**NATIONAL AND KAPODISTRIAN UNIVERSITY OF ATHENS**

**SCHOOL OF SCIENCES**

**DEPARTMENT OF CHEMISTRY**

**MASTER´S DEGREE PROGRAMMES**

**“POLYMER SCIENCE AND ITS APPLICATIONS IN INDUSTRY”**

**POSTGRADUATE DIPLOMATIC THESIS**

# Synthesis and molecular characterization of polymer bottlebrushes

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**CHEMIST**

**ATHENS**

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# Synthesis and molecular characterization of polymer bottlebrushes

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# ΜΕΤΑΠΤΥΧΙΑΚΗ ΔΙΠΛΩΜΑΤΙΚΗ ΕΡΓΑΣΙΑ

Σύνθεση και μοριακός χαρακτηρισμός πολυμερών πολυμερικών βουρτσών

**ΠΑΡΑΣΚΕΥΗ ΠΑΝΑΓΙΩΤΙΔΟΥ**

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**ΕΠΙΒΛΕΠΩΝ ΚΑΘΗΓΗΤΗΣ:** ΓΕΩΡΓΙΟΣ ΣΑΚΕΛΛΑΡΙΟΥ
**,** Αναπληρωτής Καθηγητής ΕΚΠΑ

**ΤΡΙΜΕΛΗΣ ΕΞΕΤΑΣΤΙΚΗ ΕΠΙΤΡΟΠΗ**
Γεώργιος Σακελλαρίου, Μαρίνος Πιτσικάλης, Ερμόλαος Ιατρού

ΗΜΕΡΟΜΗΝΙΑ ΕΞΕΤΑΣΗΣ 19/10/2023

# ABSTRACT

Anionic polymerization and high vacuum techniques were employed to prepare a series of well-defined polyisoprene (PI) bottlebrushes. The procedure involves: a) synthesis of macromonomer in benzene, by selective reaction of the corresponding macro-anion with the chloride of 4-(chlorodimethylsilyl)styrene (CDMSS) and b) in situ anionic polymerization of the macromonomer using *sec*-BuLi.

Intermediate and final products were characterized by Size Exclusion Chromatography (SEC), and Nuclear Magnetic Resonance (NMR) techniques. The combined characterization results showed that the synthetic procedures led to to materials with high molecular and compositional homogeneity.

Their glass transition temperatures (*Tg*) were determined via Differential Scanning Calorimetry (DSC) in order to examine the relaxation process of branches and whether this is affected by different molecular weights.

**SUBJECT AREA:** Polymer Synthesis, Characterization of polymers, Macromolecular architecture, Anionic polymerization, Bottle-brush Polymers

**KEY WORDS:** Anionic polymerization, Styrene (St), Isoprene (Is), Molecular brushes, Macromonomers, Polymer characterization, Macromolecular architecture.

# ΠΕΡΙΛΗΨΗ

Χρησιμοποιήθηκαν τεχνικές ανιονικού πολυμερισμού και υψηλού κενού για την παρασκευή μιας σειράς καλά καθορισμένων πολυμερικών βουρτσών από πολυϊσοπρένιο (PI). Η διαδικασία περιλαμβάνει: α) σύνθεση μακρομονομερούς σε βενζόλιο, με επιλεκτική αντίδραση του αντίστοιχου μακροανιόντος με το χλωρίδιο του 4-(χλωροδιμεθυλοσιλυλ)στυρένιου (CDMSS) και β) in-situ ανιοντικό πολυμερισμό του μακρομονομερούς χρησιμοποιώντας *sec*-BuLi.

Τα ενδιάμεσα και τελικά προϊόντα χαρακτηρίστηκαν με τεχνικές χρωματογραφίας αποκλεισμού μεγέθους (SEC) και πυρηνικού μαγνητικού συντονισμού (NMR). Τα αποτελέσματα χαρακτηρισμού έδειξαν ότι οι συνθετικές διαδικασίες οδήγησαν σε υλικά με υψηλή μοριακή και χημική ομοιογένεια.

Οι θερμοκρασίες υαλώδους μετάπτωσης (*Tg*) προσδιορίστηκαν μέσω Διαφορικής Θερμιδομετρίας Σάρωσης (DSC) προκειμένου να εξεταστεί η διαδικασία χαλάρωσης των κλάδων και εάν αυτή επηρεάζεται από διαφορετικά μοριακά βάρη.

**ΘΕΜΑΤΙΚΗ ΠΕΡΙΟΧΗ**: Σύνθεση πολυμερών, Χαρακτηρισμός πολυμερών, Μακρομοριακή αρχιτεκτονική, Ανιοντικός πολυμερισμός, Πολυμερή βούρτσες

**ΛΕΞΕΙΣ ΚΛΕΙΔΙΑ**: Ανιοντικός πολυμερισμός, Στυρένιο (St), Ισοπρένιο (Is), Μοριακές βούρτσες, Μακρομονομερή, Χαρακτηρισμός πολυμερών, Μακρομοριακή αρχιτεκτονική.

*To my parents*

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# PREFACE

This work was devised and took place at the Laboratory of Industrial Chemistry of the Department of Chemistry of NKUA.

First of all, I would like to thank professor Dr. Georgios Sakellariou, who is also my supervisor, for the continuous scientific guidance and enormous contribution to carrying through with the challenging experimental techniques of my work and most of all for his trust.

I would also like to express my gratitude to the director of the Laboratory of Industrial Chemistry Professor Dr. Ermolaos Iatrou for offering me the opportunity to participate in the postgraduate studies programe, but also for his effort to preserve and maintain the operation of the laboratory.

I sincerely appreciate the valuable help that professor Dr. Marinos Pitsikalis offered throughout my work, but also for the excellent courses he delivered during the postgraduate program.

I owe a big thank you to my fellow students at the laboratory, with whom I discussed my questions, and due to the great cooperation, we had, I was introduced by them to the techniques and received help with the experimental difficulties.

# CHAPTER 1
# THEORETICAL PART

## 1.1 Introduction

A polymer, by definition, is a material, consisting of repetitive atoms or groups, that are called structural or monomeric units, and are joined together by a covalent bond. These units are formed by precursor compounds known as monomers, and the chemical linking between a sufficient number, of one or more kinds of them, can lead to the display of desirable properties that remain unaltered. Polymer structures compose of a basic chain called backbone, but might also include secondary parts attached to several or to the whole extent of links on the chain, forming branching networks rather than single chains. Being more exposed than the monomers of the backbone, they define the way the polymer interacts with itself and other entities in the environment: longer side chains present higher viscosity, melting and boiling temperature etc.

The increasing demands of the technology for new polymeric materials with adjustable properties for various uses has led the researches to the discovery of new and more complex architectures. The polymers with high degree of branching are in the interest of academic and industrial applications owing to their intriguing rheological behaviour. Since the structure and domain of the branches intensely affect the properties of the final product, the synthesis of polymers comprising of well-defined branches is crucial for the comprehension of such correspondence.

Bottlebrush polymers are a type of branched or graft polymer with polymeric side-chains attached to each repeat unit of a linear polymer backbone and were first synthesized in the early 1980s. [2] The brush architecture has led to new properties for polymers, such as high grafting density including the ability of tailored side-chains for solubility or functionalization with elements for imaging, recognition and other desirable uses. The preparation of bottlebrush polymers with a specific backbone and side-chain length helps to achieve complex structures. Many advances in the field include the understanding of their physical properties, with most important, the assemblies in unique environments rather than the conformation of individual bottlebrushes. Interest in bottlebrush polymers has been increased on account of literature citations over the past two decades. [1,2] Molecular bottlebrushes can be used as building blocks for the development of unique polymers whose physical properties are governed by dense grafted structures, owing to the high concentration of side-chains. Their extensive molecular size, anisotropic conformation, and reduced chain entanglement, which is caused by the steric repulsion forces that stretch the backbone and decrease the spatial density, have been the solution to achieve applications that would have been a challenge otherwise, as of in case of linear polymers. Matyjaszewski et al., have studied the correlations between brush-type architectures and properties of the materials. [3]

Anionic polymerization is the most powerful living method for the preparation of complex architectures of macromonomers whilst using highly refined reagents, through thorough processes of purification. In the beginnings, the synthesis of bottlebrush polymers was focused on the development of strategies using controlled polymerization techniques involving radical polymerizations and ring-opening polymerizations, but only a few attempts were made with the technique of the anionic polymerization owing to the main setback of the demand of materials and apparatuses of high purity. Therefore, in this field there are only limited data and researchers utilize “living”/controlled radical polymerizations, as less time-consuming strategies.

In this work, we were able to incorporate polyisoprene (PI) macromonomers with polyisoprene (PI) to create bottle brushes with sec-butyllithium (sBuLi) in benzene, by a one-pot homopolymerization procedure. The factors affecting the reactivity of the macromonomers in this procedure are: the chemical nature of the polymerizable end group, the molecular weight of the macromonomer, the degree of polymerization (DP) of the final product and the solvent of the polymerization. [1]

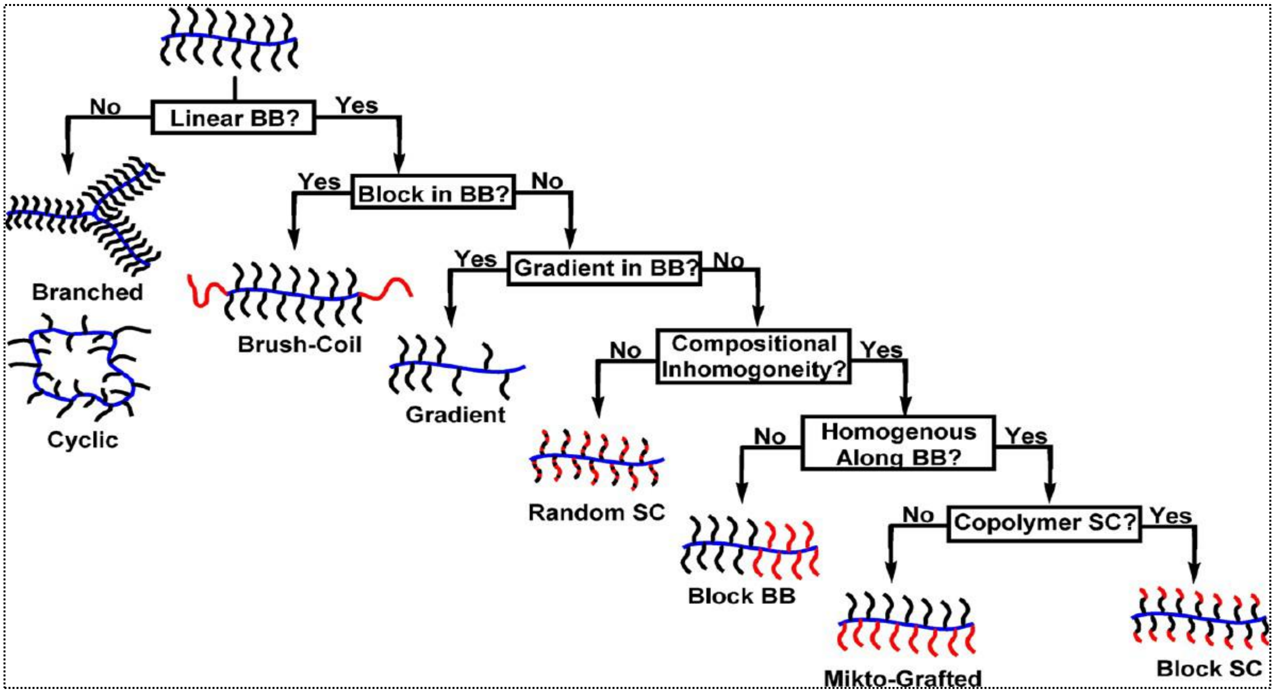
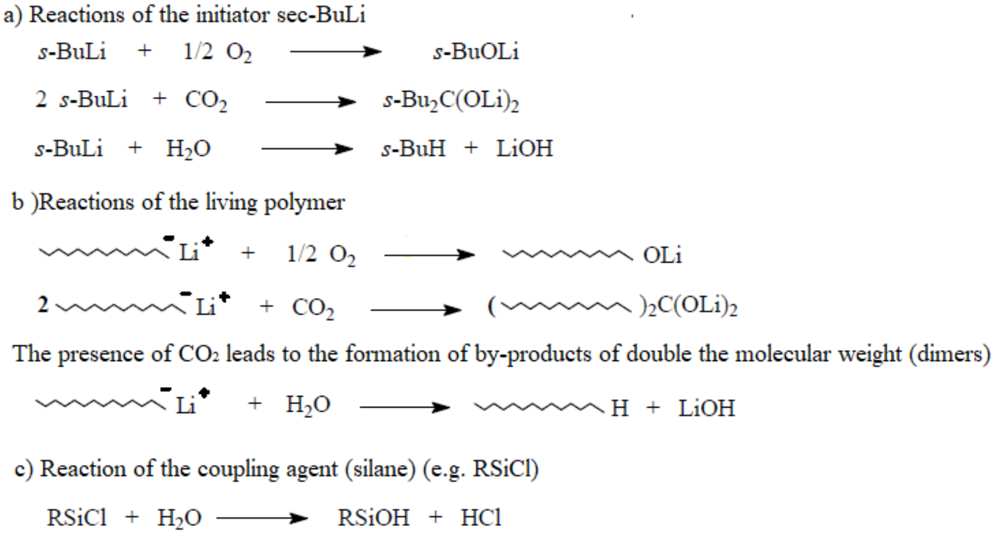


*Image 1. Schematic representation of various structures of bottlebrushes*

## 1.2 Anionic Polymerization

Through anionic polymerization synthesis of model polymers with controlled macromolecular architectures, high degree of molecular and compositional homogeneity for the study of the relationship between structure and properties are possible. However, the high reactivity of anionic centers towards atmospheric (moisture, oxygen, carbon dioxide) and other contaminants dictates specially designed apparatuses and appropriate techniques, in order to avoid premature living chain termination.



Both inert atmosphere and high vacuum techniques have been successfully employed for anionic polymerization. Nevertheless, these limitations for high-vacuum techniques can be easily overcome considering the potential of generating complex macromolecular model compounds of various architectures (linear and non-linear).

Anionic polymerization is defined as the type of polymerization in which the blocks at the end of the growing polymer chain are negatively charged. It is also called "living" polymerization because of the absolute control of the termination and/or transfer reactions, when non harming factors such as the ones mentioned above interfere. Hence, complete control of the products in terms of molecular weight, degree of polymerization and molecular weight distribution is provided. Monomers of the formula $CH_2{=}CH{-}A$, where A is an anion-stabilizing group, can be anionically polymerized by compounds, called initiators, which bestow the necessary ions (carbocations of the metal of the organometallic compound used as an initiator) to initiate the polymerization by activating the double bond of the monomer.

In anionic polymerization, two stages are distinguished: initiation and propagation, shown in Figure 1:

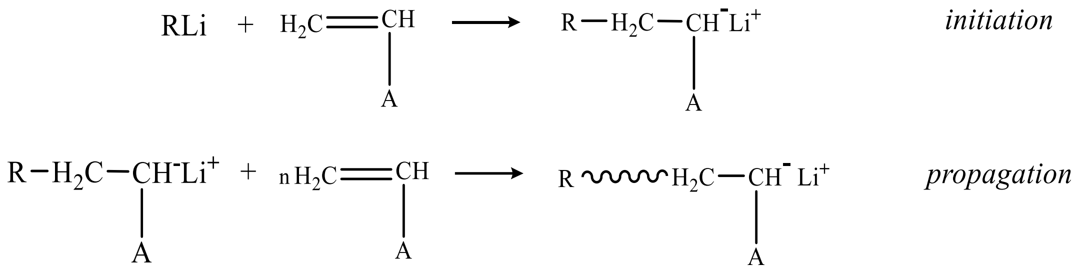


*Figure 1 General reactions during the stages of anionic polymerization*

The absence of termination stage alongside the use of suitable coupling reagents facilitates the modification of the active anionic centers, for the synthesis of well-defined macromolecules of low molecular weight dispersity and controlled molecular characteristics, including average molecular weights, composition, microstructure and architecture, such as homopolymers, copolymers and polymers of three or more blocks. The number average molecular weight can be determined by the amounts of monomer and initiator according to the equation:

$$\overline{M_n} = \frac{grams\ of\ monomer}{moles\ of\ initiator}$$

The low distribution of molecular weights (Mw/Mn=I<1,1) formulates the homogeneity of the macromolecular chains, ensured by the method of the anionic polymerization, only through careful selection of the solvent, monomer, initiator system, so that the velocity of initiation is sufficiently greater than the one of the propagation. Therefore, the initiation stage occurs almost simultaneously for all monomeric units, and the same number of structural units are added to the active macromolecular chains that are being developed. [4]

## 1.3 Initiators

The most commonly used initiators in anionic polymerization are alkyl-lithium compounds. Many of them are commercially available, soluble in hydrocarbon solvents and can be easily synthesized by the reaction between the appropriate alkyl chloride with Li. The significant characteristic of these organolithium compounds is the fact that the C-Li bond exhibits both covalent and non-covalent properties, since Li displays the smallest radius, the greatest electronegativity as well as ionization constant compared to the rest of the alkalis in the group. Alkyl lithium initiators are preferred over compounds with other alkalis, because higher velocity is achieved at the initiation stage of polymerization which leads to small molecular weight distributions of the final product ($v_{in} >> v_{pr}$). [6,7,8]

The velocity at the initiation stage of the polymerization depends on the structure of the initiator and whether the nature of the solvent is aromatic or aliphatic. The degree of aggregation and the equilibrium state also rely on the factors mentioned above. In non-polar solvents, such as benzene, the organolithium compounds from aggregates in equilibrium with the non-aggregated form. Lower degree of aggregation depicts higher reactivity and is ensured by decreasing the concentration of the polymerization solution, raising the temperature of the polymerization, using stronger solvents (aromatic are better than aliphatic). In the presence of polar components, the equilibrium is shifted to the right, leading to a rise in the concentration of free ions is observed whilst causing a dramatic increase of the propagation velocity. [10]

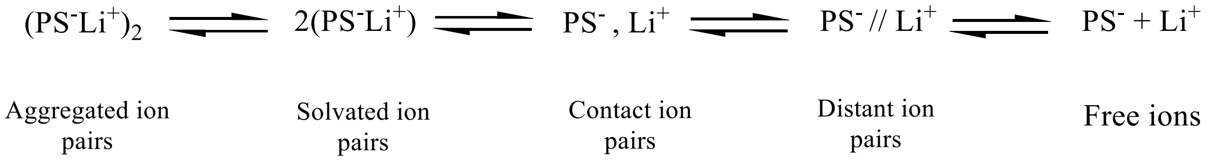


*Figure 2 Degree of aggregation of polystyrene ion pairs*

Additionally, the structure of the organolithium initiator affects the degree of aggregation. The unrestrained straight-chain initiators form hexameric aggregates in hydrocarbon solvents, whilst the branched ones at the α- or β-carbon form tetrameric. The order of reactivity and degree of aggregation of organolithium initiators for the polymerization of dienes in hydrocarbon solvents is presented below: [9]

**Methyllithium/MeLi (2) > secondary butyllithium/sec-BuLi (4)> isopropyllithium/i-PrLi (4-6)>quaternary butyllithium/t-BuLi (4) > normal butyllithium/n-BuLi (6).**

When the polymerization is carried out with particularly clean reagents, certain temperature and reaction time in a proper solvent that doesn't favour transfer reactions with the macrocarbanion, the total amount of the monomer is used up (living polymerization). Alkyl-lithium initiators are widely used in the polymerization of styrene and dienes, but are undesirable for the polymerization of methacrylates as side reactions take place, due to their excessive reactivity.[11,12,13,14] The initiation of polymerization is complete when 10-20% of the monomer has been polymerized with the suitable activator.[5]

It is important to mention that the use of a different compensating metal of the initiator, a polar solvent or the addition of polar compounds to the system of the polymerization leads to a change in the microstructure of dienes, and makes it possible to select the percentage of a specific microstructure of the resulting polydiene.[9,15,16,17,18,19,20] In general, 1,3 diene formula is $CH_2=C(R)-CH=CH_2$, and when the R substituent is H the monomer is butadiene (1,2 and 3,4 microstructures are equivalent to each other), whereas if it is $CH_3$ the monomer is isoprene. Four possible microstructures of polyisoprene are listed in

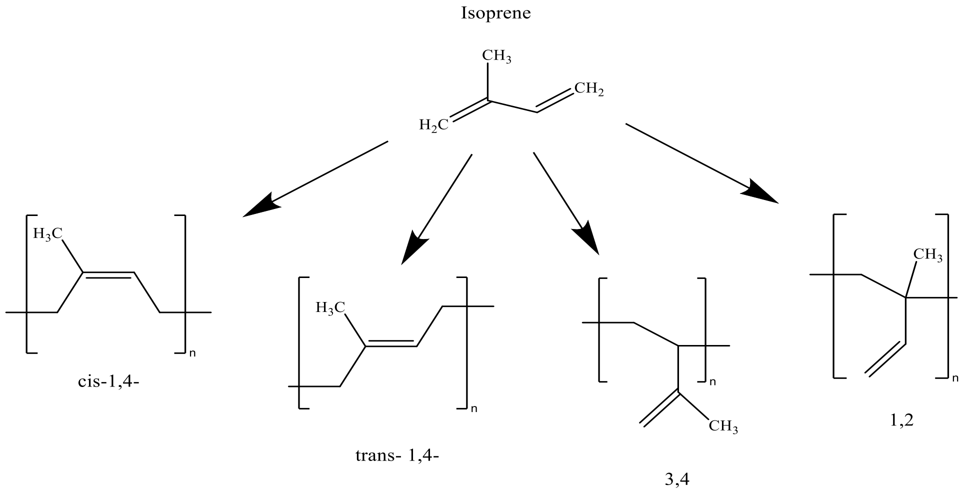


Figure 3:

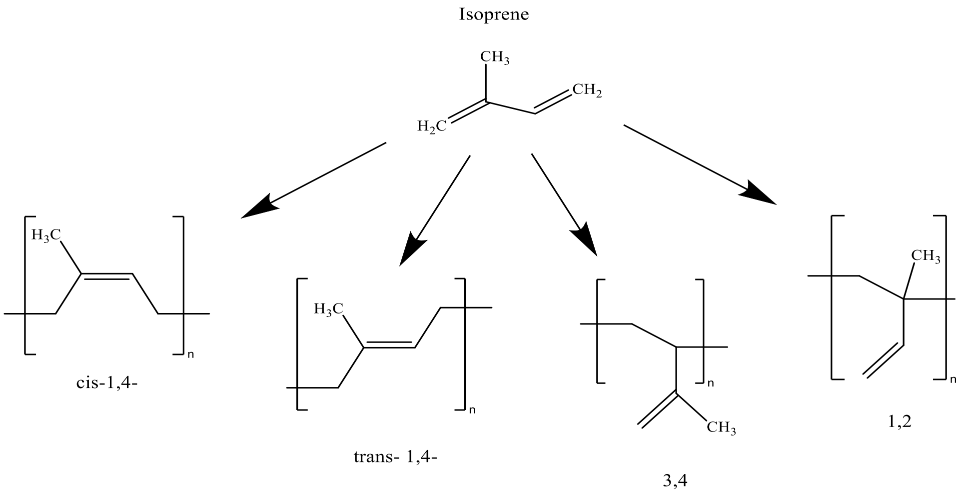


*Figure 3 Isomer microstructures of polyisoprene*

In nonpolar solvents (benzene, cyclohexane), 1,4 microstructure of high percentage (93%) is obtained, via 4,1 addition reaction of *sec*-BuLi leading to the formation of the more stable allylic species with negative charge located at the α-carbon. In the presence of a polar solvent, such as tetrahydrofuran, or by adding a certain amount of a polar component to the solution for example, triethylamine or 1,2-dipiperidinoethane, the percentages of the 1,2 and 3,4 microstructures are obtained reaching at 60%, because in this case the negative charge is mainly located on the γ-carbon leading to the predominance of the 1,2 and 3,4 microstructures.

