End-Functionalized and Branched Polymers by Anionic Ring-Opening Polymerization

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Synthesis of End-Functionalized and Branched Polymers by Anionic Ring-Opening Polymerization

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Abstract

The introduction of functional groups and branching to polymers leads to substantial changes in thermal behaviour and rheology. This work focused on two different macromonomer approaches, namely AB_2 and AB_x, to synthesise branched polysiloxanes by Williamson and hydrosilylation coupling reactions, respectively. For the AB_2 approach, anionic ring-opening polymerization (AROP) of hexamethylcyclotrisiloxane (D_3) was attempted to be initiated by using (protected) functionalized initiator molecules to introduce dihydroxyl functionality (B_2) on to the polydimethylsiloxane chain-end. The hydroxyl functionalities were protected with silyl ethers and successfully deprotected by using tetra-n-butylammonium fluoride or acetic acid after polymerization. Prior to the introduction of an alkyl halide (A-functionality) by end-capping, stability of the PDMS backbone was tested with Williamson coupling reactions. It was understood that the basic conditions of this reaction led to serious damage to the polymer and this approach was abandoned. Synthesis of ABx macromonomers was performed by copolymerizing D_3 and 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3) monomers. In this work, A and B represent Si-H and vinyl groups, respectively. The anionic copolymerization was end-capped by using chloro(methyl)phenylsilane. The resulting polymers were coupled by hydrosilylation reactions in the presence of Pt(0) catalyst. These macromonomers were successfully used to form highly branched polysiloxanes. To optimize conditions of the coupling reaction, solution concentration of the reaction was varied from 20 % to 100 % and the vinyl content of the macromonomers was varied from 11 mol% to 52 mol%. It was shown that higher solution concentrations result in higher degree of branching. On the other hand, while an increase in vinyl composition also resulted in higher level of branching, a high vinyl (>30 %) composition resulted in a decrease in branching. This is believed to happen because of poor chain end-capping for high vinyl content copolymers and/or increased likeliness of intramolecular cyclization reactions.

Table of Contents

List of Figures

List of Schemes

List of Tables

List of Equations

List of Calculations

Abbreviations

AcOH	Acetic acid
AR	Analytical reagent
AROP	Anionic ring-opening polymerization
BHT	Butylated hydroxytoluene
BPF	Bisphenol F
BPF-OSi	Triethylsilyl-protected Bisphenol F
COSY	Homonuclear correlation spectroscopy
Đ	Dispersity
D_3	Hexamethylcyclotrisiloxane
DBU	1,8-Diazabicyclo(5.4.0)undec-7-ene
DCTB	trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile
DMAC	Dimethylacetamide
DMAP	4-Dimethylaminopyridine
DME	Dimethoxyethane
DMF	Dimethylformamide
DMSO	Dimethyl sulfoxide
DPE	Diphenylethylene
DPE-OH	4,4’-Dihydroxy-1,1-diphenylethylene
DPE-OSi	t-Butyldimethylsilyl- or triethylsilyl-protected 4,4’-Dihydroxy-1,1-diphenylethylene
DPMK	Diphenylmethyl potassium
EtOH	Ethanol
GPC	Gel permeation chromatography
HMBC	Heteronuclear multiple bond coherence

HSAB	Hard soft acid base theory
HSQC	Heteronuclear single quantum coherence
IV-DP	Intrinsic viscosity – differential pressure
LiOAc	Lithium acetate
LS	Light scattering
MALDI	Matrix-assisted laser desorption/ionization
MDPS	Methyldiphenylsilyl
MeCN	Acetonitrile
MeLi	Methyllithium
M_n	Number-average molecular weight
MW	Molecular weight
M_w	Weight-average molecular weight
MWD	Molecular weight distribution
NMR	Nuclear magnetic resonance
PDMS	Polydimethylsiloxane
PEG	Polyethylene glycol
PET	Polyethylene terephthalate
PMMA	Polymethyl methacrylate
PMVS	Polymethylvinylsiloxane
PS	Polystyrene
RI	Refractive index
RT	Room temperature
SEC	Size exclusion chromatography
TBAF	Tetra-n-butylammonium fluoride
TBDMS	t-Butyldimethylsilyl

TBDMS-Cl	t-Butyl(chloro)dimethylsilane
TBDPS	t-Butyldiphenylsilyl
TBDPS-Cl	t-Butyl(chloro)diphenylsilane
TES	Triethylsilyl
TES-Cl	Chlorotriethylsilane
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMEDA	N,N,N′,N′-Tetramethylethylenediamine
TMS	Trimethylsilyl
TMS-Cl	Chlorotrimethylsilane
TOF	Time of flight
TOL-Li	Lithium initiator based toluene
UV	Ultraviolet
UV-Vis	Ultraviolet-visible light spectrum
V_3	1,3,5-Trivinyl-1,3,5-trimethylcyclotrisiloxane

Statement of Copyright

Acknowledgments

I would like to thank my supervisor Professor Lian Hutchings for giving me the opportunity to undertake this Masters programme. In addition to our monthly meetings, I cannot remember how many times I knocked his door and seek his help. He was always supportive and pointing in the right direction.

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Lastly, I would like to thank my family for the support and encouragement throughout this Masters year.

I dedicate this thesis to my high school teachers,

Noyan Erdenizci, *Semen Emirogullari* and *Zehra Ilban*

to inspire them continue believing in their students as they did
for me and changed my life in an entirely creative manner.

1 Introduction

"Nothing in chemical theory, either then apparent or later revealed, sets a limit on the number of atoms that may be thus joined together."[1] Those were the words of Paul J. Flory when he clearly pointed out the boundless nature of polymer chemistry in his 1974 Nobel Prize Lecture. Polymers have gone on to have major applications in automotive, aerospace, medical, building, consumer goods and packaging industry where they count for the 80% of the chemical industry's output worldwide.[2] Being the biggest contributor to the £2.1 trillion worldwide chemical industry attracts huge investments and massive research interests in to the field.[3] Synthetic polymer chemists all around the world aim to synthesise diverse ranges of polymers by controlling the major variables, such as molecular weight (MW), dispersity (Đ), functionality, composition and chain architecture, all of which affect macromolecular properties. The research described herein is aimed at the synthesis of end-functionalized and branched polysiloxanes, with well-controlled parameters, by living anionic ring-opening polymerization, which is a type of chain-growth polymerization.

1.1 Classification of Polymerization Mechanisms

The very first attempt to classify polymers by their mechanism of synthesis was done by W. H. Carothers[4] in 1929 who suggested two groups – *condensation* and *addition* polymers. Addition polymers were defined as polymeric molecules in which their structural unit is identical with the molecular formula of the monomer whereas condensation polymers were described as having a repeat unit with a different molecular formula to the monomer.[4] This proposal was improved greatly over the years and resulted in the currently used mechanistic classification of polymers - *step-growth* and *chain-growth* polymerizations.

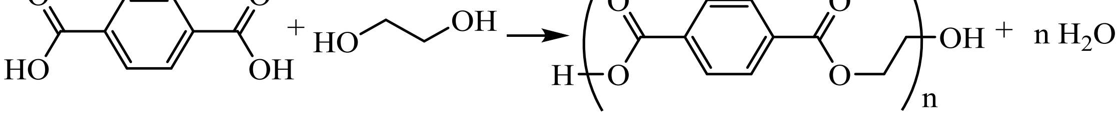


Figure 1.1: Step-growth polymerization of polyethylene terephthalate.

Step-growth polymerization, a term arising from Carothers's 'condensation polymers', can be defined as a series of stepwise reactions between monomers containing two or more functional groups that can react with each other to form macromolecules after many steps. With this methodology, monomers are consumed very quickly and the polymerization continues via the coupling of chains. This kind of polymerization does not require an initiator. Naturally occurring polypeptides, polysaccharides and nucleic acids, and synthetic polymers like polyesters, polyamides, polyurethanes, polysiloxanes, polycarbonates, polyureas and polysulfides are or can be produced by this mechanistic approach.[5] To illustrate this kind of polymerization, an example is given in Figure 1.1. Polyethylene terephthalate (PET) is synthesised by the esterification of dicarboxylic acid and diol monomers on an industrial scale. Monomers come together to form dimers and then, a dimer reacts with another monomer (or another dimer) to form a trimer (or a tetramer) and so on to form macromolecules. If a step-growth polymerization is performed with the elimination of a side-product, such as water in PET synthesis, it is called polycondensation. If it happens without the elimination of a side product, e.g. rearrangement of bonds, it is called polyaddition.

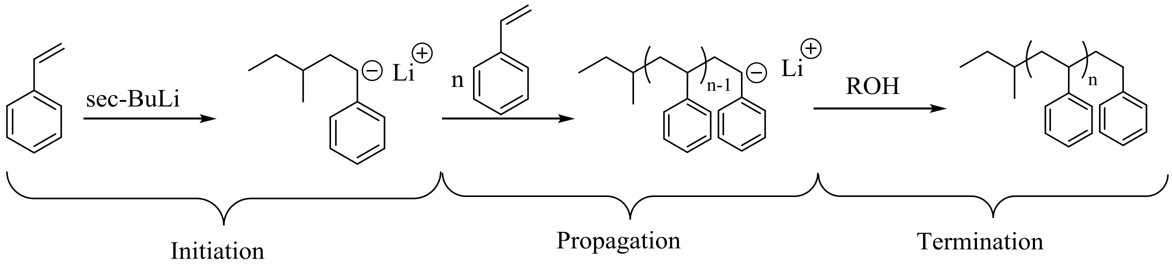


Figure 1.2: Chain-growth polymerization of styrene.

Chain-growth polymerization, arising from the term 'addition polymers', can be described as a chain reaction in which a polymer chain grows via consecutive reactions with monomers and after each growth-step, the propagating reactive centre on the chain-end is regenerated.[6] This kind of polymerization requires initiation, usually with a free radical or ionic initiator, and has distinct propagation and termination steps (Figure 1.2). Typical monomers include molecules containing alkene groups and/or strained rings. Free-radical and ionic polymerizations are both examples of chain-growth polymerization. As their names suggest, a free-radical polymerization proceeds with a propagating species bearing radicals and an ionic polymerization proceeds with ionic active centres. Ionic polymerizations are also named based on the nature of the propagating ion – anionic or cationic. Figure 1.2 shows the polymerization of styrene via living anionic polymerization.

1.2 Living Polymerizations

In 1956, Michael Szwarc and his co-workers were experimenting an electron transfer reaction between sodium-naphthalene complex and styrene to form styryl radical anions which were expected to be deactivated. The expectation of the researchers was to observe a colour change from green (the complex) to dark red (styrene anion end) which would turn to colourless eventually as the anion would "die". Moshe Levy, a PhD student of Michael Szwarc, was first to observe that the colour did not fade and, in fact, remained persistently strong. The researchers decided to add more styrene to the solution and they noted an increase in viscosity. This could only mean the radical anion did not "die" and was in the propagation step. The term "living polymers" was first used in the paper reporting this experiment, which was less than 1-page long.[7, 8] The discovery of living polymers had a major impact in the field of synthetic polymer chemistry. It enabled the synthesis of homo- and block polymers with well-defined composition, architecture and morphology. Chemists gained excellent control over molecular weight, dispersity, branching and end functionality of the chains.[9] The industrial output arising from this discovery is currently worth many billions of pounds a year.

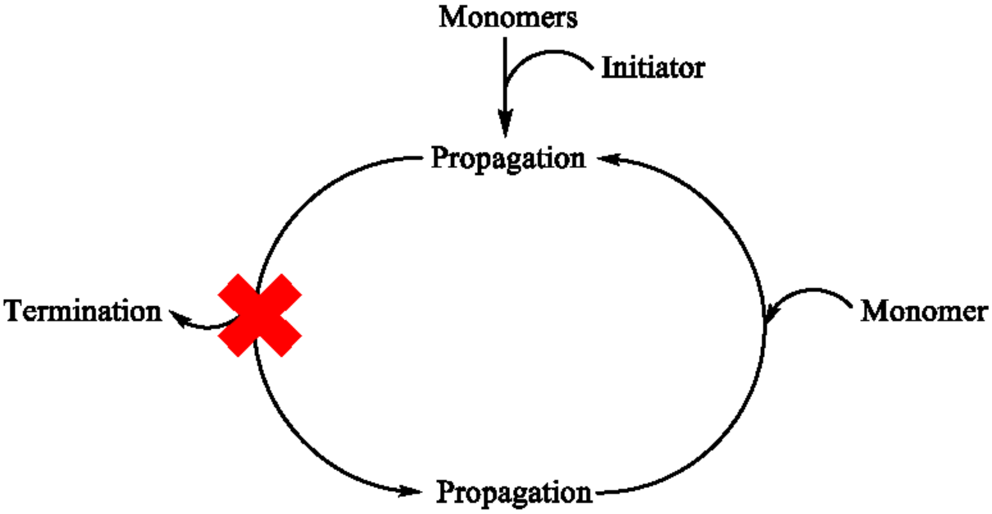


Figure 1.3: A simple illustration of living polymerization.

Ever since the first use of the word "living", there have been attempts by polymer chemists to describe the criteria which define a living polymerization. A living polymerization can simply be defined as a chain-growth polymerization in which termination and chain transfer reactions are absent (Figure 1.3). However, this is an over-simplification. There are some additional relevant criteria that have been pointed out by different researchers.[7, 10, 11]

1. The number of active centres remains constant throughout the polymerization. A living polymerization does not have an inherent termination step and continues until all monomer(s) is consumed.
2. The number average molecular weight (M_n) is a linear function of conversion and therefore, can be controlled by the stoichiometry between the amount of monomer in grams and number of moles of initiator. See Equation 1.1 for full conversion and Equation 1.2 for intermediate conversion levels. This relationship remains valid even if the termination reactions are occurring, as the number of chains is still the same (moles of initiator is same). Therefore, this criterion alone is not conclusive. However, it can be used to test for chain transfer reactions where the number of chains changes.

Equation 1.1: Definition of theoretical number-average molecular weight for 100% conversion.

$$M_n = \frac{\text{g of monomer}}{\text{moles of initiator}}$$

Equation 1.2: Definition of theoretical number-average molecular weight for intermediate conversion.

$$M_n = \frac{\text{g of consumed monomer}}{\text{moles of initiator}}$$

3. Narrow dispersity polymers (≤ 1.1) are produced. However, this condition cannot be used alone to determine whether a polymerization is living or not either. There are many polymerization mechanisms capable of producing polymers with narrow dispersity which are not accepted as living. The criterion requires all propagating chains to be equally susceptible to attack monomers, to have an initiation step with faster or comparable rate to the rate of propagation and to have an irreversible propagation step.
4. Monomers can be added sequentially and block copolymers can be prepared. This can be used diagnostically to identify living polymers as it clearly proves the absence of termination reactions during the timescale of the experiment. Size exclusion chromatography (SEC) can be used to observe this phenomenon. If a polymerization is truly living, it would give only a single peak belonging to the block copolymer. However, if there are termination reactions during the polymerization of first block, a separate peak is observed in the SEC.

5. Chain-end functionality can be introduced quantitatively with termination reactions. A living polymerization does not “die” but can be carefully “killed” with end-capping agents. These end-capping agents have one or more highly reactive bonds in the case of anionic polymerisation. For example, Si-Cl bond attached to a molecule containing a functional group can be used to introduce functionalities to the polymers.
6. A living polymerisation should display pseudo-first-order kinetics for propagation to satisfy Equation 1.3 This criterion can only be achieved if the concentration of propagating chains is constant which means there has to be no termination reactions. However, it should be noted that this criterion is insensitive to chain transfer reactions since the number of propagating species does not change with these side reactions. Criterion 6 and Criterion 2 can be used together to diagnose a living polymerization.

Equation 1.3: Definition of Pseudo-first-order kinetics for propagation, where M is monomer, k_p is the rate of propagation and P is propagating species.

$$\ln \frac{[M]_o}{[M]} = k_{obs}\, t \qquad\qquad k_{obs} = k_p\, [P^*]$$

1.3 Anionic Polymerization

Anionic polymerization is a living chain-growth polymerization in which the propagating species bears an anion. This kind of polymerization provides the ultimate control over molecular weight, molecular weight distribution (MWD), microstructure and chain-end functionality while it also enables the synthesis of block copolymers. Chain-end functionality is one of the crucial concepts of the anionic polymerization as it enables the synthesis of functionalized polymers, highly branched polymers and complex architectures.[11] Anionic polymerization has no tolerance to impurities such as water, oxygen, carbon dioxide and protic species including alcohols, acids and even primary amines, and therefore, the academic world often prefers to perform anionic polymerization under high vacuum conditions as purification steps are faster whereas the chemical industry prefers to use inert atmospheres.

Monomers

There are two main groups of monomers that are suitable for anionic polymerization. These are alkene containing monomers, specifically vinyl, diene and carbonyl-type, and cyclic monomers where the ring strain is the driving force (Figure 1.4). In almost all cases, monomers need to have substituents or functional groups which are capable of stabilizing the propagating anion. For carbanions, this happens via the delocalisation of the anion whereas for cyclic monomers usually the heteroatom carries the negative charge (Figure 1.5).[10]

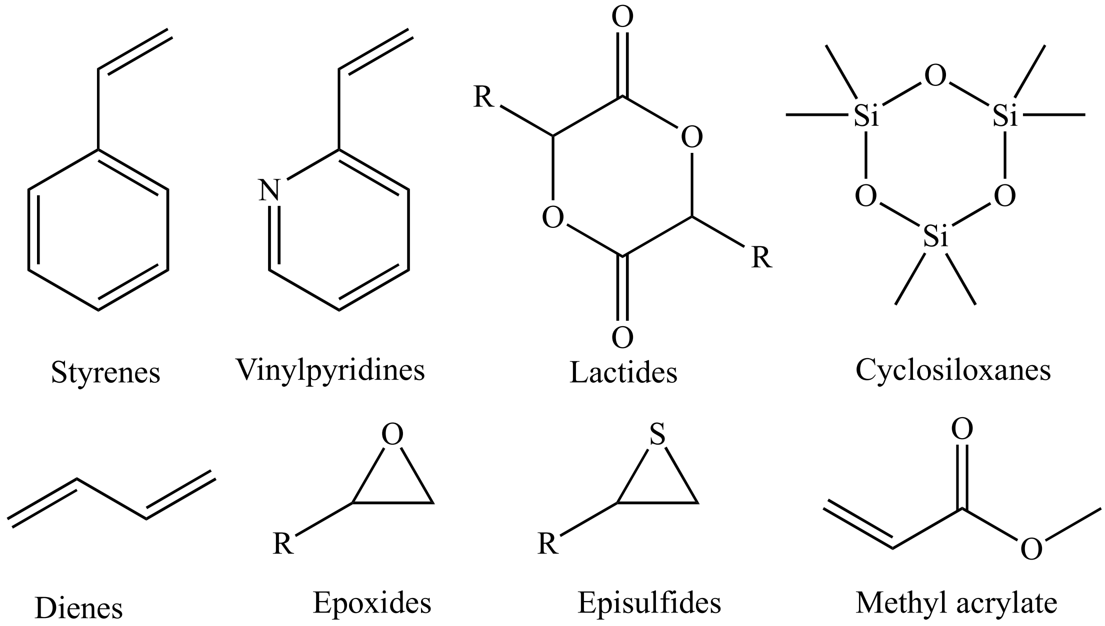


Figure 1.4: Example monomers capable of polymerizing via an anionic approach.

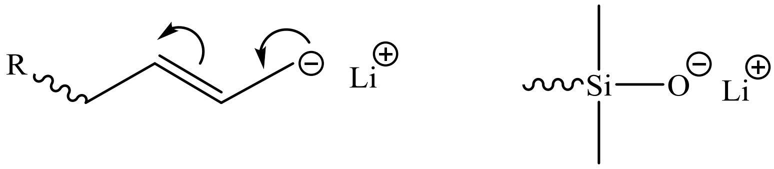
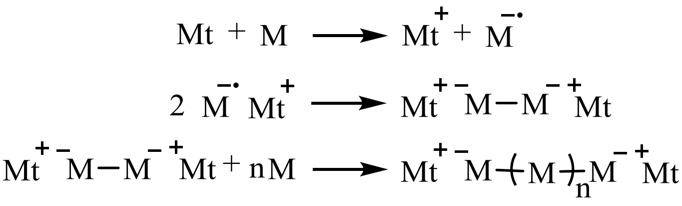


Figure 1.5: Stabilization of the anion.

The high reactivity of anionic species, specifically carbanions, results in the requirement of extremely rigorous dry and pure conditions. This means anionic polymerization of a monomer is only commercialized if it is of total success. For example, monomers with polar functional groups, such as carbonyl or nitro substituents, can undergo secondary reactions with initiating or propagating chains and this causes the loss of “living” nature of anionic polymerization. As a solution, functional groups containing acidic hydrogen atoms, such as alcohol groups, can be protected as silyl ethers to enable their polymerization. Nevertheless, the main commercialization of anionic polymerization is still limited to polystyrene (PS), polybutadiene (PBd) and polyisoprene (PI).[10, 12] Recent advances in the field however, has revealed that the anionic polymerization of strained heterocyclic monomers has tremendous applications in pharmaceutical applications (PEG) and personal care products (PDMS).

Initiator



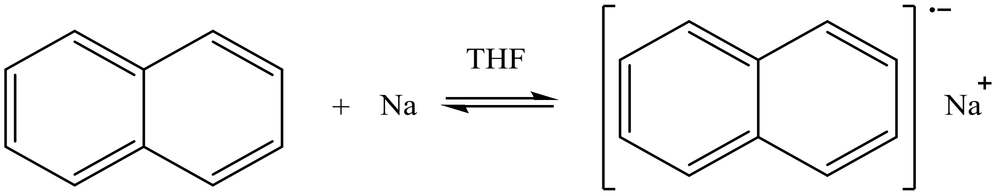
$$\mathrm{Mt} + \mathrm{M} \longrightarrow \overset{+}{\mathrm{Mt}} + \overset{-\bullet}{\mathrm{M}}$$

$$2\,\overset{-\bullet}{\mathrm{M}}\,\overset{+}{\mathrm{Mt}} \longrightarrow \overset{+}{\mathrm{Mt}}\,\overset{-}{\mathrm{M}}{-}\overset{-}{\mathrm{M}}\,\overset{+}{\mathrm{Mt}}$$

$$\overset{+}{\mathrm{Mt}}\,\overset{-}{\mathrm{M}}{-}\overset{-}{\mathrm{M}}\,\overset{+}{\mathrm{Mt}} + n\mathrm{M} \longrightarrow \overset{+}{\mathrm{Mt}}\,\overset{-}{\mathrm{M}}{-}\left(\mathrm{M}\right)_n{-}\overset{-}{\mathrm{M}}\,\overset{+}{\mathrm{Mt}}$$

Scheme 1.1: Simplified demonstration of initiation with alkali metal, where Mt is metal and M is monomer.[10]

Anionic polymerization can be initiated with one of the three types of initiator; alkali metals, radical anions and alkyllithium compounds. Initiation with alkali metals, such as lithium and sodium, are heterogeneous reactions. The initiation occurs with the transfer of an electron from metal surface to an adsorbed monomer. An example scheme is provided above (Scheme 1.1). Electron transfer from metal surface to adsorbed monomer results in the formation of a radical anion. As the radical anions are extremely reactive, two of them combine to form a dianion which is more stable. This dianion reacts with other monomer molecules and propagation starts. The initiation continues in parallel with propagation, and the control over molecular weight and dispersity is absent. Therefore, this method of initiation is no longer preferred and it is only of historic interest. [10]



Scheme 1.2: Formation of a radical anion by the reaction by naphthalene and sodium metal.

Radical anions are formed also with alkali metals but this time the metal reacts with aromatic hydrocarbon compounds (e.g. naphthalene) that can form stabilized radical anions in, of course, polar solvents. An example was given in Section 1.2 (usage of naphthalene) without pointing out the initiation mechanism. In fact, first ever living polymerization (by Szwarc[8]) was initiated by radical anions formed by the reaction of naphthalene and sodium metal (Scheme 1.2). The radical anion complex then reacts with monomers, such as styrene, dienes and epoxides, and initiates the polymerization. In a similar fashion to Scheme 1.1, dimerization between activated monomers occurs. This kind of initiation is also not highly preferred. This is mainly because of the necessity to use polar solvents which may speed up both polymerization and side reactions. This may result in a broad molecular weight. In addition, contact ion pairs, solvent-separated ion pairs and free ions are all in equilibrium during the polymerization, which causes uneven propagation and high dispersity. Beside all these, polar solvents, such as THF, can also behave as monomers under some circumstances due to the presence of polar bonds.[10]

Equation 1.4: The rate equation of the initiation of styrene in benzene, where M is monomer, x is the degree of aggregation, k_i is the rate of initiation.[10]

$$R_i = k_i \; K_d \; [RLi]^{\frac{1}{x}} \; [M] \qquad\qquad K_d = \frac{(RLi)^x}{(RLi)_x}$$

Alkyllithium initiators are predominantly the first choice in anionic polymerization. There are a variety of commercially available alkyllithiums which are readily available in solvents like cyclohexane, hexane and diethyl ether. Different alkyllithium complexes exhibit different reactivities based on their degree of association/aggregation. It is well-known that higher the degree of association, the less reactive the specific alkyllithiums (Equation 1.4). MeLi forms dimers whereas sec-BuLi and n-BuLi form aggregates of four and six, respectively. Therefore, the order of reactivity is; MeLi > sec-BuLi > n-BuLi. This also uncovers the importance of solvent. For example, the rate of initiation in aromatic solvents is 10^2-10^3 times higher than in aliphatic solvents.[10] As previously stated in Section 1.2, the rate of initiation must be faster or equal to the rate of propagation. sec-BuLi and n-BuLi are the most commonly used initiators for anionic polymerization. Sec-BuLi is often preferred in academia as the initiation reaction is much faster whereas n-BuLi, which has a lower rate of initiation is often preferred in industry as it is cheaper.

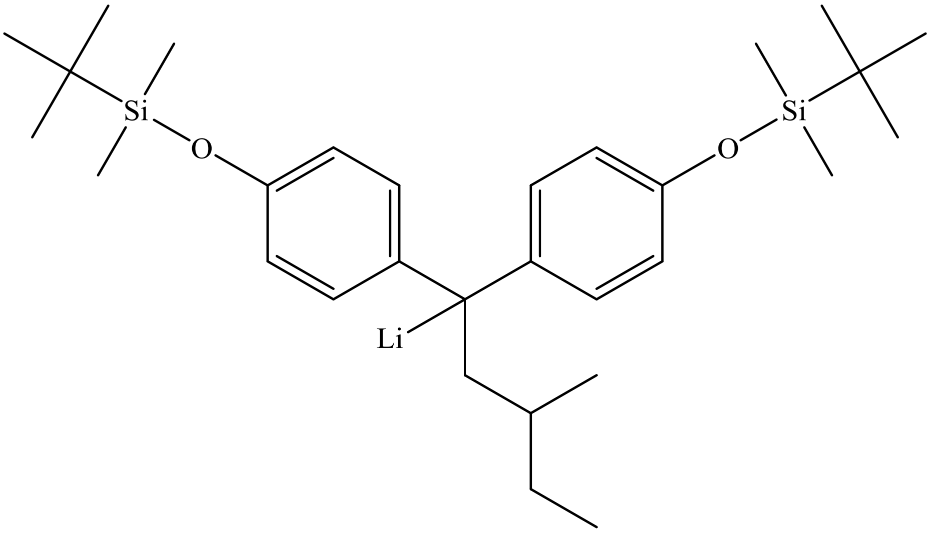


Figure 1.6: Initiator molecule used for the initiation purposes in this research.

Functionalized alkyllithium initiators enable the synthesis of end-functionalised polymers and macromonomers, a polymer capable of coupling with itself or other macromolecules. A part of our work focused on this advantage and was aimed at the introduction of hydroxyl groups to polydimethylsiloxane (PDMS) to create PDMS macromonomers. One of the functional initiators used is shown on Figure 1.6.

1.4 Polysiloxanes

1.4.1 Structure and Bonding in Siloxanes

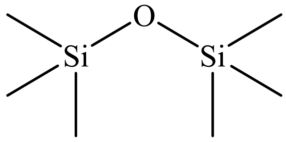


Figure 1.7: The siloxane bond.

The term "siloxane" was first suggested by German scientist Alfred Stock in 1917 to describe the Si-O bonds.[13] These bonds are of extreme importance in both nature and human practice. For example, more than half of the Earth's crust is made of silica and silicates and silicon compounds with oxygen linkages have crucial applications in construction materials, glass, etc.[14] The first polyorganosiloxanes were obtained with the high-pace progress in the siloxane chemistry in the first half of 20th century. In 1919, Stock and Somieski[15] were first to obtain polydimethylsiloxane (PDMS), the most widely used polyorganosiloxane in the world. Starting from 1940s, organosilicon chemistry have attracted huge interest and polyorganosiloxanes have been mass-produced on an industrial scale.[14] Nowadays polyorganosiloxanes are simply named polysiloxanes or silicones, for convenience. Polysiloxanes can be defined as polymeric members of organosilicon family where silicon and oxygen atoms form linkages and silicon atoms have attached alkyl groups.[16]

Equation 1.5: The additivity rule, where r is the atomic radius of an atom.

$$r_{XY} = r_X + r_Y$$

Equation 1.6: The Schomaker-Stevenson prediction, where r is the atomic radius of an atom, β is a constant (9 pm), χ is the electronegativity of an element.

$$r_{XY} = r_X + r_Y - \beta \,|\, \chi_X - \chi_Y \,|$$

The siloxanes have extraordinarily short Si-O bond lengths and wide Si-O-Si bond angles which attracted the interest of scientific world. These unusual properties are known to responsible for the backbone flexibility and thermal stability of PDMS. Early research to understand the nature of Si-O bond focussed on it in comparison to the C-O bond.[14] This may look like a justifiable approach as silicon sits below carbon in the periodic table. However, it turned out to be invalid. For example, consider the additivity rule (Equation 1.5). The additivity rule simply suggests the bond length of X-Y bond is the sum of their atomic radii. Simple molecules with no strong ionic character obey this rule, e.g., C-O bond. The radii of carbon and oxygen atoms are 77 pm and 66 pm, respectively.[17] The experimentally determined bond length of C-O is 142.6 pm and it is in a good agreement with theoretical value of 143 pm estimated by the additivity rule. However, the atomic radius of silicon atom is 117 pm and the additivity rule estimates a bond length of 183 pm. This compares the experimental value of 162.2 pm.[16] The Schomaker-Stevenson prediction (Equation 1.6) is another approach to estimate theoretical bond lengths. This prediction additionally accounts for the differences in the electronegativities of atoms.[16, 18] One may expect Equation 1.6 to better estimate Si-O bond length however, neither the additivity rule nor the prediction can get close to the experimental value of Si-O bond length. The electronegativities of silicon and oxygen atoms are 1.8 and 3.5, respectively.[17] Therefore, and the Schomaker-Stevenson prediction calculates it as 168 pm.

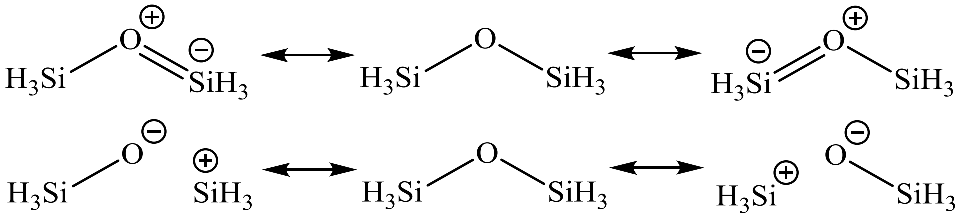


Figure 1.8: Lewis representations of back-bonding (top) and ionic (bottom) models.[19]

Two models (Figure 1.8) are put forward to explain the nature of bonding in siloxanes. The back-bonding model relies on the donation of one of the oxygen lone pairs to an empty 3d orbital of silicon atom. This (p → d) π back-bonding is believed to cause the shortening of the Si-O bond length and widening of the Si-O-Si angle. This explanation is based on the fact that silicon has a dense, positively charged nucleus (as Si electrons are withdrawn by the highly electronegative oxygen) which contracts the diffuse d-orbitals and brings them to suitable energy levels to form π-bonds with oxygen p-orbitals.[20] However, there are contradicting data to this model.[19, 21] Quantum mechanical calculations revealed that the 3d orbital of silicon does not play a substantial role in the linkages.[18] The widely accepted ionic model proposes that the Si-O bond is rich in ionic character as a result of the big difference in the electronegativity values of Si and O atoms. The presence of significant ionic character in the bonding results in the shortening of the bond length and widening of the Si-O-Si angle to satisfy the criterion of shortest distance between non-bonded atoms.[18] This model is supported by the quantum mechanical calculations and very fact that oxygen is the second most electronegative element in the periodic table.

Nevertheless, it is believed that it could be a poor approximation to assume that the empty d-orbital of silicon remains uninvolved in any kind of bonding. For example, the confirmation that cyclotrisiloxane is planar whereas the similar cyclohexane has no stable planar conformation.[20] This information supports the back-bonding model and it is noteworthy that if all oxygen atoms donate a lone pair, cyclotrisiloxane obeys the aromaticity rule of 4n + 2. Chemists have been investigating this elusive[19] bonding for more than a century and it looks like there is more we can learn from it.

1.4.2 Polydimethylsiloxane

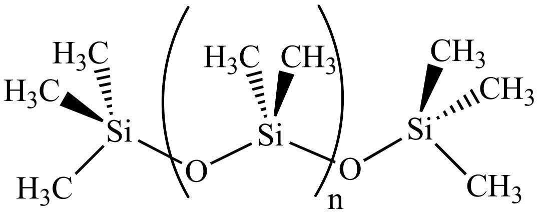
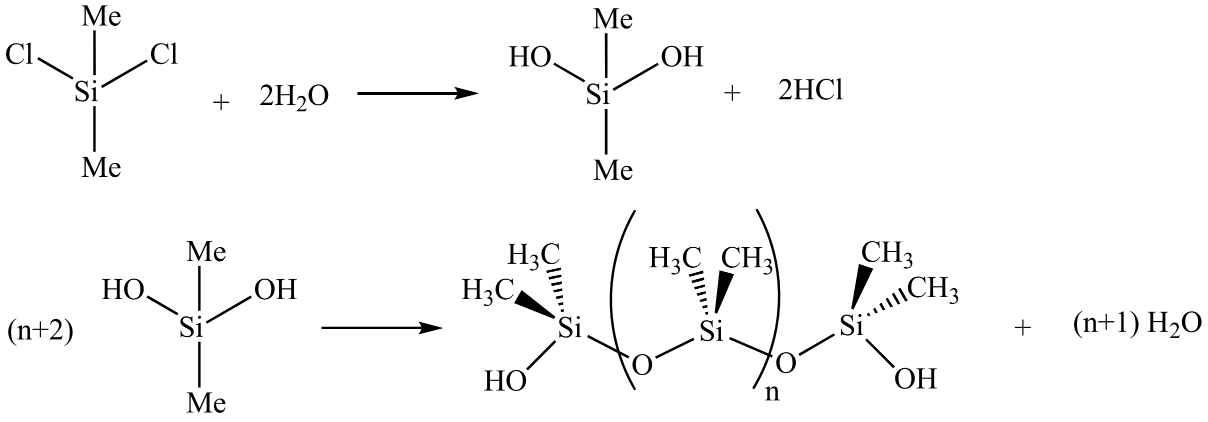


Figure 1.9: A general structure of polydimethylsiloxane.

Polydimethylsiloxane (PDMS) is one of the main polymers investigated in this research. PDMS exhibits a mixture of organic and inorganic chemistry because of its nature. The backbone is made up of polar Si-O bonds whereas the side groups are non-polar methyl groups (Figure 1.9). The importance of the siloxane bond was previously discussed in Section 1.4.1 and many of the properties of PDMS arises from the nature of this bond. PDMS is well-known to exhibit the lowest glass transition temperature (T_g) for a polymer at -125 ^{o}C.[22] High flexibility, low reactivity, low UV absorption, low surface energy, high gas permeability, biocompatibility and thermal stability are amongst its properties. PDMS is commonly used for catalysis, drug delivery, health care products, microfluidic devices, oil absorption and in surfactants and antifoaming agents.[23-29]

1.4.2.1 Conventional Synthesis of PDMS



Scheme 1.3: Conventional synthesis strategy of PDMS.

PDMS is conventionally synthesised, in two steps, by the hydrolysis of dimethyldichlorosilane followed by a condensation step-growth polymerization (Scheme 1.3). However, this method results in a high dispersity polymer with simple architecture which restricts the applications of the polymer.[30] Synthesis of PDMS via anionic polymerization enables ultimate control over architecture, molecular weight and MWD.[23, 24]

1.4.2.2 Synthesis of PDMS by Anionic Ring-Opening Polymerisation

1.4.2.2.1 Monomers for PDMS Synthesis

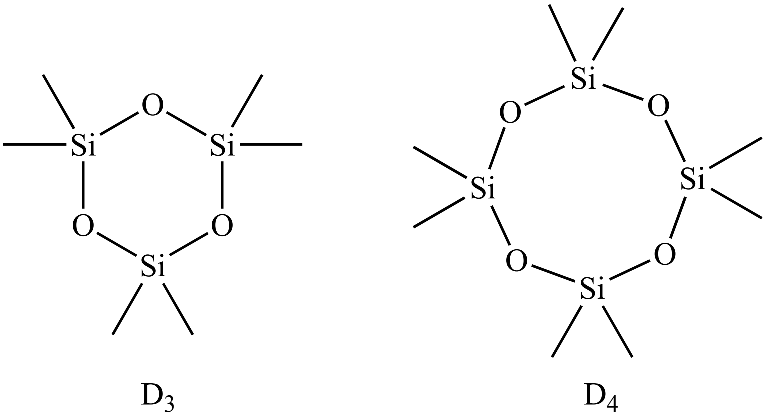


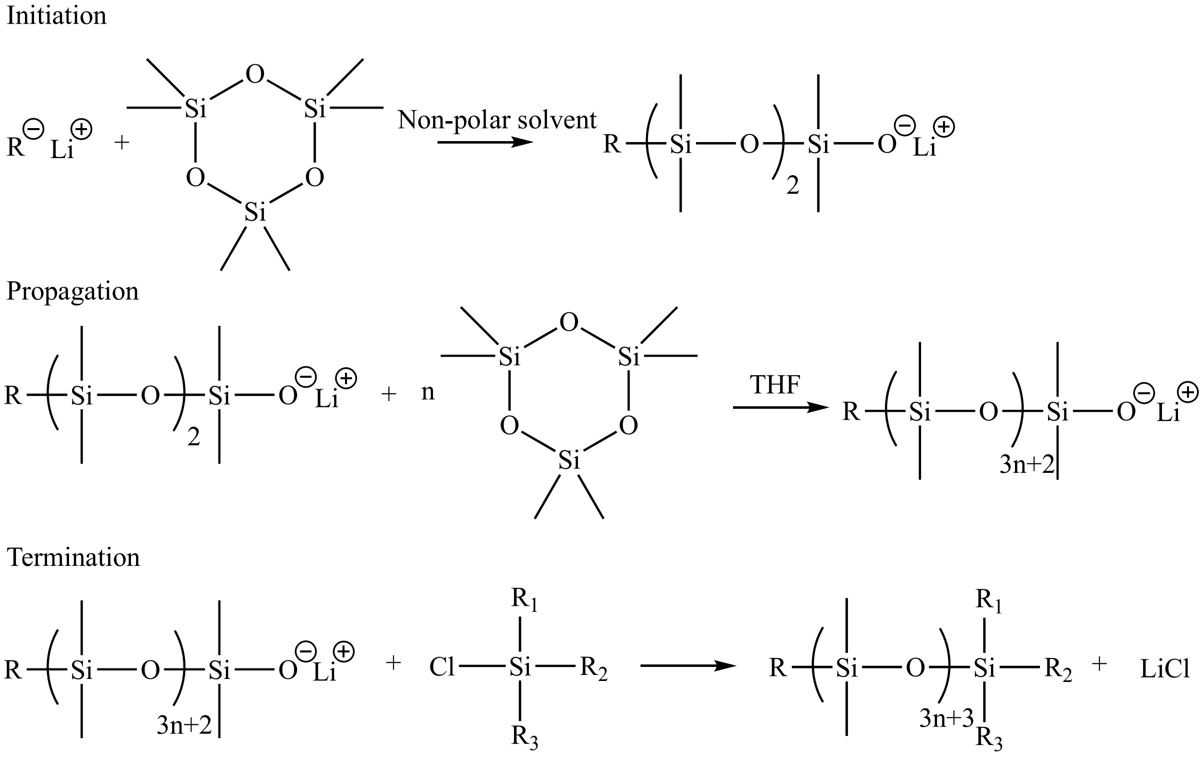
Figure 1.10: Two main monomers used for the anionic ring-opening polymerization of PDMS.

Hexamethylcyclotrisiloxane (D_3) and octamethylcyclotetrasiloxane (D_4) are the most commonly used monomers for the anionic ring-opening polymerization (AROP) of siloxanes. These two monomers polymerize in different fashions. As can be seen in Figure 1.10, D_3 has higher ring strain compared to D_4 and, as a result, anionic polymerization of D_3

is kinetically controlled whereas the polymerization of D_4 is based on an equilibrium.[23, 24, 31, 32] Other, less common, monomers include D_5, D_6, D_7 and D_8. The rate of polymerization increases with ring size (excluding the kinetically controlled D_3) since the entropic penalty to form longer chains gets smaller.[33] Among all examples, D_3 is favoured, as it provides a better control over molecular parameters. The equilibrium controlled polymerization of the other monomers leads to intra- and intermolecular side reactions and the monomer exists as a dominant component in the equilibrium.

1.4.2.2.2 Anionic Ring Opening Polymerisation of D_3

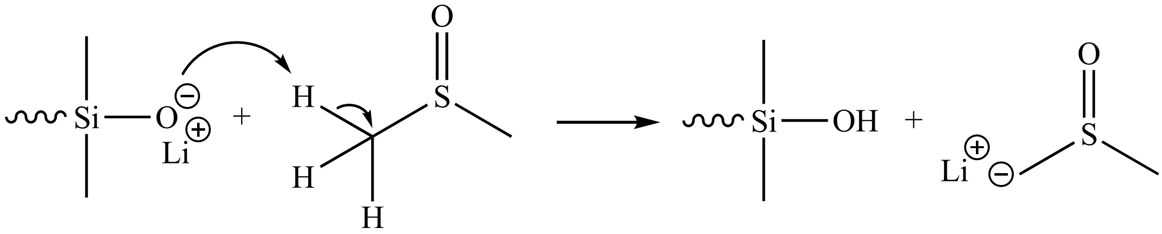
Anionic ring-opening polymerization of D_3 is usually initiated with alkyllithiums. The alkyl anion attacks the polarised Si-O bond of the strained siloxane ring. This is effectively a nucleophilic reaction and results in the opening of the ring and the formation of linear siloxane chains. The cation (Li^+) forms a monoadduct with the active chain end (Scheme 1.4). There are also reported cases where alkali metal hydroxides were used as initiators for this polymerization. However, the results indicated poor control over initiation.[24, 32, 34, 35]



Scheme 1.4: Initiation, propagation and termination steps of the AROP of D_3 monomer.

Ion-pair interaction between the living siloxane chain-end and lithium cation is so strong that propagation does not start until a promoter/complexing agent for the counterion is added. The promoter suppresses the association of living chains around the counterion.

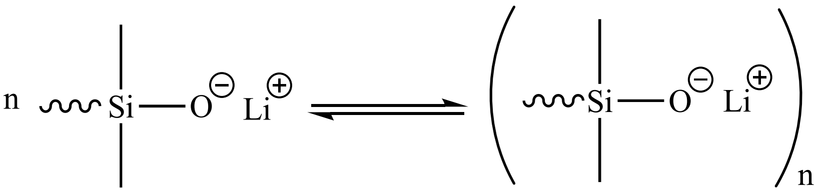
Common promoters are THF, DMSO, diglyme and triglyme. To understand how a promoter works, hard soft acid base (HSAB) theory can be adopted. According to this theory, interactions are strongest in the pairs of hard acid-hard base and soft acid-soft base. Li^+ is a hard acid and THF is a hard base. On the other hand, siloxane oxygen anion suffers from back-bonding which softens its basicity. As a result, THF complexes around the cation and weakens the interactions between the lithium counterion and living siloxane chain.[24, 33, 36] This process enables the propagation step to commence. Besides the fact that DMSO is a stronger complexing agent than THF, THF remains as the most widely-used promoter for this kind of polymerization.[36] The main reason is the simplicity of THF. For example, the presence of DMSO may trigger side reaction with itself. These reactions may form dimsyl carbanions (Scheme 1.5) which are potential chain-transfer agents.



