Synthesis of block copolymers by the conversion of living anionic polymerisation into living ROMP

Thomas Charles Castle

Synthesis of Block Copolymers by the Conversion of Living Anionic Polymerisation into Living ROMP

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by

Thomas Charles Castle

Department of Chemistry
University of Durham

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Abstract

A methodology for the synthesis of well-defined block copolymers from living anionic polymerisation and ring opening metathesis polymerisation (ROMP) using well-defined ruthenium alkylidene initiators has been developed.

Polymers synthesised by anionic polymerisation were converted into macromonomers, which were used as precursor polymers to well-defined ruthenium macroinitiators for ROMP. The macroinitiators were synthesised by an olefin metathesis reaction, involving alkylidene exchange of $RuCl_2(=CHEt)(PCy_3)_2$ with the macromonomers. The ROMP of norbornene (NBE) derivatives using the macroinitiators resulted in the synthesis of block copolymers. These copolymers possessed low polydispersity indices (typically 1.2 or less) and contained small quantities or none of the anionically polymerised homopolymer.

Poly(ethylene oxide) (PEO) macromonomers were synthesised by terminating living PEO with 4-vinylbenzyl chloride. The PEO macromonomers were used to synthesise block copolymers of ethylene oxide (EO) and NBE derivatives. Polystyrene (PS) macromonomers were prepared by Williamson coupling of hydroxyl functionalised PS and 4-VBC. The hydroxyl functionalised PS was synthesised by end functionalising living PS with EO or by incorporating a hydroxy functionality into the initiator in a protected form. Copolymers of styrene and NBE derivatives were produced using the PS macromonomers. The applicability of this methodology to other monomers that can be polymerised by an anionic mechanism was examined.

The ROMP monomers included NBE derivatives with imide, dicarboxylic ester and chloromethyl groups, illustrating the range of functionalities that can be incorporated into the ROMP block using this methodology.

Acknowledgments

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Declaration

The work reported in this thesis was carried out in the laboratories of the Interdisciplinary Research Centre (IRC) in Polymer Science and Technology, Department of Chemistry, University of Durham, between October 2001 and September 2004. This work has not been submitted for any other degree in Durham or elsewhere and is the original work of the author except where acknowledged by means of appropriate reference.

Statement of Copyright

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Contents

Abbreviations

ACS	American Chemical Society
ADMET	Acyclic diene metathesis
AROP	Anionic ring opening polymerisation
ATRP	Atom Transfer Radical Polymerisation
BO	1-Butene oxide
b.p.	Boiling point
Bu	Butyl
CK	Cumyl potassium
CM	Cross metathesis
COD	1,5-Cyclooctadiene
conc.	Concentrated
COSY	Correlation Spectroscopy
Cy	Cyclohexyl
d	Doublet
DCPD	Dicyclopentadiene
DPE	1,1-Diphenylethylene
DPMK	Diphenylmethyl potassium
DMAP	*N,N*-Dimethylaminopyridine
DMF	Dimethyl formamide
DMSO	Dimethyl sulfoxide
DP	Degree of polymerisation
EI-MS	Electron impact mass spectroscopy
EO	Ethylene oxide
Et	Ethyl
F_w	Formula weight
g	Gram(s)
GC-MS	Gas chromatography mass spectroscopy
GPC	Gel permeation chromatography (Size exclusion chromatography)
GPR	General purpose reagent
h	Hour(s)
H	Head
HSQC	Heteronuclear single quantum correlation

HMBC	Heteronuclear multiple bond correlation
I	Initiator
I_0	Initial initiator concentration (time=0 min)
IMes	1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene
IPA	Isopropyl alcohol (propan-2-ol)
k_i	Rate constant of initiation
k_p	Rate constant of propagation
lit.	Literature
M	Monomer
M_0	Initial monomer concentration (time=0 min)
MALDI-TOF	Matrix assisted laser desorption ionisation – time of flight
Me	Methyl
MeOH	Methanol
mg	Milligram(s)
MI	Macroinitiator
min	Minute(s)
mL	Millilitre(s)
mmol	Millimole(s)
M_n	Number average molecular weight
mol	Moles
m.p.	Melting point
α-MS	α-Methylstyrene
MS	Mass spectroscopy
M_w	Weight average molecular weight
NBE	Norbornene
NMR	Nuclear magnetic Resonance
PBD	Polybutadiene
PDI	Poly dispersity index
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PEP	Poly(ethylene-alt-propylene)
PES	Poly(ethylene sulfide)
Ph	Phenyl
PI	Polyisoprene

PMMA	Poly(methyl methacrylate)
PNB	Polynorbornene
ppm	Parts per million
PPO	Polypropylene oxide
PPS	Poly(propylene sulfide)
Pr	Propyl
PrS	Propylene sulfide
PS	Polystyrene
PSLi	Poly(styryl)lithium
P2VP	Poly(2-vinyl pyridine)
P4VP	Poly(4-vinyl pyridine)
q	Quartet
RCM	Ring closing metathesis
$R_{coupling}$	Rate of coupling
r.f.	Radio frequency
R_i	Rate of initiation
ROMP	Ring opening metathesis polymerisation
R_p	Rate of propagation
r.t.	room temperature
s	Singlet
t	Triplet
T	Tail
TBAF	Tetrabutylammonium fluoride
TBDMSO	*tert*-Butyldimethylsilyl ether
TBDMS	*tert*-Butyldimethylsilyl
theor.	Theoretical
THF	Tetrahydrofuran
TMEDA	*N*,*N*,*N*',*N*'-Tetramethylethylenediamine
TMS	Tetramethylsilane
3-VBC	3-Vinylbenzyl chloride
4-VBC	4-Vinylbenzyl chloride

Chapter 1

Overview and Introduction

1.1 Aims, Objectives and Overview

The aim of this research was to develop a method for the synthesis of a range of well-defined block copolymers by combining two living polymerisation techniques, anionic polymerisation and ring opening metathesis polymerisation (ROMP) initiated with well-defined ruthenium initiators. Their synthesis involved transformation of the active propagating species in anionic polymerisation, by end functionalisation of the living chain to form macroinitiators for ROMP.

This Chapter will introduce prior research that is relevant to the project. The topic of anionic polymerisation will be discussed first and examples will be used to demonstrate the unique properties of living polymerisation reactions. Olefin metathesis and ROMP in particular will then be explored. The evolution of initiators for ROMP will be discussed with particular focus on the well-defined ruthenium initiators that were used in this work. Examples of methods for combining different polymerisation techniques will be highlighted. The following chapters will outline results of this project, which were successful in developing a method for the synthesis of the block copolymers.

1.2 Synthesis and Applications of Block Copolymers

It is often highly desirable to combine the properties of two or more different polymers together. When a solid material is required, it is sometimes possible to blend the polymers together to achieve this. Unfortunately the vast majority of potential combinations of polymers are immiscible with each other, in which case phase separation of the different polymers occurs.[1] The solution to this is to covalently bond the two blocks together to form a block copolymer. Whilst microscale segregation of the polymers can occur, the covalent linkages prevent macroscale segregation. Block copolymers typically have small domain sizes together with excellent interphase adhesion, which can result in materials with high degrees of transparency and good balances of mechanical properties, provided the copolymers are substantially free from homo polymers.[1] Block copolymers are also synthesised when we wish to combine the properties of two different polymers in a single macromolecule for an application which requires its use in solution, for instance surfactants.

Block copolymers are most frequently prepared by the sequential addition of two or more monomers to a single living polymerisation reaction. Anionic polymerisation, which will be discussed in detail in Section 1.3, has historically been the most important technique for preparing block copolymers, and is probably still the most industrially important. More recently living (sometimes referred to as controlled) radical polymerisation techniques have provided a useful alternative for block copolymer synthesis. In cases where the target block copolymer structure cannot be synthesised by one polymerisation mechanism, more than one mechanism can be used (Section 1.5). This is the approach used to synthesise the new block copolymers reported in this work.

Styrene-butadiene (SB) block copolymers were first produced on a pilot plant scale in 1960.[2] They are prepared by the sequential addition of the two monomers to alkyllithium initiated anionic polymerisation. The two blocks are incompatible and hence microscale phase separation occurs. As a result the glass transitions of both polymeric blocks are detectable. However sheets moulded from the block copolymers posses a high degree of clarity. SB block copolymers have found use in a range of applications including shoe soles, floor tiles, cable insulation, conveyor belts and hoses. The transparency, high hardness and light colour of SB block copolymers means their properties lend themselves to the production of attractive floor tiles. The floor tiles have far greater wear resistance and lower mill shrinkage compared with random styrene-butadiene copolymers.

Block copolymers of poly(ethylene oxide)(PEO) and poly(propylene oxide)(PPO) are of significant industrial importance (BASF corporation trademarks Pluronic® and Tetronic®).[3] They are usually synthesised by sequential polymerisation of propylene oxide (PO) and ethylene oxide (EO) using an anionic initiator. The polymers are amphiphilic, PEO being hydrophilic and PPO being hydrophobic; the properties of the block copolymers can be tailored by adjusting the ratios of the two blocks. Thus the solubility, viscosity and physical state (liquid, paste or solid) can be adjusted by varying the lengths of the blocks. This has facilitated their use in applications as diverse as cosmetics, medicines, cleaners, and lubricants. PEO-PPO copolymers are often mixed with other polymers to increase their utility; for example addition of a bioadhesive polymer enables PEO-PPO block copolymers to be used as efficient suppositories, which can deliver insulin, or anticancer agents. Perhaps the most common use of PEO-PPO block copolymers is as surfactants, e.g. in

the demulsification of crude oils and tars, optimisation of the recovery of mineral oil from water and the de-inking of paper.

The synthesis of block copolymers can therefore be used to generate macromolecules tailored to a specific application, by adjusting the composition of the copolymers. The development of new methodologies for the synthesis of block copolymers that cannot be prepared by existing techniques is therefore of great interest.

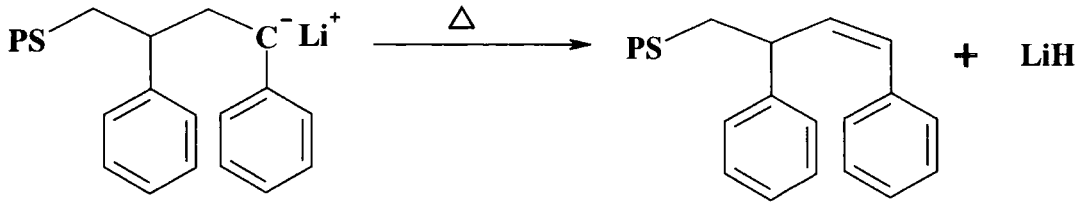
1.3 Anionic Polymerisation

The anionic polymerisation reaction is very well established. For instance diene monomers were polymerised by alkali metals as early as 1910, ethylene oxide was first polymerised by an anionic mechanism in 1878.[4] During the past 50 years or so it has evolved into a method for the synthesis of macromolecules of precisely controlled architecture. This has been possible due to the living nature of the polymerisation reactions. The fundamentals of living anionic polymerisation, the choice of initiator and reaction conditions will be reviewed. The scope of monomers that can be polymerised and the functionalisation of the polymers will be examined.

1.3.1 The Living Anionic Polymerisation of Styrene

Szwarc and his colleagues studied the polymerisation of styrene initiated by sodium naphthalene.[5] Complete conversion of the monomer to polystyrene (PS) was observed and the addition of a further batch of monomer resulted in the continuation of polymerisation. The polymerisation sites remained active during propagation and after polymerisation; there are thus no termination or chain transfer reactions inherent to the polymerisation. They coined the term living polymerisation to describe this polymerisation reaction. The anionic polymerisation reactions of styrene, and many other monomers, initiated by this and other initiators such as alkylithium compounds were also found to be living.[2] Whilst many slightly different definitions of and criteria for living polymerisation have been subsequently offered by other researchers, a living polymerisation can be simply defined as a polymerisation reaction in which chain transfer or termination does not occur during the lifetime of the experiment.[2,6-8] If the rate of initiation (R_i) is faster than that of propagation (R_p) polymers with a narrow molecular weight distribution can be synthesised, in contrast to 'conventional'

free radical polymerisation, where termination occurs throughout polymerisation leading to polymers with broad molecular weight distributions.[9] The living anionic polymerisations of styrene, butadiene and isoprene have undergone extensive investigation, most commonly using alkyllithium initiators. The living chain ends of the product of the polymerisation of styrene [poly(styryl)lithium](PSLi) possess very good stability, as do living polydienes [poly(dienyl)lithiums].[10] PSLi will remain 'alive' for many days at room temperature, although it will eventually decompose to form LiH, a process accelerated by heat (**Scheme 1.1**).



Scheme 1.1 - Thermodynamic decomposition of living polystyrene (PS).

The high stability of these carbanions means that they persist long after polymerisation is complete. Addition of a second monomer to a living anionic polymer results in the formation of a block copolymer. Further polymeric blocks can be added to the polymer chain by the sequential addition of other monomers (subject to their reactivity). As they have no inherent termination reactions living polymerisations are usually terminated in a controlled manner, e.g. using a suitable functionalisation reagent to quantitatively functionalise the polymer chains.

In addition to polymerisation reactions initiated by an anionic mechanism, living polymerisations have been reported from certain cationic,[11] radical[7,8] and metal catalysed polymerisations including ROMP.[12] Living ROMP will be discussed in Section 1.4.

1.3.2 Initiators for Living Anionic Polymerisation

Selection of the correct initiator for a polymerisation reaction allows control over the rate of initiation, the metal counter-ion of the propagating species, and the number of active sites, which in turn allow control over the molecular weight distribution of the resulting polymer and the types of postpolymerisation chemistry that can be carried out on the chain ends. In general an appropriate initiator for anionic polymerisation should have a similar reactivity to the resulting carbanion. If the reactivity is too high, side reactions, if present, will be promoted. If it is too low,

initiation will be slow or inefficient resulting in broadening of the molecular weight distribution or poor molecular weight control.

As was mentioned previously, initiation of the anionic polymerisation of dienes by alkali metals was adopted at an early stage in the history of anionic polymerisation. Indeed, the discovery that polymerisation of neat isoprene with lithium produced high *cis*-1,4-polyisoprene, with structure and properties similar to that of Hevea natural rubber, helped catalyse interest in anionic polymerisation.[2] Initiation by alkali metals is now largely of historical interest, although its mechanism will be briefly described here. Initiation is a heterogeneous process which occurs on the surface of the metal and involves electron transfer to an adsorbed monomer (**Scheme 1.2**).[13]

$$Mt + M \longrightarrow Mt^{+}\,M^{\cdot-}$$

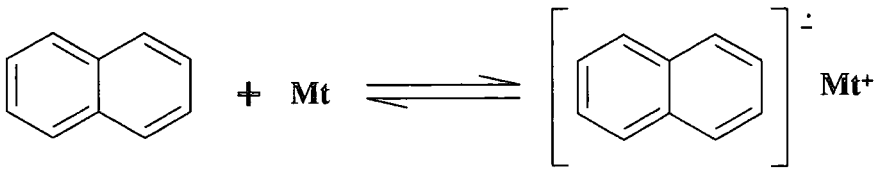
$$2\,Mt^{+}\,M^{\cdot-} \longrightarrow Mt^{+\,-}M{-}M^{-}\,Mt^{+}$$

$$Mt^{+\,-}M{-}M^{-\,+}Mt \xrightarrow{n\,M} Mt^{+\,-}M{-}M_{n}{-}M^{-\,+}Mt$$

Scheme 1.2 - Anionic polymerisation of a monomer (M) by an alkali metal (Mt).

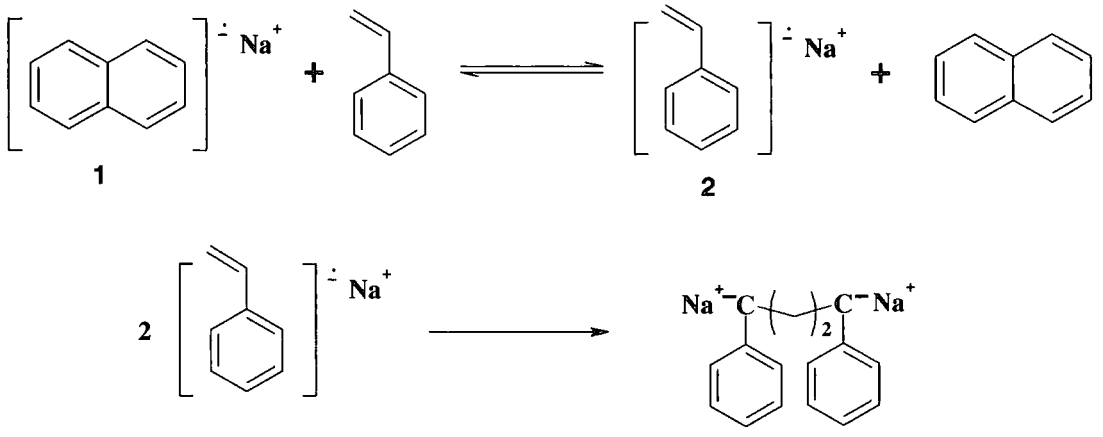
The radical anions combine quickly to form dianions. Monomer growth continues from both sites to form oligomers, which desorb into solution and propagate further to form high molecular weight polymers. The fact that initiation can continue to occur throughout the polymerisation reaction means that there is little control over the molecular weight, and polymers with broad molecular weight distributions are obtained (polydispersity index, PDI = 3-10). The reaction of α-methylstyrene (α-MS) with alkali metal is worthy of particular note. Because of the low ceiling temperature of polymerisations of this monomer 2 or 4 mers can be obtained, which can be used as bifunctional initiators for polymerisation.[14]

Radical anion initiators played an important part in the history of anionic polymerisation as they were used by Szwarc to prove the living nature of the reaction (Section 1.3.1).[5] The most important initiators of this type are based on the naphthalene radical anion system (**Scheme 1.3**).



Scheme 1.3 - Synthesis of a radical anion initiator system from napthalene and an alkali metal, Mt (Li, Na, K, Rb or Cs).

The oxidation-reduction reaction between the naphthalene and metal is reversible. The radical initiator is stabilised in tetrahydrofuran (THF) - pushing the equilibrium to the right, hence the initiator is best synthesised in that solvent.[15] Initiators of the type illustrated in **Scheme 1.3** react with monomers such as styrene by reversible electron transfer to the monomer (**Scheme 1.4**).



Scheme 1.4 - Initiation of the polymerisation of styrene using sodium naphthalene.

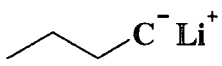
The equilibrium between the initiator **1** and the radical anion formed from the monomer **2** lies far over to the left. Initiation is still efficient, because the rate of dimerisation of **2** is very high.[13] This system can be used to prepare polymers of a fairly narrow molecular weight distribution.

The most commonly used initiators for the living anionic polymerisation of vinyl monomers are alkyllithium initiators.[2] A range of alkyllithium initiators are available commercially and these are generally used without further purification. Simple alkylithium compounds principally exist in the form of aggregates in hydrocarbon solution. The level of reactivity of initiators is closely related to their degree of aggregation, as they must first dissociate to form monomeric species prior to initiation. This reactivity trend is demonstrated by a comparison of the relative efficiency of alkyllithium compounds as polymerisation initiators and the average degree of aggregation they experience in hydrocarbon solution (shown in brackets):[2]

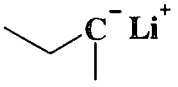
Styrene polymerisation: menthyllithium (2) > *sec*-BuLi (4) > *i*-PrLi (4-6) > *i*-BuLi > *n*-BuLi (6) > *t*-BuLi (4)

Diene Polymerisation: menthyllithium (2) > *sec*-BuLi (4) > *i*-PrLi (4-6) > *t*-BuLi (4) > *i*-BuLi > *n*-BuLi (6)

The initiator *n*-butyllithium (*n*-BuLi, **Figure 1.1**) is used very commonly in industry, although often at an elevated temperature (> 50 °C) to break down the aggregation present in the initiator. *sec*-Butyllithium (*sec*-BuLi, **Figure 1.1**) is used where a high R_i relative to R_p is of importance, for example in the synthesis of well defined styrene-butadiene copolymers.



***n*-BuLi**

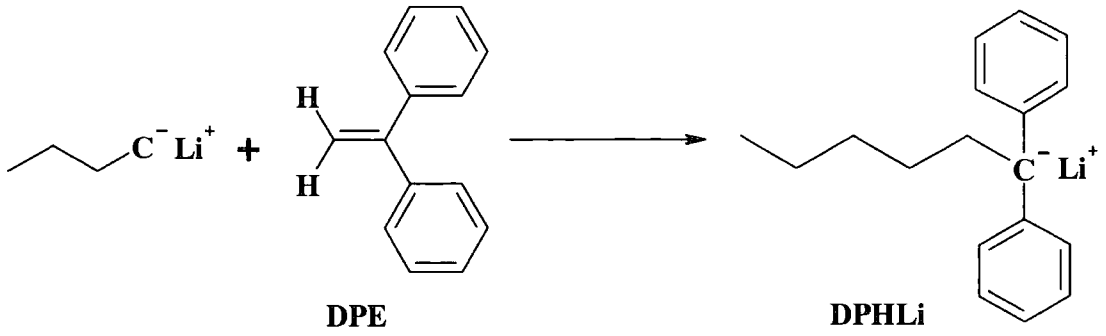


***sec*-BuLi**

Figure 1.1 - Alkyllithium initiators for anionic polymerisation that are of commercial importance.

Alkyllithium compounds decompose thermally to form LiH, although *sec*-BuLi and *n*-BuLi possess reasonable stabilities at room temperature (loss of activity occurs at a rate of 1.4% per month in the case of *sec*-BuLi), at reduced temperatures their stability is greatly enhanced.[2,16,17] Reaction with moisture and molecular oxygen leads to stoichiometric loss of initiator, producing lithium hydroxide in the case of reaction with H_2O and lithium alkoxides of the type ROLi with O_2.[16,17]

The high nucleophilicity of alkyllithium initiators means they are capable of reaction with a range of functional groups. Side reactions often occur when they are used to initiate the polymerisation of polar vinyl monomers. The reaction of alkyllithium compounds with 1,1-diphenylethylene (DPE) results in the formation of diphenylalkyllithium initiators. Conjugation of the carbanion with the two phenyl groups reduces their nucleophilicity, which coupled with the steric bulk around their active site results in a substantial reduction in reactivity. Thus 1,1-diphenylhexyllithium (DPHLi) the product of the reaction of *n*-BuLi with DPE (**Scheme 1.5**) was used to initiate the anionic polymerisation of methacrylates in a controlled manner, whereas substantial amounts of *n*-BuLi are lost to a side-reaction (Section 1.3.5.4).

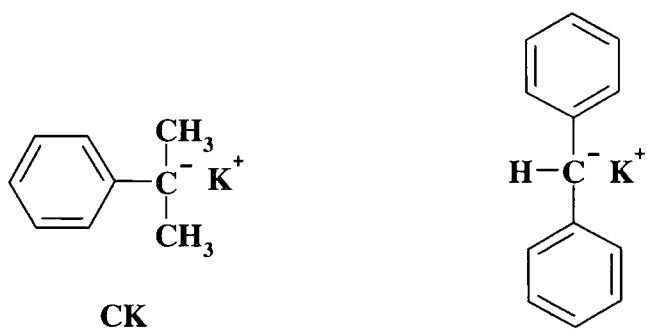


DPE DPHLi

Scheme 1.5 - Synthesis of 1,1-diphenylhexyllithium from *n*-BuLi and DPE.

Any functionality present in the alkyllithium will be incorporated into the 1,1-diphenylalkyllithium initiator synthesised from DPE, and subsequent polymers synthesised using it.

The final group of initiators that will be discussed here are alkylpotassium initiators. The two most commonly used initiators are cumyl potassium (CK) and diphenylmethylpotassium (DPMK) (**Figure 1.2**).



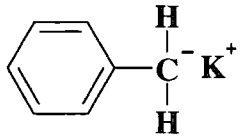
CK DPMK

Figure 1.2 – Common alkylpotassium initiators for anionic polymerisation.

They are most frequently used for the polymerisation of ethylene oxide (EO), as the potassium alkoxide propagating species formed from ring opening of EO does not encounter the same degree of aggregation in THF as that of the equivalent lithium alkoxide species formed from alkyllithium compounds. Propagation is therefore able to proceed at a reasonable pace. DPMK is not an efficient initiator of styrene, producing polymers with broad molecular weights, CK however is suitable for the polymerisation of PS.[18] CK was used to prepare polystyrene-*block*-poly(ethylene oxide) copolymers by sequential addition of the monomers.[2]

CK is prepared by reaction of cumyl methyl ether (referred to as **3**) with potassium metal, unfortunately the potassium methoxide produced as a byproduct is

difficult to remove from solution.[18] **3** is synthesised from α-methylstyrene, and can decompose back to the starting material.[19] Solutions of CK can also be contaminated with α-methylstyrene which forms difunctional initiators, via the mechanism discussed earlier in this section. Very careful preparation of CK is necessary to avoid side-reactions during the polymerisation. The synthesis of DPMK does not share these problems and it is therefore the preferred initiator for the synthesis of homo PEO.[20] The use of benzyl potassium (BK) (**Figure 1.3**) as an initiator for the anionic polymerisation of EO has been recently been reported by Hadjichristidis and co-workers.[18]



BK

Figure 1.3 - Benzyl potassium.

This initiator appears to overcome the shortcomings of CK and DPMK; it is not contaminated with any species that is harmful to polymerisation, and it is an efficient initiator of vinyl monomers. It was used to prepare a triblock copolymer of isoprene, 2-vinylpyridine and EO, by the sequential addition of the monomers. The polymer was free from homo and diblock copolymers and possessed a PDI of 1.04.

Many cyclic monomers can be polymerised by an anionic mechanism using a much wider range of initiators, for instance metal hydroxides and alkoxides, and Grignard reagents. Some of these will be discussed in more detail in Section 1.3.6.

1.3.3 The Effect of Solvents, Salts and Additives on Anionic Polymerisation

Unfortunately the high reactivity (nucleophilicity and basicity) typical of the initiators and propagating species in living anionic polymerisation limit the range of solvents that can be used. For styrene and diene monomers, the solvents of choice are alkanes, cycloalkanes and aromatic hydrocarbons.[2] Aromatic hydrocarbons such as benzene and toluene give enhanced rates of polymerisation relative to aliphatic hydrocarbons. Polymerisations of styrene and dienes in toluene are accompanied by chain transfer to the relatively acidic methyl group at elevated temperatures. Ethers often react with both the organometallic compounds used to initiate polymerisation as well as propagating species, resulting in the loss of active sites. The rate of reaction of

these species with ethers decreases in the order Li > Na > K.[2] Alkyl potassium based initiators generally posses good stability in THF. Simple alkyllithiums are however unstable in THF, *n*-BuLi decomposes completely within 2 h in THF at room temperature. Polymers initiated by alkyllithium compounds are also generally unstable in THF; it has been reported that PSLi decomposes (loss of active site) at a rate of up to a few percent each minute in THF at room temperature.[10,21]

Lewis bases such as amines, ethers and alkoxides also have an effect on the rate of polymerisation. In the case of alkyllithium initiated polymerisation they work by filling the vacant orbitals of the lithium ions, which would otherwise be involved in complexation and aggregation processes.[22] The addition of small amounts of THF to alkyllithium initiated polymerisations in hydrocarbon solvents results in an increase in rates of initiation. Crown ethers and cryptands have also been used as additives. The affect of alkoxides is more complicated, though for poly(isoprene) it was observed that their presence increased the rate of polymerisation at its early stages, although they reduce R_p at a later stage.[23] These results were explained in terms of the formation of ternary aggregates between initiator and the propagating species.

Bidentate chelating amines are frequently introduced to polymerisations. The most important of these is *N*,*N*,*N*',*N*'-tetramethylethylenediamine (TMEDA) which complexes with the lithium to form a species which is usually represented as a five-membered 1:1 complex (**Figure 1.4**).[22]

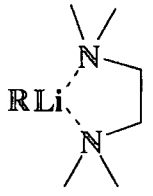


Figure 1.4 - Complex of TMEDA with Li.

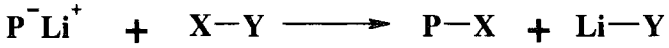
This results in a break up of the aggregation present in the lithium species, which in turn ensures efficient initiation. This can allow the polymerisation of monomers that cannot be usually polymerised via an anionic mechanism, for example ethylene.[22]

1.3.4 Functionalisation of Polymers Synthesised using Living Anionic Polymerisation

There are two main ways to functionalise polymers synthesised by anionic polymerisation. The first and most commonly used approach takes advantage of the living nature of anionic polymerisation and involves functionalising the living polymer chain end post-polymerisation. An alternative method is to introduce the functionality via the initiator.

1.3.4.1 Post-Polymerisation Functionalisation of Anionic Polymers

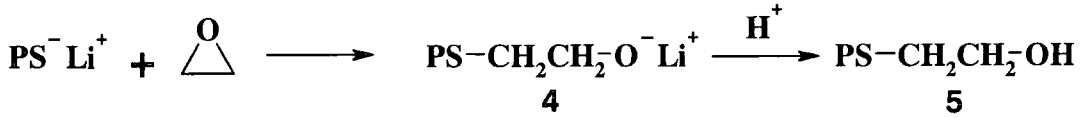
Addition of a suitable electrophilic reagent to living polymers results in the termination of polymerisation and the functionalisation of the living chain end (**Scheme 1.6**).



Scheme 1.6 - The functionalisation of living polymers using an electrophilic reagent.

These electrophilic reagents commonly include alkyl and aryl halides. Such a functionalisation agent can quantitatively functionalise the polymer chains of a living anionic polymerisation. If the functionalisation agent contains unsaturation or acidic protons, side reactions can also occur. In order to find conditions that drive the desired functionalisation reaction to close to 100% yield often requires adjustment of the structure of the chain end and the temperature, solvent, concentration, method and rate of addition of the polymer and/or functionalisation agent. Silyl halides have also proved to be useful functionalisation reagents for anionic polymerisation.

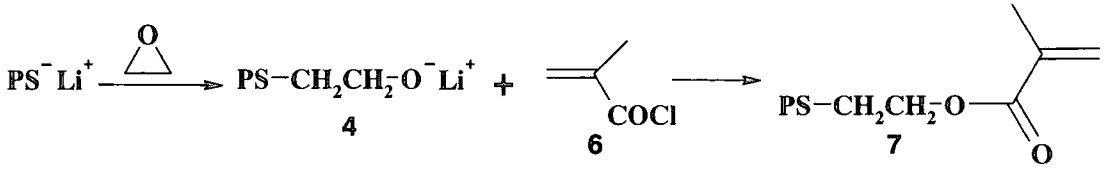
The reaction of EO with polymeric organolithium compounds is one of the few relatively simple and predictable functionalisation reactions that has been developed for anionic polymerisation. It proceeds via ring opening of the EO to form a lithium alkoxide **4**, which is then protonated to form the hydroxyethylated polymer **5**, **Scheme 1.7**.[24]



Scheme 1.7 - Synthesis of hydroxyethylated PS using EO.

It was generally accepted that oligomerisation of the EO did not occur due to the high degree of aggregation of the lithium alkoxides.[24] This has recently been revaluated and it seems that oligomerisation of the EO might occur relatively quickly.[25,26] The reaction can be used to functionalise α,ω-dilithium polymers quantitatively, although longer reaction times are required. A similar reaction takes place with PO and 1-butene oxide (BO). Unfortunately chain transfer to the alkyl group is observed with PO[27] and to a much lesser extent BO,[28] reducing the yield of functionalisation.

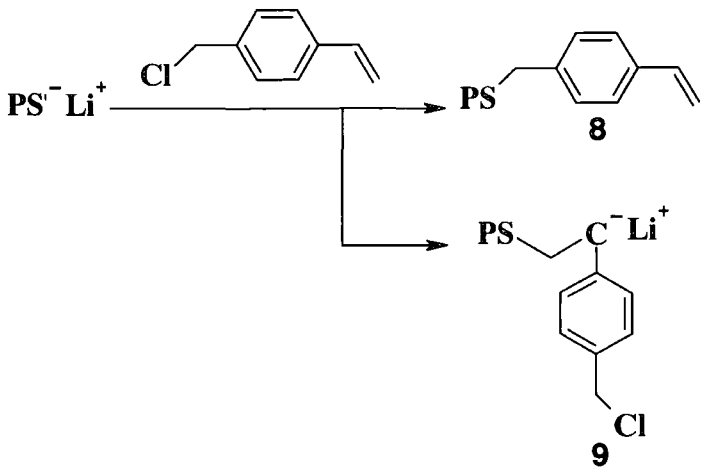
In contrast to the functionalisation reaction with alkyl halides the reaction of living polymers with EO leaves an active site – it is thus described as a living functionalisation reaction. The reaction of methacryloyl chloride **6** (**Scheme 1.8**) with poly(styryl)lithium results in vinyl addition as well as reaction with the halide. The end capped lithium alkoxide formed from PSLi and EO will attack the carbonyl chloride, without any attack on the vinyl group, to form **7**.



Scheme 1.8 - Functionalisation of PS with methacryloyl chloride.

The acidic carbonyl chloride of **6** is sufficiently electrophilic to react quantitatively with the relatively deactivated **4**. The resulting polymer **7** is functionalised with a polymerisable vinyl group. It is thus a macromolecular monomer, known as a macromonomer, and was polymerised by a radical mechanism.[2] Living anionic polymerisation has been used to prepare macromonomers which have also been polymerised using other polymerisation techniques. For instance PS was functionalised using carbonyl chloride substituted norbornene derivatives, using a methodology similar to that illustrated in **Scheme 1.8**, to form macromonomers that were polymerised by ROMP.[29-31]

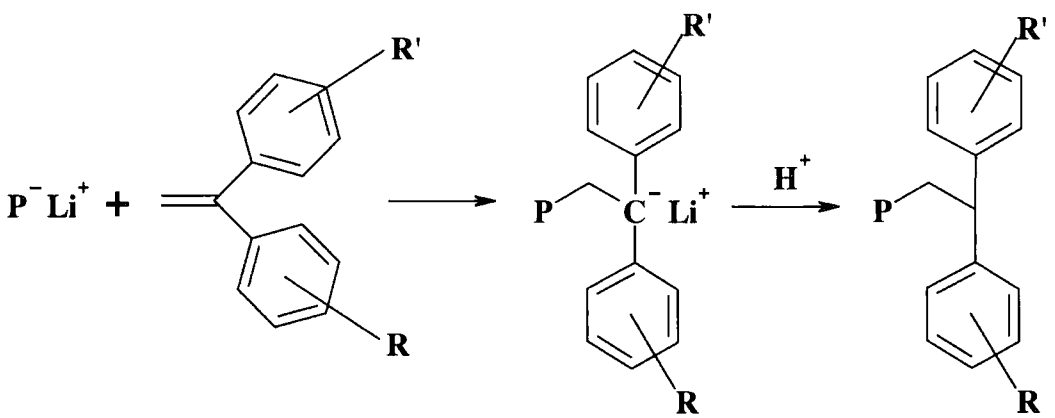
The direct addition of unsaturated less electrophilic alkyl halides like 4-VBC to living polymer chain ends was explored, in the hope that it would allow the synthesis of styryl macromonomers. However as might be expected the synthesis of the macromonomer **8** is accompanied by vinyl addition to form **9** (**Scheme 1.9**).



Scheme 1.9 - Reaction of PS-Li with 4-VBC.

Dimerisation of the PS also occurs, possibly by reaction of PS-Li or **9** with macromonomer **8**. The synthesis of the desired macromonomer can be achieved by the addition of THF and very careful control of the concentration, temperature and the method of combination of the PSLi and 4-VBC. This is discussed in more detail in Chapter 3.

The reaction of living polymers with DPE is a living functionalisation reaction that can be used to introduce functionality to the end of the chain (**Scheme 1.10**).[2,32]



10 R = $OSiMe_2Bu^t$ R' = H
11 R = $N(SiMe_3)_2$ R' = H
12 R= OCH_3 R' = OCH_3

Scheme 1.10 - Functionalisation of polymers with DPE derivatives.[32]

As many functional groups are incompatible with anionic polymerisation functional groups are often incorporated using a protecting group. Thus protected

hydroxyl **10** and amine **11** functionalities can be incorporated into polymers via means of a suitable protecting group.

There are other functionalisation reactions that, with some living polymers at least, proceed reliably such as sulfonation using sultones and aldehyde functionalisation using 4-morpholinecarboxaldehyde.[2] Many other reactions fail to yield quantitative functionalisation or give irreproducible results. The carbonation of living polymers is a useful functionalisation reaction, and an example of a functionalisation reaction that can be forced, by adjusting the reaction conditions, to approximately quantitative yield. The uncontrolled addition of CO_2 to PS-Li in C_6H_6 results in the formation of the desired carboxylated polymer (**13**, 27 - 66% yield) in addition to a ketone (**14**, 23 - 27% yield) and a tertiary alcohol (**15**, 7 - 50% yield).

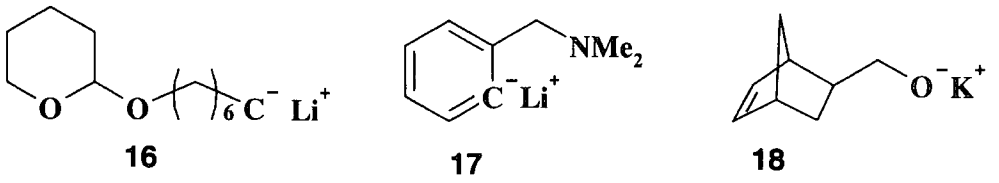
$$P^-Li^+ \xrightarrow[\text{II) } H^+]{\text{I) } CO_2} \underset{\mathbf{13}}{PCO_2H} + \underset{\mathbf{14}}{P_2CO} + \underset{\mathbf{15}}{P_3COH}$$

Scheme 1.11 - The uncontrolled carbonation of a living polymer (P) initiated by an anionic mechanism.

Aggregation of the propagating species is thought to favour the formation of the dimeric and trimeric products. The addition of sufficient quantities of a Lewis base such as THF (25 vol%) or TMEDA (46 equivalents) breaks down the aggregation of the chain ends and gives approximately quantitative yield of **13**. If the chain-ends are end-capped with DPE the resulting species will react to form carboxylated polymer (similar to **13**) in approximately quantitative yield.

1.3.4.2 Functionalised Initiators for Anionic Polymerisation

An alternative method for functionalising polymers synthesised using anionic polymerisation is to introduce the functionality in the initiating species. One way to accomplish this is to use a functionalised alkyllithium initiator. Functionalities that are incompatible with anionic polymerisation, and would lead to bimolecular decomposition of the initiator, can be incorporated into the initiators using a protecting group (**Figure 1.5**). For instance initiator **16**, which was used for the synthesis of poly(butadiene) (PBD), has a hydroxyl group protected by a tetrahydropyran ether.[32]



16 17 18

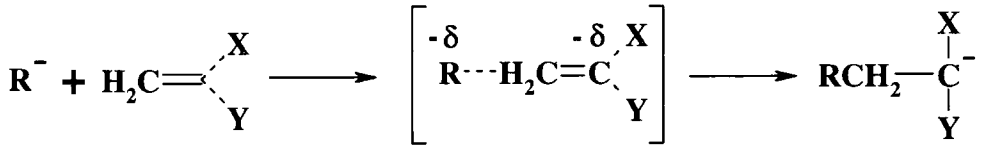
Figure 1.5 - Functionalised imitators for anionic polymerisation.

A dimethyl amino functionality can be incorporated into initiators without protection (**17**) and functionalised further with CH_3Br to form a zwitterion.[33] Gnanou synthesised initiator **18** and used it to polymerise EO; the resulting macromonomers were polymerised via ROMP, in order to synthesise graft copolymers.

In the cases of polymerisation reactions initiated by DPHLi initiators (Section 1.3.2), which are synthesised using the reaction of *n*-BuLi and DPE, we can incorporate functionality into the initiating species by replacing DPE with a functionalised DPE derivative of the type discussed in the previous section.[32]

1.3.5 Vinyl Monomers Polymerisable by Anionic Polymerisation

The range of monomers that can be polymerised by an anionic mechanism can be divided into two classes; the first is vinyl monomers, such as styrene, dienes and methacrylates, the second being cyclic monomers containing a heteroatom. It is widely accepted that there must be substituents on the double bond that can stabilise the partial negative charge that arises in the transition state of the monomer addition step (**Scheme 1.12**).

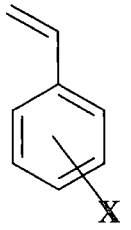


Scheme 1.12 – Formation of the intermediate in anionic polymerisation.

These are phenyl groups in the case of styrene monomers, double bonds in dienes and carbonyl groups in methacrylates. Thus simple vinyl monomers like propylene are not generally polymerisable by an anionic mechanism. The only exception to this is ethylene, where the conversion of double bonds to a single bond provides sufficient energetic driving force to allow its polymerisation under controlled circumstances (although the polymerisation is limited to producing relatively low molecular weight material).

1.3.5.1 Styrene and its Derivatives

A wide range of styrene derivatives can be polymerised by anionic polymerisation, usually initiated with alkyllithium compounds (**Figure 1.6**).



$X = CH_3$, OR, Cl, Br, -CN, SO_3R, $P(NCH_2CH_3)_2$, $Sn(C_6H_5)_3$.

Figure 1.6 – A small selection of substituted styrenes polymerisable by anionic polymerisation.[2]

The polymerisation of many of these functionalised monomers is accompanied by chain transfer to monomer or polymer; however the use of low temperatures and careful optimisation of the reaction conditions can sometimes produce polymerisations with living kinetics. The use of protecting groups can extend the range of functionalities that can be incorporated into polymers.

The polymerisation of α-methyl styrene (**Figure 1.7**) has also been studied.

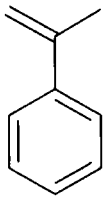
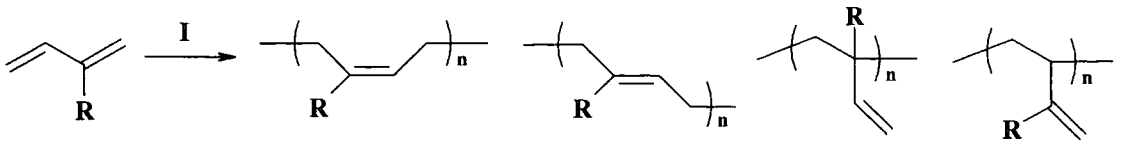


Figure 1.7 - α-Methyl styrene.

The polymerisation is fairly well behaved, although the presence of a ceiling temperature in the reaction means it must be performed at reduced temperatures. Other α-alkylstyrenes can also be used as monomers. For example α-heptylstyrene and α-nonylstyrene have been polymerised by sodium naphthalene to form low molecular weight polymers.[34]

1.3.5.2 Diene Monomers

Butadiene and isoprene are by far the most commonly polymerised diene monomers. The polymerisation results in different microstructures depending on reaction conditions (**Scheme 1.13**).

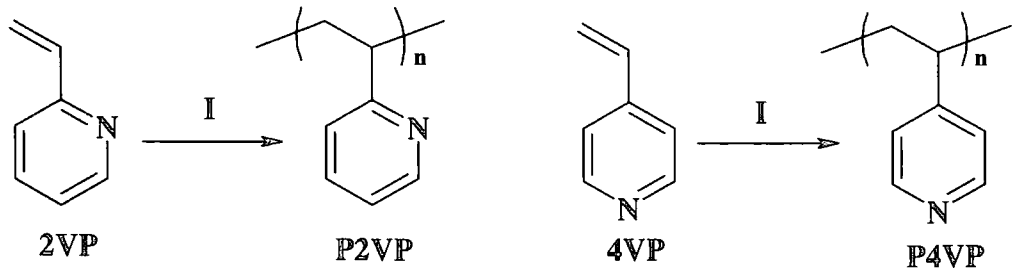


Scheme 1.13 - The microstructures of polydienes. Where I is a suitable initiator for anionic polymerisation.

Addition of the diene monomer to the living polymer can occur in one of several ways leading to the monomer being enchained in the form of one of several structures. In the case of PBD R=H, the product of 1,2-addition is equivalent to that of 3,4. A number of factors influence the microstructure of the resulting polymers including counter-ion, solvent, temperature and concentration. Most counter-ions lead to the formation of substantial amounts of 1,2 enchainment during the polymerisation of butadiene, and sizeable amounts of 3,4 and some 1,2 enchainment in the case of isoprene ($R=CH_3$). In the case of lithium counter-ions the polymerisation of dienes proceeds mainly via 1,4 addition of monomer (> 90% at r.t.) in hydrocarbon solvents (though not in THF). No 1,2 addition is observed in polyisoprene (PI), a fact that has probably increased the popularity of alkyllithium initiators (Section 1.3.2). 1,3-Pentadiene and a number of other butadiene derivatives (R in **Scheme 1.13** = ethyl, propyl, butyl, phenyl or pyridyl) have been polymerised with organolithium intiators.[2] The microstructures of the resulting products tend to be similar to PBD or PI, with the possible exception of the ratio of *cis* to *trans* 1,4 enchainment. The monomer 2-(triethylsilyl)-1,3-butadiene is reported to produce polymer with a 100% *cis*-1,4 microstructure however.

1.3.5.3 Vinylpyridines

Both 2-vinylpyridine (2VP) and 4-vinylpyridine (4VP) can be polymerised by an anionic polymerisation yielding poly(2-vinylpyridine) (P2VP) and poly(4-vinylpyridine) (P4VP) (**Scheme 1.14**).

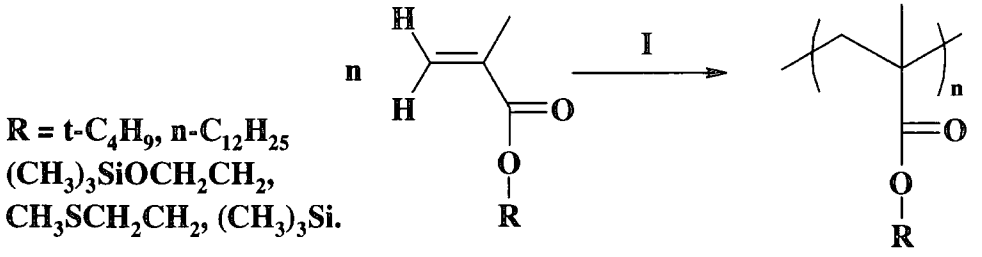


Scheme 1.14 - Polymerisation of vinylpyridines by an anionic initiator I.

The pyridine ring is subject to attack by strong nucleophiles, hence DPHLi (Section 1.3.2) is used as initiator rather than alkyllithiums. The polymerisation of 2VP can be successfully achieved at -78 °C in THF in the presence of LiCl.[35] The anionic polymerisation of 4VP is further complicated by the insolubility of medium and higher molecular weight P4VP, leading to the precipitation of the living polymer and a broad molecular weight distribution. It is however possible to synthesise P4VP with an M_n of up to a few thousand with a narrow PDI.[36]

1.3.5.4 Methacrylates and Related Monomers

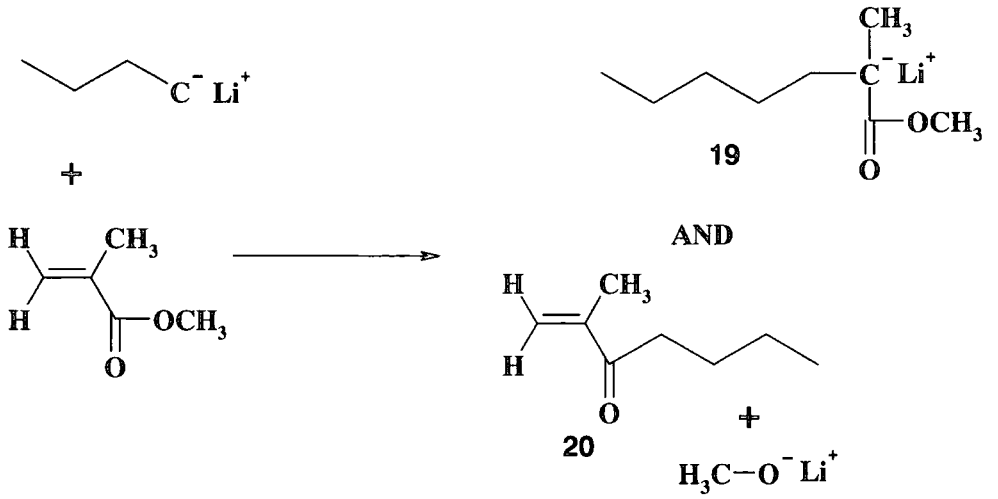
Methyl methacrylate (MMA, R=CH_3, **Scheme 1.15**) and a range of alkyl methacrylates have been polymerised to form well-defined polymers.



Scheme 1.15 - Anionic polymerisation of a selection of methacrylates by an initiator for anionic polymerisation, I.[2]

A reasonable range of functional groups can be incorporated into methacrylate polymers. There are a number of complications in the polymerisation of MMA and related monomers using an anionic mechanism which must be addressed in order to gain control over the reaction. These complications can be roughly subdivided into problems controlling the initiation, termination and propagation reactions. It will be appreciated that carbanions might be able to attack the ester group in addition to the vinyl group. The choice of initiator is therefore important. *n*-Butyllithium attacks both

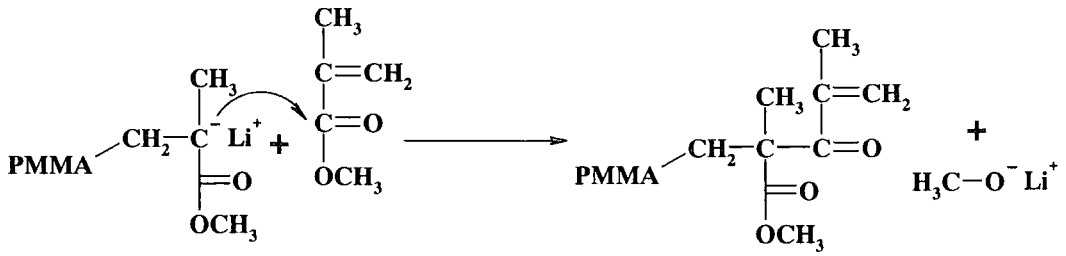
the vinyl group, forming the desired propagating species **19**, and the ester group to form butyl isopropenyl ketone **20** and lithium methoxide (**Scheme 1.16**).



Scheme 1.16 - Reaction of *n*-BuLi with MMA.

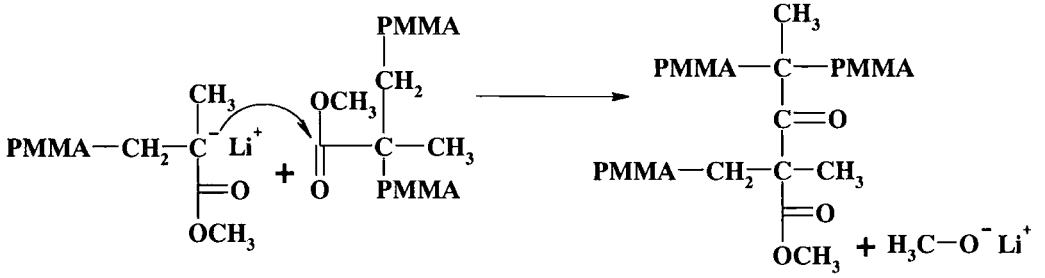
In toluene at -78 °C approximately 51% of the initiator is converted into lithium methoxide. This material is incapable of initiating polymerisation and thus 51% of initiator activity is lost. The ketone **20** is also incorporated into the polymer at an early stage. The resulting chain end is however less reactive than that from addition of MMA (**19**), and some fails to reinitiate MMA resulting in the formation of both oligomer and polymer incorporating **20**. The solution to this is to react the *n*-BuLi with 1,1-diphenylethylene (DPE) to form 1,1-diphenylhexyllithium (DPHLi) (**Scheme 1.5**). DPHLi initiates PMMA efficiently without lithium methoxide formation, allowing the synthesis of polymers of controlled molecular weight. The initiators DPMK (**Figure 1.2**) and diphenylmethylsodium have enjoyed some success as initiators; they both have similar active sites to those in DPHLi.

The propagating PMMA species can in theory terminate by chain transfer to monomer or polymer via one of three mechanisms. The propagating species can attack the carbonyl group of the monomer via a nucleophilic mechanism (**Scheme 1.17**), a reaction directly analogous to the reaction of *n*-BuLi which forms **20** (**Scheme 1.16**).



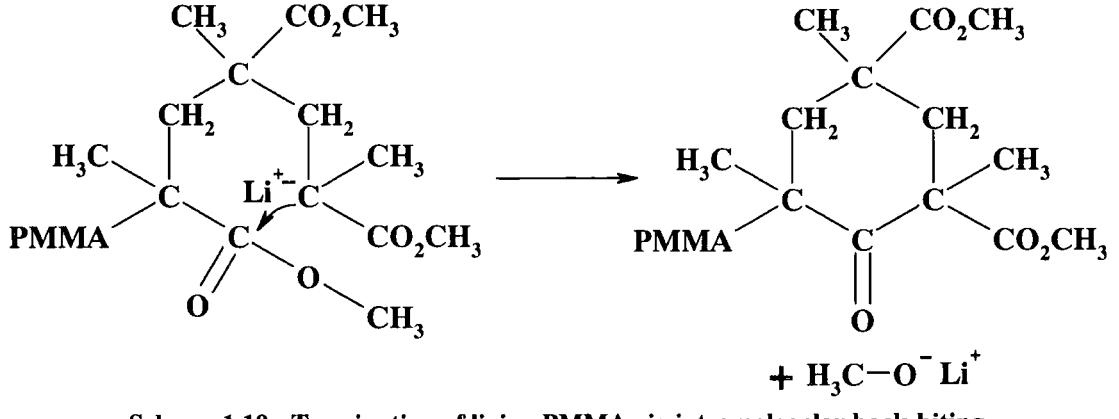
Scheme 1.17 - Termination of PMMA by attack of monomer carbonyl group.

This first mechanism was at one time regarded as the most important method of termination, although more recent results suggest it is probably not important. A similar bimolecular reaction can occur between two propagating PMMA chains (**Scheme 1.18**).



Scheme 1.18 - Termination of living PMMA by reaction with PMMA.

Studies of PMMA synthesised via an anionic mechanism using GPC indicates this mechanism is not very important. The other termination mechanism is an intra-molecular back biting reaction, resulting in the formation of a β-keto ester six-membered ring at the end of the chain (**Scheme 1.19**).



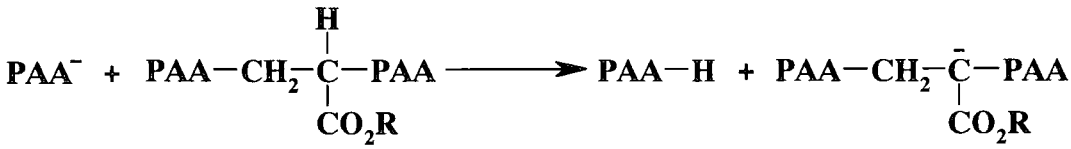
Scheme 1.19 - Termination of living PMMA via intramolecular back-biting.

This is generally accepted as the most important termination reaction in the anionic polymerisation of PMMA and other methacrylates. The rate of termination of polymer via this mechanism is insignificant when compared with the rate of propagation at low temperatures, although its significance increases at higher temperatures. Termination is also higher in non-polar solvents such as toluene,

relative to polar solvating solvents such as THF or dimethoxyethane. Polymerisation reactions are therefore typically carried out at -78 °C in THF. The PDI of the PMMA also increases when the polymerisations are carried out with cations larger than Li, which was interpreted as indicating that the rates of termination were higher in these cases.[2]

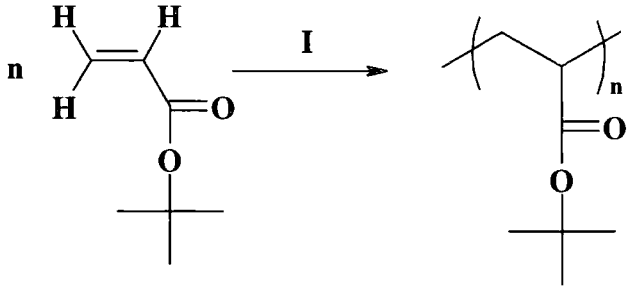
Even after efficient initiation and control of the termination reactions has been achieved, polymers with PDIs higher than those typical of anionic polymerisation are obtained (~1.2). As a result effort has gone into finding methods to control the propagation step in the reaction. The effect of Lewis base additives on the anionic polymerisation of methacylates has been thoroughly examined. The addition of lithium chloride to the polymerisation reaction of MMA initiated by DPHLi, was found to result in the synthesis of PMMA with a lower PDI compared to PMMA synthesised without any additive. Optimum results are obtained when the stoichiometry of 10 equivalents of LiCl relative to initiator is used. Thus the PDI of PMMA initiated by oligo-α-methylstyryl-Li can be lowered from 1.20 to 1.09 using 10 equivalents of LiCl. Other lithium salts such as LiF, LiBr and $LiBPh_4$ are not effective in controlling the molecular weight distribution. Whilst LiCl reduces the rate of termination by a factor of 2, it also reduces the rate of propagation by a factor of 3. The affects of lithium chloride are not therefore attributable to control of termination reactions. It is believed that in the absence of LiCl there are multiple active sites present during polymerisation, which interconvert slowly relative to propagation (possibly dimeric and tetrameric aggregates), leading to a broadening of the molecular weight distribution.[2] It is thought that in the presence of LiCl there is either only one form of active site (a mixed aggregate of living PMMA and LiCl), or alternatively there is a rapid equilibrium between aggregates which is able to successfully compete with R_p. In either case the rate of propagation is the same at all the active sites, resulting in polymers with a low PDI. Similar results have also been obtained by using lithium alkoxides in the place of LiCl. Crown ethers and cryptands have been used to increase control over the polymerisation of alkyl methacrylates initiated by sodium initiators.[37]

Acrylates can also be polymerised by an anionic mechanism. In addition to the termination reactions present in the polymerisation of MMA and other alkyl methacrylates chain transfer to the enolizable hydrogens can occur, forming in chain ester enolate ions (**Scheme 1.20**).



Scheme 1.20 Chain transfer during the polymerisation of acrylates, by attack of the enolisable hydrogens on their polymer backbone by living polymer. PAA = poly(alkyl acrylate).

Coupled with the fact that the rate of polymerisation of alkyl acrylates is higher than alkyl methacrylates; gaining control over the polymerisation of the former is very challenging. The most commonly studied monomer of this type is *t*-butyl acrylate (**Scheme 1.21**).



Scheme 1.21 - Polymerisation of *t*-butyl acrylate using an initiator for anionic polymerisation (I).

The tertiary butyl group minimises side-reactions with the ester group during polymerisation, making control over the polymerisation easier.[2] A PDI of 1.04 has been reported for this polymer, using DPHLi as initiator at -78 °C in THF solution, with $LiClO_4$ as an additive.[37]

In summary the polymerisation of alkyl methacrylates and alkyl acrylates is complicated by termination reactions and the high reactivity of the propagating species. These obstacles can however be largely overcome by careful choice of initiator, solvent, temperature and the addition of an appropriate additive, resulting in polymerisation reactions with living kinetics that can be used to produce well-defined polymers.

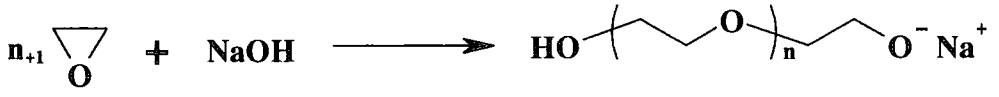
1.3.6 Anionic Ring Opening Polymerisation

Cyclic monomers are the other major class of monomers that can be polymerised by an anionic mechanism. Their polymerisation is sometimes referred to as anionic ring opening polymerisation (AROP). Epoxides, episulfides, lactones, lactams, *n*-carboxyanhydrides, and cyclic siloxanes, can all be polymerised by an anionic mechanism.[2,38,39] Not all of them can be polymerised in a well controlled

manner. The kinetics, and often the mechanism of polymerisation varies between different types of monomer. A detailed discussion of the unique characteristics of all of them is beyond the scope of this Chapter. This section will outline developments in the polymerisation of epoxides and episulfides, as they are directly relevant to this work. Both have been reported to produce living and well-defined polymerisations.

1.3.6.1 Anionic Polymerisation of Cyclic Ethers

Simple epoxides such as EO (sometimes referred to as oxirane) and PO can be polymerised via anionic polymerisation. The polymerisation of EO was probably the first AROP to be studied. It can be initiated by a number of nucleophiles including alkali hydroxides, alkali metals, and well-defined alkyl or aryl potassium initiators such as BK, CK, or DPMK (Section 1.3.3). Initiation proceeds via nucleophilic attack of the initiator on one of the methylene carbons, resulting in the formation of oxo anions. These are the propagating species in the polymerisation and attack more monomer in the same manner, resulting in high molecular weight poly(ethylene oxide)(PEO) (**Scheme 1.22**).



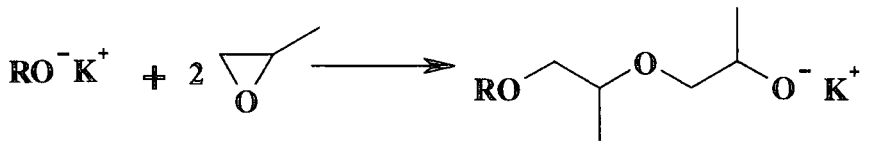
Scheme 1.22 - Polymerisation of EO using NaOH.

As with polymerisation of vinyl monomers the initiator is incorporated into the end of the polymer chain, in the case of metal hydroxide initiators leading to polymer chains with hydroxyl groups on both ends after termination. The polymerisation of EO is less sensitive to moisture than those of vinyl monomers, as an equilibrium is set up between dormant (hydroxyl functionalised) PEO and the living potassium alkoxide chain ends, which is sufficiently fast to successfully compete with propagation. In the absence of H_2O the polymerisations are truly living and thus a fresh batch of a suitable epoxide can be added and polymerisation will continue. Alternatively the oxoanions can be functionalised with a suitable terminating agent, for example an alkyl halide. The oxanions are less nucleophilic than the carbanions present during the polymerisation of vinyl monomers, potentially allowing a greater range of functionalities to be included in the terminating agents.

Attempts have been made to use alkyllithium initiators in place of alkylpotassium initiators. Under normal circumstances alkyllithium initiators such as

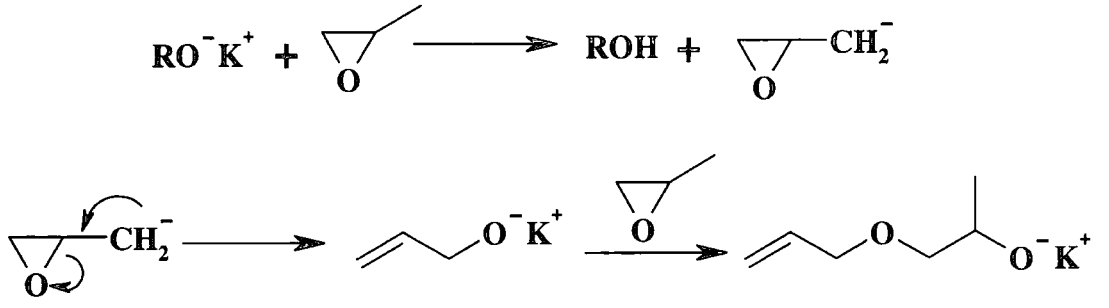
sec-BuLi ring open EO, but propagation cannot take place from the resulting lithium alkoxides due to the stability of the aggregates they form in solution, even in THF. This is because the aggregates must dissociate prior to reaction; the strength of the aggregation in lithium alkoxides results in their low reactivity. The addition of TMEDA has been reported to break down some of this aggregation allowing the successful polymerisation of EO using *n*-BuLi.[40] Unfortunately PS-Li does not initiate polymerisation, even in the presence of TMEDA.

The polymerisation of PO can be achieved using a similar range of anionic initiators to EO. The initiation and propagation reactions proceed exclusively via nucleophilic attack of the methylene rather than the methine carbon, producing a head to tail structure (**Scheme 1.23**).



Scheme 1.23 - Anionic polymerisation of PO.

This in contrast to the situation with cationic polymerisation, where attack takes place at both carbons.[41] The anionic polymerisation of PO is also accompanied by chain transfer to the methyl group (**Scheme 1.24**).



Scheme 1.24 –Chain transfer during the anionic polymerisation of PO.

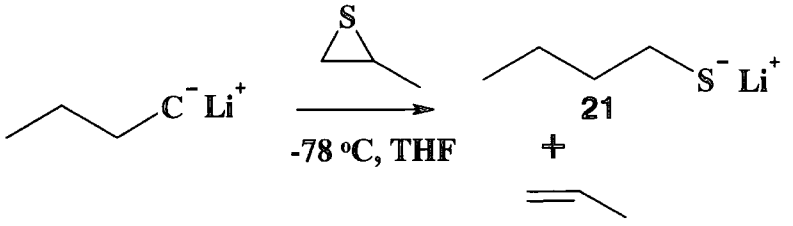
This reduces control over the molecular weight of the poly(propylene oxide)(PPO). Amphiphilic PEO-PPO block copolymers can be prepared by addition of PO to living PEO – probably accompanied by the formation of some PPO homopolymer from chain transfer.[41]

BO has also been polymerised by an anionic mechanism.[42] Chain transfer is suppressed relative to PO and hence better control over the polymerisation can be obtained.

Whilst powerful nucleophiles, such as alkyllithium initiators metallate cyclic ethers with a ring size larger than 3, it is not possible to polymerise any of them by an anionic mechanism.

1.3.6.2 Anionic Polymerisation of Cyclic Sulfides

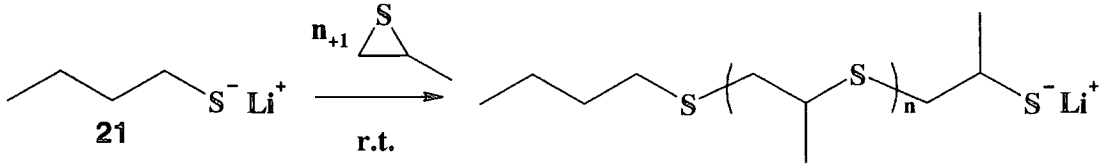
The episulfides, ethylene sulfide (thiirane) and propylene sulfide (PrS, or methylthiirane) have been polymerised by an anionic mechanism. The polymerisation of ethylene sulfide is believed to proceed via a ring opening mechanism fairly similar to that of EO. The resulting poly(ethylene sulfide)(PES) is however insoluble in all but a few solvents, and only then at temperatures exceeding 150 °C, making study of the polymerisation's kinetics and many of the properties of PES difficult. The majority of the studies of the anionic polymerisation of episulfides have been carried out on poly(propylene sulfide)(PPS). The polymerisation of PrS is free from the chain transfer reaction present in the polymerisation of PO and proceeds in a living manner. Episulfides are in general more reactive than epoxides - the living polymerisation of PrS can be achieved with a much larger range of nucleophiles than that of EO.[43] The propagating species is believed to be a thioanion in all cases. Whilst akyllithium compounds are good initiators of polymerisation, they do not do so directly; the first step is abstraction of sulfur from a molecule of PrS to form a lithium-thiolate species such as **21** (**Scheme 1.25**).



Scheme 1.25 - Formation of lithium-thiolates from PrS.

This reaction is usually carried out at -78 °C, at which temperature quantitative conversion to **21** is obtained within 30 min and propagation is negligible.[44,45] The thiolate **21** serves as the actual initiator of polymerisation. In THF

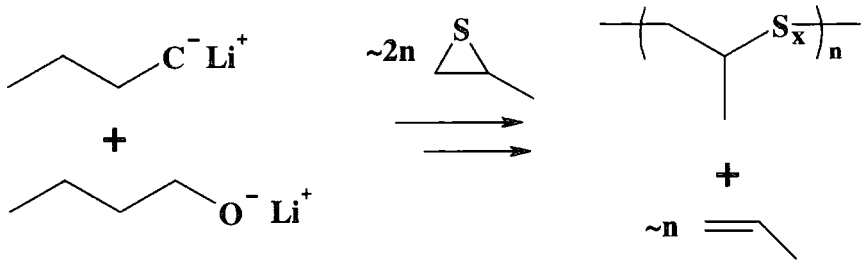
the polymerisation proceeds via a 'standard' ring opening addition mechanism involving nucleophilic attack of the PrS methylene carbon (**Scheme 1.26**).



Scheme 1.26 - Polymerisation of PrS in THF, initiated by 21.

The resulting PPS is an elastomer at room temperature. Like PES it is sensitive to oxidation and decomposes slowly at room temperature in the presence of O_2.[46] Lithium ethanethiolate (referred to as **22**) was synthesised by Morton et al. and found to be an efficient initiator of PrS, although it was unable to initiate the polymerisation of styrene.[45] Initiator **22**, like living PPS, is not believed to react with THF at room temperature. Living PPS is also not a suitable initiator for vinyl monomers. Block copolymers with styrene can be prepared by the addition of PrS to living PS, the second block being added at -78 °C to allow complete formation of the lithium macrothiolate. Via a similar method the polymerisation of PrS was initiated using living poly(*α*-methylstyrene).[45] After polymerisation was complete the living block copolymer was terminated using difunctional $COCl_2$ to yield poly(*α*-methylstyrene)-*block*-poly(propylene sulfide)-*block*-poly(*α*-methylstyrene). Living PPS is usually terminated by a suitable alkyl halide such as ethyl bromide, which avoids the presence of an unstable sulfide (mercaptan) group.[45] With the exception of these examples the functionalisation chemistry of living PPS has received very little attention.

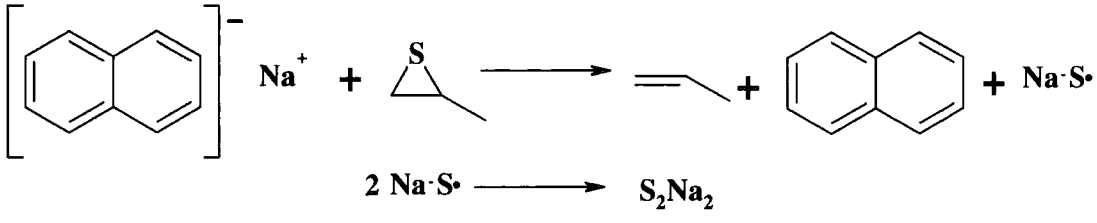
The polymerisation of PrS initiated by alkyllithiums in hydrocarbon solution or the bulk is not as simple as that in polar coordinating solvents like THF and proceeds via a 'relay mechanism' in which, in addition to the ring opening addition polymerisation reaction observed in THF, the propagating species abstracts sulfur from some of the PrS, liberating propylene. In the presence of a lithium alkoxide the desulfurisation is more prominent and the resulting polymer has approximately one S-S bond per repeat unit (**Scheme 1.27**).[47]



Scheme 1.27 - Product of the relay mechanism of PrS in the presence of lithium butoxide. x = ~2.

Work by Aliev et al. has revealed that the initiating species in these cases might not even be the lithium-alkylmonothiolate **21**, but complexes of the lithium alkoxide with lithium-alkylpolythiolates (e.g. *n*-BuS_xLi-LiOR, where x > 1).[48] It will be noted that PrS is optically active, as the methine carbon is a chiral centre. It was proposed that one isomer was selectively and completely desulfurised, whilst the other was polymerised by a ring opening mechanism. After complete consumption of monomer by the two processes, further propylene is evolved, which was interpreted as indicating that the polymer was attacked by a back biting reaction resulting in desulfurisation of the PPS.

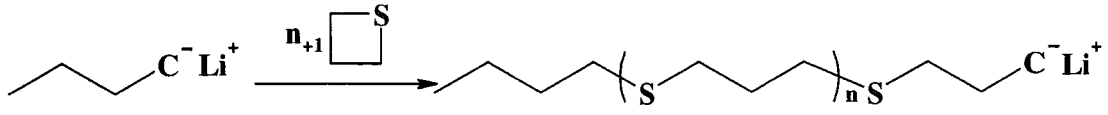
Sodium naphthalene has also served as an initiator of the polymerisation of PrS, although naphthalene is not incorporated into the polymer.[43] An electron transfer process, similar to that observed when the polymerisation of vinyl monomers is initiated by an alkali metal, was proposed (see Section 1.3.2), although this was later discounted. It is believed that the initiating species is sodium sulfide or disulfide formed by the process illustrated in **Scheme 1.28**.[47]



Scheme 1.28 - Formation of sodium sulfide and disulfide from sodium naphthalene.

Other anionic initiators for the polymerisation of PrS include alkali metals, their hydroxides and alkoxides, amongst others.[43,47] It is apparently possible to copolymerise elemental sulfur (S_8) with PrS or 2,2-dimethylthiirane, yielding something approximating to an alternating copolymer of the two.[49,50] Others have disputed these claims.[51]

The four membered heterocyclic monomer trimethylene sulfide (thietane) can also be polymerised by an anionic mechanism. The range of initiators capable of initiating its polymerisation is smaller than that with PrS. *n*-BuLi is reported to be the most efficient initiator, but alkali metals, sodium naphthalene, Grignard reagents, and presumably certain other alkyllithium initiators, are capable of initiating polymerisation.[47] The products of polymerisation have not always been thoroughly studied and in the case of Grignard reagents were limited to low molecular weights. In the case of *n*-BuLi the polymerisation appears to proceed via nucleophilic attack of one of the methylene carbons adjacent to the sulfur, resulting in the formation of a carbanion propagating species (**Scheme 1.29**).

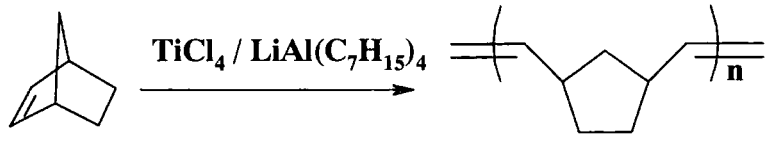


Scheme 1.29- Polymerisation of thietane.

The polymerisation of the related monomer methylthiirane is also possible by an anionic mechanism. Five and larger membered rings cannot be polymerised by an anionic polymerisation however.

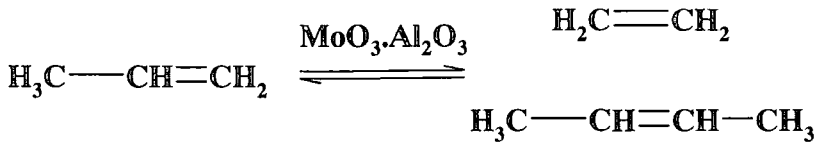
1.4 Olefin Metathesis

In 1957 workers at DuPont patented a method for the synthesis of polynorbornene (PNB) from norbornene (NBE), a bicyclic olefin, using a transition metal catalyst.[52] Truet later published a thorough examination of the product of polymerisation of NBE using titanium tetrachloride with a cocatalyst (**Scheme 1.30**).[53]



Scheme 1.30 –The metal catalysed polymerisation of NBE by $TiCl_4$ and $LiAl(C_7H_{15})_4$.

In contrast to all the addition polymerisation reactions known at the time, the product was found to contain a high degree of unsaturation. It was proposed that a ring opening mechanism might explain this result. Separately, in 1964 Banks and Bailey reported the phenomenon of what was described as 'olefin disproportionation'. This reaction resulted in two olefins exchanging substituents around their double bonds (**Scheme 1.31**).[54]

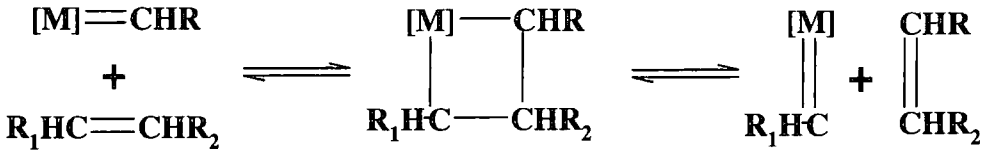


Scheme 1.31 – 'Disproportionation' of propylene using an ill-defined molybdenum catalyst.

Peters and Evering had previously disclosed this 'disproportionation' effect via a patent.[55] These two interesting but apparently distinct processes were connected by the work of Nissim Calderon in 1972.[56] He identified these two phenomena as examples of one and the same reaction, a reaction that was referred to henceforth as olefin metathesis. Put simply olefin metathesis is the process of simultaneously cleaving and reforming carbon-carbon double bonds. Over the course of the next thirty or so years olefin metathesis has developed into a powerful technique for both polymer and organic synthesis.

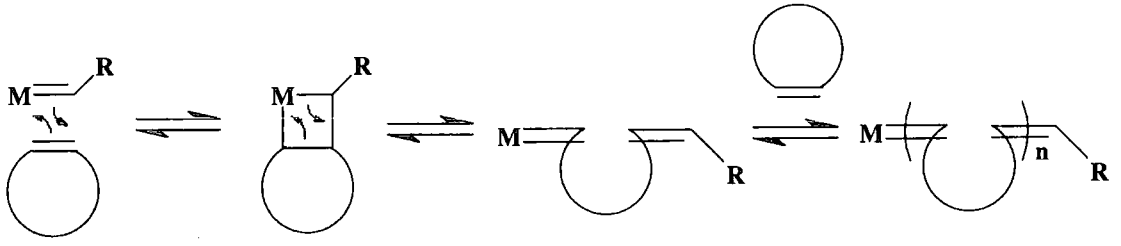
1.4.1 The Mechanism of Olefin Metathesis

The mechanism of olefin metathesis as it is currently understood was proposed by Herrison and Chauvin in 1972.[12] It involves the [2+2] cycloaddition of an olefin to a metal carbene or alkylidene resulting in the formation of a metallocyclobutane species. This metallocyclobutane can then split to either regenerate the original olefin and organometallic species resulting in non-productive metathesis, or it can form a new olefin and metal carbene species (productive metathesis) (**Scheme 1.32**).



Scheme 1.32 - The mechanism of olefin metathesis as proposed by Herrison and Chauvin.

In the case of ring opening metathesis polymerisation (ROMP) the olefin is a suitable cyclic, bicyclic or multicyclic monomer. Productive metathesis leads to ring opening of the olefin to form an unsaturated linear polymer (**Scheme 1.33**).



Scheme 1.33 - The mechanism of ROMP.

In the case of many mono cyclic compounds like cyclopentene an equilibrium is set up. The high ring strain in NBE and its derivatives means that the reaction is not reversible and polymerisation goes to completion. In some cases intra or inter molecular metathesis of the double bonds in the polymer can occur, leading to a broadening of the molecular weight distribution and possibly the formation of cyclic oligomers. This backbiting reaction is not usually as important in the polymerisation of NBE and its derivatives due to steric hindrance around the double bonds of the polymer.

1.4.2 The Microstructure of Polymers Synthesised by ROMP

The microstructure of polymers synthesised using ROMP can be quite complex and has been the subject of significant study.[12] This section will introduce the three main sources of isomerism that are found in the polymers of NBE and its derivatives. In brief they are *cis/trans* isomerism around the vinylene double bond, tacticity and in certain cases the degree of head/head, tail/tail and head/tail addition.

The monomer units can be incorporated into the polymer chain in a *cis* or *trans* position with respect to the double bond (**Figure 1.8**).

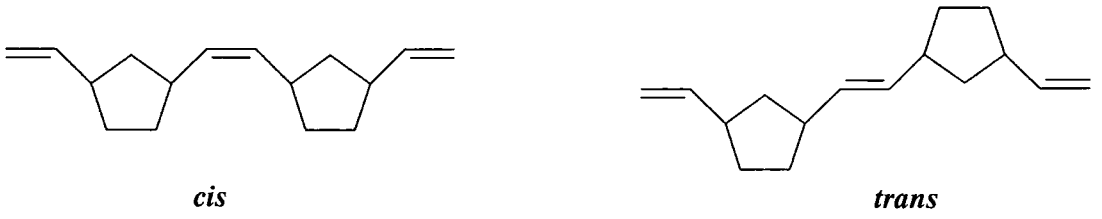


Figure 1.8 – The structure of *cis* and *trans* vinylene units from ROMP.

The degree of *cis* and *trans* vinylene units in the products of ROMP are dependent on the identity of the monomer, the initiator and in some cases other conditions like the solvent.[12]

The tertiary carbon atoms in PNB are chiral introducing tacticity into polymers of NBE and its derivatives. PNB's can potentially exist in isotactic, syndiotactic and atactic forms. The combination of *meso* and *racemic* dyads with *cis* and *trans* isomerism leads to four possibilities (**Figure 1.9**).

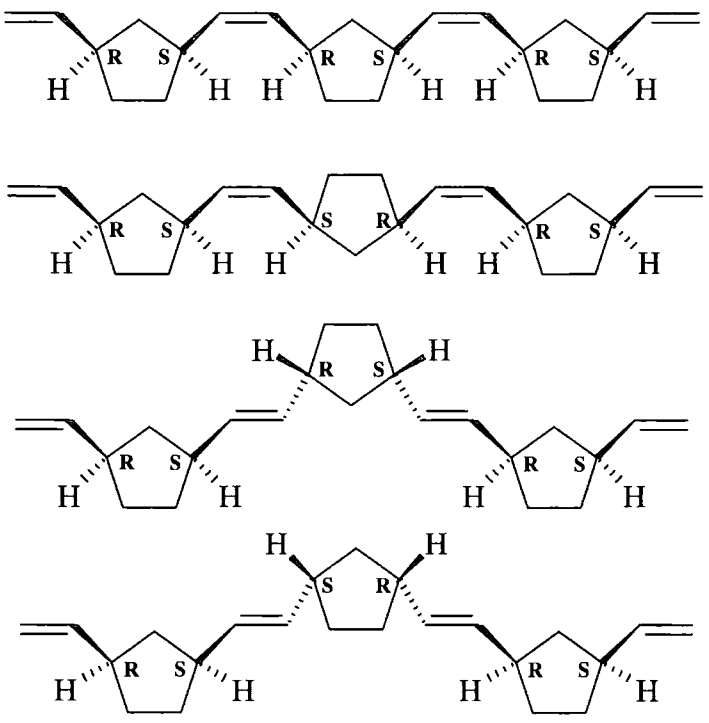


Figure 1.9 - Microstructure in ROMP polymers.

In monomers that are not symmetrical around the bridge carbon (**Figure 1.10**), head/tail (HT), head/head (HH) and tail/tail addition (TT) is possible.

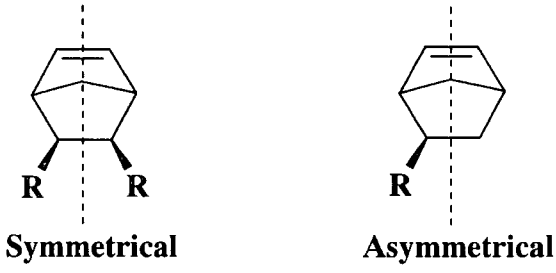


Figure 1.10 - Determination of tacticity.

Some combinations of monomer and initiator have been found to give a particular bias for one form of addition.[12]

1.4.3 An Overview of the Development of Initiators for Olefin Metathesis

This section will describe early ill-defined initiating systems before outlining developments in well-defined initiators. Ruthenium initiators, and particularly ROMP initiated by $RuCl_2(=CHPh)(PCy_3)_2$, will be discussed in greater detail as they are directly relevant to this work.

1.4.3.1 Ill-Defined Initiators for Olefin Metathesis

These initiator systems are so named because the precise nature of the active site at the metal centre is not known and is only formed *in situ* prior to reaction. All of the first catalytic systems were of this type. They can be either heterogeneous or homogenous and nearly all contain a high valence transition metal oxide or halide (non transition metal examples such as Me_4Sn/Al_2O_3 and $MgCl_2$ are very rare).[12] They usually require a co-catalyst such as $EtAlCl_2$ to generate an active centre on which polymerisation can occur, although in some cases they are able to generate it directly from the olefin. A number of systems also require a promoter such as O_2 or EtOH. Typical examples of homogeneous catalytic systems include $WCl_6/EtAlCl_2/EtOH$ and $TiCl_4/EtMgBr$, an example of a heterogeneous system is WO_3/SiO_2.

Ill-defined systems suffer from a number of disadvantages, one being that only a small percentage of the catalyst forms the active species. Once generated, the active sites are usually highly reactive, resulting in a fast rate of propagation. Thus the rate of propagation (R_p) is higher than the rate of initiation (R_i), and only poor control over the properties of the polymers can be established. The initiators are also generally highly sensitive to most polar functional groups due to the Lewis acid nature of the co-catalyst. Despite these shortcomings they are still in use in industry[57,58] and by some researchers in academia.[59]

1.4.3.2 The Development of Well-Defined Initiators for ROMP and Olefin Metathesis

In contrast to ill-defined initiators, in the case of well-defined initiators, the structure of the active site is known and the initiator is generally preformed. The arrival of well defined initiators has dramatically increased the range of applications of the olefin metathesis reaction and made possible living ROMP producing polymers with low polydispersities. A number of initiator systems of this type have been shown to be tolerant to a range of functional groups, for example the ruthenium Grubbs initiators discussed in Section 1.4.3.3.

The work of Chauvin and others led to the prediction that Fischer metal carbene complexes were active for olefin metathesis and were responsible for the initiation of ROMP.[60] Extensive research effort was put into obtaining transition metal complexes

of this sort and determining whether they were active catalysts for metathesis. As expected a number of Fischer carbenes were discovered to form active initiator systems for metathesis such as $(CO)_5W{=}CPh_2$.[12] The synthesis of the titanium complex known as Tebbe's reagent proved to be an important development in the synthesis of well-defined initiators for olefin metathesis.

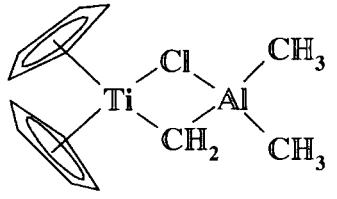
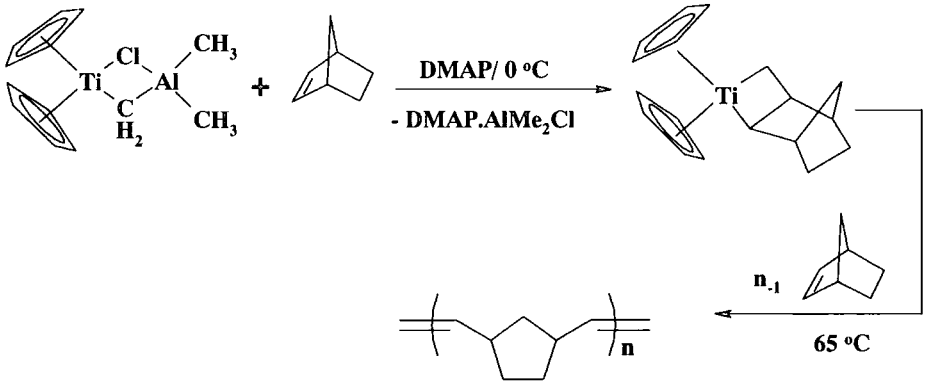


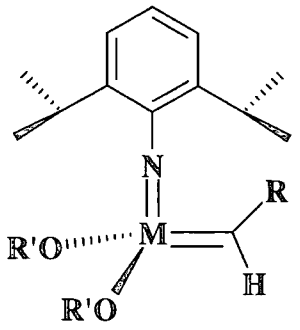
Figure 1.11 - Tebbe reagent.

Tebbe's reagent (**Figure 1.11**) may be regarded as a metal carbene complex of the type $Cp_2Ti{=}CH_2$, stabilised by $AlCl(CH_3)_2$.[12] The metallocyclobutane ring thus exists in equilibrium with its ring opened carbene form.[61] Gilliom and Grubbs discovered that the reaction of Tebbe reagent with NBE produced a titanium metallacycle that when heated at 65 °C with an excess of NBE yielded a living polymerisation that produced PNB with PDI in the region of 1.1 (**Scheme 1.34**).[62]



Scheme 1.34 - Conversion of Tebbe reagent into a titanocyclobutane initiator for ROMP and its subsequent use in the living ROMP of norbornene. DMAP = *N,N*-dimethylaminopyridine.

Unfortunately this initiator system had very little tolerance for functional groups. However its discovery increased interest in olefin metathesis and well-controlled living ROMP, and was followed by the development of well defined initiators based upon molybdenum, tungsten, and tantalum.[63,64] Schrock's Mo and W initiators are well defined initiators of the type $M(CHR)(NAr)(OR')_2$ with alkoxide and arylimido ligands that were first reported in the 1980s (**Figure 1.12**).[65]



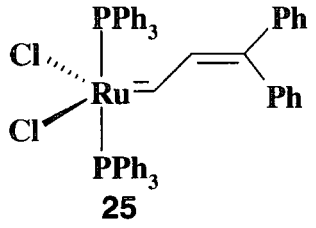
M = Mo or W
R = CMe_3 or CMe_2Ph
R' = CMe_3, CMe_2CF_3 or $CMe(CF_3)_2$

Figure 1.12 - Schrock's molybdenum and tungsten initiators.

The bulky alkoxide and arylimido ligands hinder the intermolecular decomposition reactions of the initiators, but still allow the coordination of an olefin substrate to allow formation of a metallocyclobutane ring and subsequent metathesis. The *syn* rotamer (present in crystal structures) is illustrated in **Figure 1.12**, however it exists in equilibrium with the *anti* rotamer in which the alkyl (**R**) substituent of the alkylidene ligand faces away from the arylimido ligand. The *anti* rotamer can be observed directly by ^1H NMR spectroscopy.[61,66] The tungsten initiators possess greater activity than their molybdenum counterparts, unfortunately the former are very sensitive to the presence of functional groups. The molybdenum initiators possess better functional group tolerance leading to them being widely adopted. They were used to produce polymers from NBE and norbornadiene (NBD) substituted with ethers, esters, and notably fluorine.[67-70] The activity of the Schrock initiators is greatly influenced by the nature of the alkoxide ligands; for example W(CH-*t*-Bu)(NAr)[OCMe$(CF_3)_2]_2$, **23**, metathesises *cis*-2-pentene at a rate of ~10^3 turnovers/min in toluene compared with W(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$, **24**, which only produces ~2 turnovers/h. This difference was explained by modelling the metathesis reaction as electrophilic attack of the olefin by the initiator, hence the reaction proceeds faster with the more electrophilic initiator, **23**.[68] Unfortunately Schrock initiators are extremely sensitive to both H_2O and O_2.[71]

1.4.3.3 Well-defined Ruthenium Alkylidene Initiators for Olefin Metathesis

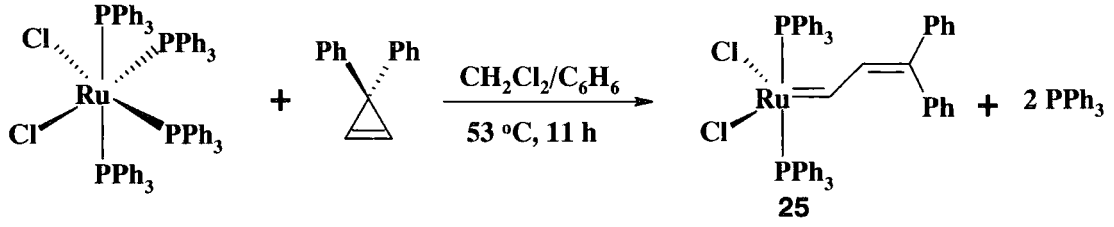
In 1992 Grubbs reported that well defined ruthenium alkylidene complex **25** was an initiator for ROMP (**Figure 1.13**).[72]



25

Figure 1.13 – A ruthenium initiator active for the ROMP of NBE.

