) Number of branches added in last grafting reaction, from the M_w^{LS} increase and M_w^{br}

2.5.3.3 Arborescent Polybutadienes

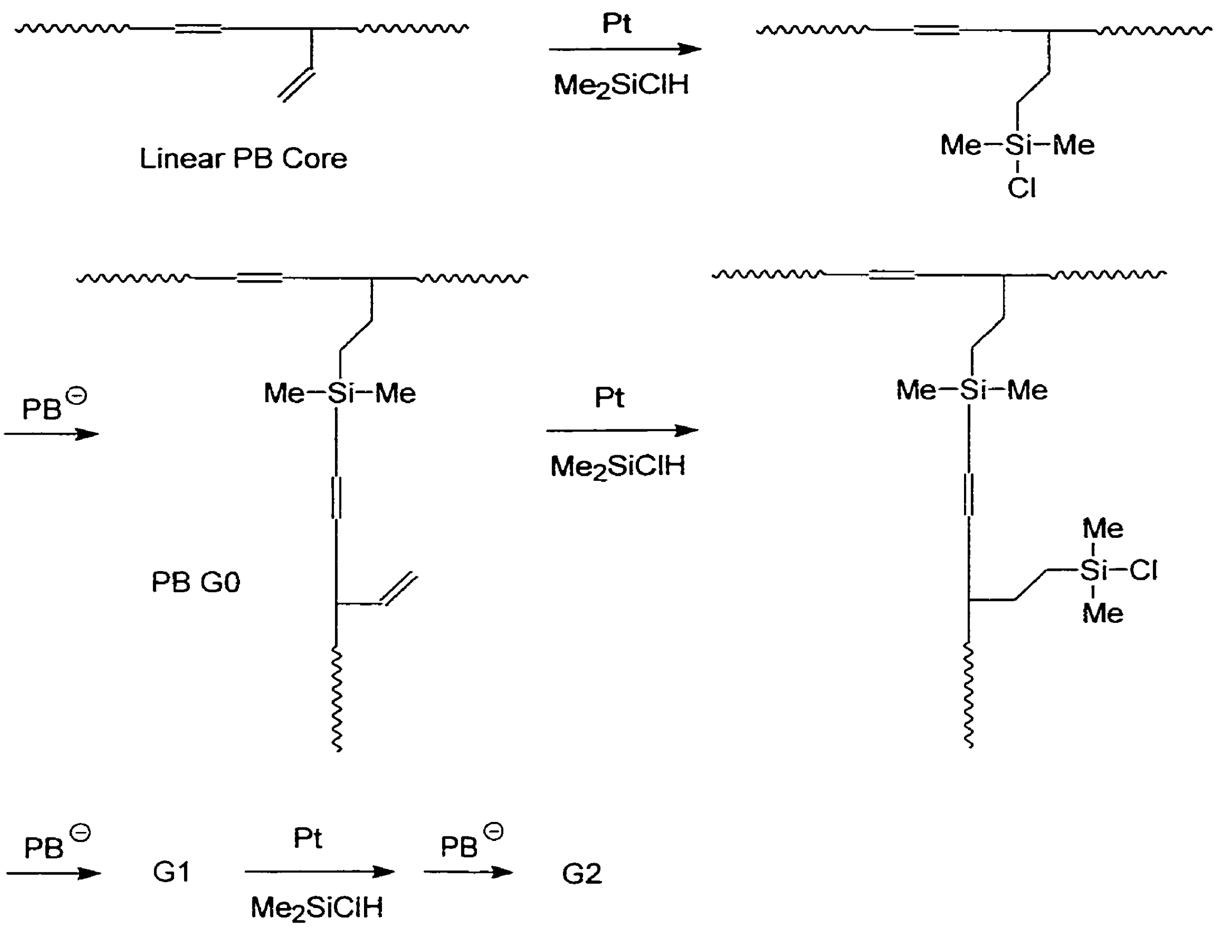
The synthesis and characterization of a series of arborescent polymers based on polybutadiene segments was reported by Hempenius *et al.*[45] The synthesis begins with a linear polybutadiene (PB) core obtained by the *sec*-butyllithium-initiated anionic polymerization of 1,3-butadiene in *n*-hexane, to give a microstructure containing approximately 6% 1,2-units (Scheme 2.12). The pendant vinyl moities are converted into electrophilic grafting sites by hydrosilylation with chlorodimethylsilane in the presence of a platinum catalyst. The hydrosilylated polybutadiene substrate is then reacted with an excess of polybutadienyllithium, to yield a comb-branched or G0 polymer. Repetition of the hydrosilylation and grafting reactions leads to the G1 and G2 polymers. Because polybutadienyl macroanions are essentially colorless, it is necessary to use a slight (20%) excess of macroanions in the grafting reaction to ensure complete reaction of the chlorosilyl coupling sites.

A series of samples was synthesized using a PB core and a side chain molecular weight $M_w \approx 10\,000$, held constant for each generation. Polymerization in *n*-hexane yields side chains with a 6% 1,2-units content, corresponding to a constant branching density of approximately 10 grafts per chain. The characteristics of the series of arborescent polybutadienes obtained are summarized in Table 2.7. With a constant PB branch molecular weight ($M_w \approx 10\,000$) and number of branching sites per chain, a geometric increase in the molecular weight and branching functionality of the graft polymers is observed up to generation G2, as predicted by Equation 2.3.

Table 2.7 Characteristics of Arborescent Graft Polybutadienes
(Adapted from Reference 45)

G	M_w^{br}	Branches / Chain [a)]	M_w^{LS}	M_w/M_n	f_w
Core	9 600	9.7	9 600	1.1	----
0	10 800	10.9	190 000	1.2	10
1	11 000	11.1	4 500 000	1.3	105
2	10 500	10.7	71 000 000	1.3	1 160

a) Calculated from M_w^{br} and 6 mol% 1-2-PB units content



Scheme 2.12 Synthesis of arborescent polybutadienes.

The graft-on-graft approach used for arborescent polybutadienes should allow for control of the composition and architecture of the molecules. The branch molecular weight is easily varied with the amount of initiator used in the polymerization reaction. Solvent polarity control in the polymerization of butadiene allows variation of the proportion of 1,2-units in the side chains, and hence the branching density.

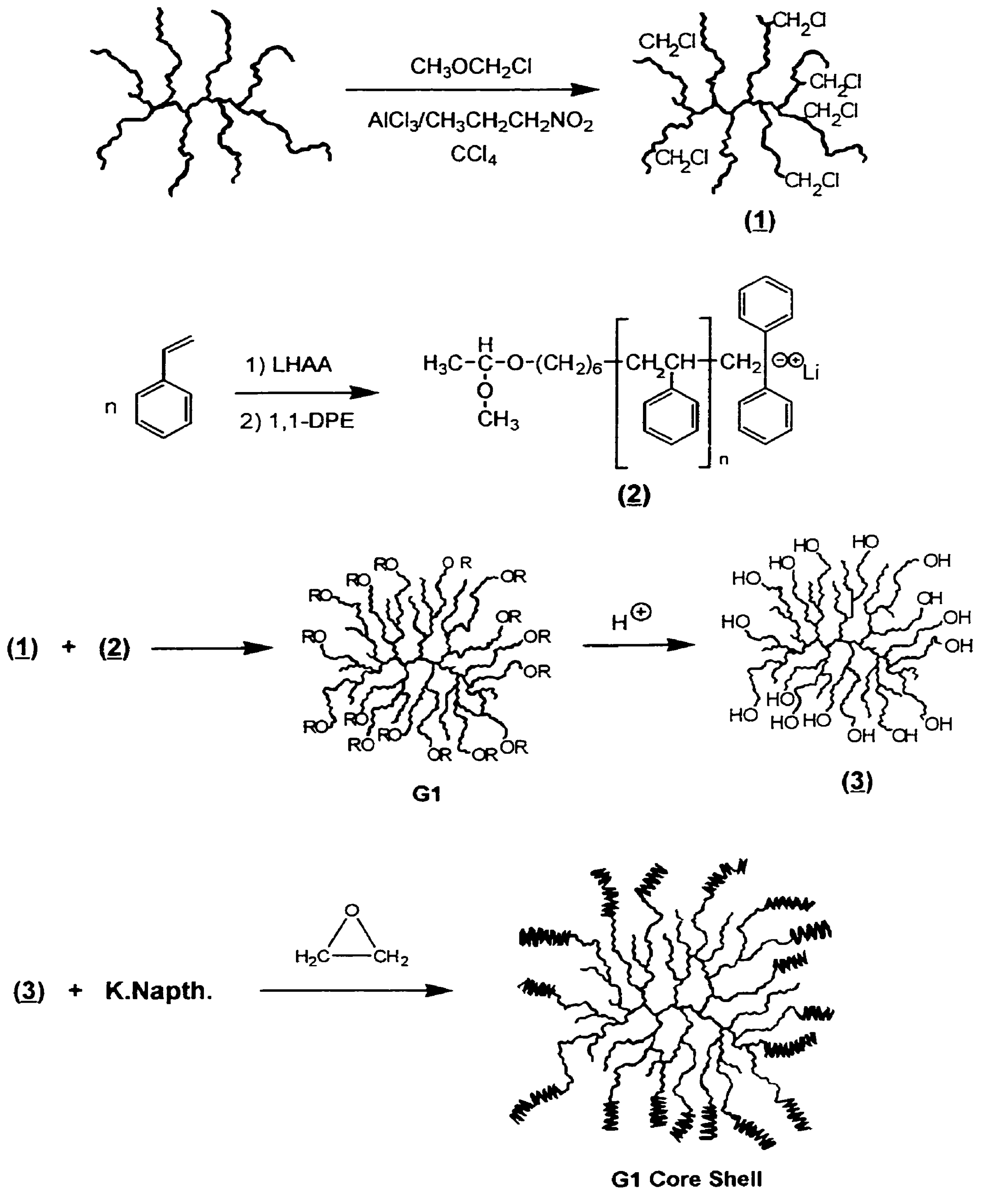
The intrinsic viscosity of arborescent polybutadienes levels off for the G1 and G2 polymers. The ratio of the radius of gyration of the molecules in solution (R_g) to their hydrodynamic radius (R_h) decreases from $R_g/R_h = 1.4$ to 0.8 from G1 to G2, close to the theoretical limit $R_g/R_h = 0.775$ for hard spheres.[46]

2.5.3.4 Arborescent Polystyrene-*graft*-Poly(ethylene oxide) Copolymers

The manner in which the architecture of arborescent homopolymers can be systematically varied is very interesting for establishing structure property relationships. When considering potential applications for arborescent polymers, however, materials with a wider range of physical and chemical properties would be more interesting. This can be achieved by incorporating other monomers in the grafting process. Since the molecular weight of arborescent polymers increases geometrically for each generation, the side chains grafted in the last generation should dominate the overall composition of copolymers. Consequently, the physical properties of the copolymers should be mainly determined by the characteristics (composition, molecular weight, and number) of these side chains.

The basic synthetic technique developed for arborescent polystyrenes was thus extended to the synthesis of graft copolymers incorporating an arborescent polystyrene core with end-linked poly(ethylene oxide) (PEO) segments using a combination of *grafting onto* and *grafting from* strategies.[47] For this purpose, arborescent PS (G0-G3) substrates are first synthesized as described in Scheme 2.13. The substrates are then partially chloromethylated and coupled with PS side chains prepared using a bifunctional alkyllithium initiator (6-lithiohexyl acetaldehyde acetal, LHAA) as shown in Scheme 2.13. Cleavage of the acetal functionalities under mildly acidic conditions yields a core carrying hydroxyl groups at the chain ends, i.e., close to the surface of the molecules. The end-linked PEO segments are introduced by titration of the hydroxyl groups with a strong base (potassium naphthalide), and addition of purified ethylene oxide. A shell of hydrophilic PEO is thus 'grown' by a chain extension reaction from the outer chains of the core polymer.

The synthesis of amphiphilic copolymers based on G1 and G4 PS cores with $M_w \approx 5\ 000$ side chains,[47] and of copolymers based on G1 PS cores with $M_w \approx 30\ 000$ side chains[48] has been demonstrated. Since living polymerization techniques are used, the structure and composition of the molecules are easily controlled. For example, the size and flexibility of the PS core can be changed by selecting different core generations, and by varying the chloromethylation level and/or the side chain molecular weight in the grafting reactions. The amount of ethylene oxide incorporated in the chain extension reaction determines the thickness of the PEO shell obtained. Evidence for a core-shell morphology is found in the solubility behavior of the molecules: Copolymers with sufficiently long PEO side chains are freely soluble in polar solvents such as water and methanol.[47]



Scheme 2.13 Synthesis of arborescent polystyrene-*graft*-poly(ethylene oxide) copolymers (G1 copolymer used as an example).

2.6 Synthesis of Other Arborescent Graft Copolymers

The highly branched structure of dendritic polymers yields unique and interesting physical properties. In particular, the physical features of arborescent polymers are unusual in that their physical behaviour resembles that of dendrimers, however their overall molecular weight is substantially higher.[41-44] A variety of unique physical properties are expected from arborescent polymers which have different chemical compositions. For example, arborescent polymers consisting of polyelectrolyte side chains would be expected to behave differently from their linear homologues. In addition, core-shell morphologies are expected from arborescent graft polymers comprised of chemically different generations.[47-48]

The assembly of dendrigraft polymer structures using *grafting onto* methodologies has received far more attention than procedures based on *grafting from* schemes. Even in the case of the arborescent ethylene oxide copolymers, the polystyrene cores were synthesized by grafting onto chloromethylated substrates, and only (linear) PEO chains were grown from the substrate in the last step. Precise control over such experimental parameters as the grafting density and side chain molecular weight is only possible using a *grafting onto* approach. Furthermore, the molecular weight of the core polymer, side chains, and graft polymer can be determined independently for each generation, resulting in a well-characterized product.

The synthesis of different arborescent graft copolymers using anionic polymerization techniques and a *grafting onto* strategy is described in the following chapters. A generalized synthetic approach has been adopted where polymeric side chains derived from selected monomers are prepared using conventional anionic polymerization techniques. These living side chains are then grafted onto suitably functionalized linear and arborescent (G0, G1 and

G2) polystyrene cores. The resulting copolymers are prepared under conditions such that the composition of the arborescent copolymers is dominated by the grafted component.

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Chapter 3

Arborescent Polystyrene-*graft*-Polyisoprene Copolymers

3.1 Abstract

A synthetic technique is presented for the preparation of a novel type of arborescent copolymer containing polyisoprene (PIP) segments. Isoprene is polymerized with *sec*-butyllithium in cyclohexane or tetrahydrofuran, to yield a predominantly *cis*-1,4- or a mixed microstructure, respectively. The graft copolymers are obtained by capping the polyisoprenyl anions with 1,1-diphenylethylene and titration with a solution of a chloromethylated polystyrene substrate. Copolymers containing PIP side chains of different molecular weights are prepared by grafting onto linear, comb-branched (G0) and twice-grafted (G1) chloromethylated polystyrenes. The samples with short ($M_w \approx 5\ 000$) PIP branches contain 77-83% polyisoprene w/w. For PIP side chains with $M_w \approx 30\ 000$ and 90 000, the polystyrene content is negligible. A low apparent polydispersity ($M_w^{app}/M_n^{app} \leq 1.15$) is maintained after grafting. Characterization of these materials using size exclusion chromatography and light scattering indicates that they have a highly compact structure. Scanning force microscopy measurements in the phase contrast mode show that the copolymers display phase-separated morphologies (glassy core surrounded by a rubbery shell) to different extents, depending on their structure.

3.2 Introduction

Dendritic polymers encompass a broad range of compounds with a cascade-branched structure including dendrimers, hyperbranched and arborescent polymers.[1] Numerous synthetic methods have been suggested for the preparation of these materials. Dendrimers are typically obtained in a series of protection-condensation-deprotection cycles (generations) of AB_n monomers. The rate of increase in molecular weight is relatively low in these systems, however, and many generations are required to reach a significant molecular weight. Hyperbranched polymers can be obtained with a high molecular weight in simple one-pot condensation procedures, but suffer from a poorly defined branched structure and a broad molecular weight distribution. Alternately, arborescent polymers can be prepared from grafting reactions using polymeric building blocks, making it possible to attain high branching functionalities and molecular weights in a few reaction steps, while maintaining a narrow molecular weight distribution.[2-4]

The synthesis of arborescent polystyrenes[2] relies on the random introduction of grafting sites (chloromethyl groups) along a linear polystyrene chain, followed by coupling with polystyryl anions to give a comb-branched (generation 0 or G0) polymer. Further chloromethylation and grafting cycles lead to higher generation arborescent polymers (G1, G2, etc.), characterized by a compact, sphere-like highly branched structure.[5] This strategy, described as a "graft-on-graft" technique, was also used for the synthesis of polyethyleneimines[3] and polybutadienes[4] with an arborescent structure. The fact that the branching density *and* the size of the branches can be varied independently for each generation is an important feature of the graft-on-graft technique.

The synthesis of arborescent *copolymers* has also been described. Amphiphilic copolymers incorporating an arborescent polystyrene core and a poly(ethylene oxide) shell were obtained in a *grafting from* approach.[6] Arborescent polystyrene molecules carrying hydroxyl groups at the *chain ends* were first synthesized. Titration of the hydroxyl groups with a strong base and addition of ethylene oxide resulted in extension of the core chains, to give covalently bound poly(ethylene oxide) segments forming a "shell" around the polystyrene core.

A new approach for the preparation of arborescent copolymers, described in this report, is based on a *grafting onto* scheme similar to the arborescent polystyrene synthesis. In this case, macroanions with a different composition are grafted on a substrate containing *randomly* distributed coupling sites. This extension of the graft-on-graft technique was used to synthesize copolymers incorporating polyisoprene segments of different molecular weights grafted onto linear, comb-branched (G0) and G1 chloromethylated polystyrene cores. For side chains with a low molecular weight, the structure expected is best described as a branched block copolymer with spherical symmetry (Figure 3.1a). For large side chains, the structure should be closer to a highly branched star-like molecule, since the dimensions of the core are small relative to the outer branches (Figure 3.1b). The combination of a narrow molecular weight distribution, a highly branched structure and a heterogeneous morphology characterizing the polystyrene-polyisoprene arborescent graft copolymers, not attainable by other synthetic methods, should lead to interesting elastomeric properties. Characterization results for these copolymers using size exclusion chromatography, light scattering, UV spectrometry and atomic force microscopy, aimed at demonstrating the success of the synthetic methods used and morphology control, are discussed in this study.

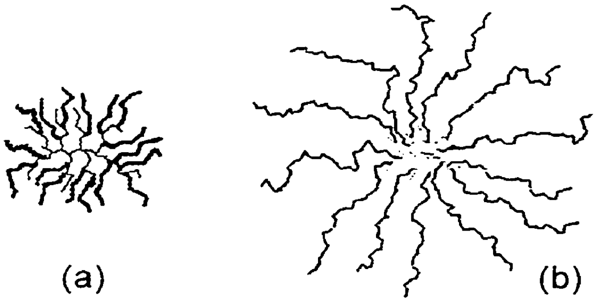


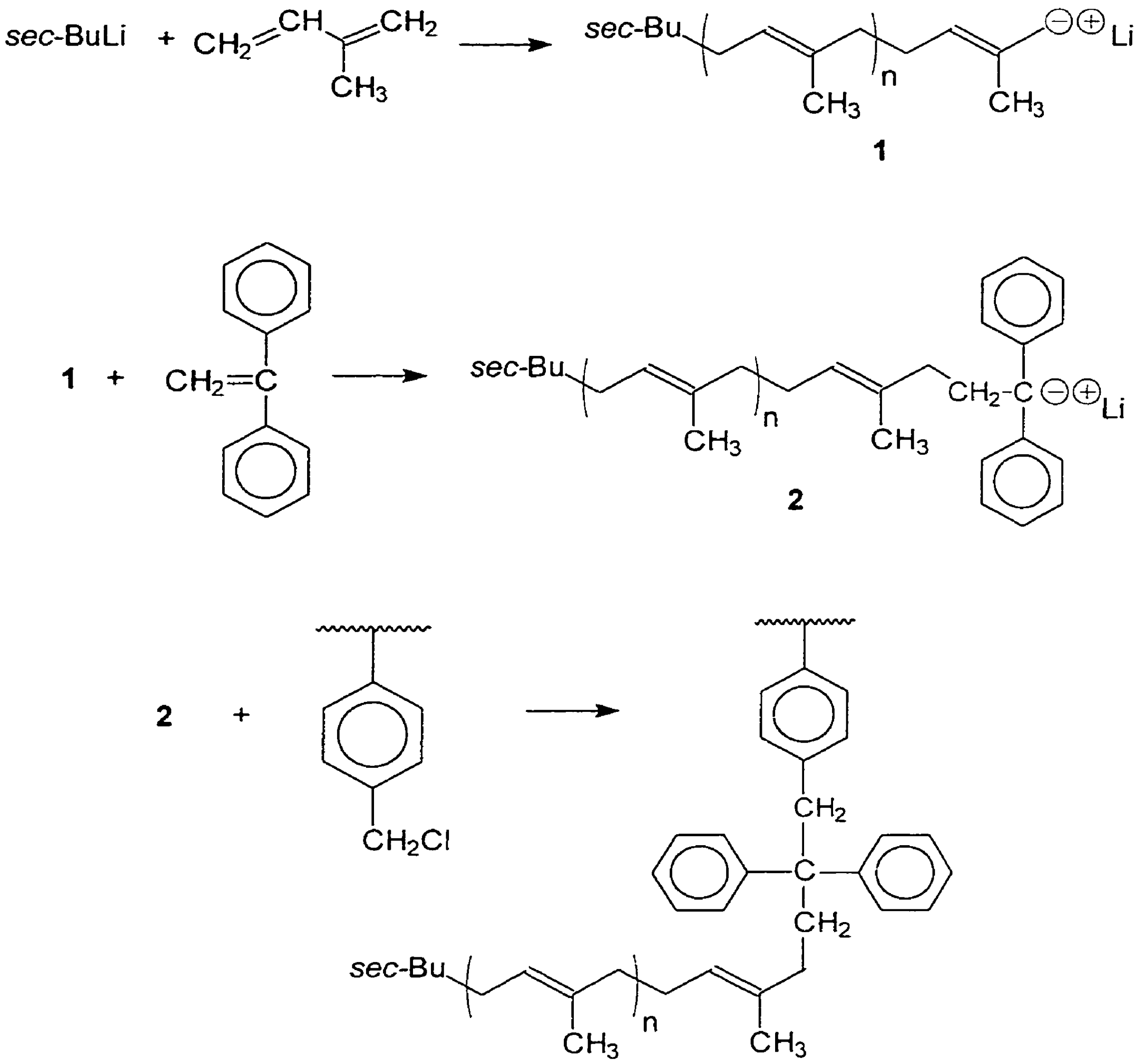
Figure 3.1 Comparison of structures obtained when a G0 (comb) chloromethylated polystyrene substrate is grafted with (a) short and (b) long polyisoprene side chains.