Scheme 1.5: Formation of dimsyl anion from DMSO.

Polymerization of hexamethylcyclotrisiloxane is usually terminated by the addition of chlorosilanes and the most common terminating agent is chlorotrimethylsilane. However, different alkyl groups can be present on chlorosilanes in order to introduce functionalities, such a C-Cl bond, or stabilize the polymer chains. The latter requirement arises from the very fact that all Si-O bonds are susceptible to hydrolysis. Termination is usually associated with a reduction of viscosity since the aggregation of chains around the counterion stops – chains disassembly. The lithium counterion is removed as LiCl.[32]

1.4.2.2.3 Aggregation of the Propagating Species



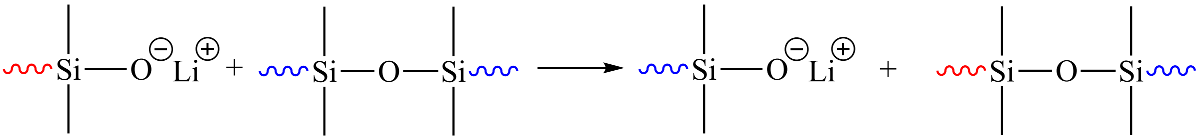
Scheme 1.6: Aggregation of propagating siloxane chains.

Aggregation (Scheme 1.6) can be defined as the association of living propagating chains around a counterion. This counterion can be any alkali metal. In general, Li^+ forms the strongest aggregates and the strength of aggregates softens with the increasing cation radius from Li to Cs. The degree of aggregation can be observed with rate experiments.[37] The kinetic order of propagation shows some variation with respect to counterion.[32] This arises from the fact that aggregated living chains are effectively dormant and exist in equilibrium with free ions. Since aggregates counteract dipoles of each other and prevent possible organizations of small molecules around free ions, aggregation is driven by entropy.[33, 37]

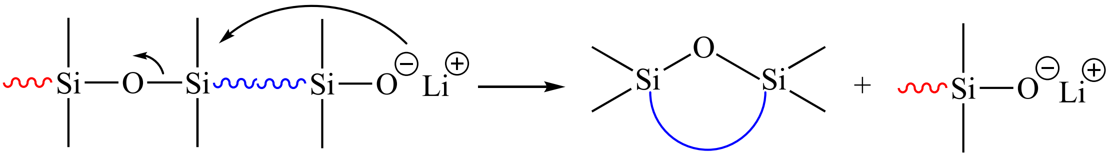
Aggregation is a problem and, at the same time, an advantage for the anionic polymerization of D_3. As mentioned, the aggregation around a lithium counterion is so strong that propagation does not start until the addition of a ‘promoter’. However, aggregation can also be used to ensure that initiation is complete before propagation commences, thereby ensuring a low dispersity. D_3 is a relatively bulky monomer because of the methyl groups and the initiation processes with bulky initiators are kinetically slow. One may wait until initiation is complete before adding the promoter. This ensures the maximum control over molecular weight and dispersity.

1.4.2.2.4 Secondary Reactions

Chain Transfer Reaction



Backbiting Reaction



Scheme 1.7: Demonstration of main side reactions in the anionic polymerization of D_3.

Chain transfer, also known as redistribution, and back-biting reactions are the main side reactions in the anionic polymerization of D_3. Both reactions arise from the nucleophilic attack by propagating siloxane chain ends on another siloxane bond. If this attack is intramolecular, the reaction is named back-biting whereas if the attack is intermolecular, the reaction is named as chain transfer. Generally, back-biting reactions are more pronounced than the chain transfer reactions. The main reason is the dilute environment, where siloxane propagating chain-ends can attack its own backbone more easily than approaching another chain. These side reactions widen the dispersity of the resulting polymer.[33]

Over the years, many studies have been performed on the backbiting reactions. A majority of these studies pointed out a significant increase in the occurrence of the side reactions at high monomer conversions (>80%).[24, 32, 38, 39] This is explained by a decrease in monomer concentration and a concomitant decrease in the rate of propagation. The rate of side reactions starts to compete with the rate of propagation in monomer starved environments. To avoid this situation, anionic polymerization of D_3 is usually terminated at around 85% monomer conversion. This solution is the most preferred but, as expected, the overall yield is decreased as a consequence.[24, 32] The introduction of strong complexation agents, such as cryptands and crown ethers, are some of the other strategies employed to address this problem.[33, 36]

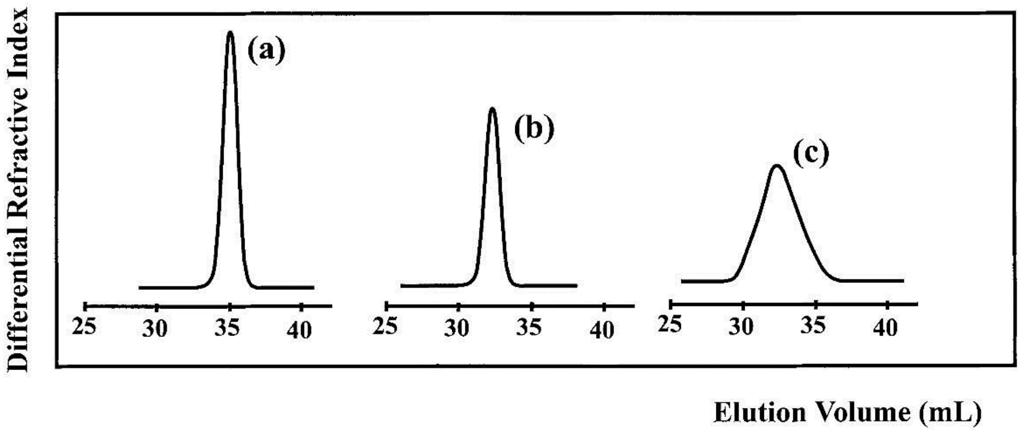


Figure 1.11: The size exclusion chromatograms reproduced from the paper of Bellas *et al.*[25], (a) at 25 °C until 50% conversion followed by (b) temperature lowered to -20 °C for 8 days to complete monomer conversion (c) 25 °C until completion.

Another approach to avoid backbiting reactions was suggested by Bellas *et al.*[25] who suggested the employment of a sequential two-step methodology for the anionic ring-opening polymerization of D_3. In this approach, the polymerizations were allowed to continue until 50% conversion at room temperature, afterwards, temperature was reduced to -20 °C and allowed to go to completion. The success of this methodology is shown by the SEC chromatograms in Figure 1.11. Figure 1.11(a) was obtained when a sample from the polymerization was obtained at 50% conversion. Then, the temperature was lowered to -20 °C and the reaction allowed to go to full conversion. As can be seen from the Figure 1.11(b), no significant change was observed in dispersity of the polymer. This clearly showed the competition between propagation and side reactions was significantly reduced at the lower temperature, if not prevented totally. This may be due to the lack of energy to rotate chains freely and overcome steric hindrance. Figure 1.11(c) shows what happened when the polymerization was allowed to go to completion at room temperature. Although this method is effective, it is not preferred to the pre-completion termination approach. The cost of D_3 monomer is rather low and usually reducing temperatures have significant effects on reaction kinetics. Also, the results of this study were challenged by Ninago *et al.*[23] who stated that this approach did not consider the synthesis of high target molecular weight samples. Ninago established that when the target molecular weight is over a million g mol^{-1}, lowering the reaction temperature actually promotes secondary reactions and leads to a broad molecular weight distribution. A possible explanation can be the movement restrictions of high MW propagating chains at low temperatures which can create insufficient monomer environment. Therefore, the approach of Bellas *et al.* is only valid if the target molecular weights are low (less than 20000 g mol^{-1}).

1.4.3 Polymethylvinylsiloxane

Polymethylvinylsiloxane (PMVS) is synthesised from the anionic ring-opening polymerization of 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (V_3) (Figure 1.12). V_3 monomer polymerizes in a similar fashion to D_3 monomer but potentially with improved kinetics. The vinyl groups around the monomer further increases the ring strain and makes the ring Si-O more susceptible to nucleophilic attack and opening of the ring. Initiation is again performed with alkyllithiums in a non-polar solvent which is followed by the addition of a promoter.[26]

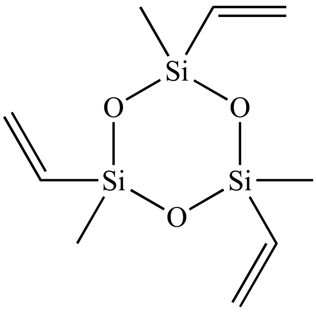


Figure 1.12: 1,3,5-Trivinyl-1,3,5-trimethylcyclotrisiloxane monomer.

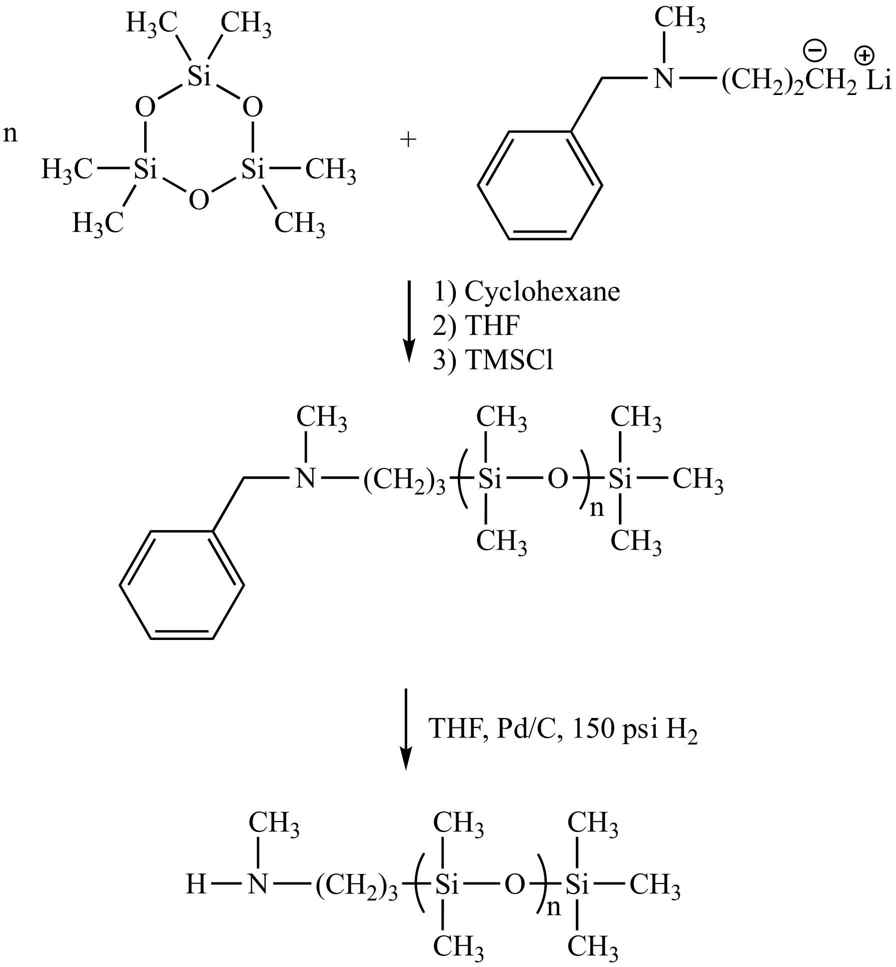
V_3 and D_3 can be copolymerized to introduce vinyl groups in to the polymer chains which can then be used subsequently for the introduction of functional groups and the synthesis of highly branched polysiloxanes (see later). Rate constants of the monomers for this copolymerization was previously determined as $r_{V3} = 17.8$ and $r_{D3} = 0.035$ at 25 °C in THF.[40, 41] These reactivity ratios indicate that V_3 monomer has a tremendous potential to homopolymerize and D_3 to copolymerize. This suggests an almost perfect block sequence of polymethylvinylsiloxane (PMVS) and polydimethylsiloxane (PDMS).

1.5 Functionalization of Polymers

The introduction of functional groups to polymers has always attracted enormous interest from the scientific community. Functional groups on polymers can participate in chain extension and branching, coupling with other reactive groups on other polymers and initiation of other polymerizations. For mechanisms like free radical polymerization, the usage of functional monomers is feasible, however, anionic polymerization cannot tolerate the functional groups on monomers and side reactions terminate the polymerization. For anionic polymerization, the two most common approaches to introduce functionality are the application of (protected) functionalized initiators and/or the end functionalization with electrophilic reagents.[10, 24]

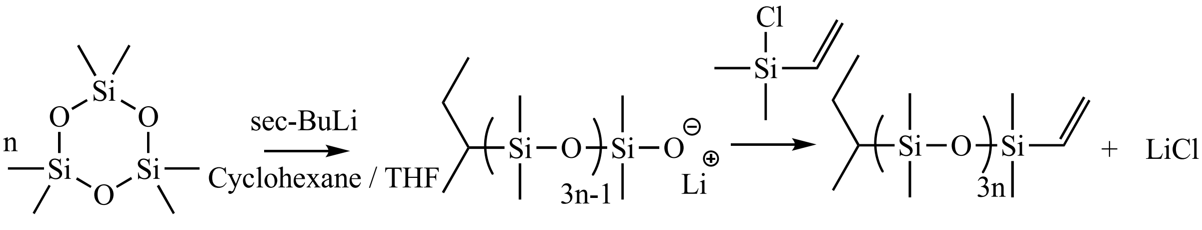
1.5.1 Functionalized Initiator Approach

In general, functionalized initiators are molecules containing functional groups, such as a hydroxyl or an amine, and they can be initiated by alkyllithiums or alkali metal. The functional groups require protection as most of the useful functional groups are not stable in the presence of organolithium reagents. A suitable protecting group is the one that can survive the polymerization conditions and can be removed easily after the polymerization without damaging the polymer backbone.[10] This approach has distinct benefits; as the macromolecule is grown from the functionalized initiator, all chains are functionalized irrespective of molecular weight. An example is given on Scheme 1.8 from the work of Elkins and Long.[24] The researchers introduced a secondary amine group to the PDMS chains by using the functionalized protected initiator 3-[(N-benzyl-N-methyl)amino]-1-propyllithium. The secondary amine was protected with a benzyl group which was removed post-polymerisation with a Pd/C catalyst with no damage to the PDMS backbone.



Scheme 1.8: The anionic ring-opening polymerization of hexamethylcyclotrisiloxane initiated by the functionalized initiator - 3-[(N-benzyl-N-methyl)amino]-1-propyllithium and the subsequent deprotection reaction.[24]

1.5.2 End Functionalization with Electrophilic Reagents



Scheme 1.9: End functionalization of living polydimethylsiloxane chains with chloro(dimethyl)vinylsilane.[39]

The most widely adopted approach to functionalize chain ends is the introduction of functionalized electrophilic reagents to terminate anionic polymerizations. An example is provided on Scheme 1.9. Hammouch *et al.*[39] used chloro(dimethyl)vinylsilane to end-capped the living chains. This approach has some inherent problems. For example, the mixing of the end-capping agent must be rapid and efficient in viscous mediums which is not always the case. Also, some chains will always die prior to induced termination as trace amounts of impurities may find a way to contaminate the reaction vessel. Therefore, in practice, complete functionalization by end-capping agents is very challenging.

1.6 Branched Polymers

A polymer consisting of more than one backbone is called a branched polymer. These polymers have chains interconnected via branch points which are also known as junction points. These points are small groups of atoms that connect two or more chains together. By definition, any polymer having more than two end groups is a branched polymer. It is well established that the polymer architecture plays an enormous role on determining the polymer properties. Branching is known to affect the crystallinity, physical properties and solution and melt viscosities of polymers. Having multiple chain-ends results in compact polymer structures, increased solubility and decreased viscosity.[10]

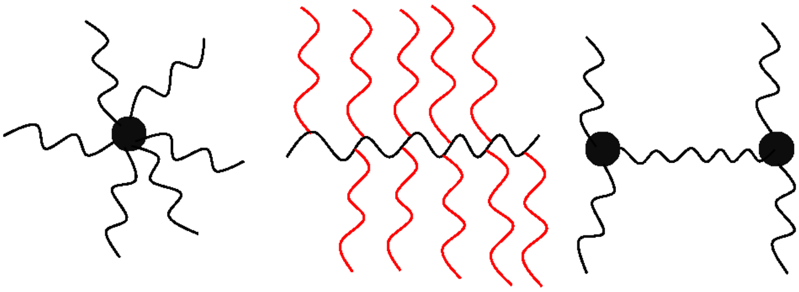


Figure 1.13: Examples of branched polymers; left – star-branched, middle – graft/comb and right – H-shaped.

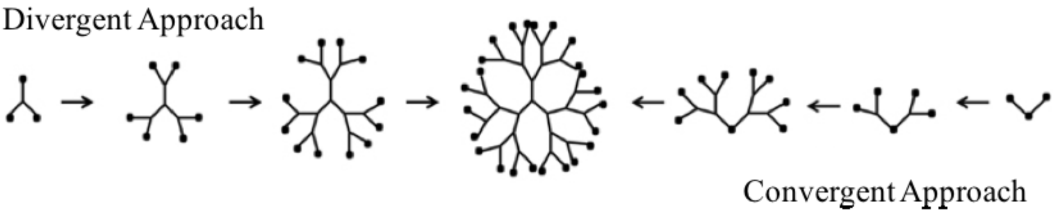


Figure 1.14: Illustrations of divergent and convergent approaches to form dendrimers.[42]

Branched polymers can be mainly divided into star-branched polymers, graft/comb polymers, H-shaped polymers (Figure 1.13) and dendritically branched polymers. Star-branched polymers consists of a single junction point where several units are linked together. Graft/comb polymers are molecules where multiple side chains (arms) are linked on to the main chain's backbone. H-shaped branched polymers contain another branch point in addition to one in star-branched polymers.[10] Dendritically (hierarchically) branched polymers include dendrimers and hyperbranched polymers. Dendrimers are perfectly branched polymers with a dispersity value of 1. They are extremely compact and contain high number of chain ends. There are two main approaches to synthesize dendrimers – divergent and convergent approach (Figure 1.14). In divergent approaches (inside out), synthesis starts from a core and monomers are added stepwise for each generation. In a convergent approach (outside in), synthesis starts by forming branches and then coupling these branches on to a multifunctional core. As one can easily understand, the synthesis of dendrimers is extremely time-consuming and a dispersity of 1 is almost impossible at high molecular weights. Hyperbranched polymers can be considered as practical alternatives to dendrimers. They are usually synthesised in one-pot reactions. They have high branching density and high number of chain-ends as in dendrimers but lack the regularity in terms of structure. They are usually synthesised by the coupling of AB_2 (macro)monomers to each other.[26, 42]

1.6.1 Branched Polysiloxanes

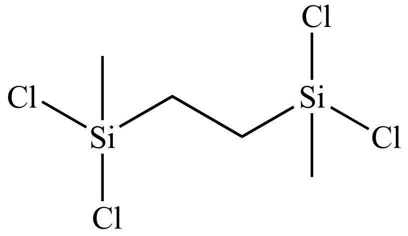


Figure 1.15: 2,2,5,5-Tetrachloro-2,5-disilahexane.

In 2003, a method was suggested by Chojnowski *et al.*[26] to synthesised highly branched polysiloxanes in which the group attempted to copolymerize D_3 and V_3 monomers, to introduce vinyl groups on to the polysiloxane chain. Anionic ring-opening polymerization was used for the preparation of these building blocks. Then, the living blocks were grafted, during the termination step, on to 2,2,5,5-tetrachloro-2,5-disilahexane (Figure 1.15) to give the star polymer (Figure 1.16). The exposed vinyl groups were then coupled with chlorodimethylsilane via a hydrosilylation reaction with Pt catalyst to add Si-Cl bonds to the branched polymer. This branched polymer was then used for the termination of other living blocks and dendrimer-like highly branched polysiloxanes were synthesised.[26]

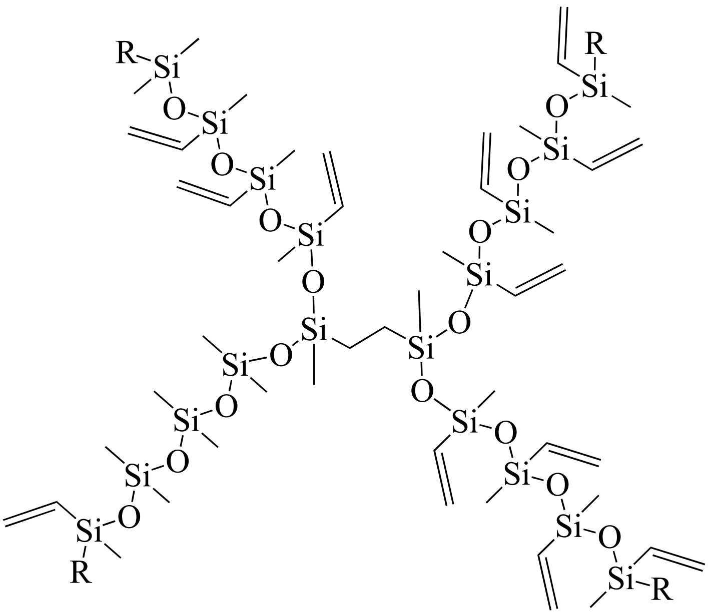


Figure 1.16: A star polymer synthesised by Chojnowski et al.[26]

1.7 Aims and Objectives

Polysiloxanes bear significant amount of essential properties and are an important class of polymers in their own right. The polymer itself is biocompatible, highly flexible, hydrophobic and has low surface energy. It is very well-known that functional groups, branching and architecture directly affects polymers' thermal behaviour, crystallization and rheology. In the present work, we aim to synthesise functionalised polysiloxanes (macromonomers) by anionic ring-opening polymerization and to couple these macromonomers to form highly branched polysiloxanes. These macromonomers are intended to be AB_2 and AB_x where A and B represent different functional groups on the polymer chain. For the AB_2 approach, A is a carbon-halogen bond and B is a hydroxyl functionality. The polymerization of D_3 is to be initiated by using protected bifunctional initiators to introduce the dihydroxyl group to one end of the chains. We would aim to deprotect the incorporated protected functionalities upon the successful completion of the polymerization. A variety of deprotection reactions is to be attempted to make sure polysiloxane backbone do not degrade during the deprotection reactions. For the AB_x approach, A is a Si-H bond and B is a vinyl group. Vinyl groups are intended to be introduced by copolymerizing the monomers D_3 and V_3. In both approaches, A functionality is intended to be introduced by end-capping reactions. For this purpose, we aim to use chlorosilane derivatives. The intended coupling reactions for AB_2 and AB_x macromonomers are Williamson and hydrosilylation couplings, respectively.

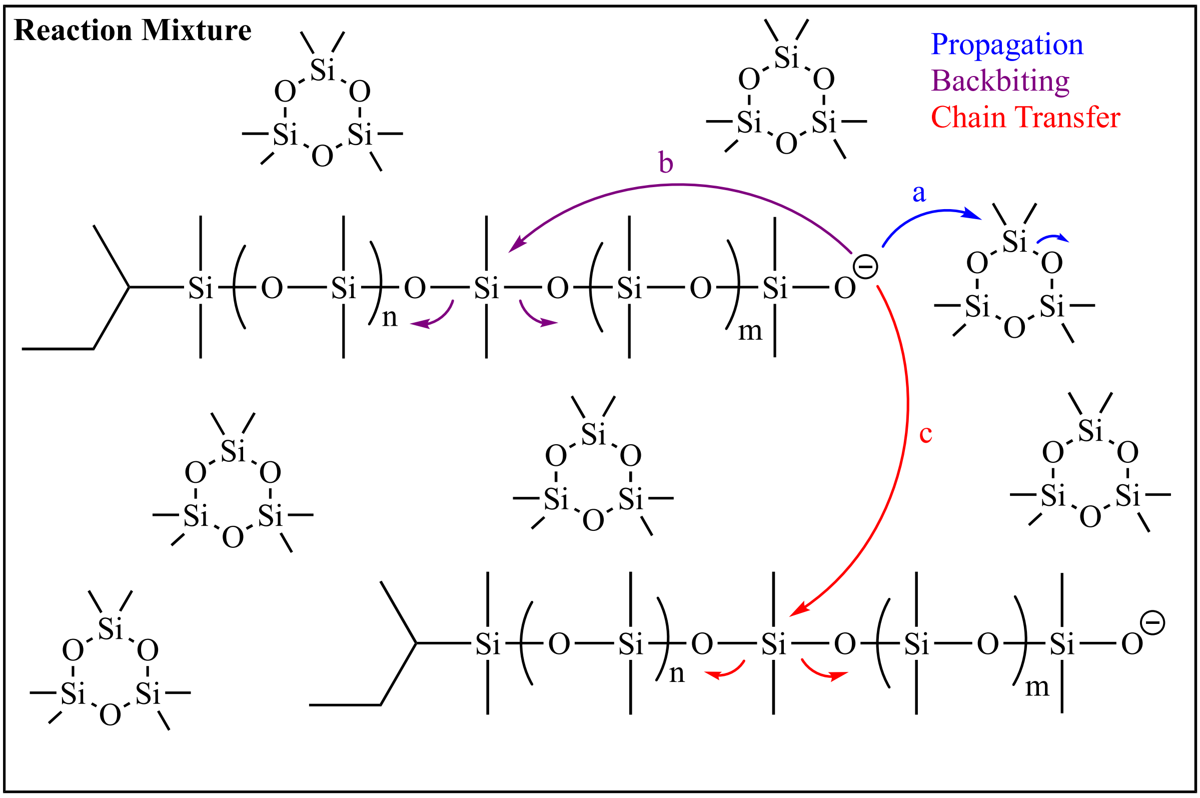
2 Results and Discussion

2.1 The Impact of Side Reactions on the Anionic Ring-Opening Polymerisation of Hexamethylcyclotrisiloxane (D_3)

Anionic polymerization is most well-known for its control over the key polymerization parameters, such as molecular weight and dispersity, as discussed in Sections 1.2 and 1.3. However, hexamethylcyclotrisiloxane is not a common anionic polymerization monomer and unlike other classical living carbanionic polymerization monomers, such as styrene and 1,3-butadiene, its polymer, PDMS, is composed of a polar backbone. This makes the polymer backbone susceptible to the nucleophilic attack of anionic species which includes its own growing chain-end, the siloxane anion. As discussed previously on Section 1.4.2.2.4, chain transfer and backbiting reactions are commonly accepted as the main side reactions competing with the anionic polymerization of D_3 and these secondary reactions are known to increase in occurrence at high monomer conversions. The initial objective therefore was to study the impact of side reactions on the control of molar mass and dispersity at high conversions for PDMS with varying target molecular weights. To gain experience and understanding of this particular anionic ring-opening polymerization, a series of polymerization reactions were carried out with increasing target molar mass. Samples were collected at intermediate times for analysis by SEC and NMR to establish the impact of conversion on dispersity.

2.1.1 The Mechanism of Propagation and Side Reactions in the AROP of D_3

There are three main reaction pathways/mechanisms that can take place during the anionic ring-opening polymerization of D_3 (Scheme 2.1). The living siloxane anion can attack a monomer (a), its own backbone (b) or another chain (c). The pathway ‘a’ results in propagation whereas the pathways ‘b’ and ‘c’ result in secondary reactions. The reactions resulting from these two pathways are known as back-biting (intramolecular) and chain transfer (intermolecular) reactions and they are known to compete with propagation at high monomer conversions. A detailed discussion, again, is provided in Section 1.4.2.2.4.



Scheme 2.1: The possible reaction pathways for the living siloxane chain-end during the AROP of D_3.

Upon the attack of the siloxane chain-end to an O-Si-O bond, there are two potential oxygen atoms to accept the electron pair. For backbiting reactions, only one of these directions forms different products from the starting propagating chain-end. These products are a dormant macrocycle and a small propagating PDMS chain. However, in the case of chain transfer reactions, the direction which electron pair moves changes the products. A chain transfer can potentially form one dormant PDMS chain and a propagating chain with two anions or two propagating chains. In all these reactions, molar mass of the chains change and this directly affects both number- and weight-average molecular weight of the resulting polymer. It is believed that the presence of these reactions could be easily followed by SEC as dispersity would change dramatically. However, the SEC analysis of PDMS is not a straightforward task.

2.1.2 Size Exclusion Chromatography of Polydimethylsiloxane

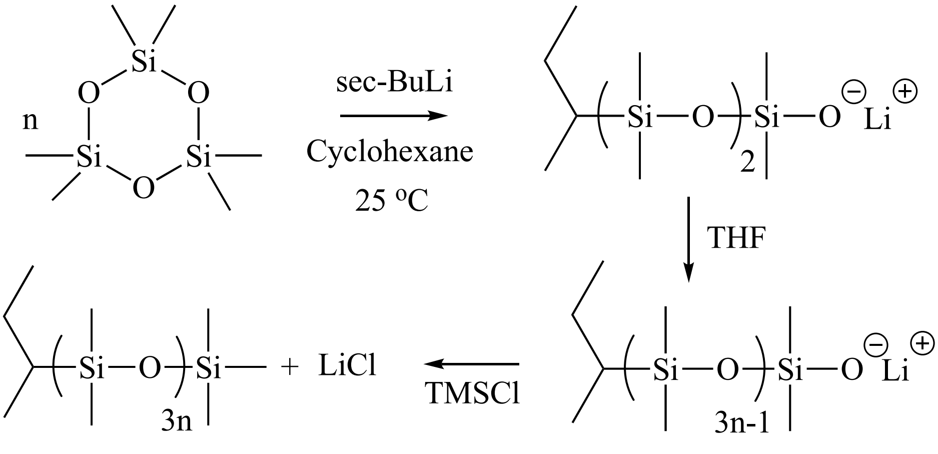
The dispersity analysis was performed by using SEC, also known as gel permeation chromatography (GPC). Information about how this technique works can be found in the literature.[43] The Hutchings' group most commonly uses a THF triple detection SEC system equipped with refractive index, viscometer and light-scattering detectors. SEC analysis of PDMS using such a system presents a significant challenge as PDMS is isorefractive with THF and, in most cases, refractive index data is very weak and no light scattering is detected. This clearly eliminates any possibility of using a triple detector calibration in this solvent. Whilst it is possible to change the solvent of the SEC machine to toluene or another solvent in which PDMS is not isorefractive, since THF is the most widely used solvent for SEC analysis, this approach was considered time-consuming and impractical and it was decided to explore the use of different calibrations – namely conventional and universal. These calibrations are both constructed from (most frequently) narrow dispersity polystyrene standards and used to estimate molecular weights.

A conventional calibration uses only refractive index (concentration) detector and a calibration curve. As such, the molar mass obtained for an unknown polymer is always relative to polystyrene standards and thus is not accurate. Moreover, since elution time is the only variable in analysis by a conventional calibration, any flow rate variation can lead to further inaccuracies. However, this calibration method is simple and fast and is useful for providing comparative data for different samples of the same type of polymer. If a reasonably intense refractive index peak can be obtained, dispersity values are reliable since any inaccuracy in number-average molecular weight (M_n) and weight-average molecular weight (M_w) would be systematic. This can be achieved by increasing the concentration of the sample from approximately 1 mg ml^{-1} (most common concentration used in the Group) to 4 mg ml^{-1}. This increases the intensity of the PDMS RI peak four times and allows a more reliable calculation of dispersity.

A universal calibration was another option. In this case, a calibration curve relating the hydrodynamic radius (volume) and retention time is constructed.[44, 45] This calibration additionally uses data from a viscometer detector which is very strong for PDMS. It assumes that two macromolecules would have the same retention volume only if their hydrodynamic volumes are the same when they are dissolved in the same solvent at the same temperature. A universal calibration needs to calculate hydrodynamic volume which requires the calculation of concentration from the refractive index signal and intrinsic viscosity from the viscometer. For the concentration calculation, it is necessary to provide the SEC analysis software with the refractive index of PDMS in THF. This value was reported by Bellas *et al.*[25] as 0.005 ml g^{-1} for PDMS in THF at 25 °C by using a refractometer at 633 nm. However, the SEC system used in Hutchings' laboratory operates at 670 nm. This means that the *dn/dc* value is also not accurate and requires a recalculation. It was attempted to obtain a reasonable light scattering signal by using a standardized sample concentration of 5.00 mg ml^{-1} to measure *dn/dc* at 670 nm. Unfortunately, even this high sample concentration did not result in a sufficiently intense light scattering signal and attempts to calculate refractive index failed. Even a small change in refractive index is important as, for example, a change of ± 0.001 ml g^{-1} means a change of ± 20% in molecular weight calculations.[43] It is possible to prepare a standard polymer solution before each SEC run, so the software do not need to calculate the concentration. However, this method is rather time-consuming and impractical considering the potential number of samples.

It was decided therefore to establish a conventional calibration using polystyrene standards and compare the results with M_n obtained from NMR data whenever M_n values are significant for analysis. NMR is not a relative technique unlike conventional calibration and therefore, the results obtained from NMR were treated as absolute. All SEC results presented in this thesis are obtained using a conventional calibration of polystyrene standards unless otherwise stated. Only M_n and M_w were reported in this thesis as they are enough to describe molecular weight distribution of a polymer (M_w/M_n).

2.1.3 The Impact of Monomer Conversion on the Extent of Side Reactions



Scheme 2.2: Procedure followed to synthesise polydimethylsiloxane polymers by AROP of D_3.

A series of polymerizations were run to explore the impact of monomer conversion on the extent of side reactions. Standard synthetic methods were used in these polymerizations (Section 1.4.2.2) - hexamethylcyclotrisiloxane monomer was initiated with sec-BuLi in cyclohexane and propagation was started by the addition of THF. Termination was achieved by the addition of chlorotrimethylsilane. All polymerizations were performed at room temperature (Scheme 2.2). Samples were collected at various times during the polymerizations of PDMS 1, PDMS 2 and PDMS 3 (Table 2.1). Molecular weights were determined by SEC and NMR. An example calculation from NMR is provided below.

Table 2.1: A summary of results obtained for initial PDMS polymerizations (SEC THF, PS conventional calibration).

PDMS 1 - 10000 g mol^{-1}	**M_n / g mol^{-1}**	**SEC**	3000	5000	13000	-
		NMR	4400	7200	11000	-
	Đ		1.06	1.09	1.09	-
	Time / h		1	2	24	-
	Conversion[1] / %		23	38	100	-
PDMS 2 - 20000 g mol^{-1}	**M_n / g mol^{-1}**	**SEC**	14000	15000	18000	27000
		NMR	12000	13000	16000	23000
	Đ		1.05	1.05	1.05	1.12
	Time / h		4	5	6	24
	Conversion[1] / %		51	55	67	100
PDMS 3 - 40000 g mol^{-1}	**M_n / g mol^{-1}**	**SEC**	30000	32000	35000	39000
		NMR	28000	-[2]	-[2]	39000
	Đ		1.11	1.12	1.14	1.20
	Time / h		7	8	9	24
	Conversion[1] / %		77	82	90	100

[1] Conversion values were predicted by assuming 24h corresponds to 100% conversion. This assumption based on the fact that target molecular weights were achieved after 24 hours. [2] Samples were lost after SEC analysis and NMR could not be run.

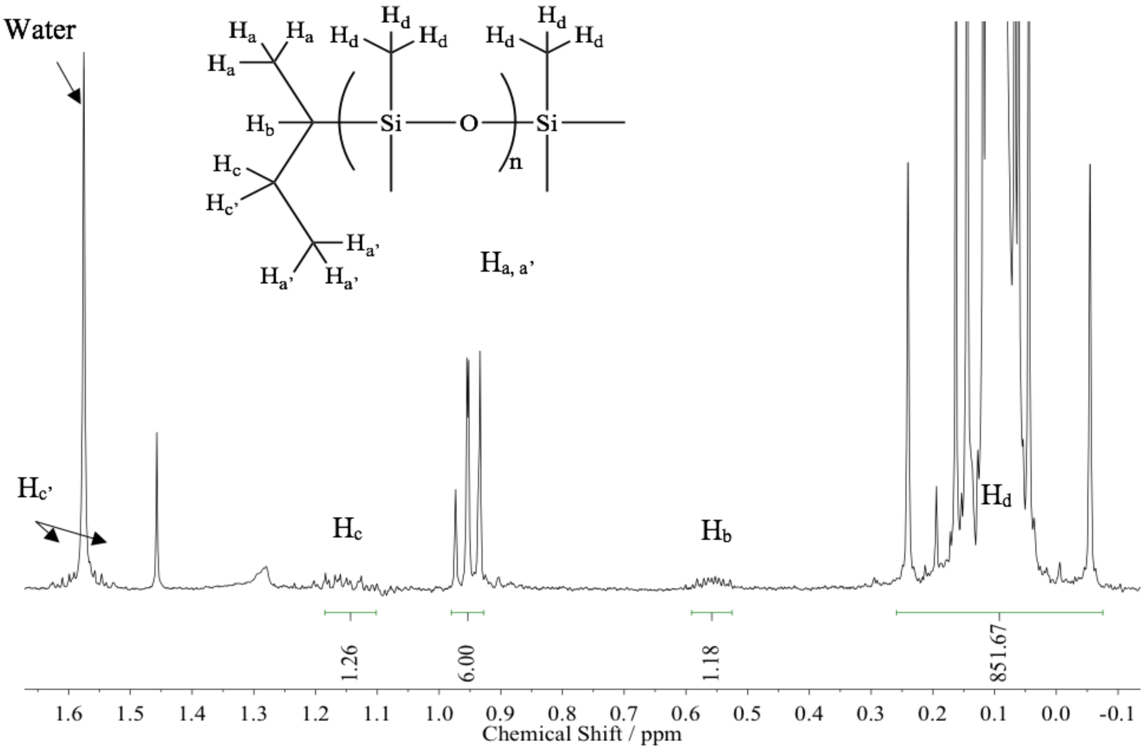


Figure 2.1: The ^1H NMR ($CDCl_3$) spectrum obtained from PDMS 1 after 24 hours.

Calculation 2.1: Calculation of number-average molecular weight of PDMS 1 from NMR.

$$\frac{\text{852 protons}}{\text{6 protons per repeat unit}} = \text{142 repeat units}$$

142 repeat units x 74 g mol^{-1} per repeat unit = 10508 g mol^{-1} ≈ 11000 g mol^{-1}

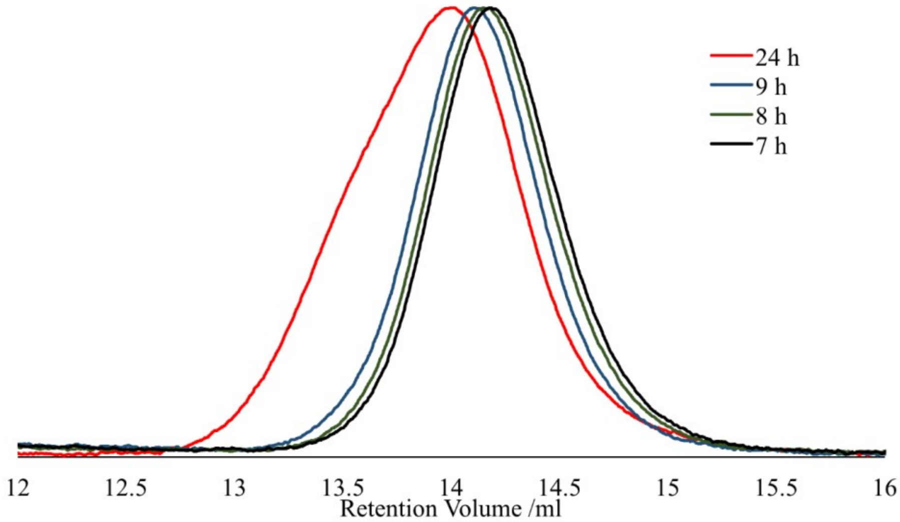


Figure 2.2: SECs obtained from PDMS 3 targeting 40000 g mol^{-1}.

The dispersity of PDMS 1 reached its maximum after 2 hours whereas PDMS 2 and PDMS 3 showed significant increases in dispersity when the polymerizations were left to continue overnight. A clear illustration of this increase is shown on Figure 2.2. SEC chromatograms obtained after 7 h, 8 h and 9 h have similar shapes. However, when the polymerization was allowed to go to higher conversions overnight, a clear change was observed in dispersity. Such a change in molecular weight distribution is a strong indication of back-biting and chain transfer reactions.

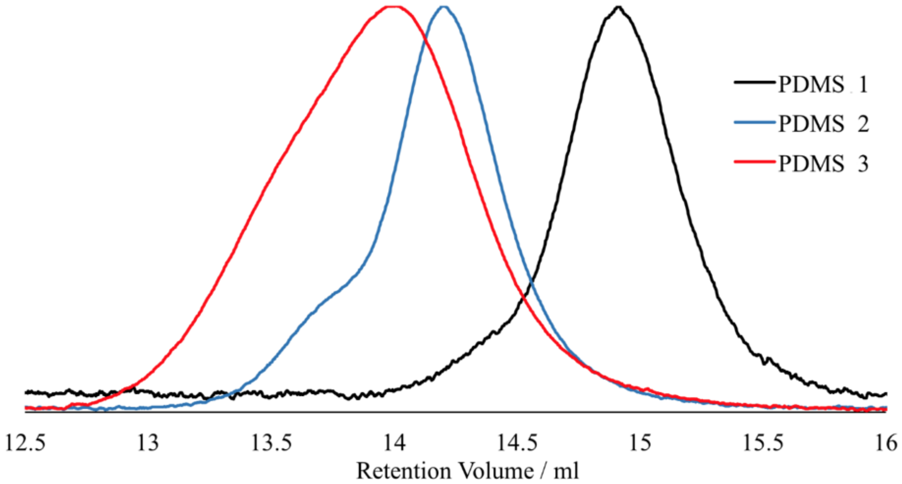


Figure 2.3: A comparison of SEC chromatograms for polymers following termination after 24 hours.

Figure 2.3 illustrates the SEC chromatograms of the samples obtained after 24 hours from PDMS 1-3. It seems like PDMS 1 did not suffer significantly from secondary reactions. One may expect that the longer the chains, the more pronounced the side reactions, such as back-biting reactions. This suggests that low molecular weight PDMS polymers are less susceptible to changes by the known secondary reactions. This might be because viscosity does not change significantly to elevate secondary reactions. Shoulders are clearly seen towards lower elution times (higher molecular weights) for PDMS 2 and PDMS 3 at completion. These shoulders may arise for several possible reasons. Firstly, the coupling of polymer chains to form a higher molecular weight polymer. These polymerizations were terminated by using chlorotrimethylsilane (TMS-Cl) and precipitated in methanol. Any excess TMS-Cl would react with methanol to form methoxide anion and HCl. Trimethylsilyl (TMS) group is well-known for its labile nature. Therefore, methoxide anion can remove TMS group from the polymer and may form a hydroxyl-terminated polymer. Two hydroxyl-terminated PDMS may combine with a condensation reaction. However, this explanation is seen unlikely to be the case, since all samples were terminated with excess TMS-Cl but their SECs do not show any shoulders or tails (Figure 2.2). However, for the sake of preventing any chain coupling reactions that might have happened in future, it was decided to use only a small excess of the end-capping agent. Secondly, chain transfer reactions may lead to the formation of these shoulders. In Scheme 2.1, it was mentioned that these side-reactions may form one very high molecular weight chain and one low molecular weight chain. This low molecular chain may be so small that it dissolves in methanol and lost during precipitation. Thirdly, the formation of knotted cyclic polymers (Figure 2.4). Since cycles formed by backbiting reactions are macrocycles, some other living polymer chains may pass through inside them and backbite themselves. This would form interconnected cyclic polymers. These connected macrocycles are more likely to be seen in PDMS polymerizations with higher molecular weight targets since these form bigger macrocycles and towards end of polymerizations viscosity increase. There is an article that reports these interconnected macrocycles may occur during the cyclization reactions of PDMS containing copolymer macrocycles.[46] However, to the best of our knowledge, these shoulders were not previously observed for back-biting reactions in literature.

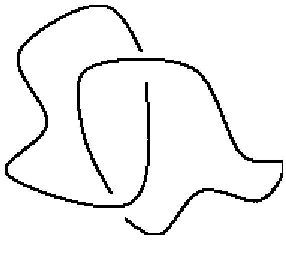


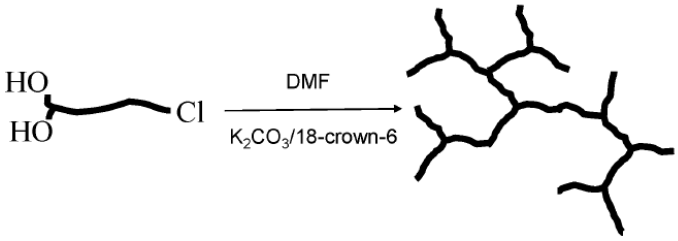
Figure 2.4: A knotted macrocycle structure.