This initiator proved to be stable with respect to H_2O and had a greater stability in the presence of O_2 than either Schrock's Mo or W initiators. Initiator **25** was synthesised by the reaction of 3,3-diphenylcyclopropene with either $RuCl_2(PPh_3)_3$ or $RuCl_2(PPh_3)_4$ (**Scheme 1.35**).



25

Scheme 1.35 - The synthesis of vinylalkylidene Ruthenium catalysts from 3,3-phenylcyclopropane.

Unfortunately this complex is unable to initiate the ROMP of less strained cyclic olefins or metathesise acyclic olefins. This resulted in the launch of an intensive research programme to try to develop more active initiators for metathesis. The effect on metathesis activity of replacing the two chlorine atoms with another species was first studied by Grubbs and co-workers by adding $Ag(OOCCF_3)$ to **25** in order to replace the two Cl ligands with trifluoroacetate groups.[73] The resulting complex was an initiator of olefin metathesis, although like its dichloro analogue it was only suitable for olefins with a high level of ring strain. The relationship between the identity of the halogen on the ruthenium initiators and their activity for olefin metathesis was also studied by Dias.[74] Initiators with bromine ligands were noticeably less active than their chlorine analogues, whereas replacing the chlorine ligands with iodine ligands produced complexes with very low or no activity for olefin metathesis (**Table 1.1**).

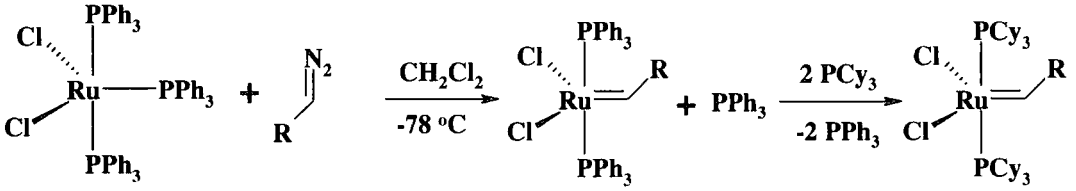
Table 1.1 - Relative activities of initiators of the type $(PR_3)_2X_2Ru=CH-CH=CPh_2$ for the ring closing metathesis of diethyl diallymalonate.[74]

PR_3	X	Activity (turnovers/h)
PCy_3	Cl	19.0
	Br	15.4
	I	1.4
PCy_2Ph	Cl	8.0
	Br	4.5
	I	*a*
P^iPr_3	Cl	17.5
	Br	13.9
	I	1.1
P^iPr_2Ph	Cl	5.5
	Br	2.3
	I	*a*

***a* Initiator showed no signs of activity for the reaction even after several hours.**

Smaller and more electron withdrawing halogen ligands thus provide the highest activity. It was established that replacement of the PPh_3 ligands with PCy_3 (Cy = cyclohexyl) led to a substantial increase in activity and allowed the ROMP of olefins with low levels of ring strain.[75,76] The relationship between the identity of the phosphine ligand and initiator activity was studied further (**Table 1.1**). The activity of initiators with different phosphines varied in the order PCy_3 > P^iPr_3 > PCy_2Ph > P^iPr_2Ph. Larger and more basic (i.e electron donating) phosphines appear to increase activity. Initiators with the combination of chloro and tricyclohexylphosphine (PCy_3) ligands possess the highest activity. Whilst various methods of naming the initiators described in this section have been used in the past, by far the most commonly used name for complexes of the type $RuX_2(=CHR)(PR_3)_2$ is Grubbs first-generation initiators (or catalysts) at the time of preparation of this report.

The discovery that alkylidene complexes of the type $RuCl_2(PR_3)_2(=CHR')$ could be obtained by the reaction of diazoalkanes led to a dramatic increase in the ease of their synthesis (**Scheme 1.36**).[76]



Scheme 1.36 - Synthesis of ruthenium initiators using diazoalkanes.

The development of this synthetic methodology provided a facile method for the synthesis of a range of initiators with different alkylidene ligands, allowing comparison of their activities as initiators of metathesis (**Figure 1.14**).

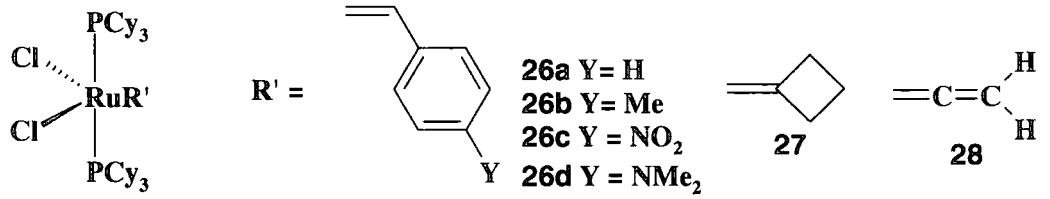


Figure 1.14 - A selection of ruthenium initiators for ROMP.[73,76]

Benzylidene ligands **26a-c** provide the most efficient initiation out of those studied, probably due to conjugation of the phenyl group with the alkylidene carbon. Benzylidene **26a** gave the best rates of initiation with **26b** following closely, in contrast the initiation constant of **26a** was a factor of 10 greater than that of **26d** in the metathesis of 1-hexene.[76] The initiator $RuCl_2(=CHPh)(PCy_3)_2$ **26a** was found to be a highly active initiator for olefin metathesis (**Figure 1.15**).

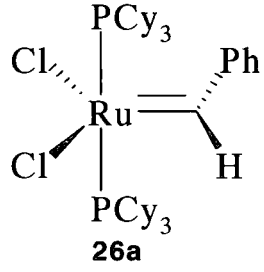
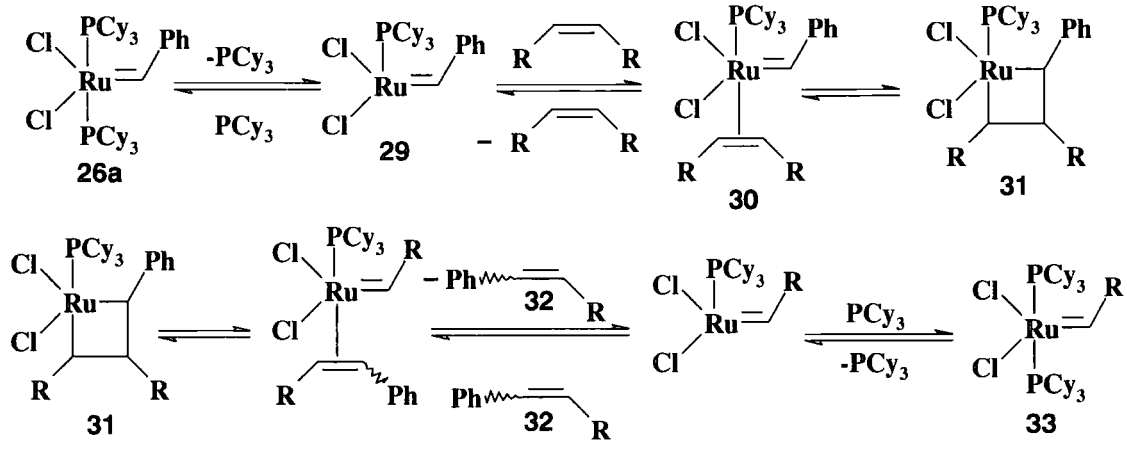


Figure 1.15 – The well defined initiator $RuCl_2(=CHPh)(PCy_3)_2$.

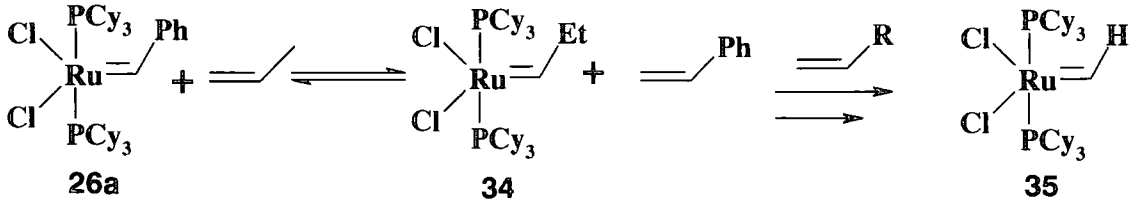
The mechanism of metathesis of this initiator, starts with dissociation of a phosphine ligand to form the active 14 electron species **29**, which allows coordination of an olefin (**30**) (**Scheme 1.37**).[77,78]



Scheme 1.37 - Mechanism of olefin metathesis with well-defined initiators.

It will be noted that in the case of productive metathesis, the metallocyclobutane species **31** cleaves to form a new olefin (**32**) and a new ruthenium initiator (**33**). The homometathesis[79] (sometimes called self-metathesis)[12] of an acyclic olefin thus leads to alkylidene exchange and the formation of new ruthenium

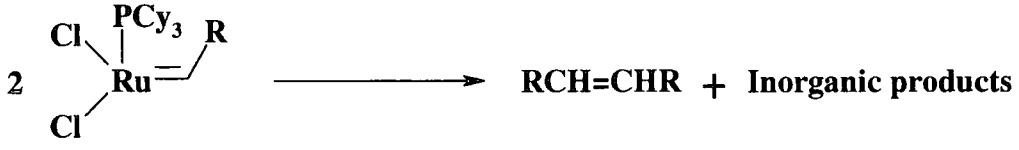
initiators.[76] As will be demonstrated in this report these initiators can themselves be synthetically useful.



Scheme 1.38 - Alkylidene exchange of 1-butene with $RuCl_2(=CHPh)(PCy_3)_2$ (26a).

The kinetic product of the reaction of a terminal alkene with $RuCl_2(=CHPh)(PCy_3)_2$ is an alkylidene initiator, a propylidene derivative (**34**) in the case of the reaction depicted in **Scheme 1.38**. The thermodynamic product of the reaction of a terminal olefin with **26a** is a methylidene complex (**35**), as it is not able to metathesise acyclic olefins.[80] In the case of terminal olefins with low steric hindrance around the olefin the second reaction is very slow, meaning the kinetic product can be isolated.[80] If the reaction involves an internal olefin which is symmetrical about its double bond like *cis*-3-hexene, only one alkylidene exchange reaction can occur and a single equilibrium is formed.[76,80] A *trans* isomer like *trans*-3-hexene can be used in place of a *cis* isomer, although the former are a little less reactive.[80]

The thermodynamic stability and method of decomposition of benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$ (**26a**) and related alkylidene initiators has been studied. The benzylidene initiator was found to possess good stability (8 days at 55 °C in solution), with other alkylidene initiators possessing a slightly lower stability. Study of the olefin byproducts of the decomposition reaction led to proposition of the mechanism shown below (**Scheme 1.39**).[81]



Scheme 1.39 - Decomposition of ruthenium alkylidene initiators.

The decomposition reaction leads to dimerisation of the organic fragment. The dimerisation reaction only occurs between mono-phosphine species and thus competes with phosphine reassociation. The addition of CuCl, a phosphine scavenger, results in a dramatic increase in decomposition.[81]

In addition to stability to H_2O and enhanced stability in the presence of O_2 relative to initiators based on other metals, $RuCl_2(=CHPh)(PCy_3)_2$ and similar well-defined ruthenium initiators also have high tolerance to substitution of the olefinic substrates with a wide range of functional groups. The functional group tolerances of well-defined Ru, Mo, W and Ti initiators is compared in the table below (**Table 1.2**).

Table 1.2 - Functional group tolerance of early and late transition metal olefin metathesis initiators.[82]

Titanium	Tungsten	Molybdenum	Ruthenium	
Acids	Acids	Acids	**Olefins**	↑
Alcohols, water	Alcohols, water	Alcohols, water	Acids	
Aldehydes	Aldehydes	Aldehydes	Alcohols, water	**Increasing**
Ketones	Ketones	**Olefins**	Aldehydes	**Reactivity**
Esters, Amides	**Olefins**	Ketones	Ketones	
Olefins	Esters, Amides	Esters, Amides	Esters, Amides	

Thus ruthenium initiators react in preference with olefins over most other functionalities. The high tolerance of $RuCl_2(=CHPh)(PCy_3)_2$ to H_2O and functional groups, and its relatively easy synthesis have made it a very popular initiator for olefin metathesis. It plays a particularly large role in metathesis polymerisation through both ROMP and acyclic diene metathesis (ADMET) mechanisms, and has been used successfully in organic syntheses utilising the ring closing metathesis (RCM) and cross metathesis (CM) reactions.[82] The use of **26a** as a ROMP initiator will be discussed in detail in Section 1.4.4.

1.4.3.4 Development of Second Generation Well-Defined Ruthenium Initiators

It was discovered that replacement of the two phosphines of $RuCl_2(=CHPh)(PCy_3)_2$ (**26a**) with two N-heterocyclic (NHC) ligands led to the synthesis of new initiators (**Figure 1.16**) that were active for the ROMP of NBE and cyclooctene as well as the RCM of 1,7-octadiene.[83,84]

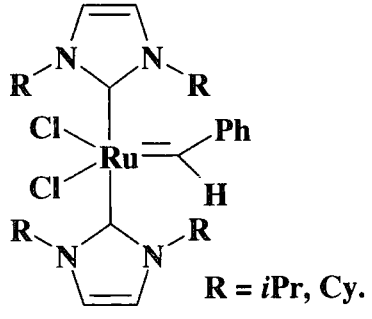


Figure 1.16 - Ruthenium bis(N-heterocyclic carbene) olefin metathesis initiators.

Work by the Grubbs,[85] Hermann,[86] and Nolan [87] groups led to the discovery that addition of the *N*-mesityl substituted imidazole ligand IMes [1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] to **26a** led to the replacement of a single phosphine ligand and the formation of stable and more active ruthenium alkylidene initiator **36** (**Figure 1.17**).

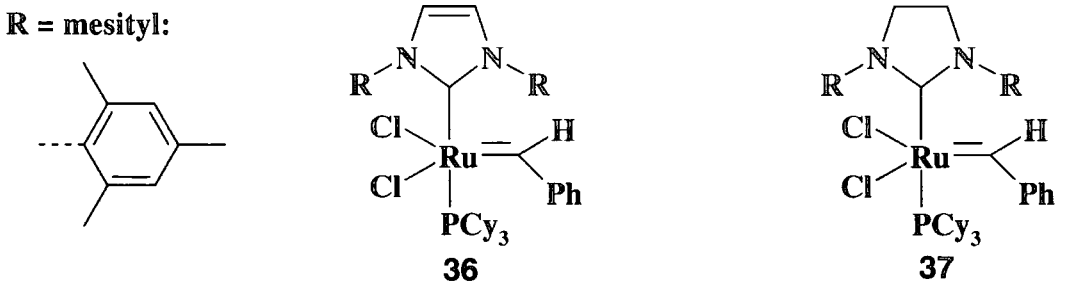


Figure 1.17 - N-heterocyclic ruthenium initiators for olefin metathesis.

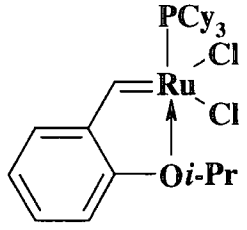
It was discovered that the closely related 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene (H_2IMes) could be used in place of IMes, resulting in the synthesis of initiator $RuCl_2$(=CHPh)(H_2IMes)(PCy_3) (**37**, **Figure 1.17**), which possesses exceptionally high activity for olefin metathesis. Early names for NHC initiator **37** included 'Super-Grubbs' or the Grubbs-Hermann initiator, it is now most commonly referred to as the Grubbs second generation initiator. The high activity of initiator **37** coupled with high functional group tolerance has resulted in it becoming a very useful and popular tool for organic synthesis, being used in both RCM[88] and CM[89] reactions. The initiator is capable of polymerising NBE derivatives by ROMP at a very fast rate. Unfortunately the rate of propagation is usually far higher than that of initiation, and backbiting may also occur to some degree.[90] Thus in more extreme cases polymers with PDIs of 29.0 have been obtained.[91]

The addition of phosphine does not enable control over ROMP initiated using this initiator.[79] Slugovc et al. have studied the effect of a wide-range of additives on ROMP with this initiator. The initiator tolerated the vast majority of them including nitriles and primary amines (which can poison **26a**), and in some cases fairly low PDIs and slightly better control over M_n was obtained. The best control was obtained with 100 equivalents of pyridine.[92,93] This result is not surprising when we consider that we would expect a bis(pyridine) initiator of the type discussed in Section 1.4.3.5 to be formed *in situ*.

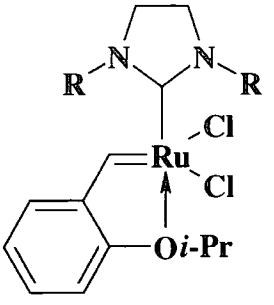
Recent work has suggested that this initiator gives inferior results to **26a** in the polymerisation of strained olefins like NBE derivatives. Initiator **37** has proven useful in the entropically driven polymerisation of large ring systems.[94] It can apparently also be useful for the polymerisation of macromolecular monomers. The high steric hindrance present in macromonomers with two polymer chains can hinder polymerisation with **26a** resulting in slow polymerisations and incomplete polymerisation of macromonomer in some cases.[90] This steric hindrance is beneficial to polymerisations initiated by **37**, lowering R_p relative to R_i and suppressing chain transfer, hence leading to well-controlled polymerisations. Whilst it seems that the second generation H_2Imes initiator might be useful for the ROMP of certain monomers for which **26a** does not show sufficient reactivity, it is generally accepted that it is not an appropriate choice of ROMP initiator for most monomer systems.

1.4.3.5 Later Developments in Well-Defined Ruthenium Initiators and their use in ROMP

The well-defined initiators **38** and **39** (**Figure 1.18**) were reported to be highly efficient initiators for olefin metathesis.[95,96]



38



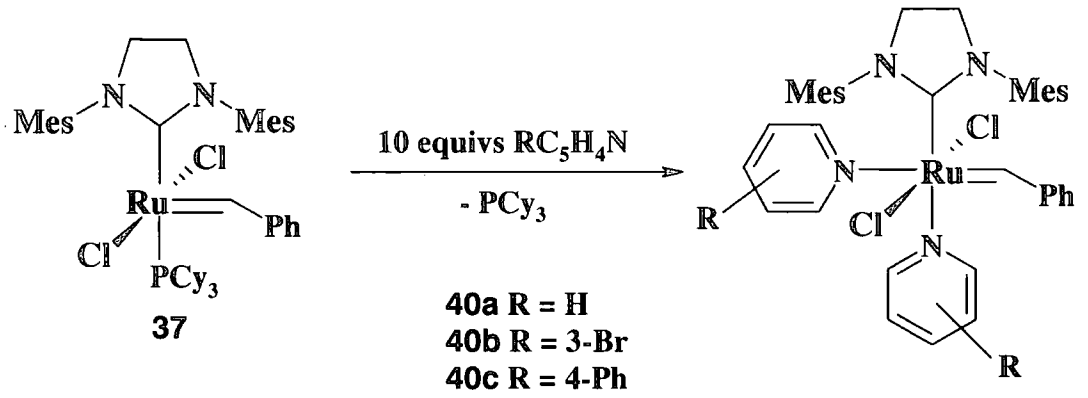
39

R = mesityl.

Figure 1.18 - Well defined ruthenium Hoveyda initiators for olefin metathesis.

Like previous initiators they possess high tolerance to functional groups, but they also have enhanced stability towards molecular oxygen. This has led to **38** and **39** becoming popular choices for organic synthesis.[96] Unfortunately studies of the ROMP of NBE derivatives by both of these initiators have indicted that they produce polymers with PDIs significantly higher to those of the corresponding polymers synthesised using $RuCl_2(=CHPh)(PCy_3)_2$ (**26a**).[97] The latter initiator is still therefore a better choice for the synthesis of well-defined polymers with a narrow molecular weight distribution.

Recently a study was undertaken to examine the effect on initiator activity of replacing the PCy_3 ligand of the second generation ROMP initiator **37** with pyridine ligands (**Scheme 1.40**).



Scheme 1.40 – Synthesis of well-defined ruthenium initiators for olefin metathesis containing pyridine ligands.

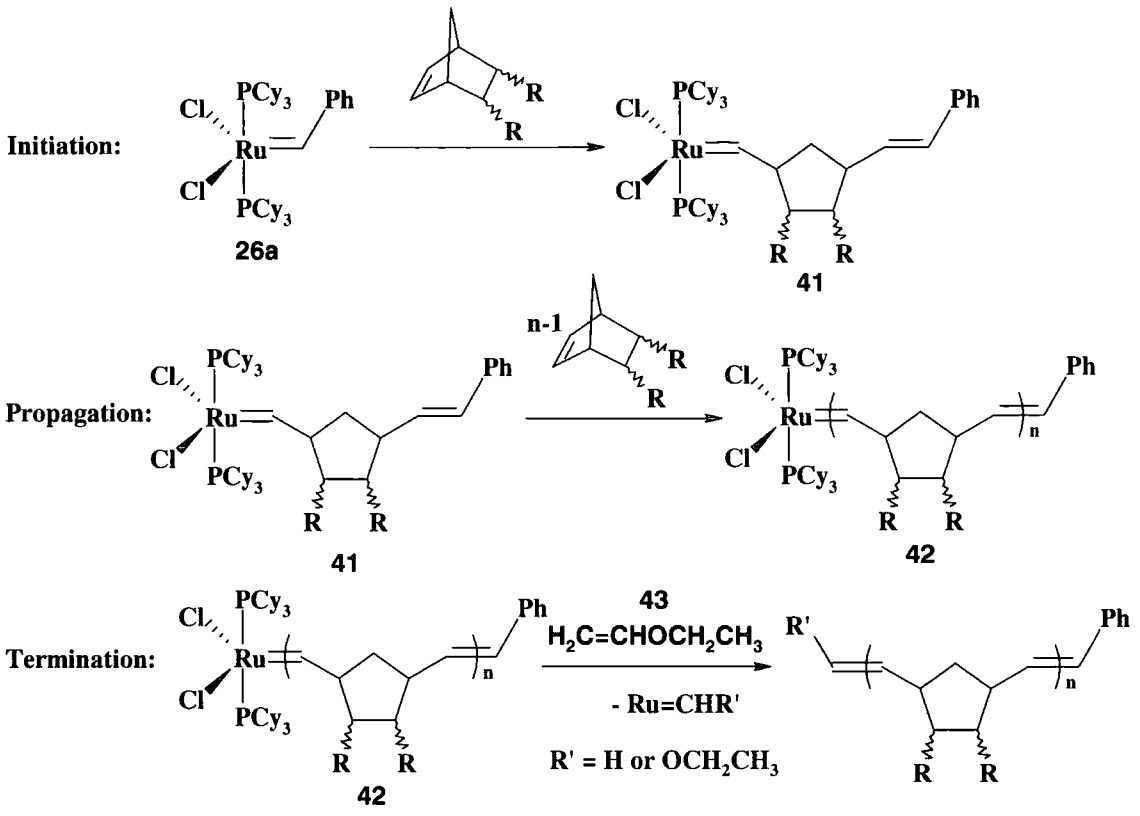
The reaction proceeds via an associative mechanism, yielding initiators where the PCy_3 ligand is replaced with two pyridine ligands.[98] The reason for the higher number of ligands in initiators of type **40** relative to **37**, is thought to be related to the lower steric bulk of the pyridine ligands compared with PCy_3.[99] The three bis(pyridine) initiators **40a-c** shown in **Scheme 1.40** have been used to initiate the CM of acrylonitrile and allylbenzene.[99] 3-Bromopyridyl derivative **40b** was found to be the most active and gave by far the best yield of product out of the three. Initiator **40b** was found to be a highly active initiator for ROMP, and in contrast to the case with **37**, polymerisations initiated by **40b** possessed a much higher rate of initiation (R_i) than propagation (R_p). The initiator appears to retain the functional group tolerance of previous initiators. Furthermore it polymerises *endo,endo* norbornene derivatives readily, which generally polymerise slowly using first (**26a**) and second (**37**) generation initiators. The polymerisation of NBE at room temperature produces polymer with a relatively broad PDI (1.65). By reducing the temperature to -20 °C the PDI was lowered to just 1.08. It has been reported that the thermal stability of the initiator is not very high, which limits its use in organic synthesis.[100] Evidence for the livingness of polymerisation reactions initiated with **40b** was obtained from its use in the synthesis of well-defined block copolymers by sequential addition of NBE monomers. The copolymers possessed narrow PDI and were free from homo-polymers or un-reacted blocks. It is noteworthy that the results of the ROMP of a NBE derivative with bis(pyridine) initiator, **40a**, and with bis(4-bromopyridine)

initiator, **40b**, were compared recently and that of **40a** produced a polymer with a slightly lower PDI.[92] A systematic study to examine the effect of changing the identity of the pyridine ligand in these initiators and their performance in ROMP has not yet been published. However it seems highly likely that Imes bis(pyridine) initiators will prove to have some place in the synthesis of polymers via ROMP in the future.

1.4.4 Living ROMP Initiated using $RuCl_2(=CHPh)(PCy_3)_2$

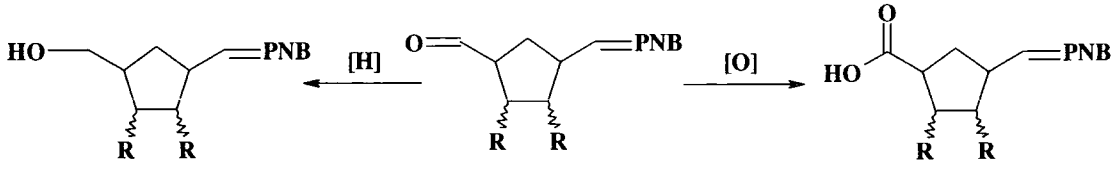
$RuCl_2(=CHPh)(PCy_3)_2$, **26a**, has become the most popular initiator for the synthesis of well-defined polymers by ROMP in recent years, typically producing polymers with a narrow, or fairly narrow, molecular weight distribution from NBE derivatives. This popularity has in part been due to the high functional group tolerance of **26a**. The ruthenium macroinitiators developed in this research are closely related analogues of **26a**, hence ROMP with **26a** will be discussed in detail as similar results are expected from ROMP reactions with the macroinitiators. It is anticipated that the range of structures described here can be reproduced with the addition of an anionically polymerised block, using the methodology divulged in this report.

The kinetics of the initiation and propagation reactions of the ROMP of NBE and its derivatives do not possess an equilibrium nature, as their polymerisation is entropically favourable due to the release of the ring strain present in the monomers. The initiation step in the polymerisation consists of the ring opening of NBE or a derivative to form 1 mer **41** (**Scheme 1.41**). Propagation proceeds by the ring opening of more monomer to form high molecular weight living polymer (**42**).



Scheme 1.41 – The ROMP of norbornene derivatives using 26a. R is any suitable alkyl or aryl group.

As they are living polymerisations another monomer can be added after propagation is complete, in order to synthesise block copolymers.[101] Polymerisations initiated by **26a** are usually terminated in a controlled manner with ethyl vinyl ether (**43**, **Scheme 1.41**). The ROMP reactions can also be terminated using a functionalised acyclic olefin to synthesise telechelic polymers.[102] ROMP reactions with **26a** are sensitive to O_2, though less so than those initiated by well-defined Mo and W initiators. The reaction of oxygen with the living chain ends can however be useful – it results in quantitative functionalisation of the polymer with an aldehyde group.[103] This can be reduced to a primary alcohol or oxidised to form a carboxylic acid (**Scheme 1.42**).



Scheme 1.42 - Reduction and oxidation of ROMP polymers synthesised by the reaction of living polymers with O_2.

Thus ROMP with **26a** can be a useful source of functionalised polymers. As further proof of the tolerance of **26a** to H_2O, the initiator was found to be suitable for the polymerisation of an aqueous dispersion of NBE derivatives using a surfactant.[104] Chlorinated solvents are usually employed as the reaction solvents, studies on the polymerisation of NBE monomers using **26a** in chloroform, methylene chloride, benzene, and toluene have generally indicated that the kinetics of the polymerisation are faster in chlorinated solvents than aromatic solvents.[97,105] The molecular weight distributions and tacticities of PNBs synthesised in these solvents were identical.[97,106] The microstructure of the polymers is largely independent of temperature.

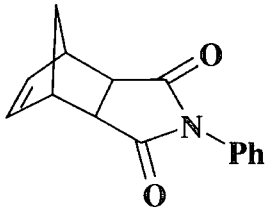


Figure 1.19 - NBE derivative used to study the effect of excess phosphine on ROMP.

Bielawski and Grubbs studied the ROMP of an NBE derivative (shown in **Figure 1.19**) with **26a**, producing a polymer with a PDI of 1.25.[107] Addition of the phosphines PCy_3, PCy_2Ph, $PCyPh_2$ to this polymerisation reaction resulted in a reduction of the PDI of the resulting polymers. The phosphine PPh_3 produced the biggest changes in polydispersity, lowering it to 1.07. It is necessary for a PCy_3 ligand to dissociate from the initiator prior to ROMP (See **Scheme 1.37**). The excess phosphine competes with the monomer and slows down polymerisation. Crucially the rate of propagation is slowed down more than initiation and hence R_i/R_p increases. The use of PPh_3 to lower PDI has not received widespread adoption, however the addition of PCy_3 has been recently used to increase control over the polymerisation of cyclopentene.[108,109]

The initiator **26a** can be used to polymerise monomers containing functional groups that are expected to be good co-ordinating ligands. It has been suggested by Grubbs[110] and most notably Demel[97] that co-ordination of the pendant groups of living polymer chains with the propagating metal centre can occur. If the co-ordination is reversible and dissociation occurs on a time scale similar to that of propagation it need not hinder the synthesis of polymers of controlled molecular

weight possessing low PDI. A selection of monomers that can be successfully polymerised using $RuCl_2(=CHPh)(PCy_3)_2$, **26a**, is shown below (**Figure 1.20**).

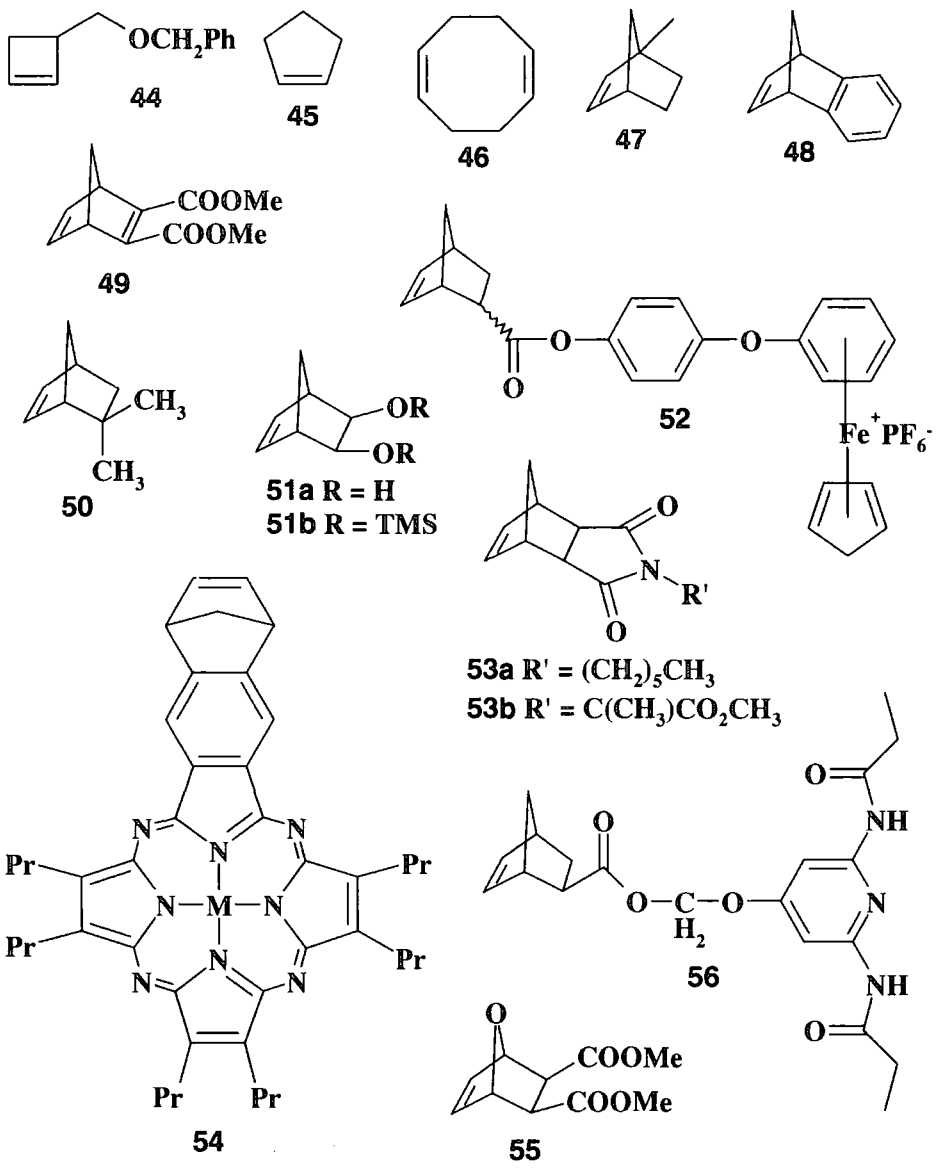
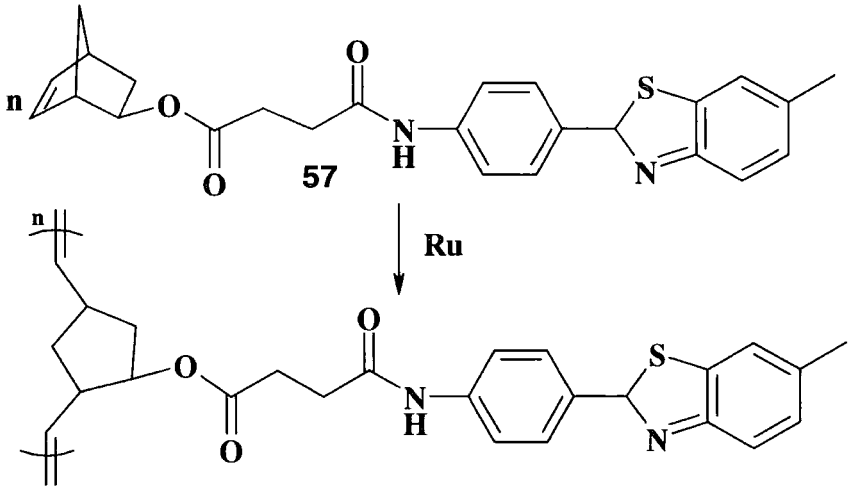


Figure 1.20 - A selection of monomers that have been polymerised using ruthenium benzylidene initiator 26a. References: 44,[110] 45,[106] 46,[110] 47-50,[106] 51a-b,[111] 52, [112] 53a,[113] 53b,[103] 54 (copolymer with NBE, where M is Mg, Cu or 2H),[114] 55,[106] 56.[115]

The complete conversion of monomers to polymer is observed in most cases. The ring opening step in the polymerisation of cyclopentene **45** has a significant equilibrium nature to it, hence in order to avoid an increase in PDI, polymerisations are often terminated before consumption of monomer is complete. Polynorbornenes synthesised using **26a** usually possess a high percentage of *trans* double bonds, most typically with only 15-20 % in a *cis* configuration.[101,106] Monomer **48** is a rare case, in

that it produces a polymer with an approximately 50:50 *cis/trans* content.[106] The functional group tolerance of **26a** allows the incorporation of 'exotic' functionalities onto a well-defined polymeric backbone.[116] For instance monomer **57** shown in **Scheme 1.43** incorporates a 2-(4-aminophenyl)-6-methylbenzothioloate functionality, a member of class of compounds that have shown activity against colon, lung, breast, and ovarian cancer.[117]



Scheme 1.43 - Synthesis of a polymeric anticancer material from ROMP.

Dendritic functionalities have been attached to NBE derivatives and polymerised by ROMP to yield dendronised polymers.[118] Barrett has carried out extensive research into immobilizing reagents for solution phase parallel organic synthesis onto a PNB backbone, producing polymers that swell in a range of solvents.[111] These materials are known as ROMPgels, and their synthesis, which involves attaching the reagent or a precursor to a NBE derivative which is then subjected to ROMP, has made extensive use of the functional group tolerance of **26a**.

The ROMP of NBE derivatives with $RuCl_2(=CHPh)(PCy_3)_2$, **26a**, has therefore proved to be a very useful tool in the synthesis of polymers incorporating a broad range of functionalities.

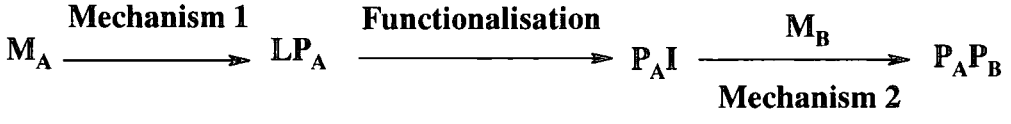
1.5 Synthesis of Block Copolymers using Two Different Polymerisation Techniques

The synthesis of block copolymers is usually achieved by the sequential addition of two or more monomers to a single living polymerisation system. There are challenges involved in this approach; the living polymer must be an efficient initiator

for the polymerisation of the second monomer and purity of the monomer is essential to avoid the presence of homopolymers as an impurity. It will be appreciated that the combination of two different polymerisation techniques to synthesise block copolymers is more technically challenging. It is however sometimes necessary and desirable to combine two different techniques to synthesise block copolymers. This is most often because the monomers cannot be polymerised by a single technique. Some monomers, e.g. NBE are polymerised into different structures depending on the polymerisation technique used; two mechanisms must be used if the desired structures cannot be obtained from a single polymerisation methodology. Alternative reasons are that the blocks cannot all be synthesised with the desired microstructures, or PDIs using a single technique. Earlier examples of this approach used post-polymerisation coupling reactions or the combination of two living polymers.[9] This section will give a brief overview of modern methods for the combination of two polymerisation techniques to synthesise block copolymers.

1.5.1 Active Site Transformation

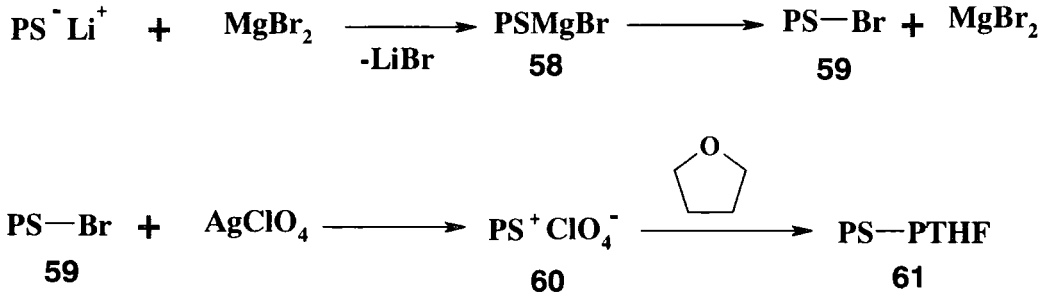
A very useful method for the combination of two polymerisation techniques, is by converting one polymerisation mechanism into another, through the use of what is quite often referred to as an active site transformation.[119] It has also been referred to recently by one author as a change of mechanism polymerisation.[120] This method involves the conversion of a polymer, synthesised by one polymerisation technique, into a species capable of initiating polymerisation via another mechanism, i.e. a macromolecular initiator – macroinitiator. The concept will be outlined below for the synthesis of AB block copolymers.



Scheme 1.44 - Synthesis of block copolymers using the macrointiator technique.

The first monomer ($\mathbf{M_A}$) is polymerised using one polymerisation mechanism to yield a living polymer ($\mathbf{LP_A}$). After polymerisation is complete, functionalisation reaction(s) are used to convert $\mathbf{LP_A}$ into a macroinitiator ($\mathbf{P_AI}$). This macroinitiator is then used for the polymerisation of the second monomer ($\mathbf{M_B}$), resulting in the synthesis of a block copolymer ($\mathbf{P_AP_B}$). For example Burgess reported a methodology

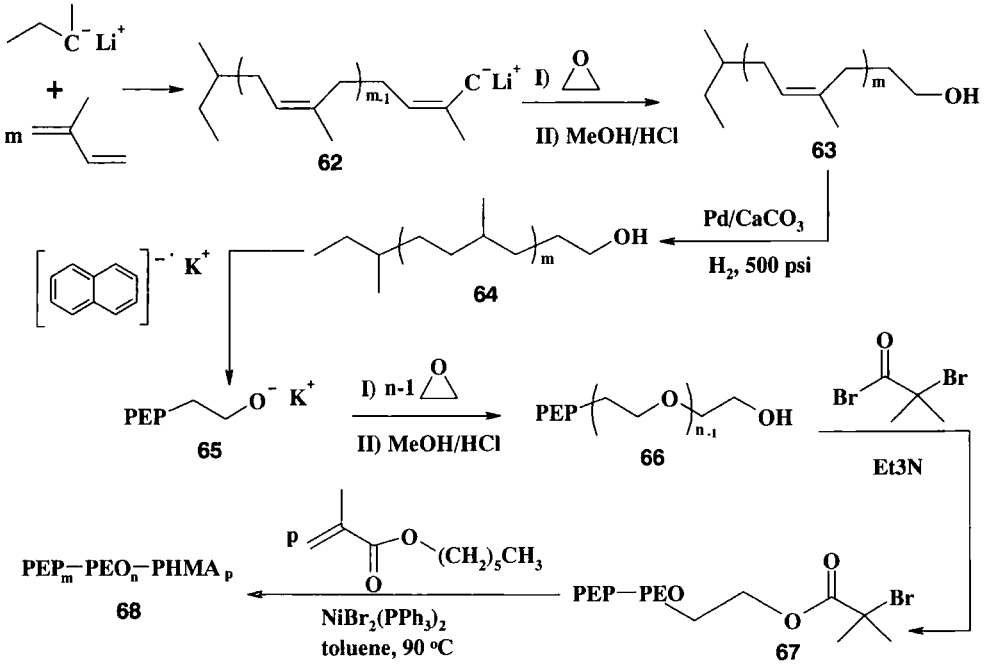
for the conversion of living anionic polymerisation into cationic polymerisation (**Scheme 1.45**).[121] The first step after the living anionic polymerisation of styrene was the synthesis of macromolecular Grignard reagent **58**, whose reaction with Br_2 produced PS-Br, **59**. This halide functionalised polymer was activated using silver salts, for example $AgClO_4$ to form a carbocation macroinitiator (**60**).



Scheme 1.45 - Transformation of living anionic polymerisation into living cationic polymerisation.

PS macroinitiator **60** was then used to initiate the polymerisation of THF to form block copolymers (**61**).

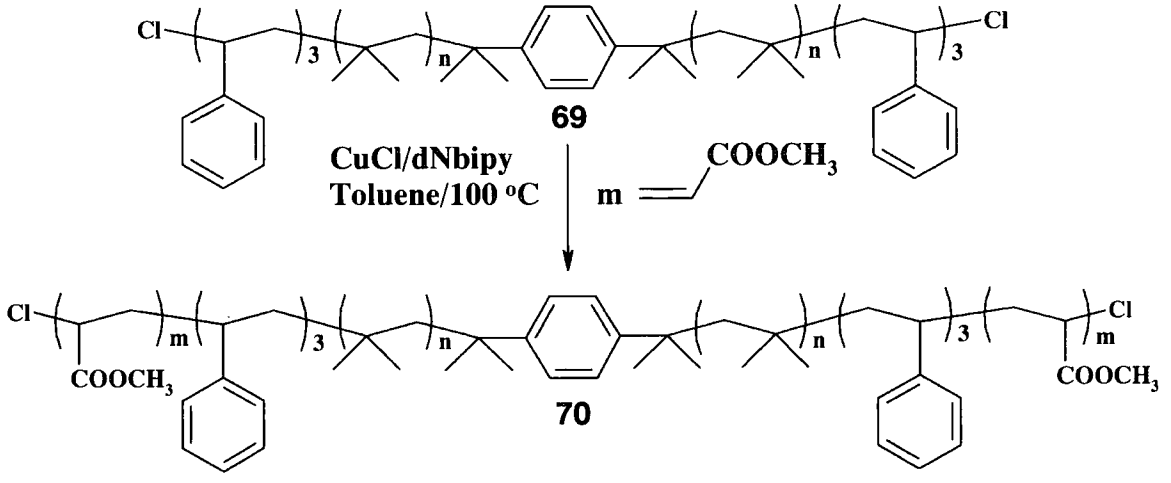
The synthesis of amphiphilic ABC triblock copolymers of poly(ethylene-alt-propylene)(PEP), EO and acrylates was achieved using anionic polymerisation and ATRP, together with a hydrogenation reaction (**Scheme 1.46**).[122] The first step involved polymerisation of isoprene via an anionic mechanism, following which the living PI **62** was functionalised with EO to introduce a hydroxyl group (**63**).



Scheme 1.46 - Synthesis of ABC block copolymers via active centre transformations.

Polymer **63** was then hydrogenated to synthesise the PEP block (**64**). The hydroxyl group of **64** was deprotonated to form alkoxide **65** using potassium naphthalenide. This macroinitiator was then used to initiate the anionic polymerisation of EO. The resulting block copolymer **66** was further functionalised resulting in the synthesis of bromide macroinitiator **67**. This macroinitiator was used to initiate the polymerisation of hexyl methacrylate via ATRP to form well-defined triblock copolymers (**68**) with PEP, PEO and poly(hexyl methacrylate)(PHMA) blocks. The triblock copolymers had polydispersities less than 1.20.

In the previous example an ABC block copolymer was produced. It is also possible to synthesise ABA block copolymer using macroinitiators of polymer B. One way to do this is to initiate the first polymerisation using a difunctional initiator. Matyjaszewski initiated the carbocationic polymerisation of isobutene using a difunctional initiator, the polymerisation reaction was then capped with a few units of styrene to form macroinitiator **69** (**Scheme 1.47**).[123]



Scheme 1.47 - Synthesis of block copolymers by the combination of cationic polymerisation and ATRP.

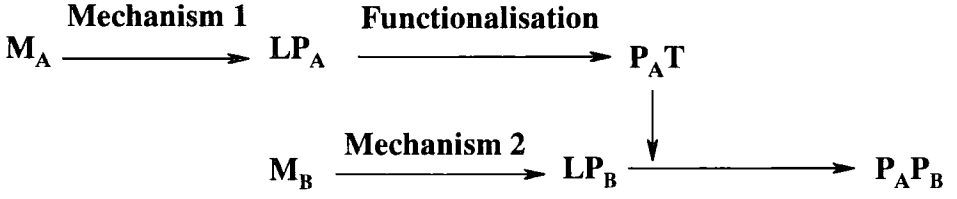
This macroinitiator was suitable for the polymerisation of styrene, methacrylates and acrylates via ATRP yielding ABA block copolymers (**70**) with a PDI of 1.2.

A general advantage of using the macroinitiator approach to synthesise block copolymers is that, provided the functionalisation reactions necessary to synthesise the macroinitiators can be achieved approximately quantitatively, block copolymers can be synthesised that are virtually free from homopolymers. As with almost any

methodology for the synthesis of block copolymers, introduction of impurities at any stage can lead to the loss of active sites, and contamination of the copolymers with homopolymer.

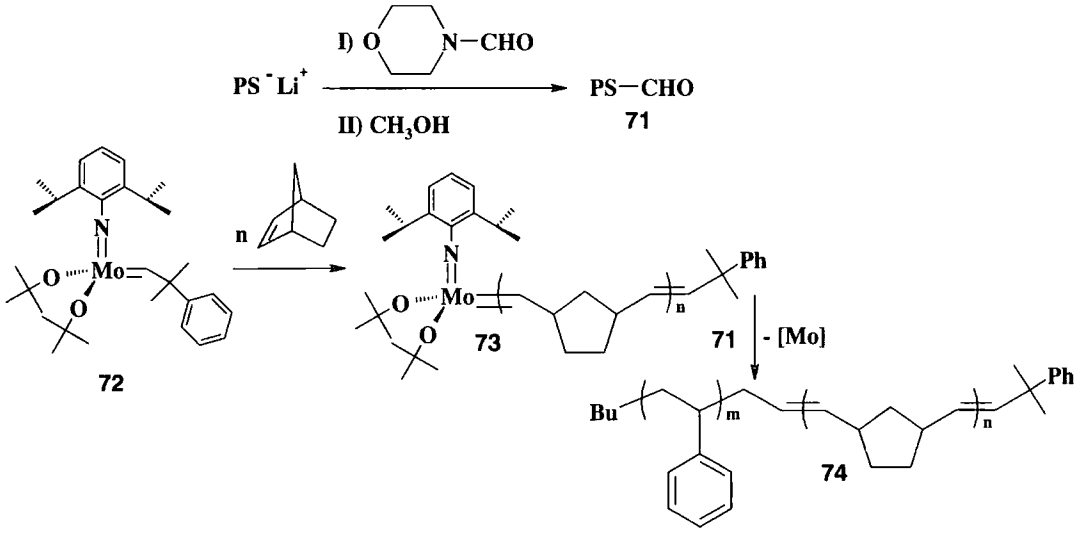
1.5.2 Use of Macroterminators to Synthesise Block Copolymers

An alternative method is to perform both polymerisations separately and couple them after polymerisation. For instance living polymers synthesised via one technique ($\mathbf{LP_A}$) can be functionalised to introduce a terminating group for another polymerisation reaction. The resulting macromolecular terminators, or macroterminators ($\mathbf{P_AT}$), can then be used to terminate a living polymer initiated via another mechanism ($\mathbf{LP_B}$) resulting in the synthesis of block copolymers ($\mathbf{P_AP_B}$) (**Scheme 1.48**).



Scheme 1.48 - Synthesis of block copolymers using macroterminators.

The synthesis of block copolymers via the combination of ROMP and anionic polymerisation was accomplished using this route with some success.[124] The living anionic polymerisation of styrene was functionalised to form a polymeric aldehyde (**71**) using the method of Quirk and Kuang (**Scheme 1.49**).[125]



Scheme 1.49 - Synthesis of block copolymers of styrene and NBE.

The polymeric aldehydes were added to living ROMP (**73**), initiated by a well-defined Mo initiator (**72**), resulting in the synthesis of the block copolymers (**74**). In all cases an excess of the polymeric aldehyde was required to completely convert the ROMP polymer to block copolymer. The excess of **71** contaminated the resulting block copolymers with homopolymer, which could only be removed through fractionation, if at all. The synthesis of a polyisoprene macroterminator was accompanied by side-reactions, which resulted in contamination of the block copolymers with a large amount of unfunctionalised homopolymer which could not be removed by purification. An advantage of using the macroinitiator technique instead of the macroterminator method is that functionalisation reactions used to convert polymer to macroinitiator in the former use reagents that are non-macromolecular, and hence unreacted reagent can be easily removed by reprecipitation. A small excess can therefore be used to drive a functionalisation reaction to completion. By contrast unreacted polymeric macroterminators are often likely to be much harder to remove from block copolymer products.

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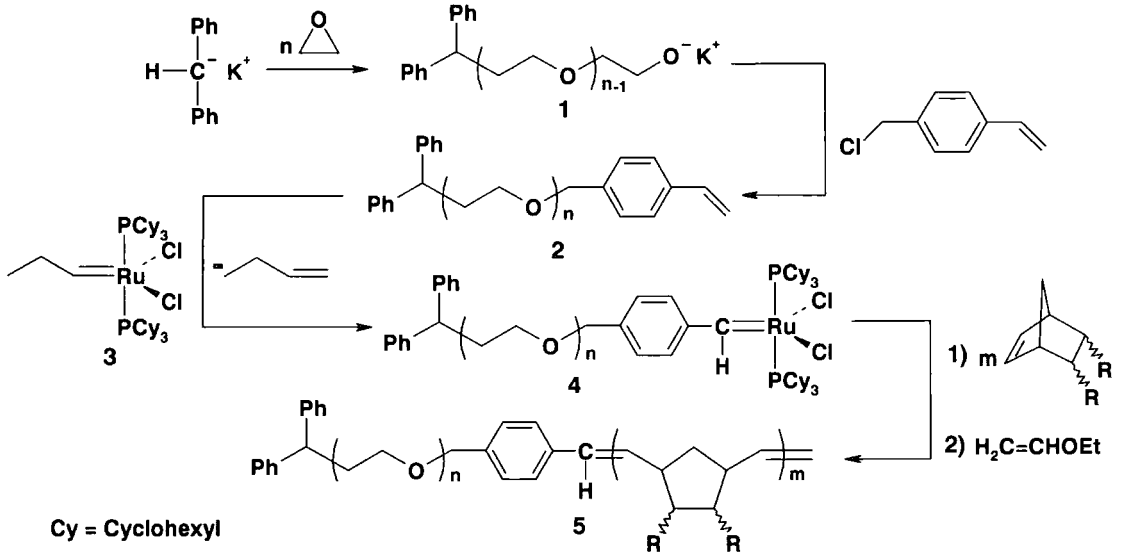
Chapter 2

Block Copolymers of Ethylene Oxide and Norbornene Derivatives

2.1 Introduction

Living anionic polymerisation and ruthenium initiated living ring opening metathesis polymerisation (ROMP) both allow the synthesis of macromolecules with a high degree of control. They are however capable of polymerising different sets of monomers with little overlap. A method for combining them to synthesise block copolymers would therefore be highly desirable. This chapter describes the first method for the synthesis of well-defined block copolymers by the combination of living anionic polymerisation with ruthenium initiated living ROMP. In order to demonstrate this principle a series of novel well-defined block copolymers have been synthesised by the transformation of the living anionic polymerisation of ethylene oxide into the living ROMP of norbornene derivatives (**Scheme 2.1**).



Scheme 2.1 – Synthesis of block copolymers of ethylene oxide with norbornene derivatives.

Ethylene oxide was polymerised anionically and end-functionalised by a controlled termination reaction with 4-vinylbenzyl chloride (4-VBC) to produce poly(ethylene oxide) (PEO) macromonomers with terminal vinyl groups (**2**, **Scheme 2.1**). The macromonomers (**2**) were transformed into the first well-defined macroinitiators (**4**) for ROMP from polymers synthesised by anionic polymerisation, using propylidene complex $RuCl_2(=CHEt)(PCy_3)_2$ (**3**) and the PEO macromonomer (**2**). Addition of norbornene derivatives to (**4**) results in the formation of block copolymers (**5**).

2.2 Results and Discussion

2.2.1 The Anionic Polymerisation of Ethylene Oxide

The first step in the synthesis of the PEO – PNB (polynorbornene) block copolymers is the synthesis of PEO macromonomers which are used as precursors to macroinitiators for ROMP. The anionic polymerisation of the epoxide ethylene oxide can be initiated using a range of nucleophiles.[1] The polymerisations are less sensitive to impurities than those of typical vinyl monomers, due to a chain transfer equilibrium between 'dead' (alcohol functionalised) and living polymer chains.[2] However high vacuum techniques were used in this work and the solvent (tetrahydrofuran, THF) and ethylene oxide were both rigorously purified. This was to ensure complete functionalisation of the PEO macromonomer. The polymerisation was carried out in a reaction vessel specially designed for anionic polymerisation (**Figure 2.1**)

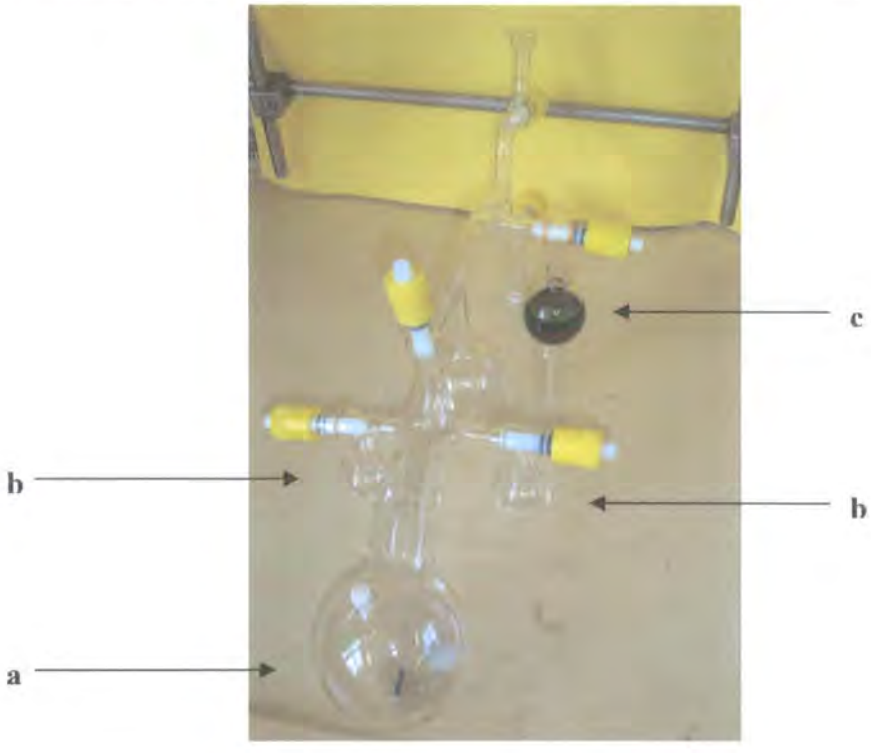


Figure 2.1 - Reaction vessel for anionic polymerisations.

The vessel consists of one central reaction chamber into which the solvent and monomer are distilled and the polymerisation reaction performed (**a**, **Figure 2.1**), as well as two side bulbs in which samples of the polymerisation reaction can be collected (**b**, **Figure 2.1**). One of these side bulbs was used to collect a sample of unfunctionalised PEO for analysis. The reaction vessel also contains a solution of polystyryllithium (PSLi, living polystyrene) in benzene (**c**, **Figure 2.1**), which is used

to wash the vessel prior to reaction, sacrificially removing any impurities that are susceptible to nucleophilic attack (and thus reaction with the living polymers). After washing the apparatus, the polystyrene was removed by distilling benzene from the wash solution into another bulb and using this to re-wash the vessel. This process was repeated a number of times (typically 4 or 5) until the washings were completely colourless and repeated a final time before all the benzene was distilled back into the wash solution.

The living anionic polymerisation of ethylene oxide is most commonly initiated using diphenylmethyl potassium (DPMK) and cumyl potassium (CK) (Section 1.3.2).[3] CK synthesised by literature methods can be contaminated with CH_3OK, which is also capable of initiating the polymerisation of ethylene oxide.[4] This problem does not affect polymerisations initiated using DPMK. In this work DPMK, in the form of a 1.0 M solution in THF, was used to initiate the polymerisation due to its availability and relatively wide use. The burgundy colour of the initiator solution disappeared fairly quickly (within approximately 5 min) on injection into freshly distilled ethylene oxide and THF. The resulting solution was almost colourless, but appeared to have a slight green or yellow hint when higher concentrations of initiator were used (i.e. lower molecular weight). This colouration could possibly stem from some interaction between the potassium ion and naphthalene residue from the potassium naphthalene used in the synthesis of DPMK. Consumption of monomer is also accompanied by an increase in viscosity. The polymerisation of ethylene oxide is a living well controlled polymerisation and thus the concentration of initiator determines the molecular weight of the resulting polymer. The propagation rate is fairly slow even in THF, due to the high degree of aggregation of lithium alkoxides.[2] A polymerisation reaction time of 24 h at room temperature (r.t.) was found to be suitable for the synthesis of polymers of M_n 2000-3000 g mol^{-1}. For polymers of higher molecular weight the reaction time was adjusted accordingly (**Table 2.1**).

Table 2.1 - Reaction times, temperatures and yields of the PEO homopolymers.

Reaction	Target M_n g mol^{-1}	Polymerisation reaction Time (Temperature)	Total yield of PEO[a] g (%)
PEO 1	1500	24 h (r.t.)	9.98 (101)
PEO 2	3000	24 h (r.t.)	10.95 (103)
PEO 3	6000	16 h (r.t), 16 h (35 °C)	12.47 (100)
PEO 4	12000	12 h (r.t.), 31 h (35 °C)	10.26 (98)
PEO 5	50000	24 h (r.t.), 96 h (35 °C)	10.16 (98)

a **After precipitation into hexane.**

Total yields of PEO after precipitation in hexane were consistent with complete consumption of the monomer, being approximately 100% prior to reprecipitation. Some of the masses of recovered polymer were greater than those expected prior to purification, due to the presence of residual potassium salts. After polymerisation was complete a sample of living PEO solution was taken into a side bulb and terminated with methyl iodide, to be used as unfunctionalised PEO for analysis. The remainder was terminated using 4-vinylbenzyl chloride (4-VBC) in order to synthesise the desired macromonomer. Polymerisations were carried out with approximately 10 g of monomer, with the initiator to monomer ratio varying in order to produce polymers with target molecular weights ranges between 1500 and 50000 (**Table 2.2**) which are discussed further in the following two sections.

Table 2.2 – Molecular weight data for PEO homopolymers.

Sample	Target M_n g mol^{-1}	M_n/DMF GPC g mol^{-1} (PDI)	M_n/^{1}H NMR g mol^{-1}	M_n/MALDI g mol^{-1} (PDI)
PEO MM 1	1500	1100 (1.09)	-	1700 (1.04)
Me PEO 1		1100 (1.10)	1460	1600 (1.05)
PEO MM 2	3000	2400 (1.06)	-	3000 (1.03)
Me PEO 2		2300 (1.08)	3000	-
PEO MM 3	6000	4600 (1.04)	-	4900 (1.04)
Me PEO 3		4500 (1.03)	5400	4700 (1.04)
PEO MM 4	12000	10400 (1.02)	-	10600 (1.01)
Me PEO 4		10300 (1.02)	12100	10800 (1.01)
PEO MM 5	50000	38800 (1.06)	-	-
Me PEO 5		38700 (1.06)	-	-

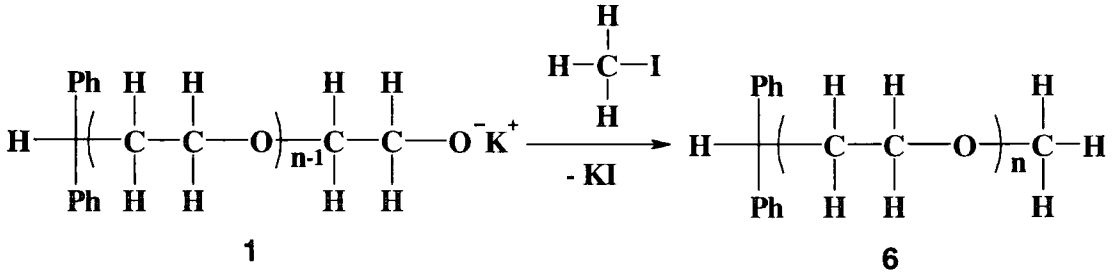
PEO MM = PEO macromonomer, Me PEO = CH_3I terminated PEO.

The polymers of target molecular weight 1500 g mol^{-1} (M_n by GPC: 1100 g mol^{-1}) were waxy solids at room temperature, which made their manipulation in the subsequent steps more difficult and reduced their recovery yields. They were thus

primarily used for assignment of the NMR data from the PEO homopolymers. No block copolymers were prepared using PEO of this molecular weight. All the PEO homopolymers precipitated from solution as powdery, or at higher molecular weights (e.g. M_n = 38700 g mol^{-1}, by GPC) fibrous, solids. PEO-PNB block copolymers were prepared from all the other macromonomers.

2.2.2 The Synthesis and Characterisation of Methyl Iodide Terminated Poly(Ethylene Oxide)

A sample of living PEO was terminated prior to addition of 4-VBC in order to provide a sample of unfunctionalised PEO for analysis. This was accomplished by the addition of an excess (approximately 1.5 equivalents relative to the concentration of living chain ends, dictated by the number of moles of initiator added) of methyl iodide (CH_3I) directly to the living PEO (**1**), yielding PEO with a terminal methyl group, **6** (**Scheme 2.2**).



Scheme 2.2 –Termination of living PEO using CH_3I.

This polymer was used to determine the molecular weight of the PEO homopolymer and to study their NMR properties. The latter shall be discussed first as it was also used to obtain an estimate of the molecular weight. NMR resonances were initially assigned using solutions of polymer in CD_2Cl_2 to avoid interference of the $CHCl_3$ peak with the aryl protons. The polymer with M_n of 1110 g mol^{-1} (GPC) was used to make the assignments with the help of 2D NMR. Regular analyses were carried out in $CDCl_3$, in which the resonances are virtually identical.

The NMR spectrum of PEO is determined by the simple structure of PEO prepared by anionic polymerisation – the polymer can be viewed as a perfect linear rod or coil, without any pendant groups or branching. Nucleophilic attack occurs only at the carbons adjacent to the oxygen, the sole method of addition is therefore head to tail. Thus the PEO does not posses tacticity of any kind and produces NMR spectra, which lack the fine structure inherent in the spectra of most polymers of vinyl

monomers for example. Whilst this simplicity might make its NMR properties of less fundamental interest, it has aided this study. It results in the peaks from the end groups being relatively sharp and well defined when compared with those from polystyrene (Chapter 3) for instance. As previously reported[3] the ^{1}H NMR spectrum is dominated by the methylene protons (A) of the backbone which form a large peak at approximately 3.6 ppm (**Figure 2.2**).

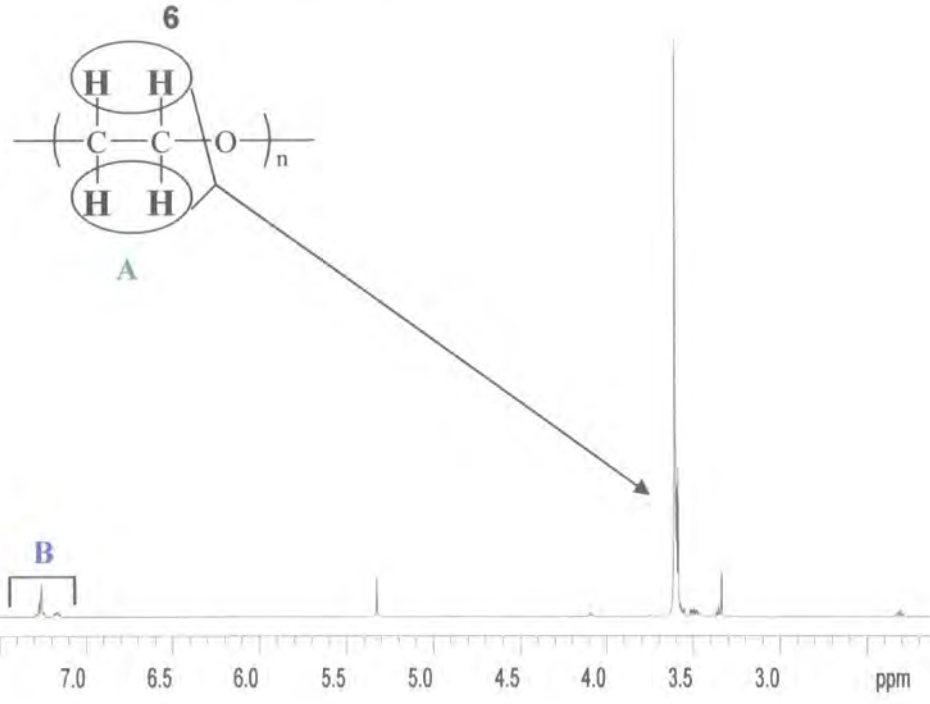


Figure 2.2 – The ^{1}H NMR spectrum of PEO (Sample Me PEO 1, CH_2Cl_2).

On the verges of this peak triplets are discernable, which are the resonances from repeat units close to the end of the polymer chain, as well as carbon satellites of the main peak. The aryl protons appear as broad multiplets between 7.28 and 7.14 ppm (B in **Figure 2.2**) and were not individually assigned. One was tentatively assigned using 2D NMR. Whilst they are partially obscured by the benzylic aryl protons in the macromonomer (Section 2.2.3) they are expected to be a good method for estimating the total integral from 10 protons in the chain of the CH_3I terminated polymer. The molecular weights of the homopolymers were therefore estimated using ^{1}H NMR, by comparing the aryl protons in the initiator residue, with the total integral of the methylene units in the polymer chain. This figure is expected to be a reasonable estimate of M_n for polymers possessing a relatively low molecular weight. A list of

these estimates is provided in **Table 2.2**. The figures are in good agreement with the predicted, although they suggest that the PEO with a target M_n of 6000 g mol^{-1} was slightly (500 daltons) below its predicted weight. No figure was calculated for the PEO synthesised with a target molecular weight of 50000 g mol^{-1} as it was believed such an estimate would be inaccurate.

No detailed assignments for the diphenylmethyl group (introduced via the DPMK initiator) attached to PEO or its effect on the chemical shift of the adjacent methylene units of the first repeat unit was located in the literature. The assignment was however important in this work, in order to use NMR as a quantitative tool for studying the functionalisation of the other end of the polymer chain using 4-VBC. The methine diphenylmethyl proton (**F**), and the methylene protons (**G** and **H**) in the first repeat unit in the polymer chain (which include the only quartet expected from the polymer), were identified and their assignments confirmed using ^{1}H-^{1}H COSY (correlation spectroscopy) (**Figure 2.3**).

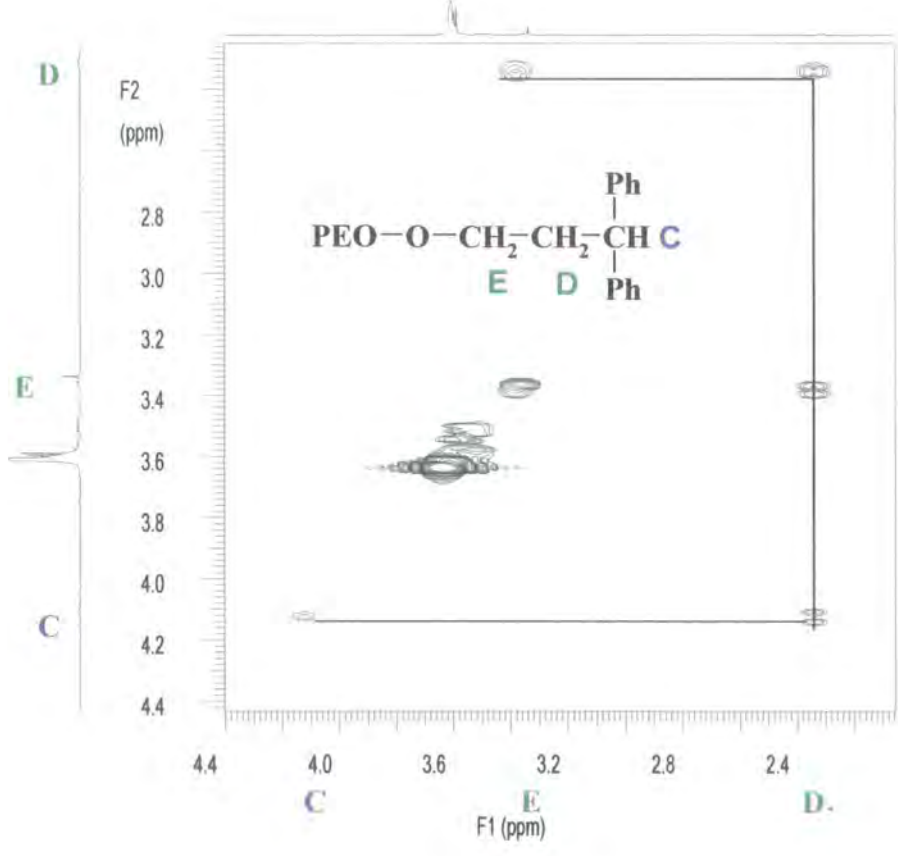


Figure 2.3 – ^{1}H-^{1}H COSY of CH_3I terminated PEO (Sample Me PEO 1, CD_2Cl_2).

^{1}H-^{13}C HMBC (heteronuclear multiple bond correlation) and HSQC (heteronuclear single quantum correlation) spectroscopy confirmed the assignments. The terminal methyl group is observed at a position approximately equivalent to the methylene group of the first repeat unit (**E**) in ^{1}H NMR. The methyl group is not present on the macromonomer discussed in the next section and thus its NMR shifts are not observed. These protons (**C**, **D** and **E** in **Figure 2.3**) therefore provide a value for the total integration from five protons attached to the polymer chain in three different chemically non-equivalent environments. This value can therefore be used to analyse the degree of functionalisation of the macromonomer.

The ^{13}C NMR resonances were mainly assigned with the aid of 2D NMR (HSQC) using the assigned ^{1}H NMR resonances. As with the ^{1}H NMR the most important peak is that of the backbone methylene units, which appear at approximately 70 ppm in ^{13}C NMR (**Figure 2.4**).

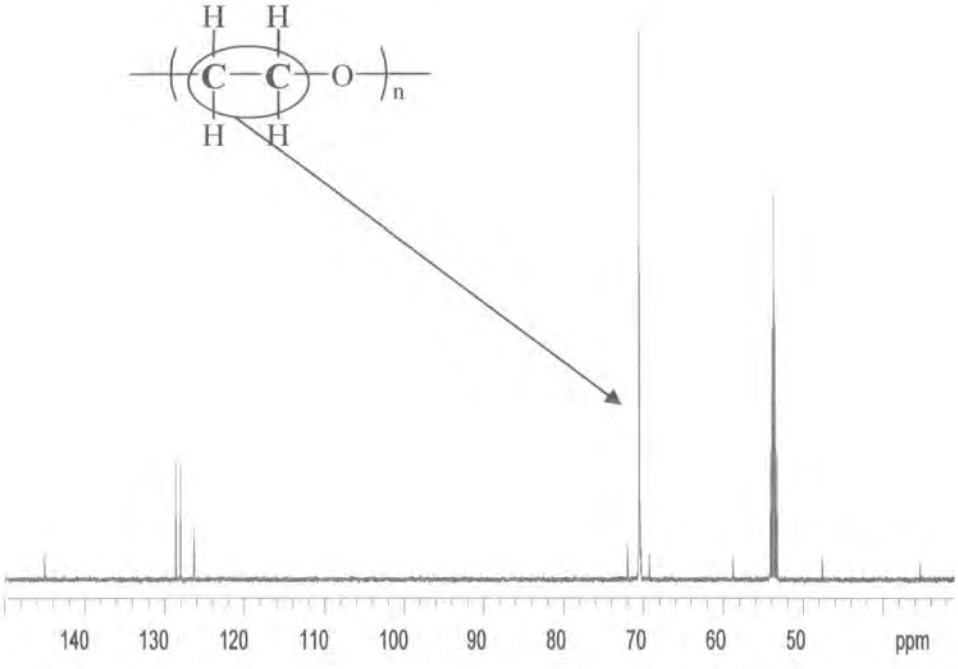


Figure 2.4 - ^{13}C NMR of CH_3I terminated PEO (Sample Me PEO 1 in CD_2Cl_2).

Whilst the aryl protons of the diphenylmethyl group could not be individually assigned, it was possible to assign the carbons of the phenyl groups using 2D NMR and the resonances of the methine proton. The carbon resonance of the terminal methyl group appears at 58.85 ppm and the signal at 72.02 ppm is assigned to the adjacent carbon ($CH_3O\mathbf{C}H_2$-) based on its absence from the ^{13}C NMR spectrum

of the 4-VBC functionalised macromonomer and is consistent with its predicted shift.[5] It was also absent in the spectrum of a sample of PEO (M_n = 2400 g mol^{-1}, by GPC) terminated using a large excess of glacial acetic acid, but whose preparation was otherwise identical. The ^{13}C spectra of methyl and acetic acid terminated PEO were otherwise almost identical, with the exception of a peak at 61.51 ppm (CD_2Cl_2) assigned to the terminal carbon CH_2CH_2OH and that at 73.02 ppm (CD_2Cl_2) assigned to the adjacent carbon CH_2CH_2OH on the basis of their predicted shifts.[5] This peak is not observed in the ^{13}C NMR spectrum of any of the samples described in **Table 2.2**.

The molecular weight of the homopolymer was determined using these CH_3I terminated samples of PEO. Functional groups can interact with GPC columns, resulting in abnormal elution and hence affect the calculated molecular weight.[3] Using unfunctionalised PEO eliminates any effect of the vinylbenzyl group of the macromonomers on GPC analysis. The preferred solvents for GPC analysis of PEO and poly(ethylene glycol) (PEG) are DMF and H_2O, the polymers having poor solubility in THF at higher molecular weights.[6,7] The use of DMF allowed comparison to be made with the PEO-PNB block copolymers – the ROMP blocks are not soluble in H_2O. The DMF GPC instrument was not equipped with a triple-detector array and thus conventional calibration was used. The GPC instrument was calibrated using narrow molecular weight distribution PEG/PEO standards with molecular weights in the range 106-273 000 g mol^{-1}. The results (**Table 2.2** and **Appendix 2.1.1**) indicate that all the samples possess a PDI below 1.1. The values for M_n are consistently slightly below the predicted values. Whilst a certain experimental error might be expected with any analytical technique, some of the GPC values appear to vary from the predicted M_n by a degree more than might be expected (~10%). It is possible that the difference is due to the molecular weight standards used to analyse the polymers being of a slightly higher molecular weight than that certified by the commercial supplier. It is also completely possible that the GPC experiments are detecting a real variation of the molecular weight from that predicted by the stoichiometry.

Most of the polymers were also studied by MALDI-TOF spectroscopy (e.g. **Appendix 2.1.2**) in order to gain another estimate for their molecular weights. PEG and PEO were amongst the first polymers to be studied by MALDI using a number of polar organic matrices.[8,9] Whilst many aspects of ion formation in MALDI are poorly understood and are the subject of current study, cationisation appears to be the major

ion formation process in the MALDI of synthetic polymers.[10] In common with many polar synthetic polymers traces of alkali metals serve as the cationisation agents.[8] PEO (and many other polar synthetic polymers) are generally cationised by trace amounts of sodium in the form of impurities, introduced either from the sample or from the matrix or solvent. They are thus observed as Na adducts in the resulting spectrum, although sometimes K adducts are present as well.[8,11] The MeI terminated polymers produced in this study appear mainly as adducts with K (**G**), and only to a much lesser degree with Na (**F**) (**Figure 2.5**).

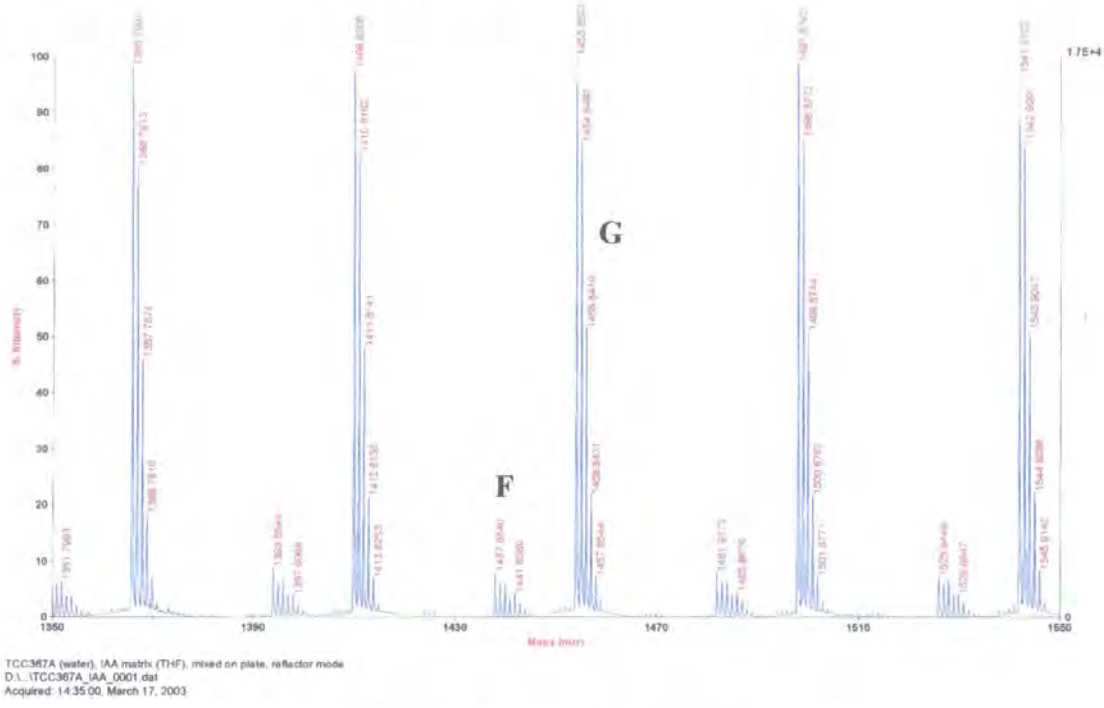


Figure 2.5 - MALDI of Me PEO 1.

The presence of trace amounts of KI (and/or other K salts) left behind as impurities from the synthesis of the polymers, is most likely to have resulted in an excess of K impurities relative to Na in the sample, thus favouring cationisation with K. The peaks were observed in the same ratios at higher molecular weight, although the resolution in the spectrum of sample of Me PEO 4, M_n: 10750 g mol^{-1} (By MALDI) was insufficient to resolve the two peaks.

Molecular weights of PEG and PMMA have been compared previously by GPC and MALDI.[11] The results from that study indicated a good comparison between the two techniques, the two producing values within 10% of each other for the two samples (PEG, M_n : 5000 g mol^{-1}, PMMA M_n: 5000 g mol^{-1}). The level of consistency between these MALDI and GPC values was of a similarly high level, for samples of

M_n 5000 g mol^{-1} and above. Intriguingly MALDI analysis of samples of lower molecular weight produced values closer to those predicted by the stoichiometry of the reaction than GPC. MALDI produced even lower values for PDI than those from GPC. However, MALDI is usually a less accurate method for determining polydispersity than GPC,[8] giving lower PDI values for PEO.[11]

The results of the analytical study of the molecular weights of the PEO samples tend to indicate that they are of a slightly lower M_n than that predicted by the reaction stoichiometry. In all cases the assumption was made that the initiator solution possessed a concentration of 1.0 M and the GPC results suggest that the actual concentration of the solution might be higher than this.

2.2.3 The Synthesis and Characterisation of Poly(Ethylene Oxide) Macromonomers

The PEO was functionalised with 4-VBC in order to produce macromonomer which was suitable for conversion to macroinitiator. The living chain ends comprising a potassiated hydroxyl group are sufficiently nucleophilic to react quantitatively with a halide functionality, even in the presence of a vinyl group.[3] 4-VBC was used as it introduced the required structure to the end of the PEO chains for conversion to macroinitiators for living ROMP (Section 2.3.5). 4-VBC supplied by Sigma-Aldrich contains impurities such as α-chloromethyl styrene (2%), dichloromethyl styrene (3%) and 3-vinylbenzyl chloride (3-VBC, 5%) in the 4-VBC. It was however the only commercially available alkyl halide, that would impart a vinylbenzyl group suitable for the macroinitiator synthesis. Functionalisation was accomplished by the addition of 1.2 equivalents of 4-VBC direct to the living chain ends, **1** (**Figure 2.6**):

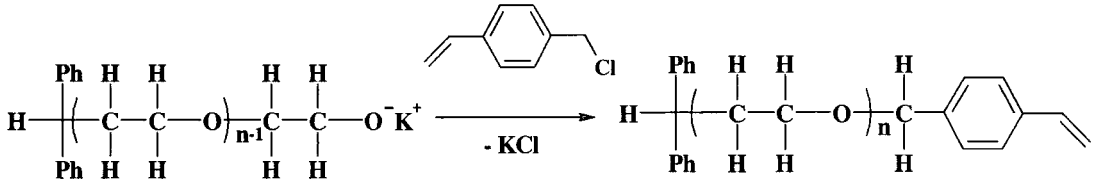


Figure 2.6 - Functionalisation of living PEO with 4-VBC.

As expected the NMR spectra of the macromonomers are very similar to that of the unfunctionalised PEO discussed in the previous section. The resonances of the vinylbenzyl functionality undergo little change upon incorporation into the PEO

macromonomer. Even the benzyl methylene group appears at a similar ^{1}H resonance, in both 4-VBC and the macromonomer, as would be expected due to the magnetic equivalence of O and Cl substituted groups in ^{1}H NMR spectroscopy.[12] They however possess different ^{13}C shifts (**Appendix 2.1.3**), the carbon falling at approximately 46 ppm in 4-VBC and 73 ppm in the PEO macromonomer. The NMR resonances of the aryl protons and carbons of the vinylbenzyl group of the macromonomer were assigned using two dimensional spectra of the macromonomer and by comparison with the spectra of 4-VBC. Unfortunately there is overlap between the aryl protons of the vinylbenzyl functionality and that of the diphenylmethyl group, precluding their use as a measure of functionalisation. Close examination of three of the peaks in the spectrum (𝕁, 𝕂 and 𝕀 in **Figure 2.7**) indicates the presence of a slight shoulder downfield on them which is attributed to 3-VBC functionalised macromonomer. This situation is similar to that observed in VBC, the vinyl and benzylic chloromethyl groups of the *meta* and *para* isomers being observed at approximately identical shifts in NMR.[13] No evidence of other end groups was found by NMR – no other peaks were observed in the ^{1}H NMR spectrum of even the lowest M_n macromonomer (PEO MM 1). The vinyl protons (𝕀, 𝕁 and 𝕂 in **Figure 2.7**) and the methylene protons (𝕀) were used to assess the degree of functionalisation of the macromonomer. The integrals of these five protons can be compared with the integrals from five protons at the other end of the chain (ℂ, 𝔻 and 𝔼 in **Figure 2.7**) in order to gain a value for the yield of functionalisation. An attempt was also made to increase the accuracy of this figure by presaturating the large PEO peak at 3.6 ppm (𝔸) with radio frequency waves prior to every scan, removing the effect of its integral from that of neighbouring peaks such as ℂ and 𝔼.

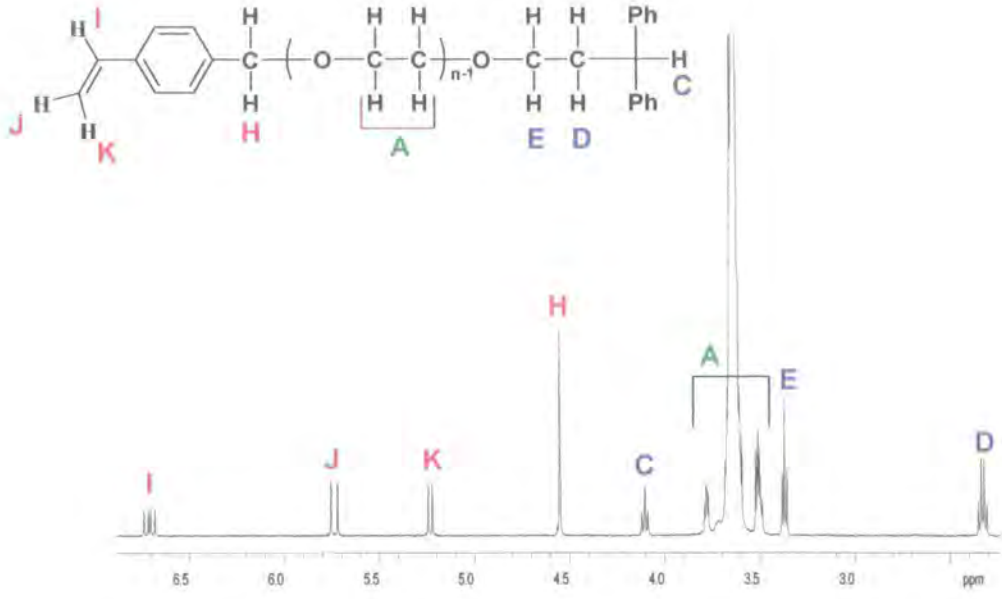


Figure 2.7 - ^{1}H NMR of end groups used for analysis of functionalisation ($CDCl_3$).

The reaction was first performed with 10 equivalents of 4-VBC in preliminary work. ^{1}H NMR indicated that the degree of functionalisation was approximately 85%. Decreasing the amount of 4-VBC increased the yield of capping, probably indicating the presence of trace amounts of an impurity in the VBC capable of reacting faster than 4-VBC with the living chain ends. Macromonomers prepared with 1.2 equivalents of 4-VBC had a yield of functionalisation of 95% or above. The end-capping reactions were left running overnight (at r.t) to ensure complete reaction. Leaving the reaction for longer (3 days) or increasing the temperature to 50 °C had no discernable effect on the functionalisation.

The macromonomers were analysed by GPC in DMF solvent using identical conditions to those used for the unfunctionalised polymers. Despite initial concern that the functional group might interfere with analysis, the results are very similar to those of the homopolymer (**Table 2.2**). The GPC traces remain mono-modal and no evidence of coupling is observed, which is expected from the reaction of dichloromethyl styrene (an impurity in 4-VBC) with the living chain ends (**Figure 2.8**).