3.3 Synthetic Strategy

There are numerous examples of star-branched polyisoprenes prepared by coupling polyisoprenyllithium with chlorosilanes.[7] In all cases the coupling reaction was efficient (often >90%), but required long reaction times. The coupling efficiency of polystyryl anions with chlorosilanes was also improved by adding a small amount of isoprene monomer to "cap" the polystyryllithium chains.[8]

Although the reaction of polyisoprenyllithium and chlorosilanes has been extensively studied, the coupling of polyisoprenyllithium with chloromethyl substituents has received little attention. In one report, the addition of linear chloromethylated polystyrene to a solution of polyisoprenyllithium in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was used to synthesize comb-branched polystyrene-*graft*-polyisoprene.[9] The amine was shown to suppress side reactions such as metal-halogen exchange and crosslinking, and to improve the overall grafting efficiency. The analogous reaction of polystyryllithium with chloromethylated polystyrene is limited to ca. 50% grafting, also because of metal-halogen exchange. In this case, it was shown that the side reaction could be virtually eliminated, and the grafting yield increased to >95% by capping the macroanions with 1,1-diphenylethylene (DPE) prior to coupling with the substrate.[2] A similar coupling efficiency would, therefore, be expected in the reaction of DPE-capped polyisoprenyllithium with chloromethylated polystyrene.

The method selected for the preparation of arborescent PIP copolymers using a grafting onto scheme is based on the arborescent polystyrene synthesis. Isoprene is first polymerized using an organolithium initiator (Scheme 3.1), and the chains are capped with DPE. The resulting deep red-coloured solution is then titrated with a solution of chloromethylated polystyrene, to fully consume the anions. This approach provides extensive control over the total molecular weight, branching functionality, and composition of the graft copolymers, by varying the chloromethylation level of the substrate, the size of the polyisoprene side chains, or using arborescent polystyrene substrates of different structures (generation and/or side chain molecular weight).



Scheme 3.1 Synthesis of arborescent isoprene copolymers by grafting onto a chloromethylated polystyrene substrate.

The microstructure of the polyisoprene side chains can be varied by selection of appropriate polymerization conditions,[10] providing further control over the physical and chemical properties of the copolymers. A high proportion of *cis*-1,4-linkages is obtained using alkyllithium initiators in hydrocarbon solvents. In polar solvents such as THF, a microstructure high in 1,2- and 3,4-units is typically obtained, the balance being primarily *trans*-1,4-polyisoprene.[11,12] The flexibility of the graft-on-graft technique in the preparation of arborescent PIP graft copolymers will be demonstrated by using side chains with either a high *cis*-1,4-content or a mixed microstructure in the grafting reaction.

3.4 Experimental Procedures

3.4.1 Reagents

Styrene (Aldrich, 99%), 1,1-diphenylethylene (DPE; Aldrich, 97%), tetrahydrofuran (THF; Caledon, ACS Reagent) and CCl_4 (Caledon, ACS Reagent) were purified as previously described.[6] Isoprene (Aldrich, 99%) was first purified by stirring with CaH_2 and distillation under nitrogen. A second purification step before polymerization, using *sec*-butyllithium, is described subsequently. Cyclohexane (BDH, ACS Reagent) was refluxed with oligostyryllithium under dry nitrogen atmosphere and distilled directly into the polymerization reactor. *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) was used as received; the exact concentration of the solution was determined by the procedure of Lipton et al.[13] Purified chloromethyl methyl ether (CMME) was prepared as described earlier.[6] The procedures using CMME should be carried out in a well-ventilated fume hood with great care, since it is a known carcinogen.[14] All other reagents were used as obtained from the suppliers.

3.4.2 Linear Core Polymer

A polystyrene sample with a weight-average molecular weight $M_w \approx 5\,000$ and a low polydispersity index was synthesized as previously described.[6] Partial chloromethylation of the linear polystyrene was achieved by dissolving the vacuum-dried polymer (5 g) in dry CCl_4 (500 mL) and CMME (50 mL), and adding a solution of anhydrous $AlCl_3$ (3 g) in 1-nitropropane (100 mL). After 30 min stirring at room temperature the reaction was quenched with glacial acetic acid (10 mL), and the solvent was removed under vacuum. The polymer residue was dissolved in $CHCl_3$, extracted with three portions of 50% (v/v) glacial acetic acid, and precipitated into methanol.

3.4.3 Comb-Branched (G0) and G1 Core Polymers

A comb-branched polystyrene was obtained by reacting the chloromethylated linear polystyrene sample with DPE-capped polystyryl anions with $M_w \approx 5\,000$, as previously described.[2] After purification by precipitation fractionation to remove non-grafted side chains, the G0 polymer was further chloromethylated and reacted with $M_w \approx 5\,000$ polystyryl anions, to yield the G1 core. Samples of the linear, G0 and G1 polystyrenes were also chloromethylated according to the method described, to serve as grafting substrates for the polyisoprenyl anions.

3.4.4 Graft Copolymers

Isoprene was purified on a high-vacuum line by three successive freezing-evacuation-thawing cycles in the presence of *sec*-butyllithium solution (0.5 mL for 50 mL monomer), and slow distillation to a glass ampule with a polytetrafluoroethylene (PTFE) stopcock. The ampule was filled with purified nitrogen and stored at –5°C until needed.

The first step in the preparation of a graft copolymer was the polymerization of isoprene (50 g) with *sec*-butyllithium. To obtain a high proportion of *cis*-1,4-units, the polymerization was performed in cyclohexane at 25°C. Alternately, polymerization was carried out at 0°C in THF to yield a mixed microstructure. When the reaction was performed in cyclohexane, the reactor was cooled to 0°C after complete conversion of the monomer, while slowly adding dry THF (for an overall THF content of ca. 30% v/v), before adding the DPE solution. If the polymerization was carried out in pure THF at 0°C, the content of the DPE ampule was simply added to the reactor after complete conversion of the monomer. The DPE was left to react 30 min before removal of a sample of the side chains for characterization. The polymer solution was cooled to –30°C, and then titrated with a solution of the chloromethylated polystyrene, over 30 min, to a pale orange-red color. Further fading of the coloration was observed after stirring was continued for 30 min. Residual anions were terminated with degassed methanol. After workup, the graft copolymer was separated from non-grafted polyisoprene side chains by precipitation fractionation in a cyclohexane-2-propanol mixture. Successful fractionation was confirmed by comparison of size exclusion chromatography (SEC) diagrams for the fractionated and non-fractionated samples.

Four series of graft copolymers with different side chain molecular weights were prepared according to the same procedure. Three series used polyisoprene side chains with a predominantly *cis*-1,4-microstructure grafted onto linear, G0 and G1 chloromethylated polystyrenes. One series of copolymers with mixed microstructure polyisoprene side chains grafted onto G0 chloromethylated polystyrene was also prepared.

3.4.5 Characterization

Size exclusion chromatography was used to characterize the polystyrene and polyisoprene side chains, the raw grafting products, and the fractionated graft copolymers. The instrument used a Waters 510 HPLC pump, a Jordi 500 mm linear mixed bed column and a Waters 410 differential refractometer (DRI) detector. Tetrahydrofuran served as the eluent, at a flow rate of 1 mL/min. Apparent molecular weights were determined for the graft copolymers and for the mixed microstructure side chain samples using a linear polystyrene standards calibration curve. Molecular weights for the linear polyisoprene side chains with a high *cis*-1,4-content were determined using a calibration curve prepared from linear polyisoprene standards having the same microstructure.

The absolute M_w of the polystyrene grafting substrates and of the arborescent graft copolymers was determined using static light scattering measurements. Refractive index increments (dn/dc) for the graft copolymers were calculated as a composition-weighted average of the values determined for the core polymers and for linear polyisoprenes with the same microstructure as the side chains.[15] The dn/dc values of the homopolymers were measured at 25.0 ± 0.1°C using a Brice-Phoenix differential refractometer equipped with a 510 nm bandpass interference filter. Measurements on the linear polyisoprene sample with a predominantly *cis*-1,4-microstructure were done in cyclohexane. The sample with a mixed microstructure was characterized in THF. A Brookhaven BI-200 SM light scattering goniometer equipped with a Lexel 2-Watt argon ion laser operating at 514.5 nm was used for the static light scattering measurements.[6] The absolute M_w was determined by Zimm extrapolation to zero angle and concentration for a series of measurements for 6-8 solutions at angles ranging from 40°-140°.

Composition and microstructure analysis was performed using ^{1}H-NMR spectra obtained on

Composition and microstructure analysis was performed using ^{1}H-NMR spectra obtained on a Bruker AM-250 nuclear magnetic resonance spectrometer. The graft copolymers prepared in cyclohexane were dissolved in $CDCl_3$, and the samples prepared in THF were dissolved in benzene-d_6. Microstructure analysis of the predominantly *cis*-1,4-polyisoprene samples was carried out according to the method described by Chen.[16] The microstructure of the polyisoprene samples prepared in THF was determined by the method of Essel and Pham.[17] The composition of the copolymers was also analyzed by UV-visible spectroscopy on a Hewlett-Packard HP8452 spectrophotometer. The characteristic polystyrene absorbance maximum at λ=262 nm was used to generate an absorbance vs. concentration curve using linear polystyrene standards ($M_w = 50\ 000$) dissolved in cyclohexane. The PIP contents reported are calculated from the polystyrene content in the graft copolymers determined in cyclohexane by comparing the absorbance at λ=262 nm to the calibration curve.

Scanning force microscopy measurements were done on a Digital Instruments Nanoscope IIIa operated in the tapping mode at a resonance frequency of ~ 360 kHz. The measurements were performed under ambient conditions using silicon probes with a spring constant of ~ 50 N/m. The samples were prepared by spincasting at 1000 rpm of a solution of the copolymer 0.05% w/w in chloroform on a freshly cleaved mica substrate.

3.5 Results and Discussion

The characteristics of the linear and branched polystyrene substrates used in the preparation of the copolymers are summarized in Table 3.1. The branching functionality of the polymers, defined as the number of chains added in the last grafting reaction, was calculated from the Equation 3.1.

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_w^{br}} \tag{3.1}$$

where $M_w(G)$, $M_w(G\text{-}1)$ and M_w^{br} are the absolute weight-average molecular weight of graft polymers of generation G, of the preceding generation and of the side chains, respectively. The number of grafting sites introduced on the substrates was calculated from their molecular weight and chloromethylation level. The nomenclature used for the polystyrene samples and the graft copolymers specifies the composition and the structure of the molecules. For example, G1PS-PIP30 refers to a copolymer with $M_w \approx 30\,000$ PIP side chains grafted onto a G1 arborescent polystyrene substrate. The suffix (THF), when used indicates that the PIP side chains were synthesized in tetrahydrofuran.

The synthesis of an arborescent copolymer (G0PS-PIP5) is demonstrated in Figure 3.2 with a series of SEC traces for (a) the chloromethylated polystyrene core (G0PS), (b) the polyisoprene side chains with $M_w \approx 5\,000$, (c) the raw grafting product, and (d) the fractionated copolymer. Three peaks can be observed in the SEC trace for the raw product (curve c). The leftmost (highest molecular weight) peak corresponds to the graft copolymer. The intermediate peak, with a molecular weight twice as high as the rightmost peak, is attributed to the formation of linear "dimer". This occurs following a metal-halogen exchange reaction with the chloromethylated polystyrene backbone,[2] to give a chlorine-terminated chain that couples with another polyisoprenyllithium molecule. The rightmost peak has the same molecular weight as the side chain sample removed from the reactor before the grafting reaction (curve b). It may correspond to either the non-reacted chlorine-terminated intermediate mentioned above, or to polymer chains deactivated by residual protic impurities present in the chloromethylated polymer solution. Comparison of curves (a) and (c) demonstrates that no excess polystyrene substrate is present in the product, because the colourimetric titration procedure used allows exact monitoring of the reaction stoichiometry.

Table 3.1 Characteristics of Arborescent Polystyrene Substrates

Polymer	M_w^{br} (SEC) [a]	M_w^{br}/M_n^{br}	M_w (LS) [b]	f_w	CH_2Cl [c] / mol %	Grafting sites
PS (linear)			4 360		27	11
G0PS	4 430	1.04	49 700	10	23	110
G1PS	5 750	1.03	797 000	130	16	1 220

[a] M_w of the side chains determined by SEC analysis

[b] Absolute M_w of the graft polymers determined by light scattering (linear sample analyzed by SEC)

[c] Chloromethylation level determined by ^{1}H-NMR spectroscopy analysis of substrate

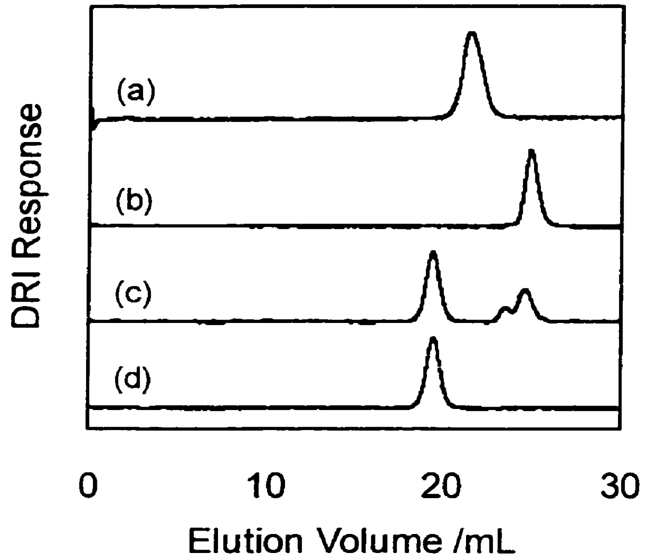


Figure 3.2 SEC chromatograms for the preparation of sample G0PS-PIP5: (a) chloromethylated G0 polystyrene, (b) polyisoprene side chains, (c) raw product from the grafting reaction, (d) fractionated graft copolymer.

The grafting efficiency can be quantified from the size exclusion chromatography trace for the raw product, if the DRI detector response due to the polystyrene component of the copolymer is considered negligible. This is done by comparing the integrated peak area for the graft copolymer to the total area of all peaks. For sample G0PS-PIP5 (Figure 3.2c), the grafting efficiency is 65%.

To demonstrate the necessity for DPE capping prior to grafting, the preparation of a comb-branched graft copolymer with short ($M_w \approx 5\ 000$) side chains was attempted without capping agent, under conditions otherwise identical with those used to synthesize sample PS-PIP5. Virtually complete reaction of the linear polyisoprene side chains and backbone polymer was observed. However, linear dimer was formed as the main product, with only 44% graft copolymer yield. In contrast, the grafting yield for the reaction using DPE was 80%.

Anionic grafting processes are known to be sensitive to the polarity of the reaction medium. For example, reduced solvent polarity was reported to have a negative influence on the coupling yield of *uncapped* polystyryllithium with polychloromethylstyrene.[18] On the other hand, grafting efficiencies of up to 96% were observed with chloromethylated polystyrene in a benzene:THF 1:2 v/v mixture, when the polystyryllithium species were capped with DPE prior to grafting. The higher grafting efficiency is clearly linked to the suppression of metal-halogen exchange reactions: In grafting DPE-capped polystyryl anions at -30°C, dimer formation is almost non-existent. In the present investigation, the grafting reaction was carried out with DPE-capped polyisoprenyl anions either in a cyclohexane:THF 7:3 v/v mixture, or in pure THF. The results obtained for both reaction conditions are compared in Figure 3.3, when $M_w \approx 5\ 000$ PIP side chains are grafted onto a G0 chloromethylated polystyrene sample. The graft polymer is not only obtained in lower yield in the less polar cyclohexane/THF mixture than in pure THF, but more dimer is also produced in the reaction. A series of copolymers was prepared by grafting different M_w PIP side chains onto a chloromethylated G0 polystyrene core in pure THF (Table 3.2). The grafting efficiencies achieved under these conditions are significantly higher than for the corresponding reactions in the cyclohexane-THF mixture, providing further evidence for the influence of solvent polarity on grafting efficiency.

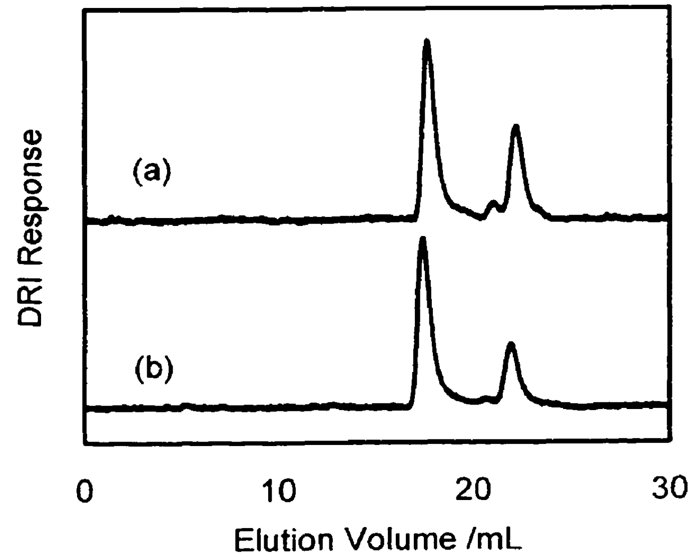


Figure 3.3 SEC chromatograms for raw grafting products: (a) G0PS-PIP5 (b) G0PS-PIP5(THF).

An alternate explanation for the lower grafting yield in less polar environments could be a decreased efficiency of the capping reaction with DPE. Chains not capped with DPE are more susceptible to metal-halogen exchange, because of the higher reactivity of the anions. According to a related study on the synthesis of epoxide-terminated styrene-butadiene block copolymers using DPE capping, however, this seems unlikely to be the source of the problem: The reaction of polybutadienyl anions with DPE was shown to proceed rapidly and quantitatively, even at low THF concentrations in the reaction mixture.[19]

It is apparent from Table 3.2 that as the molecular weight of the polyisoprene side chains increases, the grafting efficiency tends to decrease for each core polymer. The effect is most pronounced for the G1PS substrate. Since the chloromethyl sites are, presumably, randomly distributed within the core polymer, all sites should react independently from each other. However, as the core polymer becomes more highly branched, it also becomes increasingly congested. A fraction of the chloromethyl sites should become less accessible to the polyisoprenyl anions, resulting in a decreased grafting efficiency. In a recent fluorescence quenching investigation of arborescent polystyrenes, two distinct "phases" could be identified within the molecules.[20] The inner, more rigid portion of the molecule was shown to be less accessible to quencher species than the outer, more flexible portion. The fraction of less accessible material was also shown to increase for higher generation polymers. This differential accessibility effect explains the decreases in grafting efficiency observed for higher generation chloromethylated polystyrene substrates.[2] An additional factor that may have contributed to a lower grafting efficiency is the inherent immiscibility of polystyrene and polyisoprene, making the grafting sites even less accessible to the macroanions.[21]

The molecular weights determined for the polyisoprene side chains and the fractionated graft copolymers, determined either by SEC analysis or light scattering, are summarized in Table 3.2. Some M_w(LS) values are missing, due to the impossibility of purifying the copolymers in sufficiently large amounts for the light scattering measurements. The results from SEC analysis for the polyisoprene side chains demonstrate that a narrow molecular weight distribution was achieved. For the different graft copolymers prepared, the polydispersity index likewise remains relatively low ($M_w^{app}/M_n^{app} \approx 1.07\text{-}1.15$). While the polydispersity indices obtained are only apparent values based on a polystyrene standards calibration curve, they still suggest that a

Table 3.2 Characterization Data for the Arborescent Graft Copolymers Synthesized

Sample	Polyisoprene side chains			Graft Copolymers			
	M_w^{br} (SEC)[a]	M_w^{br}/M_n^{br} (SEC)[a]	Grafting Efficiency	M_w^{app} (SEC)[b]	M_w^{app}/M_n^{app} (SEC)[b]	M_w (LS)	f_w
PS-PIP5	4.5	1.07	0.80	54	1.11	50.2	11
PS-PIP30	35	1.03	0.66	222	1.10	421	12
PS-PIP100	118	1.08	0.43	733	1.13	---	---
G0PS-PIP5	4.7	1.06	0.65	169	1.07	575	112
G0PS-PIP30	32	1.06	0.63	461	1.13	2 760	85
G0PS-PIP100	112	1.03	0.35	683	1.12	4 010	35
G1PS-PIP5	5.1	1.09	0.71	393	1.11	5 640	950
G1PS-PIP30	35	1.05	0.18	666	1.11	8 180	225
G1PS-PIP100	118	1.07	0.06	901	1.07	---	---
G0PS-PIP5(THF)	5.5[b]	1.06[b]	0.92	135	1.15	825	---
G0PS-PIP30(THF)	30[b]	1.06[b]	0.69	168	1.07	3 740	---
G0PS-PIP100(THF)	99[b]	1.12[b]	0.60	540	1.13	---	---

[a] SEC calibrated using linear standards with an average microstructure of 71% *cis*-1,4-, 22% *trans*-1,4- and 7% 3,4-polyisoprene.

[b] Apparent molecular weights determined using SEC calibrated with linear polystyrene standards.

narrow molecular weight distribution was maintained for the copolymers. It is evident from Table 3.2 that the M_w^{app} values determined by SEC analysis are strongly underestimated for the graft copolymers compared with the absolute M_w(LS) values obtained from light scattering, indicating a very compact structure.