The main objective of this part of the research was to gain expertise in the practicalities of carrying out the anionic polymerization of D_3 and to determine the optimal monomer conversion to ensure that propagation is favoured over backbiting and chain transfer reactions. Although conversion data was not obtained, it can be estimated from SEC results. One can assume the polymerizations almost reached to completion in 24 hours as target molecular weights were achieved in the same period. When this assumption applied, conversion values can be obtained (Table 2.1) and it can be clearly seen from results that dispersity starts to increase at high conversions, i.e. monomer starved conditions, for high molecular weight PDMS ($\geq$ 20000 g mol^{-1}). This suggests that any polymerizations with high molecular weight target should be terminated prior to high conversions in order to keep dispersity in control. This is particularly important, since in the subsequent investigations, attempts will be made to produce end-functionalized PDMS using functionalized initiators and end-capping agents. If back-biting reactions occur, the percentage of end-functionalized chains may significantly decrease. It was decided therefore to synthesise only low molecular weight PDMS chains ($\leq$ 10000 g mol^{-1}) since a proof of concept is all we need and then this can be then applied to high molecular weight PDMS polymers. Polymerizations were terminated after 7 hours in cases where the target molecular weight was around or less than 10000 g mol^{-1}. This is believed to correspond to approximately 70-80%.

2.2 An Attempt to Synthesise PDMS AB$_2$ Macromonomers

2.2.1 Synthesis of End-Functionalized PDMS via the Use of Functionalized Initiators

One of the key objectives of this project was the synthesis of long-chain branched PDMS. Hutchings' Group have previously reported the synthesis of polystyrene and polybutadiene macromonomers which were capable of coupling under suitable conditions to form hyperbranched polymers, namely "HyperMacs" and "DendriMacs" (Scheme 2.3).[47-50] The first step in this macromonomer approach is the synthesis of dihydroxyl end-functionalised PDMS by classical anionic polymerization. To the best our knowledge, this approach has not previously been attempted for the polymerisation of PDMS.



Scheme 2.3: Synthesis of polystyrene HyperMacs.[47]

2.2.1.1 Synthesis of Functionalized Initiator Precursors

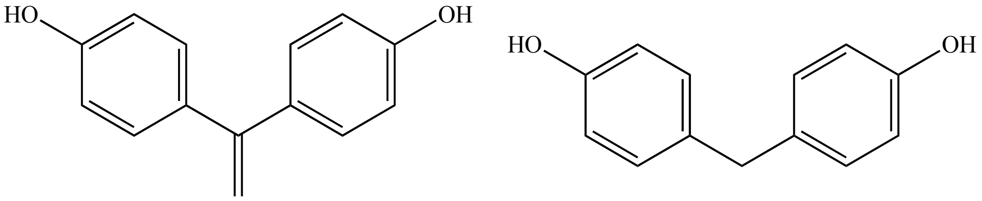


Figure 2.5: Initiator precursors 4,4'-dihydroxy-1,1-diphenylethylene (left) and Bisphenol F (right).

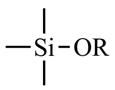
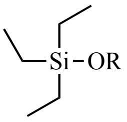
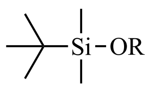
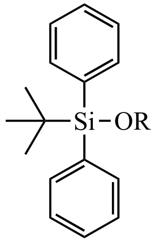
Use of functionalized initiators is a common and useful approach to introduce functional groups on to polymer chains. There are clear benefits of using a functionalized initiator compared to functionality introduced by end-capping a living polymer chain. For example, each initiator molecule generates a single macromolecule chain, whatever the molecular weight of the chain is, all macromolecules will have the functionality. Also, there are no concerns regarding the efficient and rapid mixing of reagents which is a significant problem in end-capping viscous polymer mixtures. It was decided to use the molecules 4,4'-dihydroxy-1,1-diphenylethylene (DPE-OH) and Bisphenol F (BPF) shown on Figure 2.5. Both these molecules were activated by sec-BuLi. DPE-OH was previously used in our research group (and others) to synthesise polystyrene, polymethyl methacrylate and polybutadiene macromonomers, successfully.[50] On the other hand, to the best of our knowledge, there is no previously reported case of Bisphenol F being activated by lithium to initiate a polymerization.

The use of the functionalized initiator approach with anionic polymerisation usually requires a protecting group for the functionality since most of the desirable functionalities are not stable/inert during anionic polymerization. Therefore, a requirement of this strategy is finding a suitable protecting group that will not react with the anionic propagating species and yet can be removed easily following termination.[10] Our target functionality was hydroxyl groups and a range of silyl ether groups were surveyed as potential protecting groups for the hydroxyl.

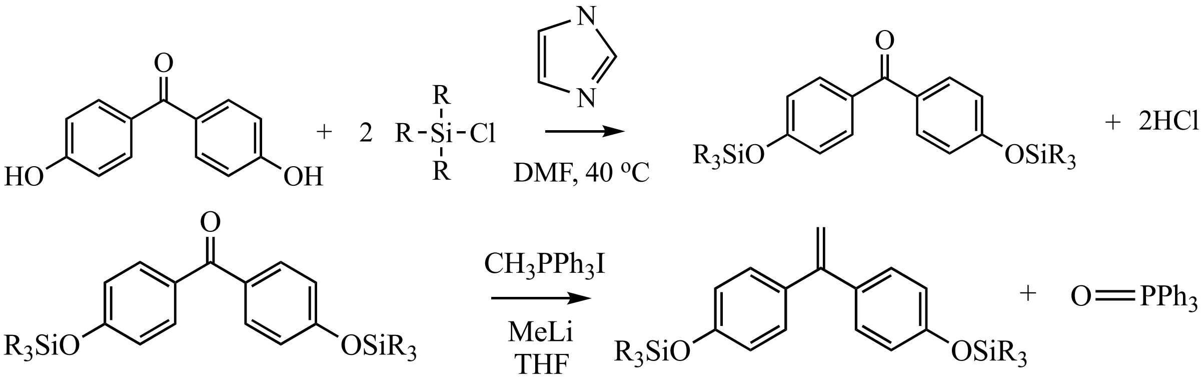
2.2.1.1.1 A Survey of Silyl Ether Protecting Groups

Since the anionic polymerization of D_3 is initiated by sec-BuLi in this case, any protecting group must be stable both to attack by sec-BuLi and the propagating anion formed after the initiation. O-silylation reactions have been widely used for this purpose for decades due to the ability to tune the stability of silyl ether protecting groups by altering the substituents on the silicon atom. A range of silyl ether protecting groups and their relative stabilities in acidic and basic mediums are shown in Table 2.2. The stability of these groups generally increases with increasing bulkiness of the substituents.[51] The trimethylsilyl (TMS) group is well-known for its labile nature and its stability against organolithium compounds is questionable and ambiguous. It is believed that TMS group would not survive the initiation reaction. Triethylsilyl (TES) group is relatively more stable than TMS because of the increased steric bulkiness and more electron-donating nature of the ethyl group. TES group is reported to be stable to organolithium reagents such as MeLi and BuLi.[52] t-Butyldimethylsilyl (TBDMS) and t-butyldiphenylsilyl (TBDPS) are very strong protecting groups with significantly less susceptibility to hydrolysis – the latter being rather too stable in many cases. For the current study, TES and TBDMS protecting groups were initially chosen for the protection reactions.

Table 2.2: Relative acidic and basic stability of different silyl ether protecting groups.[53]

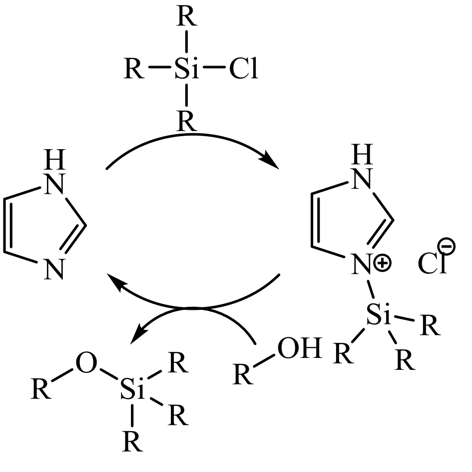
Structure				
Group	TMS	TES	TBDMS	TBDPS
Acidic Stability	1	64	20000	5000000
Basic Stability	1	10-100	20000	20000

2.2.1.1.2 Synthesis of silyl ether protected 4,4’-dihydroxy-1,1-diphenylethylene



Scheme 2.4: Synthesis of DPE-OSi.

TES and TBDMS protected 4,4’-dihydroxy-1,1-diphenylethylene (DPE-OSi) were attempted to be obtained in two steps from 4,4’-dihydroxybenzophenone (Scheme 2.4) following a previously published procedure.[54] The 4,4’-dihydroxybenzophenone was first protected by using either chlorotriethylsilane or t-butyl(chloro)dimethylsilane in the presence of imidazole to yield 4,4-bis(4-triethylsiloxy)benzophenone or 4,4-bis(4-t-butyldimetyhlsiloxy)benzophenone (I). In this reaction, imidazole acted as a base and, also, as a catalyst as it can react with Si-Cl bond and displace Cl to form a more reactive complex (Scheme 2.5). We believe the main purpose of the imidazole in this reaction was to kill (react with) any HCl produced. Imidazole was chosen as it was previously used in the literature reporting the synthesis of this initiator precursor.[54]



Scheme 2.5: Imidazole as a catalyst.

The protected ketone was then converted to an alkene by a Wittig reaction to yield 1,1-bis(4-triethylsiloxyphenyl)ethylene or 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene (II). Although, the Wittig reaction is an extremely useful reaction in organic chemistry, it requires harsh conditions and a demanding work-up and as previously stated, TES group is relatively labile. The Wittig reaction was proven to be successful for the TBDMS protected benzophenone but a very low yield (2%) was observed with the TES protected starting material. NMR analysis of both products reveals presence of a peak at 5.3 ppm, which confirms the alkene group in both molecules (Figure 2.6), however, the presence of secondary peaks at 0.95-0.74 ppm for the TES-protected alkene and at 0.96-0.25 ppm for TBDMS-protected alkene suggests the decomposition of the protecting group. One can say both protecting groups suffered from the harsh conditions of the Wittig reaction. A yield of 2% was obtained for the TES-protected product whereas the yield was 62% for the TBDMS-protected product. TES and TBDMS groups are known to be stable under conditions with excess MeLi.[52] However, it is proposed that since the formed ylide complex, being unstabilized, was extremely reactive and attacked the Si-O bond. In addition, the ylide complex with all its bulky phenyl groups may fail to approach and attack the TBDMS groups due to its steric bulk whereas the ylide may approach the TES group as it is not bulky. Since the synthesis of the TES-protected initiator precursor did not work well, whenever DPE-OSi is written in this thesis, it means TBDMS-protected 4,4'-dihydroxy-1,1-diphenylethylene, unless otherwise stated.

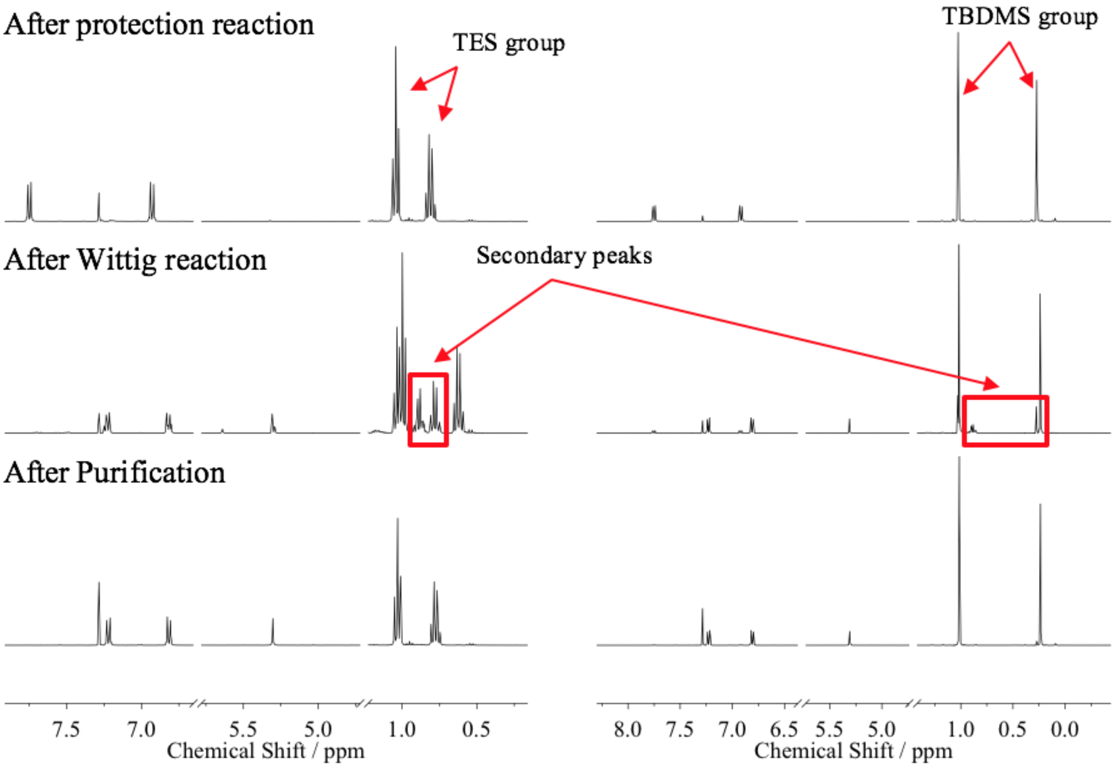
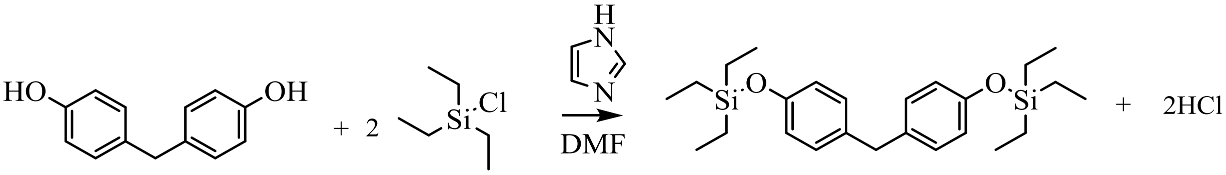


Figure 2.6: A comparison of ^{1}H NMR ($CDCl_3$) spectra before and after the Wittig reaction and the purified final product for both TES-protected (left) and TBDMS-protected (right) initiator precursor.

2.2.1.1.3 Synthesis of Protected Bisphenol F



Scheme 2.6: Protection of Bisphenol F with TES-Cl.

The hydroxyl groups of Bisphenol F were protected based on the procedure for 4,4'-dihydroxybenzophenone (Scheme 2.4). In this case only the TES protecting group was used as there is no need for a strong protecting group since the Wittig reaction is not necessary.

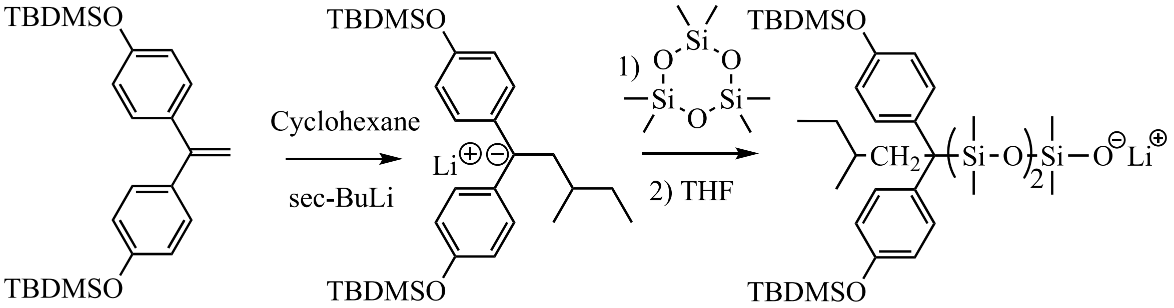
2.2.2 Initiation of PDMS Polymerization with the Functionalised Initiator Precursors

2.2.2.1 Initiation with DPE-OSi

The anionic polymerisation of D_3 is usually achieved using sec-BuLi. In order to introduce DPE-OSi at the chain end of PDMS, the DPE-OSi first needs to be "activated" by reaction with sec-BuLi in cyclohexane at room temperature – see Scheme 2.7. The kinetics of 1,1-diphenylethylene (DPE) and sec-BuLi reaction is very well studied and known to be fast and efficient. The kinetic studies showed the addition of sec-BuLi to DPE is irreversible and, almost without exception, the result is a monoaddition (even in the presence of excess DPE) because of the bulky nature of the DPE molecule.[10, 55] DPE-OSi, a derivative of DPE, has electron-donating silyl ether protecting groups on the para position of the phenyl rings. Oxygen atoms have lone pairs that they can donate into the phenyl rings which then conjugate with the double bond and deactivate it. This deactivation forms more reactive propagating species since the electron density is high and it makes DPE-OSi less reactive compared to DPE.[56] Inductive effects of oxygen are relatively weak and localised.

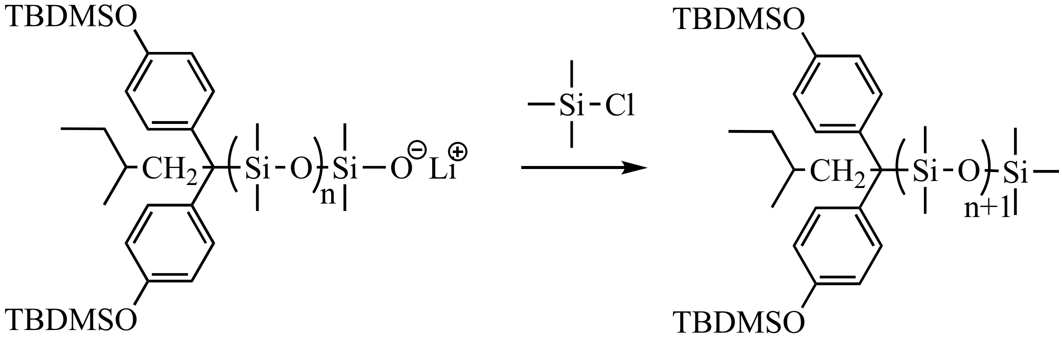
Table 2.3: The SEC results obtained from the initiation of PDMS polymerization via DPE-OSi (SEC THF, PS conventional calibration).

Experiment	Target Molecular Weight / g mol^{-1}	M_n / g mol^{-1}	Dispersity	Yield / %
DPE-PDMS 1	10000	14000	1.16	28
DPE-PDMS 2	9000	31000	1.18	84



Scheme 2.7: Initiation of hexamethylcyclotrisiloxane with the synthesised initiator, DPE-OSi.

Initially, DPE-OSi was purified by 'titration' by dropwise addition of sec-BuLi, under a nitrogen atmosphere, until a persistent red colour of the diphenylhexyllithium adduct was observed. 60 µl of 1.4 M sec-BuLi in cyclohexane was required to titrate 0.25 g DPE-OSi. The titration step ensures the removal of any impurities remaining in the reaction mixture.[50] The delocalisation of the anion formed around the phenyl groups shifts the absorption to longer wavelengths and the colour arises from the strong UV-Vis absorbance at 440 nm.[10] Then, 0.8 equivalents of sec-BuLi with respect to DPE-OSi was injected into the medium thus ensuring an excess of DPE-OSi and eliminating the possibility of the initiation of D_3 polymerization by sec-BuLi.[10] The activation reaction of DPE-OSi was initially allowed to proceed overnight but in later experiments it was considered complete after 3 hours which is known to be sufficient from previous work in the Hutchings research group.[47, 50, 57] Following the complete activation of DPE-OSi, D_3 monomer was added by vacuum distillation (Scheme 2.7). Living siloxane chains are known to be colourless and therefore, a colour change from dark red to colourless was expected. However, after 24 hours at RT no apparent colour change was observed. It was assumed that the lack of initiation could be the result of steric hindrance between the bulky phenyl groups of DPE and cyclic D_3 monomer. In an attempt to overcome this lack of reaction, the temperature was increased to 50 °C and the initiation process allowed to continue for 4 days at this temperature. The colour of the solution did change from dark red to orange and then, to yellow. This colour change may indicate either a successful reaction between activated DPE-OSi and D_3 monomer and/or termination of the living chains by impurities. 5 days in total is a long time and the environment used for the polymerization is not perfect. Septum caps may leak allowing small amounts of air to enter the reaction vessel (more information about the reaction vessel can be found in Experimental), especially if the septum cap was used for injection. It is believed both possibilities contributed to this change of colour. THF was subsequently added via vacuum distillation at this point in an attempt to instigate propagation – more information about why THF is needed can be found on Section 1.4.2.2.2. The yellow colour faded as polymerization continued (Scheme 2.8). The reaction was terminated with chlorotrimethylsilane 7 hours after the addition of THF to minimise the impact of any secondary reactions. The colour changed to colourless immediately. The polymer (DPE-PDMS 1) was recovered by precipitation in methanol. The yield was 28% and the polymer was analysed by THF SEC and NMR.



Scheme 2.8: The termination step of the DPE-OSi initiated D_3 polymerization.

The target molecular weight for this polymerization was 12300 g mol^{-1} (for 100% conversion) but since the polymerization was believed to be terminated at around 70-80% conversion, target M_n was around 10000 g mol^{-1}. SEC gave an M_n value of 14000 g mol^{-1} and therefore, it is believed that the target molecular weight was slightly missed. The initiation of DPE-PDMS 1 took 5 days and the propagation took 7 hours. This could potentially lead to a decrease in the number of active chains due to termination by impurities as discussed previously. If the number of active chains decreases, then the target molecular weight increases, so does the time required the polymerization need to go to completion. Therefore, it can be the case that this polymerization was terminated at an earlier degree of monomer conversion. However, this cannot alone explain the low yield of 28 % alone. It is quite possible that low yield was a result of loss during work-up.

The main objective of this experiment was to confirm that the polymerization of D_3 can be initiated by DPE-OSi. NMR analysis of the recovered polymer showed peaks at 6.75 and 7.07 ppm (Figure 2.7) which can be assigned to the aromatic hydrogens of the DPE rings and would appear to suggest a successful experiment. However, the NMR also exposed some problems. A perfectly (100 %) initiated polymer would have 8 aromatic DPE-OSi protons and the ratio of this peak with the polymer peak would give the number-average molecular weight of the polymer. When this fact is applied, the NMR suggests a M_n value of 34000 g mol^{-1}. However, the molar mass obtained via SEC analysis (conventional calibration, polystyrene standards), which generally agreed with NMR results during the optimization studies described above, was 14000 g mol^{-1} with a dispersity of 1.16. When M_n obtained from SEC was converted into the degree of polymerization and multiplied by the number of protons in each monomer, an approximate integral value is obtained for the polymer peak in the NMR spectrum. Integration of aromatic peaks relative to this integral value gives an estimate of percentage of chains initiated by activated DPE-OSi (Calculation 2.2 and Figure 2.7). This was calculated as 43 %. This is a rough estimation and it must be noted that although there was a good agreement between NMR and SEC, the relationship was not perfect. It can be seen from Table 2.1 that for PDMS polymers with a molecular weight higher than 10000 g mol^{-1}, SEC slightly overpredicted the M_n which means actual number of chains initiated by the activated DPE-OSi can be slightly lower than this reported percentage. The calculation suggests a high percentage of polymers was not in possession of the activated DPE-OSi. This can happen as a result of two scenarios. First, back-biting reactions could have resulted in PDMS macrocycles and second, a result of chains being initiated by sec-BuLi alone. It is believed that the amount of sec-BuLi injected during titration and initiation was actually more than the amount of DPE-OSi weighted and placed into the reaction vessel. This could happen if DPE-OSi was impure and contained some impurities contributing to its weight or during the titration with BuLi and some of the DPE-OSi might have reacted and then been deactivated by impurities. Such impurities can be trace amounts of triphenylphosphine oxide, from the Wittig reaction, and potentially deprotected alcohol containing DPE-OSi. It was shown earlier that the conditions for the Wittig reaction is harsh and this can cause the removal of the protecting groups. It is possibly that some of these side products from the Wittig reaction co-crystallized with the main product and remained as impurities. In this way, the amount of DPE-OSi available for the polymerization was reduced and it was possible that when the required amount of BuLi for initiation was added, the BuLi was in excess with respect to the DPE-OSi. If the titration end point was missed and too much sec-BuLi would be injected. Another reason can potentially be the incomplete initiation reaction between sec-BuLi and DPE-OSi. As stated before, the literature suggests reaction between DPE and sec-BuLi is fast and direct.[10, 55] Therefore, the reaction between DPE-OSi and sec-BuLi was assumed to be similar. However, this assumption could potentially be wrong as DPE-OSi is less reactive than DPE itself because of the electron-donating oxygens. The extent of the reaction between DPE-OSi and sec-BuLi was not quantified as part of this research but can be analysed by mass spectrometry in future. One may question why CH_3 protons of sec-butyl group has not been used for the calculation of percentage of chains with DPE-OSi. This is because CH_3 protons from both TBDMS and sec-butyl group appeared in the crowded regions which makes their analysis difficult and at this point, it is believed that the chemical shift of sec-BuLi peaks are unknown since there is no information suggesting a secondary butyl group around two phenyl rings would give peaks at the same chemical shift as a secondary butyl group directly attached to a siloxane chain.

Calculation 2.2: An estimation of percentage of chains initiated by the activated DPE-OSi in polymer DPE-PDMS 1.

$$\text{Degree of polymerization} \cong \frac{14000\ \text{g mol}^{-1}}{222.46\ \text{g mol}^{-1}\ \text{per monomer}} \cong 63\ \text{monomers}$$

$$\text{Number of protons in the polymer peak} \cong 63\ \text{monomers} \times 18\ \text{protons per monomer} \cong 1134\ \text{protons}$$

$$\text{Percentage of chains initiated by activated DPE - OSi} \cong \frac{3.45\ \text{aromatic protons per chain}}{8\ \text{aromatic protons per chain}} \times 100 \cong \mathbf{43\,\%}$$

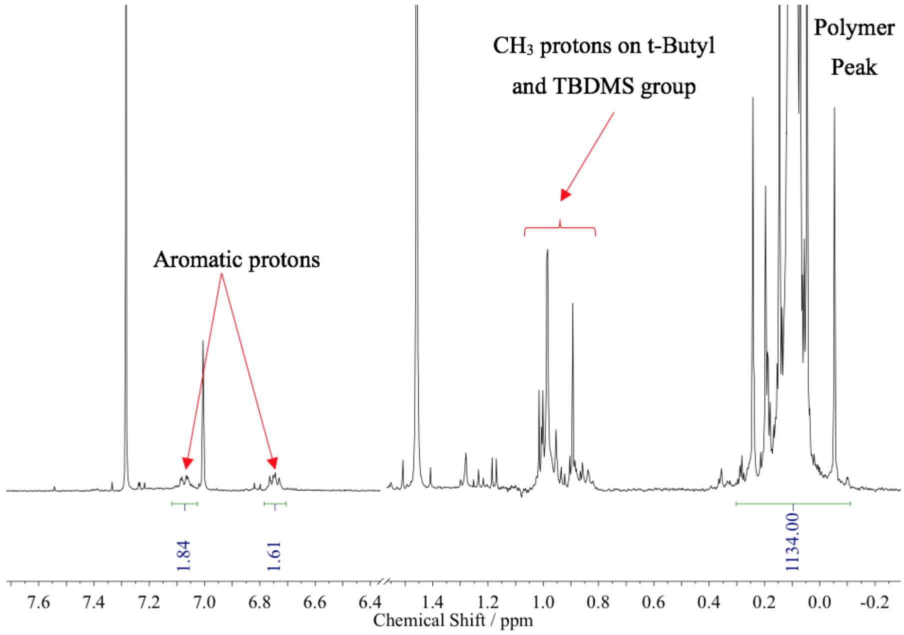


Figure 2.7: The ^{1}H NMR ($CDCl_3$) spectrum of DPE-PDMS 1.

The procedure was repeated (DPE-PDMS 2) with modifications aimed at improving the outcome. It was clear from experiment DPE-PDMS 1 that the initiation reaction between activated DPE-OSi and D_3 proceeds very slowly, possibly due to steric hindrance and, it was believed, that it could be possible to address this issue by increasing the reaction temperature. Although the usual solvent for D_3 polymerization is cyclohexane, cyclohexane has a relatively low boiling point (80.7 °C). Increasing the reaction temperature significantly above 50 °C (DPE-PDMS 1) in a sealed container may become dangerous and for this reason DPE-PDMS 2 was carried out in toluene, enabling the initiation reaction temperature to be raised safely to 90 °C.

The initiation reaction was allowed to proceed for two days at 90 °C. Unlike the previous attempt, the colour changed from dark red to yellow within 24 hours and no further colour change was observed in the next day. THF was added by vacuum-distillation at this point and the polymerization was terminated after 7 hours. The polymer was recovered by precipitation into methanol with a significantly improved yield of 84 %. However, the target molecular weight, which was 9000 g mol^{-1}, was missed and analysis by SEC indicated a molar mass (M_n) of 31000 g mol^{-1}. This clearly implies that a significant percentage of sec-BuLi molecules and/or activated DPE-OSi adduct was deactivated by impurities. A calculation similar to DPE-PDMS 1 suggests that around 40% of the chains were initiated by activated DPE-OSi complex (Calculation 2.3 and Figure 2.8). However, this data should be treated with caution, since the polymer peak is so strong and signal to noise ratio becomes a significant factor in the calculation and likely results in error. It is believed that the long initiation times are responsible for the inability to control the molar mass as the reaction mixture is more likely to be exposed to impurities during long reaction times. As a result, alternative ways to overcome the possible steric hindrance between the phenyl rings of activated DPE-OSi adduct and bulky D_3 monomer, were explored.

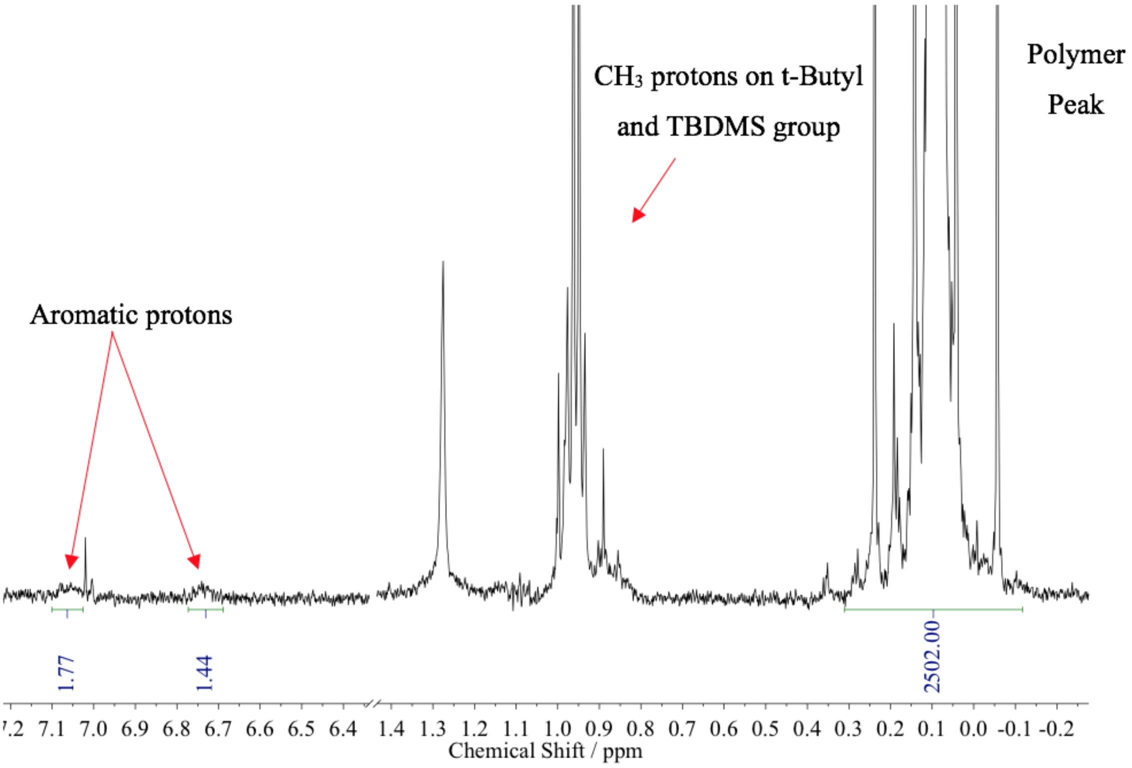


Figure 2.8: The ^{1}H NMR ($CDCl_3$) spectrum of DPE-PDMS 2, initiated at 90 °C.

Calculation 2.3: An estimation of percentage of chains initiated by the activated DPE-OSi in polymer DPE-PDMS 2.

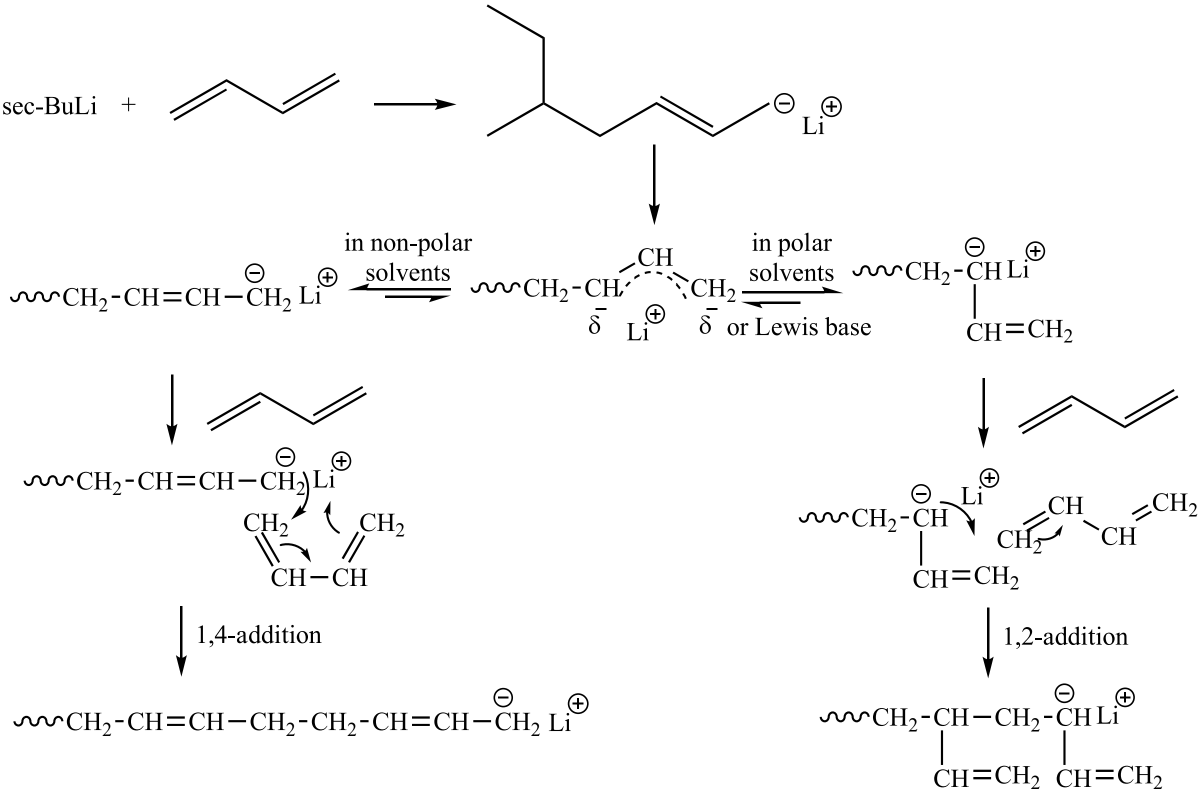
$$\text{Degree of polymerization} \cong \frac{31000 \text{ g mol}^{-1}}{222.46 \text{ g mol}^{-1} \text{ per monomer}} \cong 139 \text{ monomers}$$

$$\text{Number of protons in the polymer peak} \cong 139 \text{ monomers } \times 18 \text{ protons per monomer} \cong 2502 \text{ protons}$$

$$\text{Percentage of chains initiated by activated DPE-OSi} \cong \frac{3.21 \text{ aromatic protons per chain}}{8 \text{ aromatic protons per chain}} \times 100 \cong \mathbf{40\,\%}$$

One possible solution involves the introduction of a short “spacer” block of a different monomer to remove the steric hindrance. Thus, 1,3-butadiene (Bd) was chosen to react first with DPE-OSi before the addition of D_3. It was assumed that the activated DPE-OSi initiator would react efficiently with butadiene and that butadienyl lithium would react efficiently with D_3. It was also expected that the butadiene block would have some inherent dispersity but this was not expected to significantly impact on the molecular weight distribution of the final polymer.

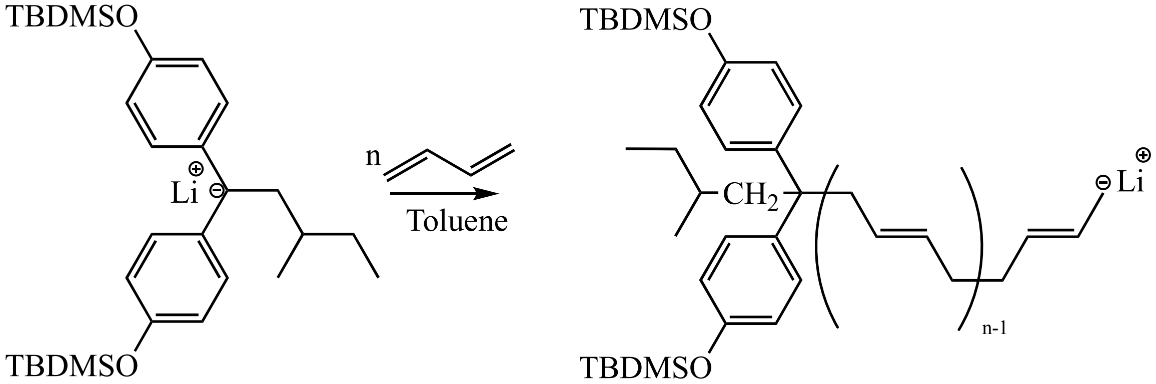
2.2.2.2 Initiation with DPE-OSi Butadienyllithium to Overcome Steric Hindrance



Scheme 2.9: Initiation and growth of butadiene chains in an anionic polymerization.[58]

1,3-Butadiene is a member of 1,3-diene monomer group which represents an extremely important class of monomers used for the preparation of many commercialised polymers. The polymerization kinetics of 1,3-butadiene are well-known. Briefly, there are two possible ways that 1,3-butadiene monomer can polymerize (Scheme 2.9). The resulting microstructures are known as 1,4- and 1,2-. The regioselectivity depends on the position of the counterion (lithium) and its coordination with the incoming 1,3-butadiene monomers. In polar solvents or in the presence of a Lewis base, monomer cannot approach to the butadiene chain-end as lithium ion is surrounded by solvent molecules (or Lewis base). This steric hindrance leads to 1,2- addition of the monomer. In non-polar solvents, lithium ion is not hindered and this addition occurs in 1,4- fashion.[58]

In an initial attempt (DPE-Bd-PDMS 1), 1,3-butadiene monomer was introduced into the polymerization 3 hours after the activation of DPE-OSi with sec-BuLi (Scheme 2.10). The number of butadiene equivalents and the choice of solvent for this approach were given careful consideration. It is expected that butadiene would polymerize in a statistical manner since reaction with all molecules of activated DPE-OSi would not be instantaneous. In other words, the number of butadiene repeat chains added to each DPE-OSi would vary and for this reason the 1,3-butadiene would need to be added in excess to ensure that every DPE-OSi carried at least one (or more) butadiene repeat unit. Thus, it was decided to add 5 equivalents of 1,3-butadiene relative to activated DPE-OSi. Toluene was chosen as the solvent. In anionic polymerization, all monomers and solvents are vacuum-distilled into the reaction mixture whenever possible which requires cooling the destination flask and its contents in a liquid nitrogen Dewar or a dry ice/acetone bath. If the contents (reactants) are frozen, then no reaction happens until melting and since the reaction mixture melts over a period of time serious heterogeneity (dispersity) can occur. If butadiene in this case is distilled in to a reaction flask containing a solution of activated DPE-OSi in cyclohexane, which has a freezing point of 6 °C, then freezing the contents is a necessity and slow melting of the solution will increase the dispersity of the short butadiene chains and some uncapped activated DPE-OSi molecules would result. Toluene has a freezing point of -95 °C which means the contents of the flask with a dry ice/acetone bath without freezing the solvent. This ensures that the distilled 1,3-butadiene is evenly mixed into the activated DPE-OSi solution and the probability of any activated DPE-OSi remaining uncapped by 1,3-butadiene is significantly limited, if not eliminated.



Scheme 2.10: Introduction of butadiene chains to avoid steric hindrance of the phenyl groups.

The addition of the 1,3-butadiene units resulted in a gradual colour change from dark red to light orange due to conversion of a diphenylhexyl carbanion (deep red) to butadienyl carbanion (pale yellow/orange). 6 hours was allowed for the reactions between the activated DPE-OSi molecules and the butadiene units based on the prior work performed on anionic polymerization of butadiene.[56] Afterwards, D_3 monomer was added by vacuum-distillation. In theory, activated butadiene units are expected to react in a similar fashion to sec-BuLi but perhaps, because of the electron donation from the double bond, in a less reactive way. This is because the butadienyl carbanion is stabilised by delocalisation. In light of this, the initiation reaction was allowed to proceed overnight. The colour of the solution changed from light orange to pale yellow overnight indicating the addition of D_3 monomer on to the chains. The anionic polymerization of D_3 has a colourless propagating species since there is no sort of conjugation present and a very weak coloured or colourless solution was expected. The pale yellow could be caused by unreacted living butadiene chains. THF was added by vacuum-distillation the next day and a gradual change in colour was observed from pale yellow to colourless. This can be a result of faster initiation reaction between the living butadiene chains and D_3 monomer in THF alongside the started propagation. The polymerization was terminated after 7 hours by the addition of chlorotrimethylsilane (TMS-Cl). Analysis of the recovered polymer by NMR indicated that the introduction of butadiene units in between DPE-OSi and D_3 monomer had been successful.

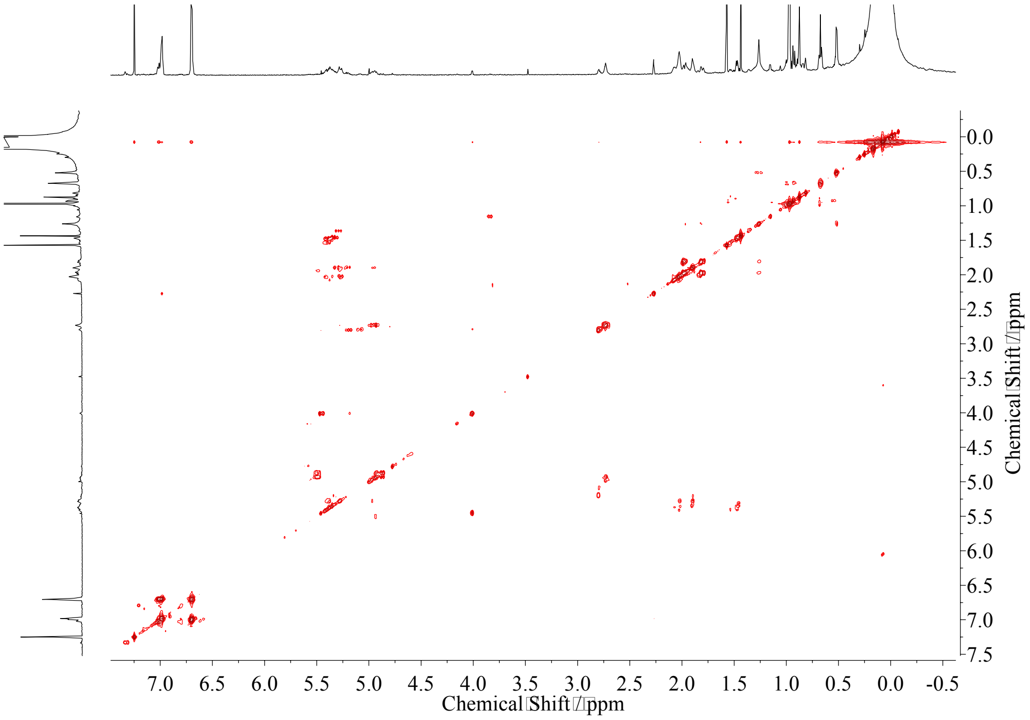


Figure 2.9: The ^1H-^1H COSY NMR ($CDCl_3$) spectrum of DPE-Bd-PDMS 1.

