Synthesis of functional stimulus responsive oligovinyl ethers and towards highly branched polymers using *ab initio* cationic polymerisation

By Rami Obaid

Department of Chemistry

The University of Sheffield

Submitted to the University of Sheffield
In fulfilment of the requirements for the award of
Doctor of Philosophy
October 2015

Declaration

This thesis is submitted to the University of Sheffield for the degree of Doctor of Philosophy, having not been submitted to any other University for any degree. I declare that all work contained herein is my own work, except where referenced and acknowledged accordingly.

....

Rami Obaid

October 2015

Acknowledgements

First of all I would like to thank Allah (God) and sincerely thanks are addressed to my parents and also, my sisters and brother: without their constant support and encouragement, I would certainly never have been able to reach the point where I am now and would not be who I am.

I would like to thank King Abdullah Scholarship Program (KASP) for funding this PhD.

Professor Stephen Rimmer is thanked for his supervision and giving me the opportunity to work in his group without whom I could not have done this project.

I am grateful to Mr. Simon Thorpe who has been very considerate and helpful on MALDI-TOF MS analysis during the whole project.

Many thanks are addressed to my great teacher Dr. Mouslim Messali who has always been ready to help me a lot during my BSc, MSc and PhD degrees.

I also want to thank my friends in Sheffield; it was a great pleasure to live with all of you.

Finally, I would like to thank the Rimmer group for their warm welcome and help during the whole project.

It was a beautiful and very rewarding for me and I liked very much to work in this laboratory on an exciting topic.

Abstract

Oligo(vinyl ethers) with functionalised end groups were produced through the alkylation of silyl enol ethers in *ab initio* cationic polymerisations. In order to obtain high degrees of chain end functionality a great deal of care was taken in choosing the monomer concentration, the reaction temperature, Lewis acids and the concentration of silyl enol ether. The experiment also required the use of highly nucleophilic species such as silyl ketene acetal, which react with carbocations at similar rates to vinyl ethers. Rapid elimination of the primary adduct produced the ester end-groups. MALDI-TOF mass spectrometry was used to analyse the oligomers obtained and to assess the side reactions and chain end functionalisation processes.

Oligo(methyl vinyl ether)s were synthesised in cationic polymerisations using the HCl-*i*sobutyl vinyl ether/$SnCl_4$ initiating system within the polymerisation temperature range -26 °C to -78 °C, and in the absence of an end-capping agent. It was observed that the use of a lower temperature yielded well-defined oligomers. Furthermore, during the polymerisation the **silyl enol ether** reactivity suppressed the termination rate and oligomethyl vinyl ether with increased levels of ester end groups were then produced. In addition, a size exclusion chromatograph was calibrated using MALDI-TOF MS to obtain molecular weights of narrow fractions (SEC-MALDI TOF). The Kuhn-Mark-Houwink relation for oligo(methyl vinyl ether) was then established. In the light of the above, it was possible to infer that the solution coil conformation is dependent on the end group structure.

Oligo(*iso*butyl vinyl ethers) were also prepared successfully at different temperatures (-26 and -78 °C) in the presence of a silyl enol ether using HCl-*i*BVE/$TiCl_4$ as the initiating system. At a lower temperature, and with a high concentration of silyl enol ether, the normal termination reactions were suppressed and oligo(*iso*butyl vinyl ethers) with a high ester group chain end functionality were produced. This phenomenon can be attributed to the fact that, at lower reaction temperatures, the rate of propagation relative to the rate of termination and the control of polymerisation was observed.

Another means by which oligo(*i*sobutyl vinyl ethers) were prepared in this experiment with ester end groups was by using continuous reaction processes. These processes are commonly applied in many industrial applications as they allow for the production of large quantities of polymer in a short period of time. These particular polymerisations were applied by using HCl-*i*BVE as an initiating system with $SnCl_4$ and $TiCl_4$ as Lewis acids at -15 °C. The production of oligomers with a high degree of ester group functionality was carried out by the use of $SnCl_4$ with a high concentration of silyl enol ether at a slow flow rate.

It was also possible to produce highly branched functional polymers by using continuous processes. In this instance, *i*sobutyl vinyl ether was used as a first monomer with diethyl divinyl ether (DEDVE) and divinyl benzene (DVBz) being used as second monomers in the presence of silyl enol ether at a temperature of -15 °C. Many different Lewis acids were used in these polymerisation reactions It was observed that the polymerisation of *i*BVE with DEDVE was only successful by using $Sc(OTf)_3$ as a Lewis acid. Highly branched polymers with ester group functionality were detected at a monomer ratio of 9:1 with a low concentration of silyl enol ether at a high feed rate. In the polymerisation of *i*BVE with DVBz, only two Lewis acids successfully aided these reactions (ZnI_2/HI and $Sc(OTf)_3$). In ZnI_2/HI, a low concentration of silyl enol ether with a high flow time was found to form highly branched polymers with the chain end group. In using $Sc(OTf)_3$, a high concentration of **SEE** with a low feed rate was shown to produce highly branched functional polymers. By analysing the aforementioned information it was possible to deduce that the feed rate and the concentration of silyl enol ether had a substantial effect on the chain end attained.

Table of Contents

Chapter 1

1.1 Cationic Polymerisation when Silyl Enol Ether is present

1.1.1 Introduction

Polymers are divided into two major groups: synthetic polymers and natural polymers. Natural polymers such as cellulose, nucleic acid and portions usually have more complex structures than synthetic polymers. Synthetic polymers generally do not contain complex structures and they have smaller repeat units. Various structural parameters are considered during the synthesis, characterisation, application and behaviour of synthetic polymers. During the nineteenth century, synthetic polymers were regarded as organic colloids. Later findings confirmed that these organic colloids were true organic macromolecules and they could be used for several applications. In our every day life, synthetic polymers are consumed in various forms such as plastics, elastomers, adhesive products, fibres and coatings.

Synthetic macromolecules were known as organic reactants until the 1960s because of their behaviour being similar to that exhibited by small organic species. Merrifield *et al.* first started using polymers as reactive molecules and solid phase techniques were employed in his subsequent experiments.[1] Up until now, many synthetic polymers with functionalised structures have been produced. These synthetic polymers possess functional groups attached within their molecular structures, endowing them with specific physical or chemical characteristics. The synthesis of functional polymers can be performed either by introducing chemical alterations in the pendant group or by bringing about chemical modifications in naturally occurring organic compounds such as polysaccharides and inorganic supports. They can be used in a variety of applications including functioning as stoichiometric reagents, biologically active agents, catalysts, substrate carriers in the process of synthesis, separators for organic compound creation, photo-resistant materials and conductive substances.

The synthetic polymer manufacturing of materials with specific properties requires a high degree of control during the various steps of the process, with good examples being the design of new monomers and polymer functionalisation.