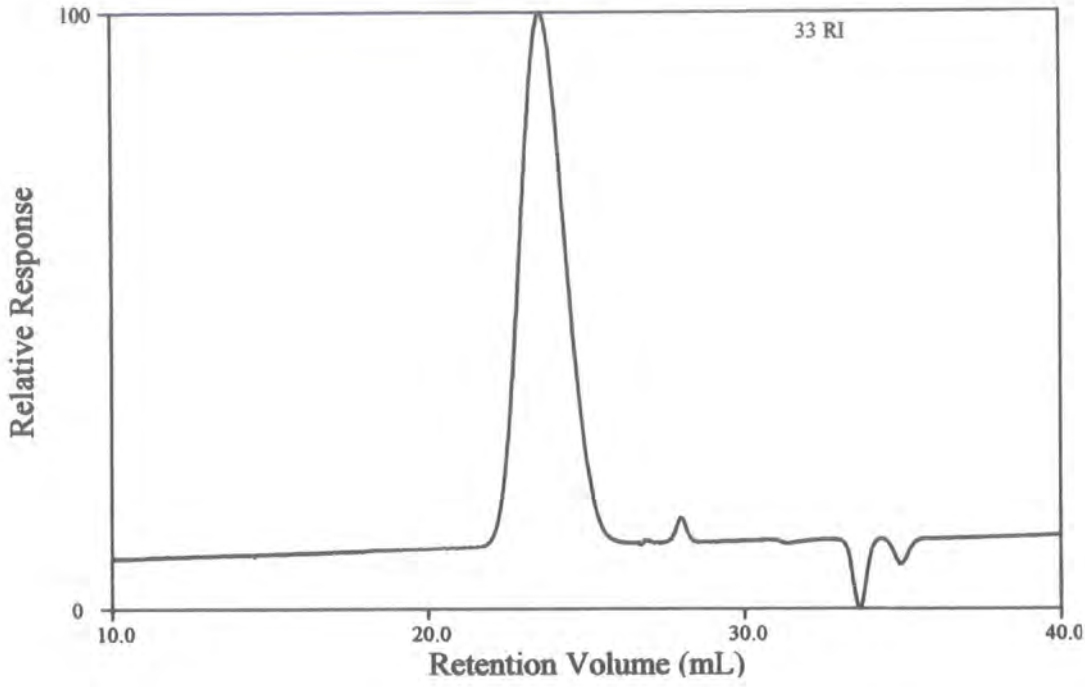


Figure 2.8 - DMF GPC Chromatogram of PEO MM 1.

The macromonomers were also studied by MALDI, producing similar results for molecular weights to those found for the CH_3I terminated polymer (**Table 2.2**). No significant difference was observed between the spectra of sample PEO MM1, obtained with the MALDI in either linear, or reflector mode. MALDI also offers the possibility of examining the end groups (**Figure 2.9, 2.10** and **Appendix 2.1.4**). KCl is generated by the reaction of 4-VBC with the living chain ends, so as with the CH_3I terminated polymer discussed in the previous section we would expect a substantial amount of the polymer to be cationised as a K adduct The ratios of Na to K adduct appear to be higher than in the CH_3I terminated PEO. This might be explained by the fact that the macromonomer contained traces of KCl rather than KI. Studies on PMMA indicate that the alkali metal iodides are slightly more efficient cationisation agents than chlorides,[10] although KCl is sufficiently effective to be used as an additive for polar synthetic organic polymers to increase their cationisation yield.[8] The principal peaks can be interpreted as 4-VBC functionalised peaks with K (L) and Na (M) adducts. Only a small amount of unfunctionalised (OH) polymer as a K adduct (N) is observed, expected from chains terminated by protic impurities. This suggests a high degree of functionalisation of the PEO macromonomer with 4-VBC. Unfortunately the corresponding Na adduct's (O) molecular weight coincides with that of the adduct of the macromonomer with K (L) (with a lower DP), and so it

cannot be observed directly.

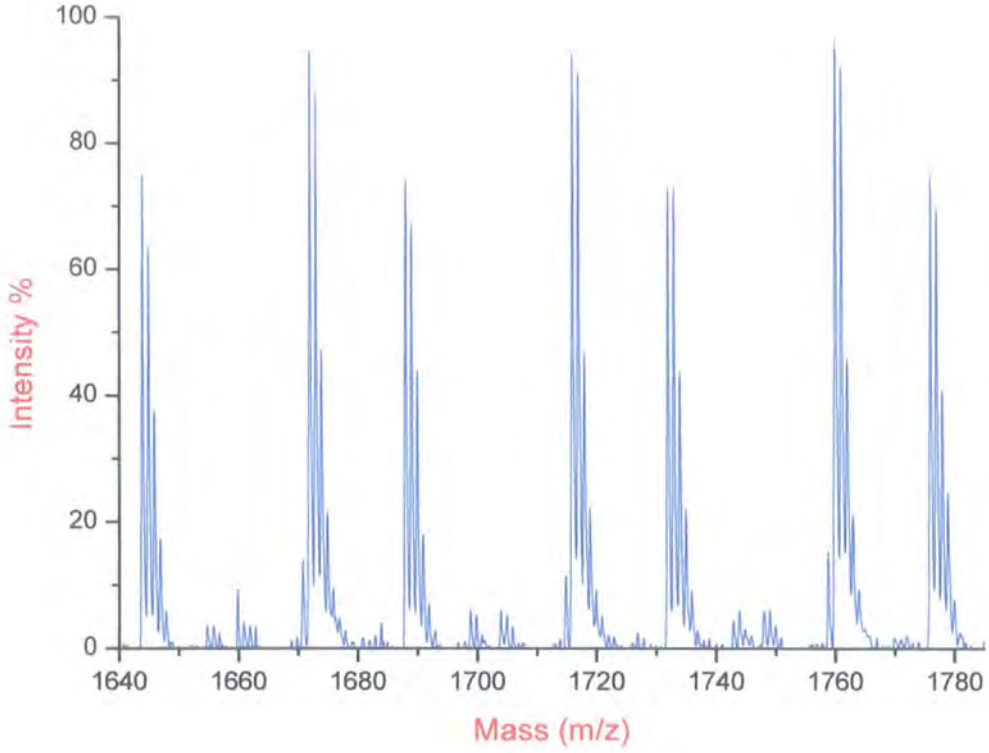


Figure 2.9 – Observed MALDI spectrum of a PEO macromonomer (PEO MM 1).

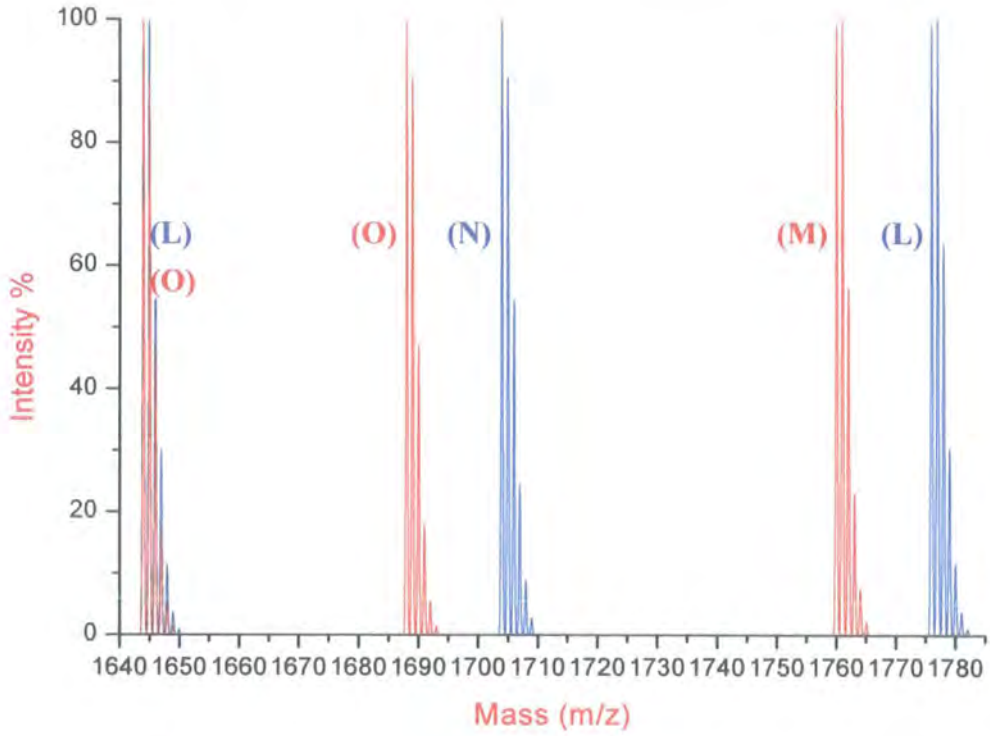
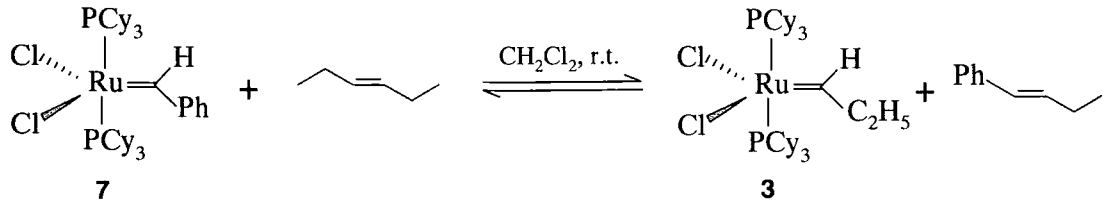


Figure 2.10 Selected possible MALDI peaks. For macromonomer (L): $C_{13}H_{11}(C_2H_4O)nC_9H_9K$, (M): $C_{13}H_{11}(C_2H_4O)nC_9H_9Na$. For unfunctionalised polymer (N): $C_{13}H_{11}(C_2H_4O)nHK$, (O): $C_{13}H_{11}(C_2H_4O)nHNa$.

An alternative interpretation is that the Na adducts are dominant and that the unfunctionalised (OH) and 4-VBC functionalised polymer are observed in almost equal quantities, because end groups can affect the efficiency of ionisation and yields of the polymer ions.[8] In other words adducts of the two polymer chains might not be observed in proportions equal to their concentration in the sample. This interpretation seems unlikely based on the previous results from NMR. In either case it is therefore not possible to quantitatively determine the ratios of the two end groups in the sample by MALDI with any certainty. The peaks were observed in very similar ratios at molecular weights higher than that in **Figure 2.9**, up until the spectrum of M_n: 10640 g mol^{-1} (by MALDI) where the resolution was insufficient to separate the peaks.

2.2.4 Synthesis and Characterisation of Ruthenium Propylidene Complex $RuCl_2(=CHEt)(PCy_3)_2$.

Schwab and co-workers[14] demonstrated that metathesis reactions of olefin substrates with well defined ruthenium initiators leads to the exchange of the alkylidene group of the initiator and the formation of a new initiator. The formation of new ruthenium alkylidene species can be observed by NMR spectroscopy, and in some cases they can be isolated as pure compounds. They reported the synthesis of $RuCl_2(=CHEt)(PCy_3)_2$ by reaction of the ruthenium benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ with an excess (10 equivalents) of 1-butene (b.p. –6.3 °C). The authors of this work also indicated that the same species could be obtained by a similar reaction with *cis*-3-hexene, a more facile reaction since *cis*-3-hexene is a liquid at room temperature. The kinetics of the formation of ruthenium propylidene initiator from the reaction of *cis*-3-hexene and *trans*-3-hexene with benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ have also been compared by ^{1}H NMR studies.[15] Although these kinetic studies indicate that the *cis* isomer is more reactive than the *trans* isomer, in the work reported here we sought to develop a synthetic protocol using *trans*-3-hexene (b.p. 67 °C). The reason for this is that the *trans* isomer is more readily available and significantly cheaper than the *cis* isomer. The alkylidene exchange reaction is an equilibrium reaction (**Scheme 2.3**):



Scheme 2.3 Synthesis of $RuCl_2(=CHEt)(PCy_3)_2$. Cy = cyclohexyl.

Due to this equilibrium, in order to drive the reaction to completion the olefin byproduct 1-phenyl-1-butene must be removed. The relatively high boiling point of the byproduct (195-200 °C)[16] makes complete extraction under vacuum at moderate temperatures difficult. The most efficient method found to clean the product was to wash it as a paste with acetone at -30 °C, just above the m.p. of the byproduct (~-40 °C). This removed the majority of the impurities from the product, although a small amount of olefinic impurities remained after the first work up, none were present in the final product.

The reaction of $RuCl_2(=CHPh)(PCy_3)_2$ and *trans*-3-hexene was first studied in $CDCl_3$, comparison with the reaction in CD_2Cl_2 indicated the former to be substantially faster to reach equilibrium. Unfortunately, whilst exposure to subsequent excesses of *trans*-3-hexene removed benzylidene from the sample, it also resulted in the growth of two further peaks in the ^1H NMR spectrum, one of which at 19.24 – 19.26 ppm (CD_2Cl_2), is assigned to the quartet of ethylidene complex $RuCl_2(=\mathbf{CHCH_3})$-$(PCy_3)_2$(**8**).[14] A small sharp singlet is observed at 18.95 ppm, which is assigned to methylidene $RuCl_2(=\mathbf{CH_2})(PCy_3)_2$(**9**).[14] This is believed to be due to the significantly higher rate of reaction of the ruthenium benzylidene and/or propylidene with traces of other hexene isomers (e.g. 2 and 1-hexene) in *trans*-3-hexene[17] when in $CHCl_3$, compared with that in CH_2Cl_2. No signs of **8** or **9** were detected in propylidene produced in dichloromethane with a similar concentration of *trans*-3-hexene, hence samples were synthesised in CH_2Cl_2. Increasing the stoichiometry from 5 to 31 equivalents of *trans*-3-hexene was also observed to have the effect of increasing the rate of conversion of benzylidene to propylidene significantly (the exact rate varied slightly). It was decided however to adopt an approach that made more efficient use of *trans*-3-hexene for preparative reactions and thus a longer reaction time was adopted.

Solubility tests on the ruthenium benzylidene and propylidene in a wide range of organic solvents, indicated that the propylidene had similar solubilities to the

benzylidene. Therefore, there appears to be no possibility of washing out substantial amounts of the benzylidene, hence virtually all of it must be consumed by reaction with *trans*-3-hexene. In total three additions of 5 equivalents of *trans*-3-hexene to $RuCl_2(=CHPh)(PCy_3)_2$ in CH_2Cl_2, were required to drive the reaction to completion. Approximately 90% conversion was observed after the first addition. This was determined by comparison of the ^1H NMR resonance of the alkylidene proton from the ruthenium benzylidene initiator at 20.62 ppm in C_6D_6 and that of propylidene at 19.61 ppm in C_6D_6 (the propylidene is observed at 19.12 ppm in CD_2Cl_2 and 19.16 ppm in $CDCl_3$). After two further additions no residual signal from the starting material at 20.62 ppm was observed by ^1H NMR (**Figure 2.11**).

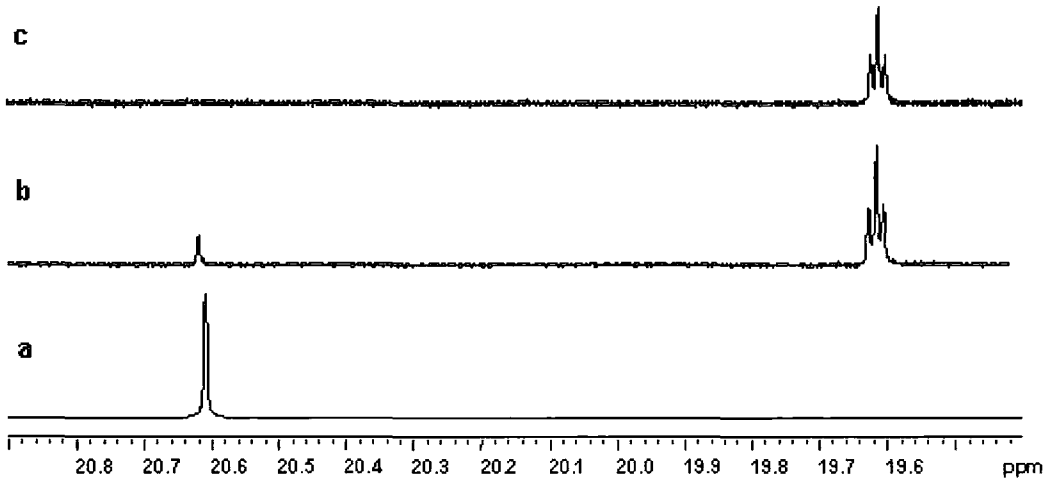
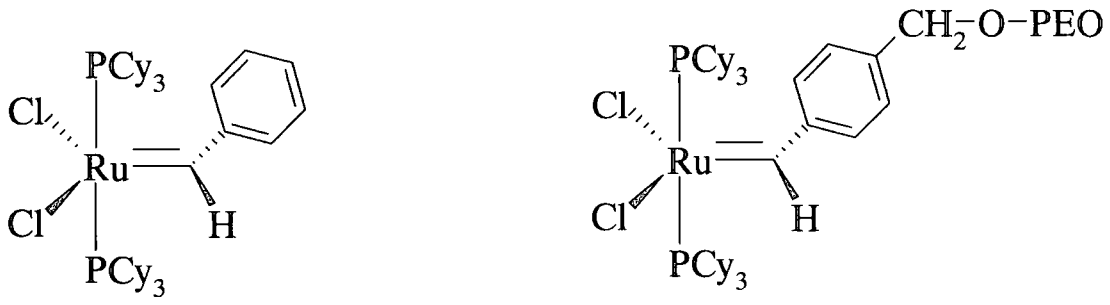


Figure 2.11 ^1H NMR analysis of alkylidene exchange reaction in the synthesis of $RuCl_2(=CHEt)(PCy_3)_2$. (C_6D_6)
a Alkylidene region for ruthenium benzylidene initiator.
b The alkylidene region after addition of 5 equivalents of *trans*-3-hexene to the benzylidene initiator.
c The alkylidene region after performing three additions of 5 equivalents of *trans*-3-hexene.

The product was isolated as a purple solid, which formed a red solution in benzene and chlorinated solvents. The sole peak in the ^{31}P NMR spectrum (**Appendix 2.2.2**) of the final product is that of the propylidene at 37.10 ppm. Only one alkylidene carbon is visible in the ^{13}C NMR spectrum (**Appendix 2.2.3**) at 322.66 ppm. It is observed as a multiplet due to its extremely low field shift, the NMR instrument was incapable of proton decoupling peaks in the spectrum at this point. Coupling between phosphorus and some of the carbons in the PCy_3 rings is also observed by ^{13}C NMR, resulting in the formation of pseudo-triplets.[14]

2.2.5 Synthesis and Properties of PEO Ruthenium Macroinitiators

The structure of the PEO ruthenium macroinitiators was chosen in order to be as similar as practically possible to that of the well-defined ruthenium initiator $RuCl_2(=CHPh)(PCy_3)_2$, which is the most commonly used initiator for living well-defined ruthenium ROMP[18,19] (**Figure 2.12**).



7 **4**

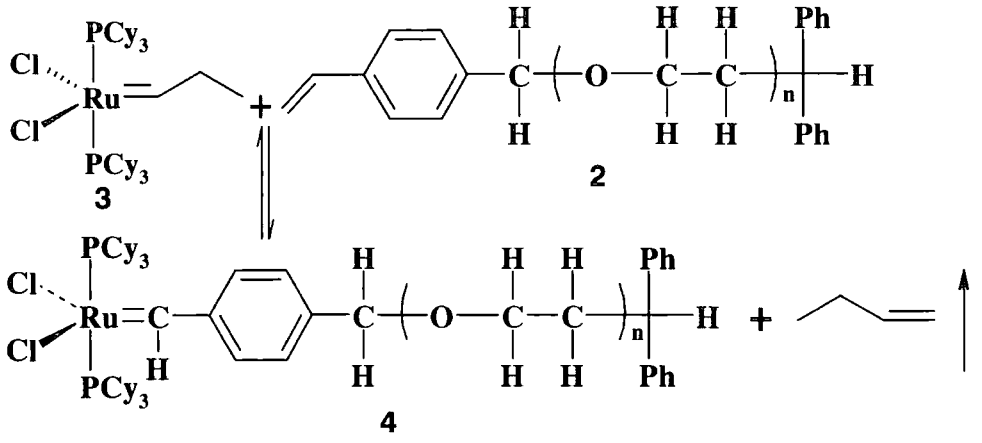
Figure 2.12 - Ruthenium benzylidene initiator and PEO ruthenium macroinitiator.

The macroinitiators (**4**) can thus be viewed as analogues of ruthenium benzylidene initiator **7**, in which the aromatic ring is substituted with PEO in a *para* position relative to the alkylidene carbon and proton.

The macroinitiators were synthesised from a metathesis reaction of the vinyl group of the 4-VBC functionalised PEO macromonomers using a well-defined ruthenium alkylidene initiator. This leads to alkylidene exchange between the two and the incorporation of the PEO into the ruthenium initiator in the form of the alkylidene ligand. In a preliminary experiment, Grubbs benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$ was used for the macroinitiator synthesis. However, the byproduct of the forward reaction in this exchange is styrene and in order to drive the reaction to completion the styrene had to be distilled from the reaction mixture, followed by addition of fresh solvent. This process was repeated six times. Whilst ^1H NMR indicated that complete exchange did occur, it was a slow and laborious process.

Using the ruthenium propylidene complex (**3**) for the macroinitiator synthesis the byproduct of the forward reaction is 1-butene, a gas at room temperature and atmospheric pressure (**Scheme 2.4**). This means that the olefin byproduct can be removed in-situ driving the reaction to completion – full conversion of **3** into the macroinitiator (**4**). This offers the advantage of preparing a number of different

macroinitiators in a single step reaction from a single batch of propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$.



Scheme 2.4 Synthesis of ruthenium PEO macroinitiators.

Initially the PEO macromonomer precursor polymer and propylidene initiator were dissolved and mixed together under a flow of nitrogen. Unfortunately methylidene $RuCl_2(=CH_2)(PCy_3)_2$ was observed in solution, the thermodynamic (though reportedly not kinetic) product of the reaction of 1-butene with ruthenium initiators.[14] This indicates that 1-butene's solubility in the reaction mixture allowed it to induce further alkylidene exchange – potentially leading to a number of side reactions. The problem was solved by bubbling a flow of an inert gas (e.g., O_2 free argon) through the solution of propylidene prior and during dropwise addition of the solution of PEO macromonomer. The flow of argon was continued for another hour to completely convert all the macromonomer into macroinitiator – no peaks were evident in the olefinic region of the ^1H NMR of the reaction mixture in C_6D_6 at this point. Complete conversion of macromonomer to macroinitiator was still not observed in experiments carried out in CD_2Cl_2 after this length of time. This could simply be due to the reduced flow rate of argon forced by the lower b.p. of this solvent, resulting in a small amount of 1-butene persisting in solution or greater solubility of the olefin in CD_2Cl_2. It was judged that a greater reaction time was undesirable, as it might lead to decomposition of the macroinitiator leading to the formation of inert PEO homopolymer as an inseparable contaminant. To avoid human exposure to benzene vapour the argon was passed out from the system through a sealed bubbler, which was exhausted into a fume cupboard. The concentrated solution of propylidene was added dropwise by cannula to chilled hexane to yield pure macroinitiator. ^1H NMR (**Figure**

2.13) shows the complete loss of the signal for the alkylidene proton of the ruthenium propylidene, a triplet at 19.61 ppm in C_6D_6, and the emergence of the new alkylidene proton signal for PEO-Ru macroinitiator, a singlet at 20.56 ppm (observed at 19.96 ppm in CD_2Cl_2 and 19.93 ppm in $CDCl_3$).

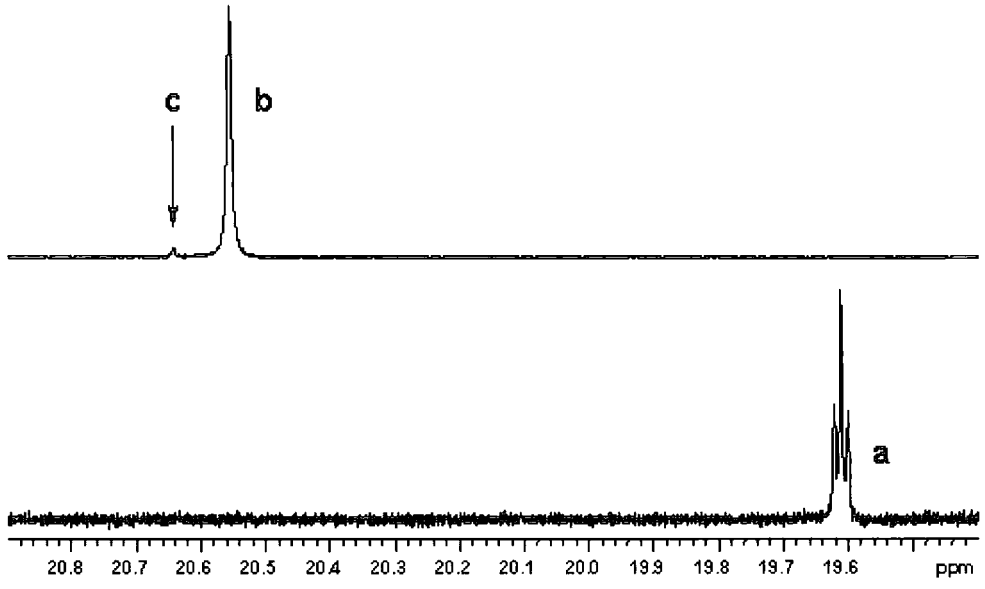


Figure 2.13 Comparison of the ^1H NMR analysis of the ruthenium propylidene initiator and the PEO macroinitiator formed as a product of the alkylidene exchange reaction between the propylidene initiator and PEO macromonomer. (C_6D_6)
a Alkylidene proton of ruthenium propylidene initiator.
b Alkylidene proton of PEO ruthenium macroinitiator from 4-VBC functionalised PEO macromonomer.
c Alkylidene proton of PEO ruthenium macroinitiator from 3-VBC functionalised PEO macromonomer.

The ^1H NMR spectrum also contains a small peak at 20.64 ppm (**c** in **Figure 2.13**), which is believed to be due to macroinitiator in which the PEO is in a *meta* position relative to the alkylidene proton. The 4-VBC used in this research contains a trace of 3-VBC. This will also react with the living PEO during the end functionalisation reaction and will eventually result in a trace of PEO ruthenium macroinitiator with *meta* substitution on the benzylidene ring. To rule out the possibility that this small peak was a trace of ruthenium benzylidene $RuCl_2(=CHPh)(PCy_3)_2$, a solution of benzylidene in C_6D_6 was added to a solution of the macroinitiator in C_6D_6 . This lead to the addition of a third peak to the ^1H NMR spectrum at approximately 20.61 ppm, the same position the alkylidene proton of $RuCl_2(=CHPh)(PCy_3)_2$ had been previously observed to fall. The other two alkylidene

peaks remained unchanged. In order to rule out the unlikely possibility that an olefin from the 4-VBC (either 4-VBC or one of the other possible impurities) used to functionalise the PEO was present in the final product, a sample of 4-VBC was added to the benzylidene. No peak was generated that was close to that of the suspected 3-VBC peak at 20.64 ppm, ruling out this as the source of the peak. The NMR resolution of the end groups is of a similarly high standard to the CH_3I terminated PEO and the macromonomers due to the absence of microstructure in PEO, as discussed earlier. A single sharp peak in ^{31}P NMR spectroscopy (**Appendix 2.3.2**) was observed at 37.14 ppm from the tricyclohexylphosphine ligands, in contrast to the broad peak observed in polystyrene macroinitiators (Chapter 3). The ^{13}C NMR (**Appendix 2.3.3**) is a combination of the PEO homopolymers and benzylidene. The alkylidene carbon was not observed, presumably due to the low concentration of the alkylidene group expected in the samples. The lack of proton decoupling of peaks at this point would lead it to be broader than is usual and might be expected to make it more difficult to differentiate between it and the baseline. As with the propylidene initiator (Section 2.2.4) coupling between some of the carbons in the PCy_3 ring and P is observed.

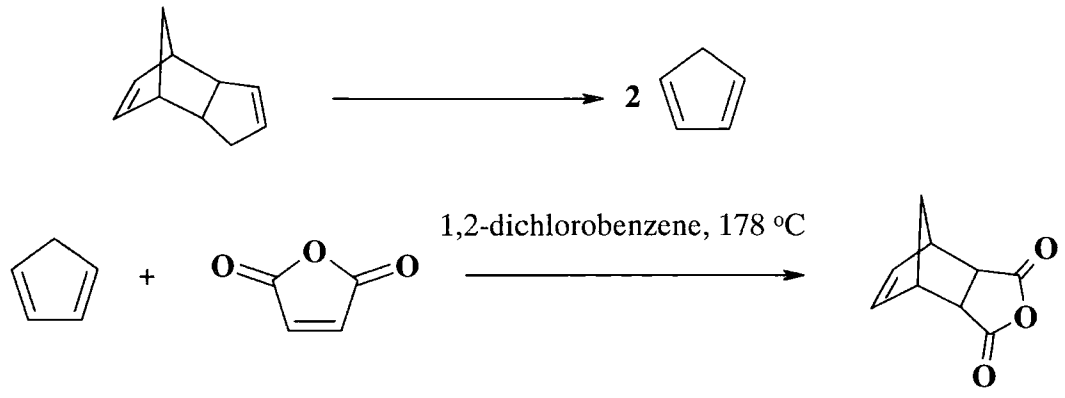
A series of PEO macroinitiators were synthesised with the number average molecular weight (M_n) of PEO ranging from 2400 to 38800 g mol^{-1}. The same reaction conditions were suitable for the preparation of macroinitiators from PEO macromonomers of all the molecular weights investigated. The only difference was the quantities of solvent used to dissolve the macromonomer and propylidene initiator. The macroinitiators were isolated as pink or light purple solids similar in physical appearance to that of the corresponding homopolymer (with the exception of colour). They possessed good solubility in C_6H_6 and CH_2Cl_2 forming purple solutions which were very similar in colour to those of benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$.

A study of the effect of adding unfunctionalised PEO to benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$ in $CDCl_3$ indicated that PEO had no effect on the stability of the initiator relative to a benzylidene control. Studies of the stability of the ruthenium PEO macroinitiators in solution in CD_2Cl_2 and C_6D_6 indicated that they also possessed a similar stability to that of a control containing the benzylidene initiator, whose stability and decomposition has been studied previously.[20] The macroinitiators

were however significantly less stable than the benzylidene in $CDCl_3$ (degassed and dried with either CaH_2 or P_2O_5), though the exact rate of decomposition varied from batch to batch of solvent (no correlation with the identity of the drying agent was observed). Chloroform reacts slowly with oxygen or oxidising agents mainly producing phosgene ($COCl_2$), Cl_2 and HCl.[21] HCl in particular is likely to be a potential agent for the decomposition of the ruthenium centre, and is likely to be present in different concentrations in batches of commercially obtained chloroform depending on their age and storage prior to being received. The reason for the greater sensitivity of the macroinitiators relative to the benzylidene to these impurities could be due to increased sensitivity of the ruthenium-alkylidene double bond caused by substitution on the benzylidene ring. A simpler explanation is that it relates to the lower concentration (in moles) of alkylidene groups in the experiments carried out with the macroinitiators, relative to those using benzylidene (both were carried out at a concentration of 14 mg/mL). All analysis of the ruthenium compounds was therefore carried out in C_6D_6 and ROMP reactions with the macroinitiator performed in CH_2Cl_2 or C_6H_6.

2.2.6 Synthesis of an *Exo* Dicarboxyimide Norbornene Monomer

Exo-N-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide was used as a monomer (**A**) in this study. Dicarboxyimides of this type are most conveniently obtained through the intermediate, *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride. The dicarboxy anhydride is prepared by the Diels-Alder reaction of 1,3-cyclopentadiene (CPD) and maleic anhydride via reflux in 1,2-dichlorobenzene at 178 °C (**Scheme 2.5**). The CPD is itself formed *in situ* from the cracking of dicyclopentadiene (DCPD) at this temperature.



Scheme 2.5 – Synthesis of *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride.

The kinetic product of this reaction as with all other Diels-Alder reactions is the *endo* isomer. Reaction of CPD with maleic anhydride at r.t. yields virtually pure *endo* isomer.[22] At higher temperatures conversion of the *endo* isomer into the *exo* isomer is thermodynamically favoured until equilibrium is reached. However, pure *exo* dicarboxy anhydride can be obtained through multiple recrystallisations from acetone. The Diels-Alder reaction is quick as the alkene (dieneophile) - maleic anhydride has electron withdrawing substituent groups (CO) which promotes reaction and the diene, DCPD, being cyclic is locked in a position where the alkenes are *cis* to each other.[23] This increases the rate of reaction because dienes must be in a *cis* position for reaction to occur. In this work the reaction was refluxed for 6 hours to ensure that equilibrium between the two adducts was reached. The product was recrystallised six times from acetone until pure *exo* adduct was obtained, as evident from the disappearance of the peak at 6.30 ppm (acetone-d_6) due to the *endo* olefinic protons, leaving just those of the *exo* derivative at 6.37 ppm (**Figure 2.14**).

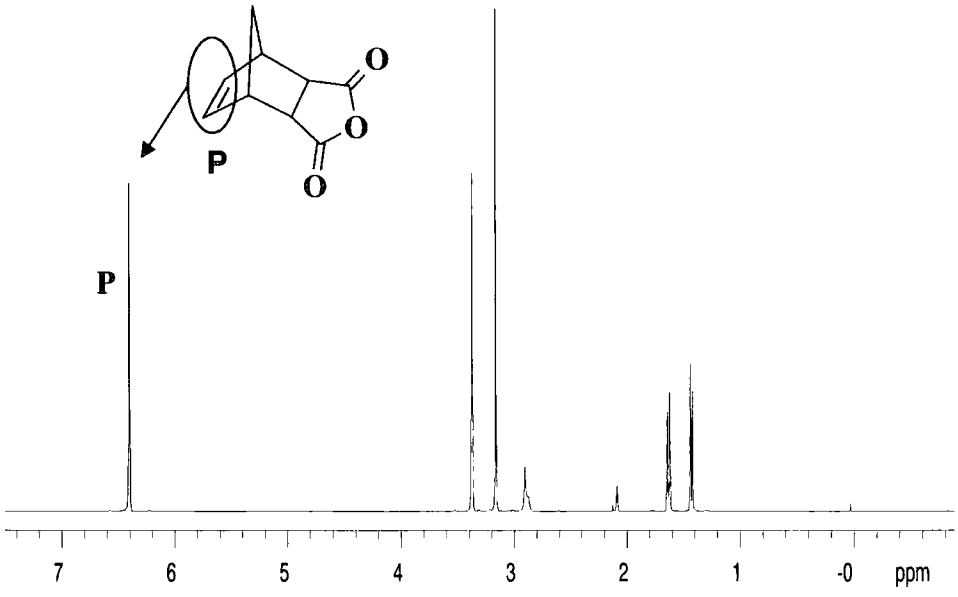
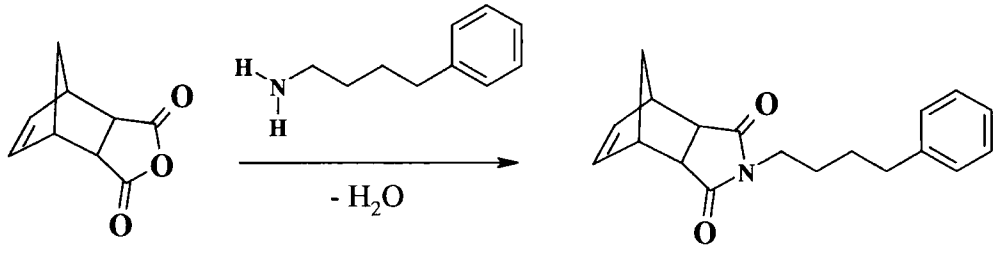


Figure 2.14 – Pure *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride in acetone-d_6.

All analytical data for the product was consistent with that previously published (**Appendix 2.4.1** and **2.4.2**).[24,25]

The condensation reaction of the dicarboxy anhydride with a primary amine has been used on a number of occasions as a source of N heterocyclic containing norbornene derivatives for use as ROMP monomers.[25,26] The reaction was used to prepare monomer **A**, *exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide which was polymerised with the ruthenium macroinitiators in this study (**Scheme 2.6**).



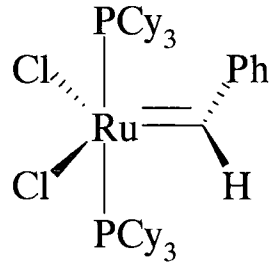
Scheme 2.6 - Synthesis of NBE monomer A

Norbornene anhydride and 4-phenylbutylamine were refluxed in glacial acetic acid and was added to H_2O. The product was extracted from the crude heterogeneous mixture using CH_2Cl_2. The CH_2Cl_2 extract was thoroughly washed using H_2O to ensure removal of acetic acid from the monomer. The solution was dried over $MgSO_4$

and the solvent was removed under reduced pressure to yield a solid whose purification is described in Section 2.4.7. All analytical data were consistent with the desired structure (**Appendix 2.4.3 – 2.4.5**).

2.2.7 Synthesis and Characterisation of PNB Homopolymers

This section describes the polymerisation of three different norbornene monomers using the well-defined first generation bis(tricyclohexylphosphine) ruthenium benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$. These monomers were used to form the ROMP blocks of the PEO-PNB block copolymers discussed in Section 2.2.6, and later the polystyrene(PS)-PNB block copolymers described in Chapter 3. The macroinitiators used to prepare these block copolymers can be viewed as derivatives of the benzylidene initiator (**Figure 2.15**).



7

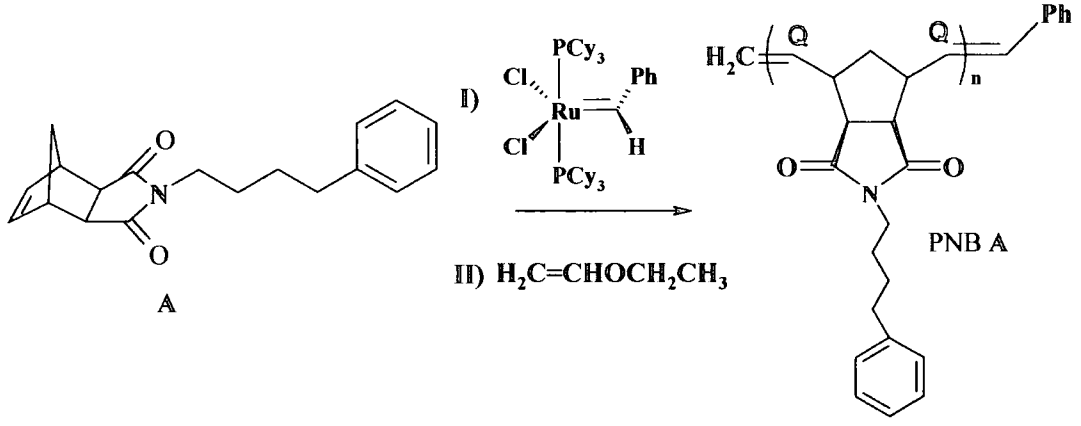
Figure 2.15 - Benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$. Cy = cyclohexyl.

The polymerisation of these monomers with benzylidene initiator (**7**) was carried out in order to predict their behaviour with the macroinitiators and provide analytical data for the resulting polymers (chiefly NMR and GPC) to allow comparison with the PEO-PNB and PS-PNB block copolymers.

2.2.7.1 The Synthesis and Characterisation of Poly(*exo*-*N*-Phenylbutylbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxyimide) – PNB A

The first of the three monomers whose polymerisation with $RuCl_2(=CHPh)(PCy_3)_2$ (**7**) was investigated is a dicarboxyimide norbornene derivative. These monomers have been investigated extensively at Durham as components of linear, branched and network polymers using well defined molybdenum and ruthenium as well as classical initiators.[18,27] Adamantyl derivatives have recently been reported to produce polymers with high glass transition

temperatures using first generation well-defined ruthenium initiators.[28,29] *Exo-N*-alkyl and *N*-phenyl alkyl dicarboxyimide norbornene derivatives have been shown to polymerise quickly with ruthenium initiators producing polymers that typically possess fairly narrow molecular weight distributions.[25,30] The alkylidene proton of the active ruthenium propagating species can be observed directly by ^{1}H NMR during the course of the reaction (which takes 10 minutes for 30 equivalents), appearing as a doublet at around 19.5 ppm.[25] This signal persists after the end of the reaction and addition of further monomer results in the growth of the polymer chain, suggesting a living polymerisation. *Exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide – NBE monomer **A**, (100 equivalents) was subjected to ROMP using 7 to form poly(*exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide) – PNB **A** with a DP of 100 (**Scheme 2.7**).



Scheme 2.7 -The ROMP of *exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (NBE monomer A) using $RuCl_2(=CHPh)(PCy_3)_2$.

ROMP was carried out in CH_2Cl_2 by combining the initiator and monomer in CH_2Cl_2 ([M]:[I] =100:1) and terminating the polymerisation reaction using ethyl vinyl ether to duplicate the conditions used to synthesise the ROMP block of the block copolymers as precisely as possible. After similarly identical purification by reprecipitation, the polymers were analysed. The structure of the polymer was confirmed by ^{1}H and ^{13}C NMR spectroscopy. As described in Chapter 1, polynorbornenes produced by ROMP possess microstructures complicated by tacticity, and the vinylene units can be in either a *cis* or a *trans* configuration. These effects have quite a profound effect on the NMR spectra of the polymers, including PNB **A** (**Figure 2.16**).

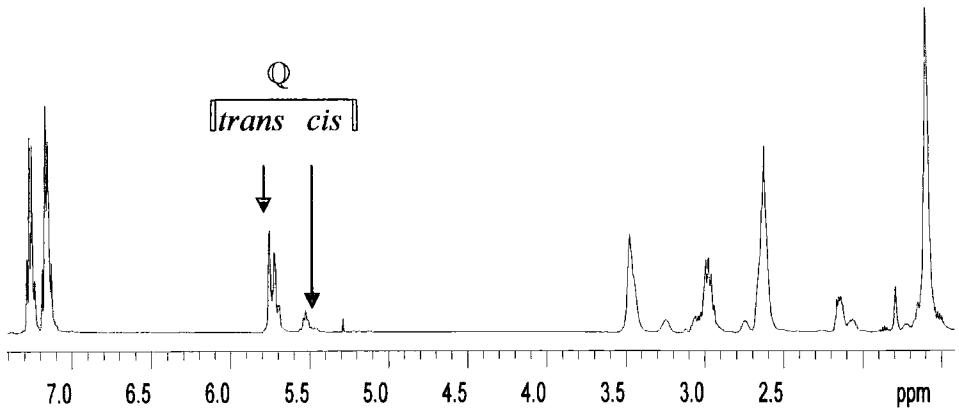


Figure 2.16 - ^{1}H NMR of PNB-A produced using $RuCl_2(=CHPh)(PCy_3)_2$. The *trans* and *cis* olefinic peaks (Q) are labelled.

Many of the *trans* and *cis* resonances of the bridge, bridgehead and vinylene protons fall at different resonances. This allows the estimation of the overall degree of *cis* and *trans* units in the polymer by comparing the integrals of the *trans* vinylene units (Q, **Scheme 2.7**) at 5.76-5.70 ppm and that of the *cis* units at 5.54-5.47 ppm. This indicates that the polymer is approximately 84% *trans* and 16% *cis*, in line with previous results for dicarboxyimides[18] and many other monomers[19] with this initiator.

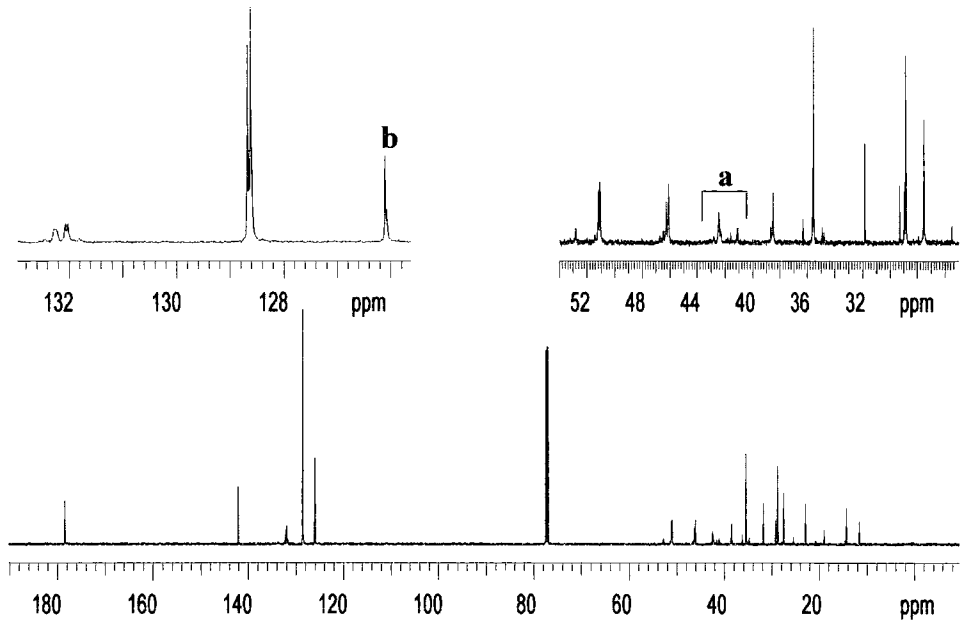


Figure 2.17 - ^{13}C NMR of PNB A produced using $RuCl_2(=CHPh)(PCy_3)_2$.

The peaks in the ^{13}C NMR spectrum (**Figure 2.17**) are also split by the presence of *cis* and *trans* units as well presumably by the presence of isotactic and syndiotactic dyads. The range marked **a** stems merely from the single bridgehead carbon (C_7, **Figure 2.18**) in various orientations due to the tacticity of the polymer chain. The peaks on the pendant phenylbutyl group are split slightly (**b** - C_{17}, for instance) though the aryl carbons appear to be split to a lesser degree than those of the alkyl groups.

The NMR assignments were made with the aid of 2D analysis (^1H and ^{13}C HSQC, HMBC and ^1H COSY) as well as by comparison with published assignments. Single and multiple bond ^1H and ^{13}C correlation spectroscopy allows for example $H_{7/7'}$, $C_{7/7'}$, H_{13}, and H_{15} to be assigned. These are similar though not identical to those described recently for this polymer,[30] in which correlation spectroscopy was not available. The major difference is in the assignment of the bridgehead protons at the positions $H_{2,3}$ and $H_{1,4}$.

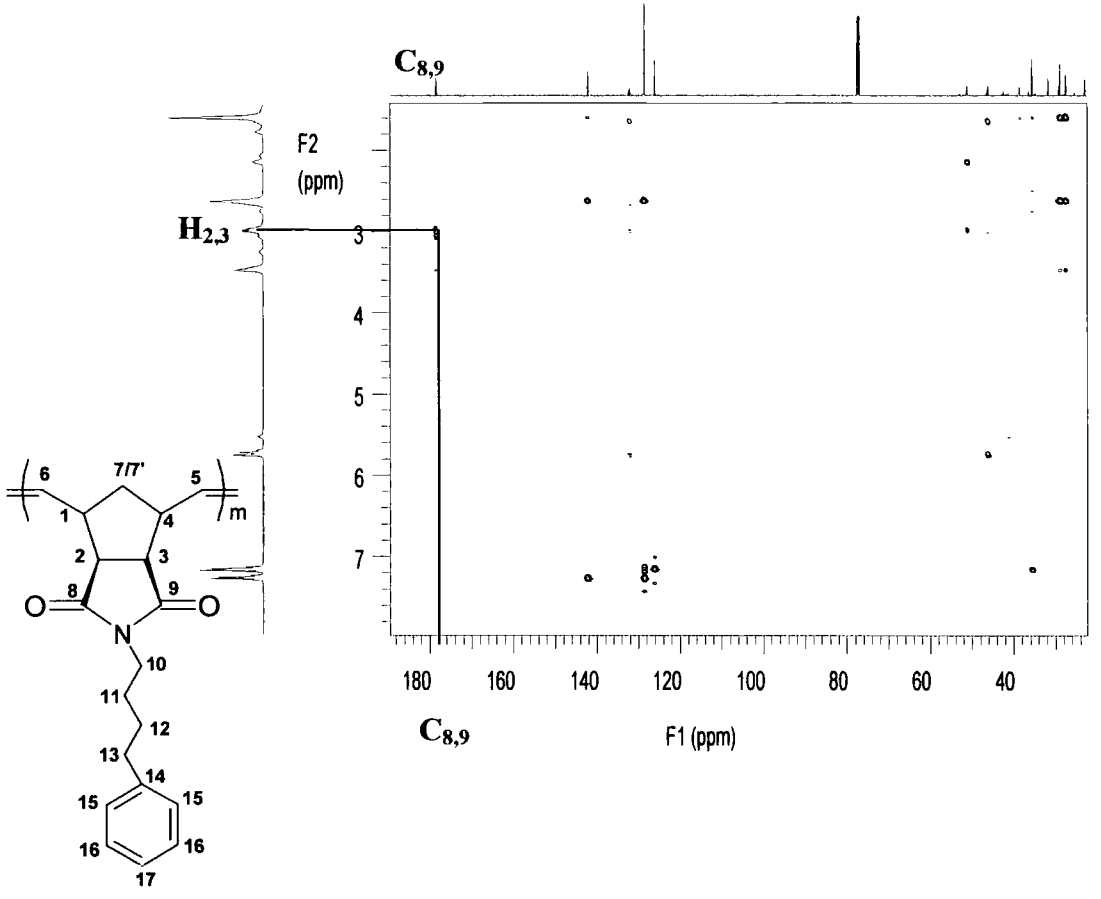


Figure 2.18 - ^1H-^{13}C HMBC of PNB A.

HMBC NMR spectroscopy (**Figure 2.18**) indicates that the carbonyl carbons ($\mathbf{C_{8,9}}$) are coupling to the peak at 3.06-2.94 ppm in the ^{1}H NMR spectrum, previously assigned to $\mathbf{H_{1,4}}$ and not the protons at 2.63 ppm which were assigned to $\mathbf{H_{2,3}}$ in the previous work. The assignments are therefore reversed in this work.

Analysis of PNB **A** (Target M_n: 29550 g mol^{-1}) by GPC using DMF as the eluent and PEO standards as calibrants indicated an M_n of 11000 g mol^{-1} and a PDI of 1.11 (**Appendix 2.5.1**) Analysis of the polymer by GPC using THF as the eluent and triple detection to calculate the molecular weights produced a M_n of 18000 g mol^{-1} (**Appendix 2.5.2**), and indicated it possessed a low PDI (1.06). The values calculated by GPC are much smaller than the predicted molecular weights. In the case of the DMF GPC, the reason for this is that the copolymers were analysed using a calibration curve generated from PEO/PEG standards. GPC columns separate the eluting polymers by molecular size (hydrodynamic volume) rather than molecular weight and as PNB **A** undoubtedly has different hydrodynamic properties to the standards we would not expect the data to be correct.[31] The THF GPC data was analysed using a triple detector, this data was calibrated using the [d*n*/d*c*] of polystyrene. The calculated figure for M_n is thus not expected to be an accurate reflection of the actual mass of the polymer, although the values for PDI will remain a good guide to the polydispersity of the sample. It should be noted that careful examination of the DMF GPC chromatogram indicates the presence of what appears to be a slight peak or shoulder next to the polymer peak at lower elution time. It is possible that this is due to a similar species to those observed in the GPC chromatograms of the anionic-ROMP block copolymers and possibly also PNB C. The peak in the block copolymers is believed to form by polymer-polymer coupling, resulting in the observation of a species which is approximately double the molecular weight of the bulk of the sample. The reader is referred to Section 2.2.8 for a discussion of the possible mechanisms of formation for these peaks.

The ROMP polymer of a fairly similar norbornene derivative was studied using MALDI spectroscopy by Davies et al. (**Figure 2.19**).[32]

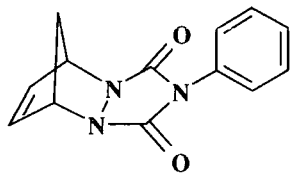
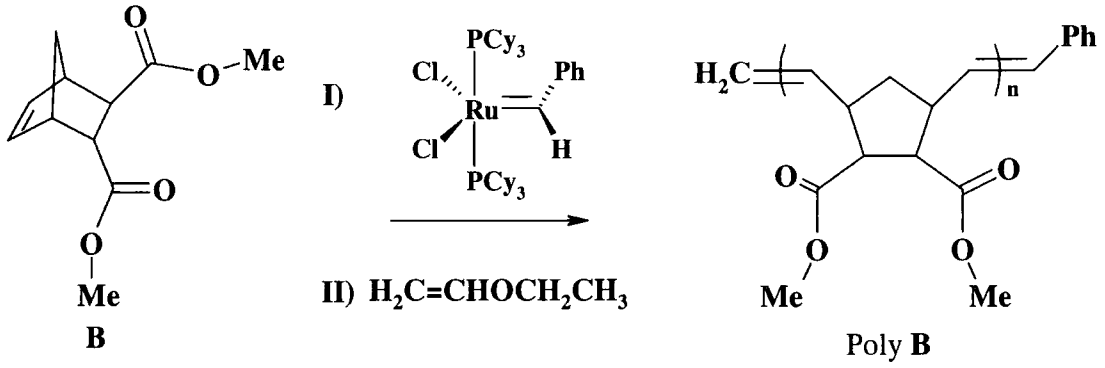


Figure 2.19 – A 2,3-diazanorborn-5-ene derivative.

It was thus thought possible that PNB **A** could be ionised by similar conditions producing an absolute, quantitative, measure of the molecular weight for this polymer. A MALDI spectrum of this polymer was obtained (**Appendix 2.5.3**) and gave a figure for M_n close to the predicted (32000 g mol^{-1}).

2.2.7.2 The Synthesis and Characterisation of Poly(*endo,exo*-Bicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxylic Acid dimethyl ester) – Poly B

The second monomer to be polymerised via ROMP with $RuCl_2(=CHPh)(PCy_3)_2$ was *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (NBE monomer **B**). This monomer has been recently polymerised with a well-defined molybdenum initiator.[24,33] The polymer produced was hydrogenated to remove unsaturation in the backbone, and the ester groups were hydrolysed using NaOH to produce water soluble sodium adducts, which were examined for effects on the crystallisation of inorganic salts from aqueous solution. The *endo,endo* and *exo,exo* adducts of this monomer have also been polymerised using $RuCl_2(=CHPh)(PCy_3)_2$,[19] though polymerisation conditions were not disclosed. The polymerisation of Monomer **B** in $CDCl_3$ solution was thus observed using ^1H NMR spectroscopy. This reaction is illustrated below in **Scheme 2.8**.



Scheme 2.8 - The synthesis of poly(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) via ROMP using $RuCl_2(=CHPh)(PCy_3)_2$.

The polymerisation of *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester using $RuCl_2(=CHPh)(PCy_3)_2$ (M_0/I_0 = 20) proceeded in a controlled manner in $CDCl_3$. No sign of the initiator (19.98 ppm in $CDCl_3$ solution) was present, indicating that complete consumption of initiator had occurred. (**Figure 2.20**)

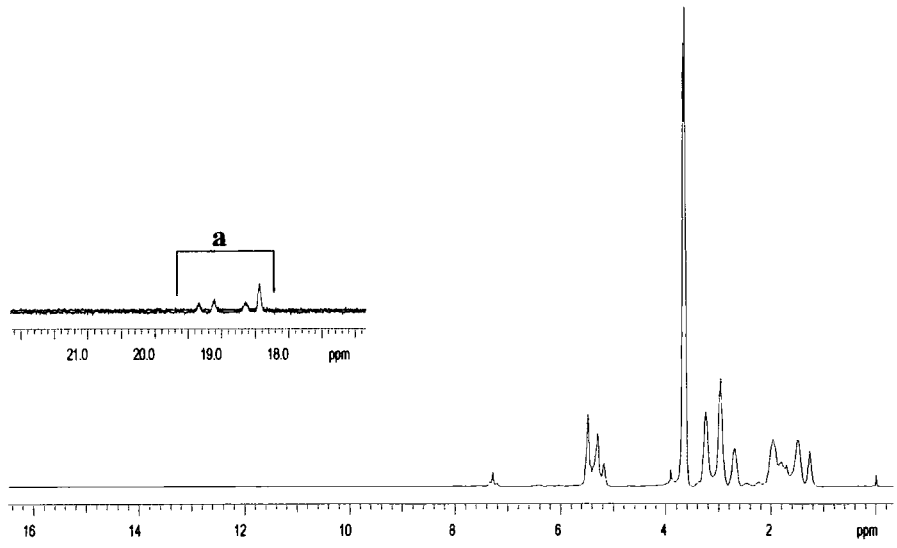
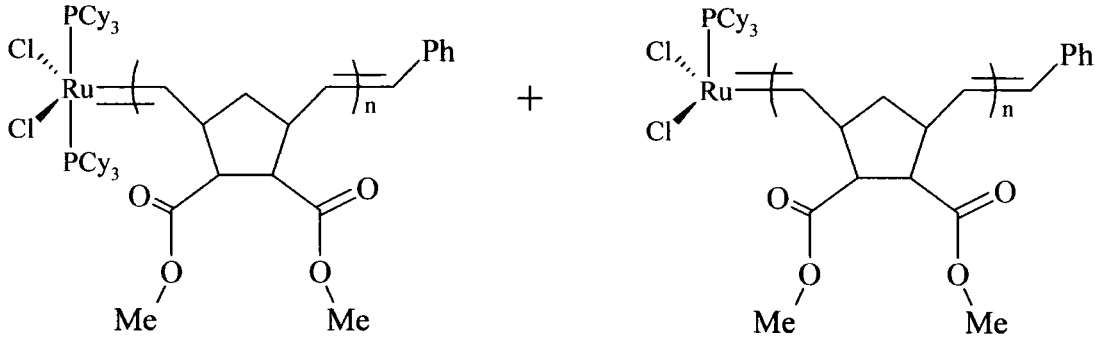


Figure 2.20 - The ^{1}H-NMR spectra of the completed polymerisation of *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester using $RuCl_2(=CHPh)(PCy_3)_2$, taken 5 hours after initiation.

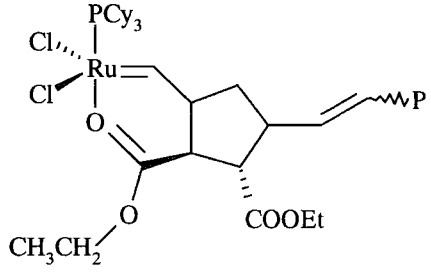
The alkylidene protons of the propagating species can be observed by ^{1}H NMR spectroscopy, most typically in the region of 20 - 18 ppm. During the polymerisation of monomer **B**, peaks at 19.32, 19.09, 18.62 and 18.41 ppm in the ^{1}H NMR spectra of the reaction are visible (**a**, **Figure 2.20**). These are present throughout the polymerisation in a similar ratio and persist for some time afterwards. The identity of all these peaks has not been conclusively identified in this work, but might be expected to include a propagating species **11**, in which one of the phosphine ligands has dissociated and a resting species **10**, in which both PCy_3 ligands are coordinated, see **Figure 2.21**.



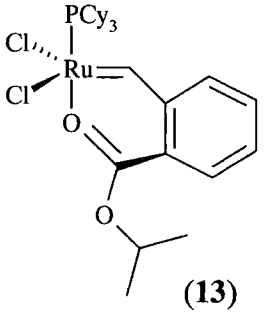
(**10**) Resting state (**11**) Propagating state

Figure 2.21 – Predicted species present during the propagation step of the ROMP polymerisation of NBE monomer B intiated by $RuCl_2(=CHPh)(PCy_3)_2$.

We might also expect to see separate peaks from alkylidene protons on units of the polymer chain with *endo* and *exo* insertion, as well as those next to *cis* and *trans* vinylene units. The broadness of the alkylidene peaks (**a, Figure 2.20**) suggests that some of the possibilities are approximately magnetically equivalent to each other. Based on studies by several researchers who have added PCy_3 to ROMP reactions which they have followed by NMR experiments,[34,35] the peaks between 19 and 20 ppm can be assigned to resting species **10** with reasonable certainty. The peaks between 18 and 19 ppm are usually assigned to propagating state **11**.[34] Recently Demel et al. have investigated the ROMP of the *exo, endo* diethyl ester analogue of NBE monomer **B** with a number of well defined ruthenium initiators including $RuCl_2(=CHPh)(PCy_3)_2$.[36] The alkylidene region of living PNB **B** is very similar to that of the living polymer of the diethyl ester derivative. The authors proposed that the two peaks between 18 and 19 ppm in their study are related to some form of chelation of an oxygen in the ester with the ruthenium (**12**) (**Figure 2.22**).



(12)



(13)

Figure 2.22 - Structure proposed by Demel et al. [36] of one of the resting states of the polymerisation of *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester with $RuCl_2(=CHPh)(PCy_3)_2$ (12), based on a similarity to (13).

This suggestion was made based on the similarity of the chemical shifts of the two peaks between 18 and 19 ppm with that of the alkylidene species of the ester stabilised ruthenium benzylidene (**13**). It was suggested that the resting states (**12**) and (**10**) exist in equilibrium with each other and that they are both capable of reacting with monomer and propagating the ROMP reaction further and therefore, importantly, remain 'living'.[35] In the case of these ester monomers oxygen co-ordination, if it occurs, does not therefore appear to have a detrimental effect on the results of their polymerisation. Their conclusions do not yet appear to have been confirmed by any other researchers. It is however interesting to note that whilst the colour of the solutions of the propagating species in the ROMP polymerisations of NBE monomers **A** and **C** with $RuCl_2(=CHPh)(PCy_3)_2$ and the macroinitiators were of a purple to red

colour (between benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ and propylidene $RuCl_2(=CHC_2H_5)(PCy_3)_2$), those of monomer **B** had a distinctly different peach colour. The termination reaction with ethyl vinyl ether, accompanied by a change in the colour of the solution to orange/yellow for PNB **A**, **B** and **C**, appeared to be slightly slower in the cases of living polymers of **B** as well.

The polymerisation of **B** in $CDCl_3$ proceeded to completion within 5 hours, with the complete disappearance of the olefinic monomer peaks at 6.28 and 6.08 ppm (**a**) and the formation of vinylene peaks at 5.48, 5.30 and 5.19 ppm (**b**) from the polymer (**Figure 2.23**).

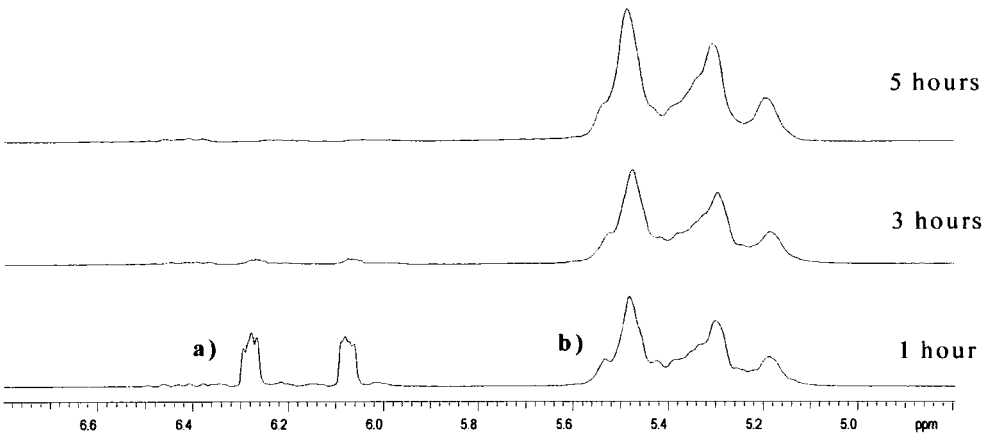


Figure 2.23 The consumption of *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester monomer a) and formation of polymer b) as shown by ^{1}H-NMR spectroscopy.

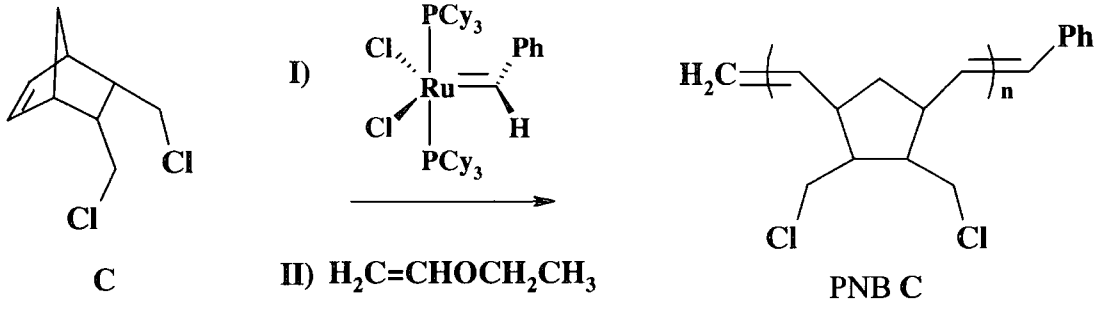
NBE monomer **B** was also polymerised on a preparative scale using conditions identical to those used later with the macroinitiators, i.e. in CH_2Cl_2 ([M]:[I] = 100:1). The ^{1}H and ^{13}C NMR spectroscopy data was assigned using the aid of published data[24,33] and confirmed with correlation spectroscopy. Unfortunately the degree of *cis* and *trans* units in the polymer cannot be easily determined from the ^{1}H spectra, as there is overlap between the peaks.[33]

Analysis of PNB **B** (Target M_n: 21050 g mol^{-1}) by GPC using DMF as the eluent and PEO standards as calibrants indicated an M_n of 17600 g mol^{-1}, and a PDI of 1.05 (**Appendix 2.5.5**). Analysis of the polymer produced by GPC using THF as the eluent, and triple detection indicated a M_n of 12700 g mol^{-1}, and a PDI of 1.02 (**Appendix 2.5.6**). Whilst the figures for PDI are likely to be a reasonable indicator of the overall polydispersity of the samples, they were calculated in the same manner as PNB **A** and are therefore not going to be quantitative or accurate reflections of the M_n

of the sample. The low polydispersity of the sample does indicate that oxygen co-ordination if present during the polymerisation, does not visibly harm the properties of the resulting polymer (as expected).

2.2.7.3 The Synthesis and Characterisation of Poly(*endo,endo*-5,6-bis[Chloromethyl]-Bicyclo[2.2.1]Hept-2-ene) – PNB C

The third monomer to be investigated by ROMP with $RuCl_2(=CHPh)(PCy_3)_2$ was *endo,endo*-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (NBE monomer C). This monomer has been investigated using ill-defined W and Mo initiators,[37] as well as well-defined molybdenum and tungsten initiators recently.[38] In general chlorinated norbornenes are less commonly studied as monomers for ROMP, compared with those bearing other functionalities. A search of the literature appears to indicate that this monomer has not been polymerised using well-defined ruthenium initiators. The monomer was chosen to add a third distinct functionality to the set of monomers investigated as components of the block copolymers. The polymerisation was studied by ^1H NMR in $CDCl_3$ to determine whether it would be suitable for ROMP with $RuCl_2(=CHPh)(PCy_3)_2$ and hence the macroinitiators. The polymerisation is illustrated in **Scheme 2.9**.



Scheme 2.9 - The synthesis of poly(*endo,endo*-5,6-bis[chloromethyl]bicyclo[2.2.1]hept-2-ene) using ruthenium initiator $RuCl_2(=CHPh)(PCy_3)_2$.

The polymerisation reaction for the ratio of M/I = 20 was complete before the acquisition of the first ^1H NMR spectrum of the reaction after 25 min. This was demonstrated by the complete conversion of the monomer signal at 6.25 ppm to that of the polymer at 5.20 ppm in the ^1H NMR spectrum of the polymerisation mixture (**Figure 2.24**). A multiplet (two overlapping doublets) was observed in the alkylidene region at 19.46 ppm (**a**, **Figure 2.24**) due to the alkylidene proton of the propagating polymer chain. This signal persisted after polymerisation was complete, indicating a

living polymerisation. Complete consumption of initiator did not occur at this M/I ratio. Comparison of the integrals of the signals of the propagating species with that of the initiator at 19.98 ppm (**b**, **Figure 2.24**), indicated that approximately 63% of the initiator remained unconsumed at the end of the reaction. This is indicative of a faster rate of propagation (R_p) than that of initiation (R_i).

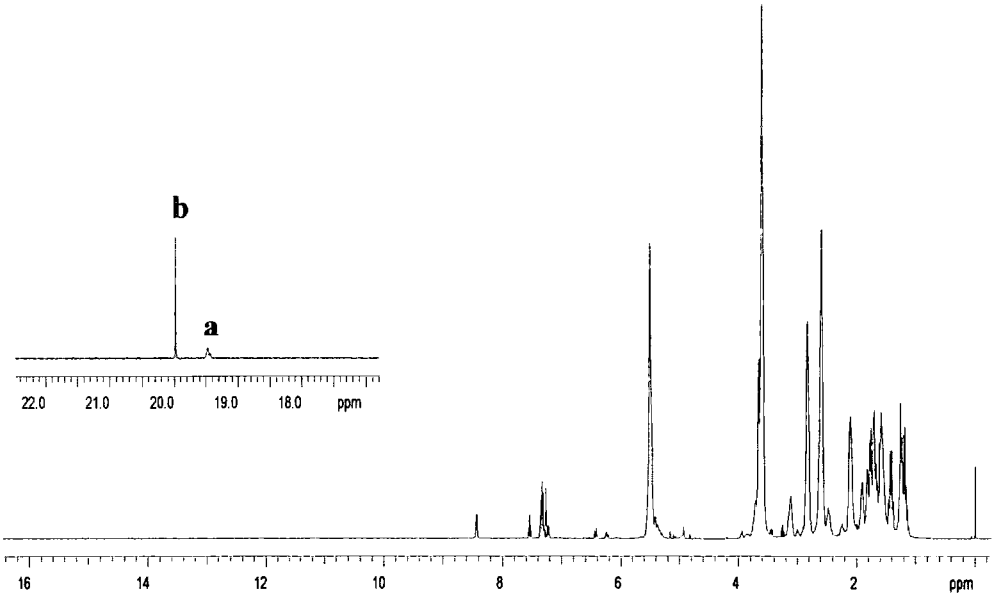


Figure 2.24 - The ^{1}H NMR spectra of the completed polymerisation of *endo,endo*-5,6-bis[chloromethyl]bicyclo[2.2.1]hept-2-ene using $RuCl_2(=CHPh)(PCy_3)_2$.

In contrast to the high rate of propagation (R_p) observed for NBE monomer **C** with $RuCl_2(=CHPh)(PCy_3)_2$, the rate of propagation of *endo* dicarboxyimides has been shown to be slow.[25] In that case several days were required for complete consumption of monomer, compared with 10 minutes for the *exo,exo* analogues ($[M_0]:[I_0] = 30:1$). The polymerisation of *endo* norbornenes using classical initiators is also either slow or impossible, which has been attributed to steric hindrance or electronic effects on the active propagating complex.[39] Recent studies on $RuCl_2(=CHPh)(PCy_3)_2$ initiated polymerisations have indicated that steric hindrance caused by the *endo*-polymer units next to the active site contributes to this effect to some degree, and in some cases co-ordination of the monomer to the active centre.[40] The difference in reactivity of NBE monomer **C** could therefore be attributed to the lower steric bulk of the chloromethyl group compared with the dicaboxyimide ring and *N*-substituent. It is also possible that the chloromethyl group had a lower, or no

tendency to co-ordinate to the active site. Both of these effects would result in the chloromethyl group having a lower tendency to interfere with the addition of monomer to the active ruthenium centre relative to many other *endo* monomers and their living polymers.

The polymerisation of NBE monomer ℂ was carried out on a preparative scale in CH_2Cl_2 to provide a comparison with the block copolymers using a ratio of [M]:[I] = 100:1. The NMR spectra of the polymer were assigned with the assistance of existing assignments.[38] The degree of *cis* and *trans* in the polymer can be estimated by comparison of the bridgehead methine protons at 3.11 and 2.83.[38] This indicates the polymer contains approximately 16% *cis* and 84% *trans* vinylene units, comparable with other results for this initiator as discussed in the previous sections.

Analysis of PNB ℂ (Target M_n: 19100 g mol^{-1}) by GPC using DMF as the eluent and PEO standards as calibrants indicated an M_n of 11000 g mol^{-1}, and a PDI of 1.58. Analysis of the polymer by triple detection GPC with THF as the eluent indicated a M_n of 18000 g mol^{-1}, and a PDI of 1.15. As with ROMP homopolymer 𝔸 and 𝔹 we would not expect the figures for M_n to be quantitatively correct, although the values for PDI should be a reasonable measure for the polydispersity of the sample. The PDIs are higher than NBE monomers 𝔸 and 𝔹 but are comparable or better than the PDIs (1.4 - 2.0) reported for samples prepared using well-defined molybdenum and tungsten initiators (obtained using GPC in THF with conventional calibration).[38] There appears to be a significant difference in the figure for PDI between the two GPC systems. Examination of the GPC trace from the DMF system reveals the presence of a peak at lower elution time at what might be approximately double molecular weight which might partly explain the PDI value (**a**, **Figure 2.25**).

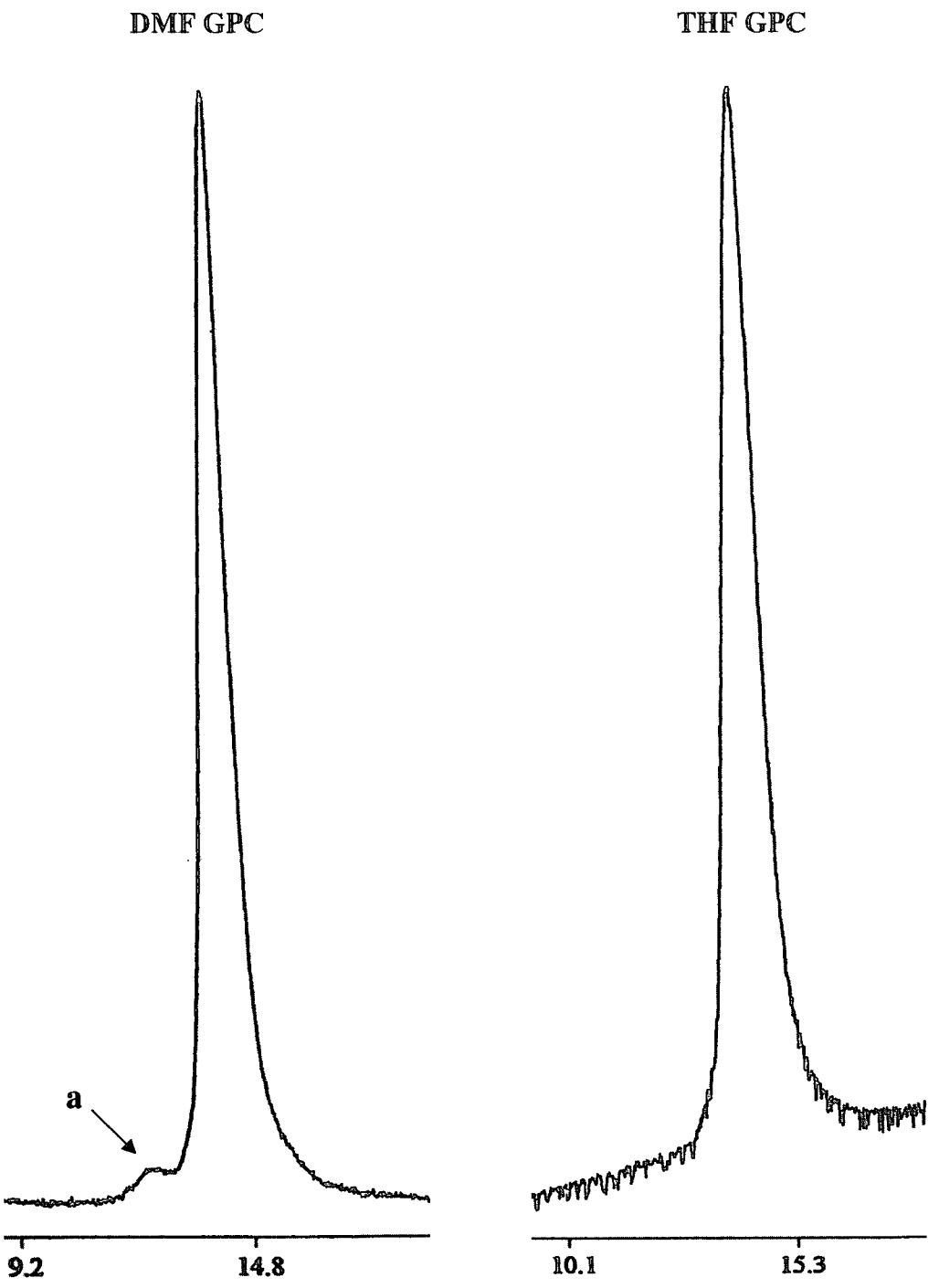


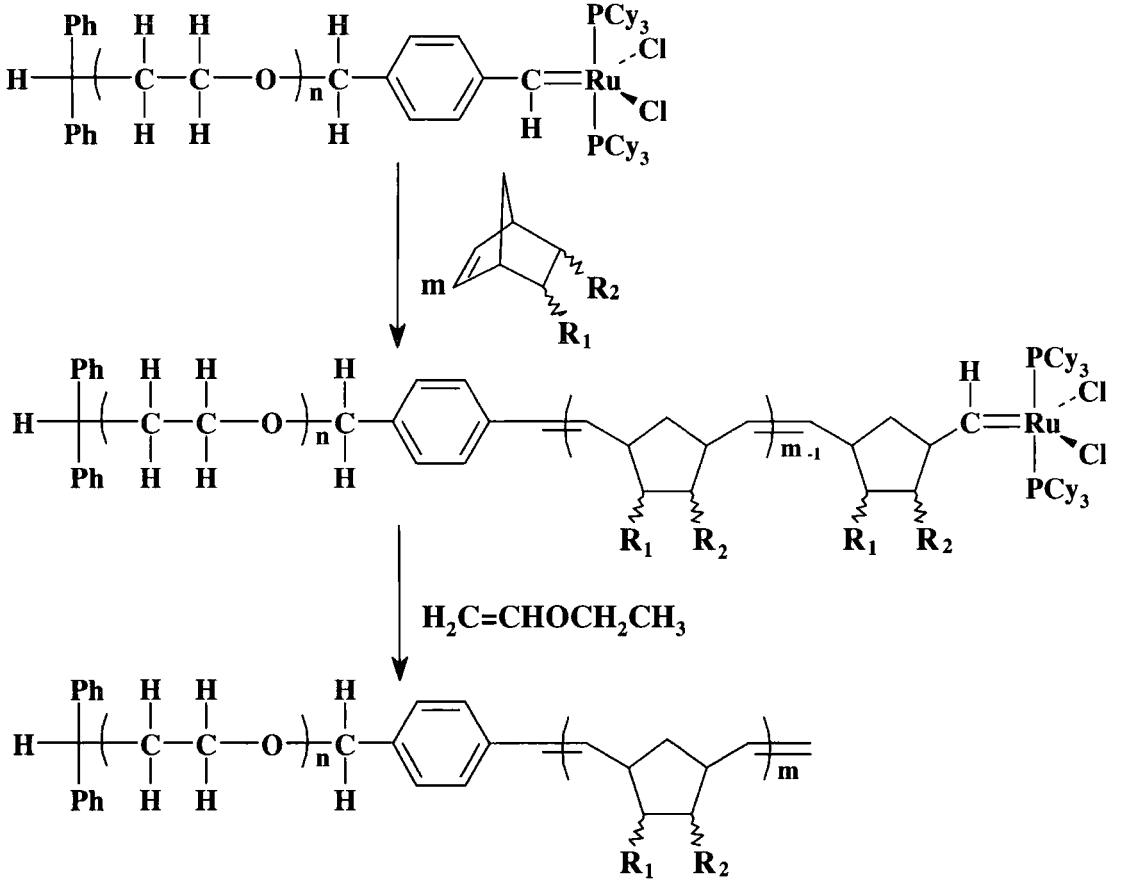
Figure 2.25 - GPC analysis of PNB C. Response vs Retention volume (mL).

This peak is not present in the THF GPC chromatogram. The reason for this could be due to the difference in the solubility behaviour of PNB **C** in the two solvents. The GPC systems also analysed the polymers differently, the DMF system used conventional calibration via a refractive index detector, and the THF GPC was measured using a triple detector, which may also contribute to the difference. The mechanism of polymer-polymer coupling is thought to involve the combination of two living ruthenium polymer chains and is discussed further in the next section.

2.2.8 Synthesis and Characterisation of PEO-PNB Block Copolymers

This section describes the ROMP of three norbornene derivatives, monomers **A**, **B** and **C** (Section 2.2.7) with PEO ruthenium macroinitiators (Section 2.2.5) to form AB PEO-PNB block polymers.

The polymerisations with the macroinitiator behave similarly to those of the benzylidene, yielding ROMP blocks. Initiation of monomers by the macroinitiator results in incorporation of the PEO into the polymer chain and the formation of living block copolymers, which were terminated using ethyl vinyl ether (**Scheme 2.10**).



Scheme 2.10 - ROMP of norbornene derivatives with a PEO ruthenium macroinitiator.

This method was successful in producing well-defined block copolymers of varying molecular weights and compositions (**Table 2.3**).

Table 2.3 - Molecular weight and composition data for a series of diblock copolymers of EO and NBE.

Sample	PEO BLOCK[a]			ROMP BLOCK		BLOCK COPOLYMER			
	M_n g mol^{-1}	M_w g mol^{-1}	PDI	Monomer	DP	M_n/Pred[b] g mol^{-1}	M_n/GPC g mol^{-1}	PDI	M_n/NMR g mol^{-1}
1	2400	2500	1.06	A	100	31900	16400	1.10	30400
2					200	61500	28400	1.21	56300
3					500	150100	63100	1.21	140500
4	4600	4800	1.04	A	100	34100	18900	1.12	30500
5	10400	10600	1.04	A	100	39900	23000	1.11	36600
6					200	69500	35500	1.15	63500
7	38800	41200	1.06	A	200	97900	62900	1.28	88300
8	2400	2500	1.06	B	100	23400	14400	1.10	23500
9	4600	4800	1.04	B	100	25600	15300	1.14	22900
10	10400	10800	1.04	B	100	31400	20700	1.13	31400
11	2400	2500	1.06	C	100	21500	10000	1.32	23700

***a* = Determined by DMF GPC. *b* Based on GPC measurements of the PEO block.**

A range of molar ratios of monomer [M] to PEO macroinitiator [MI], [M]/[MI] = 100, 200 and 500 were used to vary the composition of the block copolymers. Reaction times were identical to those of the monomers with the benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$ for [M]/[MI] = 100 and were increased accordingly for [M]/[MI] of 200 and 500. In all cases the consumption of monomer was quantitative and in almost all cases the block copolymers have a narrow molecular weight distribution (1.1-1.2), consistent with a living polymerisation technique. This suggests that the PEO macroinitiators are efficient initiators for ROMP of the norbornene derivatives used in this study. In larger scale ROMP reactions the yield of the recovered block copolymer samples were high, e.g. 96% (640 mg), after purification. The percentage yield of some of the reactions that possessed a low theoretical maximum yield (~100 mg and less) were quite low (i.e. 20-40%), due to the difficulty in recovering and purifying small quantities of samples efficiently. Elemental analysis was obtained for some of the block copolymers (see Section 2.4.7), and was generally in good agreement with that predicted, evidence that the block copolymers have compositions similar to their targets. Slight variations might be explained by the presence of residual hexane, used as the non-solvent to precipitate the polymer. The physical nature of the block copolymers was very similar to that of the corresponding ROMP homopolymers, often taking the form of a tough solid. ^{1}H NMR analysis indicated that a small amount of hexane was trapped in the

polymer and was not removed by drying the samples under vacuum for approximately a week at room temperature. The hygroscopic nature of the PEO block might also have contributed to some of the variations. The value of the PDI reported for the block copolymers includes the presence of a small peak (less than 2% of the main peak) at lower elution volumes (**b** in **Figure 2.26**), which appears to be approximately double the molecular weight of the first peak and is believed to result from some polymer-polymer coupling after the completion of polymerisation.

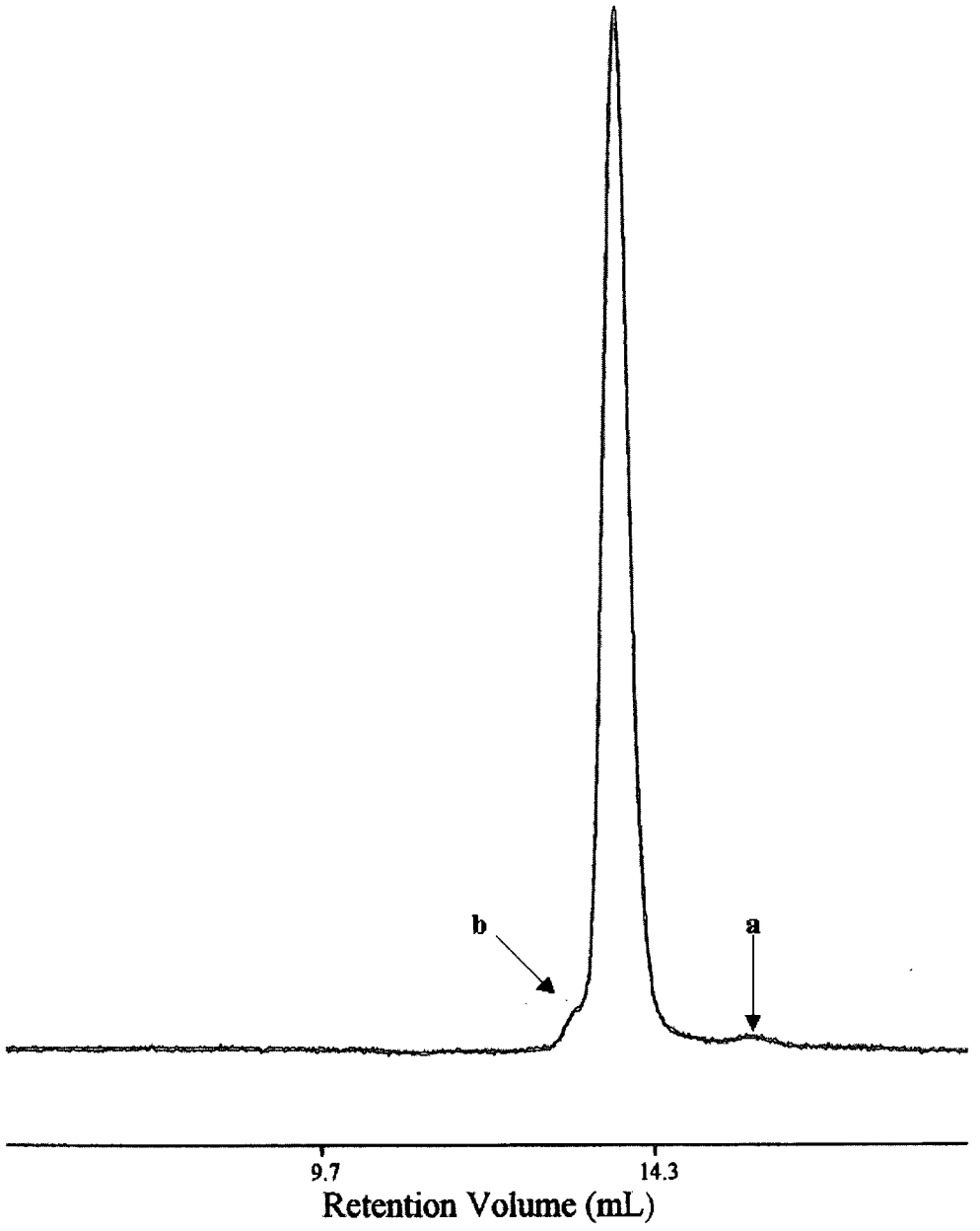
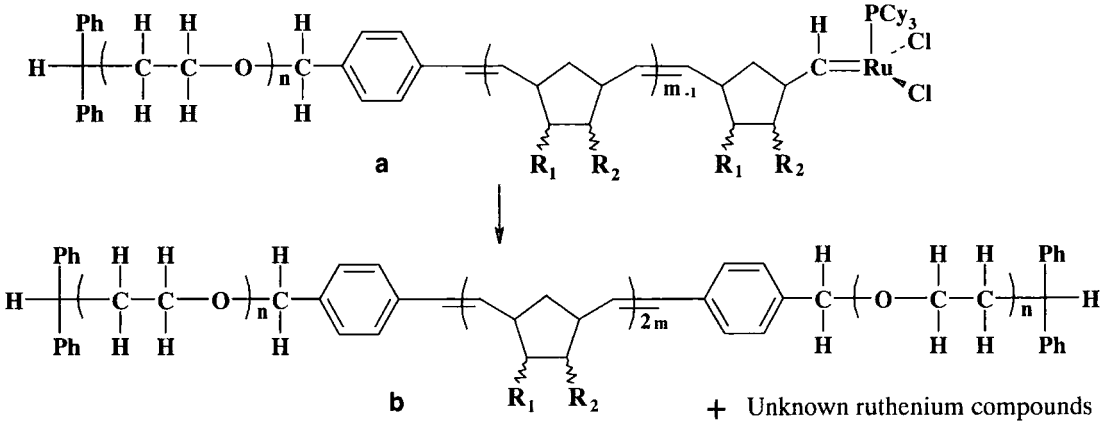


Figure 2.26- GPC chromatogram of a block copolymer containing blocks of PEO and NBE monomer B. M_n (GPC) = 14,400 g mol-1, PDI = 1.10, contaminated with a trace of PEO homopolymer M_n = 2400 g mol-1, PDI = 1.06 (a). Peak b is described in the text.

The fact that this peak is always double the molecular weight of the polymer suggests that its origin is either from a species that forms before polymerisation from the macroinitiator, or after completion of polymerisation, and not during polymerisation. Polymer-polymer coupling has been observed in some cases involving the ROMP of norbornenes and its fluorinated derivatives using Schrock's molybdenum initiators, which was attributed to reaction of the living chain end with molecular oxygen.[41] In contrast to this living ROMP polymers initiated by well-defined ruthenium initiators undergo a selective reaction with O_2 which introduces an aldehyde group onto the polymer chain.[34] Bimodal molecular weight distributions have been noted with well-defined ruthenium alkylidene initiators before, although no theory has been advanced to explain their formation.[42] The decomposition mechanism for the Grubbs ruthenium initiators is reported to involve dissociation of a phosphine ligand followed by coupling of two monophosphine species.[20] Decomposition of this metallic species is accompanied by dimerisation of the organic fragment of the alkylidene ligand. For example decomposition of propylidene $RuCl_2(=CHEt)(PCy_3)_2$ results in the formation of *trans*-3-hexene A similar decomposition pathway could presumably take place on a very small scale (less than 2%) in our system, after the polymerisation is complete, resulting in the polymer-polymer coupling (**Scheme 2.11**).



Scheme 2.11 - Possible mechanism of polymer-polymer coupling of living block copolymer (a) to produce a polymeric dimer (b).