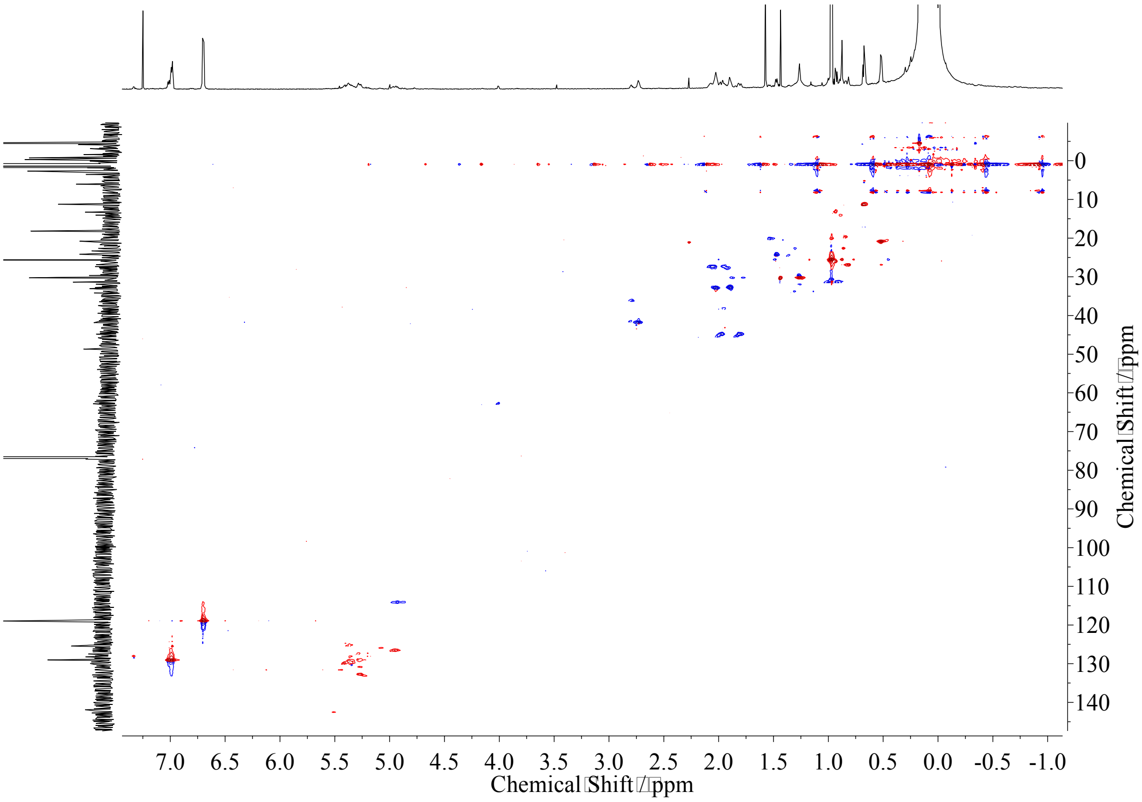


Figure 2.10: The ^{1}H-^{13}C HSQC NMR (CDCl$_3$) spectrum of DPE-Bd-PDMS 1.

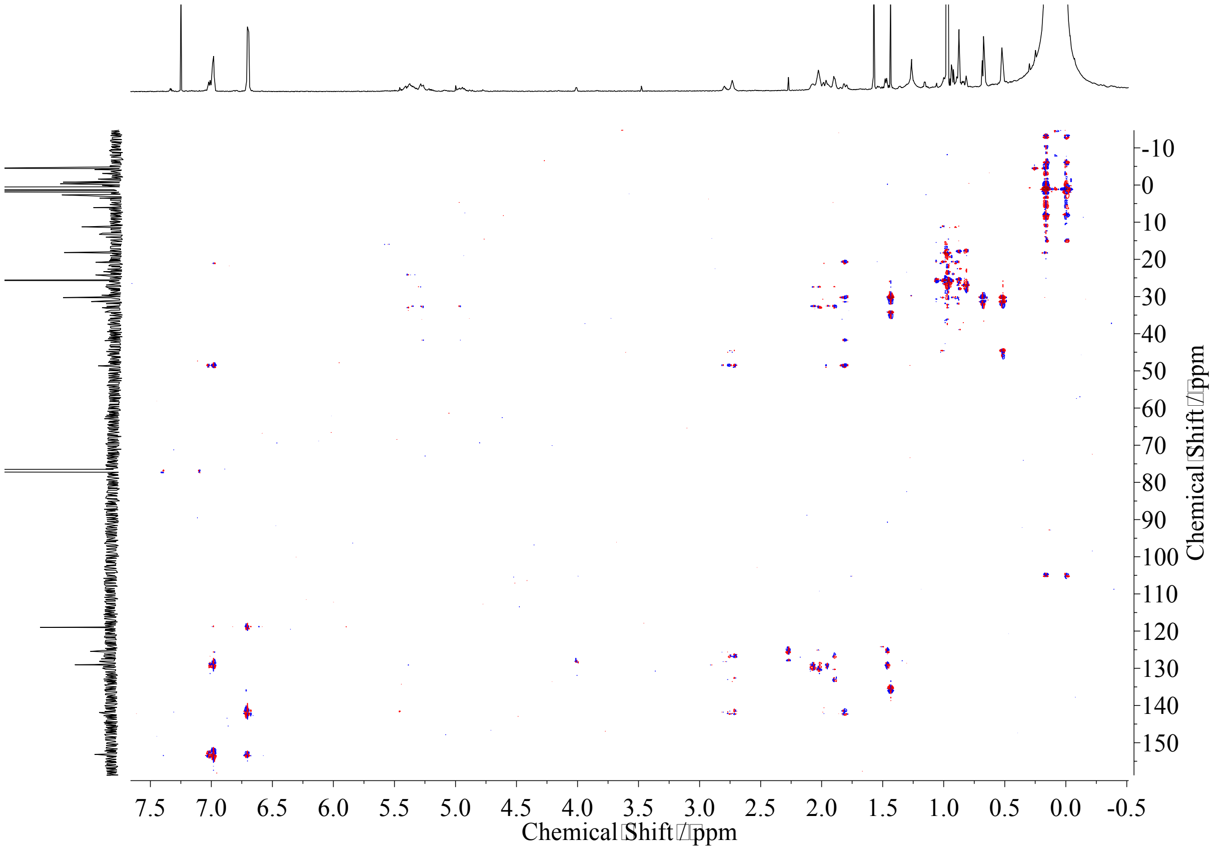


Figure 2.11: The 1H-13C HMBC NMR (CDCl$_3$) spectrum of DPE-Bd-PDMS 1.

The assignment of the proton NMR (Figure 2.12) was done with the help of ^{13}C, ^{1}H-^{1}H COSY (Figure 2.9), ^{1}H-^{13}C HSQC (Figure 2.10) and ^{1}H-^{13}C HMBC (Figure 2.11) NMR spectra obtained. The NMR spectra revealed a lot of information about the structure of the polymer. The assignment of the peaks at 7.00, 6.70, 5.38, 5.27, 4.94, 0.98 and 0.08 ppm (Figure 2.12) were straightforward as they were known from the protection reactions and the literature.[59] However, 2D NMR was needed for the assignment of other signals. The ^{13}C NMR is not provided here as most of the peaks were lost to noise because of large polymer peak. However, when the less sensitive ^{13}C nucleus was coupled to ^{1}H, the high sensitivity and abundance of protons enabled carbon atom coupled to hydrogen to be observed. The peaks were assigned by starting from H_n and H_o.

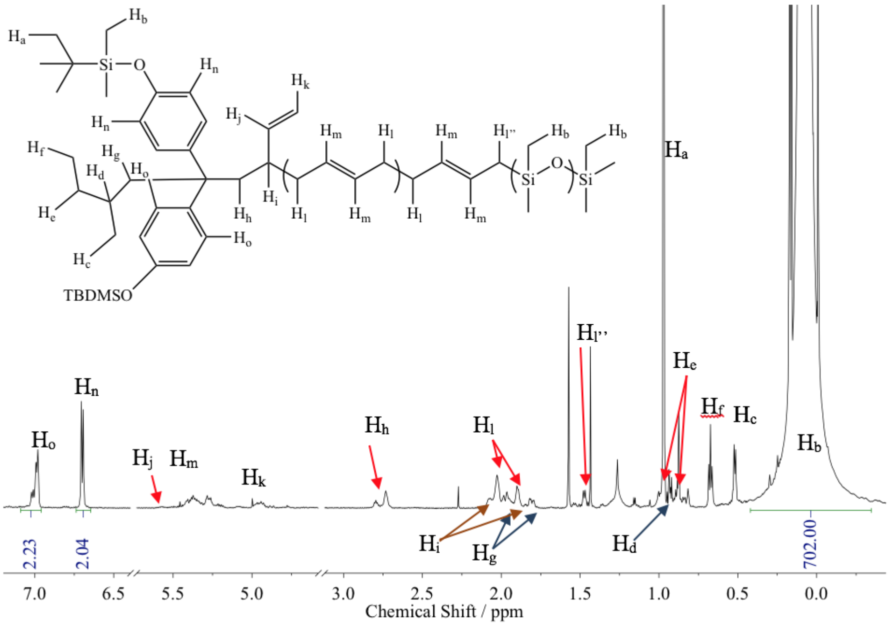


Figure 2.12: The proposed structures for the polymer DPE-Bd-PDMS 1 and the assignment of the NMR spectrum obtained in $CDCl_3$.

The protons H_h and H_g have surprisingly high chemical shifts whereas the sec-butyl group protons (H_c, H_d, H_e and H_f) had lower chemical shift values than normally expected. The reasoning behind is the shielding effect of the phenyl rings. π-Electrons of the aromatic phenyl groups are free to move around the ring and forms a loop. When an external magnetic field is applied, a ring current is induced which forms a secondary magnetic field. This induced magnetic field shields sec-butyl protons whereas it deshields the H_h and H_g protons. This give us information about the conformation of the sec-butyl group on the polymer. It is possibly sandwiched around the two phenyl groups. This is in favour of our previous statement that a secondary butyl group attached to DPE-OSi does not necessarily have the same chemical shift as a sec-BuLi group attached directly to siloxane backbone. This eliminates any possibility of using sec-butyl protons to calculate the percentage of chains initiated by activated DPE-OSi. It is also not possible to use any butadiene protons since they are in fact a mixture of 1,2- (minor) and 1,4- (major) added butadiene units where chemical shifts positions and number of protons vary. The previously used method of linking SEC results to NMR was also used in this section.

Calculation 2.4: An estimation of percentage of chains initiated by the activated DPE-OSi in polymer DPE-Bd-PDMS 1.

$$\text{Degree of polymerization} \cong \frac{8600\ \text{g mol}^{-1}}{222.46\ \text{g mol}^{-1}\ \text{per monomer}} \cong 39\ \text{monomers}$$

$$\text{Number of protons in the polymer peak} \cong 39\ \text{monomers}\ \text{x}\ 18\ \text{protons per monomer} \cong 702\ \text{protons}$$

$$\text{Percentage of chains initiated by activated DPE - OSi} \cong \frac{4.27\ \text{aromatic protons per chain}}{8\ \text{aromatic protons per chain}}\ \text{x}\ 100 \cong \mathbf{53\,\%}$$

SEC calculated an M_n value of 8600 g mol^{-1} (Table 2.4) and Calculation 2.4 was performed to estimate the success of using DPE-OSi butadienyllithium for the initiation of PDMS polymerization. The initial attempt of shortening the reaction was success. DPE-PDMS 1 took 6 days in total whereas this polymerization was terminated in less than 2 days. No elevated temperatures were needed for DPE-Bd-PDMS 1. The experimental molecular weight is in reasonable agreement with target M_n. An improved result was also noted as more chains had the intended initiator group compared to both DPE-PDMS 1 and DPE-PDMS 2 with 53 % of chains end-capped with DPE-OSi. This polymerization method was repeated to obtain the polymer DPE-Bd-PDMS 2 (Table 2.4). Although, the procedure was not changed, much higher degrees of functionalization were obtained from the repeat experiments. For DPE-PDMS 2, 98 % of chains were estimated to contain the activated DPE-OSi block. Some further results are shown on Table 2.4. In general, the initiation and introduction of the polybutadiene spacer block can be regarded as successful, as the majority of chains are believed to possess the DPE-OSi group. In a few cases, a percentage of chains end-capped with DPE-OSi (apparently) higher than 100 was observed, which is believed to be a result the slight over-prediction of M_n by THF SEC as previously discussed. This initiation procedure with TBDMS-protected DPE-OSi was performed 6 times and, in these attempts, an average of 99 ± 13 % of the chains were initiated by the activated adduct. The initiation was also attempted by using DPE (DPE-Bd-PDMS 3) and TES-protected DPE-

OSi (DPE-Bd-PDMS 7), both once only. When these results were considered with the ratio of the end-capping group to DPE-OSi (calculations demonstrated later), it was decided that initiation of PDMS polymerization with activated DPE-OSi has been successful.

Table 2.4: Experimental results for the initiation of PDMS polymerization with DPE-OSi via butadiene units (SEC THF, PS conventional calibration).

Experiment	Target MW / g mol^{-1}	M$_n$ (SEC) / g mol^{-1}	Dispersity	Yield[1] / %	End-capping Group	Chains initiated by the activated DPE-OSi adduct / %	Ratio of the end-capping group to DPE-OSi
DPE-Bd-PDMS 1	5000	8600	1.13	80	TMS	53	-
DPE-Bd-PDMS 2	10000	15000	1.09	87	TMS	98	-
DPE-Bd-PDMS 3[2]	3000	2300	1.23	68	MDPS	75	0.90
DPE-Bd-PDMS 4	6000	4200	1.16	86	MDPS	73	1.07
DPE-Bd-PDMS 5	10000	12000	1.08	76	MDPS	114	1.23
DPE-Bd-PDMS 6	8500	11200	1.14	94	MDPS	122	1.18
DPE-Bd-PDMS 7[3]	10000	15400	1.10	78	MDPS	93	1.18
DPE-Bd-PDMS 8[4]	-	-	-	-	TBDPS	-	0.13
DPE-Bd-PDMS 9	10000	13000	1.14	89	TBDPS	134	0.06

[1] Yields were calculated by assuming termination at 70 % conversion. [2] 1,1-Diphenylethylene was used to intiate the polymerization, instead of DPE-OSi. [3] TES group protected DPE-OSi was used for the initiation. [4] A separate TES group protected DPE-OSi initiated polybutadiene-block-polydimethylsiloxane copolymer was synthesised and a small sample taken from this polymer was attempted to be terminated with TBDPS. This polymer was not reported here since it was not used in the deprotection reactions.

The next objective in the synthesis of diend-functionalised PDMS polymers was the deprotection of the phenol groups of DPE-OSi and this is usually achieved by mild acid hydrolysis. Under these conditions PDMS is susceptible to depolymerisation, and depolymerisation can be random or 'initiated' at the chain end. For this reason, the PDMS ω-chain end needs to be capped, rather than leaving a Si–OH group. With this in mind, three different chlorosilane end-capping agents were tested. Increased steric bulkiness and electric donation of the Si-R end-groups are believed to increase the tolerance of the PDMS backbone to the deprotecting reaction conditions.

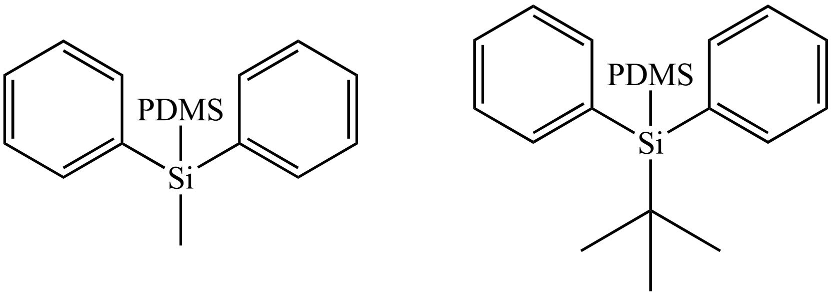


Figure 2.13: Structures of the end-capping groups MDPS and TBDPS.

The three chlorosilanes used as the end-capping agents were chlorotrimethylsilane (TMS-Cl), chloro(methyl)diphenylsilane (MDPS-Cl) and t-butyl(chloro)diphenylsilane (TBDPS-Cl). TMS does not give any distinctive peaks (Figure 2.12) in the NMR as the Si-C**H**$_3$ peak appear under the PDMS polymer peak at 0.1 ppm. Methyldiphenylsilyl group (MDPS) (Figure 2.13) contains two phenyl rings and a methyl group which are expected to give three distinctive peaks. These peaks (Figure 2.14 - top) are at 0.7 ppm (-Si(Ph)$_2$-C**H**$_3$), 7.4 ppm and 7.6 ppm (Ar-**H**). The success of the end-capping attempt by MDPS can be seen from Table 2.3. The ratio between the aromatic protons of the end-capping group to the aromatic protons of DPE-OSi was determined by using NMR. An example calculation is provided below (Calculation 2.5). It can be seen that a ratio close to 1:1 was obtained in most cases for the MDPS group. The ratio being close to 1 suggests both a successful initiation and a successful end-capping. The end-capping with MDPS-Cl was repeated 5 times and, on average, a ratio of 1.1 ± 0.1 was achieved. End-capping with TBDPS however, did not result in successful termination, and a ratio around 0.1 was observed in both trials. Since the polymerization of D$_3$ suffers from back-biting reactions (see previous discussion), the termination/end-capping step must be fast and efficient and after two trials (DPE-Bd-PDMS 8 and DPE-Bd-PDMS 9), it was decided that the TBDPS group (Figure 2.13) is not a suitable end-capping agent. It is believed that the steric bulk of this group inhibits the reaction (Figure 2.14 - bottom).

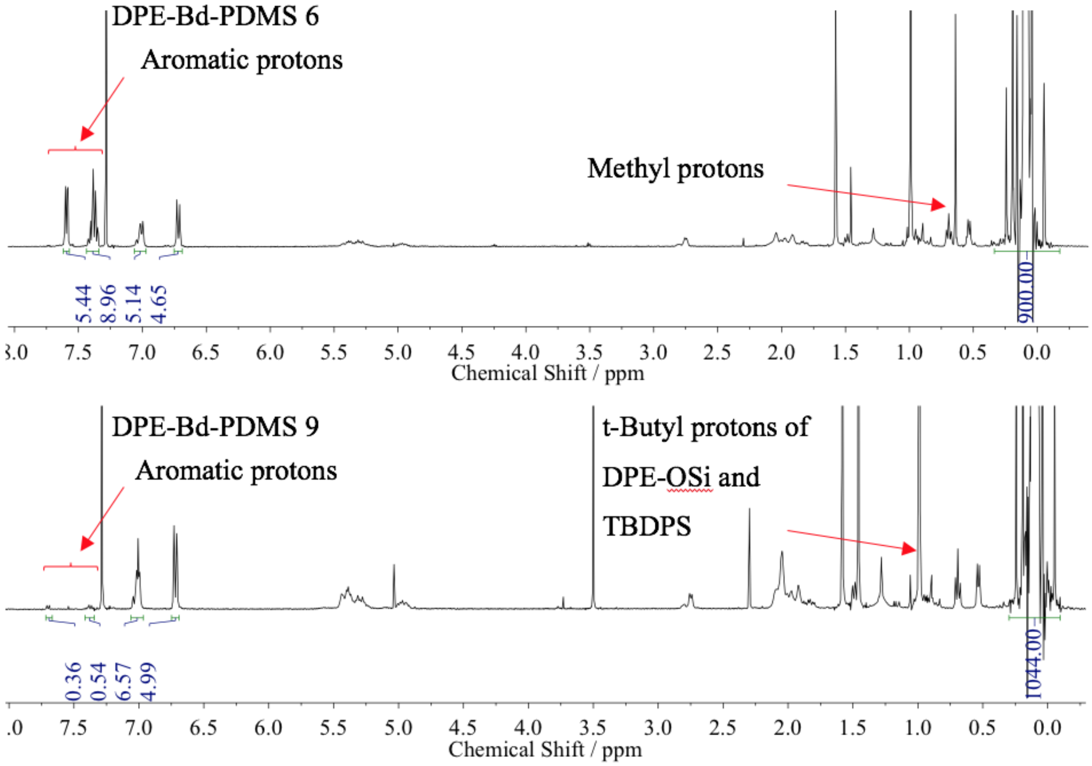


Figure 2.14: The ^{1}H NMR ($CDCl_3$) spectra of DPE-Bd-PDMS 6 (top) and DPE-Bd-PDMS 9 (bottom).

Calculation 2.5: The ratio between the aromatic protons of the end-capping group to the protons of DPE-OSi by NMR.

Ratio of the experimental number of aromatic protons of MDPS relative to the theoretical value:

$$\frac{5.44 \text{ protons} + 8.96 \text{ protons}}{10 \text{ protons}} = 1.44$$

Ratio of the experimental number of aromatic protons of DPE-OSi relative to the theoretical value:

$$\frac{5.14 \text{ protons} + 4.65 \text{ protons}}{8 \text{ protons}} = 1.22$$

$$\text{Ratio of the end-capping group to DPE-OSi} = \frac{1.44}{1.22} = \mathbf{1.18}$$

In general, yields are high. The lowest yield (68%) was obtained for DPE-Bd-PDMS 3, however, this polymer is particularly low in molecular weight and it is possible that some of the polymer chains were lost during the precipitation process as low molecular weight PDMS might be soluble in methanol.

It was also decided to run matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) experiment on the polymers obtained by this initiation method. In theory MALDI-TOF provides an accurate way of obtaining the absolute molar mass of polymer chains as no relative molecular weights are required in these calculations. However, MALDI-ToF also comes with limitations, principally, not all species "fly" to the same extent and often the detection of high molecular weight polymer chains is much less quantitative than low molecular weight chains. This is called mass discrimination and can be caused by multiple factors such as sample preparation, desorption/ionization process and detection (in)efficiency.[27, 60-64] The objective of this study was to investigate the presence of butadiene block and the nature of end groups.

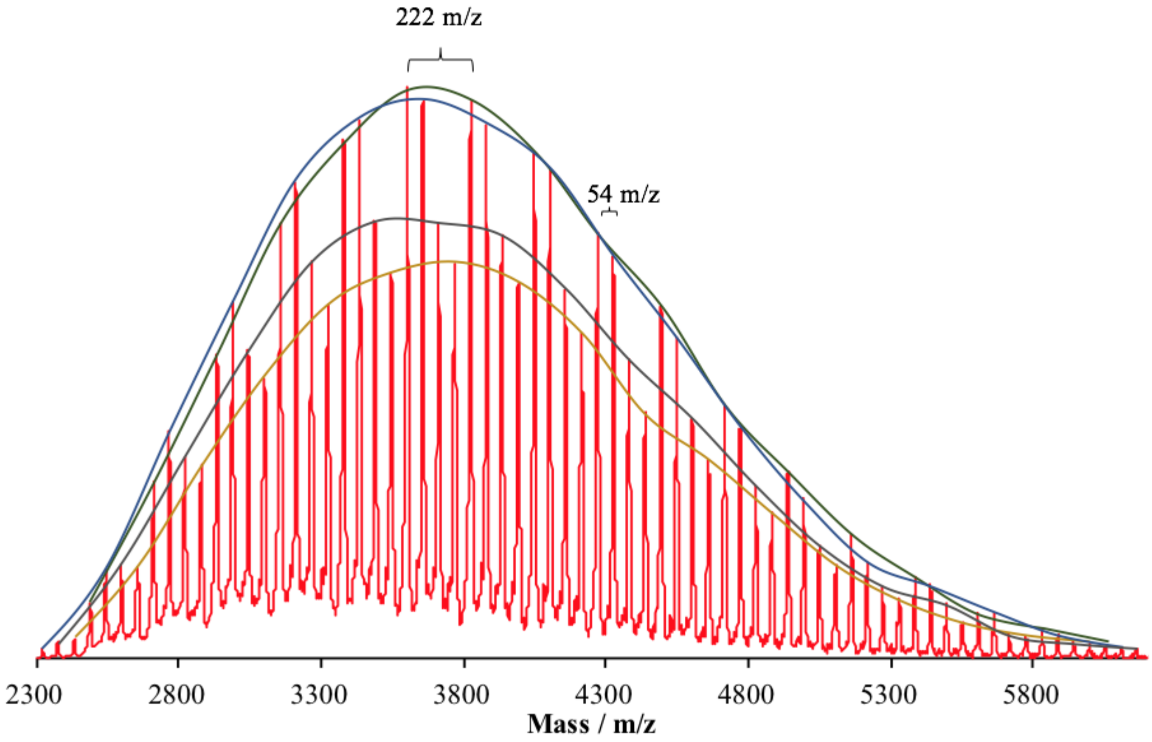


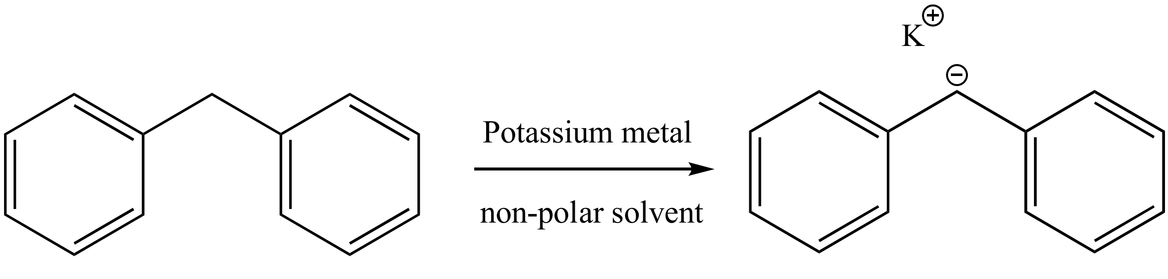
Figure 2.15: The MALDI-ToF (DCTB, K) spectrum of DPE-Bd-PDMS 3.

A low molecular weight (2300 g mol^{-1} by THF SEC) DPE-initiated polybutadiene-co-polydimethylsiloxane copolymer, DPE-Bd-PDMS 3 was synthesized as part of the broader study but was chosen for characterisation by MALDI. It revealed some information about the butadiene distribution among the polymer chains. It can be observed from Figure 2.15 that there are four main distributions each shifted by 54 m/z which is the molecular weight of a butadiene repeat unit. Peaks in each distribution are separated by 222 m/z which is the molecular weight of each D_3 monomer. MALDI-ToF shows us all chains detected are in possession of a butadiene block and all these distributions contain the PDMS block. This MALDI-ToF could not be used to determine whether all chains possess the initiator precursor DPE-OSi, since the peaks are relatively broad because of the isotopes of both carbon and silicon atoms.

In summary, the approach of introducing a short butadiene "spacer" block in between the activated DPE-OSi complex to overcome the steric hindrance was successful. The time needed to complete the polymerization was reduced from 6-7 days to about 1 day. Control over the molecular weight was gained and calculations showed that a majority of chains contained the intended DPE-OSi initiator precursor as it was demonstrated in Table 2.4. The MDPS group was shown to be the most successful end-capping strategy to (hopefully) improve the stability of the PDMS backbone.

Use of DPE-OSi to introduce functional groups to the polymers synthesised by anionic polymerization is a very common strategy adopted in our research group.[47-49] A less common strategy is the use of diphenylmethyl derivatives, such as Bisphenol F (BPF). Pagliarulo *et al.*[65] has recently published her work on the initiation of anionic polymerization of styrene by using a TBDMS-protected BPF activated with a potassium counter ion. This work resulted in a curiosity in our group whether BPF can be activated with a lithium counter ion and used for the anionic polymerization of polydimethylsiloxane. It was decided to attempt this initiation strategy as well to see if it works and how it would compare to the DPE-OSi initiation strategy.

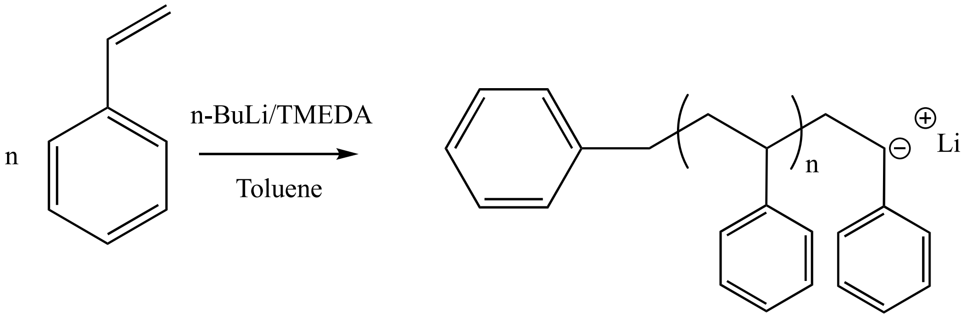
2.2.2.3 Attempted Polymerization with a Lithium Initiator based on Protected Bisphenol F



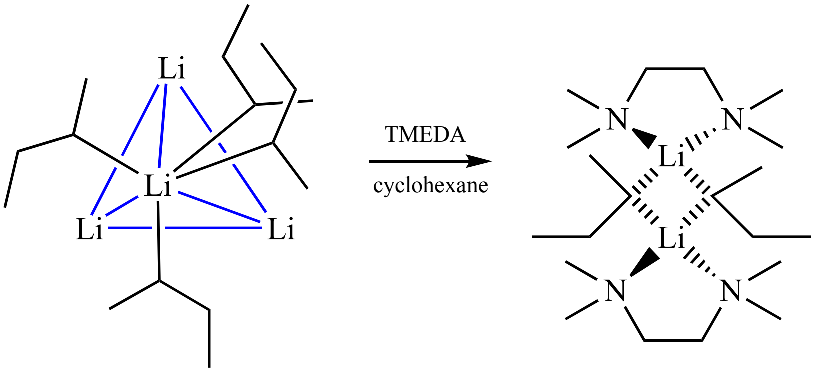
Scheme 2.11: Deprotonation of diphenylmethane by potassium metal.

Diphenylmethylpotassium (DPMK) has been widely used for the anionic ring opening polymerisation of ethylene oxide successfully[66-69] and recent work in our own group has used the protected bisphenol analogue (Bisphenol F) of DPMK for the initiation of styrene polymerization.[65] Potassium metal is known to deprotonate the diphenylmethyl group to form a stable anion on the methyl as the charge delocalizes through the ring systems (Scheme 2.11). However, D_3 polymerization with a potassium counterion causes some certain problems such as control over propagation as previously mentioned in the Introduction. This is because lithium silanolate propagating chain-ends have weaker alkalinity when compared to the propagating chain-ends with potassium counterion. Presence of potassium counterion results in an equilibrium between cyclic and linear species whereas lithium counterion always prefers to break the cyclic monomer to form linear polysiloxane chains.[70]

The paper published by Tsukahara *et al.*[71] supports the idea that diphenylmethane derivatives such as Bisphenol F (BPF) could be deprotonated to yield a lithium initiator. These researchers initiated the polymerization of styrene using an initiator formed by the reaction of toluene and n-BuLi in the presence of tetramethylethylenediamine (TMEDA) as shown on Scheme 2.12. The bidentate TMEDA ligand breaks down the aggregation of the alkyllithium complexes, which form in non-polar solvents, by forming a stronger interaction with the lithium cation (Scheme 2.13).[71] In the presence of TMEDA, BuLi is basic enough to deprotonate the methyl group of toluene to produce benzyl lithium. The use of protected Bisphenol F (BPF-OSi) as an initiator precursor to yield a lithium initiator and its use to initiate D_3 (or any other monomer) polymerization has not previously been reported to the best of our knowledge.

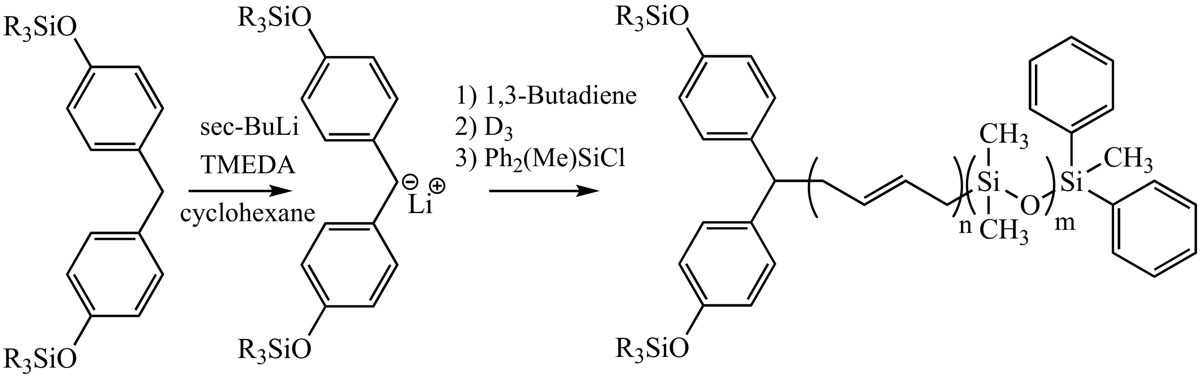


Scheme 2.12: Initiation of anionic styrene polymerization by n-BuLi/TMEDA/Toluene initiating system.[71]



Scheme 2.13: An illustration of the effect of TMEDA on sec-BuLi aggregates.

This initiation procedure was attempted three times, BPF-Li 1, BPF-Li 2 and BPF-Li 3. Previously synthesised TES-protected Bisphenol F (BPF-OSi) was dried by azeotropic distillation three times with benzene, followed by the addition of TMEDA and sec-BuLi. Upon the addition of sec-BuLi and TMEDA, the colour of the cyclohexane solution turned immediately to red, suggesting the successful formation of BHF-Li species. In an initial attempt (BPF-Li 1), the reaction between BPF-OSi and BuLi was allowed to proceed for 12 hours at room temperature. The initiation was followed (similar to the procedure with sec-BuLi) by the addition (by vacuum-distillation) of 5 equivalents of 1,3-butadiene (left for 6 hours), which was then followed by the addition of D_3 monomer into the reaction mixture. Since the solvent used was cyclohexane, it was not possible to cool the solution to -78 °C and therefore, the mixture was frozen prior to distillations. The reaction mixture melts over a period of time and serious heterogeneity (dispersity) could occur. The colour of the polymerization mixture changed from red to pale yellow in 1 hour following the distillation of butadiene monomer. The polymerization was terminated after 7 hours by the addition of chloro(methyl)diphenylsilane. This polymerization did yield a polymer which was recovered by precipitation in methanol.



Scheme 2.14: The proposed polymerization scheme.

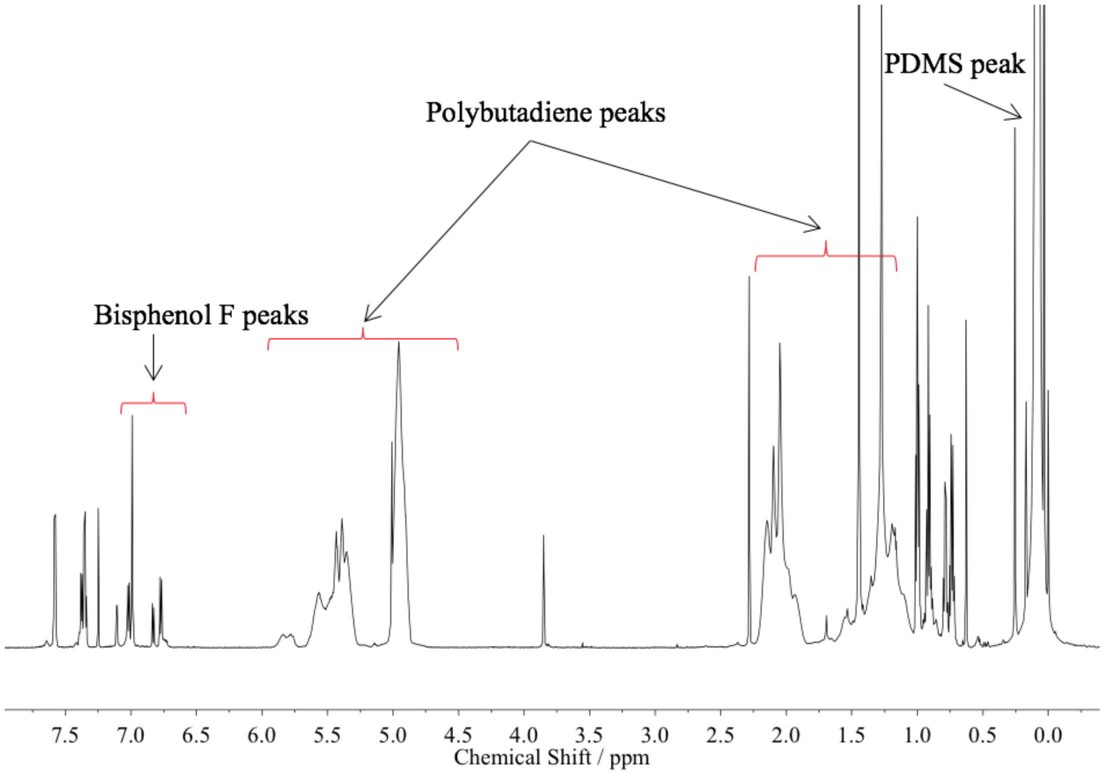


Figure 2.16: The ^{1}H NMR ($CDCl_3$) spectrum for polymer obtained from BPF-Li 1.

The NMR (Figure 2.16) indicates the presence of BPF-OSi, polybutadiene and PDMS peaks in the precipitated polymer. These were all expected peaks. The results from SEC analysis can be seen from Table 2.5 and Figure 2.17. Unexpectedly, three separate peaks, all rather narrow, were observed in the SEC. This may suggest more than one initiating system during the polymerization. Yield of the polymerization was only 12%. Although a low yield can result from all sorts of reasons, it can also arise from a low conversion. The higher the target molecular weight, the longer it takes for the polymerization to go to completion. Considering the fact that high molecular weight polymer was obtained. It is possible that the number of "initiator" molecules, which can be both sec-BuLi and BPF-Li, was lower than the injected amount and final molecular weight would be very high. This also suggests that either the BPF-OSi was impure or BPF-Li was continuously being deactivated. The SEC obtained (Figure 2.17) contains 3 peaks indicating three different polymer distributions at three different molecular weights. Of these, the two higher molecular weight polymer peaks (2 and 3) also gave a light scattering signal suggesting polymer with a substantial polybutadiene block or possibly a very high molecular weight PDMS block which can increase the intensity of light scattering signal of PDMS. This result suggests that the control over polymerization was far from good but the presence BPF-OSi aromatic protons in the NMR spectrum hints that the polymerization could potentially be initiated by this activated complex and BPF-OSi can be a viable initiator with this initiating system of TMEDA and sec-BuLi.

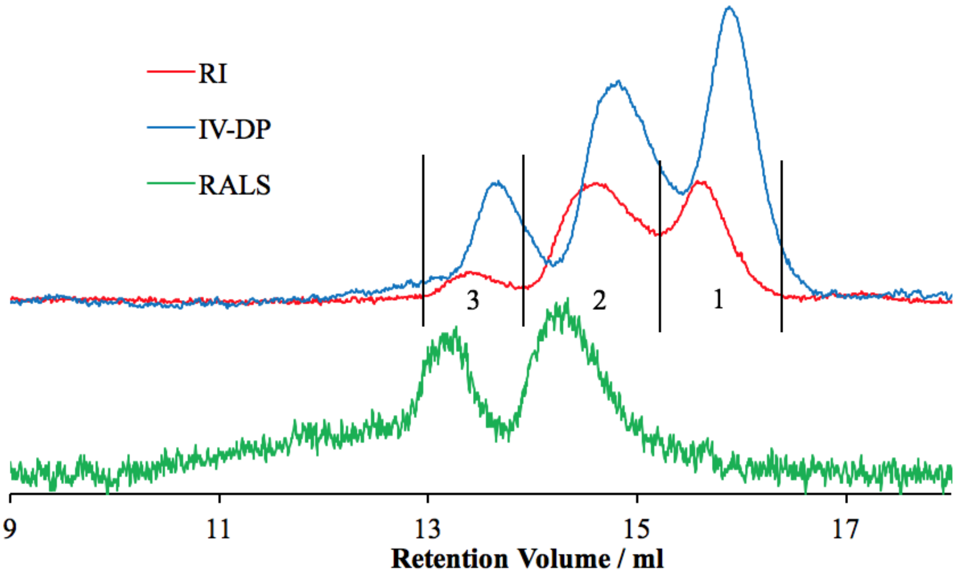


Figure 2.17: The refractive index, viscometer and light scattering data obtained from BHF-Li 1.

Table 2.5: SEC results obtained from BHF-Li 1 sample (SEC THF, PS conventional calibration).

Peak	**1**	**2**	**3**
M_n / g mol^{-1}	8200	22200	74200
M_w / g mol^{-1}	9200	24800	79600

The procedure was then amended in an attempt to tackle these problems. Thus, in an attempt to understand the initiation process it was decided to synthesise polybutadiene homopolymers using BPF-Li, instead of polybutadine-co-polydimethylsiloxane polymer. This would simplify the polymerization procedure and subsequent characterisation. Once again a red colour was obtained again upon the addition of sec-BuLi and TMEDA to the protected BPF and the (activation) reaction was allowed to proceed overnight. The mixture retained its colour. 2.7 g 1,3-butadiene monomer was vacuum-distilled into the polymerization mixture. The colour of the solution faded from red to orange, then to pale yellow and finally to colourless within 10 minutes. The polymerization was terminated after 16 hours with nitrogen-sparged methanol. It was attempted to precipitate the polymer in methanol but no polymer was recovered. At this point, it was suspected that BPF-OSi was so impure that only a small amount of sec-BuLi remains active for initiation. It is clear that the reaction between BuLi and BPF-OSi is a fast reaction since an immediate colour change from colourless to red was observed after the addition of sec-BuLi. So, it was decided to purify the protected BPF by a titration step with BuLi as used for the purification of DPE-OSi. This additional procedure was used in the third attempt. TMEDA was added into the cyclohexane solution containing BPF-OSi and BPF-OSi was titrated with dropwise addition of sec-BuLi. Upon the appearance of red colour, the solution was left for stirring for an hour. The colour of the solution turned to pale yellow and more sec-BuLi was injected to turn the solution to red again. The solution was left stirring overnight and the colour was again pale yellow in the morning. This supports of the idea of some sort of deactivation mechanism. BPF-OSi was titrated once again and the whole required amount of initiator was injected after an hour. The red colour was not significantly more intense than it was after titrations. In the case of DPE-OSi, when the entire required amount of initiator was injected the solution turned very dark red. 1,3-butadiene monomer was added to the BPF-OSi initiator solution via vacuum-distillation after 2 hours to prevent any further deactivation. The colour of the solution turned into colourless quickly again. Termination was performed after 16 hours with nitrogen-sparged methanol. No polymer was recovered.

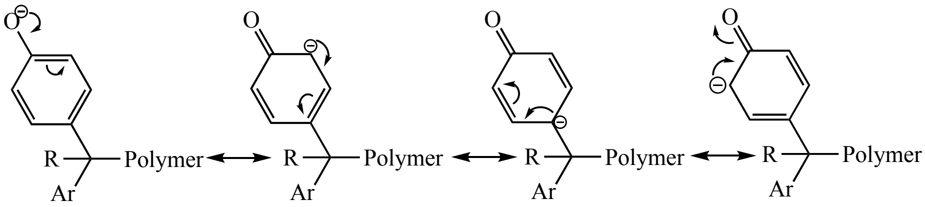
Having established a successful initiation procedure of PDMS polymerization with DPE-OSi and a short spacer block of polybutadiene in the previous step, it was decided to abandon this approach. However, it must be noted that the red colour of the solution and the presence of BPF-OSi peaks in the NMR spectrum of polymer (BPF-Li 1) in Figure 2.16 suggest that this is a concept that might be worth pursuing in future. This initiation method does produce activated BPF-OSi and some of the BPF-OSi was apparently incorporated in the polymer BHF-Li 1. The method, however, requires optimization. More details are provided in Future Work.

2.2.3 Deprotection Reactions

2.2.3.1 A Survey of Deprotection Methods

There are a variety of methods to cleave silyl ethers and deprotect hydroxyl functional groups. These protecting groups are readily removed under relatively mild conditions compared to other alcohol protecting groups such as esters, ethers and acetals.[51] A big challenge of this project was to remove the silyl ether protecting groups without degrading the polydimethylsiloxane backbone. This requires a high degree of chemoselectivity since the polymer will contain hundreds of Si-O bonds and only two of these bonds (from DPE-OSi) need to be cleaved.