On the basis of the route of synthesis, the synthesis process is divided into two types: step growth polymerisation and chain growth polymerisation. Multiple reactions of different functional groups take place step by step and in certain reactions there are chances of losing small reactant molecules, whereas in the case of chain growth polymerisation, the molecular formula of the repeat units is the same, with good examples being vinyl and other cyclic monomers. Condensation polymerisation is now regarded as step growth polymerisation and addition polymerisation is now regarded as chain growth polymerisation.

This study is focused on the manufacturing of synthetic polymers through the chain growth polymerisation process. Our objective is to synthesise highly branched functional polymers, which, according to theory, are unable to produce gels.

1.1.2 Ionic Polymerisation

On the basis of the charging of growing species, ionic polymerisation is categorised into two major types: cationic polymerisation (when growing species are positively charged) and anionic polymerisation (when growing species are negatively charged). Due to the presence of an ionic charge at the active centre, this polymerisation process is specific to the monomer structure and it is less general than free radical polymerisation. Any reacting monomers must contain a substituent, bringing about the potential of stabilising the ion and so this requires significant consideration.

The initiation of cationic polymerisation requires a cationic active centre (-C^{+} HX) to have a substituent group, with X having the delocalisation potential for positive charges or the potential to induce an electron donation process. Polymerisation by anionic active centres proceeds when the substituent group X in (-C^{-} HX) can induce an electron withdrawal or delocalisation of a negatively charged species.

1.1.3 Cationic Polymerisation

Cationic polymerisation uses a positively charged active centre, which is electrophilic in nature and is located at the end of the growing chain. It is mostly alkenes and heterocyclic monomers that undergo cationic polymerisation. This process is generally employed in commercial processes as well as some laboratory experiments where specific polymers and copolymer products are desirable. Polyindenes, polyacetal, polyvinyl ethers, polyε-caprolatam and polytetramethylene glycol are a few examples of synthetic polymers, which can be manufactured by this process in the world of commercial applications. Few of the mentioned polymers are obtained solely by the cationic polymerisation method. Currently, this route of synthesis has been modified and so polymerisation can be performed to give controlled molecular weights, while the dispersity can be narrowed. By utilising this living technique, it has been predicted that copolymers and polymers possessing reactive groups at end of their chains will become a reality and this is adaptable in the context of the commercial scale.

1.1.3.1 History of the Development of Cationic Polymerisation

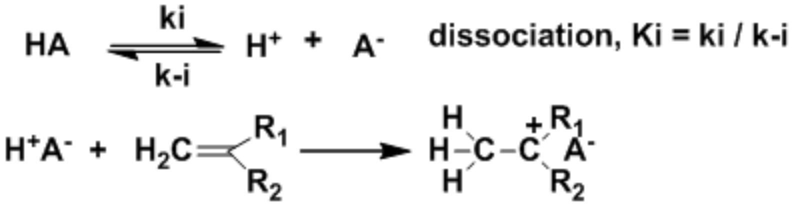
In 1877, cationic polymerisation was in a process of evolution initiated by Friedel and Crafts.[2] In their empirical study, chemical transformations were observed when $AlCl_3$ and other similar metal halides underwent the acylation and alkylation processes. The poly condensation reaction of benzyl chloride through $AlCl_3$ resulted in the formation of carbocationic polymers and it was the first reported study involving a carbocationic polymerisation process via a step growth process. In the late 1930s, Thomas Sparks synthesised cationic vinyl polymers and later on, Flory continued his research at the Esso campus.[3] In this study, heavy molecular polyisobutylenes, along with butyl rubbers and halo butyl rubbers, were employed. In 1956, Szwarc introduced the concept of living polymerisation.[4] He worked on styrene polymerisation by taking the anionic synthesis route. The reaction that was initialised by the sodium naphthalene complex later reacted with dried tetrahydrofuran. Besides this, during the process of styrene polymerisation, the molecular weight was seen to increase as conversion took place and so the reaction continued, without any termination leading to the production of copolymer blocks. These blocks then became further furnished when additional vinyl monomer was introduced (isoprene) after the initially introduced styrene became completely consumed within the reaction. Kraton was the first copolymer block manufactured by anionic polymerisation and this polymer is now widely used in designing footwear, gels and coatings.[5]

Kennedy and his fellow researchers made consistent efforts to design processes with controlled cationic initiation and termination during the 1970`s.[6] Controlled chain transfers, the manufacturing of graft polymers and well-defined blocks were also reported in subsequent research studies. In some studies, the polymer molecular weight and its distribution was controlled via hindered bases.[7] Later, in the 1980s, quasi-living and controlled cationic polymerisation were reported.[8] However, some limitations to cationic polymerisation exist, in that polymers of a low molecular weight can not be synthesised by it. This route is preferable when electrophilic end groups are the desired end product.

1.1.3.2 Cationic Polymerisation Mechanism

The use of chain growth cationic polymerisation of alkenes will be the focus of this research. The aim will be to investigate the use of continuous cationic polymerisation in the presence of silyl enol ethers, to synthesise highly branched polymer ethers by cationic polymerisation. An understanding of the cationic polymerisation process requires an explanation of the mechanism of the reactions of initiation, propagation, transfer and termination. The initiation process in cationic polymerisation involves ion generation and cationic processes that activate the species, which are then able to form the polymer chain. As opposed to free radical polymerisations, ionic polymerisations are never terminated in combination.

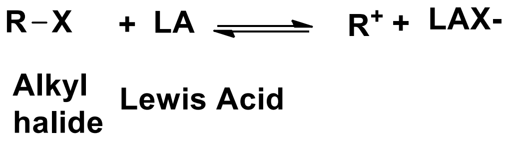
Chain Initiation: The initiation allows for control and distribution of the molecular weight and also the topology of a polymer as well. Complex initiating systems containing a protonation agent and a Lewis acid were developed to control both the overall rate of polymerisation and the molecular weight distribution. The macromonomers and telechelics can facilitate if the stable functional includes. However, the structure of the initiator may also provide a site for side reactions.[9] Generally, initiators for ionic polymerisation are only employed for certain monomers and often these initiators need to be matched to particular monomers. The active species can be prepared by different physical and chemical methods. Physical methods involve high energy irradiation and photochemically, which cations can be generated. The chemical methods for alkene cationic polymerisation involve protonic acids, Lewis acids, stable carbenium ions, oxidising reagents and other strong electrophiles.[10] The protonic acids used in cationic polymerisation depend on the nucleophilicity of the conjugate base as shown in Scheme 1.1.



Scheme 1.1: Protonic acid initiated via cationic polymerisation.