No evidence for the presence of structure **b** (**Scheme 2.11**) can be gathered by NMR as no new signals would be expected. No further work was done to study the origin of this peak in PEO-PNB block copolymers, though further work on block

copolymers of styrene (Section 3.2.3.1) confirms the suggestion that it forms from the living polymer after completion of polymerisation.

The block copolymers were precipitated into hexane, a non-solvent for PEO and the corresponding polynorbornene homopolymers. In most cases GPC analysis showed a single well-defined peak corresponding to the block copolymer, but in a couple of cases the GPC trace showed a small peak at the same elution volume as the PEO block (**a** in **Figure 2.26**). This PEO homopolymer is only present at concentrations of 1-2% of the sample and probably results from the introduction of traces of impurities, possibly with the 4-VBC resulting in PEO that has not been end-functionalised.

The number average molecular weights (M_n) of the block copolymers were calculated both by GPC and ^{1}H NMR. The values calculated by GPC are much smaller than the predicted molecular weights, the reason for this being that the copolymers were analysed using a calibration curve generated from PEO/PEG standards. GPC columns separate the eluting polymers by molecular size (hydrodynamic volume) rather than molecular weight and since the block copolymers undoubtedly have different hydrodynamic properties to the standards we would not expect the data to be correct.[31] As described in the previous section the three norbornene derivative monomers (**A-C**) were polymerised by ROMP initiated by Grubbs benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$; all three polymer samples possessed good solubility in DMF and as expected DMF GPC produced molecular weights significantly below the predicted values. Despite this the GPC data from the block copolymers is useful for qualitative analysis and determination of polydispersity.

The NMR spectra of the block copolymers (**Appendix 2.6.1 – 2.6.6**) are effectively a combination of that of the two homopolymers, the ratios of the intensity of the signals varying according to the DP of the two blocks. This ratio is directly related to the molecular weight of the block copolymers. ^{1}H NMR is therefore a useful tool for the quantitative calculation of the molecular weights of block copolymers, providing there is not too much homopolymer contaminating the sample.[43]

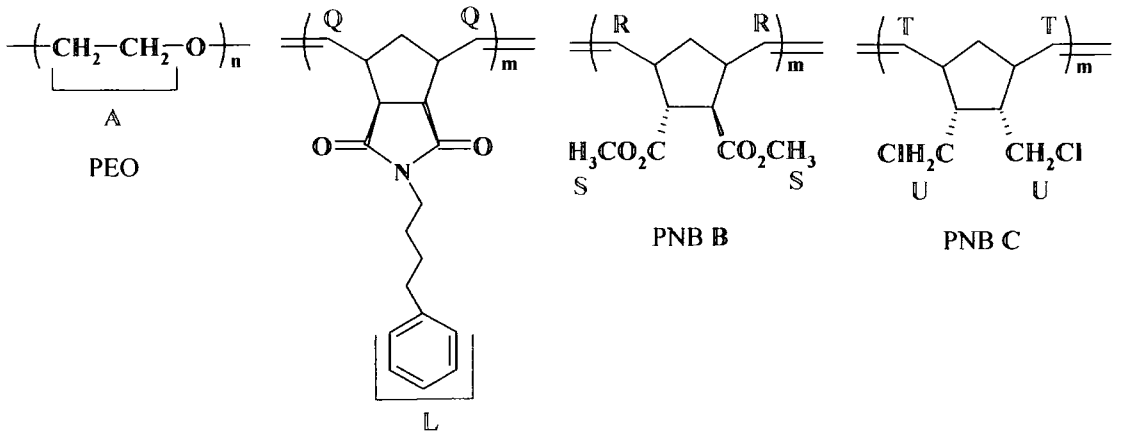


Figure 2.27 - PEO and ROMP polymer backbones labelled with environments of relevance to the calculation of M_n of PEO-PNB block copolymers using ^{1}H NMR.

The M_n of these block copolymers was measured by comparing the intensity of the methylene PEO protons (𝔸, 4H per repeat unit in the PEO block) at 3.46 ppm to the olefinic protons of the polynorbornene backbone (**Figure 2.27**) 2H per unit in the PNB block), which fall in the region of 5.75–5.51 ppm (ℚ) for blocks formed from monomer **A**, 5.48-5.19 ppm (ℝ) for monomer **B**, and 5.62-5.29 ppm (𝕋) for monomer **C**. In the case of monomers **B** and **C** the PEO peak (𝔸) overlaps with peaks from the pendant groups, at 3.70-3.63 ppm (𝕊, 6H per ROMP unit) and 3.78-3.40 (𝕌, 4H per ROMP unit). The total influence from these peaks must therefore be calculated (from the olefinic region) and removed from the total integral in order to obtain the contribution from the PEO peak. Multiplication of the ratio of PNB to PEO blocks ([PNB]/[PEO]) by the known DP (calculated from DMF GPC data) of the PEO block produces an estimate for the DP of the block copolymer. The values obtained for M_n agree well with the predicted values (**Table 2.3**). Comparison of the ^{1}H NMR spectra of the PEO-PNB block copolymers with that of the homopolymers indicates that they are similar to the ROMP polymers and contain mainly *trans* vinylene units. Blocks from monomer **A** and **C** are approximately 16 % *cis*, 84 % *trans*. As described previously the ratios cannot be determined directly from the ^{1}H NMR but comparison with the homopolymer indicates they have a similar microstructure. No difference in the microstructure of the ROMP blocks was evident in samples produced in CH_2Cl_2 or C_6H_6. Functional groups inherited from the macromonomer, i.e. the diphenylmethyl group introduced by the DPMK initiator and benzyl group, are discernable in the ^{1}H NMR of the lower molecular weight block copolymers, although their weak intensity

makes them of no practical use in estimating the weight of the copolymers in this study.

As a matrix suitable for the ionisation of samples of ROMP homopolymer A was known (dithranol), an attempt was made to see if MALDI spectra could be obtained from an example of a block copolymer of this monomer with PEO. These were successful with PEO-PNB sample 1 (**Table 2.3**), using dithranol as the matrix resulted in a figure for M_n of 31400 g mol^{-1} (**Appendix 2.6.7**), very close to the predicted M_n of 31900 g mol^{-1}. 3-Indoleacrylic acid could also be used as a matrix for PEO-PNB sample 1, producing the similar though slightly higher value of M_n = 33100 g mol^{-1} (**Appendix 2.6.8**), the resolution of the resulting spectrum was also inferior compared with the spectrum of the sample ionised using dithranol.

The primary aim of this research was to develop a technology which would allow the production of these block copolymers. The polymeric materials produced were not evaluated for suitability for any particular application. In addition to producing materials which are interesting as solids, their amphiphilic nature should give them interesting properties in solution such as the ability to form micelles.[44] The incorporation of PEO/PEG is often used to increase the water solubility of compounds.[45] Tests on block copolymers samples number 4, 7 and 10 (**Table 2.3**) produced in this study didn't display any obvious solubility in H_2O. However the potential exists for solubilising water insoluble ROMP polymers by the incorporation of a PEO chain of suitable size relative to the ROMP block. In light of the use of materials produced by ruthenium ROMP (referred to as ROMPgels) as reagents in organic synthesis by Barrett and others,[46] the modification of solubility could prove to be an interesting application of the technology.

2.3 Conclusions and Summary

Living ruthenium ROMP and anionic polymerisation were combined for the first time to make well-defined linear copolymers with narrow polydispersities. Living poly(ethylene oxide) was initiated by an anionic mechanism using diphenyl methyl potassium and successfully functionalised using 4-vinylbenzyl chloride to form PEO macromonomers. The functionalisation reaction was most efficient with a small excess of 4-vinylbenzyl chloride and was not enhanced by increasing the temperature. PEO macromonomers were synthesised with a range of molecular

weights, DMF GPC analysis indicated they possessed M_n varying between 1100 – 39000, and had polydispersities less than 1.1.

Ruthenium propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ has been synthesised from the benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ and *trans*-3-hexene. This propylidene initiator allows the facile synthesis of ruthenium PEO macroinitiators from the macromonomers by an exchange reaction. These were the first well-defined macroinitiators for ROMP synthesised from polymers obtained from an anionic polymerisation mechanism.

Three different norbornene derivatives were polymerised using ROMP initiated by $RuCl_2(=CHPh)(PCy_3)_2$, to yield homopolymers. These derivatives were then polymerised with the ruthenium PEO macroinitiators, yielding a range of block copolymers of varying molecular weights and compositions. Analysis indicated that they generally possessed a narrow polydispersity and were of the desired structure.

2.4 Experimental

2.4.1 General

2.4.1.1 Materials

All chemicals used in anionic polymerisation were degassed by five freeze-thaw-evacuate cycles, to a pressure of below $1x10^{-5}$ mm Hg prior to use, unless stated otherwise. Ethylene oxide (EO, Aldrich, 99.5+%) was purified by distillation from CaH_2 and then by distillation from $Mg(Bu)_2$ (Aldrich, 1.0 M solution in heptane) immediately before use. Tetrahydrofuran (THF, Aldrich, 99.9%, anhydrous) was passed through two columns containing alumina,[47] before being distilled from sodium/benzophenone. Diphenylmethylpotassium was synthesised in solution by the reaction of potassium naphthalene with a slight excess of diphenylmethane in THF.[48] 4-Vinylbenzyl chloride (4-VBC, Aldrich, 90 %) was stated by the supplier to be likely to contain the impurities, α-chloromethylstyrene (2%), dichloromethylstyrene (3%), and 3-vinylbenzyl chloride (3-VBC, 5%). 4-VBC was purified by vacuum distillation from CaH_2 prior to use. CH_3I (Lancaster, 99%) was distilled from 4 Å molecular sieves prior to use. Grubbs ruthenium initiator ($RuCl_2(=CHPh)(PCy_3)_2$) was synthesised according to literature procedures.[14] *trans*-3-Hexene (Aldrich, 99+%) and ethyl vinyl ether (Aldrich, 99%) were used as received. CH_2Cl_2 (Aldrich, 99.9%) was dried over calcium hydride and benzene (Aldrich, 99.9+%) was purified by passing

the solvent through a system of columns designed to remove both protic impurities and oxygen.[47] Maleic anhydride (Aldrich, 99%, briquettes), 1,2-dichlorobenzene (Aldrich, 99%), dicyclopentadiene (Acros, 95%) and 4-phenylbutylamine (Aldrich, 98%) were used as received. Hexane (Aldrich, 95+%, anhydrous) used in the precipitation of the macroinitiator was degassed by five freeze-evacuate-thaw cycles. Acetone-d_6 (Aldrich, 99.5% D, 0.03% v/v TMS), $CDCl_3$ (Aldrich, 99.9% D, 0.03% v/v TMS), and CD_2Cl_2 (Goss/Cambridge Isotope Laboratories Inc., 99.9% D, 0.03% v/v TMS) were used as received for general use. $CDCl_3$ (Aldrich, 99.9% D, 0.03% v/v TMS), and C_6D_6 (Aldrich, 99.6% D, 0.03% v/v TMS) were purified by distillation from CaH_2, and CD_2Cl_2 (Aldrich, 99.9% D, 0.03% v/v TMS) was obtained in pre-sealed ampoules, for use with air sensitive materials and polymerisation reactions.

The preparation of *exo,exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (monomer **A**) from *exo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride is described in Section 2.4.5.2. *Endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (**B**) was produced via the Diels-Alder reaction between cyclopentadiene and dimethyl fumarate.[24] *Endo,endo*-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (**C**) was obtained from the Diels-Alder reaction of cyclopentadiene with 1,4-dichlorobut-2-ene according to the method described by Bowe[49] and modified by Shahada and Feast.[37]

2.4.1.2 Analysis

Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy was performed using a Varian Inova 500 MHz or Mercury 400 MHz spectrometer. All ^1H and ^{13}C NMR resonances are quoted relative to TMS. The NMR spectra of air-sensitive materials were recorded in tubes sealed with a Young's tap. Stability studies were carried out in sealed NMR tubes using TMS as an internal reference.

Gel Permeation Chromatography (GPC)

Analysis of all of the polymers was carried out using DMF as the eluent at a flow rate of 1.0 mL/min and at a constant temperature of 80 °C. The GPC system was comprised of a Viscotek TDA 302 refractive index detector, with a guard column and 2 x 300 mL PLgel 5 μm mixed C columns. Molecular weights were obtained using a conventional calibration curve generated from narrow molecular weight distribution

polyethylene glycol (PEG)/PEO standards (Polymer Laboratories) with molecular weights in the range 106-273 000 g mol^{-1}.

The three ROMP homopolymers were also analysed using THF as the eluent at a flow rate of 1.0 mL/min and at a constant temperature of 30 °C. The GPC system was comprised of a Viscotek 200 with refractive index, viscosity and right angle light scattering detectors and 2 x 300 mm PLgel 5 μm mixed C columns. Molecular weights were obtained using triple detection, and a value of 0.185 for the [d*n*/dc] of polystyrene.

Mass Spectroscopy

Matrix assisted laser desorption ionisation – time of flight (MALDI-TOF) mass spectroscopy was performed using an Applied Biosystems Voyager-DE STR BioSpectrometry workstation. PEO samples were dissolved in H_2O and mixed on the plate with the matrix *trans*-3-indoleacrylic acid (IAA) dissolved in THF. The samples were analysed in reflector mode, except for sample Me PEO 5 which was run in linear mode. A sample of ROMP homopolymer prepared from monomer **A** was dissolved in $CHCl_3$ and premixed with the matrix dithranol dissolved in $CHCl_3$. The sample was analysed in linear mode. PEO-PNB sample number 1 was dissolved in THF and premixed with either the matrix *trans*-3-indoleacrylic acid or preferably dithranol dissolved in THF. The samples were analysed in linear mode.

Electron ionisation mass spectroscopy (EI-MS) was performed on a Micromass AutoSpec mass spectrometer.

Miscellaneous

Elemental micro-analysis (C, H and N) was carried out on an Exeter Analytical, Inc. CE-440 Elemental Analyser. Melting points were determined on an Electrothermal 9100 capillary melting point apparatus.

2.4.2 Synthesis of Poly(Ethylene Oxide) Homopolymers

2.4.2.1 Synthesis of 4-Vinylbenzyl Functionalised Poly(Ethylene Oxide) via Anionic Polymerisation.

In a typical experiment the anionic polymerisation of EO was carried out using standard high vacuum techniques. EO (12.52 g, 0.28 mol) and THF (100 mL) were distilled into the reaction vessel and polymerisation was initiated by the addition of

diphenylmethylpotassium (1.0 M solution in THF, 2.09 mL, 2.09 mmol). Polymerisation proceeded over a period of 12 h at room temperature after which the temperature was increased to 35 °C for a further 12 h before the mixture was allowed to reach room temperature. An aliquot (5 mL) of the solution was then removed from the reactor and terminated with CH_3I (0.01 mL, 0.16 mmol) in order to provide a sample of unfunctionalised PEO for analysis (see Section 2.4.3). A slight molar excess of 4-VBC (0.34 mL, 2.39 mmol, 1.2 equiv) was added to the rest and the mixture was stirred for 16 h at room temperature. The polymer was recovered by precipitation into hexane (800 mL), filtered, washed with hexane and dried *in vacuo* at r.t. for 16 h. The sample was then dissolved in CH_2Cl_2 (80 mL) and filtered through Celite (Aldrich grade 521) in order to remove the KCl formed as a byproduct of the coupling reaction of the living PEO with 4-VBC, and the solvent was removed under reduced pressure. Following this the product was redissolved in benzene (80 mL) and re-precipitated in hexane (640 mL) and dried *in vacuo*. The recovery procedure was repeated twice to ensure the complete removal of unreacted 4-VBC. Yield = 11.33 g, 95%.

Target M_n of PEO: 6000 g mol^{-1}.

DMF GPC: M_n = 4600 g mol^{-1}, PDI =1.09.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.28**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.40 (d, J_{HH}= 8.0 Hz, **H_{13}**), 7.30 (d, J_{HH}= 8.0 Hz, **H_{12}**), 7.28–7.23 (m, **$H_{3,4}$**), 7.18-7.14 (m, **H_5**), 6.72 (dd, **H_{15}**), 5.76 (dd, **H_{16}**), 5.23 (dd, **$H_{16'}$**), 4.52 (s, **H_{10}**), 4.10 (t, J_{HH}= 8.0 Hz, **H_1**), 3.60 (s, **$H_{8,9}$**), 3.35 (t, J_{HH}= 6.5 Hz, **H_7**), 2.32 (q, J_{HH}= 8.0 Hz, **H_6**).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 145.08 (s, **C_2**), 138.50 (s, **C_{14}**), 137.80 (s, **C_{11}**), 136.77 (s, **C_{15}**), 128.67 (s, **C_3**), 128.12 (s, **C_{12}**), 128.03 (s, **C_4**), 126.38 (s, **C_5**), 126.33 (s, **C_{13}**), 113.73 (s, **C_{16}**), 73.01 (s, **C_{10}**), 70.75, 70.42, 69.90 (all **C_8** and **C_9**), 69.28 (**C_7**), 47.59 (**C_1**), 35.42 (**C_6**).

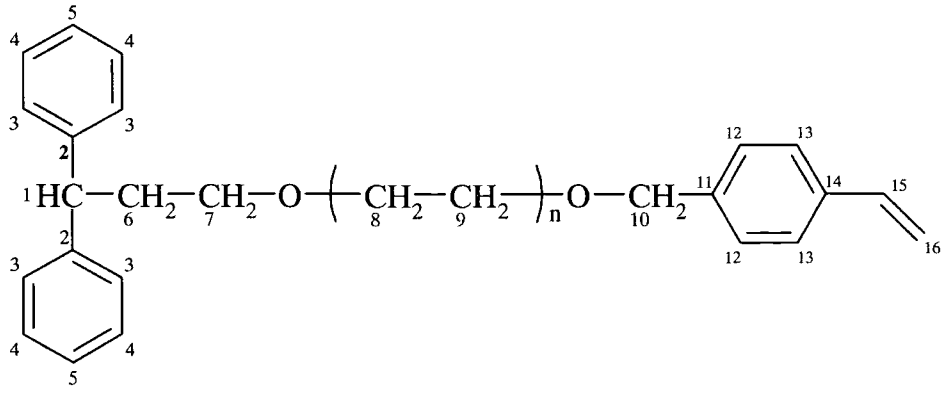


Figure 2.28 - Numbering scheme for PEO macromonomer NMR assignments.

PEO of other molecular weights were prepared in an analogous fashion. Please see **Table 2.2** for more details.

A polymer of target M_n of 1500 g mol^{-1} was made with EO (9.93 g, 0.2 mol), diphenylmethylpotassium (1.0 M solution in THF, 6.6 mL, 6.6 mmol), THF (100 mL), 4-VBC (1.05 mL, 6.3 mmol) and CH_3I (0.04 mL, 1.2 mmol). Yield of PEO: 9.98 g, 101%.

A polymer of target M_n of 3000 g mol^{-1} was made with EO (10.63 g, 0.24 mol), diphenylmethylpotassium (1.0 M solution in THF, 3.5 mL, 3.54 mmol), THF (100 mL), 4-VBC (0.53 mL, 3.2 mmol) and CH_3I (0.02 mL, 0.6 mmol). Yield of PEO: 10.95 g, 103%.

A polymer of target M_n of 6000 g mol^{-1} was made with EO (12.52 g, 0.28 mol), diphenylmethylpotassium (1.0 M solution in THF, 2.09 mL, 2.1 mmol), THF (100 mL), 4-VBC (0.34 mL, 2.4 mmol) and CH_3I (10.0 μL, 0.16 mmol). Yield of PEO: 12.47 g, 100%.

A polymer of target M_n of 12000 g mol^{-1} was made with EO (10.49 g, 0.24 mol), diphenylmethylpotassium (1.0 M solution in THF, 0.87 mL, 0.8 mmol), THF (100 mL), 4-VBC (0.14 mL, 1.0 mmol) and CH_3I (5.0 μL, 0.08 mmol). Yield of PEO: 10.26 g, 98%.

A polymer of target M_n of 50000 g mol^{-1} was made with EO (10.40 g, 0.24 mol), diphenylmethylpotassium (1.0 M solution in THF, 0.21 mL, 0.2 mmol), THF (175 mL), 4-VBC (34 μL, 0.2 mmol) and CH_3I (5.0 μL, 0.08 mmol). Yield of PEO: 10.16 g, 98%.

2.4.2.2 Recovery of Methyl Iodide Terminated Poly(Ethylene Oxide).

After being stirred with CH_3I for 16 h, the polymer was precipitated into hexane (40 mL). The sample was then dissolved in CH_2Cl_2 (10 mL) and filtered through celite to remove KI, and the solvent was evaporated. Following this the product was twice re-dissolved in benzene (7 mL) and re-precipitated in hexane (56 mL) and dried *in vacuo*. Yield = 0.19 g, 32%.

Target M_n: 6000 g mol^{-1}.

DMF GPC: M_n = 4450 g mol^{-1}, PDI = 1.03.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.29**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.28–7.23 (m, $H_{3,4}$), 7.18-7.14 (m, H_5), 4.10 (t, J_{HH} = 8.0 Hz, H_1), 3.60 (s, $H_{8,9}$), 3.35 (t, J_{HH} = 6.5 Hz, H_7), 3.34 (s, H_{10}), 2.32 (q, J_{HH} = 8.0 Hz, H_6).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 145.08 (s, C_2), 128.67 (s, C_3), 128.03 (s, C_4), 126.38 (s, C_5), 72.02, 70.75, 70.42, 69.90 (all C_8 and C_9), 69.28 (s, C_7), 58.85 (s, C_{10}), 47.59 (s, C_1), 35.42 (s, C_6).

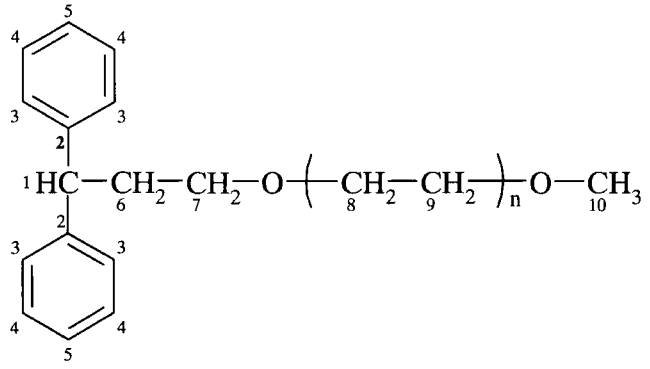


Figure 2.29 - Numbering scheme for CH_3I terminated PEO NMR assignments.

2.4.3 Synthesis of Propylidene Initiator $RuCl_2(=CHEt)(PCy_3)_2$

A sample of ruthenium benzylidene, $RuCl_2(=CHPh)(PCy_3)_2$, (0.50 g, 0.61 mmol) was dissolved in CH_2Cl_2 (6 mL) and placed in an ampoule with a magnetic stirrer. Five equivalents of *trans*-3-hexene (0.38 mL, 3.06 mmol) were added and the mixture stirred for 6 h before removing the solvent under vacuum. When the product had the consistency of a thick paste it was washed with acetone (chilled to –30 °C, 3 x 5 mL), filtered to remove side products (1-phenylbutene) and other impurities before

being dried at room temperature and a pressure of approximately $1x10^{-6}$ mbar *in vacuo* overnight. The acetone was chilled to minimise loss of the desired propylidene product, which is slightly soluble in acetone at room temperature. The solid was re-dissolved in CH_2Cl_2 (2 mL) and exposed to another five equivalents of *trans*-3-hexene (0.30 mL, 2.41 mmol) for 6 h and was worked up as described above. This procedure was repeated once more with a further 5 equivalents of *trans*-3-hexene (0.25 mL, 2.01 mmol) in order to achieve 100% conversion of benzylidene to propylidene, as shown by ^{1}H NMR spectroscopy. Yield = 0.34 g, 73%.

The initiator was fully characterised by NMR using the numbering scheme shown in **Figure 2.30**.

^{1}H NMR (C_6D_6, 500 MHz): δ 19.61 (t, J_{HH} = 5 Hz, 1H, $\mathbf{H_1}$), 3.08 (p, J_{HH} = 6.5 Hz, 2H, $\mathbf{H_2}$), 2.79-2.74, 2.03-2.00, 1.79-1.77, 1.71-1.66 and 1.32-1.21 (all m, $\mathbf{H_{5\text{-}8}}$), 1.37 (t, J_{HH} = 7.5 Hz, 3H, $\mathbf{H_3}$).

^{13}C NMR (C_6D_6, 126 MHz): δ 322.66 (t, $\mathbf{C_1}$), 54.42, (s, $\mathbf{C_2}$), 32.74 (*pseudo*-t, $\mathbf{C_5}$), 30.52 (s, $\mathbf{C_{3and7}}$), 28.69 (*pseudo*-t, $\mathbf{C_6}$), 27.44 (s, $\mathbf{C_8}$).

^{31}P NMR (C_6D_6, 162 MHz): δ 37.10 (s, $\mathbf{P_4}$).

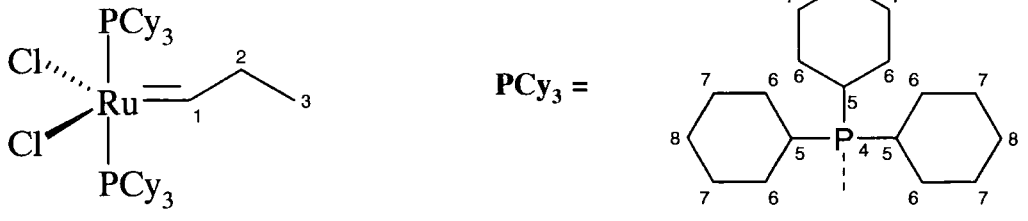


Figure 2.30 - Numbering scheme for ruthenium propylidene initiator, $RuCl_2(=CHPh)(PCy_3)_2$.

2.4.4 Synthesis of a Ruthenium PEO Macroinitiator

In a nitrogen-filled glovebox (M.Braun), PEO macromonomer (GPC M_n = 2400 g mol^{-1}, 500.0 mg, 0.2 mmol) was dissolved in C_6H_6 (2.5 mL) and placed in an ampoule. $RuCl_2(=CHEt)(PCy_3)_2$ (155.0 mg, 0.2 mmol) and C_6H_6 (5.5 mL) were added to another ampoule. Both ampoules were transferred to a vacuum line and kept under argon. The solution of PEO macromonomer was then introduced via a cannula to the agitated solution of initiator under an argon purge. Argon was bubbled through the mixture and agitation continued for a further hour. The solution was concentrated to half its original volume under vacuum and the solution was added drop-wise to vigorously stirred, degassed hexane (chilled to -78 °C, 40 mL) producing a red precipitate. The mixture was then filtered and washed thoroughly with chilled hexane

(3 x 10 mL) using standard cannula techniques. The solid obtained was dried *in vacuo* ($2x10^{-6}$ mbar) at room temperature overnight. Yield = 394 mg, 65%.

The macroinitiator was fully characterised by NMR using the numbering scheme shown in **Figure 2.31**.

^{1}H NMR (C_6D_6, 500 MHz): δ 20.56 (s, H_{15}), 8.74 (d, J_{HH} = 7.0 Hz, H_{13}), 7.31 (d, J_{HH} = 8.5 Hz, H_{12}), 7.21–7.13 and 7.06-7.00 (m, all $H_{3\text{-}5}$), 4.22 (t, J_{HH} = 8.0 Hz, H_1), 4.09(s, H_{11}), 3.50 (m, $H_{8,9}$), 3.27 (t, J_{HH} = 6.5 Hz, H_7), 2.88, 1.99-1.97, 1.74-1.71, 1.66-1.55, 1.32-1.16 (all m, $H_{17\text{-}20}$), 2.26 (q, J_{HH} = 7.5 Hz, H_6).

^{13}C NMR (C_6D_6, 126 MHz): δ 152.84 (s, C_{14}), 145.25 (s, C_2), 140.59 (s, C_{11}), 131.64 (s, $C_{13 \text{ or } 12}$), 128.71 (s, C_3), 128.41 (s, $C_{12 \text{ or } 13}$), 128.32 (s, C_4), 126.37 (s, C_5), 73.40 (s, C_{10}), 71.03, 70.63, 70.37 ($C_{8,9}$), 69.08 (s, C_7), 47.52 (s, C_1), 36.00 (s, C_6), 32.42 (*pseudo*-t, C_{17}), 30.15 (s, C_{19}), 28.14 (*pseudo*-t, C_{18}), 26.94 (s, C_{20}).

^{31}P NMR (C_6D_6, 162 MHz): δ 37.14 (s, P_{16}).

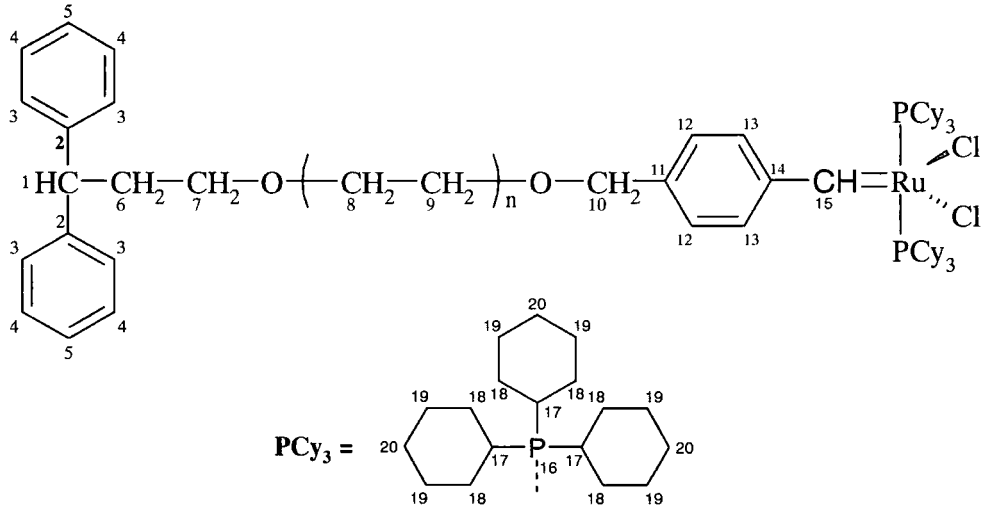


Figure 2.31 - Numbering scheme for NMR assignments of a ruthenium PEO macroinitiator.

2.4.5 Synthesis of ROMP Monomers

2.4.5.1 Synthesis of *Exo*-Bicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxy Anhydride

Maleic anhydride (490.0 g, 5.0 mol) and 1,2-dichlorobenzene (500 mL) were placed in a round bottomed flask equipped with a dropping funnel and condenser. The mixture was heated to reflux and dicyclopentadiene (335.0 mL, 330.0 g, 2.5 mol) placed in a separating funnel and added over the course of 20 min to the solution. The reflux was continued for a further 6 h during which the yellow solution turned orange and finally brown. The solution was then allowed to cool down to r.t. and was left

overnight to allow for complete crystallisation. The product was collected by filtration, yielding yellow crystals. This solid was then recrystallised five times from acetone to yield pure white crystalline *exo-* product. Yield = 75.14 g, 9.2% (lit.7.2%)[50]. m.p. 143-145 °C, lit. 143 °C[25].

Elemental analysis: Found C: 65.59%, H: 4.88 %; calculated for $C_9H_8O_3$ C: 65.85%, H: 4.91%.

The product was fully characterised by NMR using the numbering scheme shown in **Figure 2.32**.

^{1}H NMR (acetone-d_6, 500 MHz): δ 6.41 (m, 2H, $\mathbf{H_{5,6}}$), 3.38 (m, 2H, $\mathbf{H_{1,4}}$), 3.17 (m, 2H, $\mathbf{H_{2,3}}$), 1.63 (m, 1H, $\mathbf{H_7}$), 1.43 (m, 1H, $\mathbf{H_{7'}}$).

^{13}C NMR (acetone-d_6, 126 MHz): δ 172.42 ($\mathbf{C_{8,9}}$), 138.09 ($\mathbf{C_{5,6}}$), 49.15 ($\mathbf{C_{2,3}}$), 46.77 ($\mathbf{C_{1,4}}$), 44.00 ($\mathbf{C_7}$).

Mass Spectrum: (see **Appendix 2.4.2**) 164 (M+, $C_9H_8O_3$), 120 (M+-CO_2), 66 (M+-$C_4H_2O_3$).

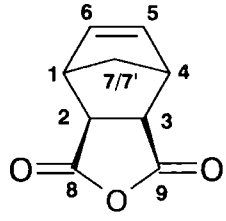


Figure 2.32 - Key for NMR assignments of *exo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride.

2.4.5.2 Synthesis of *exo-N*-Phenylbutylbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxyimide – NBE Monomer A

Exo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride (10 g, 0.061 mol) was dissolved in acetic acid (70 mL), by heating the mixture to reflux at 118 °C. 4-phenylbutylamine (9.63 mL, 0.061 mol) was then introduced over the course of 30 min. After a further two hours reflux the mixture was allowed to cool to r.t. following which the crude mixture was added to cold distilled H_2O (100 mL) producing white precipitate. The product was extracted by washing the suspension with CH_2Cl_2 (3 x 100 mL). The extract was washed thoroughly with H_2O (4 x 100 mL), dried with $MgSO_4$ and evaporated to dryness. The product was then recrystallised from petroleum ether (60-80 °C, 1250 mL), recovered by filtration, washed with chilled

petroleum ether (40-60 °C, 3 x 10 mL) and the white crystalline solid produced was dried *in vacuo*. Yield = 16.18 g, 90%. m.p. 114-116 °C, lit. 115 °C[30].

Elemental analysis: Found C: 77.32%, H: 7.21%, N: 4.63%; calculated for $C_{19}H_{21}N_1O_2$ C: 77.26%, H: 7.17%, N: 4.74%.

The monomer was fully characterised by NMR using the numbering scheme shown in **Figure 2.33**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29 - 7.13 (m, 5H, $\mathbf{H_{15\text{-}17}}$), 6.27 (m, 2H, $\mathbf{H_{5,6}}$), 3.49(m, 2H, $\mathbf{H_{10}}$), 3.26 (m, 2H, $\mathbf{H_{1,4}}$), 2.66 (m, $H_{2,3}$), 2.62 (m, H_{13}), 1.61 (m, 4H, $\mathbf{H_{11,12}}$), 1.49 (m, 1H, $\mathbf{H_{7\text{ or }7'}}$), 1.20 (m, 1H, $\mathbf{H_{7'\text{ or }7}}$).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 178.36 ($\mathbf{C_{8,9}}$), 142.17 ($\mathbf{C_{14}}$), 138.08 ($\mathbf{C_{5,6}}$), 128.65/ 128.61 ($\mathbf{C_{15,16}}$), 126.09 ($\mathbf{C_{17}}$), 48.06 ($\mathbf{C_{2,3}}$), 45.41 ($\mathbf{C_{1,4}}$), 43.00 ($\mathbf{C_{7/7'}}$), 38.69 ($\mathbf{C_{10}}$), 35.60 ($\mathbf{C_{13}}$), 29.07, 27.66 ($\mathbf{C_{11,12}}$).

Mass Spectrum: (see **Appendix 2.4.5**) 295 (M+, $C_{19}H_{21}N_1O_2$), 230 (MH+-C_5H_6), 91 (M+-C_7H_7), 66 (M+-$C_{12}H_{15}NO_2$).

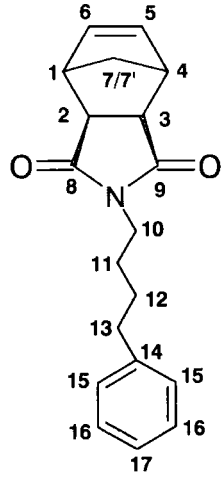


Figure 2.33 - Key for NMR assignments of *exo,exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide.

2.4.6 ROMP Homopolymerisations

2.4.6.1 NMR Scale ROMP Reactions

Polymerisation reactions were carried out with 10 mg of $RuCl_2(=CHPh)(PCy_3)_2$ and 20 equivalents of monomer and were assembled in a nitrogen-filled glovebox (M.Braun) using 7 mL screw top vials. For instance *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (monomer **B**,

52 mg, 0.2 mmol) in $CDCl_3$ (0.4 mL) was added to a stirred solution of $RuCl_2(=CHPh)(PCy_3)_2$ (10 mg, 1 $x10^{-2}$ mmol) in $CDCl_3$ (0.4 mL). The mixture was then transferred to an NMR tube which was sealed with a Young's tap to create an air tight seal. The ^1H NMR spectrum of the reaction was then collected (24 to -1 ppm) and was repeated at approximately regular intervals until complete consumption of the olefinic resonances (6-7 ppm) of the monomer was evident.

2.4.6.2 The Synthesis of Poly(*exo-N*-Phenylbutylbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxyimide) – PNB A (DP of 100).

Exo-N-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (Monomer **A**, 359 mg, 1.2 mmol) was dissolved in CH_2Cl_2 (2 mL). This solution was added to a stirred solution of ruthenium benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$ (10 mg, 0.1 mmol) dissolved in CH_2Cl_2 (1 mL). After 1 h the living polymer was terminated by the addition of a few drops of ethyl vinyl ether under a stream of N_2. The solution was stirred for a further 1 h after which it was concentrated to approximately 1.5 mL using a stream of N_2 and precipitated with vigorous agitation in hexane (15 mL). The resulting precipitate was recovered by filtration, washed with hexane (3 x 5 mL) and dried *in vacuo*. The polymer was then purified by dissolving it in CH_2Cl_2 and precipitating it in hexane twice. Yield = 0.301 g, 84%.

Target M_n: 29500 g mol^{-1}.

THF GPC: M_n = 27300 g mol^{-1}, PDI = 1.06.

DMF GPC: M_n = 17600 g mol^{-1}, PDI = 1.11.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.34**.

^1H NMR ($CDCl_3$, 500 MHz): δ 7.29 - 7.13 (brm, H_{15-17}), 5.76-5.70 (brm, *trans* $H_{5,6}$), 5.54-5.47 (*cis* $H_{5,6}$), 3.48 (brm, H_{10}), 3.25 (brm, *cis* $H_{2,3}$), 3.06-2.94 (brm, *trans* $H_{2,3}$), 2.75 (brm, *cis* $H_{1,4}$), 2.63 (brm, *trans* $H_{1,4 \text{ and } 13}$), 2.17-2.10 (brm, *trans* $H_{7 \text{ or } 7'}$), 2.10-2.03 (brm, *cis* $H_{7 \text{ or } 7'}$), 1.63 (brm, $H_{7' \text{ or } 7}$), 1.60 (brm, $H_{11,12}$).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 178.5 ($C_{8,9}$) 142.25/142.21 (C_{14}), 134 (*trans* $C_{5,6}$), 132 (*cis* $C_{5,6}$), 128.6 ($C_{15,16}$), 126.10/126.08 (C_{17}), 52.84 (*cis* $C_{2,3}$), 51.19/51.08 (*trans*, $C_{2,3}$), 46.48/46.29/46.11 (*cis/trans*, $C_{1,4}$), 42.46/42.30, 41.13 (C_7), 38.68/38.51 (C_{10}) 35.6 (C_{13}), 28.96/28.87, 27.58/27.53 ($C_{11,12}$).

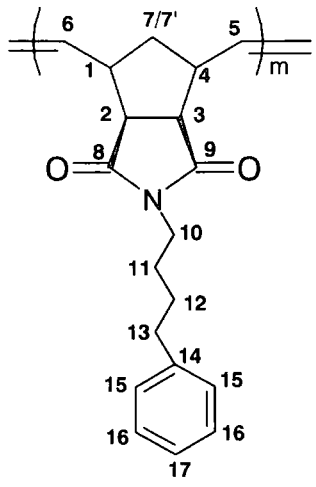


Figure 2.34 - Key for NMR assignments for poly(*exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide).

2.4.6.3 The Synthesis of Poly (*endo,exo*-Bicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxylic acid Dimethyl Ester) – PNB B (DP of 100).

The polymerisation was performed in a very similar manner to that of monomer **A**, except that *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (monomer **B**, 255 mg, 1.2 mmol) dissolved in CH_2Cl_2 (2 mL) was added to the initiator solution. The solution was stirred for 24 h prior to termination and purification as described for NBE monomer **A**. Yield = 0.205 g, 80%.

Target M_n: 21000 g mol^{-1}.

THF GPC: M_n = 12700 g mol^{-1}, PDI = 1.02.

DMF GPC: M_n = 17600 g mol^{-1}, PDI = 1.05.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.35**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.48-5.19 (3 x brm $\mathbf{H_{5,6}}$), 3.70-3.63 ($\mathbf{H_{10,11}}$), 3.24 (brm, $\mathbf{H_{2,3}}$), 2.98-2.94 (brm, $\mathbf{H_{1,4\ and\ 2,3}}$), 2.70 (brm, $\mathbf{H_{1,4}}$), 2.08-1.84 (brm, $\mathbf{H_7}$) 1.58–1.40 (brm, $\mathbf{H_{7'}}$).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 174 (*exo* $\mathbf{C_{8,9}}$), 173 (*endo* $\mathbf{C_{8,9}}$), 133.4-129.6 ($\mathbf{H_{5,6}}$), 52.75 - 52.50 ($\mathbf{C_{1,4}}$), 52.35/52.20 ($\mathbf{C_{2,3}}$), 51 ($\mathbf{C_{10,11}}$), 47-46.5 ($\mathbf{C_{1,4}}$), 45.0-44.0($\mathbf{C_{2,3}}$), 40.6-38.6 ($\mathbf{C_7}$), 39.47($\mathbf{C_{2,3}}$).

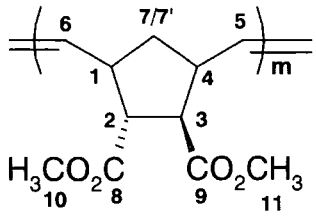


Figure 2.35 - Key for NMR assignments for poly (*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester).

2.4.6.4 The Synthesis of Poly(*endo,endo*-5,6-bis[Chloromethyl]Bicyclo[2.2.1] Hept-2-ene) – PNB C (DP of 100).

The polymerisation was performed in a very similar manner to that of NBE monomer **A**, except that *endo,endo*-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (monomer **C**, 232 mg, 1.2 mmol) dissolved in CH_2Cl_2 (2 mL) was added to the initiator solution. The solution was stirred for 1 h prior to termination and purification as described for monomer **A**. Yield = 0.138 g, 60%.

Target M_n: 19100 g mol^{-1}.

THF GPC: M_n = 18000 g mol^{-1}, PDI = 1.15.

DMF GPC: M_n = 11000 g mol^{-1}, PDI = 1.58.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.36**.

^{1}H NMR ($CDCl_3$, 500 MHz): 5.62-5.29 (brm, $\mathbf{H_{2,3}}$), 3.78-3.40 (brm, $\mathbf{H_{8,9}}$), 3.11 (brm, $\mathbf{H_{1,4}}$ *cis*), 2.83 (br, $\mathbf{H_{1,4}}$ *trans*), 2.59 (brm, $\mathbf{H_{5,6}}$ *trans*), 2.25 (brm, $\mathbf{H_{5,6}}$ *cis*), 2.16-2.04, 1.64-1.48 (brm, $\mathbf{H_{7\ and\ 7'}}$).

^{13}C NMR ($CDCl_3$, 126 MHz): 132.5-130.8 ($\mathbf{C_{2,3}}$), 49.2-48.7 ($\mathbf{C_{5,6}}$), 44.8-44.0 ($\mathbf{C_{1,4}}$), 42.9-42.6 ($\mathbf{C_{8,9}}$), 38.8-38.0 ($\mathbf{C_{1,4\ and\ 7}}$), 36.86 ($\mathbf{C_7}$).

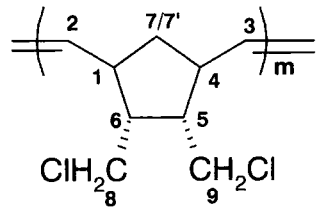


Figure 2.36 - Key for NMR assignments for poly(*endo,endo*-5,6-bis[chloromethyl]-bicyclo[2.2.1]hept-2-ene).

2.4.7 Synthesis of PEO-PNB Block Copolymers

2.4.7.1 Synthesis of Poly(Ethylene Oxide)-*block*-(*exo*-*N*-Phenylbutylbicyclo [2.2.1]Hept-5-ene-2,3-Dicarboxyimide) – PEO(DP = 55) -PNB A (DP = 100).

All ROMP reactions were performed in a nitrogen-filled glovebox (M.Braun) in screw top vials. *Exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (Monomer A, 132 mg, 0.5 mmol) was dissolved in CH_2Cl_2 (2 mL). This solution was added to a stirred solution of a ruthenium PEO macroinitiator (20.0 mg, 5 x 10^{-3} mmol, PEO macromonomer M_n = 2400 g mol^{-1}, DP = ~ 55) dissolved in CH_2Cl_2 (1 mL). After 1 h the living polymer was terminated by the addition of ethyl vinyl ether (0.1 mL, 1.1 mmol) under a stream of N_2. The solution was stirred for a further h, after which it was concentrated to approximately 0.5 mL using a stream of N_2 and precipitated with vigorous agitation in hexane (5 mL). The resulting precipitate was recovered by filtration, washed with hexane and dried *in vacuo* at room temperature overnight (Yield = 0.126 g (85%). The block copolymer was then purified by dissolving it in CH_2Cl_2 and precipitating it in hexane twice. Yield = 0.052 g, 35%.

Elemental analysis: Found C: 74.61%, H: 7.33%, N: 4.07%; calculated for $C_{2024}H_{2324}N_{100}O_{251}$ C: 75.81%, H: 7.30%, N: 4.37%.

Target M_n: 31900 g mol^{-1}.

DMF GPC: M_n = 16400 g mol^{-1}, PDI = 1.10.

The block copolymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.37**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.29-7.13 (brm, H_{15-17}), 5.76-5.70 (brm, *trans* $H_{5,6}$), 5.54-5.47 (*cis* $H_{5,6}$), 3.65 (CH_2CH_2O), 3.48 (brm, H_{10}), 3.25 (brm, *cis* $H_{2,3}$), 3.06-2.94 (brm, *trans* $H_{2,3}$), 2.75 (brm, *cis* $H_{1,4}$), 2.63 (brm, *trans* $H_{1,4 \text{ and } 13}$), 2.17-2.10 (brm, *trans* $H_{7 \text{ or } 7'}$), 2.10-2.03 (brm, *cis* $H_{7 \text{ or } 7'}$), 1.63 (brm, $H_{7' \text{ or } 7}$) 1.60 (brm, $H_{11,12}$).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 178.5 ($C_{8,9}$) 142.25/142.21 (C_{14}), 134 (*trans* $C_{5,6}$), 132 (*cis* $C_{5,6}$), 128.6 ($C_{15,16}$), 126.10/126.08 (C_{17}), 70.78 (CH_2CH_2O), 52.84 (*cis* $C_{2,3}$), 51.19/51.08 (*trans*, $C_{2,3}$), 46.48/46.29/46.11 (*cis/trans*, $C_{1,4}$), 42.46/42.30, 41.13 (C_7), 38.68/38.51 (C_{10}), 35.6 (C_{13}), 28.96/28.87, 27.58/27.53 ($C_{11,12}$).

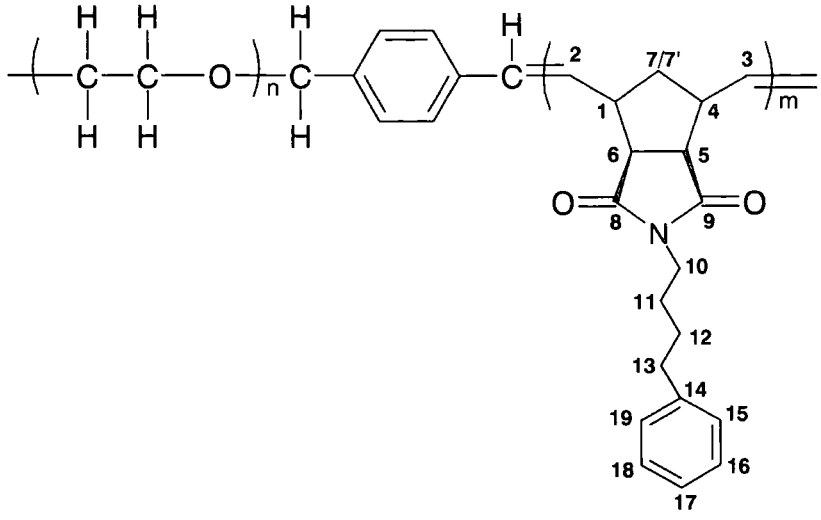


Figure 2.37 - Numbering scheme for NMR assignments of poly(ethylene oxide)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide).

2.4.7.2 Synthesis of Poly(Ethylene Oxide)-*block*-(*exo*-*N*-Phenylbutylbicyclo [2.2.1]Hept-5-ene-2,3-Dicarboxyimide) – PEO (DP = 55) - PNB A (DP = 200).

The polymerisation was performed in a similar manner to that in Section 2.4.7.1 except that Monomer A (264 mg, 0.9 mmol) dissolved in CH_2Cl_2 (4 mL) was added to the initiator solution. The solution was stirred for 2 h prior to termination with ethyl vinyl ether, stirred for a further 1 h, after which it was concentrated to approximately 1.0 mL using a stream of N_2, and purified as previously described. Yield = 0.218 g, 78 %.

Elemental analysis: Found C: 75.29%, H: 8.04%, N: 3.94%; calculated for $C_{3924}H_{4424}N_{200}O_{451}$ C: 76.50%, H: 7.24%, N: 4.55%.

Target M_n: 61500 g mol^{-1}.

DMF GPC: M_n = 28400 g mol^{-1}, PDI = 1.21.

NMR data was identical to that in Section 2.2.11 with the exception of the relative intensities of the two sets of resonances from the PEO and PNB blocks.

2.4.7.3 Synthesis of Poly(Ethylene Oxide)-*block*-(*exo*-*N*-Phenylbutylbicyclo [2.2.1]Hept-5-ene-2,3-Dicarboxyimide). PEO (DP = 55) - PNB A (DP = 500).

The polymerisation was performed in a similar manner to that in Section 2.4.7.1 except that Monomer A (661 mg, 2.3 mmol) dissolved in CH_2Cl_2 (10 mL) was added to the initiator solution. The solution was stirred for 5 h prior to termination with ethyl vinyl ether, stirred for a further 1 h, after which it was concentrated to

approximately 4.0 mL using a stream of N_2, and purified as previously described. Yield = 0.640 g, 96%.

Elemental analysis: Found C: 75.86%, H: 7.24%, N: 4.66%; calculated for $C_{9624}H_{10724}N_{500}O_{1051}$ C: 76.95%, H: 7.20%, N: 4.66%.

Target M_n: 150100 g mol^{-1}.

DMF GPC: M_n = 63100 g mol^{-1}, PDI = 1.21.

NMR data was identical to that in Section 2.2.11 with the exception of the relative intensities of the two sets of resonances from the PEO and PNB blocks.

2.4.7.4 Synthesis of Poly(Ethylene Oxide)-*block*-(*endo,exo*-Bicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxylic Acid Dimethyl Ester). PEO (DP = 55) - PNB B (DP = 100).

The polymerisation was performed in a similar manner to that in Section 2.4.7.1 except that *Endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (Monomer **B**, 66.4 mg, 0.3 mmol) dissolved in CH_2Cl_2 (2 mL) was added to the initiator solution. The solution was stirred for 24 h prior to termination with ethyl vinyl ether, stirred for a further 1 h, after which it was concentrated to approximately 0.5 mL using a stream of N_2, and purified as previously described. Yield = 0.053 g, 48%.

Elemental analysis: Found C: 61.57%, H: 7.06%; calculated for $C_{1224}H_{1624}O_{451}$ C: 62.42%, H: 6.95%.

Target M_n: 23400 g mol^{-1}.

DMF GPC: M_n = 15700 g mol^{-1}, PDI = 1.08.

The block copolymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.38**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.48-5.19 (3 x brm $\mathbf{H_{5,6}}$), 3.70-3.63 ($\mathbf{H_{10,11}}$), 3.65 ($\mathbf{CH_2CH_2O}$), 3.24 (brm, $\mathbf{H_{2,3}}$), 2.98-2.94 (brm, $\mathbf{H_{1,4\ and\ 2,3}}$), 2.70 (brm, $\mathbf{H_{1,4}}$), 2.08-1.84 (brm, $\mathbf{H_7}$) 1.58–1.40 (brm, $\mathbf{H_{7'}}$).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 174 (*exo* $\mathbf{C_{8,9}}$), 173 (*endo* $\mathbf{C_{8,9}}$), 133.4-129.6 ($\mathbf{H_{5,6}}$), 70.78 ($\mathbf{CH_2CH_2O}$), 52.75-52.50 ($\mathbf{C_{1,4}}$), 52.35/52.20 ($\mathbf{C_{2,3}}$), 51 ($\mathbf{C_{10,11}}$), 47-46.5 ($\mathbf{C_{1,4}}$), 45.0-44.0($\mathbf{C_{2,3}}$), 40.6-38.6 ($\mathbf{C_7}$), 39.47($\mathbf{C_{2,3}}$).

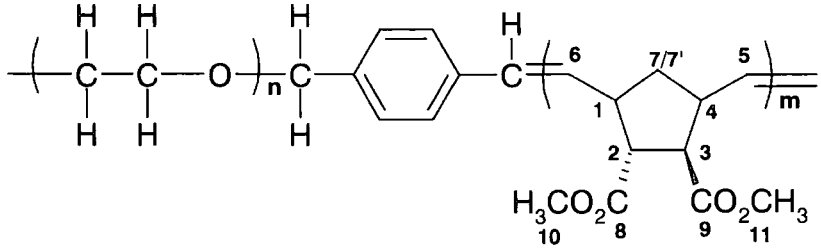


Figure 2.38 - Numbering scheme for NMR assignments of poly(ethylene oxide)-*block*-(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester).

2.4.7.5 Synthesis of Poly(Ethylene Oxide)-*block*-(*endo,endo*-5,6-bis-Chloromethyl-Bicyclo[2.2.1]Hept-2-ene) – PEO (DP = 55) - PNB C (DP = 100).

The polymerisation was performed in a similar manner to that in Section 2.4.7.1 except that *endo,endo*-5,6-bis-chloromethyl-bicyclo[2.2.1]hept-2-ene (Monomer C, 86 mg, 0.5 mmol) dissolved in CH_2Cl_2 (2 mL) was added to the initiator solution. The solution was stirred for 1 h prior to termination with ethyl vinyl ether, stirred for a further 1 h, after which it was concentrated to approximately 0.5 mL using a stream of N_2, and purified as previously described. Yield = 0.042 g, 42%.

Elemental analysis: Found C: 56.58 %, H: 6.71 %; calculated for $C_{1024}H_{1424}Cl_{200}O_{51}$ C: 56.83 %, H: 6.63 %.

Target M_n: 21500 g mol^{-1}.

DMF GPC: M_n = 10000 g mol^{-1}, PDI = 1.32.

The block copolymer was fully characterised by NMR using the numbering scheme shown in **Figure 2.39**.

^{1}H NMR ($CDCl_3$, 500 MHz): 5.62-5.29 (brm, $\mathbf{H_{2,3}}$), 3.78-3.40 (brm, $\mathbf{H_{8,9}}$), 3.65 ($\mathbf{CH_2CH_2O}$), 3.11 (brm, $\mathbf{H_{1,4}}$ *cis*), 2.83 (br, $\mathbf{H_{1,4}}$ *trans*), 2.59 (brm, $\mathbf{H_{5,6}}$ *trans*), 2.25 (brm, $\mathbf{H_{5,6}}$ *cis*), 2.16-2.04, 1.64-1.48 (brm, $\mathbf{H_{7\ and\ 7'}}$).

^{13}C NMR ($CDCl_3$, 126 MHz): 132.5-130.8 ($\mathbf{C_{2,3}}$), 70.78 ($\mathbf{CH_2CH_2O}$), 49.2-48.7 ($\mathbf{C_{5,6}}$), 44.8-44.0 ($\mathbf{C_{1,4}}$), 42.9-42.6 ($\mathbf{C_{8,9}}$), 38.8-38.0 ($\mathbf{C_{1,4\ and\ 7}}$), 36.86 ($\mathbf{C_7}$).

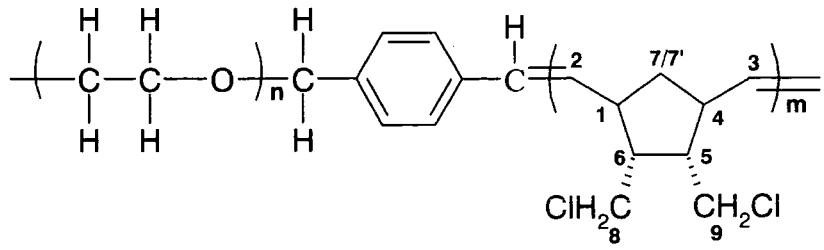


Figure 2.39 - Numbering scheme for NMR assignments of poly(ethylene oxide)-*block*-(*endo,endo*-5,6-bis[chloromethyl]bicyclo[2.2.1]hept-2-ene).

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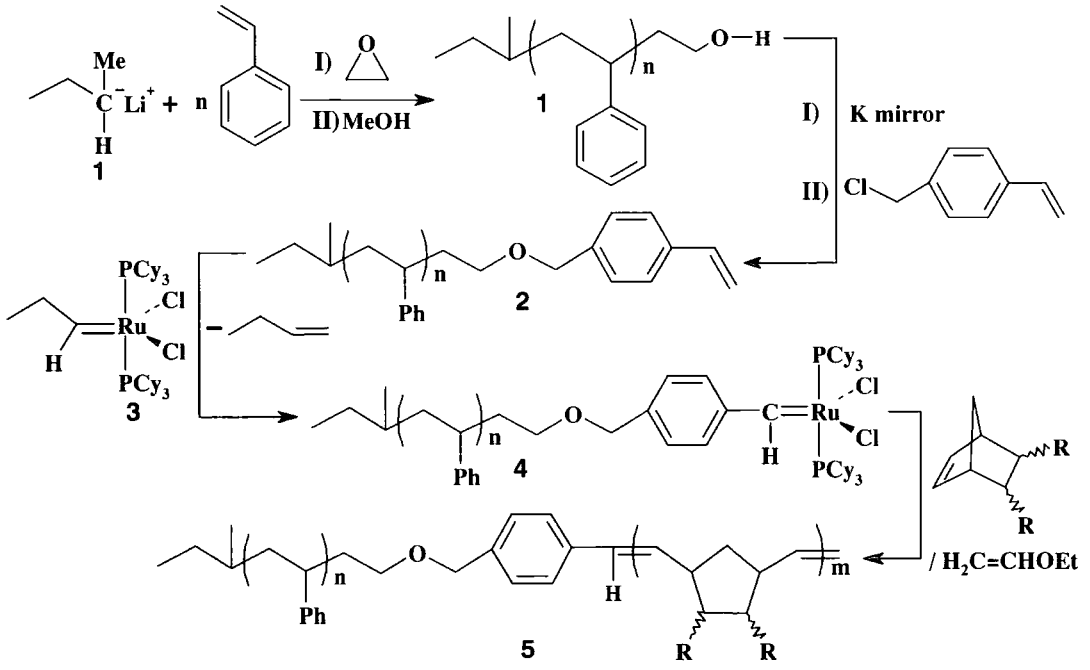
Chapter 3

Block Copolymers of Styrene and Norbornene Derivatives

3.1 Introduction

In Chapter 2 a method for the conversion of the living anionic polymerisation of ethylene oxide initiated by diphenylmethyl potassium, into living ring opening metathesis polymerisation (ROMP) was described. The majority of well-defined living anionic polymerisations are initiated using alkyllithium compounds, for example *sec*-butyllithium, and propagate via carbanion/lithium ion pairs.[1] It is thus desirable to extend the methodology to allow the combination of these polymerisations with ruthenium initiated ROMP. This concept is also demonstrated in this chapter by the synthesis of well-defined block copolymers of styrene, polymerised by an anionic mechanism initiated by an alkyllithium compound, with norbornene (NBE) derivatives polymerised by a ROMP mechanism (**Scheme 3.1**).



Scheme 3.1 - Synthesis of poly(styrene–norbornene) block copolymers. Cy= Cyclohexyl.

In one of the crucial steps of the route to the synthesis of poly(ethylene oxide)(PEO)-polynorbornene(PNB) block copolymers described in Chapter 2, the chain ends of the living PEO were functionalised to form macromonomers by the addition of 4-vinylbenzyl chloride (4-VBC) to the living polymer. This functionalisation occurred in almost quantitative yield. The high nucleophilicity of many carbanions complicates the

functionalisation of living polymers [e.g. poly(styryl)lithium (PSLi)] with 4-VBC to form analogous macromonomers. This high reactivity was overcome by end capping living polystyrene (PSLi), initiated with *sec*-butyllithium (*sec*-BuLi), with ethylene oxide in order to synthesise ω-hydroxyethylated PS (**1**). Williamson coupling reactions between, metal-alkoxides formed from the hydroxyethylated polystyrene (PS) (**1**), and 4-VBC were used to synthesise the macromonomers (**2**). The metal alkoxide was synthesised either by deprotonating **1** with K metal (**Scheme 3.1**), or alternatively was generated *in situ* using NaH and 15-crown-5. The methodology described in Chapter 2 for the conversion of PEO macromonomers into block copolymers, can then be followed to convert the PS macromonomers into PS-PNB block copolymers. The macromonomers (**2**) were used as precursors to ruthenium macroinitiators (**4**), synthesised by an alkylidene exchange reaction with the ruthenium complex $RuCl_2(=CHEt)(PCy_3)_2$(**3**). The macroinitiators were used to initiate the ROMP of NBE derivatives resulting in the synthesis of a range of block copolymers (**5**).

3.2 Results and Discussion

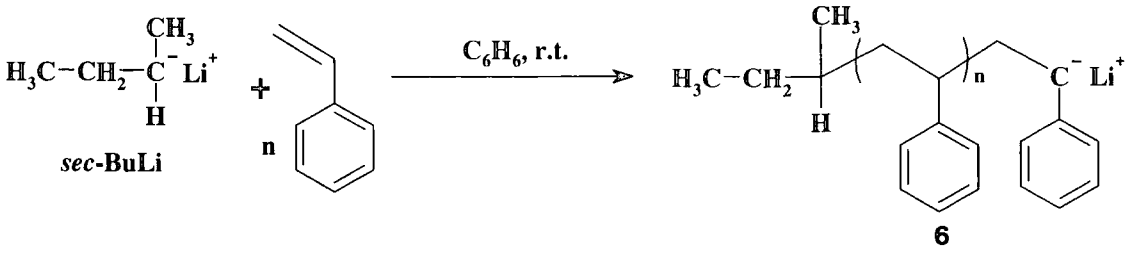
3.2.1 Synthesis and Characterisation of PS Macromonomers from PSLi

As discussed in Chapter 1 the anionic polymerisation of styrene was amongst the first living polymerisations to be discovered and was the inspiration for their name.[2] It was chosen here to be a component of the block copolymers, as it demonstrates the concept of the combination of lithium initiated anionic polymerisation with ruthenium ROMP.

3.2.1.1 Synthesis and Characterisation of Polystyrene via *sec*-Butyllithium Initiated Anionic Polymerisation

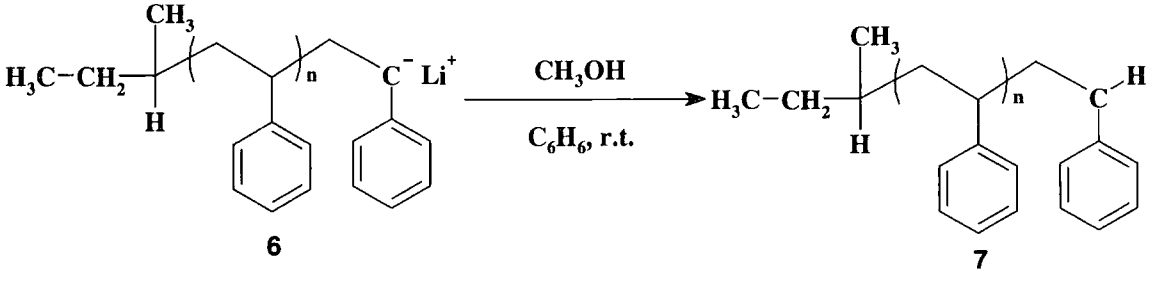
The alkyllithium initiated polymerisation of styrene proceeds in the complete absence of chain transfer or termination in benzene. The reaction is however extremely sensitive to moisture, oxygen, CO_2, and protic impurities. The monomer and benzene solvent were therefore rigorously purified to avoid loss of control (via unwanted termination reactions) over the molecular weight, polydispersity and the number of chains available for functionalisation. The reactor used for the polymerisation of ethylene

oxide (Chapter 2, **Figure 2.1**, and accompanying text) was used for the polymerisation, and prepared in the same manner, to ensure exclusion of moisture, CO_2, and oxygen. In addition to its widespread commercial availability, *sec*-BuLi was chosen as it possesses one of the highest rates of initiation (R_i), relative to that of propagation (R_p), for the polymerisation of styrene (see Section 1.3.2).[1]



Scheme 3.2 - Anionic polymerisation of styrene initiated by *sec*-BuLi.

The polymerisation is complete within a short space of time at room temperature, 30 mins reaction time being sufficient for the synthesis of polymer with a M_n of 2850 g mol^{-1}. Three different molecular weights of PS were synthesised. The majority of the poly(styryl)lithium (PSLi, **6**, **Scheme 3.2**) was end-capped with ethylene oxide (discussed in detail in Section 3.2.1.2); however an aliquot was terminated with MeOH to provide a sample for analysis. The MeOH was N_2 purged prior to injection to avoid side-reactions between the PSLi and O_2. Addition of an excess of MeOH to PSLi was observed to result in the immediate and complete loss of the red colour of the living polymer (**6**) to form a colourless solution of terminated PS (**7**).



Scheme 3.3 - Termination of living PS with MeOH.

The reaction protonates the carbanion, leaving a methylene group at one end of the polymer chain (**Scheme 3.3**). GPC analysis in THF (**Appendix 3.1.1**) of all three of the polymers indicated they had low polydispersities (**Table 3.1**).

Table 3.1 - Molecular weight data from PS homopolymers.

Sample	Target M_n g mol^{-1}	Terminating agent	M_n/THF GPC g mol^{-1}	PDI/ THF GPC g mol^{-1}
EO PS 1	2500	EO/ MeOH	2950	1.02
PS H 1		MeOH	2850	1.02
EO PS 2	5000	EO/ MeOH	5900	1.09
PS H 2		MeOH	5700	1.10
EO PS 3	10000	EO/ MeOH	10600	1.06
PS H 3		MeOH	10500	1.06

EO PS = hydroxyethylated polystyrene (Section 3.2.1.2), PS H = unfunctionalised PS.

Values for the molecular weight of the PS homopolymers were calculated using triple detection. The values for M_n are in reasonable agreement with those predicted by the reaction stoichiometry. The trend is for the molecular weights to be slightly higher than predicted – a possible contributor could be the commercially supplied *sec*-butyllithium being of a slightly lower concentration than certified. MALDI analysis of sample PS H 1 was also carried out (**Appendix 3.1.2**), from which a value for M_n of 2950 g mol^{-1} was calculated, very similar to the value calculated from GPC of 2850 g mol^{-1}.

The Polystyrenes were also studied by NMR spectroscopy (**Figure 3.1**).

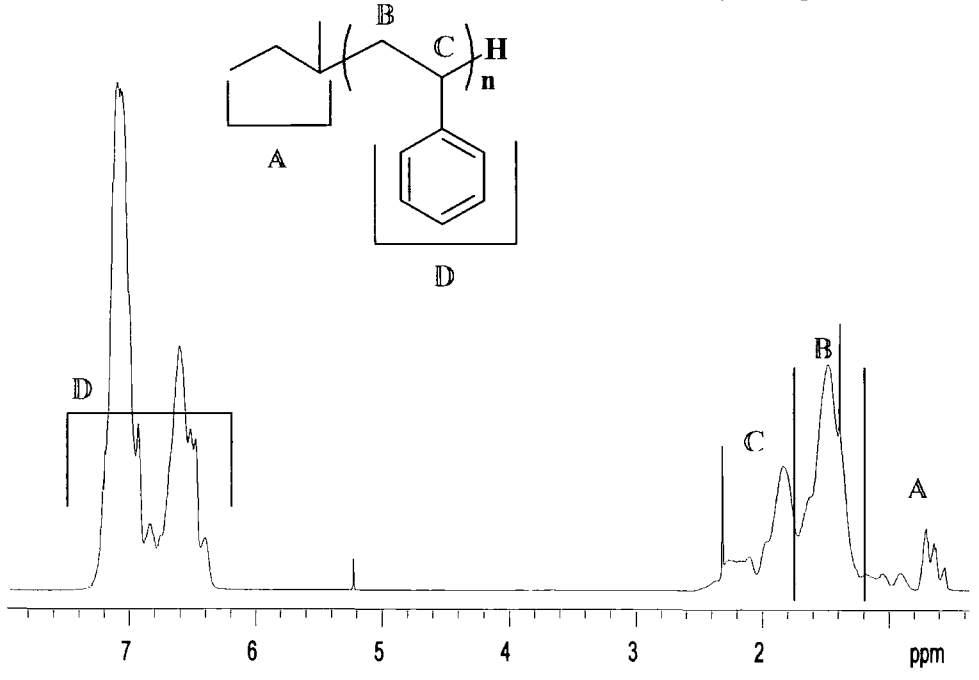


Figure 3.1 - The ^{1}H NMR spectrum of polystyrene.

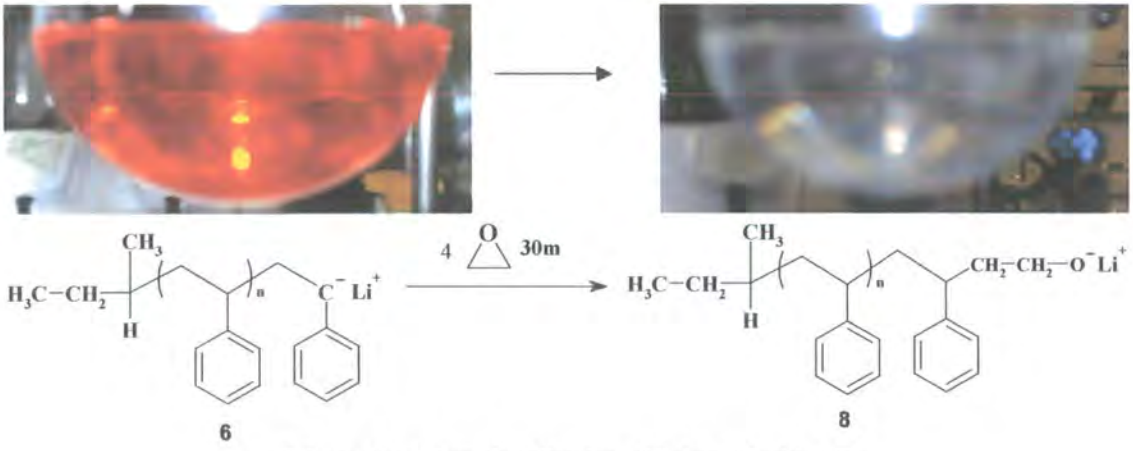
The ^{1}H NMR spectrum is dominated by the aryl protons from the pendant phenyl groups (𝔻) and the alkyl peaks from the backbone (𝔹 and ℂ). The NMR spectra of the PS discussed here is typical of that produced from living anionic polymerisation initiated with alkyllithium compounds,[3,4] suggesting the polymer is atactic.[1] The peaks in the ^{1}H (**Figure 3.1**) and ^{13}C NMR spectra (**Appendix 3.1.3**) are broadened relative to those in the spectra of the PEO homopolymers, due to the presence of the chiral centres responsible for tacticity. The NMR spectra of the polymer were principally assigned using existing assignments.[3,5] The *sec*-butyl end group, introduced from the *sec*-BuLi initiator, can be observed between 1.24 and 0.50 ppm. There was inadequate resolution to separate the peaks of the *sec*-butyl end group, in spectra recorded in chlorinated solvents on a 500 MHz spectrometer, from one another and those of the PS backbone. They are thus not of use in assessing the functionalisation of the polymer in the later steps. The *sec*-butyl group gives rise to a broad singlet and numerous clusters of peaks below 35 ppm in ^{13}C.

3.2.1.2 Synthesis and Characterisation of Hydroxyethylated PS

Carbanions are generally more nucleophilic than the ω-oxyanions present on living PEO chains. The carbanions on PSLi are amongst the most nucleophilic found on living anionic polymers.[1] The reactivity of PSLi is such that it can initiate the polymerisation of a wide range of monomers; it is therefore usually polymerised first in strategies to synthesise block copolymers by sequential addition of monomers. The high reactivity of PSLi means there are relatively few reactions available that lead to well controlled functionalisation of the polymer.[1] A number of the reactions which have been developed require extensive optimisation of the reaction conditions, and will not be applicable to other polymers without extensive optimisation. A method for the synthesis of PS macromonomers that did not require significant optimisation of the reaction parameters of the functionalisation reactions was sought. It was anticipated that such a methodology might be sufficiently flexible to form the basis of a general strategy for the synthesis of macromonomers from many lithium initiated polymerisations. 4-VBC is a styrene derivative (alternative name *p*-chloromethyl styrene) and it is commonly used as

a monomer to synthesise macromolecular materials via a radical mechanism.[6,7] It is therefore not entirely surprising that addition of 4-VBC to PSLi using the reaction conditions used to functionalise the PEO macromonomers results in vinyl addition as well as an S_N2 reaction with the chloromethyl group.[8] The S_N2 reaction with the halide is faster than the reaction with the vinyl group, but even by increasing the excess of 4-VBC relative to the chain ends to 8.25 only 50% macromonomer is formed, the other major product being a dimer of polystyrene.[8] Asami et al. have developed a method for the functionalisation of PS-Li using 4-VBC.[8] This required specially designed equipment in which the living PS-Li in C_6H_6 was pre-mixed with THF. This had the effect of creating a highly solvated ion-pair which increased the reactivity of PS-Li towards the benzylic halides, relative to the vinyl group. The 4-VBC must be used in the form of a dilute solution in THF. Furthermore the method of combination of the two requires precise control, the PS-Li solution being added dropwise to the 4-VBC solution at 0 °C, to ensure an excess of the benzylic halide with respect to living chain ends at all times. The yield of macromonomer was assumed to be quantitative when GPC indicated the product of the reaction was monomodal, and therefore free from PS dimer. The low chloride concentration of the samples was taken as further evidence of the success of the reaction, although the polymers were not apparently studied by NMR. Problems are likely to be encountered when applying this strategy to the functionalisation of other polymers, the different reactivities of the carbanion-pairs will change the relative speed of the reactions of the carbanions with the benzylic chloride and vinyl group, potentially reducing the yield of macromonomer. Whilst it has been reported that no significant termination of PSLi by THF occurs over the lifetime of the experiment when 20% (v/v) THF is used in cyclohexane,[9] a general problem with the use of THF solutions in organolithium based synthesis is metallation of the solvent[10] (PSLi is unstable in pure THF see Section 1.3.3). Different carbanions possess different stabilities in THF;[11] different living anionic polymers will react at different rates with THF, possibly resulting in significant loss of the living polymer. A method was thus sought that would avoid the design and use of new and complicated equipment, and which would not require extensive optimisation in order to generate macromonomers from different anionic polymerisations.

An alternative approach is to reduce the reactivity of the polystyryl lithium by 'end-capping' the living chain, with for example an epoxide, most typically ethylene oxide (EO), but occasionally propylene or 1-butene oxide. Chain transfer to the alkyl group is observed with propylene oxide[12] and to a much lesser extent 1-butene oxide,[13] reducing the yield of functionalisation below a quantitative level. The reaction of PS-Li with ethylene oxide (EO) proceeds quantitatively, to yield poly(styryl)hydroxyethyl lithium.[14] In all known cases where functionalisation of living polymers with EO is successful the resulting species is a lithium alkoxide, typically $RCH_2CH_2O^-Li^+$. The alkoxides exist in the form of highly stable aggregates in solution. This aggregation hinders oligomerisation of the EO, although with increased reaction times, particularly in the case of polybutadiene, oligomerisation does occur.[15] Whilst oligomerisation can be avoided by minimising the reaction time, the lithium alkoxide product of oligomerisation of EO on a polymer would be expected to have very similar reactivity to the hydroxyethylated species. Development of a method for converting the lithium alkoxide formed from reaction of EO and polystyrene (PS) into macromonomer could therefore prove to provide the basis for a general method for converting alkyllithium initiated anionic polymerisations into macromonomers. The hydroxyethylation reaction is carried out by distilling EO into the polymerisation reaction vessel. The reaction appears to be almost instant based on the quick conversion of the red PSLi (**6**) ion pairs into the approximately colourless oxo anions of **8** (**Scheme 3.4**).



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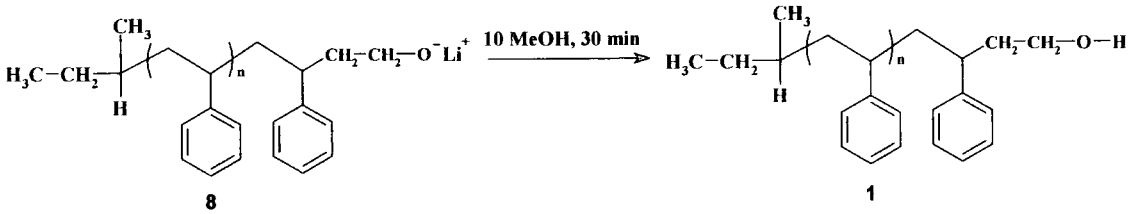
Scheme 3.4 - Functionalisation of living PS with EO.

Reaction of the ethylene oxide capped living polymer with 10 equivalents of MeOH results in the protonation of the alkoxide to form an alcohol. The resulting hydroxyethyl functionalised PS (**1**) can then be isolated and purified (**Scheme 3.5**).



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Scheme 3.5 - Synthesis of hydroxyethyl functionalised polystyrene.

The isolated hydroxyethyl functionalised PS was then characterised. Data from GPC analysis were very similar to that of the unfunctionalised PS homopolymers, and indicated the samples retain a low PDI (**Appendix 3.1.4**). The NMR of the polymer is essentially identical to that of published spectra of PS end functionalised with EO (**Figure 3.2**).[4]

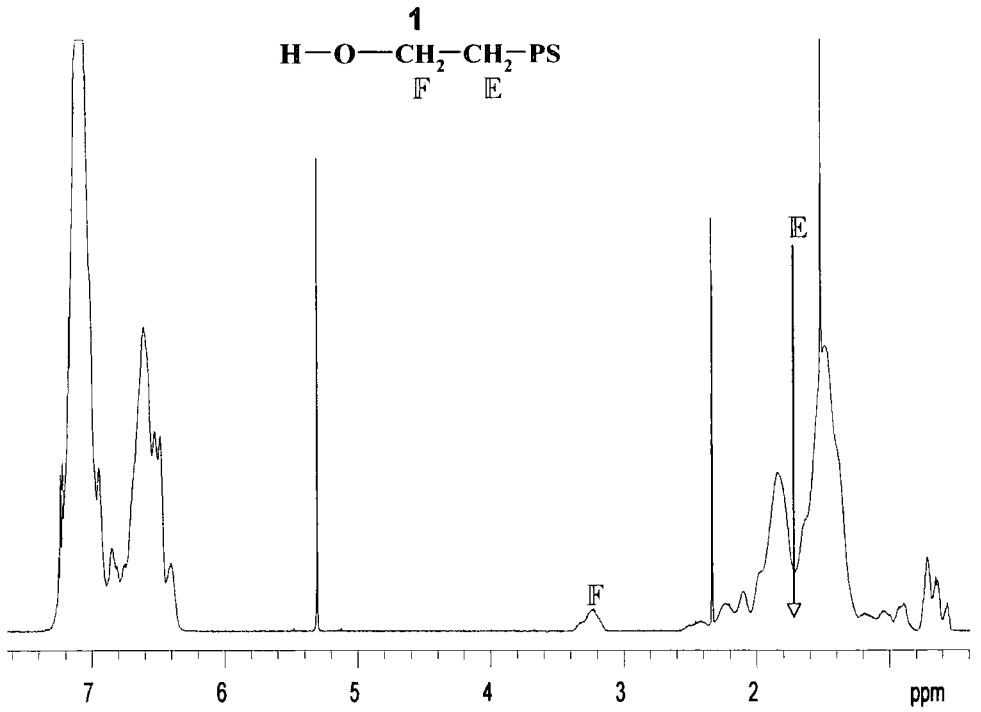


Figure 3.2 - ^{1}H NMR of hydroxyethylated polystyrene (CD_2Cl_2).

EO functionalisation only introduces one extra peak that is directly observable, which is the broad peak between approximately 3.38 – 3.10 ppm assigned to the methylene group adjacent to the hydroxyl group (𝔽). The ^{13}C shift of F is observed at 61.2-60.8 ppm (**Appendix 3.1.5**). Assignment of this allows the use of ^{1}H-^{13}C HMBC (heteronuclear multiple bond correlation) NMR spectroscopy to indirectly observe the other methylene group (𝔼), which falls at approximately 1.6-1.8 ppm (CD_2Cl_2), and is hence obscured by the polymer backbone. Integration of the peaks from the pendant phenyl groups (𝔻)(**Figure 3.1**) and methylene group (𝔽) produces values which are consistent with quantitative functionalisation (90-105%). These values are not as accurate as those of the yields of functionalisation in the PEO homopolymers, due to the substantial difference in the size of the peaks 𝔻 and 𝔽 and their breadth.

The hydroxyethylated polymer was analysed by MALDI to look for the presence of unfunctionalised PS. The study of hydrocarbon polymers, e.g. PS or polybutadiene is more complicated than that of polar polymers (for example the PEO examined in Chapter 2) and 'standard' MALDI protocols do not work.[16] Greater difficulty in finding matrices suitable for their ionisation is usually encountered.[17] Non-polar, hydrocarbon polymers are not generally cationised by Group I metal salts, probably due to the low binding energy of alkali metal ions with the polymers, and can only undergo metal cationisation with silver (Ag^+) and copper (Cu^+ or Cu^{2+}) salts.[16] Studies of the cationisation of PS have however identified a range of matrices that are suitable for obtaining MALDI spectra.[18] Silver salts are used to induce cationisation, their efficiency may stem from their affinity for the aromatic π-electrons.[19] The cationisation agent silver trifluoroacetate was used to induce silver cationisation of the homopolymers studied here. The polymer is thus observed as an adduct with Ag (**Figure 3.3**).

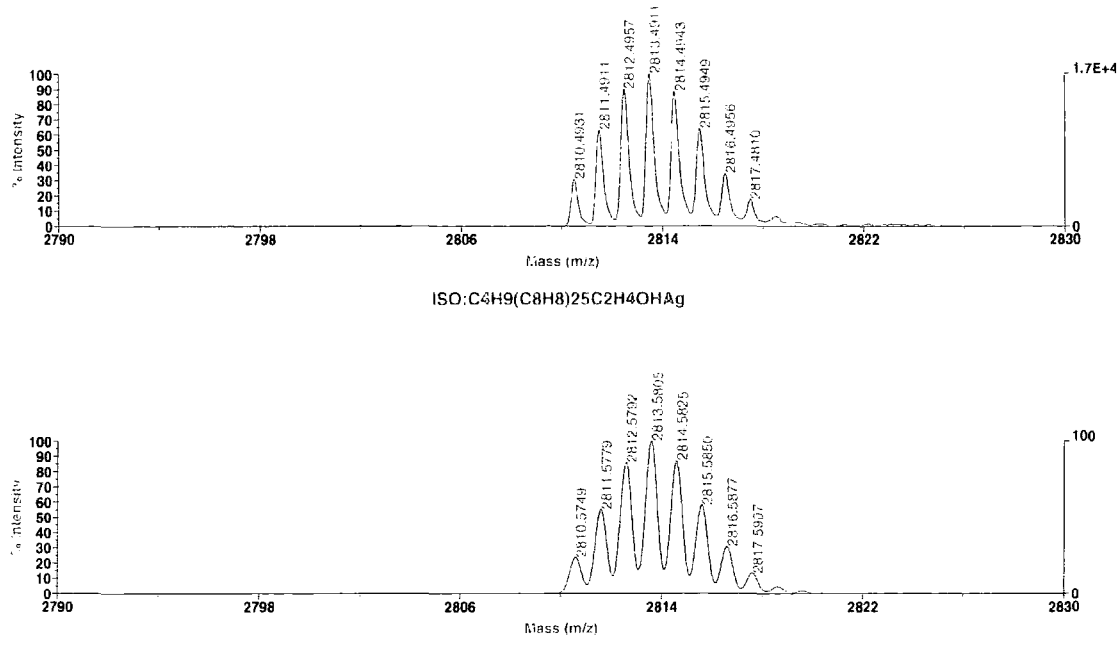
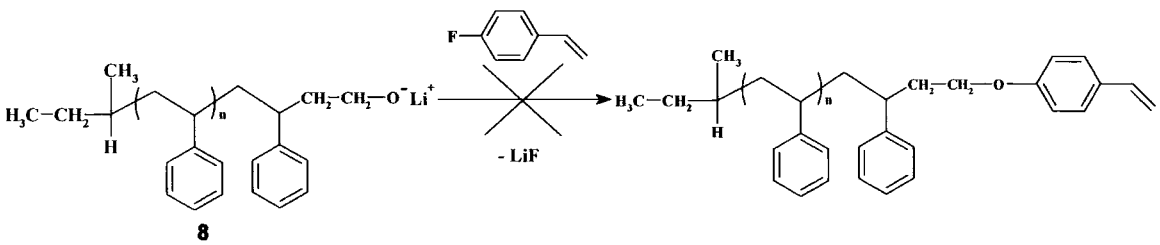


Figure 3.3 - Top: Predicted spectrum assuming sample consists of hydroxyethylated polystyrene (1) cationised as Ag adducts.
Bottom: Actual MALDI Spectrum of hydroyethylated polystyrene.

MALDI indicated that there was no or only a small amount of residual unfunctionalised PS present in the batches investigated.

3.2.1.3 Synthesis and Characterisation of PS Macromonomers

The strong aggregation present in the lithium alkoxide formed from reaction of EO with PS (**8**, **Scheme 3.6**) prevents reaction with most alkyl halide groups, with the exception of highly reactive carbonyl chlorides.[20] An attempt was made to investigate the reactivity of the hydroxy-lithium species, to see whether a PS macromonomer could be synthesised by the direct addition of 4-fluorostyrene (4-FS) to the chain ends (**Scheme 3.6**).



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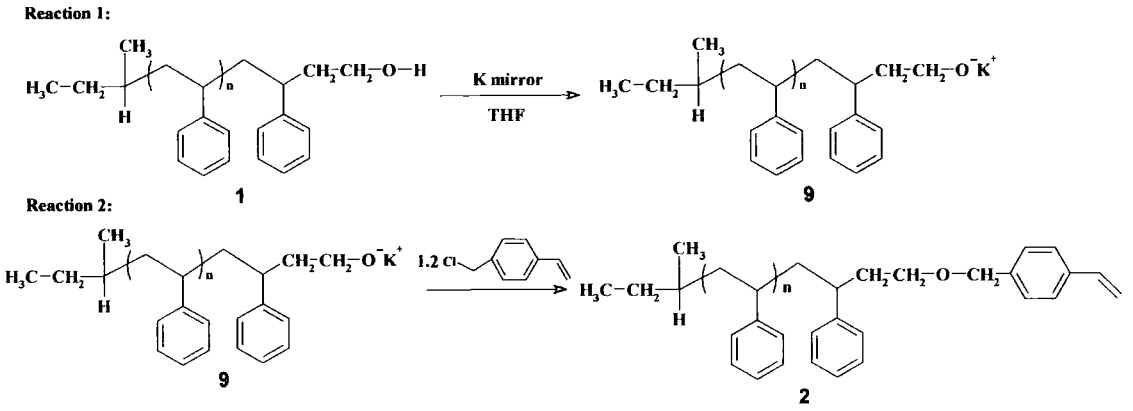
Scheme 3.6 - Attempted synthesis of PS 4-FS macromonomer.

No reaction with the 4-FS was observed. The reaction of a hydroxyl group with a halide to form an ether linkage is known as a Williamson coupling.[21] These coupling reactions involve an S_N2 reaction between a metal alkoxide, either formed *in situ* by the reaction of an alcohol deprotonated by means of a suitable base, or a preformed alkoxide (such as that present on the living PEO discussed in Chapter 2) and an alkyl or aryl halide. The reaction depicted in **Scheme 3.6** can therefore be described as an attempt at a Williamson coupling between a preformed metal alkoxide and a halide. Aryl halides are in general less receptive to nucleophilic substitution than alkyl halides. The reactivity of the aryl halides varies in the order F > Cl > Br > I.[21] Aryl fluorides are therefore the most susceptible to nucleophilic attack and formation of the required ether linkage, to the point where the reactions of aryl fluorides with primary alcohols have in some rarer cases been observed to be exothermic.[21] It was thus hoped that the 4-FS might have sufficient reactivity to functionalise the PS, avoiding the need to isolate the hydroxyethylated polymer prior to macromonomer synthesis. The reason for the failure of the reaction is probably due to the strength of the aggregation observed in the lithium alkoxides.

The hydroxyethylated PS (**1**) (discussed in the previous section) can be deprotonated into an alkali metal alkoxide of our choice, which can then be used for Williamson coupling reactions with 4-VBC. When a solution of **1** in THF was placed over a K mirror, the hydroxyl group was deprotonated leaving the oxygen in a reduced state as a potassium alkoxide (potassium-oxoanion ion pair) (**Scheme 3.7, Reaction 1**). Addition of 4-FS to this species only resulted in partial conversion (40%) to the desired macromonomer, after 26 hours reaction time. Reaction of 1.2 equivalents of 4-VBC with the polymer however, resulted in quantitative conversion of the hydroxyl group into the ether linkage, and hence the desired macromonomer (**Scheme 3.7**, **Reaction 2**).



Scheme 3.7 - Synthesis of 4-VBC PS macromonomers from hydroxyl functionalised PS deprotonated using a K mirror.

As the K mirror would be expected to react with the halide and initiate the polymerisation of the vinyl group of the 4-VBC and macromonomer,[1] the solution of polymeric metal alkoxide was removed from the mirror prior to the coupling reaction. Reaction was complete within 16 hours. It can be noted that **Reaction 2** (**Scheme 3.7**) is exceptionally similar to that used to functionalise living PEO to make macromonomers (Chapter 2). The success of the reaction was determined using ^{1}H NMR spectroscopy. Functionalisation was determined to be approximately quantitative, based on the complete conversion of the hydroxyethyl group of **1** (PC**H**$_2$OH, **F**, **Figure 3.2**), into the ether resonance of macromonomer **2** (**G**, **Figure 3.4**).