The branching functionality (f_w) of the copolymers, calculated according to Equation 2.1, ranges from 11-950. No branching functionality calculations were attempted for the copolymers prepared in THF, because only apparent characterization data were available for the side chains. The f_w values determined for the copolymers are either identical with (within error limits) or lower than the number of grafting sites calculated for the chloromethylated polystyrene substrates (Table 3.1). The trends observed among the different copolymer series are consistent with the variations in grafting efficiency discussed previously: f_w decreases relative to the theoretical (calculated) value for polymers with longer PIP side chains, and for higher generation substrates. This unfortunately leads to variations in branching functionality within a series of copolymers based on the same polystyrene grafting substrate. It would obviously be preferable, in terms of establishing structure-property correlations, to generate a series of samples for which the branching functionality remains constant and only the side chain molecular weight varies. It was shown in a previous study that 128-arm star polybutadienes can be prepared by coupling with a dense carbosilane dendrimer substrate.[22] It was also pointed out that the use of a θ-solvent is preferable to increase the coupling yield under these conditions. Unfortunately, it is not clear how this concept could be applied to the synthesis of arborescent graft copolymers, since both components are high molecular weight polymers, making it impossible to find a solvent for the grafting reaction that is simultaneously a θ-solvent for both the polystyrene and polyisoprene components.

Composition analysis for the different graft copolymer samples (Table 3.3) indicates a polyisoprene content varying from 77 % to over 98 % by weight. This demonstrates that when short PIP side chains are grafted (or alternately if grafting substrates with lower chloromethylation levels were used), copolymers containing a significant polystyrene component are obtained. When longer polyisoprene side chains are grafted on the substrate, the polystyrene component becomes essentially undetectable. This is seen in comparing the ^{1}H-NMR spectra in Figures 3.4a and 3.4b for graft copolymers with $M_w \approx 5\ 000$ and 30 000 polyisoprene side chains, respectively. The polyisoprene contents determined by UV-visible spectrophotometry are in good agreement with the values determined using ^{1}H-NMR spectroscopy. The slightly higher (3-5 mol%) values found by UV-visible analysis could be due to differences in the relaxation characteristics of the polyisoprene and polystyrene components affecting the intensity of the peaks in the NMR spectra.

The microstructure of the polyisoprene side chains determined for the copolymers prepared (Table 3.3) using ^{1}H-NMR spectroscopy consists of a high proportion of *cis*-1,4-polyisoprene units when cyclohexane is used as the polymerization solvent. The proportion of *cis*-1,4-polyisoprene varies from 63-79 mol%, while the *trans*-1,4-units content varies from 17-29 mol%, the balance of the monomer being incorporated as 3,4-units (4-8 mol%). The microstructure variations can be explained by the different initiator concentrations used in each experiment. Worsfold and Bywater[23] have shown that, for the anionic polymerization of isoprene, the proportion of 3,4-units remains constant (ca. 5-6%), while the *cis*-1,4-content decreases relative to the *trans*-1,4-content as either the initiator concentration is increased or the monomer concentration is decreased. At 20°C and with an initiator concentration on the order of 10^{-3} M, the alkyllithium-initiated polymerization of isoprene is expected to yield a *cis*:*trans*

Table 3.3 Microstructure and Polyisoprene Content Analysis

Sample	Polyisoprene / %w/w (UV)	Polyisoprene / %w/w (^{1}H-NMR)	Polyisoprene Microstructure / mol%			
			cis-1,4	*trans*-1,4	3,4	1,2
PS-PIP5	83	90	72	23	5	~ 0
PS-PIP30	94	> 98	72	22	6	~ 0
PS-PIP100	>97	> 98	63	28	8	~ 0
G0PS-PIP5	87	84	67	27	6	~ 0
G0PS-PIP30	88	94	71	24	5	~ 0
G0PS-PIP100	>97	> 98	79	17	4	~ 0
G1PS-PIP5	---	80	63	29	8	~ 0
G1PS-PIP30	---	94	70	24	6	~ 0
G1PS-PIP100	---	> 98	72	23	5	~ 0
G0PS-PIP5(THF)	77	84	34		34	29
G0PS-PIP30(THF)	91	97	38		34	28
G0PS-PIP100(THF)	>97	> 98	37		39	27

ratio of approximately 70:30, with ca. 5-6% 3,4-polyisoprene units.[24] When short polyisoprene side chains were prepared, the initiator concentration was higher than for the longer side chains ($M_w \approx 30\ 000$ and 90 000) and, consequently, the *cis*-1,4-content is somewhat lower.

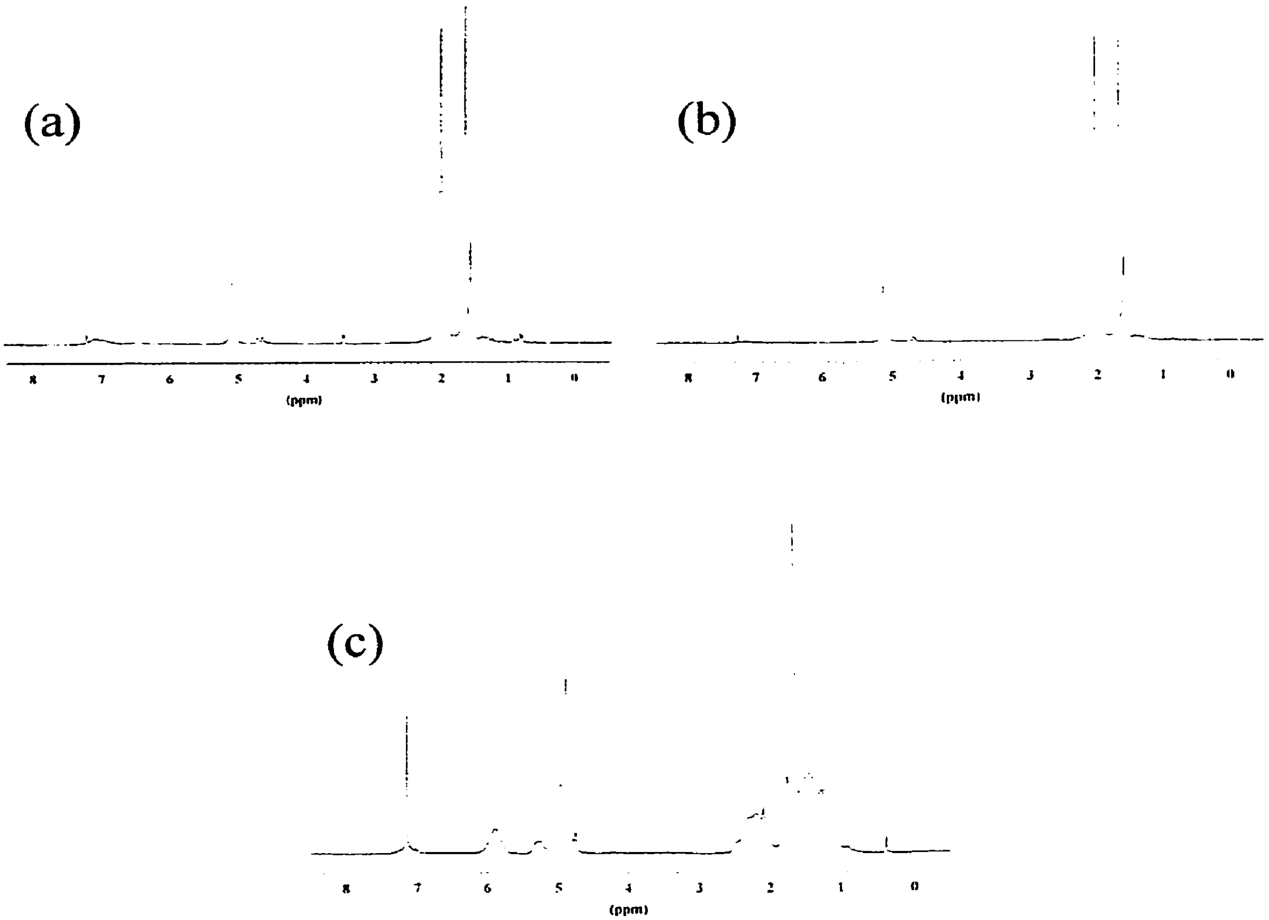


Figure 3.4 ^{1}H-NMR spectra of G1 copolymers with (a) $M_w \approx 5\ 000$ side chains, high *cis*-1,4-content (G0PS-PIP5), (b) $M_w \approx 30\ 000$ side chains, high *cis*-1,4-content (G0PS-PIP30), and (c) $M_w \approx 30\ 000$ mixed microstructure side chains G0PS-PIP30(THF).

The polyisoprene side chains prepared in THF have a mixed microstructure, with roughly equal proportions of 1,4-, 3,4- and 1,2-polyisoprene units (Table 3.3). No distinction can be made between *cis*-1,4- and *trans*-1,4-units in this case, because of peak overlap. The ^{1}H-NMR spectrum for a graft copolymer with $M_w \approx 30\ 000$ side chains prepared in THF is shown in Figure 3.4c. Individual peaks are not completely resolved in the spectrum, making it necessary to deconvolute the peaks of interest to calculate peak areas used in the microstructure analysis.[17] The calculated values are in agreement with those previously reported by Bywater and Worsfold[12] for the free-ion propagation of polyisoprenyllithium in THF.

Scanning force microscopy pictures were obtained for selected samples in the phase contrast mode. In this type of measurement, the phase lag between the stress applied on the sample by the scanning tip and the cantilever deflection are measured, in analogy to dynamic mechanical measurements. Phase contrast pictures obtained for samples G0PS-PIP5 and G1PS-PIP5 are compared in Figure 3.5. The copolymer based on a comb polystyrene substrate (G0PS-PIP5) displays little contrast, hinting at partial 'mixing', or at least at a diffuse boundary between the polystyrene and polyisoprene components of the molecules. For the sample derived from a G1 core (G1PS-PIP5), however, more pronounced phase contrast (ca. 10°-12°) is observed between the two components. Isolated nodules with an average diameter of about 15 nm, corresponding to glassy polystyrene-rich cores, are clearly visible on the picture and surrounded by a darker polyisoprene-rich shell forming a nearly continuous rubbery matrix in the film. The average polystyrene core diameter of 15 nm is close to the diameter of 19 nm measured for monomolecular films of arborescent polystyrene molecules with a similar structure.[25] Phase contrast measurements were also attempted on sample G1PS-PIP30 but no significant contrast was obtained, indicating that the film surface probed was essentially homogeneous. This is presumably due to the very low polystyrene content in the copolymer (6% w/w) making the core undetectable, as would be expected for a star-branched structure of the type shown in Figure 3.1b. The microscopy characterization results show that arborescent copolymers with different morphologies can be obtained, depending on the synthetic conditions used. Well-defined core-shell morphologies are obtained for higher generation substrates grafted with short side chains, but properties similar to branched homopolymers are observed for structures incorporating long side chains.

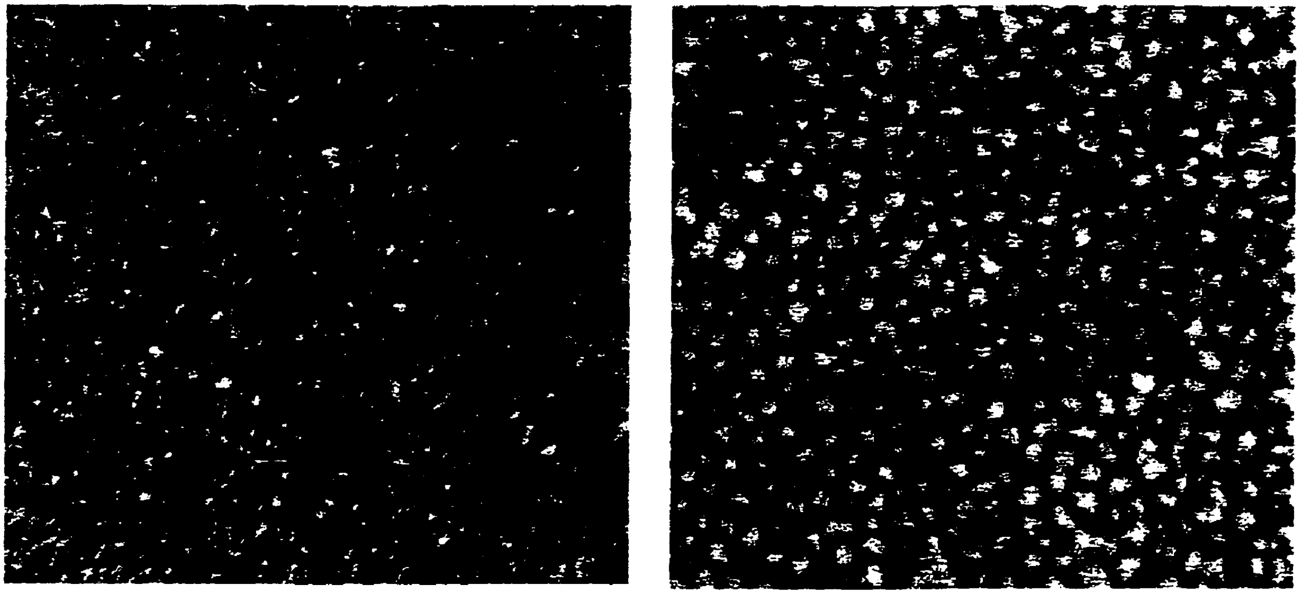


Figure 3.5 Phase contrast scanning force microscopy images for samples G0PS-PIP5 (left) and G1PS-PIP5 (right). The width of each picture is 500 nm.

3.6 Conclusions

The results reported demonstrate that it is possible to extend the graft-on-graft technique to the preparation of highly branched graft copolymers containing side chains randomly grafted on a polystyrene substrate. Control over the polyisoprene side-chain molecular weight and microstructure was achieved while maintaining a narrow apparent polydispersity for the graft copolymers ($M_w/M_n \approx 1.07$-1.15). The method was demonstrated for the special case of a dense polystyrene substrate with a high density of grafting sites. Different materials with a wider range of properties could presumably be obtained if the structure of the polystyrene substrate is varied. Likewise, the yield of the grafting reaction may be increased if grafting substrates with a lower chloromethylation level are used, to decrease the influence of steric exclusion effects. Scanning force microscopy measurements confirm the existence of microphase separation occurring to different extents for these molecules, depending on their structure. Detailed physical property investigations of these materials, in terms of dilute solution and rheological properties, will be the subject of future reports.

3.7 References and Notes

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Chapter 4

Arborescent Polystyrene-*graft*-Poly(2-vinylpyridine) Copolymers: Highly Branched Cationic Polyelectrolyte Precursors

4.1 Abstract

A technique is described for the preparation of arborescent copolymers containing poly(2-vinylpyridine) (P2VP) segments. 2-Vinylpyridine is first polymerized with 1,1-diphenyl-2-methylpentyllithium in tetrahydrofuran in the presence of N,N,N',N'-tetramethylethylenediamine (TMEDA). The graft copolymers are obtained by titration of the P2VP anions with a solution of a chloromethylated polystyrene substrate. Copolymers incorporating either short ($M_w \approx 5000$) or long ($M_w \approx 30\ 000$) P2VP side chains were prepared by grafting onto linear, comb-branched (G0), G1, and G2 chloromethylated arborescent polystyrenes. Branching functionalities ranging from 14 to 3 880 and molecular weights ranging from 8.2×10^4 to 6.7×10^7 were obtained for the copolymers, while maintaining a low apparent polydispersity ($M_w/M_n \approx 1.06$–1.15) after grafting. Characterization data for these materials from size exclusion chromatography and light scattering indicate that they have a highly compact structure. Dynamic light scattering results show that the arborescent poly(2-vinylpyridine) copolymers expand much more in solution than the linear homologous polymers when protonated with HCl. This is attributed to the higher charge density attained in the branched copolymers.

4.2 Introduction

Dendritic polymers are an interesting class of macromolecules with a cascade-branched structure including dendrimers, hyperbranched, and arborescent polymers. A variety of synthetic techniques have been employed for the preparation of these materials. Dendrimers are obtained from iterative protection-condensation-deprotection reaction cycles that incorporate AB_n monomers into structural units referred to as dendrons. Assembly of the dendrons can proceed by a divergent[1] (core first) or convergent[2] (core last) route. Dendrimers are, in general, characterized by a very low polydispersity ($M_w/M_n < 1.01$) and an exactly predictable molecular weight. Since the *Aufbau* process is based on small molecules, the rate of increase in molecular weight for each reaction cycle is low. The synthesis must be carried through many generations to achieve macromolecules with a high molecular weight. Hyberbranched polymers are obtained by one-pot polycondensation reactions of AB_n monomers. High molecular weights are easily achieved in this case, however the macromolecules obtained have a poorly defined branched structure and a high polydispersity index ($M_w/M_n \approx 2$ typically). Arborescent polymers are prepared from successive grafting reactions incorporating well-defined polymeric building blocks. This “graft-on-graft” approach makes it possible to obtain macromolecules with a high branching functionality and molecular weight in a few reaction steps, while maintaining a narrow molecular weight distribution ($M_w/M_n \approx 1.1$).

The first step in the synthesis of arborescent polymers is the random introduction of reactive grafting sites along a linear polymer chain. Living polymer chains are then coupled to the linear substrate to generate a comb-branched (generation 0 or G0) polymer. The functionalization and coupling reaction cycles are repeated to obtain the higher generation (G1, G2, etc.) arborescent polymers. This grafting strategy has been applied to the synthesis of arborescent polystyrenes[3], using cycles of chloromethylation and coupling with polystyryl anions. Similar methods have also been developed to prepare “comb-burst” polyethylenimines[4] and arborescent polybutadienes.[5] In all cases, the syntheses relied on living polymerization techniques, providing precise control over the molecular weight and polydispersity of the grafted polymer segments. The number of reactive functional groups can also be predetermined, allowing control over the branching density for each generation.

Other anionically polymerizable monomers have been incorporated into arborescent copolymers. A *grafting from* approach has been described for the preparation of arborescent polystyrene-*graft*-poly(ethylene oxide).[6] More recently, a *grafting onto* approach was used to prepare arborescent polystyrene-*graft*-polyisoprene copolymers.[7] An important feature of arborescent copolymers is that the number and size of the grafted side chains can be varied independently. This translates into extensive control over the morphology and the physical properties of the copolymers. The incorporation of monomers such as 2-vinylpyridine in the synthesis of arborescent copolymers is of considerable interest, because the pyridine moieties can undergo facile protonation to yield a polyelectrolyte.

The preparation of graft polymers containing P2VP segments has so far been limited to comb-branched structures. Copolymers consisting of a polystyrene backbone and poly(2-vinylpyridine) side chains have been prepared using both *grafting from*[8] and *grafting onto*[8,9] schemes. The *grafting from* strategy, based on the metallation of poly(*p*-bromostyrene) with lithium naphthalenide to serve as a polyfunctional initiator, suffers from the formation of a significant amount of non-grafted poly(2-vinylpyridine).

Greater control over the structure of the copolymers is attained when a *grafting onto* strategy is employed. The reaction of poly(2-vinylpyridinyl)lithium with partially chloromethylated polystyrene yielded copolymers with a poly(2-vinylpyridine) content ranging from 30-72% w/w.[8] However, a significant portion (16-29% w/w) of the poly(2-vinylpyridine) side chains was prematurely terminated by residual impurities or through side reactions.

The synthesis of a series of arborescent copolymers consisting of poly(2-vinylpyridine) segments of different molecular weights grafted onto linear, comb-branched (G0), G1, and G2 randomly chloromethylated arborescent polystyrenes is now reported. The efficiency of the coupling reaction is addressed with a systematic study of the effect of various additives and of the reaction temperature. Characterization results for the copolymers obtained from size exclusion chromatography, light scattering and ^{1}H-NMR spectroscopy measurements, demonstrating the success of the synthetic approach, are described in this study. Interesting physical properties are expected for these copolymers, due to their highly branched structure and heterogeneous morphology. For example, the very compact structure of these copolymers leads to enhanced molecular expansion upon ionization of the P2VP side chains in solution. This phenomenon was investigated using dynamic light scattering measurements.

4.3 Experimental Section

4.3.1 Reagents

Styrene (Aldrich, 99%), 1,1-diphenylethylene (DPE; Aldrich, 97%), tetrahydrofuran (THF; Caledon, ACS Reagent) and CCl_4 (Caledon, ACS Reagent) were purified as previously described.[6] N,N,N',N'-Tetramethylethylenediamine (TMEDA; Aldrich, 99%) and 2-vinylpyridine (2VP; Aldrich, 97%) were first purified by stirring with CaH_2 and distillation under reduced pressure. An additional purification step for both reagents, completed immediately before use, is described subsequently. *sec*-Butyllithium (Aldrich, 1.3 M in cyclohexane) and *tert*-butyllithium (Aldrich, 1.7 M in pentane) were used as received. The exact concentration of the *sec*-butyllithium solution was determined using the procedure of Lipton *et al.*[10] Purified chloromethyl methyl ether (CMME) was prepared as described earlier.[6] The procedures using CMME should be carried out with due caution in a well-ventilated fume hood, since CMME is a known carcinogen.[11] All other reagents were used as received.

4.3.2 Partially Chloromethylated Polystyrene Substrates

Linear, comb-branched (G0), G1 and G2 partially chloromethylated polystyrene samples were synthesized as previously described.[7]

4.3.3 Arborescent Copolymers

2-Vinylpyridine monomer was further purified, prior to polymerization, on a vacuum line using three freezing-evacuation-thawing cycles in the presence of CaH_2, followed by slow distillation to a glass ampule with a polytetrafluoroethylene (PTFE) stopcock. The ampule was then filled with purified nitrogen and stored at -5°C until needed. TMEDA was purified on a high-vacuum line using three successive freezing-evacuation-thawing cycles, titration with *tert*-butyllithium until a persistent yellow endpoint was observed, and slow distillation to a glass ampule with a PTFE stopcock.

The first step in the synthesis of a graft copolymer is the polymerization of 2-vinylpyridine in a glass reactor. After evacuation, flaming and filling of the reactor with nitrogen, purified THF and the TMEDA solution were added to the reactor, followed by the DPE solution in THF. The initiator 1,1-diphenyl-2-methylpentyllithium was generated *in situ* from *sec*-butyllithium and DPE. 2-Vinylpyridine in THF was added drop-wise to the solution, resulting in a rapid color change from bright to dark red. After 30 min, a sample of the side chains was removed from the reactor and terminated with degassed methanol. The polymer solution was then warmed to -40°C and titrated with a solution of chloromethylated polystyrene in THF until a pale orange color was observed. The polymer solution was warmed to room temperature, leading to further fading of the color over 30 min. Residual anions were terminated with degassed methanol. Non-grafted P2VP side chains were removed from the crude grafting product by precipitation fractionation using THF/methanol (4/1 v/v) as a solvent and *n*-hexane as a non-solvent.