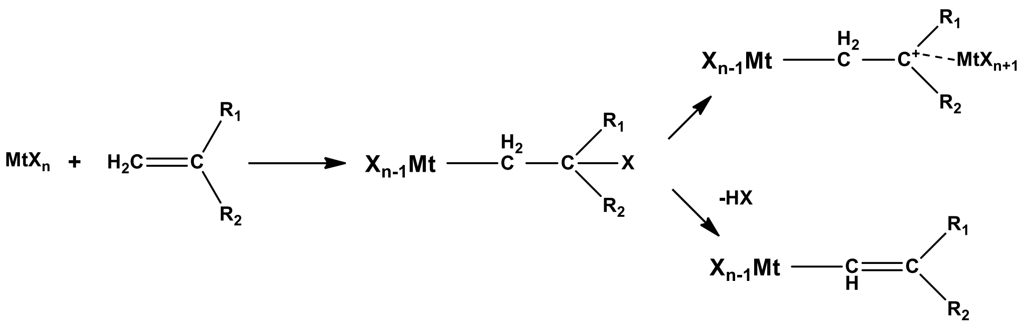
On top of this, Lewis acids, as initiators of carbocationic polymerisation, are very useful, and a number of strong Lewis acids like boron halides can initiate cationic polymerisation.[11] Lewis acid mechanisms were proposed as a way of explaining the polymerisations that were initiated without any co-reactant.

Usually, alkyl halides are used as initiators and the actual initiator is the dehalogenated carbocation. The progress of the polymerisation and susceptibility to side reactions is governed by the state of bonding between the ionic centres and thus the following equilibrium.



Scheme 1.2: The reaction of alkyl halide with Lewis acid to produce carbocation.

Yet the initiation of the Lewis acid can also happen via a halometalation process, followed by the elimination of hydrogen halide or Lewis acid ionisation. Scheme 1.3 presents the mechanism of the Lewis acid's initiation of cationic polymerisation.



Scheme 1.3: Lewis acid initiation of cationic polymerisation.

Therefore, Lewis acids are used as activators or co-initiators in most carbocationic polymerisations. The initiating species can be either an alkyl ester or halide. Lewis acids are typically used to activate dormant covalent esters, halides as well as protonic acids. In a cationic polymerisation initiated by Lewis acid, the Lewis acid is present as a co-initiator that complexes with water, or alkyl halides, for the ionisation.

Chain Propagation: the propagation step is the most important elementary reaction of a polymerisation, as it results in the formation of the entire macromolecule (except the end groups). Therefore, molecular weight, molecular weight distribution and the rate of polymerisation can be regulated if the propagation mechanism is controlled. It is important to be aware of the structure of the monomer and the growing species in order to understand the propagation mechanism.

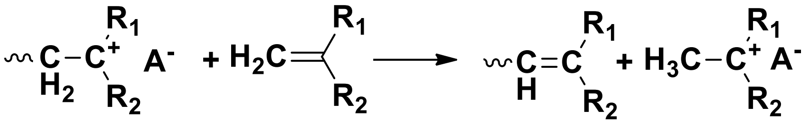
In cationic polymerisation systems, the reactivity of active centres usually correlates with their degree of ionisation. The bonds that form between carbocations and the counter-anions can vary between almost covalent, tight ion pairs through to non-interacting ions. At the start, tight ion pairs must be loosened to allow for complexation with monomers.[10]

The mechanism of insertion consists of repeated push-pull attacks by the ion pairs on the double bonds of the incoming monomers. Scheme 1.4 below shows how the cationic propagation mechanism can occur via the insertion route.

Scheme 1.4: The insertion mechanism of cationic propagation.

This mechanism provides the best control and the lowest probability for side reactions. In addition, the degree of association of the ion pairs depends on both the temperature of the reaction medium and the nature of the counter ion. Therefore, dissociated ion pairs allow for chain growth to take place free from the influence of counter ions. Carbocations add directly to the double bonds of the incoming monomers. The rate of propagation with dissociated ion pairs is higher than with the tight ion pairs.[12] During chain propagation, the monomers behave as electron donors or even as nucleophiles and an increase in electron density at the double bond increases the rates of chain propagation. The polarity of the monomer substituents and overall steric effects leads to significant effects on chain propagation. In some cases, there are various chains that might grow, even without terminal counter ions, as free propagating species. However, when more than one growing species are present during the polymerisation, the polymer may show multimodal molecular weight distributions. Matyjaszewski's research showed that bimodal molecular weight distributions have been formed with free ions and ion pairs with identical reactivity but various lifetimes. The low molecular weight fraction is formed by ion pairs and the high molecular weight fraction is formed by free ions.[10] These cationic polymerisation characteristics have created great difficulties when attempting to define rate parameters that are useful.

Chain Transfer and Chain Termination: Transfer and termination must be absent from a living polymerisation. However, in non-living polymerisation, growing chains are terminated by either a unimolecular rearrangement of the ion pair or through chain transfer. Chain transfer to monomer usually is a bimolecular reaction, as shown in Scheme 1.5.



Scheme 1.5: Chain transfer in cationic polymerisation.

In the process of chain transfer, these reactions generally reduce the polymer molecular weight by generating new chains from the same initiator. They do not, however, affect the kinetics of polymerisation because the concentration of growing species does not change. This process can be classified into bimolecular termination and unimolecular termination.

The unimolecular rearrangement process includes both hydrogen elimination and recombination processes, which irreversibly deactivate the growing species. Furthermore, the electrophilic chain ends can be functionalised via a controlled termination step, to give chain end functionalities. Polymerisations that are more under control have been used with inifers[13, 14, 15] as both initiators and transfer agents in cationic polymerisation.

1.1.3.3 Factors affecting Cationic Polymerisation

Solvent effect

The ionic polymerisation processes are greatly influenced by solvent polarity and the solvent significantly affects ion pairing; with this process taking place on an active centre. On the different solvent polarity basis, ion pairs joined through covalent bonds, intimate ion pairs and dissociated free ions can be formed. The concentration of ion pairs can be monitored through the use of solvents with varying polarities. Anion reactivity undergoes suppression when a solvation effect is produced, therefore reducing stability in chemical bond between carbocation and anion. This process improves the rate of initiation.

Studies on stopped flow provided evidence for the effect of solvents on carbenium reactivity.[16, 17] In the presence of a nucleophile solvent, carbenium reactivity was found to decrease and consequently the propagation rate was lowered in 1,2–dicholorethane, in comparison with dichloromethane.

Aside from this physical effect, in which solvent molecules with average dielectric constants behave as a continuum, some specific chemical interactions can also be introduced, good examples of which would be onium ion generation (chloronium, nitronium, oxonium and sulfonium). Due to the chemical inertness of chlorinated solvents, they are considered the best solvents to be used in cationic polymerisation. Chain propagation in dichloromethane is around one thousand times faster than in non-polar hydrocarbon solvents. Although, in more polar solvents, chain propagation by carbocationic species is slow. However, polymerisation rates have been associated with high carbenium ions concentrations, which result in an ionisation equilibrium shift.

The solvation of ionic species is promoted in highly polar solvents whereas in less polar solvents collapse. Besides this, accelerated termination reactions of propagated carbenium ions have been reported in less polar solvents that contain impurities. A reaction termination can also result if the solvent is very nucleophilic. In contrast, β-proton abstraction occurs when the solvent is very basic in nature.