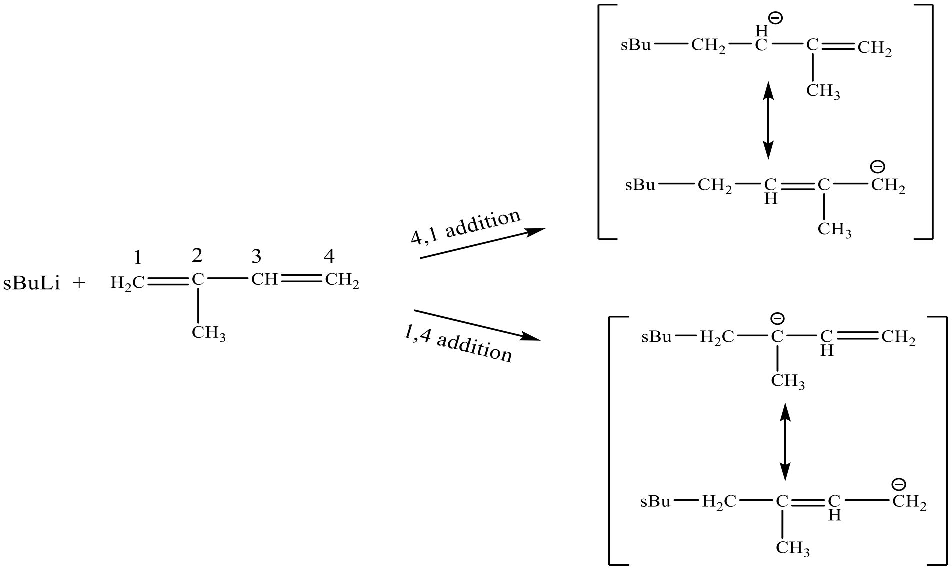


*Figure 4 Addition reactions at the initiation of isoprene polymerization*

## 1.4 Grafted Polymers

Studies conducted over the last thirty years focus on branched polymers, and more specifically, on the grafted ones. The methods for the formation of complex architectures are deemed as well-defined techniques, granting unique mechanical and thermal properties to the polymers. Their structure is also presenting intriguing behaviors in dilute solutions. Thus, their enhanced physical properties differ greatly compared to their linear counterparts.

Grafted polymers consist of a main polymer chain to which one or more side chains (branches) are chemically linked through covalent bonds. The backbone and branches can be homopolymers or copolymers. High density polymer brushes or molecular brushes are grafted polymers. Branched macromolecules in the form of a brush (also known as Bottlebrushes), consist of a polymer chain (branch) which is attached as the extent of each monomeric unit of the so called "backbone". Such polymeric brushes, due to the very dense grafting, acquire useful configurations opening new fields of research and applications.

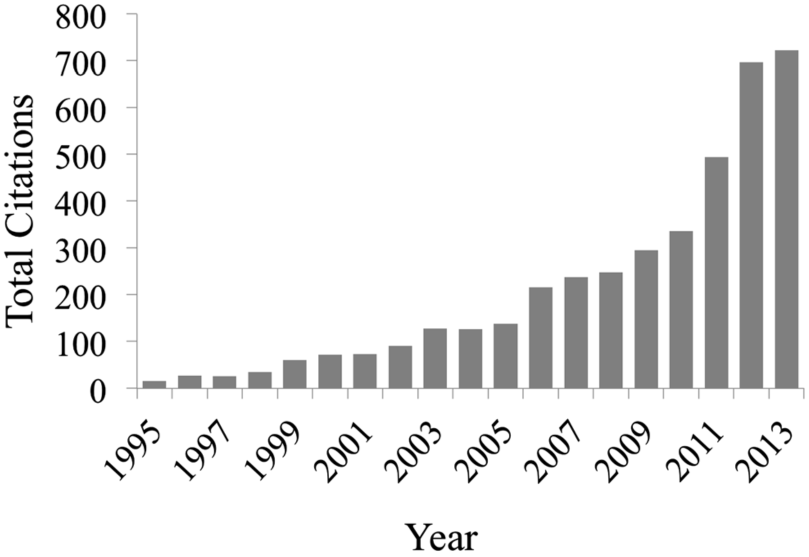


*Figure 5 Published literature citations referring to "bottlebrush" or "molecular brush" in the title, from Web of Science.*

### 1.4.1 Synthesis of brush-type polymers

The synthesis of brush-like polymers requires exquisite control of the experimental parameters and remains challenging up to now, because of the high steric hindrance between the branches. Parameters include grafting density, degree polymerization for branches and backbone as well, branch composition, length of final nanostructure, and polydispersity. The synthesis of brush-type polymers can be done through the following three methods:

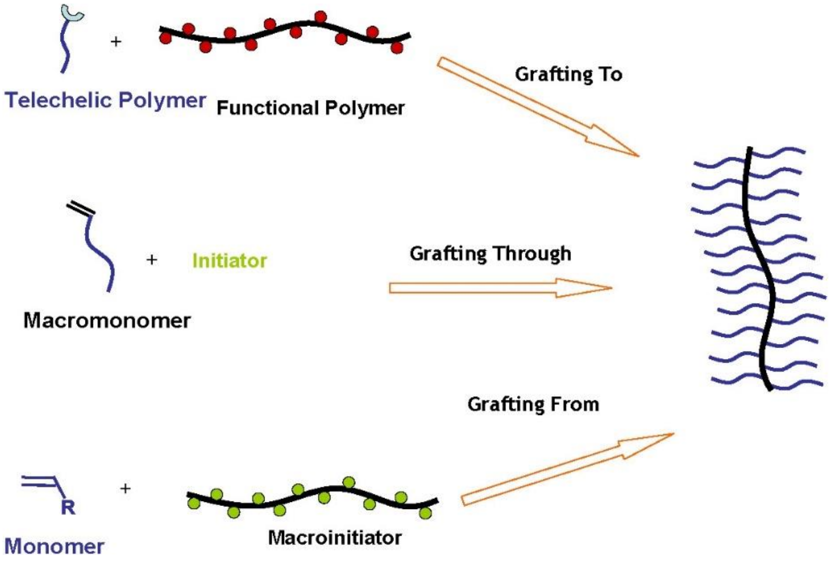


*Image 2 Three main strategies for molecular bottlebrush preparation*

Bottlebrush polymers can be synthesized by Suzuki polycondensation, chain-growth polycondensation, cyclopolymerization, sequential ROMP polymerizations, non-living transition metal catalysis, combination between grafting methods (heterograft [41]), and multiple controlled radical polymerization reactions.

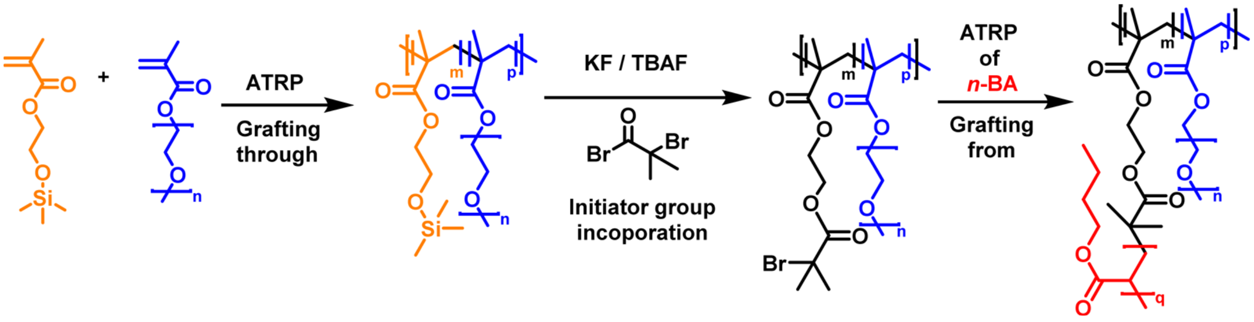


*Figure 6 Example synthesis of PEO/PBA heterografted Copolymers*

Novel bottlebrush architectures include dumbbell shaped bottlebrushes, block miktobrushes, polypseudorotaxanes, bottlebrush polymers with dendritic side-chain endgroups, and bottlebrush polymers with a redox-responsive backbone. [2]

#### 1.4.1.1 Grafting "From"

This method involves polymerization of the branches directly from predetermined active centers of the backbone chain (macroinitiator), so that the number of active sites is specific. These backbones are usually called macroinitiators. Beers et al. first reported the grafting-from synthesis of bottlebrush polymers using a controlled radical polymerization technique. The possibility of synthesizing precursor backbones with controlled and high molecular weight that can participate in the synthesis of a variety of molecular brushes with different branch lengths, along with the permittable high grafting density are the main advantages of this strategy. The grafting density can also be controlled by co-polymerizing two monomers during the synthesis of the backbone. This συvapproach would be optimal for applications involving bulk materials or bottlebrush coatings. [2,21]

Nevertheless, it is difficult to ensure that all of the active centers on the macroinitiator participate in the polymerization, as steric hindrance is presented. The high grafting density of the method, affects the degree of grafting especially in the case of bulky monomers. Also, the precise characterization of the molecular characteristics (PDI, $M_w$) of the branches is difficult, since they cannot be isolated. Another drawback is that protection and deprotection of functional groups is often required, increasing synthetic complexity. The preparation of mixed or bottlebrush block copolymers is possible using grafting-from, but three or more orthogonal polymerization chemistries (or protection–deprotection) may be required. [2,22,23]

Reversible deactivation radical polymerization (RDRP) techniques including atom transfer radical (ATRP), reversible addition−fragmentation chain transfer (RAFT), and nitroxide-mediated polymerization (NMP) have significantly facilitated the synthesis of molecular bottlebrushes via the grafting-from method. Grafting-from technique prevails through these polymerizations because of the excellent functional group tolerance and effective control of side chain growth. [3,25]

The main setback in ATRP is radical termination. Methacrylates undergo radical termination through both combination and disproportionation, whereas styrenes and acrylonitrile terminate mainly through combination. Radical termination of acrylates in

ATRP occurred predominately through bimolecular combination with a small portion of chains undergoing either backbiting to form midchain radicals or disproportionation and also some chains are terminated through catalytic radical termination (CRT) to leave behind dead, disproportionation-like products. The relative fraction of chains terminated through RT and CRT can be tuned by [Cu$^{I}$], in order to achieve 80% monomer conversion without macroscopic gelation. The reactions were relatively fast but favoured termination through CRT rather than RT, allowing the polymerization to run to high conversion with minimal coupling of brushes. High-pressure ATRP offers the ability to suppress radical termination during the formation of molecular brushes by grafting-from. [3]

This method is mainly performed by ATRP and was first introduced by the group of K. Matyjaszewski. The basic sequence of reaction involves the polymerization of 2-(trimethylsilyloxy)-ethyl methacrylate (HEMA-TMS) by ATRP, followed by esterification of the of the siloxy-group protected alcohol with the system KF/tetra-n-butylammonium fluoride (TBAF)/2-bromopropionyl bromide. This process forms the ATRP poly(initiator) PBPEM, poly (2-bromoisopropionyloxyethyl methacrylate) from which styrene (St) or n-butyl acrylate (n-BA) can be polymerized to form a molecular brush.[3,25,**Error! Reference source not found.**] The procedure is shown in Figure 7 below:

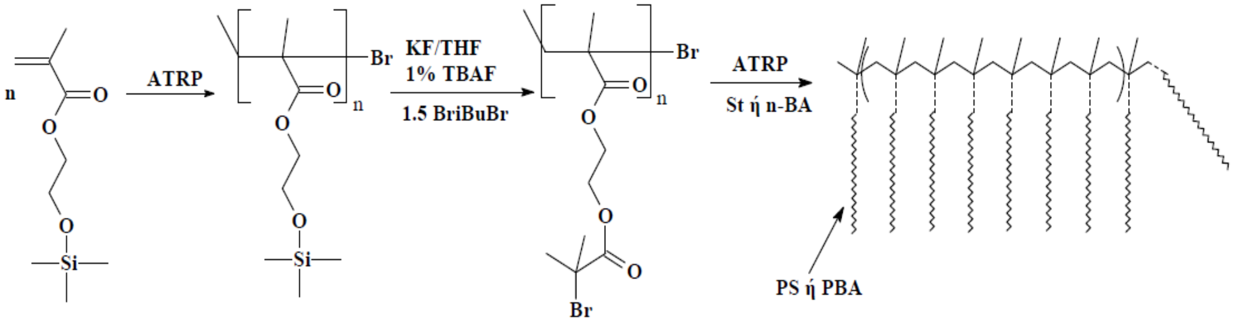


*Figure 7 Basic Grafting-from steps for bottle-brush synthesis*

In 2006, C. Feng and X. Huang et al. g developed a method to prepare amphiphilic 1D polymer brushes, whilst retaining ester groups of the polyacrylate backbone. ATRP initiators were installed onto the α-carbon of ester groups of poly(methoxymethyl acrylate) (PMOMA) backbone by treatment with lithium diisopropylamide (LDA) and α-bromopropionyl bromide. This reaction formed a macroinitiator that was further used for poly(butyl methacrylate) (PBMA) side chains with the grafting-from strategy. The side chains were connected with the backbone by C−C bonds, and the preserved ester groups were hydrolyzed to carboxyls, making brush backbone hydrophilic, but also allowing further functionalization. [27]

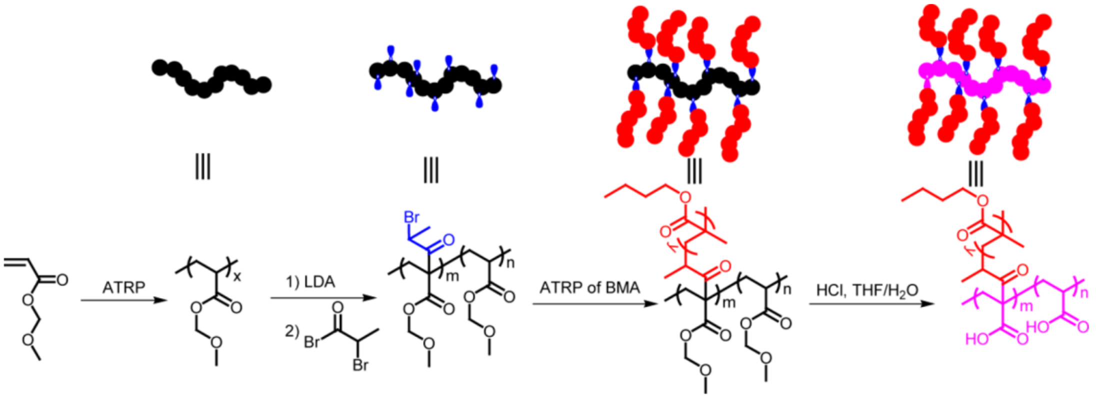


*Image 3 Synthesis of 1D polymer brushes with a carboxyl backbone.*

With variations of the method in the last decade, several macromolecular brush-like architectures have been synthesized, such as: copolymers of the type (linear)-*b*-(brush) and (linear)-*b*-(brush)-*b*-(linear). In a recent study, molecular brushes with three, four, and even six arms were prepared via grafting-from ATRP multifunctional macroinitiators. These materials could generate hierarchical inorganic nanostructured networks when used as templates, with enhanced interconnectivity and percolation properties of nanoparticles. As shown below star-shaped brushes with PHEMA-TMS backbone and poly (n-butyl acrylate) branches were prepared using tri- and tetra- functional initiators [3,25]:

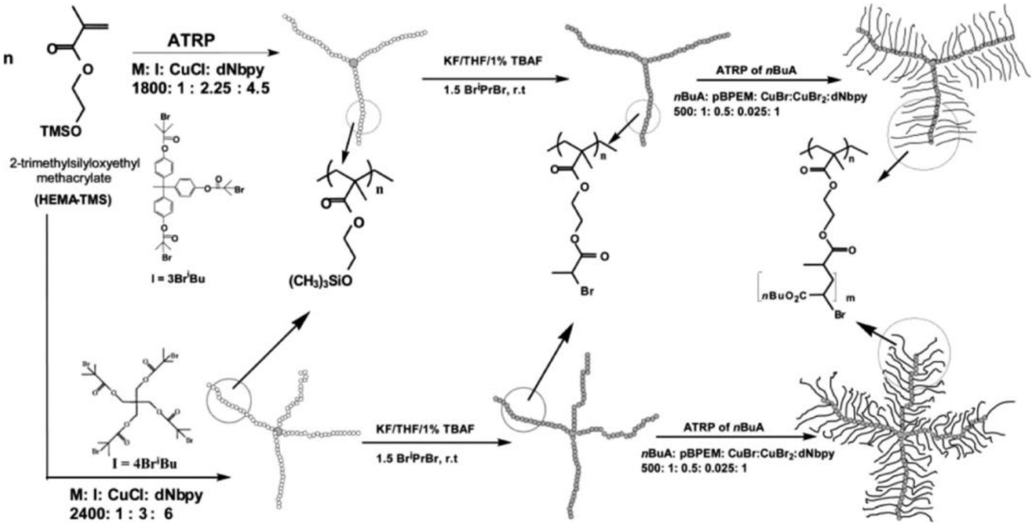


*Image 4 Synthesis of Three- and Four-Arm Star Molecular Brushes*

Four-arm molecular brushes could provide more ordered 2D structures compared to those of their corresponding linear analogues, providing a nearly perfect hexagonal ordered monolayer.

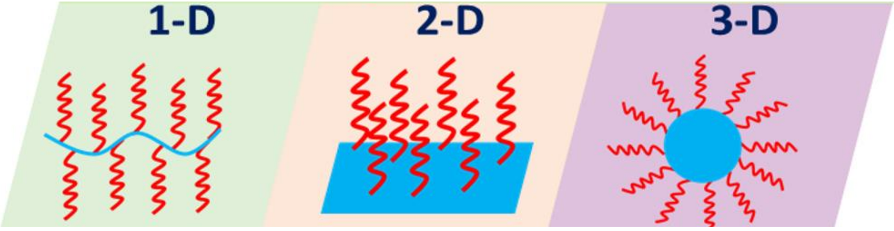


*Image 5 Molecular brush chain conformation on polymer chain (1D), surface(2D) or solid(3D)* [27]

This method also offers the possibility of synthesizing complex architectures with branches of different chemical composition (multicomponent polymers, functional group input). For example, block copolymer side-chains can be incorporated in a straightforward way through sequential polymerization reactions, resulting in densely grafted core–shell type bottlebrushes consisting of soft poly(n-butyl acrylate) cores and hard polystyrene shells. [2,25]

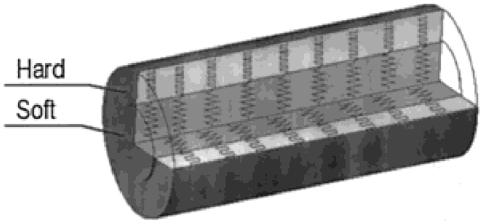


*Image 6 Cylindrical core/shell bottle brushes*

### 1.4.1.2 Grafting "Onto"

This method involves the separate preparation of backbone and side-chains with the covalent attachment of a semi-telechelic (active only at one end) macromolecular chain to a chemically modified polymeric chain (the backbone) through a coupling reaction. Advantages of this method are the precise and separate characterization of the molecular weight of the branches and the backbone. Consequently, both macromolecules can be easily controlled in terms of low PDI. The grafting-to approach produces bottlebrushes with lower grafting densities, which may be of interest for coatings and additives. [2,28]

However, the disadvantage of the method is that high degrees of grafting cannot be achieved, since the coupling reaction mentioned above is not guaranteed to occur at all active sites on the backbone, resulting to chemical heterogeneity and therefore, increase in polydispersity. Another limitation of the method is the prerequisite of branches with small $M_W$ in order to avoid steric hindrances as much as possible, Low reactivity of polymeric reagents, with the additional complication that the coupling reaction is obstructed by these steric interactions between side-chains are the main obstacles on the way to achieving satisfactory grafting degrees. As a result, this strategy usually produces polymers with grafting densities of 60% or lower, and is not suitable for synthesis of bottlebrushes. [29]

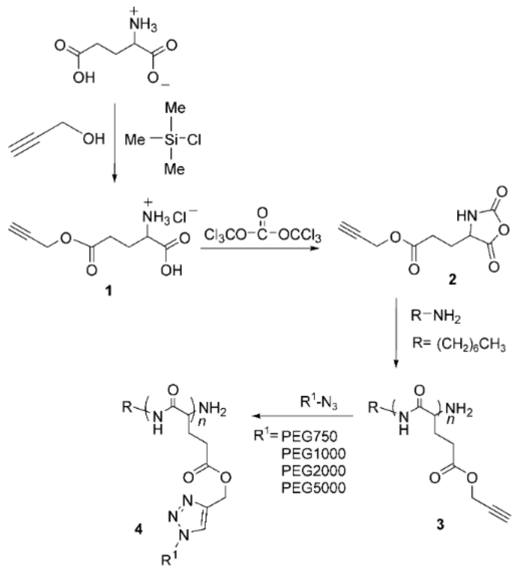


*Image 7 Synthesis of PPLG-g-PEG using click chemistry for a "grafting-to method"*

A notable exception of grafting efficiency greater than 95%, is the synthesis of poly(g-propargyl-l-glutamate) (PPLG) and the attachment of different lengths of azide-terminated poly(ethylene glycol) (PEG- $N_3$). The "grafting-to" procedure manages to maintain the a-helical conformation of the polypeptide backbone. The g-Propargyl-l-glutamate hydrochloride (1) was prepared by the reaction of a propargyl alcohol with glutamic acid, mediated by trimethylsilyl chloride, followed by reaction with triphosgene in ethyl acetate, forming the NCA monomer (2) g-propargyl-l-glutamate N-carboxyanhydride. PPLG (3) was prepared by ROP of (2) initiated by heptylamine in N,N-dimethylformamide (DMF). PEG-$N_3$ was grafted to PPLG using a CuBr/N,N,N,N',N'-Pentame- thyldiethylenetriamine (PMDETA) catalyst in DMF. [32]

In an attempt conducted by Wilhelm M., Abbasi M. et al., a series of well-defined comb-PS with loosely to densely grafted structures tending toward bottlebrush architectures were synthesized in order to quantify the effect of the number of branches on several properties. Definitions of comb and bottlebrush structures depend on the DP of side chains, as well as the average DP between branches. The anionic polymerization method was used to prepare the backbone using *s*-BuLi as initiator in toluene solution, and the termination was followed by Friedel−Crafts acetylation of the PS introducing carbonyl groups as branching points. Then, excess of “living” PS side-chains (no termination stage) was slowly added to the PS backbone that was previously diluted in THF solution, using a cooling bath. [30]

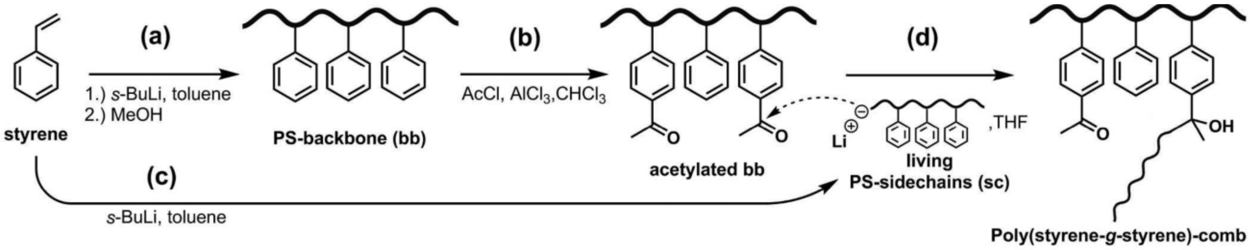


*Image 8 Grafting to process of comb-(PS-g-S)*

Macrocyclic brushes were prepared via grafting (1,1-diphenylethylene) end-capped polystyryllithium (PS-DPELi) and (1,1-diphenylethylene) end-capped polyisoprenyllithium (PI-DPELi) to cyclic poly(chloroethyl vinyl ether) (PCEVE) in heptane. They observed tubular objects as the result of intermolecular stacking of cyclic heterografted brushes. [3,31]

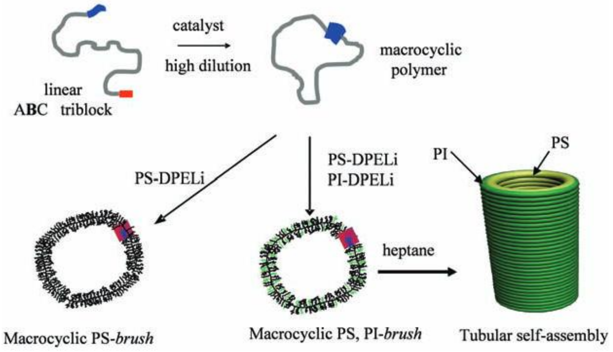


*Image 9 Cyclic comb-like copolymers grafted to PCEVE and their self-assembly.*

### 1.4.1.3 Grafting “Through”

The grafting-through synthesis approach starts with the preparation of reactive polymeric side-chains also known as macromonomers. The macromonomers are then polymerized to form a bottlebrush polymer, and different backbone lengths can be obtained by varying the relative concentration of macromonomer to initiator during polymerization. The grafting-through approach is useful for synthesis of polyolefin bottlebrush polymers, as well as bottlebrushes for imaging and detection. [2]

The synthesis of brush-type polymers through this method exclusively, quantitatively and independently of the length, structure and composition of the branch, gives such well-defined structures via single-reacting macromonomers. This strategy gives the ability to control the molecular characteristics of the branches, before the conversion to macromonomers through appropriate reactions. The polymer chain extending from each monomer unit of the backbone leads to the formation of homogeneous grafting densities of true bottlebrush-like polymers.

A disadvantage of the method, in some cases, is the relatively low velocity at the initiation stage of the polymerization that makes difficult to achieve quantitative conversion of the macromonomers leading to wide or even bimolecular distributions. Therefore, the excess of macromonomer ought to be fragmented from the final product, through time-consuming process. The backbone is formed last through the polymerization procedure. It cannot be isolated for characterization and high backbone DP cannot always be achieved. The latter factor is also governed by the demand for branches of low $M_w$, that restrain steric obstructions. Typical backbone DPs for bottlebrushes by grafting through are in the range of 100–400, in comparison to grafting-from strategies with DPs greater than 1000. [2,33]

The synthesis of molecular brushes using the grafting-through method can be achieved using various techniques such as ATRP, ROMP and anionic polymerization. Macromonomer conversion is low (30–80%) using free radical polymerization.