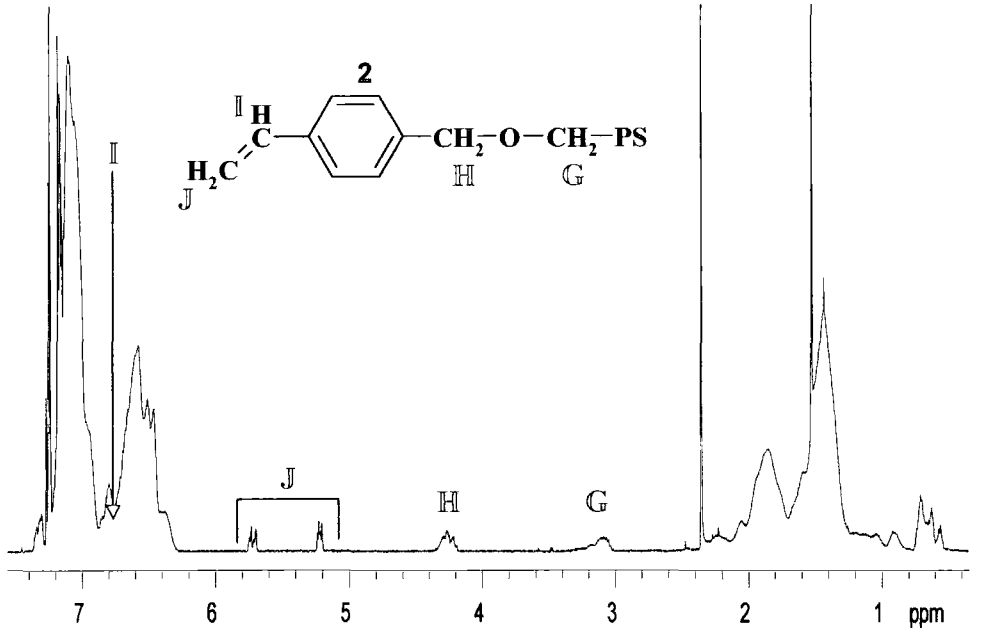


Figure 3.4 - ^{1}H NMR of polystyrene macromonomer.

The peaks from the 4-VBC are observed at very similar shifts to those in the PEO macromonomers (Chapter 2), with the exception of the vinylic peak (I), which is obscured by the aromatic protons of the polystyrene chain. As with the *sec*-butyl and hydroxyethyl end groups the resonances are broad, due to the presence of chiral centres in the polymer chain. They thus appear far broader when compared with the sharp signals observed in the PEO macromonomers. Data from GPC analysis of the macromonomers was similar to that of the unfunctionalised PS registering only a slight increase in M_n. No change was observed in polydispersity and the traces remained monomodal (**Figure 3.5**).

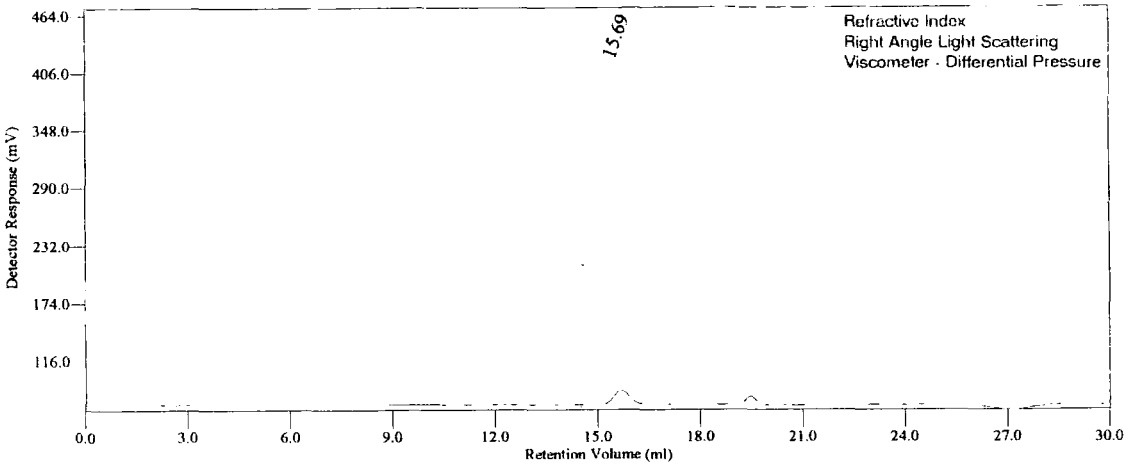
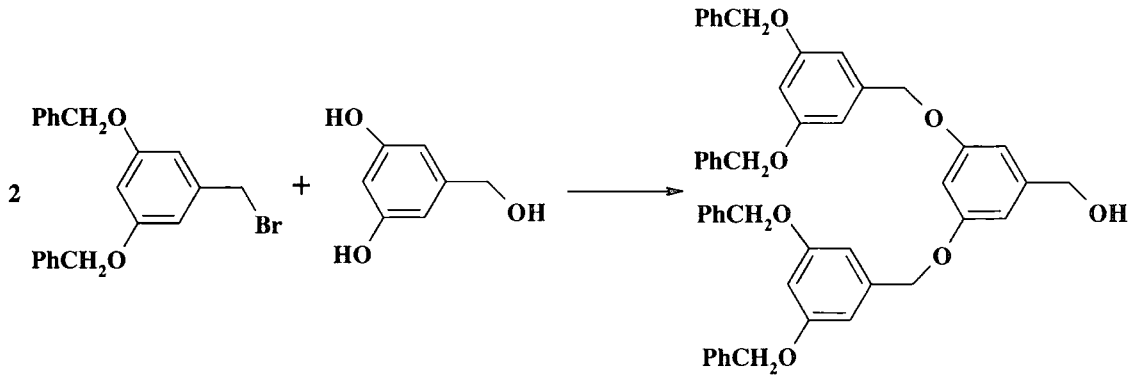


Figure 3.5 - THF GPC Chromatogram of a 4-VBC macromonomer synthesised using PS H 1 (Table 3.1) and a potassium mirror.
M_n of macromonomer = 3073 g mol^{-1} (PDI: 1.05, *THF GPC 2*).

The reaction in **Scheme 3.7** was used to convert the hydroxyethylated polystyrenes with a M_n of 2900 and 5900 g mol^{-1} into macromonomers, which were then subsequently converted into macroinitiators (Section 3.2.2). A small leak in the reaction vessel was observed when an attempt was made to convert the polymer of M_n 10500 g mol^{-1} into a macromonomer. ^{1}H analysis confirmed that some of the oxo/potassium ion pairs had been protonated by moisture resulting in incomplete functionalisation of the macromonomer (~50%). An investigation was therefore made to see if a milder set of reaction conditions could be developed which were less sensitive to air and moisture. K metal is also an exceptionally strong reducing agent, the use of a milder one might be more likely to be compatible with polymers possessing functionalities that are susceptible to nucleophilic attack.

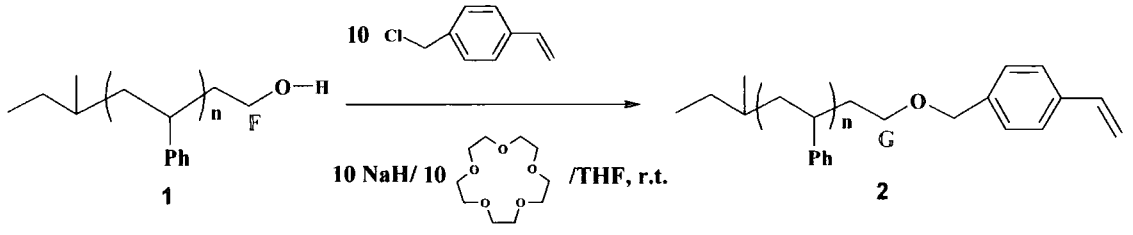
Williamson coupling reactions have been used by Hawker and Fréchet et al., in the synthesis of complex macromolecular architectures, including dendritic and hyperbranched structures.[22,23] These reactions involved the coupling of aryl hydroxyl groups with alkyl halides using a moderate (~4 equivs) excess of K_2CO_3 in the presence of catalytic amounts of the phase transfer agent 18-crown-6, in refluxing acetone under N_2. These conditions allowed the selective reaction of the alkyl bromide with aryl alcohol groups on the aromatic ring in the absence of reaction with a benzylic alcohol (**Scheme 3.8**).



Scheme 3.8 Dendritic synthesis by Williamson coupling reactions.[22]

The reaction mechanism of aryl hydroxides with alkyl halides is similar to that of alkyl hydroxides, except that the greater acidity of the alcohol on the aryl compounds means that milder bases are able to deprotonate the alcohols compared with those on alkyl hydroxides.[21] The greater reactivity of aryl hydroxides can be ascribed to the fact that the oxo-anions resulting from deprotonation of the aryl alcohols are stabilised to some degree by delocalisation.[24] Deprotonation of the alcohol to form a metal alkoxide intermediate is a key step in the reaction. It was hoped that, by increasing the levels of base and 18-crown-6 to introduce more forcing conditions, it might be possible to use this chemistry with the less reactive hydroxyethyl group (compared with the aryl oxides in **Scheme 3.8**) of **1** (**Scheme 3.7**). Unfortunately the high tendency for the radical polymerisation of 4-VBC to thermally self-initiate at elevated temperatures[7] hinders the use of Hawker's conditions. Radical auto-polymerisation is expected to reduce the amount of 4-VBC available for reaction, the polymeric material formed could also potentially couple to the PS. Attempts to convert hydroxyethylated PS (**1**) to macromonomer, using K_2CO_3 (10 equivalents), 18-crown-6 (5 equivalents) and 4-VBC (5 equivalents) in DMF at 60 °C under N_2, led to the recovery of the PS starting material. This may in part have been due to the poor solubility of K_2CO_3 in DMF at this temperature. The experiment was repeated using refluxing THF in the place of the DMF, ^{1}H NMR of the resulting material suggested that some incorporation of styrenic material into the PS occurred. In addition to indicating that incomplete functionalisation had occurred, examination of the ether region indicated that the resonances observed were not those of the correct 4-VBC macromonomer obtained using K (or later NaH).

Amongst the most commonly used reagents for Williamson coupling reactions is sodium hydride. In the case of this reagent, reaction proceeds by reduction of the alcohol by the hydride (H^-) ion to form a sodium alkoxide intermediate.[24] Recent reports have described the use of NaH in combination with 15-crown-5 to convert hindered alcohols into ethers at room temperature (r.t.).[25] The enhanced reactivity of NaH with 15-crown-5 was at least partly attributed to the activation of the sodium alkoxide intermediate that is formed *in situ*, by reducing the association between alkoxide and metal. It was believed that as these reaction conditions were suitable for the conversion of sterically hindered alkyl hydroxides into ethers, they might be sufficiently forcing for functionalisation of the hydroxyethylated polymer, without the need for elevated temperatures that could lead to decomposition (through polymerisation) of 4-VBC. The hydroxyethyl functionalised PS (M_n: 2850 g mol^{-1}), was therefore reacted with an excess of 4-VBC in the presence of an excess of NaH and 18-crown-6 at r.t (**Scheme 3.9**).



Scheme 3.9 - Synthesis of 4-VBC PEO macromonomers using NaH and 15-crown-5.

The reaction was monitored by ^1H NMR. Samples were precipitated into IPA (to avoid interference of MeOH with the NMR analysis) and dried quickly under reduced pressure. The ^1H NMR spectrum of the sample was then collected and the conversion of $\mathbb{F}$ (3.38 – 3.10 ppm, $CDCl_3$) into $\mathbb{G}$ (3.34 – 2.98 ppm) was observed. No reaction occurs in the absence of 15-crown-5, this is no doubt primarily due to the poor solubility of NaH in THF at r.t without the presence of a phase transfer agent. When 15-crown-5 was added to the reaction mixture, complete conversion of EO PS 1 (**Table 3.1**, M_n = 2850 g mol^{-1}) to macromonomer was observed after 44 h of reaction time. This method was then used to quantitatively convert the hydroxyethylated PS of M_n = 10500 g mol^{-1} into macromonomer (reaction detailed in Section 3.4.2.4). Analytical data for the macromonomers obtained from this route were essentially identical to those produced using potassium metal. The ^1H NMR resonances from the functionality introduced by 4-

VBC are observed at identical shifts. GPC indicated the macromonomers retained their low PDIs after the Williamson coupling (**Figure 3.6**).

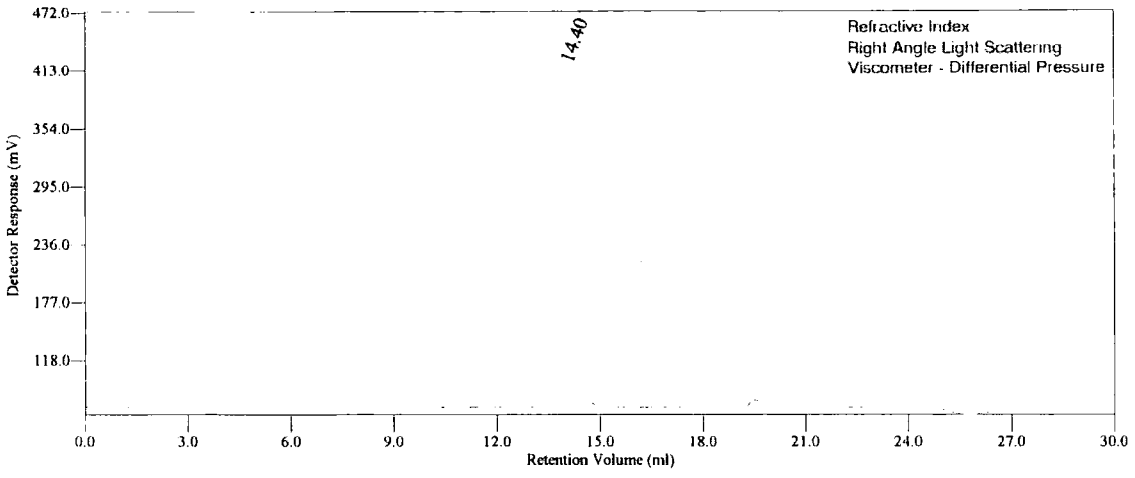
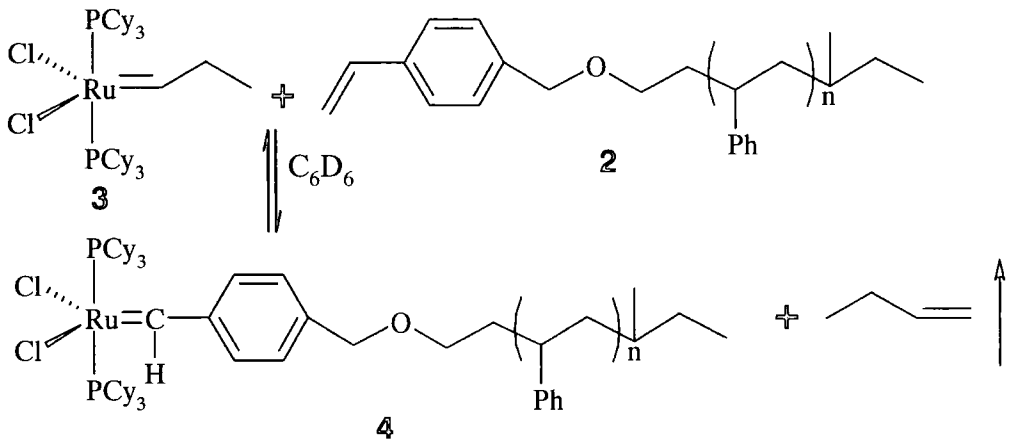


Figure 3.6- THF GPC Chromatogram of a 4-VBC macromonomer synthesised using NaH with 15-crown-5. PS M_n=10500 g mol^{-1}, M_n of macromonomer = 11530 g mol^{-1} (PDI: 1.04, *THF GPC 2*).

Another advantage of this method is that the 4-VBC requires less vigorous purification relative to the method using a K mirror. The 4-VBC was dried over $CaCl_2$, before the drying agent and inhibitors were removed by filtration through basic alumina, no distillation was required. The macromonomer with PS of M_n 10500 g mol^{-1} was used to synthesise a macroinitiator and PS-PNB block copolymers.

3.2.2 Synthesis and Properties of PS Macroinitiators

4-VBC functionalised PS macromonomer (**2**) was reacted with ruthenium propylidene $RuCl_2(=CHEt)(PCy_3)_2$ (**3**) to yield a PS ruthenium macroinitiator for ROMP (**4**, **Scheme 3.10**) in a reaction analogous with that used to prepare PEO macroinitiators.



Scheme 3.10 - Synthesis of PS macroinitiators for ROMP.

The PS macroinitiators have an identical active ruthenium centre to those of the PEO macroinitiators and can also be viewed as analogues of the initiator $RuCl_2(=CHPh)(PCy_3)_2$, in which the aromatic ring is substituted with PS in the *para* position relative to the alkylidene carbon metal double bond. Homometathesis of PS macromonomer **2** with **3** leads to the synthesis of PS macroinitiators **4**, 1-butene being the byproduct of the forward reaction. As with the PEO macroinitiators the reaction was performed by combining C_6H_6 solutions of the macromonomer and **3**. The solution containing the ruthenium initiator was purged with argon, prior to and during the reaction, to ensure complete removal of 1-butene, and the complete conversion of macromonomer to macroinitiator **4**. Higher molecular weight macromonomers required slightly larger amounts of solvent; the smaller quantities of initiator **3** necessary to convert these macromonomers meant that smaller volumes of C_6H_6 could be used to dissolve **3** in these cases (as with the PEO macroinitiators). The macroinitiators were precipitated into hexane. Whilst the precipitation of PS from C_6H_6 into hexane at r.t. leads to the formation of slightly gelatinous material, performing the same experiment with hexane chilled to -78 °C produces powdery PS. The macroinitiators precipitate in hexane at -78 °C as powdery purple materials in the same manner. Solubility tests indicated that propylidene, which must be removed by the precipitations, possessed better solubility in hexane than MeOH (used to precipitate the homopolymers), and hence hexane was adopted as the non-solvent. ^1H NMR of the macroinitiators indicated the presence of

traces of residual propylidene, which was removed by reprecipitation leaving PS macroinitiator (**Figure 3.7**).

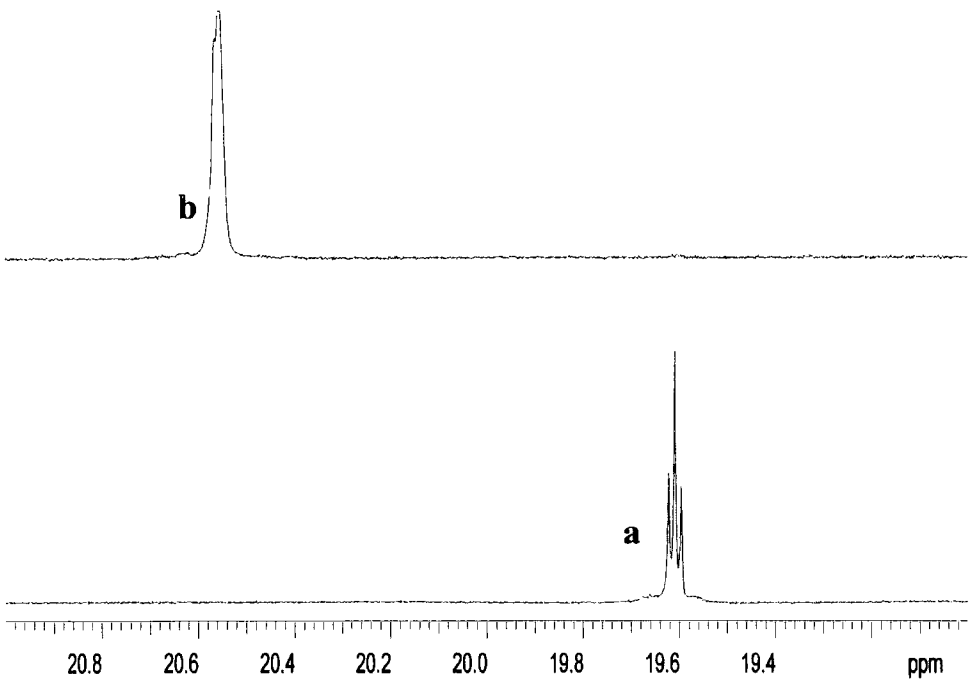


Figure 3.7 - Comparison of the ^{1}H NMR analysis of the ruthenium propylidene initiator and the PS macroinitiator formed as a product of the alkylidene exchange reaction between the propylidene initiator and PS macromonomer (C_6D_6).
a Ruthenium propylidene initiator.
b PS Ruthenium macroinitiator.

The alkylidene proton of the PS macroinitiator is observed at 20.56 ppm, and is therefore approximately equivalent to that of the ruthenium PEO macroinitiator (Discussed in Section 2.2.5). The peak is however significantly broader than that observed in the PEO macroinitiators, in keeping with the greater breadth of end groups on polystyrene observed in ^{1}H NMR spectroscopy. No peak from 3-vinylbenzyl chloride (3-VBC) functionalised macroinitiator is visible, but it is possible that the breadth of the 4-VBC peak may well result in it being obscured. The PCy_3 protons (**Appendix 3.2.1**) are observed to have a very similar shift and shape to their equivalents in the PEO macroinitiators (Section 2.2.5). The ^{31}P NMR spectrum of the PS macroinitiators contains a single sharp peak attributable to the phosphine ligands (**Appendix 3.2.2**). The ^{13}C

spectrum is comprised of the peaks expected from PS and the PCy_3 ligands (**Appendix 3.2.3**). As with the PEO macroinitiators, coupling occurs between phosphorus and adjacent PCy_3 carbons. As with the PEO macroinitiators it was not possible to observe the alkylidene carbon, presumably due to the low concentration of the alkylidene group expected in the samples.

A series of PS macroinitiators were synthesised with the number average molecular weight (M_n) of PS (THF GPC) ranging from 2850 to 10500 g mol^{-1}. All three PS ruthenium macroinitiators possessed good solubility in C_6H_6 and CH_2Cl_2 forming purple solutions which were of a similar colour to those of the PEO macroinitiators and ruthenium benzylidene initiator $RuCl_2(=CHPh)(PCy_3)_2$. The macroinitiators were subsequently used in the synthesis of block copolymers of styrene with NBE derivatives.

3.2.3 Synthesis and Properties of PS-PNB Block Copolymers

This section describes the ROMP of three norbornene (NBE) derivatives, monomers **A**, **B** and **C** (Section 2.3.7) with the PS ruthenium macroinitiators (Section 3.2.2) to form PS-PNB block polymers. ROMP reactions initiated using the PS-macroinitiators thus behave very similarly to those initiated by the benzylidene initiator and the PEO macroinitiators (Chapter 2). The major difference is that ROMP using PS macroinitiators leads to the incorporation of polystyrene chains on the end of the PNB chains, forming linear PS-PNB block copolymers (**Figure 3.8**).

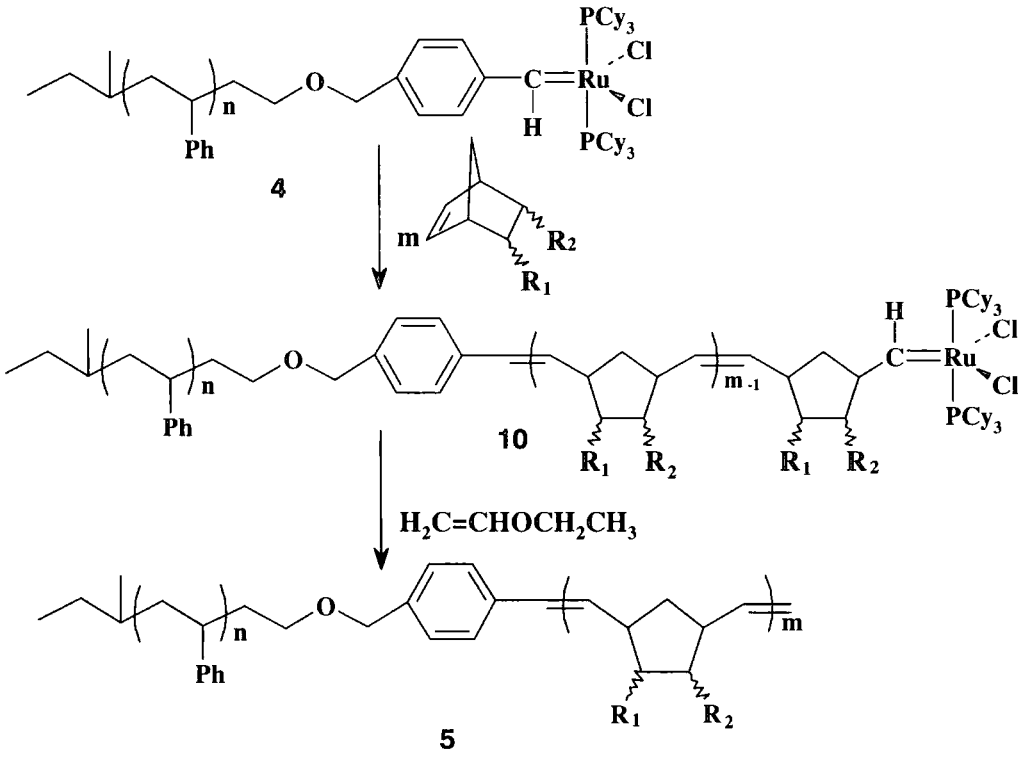


Figure 3.8 - ROMP of norbornene derivatives with PS macroinitiators.

The living polymers (**10**) were terminated using ethyl vinyl ether as with the previous systems, synthesising diblock copolymers whose molecular weight data is shown in **Table 3.2.**

Table 3.2 - Molecular weight and composition data for a series of diblock copolymers synthesised, by combining the anionic polymerisation of styrene and ROMP.

Sample	PS Block[a]			ROMP Block		Block Copolymer			
	M_n g mol^{-1}	M_w g mol^{-1}	PDI	Monomer	DP	M_n/Pred[b] g mol^{-1}	M_n/GPC g mol^{-1}	PDI	M_n/NMR g mol^{-1}
1	2850	2900	1.02	**A**	100	32500	29700	1.16	32600
2	5700	6300	1.10		100	35400	32700	1.10	34100
3	10500	11100	1.06		100	40200	38400	1.07	43100
4					200	69700	68300	1.07	68700
5					500	158400	151200	1.09	159000
6	2850	2900	1.02	**B**	100	24000	15600	1.15	23900
7	5700	6300	1.10		100	26900	20800	1.09	26200
8	10500	11100	1.06		100	31700	23100	1.05	31000
9	5700	6300	1.10	**C**	100	25000	23100	1.17	24900
10	10500	11100	1.06		100	29800	22600	1.24	30900

***a* Determined by THF GPC. *b* Based on GPC measurements of the PS block.**

A series of block copolymers were synthesised in which the composition was varied by altering the ratios of monomer [M] to macroinitiator [MI]; [M]/[MI] = 100, 200, and 500. Consumption of monomer was quantitative and in almost all cases the block copolymers have a narrow molecular weight distribution (1.05-1.2). This suggests that as with the PEO macroinitiators, these PS macroinitiators are efficient initiators for the ROMP of the NBE derivatives investigated. The block copolymers were precipitated into MeOH, a non-solvent for both the PS and PNB blocks. This means that any PS homopolymer, if present, should be observed in the GPC chromatograms. As with the PEO-PNB block copolymers a small peak was sometimes observed at an elution volume where the PS homopolymers would be expected (**a, Figure 3.9**). A shoulder was also observed at lower elution times, corresponding to approximately double the molecular weight of the block copolymers (**b, Figure 3.9**) which as with the PEO-PNB block copolymers is attributed to polymer-polymer coupling by dimerisation of the living polymer (**10**) after ROMP. Further work was carried out to examine the formation of this species (Section 3.2.3.1).

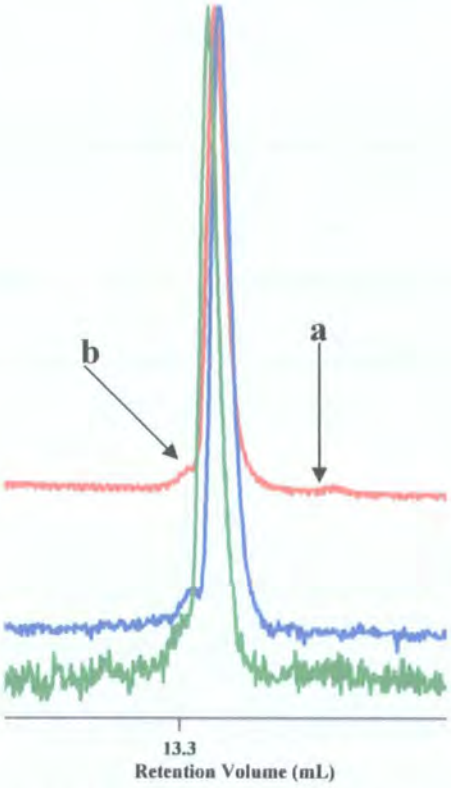


Figure 3.9 GPC chromatogram of PS PNB sample 6 prepared from PS and monomer B. M_n = 15,600 g mol^{-1}, PDI = 1.10, contaminated with a trace of PS homopolymer M_n = 2900 g mol^{-1}, PDI = 1.02 (a).

The values for M_n of the block copolymers calculated from THF GPC using triple detection (**Table 3.2**) are lower than those predicted by the stoichiometry of the reaction. The data obtained by triple detection GPC is based upon the parameters for PS measured in THF solution (e.g. refractive index [RI], specific refractive index increment [d*n*/d*c*] and intrinsic viscosity [η]), we would not therefore expect the values from GPC to be accurate. The GPC data is however important in that it gives an accurate measure of the polydispersity of the copolymers.

^{1}H and ^{13}C NMR spectra (**Appendices 3.3.1 – 3.3.6**) of the block copolymers are combinations of the spectra of PS (Section 3.2.1) and PNB (Section 2.2.7) homopolymers. As with the PEO-PNB block copolymers, the ^{1}H NMR spectra of the PS-PNB block copolymers allow the calculation of a quantitative value for the molecular weight (M_n) of the block copolymers, as we know the M_n of the PS block from GPC. To calculate the ratio of PNB to PS blocks the integrals of a peak from each of the two polymer backbones must be compared.

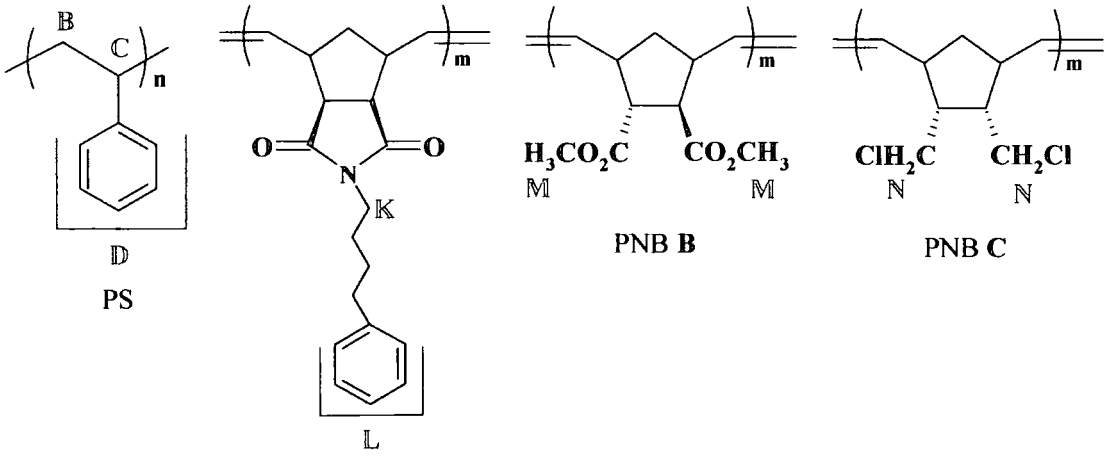


Figure 3.10 - PS and ROMP polymer backbones labelled with environments of relevance to the calculation of M_n of PS-PNB block copolymers using ^{1}H NMR.

The most suitable peak for this purpose in the ^{1}H NMR spectra of PS is that from the pendant aromatic protons (𝔻) (𝔹 and ℂ overlap with each other and the *sec*-Bu endgroup). However the residual $CHCl_3$ protons in $CDCl_3$ have a similar shift, introducing a concentration dependent error into data recorded in this solvent. ^{1}H NMR spectra of the samples in CD_2Cl_2 were thus used to perform the calculations. Residual H

in CD_2Cl_2 would interfere with the use of the olefinic resonances from some of the ROMP blocks in the copolymers, however all three of the ROMP blocks posses pendant functionalities, which have resonances in the region of 3-4 ppm. These are; in PNB **A** the methylene protons adjacent to the N on the butyl side chain at 3.50–3.36 ppm (𝕂, **Figure 3.10**, 2H in the ROMP block); in PNB **B** the methyl ester groups at 3.70-3.58 ppm (𝕄, 6H); and in PNB **C** the peak at 3.80-3.40 ppm from the chloromethyl groups (ℕ, 4H). As the calculation of M_n using NMR is more complicated in the case of block copolymers of styrene and NBE monomer **A** compared with the PEO-PNB and other PS-PNB block copolymers it will be illustrated with an example. In the case of PNB **A** the situation is complicated by the equivalence of some of the PS aryl protons (𝔻**I**) with the protons of the phenylbutyl groups (𝕃) (**Figure 3.11**).

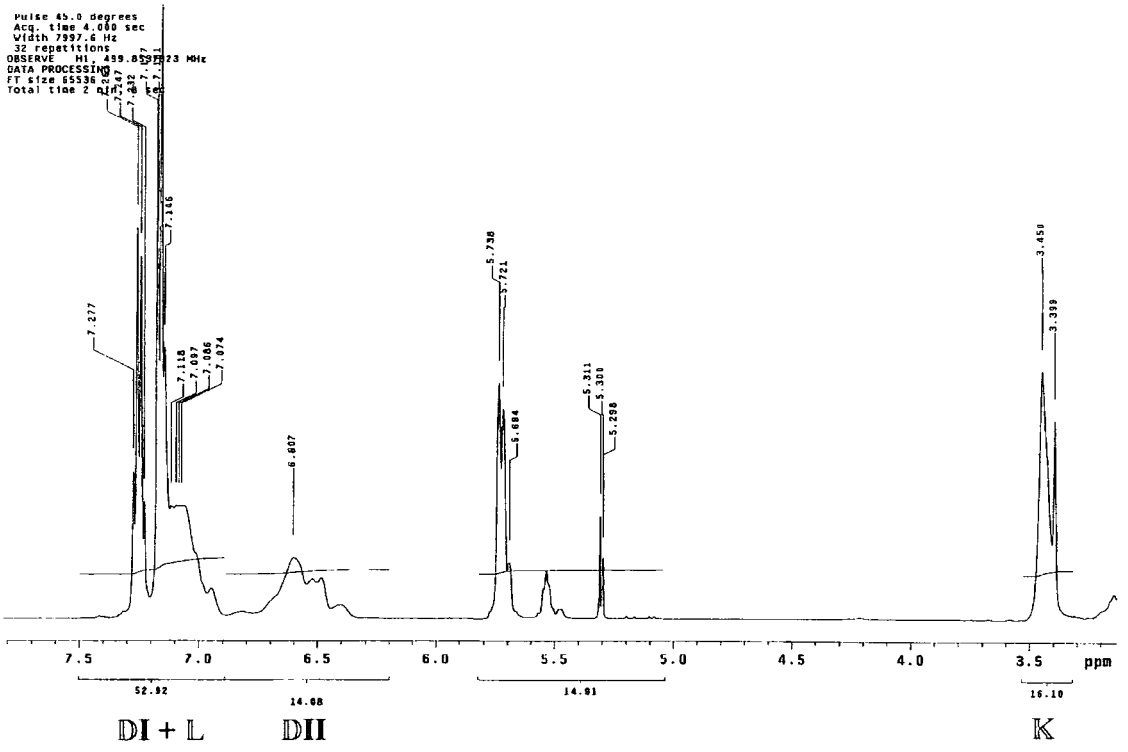


Figure 3.11 - ^{1}H NMR of PS-PNB sample 3 (Table 3.2) in CD_2Cl_2.

The aryl region of the ^{1}H NMR of homo-PS can be divided into two regions (labelled 𝔻**I** and 𝔻**II** in **Figure 3.12**).

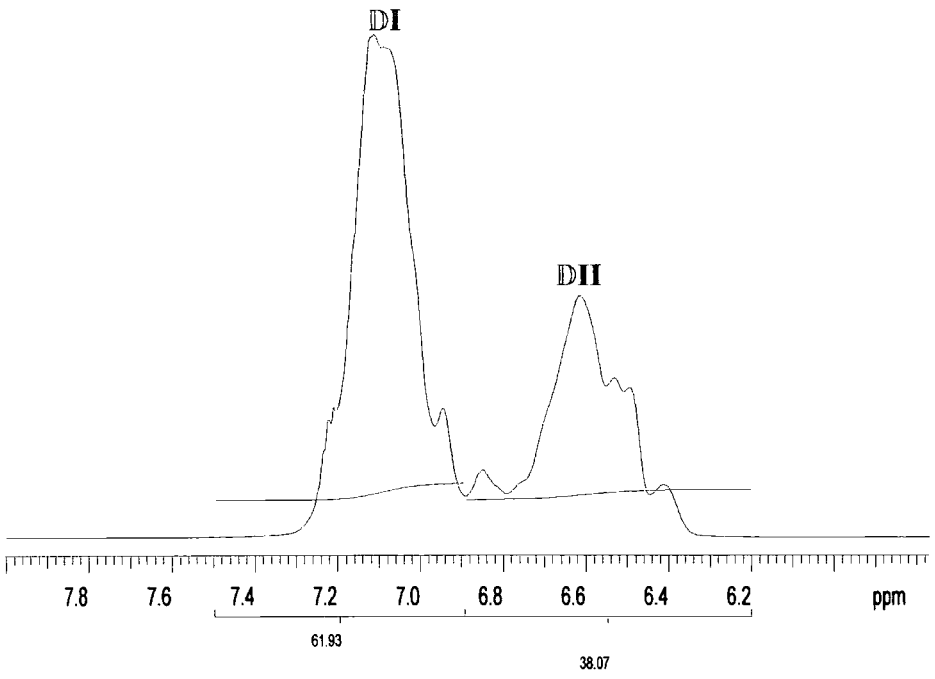


Figure 3.12 - Aromatic region of ^{1}H NMR of hydroxyethylated PS (CD_2Cl_2, M_n: 2900 g mol^{-1}).

The aryl protons from the ROMP block (𝕃) are magnetically equivalent only to those in the **𝔻I** region, and do not overlap with region **𝔻II**. Analysis of the integral of region **𝔻II** suggests that it is primarily due to two protons, although the substantial overlap between the two regions makes the integrals inaccurate. Careful integration of the aryl region of a number of homo polystyrenes (all in CD_2Cl_2) indicated that region **𝔻II** (defined as 6.89-6.20 ppm) formed 38% of the total aromatic region. This value allows us to calculate the M_n of the block copolymers, as will be demonstrated using the data contained in **Figure 3.12**. We can measure **𝔻II** from the spectra of the block copolymers directly, and hence calculate the total integral of the aryl protons 𝔻 (equal to **𝔻I** + **𝔻II**) (**Equation 3.1**):

𝔻II = 38 % of 𝔻

14.08 = 38% of 𝔻

→ 𝔻 = **𝔻II** / 0.38 (**Equation 3.1**)

𝔻 = 14.08 / 0.38 = 37.05

We have now calculated the integral of 5 protons in each repeat unit of the PS chain. It is easy to calculate the value of one proton (1H) in the PS block from this value:

$$\mathbb{D} / 5 = 1H \text{ in PS} \quad \textbf{(Equation 3.2)}$$

$$37.05 / 5 = 7.41 = 1H \text{ in PS}$$

Calculating the value of one proton in the ROMP block from $\mathbb{K}$ is comparatively trivial, as demonstrated by **Equation 3.3**:

$$1H \text{ in PNB } \mathbf{A} = \mathbb{K} / 2 \quad \textbf{(Equation 3.3)}$$

$$1H \text{ in PNB } \mathbf{A} = 16.10 / 2 = 8.05$$

The next step is calculating the ratio of PNB **A** to PS in the block copolymer:

$$1H \text{ in PNB } \mathbf{A} / 1H \text{ in PS} \quad \textbf{(Equation 3.4)}$$

$$8.05 / 7.41 = 1.09$$

We now know that there are 1.09 times the number of moles of repeat units of PNB **A** compared with PS. As we are dealing with a block copolymer we can say that the degree of polymerisation (DP) of the ROMP block is 1.09 times greater than that of the PS block. We can also calculate the DP of the PS (**Equation 3.5**) from the GPC data (**Table 3.1**, Section 3.2.1):

$$\text{DP of PS} = M_n \text{ of PS} / F_w \text{ of PS 1 mer} \quad \textbf{(Equation 3.5)}$$

$$\text{DP of PS} = 10500 / 104.15 = 100.82$$

It is now possible to calculate the DP (**Equation 3.6**) and molecular weight (**Equation 3.7**) of the ROMP block from these two values.

$$\text{DP of PNB } \mathbf{A} = (1H \text{ in PNB } \mathbf{A} / 1H \text{ in PS}) \times \text{DP of PS} \quad \textbf{(Equation 3.6)}$$

$$\text{DP of PNB } \mathbf{A} = 1.09 \times 100.82 = 109.89$$

$$M_n \text{ of PNB } \mathbf{A} = \text{DP of PNB } \mathbf{A}. \times F_w \text{ of PNB } \mathbf{A} \text{ 1 mer} \quad \textbf{(Equation 3.7)}$$

$$M_n \text{ of PNB } \mathbf{A} = 109.89 \times 295.38 = 32459 \text{ (to the nearest integer)}$$

It is now possible to calculate the M_n of the block copolymer using the M_n of both blocks, the mass introduced into the polymer chain by the functionality introduced from functionalisation of the PS with EO and 4-VBC (161 g mol^{-1}) is also considered in the calculation of the total M_n.

$$M_n \text{ of PS} + M_n \text{ of PNB } \mathbf{A} + 161 = M_n \text{ of block copolymer} \quad \textbf{(Equation 3.8)}$$

$$10500 + 32459 + 161 = 43120 \approx 43100$$

The calculated value of 43100 for M_n compares with a theoretical (theor.) value of 40200 (**Equation 3.9**).

$$\text{theor. } M_n \text{ of block copolymer} = M_n \text{ of PS} + \text{theor. } M_n \text{ of PNB } \mathbf{A} + 161 \quad \textbf{(Equation 3.9)}$$

$10500 + 29538 + 161 = 40199 \approx 40200$

This method was found to give more accurate and reproducible results for M_n than estimating $\mathbb{L}$ from the value of $\mathbb{K}$ (**Figure 3.10**), and subtracting the value of $\mathbb{L}$ from the total integral of the aryl protons in order to estimate $\mathbb{D}$ and hence 1H in the PS block, particularly in the case of copolymers where one block was substantially larger than the other one.

In the case of block copolymers containing ROMP blocks of NBE monomers **B** and **C**, calculating the ratio of PNB to PS can simply be achieved by comparing $\mathbb{M}$, or $\mathbb{N}$, respectively (**Figure 3.10**) with $\mathbb{D}$ (7.4–6.3 ppm, 5H). Once the ratio of PNB to PS has been calculated from the NMR data, the DP and hence M_n of the ROMP block are obtained using **Equations 3.6 and 3.7**. The total M_n of the block copolymers can then be determined using **Equation 3.8**. The values for M_n calculated by NMR are in good agreement with those predicted by the stoichiometry.

Comparison of the ^{1}H NMR data from the ROMP block of the PS-PNB block copolymers with the ROMP homopolymers and PEO-PNB block copolymers indicated they have similar microstructures. The *cis* and *trans* ratio of block copolymer containing poly **A** and **C** were calculated using the method described in Section 2.2.7, indicating that 10-20% of the units were *cis*.

Calculation of M_n of PS-PNB sample 3 (**Table 3.2**) using MALDI resulted in a value of 44300 g mol^{-1}, in good agreement with the predicted 40200 g mol^{-1} (**Appendix 3.3.7**). No silver salts (necessary to cationise PS) were added, and thus cationisation must have occurred on the poly **A** block. The preferential ionisation of one polymer block in copolymers is frequently observed and results in a slight bias towards the chains with relatively higher molecular weight fractions of the most easily cationised block, reducing the accuracy of the results.[26] The results here are sufficiently accurate to indicate the block copolymer is of approximately the target molecular weight and composition.

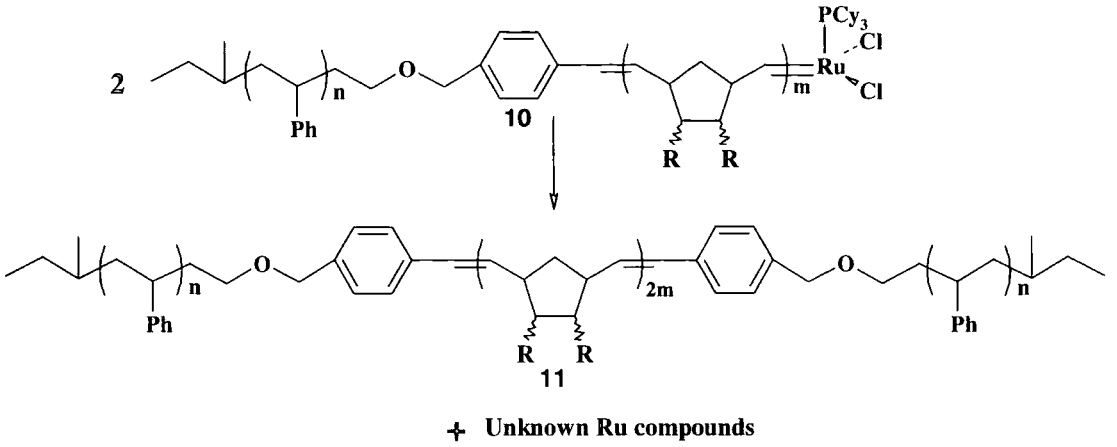
The polymers were purified by reprecipitation from CH_2Cl_2 into MeOH to produce hard solids, which were generally recovered in good yield. The recovery yield was observed to be related to the maximum yield of polymer expected, in the case of polymer reactions where a higher maximum yield was predicted (200 - 250 mg) the yields were consistent with quantitative consumption of the monomer. The recovery yield

of some of the block copolymers is a little lower where a lower maximum yield is expected, due to the reduced efficiency in handling such samples. Compositions of the block copolymers determined by elemental analysis were generally close to those predicted (Sections 3.4.4.1 – 3.4.4.5).

The aim of the work described in this chapter was to develop a generic methodology for the preparation of block copolymers, by converting living alkyllithium initiated anionic polymerisation into living ruthenium ROMP. To the author's knowledge it is the first time that block copolymers of polystyrene and a block polymerised by ruthenium initiated ROMP have been prepared with low polydispersities. Previously the combination of the polymerisation of styrene using atom transfer radical polymerisation (ATRP) and the polymerisation of 1,5-cyclooctadiene (COD) via ROMP, were used to synthesise polymers, but these had PDIs of 1.45 or higher.[27] Whilst the methodology was demonstrated using PS, this method should be suitable for the synthesis of block copolymers from other monomers whose alkyllithium initiated anionic polymerisations can be functionalised using EO. For instance poly(ethylene-alt-propylene)(PEP), synthesised from hydrogenated hydroxyl functionalised polyisoprene (Section 1.4.1), should be a suitable candidate for this methodology.

3.2.3.1 Experimental Observation of Polymer-Polymer Coupling of PS-PNB Block Copolymers

GPC analysis of both PEO-PNB and PS-PNB block copolymers has identified a small shoulder on the main block copolymer peak, which elutes after a shorter period of time. This peak appears to be from a species which is approximately double the molecular weight of the main peak (**Figure 3.9**), and is believed to arise from dimerisation of the ruthenium propagating species (**10**) leading to polymer-polymer coupling and formation of **11** (**Scheme 3.11**).



Scheme 3.11- Proposed mechanism for polymer-polymer coupling of PS-PNB block copolymers.

This phenomenon was studied to see if it could produce evidence that would confirm or disprove the mechanism shown in **Scheme 3.11**. The ROMP of 200 equivalents of NBE monomer A was initiated by a PS (M_n: 10500 g mol^{-1}) macroinitiator in CD_2Cl_2 (Section 3.4.4.6). The consumption of monomer was followed using ^{1}H NMR, by monitoring the conversion of the olefinic peak of the monomer (6.27 ppm) into that of the polymer (5.8-5.4 ppm). The rate of propagation of this monomer (R_p) was high as expected, approximately all of the monomer (98%) had been consumed within 35 min, complete conversion occurred between this point and 1h. No evidence of the sharp peak from the alkylidene proton of the macroinitiator (expected at 19.6 ppm) was observed after 35 min. A single broad signal was observed from the alkylidene proton of the propagating species at 19.45 ppm throughout the polymerisation, and could still be observed 19 h after initiation. This chemical shift is very typical of those expected of *exo*-dicarboxy imides, the ROMP propagating species of similar monomers initiated by $RuCl_2(=CHPh)(PCy_3)_2$ were observed at 19.5-19.4 ppm.[28]

Aliquots of the solutions were extracted from the NMR tube at regular intervals using a syringe, terminated with ethyl vinyl ether, and their GPC chromatogram in THF was obtained (**Figure 3.13**).

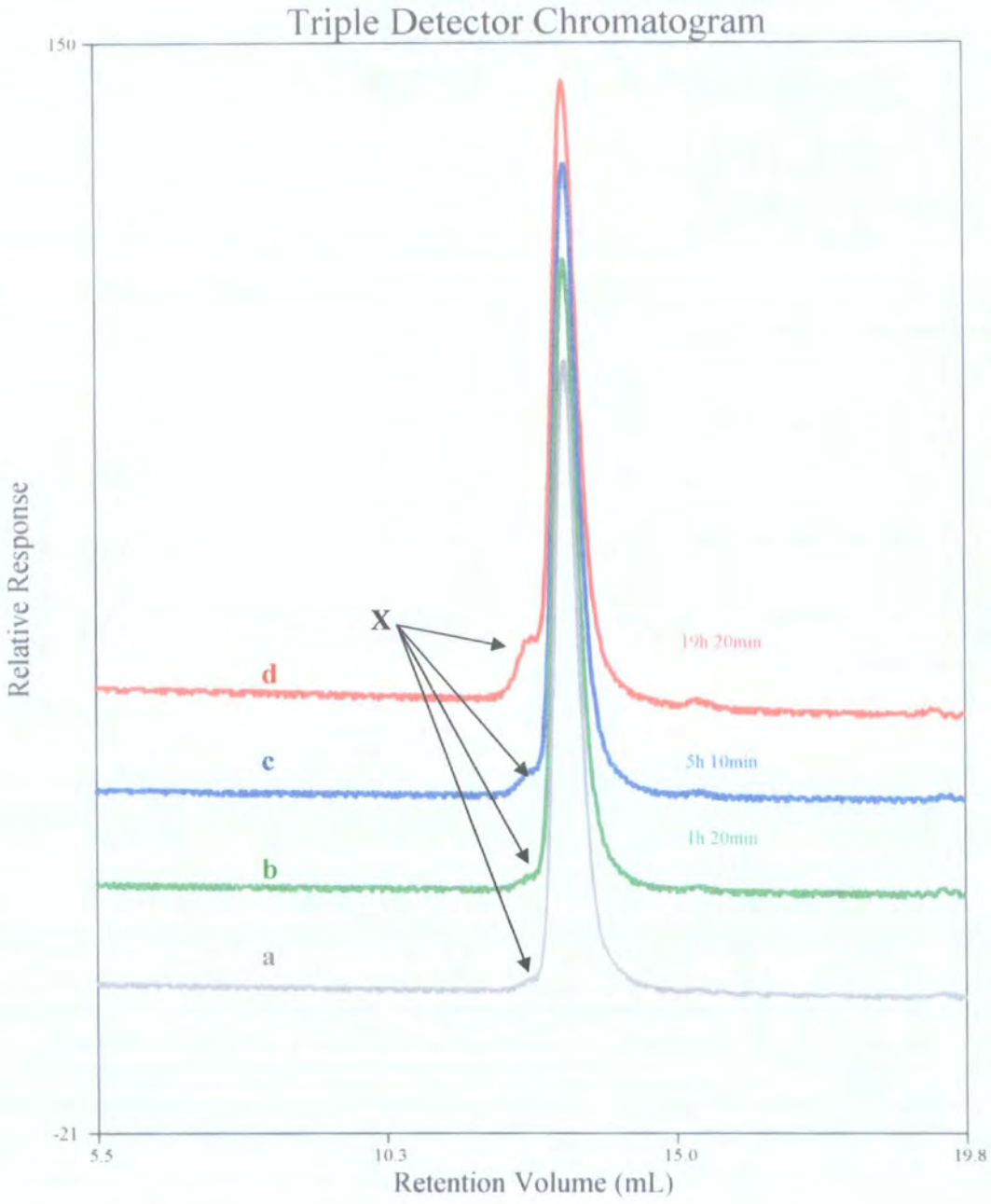


Figure 3.13 – THF GPC Chromatograms from samples of PS-PNB block copolymers (relative response vs. retention volume [mL]). X is believed to result from polymer-polymer coupling. Time after initiation, M_n, PDI;
a: 45 min, M_n: 74300 g mol^{-1}, PDI: 1.05.
b: 1h 20 min, M_n: 75200 g mol^{-1}, PDI: 1.05.
c: 5 h 10 min, M_n: 74800 g mol^{-1}, PDI: 1.05.
d: 19h 20min, M_n: 75000 g mol^{-1}, PDI: 1.09.

After 45 minutes only a very small amount of the species that elutes at a shorter time (referred to as species **X** from this point) was formed (a). Very little increase in **X** was observed after a further 35 min (b), although the chromatogram of the sample taken approximately 4 hours after complete consumption of monomer (c) shows that the amount of coupling has increased slightly. GPC analysis indicates that the increase in coupling is very small in the context of the sample as a whole – the calculated values for PDI differ by less than 0.01 with respect to the first sample (a). An increase in species **X** was observed at a point over 19 h 20 min after the complete consumption of monomer, resulting in a detectable increase in the polydispersity of the sample. These results are firmly consistent with the hypothesis that species **X** is formed via polymer-polymer coupling of the propagating species of the polymer. The rate of propagation (R_p) is far faster than that of coupling ($R_{coupling}$), the amount of coupling that occurs during polymerisation is either irrelevant or very small. Whilst the quantities of coupled polymer increase slowly after complete consumption of monomer, the results suggest that the ROMP reactions should not be left for extended periods of time prior to termination with ethyl vinyl ether.

Addition of PCy_3 to the propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ has been observed to result in a decrease in its rate of decomposition.[29] The decomposition of first-generation initiators proceeds via dimerisation of mono-phosphine ruthenium species, which are formed by dissociation of one of the PCy_3 ligands. The addition of PCy_3 reduces the availability of the mono-phosphine species in solution. The mechanism of coupling of the PEO-PNB and PS-PNB block copolymers is believed to be very similar to that of the initiators, proceeding via the mono-phosphine species. The mono-phosphine species is the active species in ROMP and productive metathesis. Grubbs and co-workers disclosed that the addition of phosphines (e.g. PPh_3 or PCy_3) to ROMP reactions results in a decrease in the rate of initiation (R_i) and an even greater decrease in R_p, a phenomenon that has been used to reduce the PDI of ROMP homopolymers.[30] We would therefore hope the addition of PCy_3 to the polymerisation reactions initiated by the macroinitiators, would result in a lowering of $R_{coupling}$ relative to R_p.

3.3 Conclusions and Summary

The anionic polymerisation of styrene in benzene was initiated using *sec*-butyl lithium. The polymers were functionalised using EO and MeOH, resulting in the synthesis of hydroxyethylated polystyrenes with narrow polydispersities. These were then converted into macromonomers by Williamson coupling reactions. The coupling reactions can be carried out by forming an alkoxide from hydroxyethylated PS using K metal, which can be quantitatively converted into macromonomer by the addition of 4-VBC. Alternatively the macromonomers can be synthesised by combining hydroxyethylated PS with 4-VBC and forming the alkoxide *in situ* from the former using sodium hydride in the presence of 15-crown-5.

Metathesis of the PS macromonomers by $RuCl_2(=CHEt)(PCy_3)_2$ led to alkylidene exchange and the formation of ruthenium PS macroinitiators for ROMP. Block copolymers of three different NBE derivatives were synthesised using the macroinitiators and the mass of the two blocks altered to change the composition of the copolymers. ^1H NMR analysis confirmed that the copolymers possessed the target compositions. GPC analysis of the block copolymers indicated they possessed low polydispersities and were substantially free of PS homopolymers, however they contained a small amount of material that eluted after a shorter time than the majority of the sample. The formation of the latter species over a period of time was examined. The results indicate that the rate of formation of this species was very low or zero during propagation, the concentration of this species in the sample increased slowly after polymerisation. The observations were consistent with the hypothesis that it forms from polymer-polymer coupling.

3.4 Experimental

3.4.1 General

3.4.1.1 Materials

All chemicals used in anionic polymerisation were degassed by five freeze-thaw-evacuate cycles, to a pressure of below $1x10^{-5}$ mm Hg prior to use, unless stated otherwise. Styrene (Aldrich, 99+%) and benzene (Aldrich, 99.9+%) were distilled from CaH_2 prior to use. Ethylene oxide (EO, Aldrich, 99.5+%) was purified by distillation from CaH_2 and then by distillation from $Mg(Bu)_2$ (Aldrich, 1.0 M solution in heptane)

immediately before use. 4-Vinylbenzyl chloride (4-VBC, Aldrich, 90%) contained the impurities, α-chloromethyl styrene (2%), dichloromethyl styrene (3%) and 3-vinylbenzyl chloride (3-VBC, 5%) and was purified as described in the appropriate section (3.4.2.3 and 3.4.2.4). 4-Fluorostyrene (4-FS, Aldrich, 99%) was passed through a short column of basic alumina and distilled from CaH_2, prior to addition to potassium or lithium alkoxy-PS anions. *sec*-Butyllithium (Aldrich, solution in hexane), potassium (Aldrich, 98%), 15-crown-5 (Aldrich, 98%) and ethyl vinyl ether (Aldrich, 99%) were used as supplied. K_2CO_3 (Aldrich, 99.99%) and 18-crown-6 (Aldrich, 99%) were dried under vacuum prior to use. Sodium hydride (Aldrich, dry, 95%) was stored in a nitrogen glovebox and handled under nitrogen at all times.

Preparation of ROMP monomers and ruthenium propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ is described in Chapter 2.

Basic alumina (activated, Brockmann 1, CA. 150 mesh) and Celite (grade 521) were used in pore 4 sintered funnels. Anionic polymerisations were terminated using MeOH (Aldrich, 99.9+%) that had been sparged with N_2 for 30 min. THF (Aldrich, 99.9%, anhydrous) used for azeotropic distillation and as a solvent for Williamson couplings was passed through two columns containing alumina.[31] Hexane (Aldrich, 95+%, anhydrous) used in the precipitation of the macroinitiator was degassed by five freeze-evacuate-thaw cycles. CH_2Cl_2 (Aldrich, 99.9%) was dried over CaH_2. CD_2Cl_2 (Goss/Cambridge Isotope Laboratories Inc., 99.9% D, 0.03% v/v TMS) and $CDCl_3$ (Aldrich, 99.9% D, 0.03% v/v TMS) were used as received for general use. C_6D_6 (Aldrich, 99.6% D, 0.03% v/v TMS) was purified by distillation from CaH_2, and CD_2Cl_2 (Aldrich, 99.9% D, 0.03% v/v TMS) was obtained in pre-sealed ampoules, for use with air sensitive materials and polymerisation reactions.

3.4.1.2 Analysis

Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy was performed using a Varian Inova-500 MHz or Mercury-400 MHz spectrometer. All ^1H and ^{13}C NMR resonances are

quoted relative to TMS unless otherwise stated. The NMR spectra of air-sensitive materials were recorded in tubes sealed with a Young's tap.

Gel Permeation Chromatography (GPC)

GPC was performed using a Viscotek 200 with refractive index, viscosity and right angle light scattering detectors and 2 x 300 mm PLgel 5 μm mixed C columns. Three samples were analysed using a Viscotek TDA 302 with refractive index, viscosity and right angle light scattering detectors equipped with the same columns, data from this system is marked *THF GPC 2* in the text. THF was used as the eluent, at a flow rate of 1.0 mL/min and at a constant temperature of 30 °C. Molecular weights were obtained using triple detection, and used a value of 0.185 for the [d*n*/d*c*], that of polystyrene. The detectors were calibrated with a single, narrow molecular weight distribution polystyrene standard (M_w = 66000 g mol^{-1}, PDI = 1.03, Polymer Laboratories).

Mass Spectroscopy

Matrix assisted laser desoportion ionisation – time of flight (MALDI-TOF) mass spectroscopy was performed using an Applied Biosystems Voyager-DE STR BioSpectrometry workstation. Polystyrene homopolymers were dissolved in $CHCl_3$ and premixed with the matrix dithranol dissolved in $CHCl_3$ and cationisation agent AgTFA dissolved in $CHCl_3$. The samples were analysed in reflector mode. Polystyrene-polynorbornene block co-polymers were dissolved in THF and premixed with the matrix *trans*-3-indoleacrylic acid (IAA) dissolved in THF. These samples were analysed in linear mode.

Elemental Analysis

Elemental micro-analysis (C, H and N) was carried out on an Exeter Analytical, Inc. CE-440 Elemental Analyser.

3.4.2 Synthesis of Polystyrene Homopolymers

3.4.2.1 Synthesis of Hydroxyethyl Functionalised Polystyrene via Anionic Polymerisation

The anionic polymerisation of styrene was carried out using standard high vacuum techniques. Styrene (10.18 g, 0.09 mol) and benzene (125 mL) were distilled into the reaction vessel and polymerisation was initiated using *sec*-butyllithium (1.4 M solution in hexane, 1.45 mL, 2.04 mmol). Polymerisation was allowed to proceed for a period of 14 h at room temperature. An aliquot (~5 mL) of the solution was then removed from the reactor, and terminated with MeOH (0.25 mL), in order to provide a sample of unfunctionalised PS for analysis (see Section 3.4.2.2). The remaining PSLi in benzene was cooled in an ice bath, and EO (0.28 g, 6.4 mmol, 3-4 equivs) was distilled into the solution. The mixture was stirred for 30 min, after which MeOH (0.83 mL, 2.0 mmol, ~10 equivs) was added. After 30 min the solvent was removed under reduced pressure. The sample was dissolved in THF (40 mL) and traces of MeOH were removed by azeotropic distillation. The solvent was removed under reduced pressure and the sample was dried for 24 h *in vacuo* at 50 °C. Yield = 10.11 g, ~101%.*

Target M_n: 5000 g mol^{-1}

THF GPC: M_n = 5900 g mol^{-1}, PDI = 1.09.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 3.14**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.3 (**H_{4-6}**), 3.38–3.10 (**H_7**), 2.4–1.7 (**H_2**), 1.7-1.24 (**H_1**), 1.24-0.5 (***sec*-Bu**).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.8-145.0, (**C_3**), 129-127.2, 126.4–125.4 (all **C_{4-6}**), 61.2-60.8 (**C_7**), 47–41.35 (**C_1**), 41.35–40.4 (**C_2**), 40.2–39.8, 39.6–39.0 (**$C_{1/2}$**), 32.0-28.4 (***sec*-Bu**), 20.1-18.4, 11.6–10.8 (all ***sec*-Bu**).

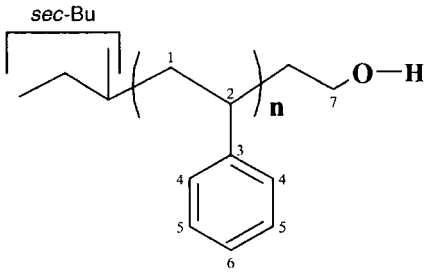


Figure 3.14 – NMR numbering scheme for hydroxyethyl functionalised polystyrene.

In a similar manner a polymer of target M_n 2500 g mol^{-1} was made with styrene (20.73 g, 0.20 mol), *sec*-butyllithium (1.3 M solution in hexane, 6.4 mL, 8.29 mmol), EO (0.58 g, 13.16 mmol), and allowing a polymerisation time of 30 min. Yield = 19.01 g, 92%.

A polymer of target M_n 10000 g mol^{-1} was made with styrene (10.13 g, 0.10 mol), *sec*-butyllithium (1.4 M solution in hexane, 0.7 mL, 1.01 mmol), EO (0.37 g, 8.39 mmol), and allowing a polymerisation time of 2 h. Yield = 10.69 g, 105%.

*The volumes of benzene solvent used in the polymerisation reaction and the volume of solution collected from the polymerisation vessel in order to provide a sample of MeOH terminated PS were not measured with a high degree of precision. Theoretical maximum and therefore percentage yields of the PS are not highly accurate as a result.

3.4.2.2 Recovery of MeOH Terminated Polystyrene

The solution of PS terminated with MeOH was precipitated into MeOH (40 mL). The polymer was filtered and dried *in vacuo*. Following this the product was twice re-dissolved in toluene (2.5 mL) and re-precipitated in hexane (20 mL), was filtered and dried *in vacuo*. Yield = 0.48 g.

Target M_n: 5000 g mol^{-1}

THF GPC: M_n = 5720 g mol^{-1}, PDI =1.10.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 3.15**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.3 (**H_{4-6}**), 2.4–1.7 (**H_2**), 1.7-1.24 (**H_1**), 1.24-0.5 (***sec*-Bu**).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.8-145.0, 143-142 (both C_3), 129-127.2, 126.4–125.4 (both $C_{4\text{-}6}$), 47–41.35 (C_1), 41.35–40.4 (C_2), 40.2–40.0, 39.5, 38.5–37.8 ($C_{1/2}$), 34.1-33.7 (C_2), 32.0–28.4 (***sec*-Bu**), 20.1-18.4, 11.6–10.8 (all ***sec*-Bu**).

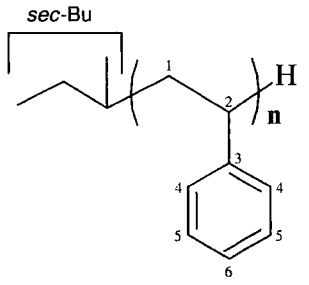


Figure 3.15 – NMR numbering scheme for unfunctionalised polystyrene.

3.4.2.3 Synthesis of PS Macromonomer - Method 1.

4-VBC was passed through a short column of basic alumina, dried and degassed over CaH_2, and purified by vacuum distillation immediately prior to use.

Hydroxyethyl functionalised PS (HOEtPS, M_n = 5900 g mol^{-1}, 5.0 g, 0.9 mmol) was dissolved in THF (100 mL) under an atmosphere of Ar in a bulb equipped with a septum. Potassium (0.2 g, 5.1 mmol, 5 equivs) was added to a second bulb under a stream of N_2 and placed under vacuum for 30 min, before being heated to form a mirror. The polymer solution was then added slowly to the K mirror and the two were allowed to remain in contact for 24 h. The solution was decanted into the first bulb and back again several times, to ensure the complete destruction of any trace amounts of protic impurities that might otherwise result in un-reacted HOEtPS contaminating the macromonomer. After this period all of the THF solution was then decanted into the first bulb, and freshly distilled 4-VBC (0.14 mL, 1.0 mmol, 1.2 equivs) was injected through the septum. The mixture was stirred for 24 h, after which air was admitted into the bulb. The polymer solution was diluted with THF (100 mL) and passed through a column of celite. It was then concentrated under vacuum (to 25 mL), and precipitated into MeOH (200 mL). It was reprecipitated from toluene (25 mL) into MeOH (200 mL) twice, to ensure the complete removal of unreacted 4-VBC. The sample was filtered and dried *in vacuo* at r.t overnight. Yield = 4.78 g, 94%.

THF GPC: M_n = 6040 g mol^{-1}, PDI =1.10.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 3.16**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4-7.2 (**$H_{10,11}$**), 7.4–6.3 (**H_{4-6}**), 5.76–5.64 (**H_{14}**), 5.24–5.16 (**$H_{14'}$**), 4.36-4.12 (**H_8**), 3.34–2.98 (**H_7**), 2.4–1.7 (**H_2**), 1.7-1.24 (**H_1**), 1.24-0.5 (***sec*-Bu**).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.8-145.0 (**C_3**), 139.0-138.8 (**C_9**), 137 (**C_{12}**), 136.9 (**C_{13}**), 129-127.2, 126.4–125.4 (both **$C_{4-6,10,11}$**), 113.8-113.6 (**C_{14}**), 72.6 (**C_8**), 68.5 (**C_7**), 47–41.35 (**C_1**), 41.35–40.4 (**C_2**), 40.2–39.8, 39.6–39.0 (**$C_{1/2}$**), 32.0-28.4 (***sec*-Bu**), 20.1-18.4, 11.6–10.8 (all ***sec*-Bu**).

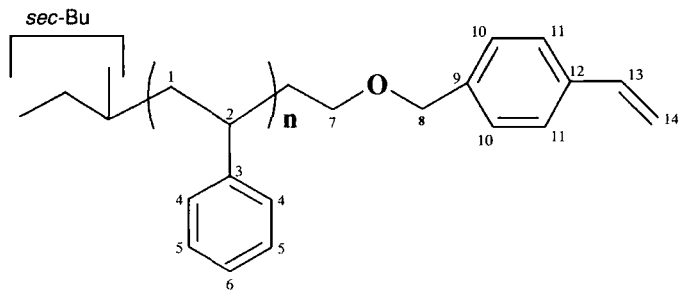


Figure 3.16 – NMR numbering scheme for 4-VBC functionalised polystyrene macromonomer.

3.4.2.4 Synthesis of PS Macromonomer – Method 2

Hydroxyethyl functionalised PS (2.0 g, 0.2 mmol, HOEtPS, PS M_n: 10600 g mol^{-1}) and NaH (0.05 g 1.9 mmol, 10 equivs) were added to a 2-neck 100 mL round bottom flask equipped with a magnetic follower, stoppered with subaseals. The flask was maintained under an atmosphere of nitrogen. The polymer was dissolved by the addition of dry THF (20 mL) to the flask, which was followed by the addition of 15-Crown-5 (0.38 mL, 1.9 mmol, 10 equivs) to the suspension. 4-VBC (0.27 mL, 1.9 mmol), which had been dried over fused $CaCl_2$ for two hours in a fridge at 4°C, was then passed through a short column of basic alumina and immediately added to the reaction. The reaction mixture was then agitated under the atmosphere of nitrogen. Periodically samples (1 mL) were removed through the subaseal using a syringe which were precipitated into IPA (10 mL), filtered, washed with IPA (5 x 10 mL) and dried briefly

under vacuum. Conversion of starting material to macromonomer was monitored using ^{1}H NMR by following the disappearance of the signal observed at 3.38–3.10 ppm (CH_2-OH, H_7, **Figure 3.14**) and the emergence of the signal in the macromonomer at approximately 3.34–2.98 ppm (CH_2-O-CH_2, H_7, **Figure 3.16**). The reaction was complete within 48 h. Residual NaH was destroyed by the addition of a few drops of MeOH. The polymer solution (16 mL) was then precipitated into MeOH (160 mL), filtered and washed with MeOH (5 x 40 mL) before being dried in vacuo. Impurities in the polymer that were insoluble in chlorinated solvents were removed by passing a dilute solution (DCM) through a short (1.5 cm) column of celite and eluting the polymer with more DCM (total 100 mL) and removing the solvent under vacuum. The polymer was reprecipitated twice from toluene (10 mL) into MeOH (100 mL), the solid produced was isolated by filtration and washed with MeOH (5 x 40 mL) and dried in vacuo at r.t. overnight. Yield = 1.40 g (86%, based on polymer left after reaction monitoring).
NMR data was identical to that from the macromonomers from K mirrors from Section 3.4.2.3.

3.4.3 Synthesis of the PS Ruthenium Macroinitiator

In a nitrogen-filled glovebox (M.Braun), PS macromonomer (M_n = 10700 g mol^{-1}, 500.0 mg, 5 x 10^{-2} mmol) was dissolved in C_6H_6 (3.0 mL) and placed in an ampoule. $RuCl_2$(=CHEt)$(PCy_3)_2$ (44 mg, 6 x 10^{-2} mmol, 1.2 equivs) was dissolved in C_6H_6 (2.00 mL) in another ampoule. Both ampoules were transferred to a vacuum line and kept under argon. The solution of PS macromonomer was then introduced via a cannula to the agitated solution of initiator under an argon purge. Argon was bubbled through the mixture and agitation continued for a further hour. The solution was concentrated to half its original volume under vacuum and the solution added drop-wise to vigorously stirred, degassed hexane (chilled to -78 °C, 25 mL) producing a red precipitate. The mixture was then filtered and washed thoroughly with chilled hexane (3 x 30 mL) using standard cannula techniques. The solid obtained was dried at room temperature and *in vacuo* (2x10^{-6} mbar) overnight. The macroinitiator was then redissolved in C_6H_6 (2 mL) in the glovebox and precipitated into hexane (-78 °C, 20 mL) and washed with hexane as

before, to ensure complete removal of unreacted ruthenium propylidene initiator. Yield = 280 mg, 53%.

The macroinitiator was fully characterised by NMR using the numbering scheme shown in **Figure 3.17**.

^{1}H NMR (C_6D_6, 500 MHz): δ 20.56 (s, H_{13}), 8.71 (br, H_{11}), 7.3-6.4 (H_{4-6} and residual H in C_6D_6), 3.92-3.70 (H_8), 3.24–2.96 (H_7), 2.90 (m ,H_{15-18}), 2.60-1.10 (H_1, H_2, all m, H_{15-18}), 1.1–0.42 (*sec*-Bu).

^{13}C NMR (C_6D_6, 126 MHz, v.s C_6D_6): δ 153.35 (s, C_{12}), 146.8-145.0 (C_3), 141.32 (s, C_9), 131.47 (s, $C_{11\ or\ 10}$), 129.4–127.8, (C_{4-6} and C_6D_6), 127.0–126.4 (C_{4-6}), 73.46 (br, C_8), 69.28 (br, C_7), 48.0–42.0 (C_1), 42.0–41.2 (C_2), 32.03 (*pseudo*-t, C_{15}), 30.76 (s, C_{17}), 28.75 (*pseudo*-t, C_{16}), 27.55 (s, C_{18}).

^{31}P NMR (C_6D_6, 202 MHz): δ 37.14 (s, P_{14}).

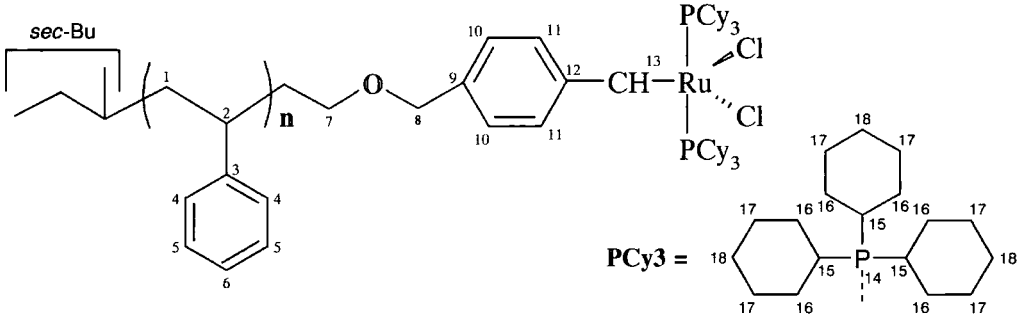


Figure 3.17 - Numbering scheme for NMR assignments of a ruthenium PS macroinitiator.

3.4.4 Synthesis of PS-PNB Block Copolymers

3.4.4.1 Synthesis of Poly(Styrene)-*block*-(*exo*-*N*-Phenylbutylbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxyimide). PS (DP = 100) - PNB A (DP = 100).

All ROMP reactions were performed in a nitrogen-filled glovebox (M.Braun) in screw top vials. *exo*-*N*-Phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (Monomer **A**, 104 mg, 0.4 mmol) was dissolved in CH_2Cl_2 (2 mL). This solution was added to a stirred solution of a PS ruthenium macroinitiator (40.0 mg, 4 x 10^{-3} mmol, PS macromonomer M_n = 10500 g mol^{-1}, DP = ~ 100,) dissolved in CH_2Cl_2 (1 mL). After 1 h the living polymer was terminated by the addition of ethyl vinyl ether (0.1 mL, 1.1 mmol) under a stream of N_2. The solution was stirred for a further h, after which it was

concentrated to approximately 1.0 mL using a stream of N_2 and precipitated into MeOH (10 mL) with vigorous agitation. The resulting precipitate was recovered by filtration, washed with MeOH and dried *in vacuo* at r.t. overnight Yield = 0.120 g (86%). The block copolymer was then purified by dissolving it in CH_2Cl_2 and precipitating it in hexane twice. The copolymer sample was finally filtered and dried *in vacuo* at r.t overnight. Yield = 0.109 g, 78%.

Elemental analysis: Found C: 80.55%, H: 7.32%, N: 3.47%; calculated for $C_{2723}H_{2930}N_{100}O_{201}$ C: 81.20%, H: 7.33%, N: 3.48%.

Target M_n: 40200 g mol^{-1}.

THF GPC: M_n = 38400 g mol^{-1}, PDI = 1.07.

The block copolymer was fully characterised by NMR using the numbering scheme shown in **Figure 3.18**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.9 ($H_{15\text{-}17,20\text{-}22}$), 6.9–6.3 ($H_{20/21/22}$), 5.78-5.66 (brm, *trans* $H_{5,6}$), 5.56-5.45 (*cis* $H_{5,6}$), 3.50–3.36 (brm, H_{10}), 3.23-3.10 (brm, *cis* $H_{2,3}$), 3.07-2.87 (brm, *trans* $H_{2,3}$), 2.69 (brm, *cis* $H_{1,4}$), 2.62 (brm, *trans* $H_{1,4 \text{ and } 13}$), 2.4–1.7 ($H_{7/7',18}$), 1.7-1.24 ($H_{7/7',11,12,23}$).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 178.56–178.2 ($C_{8,9}$), 146.8-145.0, (C_{19}), 142.53/142.44 (C_{14}), 133.6 (*trans* $C_{5,6}$), 132.4–131.8 (*cis* $C_{5,6}$), 129-127.4 ($C_{15,16,20/21/22}$), 126.4–125.4 (all $C_{17,20/21//22}$), 52.72 (*cis* $C_{2,3}$), 51.43-51.14 (*trans*, $C_{2,3}$), 47.0–40.4 ($C_{1,4,7,18,23}$), 38.51/38.35 (C_{10}) 35.54/35.50 (C_{13}), 29.03/28.96, 27.52/27.49 ($C_{11,12}$).

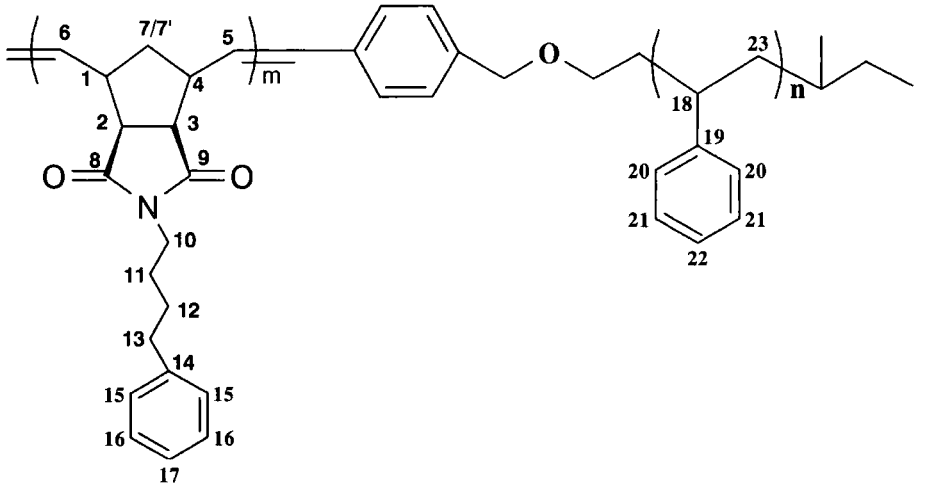


Figure 3.18 - Numbering scheme for NMR assignments of poly(styrene)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide).

3.4.4.2 Synthesis of Poly(Styrene)-*block*-(*exo*-*N*-Phenylbutylbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxyimide). PS(DP = 100) - PNB A (DP = 200).

The polymerisation was performed in a similar manner to that described in Section 3.4.4.1 except that (Monomer **A**, 207 mg, 0.7 mmol) dissolved in CH_2Cl_2 (4 mL) was added to the initiator solution. The solution was stirred for 2 h prior to termination with ethyl vinyl ether, stirred for a further h, after which it was concentrated to approximately 2.0 mL using a stream of N_2, and purified as described previously. Yield = 0.202 g, 83 %.

Elemental analysis: Found C: 78.91%, H: 7.26%, N: 3.96%; calculated for $C_{4623}H_{5030}N_{200}O_{401}$ C: 79.54%, H: 7.26%, N: 4.01%.

Target M_n: 69700 g mol^{-1}.

THF GPC: M_n = 68300 g mol^{-1}, PDI = 1.07.

NMR data was identical to that detailed in Section 3.4.4.1 with the exception of the intensities of the resonances from the PS and PNB blocks relative to each other.

3.4.4.3 Synthesis of Poly(Styrene)-*block*-(*exo*-*N*-Phenylbutylbicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxyimide). PS(DP = 100) - PNB A (DP = 500).

The polymerisation was performed in a similar manner to that described in Section 3.4.4.1 except that (Monomer **A**, 259 mg, 0.9 mmol) dissolved in CH_2Cl_2 (10 mL) was added to the stirred solution of a PS ruthenium macroinitiator (20.0 mg, 2 x 10^{-3} mmol, PS macromonomer M_n = 10500 g mol^{-1}) in CH_2Cl_2 (0.5 mL). The solution was stirred for 5 h prior to termination with ethyl vinyl ether, stirred for a further h, after which it was concentrated to approximately 3.0 mL using a stream of N_2, and purified as previously described. Yield = 0.243g, 88%.

Elemental analysis: Found C: 76.49%, H: 7.07%, N: 4.38%; calculated for $C_{10323}H_{11330}N_{500}O_{1001}$ C: 78.26%, H: 7.21%, N: 4.42%.

Target M_n: 158400 g mol^{-1}.

THF GPC: M_n = 151200 g mol^{-1}, PDI = 1.09.

NMR data was identical to that detailed in Section 3.4.4.1 with the exception of the intensities of the resonances from the PS and PNB blocks relative to each other.

3.4.4.4 Synthesis of Poly(Styrene)-*block*-(*endo,exo*-Bicyclo[2.2.1]Hept-5-ene-2,3-Dicarboxylic Acid Dimethyl Ester). PS (DP = 100) - PNB B (DP = 100).

The polymerisation was performed in a similar manner to that described in Section 3.4.4.1 except that *endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester (Monomer **B**, 74 mg, 0.4 mmol) dissolved in CH_2Cl_2 (2 mL) was added to the initiator solution. The solution was stirred for 24 h prior to termination with ethyl vinyl ether, stirred for a further h, after which it was concentrated to approximately 1.0 mL using a stream of N_2, and purified as previously described. Yield = 0.065 g, 59%.

Elemental analysis: Found C: 71.63%, H: 6.98%; calculated for $C_{1923}H_{2230}O_{401}$ C: 72.72%, H: 7.08%.

Target M_n: 31700 g mol^{-1}.

THF GPC: M_n = 23100 g mol^{-1}, PDI = 1.05.

The block copolymer was fully characterised by NMR using the numbering scheme shown in **Figure 3.19**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.3 (**$H_{14\text{-}16}$**), 5.58-5.13 (3 x brm **$H_{5,6}$**), 3.70-3.58 (**$H_{10,11}$**), 3.36-3.10 (brm, **$H_{2,3}$**), 3.10-2.86 (brm, **$H_{1,4\ \text{and}\ 2,3}$**), 2.68 (brm, **$H_{1,4}$**), 2.4–1.7 (**$H_{7/7',12}$**), 1.7-1.24 (**$H_{17/7',17}$**).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 174 (*exo* **$C_{8,9}$**), 173 (*endo* **$C_{8,9}$**), 146.8-145.0 (**C_{13}**), 133.4-129.6 (**$H_{5,6}$**), 128.8-127.6, 126.4–125.6 (both **$C_{14\text{-}16}$**), 53.20-51.60 (**$C_{1\text{-}4,10,11}$**), 47-46.5 (**$C_{1,4}$**), 45.0-44.0 (**$C_{2,3}$**), 47–41.35 (**$C_{1\text{-}4,17}$**), 41.35–40.4 (**$C_{2,3,7,12}$**).

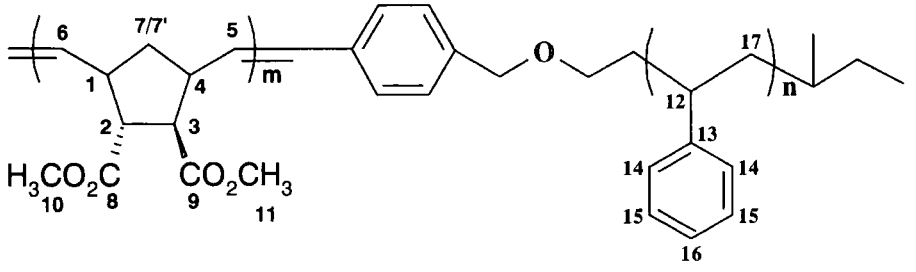


Figure 3.19 - Numbering scheme for NMR assignments of poly(styrene)-*block*-(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester).

3.4.4.5 Synthesis of Poly(Styrene)-*block*-(*endo,endo*-5,6-bis[Chloromethyl] Bicyclo[2.2.1]Hept-2-ene). PS (DP = 100) - PNB C (DP = 100).

The polymerisation was performed in a similar manner to that described in Section 3.4.4.1 except that *endo,endo*-5,6-bis(chloromethyl)bicyclo[2.2.1]hept-2-ene (Monomer **C**, 67 mg, 0.4 mmol) dissolved in CH_2Cl_2 (2 mL) was added to the initiator solution. The solution was stirred for 1 h prior to termination with ethyl vinyl ether, stirred for a further h, after which it was concentrated to approximately 1.0 mL using a stream of N_2, and purified as previously described. Yield = 0.074 g, 76%.

Elemental analysis: Found C: 67.87%, H: 6.79%; calculated for $C_{1923}H_{2230}O_{401}$ C: 69.33%, H: 6.86%.

Target M_n: 29800 g mol^{-1}.

THF GPC: M_n = 22600 g mol^{-1}, PDI = 1.24.

The block copolymer was fully characterised by NMR using the numbering scheme shown in **Figure 3.20**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.4–6.3 (**$H_{4\text{-}6}$**), 5.60-5.28 (brm, **$H_{2,3}$**), 3.80-3.40 (brm, **$H_{8,9}$**), 3.20-3.06 (brm, **$H_{1,4}$** *cis*), 2.83 (br, **$H_{1,4}$** *trans*), 2.60 (brm, **$H_{5,6}$** *trans*), 2.4–1.7 (**H_{10}**, and **$H_{5,6}$** *cis*), 1.7-1.24 (**$H_{7,7',15}$**),

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.8-145.0 (**C_{11}**), 133.0-131.8 (**$C_{2,3}$**), 129-127.4 126.4–125.6 (both **$C_{12\text{-}14}$**), 49.7–49.1 (**$C_{5,6}$**), 47–41.35 (**$C_{1,4,8,9,15}$**), 41.35–40.4 (**C_{10}**), 39.4-38.3 (**$C_{1,4\text{ and }7}$**), 37.08 (**C_7**).

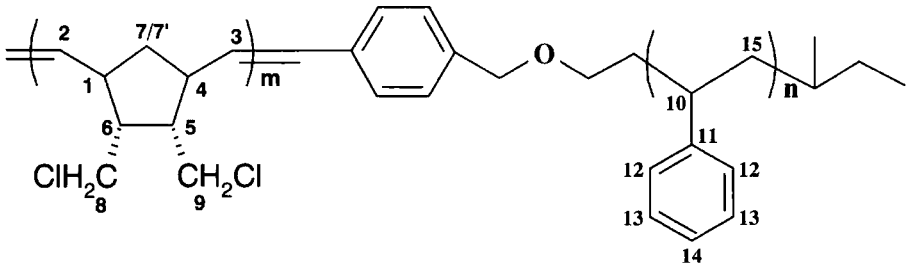


Figure 3.20 - Numbering scheme for NMR assignments of poly(styrene)-*block*-(*endo,endo*-5,6-bis[chloromethyl]bicyclo[2.2.1]hept-2-ene).

3.4.4.6 Reaction to Monitor PS-PNB Block Copolymer Coupling by NMR and GPC. PS (DP = 100) - PNB A (DP = 200).

In a nitrogen-filled glovebox (M.Braun) *exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (Monomer A, 77 mg, 0.3 mmol) was dissolved in CD_2Cl_2 (0.6 mL). This solution was added to a stirred solution of a PS ruthenium macroinitiator (15.0 mg, 1 x 10^{-3} mmol, PS macromonomer DP = 101, M_n = 10500 g mol^{-1}) dissolved in CD_2Cl_2 (0.3 mL). The mixture was diluted with CD_2Cl_2 (0.3 mL) and transferred to an NMR tube, which was sealed with a Young's tap to create an air tight seal. The ^1H NMR spectrum of the reaction was then collected 4 times periodically over 20 hours (24 to -1 ppm). At the same time as NMR data was collected a small aliquot (0.2 mL) was extracted with a syringe and terminated with a few drops of ethyl vinyl ether for GPC analysis. After an hour it was precipitated into MeOH (20 mL), washed with MeOH and dried *in vacuo*.

Target M_n: 69700 g mol^{-1}.