Additive Effect

Nucleophiles can influence many steps of cationic polymerisation, including propagation, initiation, termination, molecular weight, molecular weight distribution and the rate of polymerisation.

The reactivity of a carbenium ion is greatly reduced due to the complex of nucleophiles with active centres and so this significantly reduced both the propagation and initiation rates. The narrow molecular weight distribution is resulting in overall fast initiation rate and slow propagation rate.

Therefore, with the previous discussion in mind, the presence of nucleophiles in cationic polymerisation system, most well-defined polymers can be observed.[18, 19, 20] Moreover, the higher initiation efficiency is achieved in these processes with nucleophiles through higher reduction in the propagation rates.

Nucleophile impact on cation reactivity results in an overall effect on the cationic polymerisation process. Nucleophiles can also react with all other electrophilic species present in the system for example, carbenium ions, Lewis acids and dormant species. Controlled vinyl monomer polymerisations can be performed through the use of ether additives such as a 1, 4-dioxane, diethyl ether, tetrahydrofuran and some ester additives as well (ethyl acetate, ethyl benzoate and methyl chloroacetate). [21, 22]

The cationic polymerisation process is affected by various ion scavenger impurities in the reaction system, such as ammonia, water and amine. A β-proton loss is facilitated by these impurities and so it leads to an increased frequenting of chain transfer reactions, particularly in conditions where the concentration of the β-proton is high. One possible explanation to this could be chain transfer agent role of water in the cationic polymerisation process. Besides this water also acts as a co-initiator when the Lewis acid concentration is considerably high.[23] The type of initiator, concentrations of initiators and monomers are the few other parameters that significantly affect the reaction rate of cationic polymerisation.

Polymerisation Temperature Effect

Three degrees of loss of the translational freedom produced by monomer units connecting together makes most cationic polymerisations processes exoentropic (approximately -1200 $mol^{-1} K^{-1}$). The thermodynamic requirements for polymerisation processes are preserved through exoenthalpy, which overcomes the entropy loss. The loss of enthalpy can be prepared through isomerisation of the double bond to a single bond during the polymerisation reaction of alkenes or also occurs via relief of the ring-strain in ring-opening polymerisation process.

Different temperatures affect the individual polymerisation processes differently and can cause incremental changes in overall resultant negative activation energies.[24] Side effects, an example being chain transfers, have a high activation energy level when compared with propagation reactions and this proves that low temperatures are desirable for cationic polymerisation, most especially when your end product needs to be high molecular weight. This also explains why low temperatures are required for cationic polymerisation reactions. The carbenium ion presence produces the solvent effects during chain propagation reactions and other reactions. Temperature impacts on the reactions are considerable due to the exothermic nature of the solvation process.

Lewis Acids

In the polymerisation, Lewis acids can react with initiators to decrease electron density of the active centre and the electron acceptor is then improved. Lewis acids are typically the most common initiators of carbocationic polymerisation and they are particularly used in binary initiation systems as co-initiators or activations. There are some additional benefits of using this system, such as the good control over the polymerisation rate and the number of chains produced and their corresponding molecular weights. Instigating initiation via adapting the direct method is less effective and there is a need for activators or co-initiators (like Lewis acids) in carbocationic polymerisation processes.

The equilibrium position between carbenium ions and the associated covalent adducts greatly depends on the rate of polymerisation. Molecular weight distribution can be obtained by considering equilibrium dynamics, especially the deactivation rates of active species when they are converted to dormant species. In this cases when the exchange rate is slower than the propagation rates, a broad distribution will take place or multimodal distribution is occasionally seen. In contrast, faster exchange rate comparisons with propagation can produce Poisson distribution ($\bar{M}w / \bar{M}n \approx 1$). This indicates the significance of Lewis acids ligands and the associated nucleophilicity and basicity are very important in controlled polymerisation.

However, strong Lewis acids will not produce optimum results because they will lead to uncontrolled polymerisations. Besides this, irreversible in ion pair collapses will occur by including very strong Lewis acids, due to the strong carbenium counter ion bond, causing in termination of the reaction. Consequently, strong Lewis acids may yield lower polymerised products in comparison to weak Lewis acids. Complex formation with weak nucleophiles such as solvents, additives and monomers are also present when strong Lewis acids are used. Complex formations affect polymerisation rates directly and they are also found to be lower than those seen when weak Lewis acids are used. On top of this, with strong activators present, the necessity of a deactivator is required in order for control over polymerisation to be achieved. Nucleophiles and salts are used as deactivators because they hinder the growth of species and do not participate directly in initiation reactions. Furthermore, an atomic number is associated with increased Lewis acid strength in the similar group and their relative efficiency in initiation polymerisation are as follows: [25]

$$BF_3 > AlBr_3 > TiBr_4 > BBr_3 > SnCl_4$$

In the case of the polymerisation of vinyl ethers different Lewis acids are used, such as $TiCl_4$, which is used due to its potential for initiating polymerisation, a result of its high acidity profile.[26, 27, 28] The combination of Lewis acids with protonating agents (such as hydrogen halide and carboxylic acid) is also employed at times. Dimer formations are facilitated by $TiCl_4$ because of its high reactivity, in comparison with monomeric Lewis acid. $TiCl_4$ and alkene forms are coloured mixtures, indicating the formation of weak complexes.

In the cationic polymerisation process, $SnCl_4$ was the first Lewis acid that was used to expedite initiation.[29] Alkyl halides and esters are used in combination with it, as they yield their respective protonic acids. Complexation of $SnCl_4$ with halide anion and weak Lewis acids has been reported,[30, 31] for example, with $SnCl_5^-$ and $SnCl_6^{-2}$ when halide anion donors were present in the reaction mixture (i.e. *n*-Bu_4NCl). $SnBr_4$ is a comparatively weaker Lewis acid when compared with $SnCl_4$ and due to the increased lability of its ligands, the catalysis of cationic polymerisation takes place efficiently.[32,33] $ZnCl_2$ is a weak Lewis acid as well and it is known to have the potential to initiate polymerisation with many reactive monomers, like alkoxystyrenes, *N*-vinyl carbazole and vinyl ethers. Its use in halogenated hydrocarbons is restricted due to its reduced solubility.

1.1.3.4 Monomers used in Cationic Polymerisation

Long chains form in radical and ionic polymerisations process via addition reactions. $CH_2{=}CR_1R_2$ is the general formula for monomers, which are predisposed to rearrangement upon activation by radicals and ionic initiators due to the presence of the π-bond. If the electronegativity of the π-bond is modified then the determination of preferential stabilisation of the radicals and ions becomes easier, when one considers electron density. The type of substitution on the monomer determines the overall route of polymerisation that will be adapted to.