Two main factors that might be expected to impact upon selectivity in the deprotection reaction are the difference in the chemical structure of aryl silyl ethers and siloxane bonds, namely electronic effects, and steric effects. Electronically, an aryl silyl ether is activated because of the electron donation from the phenyl rings and the formation of the intermediate phenolate anion, which is stabilised by conjugation of the anion (Scheme 2.15), whereas a siloxane backbone is expected to remain neutral and with bulky end-capping groups to be sterically stabilized. The end-capping strategy was adopted to inhibit depolymerization initiated from chain-ends. An attempt was made to inhibit degradation of the PDMS backbone by stabilising the chain ends. This was achieved by altering the end-capping group. Trimethylsilyl (TMS) and methyldiphenylsilyl (MDPS) end-capping groups were used.



Scheme 2.15: Stabilisation of the intermediate phenolate anion.

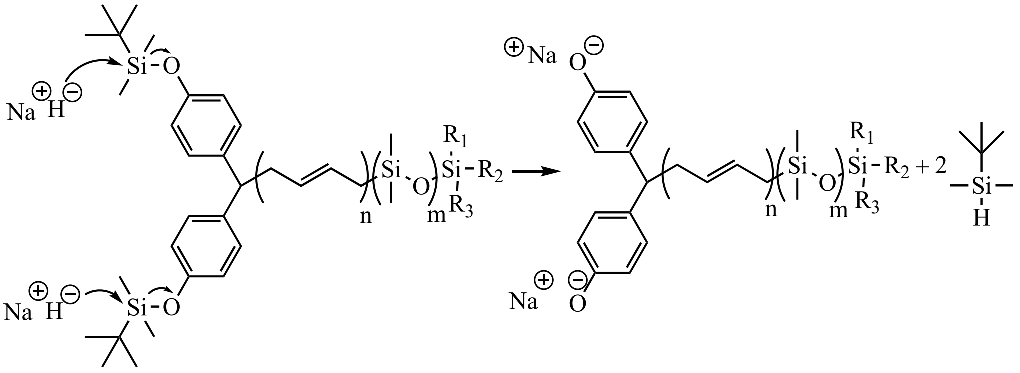
A literature survey was carried out to find the most appropriate reagents and conditions to exploit the aforementioned favourable features. There are many reported methods for the chemoselective deprotection of aryl silyl ethers in the presence of alkyl silyl ethers and it is generally accepted that basic conditions favour the deprotection of aryl silyl ethers and the acidic conditions favour the deprotection of alkyl silyl ethers.[72] The reason is the conjugation of the phenolate anion which makes an aryl silyl ether a better leaving group and a less basic species than an alkyl silyl ether.[51] Suggested methods are summarised on Table 2.6. However, most of these reactions require the use of polar aprotic solvents, such as DMF, DMSO and acetonitrile, and water, in which PDMS is insoluble. PDMS is mainly soluble in THF and non-polar solvents only, which restricts the available options for the deprotection reaction.[73] Among the reactions shown in Table 2.6, the use of NaH, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and tetra-n-butylaluminium fluoride (TBAF) were reported to be successful to some extent in THF. Therefore, it was decided to use these three methods for deprotection attempts in basic conditions. Although, PDMS is known to degrade under acidic conditions, it was also decided to attempt the deprotection reaction under mildly acidic conditions. A series of experiments were run with both hydrochloric acid and acetic acid.

Table 2.6: A summary of ideal conditions for the chemoselective aryl silyl ether deprotections. [74-85]

Reagents	Conditions	Reported Yield	Time
TBAF	THF, 0 °C	83 %	15 min
KF, Al_2O_3	DME/1,4-dioxane, 25 °C	87-96 %	4-16 h
LiOH	DMF, 25 °C	85-97 %	3-16 h
NaOH, Bu_4NHSO_4	1,4-dioxane, 25 °C	76-85%	3 h
KOH	EtOH, 25 °C	87-96 %	-
LiOAc	DMF-water (50:1), 25-70 °C	87-99 %	1.5-24 h
K_2CO_3	Ethanol-water (50:1), 75 °C	78-100 %	2-24 h
Cs_2CO_3	DMF-water (10:1), 25 °C	88-99 %	0.5-3 h
$Na_3PO_4.12H_2O$	DMF, 25 °C	76-95 %	1.5-12 h
NaH	DMF, 0-25 °C	75-100 %	2-12 min
DBU	MeCN-water (95:5), 20 °C	95-99 %	0.1-3.5 h

2.2.3.2 Attempted Deprotection Under Basic Conditions

2.2.3.2.1 Sodium Hydride



Scheme 2.16: Proposed deprotection reaction mechanism of DPE-OSi initiated PDMS with NaH.

This deprotection reaction is believed to be a nucleophilic substitution reaction (Scheme 2.16). The basic hydride anion attacks the TBDMS protecting group to form a stable phenolate anion. One may expect this nucleophilic addition to be not very selective since both TBDMS and TMS (end-capping) groups would be susceptible. However, Si-O-Si bond is stronger than a Si-H bond and hydride anion does not attack Si-O-Si bond to form a stronger bond. Therefore, the driving force for the selective deprotection reaction was believed to be the formation of the phenolate anions and not the substitution of Si-O-Si bond.[84]

Nine deprotection reactions were attempted by using varying equivalents of NaH, different solvent systems, temperature, duration and end-capping group – see Table 2.7 for details. In all cases, the dispersity of the resulting polymers increased and the number-average molecular weight decreased significantly. This clearly shows that the PDMS backbone was degraded by the hydride anion. Despite the unwanted degradation, in each experiment a degree of deprotection was observed. This was evident by NMR from the decrease in the integral of the protecting group peaks. For example, the integral of t-butyl group on TBDMS decreased from 19.82 to 12.10 relative to the peak at 6.7 ppm (aromatic protons of the DPE group) which means 39% of the DPE-OSi was deprotected (Figure 2.18).

Table 2.7: Results obtained from NaH deprotection reactions.

Reaction	End-capping group	Conditions[1]	% Removal of TBDMS	Dispersity		M_n / g mol^{-1}	
				Before	After	Before	After
NaH 1	TMS	10 eq of NaH, THF, 25 °C, 6 h	5	1.13	1.60	8600	4800
NaH 2	TMS	5 eq of NaH, THF, 25 °C, 6 h	<1	1.13	1.56	8600	3600
NaH 3	TMS	4 eq of NaH, THF, 25 °C, 3 h	<1	1.09	1.4	15000	9000
NaH 4	TMS	4 eq of NaH, THF-DMF (2:1), 25 °C, 15 min	35	1.09	1.52	15000	12000
NaH 5	TMS	3 eq of NaH, THF-DMF (2:1), 0 °C, 1 h	40	1.13	1.40	8600	2200
NaH 6[2]	MDPS	3 eq of NaH, THF-DMF (2:1), 25 °C, 15 min	-	1.23	1.28	2300	1300
NaH 7	MDPS	1.5 eq of NaH, THF-DMF (2:1), 25 °C, 30 min	27	1.16	1.36	4200	2500
NaH 8	MDPS	0.7 eq of NaH, THF-DMF (2:1), 25 °C, 30 min	39	1.16	1.25	4200	3000
NaH 9[3]	MDPS	1.5 eq of NaH, THF-DMF (2:1), 25 °C, 6 h	-	1.16	-	4200	-

[1]Number of equivalence of NaH was to the number of protected OH groups. [2]The initiator group is DPE, instead of DPE-OSi. [3]No polymer recovered.

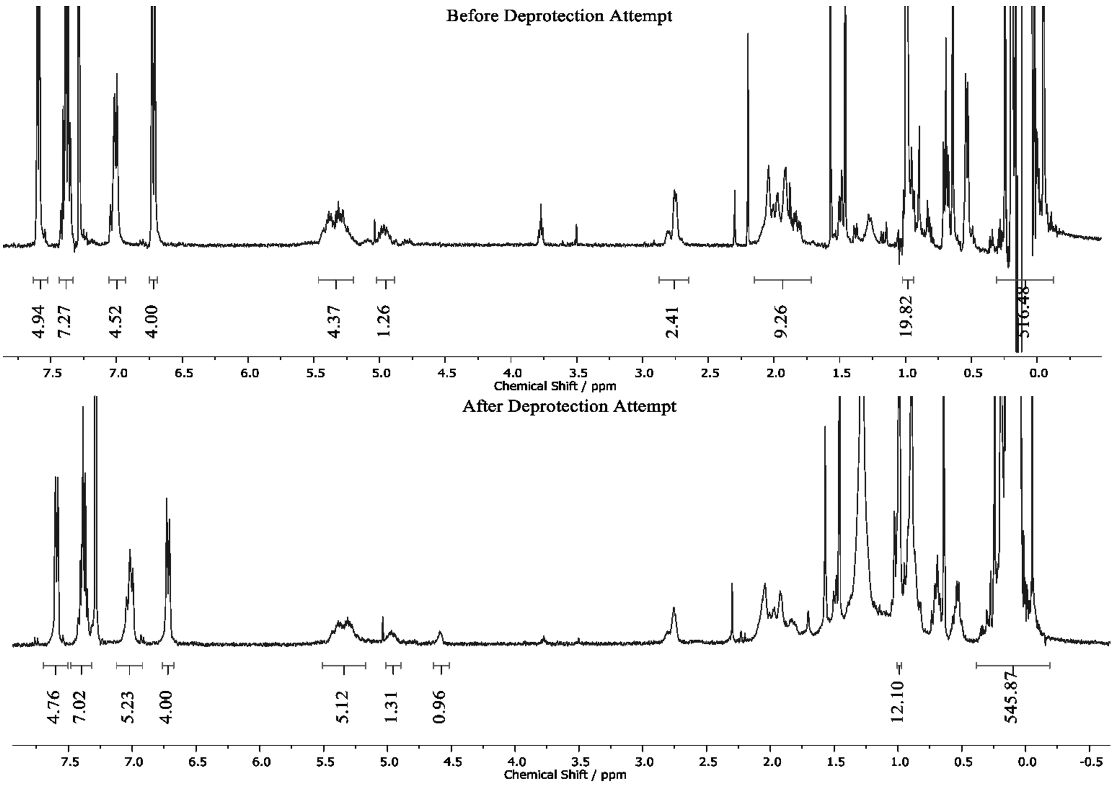


Figure 2.18: The comparison of the ^{1}H NMR ($CDCl_3$) spectra before and after the deprotection experiment NaH 8.

Fernandes *et al.* previously reported an increase in the rate of deprotection reactions with the increasing equivalences of NaH.[84] However, the number of equivalents of NaH had a significant effect on the dispersity of the resulting polymers, with an increasing dispersity arising as the equivalents of NaH increased. This is perhaps expected since a higher concentration of hydride anions will mean more frequent nucleophilic attack on both the TBDMS group and the polymer backbone. It was attempted to decrease the amount of NaH to regain the lost control over dispersity and molecular weight back. The approach did bring some degree of control and enhanced the aryl silyl ether chemoselectivity, however, the hydride anion continued to damage the backbone as can be seen from the dispersity values, and the desired deprotection reaction was far from completion. The impact of solvent (THF v THF/DMF) and reaction temperature was investigated. It was found that both increasing solvent polarity, by the use of DMF, and increasing temperature, sped up the reaction, but no improvement in chemoselectivity was observed and polymer degradation always accompanied (incomplete) deprotection. The fact that the rate of reaction increased upon a change in solvent from THF to DMF supports the idea of an S_N2 reaction as this kind of reactions are known to be favoured by polar aprotic solvents.[84, 86]

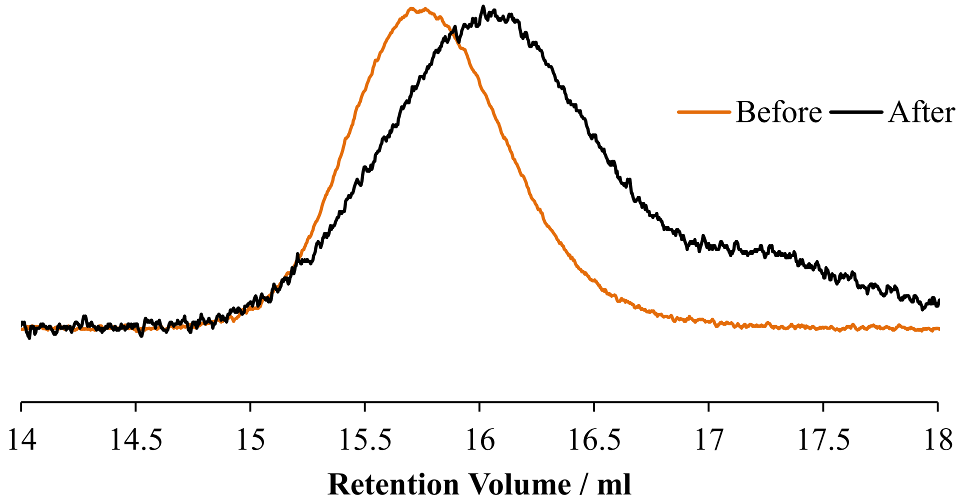


Figure 2.19: The comparison of the refractive index data, obtained from SEC (THF), before and after the attempted deprotection - experiment NaH 7.

Given that degradation could have been initiated at the chain end, another strategy adopted to inhibit degradation involved changing the end-groups of the PDMS chains from TMS to MDPS. The use of the bulkier MDPS end capping agent was successful to a degree in that the chemoselectivity towards the deprotection reaction was enhanced (Table 2.7). This suggests the idea that any depolymerisation on polysiloxane chain starts from the chain-ends, however, no such information was found in the literature to support this claim. Degradation was not eliminated and SEC analysis of NaH 7 (Figure 2.19) clearly indicates a shift towards longer retention times (lower molecular weights) and a broadening of the distribution. Despite several attempts to optimise reaction conditions the combination of incomplete deprotection and polymer degradation indicate this was not a successful strategy.

2.2.3.2.2 DBU

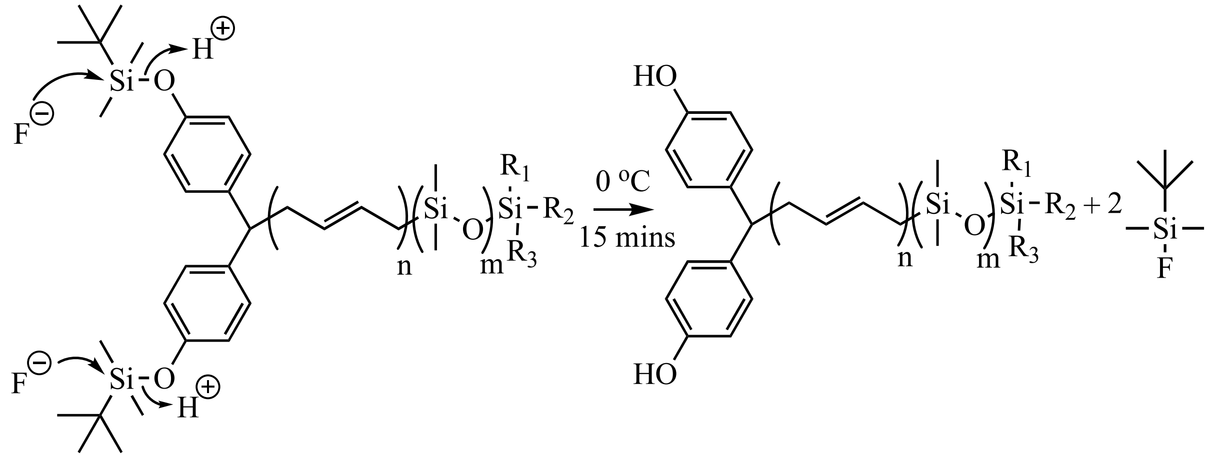
It has been reported[85] that DBU, unlike some other strong amine bases such as 4-dimethylaminopyridine (DMAP) and 1,2-diazabicyclo[2.2.2]octane, can be used as a desilylating agent. It was reported that the deprotection reaction does not go to completion in the absence of a proton source and can result in yields as low as 13-15%. Moreover, it has been reported that acetonitrile and water mixtures gave the optimal conditions for this deprotection reaction and proved that DBU acts as a catalyst, since reactions with both 0.1 and 1 equivalents of DBU went to completion. Some evidence of success was also reported when the reaction was attempted with THF, using either water or methanol as the proton source (89 % yield).[85] Thus, in the current study, it was decided to attempt the deprotection of DPE-OSi using a mixture of methanol and THF in the presence of 1 equivalent of DBU relative to TBDMS groups. Methanol rather than water was chosen as the proton source because PDMS is extremely hydrophobic and it was assumed that water may not be effective as a proton source.

Table 2.8: Results obtained from DBU-mediated deprotection reactions (SEC THF, PS conventional calibration).

Reaction	**End-capping group**	**Conditions**	**% Removal of TBDMS**	**Dispersity**		**M_n / g mol^{-1}**	
				Before	**After**	**Before**	**After**
DBU 1	MDPS	1 eq of DBU, THF-Methanol (19:1), 25 °C, 1 h	<1	1.16	1.13	4200	4600
DBU 2	MDPS	1 eq of DBU, THF-Methanol (19:1), 25 °C, 16 h	4	1.16	1.11	4200	4800
DBU 3	MDPS	2 eq of DBU, THF-Methanol (19:1), 50 °C, 72 h	15	1.16	1.13	4200	4500

The results obtained are reported in Table 2.8. The increase in molecular weight is not significant and probably due to flow-rate irregularities associated with the SEC analysis. The results indicate that whilst under the reaction conditions investigated, no degradation of the PDMS backbone was observed, the extent of deprotection was low. It was decided to abolish this strategy given the poor kinetics.

2.2.3.2.3 TBAF



Scheme 2.17: Deprotection reaction mechanism of DPE-OSi initiated PDMS with TBAF at 0 °C.

Deprotection using tetra-n-butylaluminium fluoride (TBAF) occurs via a nucleophilic substitution reaction where the fluoride anion attacks the Si-O bond to form the stronger Si-F bond. TBAF is commonly used to break down PDMS completely,[73, 87] therefore degradation of the polymer backbone is to be expected. However, Collington *et al.*[76] previously reported this deprotection strategy as chemoselective to aryl silyl ethers at 0 °C. In an attempt to minimise or even eliminate degradation, precisely 1 equivalent of TBAF with respect to TBDMS groups was attempted to be used. The number of equivalents was determined by setting the integral of phenyl peak at 6.70 ppm (NMR) to four and the molecular weight of the PDMS polymer peak was calculated from its relative integral. The deprotection reactions were performed at 0 °C and quenched with aqueous NH_4Cl after 15 minutes, as suggested by Collington *et al*[76].

Table 2.9: Results obtained from deprotection reactions using 1 equivalent of TBAF (SEC THF, PS conventional calibration).

Reaction	**End-capping group**	**Dispersity**		**M_n / g mol^{-1}**		**Yield / %**
		Before	**After**	**Before**	**After**	
TBAF 1	MDPS	1.08	1.39	11200	4400	-
TBAF 2	MDPS	1.14	1.18	13000	11500	62
TBAF 3	MDPS	1.08	1.25	12000	9400	80
TBAF 4	MDPS	1.08	1.12	12000	11300	84

NMR analysis of TBAF 1 showed that the deprotection reaction went to completion and all TBDMS groups were removed however, as indicated in Table 2.9, SEC analysis indicated that the product of TBAF 1 had suffered a sharp decrease in molecular weight and a rise in dispersity. This is a clear indication of polymer degradation. No attempt was made to calculate the yield of TBAF 1 since the initial goal was to observe the extent of degradation and deprotection. Further repeats were performed to confirm the outcome of the initial reaction. Although in subsequent repeat reactions, without changing any variables, the extent of degradation reduced, it was not eliminated and SEC data in all cases showed a decrease in molar mass and increase in dispersity compared to the starting polymer – albeit rather modest changes in the product of TBAF 4. The difference between the values obtained from the experiments are believed to be a result of difficulties in calculating the molecular weight of polymers which were subsequently used to calculate number of moles of TBAF needed. The procedures followed was same for all the polymerizations. However, these results are very promising because dispersity values of 1.12, 1.18 and 1.25 are small, indicating narrow molecular weight distribution. The results show a degree of control over dispersity is possible with this method. A detailed analysis of the SEC of TBAF 3 (Figure 2.20) shows that a tail was formed toward low molecular weights after the deprotection reaction. This tail is formed by the chains broken down in to two or more as a result of the fluoride anion attack to siloxane backbone.

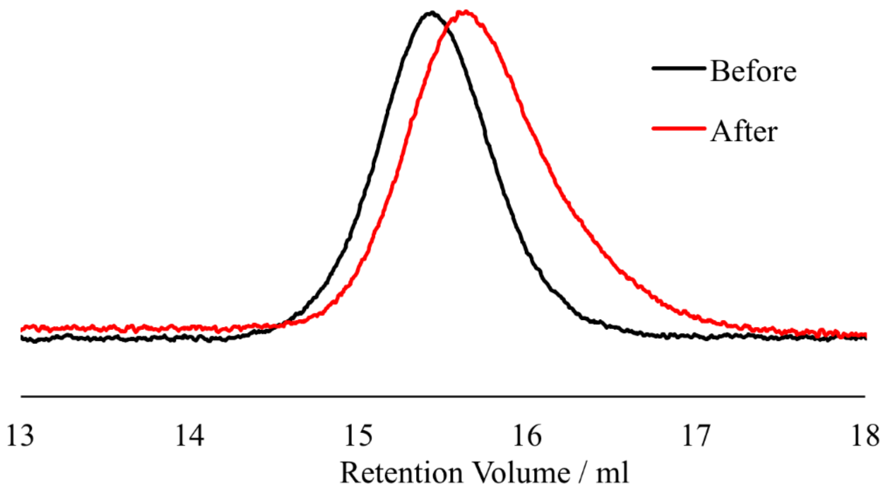


Figure 2.20: The comparison of the viscometer data, obtained from SEC (THF), before and after the deprotection experiment TBAF 3.

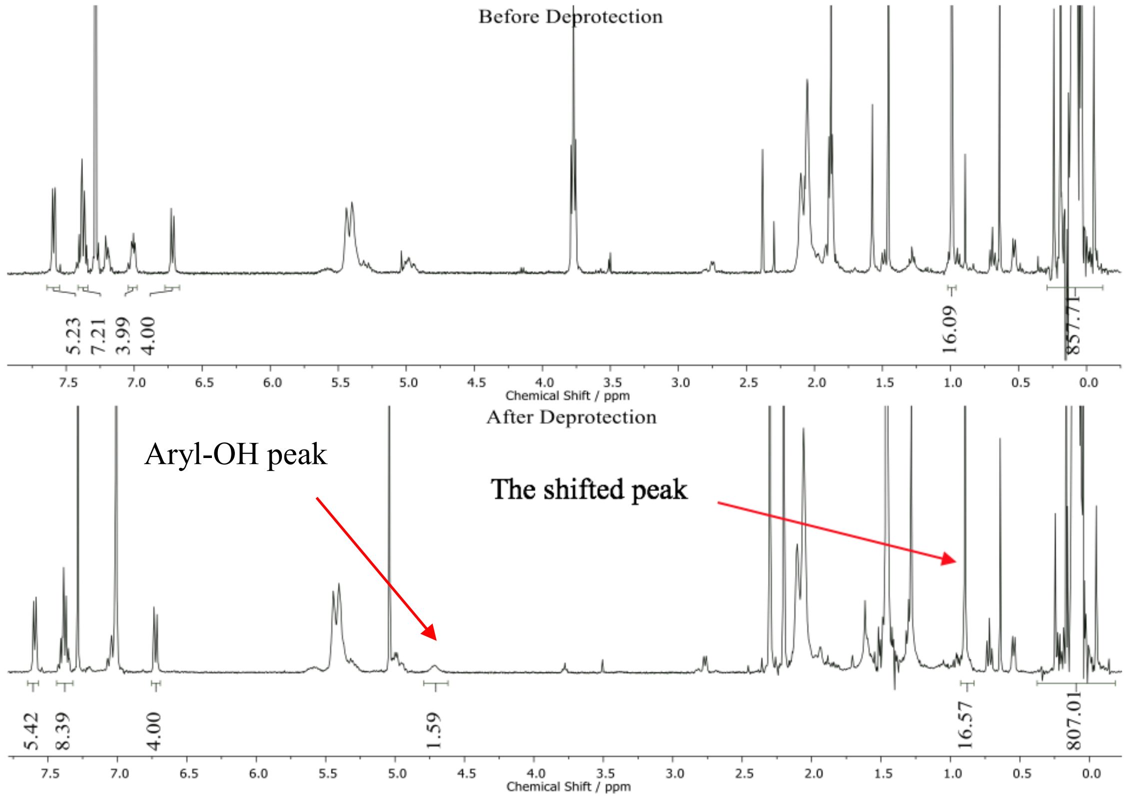


Figure 2.21: The ^{1}H NMR ($CDCl_3$) spectrum of the polymer obtained after the deprotection experiment TBAF 3.

The NMR spectra of the polymer before and after deprotection in TBAF 3 were compared and the product showed a phenolic-OH peak appeared at 4.7 ppm which clearly indicates successful deprotection (Figure 2.21). The peak for t-butyl group of TBDMS did not disappear but instead shifted from 0.99 ppm to 0.86 ppm. This indicates a new chemical environment. This information alongside the appearance of aryl-OH peak on the proton NMR spectrum confirms the deprotection. It is believed that the shifted peak can be assigned to the product of the deprotection reaction. It is possible that this product with Si-F bond was trapped inside the polymer and could not be removed during the precipitation or hydrolysed and joined to the polymer chain through condensation. Thus, although some polymer degradation did still occur during the deprotection using TBAF, deprotection of the TBDMS group was achieved to produce PDMS polymer chains functionalised with 1,1-bis(4-hydroxyphenyl)ethylene groups which might be used for coupling reactions (see the attempted coupling reactions in Section 2.2.4).

2.2.3.3 Attempted Deprotection under Acidic Conditions

2.2.3.3.1 Hydrochloric Acid

Table 2.10: Result obtained from attempted deprotection reactions using hydrochloric acid (SEC THF, PS conventional calibration).

Reaction	End-capping group	Conditions	% Removal of TBDMS	Dispersity		M_n / g mol^{-1}	
				Before	After	Before	After
HCl 1	MDPS	5 eq of HCl, THF, 25 °C, 24 h	20	1.16	Multiple Peaks	4200	Multiple Peaks

Mild-acid hydrolysis is the most commonly employed method for the cleavage of the TBDMS protecting group. However, the use of acid conditions is also known to result in the degradation of PDMS. It has previously been reported that 5 equivalents of HCl relative to Ar-OSi were used to deprotect DPE-OSi end-capped polystyrene[49] and it was decided to attempt the deprotection reaction with 5 equivalents of HCl. NMR analysis of the product indicated a low degree of deprotection and SEC analysis also indicted a multimodal molar mass distribution with an additional peak at lower molecular weights, clearly suggesting the degradation of the polymer backbone. Such was the effect of HCl upon the degradation of the polymer backbone that this strategy was taken no further.

2.2.3.3.2 Acetic Acid

Table 2.11: Results obtained from deprotection reactions using acetic acid (SEC THF, PS conventional calibration).

Reaction	End-capping group	Conditions	% Removal of Protecting Group	Dispersity		M_n / g mol^{-1}	
				Before	After	Before	After
AcOH-TBDMS	MDPS	A ratio of 0.15:1:3 Water/AcOH/THF	<1	1.08	1.08	12000	12400
AcOH-TES	MDPS	A ratio of 0.15:1:3 Water/AcOH/THF	>90	1.10	1.08	15400	16200

In the previous attempts to carry out a selective deprotection reaction using HCl in a hydrolysis reaction it was found that presence of a strong proton donor, even in low amounts, degrades the PDMS backbone harshly. Acetic acid was considered a suitable alternative because of its weakly acidic nature. It has been previously reported that acetic acid can be used to cleave a TBDMS group in the presence of water.[88, 89] The ideal conditions were reported as being water/AcOH/THF (1:3:1), however PDMS is not soluble under these conditions, although it is soluble in THF. Therefore, we investigated various ratios of this solvent mixture to find a solvent composition that was able to dissolve PDMS. Our investigations found that a ratio of 0.15:1:3 (Water/AcOH/THF) at 60 °C was suitable. The attempted deprotection reaction was allowed to continue for 3 days in this solvent mixture, at which point the polymer was recovered by precipitation in methanol and the product was analysed by SEC and NMR. The SEC chromatogram showed that the polymer did not appear to have degraded and the molar mass and dispersity remained essentially unchanged however, NMR analysis initially indicated that almost no deprotection had occurred, however, when the spectrum was expanded, a small peak can be observed at 4.75 ppm (Figure 2.22) which is where we would expect to see the Ar-OH peak following deprotection. This may suggest a low level of TBDMS deprotection. Given that no degradation had occurred and very little deprotection took place, it was decided to consider how this reaction would perform if the TBDMS group was replaced with the more labile TES protecting group. TBDMS is known to be significantly more stable to acid hydrolysis that TES and the partial success in the cleavage of the TBDMS suggested that more efficient cleavage of a TES group should be possible. TBDMS-protected DPE-OSi was therefore deprotected by using 5 equivalents of HCl in THF at 60 °C and then reprotected with the TES group. This was followed by the initiation of PDMS polymerization by using TES-protected DPE-OSi molecule. The resulting polymer (DPE-Bd-PDMS 10) had a molecular weight of 15400 g mol^{-1} with a dispersity of 1.10.

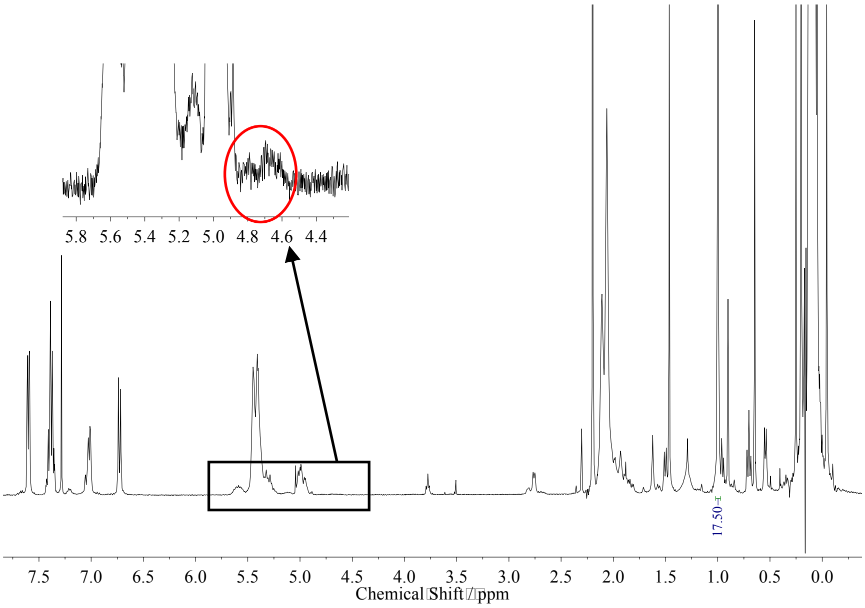


Figure 2.22: The ^{1}H NMR ($CDCl_3$) spectrum obtained from AcOH-TBDMS.

The resulting TES-protected PDMS polymer was subjected to reaction with water/AcOH/THF (0.15:1:3) at 60 °C and the reaction monitored over a week with NMR. The results are shown on Figure 2.23. The peaks in the region of 1.05-0.65 ppm arising from the TES-protecting group, which were previously assigned in Section 2.2.1.1, can be seen to diminish with time. The TES group was successfully deprotected (> 90%) by using this deprotection strategy (Figure 2.23). The reaction was slow, possibly because of the solubility problems, however, it did work. Moreover, the dispersity did not change over the course of the reaction and the molecular weight remained stable. This indicates that the TES-protected polymer can be successfully deprotected by using acetic acid and enables the synthesis of dihydroxyl end-functionalized PDMS with well-controlled molecular parameters. Although successful, this route is not terribly practical. Firstly, the rate of deprotection is slow, and, secondly the synthesis of TES-protected DPE-OSi cannot be carried out directly. As mentioned earlier, the TES protecting group does not survive the Wittig reaction required to convert the protected benzophenone to the diphenylethylene and therefore the only viable route to the TES protected DPE-OSi requires the deprotection of the TBDMS group followed by reprotection with TES group. This is far from straightforward and results in a long synthetic procedure (time-consuming) and low yields.

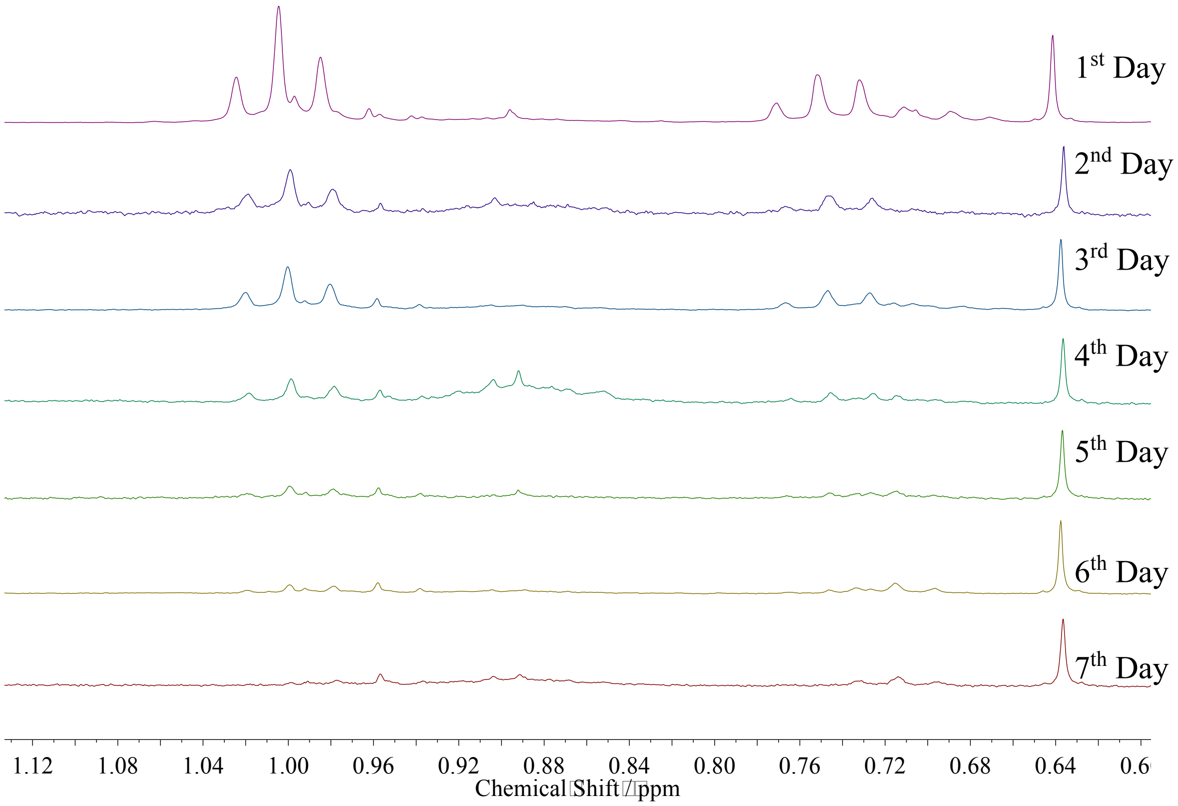


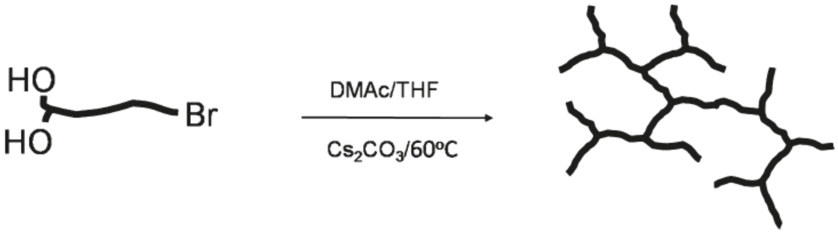
Figure 2.23: Disappearance of TES protecting groups over a week (^{1}H NMR, $CDCl_3$).

2.2.3.4 Summary

A range of deprotection strategies were attempted to obtain dihydroxyl end-functionalized PDMS with low dispersity. In most cases the PDMS backbone suffered from degradation. Deprotection reactions with NaH, DBU and HCl failed to go to completion, the latter also resulting in severe degradation. TBAF and AcOH methods were shown to successfully give dihydroxyl-functionalized PDMS with low dispersity. However, AcOH route must be preferred whenever a total control is needed over molecular parameters such as the synthesis of AB_2 macromonomers. Polymer chains are believed to remain intact with the AcOH strategy. A slight increase in the dispersity with TBAF deprotection and the presence of tail on SEC means there are chains that are not intact. However, there are limitations with the AcOH method since the synthesis of TES-protected DPE is troublesome. This is because of the multistep synthesis and the necessity of water, which results in solubility issues, to speed up the reaction. A different initiator precursor could potentially be developed to replace DPE in future. We have decided to use TBAF deprotection method for the next step, to allow a Williamson coupling for star copolymer synthesis, because of practical issues mentioned above and no necessity to keep both end-groups on the polymer chains at this point.

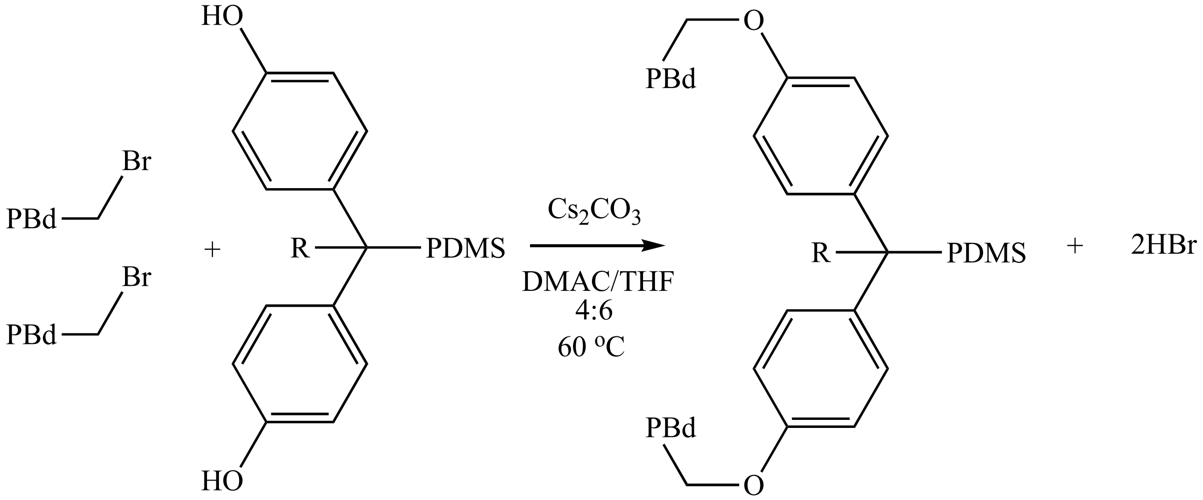
2.2.4 The Synthesis of Branched Polymers Using the End-Functionalized Polysiloxane Macromonomer Approach

The objective of synthesising end-functionalised PDMS was to produce a macromonomer capable of undergoing coupling reactions to yield branched polymers. We describe here the attempted use of a Williamson coupling reaction to produce a branched block copolymer.



Scheme 2.18: An example scheme to demonstrate the synthesis of polybutadiene HyperMacs provided by Hutchings *et al.*[50]

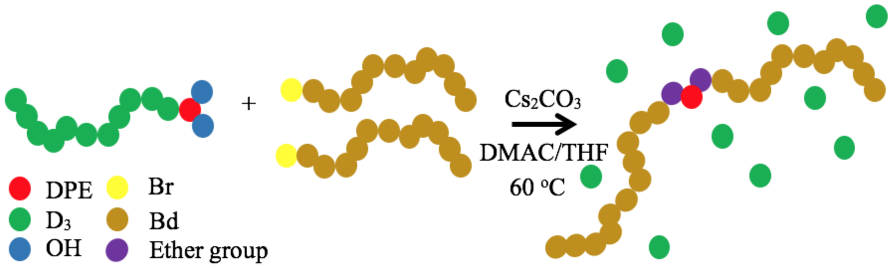
Williamson coupling, also known as Williamson ether synthesis, is a reaction between an alkoxide and an organohalide to form an ether. The reaction originates from 1850s where Alexander Williamson reported it in his paper "Theory of Etherification".[90] Ever since, it has become the most common route to synthesise ethers. The reaction involves base deprotonation of an alcohol group and the resulting alkoxide undergoing a nucleophilic substitution reaction with an electrophilic C-X bond, where X is a halogen that can stabilize the negative charge. This reaction has been widely exploited by Hutchings *et al.* to couple polymers (macromonomers) in the synthesis of HyperMacs and HyperBlocks.[48, 50, 57] The group prepared AB_2 macromonomers containing a halide group at one chain-end and two hydroxyl groups at the other chain-end (Scheme 2.18). In the present work, having established a novel method to synthesise dihydroxyl-functionalised PDMS chains, it was decided to attempt to do Williamson coupling on these chains. The ultimate goal was to study if this strategy of coupling polymers with this strategy would work with PDMS chains since PDMS chains are quite delicate and degrade easily even under mild conditions.



Scheme 2.19: Coupling of bromo end-capped polybutadiene macromonomers with dihydroxyl end-capped PDMS macromonomer.

It was decided to couple PDMS-(OH)$_2$ with bromide functionalised polybutadiene chains (PBd-Br) using the conditions shown on Scheme 2.19. It was previously reported in Section 2.3.1, that Cs_2CO_3 can potentially cleave a TBDMS group and therefore a degree of degradation of the PDMS chain was expected. Williamson coupling reactions are usually performed in polar aprotic solvents, such as DMF and DMAC, as this is an S_N2 reaction. However, since neither PDMS nor PBd is soluble in either of those solvents, a solvent mixture of DMAc and THF was used. It was found that a ratio of 4:6 DMAC/THF was a suitable solvent system for the starting materials and potentially for any block copolymers formed during the reaction. The weight-average molecular weight of the PBd and PDMS macromonomers were 20000 g mol^{-1} and 9400 g mol^{-1}, respectively. Therefore, the expected molecular weight of the coupled polymer would be around 50000 g mol^{-1} and as such a successfully coupling should be evident by SEC. However, partially coupled polymer is also a possible by-product.

Samples were removed periodically from the mixture and analysed by SEC (Figure 2.24) and NMR (Figure 2.25). After 1 hour, the only species visible in the SEC chromatogram was the unreacted polybutadiene macromonomer. The peak from PDMS macromonomer was expected to appear at around 15 ml but light scattering is very weak for PDMS as it is isorefractive with THF. It can be the case that PDMS peak is somehow omitted in the noise. The NMR analysis of the first three samples indicated that the peak at 0.08 ppm, arising due to the methyl groups on the PDMS backbone, diminished very quickly with almost no peak remaining after 2 hours (Figure 2.25). The PDMS chains appear to have broken into smaller pieces and were not recovered during precipitation. PDMS is isorefractive in THF and it is believed that its RI signal is so poor compared to PBd, it does not appear. However, after three hours a second, higher molecular weight peak can be seen with a retention volume of approximately 13.3 ml, and this peak continues to grow with time. After 19 hours, the intensity of the PBd-Br macromonomer peak (c. 13.8 ml retention volume) was less intense than the peak at 13.3 ml and a broad shoulder at lower retention volumes (higher molecular weights) has appeared. From the results, it can be seen that no further reaction appeared to have occurred after 24 hours. The presence of PBd-Br macromonomer peak after 24 hours was expected, since PBd-Br was present in excess in the mixture with 2.5 equivalent of PBd-Br used relative to PDMS-$(OH)_2$. The SEC analysis obtained for both peaks are shown in Table 2.12. The PBd-Br macromonomer and coupled polymer both gave light scattering signals and the SEC analysis could be performed by both triple detector and conventional calibration. Knowing that the PDMS did not survive in the presence of the base (from NMR), Cs_2CO_3, this suggests the coupling reaction was actually between a fragment containing the residual DPE-OH molecules and the PBd-Br (Scheme 2.20). Origin of the broad shoulder is unknown.



Scheme 2.20: Illustration of the proposed result of the Williamson coupling reaction with Cs_2CO_3.