Ring opening metathesis polymerization (ROMP) of norbornenyl macromonomers has been shown to be an effective grafting-through synthesis strategy. The reactivity of norbornenyl macromonomers in ROMP is sufficient for achieving high macromonomer conversions for a range of concentrations and macromonomer molecular weights, enabling the preparation of bottlebrush polymers with varying backbone and side-chain lengths. An advantage of the ROMP grafting-through method is its simplicity. Bottlebrush polymers can be prepared in two steps using controlled polymerization for macromonomer synthesis followed by ROMP for bottlebrush synthesis, and no protection-deprotection chemistry is required.

The hindrance between the branches due to thermodynamic and kinetic barriers, such as high viscosity, the obstructed stereochemistry and low concentration of reactive end groups make the synthesis of low dispersion molecular brushes with high DP difficult. Solution viscosities rise even at moderate concentrations, due to the high molecular weight of the macromonomers, and control over this, is necessary. [2]

The polynorbornene-g-poly-(D,L)-lactide brush polymers were synthesized by ring-opening metathesis polymerization (ROMP) of norbornenyl macromonomers. The molecular weights of the brush polymers are very high (up to 6000 kDa) and the side chains are long, however neither the side chains nor the whole polymer show evidence of entanglement. The brush polymer possesses low polydispersity (PDIs) in both backbones and side chains, and a dense distribution of branching points. Variations of this method can traditional diblock BBCPs, core−shell BBCPs, and A-branch-B BBCPs. [35,37]

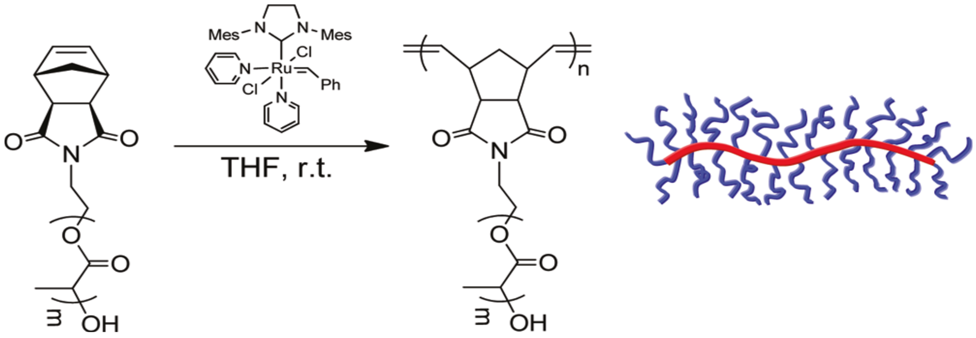


*Image 10 PNB-g-PLA brush polymer*

Amphiphilic bottle-brush block copolymerization was carried out by sequential grafting-through ROMP of norbornene-functionalized macrmonomers with a highly active third-generation Grubbs catalyst (G3) in deoxygenated DCM. This technique ensured dense side chains on every repeat unit, generated architectures with controlled DPs and different side-chain lengths of NB-PS that would affect the self-assembled morphology. The macromonomers of NB-PS and NB-PDMH were prepared by RAFT polymerization using a chain transfer agent with norbornene (NB-RAFT CTA).[38]

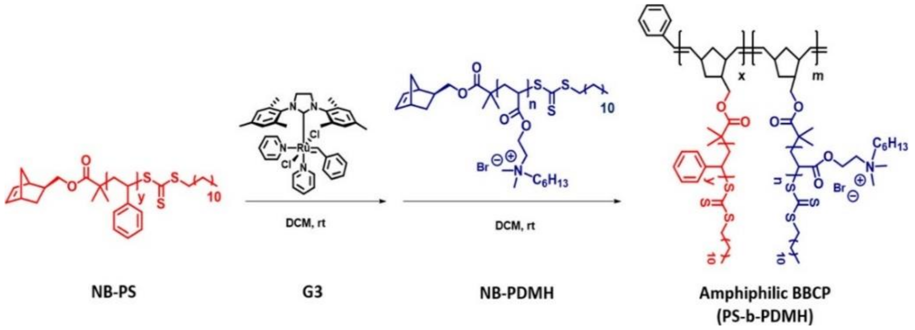


*Image 11 Synthesis of PS-b-PDMH BBCPs.*

An interesting approach in bottlebrushes, using the “grafting-through” strategy and ROMP, for UV-triggered release of anti-cancer drug molecules, is depicted below. The UV-labile “cargo”, attached to the brush “carrier” between complementary azide and alkyne moieties via click chemistry, is followed by pH-trigged release of paclitaxel (PTXL: chemotherapy drug) using acid-degradable macromonomers functionalized with PTXL pendant groups. [36]

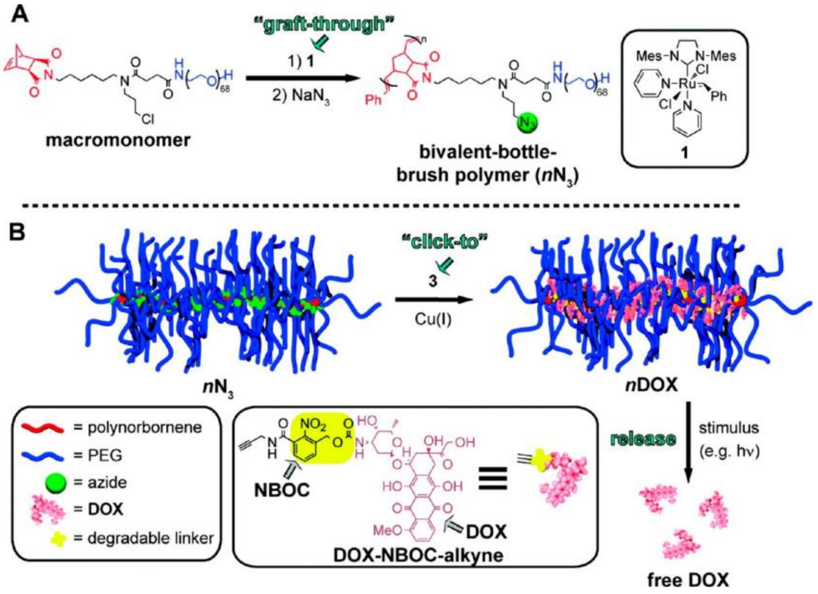


*Image 12 A) Synthesis of molecular brush carrier, B) Attachment of drug molecules via “click”*

Anionic polymerization is the most important method of living polymerization, for complex macromolecular architectures. The synthesis and polymerization of macromonomers is being carried out in the same device without requiring the isolation of the macromonomer. Additionally, a fairly controlled and “living” system is obtained. These factors highlight the supremacy of this polymerization.

Achieving large degrees of polymerization with anionic polymerization is a challenge, when it comes to long chain length and consequently strong steric hindrance effect. The the demanding experimental conditions, mainly regarding the purity of the reagents used, restrain the scientists from utilizing it. [2]

In 2004, Vazaios and Hadjichristidis, using anionic polymerization, presented a one-pot grafting-through procedure, by incorporating “living” PI, PBd and PS to 4-(chlorodimethylsilyl)-styrene, using the Grignard reaction, to prepare macromonomer branches able to polymerise into a bottlebrush structure. The reaction between CDMSS and “living” polymers lead to 99% yield, and the titration process revealed somewhat a selectivity towards the Si-Cl unit, leading to narrow molecular distributions. Hadjichristidis et al., in later studies, with the same strategy used 4-(chlorodimethylsilyl)-styrene (DCMSS), to prepare bottlebrushes with two pendant branches from each monomeric unit. [1,34]

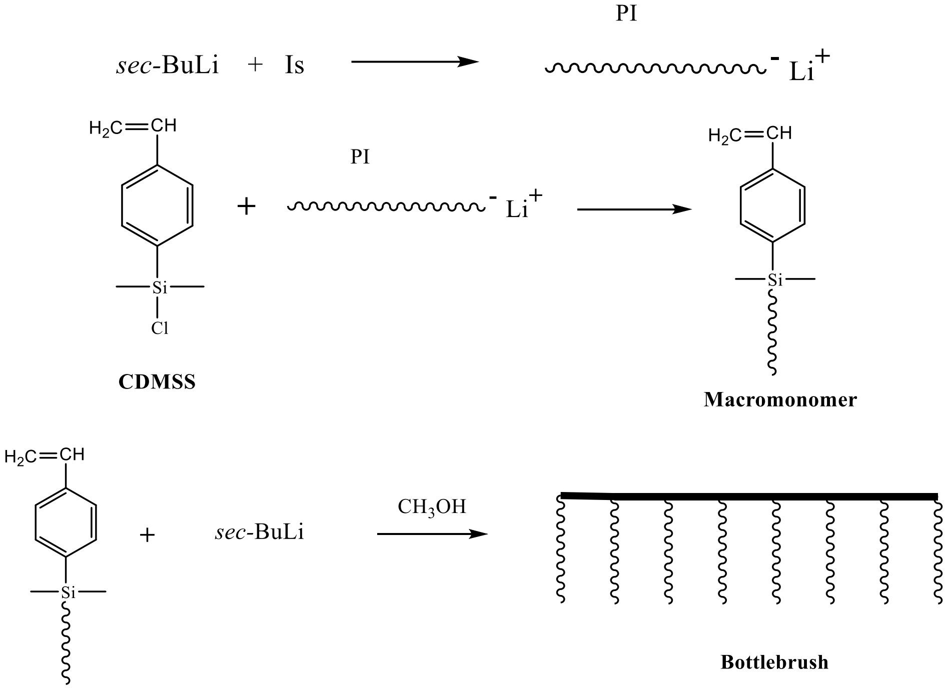


*Image 13 Grafting-through bottlebrush using anionic polymerization*

The present work is based on the synthesis of bottlebrush polymers by anionic polymerization with various lengths of macromonomer chains, a high degree of grafting, and will be analysed in the following chapters in terms of advantages and setbacks.

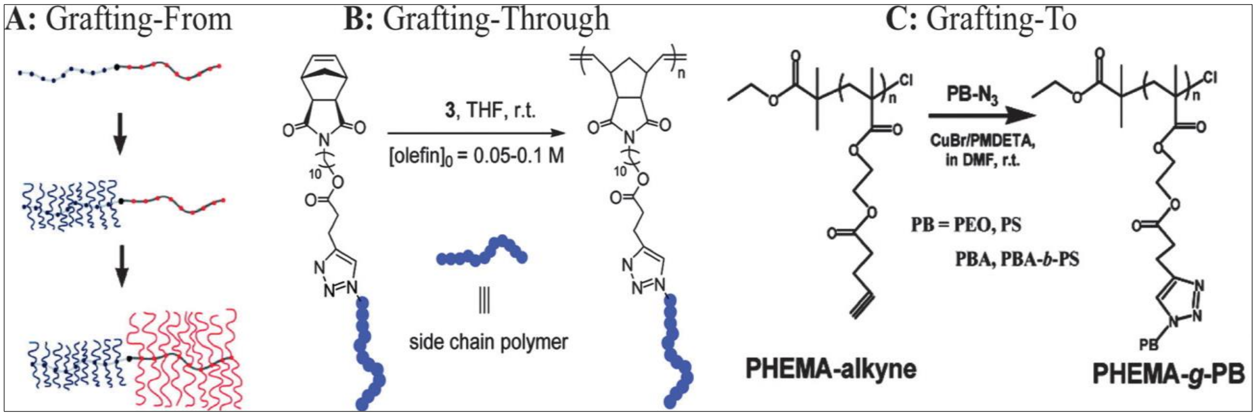


*Image 14 Bottlebrush synthesis strategies: A) Grafting-From, B) Grafting through, C) Grafting to*

### 1.4.2 Molecular Brush Properties

The molecular weight of the bottlebrush polymer is determined by the side chain molecular weight multiplied by the degree of polymerization (DP) of the macromonomers. [3,27]

#### 1.4.2.1 Structure

Bottlebrushes are classified into the following categories (*see Image 1*): linear homopolymer brushes, branched brushes, cyclic brushes, brushes with block copolymer backbones (brush-coil block copolymers), gradient brushes, brushes with random copolymer side chains, brushes with block copolymer side chains, and mikto-grafted brushes with more than one type of homopolymer side chain. Steric interactions between side chains induce two unique physical features for molecular bottlebrushes: (1) extended backbone and (2) nonoverlapping side chains. The former feature determines the cylindrical shape of the entire macromolecule. [3] It is possible to synthesize brush-like structures with a higher grafting density by incorporating dendritic monomers to the backbone. [48]

### 1.4.2.2 Molecular Conformations

When the length of side chain is shorter than that of the backbone, bottlebrushes adopt an extended and cylindrical conformation. Flexible comb-like polymers that exhibit Gaussian chain behaviour for both backbone and side chains. Molecular brushes adapt starlike conformations with side chains extending radially (length similar or greater than the backbone). The conformation of adsorbed brush molecules on surfaces is governed by the number of side chains adsorbed. If there is a significant amount of chain absorption, a ribbonlike conformation is energetically favoured, allowing more surface contacts. When side chains are not strongly adsorbed to a surface, brush molecules may switch to other conformations depending on their interactions with the surrounding environment. In a poor solvent (e.g., air), desorbed side chains attract each other and cause coiling of the backbone into a globular conformation, whilst in a good solvent, a cylindrical conformation is stabilized by steric repulsion of desorbed side chains. Spacer units in the backbone between neighbouring side chains can somewhat provide control steric congestion between side chains. [3]

### 1.4.2.3 Brushes with Segmented Backbones

Molecular brushes composed of immiscible blocks could have two possible structures: (1) brush−coil copolymers (block copolymers composed of a brush block connected to linear block(s) along a backbone) and (2) brush−brush block copolymers (BBCPs).

1. *Brush−Coil Copolymers*: The addition of linear polymer chains to a molecular brush allows for functionality to be introduced in two aspects: (1) intermolecular associations and (2) enhanced interactions with the environment. The compositionally inhomogeneous interface within a brush−coil copolymer provides amphiphilicity, allowing the molecular brush to behave as a macro-surfactant. Microphase separation, of linear-brush-linear ABA triblock copolymers, results in thermoplastic elastomers with “chameleon-like” properties, producing highly organized structures at different length from nano- to micrometres useful for fabrication of nano-porous materials with applications in absorption and filtration of toxic materials. Furthermore, the mechanical properties of these thermoplastic elastomers mimic the mechanical response of biological tissues. The surface

conformations of BCPs depend on the interactions between individual blocks, underlying substrates, and the surrounding environment. If both blocks are equally attracted to a substrate, the conformation is similar to that of a brush with homopolymer side chains (*Image 15* Adsorption of BCPs.*a*). However, if one of the blocks has preferential attraction to a substrate, the sidechains may fold (b,c). One of the most important applications of this property is the use of molecular bottlebrushes as templates to create inorganic nano-objects. [3]

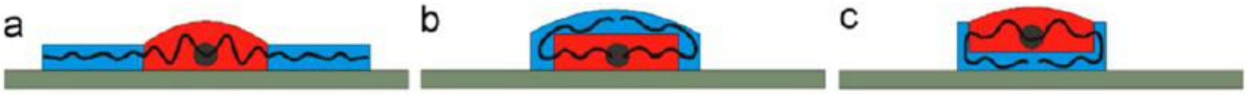


*Image 15 Adsorption of BCPs.*

2. *Brush-Brush Block Copolymers:* The combination of suppressed chain entanglement and the well-defined compositional interface in the backbone make BBCPs useful in applications, that BCPs cannot be adapted, such as lithographic templates, solid electrolytes, and photonic crystals (1D BBCPS, in bulk and thin film assembly). Bottlebrush block copolymers self-assemble to form large domains and exhibit very high order-to-disorder transition temperatures due to the extended backbone and sterically-interacting side chains, as discussed in several examples below. Mixed side-chain bottlebrush polymers have two or more chemically distinct side-chains attached to the backbone. A third type is bottlebrushes that can be both block copolymer and core–shell. BBCPS in bulk and thin film cylindrical molecules may be advantageous for increasing retention and uptake or for targeting of specific cells or tissues. Finally, bottlebrush copolymers can assemble to form micelles, vesicles, and other novel structures in solution that are potentially useful for encapsulation and delivery (primarily core–shell type bottlebrushes) [2,3]

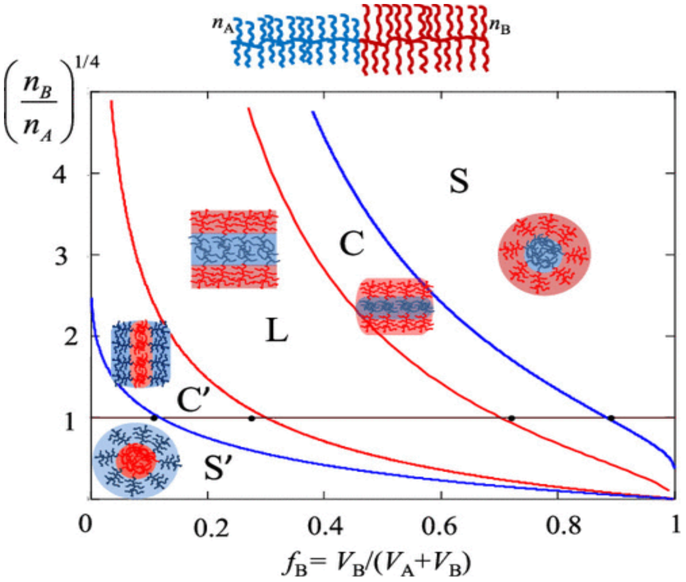


*Figure 8 Microphase Segregation in the Melts of BBCPs* [43]

Diblock bottlebrush copolymers have also found to be aligned in long range lamellar or double gyroid conformations, because of their high molecular mobility in the melt state. [40,42,] Architecturally asymmetric diblocks, such as linear-b-bottlebrush, self-assembly into cylinders, double-gyroid, and lamellar microstructures. [44] The difference in the microphase-separated states between phase-mixed bottlebrush statical copolymers BSCPs and weakly segregated bottlebrush block copolymers BBCPs can be attributed chain immiscibility when the side chains are grafted to a molecular backbone in blocks.[45] The BSCPs with symmetric volume fraction exhibit strong tendency to self-assemble into lamellar morphologies. The backbone defines the domain interface and is additionally directed by the sterically crowed side-chain packing. The topological defects in the lamellar assembly are eliminated as backbones move to the lowest free-energy conformation, in order to achieve rapid organisation into large grains. In the BSCP molecular configuration, the interface will line up directly with the backbone orientation. These self-assembly advantages over LBCPs (linear bottlebrush copolymers) suggest that BSCPs architecture packing in bulk, can be used potentially for device architectures, lithography and other applications that require well defined morphologies. [46]

#### 1.4.2.4 Brushes with Nonlinear Topologies.

The nature of cyclic polymers hinders intermolecular chain entanglement and can affect intermolecular packing in polymer melts, whereas the branched structures change intermolecular connections due to the existence of “arms”. Cyclic polymers typically have a smaller hydrodynamic volume, higher density, lower intrinsic viscosity, increased rate of nucleation and crystallization, higher glass transition temperature, and higher critical solution temperature than those of their linear counterpart. [3]

#### 1.4.2.5 Brush relaxation states in solutions and melts

Bottlebrush polymer melts exhibit unusual rheological behaviour due to their very high entanglement molecular weights. The high side-chain grafting density also leads to potentially useful phase behaviour in blends. [2]

Dilute solution characterization shows that the strong intermolecular forces between the side chains. Brush polymers show three types of sequential relaxations: glassy relaxation, relaxation of the side chains and the brush polymer backbone which is the terminal hallmark, imposing that brush polymers with side-chains of high $M_w$ are unentangled. It is expected that branched polymers should relax sequentially. The chain segments should relax first, followed by the side chains, and the whole polymer should be the last to move. The master curve of sequential relaxation is divided in three parts:

- Segmental Regime: The segmental regime covers the glassy and glass transition region of the brush polymers.
- Arm Regime: Brush polymers with the same DP shift together. This regime is affected by both the faster segmental relaxation and the slower terminal relaxation processes.
- Terminal Regime: It describes the relaxation behaviour of the backbone. The whole polymer relaxes, and the modulus values decrease with increasing DP. Arm and terminal regime don’t show entanglement, only separately existing branches therefore no excluded volume interactions (Rouse conformation).

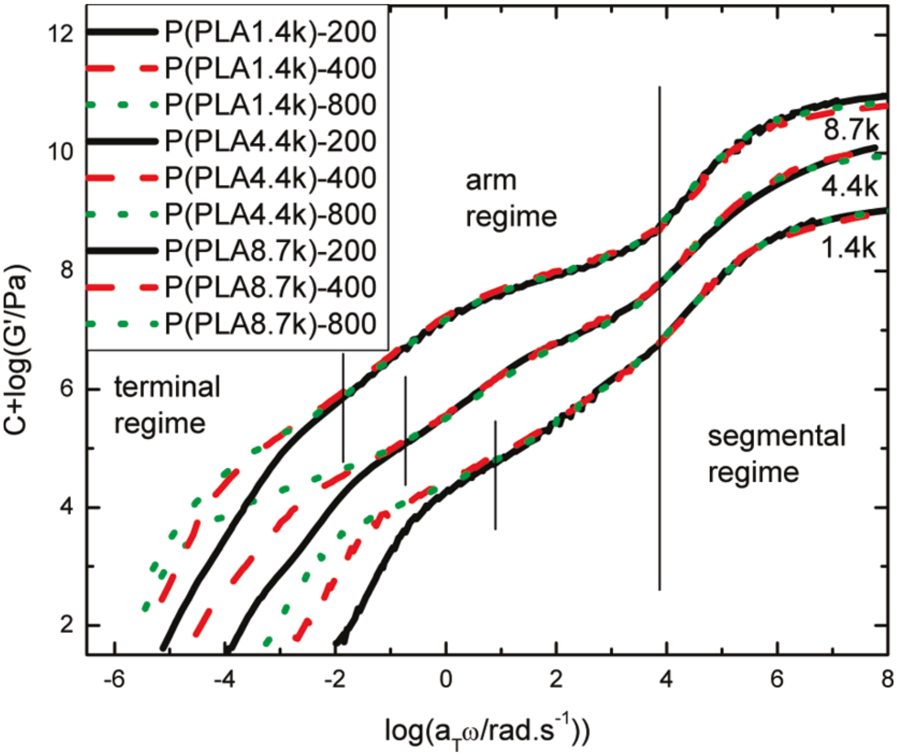


*Figure 9 Sequential relaxation of the brush polymers*

Side chain properties affect the relaxation behaviour of the whole brush polymer. For brush polymers with the same side chains but different backbone DP, their arm and segmental regimes are almost identical. The glass transition regions are shifted together and the arm regimes overlap with each other very well. The length of the arm regime increases with increasing side chain length.

In the terminal region, the curves start to deviate from each other moving to lower frequency as the DP of the backbone and side chain length increase, and the polymer becomes less flexible, because their interactions stiffen the backbone. Side chains act as solvents to dilute the polymer backbone, and dilution grows along with side chain length. There isn't a rubbery state for unentangled polymers; but it simply reflects the molecular orientation independently of entropy due to the deformation of a chain entanglement network.

The intrinsic viscosity was found to be unchanged until a critical molecular weight value was reached. The critical molecular weight for the occurrence of sharp viscosity change, increased along with side chain molecular weight. Brush-like polymers are above the region of critical molecular weight. In good solvent, the expansion of the molecular dimensions through the branch conformation due to the excluded volume effect is also considered.

For polymers with shorter side chains and extremely high grafting density, similar to the long chain branched polymers, two rubbery plateaus (phase changes): one that corresponds to the relaxation of the side chains, and another one that is regarded as the rubbery plateau of the whole polymer, which decreases with increasing side chain length, providing extremely high entanglement molecular weights to these densely branched brush polymers. The latter and very low rubbery modulus is attributed to the interactions between the densely packed side chains that stiffen the backbone as the total length of the brush chain increases with expansion of side chain density. This affects the inter-chain interactions and extends the distance between entanglements. A worm-like conformation is expected for this kind of brush polymer.

Brushes are in a transition zone from rouse conformation to fully entangled in melts. The molecular weights of the brush polymers are huge and the side chains are long, however neither the side chains nor the whole polymer show evidence of entanglement in dilute solutions. The nature of brush polymers is also confirmed by zero shear (material at rest) viscosity in the melt state. Although having very large molar masses, these brush polymer chains remain unentangled. The effect of the side chain on the conformation of the backbone also occurs in melt and in brushes with shorter side chain. [35]

#### 1.4.2.6 Rigidity of combs and brushes

Loosely grafted combs show thermorheological complexity, according to their linear viscoelasticity behaviour, because of the statistical branching distribution and the number of available potential sites for side chain reaction. As the number of branches approaches the densely grafted comb and bottlebrush architecture thermorheological complexity is reduced, since branch point distance is consequently very similar.