Alkenyl, alkoxyl and phenyl groups donating electrons to alkenes all helps facilitate cationic polymerisation as these processes augment the nucleophilicity of the monomer. Active centres undergo resonance stabilisation during cationic polymerisation. However, there are certain monomers that can undergo cationic as well as anionic polymerisation, due to the stabilisation of also anionic species. Styrene and 1, 3-butadiene are examples of such types of monomers. Vinyl ethers, *N*-vinylcarbazole, 1, 1-di-substituted alkenes (α-methylstyrene and isobutylene) and styrene are the few examples of vinyl monomers that are employed during cationic polymerisation.[34]

Different types of vinyl ether monomers were investigated in a study where cationic polymerisation was employed with reaction rates determined via polymerisation methods. The electron density was improved by the presence of certain electron donor groups such as alkoxyl as it gave nucleophilic character to the cationic centre during the stage of propagation. Similar observations were obtained with the use of different vinyl ethers, including methyl vinyl ether, ethyl vinyl ether and isobutyl vinyl ether.[35] Reduced propagation rates and high activation enthalpies were also obtained when methyl vinyl ether, ethyl vinyl ether and *i*sobutyl vinyl ether were studied. Propagation rate constants obtained for MVE, EVE and IBVE, with selected polymerisation techniques, were 1:10:48. Special conformational characteristics of MVE are thought to be responsible for this as it poses higher degrees of steric hindrance to the oncoming electrophile.

PMVE has a lower Critical Solution Temperature (LCST) in water, which makes PMVE attractive for researchers and thus it is widely used in block copolymer synthesis as a temperature responsive block.[36, 37] Different linear and non-linear copolymers are manufactured, by employing living cationic polymerisation methods. The PMVE block is used because of the need for temperature maintenance at specific levels and in some cases amphiphilic PIB-*b*-PMVE[38, 39, 40], PS-*b*-PMVE[41, 42] and di-hydrophilic block of methyl tri-ethylene glycol vinyl ether with methyl vinyl ether, PMTEGVE-*b*-PMVE are also used.[43]

1.1.3.5 Potential application of Cationic Polymerisation

Distinct polymers can be manufactured by adapting cationic polymerisation to allow for a wider commercial application. Vairon *et al.* mentioned the potential uses of polymers that were produced by cationic polymerisation at the commercial level.[44] To date, 36 different polymers and copolymers have been synthesised through alkene or heterocyclic monomers undergoing cationic polymerisation.[45] Polybutenes, polyisobutenes, polyvinyl ethers and hydrocarbon resins are the few examples of polymers that have been manufactured in vinyl polymerisation processes.

Polybutenes are lubricants that cannot be stained and show stability at high shear. As a result, polybutenes have wide industrial applications, such as in plasticisers, modifiers, concrete sealers, caulks and in personal care products. With chain end modifications of polybutenes, poly(butenylsuccinic anhydride) can be synthesised. It exhibits corrosion inhibiting characteristics and thus can be used in additives and lubricants. Polyisobutenes (PIB) with molecular weight in the moderate to high ranges can be used in the preparation of flexibility improvers in waxes, sealants, additives and more. Butyl rubbers are synthetic random copolymers, which exhibit linear cross-linked structures. These polymers have industrial applications such as: the synthesis of inner tubes, pharmaceutical stoppers, auto parts, wires and cables, tank hose lining, chewing gum formulation and more. These applications function as good damping features, with low rebound resilience, low toxicity and are overall impermeable to small sized molecules. The commercial preparation of processing aids, extenders, plasticisers and rubbers makes use of hydrocarbons. Besides this, they are also used in the formulation of rubber, coatings, adhesives and paints.

Crivello and Lam introduced the idea of photo-initiation in the 1970s and then , following this finding, a unique coating method was established. The induction of olefins and epoxies via proton-initiated polymerisation is facilitated by diaryliodonium salts in the presence of UV radiation, it was found. In many industrial coating processes UV curing is preferred, for large objects.[46, 47]

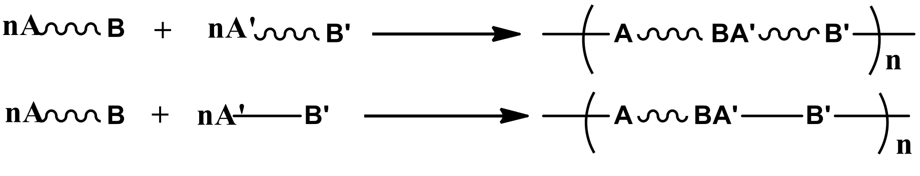
Radical polymerisation has been found to be ineffective in vinyl ether polymerisation processes and cationic polymerisation is thus preferred. When homopolymer production is desirable, cationic polymerisation is used. Vinyl ether polymers are widely used in industrial applications like viscosity index improvers in many lubricants, as a plasticiser in coatings and as non-migrating tackifiers in adhesives production.

Polymers with narrow dispersity can be produced by living cationic polymerisation technology, such as in vinyl ether polymerisation. Sequential polymerisation of hydrophilic methyl vinyl ether (MVE) is employed for copolymer block synthesis with amphiphilic nature, whereas hydrophobic octadecyl vinyl ether (ODVE) shows emulsifying behaviour when used with water and decane mixtures. Macromonomers can be synthesised by the end-capping of living polymers with hydroxyethyl acrylate.[48, 49] These compounds (polyODVE-*b*-poly(Bu-acrylate) show an improved phase separation and crystallinity features.

One of the studies shows that the living cationic polymerisation of isobutyl vinyl ether can be started when carboxyl groups along with ethylaluminum are introduced on the surface of carbon black and this reaction requires the presence of 1, 4-dioxane. Grafted PIBVE can be obtained by terminating the polymerisation reaction. In a living ionic polymerisation system, the molecular weight of surface graft can be controlled.[50] Cationic polymerisation of vinyl ethers have also been employed for the manufacturing of diblock and triblock copolymers, due to their amphiphilic nature and high water solubility.[51] With the sequential modifications of ethyl vinyl ether due to a living cationic polymerisation reaction, the Forder research group developed an alternative route for water soluble polymers, such as poly (vinyl alcohol).[52]

1.1.4 Telechelic Oligomers

Oligomers, originating from the Greek words 'oligo', meaning ‘few’, and 'mer' meaning ‘part’, are defined as short-chain polymers.[53] The differentiation between oligomer and polymer is based on the mechanical properties and bulk physical properties that significantly depend on chain length. Oligomers are polymers that include only a few monomer units. Over the last decade, the preparation of oligomers with specific terminal groups was studied, leading to new types of polymer not previously seen as accessible by conventional polymerisations, like block and graft copolymers. However, terminally reactive oligomers can be divided into two main categories, telechelic oligomers and macro-monomers, as described by Uranek *et al*, in 1960.[54] Macro-monomers generally have functionalised chain ends such as styrene, vinyl, methacroyl, epoxy and more. On the other hand, when oligomer end-groups behave as mono-functional groups, the oligomers are termed telechelic oligomers. They can take part in reactions with end-groups of different telechelic oligomers or with di-functional, small molecules to produce block copolymers, as shown in Scheme 1.6.