For a discussion of the analytical data please see Section 3.2.3.1

3.5 References

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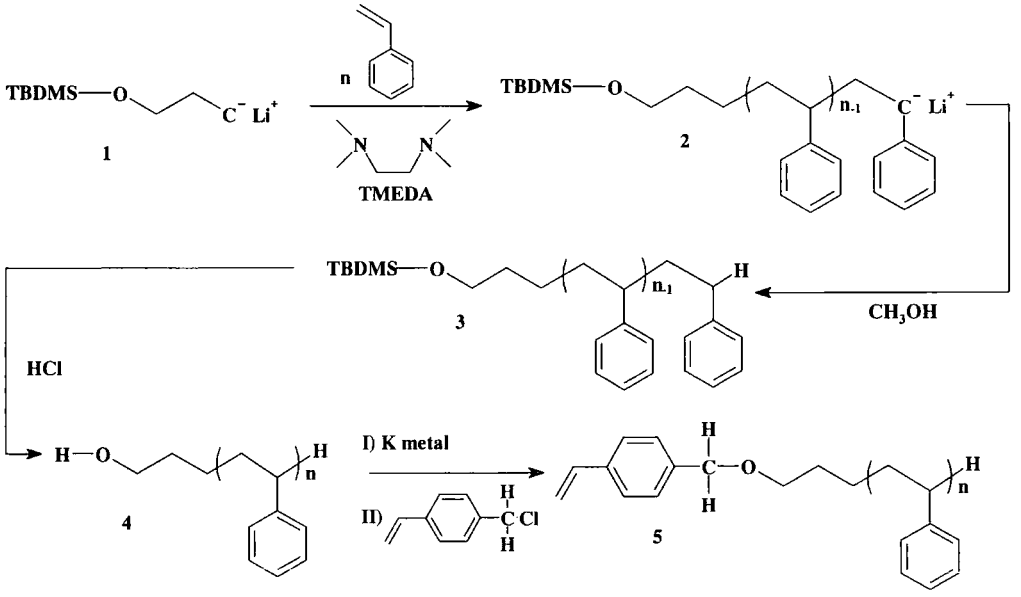
Chapter 4

Macromonomers from Hydroxyl Groups Introduced by Anionic Polymerisation using Protected initiators

4.1 Introduction

A methodology suitable for the synthesis of block copolymers by converting living anionic polymerisation into ROMP has been demonstrated in Chapters 2 and 3. Amongst the most difficult steps in the synthesis of the block copolymers is the conversion of the living anionic polymer chains into functionalised macromonomers using 4-vinylbenzyl chloride (4-VBC). Once a procedure for achieving this has been established, the conversion of the macromonomer into a macroinitiator for ROMP, and subsequent ROMP of a suitable norbornene derivative, are effectively identical to those already established. This was demonstrated in Chapter 3 with the synthesis of block copolymers of styrene and norbornene derivatives. The conversion of the living anionic polymerisation into macromonomer was accomplished in Chapter 3 by functionalising the living poly(styryl)lithium with ethylene oxide (EO) to yield hydroxyethylated polystyrene. The Williamson ether synthesis was used to convert the hydroxyethylated polystyrene (PS) into macromonomers. It is established here that an alternative to this strategy is to introduce the hydroxyl groups onto the chain ends using an initiator that contains a protected hydroxyl group, avoiding the need to end-functionalise the living polymer. The protected initiator used is a *n*-propyllithium compound incorporating a *tert*-butyldimethylsilyl ether (TBDMSO) protected alcohol functionality (**1**, **Scheme 4.1**).



Scheme 4.1 - Synthesis of macromonomers using a protected initiator. TMEDA = *N,N,N',N'*-tetramethylethylenediamine.

Polymerisation of styrene with **1** led to the formation of poly(styryl)lithium (PSLi)(**2**), which was terminated using CH_3OH to yield PS with a hydroxyl group protected by a TBDMS ether group (**3**). The polymer was deprotected by cleaving the TBDMS group using HCl (**4**). The hydroxyl functionality was converted to a metal alkoxide using K metal. Williamson coupling of this polymer with 4-VBC resulted in the synthesis of a macromonomer (**5**). These macromonomers should be suitable for the synthesis of block copolymers with norbornene derivatives – following conversion to macroinitiators.

Attempts were also made to synthesise macromonomers of poly(methyl methacrylate) and poly(propylene sulfide) using the protected initiator and convert them to macromonomers suitable for block copolymer synthesis.

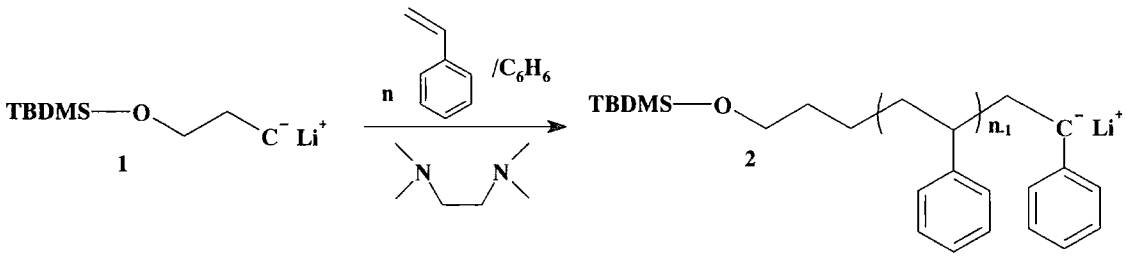
4.2 Results and Discussion

4.2.1 Polystyrene Macromonomers from a Protected Initiator

It was demonstrated in Chapter 3 that polystyrene (PS) macromonomers could be synthesised by a Williamson coupling between hydroxyl functionalised PS and 4-VBC, a reaction that proceeded via a metal alkoxide, formed using K or NaH. The hydroxyl groups were introduced by functionalising the living PS with EO, by means of a protected initiator. These materials can be used for the synthesis of macromonomers, as is demonstrated with PS. A major advantage in introducing a hydroxyl group to the polymer chains through a protected initiator is that it will be useful for the functionalisation of anionically initiated polymers that cannot be quantitatively functionalised by either direct addition of 4-VBC or EO to the living polymer chains. It will also aid the synthesis of very high molecular weight PS macromonomers, where the low concentration of living chains means that even trace amounts of impurities are likely to lead to significant termination. The termination will result in the loss of complete functionalisation.

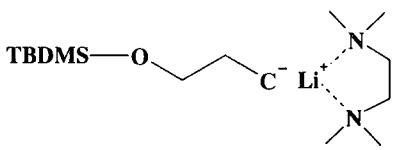
4.2.1.1 Synthesis and Characterisation of *tert*-Butyldimethylsilyl Ether Protected PS

The initiator 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (TBDMSO-PrLi)(**1**) was used to initiate the polymerisation of styrene (**Scheme 4.2**).



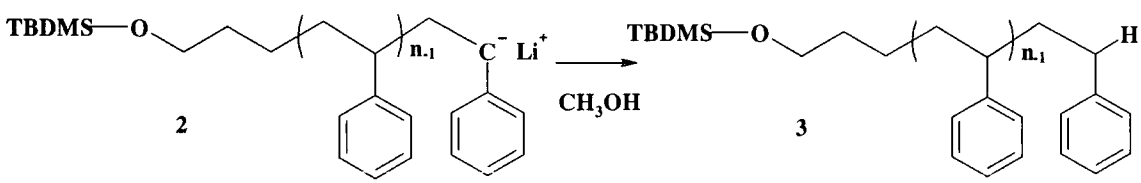
Scheme 4.2 - Synthesis of living PS using TBDMS-O-PrLi.

n-Alkylithium initiators such as propyllithium initiators are less efficient at initiating the polymerisation of styrene compared with *sec*-butyllithium, used to initiate the polymerisation of styrene in Chapter 3, due to the aggregates they form in non-polar solution.[1] *N,N,N',N'*-tetramethylethylenediamine (TMEDA) was added to the styrene prior to the addition of the initiator. TMEDA breaks up this aggregation, possibly by forming a contact ion-pair solvated by the diamine in the form of a 1:1 complex, in which the Li is in a five-membered ring (**Scheme 4.3**).[2]



Scheme 4.3 – Complexation of the lithium with TMEDA.

The propagating species, poly(styryl)lithium, had a burgundy colour in benzene. The difference in colour compared with PS initiated with *sec*-butyllithium (Chapter 3), is due to complexation of the lithium with the TMEDA. As end functionalisation of the PS is not required it can be simply terminated using MeOH (**Scheme 4.4**).



Scheme 4.4 - Termination of the living polystyrene.

The resulting polymer was analysed by Gel Permeation Chromatography (GPC) which indicated it had a low polydispersity (PDI: 1.03) (**Figure 4.1**).

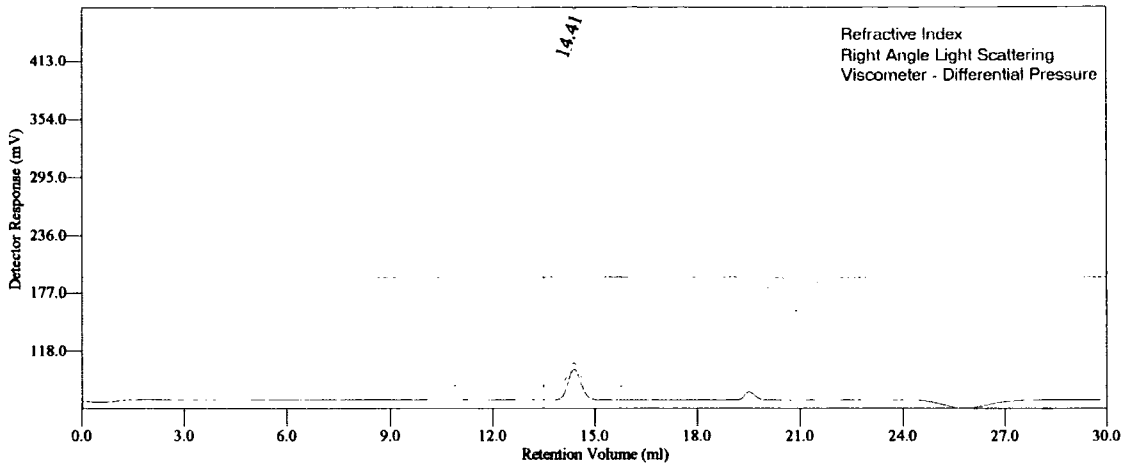


Figure 4.1 – GPC chromatograph of polystyrene initiated by TBDMSO-PrLi.

The M_n by GPC of 11600 g mol^{-1} is in good agreement with the theoretical value of 10000 g mol^{-1}.

The polymer was also studied by NMR spectroscopy. Comparison of the ^{1}H NMR (𝔸, 𝔹 and ℂ, **Figure 4.2**) and ^{13}C NMR data (**Appendix 4.1.1**) with that of PS initiated by *sec*-butyllithium (Section 3.2.1.1) suggests that the PS main chain possess a similar microstructure and is thus atactic.

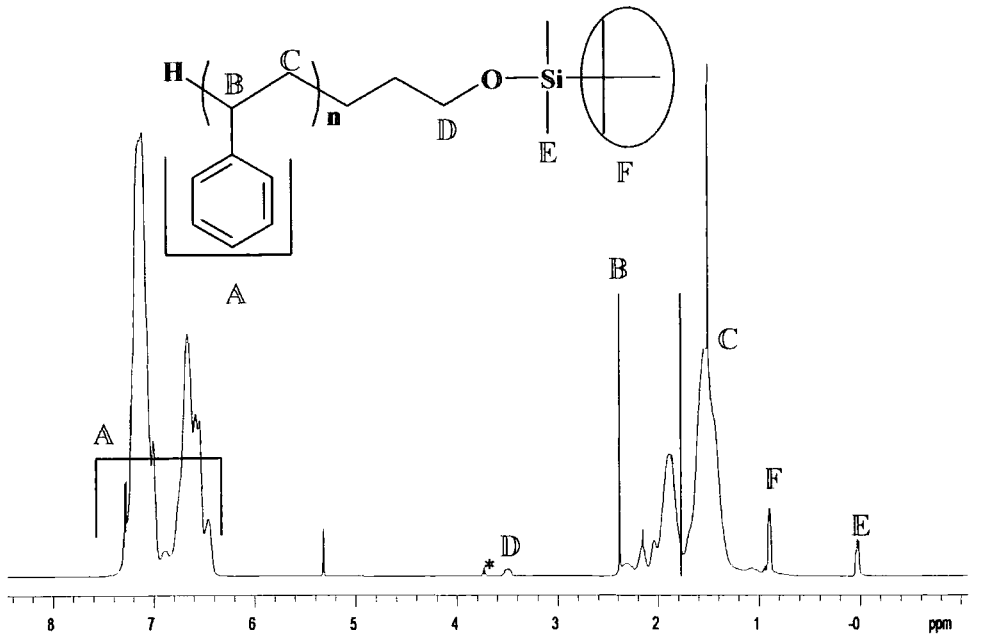


Figure 4.2 - ^{1}H NMR spectrum of polystyrene initiated using TBDMS-O-PrLi (CD_2Cl_2). *=THF.

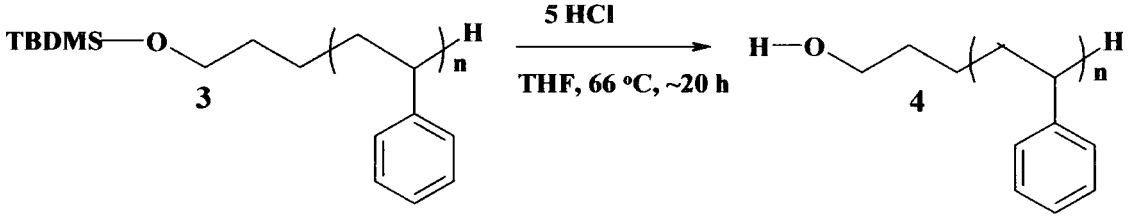
The protected alcohol functionality (𝔻) can be observed at 3.5 ppm. The TBDMS functionality is also observed; the tertiary butyl group (𝔽) at 0.9 ppm, the dimethylsilyl group (𝔼) at approximately 0 ppm. Analyses were therefore performed in solvents free from tetramethylsilane (TMS). As TBDMSO-PrLi was the only initiating species, all the polymer chains have the TBDMS ether functionality. This can be used to provide an estimate for the molecular weight of the polymer by comparing the integrals of the dimethylsilyl group (𝔼) with the pendant aryl groups (𝔸). This suggested a value for M_n of 12100 g mol^{-1}, similar to that obtained from GPC. The polymer was reprecipitated twice in order to remove impurities containing TBDMS (for example initiator that had died prior to injection into the polymerisation reaction) which would have otherwise taken part in the next step in the reaction (Section 4.2.1.2).

4.2.1.2 Deprotection of TBDMS Ether Protected PS

Use of the protected initiator TBDMSO-PrLi to initiate the polymerisation of styrene, resulted in the introduction of a protected hydroxyl group onto every chain of the PS. The TBDMS group is one of the most popular protecting groups for hydroxyl

functionalities, in part due to the ease with which it can be removed under conditions that do not attack other functional groups.[3] It is however in general very stable, being 10^4 times more stable to hydrolysis than the trimethylsilyl (frequently abbreviated TMS) group. It has excellent stability towards base, but is fairly sensitive to attack by acid. One method of cleaving the TBDMS group, is using concentrated acid, e.g. HCl or H_2SO_4.[3] Due to its wide spread use, it should be mentioned that fluoride ion is also used to cleave the TBDMS group, in the form of tetrabutylammonium fluoride (TBAF),[4] KF and 18-crown-6,[5] or even aqueous HF.[3]

In this work, the TBDMS was cleaved from the PS using HCl. The use of this acid was adopted principally because being a gas it is easier to remove from PS than many of the alternative reagents. The reaction can be performed by refluxing the polymer (**3**) in THF with 5 equivalents of HCl under a laboratory atmosphere (**Scheme 4.5**).



Scheme 4.5 - Cleavage of the TBDMS group from PS to create hydroxy functionalised PS.

The reaction was monitored by taking samples and examining them by ^{1}H NMR spectroscopy. The THF solvent was removed from the sample using a flow of N_2, the sample was redissolved in $CDCl_3$ and the ^{1}H NMR spectrum of the resulting solution collected. The resonances of the dimethylsilyl (𝔼) and *tert*-butyl groups (𝔽) of the TBDMS protected polymer were absent from the spectrum, being replaced by two new silyl and *tert*-butyl peaks, presumably from Cl-TBDMS and H-TBDMS. Both of these were removed when the aliquot was reprecipitated twice in MeOH yielding pure hydroxy functionalised polymer. The bulk of the polymer was then purified to give hydroxy functionalised polymer in good yield (94%). No sign of the protecting group is observed in the ^{1}H NMR spectrum of the final product. The ether signal is replaced by that from the CH_2OH (𝔾) at approximately 3.5-3.4 ppm (**Figure 4.3**).

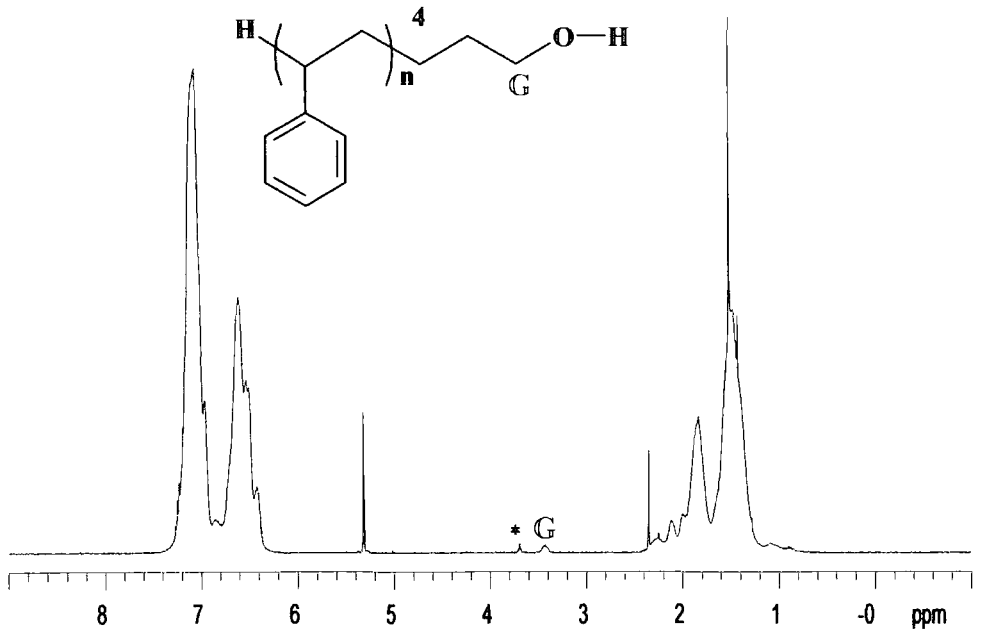


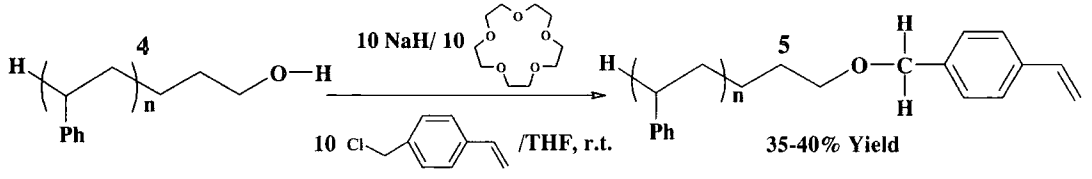
Figure 4.3 - ^{1}H NMR spectrum of deprotected polystyrene (CD_2Cl_2). *=THF.

The disappearance of the TBDMS group was also observed using ^{13}C NMR spectroscopy (**Appendix 4.1.2**). As the initiator imparted a TBDMS ether functionality to every polymer chain, complete deprotection of the TBDMS group leaves PS quantitatively functionalised with a hydroxybutyl group (when we consider functionality introduced by the initiator and the first PS repeat unit), suitable for conversion to a macromonomer by a coupling reaction based on the Williamson ether synthesis (Section 4.2.1.3). Traces of MeOH, which would react with K and NaH, were removed from the sample by azeotropic distillation using THF. The final sample was free from impurities with the exception of a trace of THF (*, **Figure 4.3**). GPC analysis of the product indicated that as expected it remained mono-modal and retained a low PDI (**Appendix 4.1.3**).

4.2.1.3 Synthesis of PS Macromonomers from Deprotected PS-OH

Attempts were made to explore whether the chemistry described in Section 3.2.1.3 could be used to convert the hydroxybutyl group of the PS-OH here (Section

4.2.1.2). The reaction of the hydroxybutyl group with 10 equivalents each of NaH, 15-crown-5 and 4-VBC in THF was carried out using conditions analogous to those used to convert the hydroxyethyl functionalised PS into macromonomer (Section 3.4.2.4) as depicted in **Scheme 4.6**.



Scheme 4.6 - Attempted synthesis of PS macromonomers (5) from PS initiated by TBDMS-O-PrLi (4) using NaH.

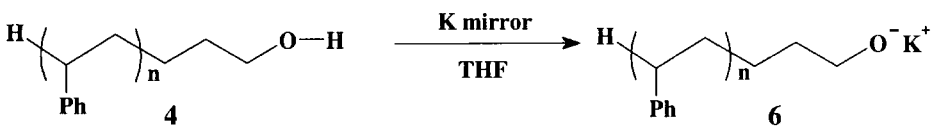
Samples were regularly collected to allow the course of the reaction to be followed by ^{1}H NMR. After 24 h of reaction time 21% conversion to macromonomer was observed. After 48 h (the time necessary to effect complete functionalisation of the macromonomer from hydroxyethylated PS) the degree of functionalisation had only grown to 32%. This increased slightly to 35% after a further 24 h, after which point further conversion was minimal (no more than 1% every 24 h). The reaction was also carried out in DMF, using the same conditions, in the hope that its higher dielectric constant relative to THF might help reduce the association of the metal ion with the alkoxide and increase the speed of reaction. Unfortunately the rate of conversion was similar or slightly slower in DMF – only 16% conversion after 24 h was detected. Reaction appeared to stop after 72 h at which point only 30-32% conversion was observed. The slightly slower rate of the reaction may be due to the tendency of DMF to undergo decomposition in the presence of base at room temperature (r.t.).[6] As a warning to the reader, it will be noted that the reaction of NaH in warm (50 °C) DMF is exothermic and can be uncontrollable,[7] presenting an explosive hazard at the temperature at which DMF refluxes.[8] The use of acetone is also precluded due to its decomposition at r.t. by NaH, which can potentially be hazardous.[8] As discussed in Section 3.2.1.3 heating 4-VBC also leads to loss of the vinyl functionality by radical autopolymerisation, which prevents the use of solvents at their reflux temperature.

The reason for the failure of NaH to work with the PS from the protected initiator is possibly related to the lower acidity of the alcohol relative to that of the EO

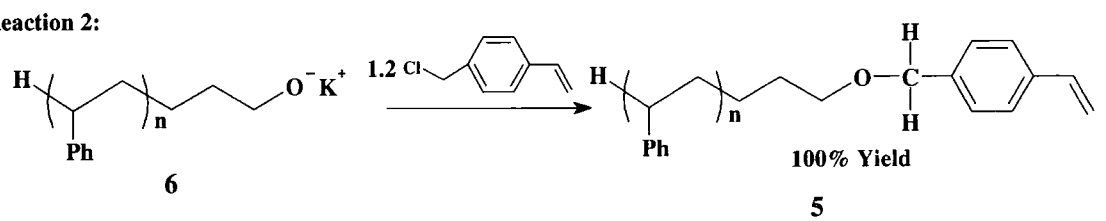
functionalised PS. Alkyl alcohols, without strongly electron withdrawing groups, possess low acidities (i.e. high pK_a) in general.[9,10] Increasing the size of the alkyl groups reduces their acidity further. The butyl alcohol (i.e $RCH(C_6H_5)$–C_4H_8OH), obtained from polymerising styrene using TBDMSO-PrLi and subsequent deprotection, is likely to be less acidic than that of the hydroxyethylated PS from ethylene oxide functionalisation (ROC_2H_4OH). This would be expected to make it slightly more difficult to deprotonate the alcohol and make the crucial sodium-alkoxide intermediate in the reaction[11] (see also Section 3.2.1.3). In the case of hydroxyethyl functionalised PS (Section 3.2.1.3) the reaction was relatively (though not prohibitively) slow, requiring 48 h to go to completion. The reduced reactivity of the hydroxybutyl group is believed to be the reason for the failure of the reaction discussed here to go to completion.

Potassium metal is one of the strongest reducing agents that is used in synthesis;[9] its reducing potential exceeds that of the hydride ion.[12] Despite the reduced acidity of the PS-OH from the protected initiator, K was still able to reduce the alcohol on the end of this chain to an oxo-anion. Reaction of the hydroxybutyl functionalised PS (**4**) with a K mirror results in the quantitative formation of potassium alkoxide **6** (**Reaction 1, Scheme 4.7**). Addition of 4-VBC to **6** results in the quantitative functionalisation of the PS with the 4-VBC to form macromonomer **5** (**Reaction 2, Scheme 4.7**).

Reaction 1:



Reaction 2:



Scheme 4.7 -Synthesis of PS macromonomers from hydroxy functionalised PS from TBDMS-O-PrLi initiated PS using a K mirror (Reaction 1) and 4-VBC (Reaction 2).

The ^{1}H (**Figure 4.4**) and ^{13}C (**Appendix 4.1.4**) NMR spectra of macromonomer **5** synthesised from TBDMS protected PS, are very similar to those synthesised from hydroxyethylated PS from ethylene oxide in Chapter 3.

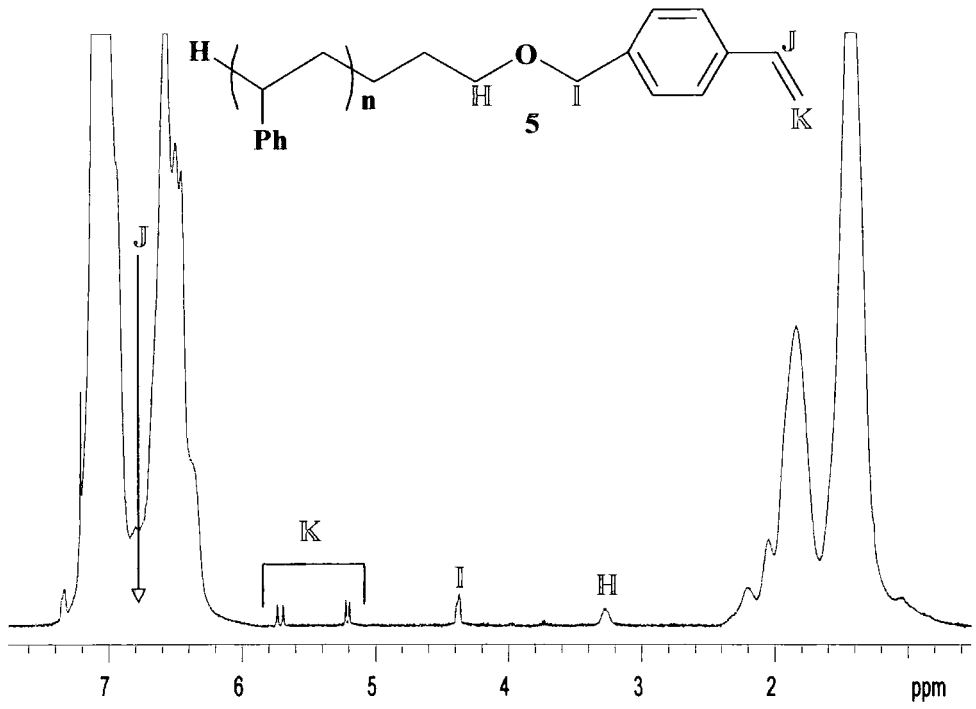
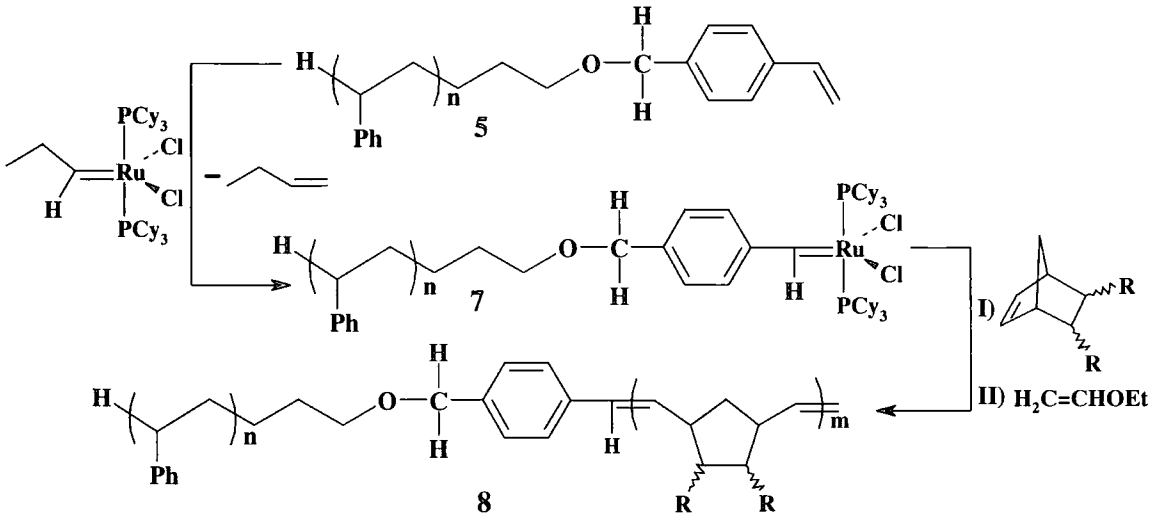


Figure 4.4 - ^{1}H NMR spectrum of PS macromonomer from TBDMSO-PrLi initiated PS ($CDCl_3$, referenced v/s TMS).

Comparison of the integrals of the peaks from a CH_2 introduced to the polymer chain from the protected initiator (ℍ, **Figure 4.4**), and the protons of the macromonomer (𝕀 and 𝕂), confirm that functionalisation is quantitative. The vinyl proton (𝕁) and the aryl protons of the chain end are obscured by the aryl protons of the PS chain as with the macromonomer obtained from hydroxyethylated PS. The PS macromonomer was examined by GPC which confirmed that it retained a low PDI as expected (**Appendix 4.1.5**).

The macromonomer synthesised by this method will be suitable for the synthesis of block copolymers of PS and PNB (polynorbornene) – after conversion to macroinitiator, by the same conditions used to synthesise block copolymers in Chapter 3 (**Scheme 4.8**).



Scheme 4.8 - Proposed route for the synthesis of PS-PNB using PS macromonomers synthesised using TCBDMSO-PrLi.

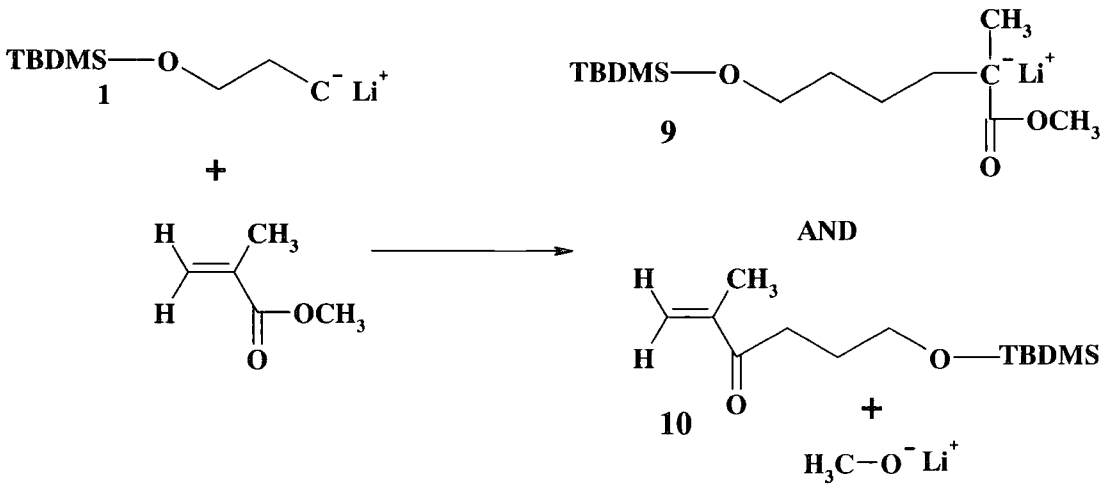
The 4-vinylbenzyl group of PS macromonomer **5** is essentially identical to that used previously to synthesise Ru macroinitiators (Section 3.2.2). Hence homometathesis of **5** with $RuCl_2(=CHEt)(PCy_3)_2$ will allow synthesis of ruthenium PS macroinitiator **7**. Addition of norbornene derivatives to **7** will result in the synthesis of poly(styrene-*block*-norbornenes) **8** (Section 3.2.3).

4.2.2 Attempted Synthesis of Poly(Methyl Methacrylate) Macromonomer

Maintaining control of the polymerisation of methyl methacrylate (MMA), and the structure of the resulting polymer, can be very challenging when an anionic mechanism is used, due to the presence of side reactions.[1] These can be effectively suppressed by careful choice of initiator, reducing the temperature to -78 °C and including additives, resulting in a reaction which has the kinetics of a living polymerisation.[13] End functionalisation of the 'living' poly(methyl methacrylate) (PMMA) is still very challenging. Attempts to functionalise PMMA with EO quantitatively have met with failure recently, probably due to the low reactivity of PMMA-Li with EO at low temperatures.[14] The use of the initiator TBDMSO-PrLi to polymerise MMA results in the incorporation of a TBDMS ether protected hydroxyl group onto every chain, avoiding the need to functionalise the living chains. Work to demonstrate the potential of the protected initiator approach in the synthesis of PMMA macromonomers has been carried out.

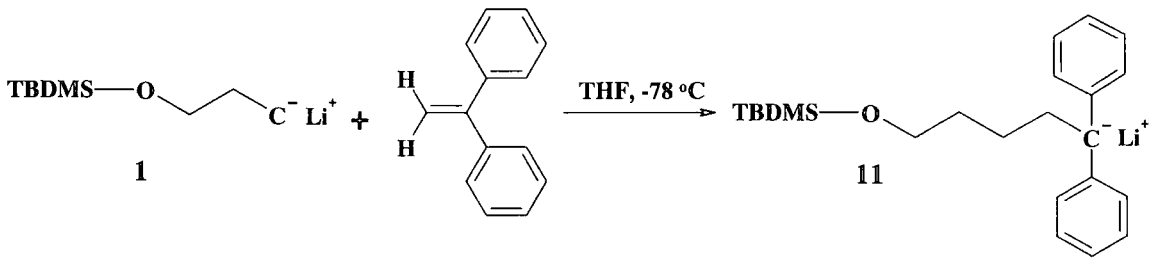
4.2.2.1 Synthesis and Characterisation of TBDMS Ether Protected PMMA

Methyl methacrylate, in common with other alkyl methacrylates, has two functional groups capable of reacting with carbanions, the vinyl and ester groups. The polymerisation is further complicated by the nucleophilicity of alkyllithium initiators, which in addition to producing the desired propagating species **9** (**Scheme 4.9**), results in attack on the carbonyl group of the monomer, resulting in the formation of ketone **10** and lithium methoxide (**Scheme 4.9**).



Scheme 4.9 - Expected reactions of the TBDMSO-PrLi initiator with MMA.

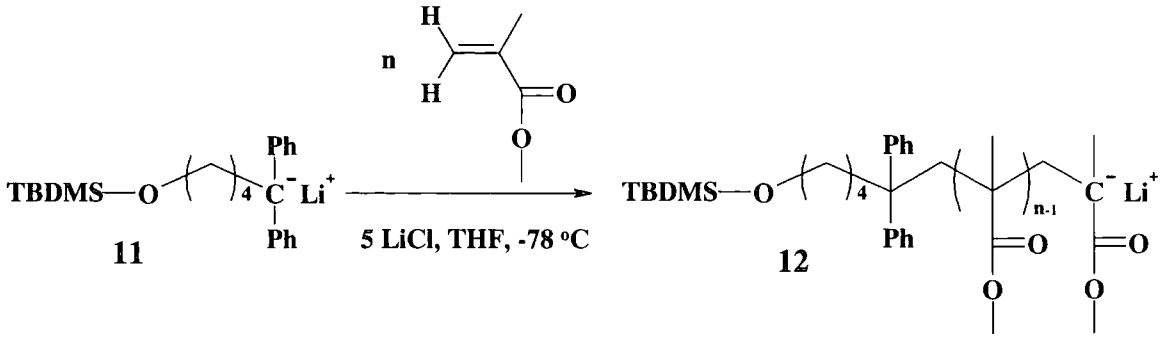
Whilst lithium methoxide, a byproduct of the formation of **10** can affect the kinetics of the propagation reaction, it is incapable of initiating polymerisation itself. The loss of initiator by this mechanism will therefore lead to a loss of control over the molecular weight. The new alkyl acrylate (**10**) can also be incorporated into the polymer chain. This could prove to be a highly undesirable complication in this work, as it would lead to the incorporation of more than one protected hydroxy group into the chain and potentially a material with two (or more) ROMP blocks incorporated into it. To prevent this side reaction, the nucleophilicity of the initiator is reduced by reacting it with 1,1-diphenylethylene (DPE), a non-homopolymerisable monomer, which results in the formation of a diphenylalkyllithium.[13] In the case of TBDMSO-PrLi the expected product is 1,1-diphenyl-5-(*t*-butyldimethylsilyloxy)-1-pentyllithium (DP*t*BPL, **11**, **Scheme 4.10**).



Scheme 4.10 – Reaction of TBDSMO-PrLi with DPE to form DP*t*BPL (11).

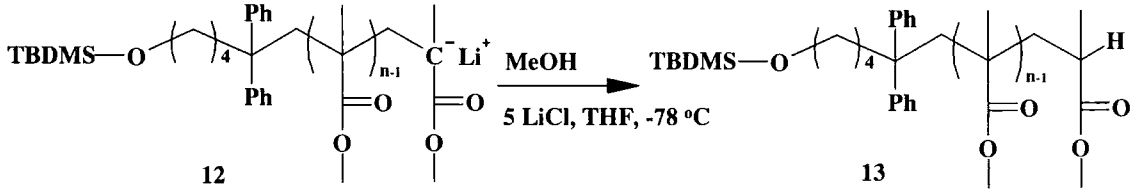
The reaction of the DPE with the TBDMSO-PrLi was allowed to proceed for 48 h, resulting in the conversion of the initial pale orange colour (due to the initiator) into a claret red solution. This colour change was taken to indicate the success of the reaction. The reduced nucleophilicity and steric hindrance around the carbanion of **11**, prevent reaction with the ester functionality and allows it to act as an efficient initiator of the polymerisation of MMA.

Termination of propagating polymer chains by their reaction with the ester groups of the monomer or polymer, was prevented by performing the polymerisation at a substantially reduced temperature (i.e. -78 °C) at which point the desired polymerisation reaction with the vinyl group is greatly preferred over addition to the ester group. The polymerisation reaction of methacrylates is very fast in THF; two propagating species, possibly dimeric or tetrameric aggregates, being present (Chapter 1). Unfortunately the rate of propagation of the two different species is significantly different leading to a PDI above 1.1. LiCl has been shown to control the rate of propagation by complexing to the propagating species, resulting in a decrease of the PDI of the resulting materials.[1] Five equivalents of LiCl were placed under vacuum in the polymerisation reactor prior to addition of the solvent and initiator. MMA was distilled into the polymerisation reactor resulting in the disappearance of the red colour of **11**, and the formation of an essentially colourless solution of living PMMA **12** (**Scheme 4.11**).



Scheme 4.11 - Polymerisation of MMA initiated by DP*t*BPL.

The polymerisation reaction was allowed to continue for 4 hours, which was expected to lead to complete consumption of the monomer. The reaction was then terminated with MeOH to yield PMMA **13** (**Scheme 4.12**).



Scheme 4.12 - Termination of the propagating species of 'living' PMMA.

Yield of polymer was consistent with complete consumption of monomer. The efficiency of purification by reprecipitation was reduced slightly by the physical properties of the PMMA, which precipitated out of solution as a fine powder, which whilst easy to collect by filtration had a tendency to stick to the sides of vessels.

The polymer was analysed by GPC which indicated it had the low PDI of 1.05 (**Figure 4.5**).

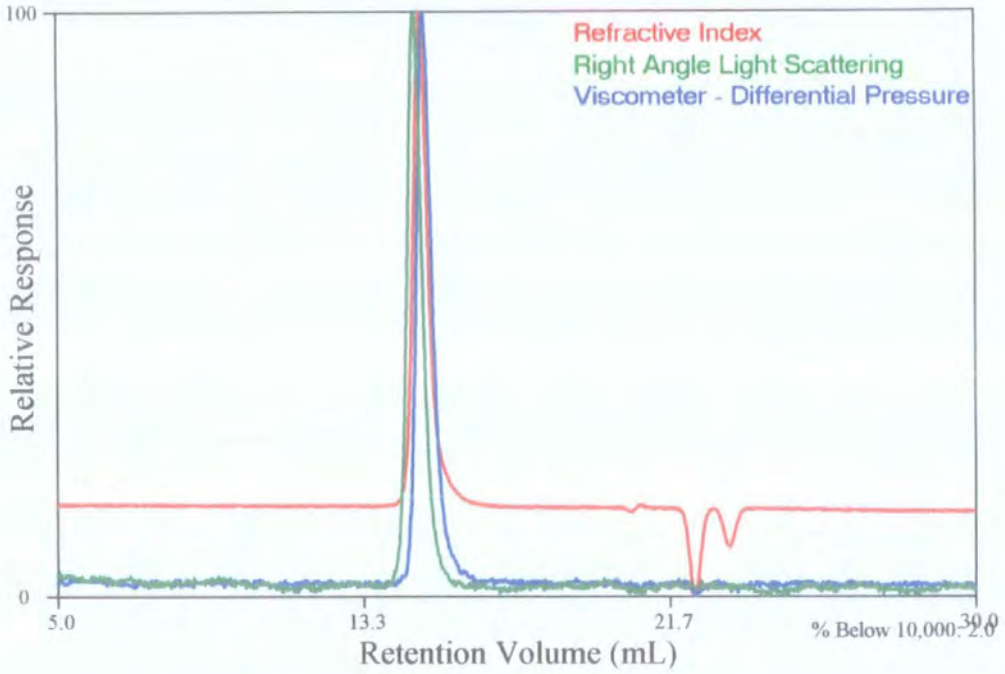


Figure 4.5 – The GPC Chromatogram of PMMA initiated by TBDMSO-PrLi.

This indicates that the propagation of the PMMA was well-controlled and is consistent with a living polymerisation. The value of M_n determined for the polymer, was just over three times that of the target of 5000. This implies that initiation was not efficient leading to a loss of control over the molecular weight. The reasons for and implications of this loss of control will be discussed later.

The PMMA was also studied by NMR spectroscopy. The ^{1}H NMR (**Figure 4.6**) and ^{13}C NMR (**Appendix 4.2.1**) spectra of the PMMA backbone were assigned using existing assignments.[15-17]

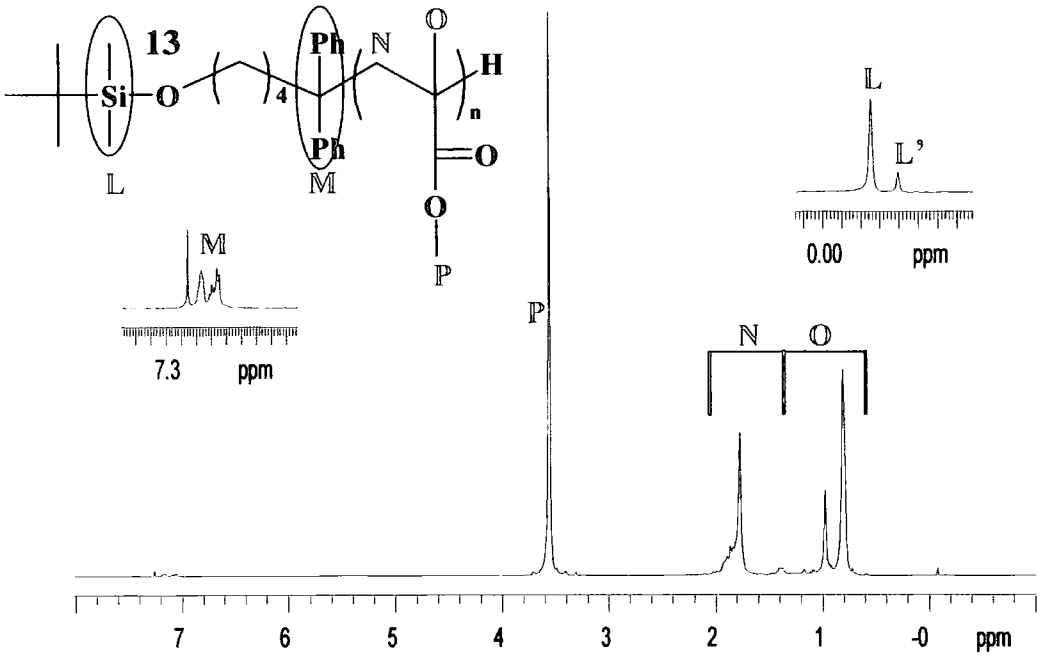


Figure 4.6 - ^{1}H NMR spectrum of PMMA initiated using TBDMSO-PrLi and DPE.

Comparison of the methylene (ℕ) protons with existing assignments indicates that the sample is predominantly syndiotactic.[15,17] The symmetry in syndiotactic units leads to the protons that would otherwise be non-equivalent, becoming equivalent and appearing as something close to a singlet. It is the most common configuration for PMMA obtained from most polymerisation mechanisms. There are a few exceptions some of which include certain anionic initiators like alkyllithium compounds and Grignard reagents in toluene, which produce highly isotactic PMMA.[15,18] Many of the expected resonances are obscured by the polymer chain, for example that of the *tert*-butyl group of the TBDMS protecting group and the ether group attached to the dimethylsilyl group. It will be noted that two peaks are observed in the silyl region, that at -0.06 to -0.12 ppm (𝕃) is 85% of the total integral of the region, whilst that at -0.15 to -0.18 ppm (𝕃') is the remaining 15%. If the two methyl silyl groups were not magnetically equivalent (due to the presence of a chiral centre for example) we would expect to see two peaks of equal intensity. The different size of the peaks observed means, this cannot explain the data. The full silyl region (i.e. peaks 𝕃 and 𝕃', expected to be 6H) was used to obtain a figure for M_n of the

polymer by comparison with the methoxy peak (ℙ, 3H per repeat unit). The resulting value of M_n - 19200 g mol^{-1} is very close to the 18500 g mol^{-1} determined by GPC. Comparing the methoxy peak with only 𝕃 or 𝕃' leads to a higher estimate for M_n. The similarity in the values of M_n calculated using the sum of 𝕃 and 𝕃' with the figure from GPC, suggests that both signals represent moieties that are incorporated into species that initiated polymerisation. The two are tentatively assigned as **13** initiated by the diphenylakyllithium formed by reaction of the TBDMSO-PrLi (**1**) with DPE (DP*t*BPL, 𝕃) and **14** initiated directly by unreacted **1** (**Scheme 4.9**) (𝕃') (**Figure 4.7**).

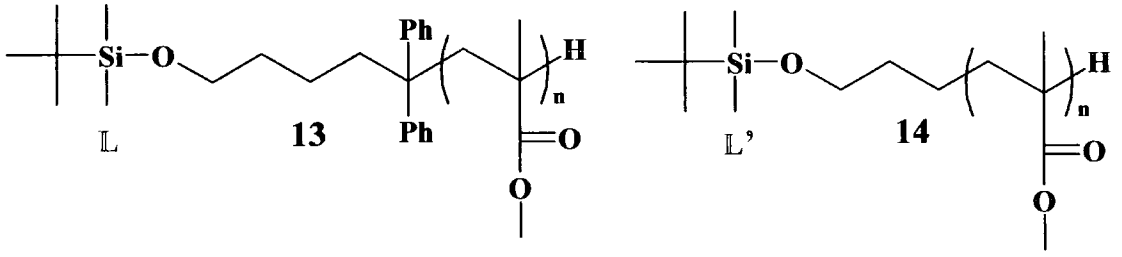


Figure 4.7 - The two proposed polymeric species from the polymerisation of MMA using TBDMSO-PrLi and DPE.

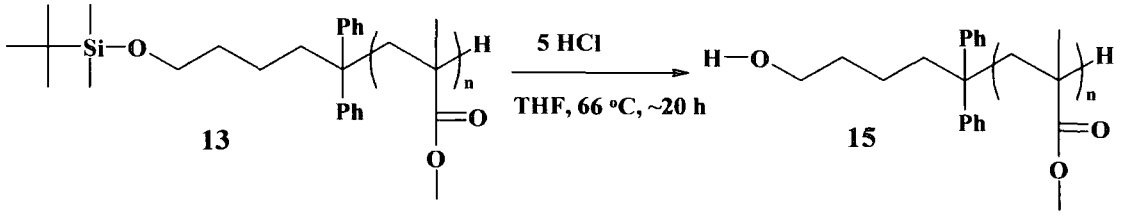
The reaction of **1** with DPE was expected to be fast, however preliminary results suggested it to be relatively slow, based on the much higher molecular weight obtained relative to that predicted by the stoichiometry. The reaction time was therefore extended to 48 h, but the lack of control over molecular weight observed suggests that efficient formation of diphenylalkyllithium initiator still did not occur. It might be possible to explain some of the loss of activity by reaction of the alkyllithium species with THF as might be expected after extended periods of time of contact between the two.[19] Subsequent results have shown however that the molecular weight can be reduced further towards that predicted by the ratio of initiator to monomer by allowing **1** and DPE to react for a further 24 h.[20] No data yet exists to confirm whether even longer reaction times of the DPE and TBDMSO-PrLi bring the M_n closer still to the predicted value. That result however suggests that un-reacted **1** was present at the end of the reaction with DPE. Residual **1** thus initiated polymerisation yielding **14**, when MMA was distilled in. The high reactivity of the TBDMSO-PrLi is also likely to lead to reaction with carbonyl group resulting in the formation of a new unsaturated species (**10**, **Scheme 4.9**) containing the protected functionality and lithium methoxide as discussed previously.

Assuming the assignment of L and L' in **Figure 4.7** are correct no evidence of incorporation of this material was observed by NMR spectroscopy, although the presence of trace amounts cannot be ruled out. This may be due to the reduced reactivity of this species with the propagating species. The ^{13}C NMR shifts of the TBDMS group of **13** (**Appendix 4.2.1**) were assigned by the aid of those of TBDMS functionalised PS **3** (Section 4.2.1). In addition to a trace of THF the spectrum contains a small peak at 22.54 ppm assigned to the three methyl groups of the *tert*-butyl group of **14**. No other shifts that are unique to **14** are observed, probably due to their very low concentration.

As both of the polymeric species depicted in **Figure 4.7** contain a single TBDMS protected hydroxyl group, it is believed that all the polymer chains were quantitatively functionalised with the desired moiety.

4.2.2.2 Deprotection of TBDMS Ether Protected PMMA

Deprotection of the PMMA is expected to leave the PMMA chains with a single hydroxyl group on every chain. The reaction was carried out using HCl (**Scheme 4.13**) in a very similar manner to that used to cleave the TBDMS group from the PS.



Scheme 4.13 - Deprotection of TBDMS ether functionalised PMMA.

The reaction was followed by ^{1}H NMR spectroscopy. No signs of the dimethylsilyl groups from the TBDMS groups (observed at -0.06 to -0.12 and -0.15 to -0.18 ppm) are present in the NMR spectrum of the final product (inset, **Figure 4.8**).

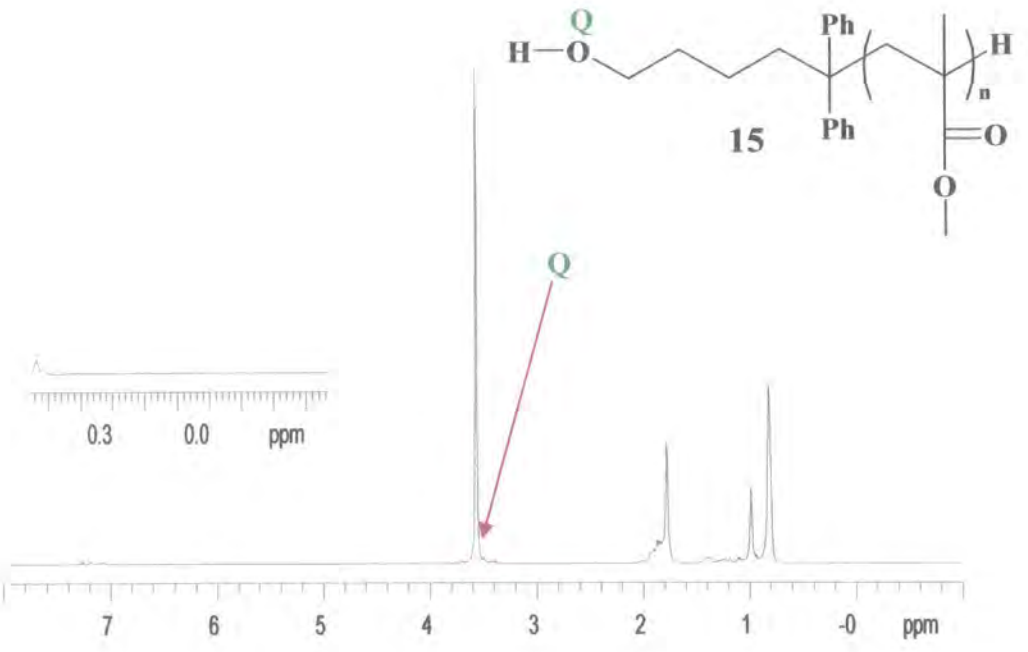


Figure 4.8 - ^{1}H NMR spectrum of deprotected PMMA ($CDCl_3$).

The hydroxy group (Q) of the deprotected PMMA is expected where the methoxy groups of the PMMA fall. It is however directly observable by ^{13}C NMR spectroscopy at 62.3 ppm (**Appendix 4.2.2**). Deprotection of the hydroxyl group was not observed to result in any change of the ^{1}H or ^{13}C NMR resonances of the polymer backbone. GPC proved that the sample retained a monomodal trace with a narrow polydispersity (**Appendix 4.2.3**). The deprotection was thus completed successfully yielding PMMA quantitatively functionalised with a hydroxyl group. Whilst **Scheme 4.13** depicts the deprotection of **13**, the absence of TBDMS in the final product indicates the deprotection of **14** (**Figure 4.7**) was also completely successful, forming **16** (**Figure 4.9**).

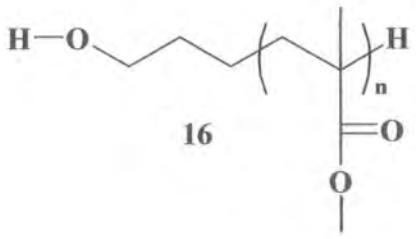
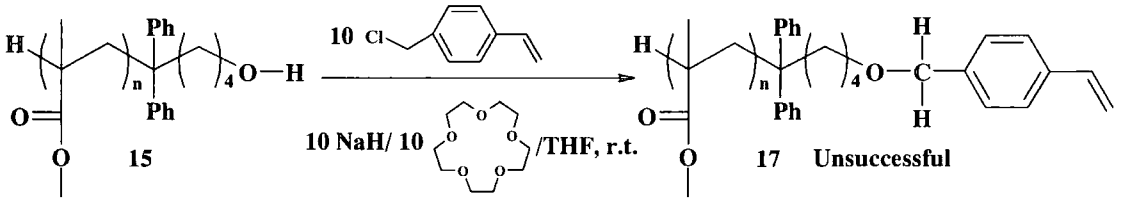


Figure 4.9 – Deprotected TBDMSO-Pr-PMMA.

Based on evidence from NMR spectroscopy (discussed in Section 4.2.2.1) the species depicted in **Figure 4.9** is expected to comprise approximately 15% of the sample.

4.2.2.3 Attempts to Synthesise PMMA Macromonomers from Deprotected TBDMS Ether Protected PMMA

The *tert*-butyldimethylsilyl ether functionalised PMMA was synthesised and deprotected in the hope that it could be functionalised with 4-VBC to form macromonomers via a Williamson ether synthesis. Attempts to convert it into a macromonomer were carried out in parallel with that which successfully converted hydroxy functionalised PS into a macromonomer (Section 4.2.1.3). It was envisioned that the pendant ester groups might be susceptible to attack by a strong base. It was hoped that NaH might prove to be suitable for the synthesis of macromonomer **17** from PS-OH **15** (**Scheme 4.14**), in the absence of any significant deterioration of the polymer.



Scheme 4.14- Attempted synthesis of PMMA macromonomers from PS-OH using NaH.

These reaction conditions were successful in converting PS with a hydroxyethyl group into macromonomers in Chapter 3. The PMMA (**15** in **Scheme 4.14** and **16** in **Figure 4.9**) synthesised in this work possesses hydroxybutyl groups. It was not possible to prepare macromonomers from the PMMA, but the results illustrate that side-reactions during the Williamson coupling can present an obstacle to the synthesis of macromonomers using the methodology as it currently stands.

A trial Williamson coupling was carried out on a small scale using large excesses of NaH, 15-crown-5 and 4-VBC (300 equivalents of each). The resulting polymer was studied by ^{1}H NMR spectroscopy (**Figure 4.10**).

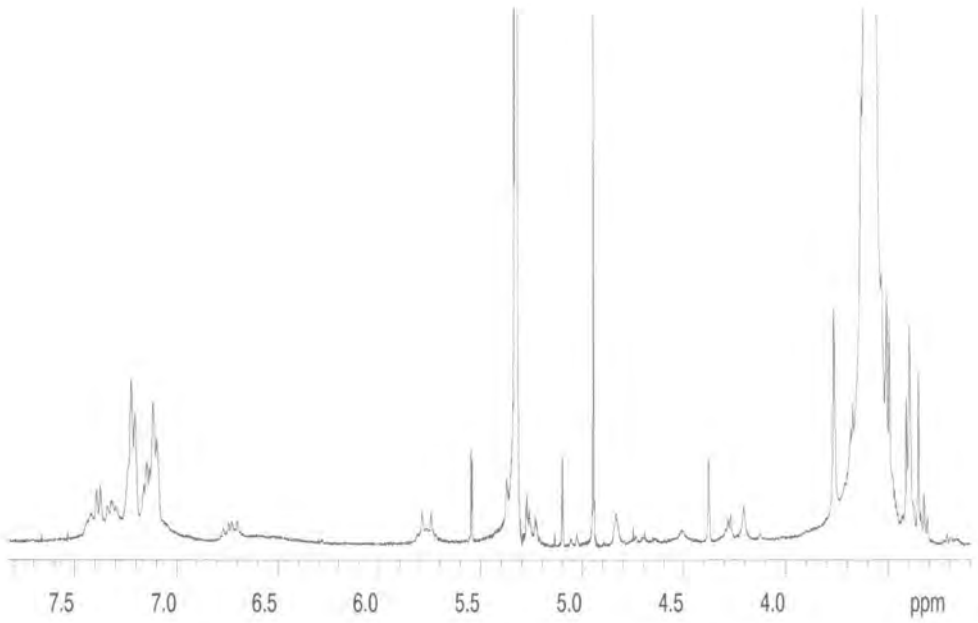


Figure 4.10 - ^{1}H NMR of a trial attempt to synthesise PMMA macromonomers.

This indicated some incorporation of vinyl material into the polymer had occurred, although a variety of unidentified extraneous peaks were present. The shape of the vinyl peaks suggests that they are in two or more different environments – possibly indicating they have been incorporated into the ester groups. A GPC chromatogram (**Appendix 4.2.4**) showed a polymeric species present at a lower elution time than the bulk of the sample, presumably due to deterioration of the PMMA. The polymeric species detected by GPC will be discussed in more detail later.

In the hope that the large excess of NaH was responsible for the apparent deterioration of the polymer chain, the experiment was repeated on a larger scale using far more moderate excesses of the reagents (Section 4.4.3.3). ^{1}H NMR spectroscopy revealed the presence of weak signals where the vinyl groups of the macromonomer are expected (**R**, **Figure 4.11**).

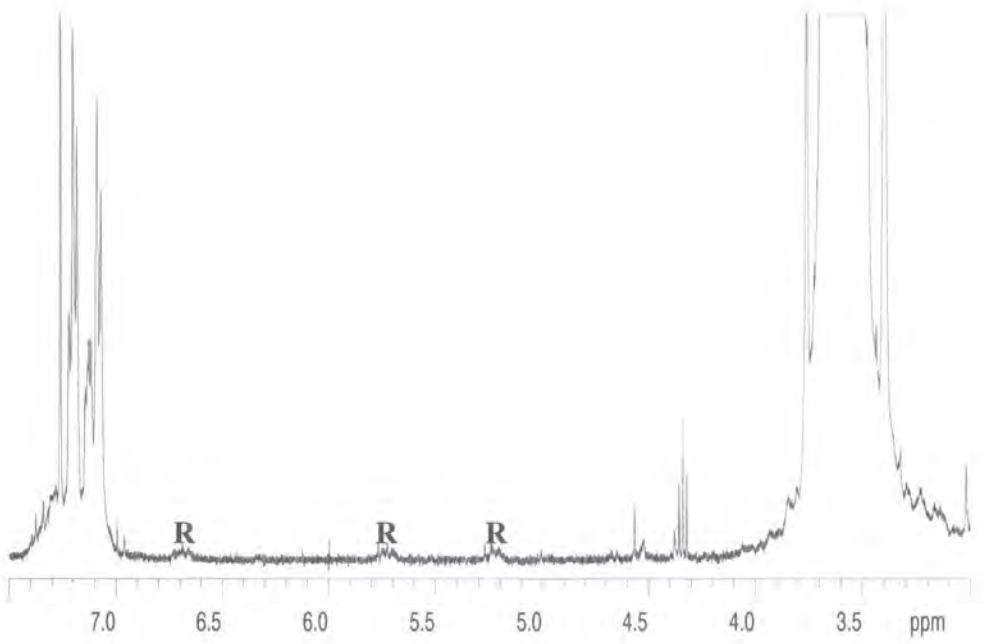


Figure 4.11 - ^{1}H NMR spectrum of the product of the attempted synthesis of PMMA macromonomers ($CDCl_3$).

The signals are far too broad to be un-reacted 4-VBC and were not altered by reprecipitation. It is possible therefore that these peaks are from the correct macromonomer. Their intensity is inconsistent with complete functionalisation. The sample was studied by ^{13}C NMR spectroscopy (**Appendix 4.2.5**). The hydroxy group of the deprotected PS **15** (observed at 62.3 ppm) is observed to remain unchanged. The ^{13}C NMR shift of this carbon and its equivalent in the TBDMS ether group on PMMA **13** (Section 4.2.2.1), were observed to be very similar to those of the corresponding PS polymers. Based on this analogy we would expect the signals from the ether carbons in the PMMA macromonomer to be observed at approximately 70 ppm, unfortunately no signals are observed in this area. This means that the concentration of ether groups was insufficient in the sample for them to be detected by ^{13}C NMR spectroscopy. This confirms that the level of conversion of PS-OH to macromonomer was very low.

Study of the polymer by GPC (**Figure 4.12**) produced a very similar trace to that from the previous small scale reaction.

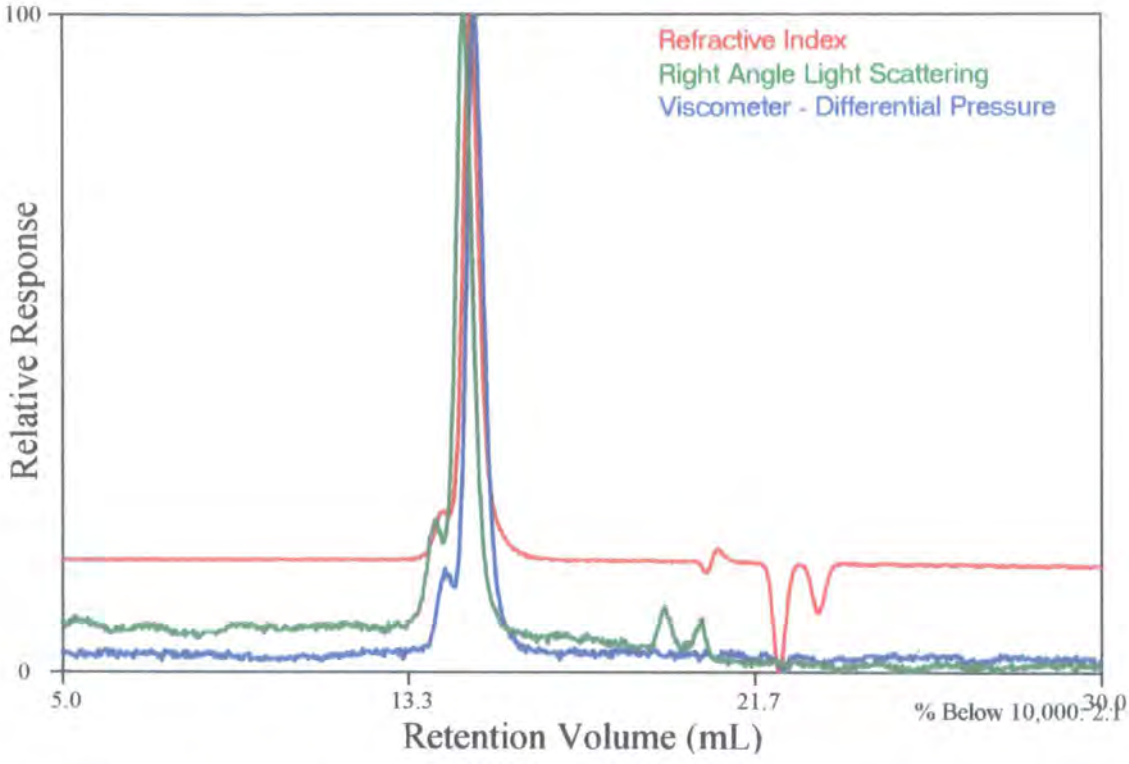


Figure 4.12 –THF GPC of the product of an attempt to synthesise PMMA macromonomers using NaH and 15-crown-5.

GPC cannot differentiate between the bulk of the polymer and hydroxyl functionalised PMMA. A new peak at lower elution time is observed which probably corresponds with a species which possesses double the molecular weight of the majority of the sample. It is believed that NaH induced polymer-polymer coupling. The exact mechanism is unknown but might involve reduction of the carbonyl group to form an oxoanion, which might then attack an ester group on the polymer chain. No changes could be definitely identified in the NMR spectrum of the polymer backbone. This is not particularly surprising, when we consider that the majority of the polymer chains remain uncoupled and that in the case of those that have coupled only a single ester group, out of the approximately 185 ester units on average on each polymer chain (based on M_n by THF GPC), need be involved.

The use of K metal was considered, but its greater potency as a reducing agent was thought to be likely to lead to an even greater degree of coupling than that observed

using NaH. It was not attempted in case this should result in a hazardous exothermic reaction. Diphenylmethylpotassium (DPMK) used as an initiator for the polymerisation of EO in Chapter 2, was investigated as a reducing agent for the hydroxyl group. It can be used to potassiate the hydroxyethyl groups introduced by functionalisation of living polymers with EO in order to synthesise block copolymers with a poly(ethylene oxide) block by two different anionic mechanisms.[14] The steric hindrance around the carbanion in DPMK, led to the suggestion that it might react with the alcohol without attacking the ester. The small concentration of chain ends in the polymer, of M_n = 18500, makes the use of a stoichiometric amount of DPMK very difficult. Trace amounts of impurities would be expected to result in the loss of a significant amount of chain ends and the formation of unfunctionalised material. A substantial excess was used to ensure destruction of impurities and hopefully produce the desired potassium alkoxide. Excess DPMK would be expected to initiate polymerisation of the macromonomer and 4-VBC. An excess of 4-VBC (1.2 equivalents) relative to the total amount of DPMK was used in the hope that functionalisation of both species would be faster than their polymerisation.

Analysis of the polymer by THF GPC (**Appendix 4.2.6**) produced a trace with a similar shape to that from the experiments using NaH. The polymer was also analysed by ^{1}H NMR spectroscopy (**Figure 4.13**).

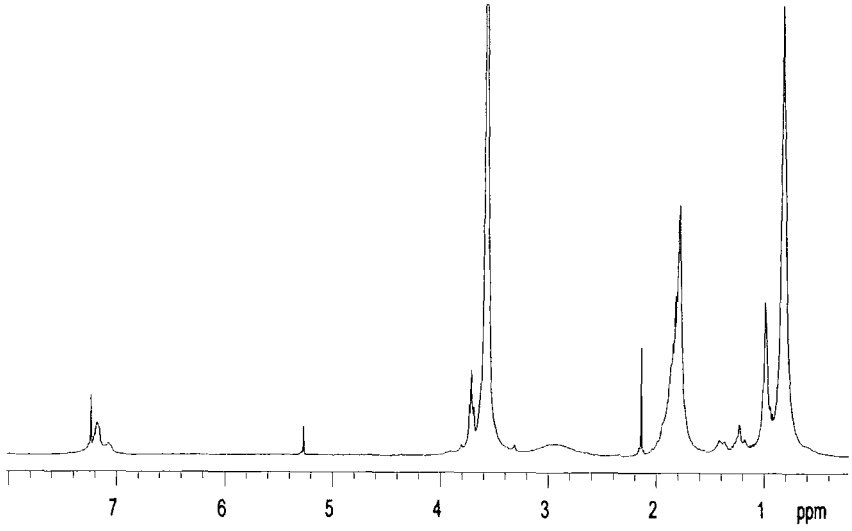


Figure 4.13 - ^{1}H NMR spectrum of the product of reaction of DPMK and PMMA.

No evidence of styrenic peaks from the vinylbenzyl functionality is evident. The aryl region (7.5-7.0 ppm) has clearly changed and grown in intensity. This might be explained by the attack on the carbonyl carbon resulting in the formation of a bond between it and the DPMK, accompanied by elimination of potassium methoxide, in analogy to the reactions expected with butyllithium (Section 4.2.2.1). Comparison of the ^{1}H NMR spectrum of this product (**Figure 4.13**) with that of PMMA-OH prior to reaction with DPMK (**Figure 4.8**), suggests the presence of a new broad peak at around 3.0 ppm. This shift is similar to that of the main methoxy peak of the polymer backbone, which would not be expected if the only reaction that had occurred was incorporation of a diphenylmethyl group and elimination of methoxide.

It was not possible to detect any difference in the reactivity of the two proposed PMMA-OH species **15** and **16**. As it is not possible to differentiate between the two by NMR and that conversion of the hydroxy group into macromonomer was not quantitative, a difference in the ease with which they can be deprotonated might exist. Such a difference would be expected to be small, possibly insignificantly so. The ultimate reason for the failure of this approach to the synthesis of PMMA macromonomers and hence PMMA-PNB block copolymers, is the inability to bring about the desired Williamson coupling to synthesise the macromonomer without side reactions. A possible solution is to modify the methodology to incorporate a more acidic group such as an aryl alcohol onto the polymer chain, which should allow the use of mild bases such as potassium carbonate to perform the coupling. A possible method for doing this will be discussed in Chapter 5.

4.2.3 Attempted Synthesis of Poly(Propylene Sulfide) Macromonomers

Ethylene sulfide (commonly referred to as thiirane) and propylene sulfide (methylthiirane) can be polymerised using either anionic or cationic ring opening polymerisation. Poly(ethylene sulfide) (PES) is insoluble in most solvents, although it has been noted to be soluble in DMSO at 170 °C and nitrobenzene and *o*-dichlorobenzene at 180 °C.[21] These conditions are not suitable for carrying out the synthesis of the macromonomer, or any of the further steps necessary to carry out the synthesis of PES-PNB block copolymers. By contrast poly(propylene sulfide) (PPS) initiated by anionic

polymerisation is usually atactic and an elastomer at r.t.[21] The conversion of such a material into a PPS-PNB block copolymer would also present the technical challenge of working with an elastomeric material.

In contrast to the polymerisation of propylene oxide, which is accompanied by chain transfer to the methyl group, propylene sulfide (abbreviated as PrS to avoid confusion with polystyrene) initiated by alkyllithium compounds possess living kinetics.[21,22] The ability of the thioanions, the propagating species in the polymerisation, to undergo quantitative functionalisation has received little assessment. The thioanions appear to be more tolerant to impurities than those of carbanion based polymerisations in general and appear to be insufficiently nucleophilic to initiate the polymerisation of vinyl monomers like styrene,[21] in keeping with the reactivity of alkylthiolatelithium initiators.[23] The living chain ends are however capable of reacting with elemental sulfur to form copolymers, and would be expected to quantitatively consume any sulfur present in the system resulting in the formation of sulfur-sulfur bonds.[24] Unfortunately the polymer was not quantitatively functionalised with the TBDMS group; the synthesis of PPS is discussed as it demonstrates another potential problem in the synthesis of macromonomers for conversion to macroinitiators for ROMP, using the protected initiator strategy.

4.2.3.1 Polymerisation and Characterisation of PPS using the TBDMS Ether Protected Initiator

Purification of the commercially available PrS monomer is more challenging than is usual. ^{1}H NMR spectra of the monomer indicated the presence of signals between 7 and 5 ppm, probably due to unsaturated compounds from PrS' thermodynamic decomposition.[25,26] Some of this material remained after fractional distillation, it was hoped it might be eliminated by the multiple distillations necessary to dry the material. Whilst it is possible that this material might have resulted in the loss of some initiator, it is not known to have had any other effect on the polymerisation. In common with many anionic ring opening polymerisations (AROP), the propagating species does not appear to be as reactive towards unsaturated compounds as that of vinyl polymers. Anionic polymerisation of PrS is initiated by a variety of bases and cationic polymerisation by

acidic materials, which includes many metal compounds. This introduces complications in the drying of PrS; CaH_2 has been previously reported to be an initiator for PrS[23] and was observed to initiate polymerisation here. Molecular sieves (Aldrich, 4Å) also initiated polymerisation, possibly due to the metal compounds in the sieve structure. $CaCl_2$ and $MgSO_4$ were not observed to cause polymerisation. In the final purification procedure the monomer was first thoroughly degassed over an excess of $MgSO_4$ in an ampoule without a septum. The PrS was thus distilled off the $MgSO_4$ onto CaH_2 in an ampoule with a septum (to allow escape of pressure and termination of uncontrolled polymerisation should it have occurred) and dried at 0 °C for 2 hours. It was then degassed once more to remove evolved H_2 and distilled into an ampoule in which it was weighed. It was immediately distilled into the polymerisation reactor and used.

The first step in the polymerisation of PrS by alkyllithium compounds such as **1** is the abstraction of sulfur from a molecule of PrS by the alkyllithium to form a lithium-thiolate species, TBDMSO-PrSLi (**18**, **Figure 4.14**) in this case.[27]

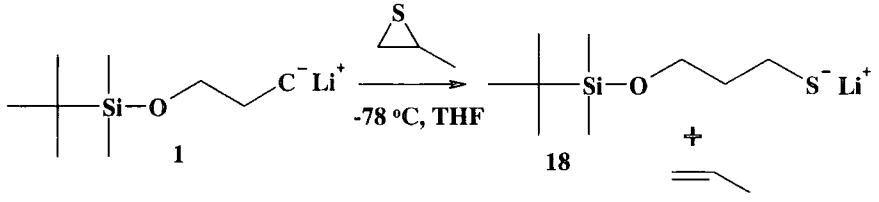


Figure 4.14 Abstraction of sulfur from PrS by TBDMSO-PrLi to form TBDMSO-PrSLi.

The reaction was carried out at -78 °C, at this temperature propagation is negligible.[23] The propene plays no known further role in the polymerisation. Crucially the alkyl group from the alkyllithium (**1**) is incorporated into the lithium-thiolate (**18**) which serves as the actual initiator of polymerisation, yielding **19** (**Figure 4.15**).

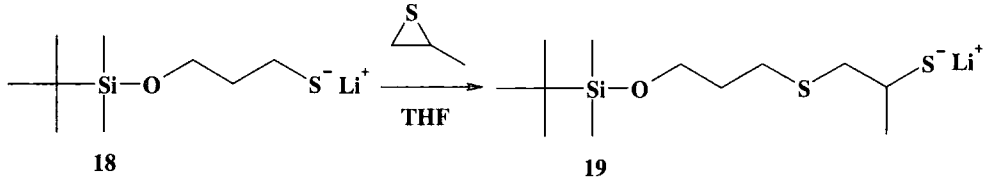


Figure 4.15 -Initiation of PrS by TBDMSO-PrSLi.

All polymer chains initiated by TBDMSO-PrSLi thus have the desired TBDMS functionality. The propagation reaction was allowed to proceed by warming the

polymerisation reactor to room temperature. The propagating step of the polymerisation is via a ring opening mechanism of PrS in THF solvent (**Figure 4.16**).

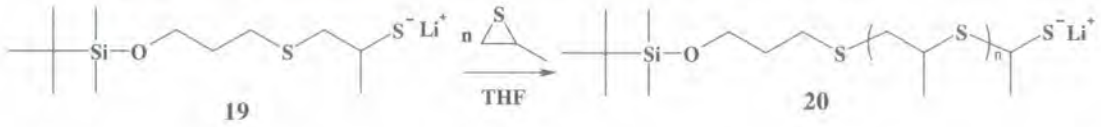


Figure 4.16 - Propagating step in the polymerisation of PrS.

Propagation was allowed to proceed for 20 hours. The resulting living polymer **20** were terminated with CH_3I, chosen in part because it should result in the synthesis of methyl functionalised PPS **21**, rather than the thiol functionalised PPS expected from termination with MeOH (**Figure 4.17**).

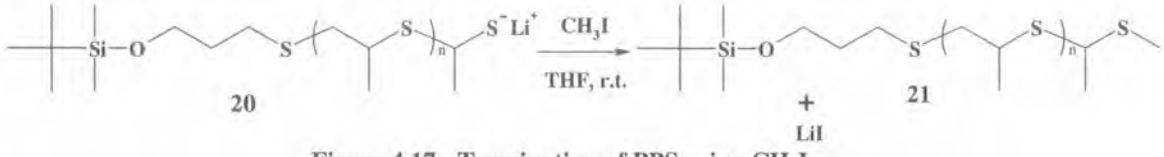


Figure 4.17 - Termination of PPS using CH_3I.

The presence of a thiol group on the end of poly(propylene sulfide) has been reported to lower the stability of the resulting PPS, introducing an alkyl group gives the resulting polymer better stability.[22] The elastomeric nature of the PPS hindered purification slightly. Efficient reprecipitation of the polymer was however possible by adding a solution of PPS in CH_2Cl_2 to hexane, both chilled to -78 °C. The polymer precipitated as a white powder, which could be efficiently recovered by vacuum filtration using chilled filtration apparatus. Crude PPS was observed to possess the properties of a highly viscous liquid and could be transferred between vessels using a Pasteur pipette. Successive purifications led to an increase in viscosity to an almost clear and colourless elastomeric material that could be easily manipulated by a spatula. The PPS flowed slowly in glassware at r.t, but took the form of a fairly hard solid when stored in a freezer at -40°C. Resulting yields of the PPS polymerisations were consistent with quantitative conversion of monomer to polymer.

PPS is highly prone to oxidation at elevated (approaching 200 °C) temperatures, although it has better stability at r.t.[22] It is generally agreed that the polymer is stable at low temperatures, particularly in the dark. The PPS was therefore stored in the dark at approximately -40 °C. PPS can also be stored under vacuum for extended periods of time.

No evidence of an increase in PDI measured by GPC was detected from samples taken during the purification of PPS.

The PPS was studied by ^{1}H NMR and ^{13}C NMR (**Appendix 4.3**) spectroscopy. What might first appear to be two separate peaks at 2.9 and 2.6 ppm in the ^{1}H NMR spectrum (**Figure 4.18**) of the polymer are in fact a combination of the methine (V), and methylene (U) peaks [confirmed by Heteronuclear Single Quantum Correlation (HSQC) and Heteronuclear Multiple Bond Correlation (HMBC)].

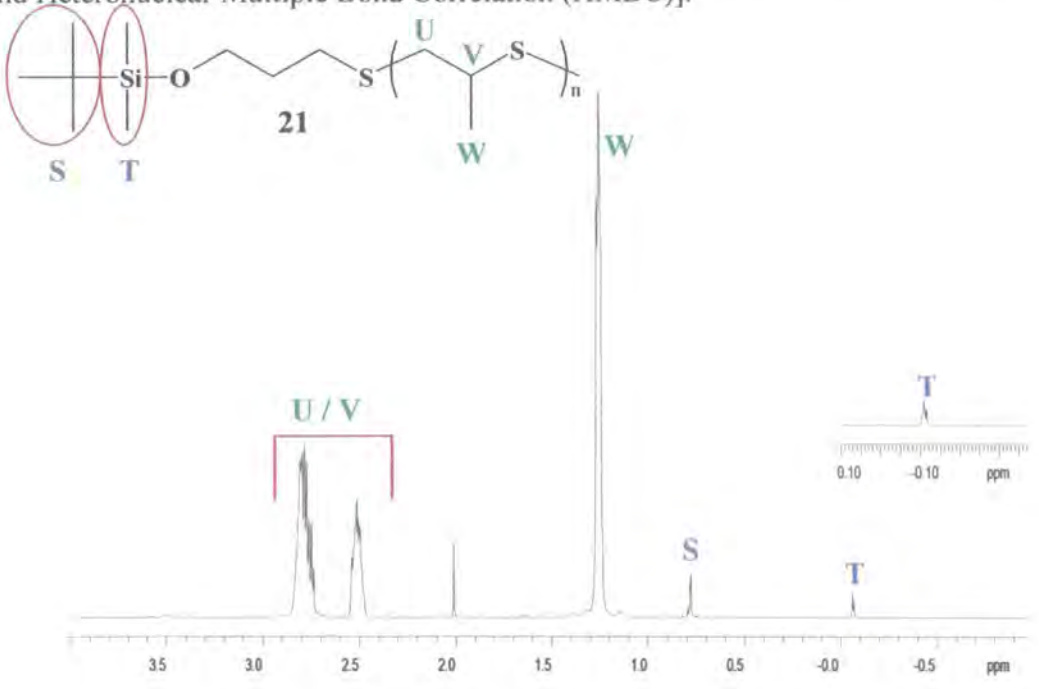


Figure 4.18 - ^{1}H NMR spectrum of poly(propylene sulfide).

Studies by Ivin and others have demonstrated that the methylene (U) protons are non-equivalent and are observed as two multiplets, one of which coincides with the principal CH (V) peak.[28,29] The similarity of the ^{1}H NMR spectrum (**Figure 4.18**) to that of PPS initiated by Na metal suggests the polymer is atactic, with approximately equal numbers of isotactic and syndiotactic units.[29] The dimethylsilyl and *tert*-butyl protecting group (S and T) is observed as expected, although it is split to a slightly greater degree that those from the TBDMS groups located on PS and PMMA. It is possible that this splitting is due to the presence of two slightly different TBDMS groups on the polymer, one introduced by initiation of PPS by the lithium-thiolate product of the alkyllithium

(TBDMSO-PrSLi) and one from an alkoxide as will be discussed later. It was expected that as with PS and PMMA synthesised using the TBDMSO-PrLi initiator it would be possible to obtain a value for M_n by comparing the integral of the TBDMS group with that of the polymer backbone using ^{1}H NMR spectroscopy. This was achieved by comparing the dimethylsilyl group T with the methyl group W (**Figure 4.18**) or the total integral from U and V. In both cases a value of 11500 g mol^{-1} was obtained. Figures for M_n obtained by comparing the same PPS groups with the *tert*-butyl protons S were close to 10000 g mol^{-1}. These estimates for M_n are substantially different from that of 2500 g mol^{-1} predicted by the stoichiometry. It was first thought this was due to a loss of control over M_n caused by the loss of initiator to impurities or poor initiator efficiency, subsequent results from GPC and MALDI suggested the situation was more complicated.

It was possible to measure a value for the [d*n*/d*c*] of the polymer using a solution of known concentration (Section 4.4.1.2). GPC produced a value of 5370 g mol^{-1} for M_n, significantly lower than that from NMR. It indicated the polydispersity of the overall sample was relatively low - 1.18 (**Figure 4.19**).

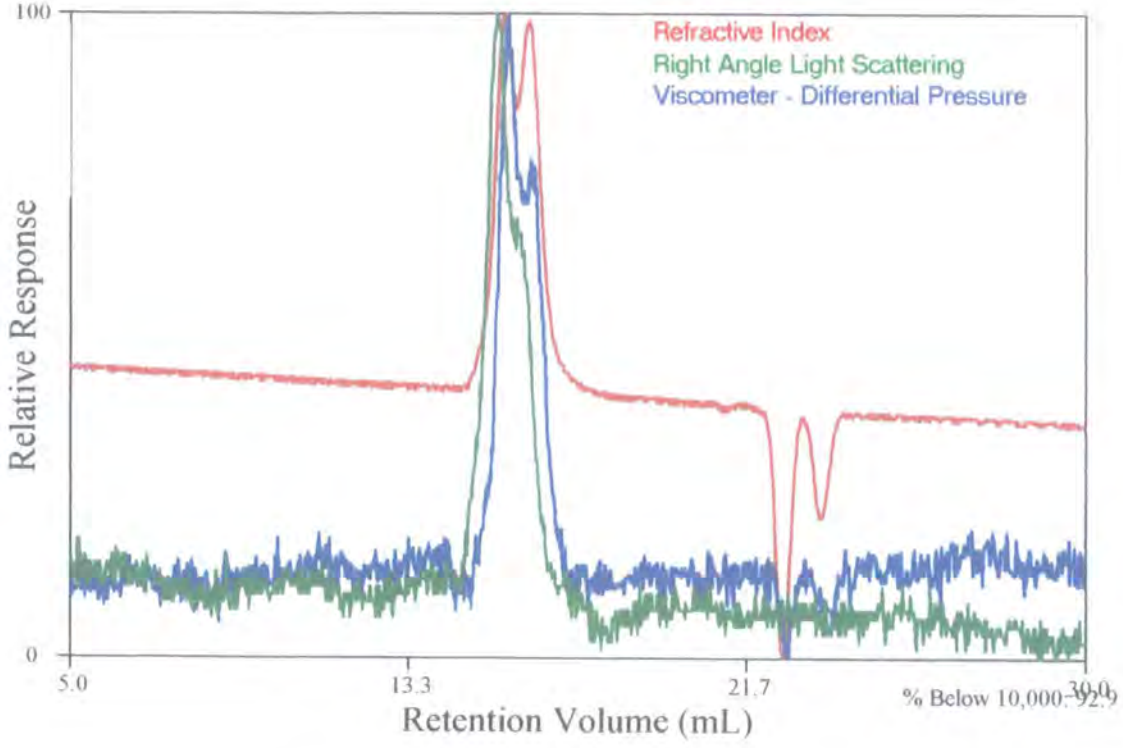


Figure 4.19 - GPC trace of poly(propylene sulfide).

The trace is bimodal, which could be explained by the occurrence of two or more initiation reactions, caused by the presence of more than one initiating species. If the initiating species did not possess the TBDMS ether group, it would subsequently not be incorporated into the polymer chain. This would result in any estimates of M_n by NMR, which were based on the TBDMS group, being too high. TBDMSO-PrLi as received from the commercial supplier was not contained in an appropriate vessel. During transfer of this material to a more suitable container some initiator was deactivated through reaction with H_2O and O_2 from the air. The expected reactions are detailed below (**Figure 4.20**).[19,30]

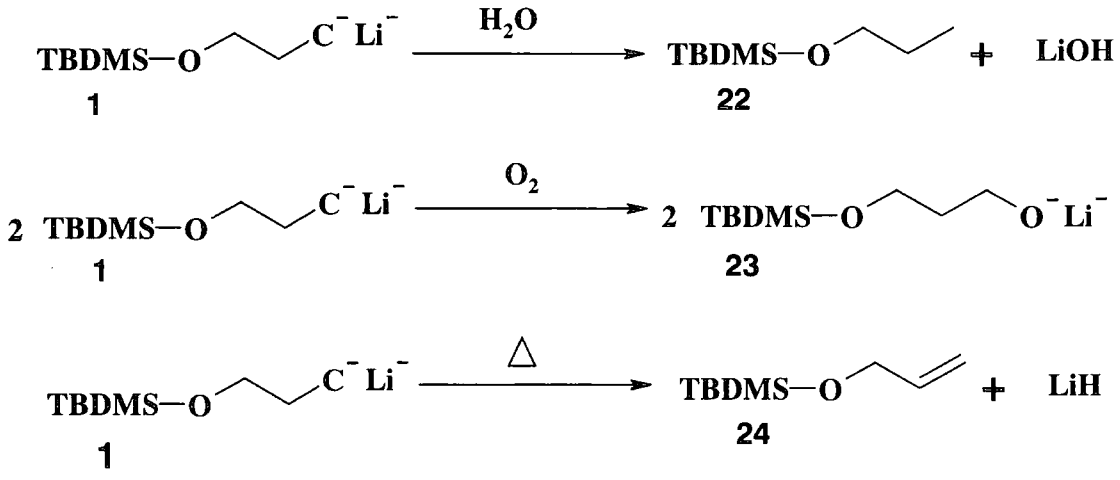


Figure 4.20 - Expected decomposition reactions of the TBDMSO-PrLi initiator.

The presence of the alkoxide is also expected to catalyse the thermodynamic decomposition of the initiator which produces LiH.[1] The species depicted in **Figure 4.20** are frequently ignored for the purposes of anionic polymerisation as they are incapable of initiating the polymerisation of vinyl monomers, although they can have some effect on the kinetics of the polymerisations.[1] Anionic polymerisation of PrS can however be initiated by a much larger range of nucleophiles including metal hydroxides, alkoxides and hydrides.[21,22] The possibility that LiOH was initiating polymerisation was examined first. Polymerisation of PrS can be readily initiated by KOH and to some degree by NaOH,[21,22] but a search of the literature did not result in the discovery of a report into the behaviour of LiOH. A small amount of LiOH was sealed in a vial with neat PrS under N_2. For comparison a pellet of KOH was added to a vial containing PrS under the same

conditions. Within 24 hours the KOH had converted the PrS to a viscous yellow polymer, whose ^{1}H NMR spectrum was very similar to that of the PPS produced using TBDMSO-PrLi (**Figure 4.18**). However no sign of change was observed in the vial containing LiOH and ^{1}H NMR spectroscopy confirmed no polymerisation or other reaction had taken place. This tends to suggest that polymerisation of PrS is certainly not as readily initiated by LiOH as it is by KOH.