In extensional rheology measurements, the more the number of branches is the stiffer the polymers become, raising the strain hardening factor (SHF), that describes the increase in hardness and strength, caused by plastic deformation while stretching the backbone.

This implies that densely grafted bottlebrush topologies, show large degree of SHF and an almost unobtainable steady state at the maximum extensional viscosity. This means that bottlebrush structures might not have good processability compared to the comb ones in the melt state under extensional deformations. However, solution processing of such bottlebrushes, e.g. electrospinning, might be a possible alternative. [30]

#### 1.4.2.7. Structure of bottlebrushes in melts

The bottlebrush side-chain conformations vary in different states (adsorbed, solvent, melt), and so do their potential applications. [2]

Bottlebrushes behave as a melt of flexible filaments depending on the grafting density, side chain length and rigidity. Dense branching results in distinct shape of individual molecules and reduces overlap of neighbouring molecules in dense systems (concentrated solutions and melts). In bulk melts, wormlike conformation promotes reduction of entanglement density. Short backbones lead to rod-like polymers. These fundamental changes in physical properties are achieved only through architectural control without changing the chemical composition. These unique features inspire the design of new materials with physical properties that are different from properties of conventional linear polymers. Branched macromolecules were explored as molecular pressure sensors, pH-sensitive probes, super soft solvent-free elastomers (for low voltage actuators, vibration damping, soft robotics, and drug delivery agents), and materials mimicking mechanical properties of biological tissues.

Conformations of combs and bottlebrushes depend on the DP of the side chains and their grafting density and can be classified as: (i) loosely grafted combs (LCs) with long backbone spacers between side chains and with strongly interpenetrating neighbouring molecules and (ii) densely grafted combs (DCs) with weak interpenetration between molecules. There are also two regimes at higher grafting density: (iii) loosely grafted bottlebrushes (LBs) with extended backbones and Gaussian side chains for intermediate grafting density and (iv) densely grafted bottlebrushes (DBs) with extended backbones and side chains for high grafting density.

The space-filling condition is the boundary between combs and brushes regarding the interpenetration of side chains from neighbouring molecules. Densely grafted combs (DC), with spacers shorter than the side chains, allow only partial interpenetration of the side chains because there is not enough space to accommodate side chains of neighbouring molecules near the backbone of a host molecule. Both the side chains and backbones in melts of combs (LC and DC) are in almost unperturbed Gaussian conformations.

The bottlebrush regime describes the excluded volume interactions between densely grafted side chains, which cause (i) extension of backbone and side chains, (ii) stiffening of a graft macromolecule, and (iii) withdrawal of its side chains from neighbouring macromolecules., The stiffening of the backbone is responsible for decrease of entanglement. In the comb regime, this state is achieved due to the predominance of dilution effect.

The bottlebrush regime is the lack of space for side chains emanating from the unperturbed Gaussian backbone. Interpenetration of these side chains without their significant deformation is only possible upon extension of the backbone. In melts, reduced interpenetration of side chains from neighbouring macromolecules distinguishes segregated filaments (bottlebrushes) from overlapped molecules (linear chains and combs with long side chains). The terminal monomers are in the interpenetration zone between two bottlebrushes. This zone contains 50:50 composition of monomers from both molecules.

Bottlebrush backbones are shielded by densely grafted side chains and do not approach each other. The backbone stretches and stiffens, indicating stronger intramolecular correlations. The existence of this local structure for bottlebrush melts is due to long-range interactions between backbone monomers induced by side chains. The longer the side chains are, the stronger the interaction is between backbone monomers and the longer the range of these interactions is. The interaction range along the backbone is comparable to the size of the persistence segment.

Particular attention was paid to the bending rigidity of bottlebrush macromolecules, key feature behind physical properties of bottlebrush melts and elastomers. The entanglement modulus of bottlebrush melts decreases, and their backbones of in a melt state obey Gaussian statistics. Limited interpenetration of side chains of neighbouring molecules and the existence of individually formed bottlebrushes inside melt, displays them as melts of thick and flexible filaments, with a persistence length proportional to the size of the side chains. The rigidity of bottlebrush is only due to the mutual repulsion of the crowded side chains creating a cylindrical-like persistent segment. The conformations of bottlebrush backbones, at small length scales are similar to those of flexible polyelectrolytes, meaning that on small length scales and have large persistence length, induced by side-chain repulsion, on intermediate length scales.

The size of a bottlebrush in a melt state can be estimated by conformational transformation from a random coil to a rod as the grafting density increases. If grafting density is too high, side chains grafted to the undeformed section of the backbone can no longer fit in the pervaded volume, forcing the backbone to extend. The size of side chains of densely grafted bottlebrushes with almost fully stretched backbones increases with degree of polymerization and grafting density along the backbone. As a result of side chains that do not extend to large radial distances from the backbone, the crowding of remaining chains at these large radial distances decreases. This decrease in crowding weakens the stretching of the remote side-chain sections, resulting in a relatively smaller average extension of chain sections. The stretching vanishes at the free side-chain ends in the overlapping zone of neighbouring bottlebrushes. [47,48]

#### 1.4.2.8 Applications of polymer brushes

Polymer brushes tethered to another polymer chain (one-dimensional, 1D) or the surface of a planar (two-dimensional, 2D), spherical or cylindrical (three-dimensional, 3D) solid via a stable covalent or noncovalent bond linkage (*see Image 5*), can be used in catalysis, nanolithography, biomineralization, drug delivery, medical diagnosis, optoelectronics etc. Linear 1D amphiphilic BBCPs are used as building blocks of nanostructures with diverse morphologies, such as fibular and tubular structures, owing to the wormlike configuration and can be utilised as templates to prepare organo-silica hybrid nanowires. Polymer brushes, 2D and 3D, combine the functionalities of matrix of inorganic nanostructures, such as magnetic, optical, electronic, and mechanical properties, and the properties of tethered polymers, including stimuli-responsiveness, super-hydrophobicity, antifouling, corrosion protection, colloid stability, adhesive behaviour, lubrication and friction.

Brush-like nanoparticles in solution, are designed to target tumours, carry and release, precise ratios of anti-cancer drug molecules, simultaneously.[3,27] Polymer film formed by spin-casting can mitigate biofouling effectively, due to limited adsorption events. The formation of polymer brushes on the surface of graphene and RGO (reduced graphene oxide) is an effective route to prevent RGO from restacking, and polymers can be used as cathode for lithium-ion batteries (LIBs). [27] Adsorption of brush macromolecules into an interface, results in enhanced steric repulsion between adsorbed side chains, which causes significant tension in the brush backbone. When brushes undergo lateral compression on a substrate, the backbones coil due to desorption of side chains. This causes each macromolecule to occupy less area on the surface of the substrate. This adsorption-induced behaviour has allowed molecular brushes to be used as pressure sensors. [3]

## 1.5 Molecular Characterization

### 1.5.1 Size Exclusion Chromatography (SEC)

Early in their work Wheaton and Bauman separated non-ionic substances of low molecular weight were separated by elution with water through a column packed with ion-exchange resin particles. Since that time the techniques of column chromatography on crosslinked gels have become broadly applicable to separations of large from small molecules in aqueous solutions. Lathe and Ruthen showed that the separating range could be greatly extended by using swollen starch grains as column packing, for differentiation between a globulin and hemoglobin, of molecular weights 150kDa and 67kDa. Porath and Flodin, produced a series of hydrophilic gel column packings, introducing the term “gel filtration” for this process. However, their use is limited to the separation of water-soluble substances.

Hydrophobic gels of high permeability weren’t available. Several interesting separations were reported by Cortis Jones on columns packed with crosslinked polystyrene, however, thy didn’t extend to large molecule separation. Vaughan showed that separation of low molecular weight polystyrenes did occur when they were eluted with benzene through polystyrene beads, lightly crosslinked and therefore, swollen in benzene. Gel networks of altered structure are produced by crosslinking in the presence of a diluent which is a solvent for the monomer. It appeared likely that preparation of polystyrene beads, with sufficient crosslinking to confer a desirable amount of rigidity, is possible, whilst regulating the permeability of the network over a wide range by varying the mount and nature of the diluent present at the time of crosslinking.

In 1964, Moore went a step further in the direction of improving these techniques. Using electron microscopy (observation of the columns) and by changing both the type and the amount of solvent, that is used to swell the column packing material, he proved that the chromatographic separation is in an equilibrium process, where the dissolved and ready to be separated molecules diffuse rapidly throughout the gel lattice. Using small samples and slow flow rates, revealed symmetrical peaks in the chromatograms. On the contrary, larger samples or at faster flow rates the peaks showed broadening that did not appear at shorter times, which made it clear that the the separation of the molecules isn’t based on the diffusion speed of the molecules in the lattice. It was also observed that homologous series of polymers weren’t separated just as well as the separation of polymers with identical monomer but different molecular weight. For larger molecules, the main separating factor is size while for smaller molecular weights the difference in polarity dominates. The term “gel chromatography” was proposed by Moore (in 1964), describing a mechanism of molecule separation according to their different size, owing to their different permeability through pores of a certain size.

The properties and uses of polymeric materials are influenced by characteristics such as chemical structure, average molecular weight, molecular weight distribution, degree of branching, regularity, and crystallinity. Size Exclusion Chromatography (SEC) or Gel Permeation Chromatography (GPC), appeared as the most reliable method for determining the molecular weight distribution of polymers (MWD=Molecular Weight Distribution), the most important quality factor of macromolecules. Smaller distributions (PDI=1) are equal to polymers of good mechanical and chemical properties. SEC is a type of High-Performance Liquid Chromatography (HPLC) adapted to the sizes of polymers which are characterized by molecular weights much greater than those of simple chemical compounds. The conditions to be met by a polymeric substance in order to be determined through this method are the following:

A. Good solubility in the solvent used in the set-up.
B. Inability to react with the solvent.
C. Inability to react with the separation medium.

Polymer solution is passed through columns containing a separation medium, usually spherical pores of crosslinked polystyrene known under the trade name styragel (of course there are also columns filled with porous glass but these show some disadvantages in terms of accurate determination of the average molecular weight, since secondary interactions occur, during the passage of the substances through the columns, increasing the elution time presenting the molecular weight of the polymer lower than the real one). The styragel gel has pores that range in size from 60-$10^7$Ǻ (average diameter). The gel is completely immersed in the device solvent without the presence of gases. When polymer solution enters the columns, the polymer molecules pass through pores, that are large enough in order to fit big molecules such as polymers inside. Therefore, since the columns are packed with material exhibiting a pore size distribution, the separation of polymer molecules based on their size difference. Large molecules pass only through a small amount of pores, resulting in earlier elution, in contrast to the elution time of smaller ones, which remain in more pores. Essentially the hydrodynamic volume is the magnitude, that defines the elution time of the polymer. If the “good” solvent is used, then the polymer swells, acquiring volume (hydrodynamic volume), directly linked to the elution time in the case of linear monomolecular polymers. However, this not the case describing mixtures of homopolymers, copolymers, and branched homopolymers or copolymers because:

A. For a certain molecular weight, the hydrodynamic volume of a branched homopolymer is smaller than that of its linear counterpart.
B. In a copolymer, the partial molecular volume, $M_i/V_h$, for each of the repeating units, is different.

Size exclusion chromatography is not an absolute method and therefore calibration of the chromatograph with standard samples is necessary. Polystyrene homopolymers of different molecular weights prepared by anionic polymerization, are adequate templates, exhibiting narrow distributions for greater chromatograph accuracy in determining molecular weight and molecular weight distribution ($I = M_w/M_n$). The calibration curve obtains a region of linearity, in which good precision in molecular weight can be acquired. At very low or very high molecular weights, the separation capacity of the method decreases, resulting in an increase in the probability of error, which in any case reaches 10% in GPC. This is the reason behind the identification of the titre of the initiator, using styrene and *s*-BuLi (initiator), in an attempt to prepare a polymer with a molecular weight above 15K, within the linear region of the calibration curve, avoiding large deviations in the calculation of the concentration (*see section 2.6*).

A branched homopolymer (e.g. PS star) with the same molecular weight as the linear one, elutes first since its hydrodynamic volume is smaller. This indicates that the elution time of a polymer is directly dependent on the architecture as well, which makes the molecular weight determination by SEC perplexing. The solution was proposed by Albert

Einstein who first related the elution time to the molecular weight M and the intrinsic viscosity [η] according to the following equation:

$$[n]M = 0{,}025N_AV_h$$

Therefore, if the intrinsic viscosity [n] of several standards and the polymer of interest, are determined independently, the molecular weight of the unknown sample can be calculated from the calibration curve of the product [n]×M versus the elution volume ($V_e$), whereas $N_A$ is Avogadro's number and $V_h$ stands for the hydrodynamic volume of the polymer in a particular solvent.[49,50,51]

The detector or detectors in size exclusion chromatography are very important. The detectors used are divided into two categories according to the size they determine. Concentration-mass sensitivity detectors such as UV, IR and DRI are used. Molecular mass sensitivity detectors such as the light scattering detector and the viscometric detector are also used. [52]

The UV detector is used when the polymers have chromophore groups that absorb in UV (between 190 - 400 nm). Combined with the DRI detector, they jointly provide information on the composition of a copolymer that obtains UV-absorbing clusters. It works well below average temperatures, but solvents used should not absorb in this range.

The DRI detector (Differential Refractometer Index) is considered a universal detector, because of its sensitivity to differences in the refractive index of the solvent and the dissolved polymeric substance. Used even at high temperatures, offers linear responses over a wide range of concentrations but is very sensitive to atmospheric conditions.

The IR detector is suitable for polymers with ligands that absorb in the infrared region such as the sulfonic group ($SO_3H$), and polymer composition as a function of molecular mass can be defined.

On the other hand, the scattering detectors used in size exclusion chromatography show great accuracy in determining the actual molecular weight, but also in determining the distribution of molecular weights at all elution times, since they consist of small detectors that can measure the intensity of the scattering radiation at various angles, and with a special processing of the results, in order to give the actual molecular weight $M_w$ since the Rayleigh ratio determined is related to it through the following relationship (C:the weight-by-volume concentration of the polymer in the solution, $A_2$ and $A_3$ the second and third virial coefficients and with $M_w$ the average molecular weight-by-weight):

$$K_c/\Delta R_\theta = 1/M_w + 2A_2C + 3A_3C$$

The viscometric detector is used in a row with one of the mass-concentration sensitive detectors mentioned above, giving fine information about the absolute average molecular mass, the intrinsic viscosity and the degree of branching. In these probes, the intrinsic viscosity of the polymer solution is determined by the pressure difference across a capillary, recorded by a differential pressure transducer. The great advantage this detector is the ability to obtain average molecular weights based on the global calibration curve for polymers of different composition, so that the hydrodynamic volume independent of the architecture factor.[49,50,51] The SEC intrumentation is represented at Image 16 below:

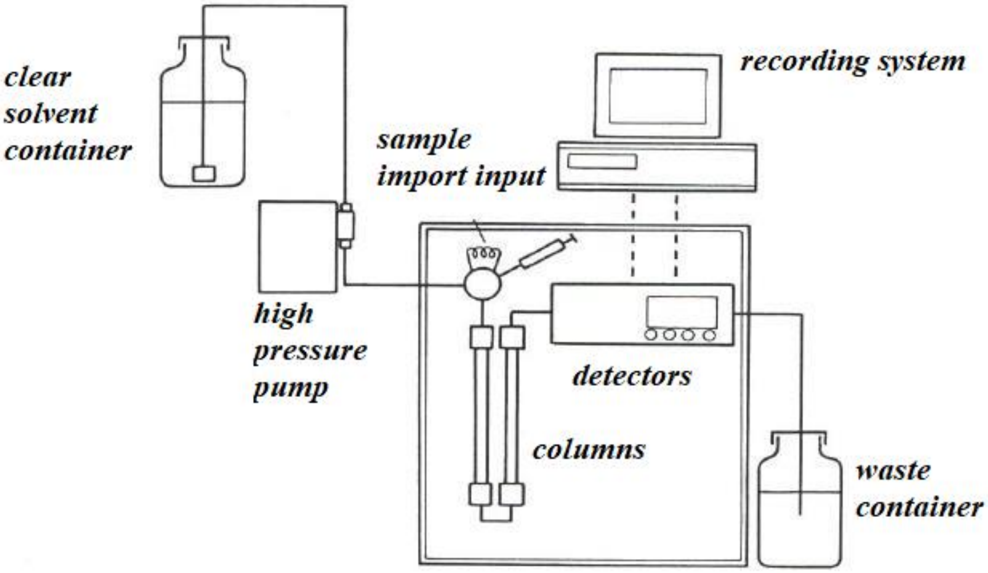


*Image 16 Size Exclusion Chromatography instrumentation*

### 1.5.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most important methods for finding the structure of matter and is widely used in almost all branches of chemistry. In the field of polymers, pioneered by Bovey and his classic works, the NMR technique has found enormous application in finding the stereochemical imaging (regularity) of the polymer, as well as the geometric isomerism, structure and composition of the copolymers, while recent studies regarding the movement of macromolecules in solution and in solid state have also been developed. The theoretical basis for nuclear magnetic resonance spectroscopy was proposed in 1924 by W. Pauli, who said that the nucleus of an atom must have spin and magnetic moment so that when exposed to a magnetic field, its energy levels are crossed. During the next decade, the correctness of the above propositions was experimentally proven.

In the next decades, following the discovery of nuclear magnetic resonance, chemists saw that the molecular environment affects the absorption of radiation in the radio frequency range (4 to 600 MHz) of a nucleus in a magnetic field. This influence can be related to the chemical structure. In 1953, the first nuclear magnetic resonance spectrophotometer was built to study the structure of chemical compounds. Today two types of spectrophotometers exist: continuous wave (CW) spectrophotometers and pulse or Fourier transform spectrophotometers. CW spectrophotometers are governed by the same principle as optical spectrophotometers, in which the absorption signal is recorded as a function of source frequency. In pulses, the sample is periodically irradiated, resulting in a signal that decays over time. This signal is then Fourier transformed into a signal in the frequency domain, resulting in a spectrum, similar to that obtained by continuous wave spectrophotometers.

The $^1$H-NMR proton spectrum, which is widely used to study polymers, consists of a group of spectral lines due to the different types of protons in the sample. There are three basic pieces of information that can be determined from a spectrum:

I. The position of the spectral line or as it is called the chemical shift, which is characteristic of the type of proton.
II. The area of the region under each spectral line, which is proportional to the number of particles present in the sample.
III. The range of the spectral line which is related to the molecular environment of the specific proton.

The resonance of each nucleus at each different frequency is due to the existence of electrons that surround it. These electrons create local magnetic fields which protect it, with the result that the nucleus feels a $B_{loc}$ field different from the applied B:

$$B_{loc} = B\,(1 - \sigma)$$

where σ is the shielding or screening constant, a dimensionless magnitude that determines the electronic density around the nucleus, and therefore, its degree of shielding.

The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and a standard reference substance. The substance commonly used as a reference for the proton spectrum is tetramethyl silane ($Si(CH_3)_4$), referred to as TMS, which has twelve equivalent and strongly shielded protons. However, for the present work, we used deuterated chloroform as solvent. The chemical shift δ is defined as:

$$\delta = \frac{B_\alpha - B_\delta}{B_\delta} \times 10^6\,ppm$$

$$\delta = \frac{v_\alpha - v_\delta}{v_\delta} \times 10^6\,ppm$$

where $B_\alpha$ and $B_\delta$, the resonance fields of the nuclei of the reference substance and of the sample respectively, while $v_\alpha$ and $v_\delta$ are the frequencies of the reference substance and of the sample respectively. Generally, if a core is more protected (large value of σ), resonance is achieved at higher applied magnetic fields and lower frequency. The basis of quantitative analysis is fact that the area under the spectral line, is proportional to the number of particles in the sample. Taking into account different spectral lines, due to different kinds of particles, it is possible the composition of the copolymers.

Finally, knowing the degree of peak crossing leads to its respective identification. The number of spectral lines displayed, is given by the formula ($2n_xI_x + 1$), where $n_x$ is the number of equivalents of neighbouring nuclei, and $I_x$ the spin of the nucleus. In the case of $^1H$ and of $^{13}C$, the spin is I = ½, and the formula reduces to $n_x+1$ and the relative intensities of the peaks are the coefficients of the expansion $(1 + x)^n$ ; for example, a split core from two other vicinal cores will give a triple peak with peak intensities 1:2:1. [52,53]

## 1.6 Differential Scanning Calorimetry (DSC)

For the comprehension of the thermomechanical properties of polymers, it is necessary to first understand the various types of transitions that occur in the natural state of these materials. These transitions occur as the temperature, the external mechanical stress, or the time scale of the experiment used, to measure each transition, change. These include: crystal melting, first-order crystal transitions, glass transitions, and secondary glass transitions. Almost all mechanical properties of polymers are primarily determined by these transitions and the temperatures at which they occur.

Polymers in the solid state behave as amorphous and crystalline bodies [69]. The mobility of polymer chains is characterized by: the glass transition temperature $T_g$ (the temperature at which certain properties of the polymer such as viscosity, heat capacity, coefficient of thermal expansion, etc. undergo abrupt changes, while some others such as volume, enthalpy and entropy change gradually) and the melting point (melting point) $T_m$, which relate to the amorphous and crystalline part of the polymer respectively. $T_g$ and $T_m$ are usually determined by Differential Scanning Calorimetry (DSC).

DSC gives results for these temperatures with the help of a reference sample. At these temperatures, the heat capacity of the polymer increases, as the corresponding parts of the chains move more easily, absorbing larger amounts of energy. The transition from the glassy to the elastomeric state occurs in a range of temperatures, therefore the value of $T_g$ for the same polymer can vary.

Differential Scanning Calorimetry[70] (DSC) belongs to the methods of thermal analysis and is used for measurement of temperatures and heat flows, related to material transitions, as a function of temperature and time. With differential scanning calorimetry, qualitative and quantitative information can be obtained on the physicochemical changes of the sample, involving endothermic and exothermic processes or changes in heat capacity.

There are two very important temperatures that reflect changes in the mobility of polymeric materials. It is the glass transition temperature ($Tg$) that refers to the amorphous parts of solid-state polymers and is related to movement of very small parts of the chain, and the melting temperature ($T_m$) that refers to the areas that show crystallinity and is related to movement of the entire macromolecule.

Experimentally, the polymer sample is enclosed in a special capsule ($Al_2O_3$) and along with the reference capsule (empty) are placed in two separate heating cells. The whole system is heated at a rate of 10-20$^o$C/min. Changes in the thermal behaviour of the sample are calculated as changes in current power. At glass transition temperature, a sharp increase in the heat capacity of the material appears, because the chain segments begin to move more easily, absorbing larger amounts of energy. The glass transition temperature is considered to be a free volume phenomenon, since empty space around the chains is required for the movement of their segments. When there is a decrease in temperature, in order to cover the minimum energy requirement, the free volume decreases and the bonds of the chain retain only a small number of their configurations. The chain becomes more rigid and the entropy of the system is reduced Therefore, the glass transition phenomenon can be studied by observing the entropy or free volume change of the system. Thus, decrease in temperature, and therefore decrease in free volume, a restriction of the movement of the chain segments is observed, until they are no longer detectable in the corresponding range of observation times.

As reported in the literature, the $T_g$ values for the same sample show range of 5-10$^o$C, because the glass transition state doesn’t occur at any specific well-defined temperature. Also, the observed $T_g$ depends on the thermal history of the sample, the heating or cooling rate, and also on the method used to determine it. The glass transition temperature is described as a thermodynamic transition, because there is a discontinuity in the specific heat under constant pressure ($C_p$), but also as a kinetic phenomenon, strongly dependent on the cooling rate. Generally rapid cooling leads to higher $T_g$. Additionally, polymers with flexible segments in their chains display low $T_g$, while those with rigid one quite high. Flexibility occurs when the chains include a sequence of bonds that can rotate. Polymers with $-CH_2CH_2-$, $CH_2OCH_2-$, -SiOSi- bonds have a fairly low $T_g$. In polymers with flexible chains, the presence of bulky end-groups hinders rotation, resulting in an increase in $T_g$. Flexibility also plays affects the melting temperature, $T_m$, and there is correlation between $T_g$ and $T_m$ for a large number of polymers.

High molecular weight polymers, display unassociated $T_g$ and molecular weight, but as the length of the polymer chain decreases, a decrease in $T_g$ is also observed. The two ends of the chain exhibit greater mobility than a monomeric group within the chain. The end chains contribute to the free volume, considerably, causing decrease of density with decreasing polymer chain length. The equation between $T_g$ and number average molecular weight is:

$$T_g = T_{g\infty} - \frac{K}{\overline{M}_n}$$

where $T_{g\infty}$ is the glass transition temperature in the limit of infinite molecular weight, and K, a constant correspondent to the increased free volume near the ends of the chain.

# CHAPTER 2
# EXPERIMENTAL PART

## 2.1 Anionic polymerization high vacuum technique

Anionic polymerization, as already mentioned, is an important “tool” for the synthesis of well-defined polymers, i.e., polymers with narrow molecular weight distribution, predictable molecular weight, desired architecture and microstructure. These polymers are ideal for determining the relationship between structure and properties.