Scheme 1.6: Telechelic oligomer with di-functional molecule, to give block polymers.

1.1.5 Living Cationic Polymerisation

Living polymerisation means that there are no termination reactions during propagation. It is very useful for the synthesis of polymers such as block copolymers and mono-disperse polymers. In a living polymerisation system, controlling the degree of polymerisation and molecular weight distribution can be achieved. To create narrow polymers, it is necessary to pick the right initiator and solvent to create a rate of initiation that is faster than the rate of propagation.[55]

Controlled polymerisation systems can be produced by using cationic polymerisation, anionic polymerisation and coordination polymerisation, which all utilise Ziegler-Natta catalysts, group transferral, metathesis or radical polymerisation. This allows for the production of well-defined architectures, from a wide variety of monomers of commercial interest. On top of this, these polymers could be block copolymers, they could have pendant functional groups, they could possess terminal functional groups, they could be formed from oligomers and polymers with regulated sequences of repeat units, they could be graft polymers, multi-armed polymers, amphiphilic polymers or macro-cyclic polymers. Various potentially useful and well-defined new materials have resulted from controlled living cationic polymerisations, with examples being polyisobutylenes, hydroxy-telechelic polyisobutylenes and highly branched butyl rubbers (that have already been made commercially available).

Winstein *et al* defined different types of ionic species that are found in cationic polymerisation in 1956.[56] Four species in equilibrium, were reported, involving covalent electrophiles, contact ion pairs, solvent-separated ion pairs and free ions, as shown in Scheme 1.7.

$$\sim C^{\delta+} - X^{\delta-} \Leftrightarrow \sim C^{\delta+} - - X^{\delta-} \Leftrightarrow \sim C^{+} \cdot X^{-} \Leftrightarrow \sim C^{+} / X^{-} \Leftrightarrow \sim C^{+} // X^{-} \Leftrightarrow \cdots \Leftrightarrow \sim C^{+} + X^{-}$$

Polar Covalent Bond	**Stretched polarised covalent bond**	**Contact ion pair**	**Solent separated ion pairs**	**Solvated free ions**

Dormant Species

Living carbocationic polymerisations

Conventional uncontrolled carbocationic polymerisations

Scheme 1.7: The different spectra of ionicities of propagating species in carbocationic polymerisation, presented by Winstein.

In the 1980s, Kennedy and his co-workers[6] proposed the concept of 'quasi-living polymerisation', which is related to the concept of living polymerisations. These processes included slow and continuous monomer addition to a solution at a low temperature. The monomers employed involved isobutene, styrene, α-methoxystyrene and alkyl vinyl ethers. More importantly, the average molecular weight increased along with the added weight of each monomer. In addition to this, the formed polymers had narrow molecular weight distributions.

In 1982, Higashimura *et al*[57] focused on the development of the living cationic polymerisation of vinyl monomers. They used isobutyl vinyl ether and the related alkyl ethers as monomers, which were used to form alkoxy-stabilised growing carbocations. Moreover, Nuyken *et al*[58] also studied the living polymerisation of vinyl monomers. They observed that living vinyl ether polymerisation systems have several properties that can confirm whether a polymerisation is living or not, as listed below.

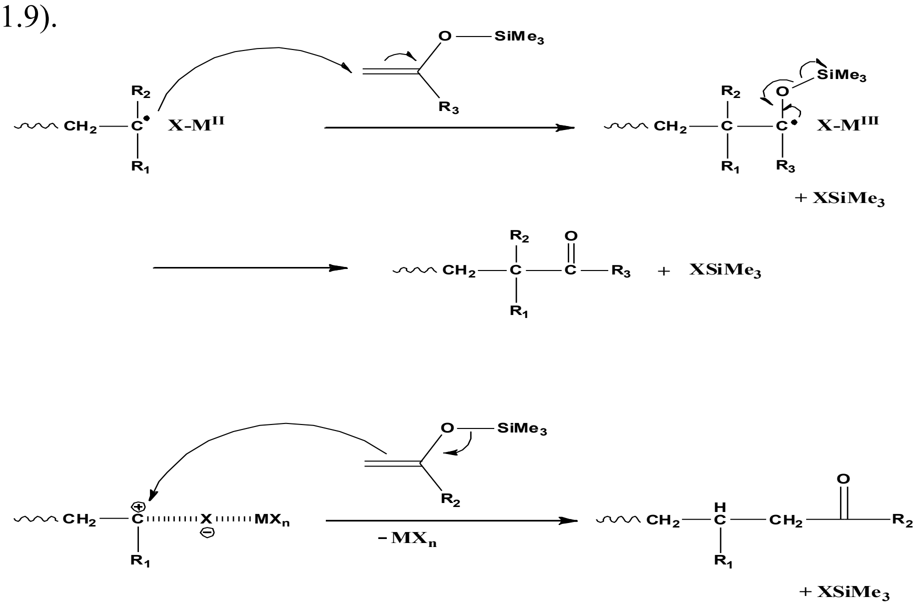
- Their initiation is spontaneous.
- Molecular weight is controlled by the propagation of monomer and initiator concentration.
- Molecular weight increases with conversion.
- Molecular weight increases by the sequential addition of monomers.
- Molecular weight distribution is narrow.
- The well-defined distribution and controlled termination allows the synthesis of macromonomers and telechelics.

1.1.6 Alkylation reactions of Silyl Enol Ethers and the Aldol reaction

Silyl enol ethers are the stable equivalent of enols. They have electron rich double bonds that react with electrophiles in a similar way to alkenes. McGrath and Riffle initially took silyl enol ether as an example in living cationic polymerisation and then trimethylsilyl ketene acetal was used as a SEE and HI/ZnI_2 initiated vinyl ether.[59] After that, Sawamoto's group used SEE in end-capping agents in the process of living cationic polymerisation for many architectures such as linear[60] and stars polymers.[61, 62] In this case, SEE was also used in non-living cationic polymerisation to receive oligovinyl ethers with reactive end-capping.[63] These then have a reaction with the carbocations to the overall result being the terminal ketones release trimethyl silyl halide, as outlined in Scheme 1.8. (via an addition elimination process).