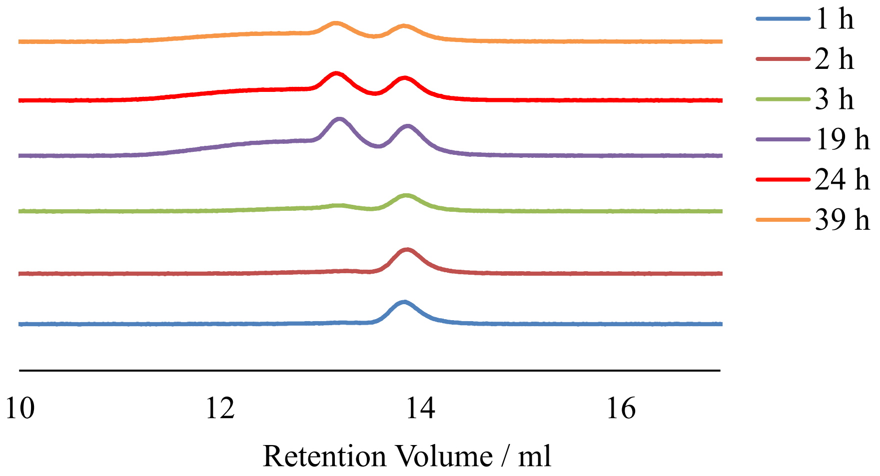


Figure 2.24: The light scattering data obtained from SEC (THF) analysis of samples taken from the coupling reaction at various intervals.

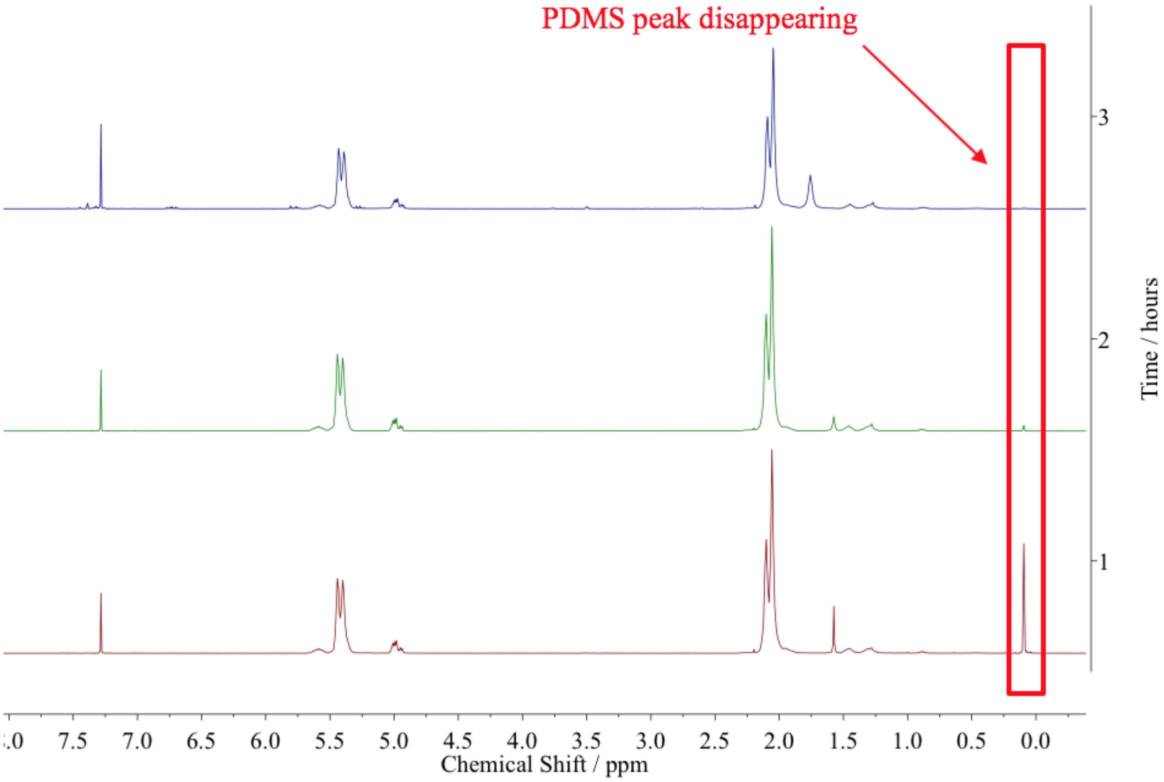


Figure 2.25: The ^{1}H NMR ($CDCl_3$) spectra obtained from samples taken during the coupling reaction after 1, 2 and 3 hours following the addition of Cs_2CO_3.

Table 2.12: The molecular weight and dispersity analysis of the chromatograms shown on Figure 2.24 (SEC THF, PS conventional calibration).

Peak	M_n / g mol^{-1}		M_w / g mol^{-1}		Dispersity	
	Conventional Calibration	Triple Detector	Conventional Calibration	Triple Detector	Conventional Calibration	Triple Detector
1	38500	22700	40100	24000	1.04	1.05
2	89800	54900	99200	70300	1.17	1.28

Williamson coupling reactions require a base as a reaction between an alcohol and an organohalide is extremely slow in the absence of a base. This base need to be basic enough to deprotonate an Ar-OH group which is believed to has a tendency to lose its proton because of the possible delocalisation of the anion in the ring system. Therefore, it was decided to try a weaker base than Cs_2CO_3 with a view to avoid PDMS degradation. Hutchings *et al.* previously reported the use of K_2CO_3 with 18-crown-6 ether for their Williamson (polymer) coupling reactions.[49] A potassium cation is significantly smaller than a caesium cation and therefore, it holds to the carbonate anion more strongly than the caesium which makes it significantly less basic, but it is still basic enough to deprotonate an Ar-OH group. Moreover, Paul *et al.* has reported that Williamson ether synthesis can be catalysed by zinc in the absence of a base.[91] To the best of our knowledge, this approach has not been used to couple polymer chains before. However, before proceeding it was decided to carry out some preliminary reactions to confirm the extent to which PDMS degrades in the presence of Cs_2CO_3 and then to repeat this experiment with K_2CO_3 and Zn. Hence, PDMS was subjected to the same reaction conditions as described above for the coupling reaction, except no polybutadiene macromonomer was added. About 0.25 g of PDMS was used in each case and a 10% solution was prepared. The solvents were DMAC/THF (4:6) for Cs_2CO_3 and K_2CO_3 and THF was used as the solvent for reaction with Zn. 5 equivalents of the carbonate and 1 equivalent of Zn relative to PDMS were used. Each of the mixtures were stirred for 8 hours at 60 °C and the results are shown in Table 2.13.

Table 2.13: The results obtained from the stability experiments performed on PDMS with various deprotonation agents (SEC THF, PS conventional calibration).

Deprotonating Agent	Dispersity		Molecular Weight (M_n) / g mol^{-1}	
	Before	**After**	**Before**	**After**
Cs_2CO_3	1.14	-	12000	-
K_2CO_3	1.14	1.23	12000	11800
Zn	1.14	1.14	12000	11500

No polymer was recovered when Cs_2CO_3 was used. This clearly confirms that the PDMS chains do not survive when Cs_2CO_3 is the base. A small increase in dispersity and decrease in molecular weight was observed when K_2CO_3 was used. It can be said that potassium carbonate can potentially degrade the polymer but this degradation is slow. No change in dispersity was observed when zinc was used. It was decided to repeat the Williamson coupling between PDMS-$(OH)_2$ and PBd-Br using K_2CO_3 with 18-crown-6 ether, and also using zinc. The optimum conditions are not known for neither of the reagents however, an analogous synthesis with potassium carbonate was previously reported by Hutchings *et al.* using 5 equivalents of both the carbonate and the crown ether.[49] It was decided to use these reported quantities but it must be noted that optimization may again be necessary to ensure minimal degradation to PDMS chains whilst maximising the degree of coupling. Zn-catalysed Williamson coupling was performed with small molecules only and the report in question used 0.25 equivalents of Zn relative to Ar-OH group to be used.[91] However, polymers are macromolecules and reactivity is often lower compared to small molecules. It was decided therefore to use 1 equivalent of Zn, about 4 times the suggested value in literature.

Table 2.14: The results obtained from the Williamson coupling reactions performed with Zn and K_2CO_3 deprotonation agents (SEC THF).

Reagent	Peak	Triple Detector SEC		
		M_n / g mol^{-1}	M_w / g mol^{-1}	Dispersity
K_2CO_3	1	20900	21700	1.04
	2	33900	35000	1.03
	3	57800	61500	1.07
Zinc	1	18600	19700	1.06
	2	47700	51900	1.09

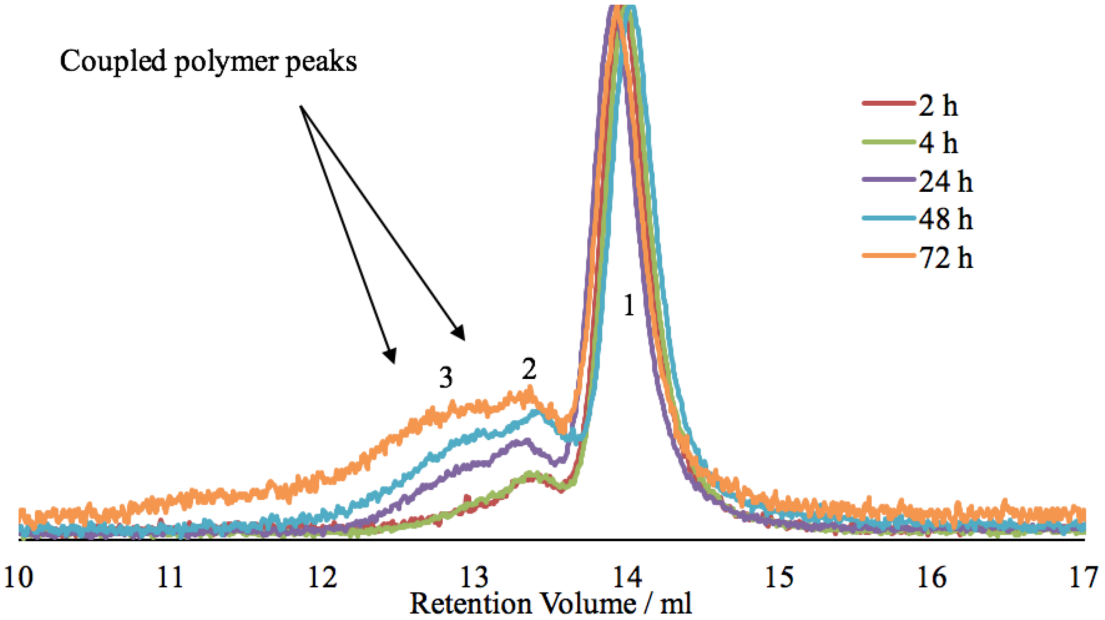


Figure 2.26: The light scattering data obtained from SEC for the Williamson coupling reaction performed with K_2CO_3 and 18-crown-6 ether.

The results obtained with potassium carbonate/18-crown-6 ether and zinc are shown on Table 2.14, Figure 2.26 and Figure 2.28. As a light scattering signal was obtained, it was decided to use triple detector to analyse the coupled polymers. It must be noted that the dispersity values stated on the table for coupled polymers are artificially narrow because of the limits chosen to analyse the peak molecular weights. It can be clearly seen in Figure 2.26 that the coupling did happen, although not to any great extent. Unlike the coupling attempt with Cs_2CO_3, where a single coupled polymer distribution was observed, this attempt resulted in a broad, multimodal peak to lower retention volumes which suggests some chain coupling. The peak appearing at 13.3 ml gave a M_n of 33900 g mol^{-1} and it is believed to be associated with HO-PDMS-PBd, partially branched copolymer, since PBd had a molecular weight of 20900 g mol^{-1} and PDMS-$(OH)_2$ had a molecular weight of 9400 g mol^{-1}. The SEC analysis of the peak at 12.8 ml gave a M_n of 59200 g mol^{-1} indicated that this peak is likely to be associated with $(PBd)_2$-PDMS star block copolymers. Despite these promising results, it must be noted that the extent of coupling was not high – the reaction did not go to completion. This was not unexpected and, in fact, the preference of Cs_2CO_3 over K_2CO_3 for polymeric Williamson coupling reactions is usually solely based on better reaction kinetics obtained with the former.

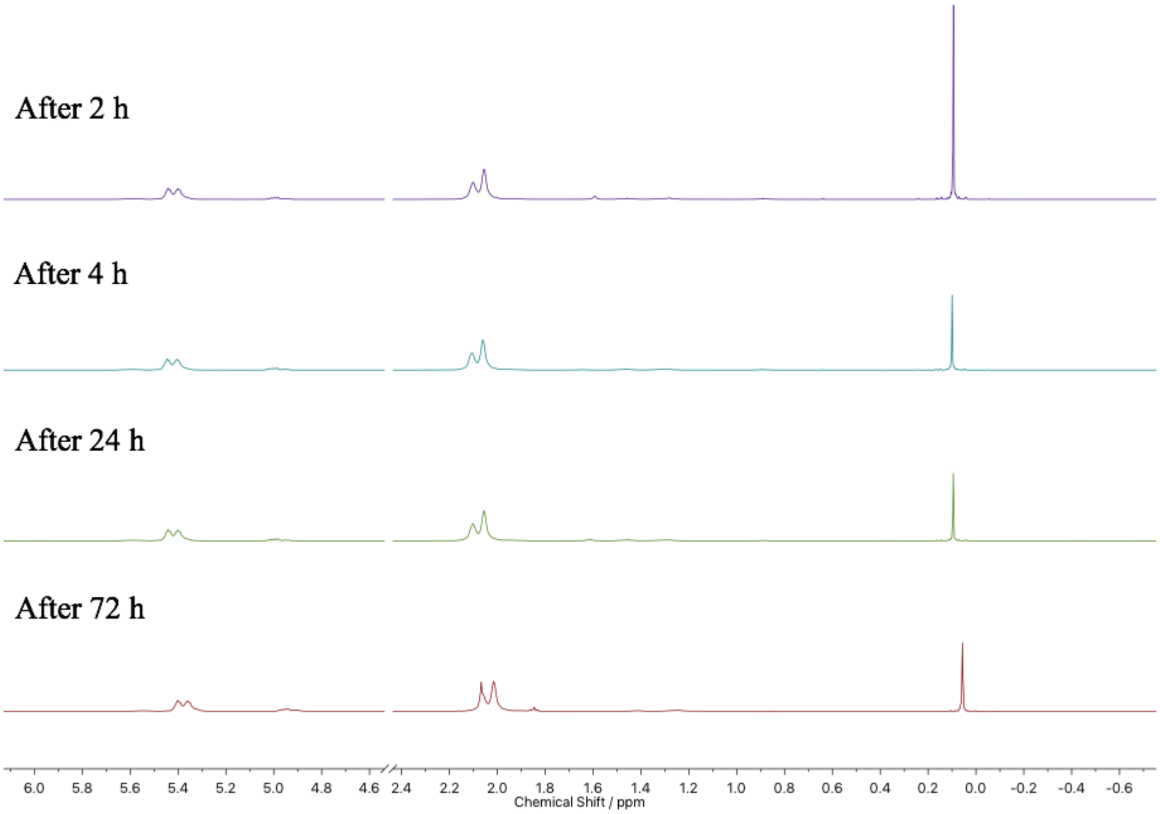


Figure 2.27: The ^1H NMR ($CDCl_3$) spectra obtained from the samples taken during the Williamson coupling using K_2CO_3 and 18-crown-6 ether. The PBd peak at 2.05 ppm was normalized to be the same intensity in all spectra.

The NMR spectra obtained (Figure 2.27) were examined to establish if PDMS was degraded, as it was with Cs_2CO_3. The PBd peak at 2.05 ppm was normalized to be of constant intensity in all spectra and change in the intensity of PDMS peak (0.06 ppm) was assessed. It can be seen that the intensity of the PDMS peak more than halved between samples taken after 2 hours and after 4 hours. This result agrees with the results obtained from the stability test to some extent (Table 2.13). Potassium carbonate does degrade the PDMS polymer, albeit more slowly than Cs_2CO_3. However, the degradation seemed to stop after 4 hours and the intensity of the PDMS peak remained stable until the precipitation which was performed after 72 hours. This observation likely suggests that all the base was consumed by the reaction after 4 hours or some PDMS chains containing the MDPS end-capping does survive K_2CO_3 and other that do not possess the end-capping group degrades.

For the zinc-catalysed system, Williamson coupling was observed to some extent but the extent of coupling was even poorer (Figure 2.28) than the Williamson coupling with potassium carbonate. It was previously stated that this zinc-catalysed Williamson coupling reaction was not used to couple polymers and, therefore, requires optimization.

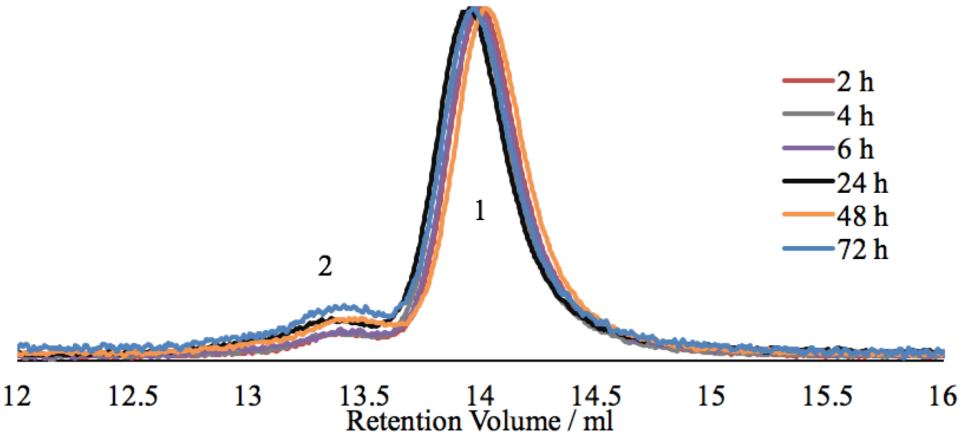


Figure 2.28: The light scattering data obtained from SEC (THF) for the Zn-catalysed Williamson coupling.

The results with zinc were encouraging but further work is required to establish whether this is a viable route to chain coupling via a Williamson reaction. However, it is also worth noting that NMR analysis of the product of the Williamson ether synthesis with zinc, showed that PDMS backbone does not degrade (Figure 2.29). The intensity of the PDMS peak remained stable even after 24 hours.

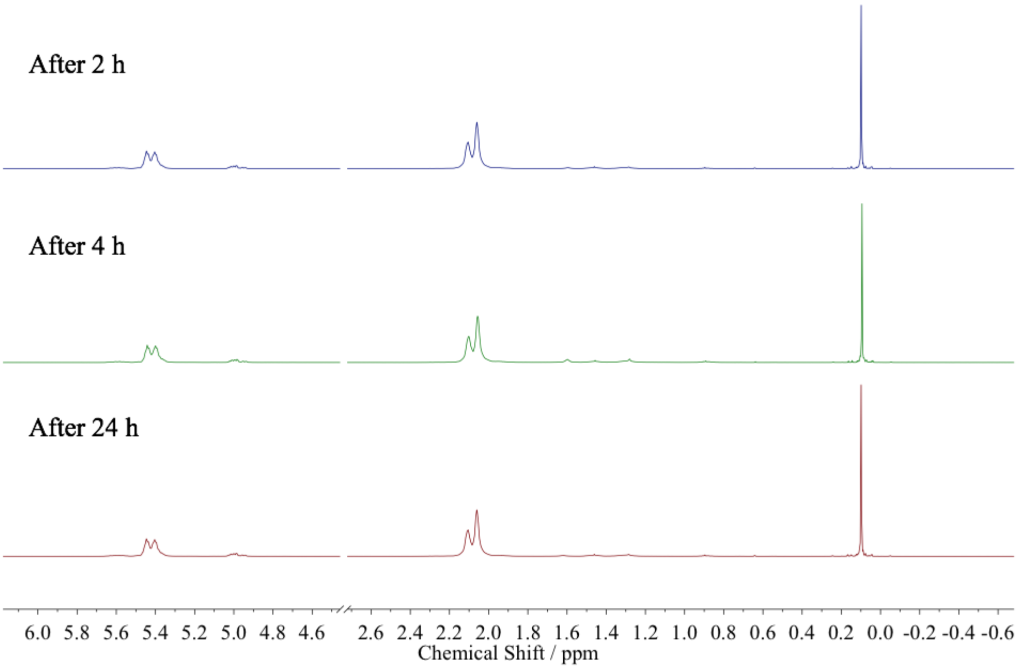
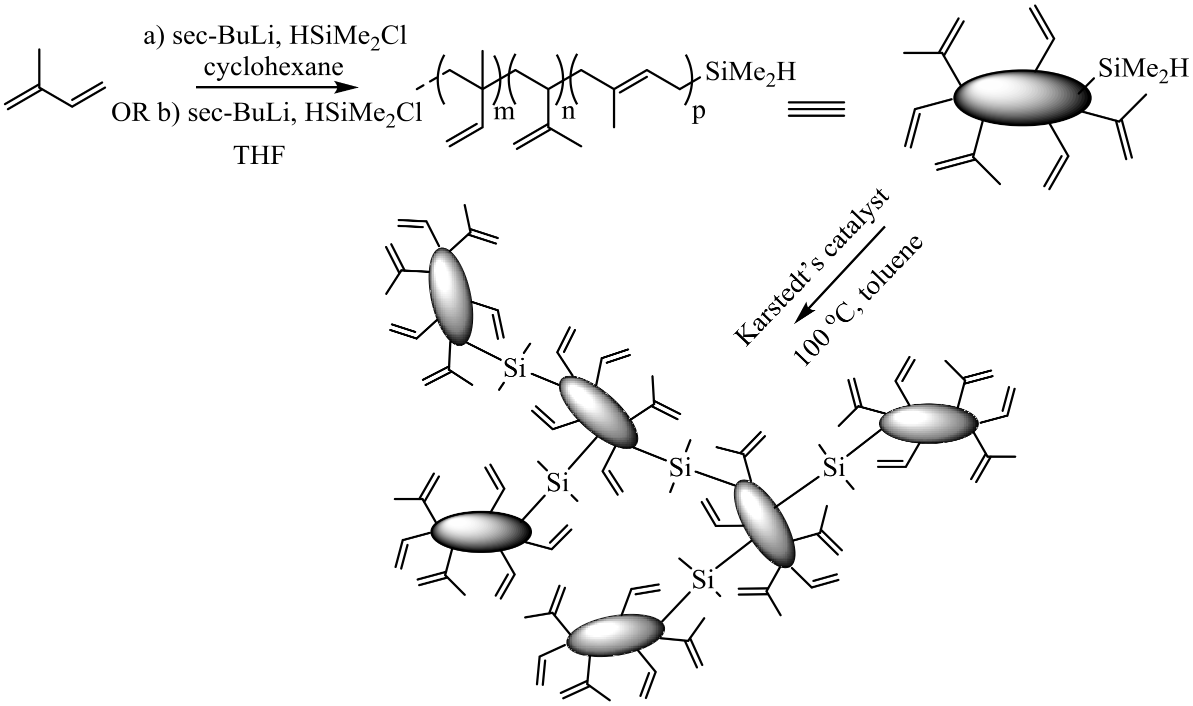


Figure 2.29: The ^1H NMR ($CDCl_3$) spectra obtained from the samples taken during the zinc-catalysed Williamson coupling. The PBd peak at 2.05 ppm was normalized to be the same intensity in all spectra.

It was demonstrated that the necessity of a base in these etherification reactions caused significant degradation and kinetic issues. We have decided to stop proceeding with this AB_2 macromonomer approach as the coupling reactions attempted failed to yield branched polymers with well-defined blocks.

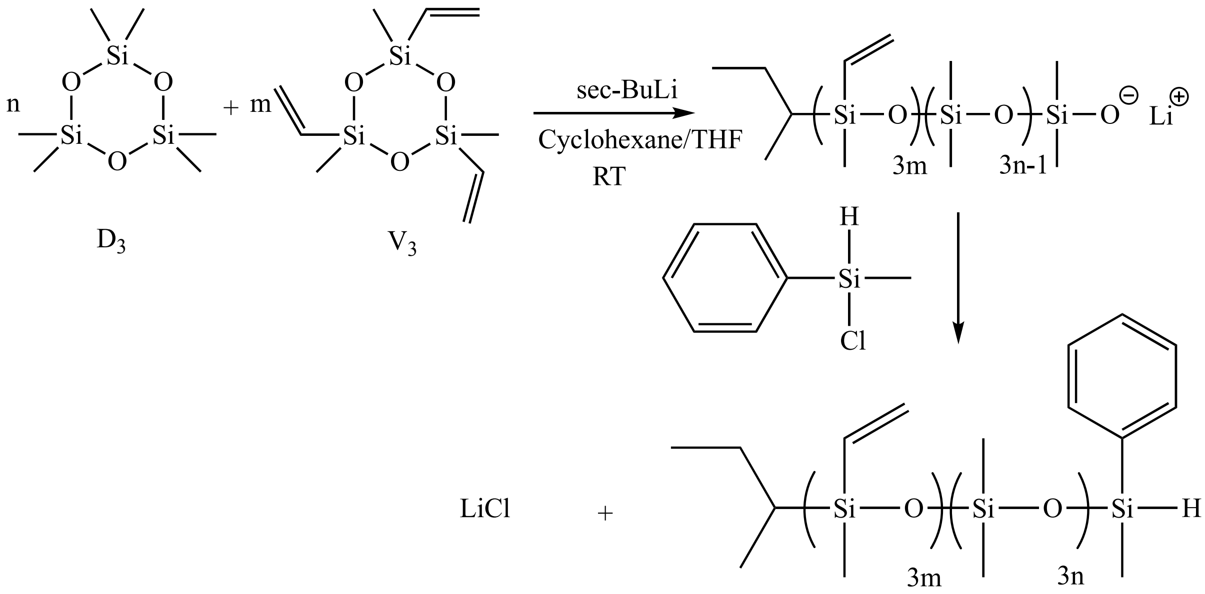
2.3 Synthesis and Coupling of AB_x Polysiloxane Macromonomers to Form Highly Branched Polysiloxanes

It is well-established in polymer chemistry that the physical properties of macromolecules are governed by chemical structure, such as functional groups, and molecular architecture, such as branching.[26] Highly branched polymers have always attracted significant attention as these polymers possess significantly different characteristics from their linear polymers of similar molecular weight in terms of their thermal behaviour, crystallization and rheology.[92] Inspired by a previous report by Frey *et al*.[93] who reported the coupling of AB_x polyisoprene macromonomers via a platinum catalysed hydrosilylation reaction (Scheme 2.21), an analogous strategy has been developed for the synthesis of highly (hyper)branched PDMS. The Frey Group synthesised several Si-H end-functionalised polyisoprene macromonomers with varying alkene microstructure by anionic polymerisation. The resulting polymers were comprised of a mixed microstructure of both 1,4 and 1,2 (or 3,4) repeat units, the former containing an alkene bond in the polymer backbone and the later a pendant/terminal vinyl double bond. Only the pendant double bonds is able to react during the hydrosilylation reaction. The group altered the ratio of cyclohexane, which favours 1,4-polymerization, and THF, which favours 1,2- and/or 3,4- polymerization, and obtained polyisoprene macromonomers with varying microstructure. These macromonomers were then coupled by a hydrosilylation reaction to form highly branched polyisoprene and the impact of microstructure on the coupling reaction reported.[93] It was decided to develop an analogous approach in the current work and we have incorporated vinyl groups in to the polysiloxane chain by the anionic copolymerization of D_3 and V_3 monomers. This section is divided into two parts; synthesis of Si-H chain-end functionalized statistical copolymers of PDMS-co-PMVS as AB_x macromonomers and secondly, the hydrosilylation coupling reactions of the aforementioned macromonomers.



Scheme 2.21: The work performed by Frey Group to synthesise branched polyisoprenes.[93]

2.3.1 Synthesis of Si-H Functionalized PDMS-co-PMVS AB_x Macromonomer



Scheme 2.22: Synthesis of Si-H functionalized PDMS-co-PMVS polymer.

Well-defined AB_x polysiloxane macromonomers, where A and B represent Si-H and the V_3 vinyl groups respectively, with exact molecular weight and narrow dispersity can be prepared by anionic ring-opening copolymerization (AROP) of D_3 and V_3 monomers (Scheme 2.22). As in the case of AROP of D_3 monomer, anionic polymerization of V_3 monomer is driven by the ring strain. V_3 monomer is more strained than D_3 because of the vinyl groups and this results in greater tendency for V_3 monomer to be opened – V_3 is a more reactive monomer.[26] As mentioned in the Introduction, the reactivity ratios of V_3 and D_3 monomers are 17.8 and 0.036 at 25 °C in THF, respectively.[26, 41] These reactivity ratios mean that V_3 shows a very strong tendency to homopolymerise and D_3 a strong tendency to copolymerise. As such, the resulting copolymers will be far from random and an equimolar feed ratio would lead to a block-like sequence despite the fact that both monomers are present at the same time.

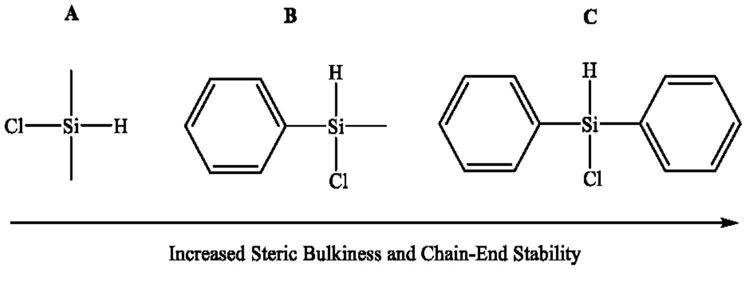


Figure 2.30: Chemical structures of the end-capping molecules considered and the trends in steric bulkiness and chain-end stability.

Living anionic ring-polymerization allows the synthesis of Si-H end-functionalised polysiloxanes by the use of modified termination agents. There were two concerns in choosing a suitable end-capping agent; stability of the copolymer backbone and the steric hindrance at the Si-H group containing chain end. Three molecules (Figure 2.30), chlorodimethylsilane (A), chloro(methyl)phenylsilane (B) and chlorodiphenylsilane (C), were considered as the end-capping agent. There are two expected trends among these molecules. Chain stability would increase as A < B < C while steric bulkiness would increase as A < B < C. It is desirable for the PDMS chain-end to gain some stability however steric hindrance of Si-H bond would result in poor coupling kinetics. It was decided to use chloro(methyl)phenylsilane as the end-capping agent. It is believed that a single phenyl group would provide the needed stability without affecting the kinetics of the reaction. In addition, the presence of phenyl group also helps to the quantization of the end-capping reaction.

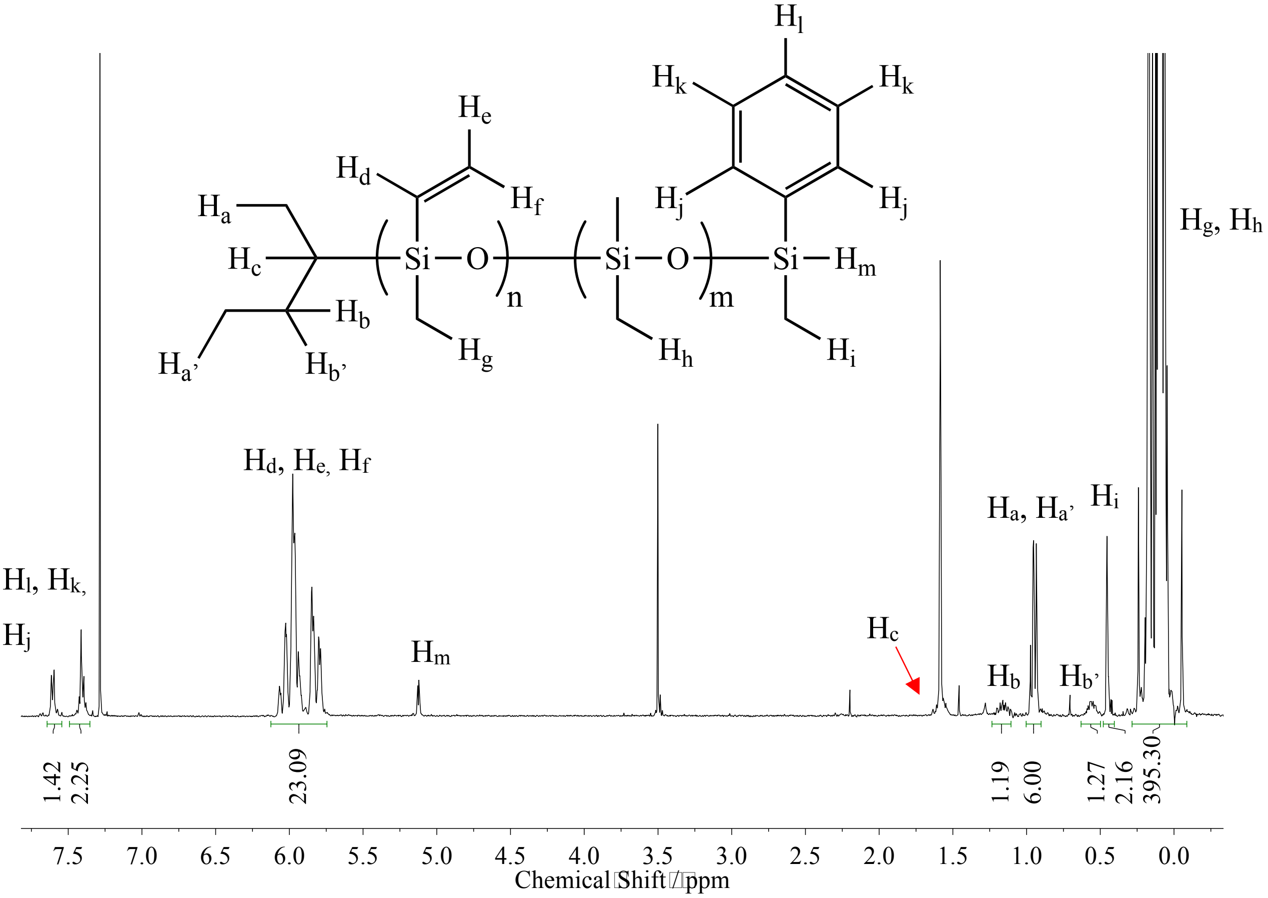


Figure 2.31: The ^{1}H NMR ($CDCl_3$) spectrum of PDMS-PMVS 1.

Calculation 2.6: Determination of M_n and composition of PDMS-PMVS 1 from the NMR spectrum on Figure 2.31.

M_n calculation from NMR :

Molar mass of each $(CHCH_2)(CH_3)Si\text{-}O$ unit = 86.17 g mol^{-1} per unit

Molar mass of each $(CH_3)_2Si\text{-}O$ unit = 74.15 g mol^{-1} per unit

$$\text{Number of }(CHCH_2)(CH_3)Si\text{-}O\text{ units in the chain} = \frac{\text{Vinyl integral}}{\text{Protons in each vinyl unit}} = \frac{23.09\text{ protons}}{3\text{ protons per unit}} = 7.7\text{ units}$$

Total molar mass of $(CHCH_2)(CH_3)Si\text{-}O$ units in the chain = 7.7 units x 86.17 g mol^{-1} per unit = 663.5 g mol^{-1}

$$\text{Number of }(CH_3)_2Si\text{-}O\text{ units in the chain} = \frac{\text{Methyl integral - Vinyl integral}}{\text{Number of protons in in each }(CH_3)_2Si\text{-}O\text{ unit}}$$

$$□\ \frac{395.30\text{ protons - }23.09\text{ protons}}{6\text{ protons per unit}} = 62.0\text{ units}$$

Total molar mass of $(CH_3)_2Si\text{-}O$ units in the chain = 62.0 units x 74.15 g mol^{-1} per unit = 4597 g mol^{-1}

M_n of PDMS-PMVS 1 = 663.5 g mol^{-1} + 4597 g mol^{-1} = 5260 g mol^{-1} $\cong$ 5300 g mol^{-1}

V_3 composition in PDMS - PMVS 1 :

$$\text{weight \%} = \frac{663.5\text{ g mol}^{-1}}{5260\text{ g mol}^{-1}} \text{ x } 100 = \mathbf{13\%} \qquad \text{mol \%} = \frac{7.7\text{ units}}{62\text{ units} + 7.7\text{ units}} \text{ x } 100 = \mathbf{11\%}$$

A total of 5 copolymeric macromonomers were synthesised with varying ratios of V_3 and D_3 monomers. A general aim was to keep the V_3 mole fraction low in the macromonomers since this is an expensive monomer whereas D_3 is relatively cheap. A low mole fraction of V_3 is also believed to result in a less block-like structure. The mole fraction of V_3 in each copolymer, along with SEC and NMR results, and the extent of end-capping, are shown on Table 2.15. Molecular weight and V_3 compositions were calculated from NMR (Figure 2.31) as shown on Calculation 2.6. Integral of the NMR peaks arising from H_a and $H_{a'}$ was set to be 6 protons as these are the protons of sec-butyl initiator group. Degree of the end-capping was calculated by using the aromatic protons (Calculation 2.7).

Calculation 2.7: Degree of the end-capping for PDMS-PMVS 1.

$$\frac{\text{Combined integral of the aromatic peaks}}{\text{Theoretical integral of the aromatic peaks}} = \frac{2.25\text{ protons} + 1.42\text{ protons}}{5\text{ protons}} = 73\ \%$$

Low molecular weights were generally targeted and achieved (5400-10200 g mol^{-1}). Polymerizations were terminated after 4 hours with 3 equivalents of chloro(methyl)phenylsilane. A detailed typical synthetic procedure is provided in Experimental. Dispersity values were a little high for an anionic polymerization but this is probably a result of previously discussed back-biting reactions. A series of copolymers were prepared with 11 mol% to 52 mol% V_3 composition. Chain-end functionalization was reasonably successful, with the exception of PDMS-PMVS 4 in which only 42 % of the chains functionalized with Si-H group. This could have happened as a result of impurities injected into the polymerization during termination step or the enhanced rate with high V_3 monomer content in the reaction. The enhanced reactivity means the reaction reaches to higher conversions quickly and suffers more from backbiting. This may result in large macrocycles, without the end-capping group, and small polymer chains and would be terminated by chloro(methyl)phenylsilane but they might be soluble during precipitation. However, as dispersity values are relatively lower for polymers with high V_3 composition, it can be hypothesised that backbiting is less likely to occur as a result of the steric bulk of the vinyl group. Poor end-capping results in the lack of Si-H group which means these macromonomers lack the A group and can only couple to other polymers via their B_x vinyl groups.

Table 2.15: SEC (THF, PS conventional calibration) and NMR ($CDCl_3$) results obtained for the macromonomers and their analysis.

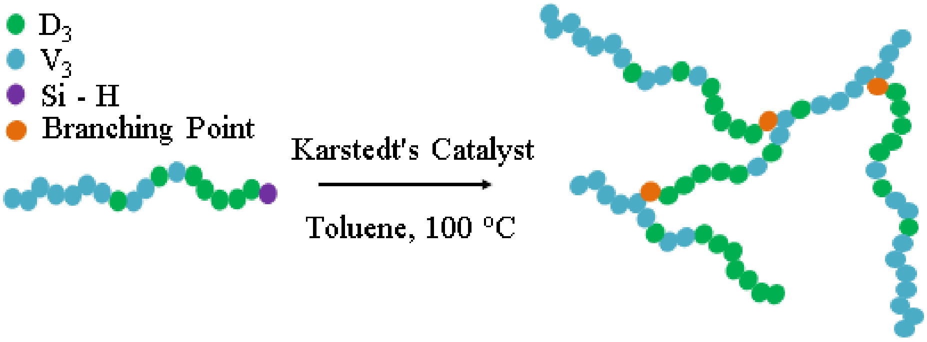
Polymer	SEC			NMR
	M_n / g mol^{-1}	**M_w / g mol^{-1}**	**Đ**	**M_n / g mol^{-1}**
PDMS-PMVS 1	7200	8900	1.25	5300
PDMS-PMVS 2	9600	12700	1.32	10200
PDMS-PMVS 3	8000	9400	1.17	5300
PDMS-PMVS 4	7000	8300	1.19	5200

Polymer	Composition / mol % V_3	Degree of End-capping / %	Yield / %
PDMS-PMVS 1	11	73	81
PDMS-PMVS 2	22	75	78
PDMS-PMVS 3	35	63	68
PDMS-PMVS 4	52	42	71

2.3.2 Hydrosilylation Coupling Reaction

Hydrosilylation is the name given to the addition of Si-H bonds to alkenes. The reaction was first reported in 1947 by Sommer *et al.*[94] In Ullmann's Encyclopedia of Industrial

Chemistry[95], it was described as the "most important application of platinum in homogeneous catalysis".



Scheme 2.23: Synthesis of highly branched polysiloxanes by hydrosilylation coupling reaction.

As hydrosilylation is a well-used reaction in organic chemistry and, based on the previous work of Frey Group[93], some chain coupling was expected. However, the extent of branching was a matter of speculation. One of the main aims of this work was to explore the conditions which would lead to highest degree of chain branching and two variables were explored, namely macromonomer solution concentration and the mole fraction of V_3 in the macromonomers. The former variable is relevant since macromonomer solution concentration will impact on the balance of intermolecular chain coupling and intramolecular chain cyclisation[49] and the latter is relevant since the mole fraction of V_3 will determine the value of 'x' in the AB_x macromonomer. Therefore, a series of experiments were run to find the optimal conditions. Since one target of this method was to use the minimal amount of (expensive) V_3 units in the macromonomer, the experiments exploring different concentrations, were run on PDMS-PMVS 1 macromonomer. The hydrosilylation reaction was performed at 20 %, 40 %, 60 %, 80% (w/w) solutions and in bulk. In most cases the reaction was carried out in duplicate and in some cases in triplicate. The concentration optimization experiments were followed by NMR (Figure 2.32). In all cases, complete removal of Si-H was observed. The peaks corresponding to the phenyl group (7.3-7.7 ppm) on the end-group has become broader as a result of coupling. This was expected as now there are more than one phenyl group in the resultant branched polymers and their peaks overlap. Another apparent change upon the hydrosilylation reaction is the disappearance of the peak at 0.43 ppm. This peak is associated with H_i protons of the starting material (Figure 2.31). The environment around this peak changes as Si-H bond react with a vinyl group. This reaction also results in the alkylation of the vinyl group and the two newly formed alkane CH_2 groups give peaks at around 0.47 - 0.27 ppm alongside the H_i proton. A final difference in the NMR spectra is the decrease in the intensity of the peaks belonging to the vinyl groups (5.9 ppm). In Figure 2.32, intensity of the vinyl group peak decreased from 22.6 protons to 15.1 protons upon the coupling reaction. Coupling of each vinyl group means a decrease of 3 protons from the vinyl peak and suggesting an average degree of branching of 2.5 ([22.6 protons - 15.1 protons] / 3 protons). However, NMR provides number-average values and not weight-average values. Also, the value of 2.5 does not change significantly between the different concentrations as Si-H peak was completely disappeared in all of these coupling reactions. Therefore, the reactions went to completion. An arising question is, however, whether the hydrosilylation reactions occur in an intramolecular or an intermolecular fashion. The results of SEC analysis are reported in Table 2.16. It can be seen from SEC M_n that the number-average molecular weights did not change significantly. However, the M_w results did. These are believed to be (qualitatively) representative of the branching as higher molecular weight polymers contribute more to the M_w. It is expected that intramolecular reactions would result in lower molecular weights than intermolecular reactions, because of the smaller volume of the cyclic polymers. However, it should be noted that it is not possible to be fully quantitative with SEC. This is discussed in more detail later in the section.