4.3.4 Characterization

Size exclusion chromatography served to characterize the polystyrene substrates and poly(2-vinylpyridine) side chains, the raw grafting products, and the fractionated graft copolymers. The instrument used consists of a Waters 510 HPLC pump, a Jordi 500 mm DVB linear mixed bed column, and a Waters 410 differential refractometer detector. Tetrahydrofuran containing TMEDA (5% v/v, to prevent the adsorption of P2VP on the column)[12] served as eluent at a flow rate of 1 mL/min. A linear polystyrene standards calibration curve was used to provide apparent (polystyrene-equivalent) molecular weights and molecular weight distributions for the grafting substrates, the graft copolymers, and the poly(2-vinylpyridine) side chains.

The composition of the arborescent copolymers was determined by ^{1}H-NMR spectroscopy on a Bruker AM-250 spectrometer after dissolution in $CDCl_3$ at a concentration of 5% w/v.

The absolute weight-average molecular weight (M_w) of the polystyrene grafting substrates and of the arborescent graft copolymers was determined from static light scattering measurements. Refractive index increments (dn/dc) for the graft copolymers were measured in methanol at 25.0 ± 0.1°C using a Brice-Phoenix differential refractometer with a 510 nm bandpass interference filter. A Brookhaven BI-200 SM light scattering goniometer equipped with a Lexel 2-Watt argon ion laser operating at 514.5 nm was used for the static light scattering measurements.[6] The absolute M_w was determined by Zimm extrapolation to zero angle and concentration for a series of measurements for 6-8 samples at angles ranging from 30-150°.

The hydrodynamic radius of the graft copolymers was determined from dynamic light scattering measurements, for comparison to values obtained for linear poly(2-vinylpyridine) samples (Polymer Source, Inc.). A Brookhaven BI-2030AT 201-channel correlator was used for the measurements. The hydrodynamic radius was determined from the z-average diffusion coefficient obtained from cumulant analysis. The results from the first- and second-order cumulant analyses were always compared, to ensure that aggregation of the macromolecules did not occur. Solutions of the copolymers and linear P2VP samples were prepared in pure methanol and in methanol containing 0.1 N HCl. The concentration of the solutions was adjusted to <1% (w/v) to provide a reasonable photon counting rate ($\approx 10^5$ counts/sec). Prior to analysis, each polymer sample was filtered three times through a 0.5 μm PTFE membrane filter into a scintillation vial.

4.4 Results and Discussion

The characteristics of the linear and branched polystyrene substrates used in the preparation of the graft copolymers are summarized in Table 4.1. The branching functionality of the polymers, defined as the number of chains added in the last grafting reaction, is calculated from Equation 4.1.

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_w^{br}} \tag{4.1}$$

where $M_w(G)$, $M_w(G\text{-}1)$ and M_w^{br} are the absolute weight-average molecular weight of graft polymers of generation G, of the preceding generation and of the side chains, respectively. All grafting substrates were synthesized using $M_w^{br} \approx 5\,000$ side chains. The number of potential grafting sites introduced on the substrates is calculated from their molecular weight ($M_w(G)$) and chloromethylation level. In keeping with previous nomenclature,[7] the sample identification for the grafting substrates and the graft copolymers specifies their composition and structure. For example, G1PS-P2VP30 refers to a graft copolymer with $M_w^{br} \approx 30\,000$ poly(2-vinylpyridine) (P2VP) side chains grafted onto a G1 (twice-grafted) arborescent polystyrene substrate.

Table 4.1 Characteristics of the Polystyrene Substrates

Polymer	M_w^{br} (SEC) [a]	M_w/M_n^{br} (SEC)[a]	M_w (LS) [b]	f_w	CH_2Cl [c] / mol%	Grafting Sites
PS (linear)	5 420	1.09	n/a	1	26	14
G0PS	5 220	1.07	66 700	12	22	140
G1PS	6 160	1.06	727 000	108	20	1390
G2PS	5 210	1.07	5 030 000	826	16	7730

[a] Values from SEC analysis using linear PS standards calibration
[b] Absolute M_w of the graft polymers from laser light scattering
[c] Chloromethylation level from ^{1}H-NMR spectroscopy

The synthesis of an arborescent copolymer sample is illustrated in Figure 4.1 with a series of SEC traces corresponding to a chloromethylated polystyrene substrate (G0PS), P2VP side chains with $M_w \approx 5000$, the raw grafting product, and the fractionated arborescent graft copolymer. Two peaks are present in the SEC trace for the raw grafting product (curve c). The leftmost (highest molecular weight) peak corresponds to the graft copolymer. The rightmost peak has the same elution volume as the side chain sample removed from the reactor prior to grafting (curve b), and corresponds to non-grafted side chains. These chains are presumably deactivated by residual protic impurities present in the chloromethylated polymer solution, or else through side reactions. A comparison of curves a and c indicates that no excess grafting substrate is present in the raw product. This is a consequence of the colorimetric titration procedure used, which allows precise control over the stoichiometry of the grafting reaction. Curve d confirms complete removal of the non-grafted side chains by fractionation.

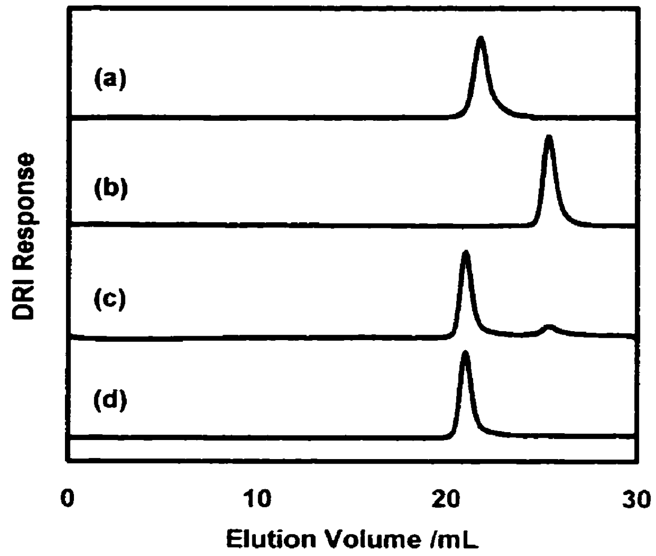

Figure 4.1 Preparation of sample G0PS-P2VP5: SEC traces for (a) chloromethylated G0 polystyrene, (b) poly(2-vinylpyridine) side chains, (c) raw product from the grafting reaction, (d) fractionated graft copolymer.

The fraction of P2VP side chains in the reaction mixture that becomes grafted onto the polystyrene substrate, defined as the ***grafting yield***, can be determined from the SEC trace obtained for the raw product. The refractive index increments in THF for polystyrene (dn/dc = 0.196 at 514.5 nm) and poly(2-vinylpyridine) (dn/dc = 0.180 at 514.5 nm) are comparable, and therefore the response of the DRI detector can be assumed to be equivalent for each component. Furthermore, the overall composition of the graft copolymers is dominated by the P2VP component. Under these conditions, the ratio of the peak area for the graft copolymer and the total area for both peaks in the SEC trace yields the fraction of P2VP side chains grafted. For example, 89% of the P2VP side chains generated were grafted onto the G0PS substrate in the synthesis of sample G0PS-P2VP5 (Figure 4.1c). The grafting yield for each reaction can be compared to optimize the grafting conditions.

For the grafting reaction to proceed in high yield, the macroanions must remain 'living' during the time required to complete the reaction, and coupling must be favored over side reactions leading to premature termination of the chain ends. This requires the macroanions to be stable, but nonetheless highly nucleophilic, which may be difficult to achieve when attempting to graft macroanions derived from polar monomers such as 2-vinylpyridine. The stability of the macroanions and the rate of the coupling reaction can be controlled to some extent using additives to modify the reactivity of the chain ends, and by varying the temperature at which the grafting reaction is carried out. These parameters were systematically investigated to maximize the efficiency of the grafting reaction. For each test reaction, a copolymer was prepared consisting of short ($M_w \approx 5000$) P2VP side chains grafted onto a partially chloromethylated $M_w \approx 5000$ linear polystyrene substrate.

4.4.1 Effect of Additives

The reactivity of P2VP anions may be increased or decreased, depending on the additive selected. The stability of the macroanions is expected to improve if the nucleophilic character is reduced; however the rate of the coupling reaction should also decrease. The coupling reaction was attempted at -78°C in the absence of additives, and in the presence of either lithium chloride or *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The results obtained in these experiments are summarized in Table 4.2.

The presence of excess lithium ions during the anionic polymerization of acrylates and methacrylates in polar solvents has been shown to prevent side reactions that lead to premature chain termination.[14] The addition of LiCl to the polymerization of 2-vinylpyridine has also been shown to have no detrimental effect on the living character of the anions, and to facilitate the preparation of block copolymers incorporating poly(*tert*-butyl acrylate) end-blocks.[15] The reactivity of the chain ends is expected to decrease in the presence of excess lithium ions, thereby preventing detrimental side reactions. Experimentally, the grafting yield decreases from 84% in the absence of additives, to 77% when a 10-fold excess of lithium ions is present (Table 4.2). Different side reactions may occur during the anionic polymerization of 2-vinylpyridine: For example, proton transfer from the polymer backbone to the living macroanion results in chain termination,[16] and nucleophilic attack at the carbon α to the nitrogen atom within the pyridine ring can subsequently lead to chain cleavage or the formation of branched products.[17] Based on the grafting yield observed, it appears that the presence of excess lithium cations, while decreasing the reactivity of the macroanions, also reduces the rate of the coupling reaction even more than the rate of side reactions.

Table 4.2 Effect of Additives and Reaction Temperature on the Coupling Efficiency

Sample	Additive	$[A]/[LE]^d$	Grafting Temperature / °C	Side Chains[a] M_w^{app}	Side Chains[a] M_w/M_n^{app}	Grafting Yield[e]	Graft Copolymer[a] M_w^{app}	Graft Copolymer[a] M_w/M_n^{app}
1	none	0	-78	4 800	1.08	0.84	31 900	1.15
2	LiCl	10	-78	5 300	1.10	0.77	33 500	1.15
3	TMEDA[b]	10	-78	5 270	1.09	0.92	33 000	1.11
4	TMEDA[c]	10	-78	5 190	1.08	0.93	33 100	1.16
5	TMEDA[c]	10	-30	5 760	1.08	0.92	34 100	1.11
6	TMEDA[c]	10	0	4 400	1.09	0.85	28 600	1.16

[a] Apparent values calculated by SEC analysis using a linear polystyrene standards calibration curve

[b] TMEDA added after complete polymerization of 2-vinylpyridine

[c] TMEDA added prior to the polymerization of 2-vinylpyridine

[d] Ratio of concentration of additive [A] to concentration of living ends [LE]

[e] Calculated from relative peaks areas in the SEC trace for the raw product

Considering the negative influence of an increased lithium ion concentration, an alternate method to perturb the dissociation equilibrium using TMEDA was also investigated with the aim of reducing side reactions. It is well known that TMEDA is an efficient ligand for the lithium counterion.[18] Consequently, in the presence of excess TMEDA, the nucleophilic character of the P2VP macroanions is expected to increase, due to the complexation of the lithium ions. For example, the addition of TMEDA prior to grafting polyisoprenyllithium onto partially chloromethylated polystyrenes was shown to enhance the coupling reaction and suppress side reactions.[19] Similarly, the addition of TMEDA was reported to disrupt the aggregation of living polymer chains, leading to increased reactivity for anions derived from ethylene, isoprene, and styrene.[20] The effect of adding TMEDA either prior to polymerization or immediately before grafting of the P2VP chains was examined. In both cases, the grafting yield was increased from 84% in the absence of additives to 92-93% at –78°C with TMEDA (Table 4.2).

4.4.2 Effect of Grafting Temperature

It has been shown that the temperature at which the grafting reaction is carried out can influence the grafting yield in the preparation of arborescent polystyrenes.[3] This is a consequence of metal-halogen exchange competing with coupling. Capping the highly nucleophilic polystyryl anions with 1,1-diphenylethylene was shown to suppress metal-halogen exchange and increase the grafting yield. On the other hand, it has also been reported that the grafting yield for the reaction of P2VP anions with chloromethylated polystyrene proceeds in high yield, essentially independently of the reaction temperature, when potassium is used as a counterion.[8] Since the addition of TMEDA lead to increased grafting yields, the effect of grafting temperature in the presence of TMEDA was re-examined in this study.

In the presence of TMEDA, the grafting yield is maximized in the low temperature range (–78°C to –30°C) (Table 4.2), decreasing slightly at higher temperatures (0°C). Based on these results, all coupling reactions discussed subsequently were carried out at –30°C in the presence of TMEDA.

4.4.3 Arborescent Polystyrene-*graft*-Poly(2-vinylpyridine) Copolymers

Two series of arborescent polystyrene-*graft*-poly(2-vinylpyridine) copolymers were synthesized by grafting either short ($M_w \approx 5\ 000$, P2VP5) or long ($M_w \approx 30\ 000$, P2VP30) poly(2-vinylpyridine) side chains onto partially chloromethylated polystyrene substrates of different generations (Table 4.1). Characterization data for the copolymers obtained are summarized in Table 4.3. The data demonstrate that good control was maintained over the molecular weight distribution of the P2VP side chains under the conditions used: The low apparent polydispersity index values obtained ($M_w/M_n \leq 1.12$) show that the polymerization proceeded free of side reactions.

When P2VP side chains are grafted onto randomly chloromethylated polystyrene substrates of different generations, the grafting yield (the fraction of available P2VP side chains that is grafted onto the substrate) ranges from 40 to 92% (Table 4.3). One important factor contributing to the deactivation of living P2VP anions may be their reaction with residual protic impurities introduced with the substrate polymer solution. The grafting yield decreases in both the P2VP5 and P2VP30 series when the polystyrene substrates are more highly branched (G0, G1 and G2). A dependence of the grafting yield upon the length of the

Table 4.3 Characterization Data for Arborescent Poly(2-vinylpyridine) Graft Copolymers

	Side Chains			Graft Copolymer					
Copolymer Sample	M_w^{app} (SEC) [a]	M_w/M_n^{app} (SEC) [a]	Grafting Yield [b]	Copolymer Composition [c] / mol% P2VP	M_w^{app} (SEC) [a]	M_w/M_n^{app} (SEC) [a]	M_w (LS)	f_w	Coupling Efficiency [d]
PS-P2VP5	5 200	1.08	0.92	86	33 100	1.15	81 500	14	100
G0PS-P2VP5	5 820	1.08	0.89	90	105 300	1.11	718 000	112	80
G1PS-P2VP5	5 050	1.06	0.81	86	---	---	5 730 000	991	72
G2PS-P2VP5	5 200	1.12	0.76	81	---	---	25 200 000	3 880	50
PS-P2VP30	27 200	1.07	0.80	97	165 200	1.09	415 000	14	100
G0PS-P2VP30	28 600	1.08	0.65	97	385 700	1.06	3 240 000	111	79
G1PS-P2VP30	32 400	1.09	0.56	96	---	---	26 900 000	808	58
G1PS-P2VP30[e]	34 400	1.09	0.26	96	---	---	26 800 000	758	55
G2PS-P2VP30	31 200	1.10	0.40	92	---	---	67 100 000	1 990	26

[a] Apparent values based on a linear polystyrene standards calibration curve

[b] Calculated from relative peak areas in the SEC trace for the raw product

[c] Copolymer composition determined using ^{1}H-NMR spectroscopy

[d] Calculated from branching functionality, f_w, and potential grafting sites available

[e] Grafting reaction allowed to proceed for six hours with 25 mol% excess of P2VP anions

P2VP grafts is also observed: Comparison of the grafting yield for substrates of the same generation shows that the yield is always lower for the P2VP30 copolymers. This effect is most noticeable for the G2 polystyrene substrates for which the grafting yield decreases from 76% to 40% for samples G2PS-P2VP5 and G2PS-P2VP30, respectively (Table 4.3). This large decrease is attributed to the lower concentration of living ends present when grafting P2VP30 side chains.

Weight-average molecular weights ranging from M_w = 8.2×10^4-2.5×10^7 and 4.2×10^5-6.7×10^7 are obtained using static light scattering measurements for the P2VP5 and P2VP30 copolymer series, respectively. The corresponding branching functionalities (f_w, calculated using Equation 4.1) range from 14-3880 for the P2VP5 series, and from 14-1990 for the P2VP30 series. The ***coupling efficiency*** (Table 4.3), defined as the fraction of available chloromethyl sites consumed in the coupling reaction, is calculated by comparing f_w and the number of available grafting sites on the substrate (Table 4.1). The trends observed for f_w and the coupling efficiency are consistent with those obtained for the grafting yield: Both decrease for longer P2VP side chains and for higher polystyrene substrate generations. In the case of the linear polystyrene substrate, all available grafting sites are reacted.

Since the chloromethyl groups are presumably distributed randomly throughout the polystyrene substrate, all sites should have the same reactivity. On the other hand, when the substrate becomes more highly branched, the structure becomes more congested. As the grafting reaction proceeds, steric congestion leads to differential accessibility for the remaining chloromethyl sites, and the coupling efficiency decreases. The morphology of arborescent polystyrenes was probed using fluorescence quenching techniques to show that the inner portion of the molecule was less accessible to quencher molecules than chains in the outer layer.[21] The fraction of less accessible material was found to increase for higher generation polymers.

A grafting reaction, aimed at increasing the *coupling efficiency*, was allowed to proceed for six hours with a 25 mol% excess of poly(2-vinylpyridine) macroanions. The reaction of the G1PS substrate and $M_w \approx 30\ 000$ P2VP side chains was used for this purpose. In contrast, the standard method consists of titrating the living P2VP anions solution with a solution of the chloromethylated substrate over approximately one hour. In the presence of excess living ends, the deep red coloration of the solution persists over the course of the reaction. Residual anions are then terminated with degassed methanol to yield a clear solution. As expected, the grafting yield decreases from 56% to 26%, due to the excess of living ends present. However, the absolute molecular weight, branching functionality, and coupling efficiency obtained are virtually identical to those for a 1-hour reaction time (Table 4.3). This confirms that the coupling efficiency is limited by the extent of steric congestion within the molecules, and not by the experimental conditions used. Based on these results, grafting shorter P2VP side chains, grafting onto a less congested polystyrene substrate, or decreasing the chloromethylation level would be expected to increase the coupling efficiency.

Composition analysis indicates that the graft copolymers are dominated by the P2VP component, ranging from 81-90 mol% and 92-97 mol% for the P2VP5 and P2VP30 series, respectively (Table 4.3). This demonstrates that graft copolymers with a significant polystyrene component can be prepared if short P2VP (or alternately fewer) segments are grafted. The polystyrene content becomes negligible when longer P2VP segments are used.

It is thus possible to control the composition of the copolymers, depending on the size and number of P2VP segments used.

4.4.4 Solution Properties

Comparison of the absolute molecular weights obtained from light scattering measurements with the apparent values from size exclusion chromatography (SEC) shows that the graft copolymers have a very compact structure (Table 4.3). The copolymers based on the G1PS and G2PS substrates do not elute from the SEC column. The molecular weights are significantly underestimated using SEC, but the apparent molecular weight distribution remains narrow ($M_w/M_n \leq 1.15$) for all generations characterized. The compact molecular structure and narrow molecular size distribution of the arborescent P2VP copolymers should lead to interesting solution behaviour. In particular, changes in the molecular dimensions upon ionization of the P2VP side chains were investigated in dilute solutions using dynamic light scattering (DLS) measurements.

All the copolymer samples synthesized are freely soluble in methanol, and in dilute HCl solutions in methanol and water. Clear solutions are obtained for the copolymers based on linear, G0, and G1 polystyrene cores. Solutions of the copolymers based on the G2 polystyrene core are opalescent. To investigate molecular expansion upon ionization, the hydrodynamic radius of the arborescent copolymer molecules was determined using dynamic light scattering measurements in pure methanol and in methanol containing 0.1 N HCl. The hydrodynamic radius of the neutral and ionized copolymers is compared in Table 4.4. Reproducible results could not be obtained for the PS-P2VP5 sample, presumably due to the small dimensions of the molecules (R_h < 10 nm). The values obtained from first-and second-order cumulant analysis were in excellent agreement for all samples measured, as expected for molecules of uniform size. Furthermore, in all cases, the increase in hydrodynamic radius upon ionization was much less than would be expected in the presence of molecular aggregation. The increase in hydrodynamic radius upon protonation, attributed to the polyelectrolyte effect, can be expressed as the ratio of hydrodynamic volumes in methanol/HCl and in pure methanol. The influence of structure on molecular expansion can be explored by comparing these volume expansion factors to the hydrodynamic volume ratios determined for linear P2VP samples ($M_w = 1.73\text{–}9.38\times10^5$), selected for their hydrodynamic radius that is comparable to some of the branched copolymers in the neutral state.

Table 4.4 Dynamic Light Scattering Results

Sample	R_h (MeOH) /nm	R_h (0.1 N HCl in MeOH) /nm
G0PS-P2VP5	12.8	14.9
G1PS-P2VP5	25.1	28.4
G2PS-P2VP5	34.4	37.2
PS-P2VP30	12.6	17.4
G0PS-P2VP30	26.8	36.5
G1PS-P2VP30	38.9	48.8
G2PS-P2VP30	44.5	56.3
P2VP173	13.9	14.7
P2VP370	18.4	19.3
P2VP938	23.9	25.4

The hydrodynamic volume expansion factors determined for the linear P2VP samples and the two series of graft copolymers with $M_w \approx 5000$ (P2VP5) and $M_w \approx 30\ 000$ (P2VP30)

P2VP side chains are compared in Figure 4.2. The increase in hydrodynamic volume upon protonation is much greater for the copolymer samples than for linear P2VP. This effect is attributed to increased charge density and electrostatic repulsions inside the branched copolymers, due to the compact structure of the molecules, leading to enhanced molecular expansion. The expansion is greatest for the protonated graft copolymers with long, flexible P2VP30 side chains.