Nevertheless, an important drawback of the method is the high reactivity displayed by the anionic centres, the coupling agents and the polymerization initiators with atmospheric oxygen, carbon dioxide, moisture and impurities that may be present in the reagents used.

It is considered necessary to use specially designed devices, as well as the high vacuum technique in order to remove from the reaction system unwanted substances that will cause premature termination of the living chains, as shown below. All procedures for the synthesis of polymers in this work were carried out using the above technique [24,26].

The high vacuum line as shown in Image 17, consists of glass tubes (Pyrex) (D), high vacuum valves (Rotaflon HP 10mm, $10^{-8}$mmHg) (E), an oil pump (A) and a mercury diffusion pump (B). The oil pump creates a preliminary vacuum of the order of $10^{-2}$-$10^{-3}$ mmHg, which is necessary for the distillation of the mercury, located in the diffusion pump (Image 18), at a low temperature.

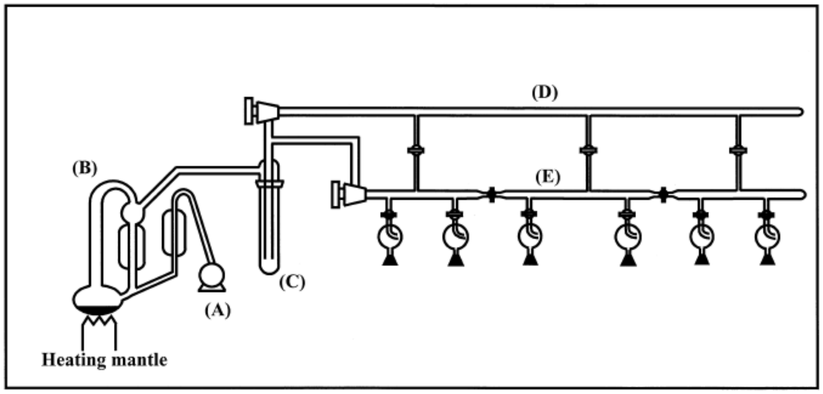


*Image 17 Schematic representation of high vacuum line*

The mercury molecules pass through the constriction, located in the diffusion pump (Image 18), which causes their velocity to increase and, by extension, their pressure to decrease, according to Bernoulli's principle. The velocity of an incompressible fluid must change as it flows along a pipe of no fixed diameter. Elements of the incompressible fluid accelerate, moving from a region of high pressure to another of low pressure so that it accelerates it forward, as an effect of net force. When the diameter of the flow pipe is changed, the pressure should also change even if there is no difference in height. Thus, during the passage of mercury molecules through the constriction, an increase in their speed is caused, and due to the decrease in pressure caused by the same action, pressure difference (vacuum) is noted at the ends of the column. During its contact with the walls of the cooler, the mercury condenses and returns to the bottle, where the process is repeated. This creates a vacuum of the order of $10^{-6}$ mmHg, equal to the mercury vapor pressure.

In order to protect the diffusion pump and the oil pump from volatile components there is a liquid nitrogen trap. The diffusion pump is connected to the main part of the vacuum line, which is made of glass tubes (Pyrex) with high vacuum Teflon stopcocks, that aid to the direction of vacuum to specific sites of the line, simultaneously isolating isolate other sites. The connection to the vacuum line is done using ground glass joints, in order for devices to be adapted to perform various experimental processes (distillations of solvents, monomers, degassing, etc.). High vacuum distillations are facilitated by slightly heating the liquid to be distilled (facilitated by constant stirring), while simultaneously cooling the receiving flask with liquid nitrogen (-196 $^{o}$C) or with an isopropanol-liquid nitrogen bath (- 78$^{o}$C). Special safety measures must be taken when conducting experiments in the high vacuum line.

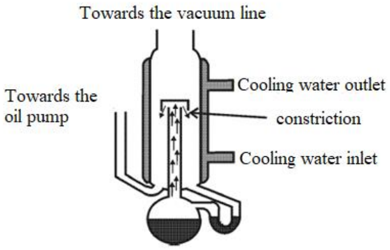


*Image 18 Schematic representation of the diffusion pump*

The quality of the vacuum can be checked with the Tesla coil. When the high vacuum line is satisfactorily degassed, then coil noise near the glass sections of the line is negligible. Details of the use of the high vacuum line and the necessary precautions to be taken are given in the literature. Before starting any distillation or purification process in the vacuum line, it is necessary to check the apparatus used to find possible micro-holes, the presence of which allows moisture or oxygen to enter the purification apparatus leading to undesirable results for both reagents and mercury (oxidation). Also, the mechanical pump can be damaged, whether large amounts of air flow into it. The test for the existence of holes is done with the help of the tesla-coil, as mentioned above, the sound of which indicates the existence of a vacuum or air. [63]

## 2.2 Purification of solvents

Anionic polymerization is a synthesis method particularly sensitive to impurities, therefore all reagents used in the synthetic routes described in this work were of high purity. In addition, all of the reagents ought to be undergone further purification processes, proportionate to the nature and intended use of the reagent, which are listed explicitly in the next sections. Any reagents not listed in the purifications were used directly as received commercially.

*Image 19 Benzene molecule*

### 2.2.1 Benzene

The purification of benzene initially involves stirring it with a concentrated solution of sulfuric acid ($H_2SO_4$), in a conical flask, for a period of one week. This process exempts benzene from unsaturated compounds such as thiophene and toluene, which are contained as by-products in commercially available benzene and can negatively affect the course of anionic polymerization. Thiophene increases the polarity of the solvent resulting in a change in the diene microstructure, while toluene is able to give termination reactions. Their removal is done according to the reactions on Image 20:

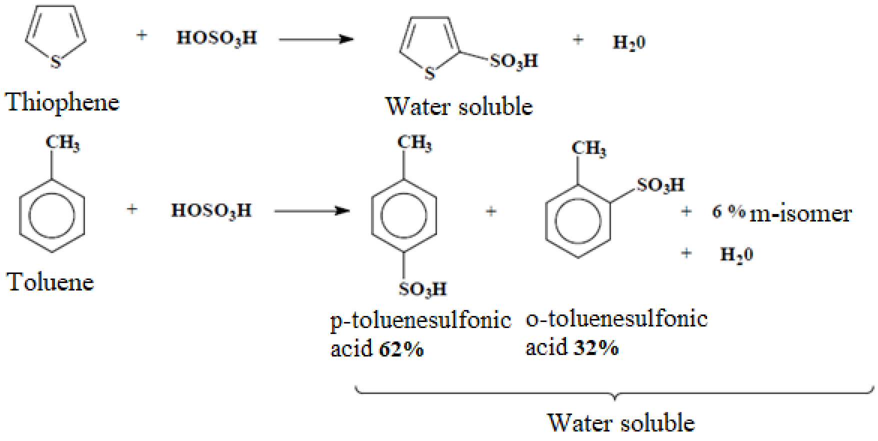


*Image 20 Removal of unsaturated compounds in commercially available benzene solvent*

A quantity of benzene is then transferred to a round-bottomed flask, which contains finely compartmentalised calcium hydride ($CaH_2$), as a drying agent, and is left under stirring overnight, so that all traces of moisture may be removed. The next day the benzene flask is placed on the vacuum line, degassed several times and distilled into a volumetric cylinder, which contains a suitable amount of *n*-BuLi that reacts with the last traces of impurities and a small amount of styrene monomer. The benzene is degassed once (or more times) in the cylinder and left for another day under stirring. The intense orange colour is distinct for polystyrene and indicates the purity of benzene. The benzene contained in the cylinder is also the polymerization solvent used in this work.

### 2.2.2 Tetrahydrofuran (THF)

Tetrahydrofuran (THF), is used as a polymerization solvent, as well as a polar additive in anionic polymerization coupling reactions, because it improves the initiation of polymerization since by fracturing the aggregates created between the active centres of the macro-anions (electrostatic interactions). In order to achieve the desired degree of purity, the following cleaning procedure is followed.

Firstly, in a spherical flask, finely compartmentalised calcium hydride is added along with tetrahydrofuran. The flask equipped with ground glass joint adaptor, is placed on the high-vacuum line and the THF is sufficiently degassed (twice). Understirring, hydride reacts with the moisture for a day. In the next step, we distil the THF into a flask to which we have previously added chipped sodium parts, removed the air by degassing twice and left under stirring for one more day. It is worth noting that the process of adding the pieces of Na to the flask requires special attention. Na is kept in a capsule with hexane solvent covering all the pieces, otherwise there is a risk of fire due to the strong reaction of sodium with atmospheric moisture. The pieces are carefully added to the flask, and excess hexane is received at the trap of the high vacuum line.

The final stage of the process involves distilling the tetrahydrofuran into a flask containing a liquid sodium/potassium “alloy” solution in a ratio of 1:3. Finally the THF is degassed and left under vigorous stirring. The blue colour as seen on Image 21 acquired after stirring has been proposed to originate from complexes of the pure solvent with negative metal ions, mainly potassium, due to electron transfer through THF (solvated electrons) according to the reaction:

$$2K \xrightarrow{THF} K^+ + K^-$$

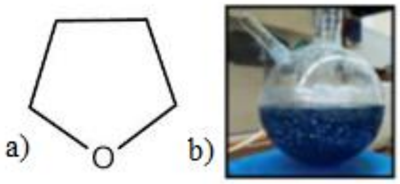


*Image 21 a) THF molecule b) THF alloy solution*

Tetrahydrofuran in the present work was used as a solvent for the synthesis of the coupling reagents chloro(dimethyl)(4-vinylphenyl) silane (CDMSS).

### 2.2.3 Hexane

The hexane is allowed to stir overnight in a round-bottomed flask in the presence of a quantity of finely divided calcium hydride and the next day is degassed in the vacuum line and distilled into a second round-bottomed flask containing a quantity of n-BuLi. It is degassed again and left under stirring for at least three hours so that all the impurities contained in the solvent react with the normal butyl-lithium. Retention of a faint yellow colour is an indication of the purity of the hexane. In the present work hexane was used as a solvent in the synthesis of sec-BuLi initiator.

## 2.3 Purification of monomers

The monomers used in anionic polymerization should also be purified for evasion of the possibility of undesirable reactions, between impurities and polymerization reagents. This process is followed by distillation and finally, ampulization in apparatuses made using scientific glass-blowing techniques and precalibrated using deionized water.

### 2.3.1 Styrene (St)

Styrene (b.p.: 145 °C, d = 0.909 g/mL) is placed in a round bottom flask in the presence of $CaH_2$ granules and left under stirring overnight. It is then transferred to the vacuum line, degassed and distilled, using short-path apparatus, into another flask containing a solution of normal di-n-butyl magnesium $(n\text{-Bu})_2Mg$ (1M) in heptane (amount[monomer]/[DBMg]=20/1), from which the solvent has been quantitatively removed. The styrene is left under stirring in $n\text{-Bu}_2Mg$ for a minimum of 4 hours up to overnight, at room temperature. The appearance of a yellow-green colour is an indication of the purity of the styrene. It is then distilled into ampules and stored at -20°C for approximately six months.

It should be noted that there is a risk of polymerization after a prolonged stay at this temperature, $(n\text{-Bu})_2Mg$, although slow, can initiate anionic polymerization of styrene. Furthermore, for the purification of styrene, organolithium compounds are not used, as in the case of dienes and ethylene oxide, styrene is polymerised quickly through an exothermic process, at a risk of explosion. The Mg compound having one n-butyl and one iso-butyl group is preferred due to its higher solubility in hydrocarbon solvents. The image below shows the devices we use to purify and store pure styrene. All ampules are calibrated so that we know the exact amount we receive each time. In each ampule we distil the desired amount of styrene and after freezing and degassing.

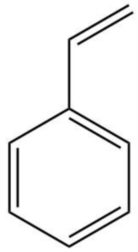


*Image 22*
*Styrene molecule*

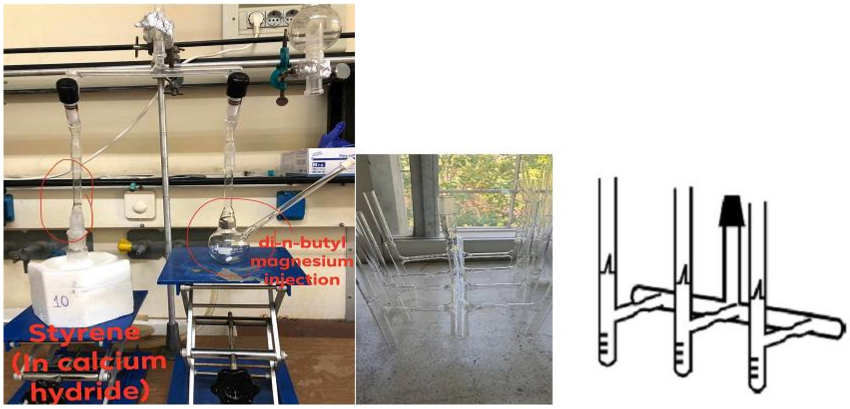


*Image 23 Apparatuses used during styrene purification*

### 2.3.2 4-Chlorostyrene (4-St-Cl)

The 4-chlorostyrene is introduced into a suitable apparatus which contains granules of calcium hydride. The apparatus is attached to the vacuum line, degassed, and the 4-chlorostyrene is left under stirring overnight, so that moisture reacts with the desiccant. The next day it is degassed again, distilled into the calibrated ampules of the apparatus below and stored at -20°C. An important observation is that the high boiling point of 4-St-Cl makes it difficult to distil to the ampules.

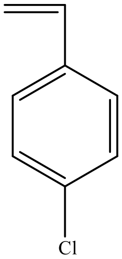


*Image 25 p-Chlorostyrene*

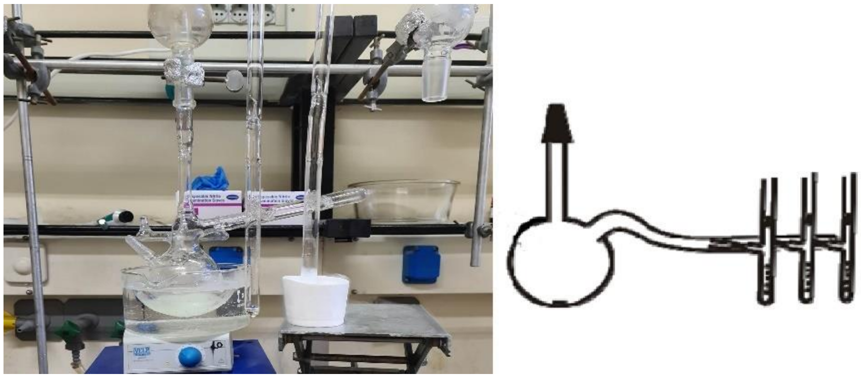


*Image 24 Apparatus used for the purification of 4-St-Cl*

### 2.3.3 Isoprene (Is) / 2-Methyl-1,3 Butadiene

A quantity (50-70mL) of isoprene (b.p: 34.07°C, d=0.681 g/mL) is transferred to a round-bottomed flask containing coarse granules of calcium hydride and left under stirring overnight, so that any traces of moisture present may react with the desiccant.

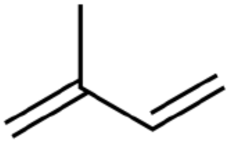


*Image 26 Isoprene molecule*

The next day the spherical flask is placed on the vacuum line, the isoprene is degassed and distilled into a second flask, which contains an appropriate amount of *n*-BuLi. The solution is left under stirring for approximately 20 minutes, with purpose of with purpose of reaction between *n*-BuLi and impurities, that are contained on the monomer, at a temperature of 0$^{o}$C (ice/water bath). The low temperature in this step is necessary, as n-BuLi is an initiator for diene polymerization.

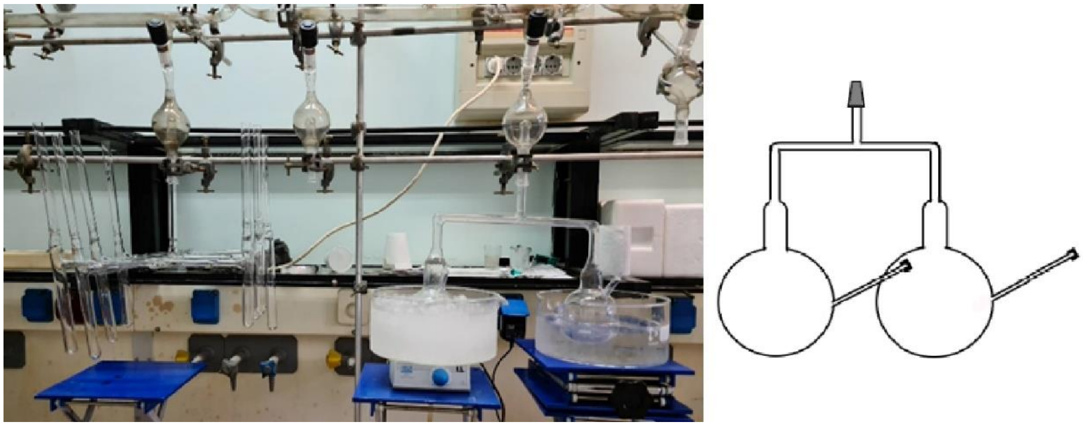
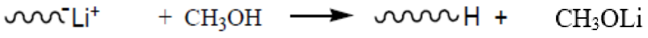


*Image 27 Apparatus used for the purification of Isoprene*

Then, the solution is degassed and distilled in a third spherical flask that also contains a quantity of *n*-BuLi, where the same procedure is followed (stirring at 0$^{o}$C, degassing). In the last stage, the isoprene is distilled in glass, calibrated ampules in the apparatus of Figure 4.5 and stored in -20$^{o}$C.  In contrast to the purification of styrene, the purification of dienes is done with organolithium compounds, because their polymerization by these compounds is not as fast and exothermic as in the case of styrene.

## 2.4 Purification of termination reagent: Methanol

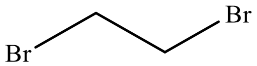
A quantity of methanol is degassed at least twice in the vacuum line and then distilled into glass ampules also thoroughly degassed. Degassing is a necessary procedure, as possible presence of unwanted impurities in the ampule (e.g., $CO_2$, or traces of moisture), doubles the molecular weight of the terminated macro-anion up, at a high percentage. Methanol is used as a means of terminating the polymerization reaction, as shown schematically below:



## 2.5 Purification of other reagents

### 2.5.1 1,2-Dibromoethane

A minimum amount (roughly 0,5mL, few drops) of 1,2-dibromoethane is introduced by syringe through the rubber stopper into the reaction flask (see later sections) and the glassware bearing the rubber stopper is removed by heat-sealing and the 1,2-dibromoethane is cooled with liquid nitrogen, and degassed, because all of the magnesium is coated with a passivating layer of magnesium oxide and 1,2-dibromoethane acts as an activating agent, that produces bubbles of ethylene:

Mg +  ⟶ $C_2H_4\uparrow + MgBr_2$

The amount of Mg consumed by this reagent is insignificant.

### 2.5.2 Dichlorodimethylsilane

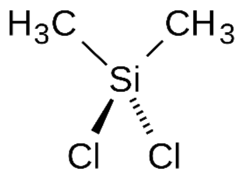
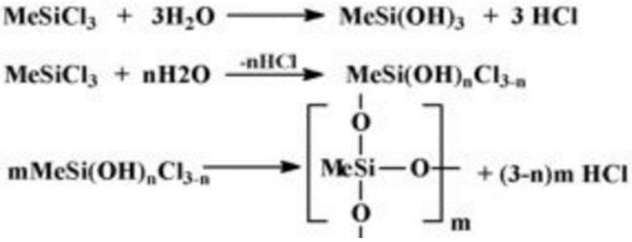


*Image 28*
*Dichlorodimethylsilane molecule*

The dichlorodimethylsilane is transferred by syringe into a spherical flask already fitted to the vacuum line and is degassed at least twice, to remove not only the air but also the hydrogen chloride gas that may be formed. Afterwards, a small amount of the trichloromethyl silane is injected into an apparatus with ampules in order to remove impurities, transferring the amount of silane to all its parts, after the constriction (from which the injection was carried out), is sealed off. Any impurities present react with the silane and are converted into inert compounds, while the remaining silane is removed off the same device, that is already fitted to the vacuum line, using the second ground glass joint that consists of an internal ampule. The $Me_2SiCl_2$ is distilled afterwards into the purged apparatus, and the ampules received are also stored at room temperature until the synthesis of the coupling reagent chloro(dimethyl)(4-vinylphenyl) silane, CDMSS.

*Image 29 Apparatus for the purification of $Me_2SiCl_2$*

The reaction of the silane with the impurities produces either inert precipitates (silicones), or HCl gas, which is removed along with the unreacted silane through the vacuum line. The $Me_3SiCl$ is preferred as purging reagent over the other three related types of silanes, because in the case of residue quantity, that might not have been fully removed off, the ampules will contain both $Me_3SiCl$ and $Me_2SiCl_2$. Only the latter silane should be intended to react with the 4-St-Cl, otherwise 4-(methyldichlorosilyl) styrene (DCMSS) will be produced, which not only will it lead to a lower yield in the CDMSS reaction (which by nature is already a low yield Grignard reaction), but it will also “consume” a portion of the $PI^-Li^+$ producing a macromonomer with 2 branches (due to selectivity for the Si-Cl bond). Therefore, we wouldn’t be able synthesise a bottlebrush, but statistical brushes.



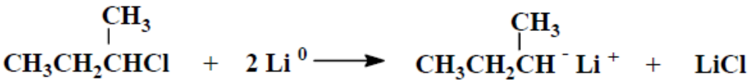
$$MeSiCl_3 + 3H_2O \longrightarrow MeSi(OH)_3 + 3\,HCl$$

$$MeSiCl_3 + nH2O \xrightarrow{-nHCl} MeSi(OH)_nCl_{3-n}$$

$$mMeSi(OH)_nCl_{3-n} \longrightarrow \left[ \overset{|}{\underset{|}{\overset{O}{\underset{O}{MeSi}}}}-O- \right]_m + (3-n)m\,HCl$$

## 2.6 Synthsis of secondary butyl-lithium (*sec*-BuLi)

The initiator widely used in anionic polymerization is secondary butyllithium (sec-BuLi). It is prepared under vacuum from the corresponding secondary butyl chloride and metallic lithium, according to the following reaction:



$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCl + 2\,Li^0 \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}H^- Li^+ + LiCl$$

The apparatus for the synthesis is shown on Image 30. The lithium metal (10:1 butyl-chloride) is introduced from the lithium receiver as which is then removed by heat-sealing at point C. The device is then placed into the vacuum line, degassed (three flame-drying processes are carried out in order to remove traces of moisture from the device) and using the rubber stopper an amount of *n*-BuLi solution in 1,6 M hexane is injected with a syringe. By heat-sealing the point, A, the rubber stopper is removed and hexane solvent is distilled into the apparatus. The hexane is cooled and the device is degassed again, sealed at point D and removed off the vacuum line. The device is then purged with the solution of *n*-BuLi in order to remove any reactive impurity present on the surface of the glass. The excess of *n*-BuLi as well as its reaction products are removed from the various parts of the apparatus by proper vertical positioning and repeated distillation of the solvent in the main part of the apparatus while, finally, all the *n*-BuLi is concentrated in the cleansing department. The hexane is distilled towards the main part of the apparatus (flask F) and the purge-section with *n*-BuLi is removed, leaving the main reaction apparatus clean and free of reactive impurities. The hexane-lithium mixture is cooled to 0°C and by breaking the ampule G, *s*-BuCl is distilled. Secondary butyl chloride is slowly distilled into the hexane-lithium mixture, which is under constant stirring and left at 0 °C overnight. The resulting solution is filtered through the glass filter and the now clear solution is divided into ampules which are kept at -20 ºC, because at room temperature *s*-BuLi is unstable. The yield of the reaction is in the order of 70%-80%.