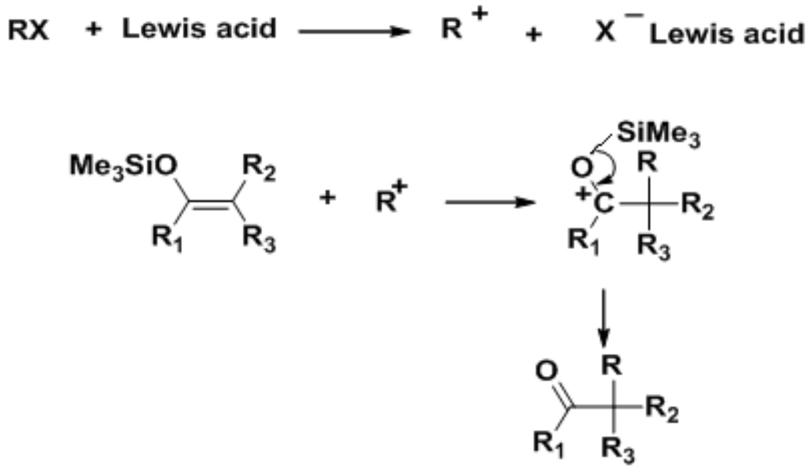
Scheme 1.8: Silyl enol ether used as end-capping agents.

Later, a new polymerisation method was developed. This technique was termed *ab initio* cationic polymerisation and it required one to add all the reactants, including the end-capping agent at the start of the polymerisation rather than in the method at the end of living cationic polymerisation. However, silyl enol ethers can react with both radicals and cationic polymerisation, to produce functional end groups (as seen in Scheme 1.9).



Scheme 1.9: Capping process of silyl enol ether on radical (top) and cationic polymerisation (below).

Furthermore, in the presence of Lewis acids and alkyl halides, α-alkylated carbonyl compounds can be produced, as shown in Scheme 1.10.



Scheme 1.10: The reaction in the presence of Lewis acid, alkyl halide complex, α-alkylated carbonyl compounds.

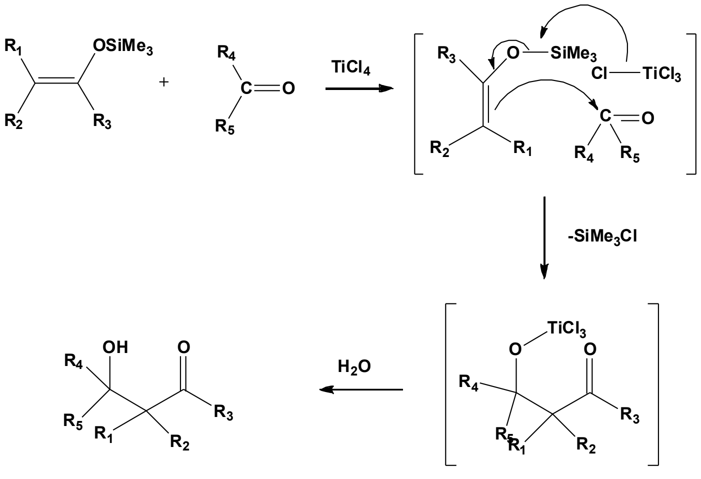
Silyl enol ethers are neutral nucleophiles, which are alkylated by electrophiles in the presence of Lewis acids. The most common alkylating agents for silyl enol ethers are tertiary alkyl halides. They generate stable carbocations from Lewis acids, such as $SnCl_4$ or $TiCl_4$.

Table 1.1, shows the yields from alkylation of silyl enol ethers, by using various Lewis acids at -45 °C in dichloromethane as a solvent.

Carbonyl Compounds	Alkyl halide	Lewis acids	Products	Yield (%)
1-Trimethylsilyloxy-Cyclohexene	t-Butyl chloride	$TiCl_4$	2-tert Butyl-Cyclohexanone	85
		$FeCl_3$		70
1-Trimethylsilyloxy-Cyclopentene		$TiCl_4$	2-tert Butyl-Cyclopentanone	78
1-Trimethylsilyloxy-6-ethylcyclohexene		$TiCl_4$	2-tert-Butyl-6-methylcyclohexanone	67
1-Trimethylsilyloxy-2-ethylcyclohexene		$TiCl_4$	2-tert-Butyl-2-methylcyclohexanone	86
2-Trimethylsilyloxy-3-methyl-2-butene		$TiCl_4$	3,3,4,4-Tetramethyl-2-pentanone	95
2-Trimethylsilyloxy-propene		$ZnCl_2$	4,4-Dimethyl-2-pentanone	40
1-Trimethylsilyloxy-1-butene		$ZnCl_2$	2-Ethyl-3,3-dimethylbutanal	30

Table 1.1: Alkylation of silyl enol ethers via different Lewis acids, in dichloromethane at -45 °C.[64]

The Aldol reaction is one of the most useful techniques for carbon-carbon bond formation in organic synthesis. It also creates by-products, such as di-, poly- or self-condensation products. Several efforts have been made to alleviate this difficulty, involving Mukaiyama and his co-workers.[65] This group obtained a new cross-Aldol reaction of silyl enol ethers with carbonyl compounds and the resulting research indicated silyl enol ethers can be prepared from various carbonyl compounds through a reaction with ketones and aldehydes, in the presence of titanium tetrachloride ($TiCl_4$), to create additional products like mono-methylol cross-Aldol, as shown in Scheme 1.11.

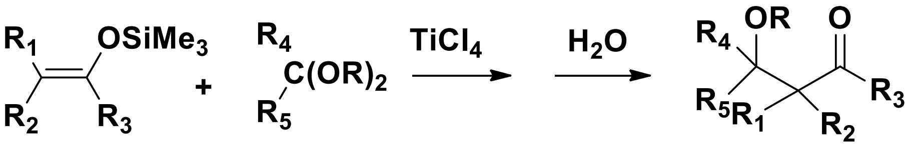


Scheme 1.11: Mukaiyama Aldol reaction.

Many Lewis acids were employed as catalysts in this new Aldol reaction. For example, $ZnCl_2$, $AlCl_3$, BCl_3 and $SnCl_4$ give different product yields. Dichloromethane, as a solvent, gave the best yields, whereas the product could not be obtained in THF or diethyl ether and also gave a low yield in benzene and n-hexane.^{66}

Silyl enol ethers reacting with aldehydes only gave excellent yields at a low temperature of -78 ℃, whilst at room temperature the same reaction gave very poor yields. In contrast, the reaction of silyl enol ethers with ketones only actually occurred at zero or room temperature.

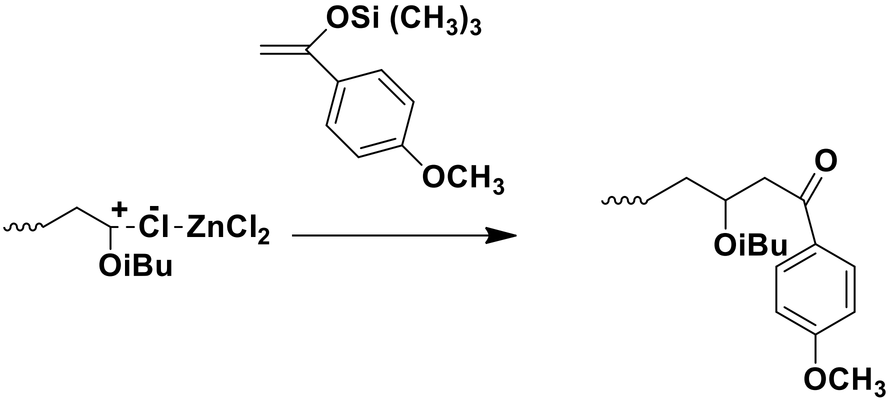
Mukaiyama and his team showed that the reaction of silyl enol ethers with aldehydes was more rapid than with ketones or esters. Moreover, silyl enol ethers reacted selectively with aldehyde functions, rather than ketones, at low temperatures, when using $TiCl_4$. In addition, silyl enol ethers may react smoothly with methyl orthoformate or acetals at low temperatures, in the presence of $TiCl_4$, to produce β-alkoxy ketones or β-keto acetals in a good yield as what is shown in Scheme 1.12.