Initiation by alkoxylithium species is apparently possible,[1] so TBDMSO-PrOLi (**23**) could serve as an initiator for the polymerisation of PrS. Initiation by this species will result in an increase in PDI if the rate of initiation differs significantly to that of TBDMSO-PrSLi (**18**, **Figure 4.15**). Initiation by this alkoxide would however result in the incorporation of a TBDMS ether group into every chain, and these chains would thus be available for deprotection and conversion to macromonomer. Initiation of the polymer by TBDMSO-PrOLi would therefore not be expected to affect the estimate of M_n by ^{1}H NMR.

A comprehensive study of which metal hydrides initiate the polymerisation of PrS and whether the hydride ion initiates polymerisation directly or somehow abstracts sulfur to form an initiating species does not seem to have been undertaken. The polymerisation of PrS by CaH_2, frequently used as a drying agent, is well-known and was observed to result in the polymerisation of the majority of PrS left in an ampoule overnight at r.t. It would also be expected that the more nucleophilic alkyl metal hydrides would initiate polymerisation, though no study seems to have been carried out. We might therefore expect the polymerisation of PrS to be initiated by LiH. The resulting polymer will not have the TBDMS ether functionality or any other group available for conversion to macromonomer. Initiation of PrS by LiH would lead to the calculation of erroneous values of M_n using the NMR data.

The polymer was also analysed by MALDI mass spectroscopy (**Figure 4.21**).

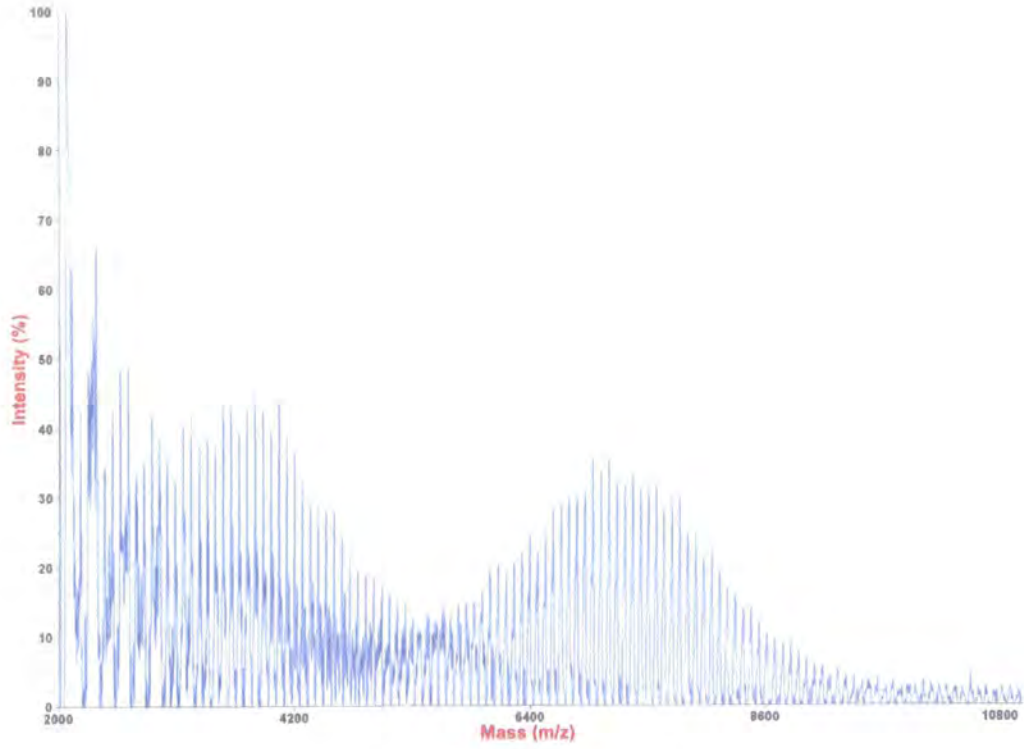


Figure 4.21 - MALDI spectrum of PPS.

The bimodal nature of the polymer sample can be viewed very clearly. The spectrum indicates there at least two main polymeric species or distributions; one centred around 3500 g mol^{-1} and one at around 7200 g mol^{-1}. Definite identification of the different species is rather challenging due to the breadth of the peaks and by the number of species whose existence could be sensibly predicted.

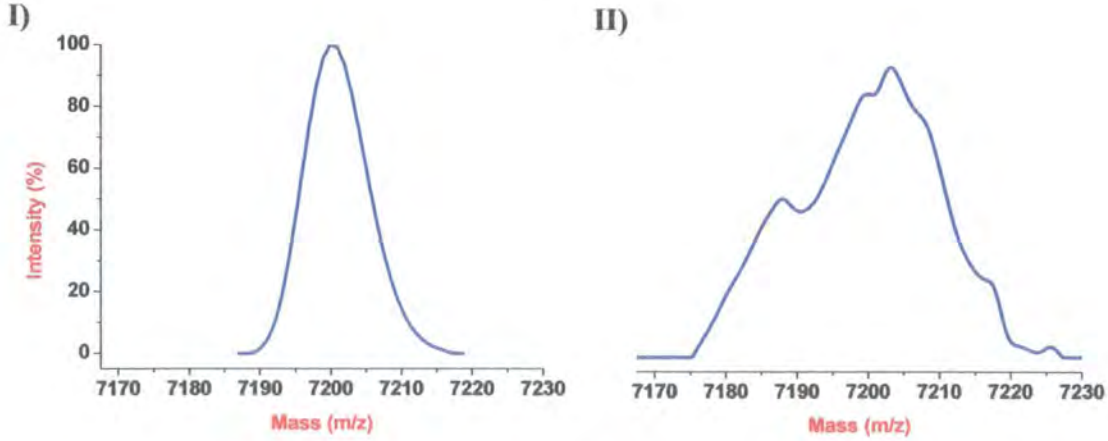


Figure 4.22 - I) Predicted isotope pattern for $C_8H_{21}SiOS(C_3H_6S)_{94}CH_3Na$. II) Observed isotope pattern in this region.

The predicted isotope pattern (**I**, **Figure 4.22**) of TBDMSOPrS(C_3H_6S)$_{94}CH_3Na$ (**21-Na**), the polymeric species formed as a result of initiation by TBDMSO-PrSLi (**Figure 4.17**) is broadly consistent with that observed (**II**, **Figure 4.22**). The shoulder at lower molecular weight is consistent with TBDMS-OPrO(C_3H_6S)$_{94}CH_3Na$ a species that might be formed if polymerisation was initiated by TBDMSO-PrOLi (**23**, **Figure 4.20**). The same shoulder is attributable to the species TBDMSOPrS(C_3H_6S)$_{94}HNa$, i.e. thiol rather than methyl functionalised PPS. The lower molecular weight region is even broader, making it more difficult to make meaningful comparisons with predicted species. The species H(C_3H_6S)$_n CH_3Na$, thought to be a possible product of initiation of PrS by LiH, seems to fit well with one of the maxima in the peaks in the lower molecular weight region. The breadth of the peaks could also be as a result of the ability of the propagating species of living PPS to enchain further sulfur in the form of S-S bonds, resulting in ($C_3H_6S_x$)$_n$ where $x > 1$. This can occur either through reaction of the propagating species with any traces of sulfur (formed from the thermal decomposition of PrS) or through abstraction of sulfur from PrS. The latter is not thought to be a significant factor in the polymerisation of PrS initiated by alkyllithiums in THF.[31] The breadth of the distribution of polymer chains could also be caused by degradation of the polymer chains, consistent with PPS's reported instability,[21] although as discussed earlier no increase in PDI was noticed in PPS when monitored by THF GPC.

In conclusion GPC and MALDI data suggest that more than one initiation event has occurred leading to a polymeric material with two molecular weight distributions. Estimates of M_n by NMR when compared to those from GPC, suggest that not all of the species have the desired TBDMS ether group. This means that not all of the chains are available for conversion to macromonomer. The protected initiator strategy to macromonomers discussed in this chapter requires that TBDMSO-PrLi (**1**) is the only species present capable of initiating polymerisation and that initiation results in incorporation of the TBDMS group onto the polymer. The strategy will prove unsuccessful in quantitatively functionalising polymers in cases where **1** is not the only initiating species, as observed here with PPS. This is more likely to be a problem associated with the polymerisation of cyclic monomers by anionic ring opening

polymerisation than with vinyl monomers, as many cyclic monomers can be ring opened by a range of weaker nucleophiles.

Concurrent to the analytical studies overleaf the compatibility of the PPS with ruthenium benzylidene $RuCl_2(=CHPh)(PCy_3)_2$ was examined. A solution of the two in C_6D_6 was analysed over time by NMR and compared with a solution of the ruthenium benzylidene initiator, which showed the presence of PPS did not accelerate decomposition of the initiator. Providing a way can be found to quantitatively functionalise the PPS, it is possible that block copolymers with PNB might be synthesised by the methodology developed in Chapters 2 and 3. As mentioned earlier the functionalisation chemistry of living PPS has received very little attention. It would be interesting to examine the possibility of functionalising the polymer directly after polymerisation possibly with 4-VBC. As an alternative it might also be possible to synthesise block copolymers containing a trimethylene sulfide (**Figure 4.23**, more commonly referred to as thietane) block synthesised by anionic polymerisation and a PNB block using the macroinitiator technique examined in this chapter.

Figure 4.23 - Trimethylene sulfide.

This monomer behaves rather differently with alkyllithium initiators compared with PrS, undergoing ring opening polymerisation to form a carbanion which is sufficiently nucleophilic to initiate the polymerisation of styrene. Crucially whilst polymerisation with n-butyllithium is very fast, the range of compounds capable of initiating polymerisation is far lower than PrS.[22] Sodium naphthalene and alkali metals being the other efficient initiators for polymerisation apart from alkyllithium compounds that have been reported. The TBDMS ether group should thus be incorporated into every polymer chain if TBDMSO-PrLi is used to initiate polymerisation.

4.2.4 Applicability of this Methodology to the Synthesis of other Block Copolymers

This section will give an overview of the range of block copolymers that can be prepared using the methodology developed in this report in light of the results presented in this Chapter.

It should be possible to prepare block copolymers from most living anionic polymerisations where a hydroxyl group can be introduced quantitatively using the methods described in this and the previous Chapter. These will include polymers of styrene derivatives, for example poly(α-methylstyrene), as well as poly(vinylpyridine). It was anticipated that poly(vinyl pyridine) might co-ordinate to the ruthenium macroinitiators, in light of the recent synthesis of well-defined ruthenium initiators with bis(pyridine) ligands.[32] A solution of poly(2-vinylpyridine) (P2VP, Aldrich, certified as M_n = 4800 g mol^{-1}) and $RuCl_2(=CHPh)(PCy_3)_2$ in C_6D_6 was studied by ^1H NMR, and no change was observed in the shift or stability of the alkylidene proton. It should be possible to synthesise block copolymers of P2VP and ROMP monomers using this method.

It will be difficult to synthesise block copolymers containing anionically polymerised methacrylate derivatives using the methodology developed in this research. This is due to the high nucleophilicity of the bases used to perform the conversion of the hydroxyl functionalised polymers to macromonomers, which can result in deterioration of the polymer chain as demonstrated using PMMA. It is possible that this might not be a problem with some other methacrylates for example *tert*-butyl methacrylate, where steric hindrance might prevent the decomposition reaction. A method for solving this problem is discussed in the next section.

Poly(butadiene) (PBD) cannot be combined with ROMP using this methodology, due to the great efficiency with which $RuCl_2(=CHPh)(PCy_3)_2$ depolymerises PBD.[33,34] The polymer backbone of poly(1,4-isoprene) and other dienes in which there are substituents around the double bond is far more resilient to metathesis by $RuCl_2(=CHPh)(PCy_3)_2$.[35,36] However the anionic polymerisation of dienes leads to some degree of pendant unsaturation on the resulting polymers (as a result of 1,2 or 3,4 enchainment of the monomer during propagation, depending on the monomer), with the apparent exception of a few less common monomers such as 2-(triethylsilyl)-1,3-

butadiene.[1] As well-defined ruthenium initiators will metathesise this pendant unsaturation, this would also prevent the combination of most or all dienes with ROMP using this methodology.

4.3 Conclusions and Summary

We have successfully developed a method for the synthesis of macromonomers via anionic polymerisation, using an initiator with a protected functionality. This initiator was a propyllithium compound bearing a *tert*-butyldimethylsilyl (TBDMS) ether group. The anionic polymerisation of styrene was achieved using this initiator resulting in the synthesis of polystyrene of low polydispersity (PDI: 1.03 by GPC). This TBDMS ether group was deprotected using HCl yielding PS quantitatively functionalised with a hydroxyl group. This hydroxyl group could be converted into a macromonomer via a Williamson coupling reaction using K and 4-VBC.

Attempts to synthesise macromonomers from the monomers methyl methacrylate, and propylene sulfide, highlighted some limitations of this technique. Poly(methyl methacrylate) was successfully synthesised using the protected initiator. The resulting polymer possessed a narrow PDI (PDI: 1.05, by THF GPC), although a lack of control over molecular weight was apparent. The resulting polymer was successfully deprotected leaving a hydroxyl group on every chain. Attempts to synthesise a macromonomer using a Williamson coupling reaction, were accompanied by polymer-polymer coupling, probably due to attack on the ester groups of the polymer by the base.

Poly(propylene sulfide) was also synthesised using the protected initiator. Study of the resulting polymer by GPC and MALDI indicated bimodal traces (PDI: 1.18, by GPC), suggesting the presence of two different molecular weight distributions. Calculation of the M_n of the polymer by NMR spectroscopy suggested that some of the polymer did not have the TBDMS ether group, implying that some polymer was initiated by another Li salt present in the initiator solution. The polymer was not quantitatively functionalised with the TBDMS group and could thus not be used in the synthesis of macromonomer or block copolymers.

4.4 Experimental

4.4.1 General

4.4.1.1 Materials

All anionic polymerisations were carried out using standard high vacuum techniques in the polymerisation reactor described in Chapter 2 (**Figure 2.1** and accompanying text). All chemicals used in anionic polymerisation were degassed by five freeze-thaw-evacuate cycles, to a pressure of below $1x10^{-5}$ mm Hg prior to use, unless stated otherwise. Styrene (Aldrich, 99+%), 1,1-Diphenylethylene (DPE, Aldrich, 97%), and benzene (Aldrich, 99.9+%) were distilled from CaH_2 prior to use. Propylene sulfide (PrS, Aldrich, 96+%) was fractionally distilled, dried over $MgSO_4$ for 16 h, and thoroughly degassed. It was then distilled onto CaH_2, and dried at 0 °C for 2 h, following this it was degassed once more and immediately re-distilled into another ampoule. It was then weighed and used immediately. Methyl methacrylate (Aldrich, 99%) was purified by distillation from CaH_2 and then by distillation from $Al(Et)_3$ (Aldrich, 1.0 M solution in heptane) immediately before use. THF for use in azeotropic distillation and as a solvent for Williamson couplings (Aldrich, 99.9%, anhydrous) was passed through two columns containing alumina.[37] The same procedure was used to obtain solvent for use in anionic polymerisation, except it was purified further by distillation from sodium/benzophenone. Tetrahydrofuran (THF, Fisher, HPLC grade) was used as a solvent for the deprotection of polymers using HCl. 4-Vinylbenzyl chloride (4-VBC, Aldrich, 90%) was stated by the supplier to contain the impurities, α-chloromethyl styrene (2%), dichloromethyl styrene (3%) and 3-vinylbenzyl chloride (3-VBC, 5%) and was purified as described in the relevant section. CH_3I in a foil covered ampoule (Aldrich, 99.5%) was dried and distilled from CaH_2. 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (FMC Lithium Division, solution in cyclohexane), potassium (Aldrich, 98%), *N,N,N',N'*-tetramethylethylenediamine (Aldrich, 99.5+% under N_2, TMEDA), lithium chloride (Aldrich, 99.99%), 15-crown-5 (Aldrich, 98%) and decolourising activated carbon were used as supplied. Sodium hydride (Aldrich, dry, 95%) was stored in a nitrogen glovebox and handled under nitrogen at all times. Diphenylmethylpotassium (DPMK) was synthesised in solution by the reaction of potassium naphthalene with a slight excess of diphenylmethane in THF.[38] LiOH (Fisons, 99.5+%) and KOH (Fisher, reagent grade)

were dried *in vacuo* at 100 °C for 24 h prior to addition to PrS. Basic alumina (activated, Brockmann 1, CA. 150 mesh) and celite (grade 521) were obtained from Aldrich and used in pore 4 sintered funnels. MeOH (Aldrich, 99.9+%), used to terminate anionic polymerisations, was purged with N_2 for 30 min prior to injection. $CDCl_3$ (Aldrich, 99.9% D) with and without TMS (0.03% v/v) and CD_2Cl_2 (Goss/Cambridge Isotope Laboratories Inc., 99.9% D,) with and without TMS (0.03% v/v) were used as received.

4.4.1.2 Analysis

Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance (NMR) spectroscopy was performed using a Varian Inova 500 MHz or Mercury 400 MHz spectrometer. All ^1H and ^{13}C NMR resonances are quoted relative to residual H or to C of the solvent unless otherwise stated.

Gel Permeation Chromatography (GPC)

GPC of the poly(methyl methacrylate) (PMMA) and poly(propylene sulfide) (PPS) samples using a Viscotek 200 with refractive index, viscosity and right angle light scattering detectors and 2 x 300 mm PLgel 5 μm mixed C columns. The polystyrene (PS) samples were studied using a Viscotek TDA 302 with refractive index, viscosity and right angle light scattering detectors equipped with the same columns. THF was used as the eluent, at a flow rate of 1.0 mL/min and at a constant temperature of 30 °C. Molecular weights were obtained using triple detection, and a value of 0.185 for the [d*n*/d*c*] of PS was assumed. The detectors were calibrated with a single narrow molecular weight distribution PS standard (M_w = 66000 g mol^{-1}, PDI = 1.03, Polymer Laboratories). A figure of 0.167 for the [d*n*/d*c*] of the PPS was determined. This was calculated using a solution of the sample described in Section 4.4.4 dissolved in THF of a known accurate concentration, using the right angle light scattering detector precalibrated using a sample of known molecular weight and [d*n*/d*c*].

Mass Spectroscopy

Matrix Assisted Laser Desoprtion Ionisation – Time of Flight (MALDI-TOF) mass spectroscopy was performed using an Applied Biosystems Voyager-DE STR

BioSpectrometry workstation. PPS was dissolved in THF and premixed with the matrix 2-(4-hydroxyphenylazo)-benzoic acid (HABA) dissolved in THF. Spectra were obtained in linear mode.

4.4.2 Synthesis of Polystyrene Homopolymers using a Protected Initiator

4.4.2.1 Synthesis of *tert*-Butyldimethylsilyl Ether Polystyrene via Anionic Polymerisation

Styrene (15.40 g, 0.15 mol) and benzene (125 mL) were distilled into the reaction vessel and TMEDA (0.23 mL, 1.54 mmol, 1 equiv) added by injection. Polymerisation was then initiated by the addition of 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (0.3 M solution in cyclohexane, 5.13 mL, 1.54 mmol). Polymerisation was allowed to proceed over a period of 8 h at room temperature. The poly(styryl)lithium was then terminated by the injection of N_2 purged MeOH (1.00 mL), and then precipitated into MeOH (1250 mL). The polymer was filtered and the sample dried for 24 h *in vacuo* at r.t. (Yield:15.42 g, ~100%). The sample was dissolved in CH_2Cl_2 (500 mL) and filtered through Celite in order to remove Li salts from the sample, and the solvent was removed under vacuum. The product was twice redissolved in toluene (75 mL), re-precipitated in MeOH (750 mL) and dried *in vacuo*. Yield = 13.60 g, 88%.

Target M_n: 10000 g mol^{-1}.

THF GPC: M_n = 11600 g mol^{-1}, PDI = 1.03.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 4.24**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.5–6.2 (**$H_{3\text{-}5}$**), 3.56-3.43 (**H_7**), 2.5–1.7 (**H_1**), 1.7-1.20 (**H_2**), 0.92–0.87 (**H_{10}**), 0.05–0.00 (**H_8**).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.5-144.8 (**C_2**), 128.5-127.0, 125.8–125.3 (both **$C_{3\text{-}5}$**), 63.06 (**C_7**), 46.8–41.0(**C_2**), 41.0–40.2 (**C_1**), 26.09 (**C_{10}**), 18.54 (**C_9**), -5.23 (**C_8**).

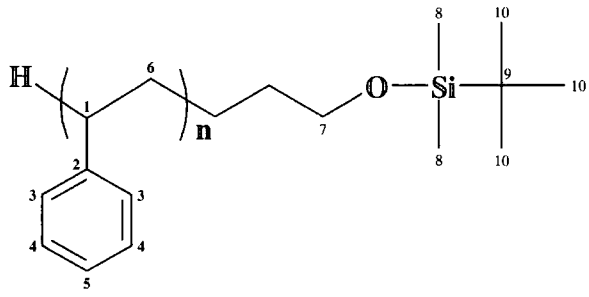


Figure 4.24 - Numbering Scheme for NMR assignments of TBDMS ether PS.

4.4.2.2 Deprotection of *tert*-Butyldimethylsilyl Ether Polystyrene

tert-Butyldimethylsilyl ether PS (THF GPC M_n = 11600 g mol^{-1}, 10 g, 0.9 mmol) was dissolved in THF (75 mL) and conc. HCl (35% , 0.5 mL, ~5 equivs) added to the solution. The solution was refluxed for 17 h after which it was allowed to cool to r.t., a small sample of the solution was collected and further HCl (0.5 mL) was added. The reflux was then restarted and continued for a further 2 h to ensure complete deprotection of the PS. Analysis by ^{1}H NMR of the sample of the PS solution (precipitated into MeOH and dried) indicted the absence of the chemical shifts from the protecting group (0.92–0.87 and 0.05–0.00 ppm). The bulk of the polymer solution was then precipitated into MeOH (750 mL). The polymer was filtered and the sample was dried for 24 h *in vacuo* at r.t. Following this the product was twice redissolved in toluene (65 mL), re-precipitated in MeOH (650 mL) to remove TBDMS residues and dried *in vacuo*. The sample was dissolved in THF (50 mL) and traces of MeOH were removed by azeotropic distillation. The solvent was then removed under reduced pressure and the polymer was dried in vacuum at r.t. overnight (Yield: 9.36 g, 94%).

THF GPC: M_n = 11500 g mol^{-1}, PDI = 1.05.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 4.25**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.5–6.2 (**$H_{3\text{-}5}$**), 3.50-3.37 (**H_7**), 2.5–1.7 (**H_1**), 1.7-1.20 (**H_2**).

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.5-144.8 (**C_2**), 128.5-127.0, 125.8–125.3 (both **$C_{3\text{-}5}$**), 62.91 (**C_7**), 46.8–41.0 (**C_2**), 41.0–40.2 (**C_1**).

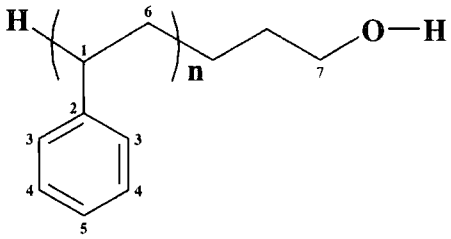


Figure 4.25 - Numbering Scheme for NMR assignments of deprotected PS.

4.4.2.3 Synthesis of 4-Vinylbenzyl Functionalised Polystyrene Macromonomer

4-VBC was passed through a short column of basic alumina, dried and degassed over CaH_2, and purified by vacuum distillation immediately prior to use.

Hydroxy functionalised PS (THF GPC M_n = 11600 g mol^{-1}, 2.0 g, 0.2 mmol) was dissolved in THF (40 mL) under an atmosphere of Ar in a bulb equipped with a septum. Potassium (0.04 g, 1.0 mmol, 5 equivs) was placed under vacuum for 30 min in a second bulb, before being heated to form a mirror. The THF solution was then added slowly to the K mirror and allowed to remain in contact with the K for 24 h. At several points the solution was decanted into the first bulb and back again, to ensure the complete consumption of any trace amounts of protic impurities that might otherwise result in residual hydroxy functionalised PS in the macromonomer. After this period all of the THF solution was then decanted into the first bulb, and freshly distilled 4-VBC (0.03 mL, 0.2 mmol, 1.2 equivs) was injected through the septum. The mixture was stirred for 24 h, after which air was admitted into the bulb. It was then precipitated into MeOH (400 mL) and dried *in vacuo*. It was reprecipitated from toluene (10 mL) into MeOH (100 mL) twice, to ensure the complete removal of unreacted 4-VBC. Yield = 1.61 g, 81%.

THF GPC: M_n = 11600 g mol^{-1}, PDI = 1.05.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 4.26**.

^{1}H NMR (CD_2Cl_2, 500 MHz): δ 7.44-7.38 (**H_{11}**), 7.38–6.2 (**$H_{3\text{-}5}$**), 5.82–5.74 (**H_{14}**), 5.28–5.22 (**$H_{14'}$**), 4.36-4.18 (**H_8**), 3.40-3.28 (**H_7**), 2.5–1.7 (**H_1**), 1.7-1.20 (**H_2**)

^{13}C NMR (CD_2Cl_2, 126 MHz): δ 146.5-144.8 (**C_2**), 139.04 (**C_9**), 137 (**C_{12}**), 136.94 (**C_{13}**), 128.5-127.0, 125.8–125.3 (**$C_{3\text{-}5,10,11}$**), 113.79 (**C_{14}**), 72.7 (**C_8**), 70.6 (**C_7**), 46.8–41.0(**C_2**), 41.0–40.2 (**C_1**).

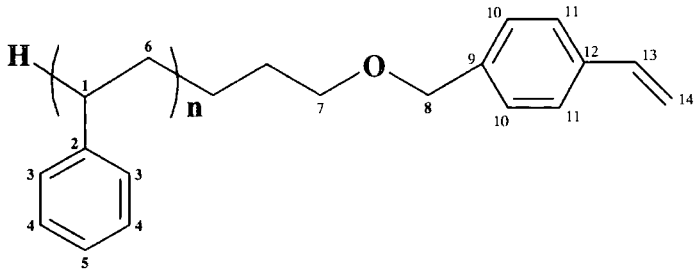


Figure 4.26 - Numbering Scheme for NMR assignments of PS macromonomer.

4.4.3 Synthesis of Poly(Methyl Methacrylate) Homopolymers using a Protected Initiator

4.4.3.1 Synthesis of *tert*-Butyldimethylsilyl Ether Poly(Methyl Methacrylate) via Anionic Polymerisation

LiCl (0.21 g, 5 mmol, 5 equivs) was added to the polymerisation reactor which was then placed under vacuum for 16 h. THF (100 mL) was distilled into the vessel, and maintained at -78 °C. Freshly distilled DPE (0.35 mL, 2.0 mmol, 2 equivs) and 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (0.35 M solution in cyclohexane, 2.86 mL, 1.0 mmol) were added by injection and the solution was stirred for 48 h. Methyl methacrylate (5.01 g, 0.05 mol) was then distilled into the reaction vessel. Polymerisation was allowed to proceed for a period of 4 h. The polymerisation was then terminated by the injection of N_2 purged MeOH (1.00 mL) before the solution was allowed to warm to r.t. The polymer was precipitated into MeOH (1000 mL), filtered and dried for 24 h *in vacuo* at r.t (Yield: 4.76 g, 95%).

The protected polymer (1.98 g) was then dissolved in CH_2Cl_2 (300 mL) and filtered through Celite in order to remove Li salts from the sample, and the solvent was removed under vacuum. The product was then twice redissolved in THF (20 mL), re-precipitated in hexane (200 mL) and dried *in vacuo*. Yield: 1.32 g, 67%.

Target M_n: 5000 g mol^{-1}.

THF GPC: M_n = 18500 g mol^{-1}, PDI = 1.05.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 4.27**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.2-6.96 (**H_{7-9}**), 3.8-3.0 (**H_4**), 2.1–1.3 (**H_5**), -0.06 – -0.12 (**H_{11}**), -0.15 – -0.18 (**dimethylsilyl,** see Section 4.4.2.1).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 178.2-177.6, 177.4-176.8 (**C_3**), 128.2-127.5, 126.0-125.4 (**C_{6-9}**), 62.9 (**C_{10}**), 55.0-52.90 (**C_5**), 51.75 (**C_4**), 45.0-44.0 (**C_1**), 25.86 (**C_{13}**), 18.90 (**C_{12}**), 18.6, 16.8-16.0 (**C_2**), -5.38 (**C_{11}**).

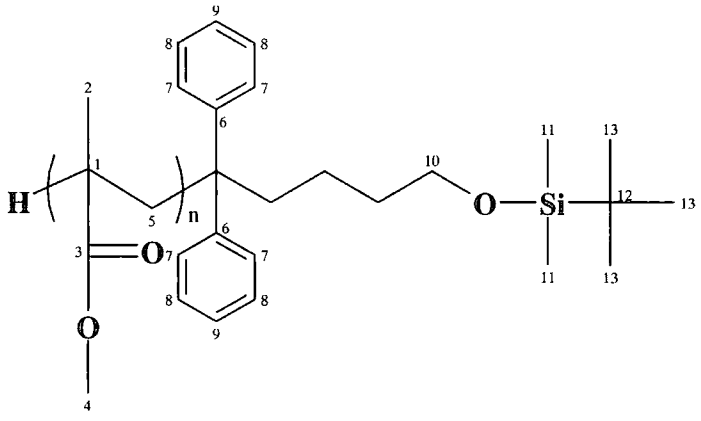


Figure 4.27 - Numbering Scheme for NMR assignments of PMMA initiated by the product of TBDMSO-PrLi and DPE.

4.4.3.2 Deprotection of *tert*-Butyldimethylsilyl Ether Poly(Methyl Methacrylate)

tert-Butyldimethylsilyl ether PMMA (THF GPC M_n = 18500 g mol^{-1}, 1.35 g, 0.1 mmol) was dissolved in THF (30 mL) and conc. HCl (35%, 0.5 mL, 5.6 mmol) was added to the solution. The solution was refluxed for 18 h then cooled to r.t. and a small sample (0.5 mL) of the solution was collected, precipitated into hexane and dried. NMR analysis of the sample showed no evidence of the shift from the protecting group on the polymer (-0.15 – -0.18 ppm). The bulk of the polymer solution was then reduced in volume under vacuum (to a total of 15 mL) and precipitated into hexane (150 mL) and dried for 24 h *in vacuo* at 50 °C. The product was then twice redissolved in THF (10 mL), re-precipitated in hexane (100 mL) to remove TBDMS residues and dried *in vacuo*. (Yield: 1.22 g, ~90%).

THF GPC: M_n = 18200 g mol^{-1}, PDI = 1.05.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 4.28**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.2-6.96 (**H_{7-9}**), 3.8-3.0 (**H_4**), 2.1–1.3 (**H_5**).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 178.2-177.6, 177.4-176.8 (C_3), 128.2-127.5, 126.0-125.4 (C_{6-9}), 62.3 (C_{10}), 55.0-52.90 (C_5), 51.75 (C_4), 45.0-44.0 (C_1), 18.6, 16.8-16.0 (C_2).

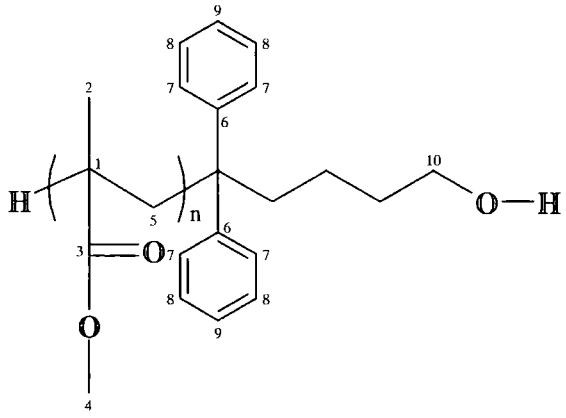


Figure 4.28- Numbering Scheme for NMR assignments of deprotected PMMA (initiated by the product of TBDMSO-PrLi and DPE).

4.4.3.3 Attempted Synthesis of PMMA Macromonomer using Sodium Hydride

Deprotected hydroxy functionalised PMMA (THF GPC M_n = 18500 g mol^{-1}, 0.5 g, 3 x 10^{-2} mmol) and NaH (7.0 mg, 0.3 mmol, 10 equivs) were added to a 2-neck round bottom flask (100 mL) equipped with a magnetic follower and stoppered with subaseals. The flask was placed under an atmosphere of N_2. The polymer was dissolved by addition of dry THF (10 mL) to the flask, following which 15-Crown-5 (55 μL, 0.3 mmol, 10 equivs) was added to the suspension. 4-VBC (40 μL, 0.3 mmol), which had been dried over fused $CaCl_2$ for a couple of hours in a fridge at 4 °C, was then passed through a short column of basic alumina and immediately added to the reaction. The reaction mixture was then agitated under the atmosphere of nitrogen. A small sample (0.5 mL) was removed after 24 hours of reaction and precipitated into hexane (5 mL). Analysis of this sample by THF GPC suggested that polymer-polymer coupling had already started to take place. After a total of 48 h of reaction time, residual NaH was destroyed by the addition of a few drops of MeOH. The Polymer was collected by precipitation into hexane (100 mL), filtered and washed with hexane before being dried in vacuo. Yield = 0.35 g (78%).

The polymer was reprecipitated twice from THF (4 mL) into hexane (40 mL), the solid was isolated by filtration and washed with hexane and dried *in vacuo* at r.t.

overnight and the polymer was analysed by GPC and NMR spectroscopy. Reprecipitation was observed to have no clear effect on analytical data.

THF GPC: M_n = 19500 g mol^{-1}, PDI = 1.09.

NMR data was essentially identical to that from the deprotected hydroxy functionalised PMMA disclosed in Section 4.4.3.2, with the exception of the presence of small amounts of vinyl substitution (see Section 4.2.2.2).

4.4.3.4 Attempted Synthesis of PMMA Macromonomer using DPMK

4-VBC was passed through a short column of basic alumina, dried and degassed over CaH_2, and purified by vacuum distillation immediately prior to use.

Hydroxy functionalised PMMA (THF GPC M_n = 18500 g mol^{-1}, 0.05 g, 3 x 10^{-3} mmol) was dissolved in THF (10 mL) under an atmosphere of Ar in a bulb equipped with a septum. DPMK (1.0 M solution in THF, 70 μL, 0.07 mmol) was then added by injection into the stirred solution of PMMA. After 5 min reaction time, freshly distilled 4-VBC (13 μL, 0.08 mmol, 1.2 equivs relative to DPMK) was injected through the septum. The mixture was stirred for 30 min, after which MeOH (200 μL) was added to ensure no potassiated PMMA or DPMK remained – no change was observed. The solvent was then reduced to 5 mL and the polymer was precipitated by addition of the solution to hexane (50 mL). The polymer was then filtered and dried. It was then purified by precipitating a solution of the polymer in THF (1 mL) into hexane (10 mL). The polymer was finally filtered and dried *in vacuo* at r.t overnight. Yield = 0.021 g, 42%.

THF GPC: M_n = 18000 g mol^{-1}, PDI = 1.08.

NMR data was similar to that from the deprotected hydroxy functionalised PMMA disclosed in Section 4.4.3.2, please see Section 4.2.2.2 for further discussion.

4.4.4 Synthesis of Poly(Propylene Sulfide) by Anionic Polymerisation

Propylene sulfide (6.90 g, 93.1 mmol) and THF (125 mL) were distilled into the reaction vessel and the resulting solution chilled to -78 °C. 3-(*t*-butyldimethylsilyloxy)-1-propyllithium (0.3 M solution in cyclohexane, 9.20 mL, 2.8 mmol) was added by injection. The resulting yellow solution was stirred at -78 °C for 30 min, before it was allowed to reach r.t. The polymerisation reaction was stirred for a further 20 h, after

which it was terminated using MeI (0.34 mL, 5.5 mmol, 2 equivs). After 30 min air was admitted and the solvent was removed under vacuum. The elastomeric product formed was dissolved in CH_2Cl_2 (250 mL) and slurried with decolourising activated carbon, before filtration through a column of celite. This process was repeated once more in order to remove Li salts and yellow compounds with a sulfurous odour from the polymer. It was then redissolved in CH_2Cl_2 (40 mL), which was chilled to -78 °C and precipitated in hexane (400 mL, -78 °C). Filtration equipment was chilled by the passage of hexane at -78 °C and the product was quickly filtered and washed with chilled hexane. The solid was dried, and dissolved in CH_2Cl_2 (100 mL). The solution was reduced (to 40 mL) and was added into hexane once more. The precipitate was filtered and dried. Finally the polymer was dissolved in CH_2Cl_2 (200 mL), dried over $MgSO_4$ and then filtered through celite, following which the solvent was removed. Yield = 5.88 g, 85%.

Target M_n: 2500 g mol^{-1}.

THF GPC: M_n = 5370 g mol^{-1}, PDI =1.18.

The polymer was fully characterised by NMR using the numbering scheme shown in **Figure 4.29**.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.60-3.45 (**H_4**), 3.0-2.3 (**$H_{1,3}$**), 1.4–1.1 (**H_2**), 0.86-0.83 (**H_6**), 0.01 – -0.01 (**H_4**).

^{13}C NMR ($CDCl_3$, 126 MHz): δ 63.2-62.8 (**C_5**), 41.5-40.9 (**C_1**), 38.6-38.2 (**C_3**), 21.8-19.9 (**C_2**), 26.2-25.8 (**C_6**), -5.28 – -5.53, -7.52 (**C_5**).

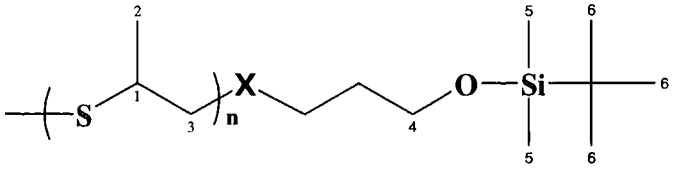


Figure 4.29- Numbering Scheme for NMR assignments of TBDMS ether PPS. X=S or O. A significant fraction of the sample did not possess the TBDMS ether functionality.

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Chapter 5

Conclusions and Future Work

5.1 Conclusions

This work was successful in producing a range of well-defined block copolymers of low polydispersity, which contained a block polymerised by an anionic mechanism and a block from Ring Opening Metathesis Polymerisation (ROMP) using well-defined ruthenium alkylidene initiators.

The first anionically polymerised block to be incorporated into the block copolymers was poly(ethylene oxide)(PEO), which could be functionalised by the reaction of 4-vinylbenzyl chloride (4-VBC) with the living PEO polymer to create macromonomers. These were converted into PEO macroinitiators via alkylidene exchange with the ruthenium propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$, and in turn were used to initiate the polymerisation of norbornene derivatives, resulting in a series of block copolymers. The ROMP monomers were substituted with imide, dicarboxylic acid ester, and chloromethyl functionalities illustrating the range of functionalities that can be incorporated into the ROMP block, due to the high tolerance of the macroinitiators to functional groups. Block copolymers with varying lengths of both the PEO and ROMP block were synthesised to demonstrate the versatility of the methodology.

The synthesis of block copolymers of styrene and norbornene derivatives required a slightly modified methodology, due to the greater reactivity of living polystyrene (PS) compared to PEO, which prevents clean reaction of PS with 4-VBC. This problem was overcome by functionalising the polymer with ethylene oxide to form hydroxyethylated PS. The hydroxyethylated PS could then be converted to macromonomer by means of a Williamson coupling reaction with 4-VBC using either K metal, or NaH and 15-crown-5, to form the metal alkoxide intermediate. These macromonomers were converted to PS macroinitiators, by alkylidene exchange with $RuCl_2(=CHEt)(PCy_3)_2$, which could then initiate the ROMP of the same range of norbornene derivatives as the PEO macroinitiators, resulting in a second series of block copolymers of varying molecular weight and composition.

PS was also synthesised by anionic polymerisation initiated by a propyl lithium initiator with a hydroxyl group protected by a *tert*-butyldimethylsilyl (TBDMS) group. Deprotection of this group with HCl regenerated the hydroxyl group. This could then be used in the synthesis of macromonomers by a Williamson coupling reaction with 4-VBC. Attempts to apply this methodology to other monomer

groups that can be polymerised by anionic polymerisation such as methyl methacrylate and propylene sulfide met with limited success – although poly(methyl methacrylate)(PMMA) could be polymerised with the protected initiator it was not possible to prepare PMMA macromonomers due to deterioration of the polymer during the Williamson coupling. The initiation of poly(propylene sulfide) was not well-controlled leading to less than quantitative functionalisation of the polymer chains with the protected hydroxyl groups.

5.2 Future Work

One problem highlighted in the synthesis of PMMA macromonomers was that the strength and nucleophilicity of the bases that are necessary to affect the Williamson coupling can cause side reactions. One way to reduce the required level of reactivity of these bases would be to introduce a more acidic arylhydroxide group onto the polymer chains, allowing the use of mild bases like potassium carbonate to produce the metal alkoxide intermediates. This could be achieved either by end-functionalisation or by incorporation of arylhydroxide into the initiating species in a protected form. Both of these options are synthetically feasible and will be explored to broaden the scope of monomers that can be incorporated using anionic polymerisation, especially methacrylates.

Analogous macroinitiators based on the bis(pyridine) initiators discussed in Section 1.3.3.4 could be synthesised, allowing the ROMP of the majority of the *endo* substituted norbornene monomers to be carried out quickly. It would be interesting to see whether the poor thermal stability reported for the bis(4-bromopyridine) initiator, would result in block copolymers synthesised using these macroinitiators being contaminated with significant amounts of homopolymer.

It would be interesting to extend this methodology to the synthesis of A-B-A triblock copolymers, where block B is synthesised from an α,ω-difunctionalised polymer polymerised via an anionic mechanism, possibly initiated by means of a difunctional initiator. Block B would then be converted into a difunctional macroinitiator for ROMP, and could be used to synthesise a range of block copolymers.

Appendix 1

Publication and Conference Record

Publication Record

This work has led to the following publications and preprints at the date of preparation of this report:

- Castle, T. C.; Hutchings, L. R.; Khosravi, E. *Macromolecules* **2004**, *37*, 2035-2040.
- Castle, T. C.; Khosravi, E.; Hutchings, L. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2004**, *45*, 547-548.

Conference Record

Elements of this research were presented by the author of this report at the following conferences and meetings:

Oral papers

- August 2004, 228th American Chemical Society National Meeting, Philadelphia, Pennsylvania, USA. "Block Copolymers by the Conversion of Living Lithium Anionic Polymerization into Living Ruthenium ROMP", Tom C. Castle, Ezat Khosravi, and Lian R. Hutchings.

- April 2003, MacroGroup UK Young Researchers' Meeting, University of Durham, UK. "The Synthesis of Block Copolymers Through the Combination of Living Ring Opening Metathesis and Anionic Polymerisation" Tom Castle.

- September 2002, NATO Advanced Science Institute on Novel Metathesis Chemistry, Antalya, Turkey. "The Synthesis of Block Copolymers Through the Combination of Living Ring Opening Metathesis and Anionic Polymerisation", Tom Castle, Lian Hutchings, and Ezat Khosravi.

Poster Papers

- September 2004, UK Polymer Showcase, Wakefield, UK. "The Synthesis of Block Copolymers Through the Conversion of Living Anionic Polymerisation into Ring Opening Metathesis Polymerisation." Tom C. Castle, Ezat Khosravi and Lian R. Hutchings.

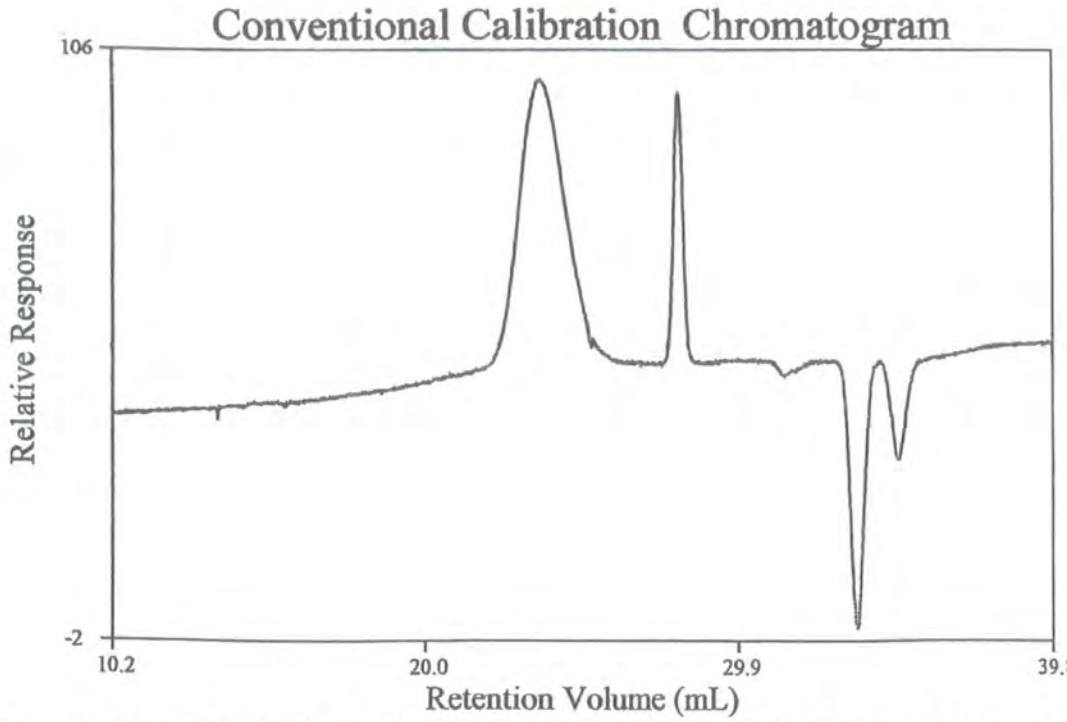
- September 2003, IRC in Polymer Science and Technology Industrial Club Meeting, Leeds, UK. "The Synthesis of Block Copolymers Through the Combination of Living Ring Opening Metathesis and Anionic Polymerisation", Thomas C. Castle, Lian Hutchings and Ezat Khosravi.

The author also attended the following meeting:

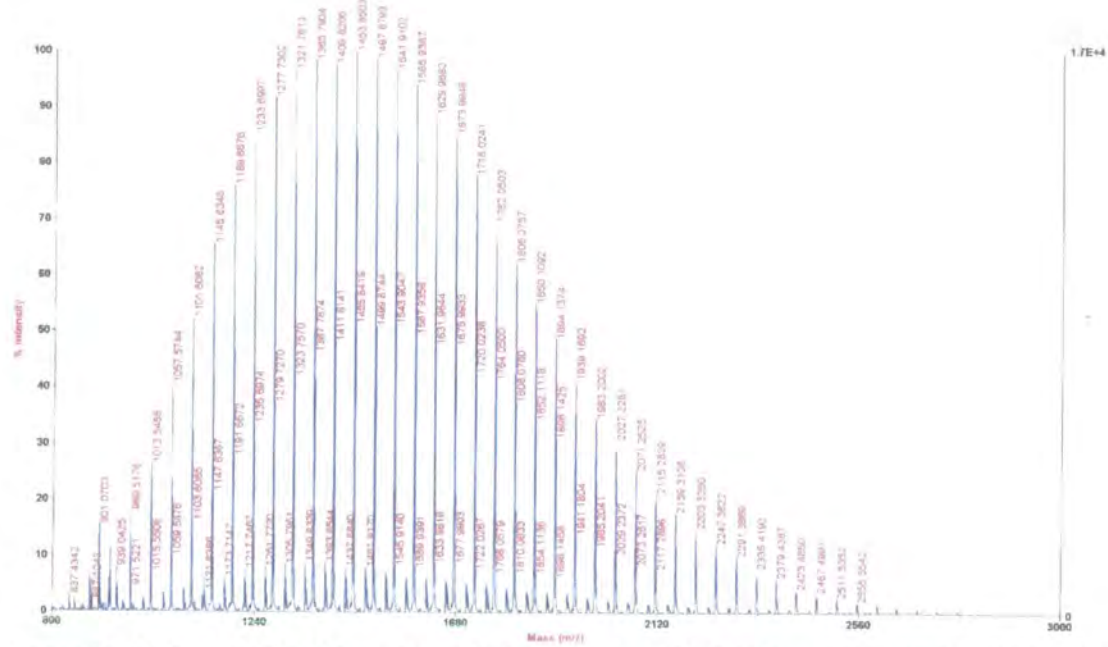
- August - September 2001, Euro Summer School: 4th International School on Molecular Catalysis, Poznań, Dymaczewo, Poland.

Appendix 2

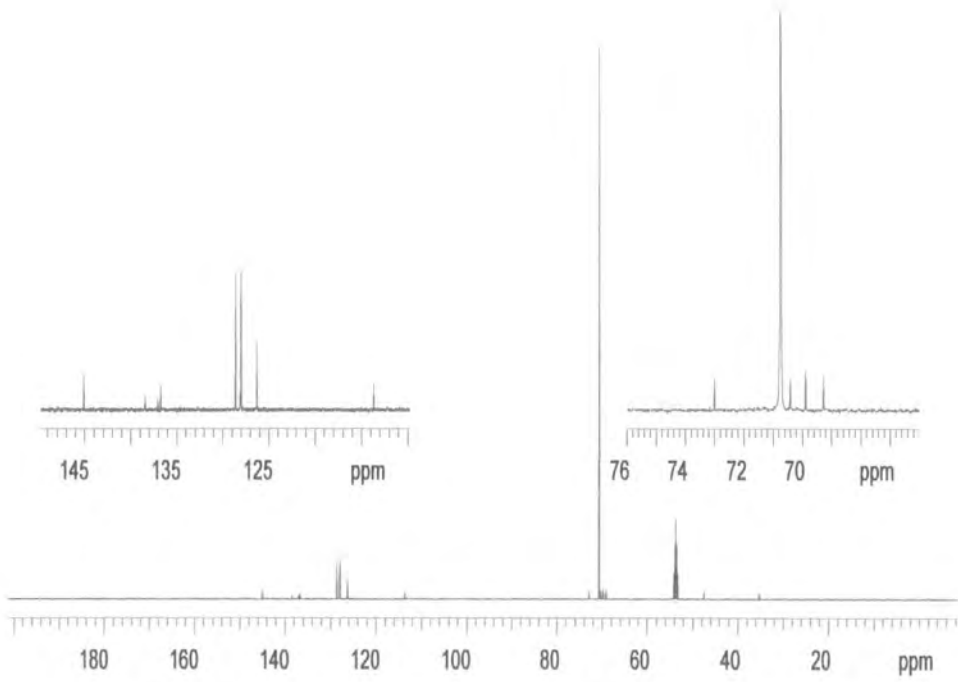
Appendices for Chapter 2



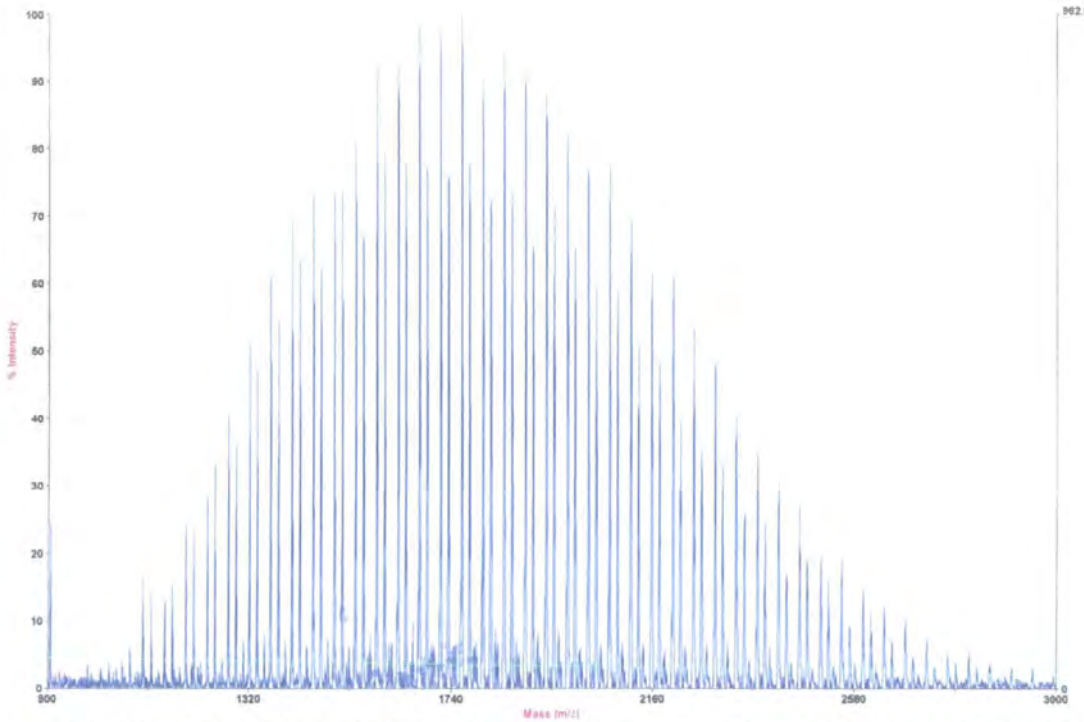
Appendix 2.1.1 - GPC (DMF eluent) of CH_3I terminated PEO (Sample Me PEO 1, Table 2.2). M_n: 1100 g mol^{-1}, PDI: 1.10.



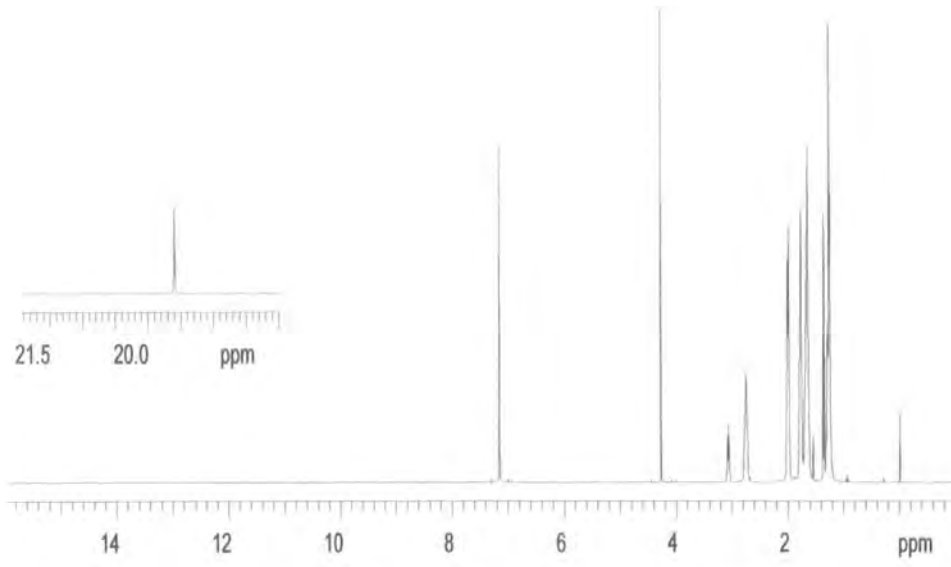
Appendix 2.1.2 - MALDI MS spectrum of CH_3I terminated PEO (Sample Me PEO 1, Table 2.2). M_n: 1600 g mol^{-1}, PDI: 1.05.



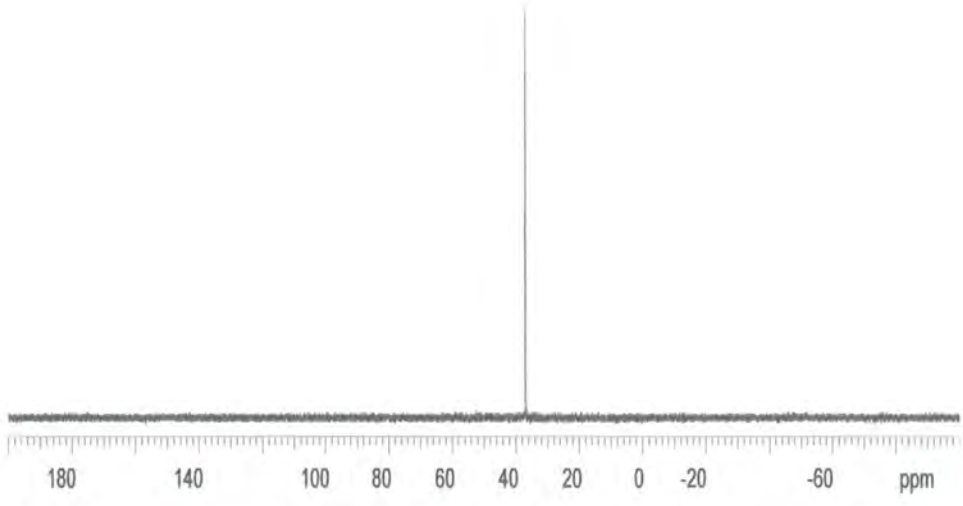
Appendix 2.1.3 - ^{13}C NMR of PEO macromonomer (Sample PEO MM 1, Table 2.2) in CD_2Cl_2.



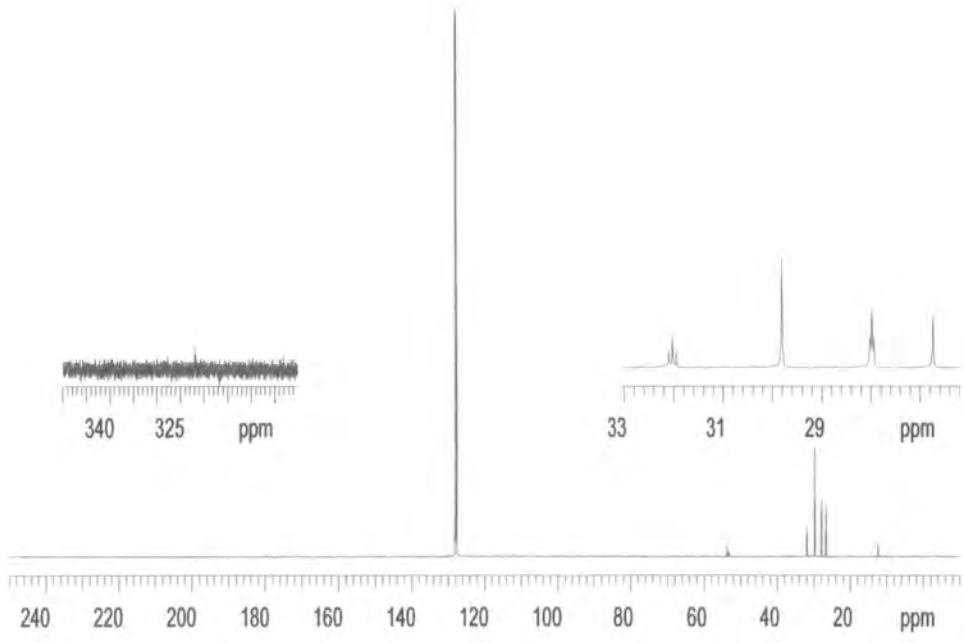
Appendix 2.1.4 - MALDI MS spectrum of PEO Macromonomer (Sample PEO MM 1, Table 2.2). M_n: 1700 g mol^{-1}, PDI: 1.04.



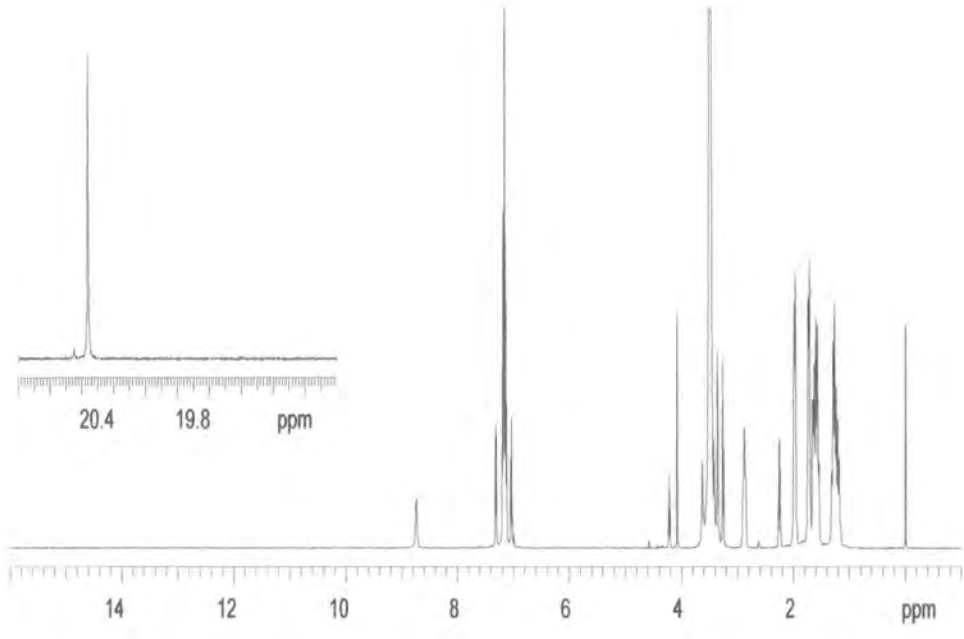
Appendix 2.2.1 - ^{1}H NMR spectrum of propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ in C_6D_6.



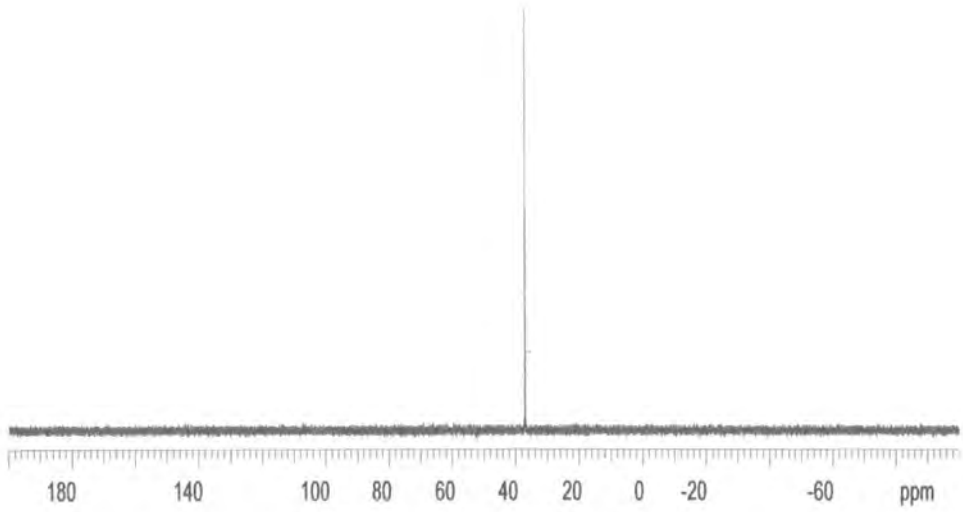
Appendix 2.2.2 - ^{31}P NMR spectrum of propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ in C_6D_6.



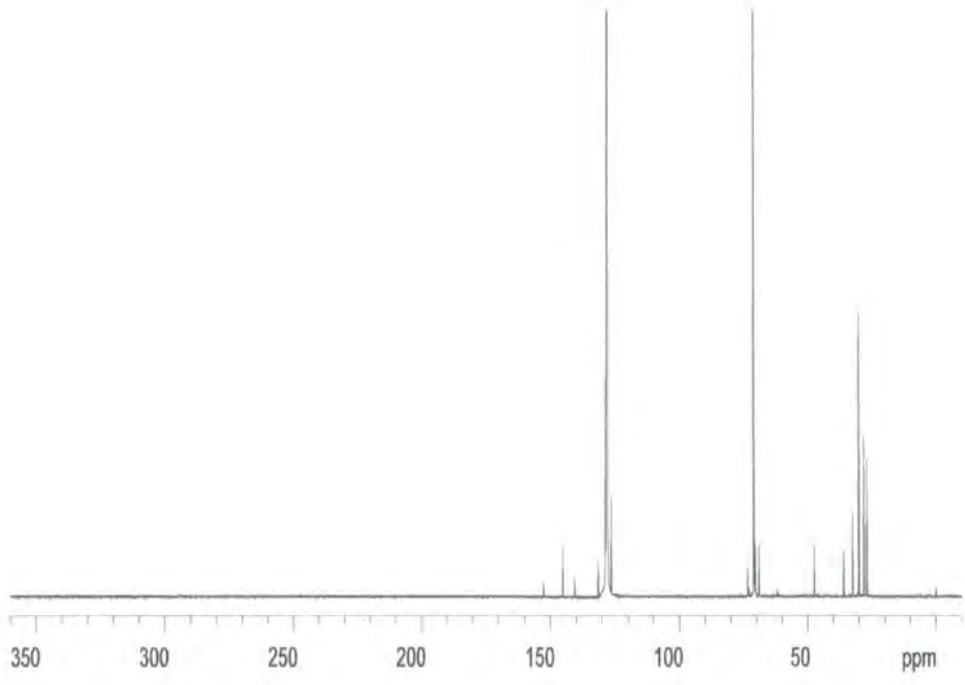
Appendix 2.2.3 - ^{13}C NMR spectrum of propylidene initiator $RuCl_2(=CHEt)(PCy_3)_2$ in C_6D_6.



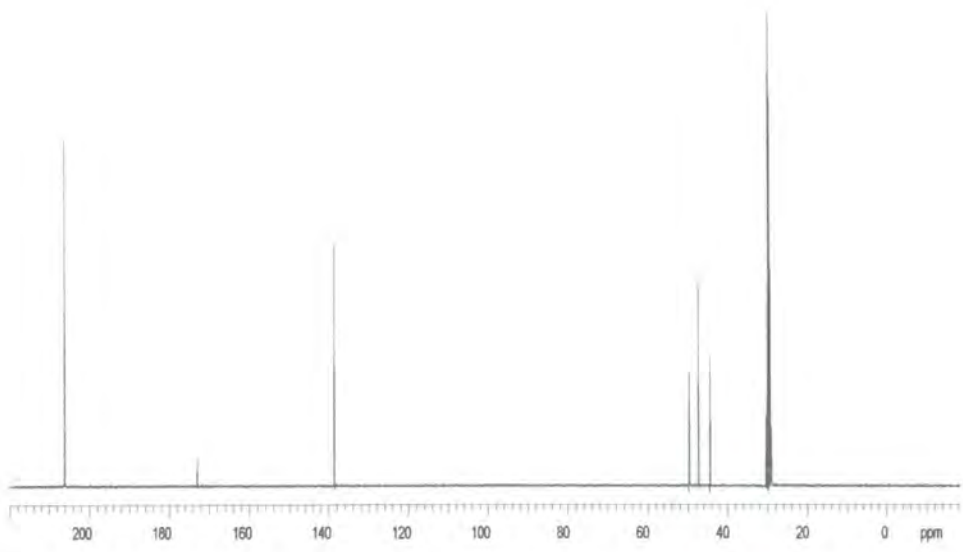
Appendix 2.3.1 - ^{1}H NMR spectrum of PEO ruthenium macroinitiator (M_n of PEO = 2300 g mol^{-1}) in C_6D_6.



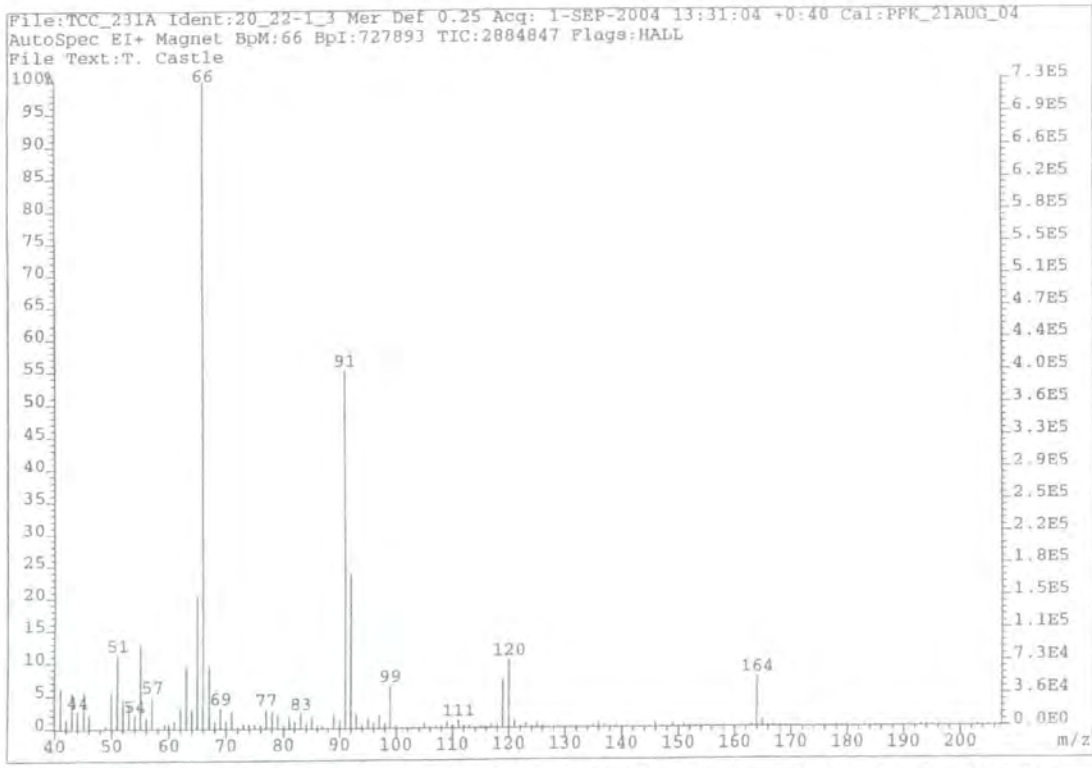
Appendix 2.3.2 - ^{31}P NMR spectrum of PEO ruthenium macroinitiator (M_n of PEO = 2300 g mol^{-1}) in C_6D_6.



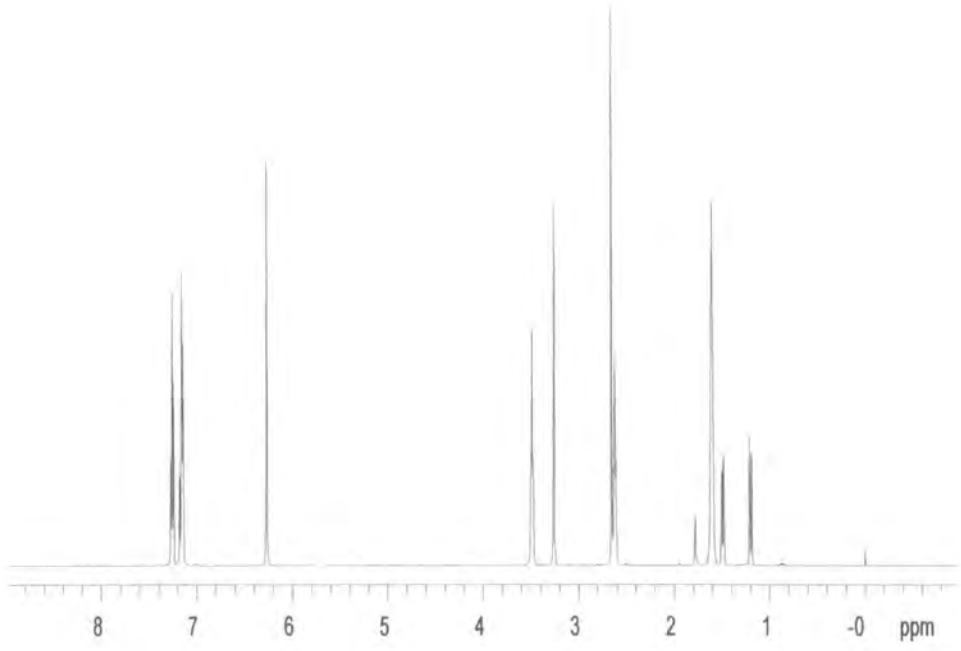
Appendix 2.3.3 - ^{13}C NMR spectrum of PEO ruthenium macroinitiator (M_n of PEO = 2300 g mol^{-1}) in C_6D_6.



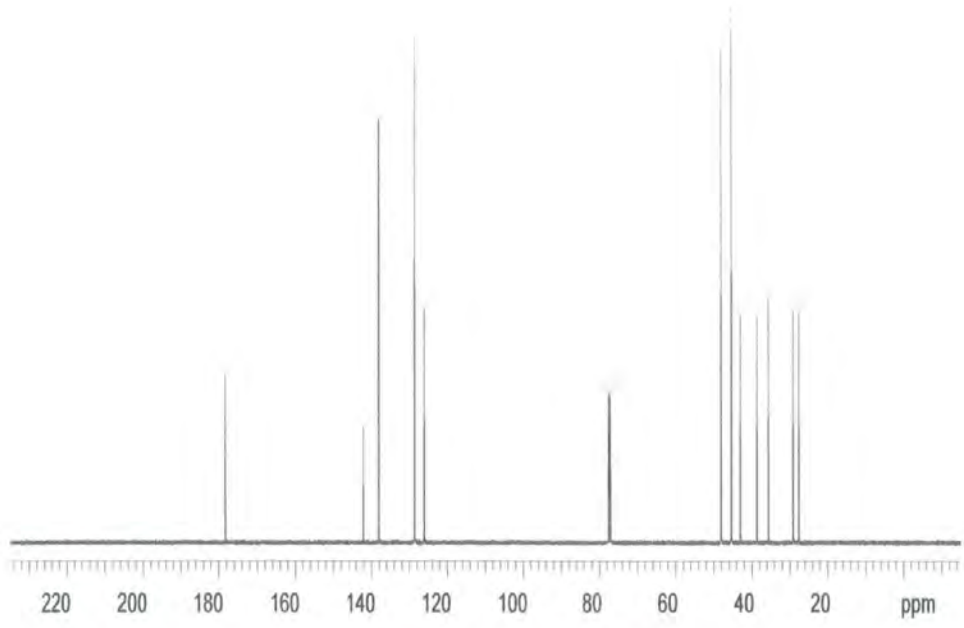
Appendix 2.4.1 - ^{13}C NMR spectrum of *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride in acetone-d_6.



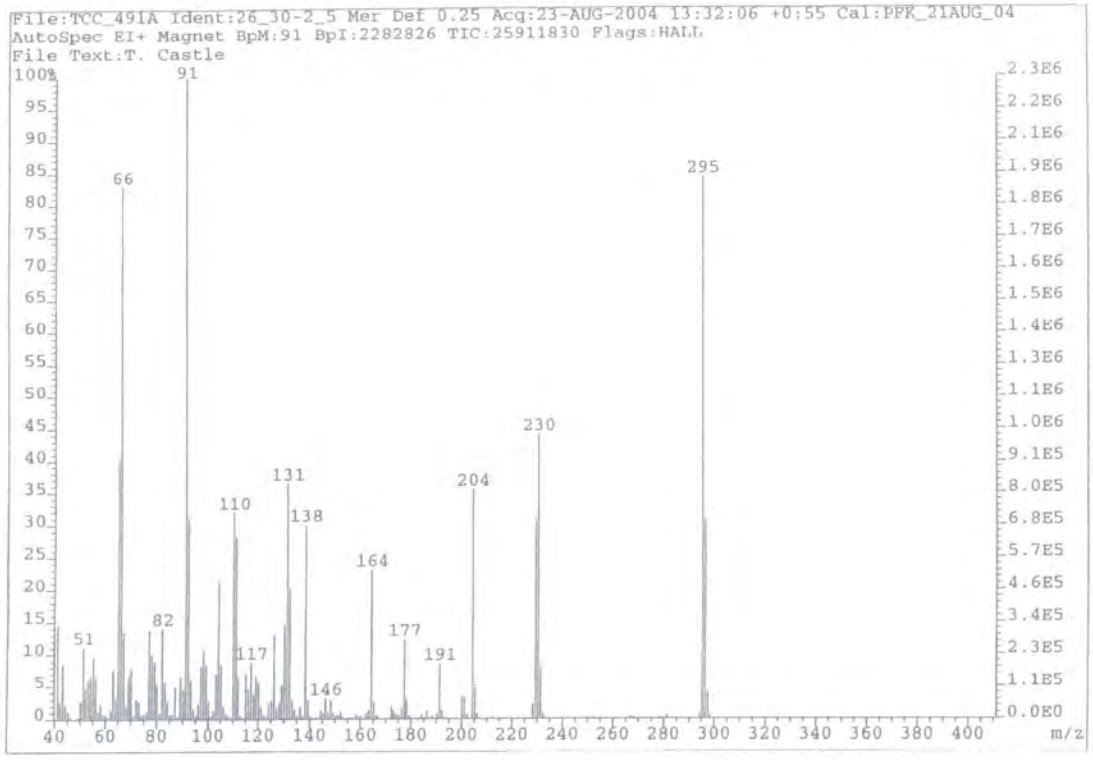
Appendix 2.4.2 – EI-MS spectrum of *exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxy anhydride.



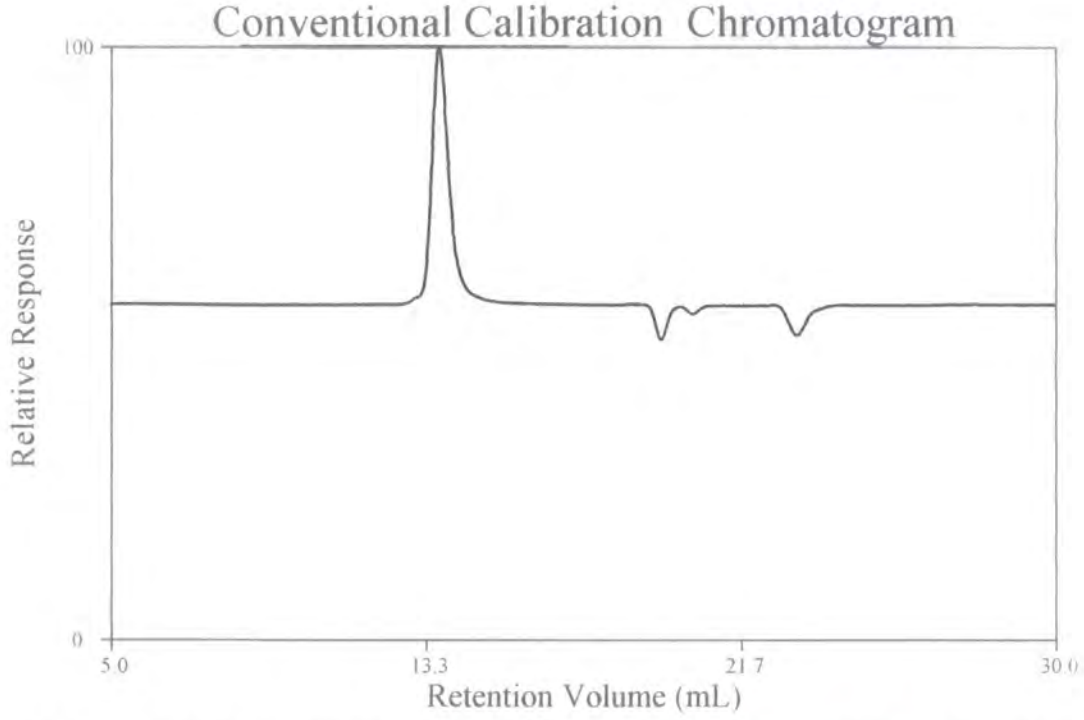
Appendix 2.4.3 – ^{1}H NMR spectrum of *exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (NBE Monomer A) in $CDCl_3$.



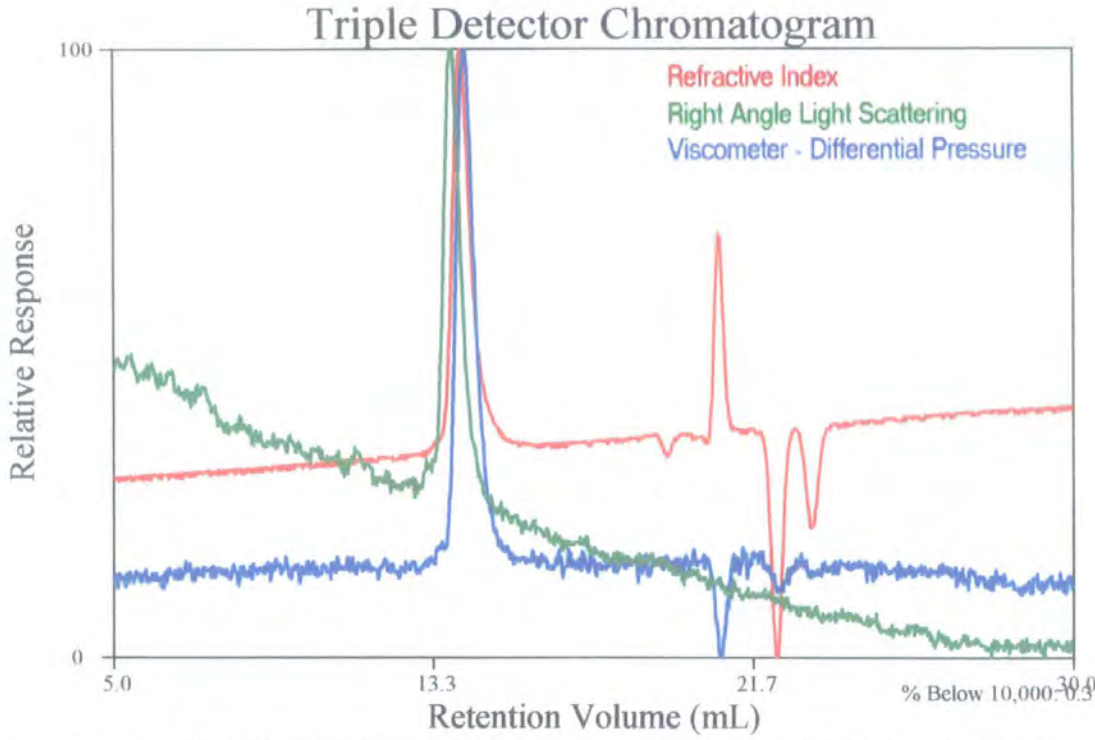
Appendix 2.4.4 – ^{13}C NMR spectrum of *exo-N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide (NBE Monomer A) in $CDCl_3$.



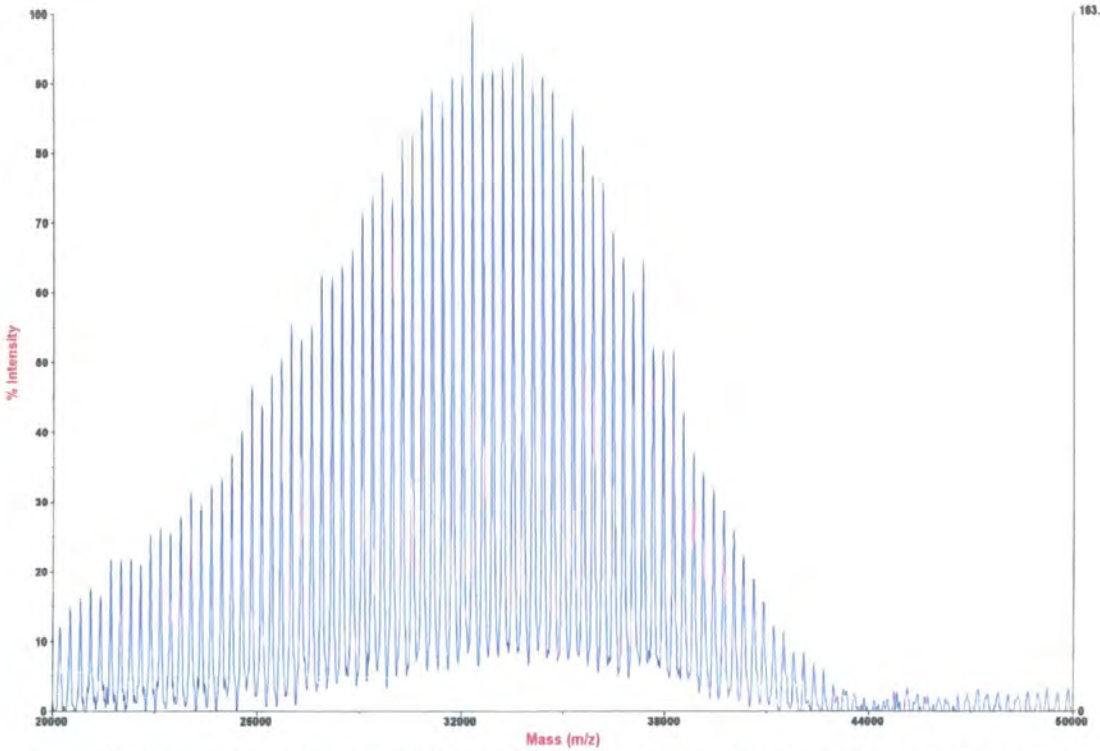
Appendix 2.4.5 – EI-MS spectrum of exo-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide – NBE Monomer A (in $CDCl_3$).



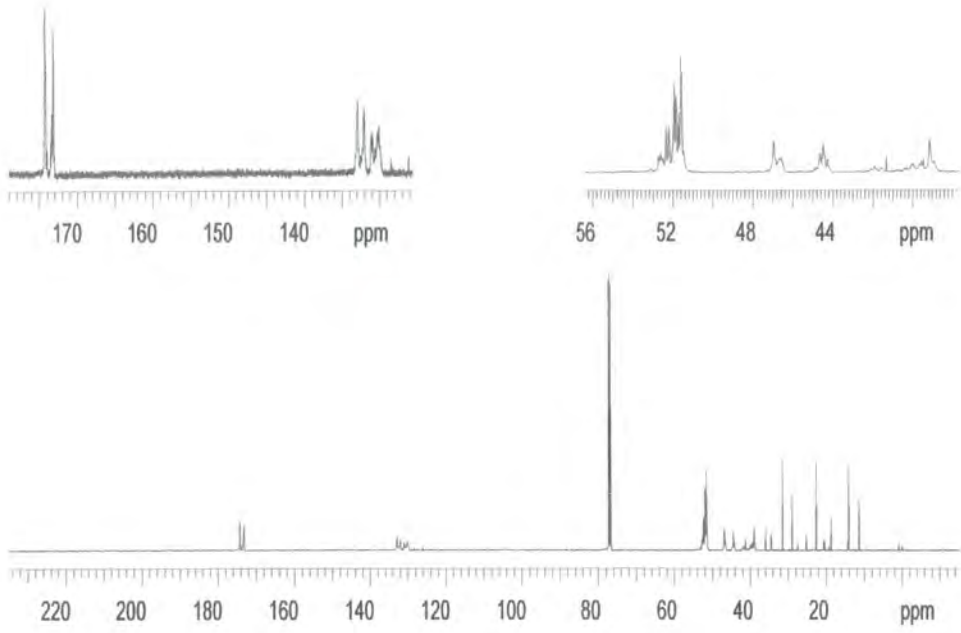
Appendix 2.5.1 GPC (DMF eluent) of poly(*exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide) (PNB A). M_n: 11000 g mol^{-1}, PDI: 1.11.



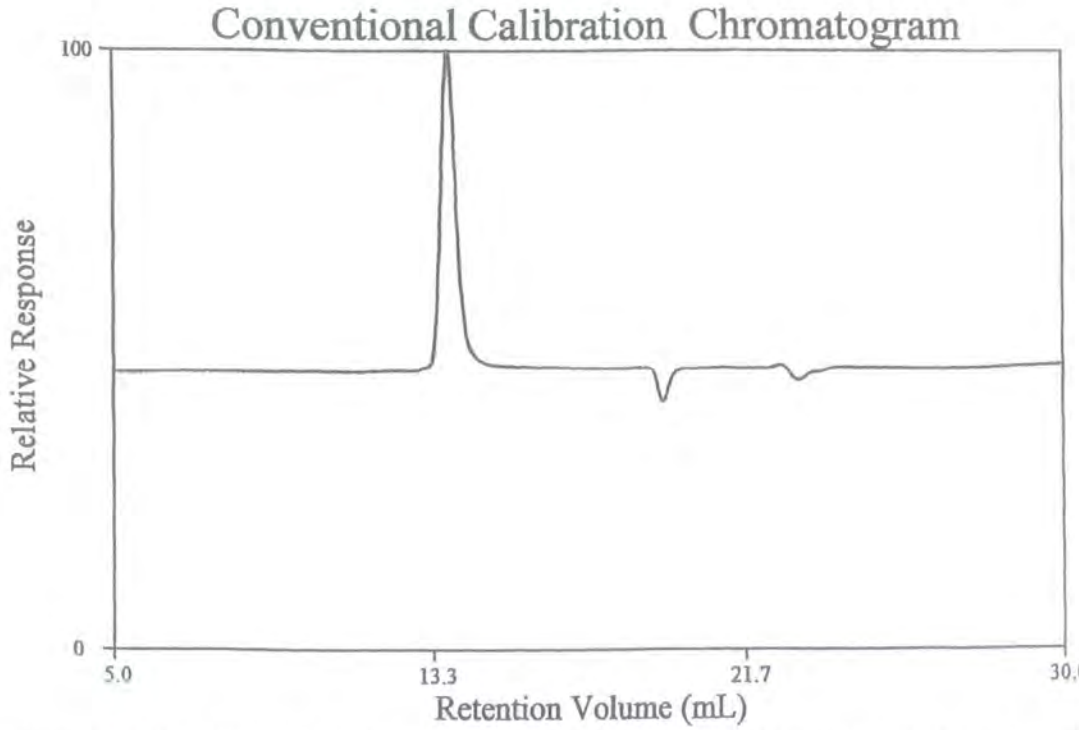
Appendix 2.5.2 GPC (THF eluent) of poly(*exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide) (PNB A). M_n: 18000 g mol^{-1}, PDI: 1.06.