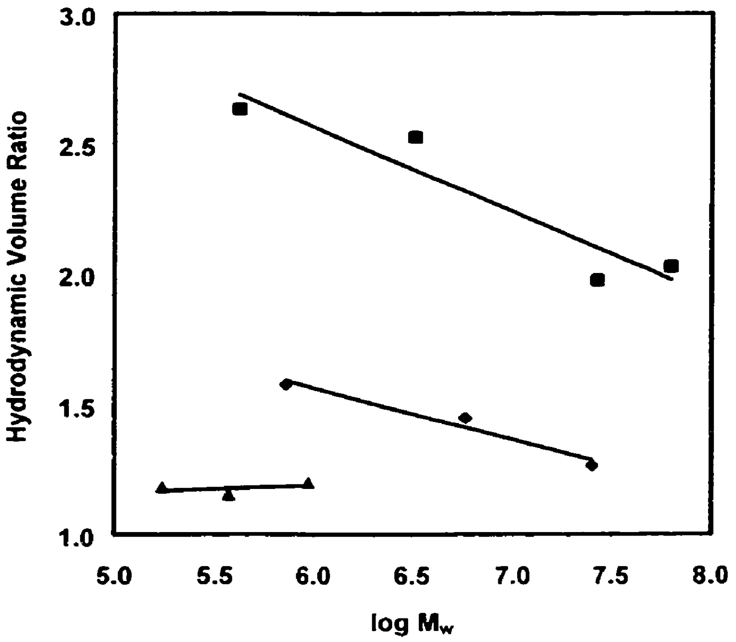

Figure 4.2 Molecular weight dependence of hydrodynamic volume expansion for linear P2VP (▲), P2VP5 (◆) and P2VP30 (■) arborescent copolymers.

Interestingly, within each series of graft copolymers, the hydrodynamic volume expansion ratio decreases for higher generations (Figure 4.2). Two factors may contribute to the differences observed among the two series, namely variations in the polystyrene content and in the structural rigidity of the molecules. The arborescent copolymers with short ($M_w \approx 5\,000$) P2VP side chains have a higher polystyrene content (10–19 mol%) and expand proportionately less upon protonation than the copolymers with long P2VP side chains. The increasing polystyrene content of the copolymers correlates with the decreasing tendency for the molecules to expand for higher generations. Increased structural rigidity is also expected for copolymers with short P2VP side chains, due to their high branching density. A study of the solution behaviour of arborescent polystyrenes demonstrated that molecules with short ($M_w \approx 5000$) polystyrene side chains become progressively more rigid for higher generations.[22] Under these conditions, the enhanced molecular expansion effect expected due to electrostatic repulsion may be opposed by elastic forces linked to increased structural rigidity within the molecules.

It is interesting to note that a decrease in molecular expansion is also observed for the arborescent copolymers with long P2VP side chains. The composition of these copolymers is strongly dominated by the P2VP component (92–97 mol%), and solution properties consistent with P2VP homopolymers would be expected for these samples. It seems therefore, that the increased structural rigidity of higher generation molecules may be a dominant factor leading to the trends observed.

4.5 Conclusions

The results reported demonstrate that it is possible to prepare arborescent graft copolymers consisting of poly(2-vinylpyridine) side chains randomly grafted onto a partially chloromethylated arborescent polystyrene substrate. The efficiency of the coupling reaction between poly(2-vinylpyridine) anions and chloromethyl sites improves in the presence of TMEDA, presumably due to the increased reactivity of the anions. Dynamic light scattering measurements indicate that the arborescent poly(2-vinylpyridine) copolymers expand considerably more than linear homologous polymers when protonated with HCl. This effect is attributed to the higher charge density attained for the highly branched copolymers.

The data obtained suggest that by varying the structure of the copolymers, the physical properties of arborescent P2VP copolymers in solution can be controlled to a large extent. One way this can be achieved is by varying parameters such as the length and number of the P2VP segments, and the size (generation) of the polystyrene substrate. Control over these parameters may enable the design of pH-sensitive reversible gels with controllable properties such as sol-gel transition points and gel modulus.

4.6 References

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Chapter 5

Arborescent Polystyrene-graft-Poly(*tert*-butyl methacrylate) Copolymers: Highly Branched Anionic Polyelectrolyte Precursors

5.1 Abstract

A technique is described for the preparation of arborescent graft copolymers containing poly(*tert*-butyl methacrylate) (PtBuMA) segments. For this purpose, *tert*-butyl methacrylate is first polymerized with 1,1-diphenyl-2-methylpentyllithium in tetrahydrofuran. The graft copolymers are obtained by addition of a solution of a bromomethylated polystyrene substrate to a living PtBuMA macroanion solution. Copolymers incorporating either short ($M_w \approx 5000$) or long ($M_w \approx 30\ 000$) PtBuMA side chains were prepared by grafting onto linear, comb-branched (G0), G1, and G2 bromomethylated arborescent polystyrenes. Branching functionalities ranging from 9–4 508 and molecular weights ranging from 8.8×10^4–6.3×10^7 were obtained for the copolymers, while maintaining a low apparent polydispersity index ($M_w/M_n \approx 1.14$–1.25). Characterization data for these materials from size exclusion chromatography and light scattering indicates that they have a highly compact structure. Arborescent polystyrene-*graft*-poly(methacrylic acid) (PMAA) copolymers were obtained by hydrolysis of the *tert*-butyl methacrylate segments. Dynamic light scattering measurements show that the arborescent poly(methacrylic acid) copolymers expand considerably more than homologous linear polymers when neutralized with NaOH. This effect is attributed to the higher charge density and compact structure of the arborescent copolymers.

5.2 Introduction

Dendritic polymers are an interesting class of macromolecules with a cascade-branched structure comprising dendrimers, hyperbranched, and arborescent polymers. A wide range of synthetic techniques has been developed for the preparation of these materials.[1-5] Arborescent polymers are prepared from successive grafting reactions incorporating well-defined polymeric building blocks. This "graft-on-graft" approach yields macromolecules with a high branching functionality and molecular weight in a few reaction steps, while maintaining a narrow molecular weight distribution ($M_w/M_n \approx 1.1$). The synthesis of arborescent polymers first requires the random introduction of reactive grafting sites along a linear polymer chain. Living polymer chains are then coupled with the linear substrate to generate a comb-branched (generation 0 or G0) polymer. Repeating the functionalization and coupling reaction cycles leads to higher generation (G1, G2, etc.) arborescent polymers. This synthetic strategy has been applied to the synthesis of arborescent polystyrenes[3] using cycles of chloromethylation and coupling with polystyryl anions. Analogous methods have also been developed to prepare comb-burst polyethylenimines[4] and arborescent polybutadienes.[5] In all cases the syntheses relied on living polymerization techniques, to achieve precise control over the molecular weight and polydispersity of the grafted polymer segments.

Incorporation of other monomers into the "graft-on-graft" approach has led to the preparation of arborescent copolymers with a wide range of chemical compositions. The preparation of arborescent polystyrene-*graft*-poly(ethylene oxide) has been described using a *grafting from* approach.[6] More recently, a *grafting onto* approach was used to prepare arborescent polystyrene-*graft*-polyisoprene[7] (Chapter 3) and polystyrene-*graft*-poly(2-vinylpyridine) copolymers (Chapter 4).[8] The key feature of arborescent copolymers is that the number and size of the grafted side chains can be varied independently, resulting in extensive control over the morphology and the physical properties of the copolymers.

The incorporation of other monomers such as *tert*-butyl methacrylate, that can be readily hydrolyzed to yield methacrylic acid-based polyelectrolytes, is of considerable interest.

Interesting physical properties are expected for these copolymers, due to their highly branched structure and heterogeneous morphology. For example, dynamic light scattering results show that arborescent poly(2-vinylpyridine) copolymers expand much more in solution than linear homologous polymers when protonated with HCl (Chapter 4). This was attributed to the higher charge density attained in the branched copolymers. Hydrolysis of the PtBuMA side chains will yield arborescent poly(methacrylic acid) (PMAA) copolymers, that are expected to have interesting solution behaviour due to their compact structure and high charge density in the ionized state.[9]

The synthesis of two series of arborescent copolymers incorporating PtBuMA side chains of different molecular weight grafted onto linear, comb-branched (G0), G1, and G2 randomly bromomethylated arborescent polystyrenes is now reported. A method by which chloromethyl sites on polystyrene are conveniently converted to bromomethyl functionalities is described. The coupling yield is compared for reactions using partially chloromethylated and bromomethylated substrates. Characterization results for the copolymers obtained from size exclusion chromatography, light scattering and ^{1}H-NMR spectroscopy measurements, demonstrating the success of the synthetic approach, are described in this study. The interesting solution behaviour of these copolymers is demonstrated in an investigation of the polyelectrolyte effect using dynamic light scattering measurements.

5.3 Experimental Procedures

5.3.1 Reagents

Styrene (Aldrich, 99%), 1-1-diphenylethylene (DPE; Aldrich, 97%), tetrahydrofuran (THF; Caledon, ACS Reagent) and CCl_4 (Caledon, ACS Reagent) were purified as previously described.[6] *tert*-Butyl methacrylate (tBuMA; TCI, 98%) was first purified by stirring with CaH_2 and distillation under reduced pressure. To obtain *tert*-butyl methacrylate monomer of sufficient purity for anionic polymerization, an additional purification step, using triethylaluminum (TEA; Aldrich, 1.9 M in toluene) and diisobutylaluminum hydride (DIBAH; Aldrich, 1.0 M in toluene) is described subsequently. A *sec*-butyllithium solution (Aldrich, 1.3 M in cyclohexane) was analyzed by the procedure of Lipton *et al.*[18] to determine the exact concentration of the reagent. All other reagents were used as received.

5.3.2 Partially Chloromethylated Polystyrene Substrates

Linear, comb-branched (G0), G1, and G2 polystyrene samples were synthesized as previously described.[6] Partial chloromethylation of the substrates was carried out by a known procedure.[7]

5.3.3 Partially Bromomethylated Polystyrene Substrates

Linear, comb-branched (G0), G1 and G2 partially chloromethylated polystyrene samples were converted to bromomethylated substrates using a modification of a known procedure.[19] A chloromethylated polystyrene sample (5 g; 12 meq chloromethyl functionalities) and sodium bromide (3.09 g, 30 mmol) were dissolved in DMF:dibromomethane (100 mL, 2:1 v/v). The solution was warmed to 85°C and stirred for 24 hours. After cooling to room temperature, the polymer solution was filtered to remove residual salts, and precipitated in methanol (1.5 L). Redissolution in THF and precipitation in methanol was used to further purify the polymer. Prior to the grafting reaction, the vacuum-dried bromomethylated polystyrene sample was transferred to a glass ampule equipped with a poly(tetrafluoroethylene) (PTFE) stopcock and further purified on a vacuum line using three azeotropic distillation cycles with purified THF. After redissolving the polymer in purified THF, the ampule was filled with nitrogen.

5.3.4 Arborescent Copolymers

tert-Butyl methacrylate was purified on a vacuum line immediately prior to anionic polymerization first by degassing with three freezing-evacuation-thawing cycles, followed by titration with a solution of TEA:DIBAH 1:1 v/v at 0°C until a persistent yellow-green endpoint was observed.[10,20] Three additional freezing-evacuation-thawing cycles were performed, and the monomer was stirred at 0°C and slowly distilled to a glass ampule with a PTFE stopcock. The ampule was filled with nitrogen and stored at -5°C until needed.

The first step in the synthesis of a graft copolymer is the anionic polymerization of tBuMA. The polymerization was carried out under nitrogen atmosphere in a 2-L glass reactor at –78°C. Purified THF was added to the reactor, followed by a solution of DPE in THF. The initiator, 1,1-diphenyl-2-methylpentyllithium, was generated *in situ* from the reaction of *sec*-butyllithium with DPE. The monomer was then added drop-wise to the solution, resulting in a rapid colour change from bright red to faint yellow-green. After 30 min, a sample of the side chains was removed from the reactor and terminated with degassed methanol. The polymer solution was warmed to 0°C and a solution of bromomethylated polystyrene in THF was added. After 12 h, residual anions were terminated with degassed methanol, yielding a clear, colourless solution. Non-grafted poly(*tert*-butyl methacrylate) side chains were removed from the crude grafting reaction product by repeated precipitation fractionation using a THF/methanol mixture. The fractionated product was dissolved in THF and was precipitated in methanol/water 4/1 v/v.

5.3.5 Hydrolysis of Arborescent Copolymers

A vacuum-dried sample of fractionated graft copolymer (1.0 g, 7.0 meq tBuMA units) and dichloromethane (20 mL) were loaded in a 100 mL round–bottomed flask with a stirring bar. The flask was fitted with a rubber septum, purged and pressurized with nitrogen. Trimethylsilyliodide (5.0 mL, 35 mmol; Aldrich) was added to the flask with a syringe and the solution was stirred for 12 h at room temperature. The solvent was removed under vacuum and the residue was redissolved in methanol containing 50% v/v 1 N HCl (20 mL). The polymer was then precipitated in diethyl ether, and further purified by three cycles of dissolution in methanol and precipitation into diethyl ether.

5.3.6 Characterization

Size exclusion chromatography was used to characterize the polystyrene and poly(*tert*-butyl methacrylate) side chains, the raw grafting products, and the fractionated graft copolymers. The instrument used consists of a Waters 510 HPLC pump, a Jordi 500 mm DVB linear mixed bed column and a Waters 410 differential refractometer detector. Tetrahydrofuran served as eluent at a flow rate of 1 mL/min. A linear PtBuMA standards (Polymer Source) calibration curve was used to determine absolute molecular weights for the PtBuMA side chains and apparent molecular weights for the arborescent copolymers. A linear polystyrene standards (Pressure Chemical Co.) calibration curve was used to determine absolute molecular weights for the polystyrene side chains and apparent values for the arborescent polystyrene grafting substrates.

Completion of the halogen exchange reaction was verified using FT-IR spectroscopy on a Bomem Michelson MB-100 FT-IR spectrometer with a resolution of 4 cm^{-1}. A thin film of the functionalized polystyrene substrate was cast from a chloroform solution onto a NaCl disk for this purpose.

The degree of functionalization of the chloromethylated and bromomethylated arborescent polystyrene substrates, and the composition of the graft copolymers were determined using ^{1}H-NMR spectroscopy on a Bruker AM-250 spectrometer. The polymers were dissolved in $CDCl_3$ at a concentration of 5% w/v for the measurements. Complete hydrolysis of the graft copolymers was also verified using ^{1}H-NMR spectroscopy, after dissolution in methanol-d_4 at a concentration of 5% w/v.

The composition of the graft copolymers was also verified by UV spectroscopy on a Hewlett-Packard HP8452 spectrophotometer. The characteristic polystyrene absorbance maximum at $\lambda = 262$ nm was used to generate an absorbance *vs.* concentration curve using linear polystyrene standards (M_w = 5 000) dissolved in *n*-butyl acetate. The PtBuMA contents reported are calculated from the polystyrene content in the graft copolymers determined in *n*-butyl acetate, by comparing the absorbance at $\lambda = 262$ nm to the calibration curve.

The absolute weight-average molecular weight (M_w) of the polystyrene substrates and of the arborescent copolymers was determined from static light scattering measurements. The refractive index increments (dn/dc) for linear polystyrene ($M_w \approx 50\ 000$), linear poly(*tert*-butyl methacrylate) ($M_w \approx 30\ 000$) and the graft copolymers were measured in *n*-

butyl acetate at 25.0 ± 0.1°C using a Brice-Pheonix differential refractometer equipped with a 510 nm bandpass interference filter. A Brookhaven BI-200 SM light scattering goniometer with a Lexel 2-Watt argon ion laser operating at 514.5 nm was used for the light scattering measurements.[6] The absolute M_w was determined by Zimm extrapolation to zero angle and concentration for a series of measurements for 6-8 samples at angles ranging from 30-150°.

The hydrodynamic radius of the graft copolymers was determined from dynamic light scattering measurements using a Brookhaven BI-2030AT 201–channel correlator. The hydrodynamic radius was determined from the z-average diffusion coefficient obtained from second-order cumulant analysis of the normalized electric field correlation function $|g_1(\tau)|$, to better account for polydispersity effects. First and second-order cumulant analyses were always compared, to ensure that aggregation of the macromolecules was not occurring. Solutions of the copolymers and linear polymers were prepared in methanol:water 95:5 v/v containing 0.05 N NaCl, and in methanol:water 95:5 v/v containing 0.05 N NaCl and 0.01 N NaOH. The concentration of the polymer solutions was adjusted to provide a reasonable photon counting rate ($\approx 10^5$ counts/sec), but was always <1% w/v. Prior to analysis, each polymer sample was filtered three times through a 0.5 μm PTFE membrane filter into a scintillation vial.

5.4 Results and Discussion

The synthesis of PtBuMA of controllable molecular weight has been previously reported.[10,11] Narrow molecular weight distributions can only be achieved if the monomer is appropriately purified and the polymerization is initiated with a species that reacts exclusively with the vinyl bond. Under these conditions, PtBuMA samples with narrow molecular weight distributions (M_w/M_n=1.12–1.32) have been prepared at temperatures up to 37°C.[10] The presence of lithium chloride (LiCl) has been shown to enhance the living character of the polymerization, and to result in a narrower molecular weight distribution (M_w/M_n=1.05-1.10).[11]

Anionic grafting techniques have been applied to the preparation of comb-branched graft copolymers from moderately nucleophilic macroanions such as poly(ethylene oxide)[12] and poly(2-vinylpyridine)[13,14] and partially chloromethylated linear polystyrene. The reactivity of poly(alkyl methacrylate) anions is lower than that of poly(2-vinylpyridine) anions, but is greater than for poly(ethylene oxide) anions.[15] This suggests that graft copolymers could be prepared from PtBuMA anions and partially chloromethylated polystyrene substrates. Alternately, more electrophilic coupling sites could be selected to increase the grafting yield. For example, the reaction of excess poly(methyl methacrylate) anions with 1,4-bis(bromomethyl)benzene proceeds with 90% consumption of the available bromomethyl groups.[16] In a related study, 4-arm star polymers with either poly(2-vinylpyridine), poly(methyl methacrylate) or PtBuMA side chains have been prepared by reacting a 50 mol% excess of the corresponding living macroanion with 1,2,4,5-tetra(bromomethyl)benzene.[17] The synthesis of graft copolymers consisting of PtBuMA side chains has been reported very recently, but only for comb-branched structures.[17] In this case, the coupling efficiency was limited to 70% for the reaction of PtBuMA side chains with partially bromomethylated linear polystyrenes.

5.4.1 Grafting Substrates

The characteristics of the linear and branched polystyrene substrates used in the preparation of the graft copolymers are summarized in Table 5.1. The branching functionality (f_w) of the polymers, defined as the number of chains added in the last grafting reaction, was calculated from the equation

$$f_w = \frac{M_w(G) - M_w(G-1)}{M_w^{br}} \tag{5.1}$$

where $M_w(G)$, $M_w(G-1)$ *and* M_w^{br} are the absolute weight-average molecular weight of graft polymers of generation *G*, of the preceding generation and of the side chains, respectively. The number of potential grafting sites introduced on the substrates was calculated from their molecular weight ($M_w(G)$) and chloromethylation level.

Table 5.1 Characteristics of the Polystyrene Substrates

Polymer	M_w^{br} (SEC)[a]	M_w/M_n^{br} (SEC)[a]	M_w (LS)[b]	f_w	CH_2Cl[c] / mol%	Grafting Sites
PS (linear)	5 420	1.09	n/a	1	26	14
G0PS	5 220	1.07	66 700	12	22	140
G1PS	6 160	1.06	727 000	108	20	1390
G2PS	5 210	1.07	5 030 000	826	16	7730

[a] Values from SEC analysis using linear PS standards calibration

[b] Absolute M_w of the graft polymers from laser light scattering (linear sample analyzed using SEC)

[c] Chloromethylation level from ^{1}H-NMR spectroscopy

5.4.2 Halogen Exchange Reaction

Linear, comb-branched (G0), G1, and G2 partially bromomethylated polystyrene substrates were prepared from chloromethylated samples by halogen exchange. Complete conversion was verified using ^{1}H-NMR and IR spectroscopy. A representative ^{1}H-NMR spectrum for a partially chloromethylated G0 polystyrene is shown in Figure 5.1. The peak corresponding to the chloromethyl protons ($\delta = 4.54$ ppm) in the ^{1}H-NMR spectrum for chloromethylated polystyrene appears upfield ($\delta = 4.41$ ppm) with the same relative intensity after bromomethylation (inset; Figure 5.1). IR spectra for the chloromethylated and bromomethylated polystyrenes are distinct. The absorbance at 1265 cm^{-1} in the FTIR spectrum of the chloromethylated sample, corresponding to the methylene wag of the chloromethyl group (Figure 5.2a), is absent from the spectrum of the bromomethylated sample (Figure 5.2b). The absorbance at 1200 cm^{-1} in the FTIR spectrum for the bromomethylated sample (Figure 5.2b) is attributed to the methylene wag of the bromomethyl group. In all cases, SEC analysis indicates that there is no change in the apparent molecular weight of the substrates after the halogen exchange reaction. Based on these results, the conversion of the chloromethyl sites to bromomethyl sites appears to proceed quantitatively without side reactions.