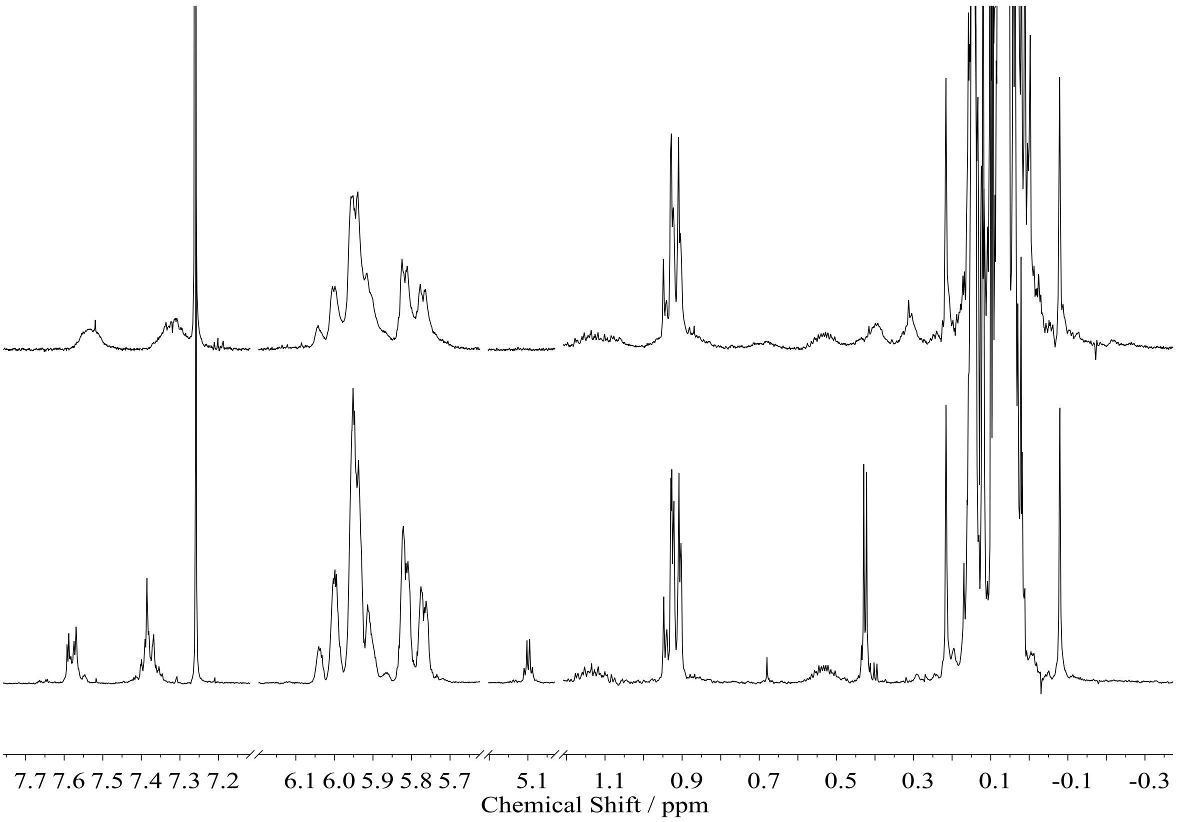


Figure 2.32: A comparison of ^{1}H NMR ($CDCl_3$) spectra before and after the coupling of PDMS-PMVS 1 at 20 % (w/w).

Table 2.16: SEC results obtained from the hydrosilylation coupling experiments at varying macromonomer solution concentration by using PDMS-PMVS 1; M_n 7200, M_w 8900, Đ 1.25 (SEC THF, PS conventional calibration).

Concentration / % (w/w)	**M_n / g mol^{-1}**	**Average M_n / g mol^{-1}**	**M_w / g mol^{-1}**	**Average M_w / g mol^{-1}**	**Đ**	**Average Đ**
20(1)	14800	14100	28100	28050	1.90	2.00
20(2)	13400		28000		2.10	
40(1)	15500	14550	32300	30700	2.09	2.11
40(2)	13600		29000		2.13	
60(1)	20200	18000	43600	42300	2.16	2.37
60(2)	17000		44000		2.59	
60(3)	16800		39400		2.35	
80(1)	14300	14700	42600	41300	2.97	2.82
80(2)	14800		43500		2.94	
80(3)	14900		38000		2.55	
BULK	16300	16300	41700	41700	2.56	2.56

[1] SEC results were obtained by using a conventional calibration of polystyrene standards.

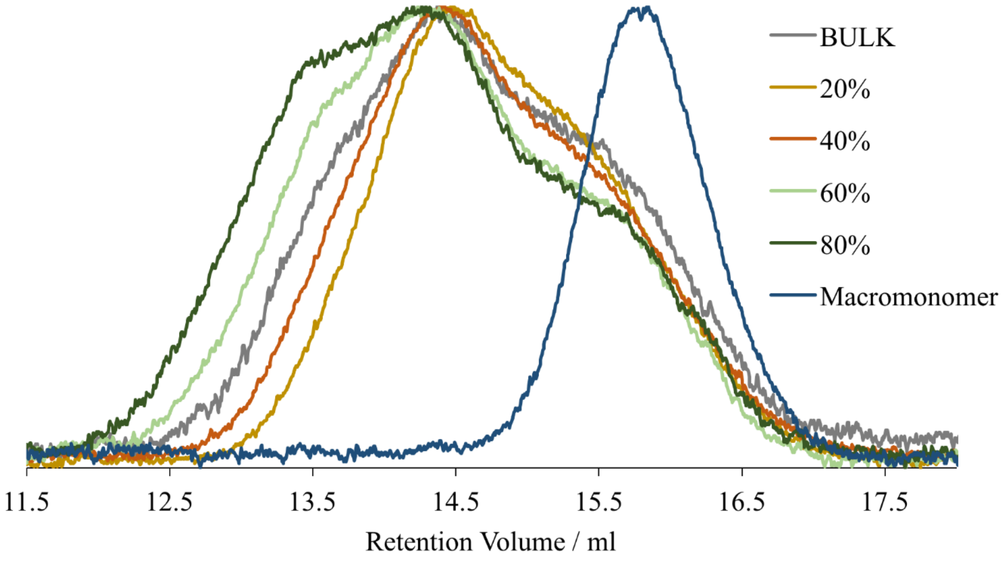


Figure 2.33: Data obtained from the SEC (THF) viscometer at varying macromonomer solution concentrations (1).

One may state that SEC only detects the hydrodynamic volume and branching at different locations of a polymer may led to different polymer sizes. This is a fact as branched polymers have lower hydrodynamic volumes than linear polymers with the same molar mass and a conventional calibration will always underestimate the molar mass of a branched polymer. However, despite these obvious inaccuracies, the SEC data (molar mass and dispersity) can be used for qualitative comparisons about the degree of branching. For clarity of presentation the viscometer data are shown on Figure 2.33 and Figure 2.36 rather than the RI data which has lower intensity. In all cases, it can be seen that the intensity of the macromonomer peak was diminished and the hydrosilylation reaction has successfully yielded branched polysiloxanes. However, as one may expect, reactions with different macromonomer solution concentrations yielded different degrees of branching. It can be seen from Table 2.16 and the plot on Figure 2.33 that an increase in concentration initially resulted in an increase in branching; higher concentrations favouring intermolecular chain coupling over intramolecular cyclisation. Concentrations of 60 % and 80 % can be regarded as the best performing reactions. It can be seen in Figure 2.33 that using 80 % concentration resulted in slightly higher molecular weight polymers than 60 % concentration in the first trial but this difference is not reflected on Table 2.16 as viscometer data was not used for the calculation of molecular parameters. As stated previously, all calculations were performed by using a conventional calibration of PS standard from the refractive index data. Repeats experiments were done and Figure 2.34 was plotted to observe any trends. It can be clearly seen that 60% and 80% solution concentrations and bulk coupling behaved in similar manners and clearly outperformed the lower concentrations.

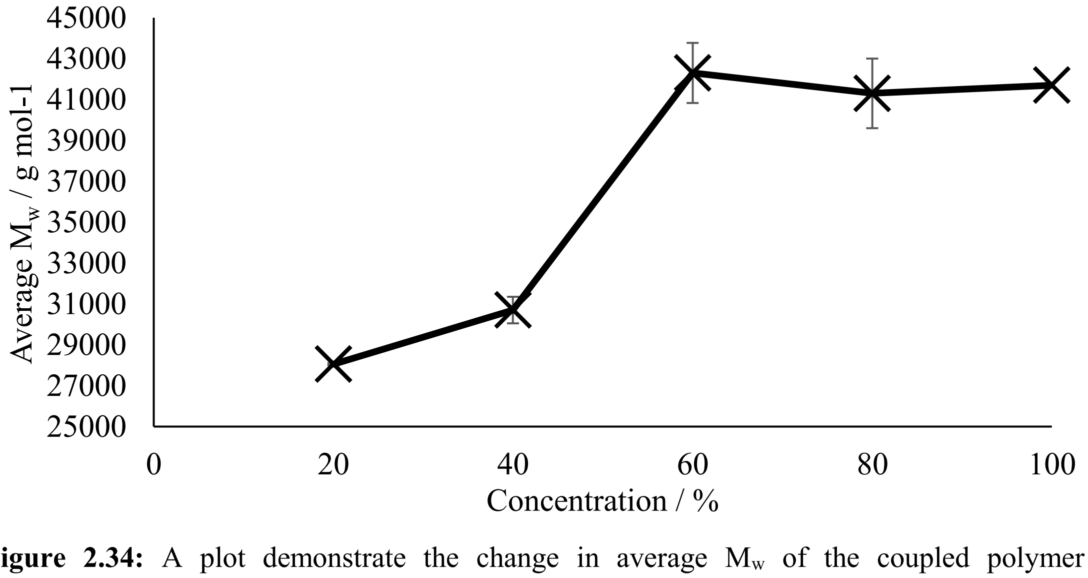


Figure 2.34: A plot demonstrate the change in average M_w of the coupled polymer with concentration.

In subsequent reactions, it was decided to use a solution concentration of 60% to explore the impact of copolymer composition (Table 2.15). It was anticipated that when there is a higher mole fraction of V_3 monomer in the copolymer, the result might be a higher degree of coupling and higher molecular weights. This is in turn might lead to higher viscosity and the higher viscosity at 80% might start to inhibit the coupling reaction. Frey *et al.*[93] used 50% concentration and bulk for all the coupling reactions although the authors did not provide any justification for this choice of 50% concentration.

Table 2.17: The results obtained from composition experiments (SEC THF, PS conventional calibration).

Composition / mol % V_3	M_n / g mol^{-1}		M_w / g mol^{-1}		Dispersity
	Before	After	Before	After	
11	7200	17000	8900	44000	2.59
22	9600	25700	12700	91600	3.56
35	8000	11000	9400	19000	1.69
52	7000	9900	8300	16000	1.62

Results of the coupling reactions on copolymers with varying copolymer composition are shown in Table 2.17. If the molar masses of the macromonomers were the same, a plot of M_w vs V_3 mol fraction could be used to show the extent of branching reactions but since the molar mass of the macromonomer varies that would be misleading and unscientific. Instead a plot of degree of polymerization of the macromonomer (DP_w) vs V_3 mole fraction was plotted (Figure 2.35) – which essentially normalizes the data. This approach was also previously used by Hutchings *et al.*[49] It can be clearly seen that, unexpectedly, an increase in V_3 composition did not necessarily resulted in an increase in chain coupling (Figure 2.35). It can be deduced that an increase in vinyl composition does initially increase branching and the macromonomer containing 11 mol% V_3 had a DP_w of 4.9, which rose to 7.2 as the V_3 content increased to 22 mol%. However, further increases in the V_3 content did not result in further increases in coupling. In fact, the result was lower degrees of coupling with DP_w dropping to about 2.0. This can be a result of the poor success of the end-capping reaction for PDMS-PMVS 3 and PDMS-PMVS 4. However, it is also possible that high vinyl composition promotes backbiting reactions and results in lower degrees of branching.

Especially, for PDMS-PMVS 3 where degree of end-capping is only 10% lower than the PDMS-PMVS 2.

A part of our results is in line with the Frey Group's findings. As it can be seen from Figure 2.36, the group reported an increase in branching with increased concentration (from 50% solution concentration to bulk) as the likelihood of intramolecular cyclisation reaction decreases. The group also reported that an increase in the presence of terminal vinyl bonds led to higher degrees of branching as we reported for 12 mol % and 22 mol % V_3 compositions. However, Frey *et al.*[93] did not report that an excessive increase in terminal vinyl content would decrease the degree of branching. This can be because of a number of reasons. First, low degree of end-capping achieved with high vinyl content PDMS-PMVS macromonomers which potentially inhibited the branching. Second, the polymers synthesised by the Frey group were much lower in molecular weight compared to the polymer investigated in our research. This means viscosity was not a problem. This potentially prevented the inhibition of coupling reactions and avoided the promotion of intramolecular cyclisation reactions. Third, chemical nature of the polyisoprene macromonomers investigated by the Frey Group are completely different to the polysiloxanes. Polysiloxanes are well-known to be highly flexible which makes it much more susceptible to the back-biting reactions. It is believed the first reasoning stated has the potential to be a key factor and further repeats need to be done in future to obtain macromonomer with similar vinyl composition but higher degree of end-capping.

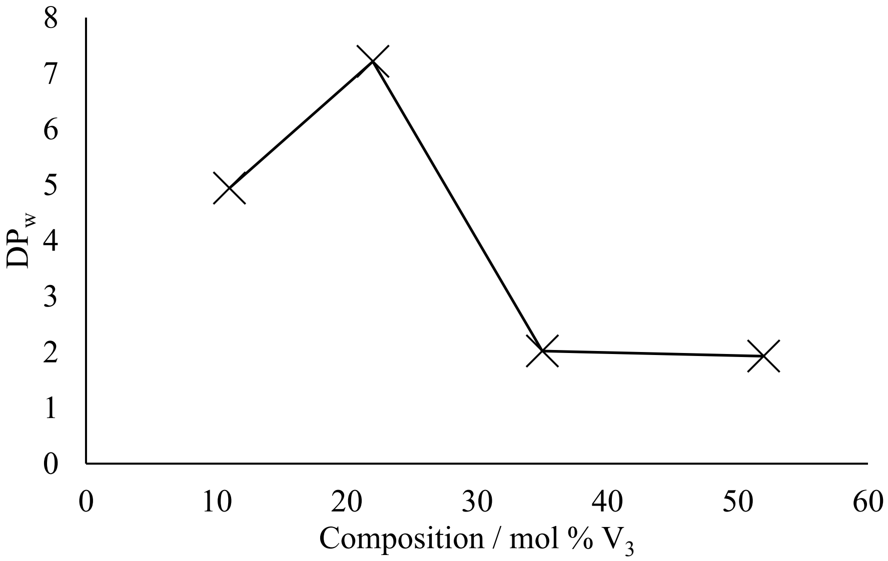


Figure 2.35: A plot of molar mass versus mol % V_3 where molar mass is represented by DP_w and DP_w is the ratio of the M_w of the branched polymer to the M_w of the macromonomer.

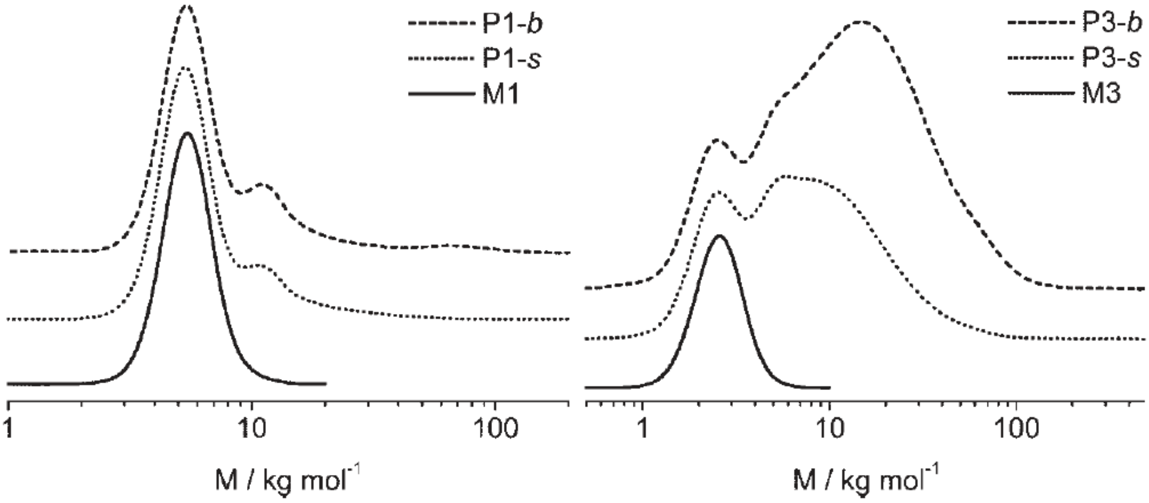


Figure 2.36: The SEC results provided in the work of Frey Group.[93] M1 represents the macromonomer 1 (M_n 3500 g mol^{-1}) containing 3 pending and 48 internal alkene bonds, M3 represents the macromonomer 2 (M_n 2100 g mol^{-1}) containing 27 pending and 4 internal alkene bonds. P attributes to the coupling reaction and b and s represents bulk and solution (50% concentration) coupling reactions.

In summary, a facile method was established to synthesise highly and randomly branched polysiloxanes. The optimal macromonomer solution concentration for the hydrosilylation coupling reaction was explored using a macromonomer with (11 mol% V_3) and was determined to be 60% (w/w). It was unsurprising that lower solution concentrations resulted in lower degrees of chain branching. This solution concentration was then used to explore the optimal copolymer composition for the highest degree of chain coupling. In the current work the highest degree of chain coupling was observed for the copolymer containing 22 mol % V_3 – however, chain coupling in samples containing higher amounts of V_3 monomer was probably inhibited by a low degree of chain end-capping with the required Si-H group. In both cases (concentration and composition) there will be a competition between intermolecular chain coupling (branching) and intramolecular cyclisation. An increase in V_3 composition initially resulted in higher degrees of branching, however, the degree of branching reduced for the higher vinyl content macromonomers. It can be hypothesised that excessive high vinyl content promotes intramolecular cyclisation reaction but this cannot be tested given the poor end-capping. Also, we wish to stress, again, that it is not possible to be fully quantitative with SEC as branched polymers have lower hydrodynamic volumes than linear polymers with the similar molecular weights. There is definitely scope for further investigation into this system.

3 Experimental

3.1 Materials

Tetrahydrofuran (in-house purification) was stirred and degassed over sodium wire (Aldrich, 99.9%) and benzophenone (Aldrich, 99 %) by freeze-pump-thaw cycles, until the solution turned purple, and stored under high-vacuum. Anhydrous N,N-dimethylformamide (Sigma-Aldrich, 99.8 %) dried over molecular sieves and N,N-dimethylacetamide (Sigma-Aldrich, 99.8%) was used as received. Cyclohexane (Aldrich, ≥ 99.9%), toluene (Aldrich, 99.8%), benzene (Aldrich, ≥ 99%), hexamethylcyclotrisiloxane (Aldrich, 98%), styrene (Sigma-Aldrich, ≥ 99%) 1,3,5-trivinyl-1,3,5-trimethylcyclotrisiloxane (Fluorochem, > 95%) were dried and degassed over calcium hydride (Acros Organics, 93%) by freeze-pump-thaw cycles and stored under high-vacuum. 1,3-Butadiene (Aldrich, ≥ 99.6%) was purified by passing monomer through columns of Carbosorb (Aldrich) and molecular sieves (Sigma-Aldrich) to remove any inhibitor and moisture. All solvents and monomers were freshly distilled prior to use. 4,4`-Dihydroxybenzophenone (Aldrich, 99%), t-butyldimethylsilyl chloride (Aldrich, 97%), chlorotriethylsilane (Aldrich, 99%), imidazole (Aldrich, ≥99%), sodium carbonate (Sigma-Aldrich, ≥99.5%), magnesium sulphate (Fisher Chemical, >95%), silica gel 60 Å (Fluorochem), 1.6M methyllithium in anhydrous diethyl ether (Aldrich), methyltriphenylphosphonium iodide (Aldrich, >97%), hydrochloric acid (Fisher Chemical, 32-35%), sec-butyllithium 1.4 M in cyclohexane (Sigma-Aldrich), n-butyllithium 2.5 M in hexanes (Aldrich), trimethylchlorosilane (Sigma Aldrich, ≥ 99%), chloro(methyl)diphenylsilane (Aldrich, 98%), tert-butyl(chloro)diphenylsilane (Aldrich, ≥ 98%) and chloro(methyl)phenylsilane (Aldrich, ≥ 93%), butylated hydroxytoluene (Aldrich, ≥ 99%), sodium hydride 60% dispersion in mineral oil (Aldrich), 1,8-diazabicyclo(5.4.0)undec-7-ene (Aldrich, 98%), tetra-n-butylammonium fluoride 1.0 M in THF (Aldrich), acetic acid glacial (Fisher Chemical), ammonium chloride (Sigma, ≥ 99.5%), caesium carbonate (Aldrich, 99%), potassium carbonate (Sigma, ≥ 99%), 18-crown-6 ether (Sigma-Aldrich, ≥ 99%), Zinc powder (AlliedSignal), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane in xylene, Pt ~2 % (Aldrich) were used as received. Tetramethylethylenediamine (Aldrich, ≥ 99.5%) was stirred over sec-BuLi and distilled to a separate flask prior to injection. C-Br functionalised polybutadiene was synthesised in our laboratory as part of a different project. Light petroleum, acetone, toluene, hexane, ethyl acetate, tetrahydrofuran and methanol (Fisher Scientific, AR grade) were used as received.

3.2 Analysis

3.2.1 Size Exclusion Chromatography

Molecular weights and dispersity of the synthesised polymers were calculated by size exclusion chromatography (SEC) using a Viscotek TDA 302 with refractive index, light scattering and viscosity detectors. The instrument was equipped with 2 PLgel 2 x 300 mm 5 µm mixed C columns. The solvent was THF with a flow rate of 1.0 ml/min at 35 °C. Only refractive index data was used for the calculations. A conventional calibration was generated using narrow dispersity polystyrene standards obtained from Polymer Laboratories with a molecular weight range of 192 – 1,112,000 gmol^{-1}. Molecular weight analysis was carried out with OmniSEC software.

3.2.2 Nuclear Magnetic Resonance Spectroscopy

1D NMR were run on Bruker Avance 400 MHz or Varian VNMRS 700 MHz spectrometer and 2D NMR spectra were run on Varian VNMRS 700 MHz or Varian VNMRS 600 spectrometer. All samples, except DPE-OH, were dissolved in $CDCl_3$ (Apollo Scientific, ≥ 99.96% D). DPE-OH was dissolved in DMSO (Sigma Aldrich, ≥ 99.9% D).

3.2.3 Mass Spectrum

Mass spectrum was obtained by using an Autoflex II matrix assisted laser desorption ionization-time-of-flight/time-of-flight (MALDI-TOF/TOF) tandem mass spectrometer (MS/MS; Bruker).

3.3 Synthesis of Initiator Precursors

3.3.1 Synthesis of 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene

Protection: A solution of 19.40 g (90.6 mmol) 4,4`-dihydroxybenzophenone in 35 ml of dry N,N-dimethylformamide (dried with molecular sieves under vacuum) was prepared under a nitrogen atmosphere resulting in an orange solution. 29.59 g (196 mmol) of t-butyldimethylsilyl chloride and 14 g of imidazole were added to the solution under nitrogen atmosphere. The mixture was heated overnight at 40 ºC. 120 ml of hexane was added to the flask and the solution was washed with 5% $NaHCO_3$. The hexane solution was recovered and dried over $MgSO_4$ over weekend. Solid was removed by filtration. The solvent was removed from the filtrate and the product was purified by SiO_2 chromatography using toluene as the eluent. The solvent was removed in vacuo to give a colourless solution, which was dried under vacuum to yield white crystals (34.23 g, 85.4%), TLC (SiO_2, toluene): R_f = 0.4, ^1H NMR ($CDCl_3$): δ = 0.30 (s, Si-C**H**$_3$), 1.05 (s, Si-C-(C**H**$_3$)$_3$), 6.92-7.79 ppm (m, aromatic C-**H**).

Wittig Reaction: A ylide solution of 60.0 ml (96.0 mmol) of 1.6M methyllithium in anhydrous diethyl ether and 33.2 g (84.2 mmol) methyltriphenylphosphonium iodide was prepared under dry conditions. A solution of 34.2 g (77.2 mmol) 4,4-bis(t-butyldimethylsiloxy)benzophenone in 100 ml of dry THF was added to the ylide solution via a dropping funnel at 0 °C. The reaction was stirred overnight and then quenched with 60 ml of acetone AR. The solid formed was removed by filtration and the solvent was evaporated from the filtrate in vacuo. 200 ml of petroleum ether was added to the resulting oily liquid and the solid formed was removed by filtration. The petroleum ether was evaporated from the filtrate and the product purified by recrystallization from ethanol to give a white powder of 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene (20.2 g, 59%), TLC (SiO_2), toluene): R_f = 0.9, ^1H NMR ($CDCl_3$): δ = 0.24 (s, Si-C**H**$_3$), 1.02 (Si-C-(C**H**$_3$)$_3$), 5.30 ppm (s, C=C**H**$_2$), 6.78-7.26 ppm (m, aromatic C-**H**).

3.3.2 Synthesis of 1,1-bis(triethylsiloxyphenyl)ethylene

Method 1

Protection: A solution of 8.00 g (37.3 mmol) 4,4`-dihydroxybenzophenone in 15 ml of dry N,N-dimethylformamide was prepared under nitrogen atmosphere. An orange solution was formed. 12.6 g (83.4 mmol) of chlorotriethylsilane and 5 g (73.4 mmol) of imidazole was added to the solution under nitrogen. The mixture was heated overnight at 40 °C. 120 ml of hexane was added to the cooled flask and the solution was washed with 5% $NaHCO_3$ (3 x 50 ml). Hexane solution was recovered and dried over $MgSO_4$ overnight. Solid was filtered off. The solvent was removed and the product was purified with SiO_2 chromatography using toluene as eluent. The solvent was removed in vacuo. Colourless liquid was dried under vacuum to provide the colourless liquid, 4,4-bis(triethylsiloxy)benzophenone (12.2 g, 74%), TLC (SiO_2, toluene): R_f = 0.4, ^1H NMR ($CDCl_3$): δ = 0.81 (q, Si-C**H**$_2$CH$_3$), 1.04 (t, Si-CH$_2$C**H**$_3$), 6.92-7.79 ppm (m, aromatic C-**H**).

Wittig Reaction: A ylide solution of 22.0 ml (35.2 mmol) of 1.6M methyllithium in anhydrous diethylether and 12.7 g (31.2 mmol) methyltriphenylphosphonium iodide was prepared under dry conditions. A solution of 12.2 g (28.2 mmol) of 4,4-bis(triethylsiloxy)benzophenone in 60 ml of dry THF was added to the ylide solution via a dropping funnel at 0 °C. The reaction was left overnight and terminated with 40 ml of acetone AR. The resulting solid was removed by filtration and the solvent was evaporated from the filtrate in vacuo. 200 ml of petroleum ether was added into the oily liquid and the solid formed removed by filtration. The petroleum ether was evaporated and the product purified with SiO_2 chromatography using toluene as eluent. The solvent was removed in vacuo and the colourless liquid dried under vacuum to give 1,1-bis(triethylsiloxyphenyl)ethylene (0.08 g, 2%), TLC (SiO_2), toluene): $R_f = 0.8$, ^{1}H NMR ($CDCl_3$): $\delta = 0.77$ ppm (q, Si-C**H**$_2$CH$_3$), 1.03 (t, Si-CH$_2$C**H**$_3$), 5.30 ppm (s, C=C**H**$_2$), 6.78-7.26 ppm (m, aromatic C-**H**).

Method 2

Deprotection of TBDMS-protected DPE-OSi: A solution of 1 g (2.26 mmol) of 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene was prepared in 5 ml of THF. 1 ml of 10M HCl was added into the solution resulting in the formation of black solids. The reaction was stirred for 2 days at room temperature. 20 ml of ethyl acetate was added into the solution which changed to a green colour. The solution was washed with saturated $NaHCO_{3(aq)}$ (4 x 20 ml) and dried over $MgSO_4$. The solution turned red. The solvent was removed in vacuo and a black liquid was obtained. The product was purified with SiO_2 chromatography using hexane/ethyl acetate (4:1 at first, then 6:4) as eluent. The solvent was removed and the colourless liquid was dried under vacuum to give 4,4'-dihydroxy-1,1-diphenylethylene (0.23 g, 48%), TLC (SiO_2), hexane/ethyl acetate (6:4): $R_f = 0.5$, ^{1}H NMR (DMSO): $\delta = 5.17$ ppm (s, C=C**H**$_2$), 6.68-7.18 ppm (m, aromatic C-**H**).

Reprotection: A solution of 0.23 g (1.08 mmol) 4,4'-dihydroxy-1,1-diphenylethylene in 0.5 ml of dry N,N-dimethylformamide was prepared under nitrogen atmosphere. 0.63 g (4.17 mmol) of chlorotriethylsilane and 0.16 g (2.35 mmol) of imidazole was added into the solution under nitrogen atmosphere. The mixture was heated overnight at 40 °C. 30 ml of hexane was added to the flask and the solution was washed with 5% $NaHCO_3$ (3 x 15 ml). The hexane solution was recovered and dried over $MgSO_4$ overnight. The solid was filtered off, the solvent was removed from the filtrate and the product was purified with SiO_2 chromatography using toluene as eluent. The solvent was removed in vacuo to yield 1,1-bis(triethylsiloxyphenyl)ethylene (0.36 g, 77%), TLC (SiO_2, toluene): $R_f = 0.8$, ^{1}H NMR

($CDCl_3$): δ = 0.77 (q, Si-C**H**$_2$CH$_3$), 1.03 (t, Si-CH$_2$C**H**$_3$), 5.30 ppm (s, C=C**H**$_2$), 6.78-7.26 ppm (m, aromatic C-**H**).

3.3.3 Protection of Bisphenol F

A solution of 3.00 g (15.0 mmol) Bisphenol F in 8 ml of dry N,N-dimethylformamide was prepared under a nitrogen atmosphere. 5.28 g (35.0 mmol) of chlorotriethylsilane and 2.1 g (30.8 mmol) of imidazole was added into the solution under nitrogen. The mixture was stirred overnight at 40 °C. 60 ml of hexane was added to the cooled flask and the solution was washed with 5% $NaHCO_3$ (3 x 40 ml). The organic layer was dried over $MgSO_4$ over the weekend. The $MgSO_4$ was removed by filtration, the solvent removed from the filtrate and the product purified with SiO_2 chromatography using toluene as eluent. After removal of the toluene by rotary evaporation, the colourless liquid was dried under vacuum to provide 4,4-bis(triethylsiloxy)phenol (4.5 g, 70%), TLC (SiO_2, toluene): $R_f = 0.8$, ^{1}H NMR ($CDCl_3$): δ = 0.75 (q, Si-C**H**$_2$CH$_3$), 1.02 (t, Si-CH$_2$C**H**$_3$), 3.87 ppm (s, Ar-C**H**$_2$-Ar), 6.76-7.06 ppm (m, aromatic C-**H**).

3.4 Polymerizations

3.4.1 Reaction vessel and preparation procedure

Figure 3.1: The “Christmas tree” reaction vessel.

All polymerizations were carried out in a specifically designed reaction apparatus for living anionic polymerizations – locally known as a “Christmas tree” (Figure 3.1). The tree consists of one main reaction flask (1), small side flasks (2), a sealed flask containing a cleaning solution of living polystyryl lithium in benzene (3) and a washing vessel (4).

Anionic polymerization is extremely susceptible to trace amount of impurities and therefore, the reaction vessel is thoroughly cleaned before using. Firstly, the vessel is washed with THF, methanol and acetone, respectively. Then, the vessel is dried. Upon drying, septum caps are inserted and securely tightened with metal wires. The sealed Christmas tree is evacuated and left under high-vacuum for one hour to remove all traces of air and moisture. The tree is then closed by sealing all the Young's taps and removed from the high vacuum-line. All parts of the apparatus are thoroughly washed with the living PSLi solution in flask 3. After the wash, as much as possible of the living solution is transferred back in to flask 3 and the remaining PSLi solution on the walls of the vessels is washed with benzene. Benzene is distilled from the living solution into flask 4 and then used to wash the living solution around the Christmas tree back in to flask 3. This benzene wash is repeated until the post-wash colour of benzene is colourless. This is followed by freezing the living solution and heating all other parts of the Christmas tree to distil any remaining benzene outside the flask 3. The reaction vessel is again connected to the high-vacuum line and left overnight for evacuation.

3.4.2 Anionic Polymerization of Hexamethylcyclotrisiloxane (D_3)

The christmas tree was washed and prepared for the polymerization by the procedure outlined in Section 3.4.1. In a typical reaction, 4.26 g (19.1 mmol) of D_3 monomer was vacuum-distilled into a transfer flask. The reaction solvent, cyclohexane, was vacuum-distilled into a purification flask containing living PSLi solution. 20 ml of cyclohexane, to form a solution concentration of about 20% w/w of monomer, was vacuum-distilled into the transfer flask. The monomer solution was purified by injecting 40 µl of 2.5 M n-BuLi solution in hexanes, with a gas-tight syringe, immediately before the distillation into the Christmas tree. The monomer solution was then vacuum-distilled into the main reaction compartment (1) of the tree. 300 µl (0.43 mmol) of 1.4 M sec-BuLi was injected by using a gas-tight syringe to initiate the polymerization at room temperature. 2 hours was given for the initiation reaction and then, 20 ml of THF was freshly distilled to promote propagation. Samples of approximately 10 ml were collected after 1 and 2 hours and terminated with 34 µl (0.27 mmol) chlorotrimethylsilane, injected with a gas-tight syringe each time. 68 µl (0.54 mmol) of chlorotrimethylsilane was injected with a gas-tight syringe to terminate the polymerization after 24 hours. Polymers were recovered by precipitation in methanol.

PDMS 1 (target M_n 10000 g mol^{-1}) - M_n 3000 g mol^{-1}, Đ 1.04 (1 h), M_n 5000 g mol^{-1}, Đ 1.09 (2 h) and M_n 13000 g mol^{-1}, Đ 1.09 (24 h).

PDMS 2 (target M_n 20000 g mol^{-1}) - M_n 14000 g mol^{-1}, Đ 1.05 (4 h), M_n 15000 g mol^{-1}, Đ 1.05 (5 h), M_n 18000 g mol^{-1}, Đ 1.05 (6 h) and M_N 27000 g mol^{-1}, Đ 1.12 (24 h).

PDMS 3 (target M_n 40000 g mol^{-1}) - M_n 30000 g mol^{-1}, Đ 1.11 (7 h), M_n 32000 g mol^{-1}, Đ 1.12 (8 h), M_n 35000 g mol^{-1}, Đ 1.14 (9 h) and M_n 39000 g mol^{-1}, Đ 1.20 (24 h);

1H NMR ($CDCl_3$): δ = 0.04-0.24 ppm ($C\mathbf{H}_3)_2OSi$, 0.55 ppm $(CH_2CH_3)(CH_3)C\mathbf{H}$-SiO, 1.05-1.20 ppm $(CH_2C\mathbf{H}_3)(C\mathbf{H}_3)CH$-SiO, 1.15 ppm $(C\mathbf{H}HCH_3)(CH_3)CH$-SiO and 1.50-1.60 ppm $(CH\mathbf{H}CH_3)(CH_3)CH$-SiO.

3.4.3 Anionic Polymerization of Hexamethylcyclotrisiloxane using DPE-OSi

For DPE-PDMS 1, 0.26 g (0.59 mmol) initiator precursor DPE-OSi was placed into one of the side flasks of the tree. The Christmas tree was evacuated and cleaned as outlined in Section 3.4.1 with the exception of keeping the side flask's Young's tap closed during washes. 60 ml of benzene was vacuum-distilled into a purification flask containing living PSLi solution. 20 ml of benzene was vacuum-distilled into the Christmas tree to wash the DPE-OSi azeotropically and then distilled out of the tree to a waste flask. This procedure was repeated 3 times. 5.5 g (25 mmol) of D_3 monomer was vacuum-distilled into a flask. Cyclohexane was vacuum-distilled into a purification flask containing living PSLi solution and then 20 ml of cyclohexane was vacuum-distilled into the tree. The Christmas tree was raised to atmospheric pressure with dry nitrogen gas and the DPE-OSi was "titrated" with 1.4 M sec-BuLi until a persistent red colour was obtained. 320 μl (0.448 mmol) of 1.4 M sec-BuLi was injected using a gas-tight syringe to initiate the polymerization at room temperature. After 4 hours, 10 ml of cyclohexane was vacuum-distilled into the transfer flask containing the D_3 monomer. The mixture was purified by injecting 40 μl (0.10 mmol) of 2.5 M n-BuLi solution in hexanes with a gas-tight syringe right before the vacuum-distillation into the Christmas tree. The contents of the transfer flask were vacuum-distilled into the tree. The reaction between the activated DPE-OSi and the monomer was allowed to proceed for 24 hours and then heated to 50 °C for another 4 days. This was followed by the addition of 30 ml THF. After 7 hours at room temperature 142 μl (1.12 mmol) trimethylchlorosilane was injected with a gas-tight syringe to terminate the polymerizations. The polymer was recovered by precipitation in methanol. Yield; 28 %. M_n 14000 g mol^{-1}, Đ 1.16. For DPE-

PDMS 2, the nonpolar solvent was changed from cyclohexane to toluene and the reaction between D_3 monomer and activated DPE-OSi complex was allowed to proceed for two days at 90 ^{o}C. Yield; 84 %. M_n 31000 g mol^{-1}, Đ 1.18. 1H NMR ($CDCl_3$): $\delta = 0.04\text{-}0.24$ ppm $(C\mathbf{H}_3)_2OSi$, 0.98 ppm $Si(CH_3)_2C(C\mathbf{H}_3)_3$, 6.70-7.15 ppm Ar-**H**.

3.4.4 Anionic Polymerization of Hexamethylcyclotrisiloxane using DPE-OSi and Polybutadiene Spacer Block

The polymerization was performed according to the procedure described above (3.4.3) with the exception of 5 equivalents of 1,3-butadiene monomer (relative to initiator) which was added immediately after the reaction of DPE-OSi and sec-BuLi but before the addition by distillation of the D_3 monomer. Thus, 1,3-butadiene was vacuum-distilled into a transfer flask and purified with the injection of 20 μl (0.05 mmol) of 2.5 M n-BuLi solution in hexanes via a gas-tight syringe right before distillation into the tree (with acetone/CO_2 bath). 6 hours was given for the polymerization between the activated DPE-OSi and 1,3-butadiene monomers at room temperature. A series of reactions were carried out and the polymers were terminated with one of three end-capping agents after 7 hours followed by the vacuum-distillation of D_3 monomer; chlorotrimethylsilane for DPE-Bd-PDMS 1 and 2, chloro(methyl)diphenylsilane for DPE-Bd-PDMS 3-7 and t-butyl(chloro)diphenylsilane for DPE-Bd-PDMS 8 and 9.

DPE-Bd-PDMS 1 (target M_n 5000 g mol^{-1}); Yield 80 %, M_n 8600 g mol^{-1}, Đ 1.13.

DPE-Bd-PDMS 2 (target M_n 10000 g mol^{-1}); Yield 87 %, M_n 15000 g mol^{-1}, Đ 1.09.

DPE-Bd-PDMS 3 (target M_n 3000 g mol^{-1}); Yield 75 %, M_n 2300 g mol^{-1}, Đ 1.23.

DPE-Bd-PDMS 4 (target M_n 6000 g mol^{-1}); Yield 86 %, M_n 4200 g mol^{-1}, Đ 1.16.

DPE-Bd-PDMS 5 (target M_n 10000 g mol^{-1}); Yield 76 %, M_n 12000 g mol^{-1}, Đ 1.08.

DPE-Bd-PDMS 6 (target M_n 8500 g mol^{-1}); Yield 94 %, M_n 11200 g mol^{-1}, Đ 1.14.

DPE-Bd-PDMS 7 (target M_n 10000 g mol^{-1}); Yield 78 %, M_n 15400 g mol^{-1}, Đ 1.10.

The SEC results of DPE-Bd-PDMS 8 is not of any importance as it was synthesised as part of a wider project.

DPE-Bd-PDMS 9 (target M_n 10000 g mol^{-1}); Yield 89 %, M_n 13000 g mol^{-1}, Đ 1.14.

DPE-Bd-PDMS 10 (target M_n 10000 g mol^{-1}); Yield 81 %, M_n 15400 g mol^{-1}, Đ 1.10.

1H NMR ($CDCl_3$) δ = 0.04-0.24 ppm ($(CH_3)_2OSi$), 2.60-2.75 ppm and 4.80-5.70 ppm polybutadiene block, 6.70-7.15 ppm Ar-**H**. A detailed NMR assignment is provided in Figure 2.12. End-capping groups: Methyldiphenylsilyl; 1H NMR ($CDCl_3$) δ = 0.64 ppm $(Ph)_2Si-CH_3$, 7.32-7.64 ppm Ar-**H**. t-Butyldiphenylsilyl; 1H NMR ($CDCl_3$) δ = 0.99 ppm $(Ph)_2Si-C(CH_3)_3$, 7.34-7.72 ppm Ar-**H**.

Anionic Polymerization of Hexamethylcyclotrisiloxane using TES-protected Bisphenol F

In a typical procedure (BPF-Li 1), 0.25 g (0.58 mmol) of TES-protected Bisphenol F (BPF-OSi) was placed in to the one of the side flasks of the Christmas tree. BPF-OSi was azeotropically washed by benzene three times and dried under high vacuum overnight. 2.40 g (10.8 mmol) of D_3 monomer was vacuum-distilled into a transfer flask. Cyclohexane was vacuum-distilled into a purification flask containing living PSLi solution. 10 ml of cyclohexane was vacuum-distilled into the tree. 320 µl (2.1 mmol) of TMEDA was injected into a transfer flask followed by 50 µl (0.13 mmol) of 2.5M n-BuLi in hexanes. The purified TMEDA was then distilled to a dry clean flask under high vacuum. 320 µl (0.448 mmol) of 1.4M sec-BuLi in cyclohexane and 120 µl (0.79 mmol) purified TMEDA were injected into the Christmas tree. A red colour was observed at this point. The reaction continued for 12 hours at RT before 0.20 g (3.7 mmol) of 1,3-butadiene was distilled into the mixture and a slow colour change from red to pale yellow was observed over 1 hour. The reaction between butadiene and the activated BPF-OSi was allowed to proceed for 6 hours at room temperature. 5 ml of cyclohexane was vacuum-distilled into the transfer flask containing D_3 monomer and the mixture purified by injecting 20 µl (0.05 mmol) of 2.5 M n-BuLi solution in hexanes with a gas-tight syringe right before D_3 solution in cyclohexane was distillation into the Christmas tree. D_3 monomer was left for initiation overnight. 15 ml of THF was then distilled in to the tree to instigate propagation at RT. The polymerization was terminated by 235 µl (1.12 mmol) chloro(methyl)diphenylsilane after 6 hours. The polymer was recovered by precipitation in methanol with a spoonful of added butylated hydroxytoluene (BHT) to prevent the oxidation of the double bonds in polybutadiene block. BPF-PDMS 1: Yield 12 %; Three peaks appread on THF SEC, Peak 1 M_n 8200 g mol^{-1}, Peak 2 M_n 22200 g mol^{-1} and Peak 3 M_n 74200 g mol^{-1}; 1H NMR ($CDCl_3$) δ = 0.04-0.24 ($(CH_3)_2OSi$), 1.84-2.29 ppm and 4.80-5.95 ppm polybutadiene block, 6.70-7.15 ppm Ar-**H** (BHF), 7.33-7.73 ppm Ar-**H** (MDPS).

3.4.5 Copolymerization of Hexamethylcyclotrisiloxane and 1,3,5-Trivinyl-1,3,5-trimethylcyclotrisiloxane

In a typical reaction (PDMS-PMVS 1), 9.86 g (44.3 mmol) of D_3 and 1.28 g (4.92 mmol) of V_3 were vacuum-distilled in to separate transfer flasks. 50 ml of cyclohexane was vacuum-distilled in to a purification flask containing PSLi. 40 ml and 10 ml of cyclohexane were vacuum-distilled from the purification flask to the transfer flasks containing the D_3 and V_3 monomers, respectively, followed by the injection of 100 μl (0.25 mmol) and 20 μl (0.05 mmol) of 2.5M n-BuLi in hexanes to purify the monomers further, respectively. The contents of the transfer flasks were distilled into the Christmas tree. The polymerization was initiated by the injection of 1.32 ml (1.86 mmol) of 1.4 M sec-BuLi via a gas-tight syringe. The initiation reaction was allowed to proceed for 2 hours at RT after which 50 ml of THF was added to instigate propagation. The polymerisation reaction was terminated after 4 hours by the addition of 700 μl (4.65 mmol) chloro(methyl)phenylsilane. The polymer was recovered by precipitation in methanol with a spoon of added butylated hydroxytoluene (BHT) to prevent the oxidation of the double bonds in the structure. The feed ratio of D_3 and V_3 was varied to produce a series of copolymers with different compositions. Target molecular weight was 6000 g mol^{-1} for all copolymerizations.

PDMS-PMVS 1; Yield 81%; (NMR) Composition 11 mol %, M_n 5300 g mol^{-1}, degree of end-capping 81 %; (SEC) M_n 7200 g mol^{-1}, M_w 8900 g mol^{-1}, Đ 1.25.

PDMS-PMVS 2; Yield 78%; (NMR) Composition 22 mol %, M_n 10200 g mol^{-1}, degree of end-capping 78 %; (SEC) M_n 9600 g mol^{-1}, M_w 12700 g mol^{-1}, Đ 1.32.

PDMS-PMVS 3; Yield 68%; (NMR) Composition 35 mol %, M_n 5300 g mol^{-1}, degree of end-capping 63 %; (SEC) M_n 8000 g mol^{-1}, M_w 9400 g mol^{-1}, Đ 1.17.