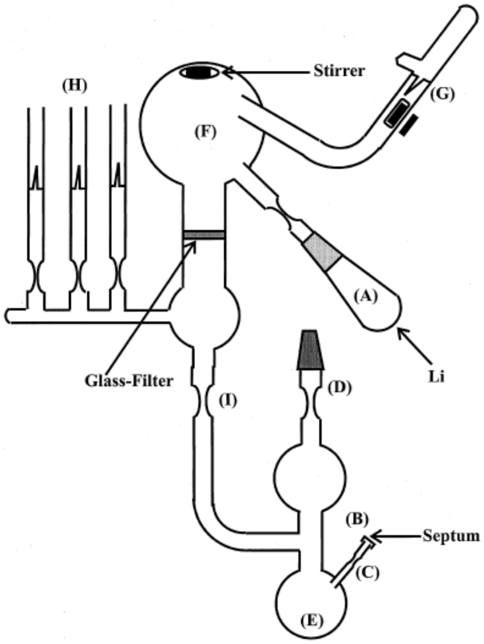


*Image 30 Sec-BuLi preparation apparatus*

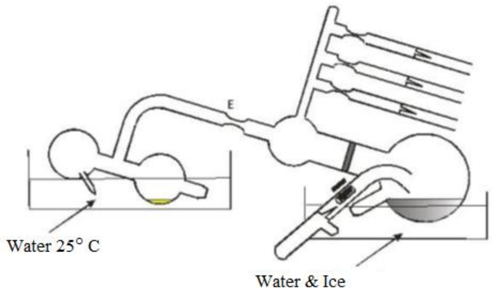


*Image 31 Hexane distillation*

The concentration (titre) of the solution is calculated by neutralizing the C–Li bonds with $H_2O$, producing LiOH, which is titrated with standard HCl solution (in the presence of phenolphthalein indicator):

$$\text{sec-BuLi} + H_2O \longrightarrow \text{sec-BuH} + \text{LiOH}$$
$$\text{LiOH} + \text{HCl} \longrightarrow \text{LiCl} + H_2O$$

This method gives an approximate value of the titre of the *s*-BuLi solution, because in this way the total titre in terms of lithium is calculated. However, there is a case where lithium exists in the solution in another form (e.g. BuOLi that comes from the reaction of *s*-BuLi with oxygen when the sampler is opened) that is not a polymerization initiator, a substance that cannot be separated by the method mentioned previously. Polymerization of a known amount of monomer (usually styrene) provides greater accuracy. Based on the fact that the yield of anionic polymerization is 100%, the amount of polymer obtained is equal to the monomer used. By determining the number average molecular weight (retrieved from SEC data) along with a specific amount of monomer used, the moles of initiator are calculated based on the equation:

$$\text{moles}_{of\ initiator} = \frac{g_{monomer}}{\overline{M_n}}$$

Mathematic reduction of the volume used, leads to the calculation of the exact concentration of the initiator solution (*s*-BuLi).

## 2.7 Dilution of reagents

The acknowledgement of the concentration of the various reagents used in polymerizations is crucial for preparation of products with desired molecular weights. This dictates the need of more dilute solutions of these reagents. The dilution process requires attention and strict precision in the volumes added. The apparatus mainly used for dilutions of reagents in anionic polymerization is shown on Image 32 below:

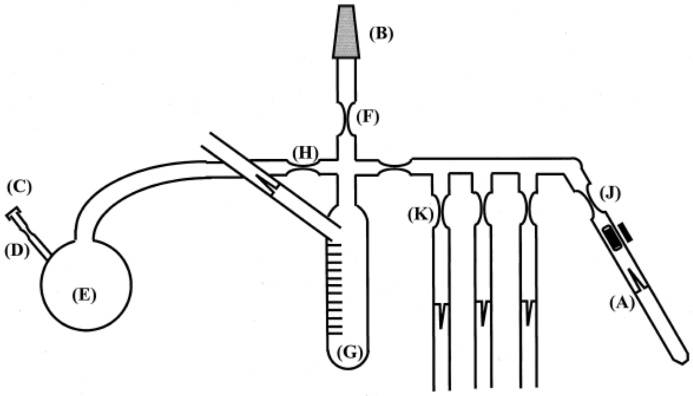


*Image 32 Dilution apparatus*

The apparatus in the figure is attached to the high vacuum line from the special ground glass joint located at position (B), and through scientific glass-blowing technique the reagent to be diluted is attached to the apparatus at position (J). The presence of micro-holes is checked by bringing the tesla spark-coil close and all over the apparatus, and the moisture must be removed applying the flame-drying process for three times over a ten-minute break between each time Normal butyllithium in hexane is then introduced into the device through the rubber stopper, we seal the constriction at position (D). Then, hexane is deducted in the vacuum line by opening the stopcock connecting the apparatus to the line, and solvent is distilled in the purge section.

Degassing is necessary before we remove the device from the line by heat-sealing position (F). After frozen solvent melts, we shake the device appropriately so that the solution (*n*-BuLi-solvent) is brought to all of the parts of the device, so that it reacts with moisture and impurities. We purge the device with the help of liquid nitrogen in order to remove the traces of normal butyllithium from all its parts (bringing the solvent to the different parts of the device), paying attention to avoid solution passage from the cleaning part to the main part of the diluting device. After two hours of attentive washing, we place the apparatus appropriately; the flask of the cleaning section in a 40ºC bath, and the precalibrated cylinder on ice, so that the solvent is slowly distilled in the main apparatus in. If we use liquid nitrogen, there is a risk of abrupt nBuLi entrance, contaminating the main device, by reacting with the coupling reagent and contaminate it with by-products, or in the case of initiation dilution, two types of active centres will exist with disastrous consequences for the polymerization, since the polymers that will be prepared will show large distributions but also a deviation from the desired molecular weights.

After distilling the desired amount of solvent into the main part of the diluting apparatus, purging and sealing (H) is done to remove the purge section. Then, ampule of reagent is shuttered entering in the device. After washing point (J) with solvent, the empty ampule is sealed and removed. The diluted solution ready for use (stored at -20°C). The calculation of the concentration in the diluted component is done very simply according to Ostwald's dilution law: $C_{IN} \times V_{IN} = C_{FIN} \times V_{FIN}$.

## 2.8 Synthesis of chloro(dimethyl)(4-vinylphenyl) silane, CDMSS

The synthesis of CDMSS (also referred to as p-chlorodimethylsilyl styrene) will be described in this section. The 4-St-Cl (4,8mL, 0,0384mol) is placed in a precalibrated glass cylinder apparatus, attached to the vacuum line through the ground glass joint and 43,2 mLTHF are diluted in the apparatus. It is then degassed, removed from the line and after shuttering the ampule and mixed with the solvent for dilution, by shuttering the ampule. Afterwards, the cylinder containing the diluted solution is attached to the apparatus where the Grignard reaction will take place.

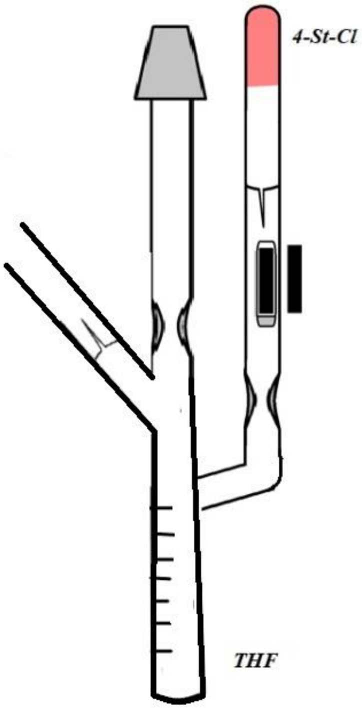


*Image 33 Apparatus for 4-St-Cl dilution*

The next step requires the purging of the device shown on Image 34 with trimethylchlorosilane ($(CH_3)_3SiCl$) to remove impurities that may be present. A small amount of $(CH_3)_3SiCl$ is added using a syringe through a rubber stopper. The silane is frozen with liquid nitrogen, the apparatus is degassed for a few minutes, and the first piece of glass container is removed by sealing at point A. The apparatus is left in the vacuum line for a little more time for complete elimination of moisture and removed from the line by heat-sealing at point B.

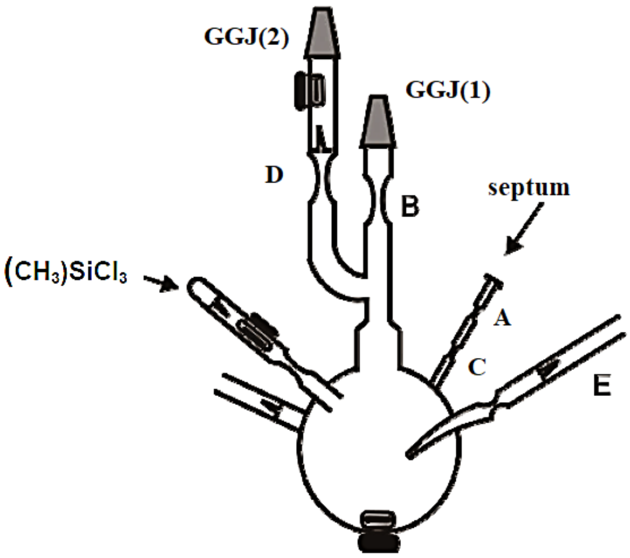


*Image 34 Initial apparatus (1) for CDMSS*

The apparatus is purged by moving the (CH$_3$)$_3$SiCl from side to side, and then the silane is collected in the remaining piece of receiver, which is removed by sealing at C. The apparatus is readjusted to the vacuum line using the second ground glass joint and left overnight, to remove the last traces of (CH$_3$)$_3$SiCl. The next day it is removed from the line by heat-sealing at B and attached to the device shown on Image 35 via break-seal E, for the next stage of the process.

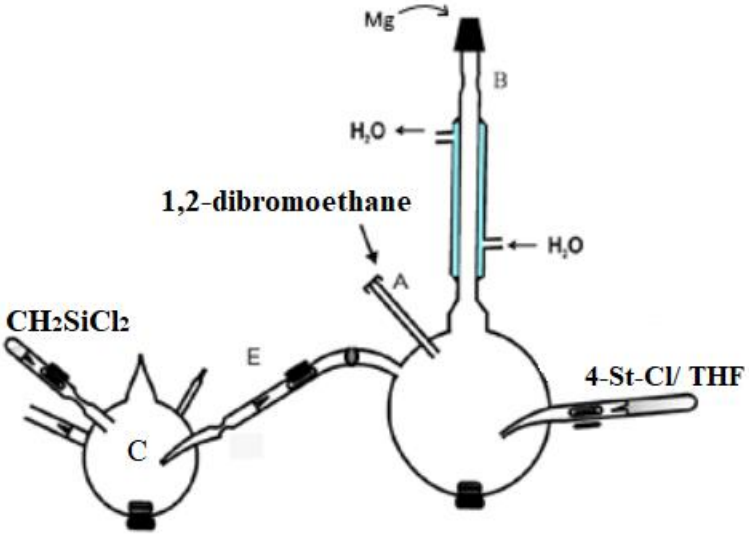


*Image 35 Final apparatus of CDMSS*

The special device with the condenser is attached to the vacuum line and metallic magnesium (1,0619g, 0,044 mol) is introduced into it. The Mg has already been purged several times using a Buchner filter and THF, and then left to dry overnight inside a vacuum oven (without heat). The 1,2-dibromoethane (few drops of it) is added to the flask via heavy-wall tube A, which is then removed by heat-sealing, and degassing is necessary in order to remove air, moisture and the gas that is produced (ethane) through its reaction with Mg. Pure THF (alloy solution ~30mL) is distilled into the flask and the mixture is stirred for a few minutes to activate the magnesium. During this time, the stopcock of the line to which the device is attached is opened and closed, at intervals, to remove the gas formed. This is followed by thorough degassing of the device and removal from the vacuum line by heat-sealing at point B.

The device is then placed in a 35ºC-40ºC water bath and the solution of 4-St-Cl in THF is added dropwise to the magnesium, after breaking the glass of the corresponding ampule. The addition is done in such a way as to maintain constant reflux of the solvent (THF) and constant boiling of the solution in the reactor flask. After the end of the addition, which lasts about 2 hours, the solution turns to green-blue colour. The apparatus is left under stirring for another 1 hours at 35-40ºC to complete the Grignard reaction.

*Image 36 Final apparatus of CDMSS during the experiment*

The flask C is placed in ice-water bath and the glass ampule of $Me_2SiCl_2$ (6,7 mL, 0,052mol) is shuttered. The ampule E is cooled with $N_2$(l) and the dropwise addition of the Grignard to the flask C, passing through the glass constriction is done, while solution immediately turns yellow. The addition is complete within one hour, the solution is left under stirring for another half hour at 0°C and at the end the two flasks are frozen with liquid nitrogen and separated by heat-seal at constriction E. Flask C containing the desired CDMSS reaction product, as well as THF and excess $Me_2SiCl_2$, is connected to the already purged with $(CH_3)_3SiCl$ and dried flask D through a glass filter, as shown on Image 37. The apparatus is attached to the vacuum line. This small section is degassed, and afterwards the ampule B is shuttered and the solution is condensed through the line. Next, ~80mL of hexane is distilled into flask C, the apparatus is degassed again, and by heat-seal at point E it is removed from the vacuum line. The solution is kept for two days at -20$^o$C until partial precipitation of MgBrCl is achieved and then Z ampule is shuttered and the solution is filtered through the glass filter into flask D.

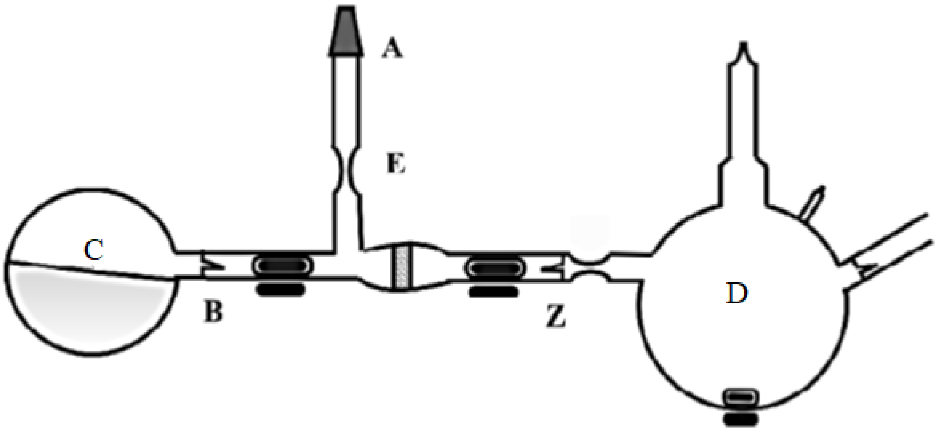


*Image 37 Apparatus equipped with filter for CDMSS purging*

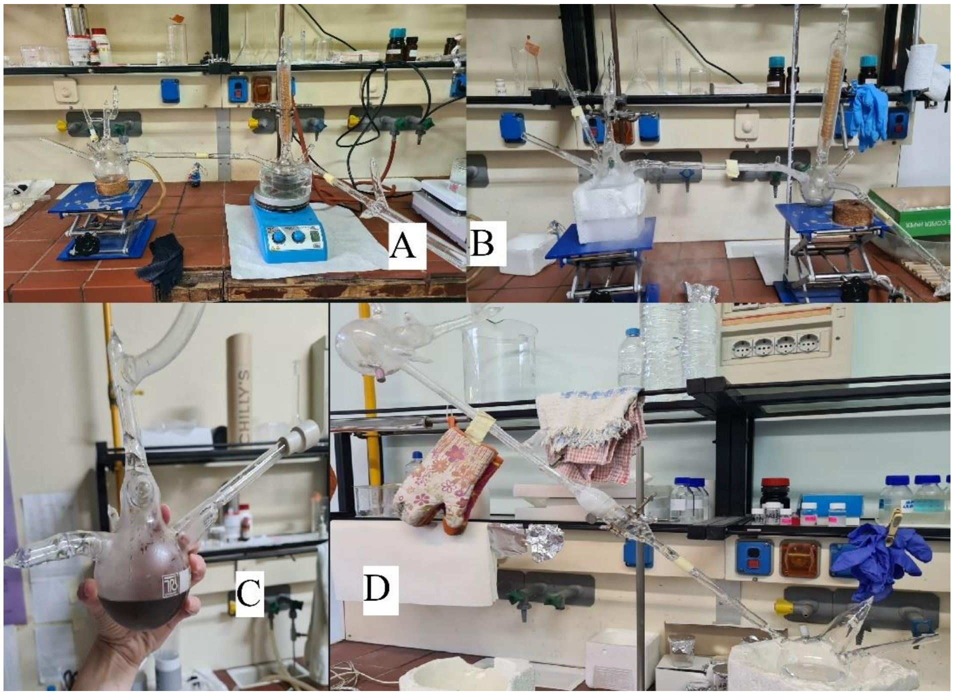


*Image 38 Experimental procedure representation*

Flask D is connected to the also pure of $(CH_3)_3SiCl$ and dry flask E of Image 39 and after degassing the short space, the ampule A is broken and the solution is concentrated through the vacuum line for almost three hours under constant stirring at 40°C to eliminate all traces of hexane, THF and $CH_2SiCl_2$.The final step involves purifying the reagent from existing by-products by fractional distillation and diluting it with benzene solvent. The temperature rises to 140-150ºC (using an oil bath and heatgun) and the product distils into E, after previously breaking the glass membrane that connects the two parts of the device. The flask E, containing the desalted product, is removed from by heat-sealing at B. The new piece of apparatus is readjusted to the line (through the already purged flask E) and finally pure CDMSS (1,32g, $6,67\times10^{-3}$ mol) is distilled into (b.p.>110°C) in precalibrated ampules. As shown on the image below, the ampules are equipped with aliquots, for identification by $^{1}H$-NMR.

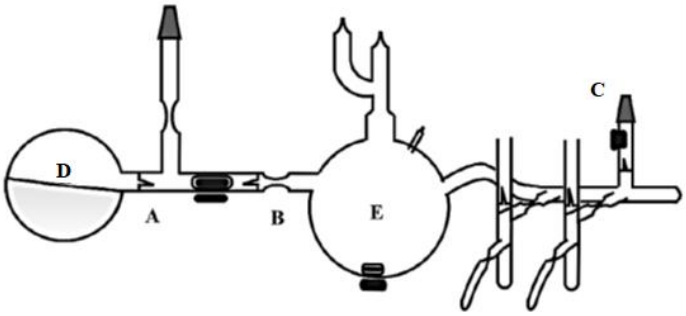


*Image 39 Final apparatus for purge and ampulization of CDMSS*

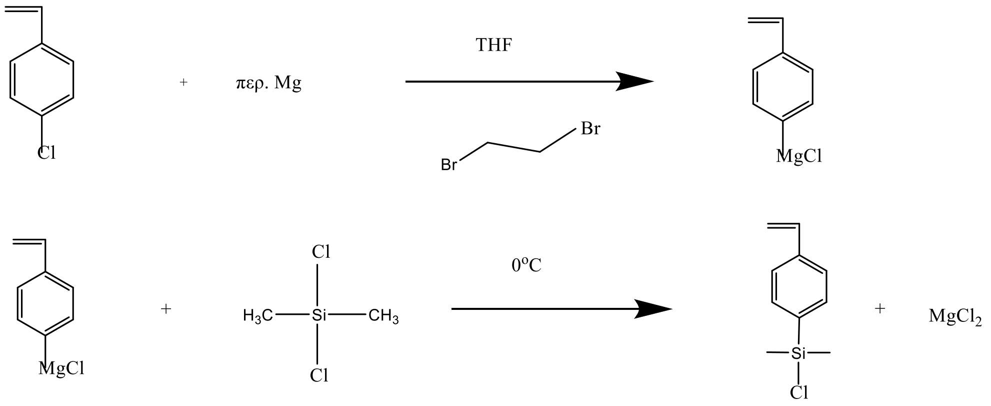
It is important to note that exquisite scientific glass-blowing be done and the sections that CDMSS would be distilled should be properly attached with a slight tilt (as shown on Image 38D) onto each apparatus, in order to facilitate the process because the product is difficult to be distilled, owing to its high boiling point (>100$^o$C). The desired product CDMSS is diluted with benzene in a suitable ampule apparatus previously purged with *n*BuLi in benzene solution, divided into ampules and stored at -20°C. The synthesis and purification of chloro(dimethyl)(4-vinylphenyl) silane are carried out in THF solvent, while its dilution in benzene solvent, under high vacuum conditions and in appropriately designed devices.

### 2.8.1 Dilution of the CDMSS

The CDMSS coupling reagent dilution is carried out with benzene solvent and in the apparatus of Image 40 in section of dilution. Benzene is less polar and the coupling reagent is more stable at the polymerization to bottlebrush polymer. On the contrary, the styrenic monomer in presence of THF may later lead to higher PDI during the bottlebrush synthesis, because it favours the propagation stage instead of the initiation one, since it lowers the degree of aggregation, even with a small amount present.

*Image 40 Apparatus for CDMSS dilution*

The apparatus is attached to the vacuum line, checked for holes, degassed, *n*BuLi is injected and the constriction of the rubber stopper is sealed and removed, followed by degassing, benzene distillation into the purge section, thorough degassing and finally remove from the line by heat-seal. The purging is accomplished by transferring the cleaning agent to all parts of the device, so that *n*BuLi reacts with all the impurities from side to side, and then every section of the apparatus is cooled with $N_2$, which leads to solvent distillation to the correspondent parts, a process which drifts the remaining *n*BuLi away from the apparatus and into the purge section. After this time-consuming process (3 hours long) the ampule of CDMSS, which is attached under the first constriction (as seen on Image 40 from left to right) is shuttered and the concentrated coupling reagent is mixed with the amount of solvent. The constriction that contained the CDMSS is purged by distilling a quantity of solvent and this part is removed by flame seal. The diluted coupling reagent is stored at -20$^{o}$C.



## 2.9 Synthesis of "living" polyisoprene ($PI^-Li^+$)

The main apparatus used for the synthesis of the “living” polymer branches used to prepare the macromonomers is shown on Image 41 (and Image 42, for the preparation a series of branches with identical characteristics, such as a specific $M_w$). The apparatus contains the ampule of initiator (*s*-BuLi), the ampules of the monomer (Is) and the termination reagent (MeOH), and a cylinder for the isolation of the $PI^-Li^+$ branch. The final polymer is collected in calibrated cylinders; it is equipped with a break-seal in order to be attached to the bottlebrush apparatus; and stored until used in the next stage of synthesis. As seen on the image below, the device consists of two parts, the main part of the reactor (D) and the purge section (B).

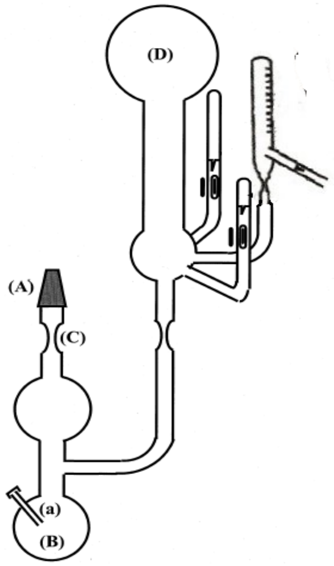


*Image 41 Apparatuses for PI-Li+ branches polymerization*

The device is attached to the vacuum line and degassed. Through the septum and with the help of a syringe, 3-4mL of *n*-BuLi (1,6M solution) in hexane is introduced and the glass tube on which the stopper is located is removed by heat-sealing at point (a). The solution solvent and the air imported into the apparatus, while performing the injection is removed through the vacuum line. By freezing with liquid nitrogen, the appropriate amount of benzene, the polymerization solvent from the volumetric cylinder fitted to another grinding of the vacuum line, is distilled into the flask B of the purification section, Due to the low temperature, the benzene solidifies and after the device is degassed, it is removed from the line.

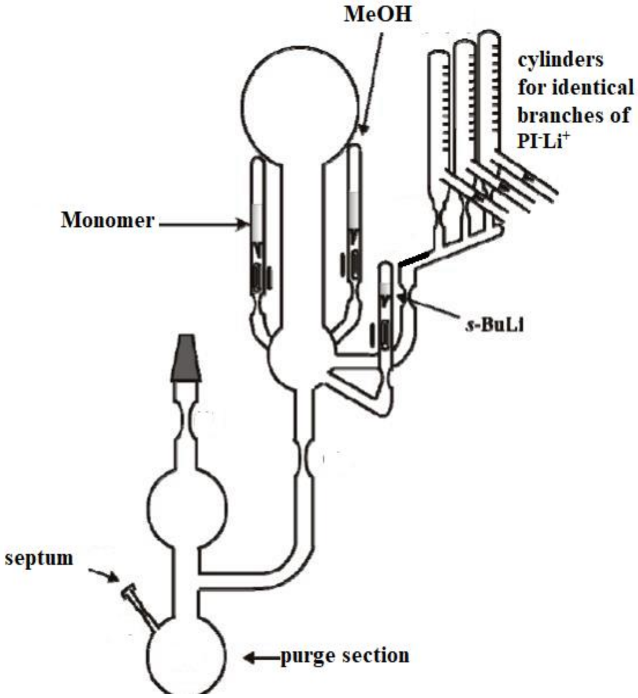


*Image 42 Apparatus for the preparation of identical "living" branches*

*Image 43 From left to right: Polymerization apparatus and volumetric cylinder of pure benzene*

When the solvent thaws, *n*-BuLi in benzene is transferred to each section of the apparatus, so that all impurities present on the walls react with the organolithium reagent.

This procedure is done at least three times, all the solution is transferred to the flask D and placed in an upright position in a 40-50°C water bath. In this way, the distillation is achieved by refluxing the solvent throughout the volume of the apparatus, thus entraining the traces of *n*-BuLi and the products of its reaction with the impurities, into flask B. The process is repeated several times so that the removal of *n*-BuLi and by-products from the polymerization apparatus. Any residual *n*-BuLi can lead to polymerization of isoprene, while the presence of impurities contributes to changing the initiator concentration. The solvent is then distilled from the cleaning section into the main part of the polymerization apparatus as shown below.