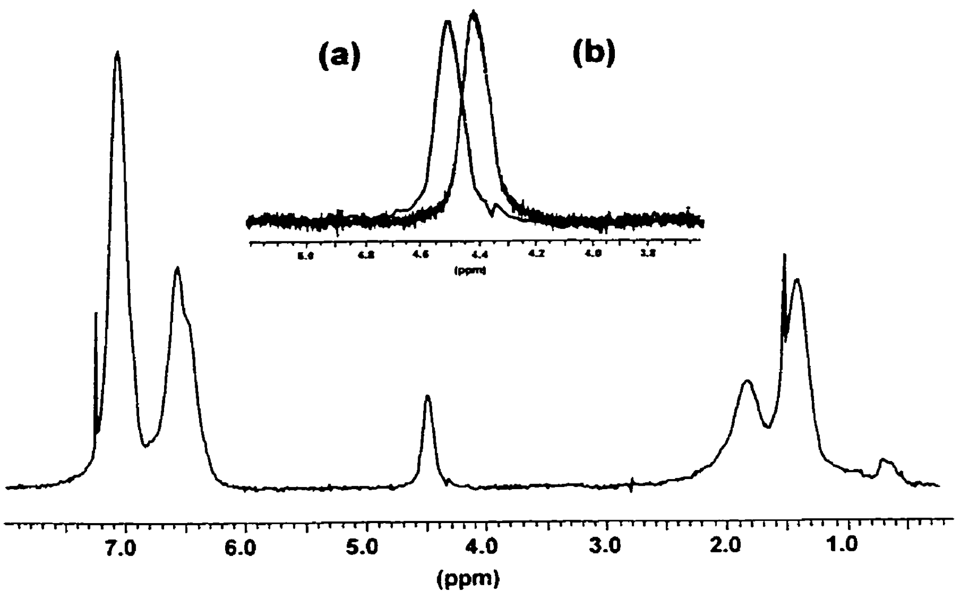

Figure 5.1 ^{1}H-NMR spectra for (a) chloromethylated and (b) bromomethylated G1 arborescent polystyrenes.

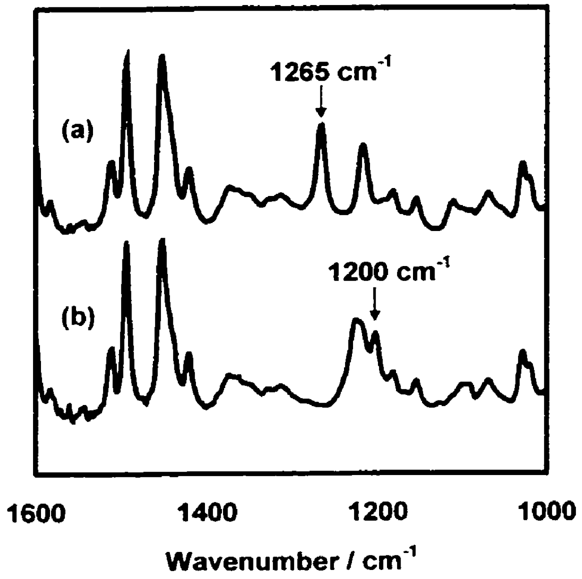

Figure 5.2 IR spectra for partially functionalized G1PS, comparing the methylene absorptions for (a) chloromethylated and (b) bromomethylated G1PS.

5.4.3 Optimization of the Grafting Yield

There are three important requirements for the synthesis of graft copolymers using a *grafting onto* strategy: Firstly, the polymeric side chains must remain living during the time required to complete the reaction. Secondly, grafting must proceed in the absence of side reactions. Thirdly, the reactivity of the macroanions serving as side chains must be matched to the reactivity of the grafting sites. Anionic polymerization techniques are ideally suited to the preparation of graft polymers, since a variety of polymeric macroanions are highly nucleophilic and have good "living" characteristics.[21] Furthermore, many macroanions have sufficient reactivity to graft onto suitably functionalized polymeric substrates.[22]

The fraction of available PtBuMA side chains that becomes grafted onto a polystyrene substrate is defined as the ***grafting yield***. It can be approximated using the SEC trace for the raw product from each grafting reaction. A series of SEC elution curves are provided in Figure 5.3 to illustrate the synthesis of sample G0PS-PtBuMA5. The sample identification used for the graft copolymers specifies their composition and structure. For example, G0PS-PtBuMA5 refers to a graft copolymer with $M_w^{br} \approx 5\ 000$ PtBuMA side chains grafted onto a G0 (comb-branched) arborescent polystyrene substrate. Since the overall composition of the graft copolymers is dominated by the PtBuMA component, a comparison of the peak area for the graft copolymer (leftmost peak, Figure 5.3c) to the total area for both peaks in the SEC trace for the crude grafting product (Figure 5.3c) yields the fraction of PtBuMA side chains grafted. Thus 67% of the available PtBuMA side chains were grafted onto the G0PS substrate. However, this value is in fact slightly overestimated, because the refractive index increment (dn/dc) for polystyrene in THF (dn/dc = 0.196 at 514.5 nm) is larger than for poly(*tert*-butyl methacrylate) (dn/dc ≈ 0.080 at 514.5 nm). Because of this, the intensity of the graft copolymer peak is exaggerated when compared to the peak corresponding to the non-grafted side chains, due to the proportionally larger response for the polystyrene component of the copolymer. Nevertheless, the approximate fraction of non-grafted PtBuMA side chains may be compared on a relative basis.

Grafting yields were compared for the reaction of excess living PtBuMA macroanions (1.25 eq with respect to the coupling sites) with linear partially chloromethylated and bromomethylated polystyrene substrates, respectively. A grafting yield of 45% was obtained for the reaction with the partially chloromethylated substrate. Under the same reaction conditions, the grafting yield increased to 67% after conversion to bromomethyl sites. Thus, the modest reactivity of the living PtBuMA anions is more closely matched to the increased reactivity of the bromomethyl sites.

Two factors may contribute to the deactivation of living PtBuMA anions. Residual protic impurities introduced with the substrate polymer solution can terminate the chains. In addition, premature self-termination of the macroanions can occur by an intramolecular "backbiting" reaction, resulting in the formation of a β-keto ester and a six-membered ring at the chain terminus.[23] In the absence of LiCl the chain ends are less stable, and termination may occur at an appreciable rate in THF at 0°C.[24] In the presence of a large excess of living chains, the coupling reaction is less sensitive to residual protic impurities and the overall rate of the grafting reaction may increase. Increasing the rate of the grafting reaction is desirable, due to the limited reactivity and temperature-dependent stability of PtBuMA anions.

The dependence of the grafting yield on the PtBuMA side chains excess used was investigated in a series of four reactions. In each case, PtBuMA side chains ($M_w \approx 30\ 000$) were reacted with the bromomethylated G0PS substrate. The ratio of PtBuMA side chains to grafting sites was varied from 1:1 to 2:1. The grafting yields attained are compared in Table 5.2. As the ratio of living PtBuMA anions to grafting sites increases from 1:1 to 1.5:1, the grafting yield increases. However, at a ratio of 2:1 the grafting yield is reduced due to the large excess of side chains. Interestingly, the apparent weight-average molecular weight (M_w^{app}) of the graft copolymers increases as the ratio of living PtBuMA anions to grafting sites tends to increase, suggesting that more side chains were grafted onto the substrate.

Table 5.2 Effect of Excess PtBuMA Side Chains on Grafting Yield for G0PS-PtBuMA30 Copolymers

[PtBuMA]/[Br]	M_w^{br} (SEC) [a]	M_w/M_n^{br} (SEC)[a]	Grafting Yield / %	M_w^{app} (SEC) [b]	M_w/M_n^{app} (SEC)[b]
1	31 300	1.10	19	550 000	1.19
1.25	30 400	1.09	38	530 000	1.17
1.5	29 700	1.09	62	572 000	1.13
2	31 600	1.11	43	583 000	1.12

[a] Values for the side chains from SEC analysis using linear PtBuMA standards calibration
[b] Apparent values for the copolymers from SEC analysis using linear PtBuMA standards calibration

The ***coupling efficiency***, defined as the fraction of available grafting sites that react, is determined by the accessibility of the grafting sites. On the basis of the trends observed, excess PtBuMA side chains (25-100%) were used for the PtBuMA5 series of arborescent copolymers prepared. A larger excess of side chains (25-200%) was used for synthesis of the PtBuMA30 series than for the PtBuMA5 series, to account for the expected decrease in coupling efficiency with increasing side chain M_w.

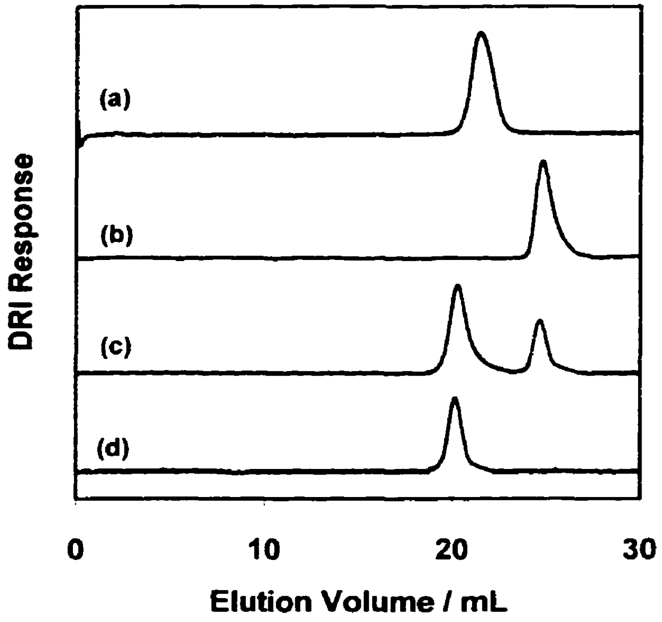

Figure 5.3 Preparation of sample G0PS-PtBuMA5: SEC traces for (a) bromomethylated G0 polystyrene, (b) poly(*tert*-butyl methacrylate) side chains, (c) raw product from the grafting reaction, (d) fractionated graft copolymer.

5.4.4 Arborescent Polystyrene-*graft*-Poly(*tert*-butyl methacrylate) Copolymers

The synthesis of an arborescent graft copolymer is illustrated in Figure 5.3 using a series of SEC traces corresponding to the bromomethylated polystyrene substrate (G0PS), PtBuMA side chains with $M_w \approx 5000$, the raw grafting product, and the fractionated arborescent graft copolymer. Two peaks can be observed in the SEC trace for the raw product (curve c). The leftmost (highest molecular weight) peak corresponds to the arborescent copolymer. The rightmost (lowest molecular weight) peak has the same elution volume as the side chain sample removed from the reactor prior to grafting (curve b). This peak corresponds to non-grafted side chains that were either prematurely terminated or did not react in the grafting reaction. Termination of the living polymer chains may occur according to the self-termination reaction described above or through reaction with residual protic impurities present in the bromomethylated polymer solution. Curve d demonstrates that complete removal of the non-grafted side chains can be readily achieved through fractionation.

Two series of arborescent copolymers were prepared by grafting either short ($M_w \approx$ 5 000, PtBuMA5 series) or long ($M_w \approx$ 30 000, PtBuMA30 series) side chains onto bromomethylated polystyrene substrates of different generations. Characterization results obtained for the copolymers are summarized in Table 5.3. The narrow molecular weight distributions obtained ($M_w/M_n \leq 1.11$) demonstrate that precise control was maintained over the molecular weight of the PtBuMA side chains under the conditions used, and that the polymerization proceeded free of side reactions.

Compositional analysis was carried out using both ^{1}H-NMR and UV spectroscopy. The results from both methods are in close agreement, and indicate that the composition of the graft copolymers is dominated by the PtBuMA component, ranging from 81-91 mol% and 90-98 mol% for the PtBuMA5 and PtBuMA30 series, respectively (Table 5.3). This demonstrates that graft copolymers with a significant polystyrene component can be prepared if short PtBuMA (or alternately fewer) chains are grafted. The polystyrene component becomes negligible when longer PtBuMA chains are used. For example, in the ^{1}H-NMR spectrum obtained for sample G1PS-PtBuMA30 shown in Figure 5.4a, the characteristic peaks attributable to the aromatic protons of the polystyrene component are very weak.

The branching functionality (f_w, calculated using Equation 5.1) ranges from 11–4 508 within the PtBuMA5 series and from 9–1 599 within the PtBuMA30 series. The ***coupling efficiency***, also reported in Table 5.3, defined as the fraction of available bromomethyl sites consumed in the coupling reaction, is calculated by comparing the f_w values and the number of available grafting sites on the substrates (Table 5.1). The coupling efficiency decreases for longer PtBuMA side chains and for higher polystyrene substrate generations. The same variations in coupling efficiency were observed in the preparation of arborescent polystyrene-*graft*-polyisoprene[7] and arborescent polystyrene-*graft*-poly(2-vinylpyridine)[8] copolymers. The coupling sites are presumably distributed randomly throughout the polystyrene substrate and should have equivalent reactivity. On the other hand, higher generation substrates are more highly branched and their structure is much more congested. As the grafting reaction proceeds, increased steric congestion should lead to differential accessibility for the remaining coupling sites, and a decreased coupling efficiency.

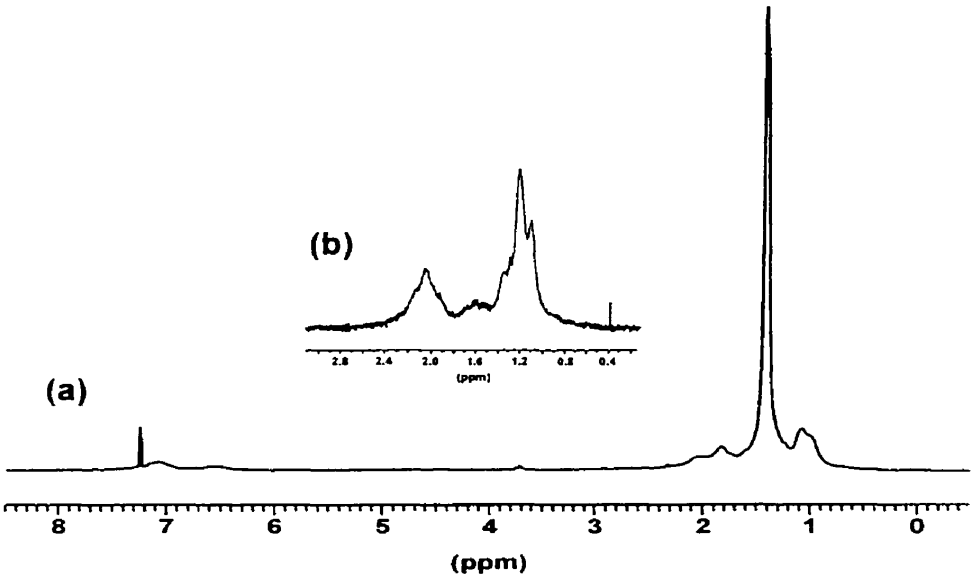

Figure 5.4 ^{1}H-NMR spectra for sample G1PS-PtBuMA30 (a) prior to hydrolysis and (b) (inset) after hydrolysis.

Table 5.3 Characterization Data for Arborescent Poly(*tert*-butyl methacrylate) Graft Copolymers

	Side Chains			Graft Copolymers						
Copolymer Sample	M_w (SEC)[a]	M_w/M_n (SEC)[a]	PtBuMA: Coupling Sites	M_w^{app} (SEC)[b]	M_w/M_n^{app} (SEC)[b]	M_w (LS)	Composition (NMR)[c] / %w/w PtBuMA	Composition (UV)[d] / %w/w PtBuMA	f_w[e]	Coupling Efficiency[f] / %
PS-PtBuMA5	5 100	1.11	25	39 300	1.18	87 900	89	91	11	78
G0PS-PtBuMA5	5 300	1.07	25	112 800	1.20	712 000	88	89	102	73
G1PS-PtBuMA5	5 500	1.08	50	476 300	1.25	7 240 000	83	85	750	54
G2PS-PtBuMA5	5 100	1.07	100	---	---	42 000 000	82	81	4 508	58
PS-PtBuMA30	30 500	1.10	25	186 000	1.20	278 000	98	98	9	64
G0PS-PtBuMA30	29 700	1.09	50	572 000	1.13	1 610 000	96	95	43	30
G1PS-PtBuMA30	29 400	1.10	100	1 250 000	1.14	15 600 000	94	93	329	24
G2PS-PtBuMA30	31 500	1.08	200	---	---	63 000 000	91	90	1 599	21

[a] Values from SEC analysis using linear PtBuMA standards calibration
[b] Values from SEC analysis using linear PtBuMA standards calibration
[c] Copolymer composition determined using ^{1}H-NMR spectroscopy
[d] Copolymer composition determined using UV spectroscopy
[e] Average number of branches calculated from M_w (LS) and absolute side chain M_w (Column 2)
[f] Fraction of grafting sites reacted calculated from f_w and grafting sites available

The segmental density of arborescent polystyrenes was probed using fluorescence quenching techniques, to show that the inner portion of the molecule is less accessible to quencher molecules than chains in the outer layer.[25] The fraction of less accessible material is found to increase for higher generation polymers. On this basis, a lower accessibility is predicted for coupling sites on higher generation substrates, in agreement with the coupling efficiency variations observed.

5.4.5 Copolymer Hydrolysis

The arborescent polystyrene-*graft*-poly(*tert*-butyl methacrylate) (PS-PtBuMA) copolymers were treated with TMSI and hydrolyzed with HCl to yield the corresponding polystyrene-*graft*-poly(methacrylic acid) (PS-PMAA) copolymers. Complete hydrolysis was verified using ^{1}H-NMR spectroscopy. For example, ^{1}H-NMR spectra are compared in Figure 5.4 for sample G1PS-PtBuMA30 before and after hydrolysis (aliphatic region; inset). The absence of the methyl proton resonance ($\delta = 1.42$ ppm) from the aliphatic region of the spectrum for the hydrolyzed sample is noted.

5.4.6 Solution Properties

A comparison of the absolute molecular weights obtained from light scattering measurements with the apparent values from size exclusion chromatography indicates that the arborescent copolymers have a very compact structure (Table 5.3). The molecular weights are significantly underestimated using SEC, but the apparent molecular weight distribution remains narrow ($M_w/M_n \leq 1.25$) for all generations characterized. The copolymers based on the G2PS substrate do not elute from the SEC column. Absolute weight-average molecular weights $M_w = 8.8\times10^4$–4.2×10^7 and 2.8×10^5–6.3×10^7 are obtained using light scattering for the PtBuMA5 and PtBuMA30 copolymer series, respectively. The refractive index increment (dn/dc) was measured for each copolymer. The values measured (in *n*-butyl acetate at 25°C) are consistent with values calculated using the equation:[26]

$$\frac{dn}{dc} = x_{PS}v_{PS} + x_{PtBuMA}v_{PtBuMA} \tag{2}$$

where x_{PS} and x_{PtBuMA} are the weight fractions of polystyrene (PS) and PtBuMA in the copolymer sample, respectively; v_{PS} and v_{PtBuMA} are the measured *dn/dc* values for styrene and tBuMA homopolymers.

After complete hydrolysis, all the arborescent polystyrene-*graft*-poly(methacrylic acid) copolymer samples synthesized were freely soluble in methanol containing 5% v/v water and 0.05 N NaCl. Clear solutions were obtained for the copolymers (0.5-2% w/v) based on linear, G0, and G1 polystyrene cores. Solutions containing 0.5% (w/v) copolymers based on the G2 polystyrene core were opalescent. To investigate molecular expansion upon ionization due to the polyelectrolyte effect, the hydrodynamic radius of the arborescent copolymer molecules was measured using dynamic light scattering before and after neutralization with NaOH. Hydrodynamic radii for samples in the neutral state were determined in methanol containing 5% (v/v) water and 0.05 N NaCl. Neutralization was achieved by preparing solutions of the copolymers in methanol containing 5% (v/v) water, 0.05 N NaCl and 0.01 N NaOH. The hydrodynamic radii of the copolymers before and after ionization are compared in Table 5.4. The values obtained from first- and second-order cumulant analysis were in excellent agreement (± 2–4%) for all samples measured, suggesting that aggregation was not occurring in solution in both the neutral and neutralized state.

The increase in hydrodynamic radius upon ionization, due to the polyelectrolyte effect, can be expressed as the hydrodynamic volume ratio ($V_{h,NaOH}/V_h$) for the ionized ($V_{h,NaOH}$) and neutral (V_h) molecules obtained using dynamic light scattering. The influence of structure on molecular expansion can be explored by comparing these values to the hydrodynamic volume ratios determined for linear poly(methacrylic acid) (PMAA) samples ($M_w = 8.5\times10^4$–2.75×10^5) with a hydrodynamic radius comparable to some of the branched copolymers in the neutral state (Table 5.4). The hydrodynamic volume ratios ($V_{h,NaOH}/V_h$) determined for homologous linear PMAA samples and the two series of arborescent copolymers are compared in Figure 5.5.

The increase in hydrodynamic radius (Table 5.4) and hydrodynamic volume (Figure 5.5) upon ionization is considerably greater for the arborescent copolymer samples than for linear PMAA samples. This effect is attributed to the compact structure of the copolymers, leading to increased charge density and electrostatic repulsion along the backbone, and enhanced expansion of the molecules. Arborescent copolymers with longer ($M_w \approx$ 30 000, PMAA30 series) side chains expand considerably more than copolymers with short ($M_w \approx$ 5 000, PMAA5 series) side chains. Interestingly, the hydrodynamic volume ratio decreases for higher generations and for both copolymer series. Furthermore, the decrease is larger for the PMAA30 series.

Two factors may have contributed to the differences observed among the two series of arborescent copolymers, namely variations in the polystyrene content and in the structural rigidity of the molecules. Within each series of copolymers, the polystyrene content increases slightly for higher generations (Table 5.3). At the same time, the molecules expand proportionately less upon ionization. On the other hand, increased structural rigidity, due to a high branching density, is expected for copolymers with short (PMAA5) side chains. An examination of the solution behaviour of arborescent polystyrenes by static light scattering demonstrated that the molecules become progressively more rigid for higher generations.[27] Under these conditions, enhanced molecular expansion due to electrostatic repulsion may be opposed by steric restrictions resulting from increased structural rigidity for higher generations. The influence of increased structural rigidity appears to be more significant for the PMAA30 series, showing larger variations in molecular expansion for successive generations. In conclusion, the data obtained suggest that variation in the structure of the copolymers provides a facile way to control the physical properties of arborescent copolymers.

Table 5.4 Dynamic Light Scattering Results

Sample	R_h[a] / nm	$R_{h,NaOH}$[b] / nm
PS-PMAA5	13.2	21.5
G0PS-PMAA5	15.4	23.4
G1PS-PMAA5	30.9	44.1
G2PS-PMAA5	41.0	58.1
PS-PMAA30	15.9	32.1
G0PS-PMAA30	24.9	46.9
G1PS-PMAA30	42.2	72.3
G2PS-PMAA30	62.9	105.2
PMMA86	13.6	18.2
PMAA120	15.3	20.9
PMAA140	17.4	24.0
PMAA275	22.4	31.4

[a] R_h for neutral samples measured in 95/5 v/v MeOH:H_2O with 0.05 NaCl

[b] $R_{h,NaOH}$ for samples ionized with 0.01 N NaOH measured in 95/5 v/v MeOH:H_2O with 0.05N NaCl

A comparison of the hydrodynamic volume expansion ratios obtained for PMAA and P2VP homo- and copolymers highlights the enhanced expansion of the PMAA polymers. The differences in volume expansion ratios between arborescent PMAA and P2VP copolymers are even more noteworthy. For example, even the PMAA5 series copolymers expand more upon neutralization than the P2VP30 copolymer series upon protonation (Figure 5.5). This difference could be attributed to the greater flexibility of the PMAA side chains.