PDMS-PMVS 4; Yield 71%; (NMR) Composition 52 mol %, M_n 5200 g mol^{-1}, degree of end-capping 42 %; (SEC) M_n 7000 g mol^{-1}, M_w 8300 g mol^{-1}, Đ 1.19.

H NMR ($CDCl_3$): 0.04-1.15 ppm $(C\mathbf{H}_3)_2SiO$, 0.15-0.20 ppm $(C\mathbf{H}_3)(CHCH_2)SiO$, 0.45 ppm $(C\mathbf{H}_3)(Ph)SiH$, 0.50-0.61 ppm $(CH_2CH_3)(CH_3)C\mathbf{H}$-SiO, 0.88-0.99 ppm $(CH_2C\mathbf{H}_3)(C\mathbf{H}_3)CH$-SiO, 1.10-1.20 ppm $(C\mathbf{H}HCH_3)(CH_3)CH$-SiO, 1.50-1.60 ppm $(CH\mathbf{H}CH_3)(CH_3)CH$-SiO, 5.68-6.11 ppm $(CH_3)(C\mathbf{H}C\mathbf{H}_2)SiO$, 7.33-6.64 ppm Ar-**H** (MDPS).

3.5 Attempted Deprotection of DPE-OSi End-capped PDMS

3.5.1 Deprotection using Sodium Hydride

For NaH 1, 0.50 g (0.058 mmol) of DPE-OSi initiated PDMS was dried under high vacuum for 48 hours before dissolving it in 5 ml dry THF to form a 10% w/v concentration of the polymer. 46 mg (1.16 mmol) NaH 60% dispersion in mineral oil was added into the solution under N_2 atmosphere. The reaction was allowed to occur for 6 hours at RT. The reaction was quenched by methanol and the polymer was recovered by precipitation in methanol with BHT. A variety of conditions were attempted – see below.

NaH 1; M_n 8600 g mol^{-1} Đ 1.13 (before), 4800 g mol^{-1} Đ 1.60 (after).

NaH 2 (5 eq of NaH, THF, RT, 6h); M_n 8600 g mol^{-1} Đ 1.13 (before), 3600 g mol^{-1} Đ 1.56 (after).

NaH 3 (4 eq of NaH, THF, RT, 3h); M_n 15000 g mol^{-1} Đ 1.09 (before), 9000 g mol^{-1} Đ 1.40 (after).

NaH 4 (4 eq of NaH, THF-DMF 2:1, RT, 15 mins); M_n 15000 g mol^{-1} Đ 1.09 (before), 12000 g mol^{-1} Đ 1.52 (after).

NaH 5 (3 eq of NaH, THF-DMF 2:1, 0 °C, 1 h); M_n 8600 g mol^{-1} Đ 1.13 (before), 2200 g mol^{-1} Đ 1.40 (after).

NaH 6 (3 eq of NaH, THF-DMF 2:1, RT, 15 mins); M_n 2300 g mol^{-1} Đ 1.23 (before), 1300 g mol^{-1} Đ 1.28 (after).

NaH 7 (1.5 eq of NaH, THF-DMF 2:1, RT, 30 min); M_n 4200 g mol^{-1} Đ 1.16 (before), 2500 g mol^{-1} Đ 1.36 (after).

NaH 8 (0.7 eq of NaH, THF-DMF 2:1, RT, 30 min); M_n 4200 g mol^{-1} Đ 1.16 (before), 3000 g mol^{-1} Đ 1.25 (after).

NaH 9 (1.5 eq of NaH, THF-DMF 2:1, RT, 6h); M_n 4200 g mol^{-1} Đ 1.16 (before), no polymer recovered (after).

3.5.2 Deprotection using DBU

0.50 g (0.12 mmol) of DPE-OSi initiated PDMS was dissolved in 5 ml THF/methanol (19:1) mixture to form a 10% w/v concentration of the polymer. 36 μl (0.24 mmol) DBU was added into the solution. The reaction was allowed to proceed at RT for 1 hour. The polymer was recovered by precipitation in methanol with BHT. A variety of conditions were explored – see below.

DBU 1; M_n 4200 g mol^{-1} Đ 1.16 (before), 4600 g mol^{-1} Đ 1.13 (after).

DBU 2 (1 eq of DBU, THF-Methanol 19:1, RT, 16 h); M_n 4200 g mol^{-1} Đ 1.16 (before), 4800 g mol^{-1} Đ 1.11 (after).

DBU 3 (2 eq of DBU, THF-Methanol 19:1, 50 °C, 72 h); M_n 4200 g mol^{-1} Đ 1.16 (before), 4500 g mol^{-1} Đ 1.13 (after).

3.5.3 Deprotection using TBAF

0.50 g (0.045 mmol) of DPE-OSi initiated PDMS was dissolved in 5 ml THF to form a 10% w/v concentration of the polymer. The temperature was lowered to 0 °C and 89 μl (0.090 mmol) TBAF was injected into the solution. The reaction was quenched after 15 mins with $NH_4Cl_{(aq)}$ and the polymer was recovered by precipitation in methanol, with a teaspoon of butylated hydroxytoluene.

TBAF 1; M_n 11200 g mol^{-1} Đ 1.08 (before), 4400 g mol^{-1} Đ 1.39 (after).

TBAF 2; Yield 62%, M_n 13000 g mol^{-1} Đ 1.14 (before), 11500 g mol^{-1} Đ 1.39 (after).

TBAF 3; Yield 80%, M_n 12000 g mol^{-1} Đ 1.08 (before), 7400 g mol^{-1} Đ 1.25 (after).

TBAF 4; Yield 84%, M_n 12000 g mol^{-1} Đ 1.08 (before), 11300 g mol^{-1} Đ 1.12 (after).

3.5.4 Deprotection using Hydrochloric Acid

0.50 g (0.12 mmol) of DPE-OSi initiated PDMS was dissolved in 5 ml THF to form a 10% w/v concentration of the polymer. 120 μl (0.60 mmol) of 10 M HCl was added into the solution. The reaction was allowed to proceed at RT for 24 hours. The polymer was recovered by precipitation in methanol with BHT.

HCl 1; M_n 4200 g mol^{-1} Đ 1.16 (before), multiple peaks (after).

3.5.5 Deprotection using Acetic Acid

0.50 g (0.042 mmol) of DPE-OSi initiated PDMS was dissolved in water/AcOH/THF (0.25:1:3) to form a 10% w/v concentration of the polymer. The reaction was heated at 60 °C and left until complete deprotection. The polymer was recovered by precipitation in methanol with a teaspoon of butylated hydroxytoluene.

AcOH-TBDMS; M_n 12000 g mol^{-1} Đ 1.08 (before), M_n 12400 g mol^{-1} Đ 1.08 (after).

AcOH-TES; M_n 15400 g mol^{-1} Đ 1.10 (before), M_n 16200 g mol^{-1} Đ 1.10 (after).

3.6 Attempted synthesis of PDMS-PBd star block copolymers via Williamson Coupling Reactions

3.6.1 Williamson Coupling Attempt with Caesium Carbonate

0.50 g (0.053 mmol) of TBAF-deprotected PDMS was dissolved with 2.33 g (0.12 mmol) bromine end-capped polybutadiene in a mixture of 30 ml dry THF/DMAC (6:4) at 60 °C. 17 mg (0.53 mmol) of Cs_2CO_3 was added into the reaction under N_2 atmosphere. Samples were taken at various intervals. The starting materials and the coupled polymer were recovered by precipitation in methanol containing BHT.

^{1}H NMR ($CDCl_3$): δ = 5.7-5.3 (=C**H**), 5.1-4.9 (=C**H** vinyl), 2.97 (C**H**$_2$Br), 2.4-1.8 (C**H**$_2$CH=CH); SEC (THF): M_n 38500 g mol^{-1} M_w 40100 Đ 1.04 (Peak 1 – Conventional Calibration), M_n 22700 g mol^{-1} M_w 24000 Đ 1.05 (Peak 1 – Triple Detector), M_n 89800 g mol^{-1} M_w 99200 Đ 1.17 (Peak 2 – Conventional Calibration), M_n 54900 g mol^{-1} M_w 70300 Đ 1.28 (Peak 2 – Triple Detector).

3.6.2 Williamson Coupling Attempt with Potassium Carbonate and 18-Crown-6 Ether

0.50 g (0.053 mmol) of TBAF-deprotected PDMS was dissolved with 2.33 g (0.12 mmol) bromine end-capped polybutadiene in a mixture of dry THF/DMAC (6:4) at 60 °C. 37 mg (0.27 mmol) K_2CO_3 and 7 mg (0.27 mmol) 18-crown-6 ether was added into the reaction mixture under N_2 atmosphere. Samples were taken at various interval. The starting materials and the coupled polymer were recovered by precipitation in methanol containing BHT.

^{1}H NMR ($CDCl_3$): δ = 7.6-6.6 (Ar-**H**), 5.7-5.3 (=C**H**), 5.1-4.9 (=C**H** vinyl), 2.97 (C**H**$_2$Br), 2.4-1.7 (C**H**$_2$CH=CH), 0.02 ppm ((C**H**$_3$)$_2$SiO); SEC (THF): M_n 20900 g mol^{-1} M_w 21700 Đ 1.04 (Peak 1 – Triple Detector), M_n 33900 g mol^{-1} M_w 35000 Đ 1.03 (Peak 2 – Triple Detector), M_n 57800 g mol^{-1} M_w 61100 Đ 1.07 (Peak 3 – Triple Detector).

3.6.3 Williamson Coupling Attempt with Zinc

0.50 (0.053 mmol) g of TBAF-deprotected PDMS was dissolved with 2.33 g (0.12 mmol) bromine end-capped polybutadiene in dry THF at 60 °C. 3 mg (0.053 mmol) Zn powder was added into the reaction mixture under N_2 atmosphere. Samples were taken at various interval. The starting materials and the coupled polymer were recovered by precipitation in methanol containing BHT.

^{1}H NMR ($CDCl_3$): δ = 7.6-6.6 (Ar-**H**), 5.7-5.3 (=C**H**), 5.1-4.9 (=C**H** vinyl), 2.97 (C**H**$_2$Br), 2.4-1.7 (C**H**$_2$CH=CH), 0.02 ppm ((C**H**$_3$)$_2$SiO); SEC (THF): M_n 18600 g mol^{-1} M_w 19700 Đ 1.06 (Peak 1 – Triple Detector), M_n 47700 g mol^{-1} M_w 51900 Đ 1.09 (Peak 2 – Triple Detector).

3.7 Synthesis of Randomly Branched Polysiloxanes via Hydrosilylation Chain Coupling

In a typical example, 1 g of PDMS-PMVS (D_3-V_3) copolymer (10 weight % V_3) with M_n 7200 g mol^{-1} was dissolved in 0.6 g dry toluene to form a 60% w/w concentration. The mixture was heated to 100 °C before the injection of 160 µl (4% by mol) of 2% platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst in xylenes under N_2 atmosphere. The reaction was refluxed for 2 hours before cooling to room temperature. The product was recovered by precipitation in methanol containing a teaspoon of butylated hydroxytoluene.

A series of PDMS-PVMS copolymers were subjected to the same procedure at varying solution concentrations, 20%, 40%, 60%, 80% (w/w) and in the bulk, and using copolymers with varying weight fractions of V_3 - 10%, 22%, 25%, 48% and 56 %. Reactions at varying concentration used copolymer; M_n 7200 g mol^{-1} M_w 8900 g mol^{-1} Đ 1.25, 10 weight % V_3):

Bulk; M_n 16300 g mol^{-1}, M_w 41700 g mol^{-1}, Đ 2.56.

20% (1); M_n 14800 g mol^{-1}, M_w 28100 g mol^{-1}, Đ 1.90.

20% (2); M_n 13400 g mol^{-1}, M_w 28000 g mol^{-1}, Đ 2.10.

40% (1); M_n 15500 g mol^{-1}, M_w 32300 g mol^{-1}, Đ 2.09.

40% (2); M_n 13600 g mol^{-1}, M_w 29000 g mol^{-1}, Đ 2.13.

60% (1); M_n 20200 g mol^{-1}, M_w 43600 g mol^{-1}, Đ 2.16.

60% (2); M_n 17000 g mol^{-1}, M_w 44000 g mol^{-1}, Đ 2.59.

60% (3); M_n 16800 g mol^{-1}, M_w 39400 g mol^{-1}, Đ 2.35.

80% (1); M_n 14300 g mol^{-1}, M_w 42600 g mol^{-1}, Đ 2.97.

80% (2); M_n 14800 g mol^{-1}, M_w 43500 g mol^{-1}, Đ 2.94.

80% (3); M_n 14900 g mol^{-1}, M_w 38000 g mol^{-1}, Đ 2.55.

Composition experiments at 60% (w/w) concentration:

11 mol% V_3; M_n 7200 g mol^{-1}, M_w 8900 g mol^{-1}, Đ 1.25 (before), M_n 17000 g mol^{-1}, M_w 44000 g mol^{-1}, Đ 2.59 (after).

22 mol% V_3; M_n 9600 g mol^{-1}, M_w 12700 g mol^{-1}, Đ 1.32 (before), M_n 25700 g mol^{-1}, M_w 91600 g mol^{-1}, Đ 3.56 (after).

35 mol% V_3; M_n 8000 g mol^{-1}, M_w 9400 g mol^{-1}, Đ 1.17 (before), M_n 11000 g mol^{-1}, M_w 19000 g mol^{-1}, Đ 1.69 (after).

52 mol% V_3; M_n 7000 g mol^{-1}, M_w 8300 g mol^{-1}, Đ 1.19 (before), M_n 9900 g mol^{-1}, M_w 16000 g mol^{-1}, Đ 1.62 (after).

H NMR ($CDCl_3$): 0.04-1.15 ppm $(C\mathbf{H}_3)_2SiO$, 0.15-0.20 ppm $(C\mathbf{H}_3)(CHCH_2)SiO$, 0.27-0.50 ppm $(O(Ph)(C\mathbf{H}_3)SiC\mathbf{H}_2C\mathbf{H}_2Si(CH_3)O)$, 0.50-0.61 ppm $(CH_2CH_3)(CH_3)C\mathbf{H}\text{-}SiO$, 0.88-1.00 ppm $(CH_2C\mathbf{H}_3)(C\mathbf{H}_3)CH\text{-}SiO$, 1.04-1.25 ppm $(C\mathbf{H}HCH_3)(CH_3)CH\text{-}SiO$, 1.50-1.60 ppm $(CH\mathbf{H}CH_3)(CH_3)CH\text{-}SiO$, 5.56-6.22 ppm $(CH_3)(C\mathbf{H}C\mathbf{H}_2)SiO$, 7.33-7.54 ppm Ar-**H** (MDPS).

4 Conclusions

In this thesis, we have reported the synthesis of well-defined dihydroxyl end-functionalized polydimethylsiloxane (PDMS) polymers, with attempts to couple those polymers to form star polymers via Williamson coupling reactions, and the synthesis of highly (randomly) branched polysiloxanes by AB_x macromonomer approach.

Two different initiator precursors, 4,4’-dihydroxy-1,1-diphenylethylene and Bisphenol F, were protected and used to initiate the polymerization of hexamethylcyclotrisiloxane (D_3). The precursor compounds were protected by forming silyl ethers, specifically triethylsilyl (TES) and t-butyldimethylsilyl (TBDMS) groups. The synthesis of protected 4,4’-dihydroxy-1,1-diphenylethylene (DPE-OSi) was performed in two steps via the protection of 4,4’-dihydroxybenzophenone followed by the conversion of the ketone group to an alkene via a Wittig reaction. It was observed that the TES group did not survive the Wittig reaction and only TBDMS-protected 4,4’-dihydroxy-1,1-diphenylethylene was successfully prepared with this synthetic procedure. Bisphenol F was protected by using TES-Cl only since this synthesis did not require harsh conditions such as a Wittig reaction.

Initiation of D_3 polymerization with activated DPE-OSi did not work initially, we believe due to steric hindrance, however, this problem was overcome by the introduction of a short polybutadiene spacer block in between DPE-OSi and PDMS block. Several end-functionalised polymers were subsequently synthesised and NMR analysis showed that a majority of chains were in possession of the intended DPE-OSi end-group. In addition to the commonplace terminating (end-capping) agent chlorotrimethylsilane, two other end-capping agents, chloro(methyl)diphenylsilane and t-butyl(chloro)diphenylsilane, were also used in attempt to increase the stability of the PDMS polymer to degradation during a subsequent deprotection reaction. The end-capping with chloro(methyl)diphenylsilane did work whereas the end-capping with t-butyl(chloro)diphenylsilane was believed to suffer from steric problems. The initiation reaction of Bisphenol F with sec-BuLi/TMEDA was not completely successful, but appeared to be a promising approach given the incorporation of protected Bisphenol F was confirmed with NMR analysis.

A variety of deprotection reactions were attempted under both basic (NaH, DBU and TBAF), and acidic (HCl and AcOH), conditions. Two successful methods were established as a result of these trials. First, TBAF deprotection of TBDMS-protected DPE-OSi initiated PDMS and second, AcOH deprotection of TES-protected DPE-OSi initiated PDMS. The TES-protected

DPE-OSi was prepared and used for polymerization prior to this reaction by following a deprotection-reprotection strategy. Both methods resulted in almost complete removal of aryl silyl ether group. TBAF deprotection was straightforward but degradation of the PDMS backbone occurred as evidenced by a rise in dispersity in all cases. The AcOH deprotection approach was rather time-consuming and suffered from polymer solubility issues but yielded a dihydroxyl end-functionalised PDMS with no damage to the siloxane backbone. It is believed that both methods are potentially valuable, depending on what is intended for the macromonomer.

An attempt was made to couple TBAF-deprotected PDMS macromonomers with bromine end-capped polybutadiene chains via a Williamson coupling reaction to test if the macromonomer would survive the reaction. In the initial reaction with Cs_2CO_3, the PDMS backbone suffered significant degradation, probably due to attack by the base. This started a search for another suitable base to deprotonate the phenol group. K_2CO_3/18-crown-6 ether and zinc were tried for this purpose. The reaction with K_2CO_3/18-crown-6 did result in a degree of coupling and a portion of PDMS chains survived the coupling reaction. However, the reaction cannot be considered as a great success since only a small portion polymers coupled. Zinc, which was never used to catalyse the Williamson coupling of polymers, also performed badly, however, the results show PDMS backbone is stable in the presence of Zn metal.

In the final three months of the project, we have successfully synthesised highly and randomly branched polysiloxanes, via AB_x macromonomer approach. Initially, copolymers of D_3 and V_3 monomers were produced, to introduce some vinyl groups to the polymer backbone, and the polymerizations were terminated with chloro(methyl)phenylsilane to introduce Si-H bond to the end of polymer chains. A number of polydimethylsiloxane-polymethylvinylsiloxane (PDMS-PMVS) copolymers with varying V_3 composition were synthesised. The goal of this approach was to achieve the highest degree of branching with lowest vinyl composition since V_3 was the expensive monomer. A series of experiments were performed, at varying solution concentrations, on the copolymer containing 12 mol% V_3. The optimal concentrations were determined as 60% and 80% (w/w). 60% was chosen for a series of subsequent experiments on PDMS-PMVS copolymers of varying composition, to minimise any problems of high viscosity. An increase in V_3 content from 11 mol% to 22 mol% did result in greater branching, however further increase in V_3 content resulted in lower degrees of branching. This was believed to be a result of poor end-capping and possible increased likelihood of intramolecular cyclization reactions. In overall, a facile two-step method was established to synthesise highly branched polysiloxanes via a hydrosilylation reaction of AB_x PDMS-PMVS macromonomers.

5 Future Work

Possible future work could include further investigations into the development of the BPF/TMEDA/sec-BuLi initiation system and separately in the field of well-defined functionalised PDMS macromononers, and crosslinked silicones.

BPF/TMEDA/sec-BuLi

We have attempted, for the first time, to create a novel functionalised BPF-Li initiator for the anionic ring-opening polymerisation of PDMS, by using an initiating/chain transfer system which has previously been shown as efficient for toluene.[71] One of the main ideas of this strategy was the stabilization of the anion by the ring system. As it can be seen from Figure 5.1, that Bisphenol F has two phenyl groups and therefore, more resonance structures are possible for lithium initiator based Bisphenol F (BPF-Li) compared to a lithium initiator based toluene (TOL-Li). TOL-Li is known to give a yellow colour when the species is present in the solution and the fact that a red colour was observed with BPF-Li is very promising for the field of anionic polymerization. TMEDA is a basic species capable of making BuLi more reactive. It is hypothesised the relatively weak TES protecting group did not survive the initiation reaction and killed the living species in the medium. It is believed that this initiation mechanism can be attempted by using a TBDMS protecting group and this initiator can be used to initiate anionic polymerization of styrene or 1,3-butadiene monomers as they are known to be resistant to acidic conditions required to remove the TBDMS group.[50]

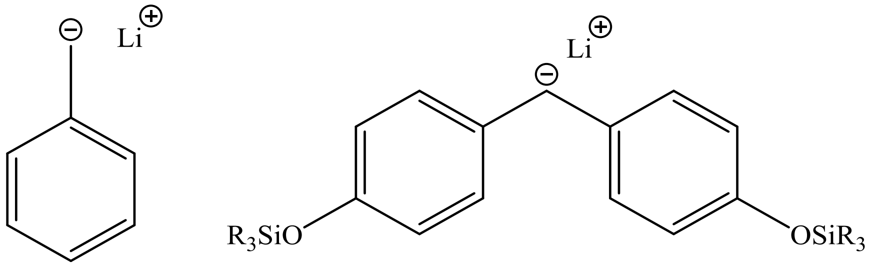
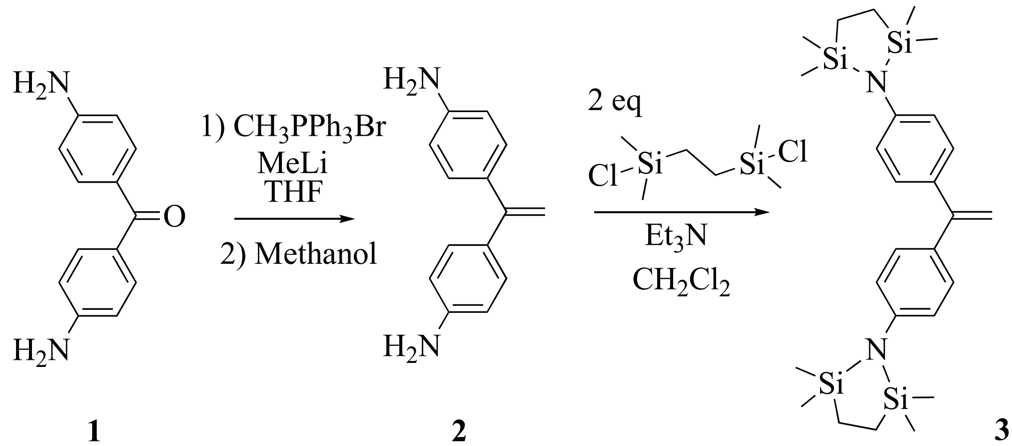


Figure 5.1: The structures of lithium initiator based toluene and Bisphenol F.

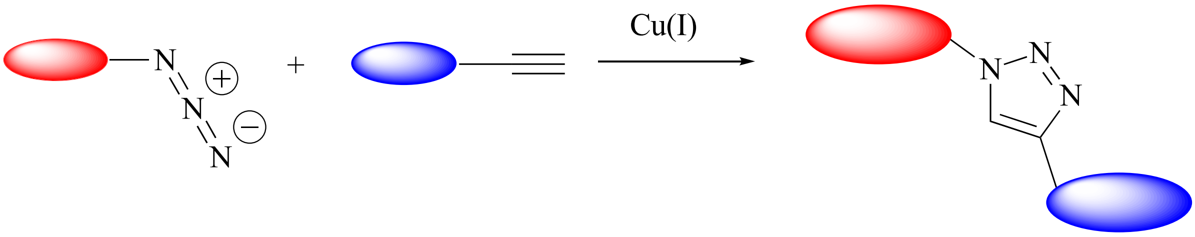
Synthesis of Diamine End-functionalised PDMS

There has been an increasing interest in synthesising branched polymers as these polymers may find use in a variety of fields including catalysis, chromatography, electronic and paints.[33, 41] Flexibility and hydrophobicity of polydimethylsiloxane can be beneficial towards these applications. In addition, an end-functionalized PDMS macromonomer can be coupled to different polymers, such as polyethylene glycol (PEG). PEG is a hydrophilic polymer and a PDMS macromonomer coupled to a PEG chain would form an amphiphilic copolymer. These copolymers can be useful for shipping industries. Algae formation on ships is a very serious problem slowing down the ships. This branched polymer can be incorporated into paints used to paint ships. PEG part of the polymer would face the water and PDMS part of the polymer would attach to the ship, potentially preventing the growth of algae. We have managed to synthesise dihydroxyl end-functionalised PDMS with well-controlled molecular parameters, however, our attempts to couple this PDMS macromonomer with other macromonomers through etherification has failed. Therefore, alternative functionalities need to be considered. It is suggested here to introduce amine groups to the PDMS chain which can then later be used for "click" chemistry. Scheme 5.1 shows a suggested procedure for the synthesis of a new initiator precursor, **3**, and its polymerization. Synthesis of 4,4'-bis(benzenamine)ethenylidene, **2**, was previously reported in the literature.[96] The protecting group, 1,2-bis(chlorodimethylsilyl)ethane, is suggested as it was reported to be stable in the presence of s-BuLi at – 25 °C and can be easily removed in the presence of 0.1 M HCl or AcOH.[97] This initiator precursor can then be used to initiate the polymerization of D_3 monomer by the previously described method in this thesis. Low temperatures may be necessary to retain the protecting group throughout the polymerization.



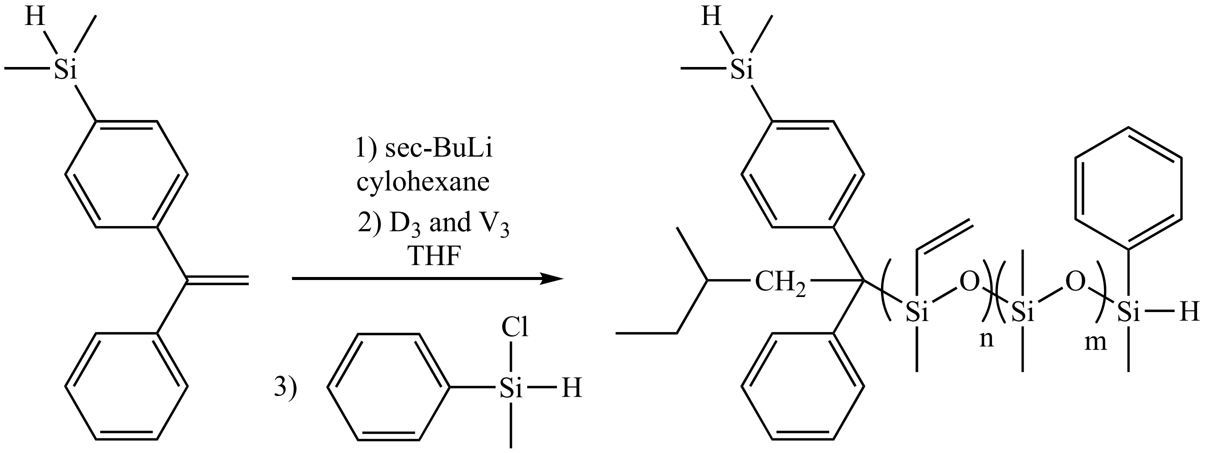
Scheme 5.1: Proposed initiator precursor (3) and its suggested synthesis.[96, 97]

The presence of amine functionality enables the introduction of azide moiety on to the polymer chains by using NaN_3. This reagent was previously used with PDMS polymer to convert C-I and C-OTs bond to N_3 moiety.[98] The mentioned paper did not report any damage to the polymer chain and reported yields over 90% which suggests the reaction happens without damaging the polymer backbone. If the functionality can be introduced on to the polymer chains, then these macromonomers can be coupled to any polymer chain containing an alkyne group via click chemistry (Scheme 5.2). It is also possible to end-cap the PDMS polymer chains with a chlorosilane derivative containing an alkyne group.



Scheme 5.2: A demonstration of click chemistry reaction between an azide and an alkyne group.

Crosslinked Silicones



Scheme 5.3: An example scheme to illustrate the synthesis of di-“Si-H”-endfunctionalised PMVS-PDMS copolymer. A PBd spacer block may be needed but omitted in this scheme.[99]

Silicones, such as PDMS, are unique biomaterials with a variety of applications in biomedicine and healthcare. Although silicone “fluids” can be used without any curing, in most cases silicones need to be specifically tailored for a desired application. Crosslinking is one of the most common curing methods to meet this design challenge as it is possible to vary the silicones strength and elasticity.[100] It is believed that the hydrosilylation coupling of the anionically synthesised polysiloxane macromonomers might be a useful way of making crosslinked silicones if both ends of the polymers were end-capped with an Si-H group. An example scheme is provided above. Information regarding the synthesis of the 1-(4-dimethylsilylphenyl)-1-phenylethylene initiator precursor can be found on the paper published by Quirk *et al.*[99] A small spacer unit may be necessary with this initiator again. Alternatively, PDMS-PMVS macromonomers can also be coupled with a difunctional silane

(Figure 5.2). Crosslink density in the final silicones can potentially be controlled by V_3 content of the macromonomer in both cases.

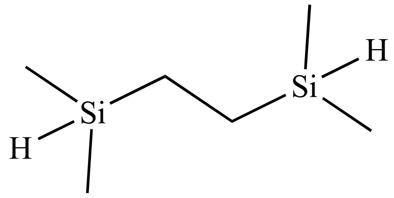


Figure 5.2: An example of a potential crosslinking agent.

References

1. Nobel Prize Website, http://www.nobelprize.org/nobel_prizes/chemistry/laureates/1974/flory-lecture.html, (accessed April 2017).
2. K. Singh, in *Chemistry in Daily Life*, PHI Learning Private Limited, New Delhi, 3rd edn., 2012, p. 132.
3. R. S. o. Chemistry, http://www.rsc.org/learn-chemistry/resources/business-skills-and-commercial-awareness-for-chemists/docs/businessdoc1.pdf, (accessed June 2017).
4. W. H. Carothers, *Journal of American Chemical Society*, 1929, **51**, 2548-2559.
5. S. Ito, *Polymer Journal*, 2016, **48**, 667-677.
6. A. D. Jenkins, P. Kratochvil, R. F. T. Stepto and U. W. Suter, *Pure and Applied Chemistry*, 1996, **68**, 2287-2311.
7. M. Szwarc, *Nature*, 1956, **178**, 1168-1169.
8. M. Szwarc, M. Levy and R. Milkovich, *Journal of American Chemical Society*, 1956, **78**, 2656-2657.
9. K. Matyjaszewski and A. H. E. Muller, *Progress in Polymer Science*, 2006, **31**, 1039-1040.
10. H. L. Hsieh and R. P. Quirk, *Anionic Polymerization: Principles and Practical Applications*, Marcel Dekker, Inc., New York, 1996.
11. R. P. Quirk and B. Lee, *Polymer International*, 1992, **27**, 359-367.
12. H. L. Hsieh, in *Applications of Anionic Polymerization Research*, ed. R. Quirk, Americal Chemical Society, Washington, DC, 1998, pp. 28-33.
13. A. Stock, *Berichte Der Deutschen Chemischen Gesellschaft*, 1917, **50**, 169-170.
14. M. G. Voronkov, V. P. Mileshkevich and Y. A. Yuzhelevskii, in *The Siloxane Bond: Physical Properties and Chemical Transformations*, Consultants Bureau, New York, 1978, pp. 1-47.
15. A. Stock and C. Somieski, *Berichte Der Deutschen Chemischen Gesellschaft*, 1919, **52**, 695-724.
16. E. Yilgor and I. Yilgor, *Progress in Polymer Science*, 2014, **39**, 1165-1195.
17. A. Ede, in *The Chemical Element: A Historical Perspective*, Greenwood Publishing Group, Inc., Connecticut, USA, 2006, pp. 115, 122, 123, 134

18. H. Oberhammer and J. E. Boggs, *Journal of American Chemical Society*, 1980, **102**, 7241-7244.

19. S. Grabowsky, M. F. Hesse, C. Paulmann, P. Luger and J. Beckmann, *Inorganic Chemistry*, 2009, **48**, 4384-4393.

20. R. J. Abraham and G. H. Grant, *Journal of Computer-Aided Molecular Design*, 1988, **2**, 267-280.

21. R. J. Gillespie and S. A. Johnson, *Inorganic Chemistry*, 1997, **36**, 3031-3039.

22. J. C. Lotters, W. Olthuis, P. H. Veltink and P. Bergveld, *Journal of Micromechanics and Microengineering* 1997, **7**, 145-147.

23. M. D. Ninago, A. J. Satti, J. A. Ressia, A. E. Ciolino, M. A. Villar and E. M. Valles, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2009, **47**, 4774-4783.

24. C. L. Elkins and T. E. Long, *Macromolecules*, 2004, **37**, 6657-6659.

25. V. Bellas, H. Iatrou and N. Hadjichristidis, *Macromolecules*, 2000, **33**, 6993-6997.

26. J. Chojnowski, M. Cypryk, W. Fortuniak, M. Scibiorek and K. Rozga-Wijas, *Macromolecules*, 2003, **36**, 3890-3897.

27. M. Barrere, F. Ganachaud, D. Bendejacq, M. A. Dourges, C. Maitre and P. Hemery, *Polymer* 2001, **42**, 7239-7246.

28. M. Liu, A. Ragheb, P. Zelisko and M. A. Brook, in *Colloidal Biomolecules, Biomaterials and Biomedical Applications*, ed. A. Elaissari, Marcel Dekker Inc., New York, 2004, vol. 116, pp. 7239-7246.

29. C. Sun, M. Shen, L. Deng, J. Mo and B. Zhou, *Chinese Chemical Letters*, 2014, **25**, 621-626.

30. J. E. Mark, H. R. Allcock and R. West, Oxford University Press, New York, 2 edn., 2005.

31. R. G. Jones, W. Ando and J. Chojnowski, in *Silicon-Containing Polymers: The Science and Technology of Their Synthesis and Applications*, Kluwer Academic Publishers, Netherlands, 2000, p. 58.

32. J. G. Zilliox, J. E. L. Roovers and S. Bywater, *Macromolecules*, 1975, **8**, 573-578.

33. J. Chojnowski, *Journal of Inorganic and Organometallic Polymers*, 1991, **1**, 299-323.

34. A. K. Sutar, T. Maharana, S. Dutta, C. Chen and C. Lin, *Chemical Society Reviews*, 2010, **39**, 1724-1746.

35. J. Goff, E. Kimble and B. Arkles, in *Silicones and Silicone-Modified Materials: Living Polymerization routes to Siloxane Macromers and Higher Order Silicone Structures*, ACS Symposium Series, Washington, 2013, pp. 59-78.
36. T. Zundel, J. M. Yu, L. Lestel, D. Teyssie and S. Boileau, *Macromolecular Symposia*, 1994, **88**, 177-189.
37. L. Wilczek and J. P. Kennedy, *Polymer Journal*, 1987, **19**, 531-538.
38. A. Molenberg, H. Klok and M. Moller, *Macromolecules*, 1997, **30**, 792-794.
39. S. O. Hammouch, G. J. Beinert, J. G. Zilliox and J. E. Herz, *Polymer*, 1995, **36**, 421-426.
40. J. Bauer, N. Husing and G. Kickelbick, *Journal of Polymer Science: Part A: Polymer Chemistry*, 2004, **42**, 3975-3985.
41. J. Chojnowski, M. Cypryk, W. Fortuniak, K. Rozga-Wijas and M. Scibiorek, *Polymer*, 2002, **43**, 1993-2001.
42. P. K. Avti and A. Kakkar, *Brazilian Journal of Pharmaceutical Sciences*, 2013, **49**, 57-65.
43. M. G. Neira-Velazquez, M. T. Rodriguez-Hernandez, E. Hernandez-Hernandez and A. R. Y. Ruiz-Martinez, in *Handbook of Polymer Synthesis, Characterization and Processing*, eds. E. Saldivar-Guerra and E. Vivaldo-Lima, John Wiley & Sons, Inc., New Jersey, First edn., 2013, ch. 17, pp. 355-366.
44. J. C. Giddings, *Analytical Chemistry*, 1994, **66**, 2783-2787.
45. M. Gaborieau and P. Castignolles, *Analytical and Bioanalytical Chemistry*, 2011, **399**, 1413-1423.
46. R. Yin and T. E. Hogen-Esch, *Macromolecules*, 1993, **26**, 6952-6957.
47. L. R. Hutchings, *Soft Matter*, 2008, **4**, 2150-2159.
48. L. R. Hutchings and S. J. Roberts-Bleming, *Macromolecules*, 2006, **39**, 2144-2152.
49. L. R. Hutchings, J. M. Dodds and S. J. Roberts-Bleming, *Macromolecules*, 2005, **38**, 5970-5980.
50. L. R. Hutchings, J. M. Dodds, D. Rees, S. M. Kimani, J. J. Wu and E. Smith, *Macromolecules*, 2009, **42**, 8675-8687.
51. P. J. Kocienski, in *Protecting Groups*, eds. D. Enders, R. Noyori and B. M. Trost, Georg Thieme Verlag, Germany, 1994, pp. 28-41.
52. G. S. Buchanan, K. P. Cole, Y. Tang and R. P. Hsung, *The Journal of Organic Chemistry*, 2011, 7027-7039.

53. P. G. M. Wuts and T. W. Greene, in *Greene's Protective Groups in Organic Synthesis*, John Wiley & Sons, Inc., New Jersey, 4th edn., 2006

ch. 2, pp. 16-366.

54. R. P. Quirk and Y. Wang, *Polymer International*, 1993, **31**, 51-59.

55. R. P. Quirk, T. Yoo, Y. Lee, K. Kim and B. Lee, in *Advances in Polymer Science*, eds. A. Abe, A. C. Albertsson, G. W. Coates, J. Genzer, S. Kobayashi, K. S. Lee, L. Leibler, T. E. Long, M. Moller, O. Okay, V. Percec, D. Z. Tang, E. M. Terentjev, P. Theato, M. J. Vicent, B. Voit, U. Wiesner and X. Zhang, Springer-Verlag, Berlin, 2000, vol. 153, pp. 68-154.

56. L. R. Hutchings, P. P. Brooks, D. Parker, J. A. Mosely and S. Sevinc, *Macromolecules*, 2015, **48**, 610-628.

57. L. R. Hutchings, S. Agostini, I. W. Hamley and D. Hermida-Merino, *Macromolecules*, 2015, **48**, 8806-8822.

58. D. Baskaran and A. H. E. Muller, in *Controlled and Living Polymerization*, eds. A. H. E. Muller and K. Matyjaszewski, Wiley-VCH, Weinheim, 2009, ch. 1, pp. 1-56.

59. M. A. Hillmyer and F. S. Bates, *Macromolecules*, 1996, **29**, 6994-7001.

60. K. J. Wu and R. W. Odom, *Characterizing Synthetic Polmers by MALDI MS*, 1998.

61. G. Montaudo, M. S. Montaudo, C. Puglisi and F. Samperi, *Rapid Communications in Mass Spectrometry*, 1995, **9**, 453-460.

62. C. Jackson, B. Larsen and C. McEwen, *Analytical Chemistry*, 1996, **68**, 1303-1308.

63. P. M. Lloyd, K. G. Suddaby, J. E. Varney, E. Scrivener, P. J. Derrick and D. M. Haddleton, *European Mass Spectrom*, 1995, **1**, 293-300.

64. G. Montaudo, F. Samperi and M. S. Montaudo, *Progress in Polymer Science*, 2006, **31**, 277-357.

65. A. Pagliarulo and L. R. Hutchings, *Macromolecular Chemistry and Physics*, 2017, **Advance Online Publication**, 1700386.

66. X. Pang, R. Jing and J. Huang, *Polymer*, 2008, **49**, 893-900.

67. J. He, J. Li and S. Yang, in *Anionic Polymerization: Principles, Practice, Strength, Consequences and Applications*, eds. N. Hadjichristidis and A. Hirao, Springer, Japan, 1st edn., 2015, pp. 719-752.

68. Y. Zhang, G. Wang and J. Huang, *Journal of Polymer Science: Part A, Polymer Chemistry*, 2010, **48**, 5974-5981.

69. T. C. Castle, L. R. Hutchings and E. Khosravi, *Macromolecules*, 2004, **37**, 2035-2040.

70. Z. Zhang, N. Zhou, C. Xu and Z. Xie, *Chinese Journal of Polymer Science*, 2001, **9**, 7-11.

71. T. Tsukahara, J. Inoue, Y. Ohta, S. Kohjiya and Y. Okamoto, *Polymer Journal*, 1994, **26**, 1013-1018.

72. T. D. Nelson and R. D. Crouch, *Synthesis*, 1996, **9**, 1031-1069.

73. J. N. Lee, C. Park and G. M. Whitesides, *Analytical Chemistry*, 2003, **75**, 6544-6554.

74. E. J. Corey and A. Venkateswarlu, *Journal of American Chemical Society*, 1972, **94**, 6190-6191.

75. B. E. Blass, C. L. Harris and D. E. Portlock, *Tetrahedron Letters*, 2001, **42**, 1611-1613.

76. E. W. Collington, F. H and I. J. Smith, *Tetrahedron Letters*, 1985, **26**, 681-684.

77. S. V. Ankala and G. Fenreany, *Tetrahedron Letters*, 2002, **43**, 4729-4732.

78. Z. Jiang and Y. G. Wang, *Chemistry Letters*, 2003, **32**, 568-569.

79. R. D. Crouch, M. Stieff, J. L. Frie, A. B. Cadwallader and D. C. Bevis, *Tetrahedron Letters*, 1999, **40**, 3133-3136.

80. B. Wang, H. X. Sun and Z. H. Sun, *Journal of Organic Chemistry*, 2009, **74**, 1781-1784.

81. Z. Jiang and Y. G. Wang, *Tetrahedron Letters*, 2003, **44**, 3859-3861.

82. N. S. Wilson and B. A. Keay, *Tetrahedron Letters*, 1997, **38**, 187-190.

83. L. Yan, F. Zhao, Y. Gan, J. Zhao and Z. Jiang, *Synthetic Communications*, 2012, **42**, 285-291.

84. R. A. Fernandes, S. P. Gholap and S. V. Mulay, *RSC Advances*, 2014, **4**, 16438-16443.

85. C. Yeom, H. W. Kim, S. Y. Lee and B. M. Kim, *Synlett*, 2007, **1**, 146-150.

86. S. W. Wright, *Journal of Chemical Education*, 1992, **69**, 235.

87. M. Kleiman, K. A. Ryu and A. P. Esser-Kahn, *Macromolecular Chemistry and Physics*, 2016, **217**, 284-291.

88. W. R. Li, W. R. Ewing, B. D. Harris and M. M. Joullie, *Journal of American Chemical Society*, 1990, **112**, 7659-7672.

89. J. A. Marshall and R. J. Sedrani, *Journal of Organic Chemistry*, 1991, **56**, 5496-5498.

90. A. Williamson, *Philosophical Magazine*, 1850, **37**, 350-356.

91. S. Paul and M. Gupta, *Tetrahedron Letters*, 2004, **45**, 8825-8829.

92. B. Liu, X. Gao, Y. Zhao, L. Dai, Z. Xie and Z. Zhang, *Macromolecular Chemistry and Physics*, 2017, **218**, 1700005(1700001 to 1700011).

93. F. Lopez-Villanueva, F. Wurm, A. F. M. Kilbinger and H. Frey, *Macromolecular Rapid Communications*, 2007, **28**, 704-709.

94. L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, *Journal of American Chemical Society*, 1946, **69**, 188.

95. H. Renner, G. Schlamp, I. Kleinwachter, E. Drost, H. M. Luschow, P. Tews, P. Panster, M. Diehl, J. Lang, T. Kreuzer, A. Knodler, K. A. Starz, K. Dermann, J. Rothaut and R. Drieselman, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Germany, 2002, vol. 28, pp. 319-382.

96. G. J. Summers, M. P. Ndawuni and A. C. Carol, *Polymer International*, 2014, **63**, 876-886.

97. S. Djuric, J. Venit and P. Magnus, *Tetrahedron Letters*, 1981, **22**, 1787-1790.

98. M. J. Isaacman, K. A. Barron and L. S. Theogarajan, *Journal of Polymer Science: Part A, Polymer Chemistry*, 2012, **50**, 2319-2329.

99. R. P. Quirk and S. Shaoo, *Macromolecular Symposia*, 2013, **325-326**, 77-88.

100. J. M. Lambert, *Journal of Biomedical Materials Research. Part B: Applied Biomaterials*, 2006, **78B**, 167-180.