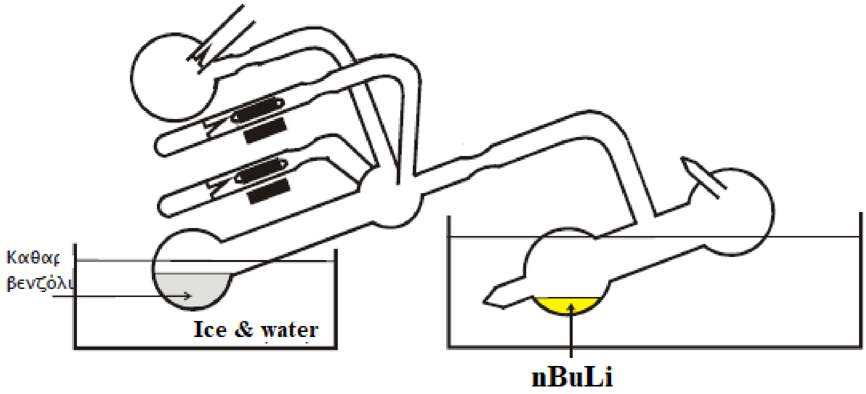


*Image 44 Benzene distillation into Roovers*

The purge section is placed in a 30-40°C water bath, while the main flask of the polymerization device is placed in ice water, resulting in distillation of the benzene. This stage is quite dangerous and must be done with care, because if even traces of *n*-BuLi pass through, the molecular weight and molecular weight distribution will change, since it is known that *n*-BuLi exhibits different initiation kinetics compared to *s*-BuLi which is the polymerization initiator. After the completion of the distillation, the purification part, in which the total amount of *n*-BuLi and impurities have remained, is removed by heat-sealing. In the polymerization flask, the solvent is mixed with the monomer, after breaking the glass of the ampule with the help of glass magnet. In the same way, the initiator mixing with the solution is done as quickly as possible, so that all molecules of the initiator react with the monomer immediately.

The solution is left in order for anionic polymerization to be accomplished (~24h for styrene and isoprene). Finally, the solution is collected in a precalibrated cylinder by heat-seal in the constriction above and a predetermined amount is removed. The remaining polymer is deactivated with methanol and precipitated in “bad” solvent that is mixed with the solvent of polymerization when poured (10mL of good solvent, i.e. in this case benzene, into 100mL of bad solvent, methanol) for molecular characterization. The polymer is left to settle down as gel (in this case because of the rubbery nature of polyisoprene) in a beaker stored at the -20$^o$C freezer. After a day or two the methanol is poured out and the polymer residue is dried and stored in a vial at the freezer. Cylinders with living polymers are also stored at -20°C until use.

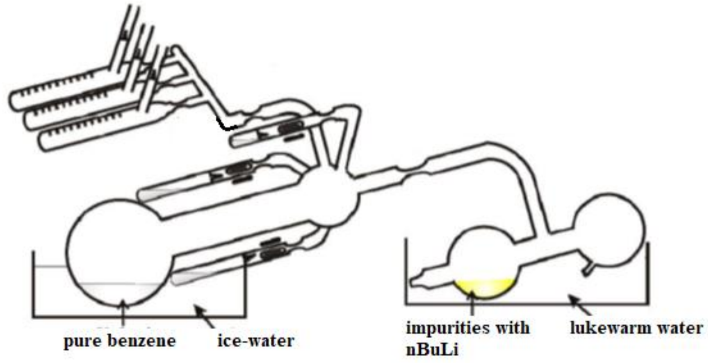


*Image 45 Distillation of benzene into polymerization apparatus for identical branches*

## 2.10 Synthesis of Macromonomers and Molecular Brushes through Anionic Polymerization

The synthesis of macromonomers and molecular brushes is performed in the same apparatus, without prior isolation of the macromonomers. The “living” macromonomers are coupled with the 4-(chlorodimethylsilyl)-styrene (CDMSS) and are later used at the synthesis of bottlebrushes.  These reactions are carried out in a specifically designed apparatus (Image 46), which is attached to the vacuum line. Then, *n*-BuLi is injected into the septum f the purge section, and the same procedure that has already been mentioned in the previous section is followed. Benzene is distilled, frozen with liquid nitrogen, degassed, and removed from the line by heat-sealing. The normal butyllithium solution is then transferred to all of parts the apparatus, the apparatus is purged, and all of the benzene is distilled from the purge section into the main flask, following procedures similar to those described above during the synthesis of the living branches. The purge section is flame-sealed at the appropriate constriction. The final apparatus used to synthesize the macromonomers and molecular brushes (after the removal of the purging section) is shown on Image 47.

The solution of CDMSS is added to the solvent by breaking the corresponding ampule, and the interior of it is purged by solvent condensation. The stirring must be vigorous, because afterwards, the living polymer is titrated dropwise to the CDMSS solution by shuttering the ampule of the cylinder which contains it.

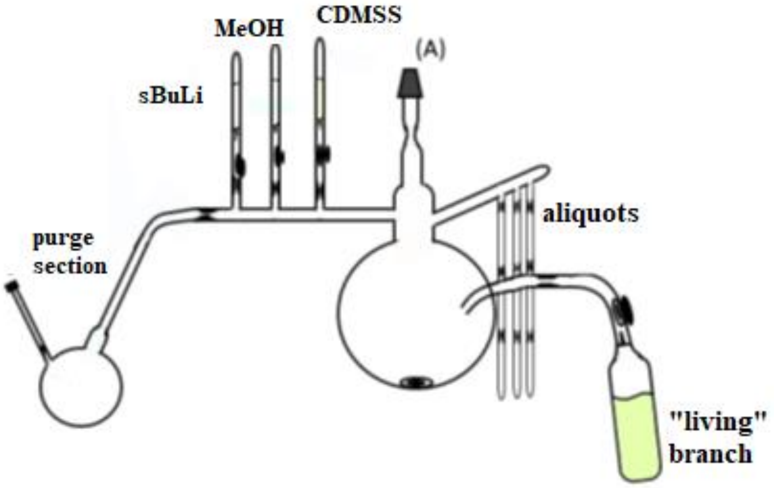


*Image 46 Initial apparatus for the synthesis of macromonomers and molecular brushes*

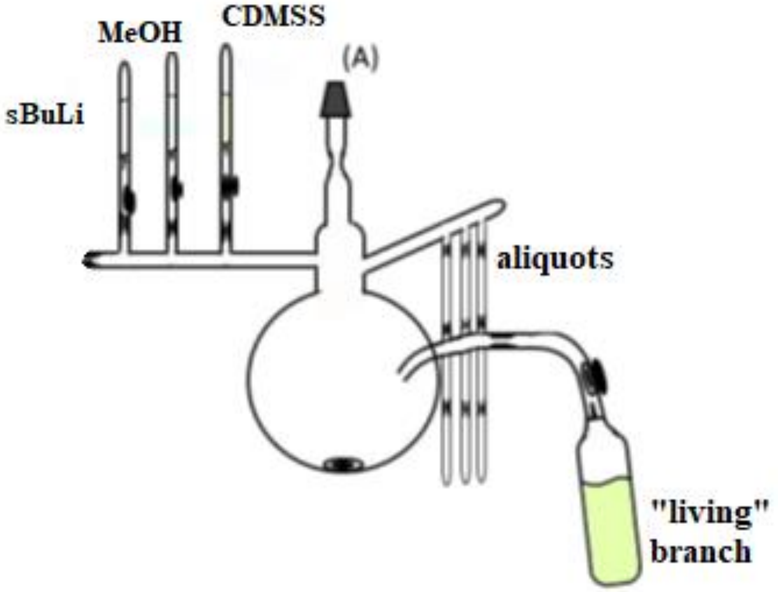


*Image 47 Final apparatus for the synthesis of macromonomers and molecular brushes*

Every time a small quantity of the $PI^{-}Li^{+}$ is added to the CDMSS, the living anionic centres are terminated, and the solution slowly acquires a light yellowish colour. The progress of the coupling is monitored by size exclusion chromatography (SEC) by taking samples, at regular intervals, into the aliquots and removing them by flame-sealing. From the chromatograms, the peak appearing at a certain elution time, corresponding to the molecular weight of the living $PI^{-}Li^{+}$ branch (macromonomer with a linear branch), doesn't change its position or decrease during the macromonomer formation due the fact that the CDMSS is of a very little $M_w$ compared to high $M_w$ of the branch. The disappearance of the first peak, though, cannot be noted easily, because the change in $M_w$ is insignificant. The titration lasts ~8 hours and 70% of the calculated amount is added in the first five hours. Then the remaining amount is added very slowly, since in this case the $PI^{-}Li^{+}$ branch centres, are likely to act as an initiator. Thus, near the critical point, the rate of addition slows down dramatically, so that local excess of the "living" PI branch is avoided, because the $Li^{+}$ might cause the opening of the double bond of the monomer. The addition is stopped when we observe that a minimal percentage of macromonomer has remained in the solution (5~10%). At this point, the cylinder of the living branch is removed by heat-sealing, the initiator (*s*-BuLi) is then added and the solution immediately acquires a bright yellow colour. The solution is left, at room temperature, for about 7 days to complete the polymerization where it takes on a yellow-gold colour.

After the end of polymerization, the bottlebrush polymer is terminated with methanol, and is also precipitated in methanol solvent. The obtained polymer is placed in a vacuum oven and dried to constant weight. The final product is separated from the excess unreacted styrenic macromonomer by fractionation with a solvent (toluene)/non-solvent (methanol) system. The fractionated polymer is finally precipitated in an excess of stabilized methanol (0.1% w/v cresol), and after outpouring the supernatant, the obtained desired polymer is placed in a vacuum oven and dried to constant weight.

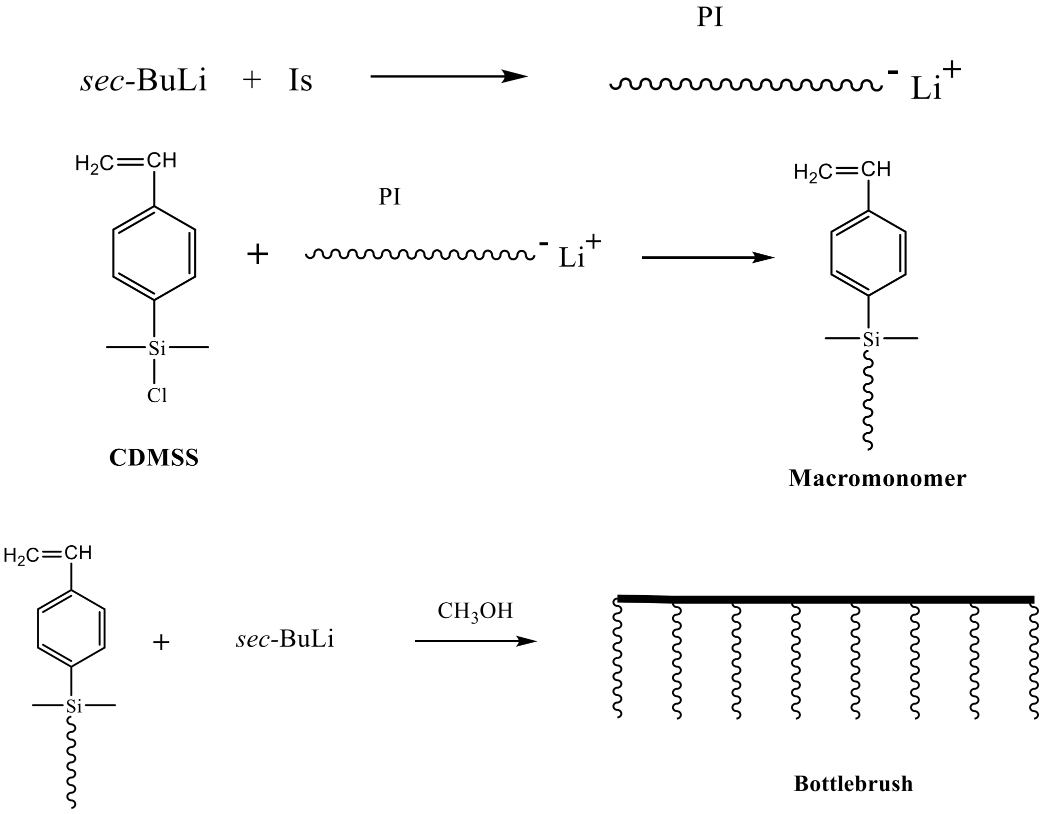


*Figure 10 Bottlebrush synthetic strategy*

## 2.11 Instrumentation of molecular and morphological characterization

### 2..11.1 Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was performed using a Waters 510 pump, with a U6K sample holder and a Waters 401 differential refractometer as detector. Five m-Styragel type columns were used, with porous material (poly(styrene-co-divinylbenzene) monoliths) with pore size from 500 to $10^6$ Å. The carrier solvent was chloroform at a flow rate of 1ml/min at room temperature. The instrument was calibrated with nine PS standards having a molecular weight ranging from 970 - 600,000 Da.

### 2.11.2 Nuclear Magnetic Resonance Spectroscopy ($H^1$NMR)

A Varian Unity Plus 300/54 instrument was used for NMR spectroscopy. The $^1$H-NMR spectra were obtained at room temperature. The analysis was performed on dilute solutions of the polymers in the solvent deuterated chloroform, $CDCl_3$.

### 2.11.3 Differential Scanning Calorimetry (DSC)

The calorimetric measurements were performed employing a TA Q200 DSC apparatus (TA Instruments, USA), calibrated with sapphires for heat capacity and indium for temperature and enthalpy, on samples of ~5-7 mg in mass closed in Tzero aluminium TA pans (Hermetic with a hole on the top), in the temperature range from –140 oC to RT in helium atmosphere of high purity (99.9995%). Two heating scans were performed at rate of 10 oC/min.

# CHAPTER 3

# RESULTS & DISCUSSION

## 3.1 Synthesis and Characterization of Macromonomers and Molecular Brushes

The synthesis of grafted polymers with a single branch at each monomeric unit was used in order to define their conformational behaviour in confinement. The kinetics and dynamics of their rigid configuration can be studied while bottlebrushes "enter" nanopores with dimensions similar to those of the main chain.

Firstly, the synthesis of "living" polymer branches was conducted at target molecular weights of 2500Da and 7500Da, with the latter one produced as part of a series of 4 polymers with identical molecular characteristics. Secondly, the synthesis of the coupling reagent chloro(dimethyl)(4-vinylphenyl), which carries a silane group is carried out. A linear $PI^-Li^+$ branch is then coupled to the chloride atom of the CDMSS reagents, a reaction with almost 99% yield, towards the formation of a vinylic macromonomer. The double bond "opening" is accomplished by the addition of an amount of initiator, which, in-situ, leads to brush-like architecture. The synthetic strategy is described in the next sections.

### 3.1.1 Synthesis of CDMSS

Firstly, the synthesis of the Grignard reagent [64] takes place during the reaction of 4-chlorostyrene with metallic magnesium. The activation of magnesium is also carried out in this case by adding a few drops of 1,2-dibromoethane onto the metal (iodine can also be used as an alternative). To facilitate magnesium activation, the metal is first washed with THF and dried overnight in a vacuum oven. An indication of the successful synthesis of the Grignard reagent is the achievement of continuous boiling throughout the addition of the 4-St-Cl and reflux of the solvent without external heating of the solution. After the addition of the amount of 4-chlorostyrene within an hour, the solution is left under stirring for about 2 hours and then the reaction of the Grignard reagent with excess dichlorodimethylsilane is carried out at a temperature of $0^oC$. Afterwards, the solution is left under stirring for 1 hour, as there is a risk of homopolymerization of the styrene Grignard reagent formed, if left for more time. The solvent used in the whole procedure is THF. The reactions are carried out in properly designed devices, under vacuum, to avoid the presence of moisture and the formation of by-products.

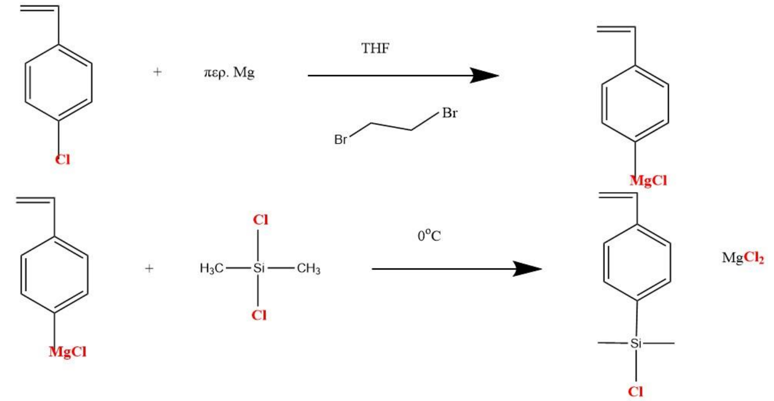


*Figure 11 Schematic representation of the reaction for CDMSS synthesis*

Figure 12 displays $^1$H NMR spectrum of the final product, the coupling reagent CDMSS. The two double peaks at 7,46-7,60 ppm correspond to the aromatic protons ($C_6\mathbf{H}_4$), the two double peaks at 5,33-5,85 ppm to the two protons of the double bond ($C\mathbf{H}_2=CH$), the quadruple peak at 6,69-6,77 ppm to the proton of the double bond ($CH_2=C\mathbf{H}$) and the single peak at 0,68 ppm to the six protons of the two methyl groups of silane ($(C\mathbf{H}_3)_2Si$). Integration of the peaks at 6,69-6,77 ppm and 0,68 ppm (quadruple to singlet) is of ratio of 1/6 as expected.

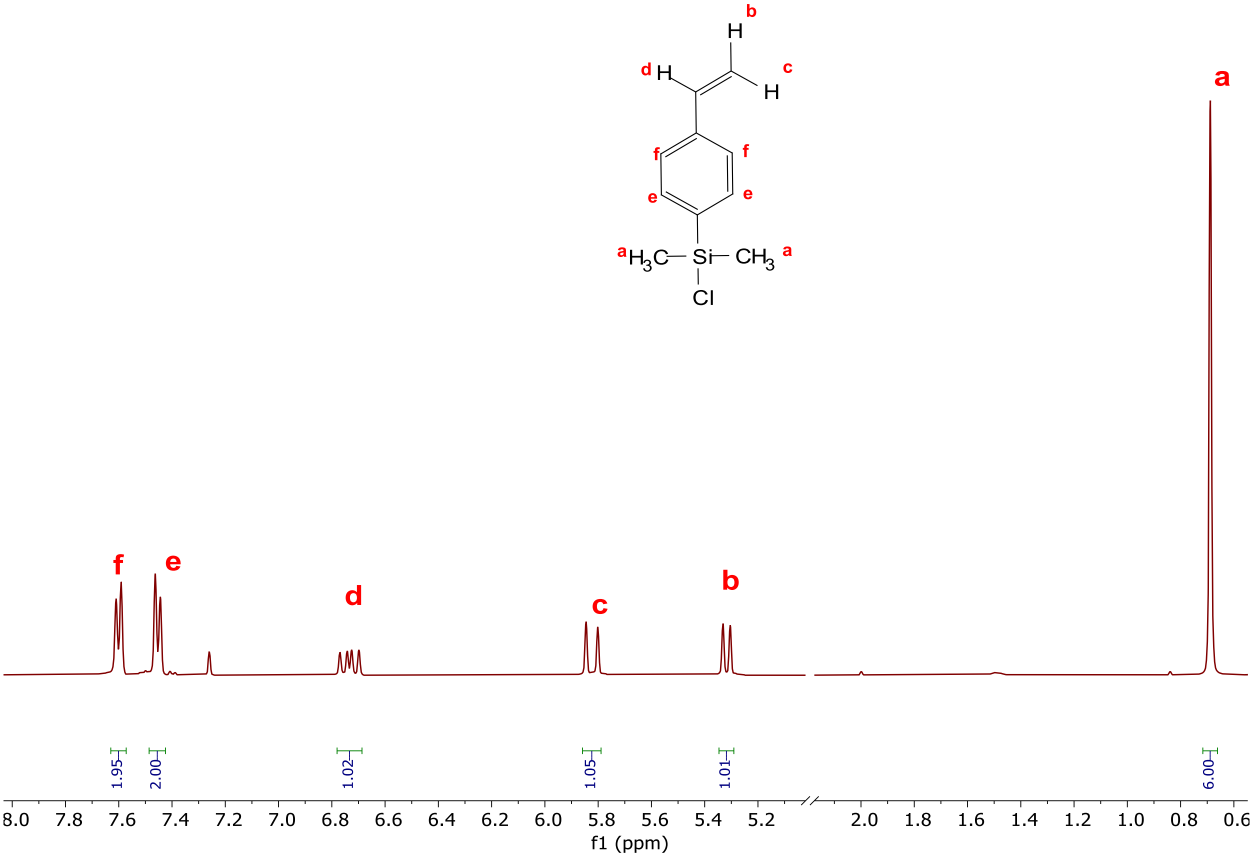


*Figure 12 $^1$H-NMR of the coupling reagent CDMSS, (solvent: $CDCl_3$)*

### 3.1.2 Synthesis of Macromonomers and Molecular Brushes

A very important role for the successful synthesis of molecular brushes is the selectivity of the living branch towards the coupling reagent. The 4-(chlorodimethylsilyl)-styrene (CDMSS) [72,73,74,], used as the coupling reagent, is a bifunctional reagent since it incorporates a chlorosilyl group (-Si-Cl) and a double bond (C=C). The two functional groups of CDMSS are reactive towards the “living” branch $PI^-Li^+$. Thus, the successful synthesis of macromonomers is based on the selective reaction of the anion with the -Si-Cl group, which is favoured over the reaction with the vinylic bond. [75]

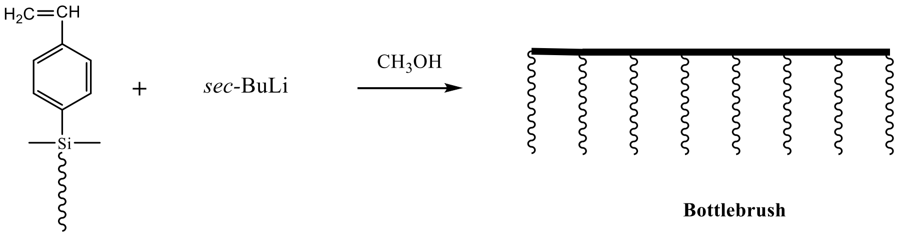


*Image 48 In-situ polymerization of macromonomer 4-St-Si-$PI^-Li^+$ with sBuLi*

Also, an important role in the present experiment is the rate of addition of the “living” branch. The stoichiometry of the reaction requires one mole of “living” polymer for each mole of coupling reagent. In previous work [76,77], it was observed that the rapid addition of the living branch targets the double bond. The difference at the reaction velocity between $PI^{-}Li^{+}$ and -Si-Cl or the double bond, doesn’t only require an equivalent stoichiometry, but also dropwise addition of a dilute solution of the branch to diluted solution of the coupling reagent, under constant and vigorous stirring. The addition lasts for 5-8 hours, with 70% of the calculated amount added in the first two hours, while the remaining quantity is added at a very slow rate. These precautions are taken to avoid local branch excess present at the solution mixture, and according to that, the styrenic reagent excess is ensured over branch excess, which favours the reaction with the silyl group over the reaction of the double bond. [78,79]

The completion of the reaction can be verified visually, since the light-yellow colour of the mixture disappears, immediately after the addition to the CDMSS solution. When the chlorosilyl groups have reacted quantitatively, the $PI^{-}Li^{+}$ begins to “attack” the double bonds of the macromonomers, which is best avoided since in this way there is no control over the molecular weight of the final product. In these conditions, we can manage to achieve almost quantitative synthesis of the macromonomer (~97%). To confirm that the CDMSS has reacted quantitatively, the progress of the reaction was monitored by taking samples during the addition and analysing them by size exclusion chromatography.

The addition of 70% out of the total quantity and after approximately one hour has passed, the first aliquot is taken. The molecular brush has not started to form and the peak that appears corresponds to the macromonomer. From this point onwards the branch is added at an even slower rate and 2 more SEC samples are taken until the solution changes colour (either by breaking an ampule containing *sec*-BuLi or by continuing to dropwisely pour the branch till double bond opening).

If the solution changes colour, prematurely, the next aliquot about to be heat-sealed off indicates the existence of bottlebrush as well as macromonomer. This is probably due to the fact that it takes more time for the entire amount of macromonomer to react, owing to the very strong steric hindrance of the molecular brush that forms simultaneously, that blocks the consumption of the additional macromonomer. In this case, it is chosen to initiate the bottlebrush polymerization by releasing the *s*-BuLi initiator. The consequence of receiving a smaller amount final product, is not considered as a drawback over the control of the molecular weight, which is more crucial. When the observed peaks do not change after a week the reaction is considered complete. From the course of the sampling, it is concluded that during the synthesis of molecular brushes it is difficult to control the molecular weight and its distribution as well as to control the amount of the final product. The final product is precipitated in methanol, and separated from the excess macromonomer by fractionation with solvent (toluene)/non-solvent (methanol) system.