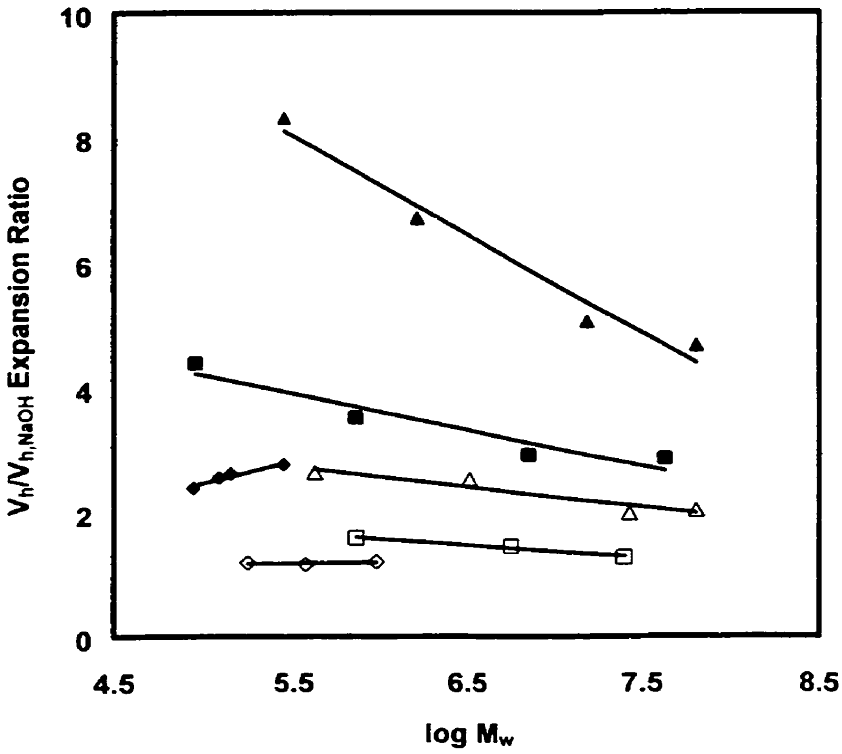

Figure 5.5 Molecular weight dependence of hydrodynamic volume expansion ratio: ($V_{h,NaOH}/V_h$) for linear and arborescent PMAA graft copolymers dissolved in MeOH/H_2O 95/5 with 0.05 N NaCl and neutralized with NaOH. Symbols: ◆ Linear PMAA; ■ PMAA5 Series; ▲ PMAA30 Series. Also shown: ($V_{h,HCl}/V_h$) for linear P2VP (◇), P2VP5 series (□) and P2VP30 series (△) arborescent copolymers.

5.5 Conclusions

A convenient method for converting randomly chloromethylated arborescent polystyrenes to bromomethylated products was developed. Two series of arborescent polystyrene-*graft*-poly(*tert*-butyl methacrylate) copolymers with short ($M_w \approx$ 5 000; PtBuMA5) and long ($M_w \approx$ 30 000; PtBuMA30) segments were prepared by grafting onto bromomethylated polystyrene substrates. The efficiency of the coupling reaction between the PtBuMA anions and bromomethyl sites ranges from 21-78%. A comparison of molecular weight data obtained using SEC and static light scattering confirms the compact structure of these molecules. Hydrolysis of the PtBuMA segments yielded arborescent polystyrene-*graft*-poly(methacrylic acid) copolymers. Dynamic light scattering results indicate that the arborescent poly(methacrylic acid) copolymers demonstrate enhanced expansion compared to linear homologous polymers when neutralized with NaOH. This is attributed to the higher charge density attained for the highly branched copolymers.

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Chapter 6

Preliminary Investigation into the Synthesis of Arborescent Polystyrene-*graft*-Poly(methyl methacrylate) Copolymers

6.1 Abstract

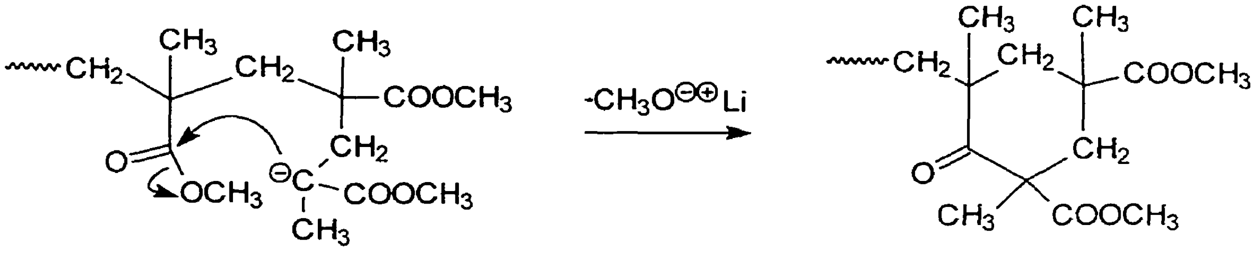
A technique is described for the preparation of arborescent graft copolymers containing poly(methyl methacrylate) (PMMA) segments. Methyl methacrylate is polymerized in the presence of LiCl using 1,1-diphenyl-2-methylpentyllithium in tetrahydrofuran, and the PMMA side chains are "capped" with 5 units of *tert*-butyl methacrylate (tBuMA). The graft copolymers are obtained by drop-wise addition of a solution of a bromomethylated comb-branched (G0) polystyrene substrate to the living PMMA anion solution. A copolymer with $M_w \approx 30\ 000$ PMMA side chains and a low apparent polydispersity index ($M_w/M_n = 1.16$) was prepared in 58% yield.

6.2 Introduction

The synthesis of arborescent copolymers relies on the anionic polymerization of the selected monomer, followed by grafting of the living side chains onto either a partially chloromethylated or bromomethylated arborescent polystyrene substrate. Using a similar approach, novel graft polymers consisting of poly(methyl methacrylate) (PMMA) side chains grafted onto arborescent polystyrene cores were prepared. Established techniques for the anionic polymerization of methyl methacrylate and the synthesis of arborescent copolymers were adapted for the synthesis of the PMMA copolymers. This Chapter summarizes a preliminary investigation into the synthesis of arborescent polystyrene-*graft*-poly(methyl methacrylate) copolymers.

6.3 Synthetic Strategy

For the grafting reaction to proceed in high yield, the PMMA anions must remain living during the time required for completing the reaction. The living characteristics of the macroanions depend on two important experimental factors: The monomer must be extremely pure and the reaction conditions must be carefully selected. The synthesis of poly(methyl methacrylate) (PMMA) with a predictable molecular weight and a narrow molecular weight distribution has been reported for alkyllithium-initiated anionic polymerizations carried out at low temperatures.[1] The anionic polymerization of MMA must be initiated with a sterically hindered initiator, to avoid reaction of the ester carbonyl function of the monomer.[2] At temperatures above –78°C the macroanions are susceptible to side reactions leading to premature termination of the chains and broadening of the molecular weight distribution.[3] The predominant side reaction has been identified as an intramolecular "backbiting" reaction resulting in the formation of a cyclic β-keto ester at the chain terminus (Equation 6.1).[4] To avoid premature termination reactions, the polymerization of MMA is typically carried out in the presence of at least a five-fold excess of lithium chloride, to stabilize the propagating anions.[5]



Equation 6.1 Intramolecular backbiting reaction that leads to termination of PMMA.

Anionic grafting techniques have been applied to the preparation of comb-branched graft copolymers from the reaction of moderately nucleophilic macroanions such as poly(ethylene oxide)[6] and poly(2-vinylpyridine)[7] with partially chloromethylated linear polystyrene substrates. When lithium is selected as a counterion, the reactivity of poly(methyl methacrylate) anions is slightly less than that of poly(2-vinylpyridine) anions, but is very similar to poly(ethylene oxide) anions.[8] This suggests that graft copolymers consisting of PMMA side chains grafted onto partially chloromethylated polystyrene substrates could be prepared. Alternately, more electrophilic coupling sites could be selected to enhance the grafting yield. For example, comb-branched graft copolymers consisting of poly(*tert*-butyl methacrylate) side chains were recently prepared by *grafting onto* partially bromomethylated linear polystyrenes. The ***coupling efficiency***, defined as the fraction of available grafting sites reacted, was limited to 70% under these conditions.[9] In the presence of 25-200 mol% excess side chains, arborescent polystyrene-*graft*-poly(*tert*-butyl methacrylate) copolymers were prepared by *grafting onto* bromomethylated arborescent polystyrene substrates with coupling efficiencies up to 78% (Chapter 5).

To illustrate the preparation of arborescent copolymers with PMMA segments, the synthesis of copolymers with $M_w \approx 30\,000$ side chains grafted onto comb-branched (G0) arborescent polystyrene was attempted using randomly chloromethylated and bromomethylated substrates. The grafting yield was increased by "capping" the living PMMA anions with a few *tert*-butyl methacrylate units.

6.4 Experimental Procedures

6.4.1 Reagents

Purified chloromethyl methyl ether (CMME) was prepared according to a previously described method.[10] The procedures using CMME should be carried out with due caution in a well-ventilated fume hood, since CMME is a known carcinogen.[11] Styrene (Aldrich, 99%), 1-1-diphenylethylene (DPE; Aldrich, 97%), tetrahydrofuran (THF; Caledon, ACS Reagent) and CCl_4 (Caledon, ACS Reagent) were purified as previously described.[10] Methyl methacrylate (MMA; Aldrich, 99%) and *tert*-butyl methacrylate (tBuMA; TCI, 98%) were first purified by stirring with CaH_2 and distillation under reduced pressure. To obtain methyl methacrylate and *tert*-butyl methacrylate monomers of sufficient purity for anionic polymerization, an additional purification step with triethylaluminum (TEA; Aldrich, 1.9 M in toluene) and diisobutylaluminum hydride (DIBAH; Aldrich, 1.0 M in toluene) was used. Dibromomethane (Aldrich, 99%), *N,N*-dimethylformamide (DMF; BDH, ACS Reagent), sodium bromide (Fisher) and *sec*-butyllithium (Aldrich, 1.3 M in cyclohexane) were used as received. The exact concentration of the *sec*-butyllithium solution was determined using the procedure of Lipton *et al.*[12]

6.4.2 Partially Chloromethylated G0 Polystyrene

A comb-branched (G0) polystyrene sample with a M_w = 5 420 backbone and M_w = 5 220 side chains was synthesized as described in Chapter 3. Partial chloromethylation was achieved using a modification of a previously reported procedure.[13] A comb-branched (G0) polystyrene sample (5 g) was dissolved in CCl_4 (500 mL), and a solution of aluminum chloride (Aldrich; 7 g), 1-nitropropane (Aldrich, 98%; 50 mL), and CCl_4 (50 mL) was slowly added. After stirring for 30 min, glacial acetic acid (10 mL) was added to the solution and the solvent was evaporated under reduced pressure. The residue was dissolved in chloroform, extracted with one portion of HCl (50% v/v), two portions of acetic acid (50% v/v), and precipitated into methanol. The precipitate was isolated, and purified twice by dissolution in toluene and precipitation into methanol.

6.4.3 Partially Bromomethylated G0 Polystyrene

The partially chloromethylated comb-branched (G0) polystyrene sample was converted to bromomethylated substrate using a modification of a previously reported procedure.[14] A chloromethylated polystyrene sample (5 g, 12 meq chloromethyl groups) and sodium bromide (3.09 g, 30 mmol) were dissolved in DMF:dibromomethane (100 mL, 2:1 v/v). The solution was warmed to 85°C and stirred for 24 h. After cooling to room temperature, the polymer solution was filtered to remove precipitated salts, and added drop-wise to methanol (1.5 L). The precipitate was isolated, and purified twice by dissolution in THF and precipitation into methanol.

Prior to the grafting reaction, the vacuum-dried bromomethylated polystyrene sample was transferred to a glass ampule equipped with a polytetrafluoroethylene (PTFE) stopcock and further purified on a vacuum line using three azeotropic distillations of purified THF. After dissolving the polymer in purified THF, the ampule was finally filled with nitrogen.

6.4.4 Arborescent Copolymers

Anionic polymerization–grade *tert*-butyl methacrylate and methyl methacrylate were obtained by purification on a vacuum line, first using three freezing-evacuation-thawing cycles, followed by titration with a solution of TEA:DIBAH 1:1 v/v at 0°C until a persistent yellow-green endpoint was observed.[15] Three additional freezing-evacuation-thawing cycles were performed, and the monomer was slowly distilled to a glass ampule while stirring at 0°C. The ampule was filled with nitrogen and stored at –5°C until needed. Purified THF (90% v/v) was added to the ampule containing *tert*-butyl methacrylate.

The first step in the synthesis of a graft copolymer is the anionic polymerization of methyl methacrylate. Prior to the polymerization, LiCl (5 mmol) was added to a 2–L glass reactor, which was then flamed under vacuum and filled with purified nitrogen. The polymerization was carried out under nitrogen atmosphere at –78°C. Purified THF (500 mL) was added to the reactor followed by a solution of DPE in THF. The initiator, 1,1-diphenyl-2-methylpentyllithium, was generated *in situ* through the reaction of *sec*-butyllithium with DPE. After 30 min, methyl methacrylate monomer was added drop-wise to the solution, resulting in a rapid colour change from bright red to colourless. After 30 min, the solution of *tert*-butyl methacrylate monomer in THF was added drop-wise to the solution. After 30 min, a sample of the side chains was removed from the reactor and terminated with degassed methanol. The solution of bromomethylated polystyrene (750 mg) in THF (50 mL) was then added drop-wise to the solution. The reaction was allowed to proceed for 24 h as the solution slowly warmed to 0°C. Residual anions were terminated with degassed methanol. The crude product was isolated, dissolved in THF and precipitated into methanol. Non-grafted poly(*tert*-butyl methacrylate)-capped PMMA side chains were removed from the crude grafting product by precipitation fractionation from a solvent/non-solvent (THF/methanol) mixture.

6.4.5 Characterization

Size exclusion chromatography (SEC) was used to characterize the polystyrene and poly(methyl methacrylate) side chains, the raw grafting products, and the fractionated graft copolymers. The instrument used consisted of a Waters 510 HPLC pump, a Jordi DVB 500 mm linear mixed bed column and a Waters 410 differential refractometer detector.

Tetrahydrofuran served as eluent at a flow rate of 1 mL/min. Apparent molecular weights for the PMMA side chains and graft copolymers were determined using a linear polystyrene standards calibration curve.

Completion of the halogen exchange reaction was verified using FT-IR spectroscopy on a Bomem Michelson FT-IR spectrometer. A thin film of the functionalized polystyrenes was cast from a chloroform solution onto a NaCl disk for the analyses.

The degree of functionalization of the chloromethylated and bromomethylated arborescent polystyrene substrates, and the composition of the graft copolymers were determined using ^{1}H-NMR spectroscopy on a Bruker AM-250 spectrometer. The polymers were dissolved in $CDCl_3$ at a concentration of 5% w/v for the measurements.

The composition of the graft copolymers was also verified using UV spectroscopy on a Hewlett-Packard HP8452 spectrophotometer. The characteristic polystyrene absorbance maximum at $\lambda = 262$ nm was used to generate an absorbance *vs.* concentration curve from linear polystyrene standards ($M_n = 5\ 000$) dissolved in THF. The PMMA contents reported were calculated from the polystyrene concentration determined in THF by comparing the absorbance at $\lambda = 262$ nm to the calibration curve.

6.5 Results and Discussion

The synthesis of arborescent copolymers with PMMA side chains grafted onto a G0 (comb-branched) arborescent polystyrene substrate was attempted to demonstrate the synthesis of these materials. The composition of the copolymers should be dominated by the PMMA component. For example, a comb-branched polystyrene (G0PS) sample with a total weight–average molecular weight $M_w = 66\ 700$ was partially chloromethylated (21 mol%) to yield a grafting substrate bearing 140 potential grafting sites. If 140 PMMA side chains with $M_w \approx 30\,000$ were grafted onto the G0PS substrate, the total molecular weight of the copolymer would be $M_w \approx 4\,250\,000$ and the PMMA content would be 98% w/w.

The synthesis of a G0PS-PMMA30 copolymer was first attempted by direct grafting of PMMA side chains onto a chloromethylated substrate. Addition of a solution of chloromethylated G0PS to a solution of living PMMA anions in THF at −78°C failed to yield any copolymer. The absence of product is attributed to the reduced reactivity of the macroanions in the presence of LiCl. The grafting reaction may not proceed at −78°C under these conditions. Furthermore, a five-fold excess of lithium counterions with respect to the living end concentration has been shown to significantly decrease the contribution of free-ions to the polymerization rate through the common ion effect.[16] Termination of the PMMA anions may occur by reaction with residual protic impurities added with the polymer substrate, or by the intramolecular termination reaction described in Equation 6.1. Since a solution of the G0PS substrate at ambient temperature is added drop-wise to a solution of the living PMMA anions at −78°C, small increases in temperature are expected when the solution is added. Despite the presence of a five-fold excess of LiCl, an increase in the rate of self-termination is expected. The reaction mixture must remain at −78°C to avoid termination of the PMMA side chains.[4]

In a second attempt, the chloromethylated G0PS sample was converted to a more reactive bromomethylated substrate to increase the ***grafting yield***, defined as the fraction of available side chains that become grafted onto the substrate. For example in Chapter 5, the synthesis of an arborescent copolymer from a partially bromomethylated linear PS substrate and an excess (25 mol%) of poly(*tert*-butyl methacrylate) side chains ($M_w \approx 30\,000$) was described.

The grafting yield increased from 45% to 67% when changing the grafting substrate from chloromethylated to bromomethylated polystyrene. On this basis, the synthesis of a G0PS-PMMA30 sample was also attempted using the partially bromomethylated G0PS substrate and an excess (25 mol%) of side chains. A grafting yield of 14% was observed under these conditions. The low grafting yield is attributed to a competition between the slow coupling reaction and side reactions that result in premature termination of the PMMA anions.

The fraction of available PMMA side chains that is grafted onto the polystyrene substrate can be approximated using the SEC trace for the raw product from each grafting reaction. Two peaks are observed in the SEC trace for the raw grafting product: The leftmost (highest molecular weight) peak corresponds to the arborescent copolymer. The rightmost (lowest molecular weight) peak corresponds to non-grafted side chains. Since the overall composition of the copolymers is dominated by the PMMA component, the ratio of the peak area for the graft copolymer to the total area for both peaks in the SEC trace yields the approximate fraction of PMMA side chains grafted. For example, 34% of the available PMMA side chains were grafted onto the G0 PS substrate in the synthesis of sample G0PS-PMMA30c (Figure 6.1). The shoulder on the right-hand side of the peak (higher elution volume) for the graft copolymer is likely due to a decrease in living end concentration throughout the grafting reaction. As the concentration of the living ends decreases, the rate of the coupling reaction decreases, leading to the formation of graft copolymers with fewer PMMA side chains.

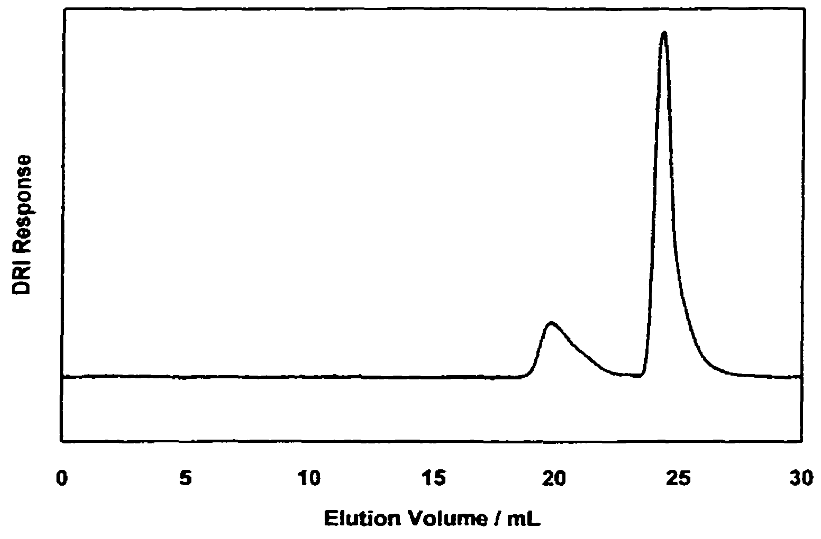


Figure 6.1 SEC trace for sample G0PS-PMMA30c.

The grafting yield could be increased if the PMMA anions were less sensitive to temperature increases that favour termination reactions. One way to accomplish this is by "capping" the PMMA anions with a few *tert*-butyl methacrylate (tBuMA) units. Poly(*tert*-butyl methacrylate) (PtBuMA) anions remain living at temperatures up to 37°C for extended periods of time.[17] The reaction of PMMA anions with *tert*-butyl methacrylate is rapid and quantitative at –78°C.[18] Further increases in grafting yield were observed for PMMA side chains that were "capped" with either 2.9 or 4.8 *tert*-butyl methacrylate units before grafting onto the bromomethylated G0PS substrate. The grafting yield obtained for all reactions are compared in Table 6.1. When the PMMA side chains were "capped" with 2.9 tBuMA units, a grafting yield of 34% was observed (Figure 6.1). However, when 4.8 tBuMA units were used, the grafting yield further increased to 58% (Figure 6.2c). Under the same conditions, a grafting yield of 62% was observed for synthesis of sample G0PS-PtBuMA30 (Chapter 5).

These results suggest that intramolecular backbiting (Equation 6.1) is the dominant termination reaction. It can be minimized if more than 3-5 tBuMA units on average are used to "cap" the chain termini prior to grafting.