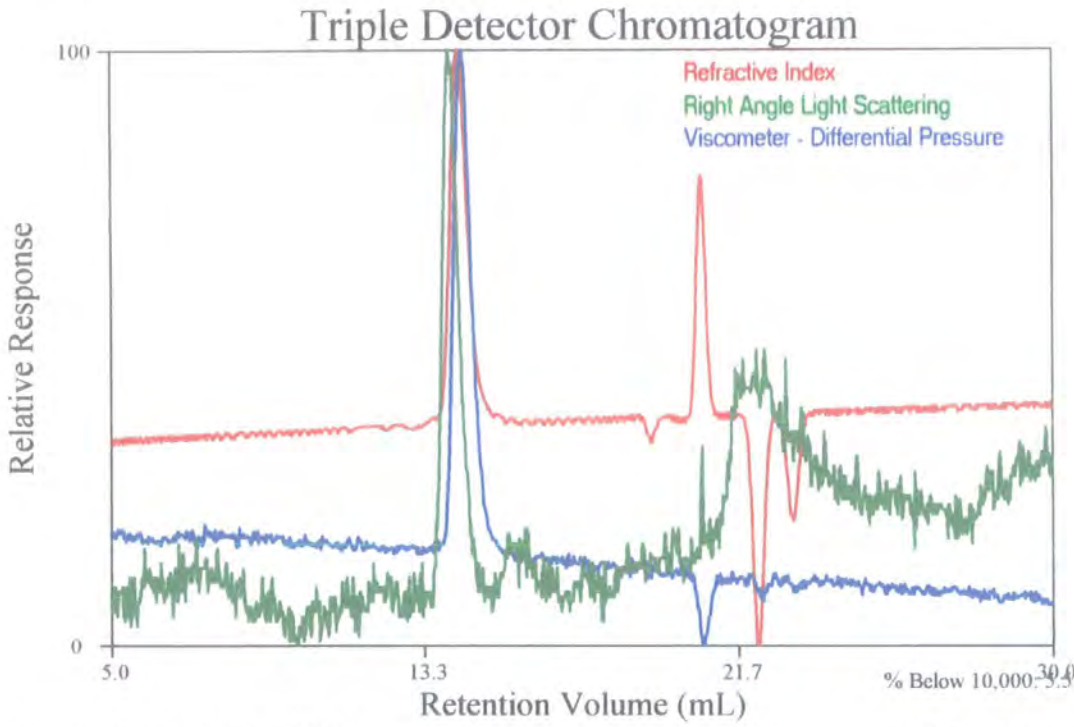
Appendix 2.5.3 MALDI MS spectrum of poly(*exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide) (PNB A). M_n: 32000 g mol^{-1}, PDI: 1.03.



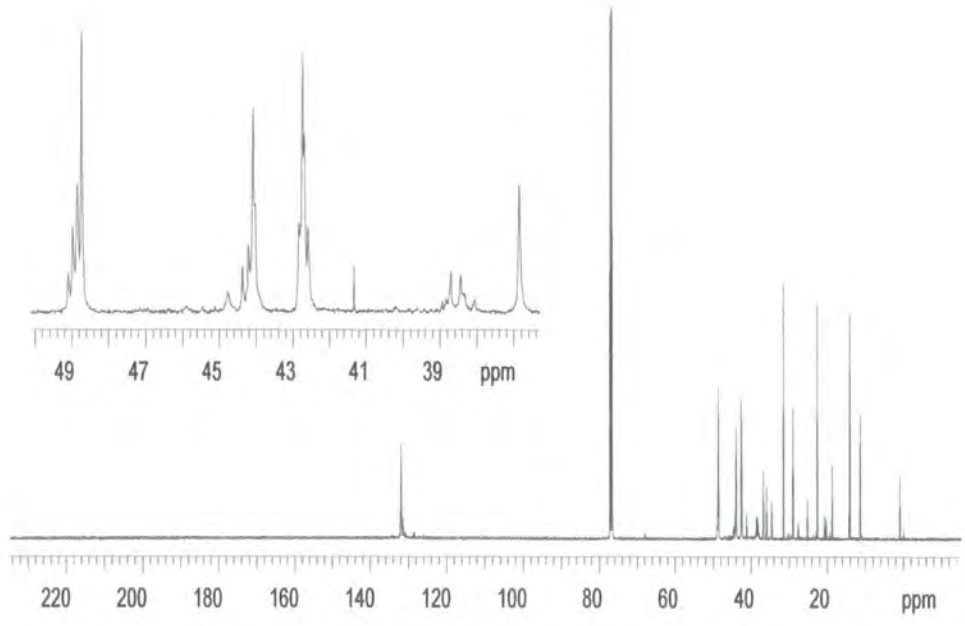
Appendix 2.5.4 - ^{13}C NMR spectrum of poly(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) (PNB B) in $CDCl_3$.



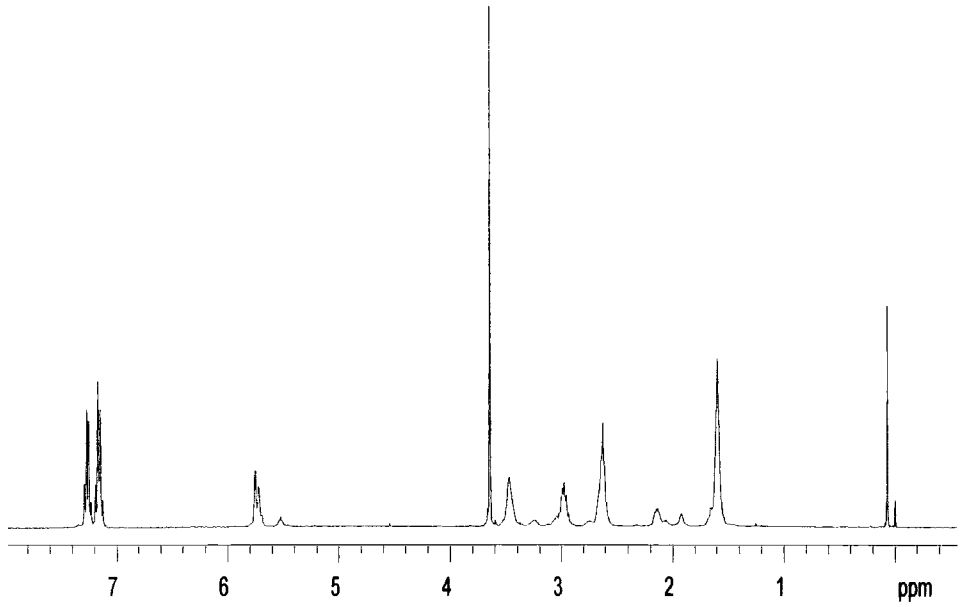
Appendix 2.5.5 - GPC (DMF eluent) of poly(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) (PNB B). M_n: 17600 g mol^{-1}, PDI: 1.05.



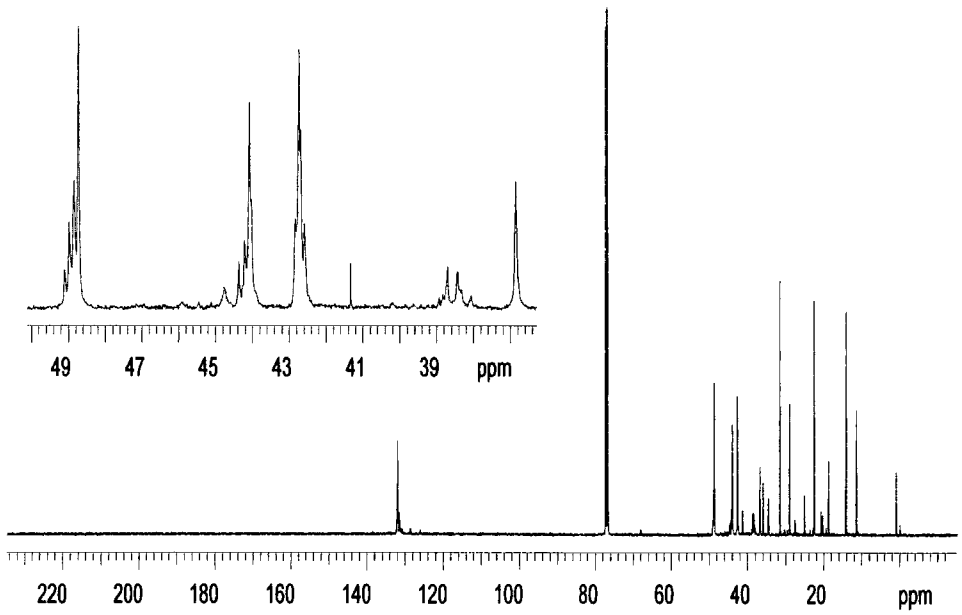
Appendix 2.5.6 - GPC (THF eluent) of poly(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) (PNB B). M_n: 12700 g mol^{-1}, PDI: 1.02.



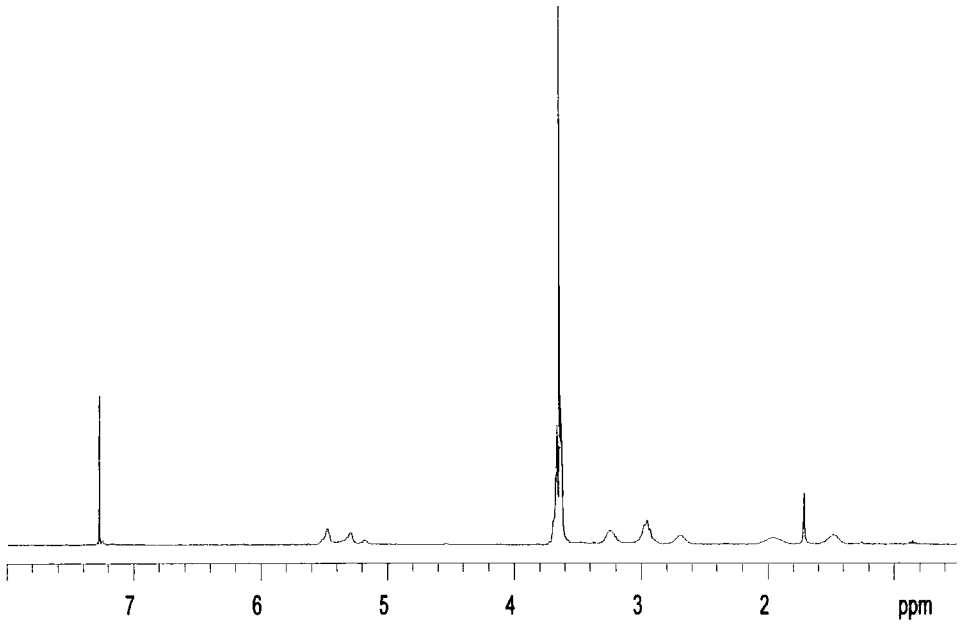
Appendix 2.5.7 - ^{13}C NMR spectrum of poly(*endo,endo*-5,6-bis[chloromethyl]bicyclo[2.2.1]hept-2-ene) (PNB C) in $CDCl_3$.



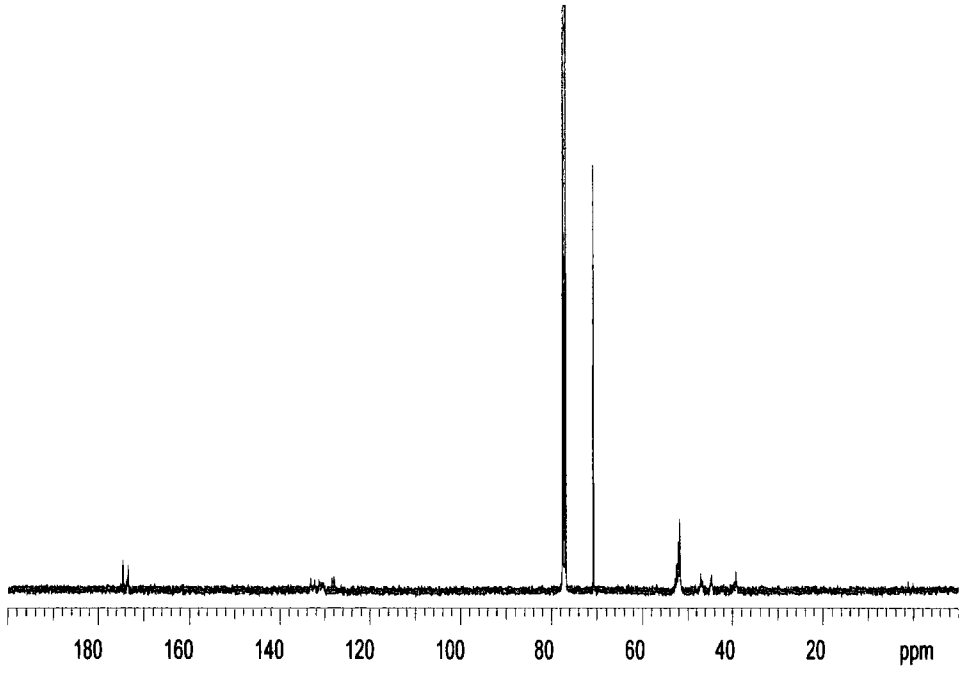
Appendix 2.6.1 - ^{1}H NMR spectrum of poly(ethylene oxide)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide) in $CDCl_3$. Sample PEOPNB 1, Table 2.3 [PEO (DP = 55) - PNB A (DP = 100)].



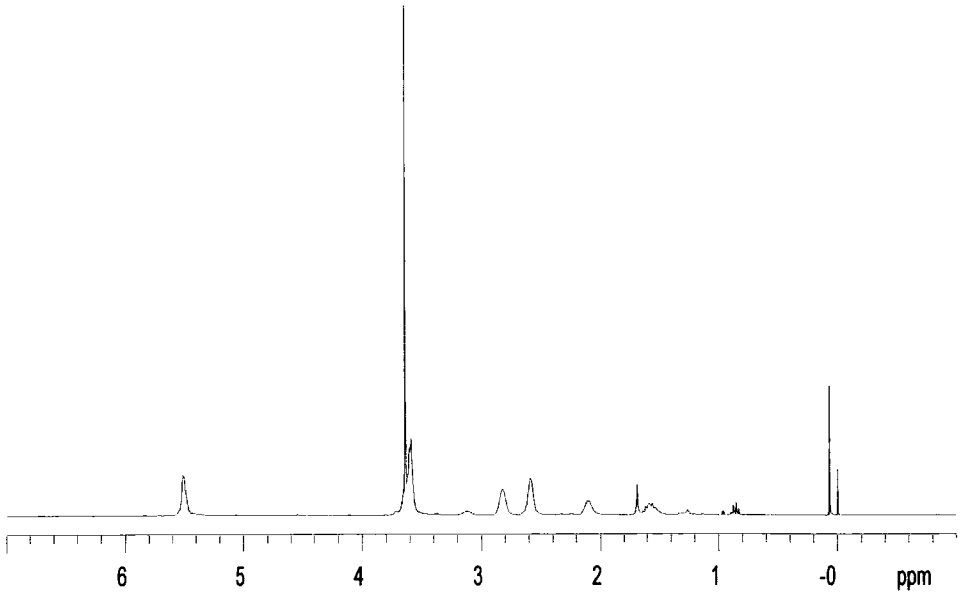
Appendix 2.6.2 - ^{13}C NMR spectrum of poly(ethylene oxide)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide) in $CDCl_3$. Sample PEOPNB 1, Table 2.3 [PEO (DP = 55) - PNB A (DP = 100)].



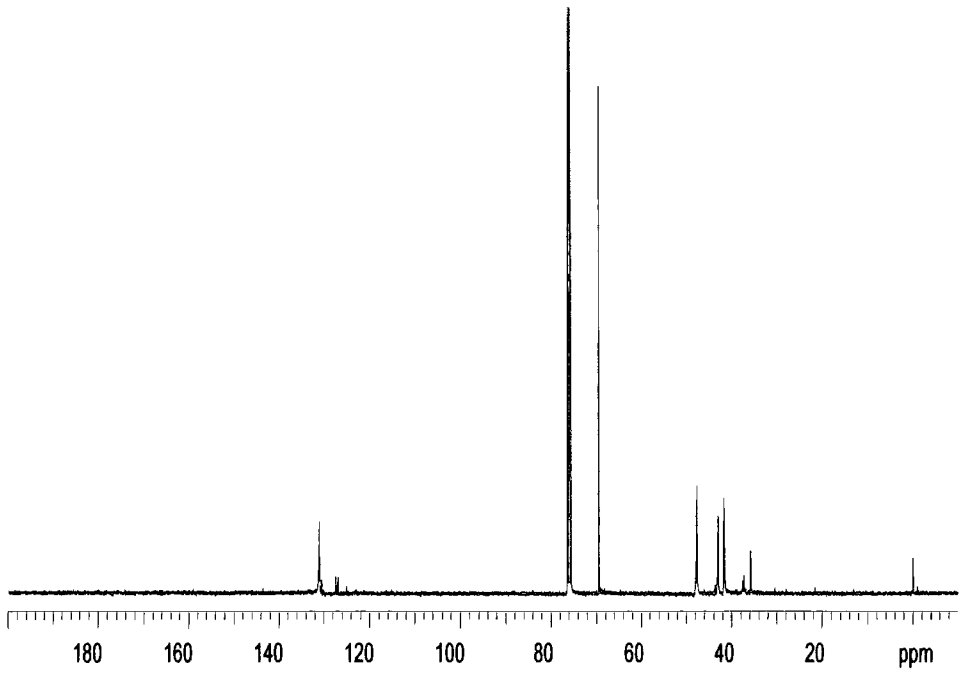
Appendix 2.6.3 - ^{1}H NMR spectrum of poly(ethylene oxide)-*block*-(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) in $CDCl_3$. Sample PEOPNB 8, Table 2.3 [PEO (DP = 55) - PNB B (DP = 100)].



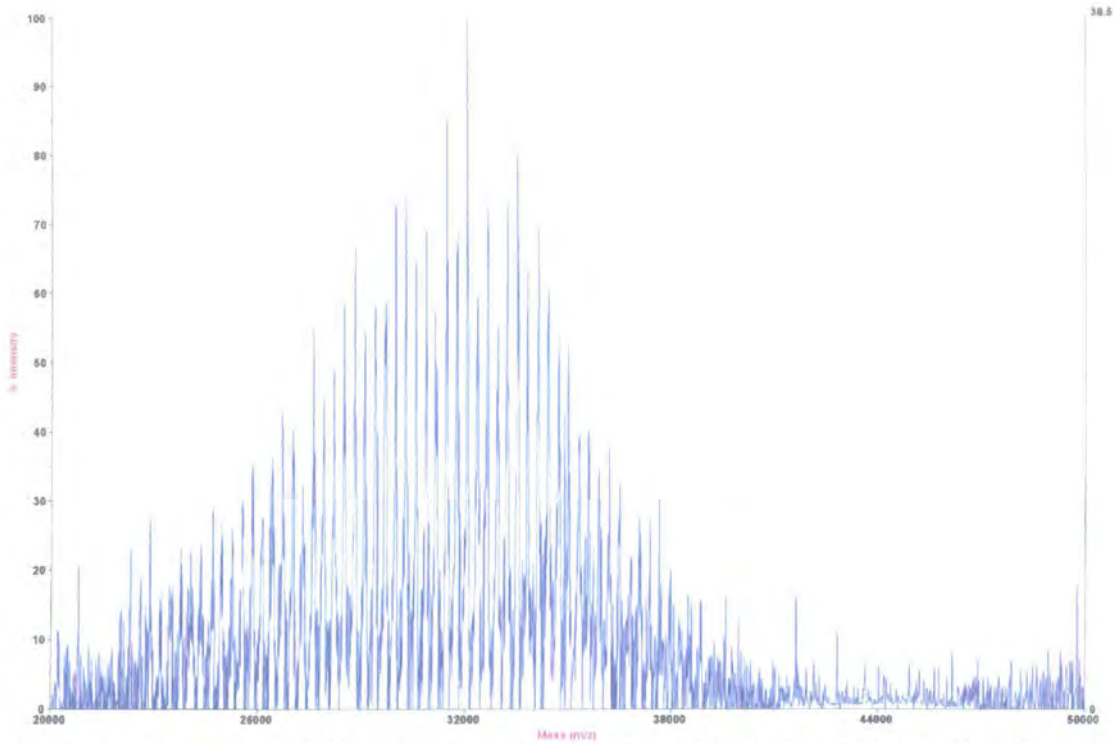
Appendix 2.6.4 - ^{13}C NMR spectrum of poly(ethylene oxide)-*block*-(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) in $CDCl_3$. Sample PEOPNB 8, Table 2.3 [PEO (DP = 55) - PNB B (DP = 100)].



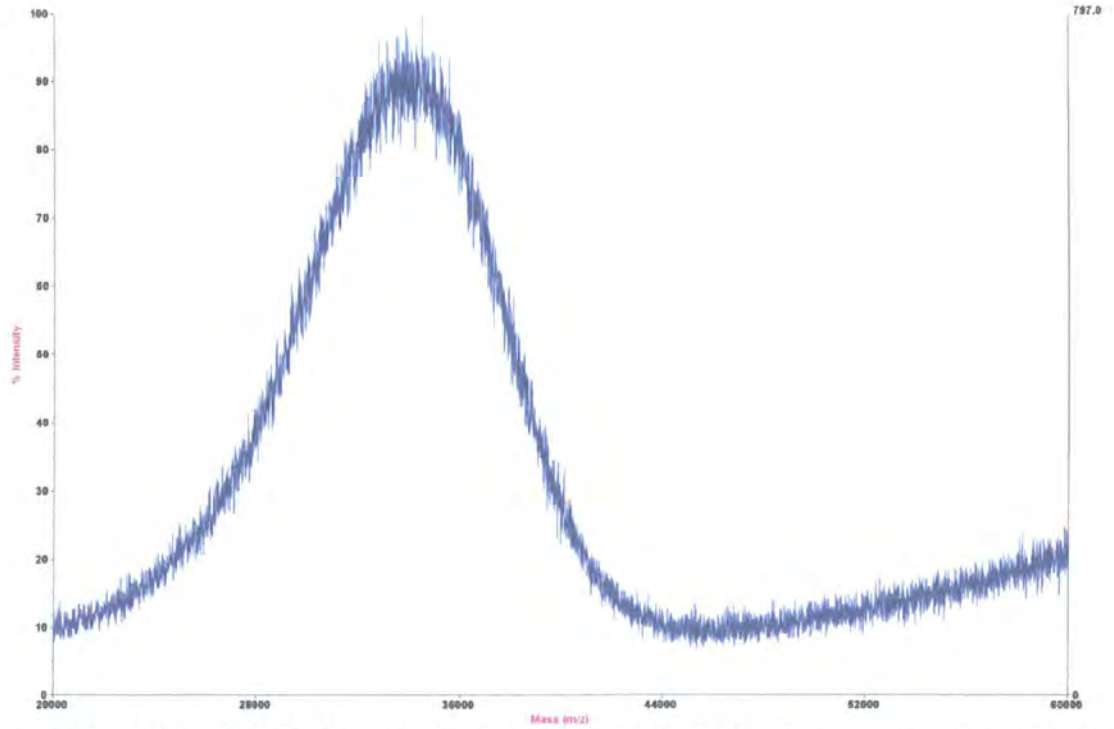
Appendix 2.6.5 - ^{1}H NMR spectrum of poly(ethylene oxide)-*block*-(*endo*,*endo*-5,6-bis-chloromethyl-bicyclo[2.2.1]hept-2-ene) in $CDCl_3$. Sample PEOPNB 11, Table 2.3 [PEO (DP = 55) - PNB C (DP = 100)].



Appendix 2.6.6 - ^{13}C NMR spectrum of poly(ethylene oxide)-*block*-(*endo*,*endo*-5,6-bis-chloromethyl-bicyclo[2.2.1]hept-2-ene) in $CDCl_3$. Sample PEOPNB 11, Table 2.3 [PEO (DP = 55) - PNB C (DP = 100)].



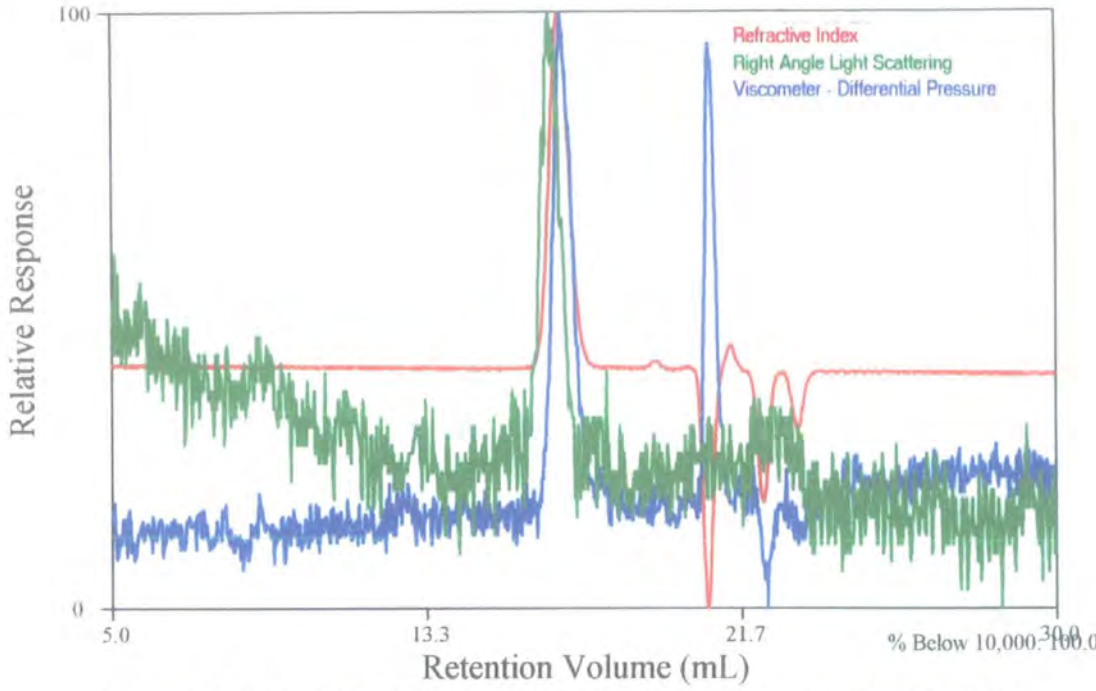
Appendix 2.6.7 - MALDI MS spectrum of poly(ethylene oxide)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide). Sample PEOPNB 1, Table 2.3 [PEO (DP = 55) - PNB A (DP = 100)]. Spectrum obtained using dithranol as the matrix. M_n: 31400 g mol^{-1}, PDI: 1.03.



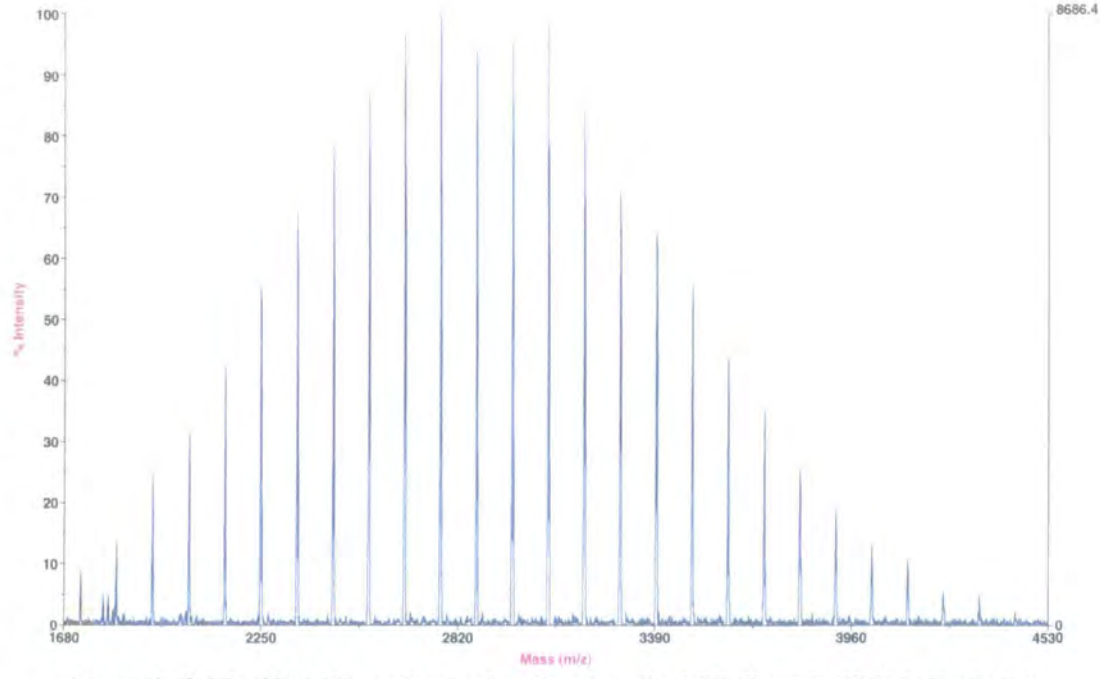
Appendix 2.6.8 - MALDI MS spectrum of poly(ethylene oxide)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide). Sample PEOPNB 1, Table 2.3 [PEO (DP = 55) - PNB A (DP = 100)]. Spectrum obtained using *trans*-3-indoleacrylic acid as the matrix. M_n = 33100 g mol^{-1}, PDI: 1.02.

Appendix 3

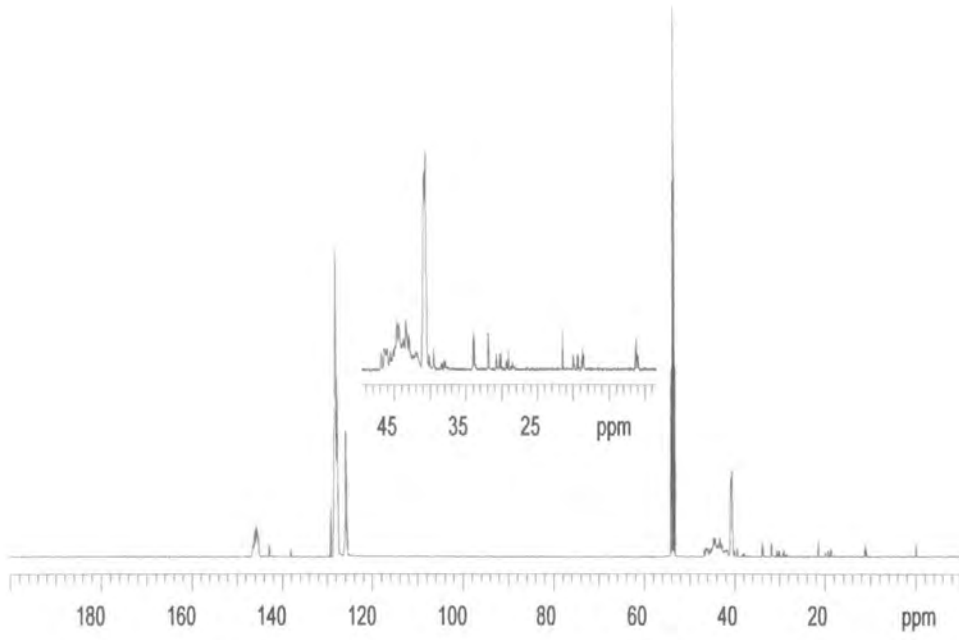
Appendices for Chapter 3



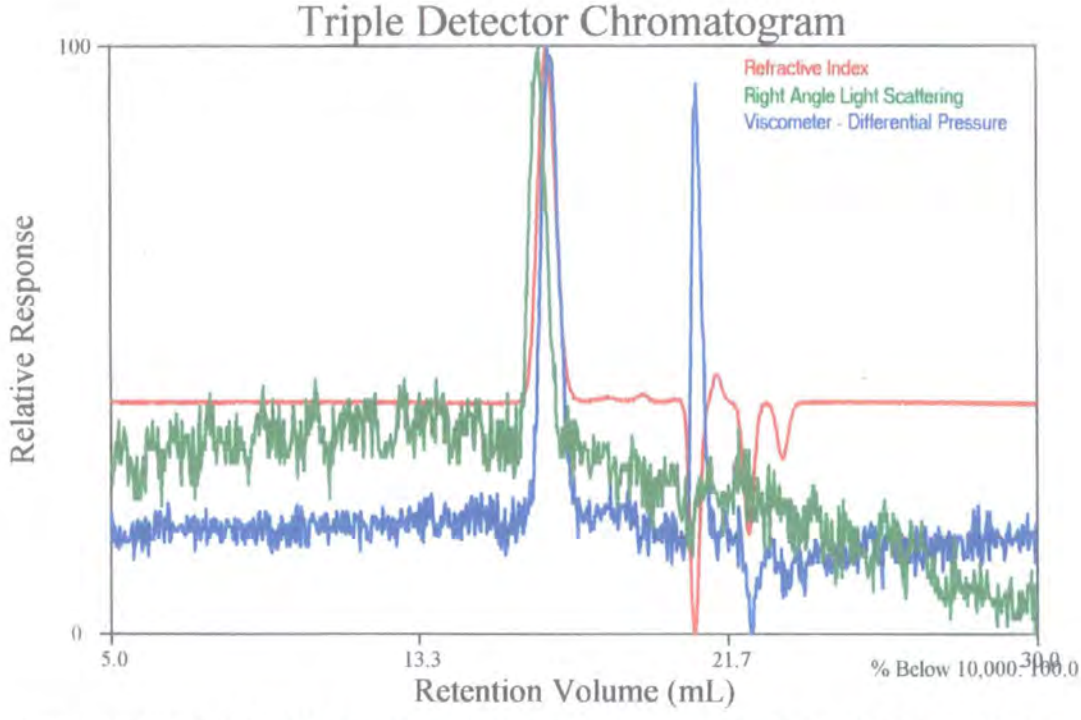
Appendix 3.1.1 - GPC in THF of unfunctionalised PS (Sample PS H 1, Table 3.1). M_n: 2850 g mol^{-1}, PDI: 1.02.



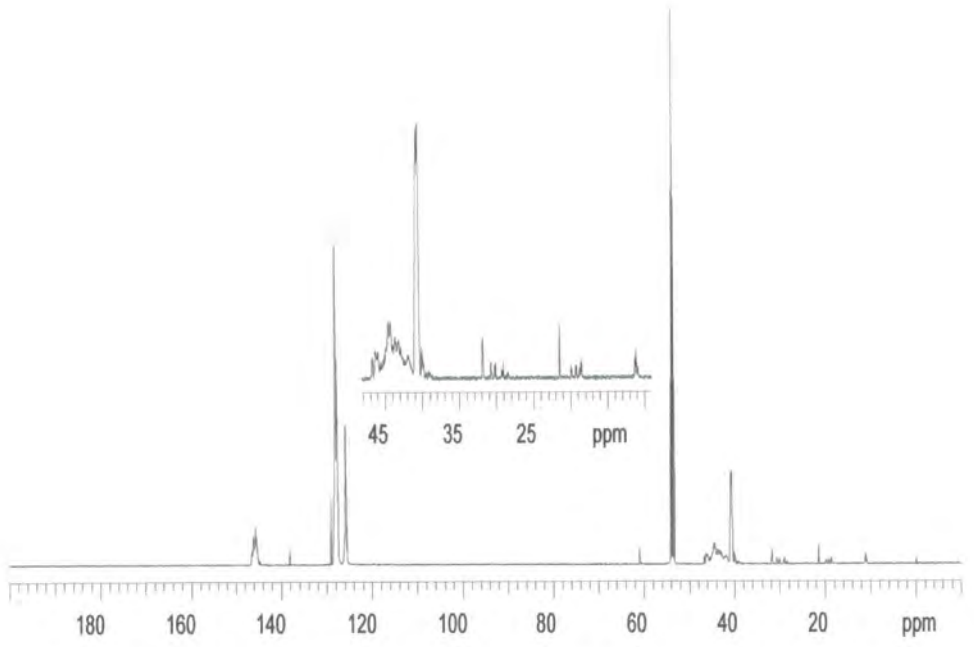
Appendix 3.1.2 - MALDI spectrum of unfunctionalised PS (Sample PS H 1, Table 3.1). M_n: 2950 g mol^{-1}, PDI: 1.04.



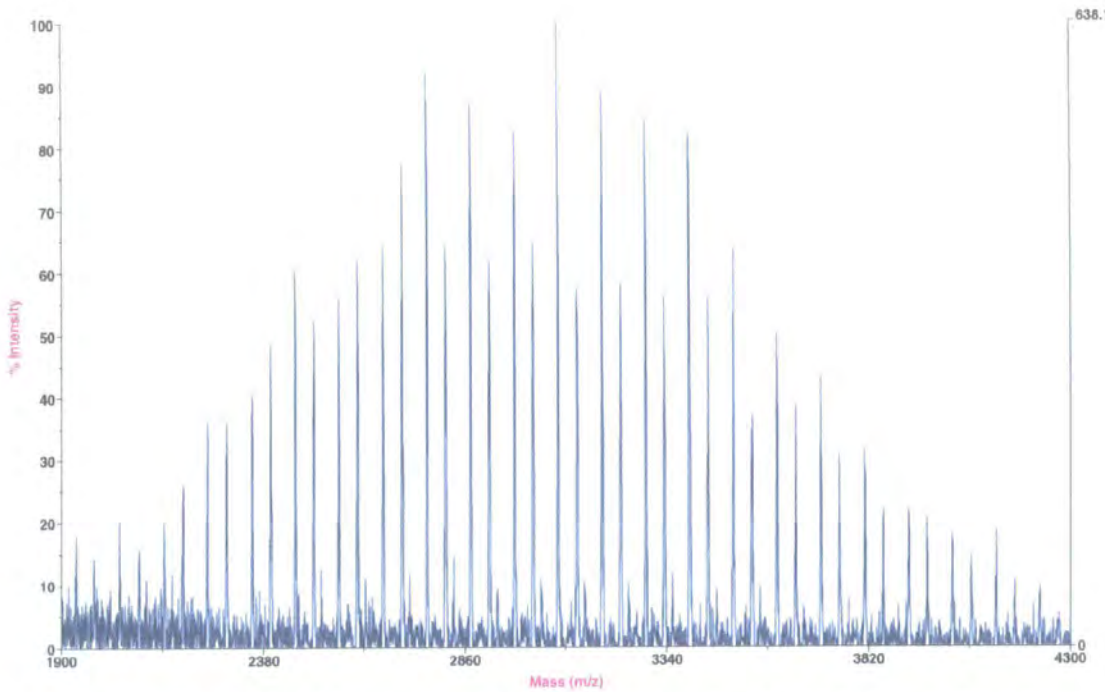
Appendix 3.1.3 - ^{13}C NMR spectrum of unfunctionalised PS (Sample PS H 1, Table 3.1) in CD_2Cl_2.



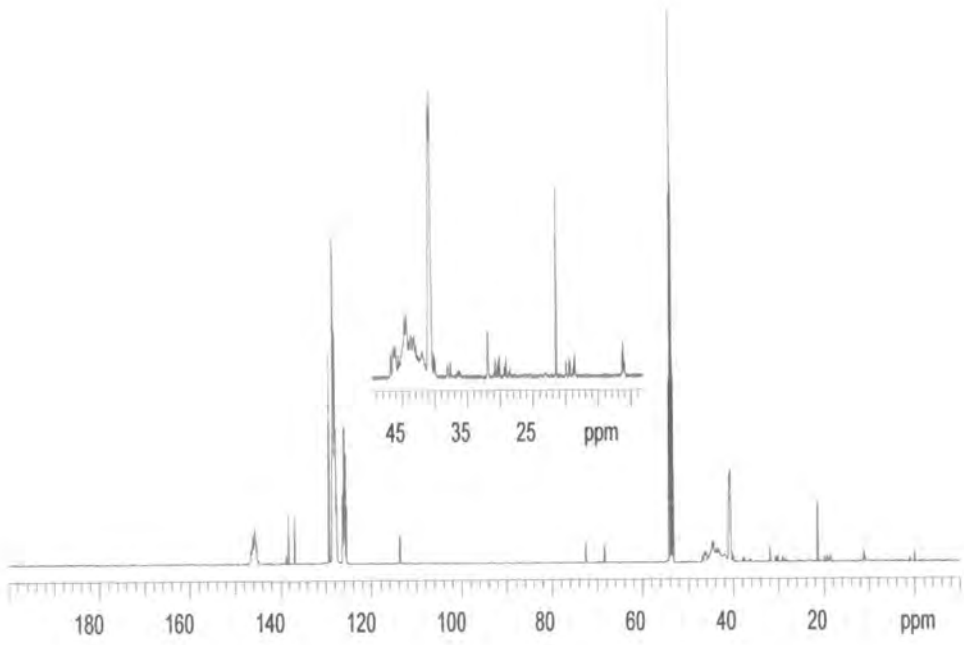
Appendix 3.1.4 GPC (THF eluent) of ethylene oxide functionalised PS (EO PS 1, Table 3.1). M_n: 2950 g mol^{-1}, PDI: 1.02.



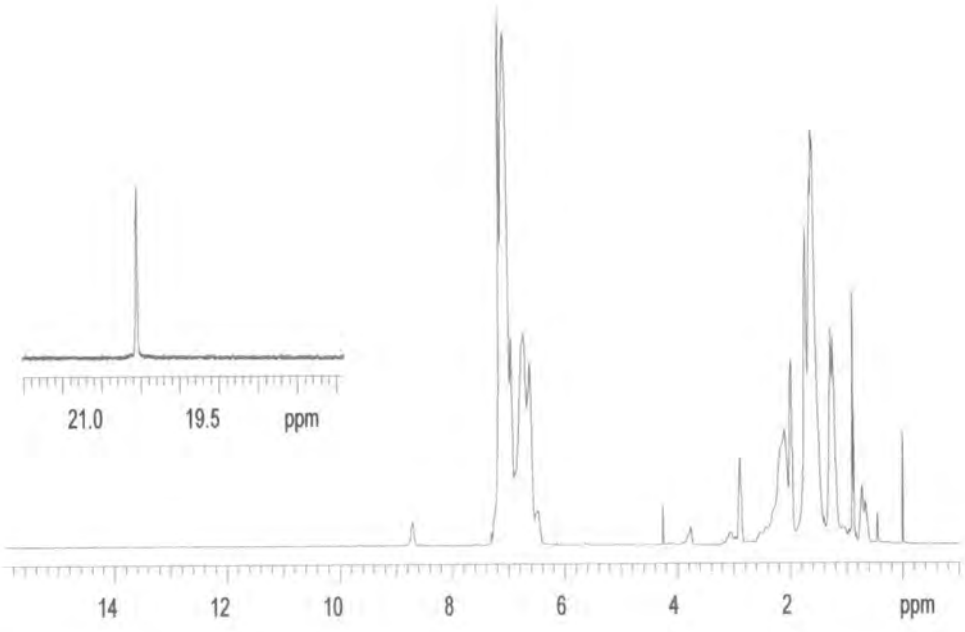
Appendix 3.1.5 - ^{13}C NMR spectrum of hydroxyethyl functionalised PS (Sample EO PS 1, Table 3.1) in CD_2Cl_2.



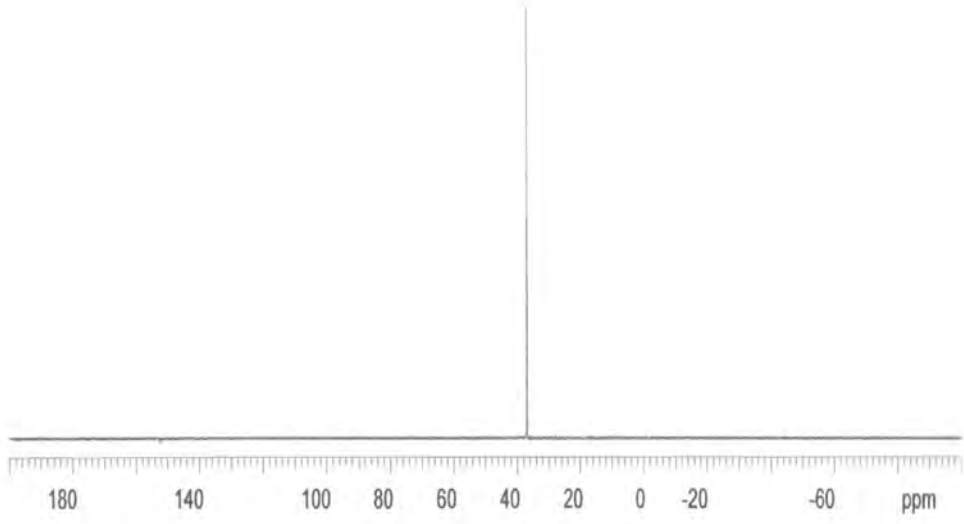
Appendix 3.1.6 - MALDI spectrum of hydroxyethyl functionalised PS (Sample EO PS 1, Table 3.1). M_n: 3000 g mol^{-1}, PDI: 1.03.



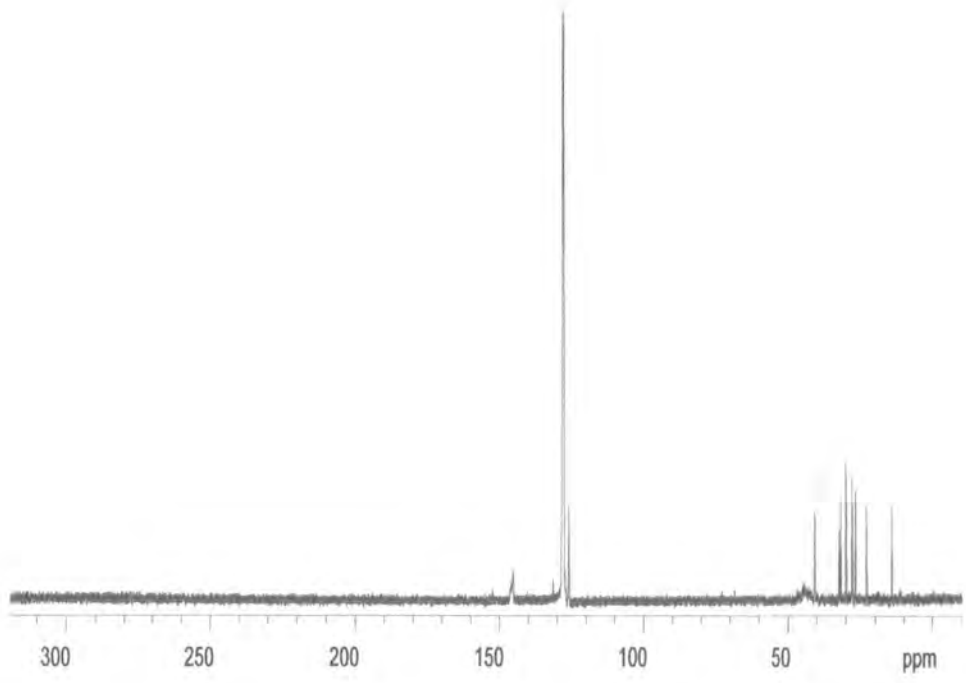
Appendix 3.1.7 - ^{13}C NMR spectrum of PS Macromonomer in CD_2Cl_2 (Synthesised using K metal and Sample EO PS 1, Table 3.1).



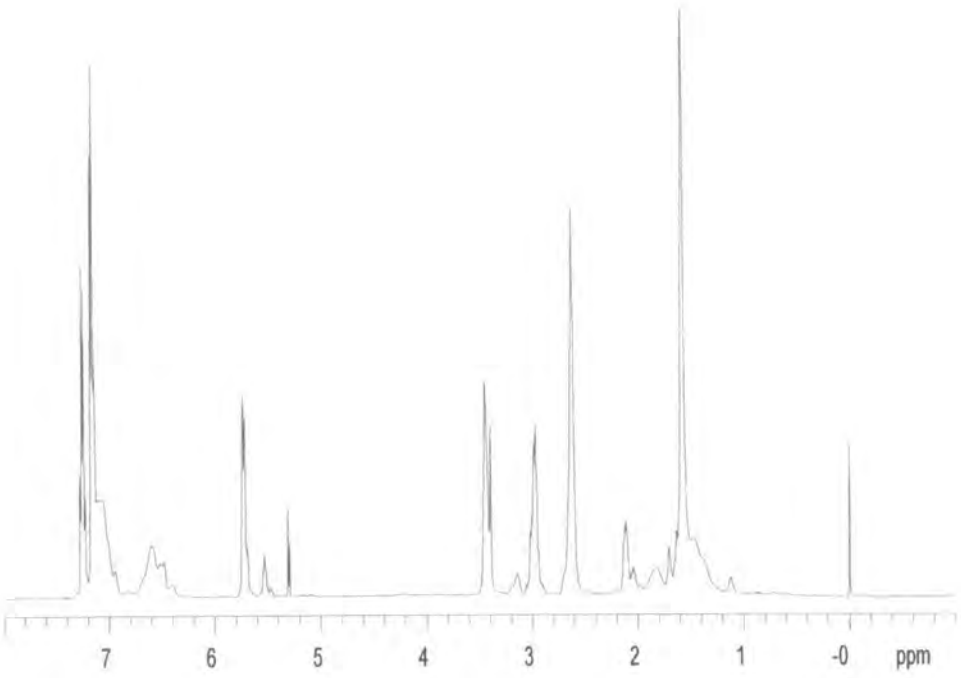
Appendix 3.2.1 - ^{1}H NMR spectrum of PS ruthenium macroinitiator (M_n of PS = 2900 g mol^{-1}) in C_6D_6.



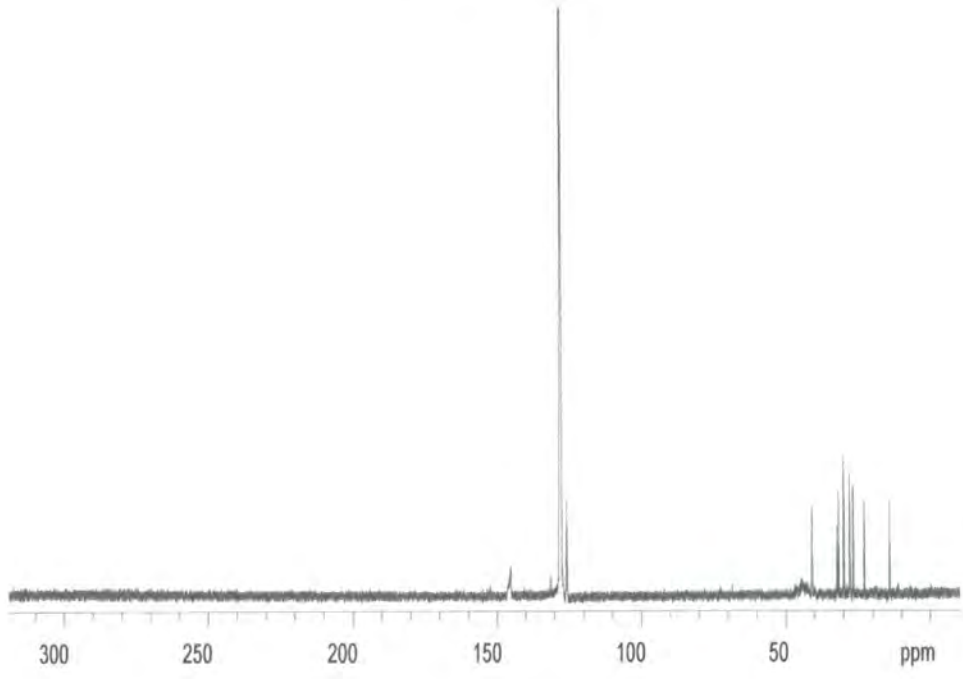
Appendix 3.2.2 - ^{31}P NMR spectrum of PS ruthenium macroinitiator (M_n of PS = 2900 g mol^{-1}) in C_6D_6.



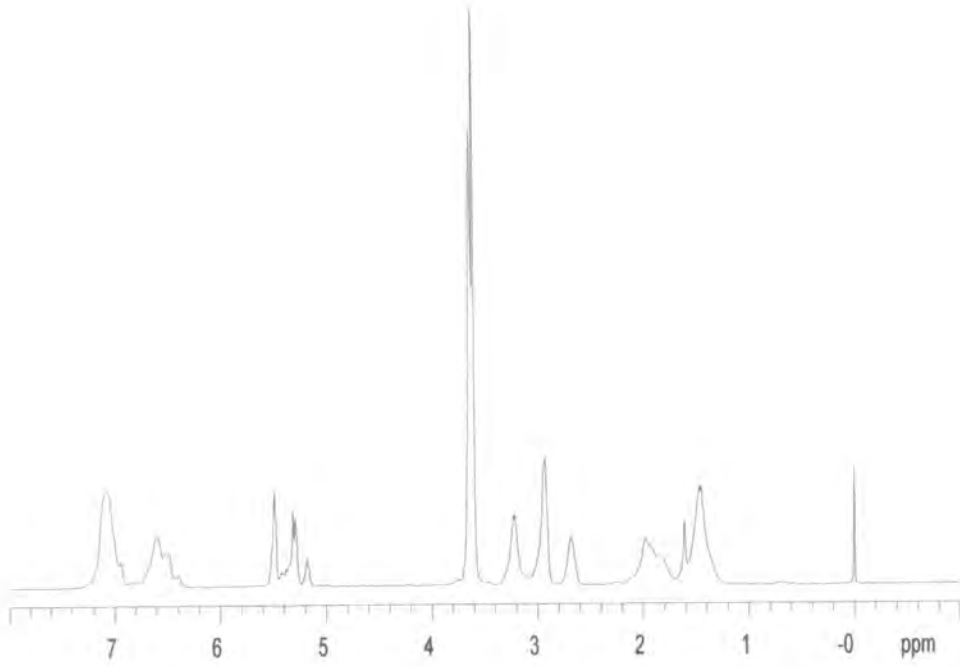
Appendix 3.2.3 - ^{13}C NMR spectrum of PS ruthenium macroinitiator (M_n of PS = 2900 g mol^{-1}) in C_6D_6.



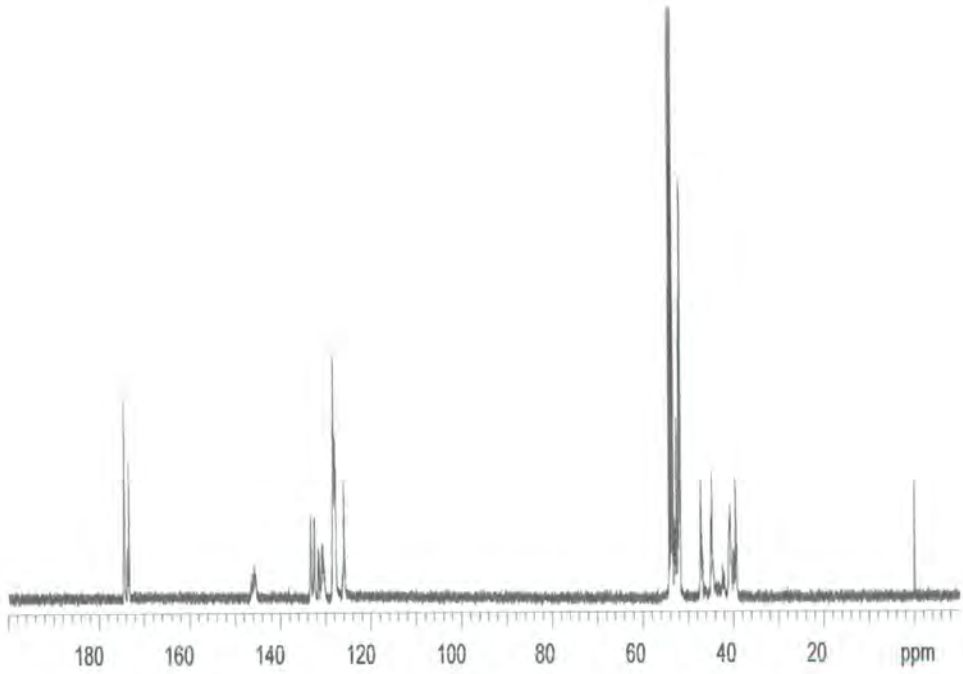
Appendix 3.3.1 - ^{1}H NMR spectrum of poly(styrene)-*block*-(*exo*-*N*-phenylbutylbicyclo[2.2.1]hept-5-ene-2,3-dicarboxyimide) in CD_2Cl_2. Sample PSPNB 3, Table 3.2 [PS (DP = 100) - PNB A (DP = 100)].



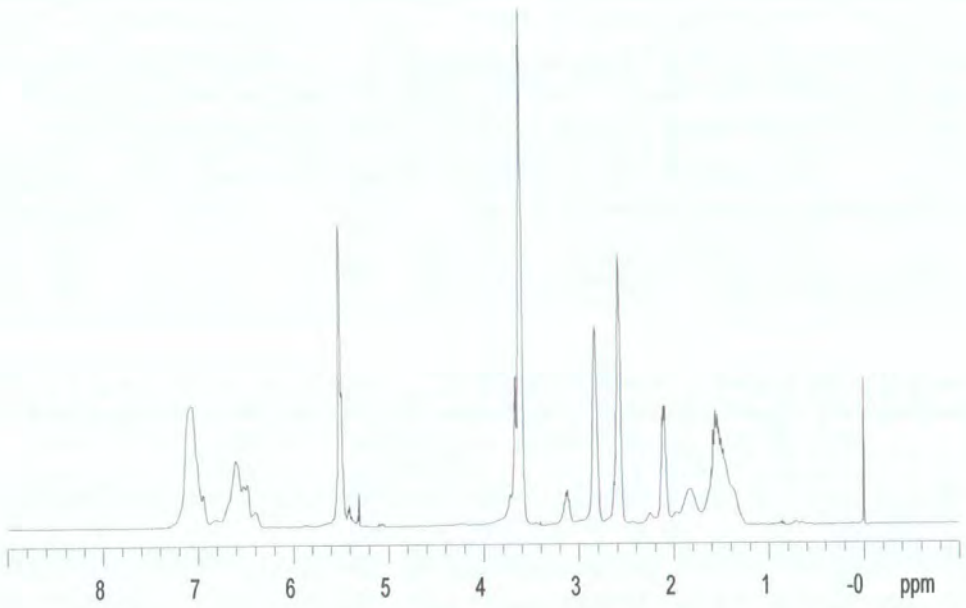
Appendix 3.3.2 - ^{13}C NMR spectrum of poly(styrene)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide) in CD_2Cl_2. Sample PSPNB 3, Table 3.2 [PS (DP = 100) - PNB A (DP = 100)].



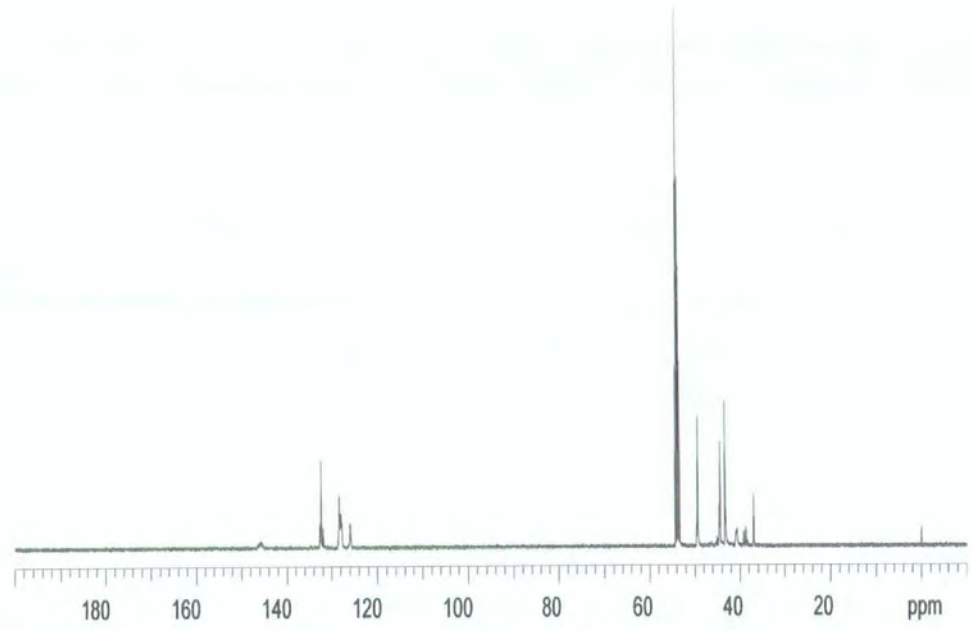
Appendix 3.3.3 - ^{1}H NMR spectrum of poly(styrene)-*block*-(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) in CD_2Cl_2. Sample PSPNB 8, Table 3.2 [PS (DP = 100) - PNB B (DP = 100)].



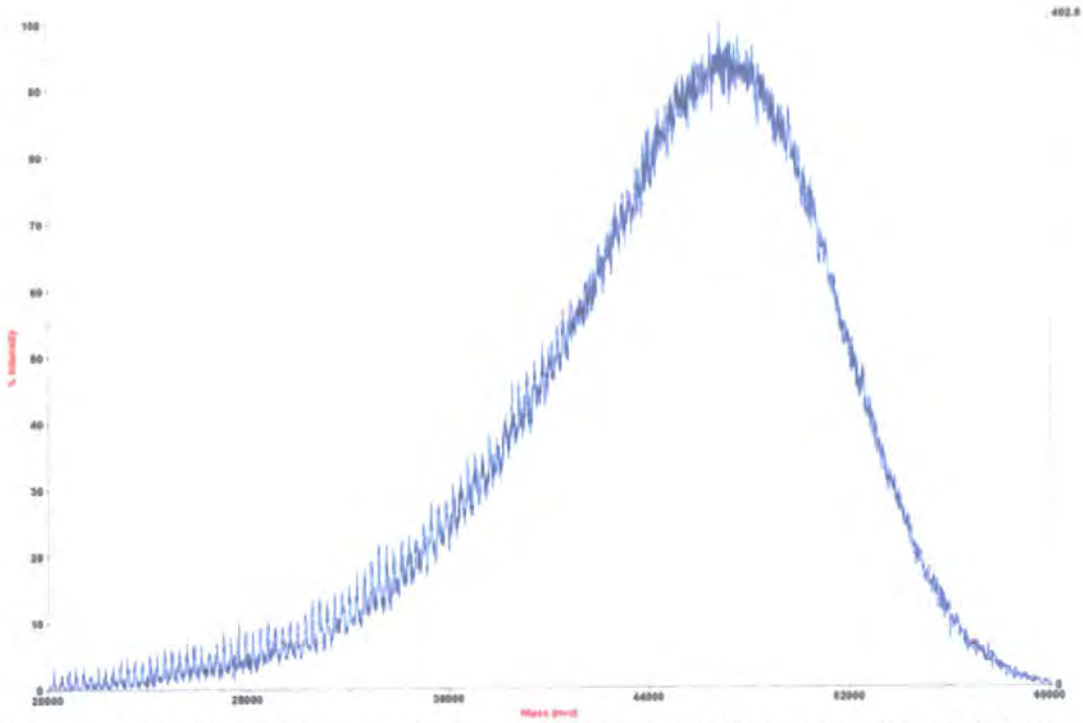
Appendix 3.3.4 - ^{13}C NMR spectrum of poly(styrene)-*block*-(*endo,exo*-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid dimethyl ester) in CD_2Cl_2. Sample PSPNB 8, Table 3.2 [PS (DP = 100) - PNB B (DP = 100)].



Appendix 3.3.5 - ^{1}H NMR spectrum of poly(styrene)-*block*-(*endo*,*endo*-5,6-bis[chloromethyl] bicyclo[2.2.1]hept-2-ene) in CD_2Cl_2. Sample PSPNB 10, Table 3.2 [PS (DP = 100) - PNB C (DP = 100)].



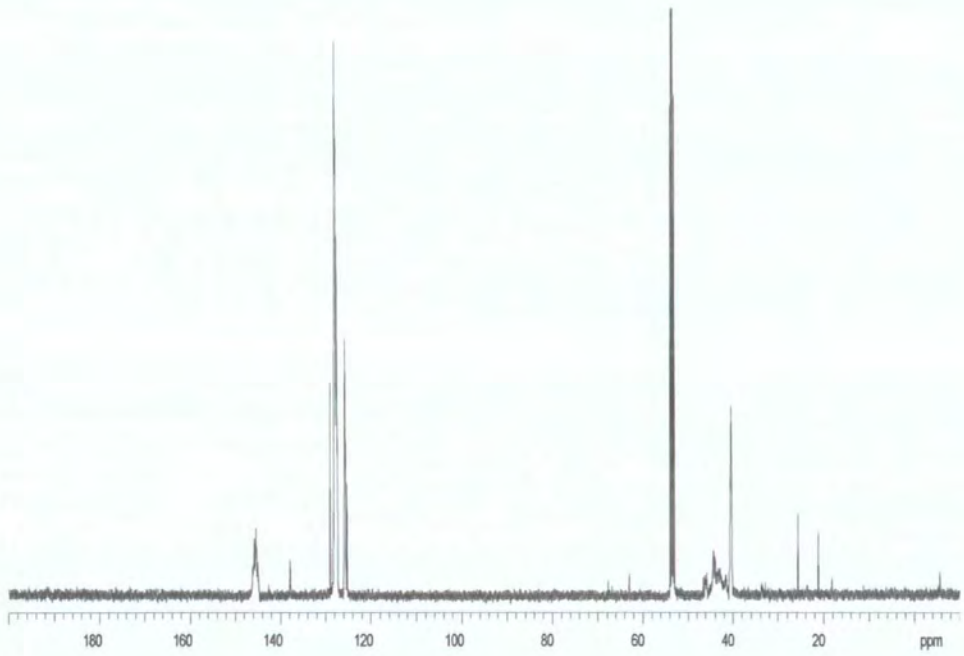
Appendix 3.3.6 - ^{13}C NMR spectrum of poly(styrene)-*block*-(*endo*,*endo*-5,6-bis[chloromethyl] bicyclo[2.2.1]hept-2-ene) in CD_2Cl_2. Sample PSPNB 10, Table 3.2 [PS (DP = 100) - PNB C (DP = 100)].



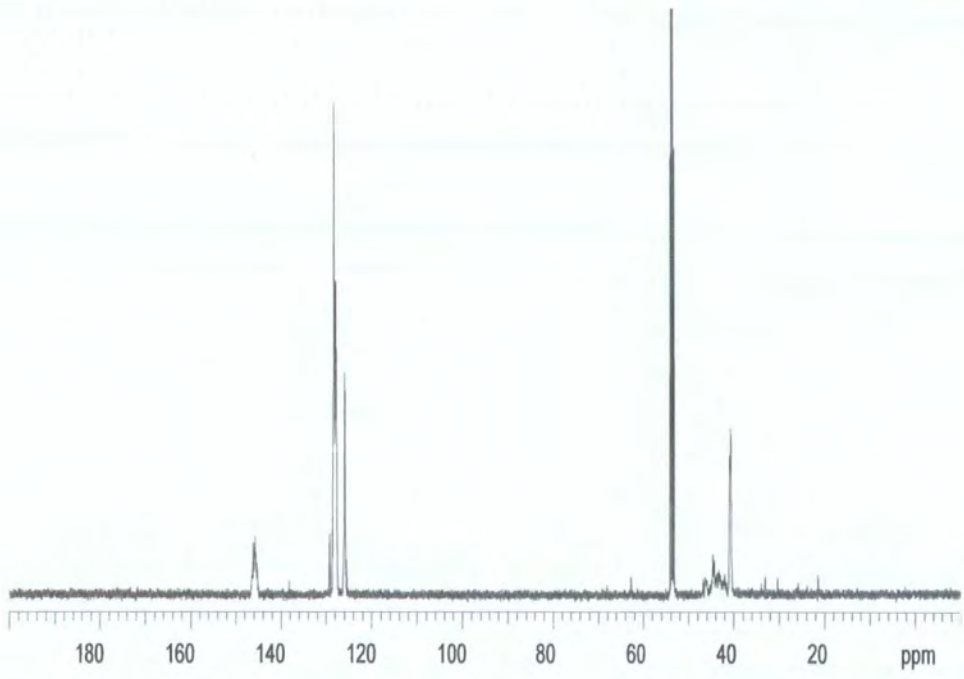
Appendix 3.3.7 – MALDI spectrum of poly(styrene)-*block*-(*exo*-*N*-phenylbutylbicyclo [2.2.1]hept-5-ene-2,3-dicarboxyimide). Sample PSPNB 3, Table 3.2 [PS (DP = 100) - PNB A (DP = 100)]. M_n: 44300 g mol^{-1}, PDI: 1.02.

Appendix 4

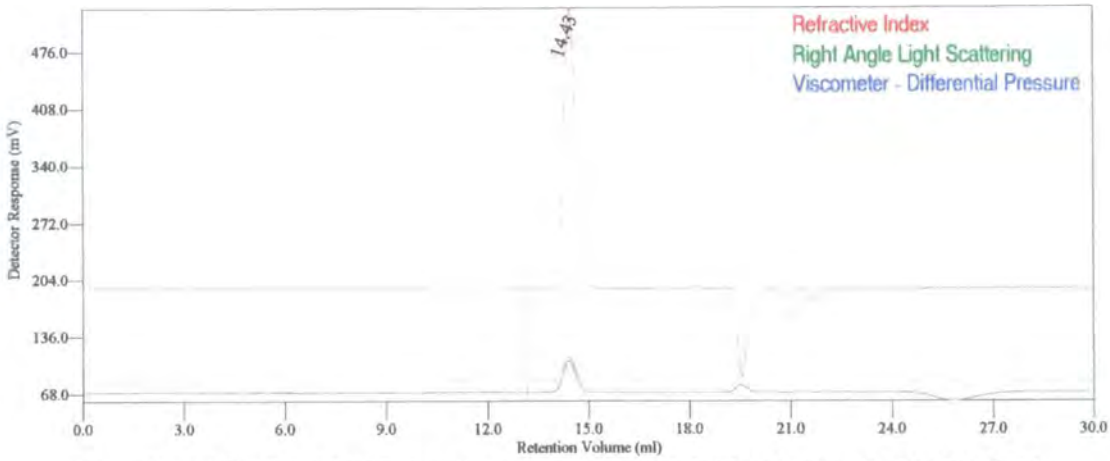
Appendices for Chapter 4



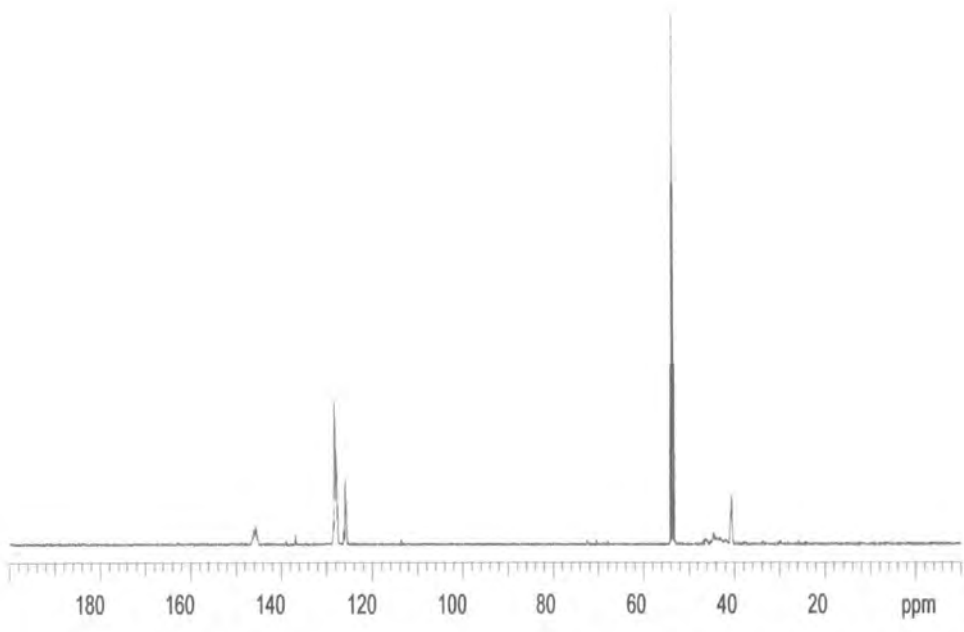
Appendix 4.1.1 - ^{13}C NMR spectrum of PS initiated using TBDMSO-PrLi in CD_2Cl_2.



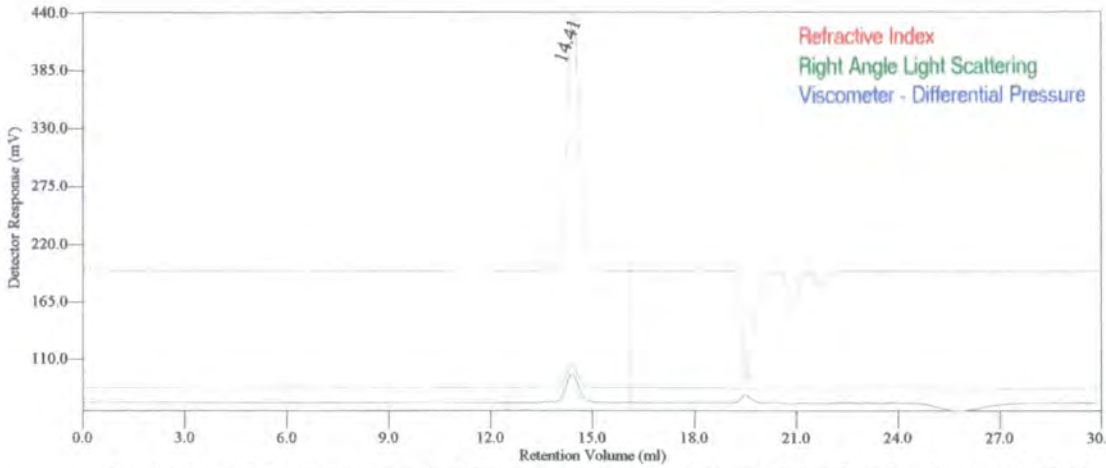
Appendix 4.1.2 - ^{13}C NMR spectrum of deprotected PS initiated using TBDMSO-PrLi in CD_2Cl_2.



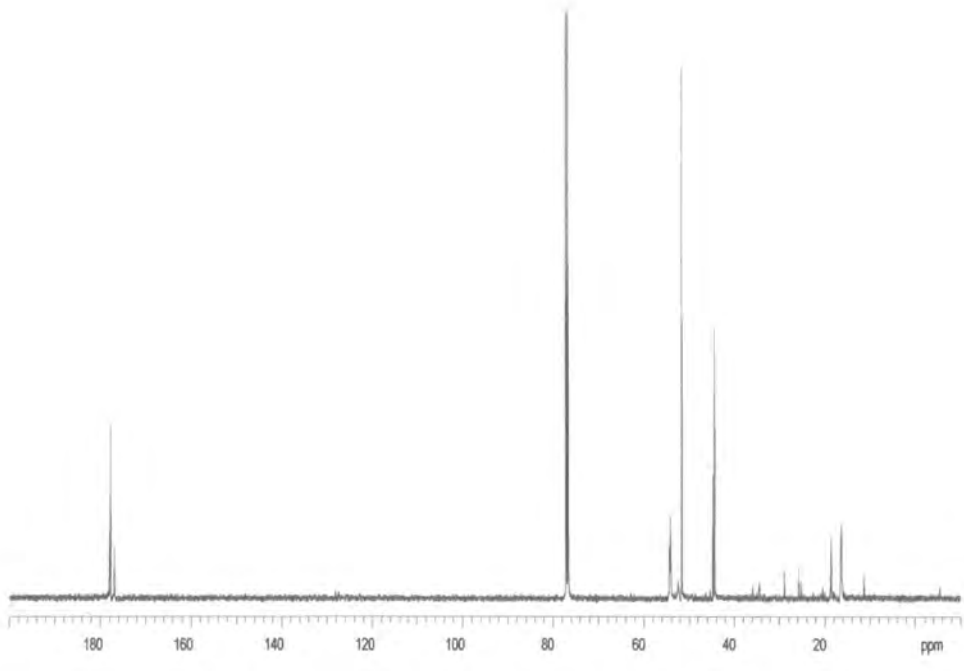
Appendix 4.1.3 – GPC (THF eluent) of deprotected PS initiated using TBDMSO-PrLi. M_n: 11600 g mol^{-1}, PDI: 1.05.



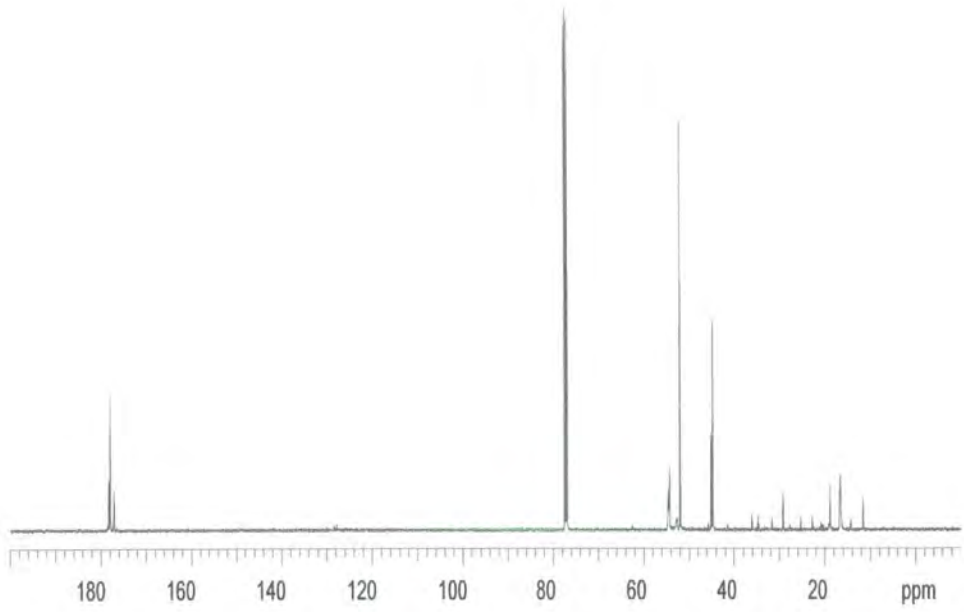
Appendix 4.1.4 - ^{13}C NMR spectrum of PS macromonomer from PS initiated using TBDMSO-PrLi in CD_2Cl_2.



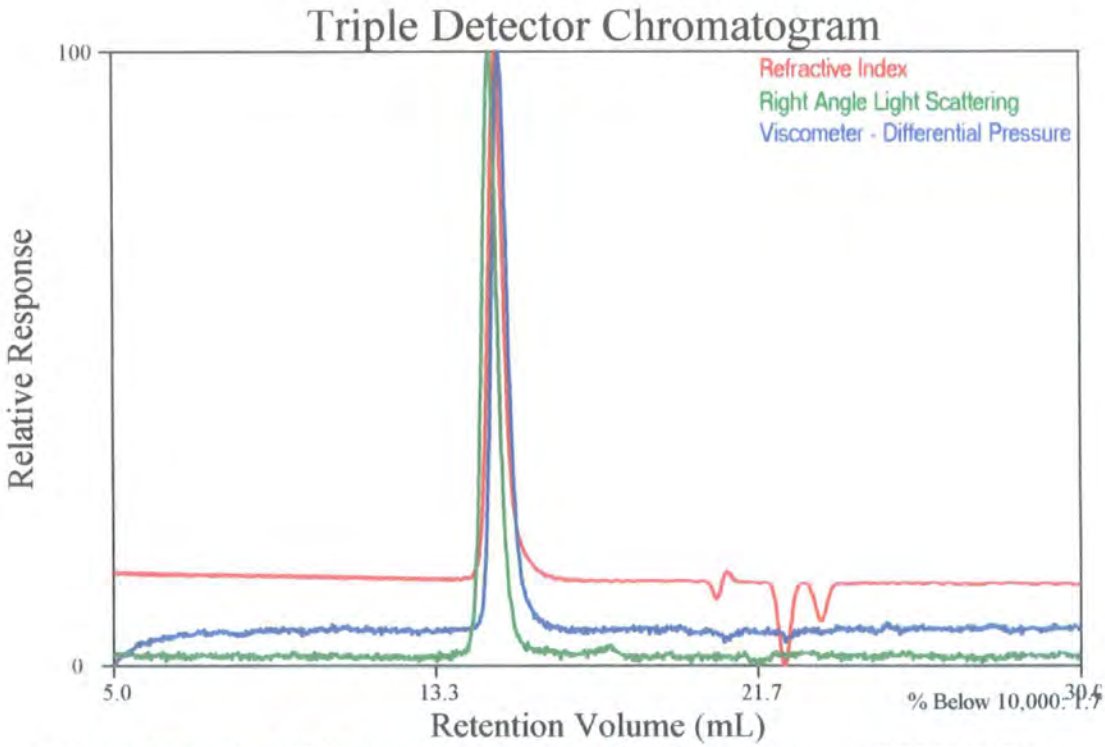
Appendix 4.1.5 – GPC (THF eluent) of PS macromonomer from PS initiated using TBDMSO-PrLi. M_n: 11700 g mol^{-1}, PDI: 1.05.



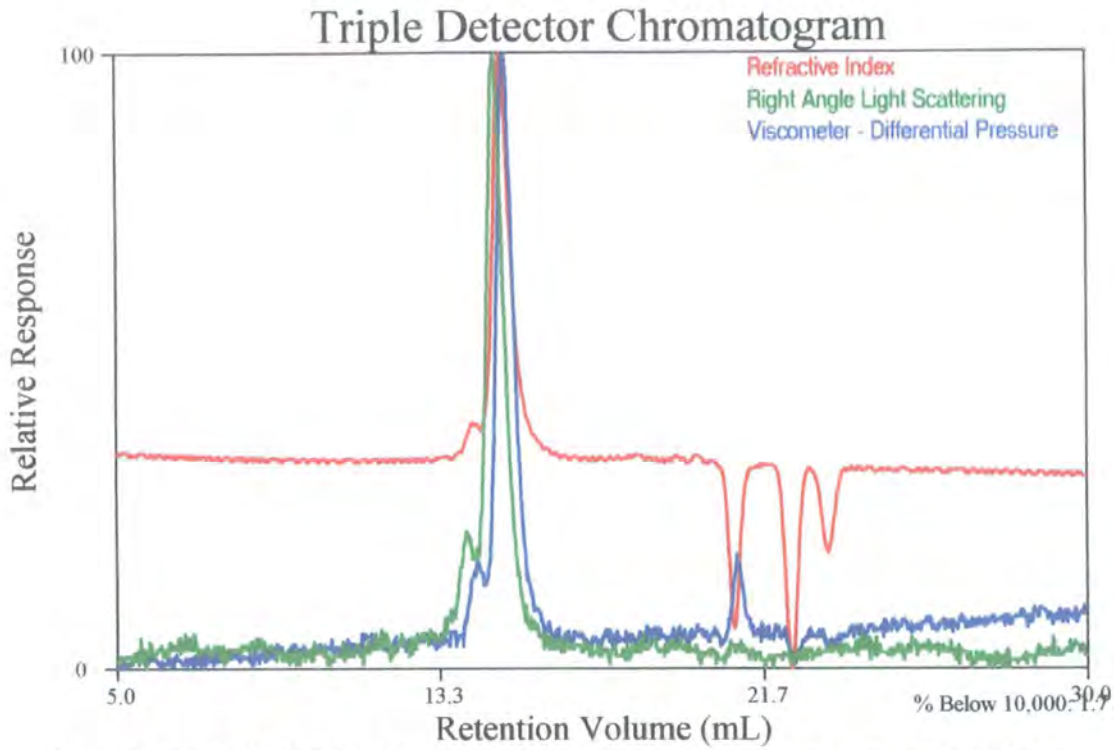
Appendix 4.2.1 - ^{13}C NMR spectrum of PMMA initiated using TBDMSO-PrLi in $CDCl_3$.



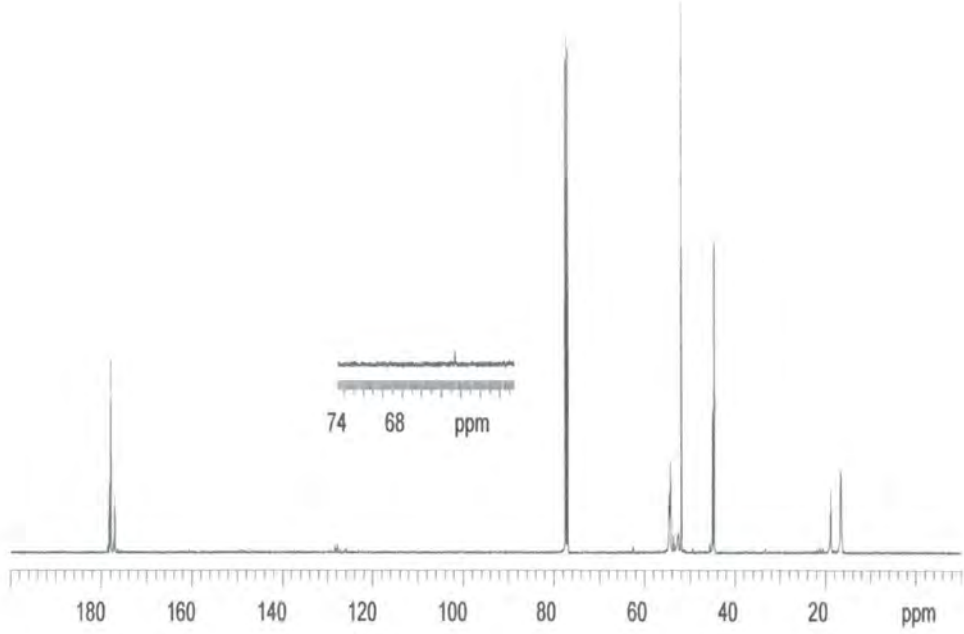
Appendix 4.2.2 - ^{13}C NMR spectrum of deprotected PMMA initiated using TBDMSO-PrLi in $CDCl_3$.



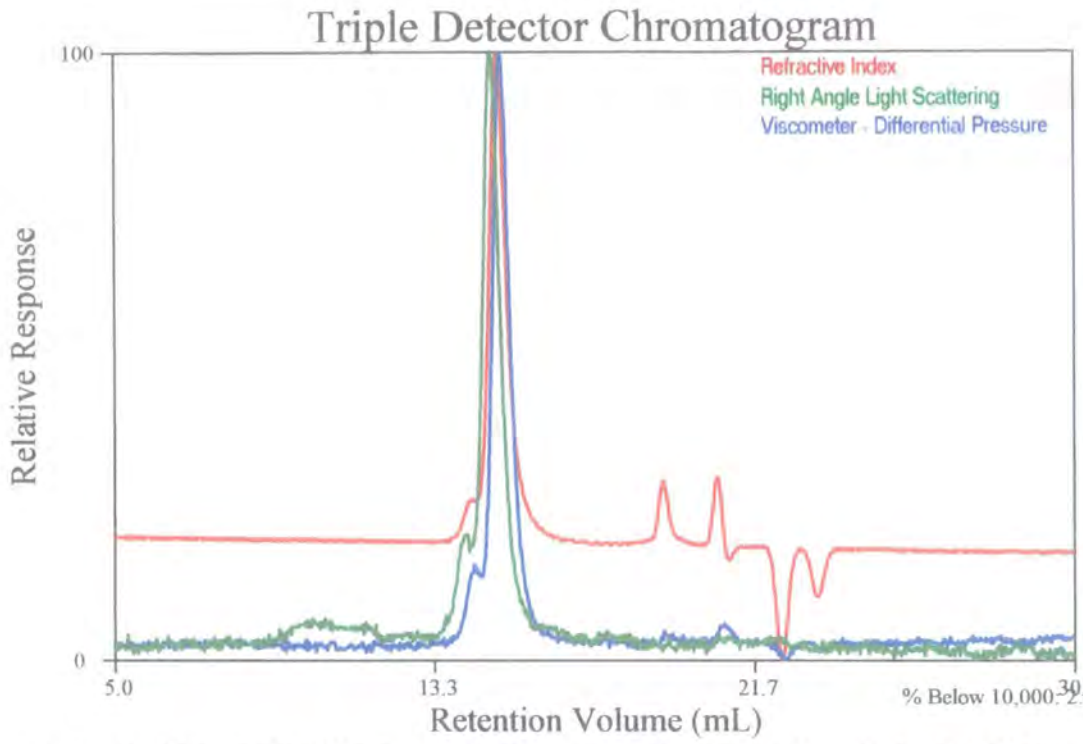
Appendix 4.2.3 - GPC (THF eluent) of deprotected PMMA initiated using TBDMSO-PrLi. M_n: 18200 g mol^{-1}, PDI: 1.05.



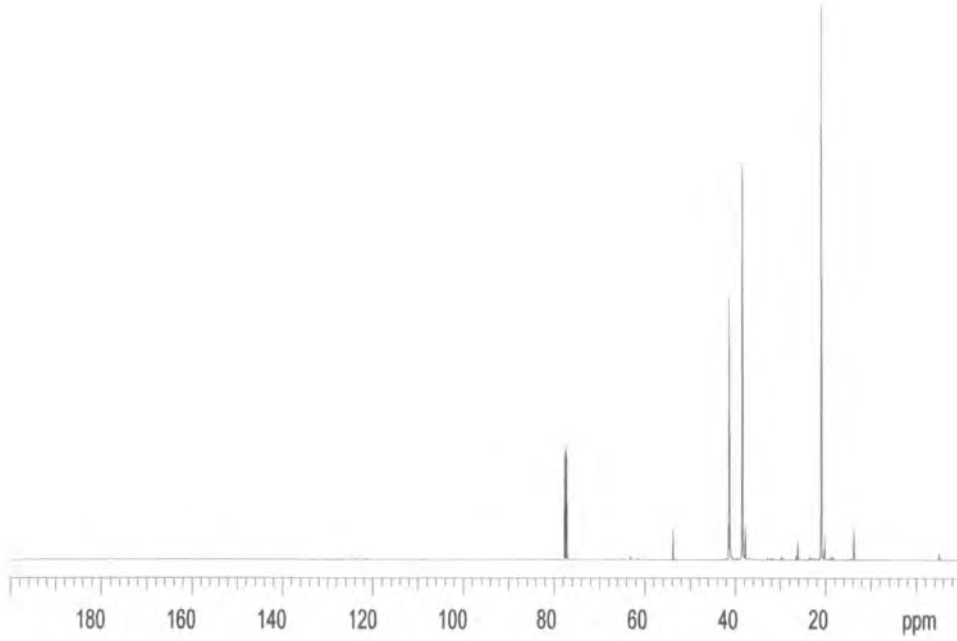
Appendix 4.2.4 – GPC (THF eluent) of polymer from the attempted synthesis of a PMMA macromonomer using hydroxy functionalised PMMA and 300 equivalents of NaH, 15-crown-5 and 4-VBC each (Section 4.2.2.3). M_n: 18800 g mol^{-1}, PDI: 1.07.



Appendix 4.2.5 - ^{13}C NMR spectrum ($CDCl_3$ solvent) of polymer from the attempted synthesis of a PMMA macromonomer using hydroxy functionalised PMMA, 4-VBC and 10 equivalents of NaH, 15-crown-5 (Section 4.4.3.3).



Appendix 4.2.6 – GPC (THF eluent) of polymer from the attempted synthesis of a PMMA macromonomer using hydroxy functionalised PMMA, 4-VBC and DPMK (Section 4.4.3.4). M_n: 18000 g mol^{-1}, PDI: 1.08.



Appendix 4.3 - ^{13}C NMR spectrum of poly(propylene sulfide) in $CDCl_3$.