### 3.1.3 Characterization of Macromonomers and Molecular Brushes

The initial characterization of these polymers is the determination of the $M_w$ through GPC. The size exclusion chromatography instrument is suitably calibrated, to determine the molecular weight of linear polystyrene homopolymers. Therefore, the molecular weight for the branch, as well as the molecular brushes does not correspond to the real $M_w$, but the relative one. The data about the $M_w$ and $M_n$ obtained by the GPC instrument must be calculated by dividing them with this constant [$M_w$ (or $M_n$) ÷ 1.6]. Nevertheless, the determination of the polydispersity of the polymers ($I = M_w/M_n$) is possible, in addition to tracking fractionation procedures as well comparison of molecular weights. Throughout the coupling reaction, a unimodal narrow peak appeared along with the appearance of a new small peak, almost at the exact elution volume as the PI branch. The latter peak corresponded to the PI macromonomer. At the end of the titration (colour change), a very small amount (<5%) of byproducts (dimer and oligomacromonomer) was detected in the SEC chromatogram. In all the final SEC chromatograms of the bottlebrushes, a residual 5–10% of 4-St-Si-PI was always present. This macromonomer that never reacted with CDMSS, due to steric hindrance, has to be removed with fractionation.

Comparing results of the present work with those of previous ones, the synthesis of macromonomers by coupling the CDMSS reagent with a linear branch of polyisoprene, after the opening of the first double bonds of the CDMSS, we notice that the homopolymerization towards the formation of bottlebrush polymers is considerably slower than that of linear polymers, possibly due to greater steric hindrance. In the experiments, it was observed that after the opening of the first double bonds and for a time period greater than half an hour, the percentage of the formed polymer increased slightly and according to size exclusion chromatography, its peak appeared at an elution time earlier than that of the linear macromonomer $M_w$ and also wider. The high selectivity of $PI^-Li^+$ to the chlorosilyl group of CDMSS can be explained by its known inability to properly initiate styrene polymerization in nonpolar solvents because of strong association effects. [1,80]

As the molecular weight of the PI branch increased, a larger excess of living PI was required for noticeable colour change. This problem was solved by slowing the rate of addition (an extra hour), which provided the necessary time for the coupling reaction.

#### 3.1.3.1 Characterisation of Bottlebrush with branch of PI 2500Da

The macromonomer with branch of theoretical $M_w$=2.500Da (g/mol) was targeted for synthesis of a bottlebrush of desired $M_w \approx$160.000 Da, roughly 64-70 branches, though we managed to receive a relative $M_w$=63.800 g/mol. After the coupling reaction, the *s*-BuLi ampule was shuttered, and subsequently, in order to avoid further expansion of the bottlebrush peak at the chromatogram, the polymerization was terminated only an hour after the initiation with *s*-BuLi, so as to prevent the bottlebrush synthesis exceeding the theoretical molecular weight.

Another important remark is the excess quantity left that was more than the expected one. Theoretical calculations were conducted with purpose of 10% remains of the branch. Instead, a percentage of 20% of the branch didn't react. The conclusion that an error of also 20% occurred was attributed to the difficulty of the determination of very small molecular weights using SEC.

The massive dimensions of the bottlebrush lead to high steric hindrance and as the time passes the macromolecules are not "able" to be directed to connect with the forming backbone. In the below the bottlebrush synthesis procedure monitored by chromatograms is represented. The polymerization due to double bond opening began after 8 hours, during which the coupling reaction with CDMSS preceded. We started taking samples, after an hour of the appearance of the yellow hue at the solution. The final chromatogram line (green) indicated the sample taken an hour after the initiation with *s*-BuLi. The rise of the height between the peaks implies the consumption of the macromonomer.

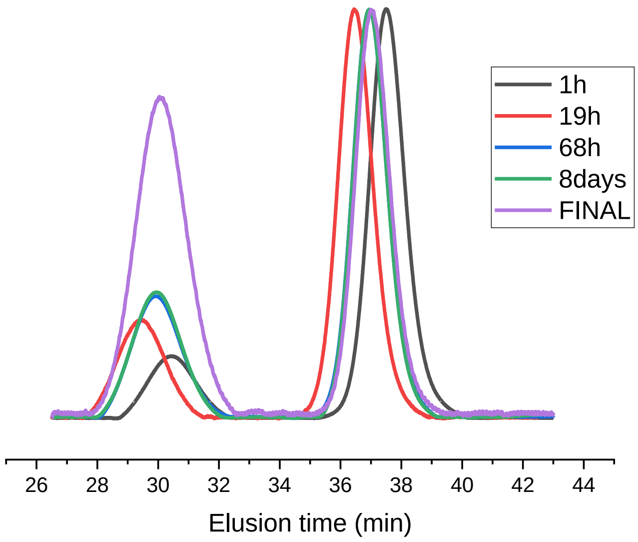


Figure 13 Bottlebrush procedure of PI 2,5kDa macromonomer

### 3.1.3.2 Characterisation of Bottlebrush with branch of PI 2500Da

The use of living PI branch of Mw≈7500Da was intended for the synthesis of a brush with DP=20 and Mw=150.000g/mol, approximately. The synthesis of CDMSS was conducted extremely carefully, with the whole procedure of the coupling reaction lasting more than 8 hours. The solution inside the flask started to acquire a yellowish colour, but not as vibrant as the one from the synthesis of the bottlebrush mentioned in the previous section. The colour fade of the solution is an indication of chlorosilyl groups of CDMSS not reacting quantitatively. [1]

Since the total amounts of the reagents was consumed, we made a false assumption that the reaction between CDMSS and $PI^{-}Li^{+}$ was terminated, therefore we release the initiator into the solution. The chromatograms from 1-8 hours (black,red,blue) include two samples taken during the macromonomer synthesis, and a third one at 8 hours after the so thought initiation of the polymerization. The bottlebrush formation is a long-lasting procedure and the target $M_w$ is obtained after a week or so. Upon checking with the solution of the reaction by SEC aliquot after 3 days, we noticed that only a small and very wide peak was displayed. After almost half of the time needed for the ending of the polymerization, we should have expected to see a sharper peak. This led to the conclusion that the polymerization might not have started properly, and the *s*-BuLi addition may have resulted in the addition of $PI^-Li^+$ to the double bond of CDMSS and the sequential addition of the intrachain anion to another CDMSS. The reason for that kind of reactions is the existence of high steric hindrance of the long macromonomer chains, that are “unable to locate” the silyl group easily. This obstacle could have been avoided if the reaction solution was more dilute. Nonetheless, the exact same incident was also observed at a previous attempt of synthesis of a bottlebrush, with a branch from the series of 7500Da living polymers. The predominant problem is the inability of SEC to determine accurately low molecular weights of polymers, because very small molecules are eluded at a period of time close to the time when the general sample measurement finishes. The living by-products might form small wide peaks on the chromatogram that appear in-between the peak of the bottlebrush and that of the macromonomer, as shown on

Figure *13* below. [1]

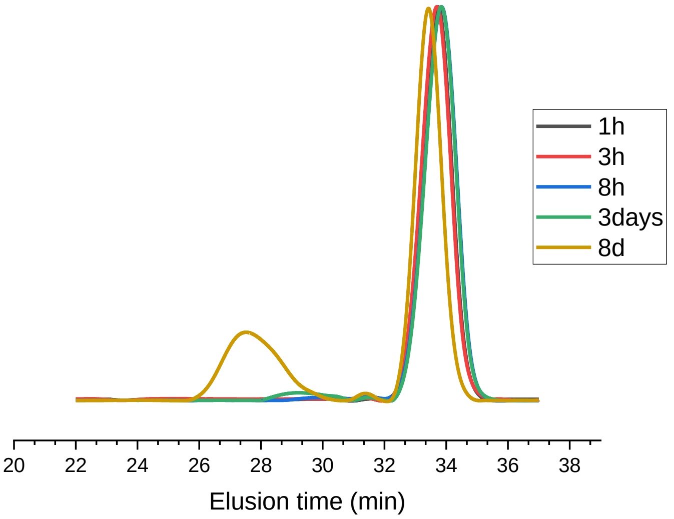


*Figure 13 Bottlebrush procedure of PI 7,5kDa macromonomer*

After the termination of the polymerization (7 days), the final product had to be separated by the undesirable products (oligomers or macromonomers that may exist). The separation is quite easy in this case, because such a high molecular weight blurs during the fractionations, and precipitates immediately, in solvent/non-solvent mixture and non-solvent, respectively.

### 3.1.4 Unsuccessful attempts during the synthesis of bottlebrushes

For this work, we intended to synthesize a series of bottlebrushes with different DPs and lengths of "living" branches. Two "living" polymers with molecular weights of 2500Da and one of 14000Da were prepared, along with the set of 4 polymers with $M_w$=7500Da. One 2500Da and a 7500Da polymer were used for the preparation of the bottlebrush mentioned in sections 3.1.3 above. One out of the four linear homopolymers was used for the exact synthesis as the bottlebrush with the 7,5kDa $PI^-Li^+$. The same obstacles coincided with the first preparation, therefore it was used as "test" process, through which we corrected previously mentioned synthesis. The rest of the branches, 2500, 14.0000, and two of 7500Da, weren't used, because of a laboratory accident that led to premature reaction of the silyl group of the coupling reagent with oxygen of the air. The remaining "living" branches and the polymers are stored alongside at -20°C until future use.

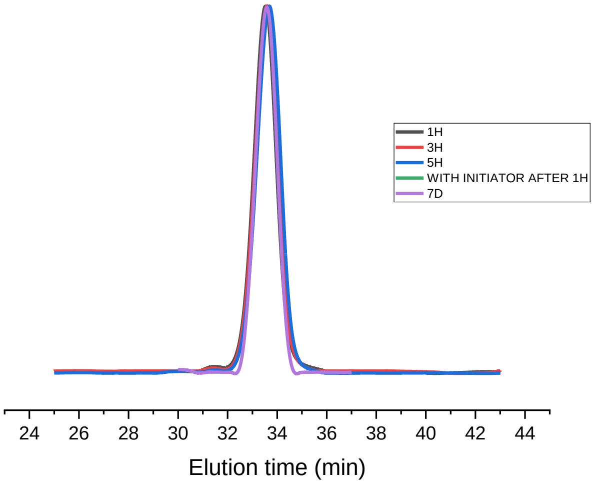


*Figure 14 Failed bottlebrush synthesis using PI 7,5kDa macromonomer*

### 3.1.5 Differential Scanning Calorimetry Results

From the results it is evident that the *Tg* of the bottlebrush is dependent on the behaviour of the *Tg* of the linear counterpart. As the molecular weight decreases, so does the *Tg* of both the branch and the bottlebrush.

| Sample (g/mol) | $T_g$ (ºC) |
|---|---|
| PI branch 2200 | -75 |
| Bottlebrush of 2200 | -128 |
| PI branch 9300 | -67 |
| Bottlebrush of 9300 | -67 |

Table 1 Glass transition temperatures of branches and bottlebrushes

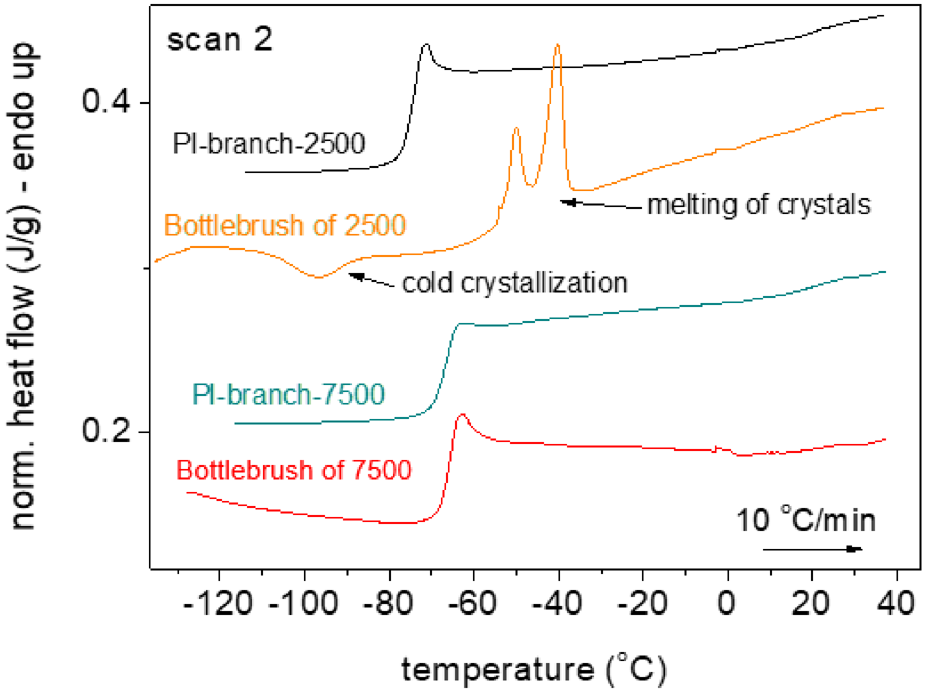


Figure 15 Calorimetric measurements of bottlebrushes and the respective branches

# CHAPTER 4

# CONCLUSIONS

This work presents the synthesis of polyisoprene molecular brushes, by anionic polymerization of macromonomers. The originality of the method lies in the fact that the synthesis of the macromonomers and their polymerization are done in the same device, without prior isolation of the macromonomer. The synthetic process includes three steps a) synthesis of living branches ($PI^{-}Li^{+}$) by anionic polymerization, b) synthesis of styrenic macromonomers by selective reaction of living macro-anions with the chlorosilyl group of 4-(chlorodimethylsilyl)-styrene (CDMSS) and c) in situ polymerization of the macromonomers with sBuLi. All reactions were performed in benzene, using high vacuum techniques and specially designed apparatus.

A basic condition for the synthetic process to work is the quantitative reaction of the living polyisoprene with the chlorosilyl group of CDMSS selectively, without reacting with the double bond of the reagent. The reaction must also be carried out with stoichiometric amounts, in order to enable the subsequent in situ polymerization of the macromonomers. Due to the selectivity of the macroanions for the Si-Cl group, it was found that with appropriate control of the reaction conditions (dropwise addition of a dilute solution of the living branch to a solution of the coupling reagent), it is possible to prepare the macromonomer quantitatively, with only a small percentage of by-products.

The molecular brushes synthesized in this way are characterized by narrow molecular weight distributions ($M_w/M_n<1.15$). Degrees of polymerization up to 20 were achieved with this method, making them comparable to similarly high grades reported in the literature with anionic polymerization, while also with this method we have a quite controllable system.

The molecular characterisation for all of the possible isolated products was conducted by size exclusion chromatography (SEC) and nuclear magnetic resonance spectroscopy (NMR).

# ABBREVIATIONS – ACRONYMS

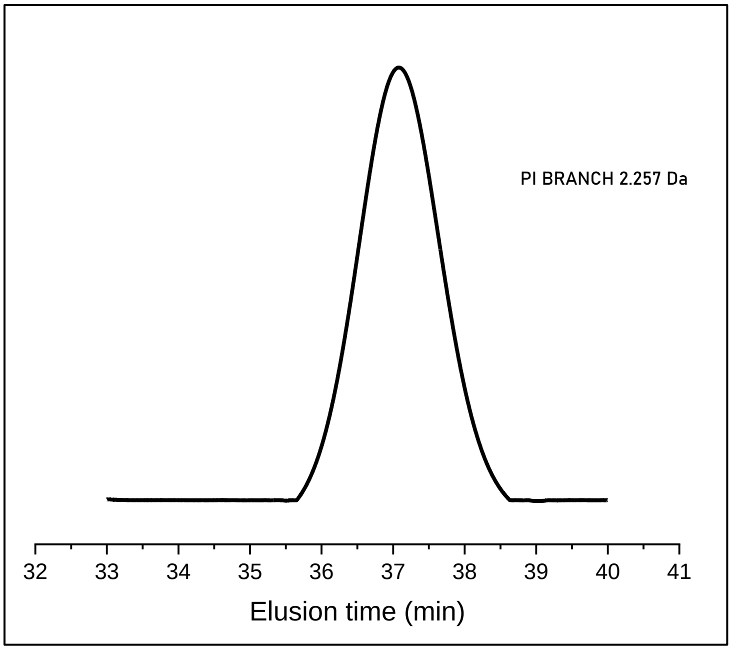
| | |
|---|---|
| PI | Polyisoprene |
| PBd | Polybutadiene |
| $PI^-Li^+$ | “living polyisoprene” |
| sBuLi | Secondary butyl-lithium |
| n-BuLi | Normal butyl-lithium |
| DP | degree of polymerization |
| Li | Lithium |
| THF | tetrahydrofuran |
| Đ | polydispersity |
| $M_w$ | Molecular weight |
| ATRP | Atom Transfer Radical Polymerization |
| ROMP | Ring-Opening Metathesis Polymerization |
| RDRP | Reversible deactivation radical polymerization |
| RAFT | Reversible addition−fragmentation chain transfer |
| NMP | Nitroxide-mediated polymerization |
| PS | Polystyrene |
| CDMSS | 4-(chlorodimethylsilyl)-styrene |
| BBCPs | Bottlebrush Copolymers |
| kDa | kilo-Dalton |
| SEC | Size Exclusion Chromatography |
| GPC | Gel Permeation Chromatography |
| HPLC | High Performance Liquid Chromatography |
| 4-St-Cl | 4-Chlorostyrene |
| GGJ (also as ggj) | ground glass joint |

# APPENDIX I

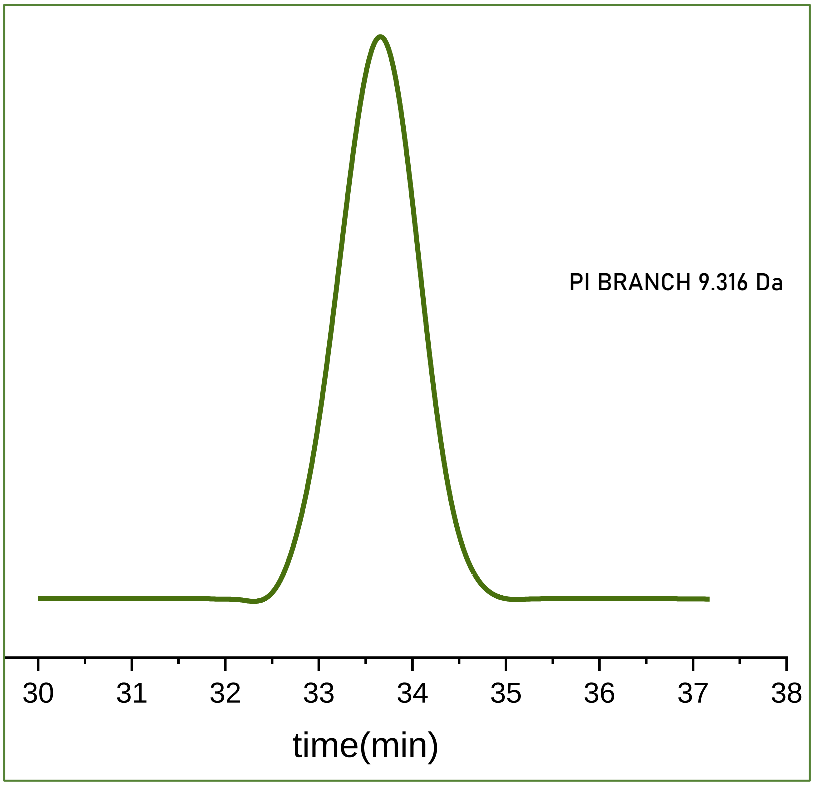
*Table 2 Molecular characteristics of the branches used in bottlebrush synthesis*

| *$Mw_{theoretical}$ (g/mol ή Da)* | *Mw (Da)* | *Mw/1,6 (Da)* | *PDI* |
|---|---|---|---|
| *2500* | *3600* | *2.200* | *1,07* |
| *7500* | *14.900* | *9.300* | *1,03* |
| *14.000* | *28.300* | *17.700* | *1,02* |

*PI $M_{w,theoretical}$=2500Da*



PI $M_{w,theoretical}$=7500Da



PI $M_{w,theoretical}$=14.000Da

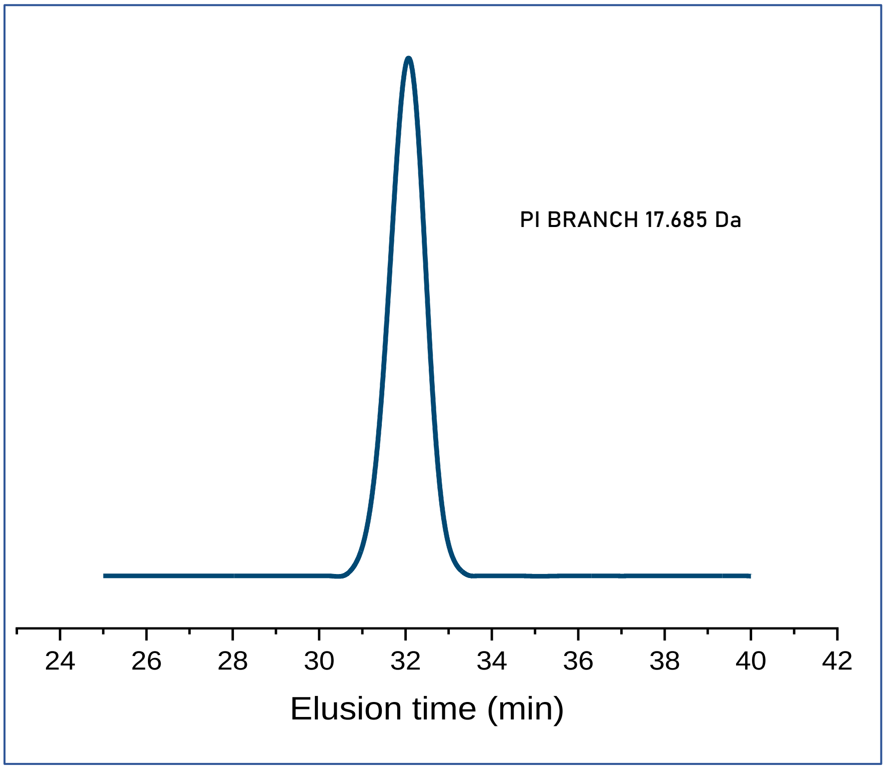


*Table 3 Mw=63.800 g/mol Bottlebrush*

| *$Mw_{theoretical}$(g/mol ή Da)* | *Mw (Da)* | *Mn (Da)* | *PDI* |
|---|---|---|---|
| *150.000* | *63.800* | *57.200* | *1,11* |

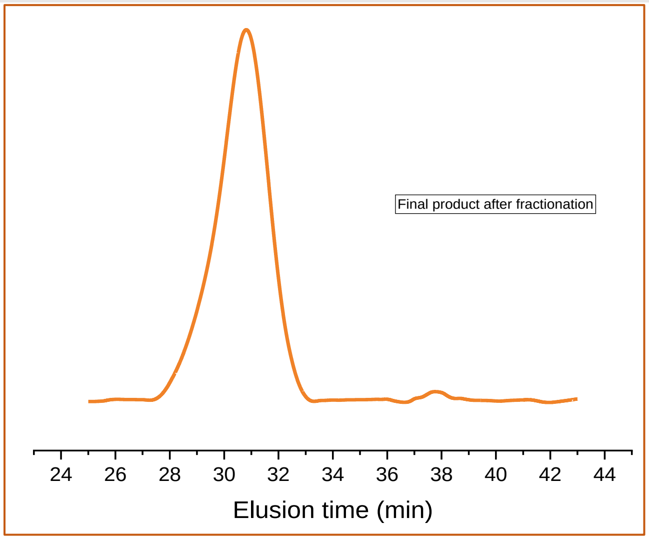
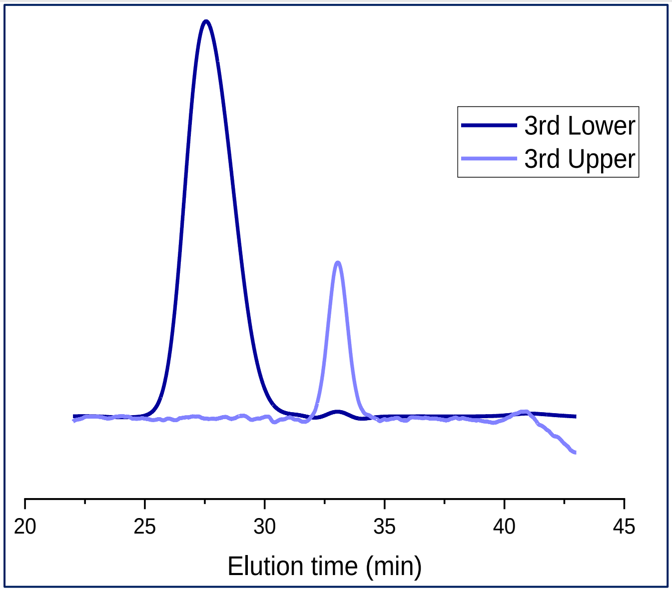


*Table 4 Mw=177.200 g/mol Bottlebrush*

| *$Mw_{theoretical}$ (g/mol ή Da)* | *Mw (Da)* | *Mn (Da)* | *PDI* |
|---|---|---|---|
| *150.000* | *177.200* | *152.500* | *1,16* |



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