Table 6.1 Characterization Results for Arborescent G0PS-PMMA30 Copolymers

Arborescent	PMMA Side Chains			Graft Copolymers		
Copolymer Sample	M_w (SEC)[c]	M_w/M_n[c] (SEC)	PtBuMA Units	M_w (SEC)[c]	M_w/M_n[c] (SEC)	Grafting Yield %
G0PS-PMMA30a[a]	29 900	1.07	0	---	---	0
G0PS-PMMA30b[b]	31 300	1.05	0	547 000	1.14	14
G0PS-PMMA30c[b]	30 200	1.06	2.9	558 000	1.11	34
G0PS-PMMA30d[b]	32 400	1.09	4.8	536 000	1.16	58

[a] Chloromethylated G0PS substrate
[b] Bromomethylated G0PS substrate
[c] Apparent values from SEC analysis using linear polystyrene standards calibration

The synthesis of an arborescent G0PS-PMMA30 copolymer is illustrated in Figure 6.2 using a series of SEC traces corresponding to the bromomethylated polystyrene substrate (G0PS), a sample of poly(*tert*-butyl methacrylate)-capped PMMA side chains with $M_w \approx 30\ 000$, the raw grafting product, and the fractionated arborescent copolymer.

The PMMA side chains constitute the major component of the arborescent copolymers. The fractionated G0PS-PMMA30d sample was analyzed using ^{1}H-NMR spectroscopy and UV-visible spectrophotometry. The composition was 98 and 97% w/w determined by ^{1}H-NMR and UV analysis, respectively. The ^{1}H-NMR spectrum for the copolymer is shown in Figure 6.3. The peaks at $\delta = 6.7\text{-}7.3$ ppm, corresponding to the aromatic protons of the G0PS substrate, are barely detectable.

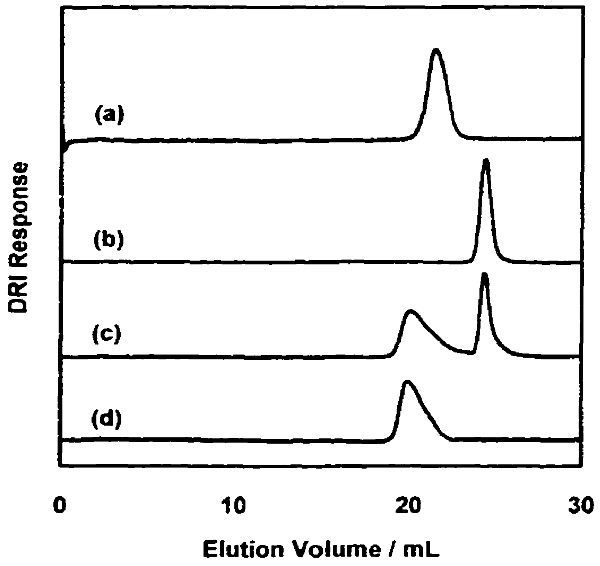


Figure 6.2 Synthesis of G0PS-PMMA30d: SEC traces for (a) the bromomethylated polystyrene substrate (G0PS), (b) poly(*tert*-butyl methacrylate)-capped PMMA side chains with $M_w \approx 30\ 000$, (c) raw grafting product and, (d) fractionated arborescent copolymer.

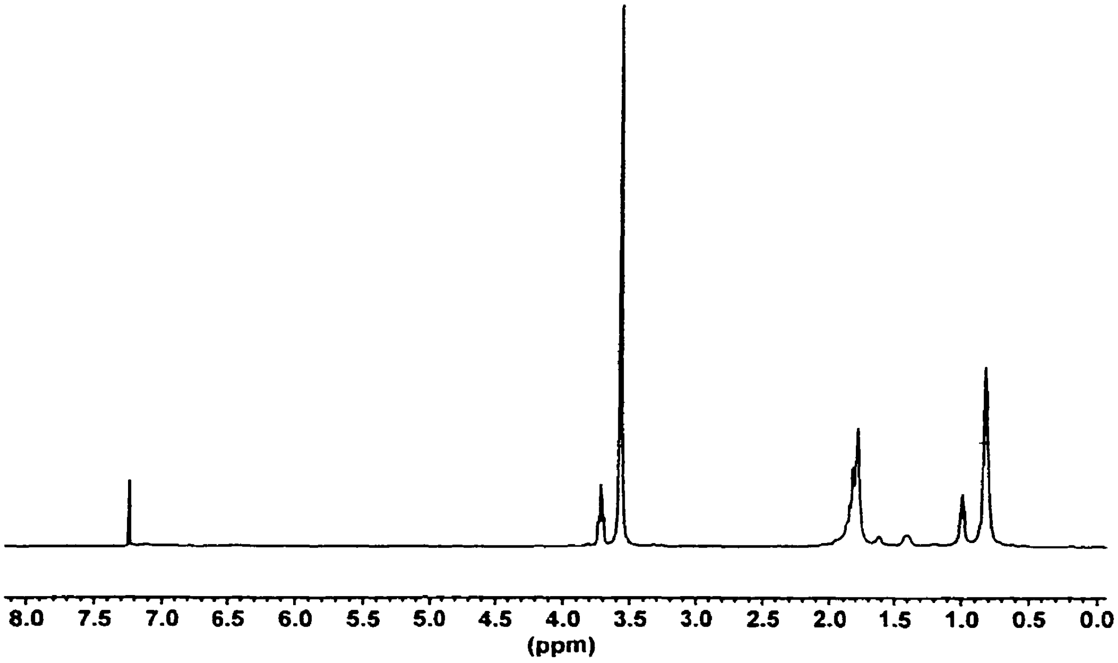


Figure 6.3 ^{1}H-NMR spectrum for fractionated sample G0PS-PMMA30d.

6.6 Conclusions

The synthesis of arborescent polystyrene-*graft*-poly(methyl methacrylate) copolymers has been demonstrated by grafting PMMA side chains ($M_w \approx 30\ 000$) onto a partially bromomethylated G0 polystyrene substrate. Direct reaction of PMMA side chains with chloromethylated G0PS failed to yield a grafted product. Capping the living PMMA side chains with 5 units of *tert*-butyl methacrylate on average significantly increases the grafting yield. The arborescent copolymer composition is dominated by the PMMA component. A series of arborescent PMMA copolymers could be prepared, based on the techniques described herein. As in the previous examples, copolymers with both short and long PMMA side chains grafted onto arborescent cores up to G2 could be prepared, to help establish structure-property correlations for these materials.

The grafting yield would be improved if either the rate of the grafting reaction could be increased or if the macroanions were less susceptible to termination reactions. Recently, the anionic polymerization of methyl methacrylate was reported to proceed without side reactions when the polymerization is initiated using tetraphenylphosphonium triphenylmethanide ($Ph_3C^{-}\ {}^{+}P\ Ph_4$) in THF at 20°C.[19] The monomer is rapidly added to the reaction and the polymerization proceeds to complete conversion in a few minutes. The initiator efficiency can be a bit low (75-100%), although predictable molecular weights and narrow molecular weight distributions are possible ($M_w/M_n \leq 1.08$). The preparation of PMMA side chains under these conditions may minimize the premature termination of the side chains and improve the grafting yield.

6.7 References

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Chapter 7

General Conclusions
and
Suggestions for Future Work

7.1 General Conclusions

The synthesis of four different types of arborescent copolymers using a *grafting onto* scheme was demonstrated using polystyrene substrates functionalized with either chloromethyl or bromomethyl coupling sites. Polyisoprene and poly(2-vinylpyridine) macroanions can be reacted directly with the chloromethylated substrates in high yield. A convenient method for converting chloromethylated polystyrenes to their bromomethylated analogues was developed. The more reactive bromomethyl sites are necessary for the synthesis of arborescent copolymers with either poly(*tert*-butyl methacrylate) or poly(methyl methacrylate) side chains. In each example provided, the *graft-on-graft* approach used provides control over the side chain molecular weight and the branching density, while a low apparent polydispersity is maintained for the graft copolymers.

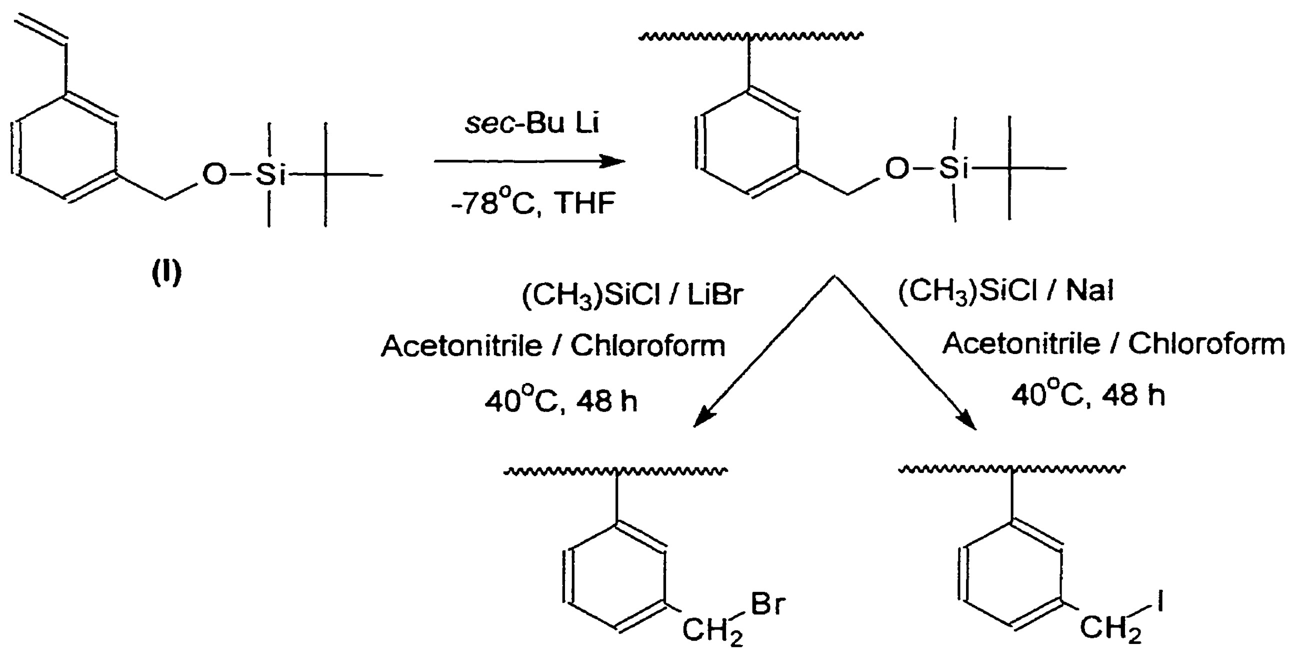
The arborescent copolymers are characterized by a compact, highly branched structure that should lead to interesting physical properties that are strongly influenced by the chemical composition of the grafted side chains. For example, scanning force microscopy measurements in the phase contrast mode have shown that the isoprene copolymers display phase-separated morphologies (glassy core surrounded by a rubbery shell) to different extents, depending on their structure. In the case of arborescent poly(2-vinylpyridine) copolymers, dynamic light scattering measurements indicated that the molecules expand considerably more than their linear homologues when protonated with HCl. This enhanced polyelectrolyte effect is attributed to the higher charge density attained in the branched copolymers. This effect is even more noticeable for arborescent copolymers with poly(methacrylic acid) side chains neutralized with NaOH, after hydrolysis of the poly(*tert*-butyl methacrylate) copolymers.

7.2 Suggestions for Future Work

7.2.1 Bromomethylation of Arborescent Polystyrenes

Bromomethylated polystyrene substrates were shown to be useful for the preparation of arborescent copolymers from macroanions with modest nucleophilic character such as poly(*tert*-butyl methacrylate). Direct bromomethylation of the polystyrene substrates would circumvent the need for chloromethylation followed by conversion to bromomethyl groups. Such a method was recently reported using trimethylsilylbromide and trioxane in bromoform (CH_3Br) at 5°C, followed by stirring at room temperature for 24 h.[1]

Alternately, side chains bearing one functional group per monomer unit could be grafted onto a chloromethylated polystyrene substrate to generate a large number of coupling sites. For example, the living anionic polymerization of *m*-(*tert*-butyldimethylsilyl)-1-oxymethylstyrene can be achieved by initiation with *sec*-butyllithium in THF at -78°C (Scheme 7.1).[2] The *m*-(*tert*-butyldimethylsilyl)-1-oxymethyl functionalities are readily transformed to bromomethyl groups by reaction with trimethylsilylchloride and lithium bromide in a mixture of acetonitrile and chloroform at 40°C for 48 h. Similarly, the *m*-(*tert*-butyldimethylsilyl)-1-oxymethyl functionalities can be converted to iodomethyl groups by reaction with trimethylsilylchloride and sodium iodide under the same conditions.



Scheme 7.1 Polymerization of *m*-(*tert*-butyldimethylsilyl)-1-oxymethylstyrene and conversion to bromomethylated and iodomethylated polystyrene.

7.2.2 Arborescent Copolymers Incorporating Other Monomers

A wide range of arborescent copolymers could be prepared using the graft-on-graft approach described in the preceding chapters. In each of the four cases investigated, established anionic polymerization and grafting techniques were adapted for the synthesis of the copolymers. Based on these results, it should be possible to prepare other arborescent copolymers from anionically polymerizable monomers. By selection of the appropriate polymerization conditions and coupling site type, a wider range of copolymers with interesting properties should be attainable.

7.2.2.1 Arborescent Poly(ethylene oxide) Copolymers

The synthesis of arborescent copolymers with poly(ethylene oxide) (PEO) side chains has been previously reported.[3] The method consists of coupling a chloromethylated substrate with polystyrene side chains prepared using a bifunctional alkyllithium initiator (6-lithiohexyl acetaldehyde acetal). Cleavage of the acetal functionalities under mildly acidic conditions yields an arborescent core carrying hydroxyl groups at the chain ends. End-linked PEO segments are introduced by titration of the hydroxyl groups with a strong base (potassium naphthalide) and addition of purified ethylene oxide. A shell of hydrophilic PEO is thus 'grown' by a chain extension reaction from the outer chains of the core polymer. Using this approach, the number of polystyrene side chains grafted during the final grafting cycle determines the number of PEO segments in the copolymer. Furthermore, since a *grafting from* strategy is used, the molecular weight of the PEO segments cannot be precisely determined.

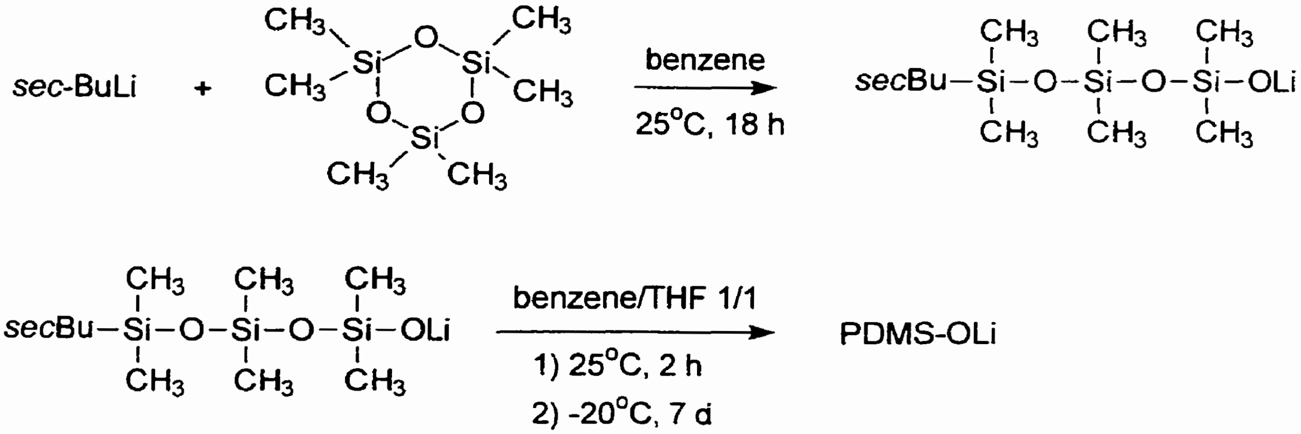
The direct coupling reaction of living PEO macroanions with either a chloromethylated of bromomethylated polystyrene core by a *grafting onto* strategy would yield better-defined molecules. The preparation of comb-branched copolymers consisting of PEO side chains grafted onto chloromethylated polystyrene has been reported.[4] The method was based on the diphenylmethylpotassium-initiated anionic polymerization of ethylene oxide at 20-30°C, followed by coupling with chloromethylated polystyrene. Grafting yields ranging from 73 to 100% were reported. Using a similar approach, it should be possible to prepare well-defined arborescent copolymers consisting of PEO side chains grafted onto either chloromethylated or bromomethylated polystyrene cores.

7.2.2.2 Arborescent Poly(4-vinylpyridine) Copolymers

The synthesis of arborescent polystyrene-*graft*-poly(2-vinylpyridine) copolymers was described in Chapter 4. Although protonation of the poly(2-vinylpyridine) (P2VP) side chains led to interesting polyelectrolyte behavior, the synthesis of arborescent copolymers with poly(4-vinylpyridine) (P4VP) side chains would also be of considerable interest. For example, P4VP can be more readily quaternized than P2VP to afford polyelectrolytes.[5] The synthesis of comb-branched polystyrene-*graft*-poly(4-vinylpyridine)s by reaction of P4VP macroanions with chloromethylated polystyrene has been reported.[6] Quantitative grafting yields were reported, however the molecular weight of the P4VP side chains was limited to $M_w \approx 10\ 000$ due to poor solubility of the side chains in the polymerization medium. More recently, the controlled diphenylmethyllithium-initiated anionic polymerization of 4-vinylpyridine has been demonstrated at 0°C in a 9/1 v/v pyridine/THF mixture.[7] High molecular weight ($M_n > 50\ 000$) P4VP could be prepared under homogeneous conditions in this solvent mixture. Based on these new developments, the reaction of P4VP macroanions in 9/1 pyridine/THF with choloromethylated polystyrene substrates should yield the corresponding arborescent copolymers in high yield. The subsequent N-alkylation of the copolymers would yield branched quaternary ammonium polyelectrolytes likely to display unusual physical characteristics.

7.2.2.3 Arborescent Polydimethylsiloxane Copolymers

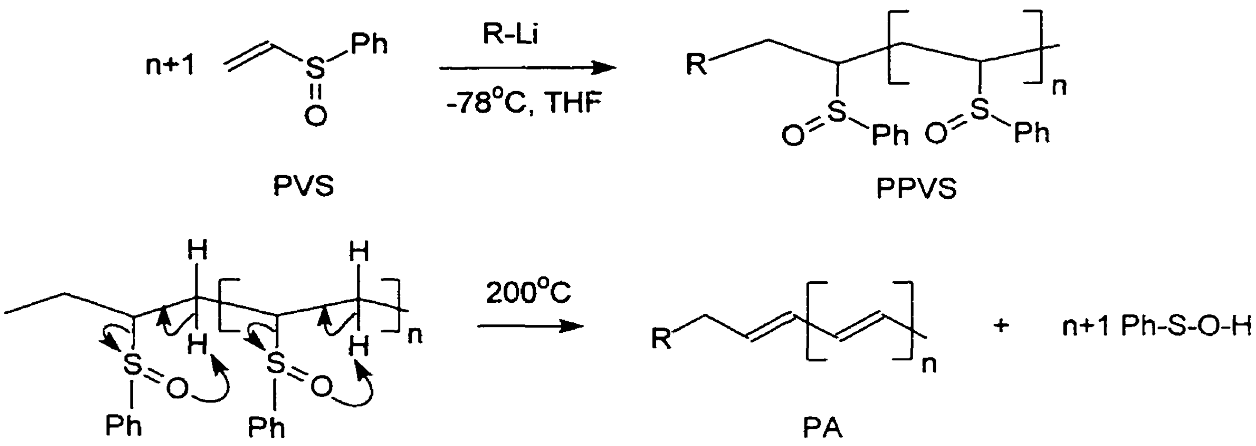
Well-defined linear polydimethylsiloxane (PDMS) samples of predictable molecular weight and with a narrow molecular weight distribution ($M_w/M_n \leq 1.3$) after complete monomer conversion have been synthesized.[8,9] The polymerization method used is described in Scheme 7.2. The monomer, hexamethylcyclotrisiloxane (D_3; 1 meq) is first reacted with *sec*-butyllithium (1 meq) in benzene at 25°C for 24 h. The propagation reaction is then carried out by adding the remaining monomer and an equal volume of THF. The polymerization is initially allowed to proceed to 50% conversion, and the temperature is then reduced to –20°C for complete conversion of the monomer. Arborescent copolymers could be prepared by direct coupling of living PDMS macroanions with bromomethylated or iodomethylated polystyrenes.



Scheme 7.2 Alkyllithium-initiated anionic polymerization of hexamethylcyclotrisiloxane.

7.2.2.4 Arborescent Poly(vinyl phenyl sulfoxide) Copolymers

Arborescent copolymers incorporating electrically conductive side chains may be of considerable interest due to their compact, globular structure. The anionic polymerization of phenyl vinyl sulfoxide (PVS) and subsequent elimination of phenylsulfenic acid has been described as a convenient route to polyacetylene (PA).[10] The anionic polymerization of PVS proceeds through a stable carbanion and typically yields unimodal molecular weight distributions ($M_w/M_n < 1.4$). It is also possible to prepare high molecular weight ($M_w > 30\,000$) PPVS chains of predictable molecular weight using alkyllithium initiators at –78°C in THF. The polymerization of PVS is described in Scheme 7.3. The thermal elimination of phenylsulfenic acid in air at 110-200°C (Scheme 7.3) yields PA units in high yield (>95%).[11,12] Conductivity values ranging from 0.2-4.4 S/cm at 11.7 Hz were reported for linear samples doped with iodine.[12] The synthesis of arborescent copolymers with PA side chains should be possible by grafting PPVS macroanions onto either chloromethylated or bromomethylated polystyrene cores, followed by thermal elimination of phenylsulfenic acid from the PVS units. The copolymers may exhibit conductivity behaviour distinct from their linear counterparts, due to their globular shape.



Scheme 7.3 Alkyllithium-initiated anionic polymerization of phenyl vinyl sulfoxide and elimination of phenylsulfenic acid to yield polyacetylene.

7.3 References

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