Scheme 1.12: The reaction of silyl enol ethers with acetals.

1.1.7 *Ab initio* end capping by Silyl Enol Ethers

Silyl enol ethers have been shown to be effective mono-functional and multifunctional terminating reagents for the living cationic polymerisation of vinyl ethers, by H. Fukui, in 1994.[67] For an illustration of this, see Scheme 1.13.



Scheme 1.13: Silyl enol ethers used as mono-functional and multifunctional terminating reagents for living cationic polymerisation.

Typically, in conventional, living cationic polymerisation, silyl enol ethers can be added after the consumption of the monomers.

The term of *ab initio* refers to reaction formulations in which all of the reactants (Lewis acid, initiator, monomer and also end capping) need to be added at the start of the reaction. More importantly, the production of a polymer relies on the rate of termination being less than the rate of propagation. Thus, the idea of *ab initio* end capping of silyl enol ethers methodology was proposed. This technique could help control the molecular weight of the polymer with high degrees of chain end capping. The rate constants of addition to either the vinyl or silyl enol ethers were compared, using Mayr and his co-workers' results from the reaction of carbocations with nucleophiles. They compared the reactivity of alkyl vinyl ethers and silyl enol ethers, in similar model reactions with electrophiles. Table 1.2 shows the rate constant data from Mayr and his co- workers.[68] It gives a range of structurally diverse silyl enol ethers and the rate constants for the addition of a carbocation, at 20 °C. Clearly these are fast reactions, with rate constants close to the diffusion limit.[69]

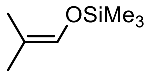
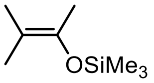
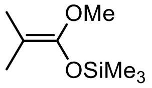
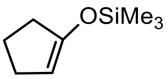
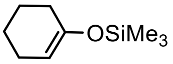
Nucleophiles	k_2 L $mol^{-1}sec^{-1}$
	1.5×10^9
	2.1×10^9
	3.0×10^9
	2.4×10^9
	2.5×10^9
	2.3×10^9

Table 1. 2: Second order rate constant, for the reaction of (p-$ClC_6H_4)_2CH^+$ with π-nucleophiles in acetonitrile, at 20 °C.

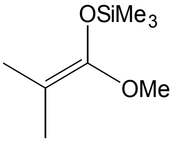
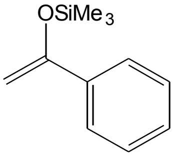
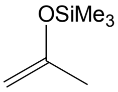
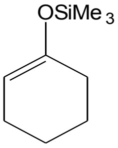
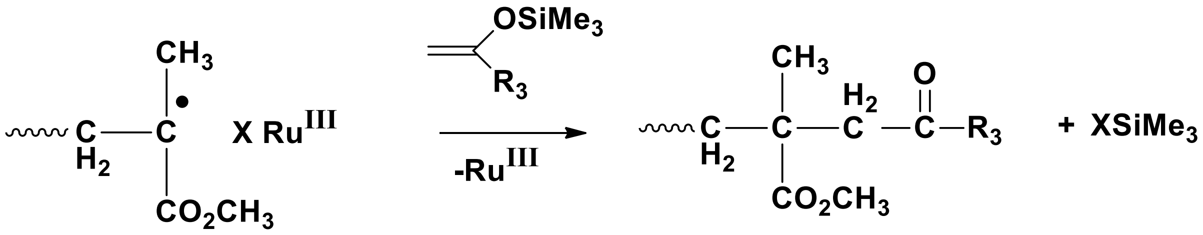
Silyl enol ether	k_2 L $mol^{-1}sec^{-1}$	Relative reactivity
	8.02×10^1	418
	1.73×10^{-1}	9
	3.53×10^{-2}	2
	1.92×10^{-2}	1

Table 1. 3: Second-order rate constants for reactions of silyl enol ethers with (p-Me_2N-$C_6H_4)CH^+$ in DCM, at 20 °C.

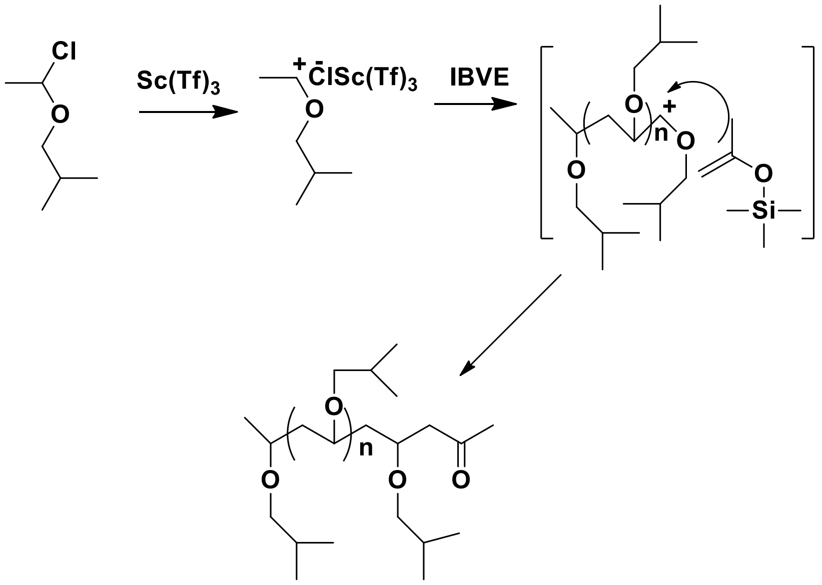
Mayer and his co-workers[69] presented the reaction rates of model reactions of silyl enol ethers with carbocations. (*p*-Me_2N-$C_6H_4)CH^+$ was used as a weak electrophile attack by the double bond of silyl enol ethers. Table 1.3. shows the relative reactivities of silyl enol ethers that can be given from their second order rate constants. However, silylated enol ethers rapidly desilyate and so the carbonyl bond is formed after the electrophilic addition. In this sense, silyl enol ethers can prevent further polymerisation and so can be applied as end-capping agents in the process of *ab initio* cationic polymerisation.

Furthermore, silyl enol ethers could react with carbon radicals at the end of living radical polymerisations, when transition metal salts (such as Ruthenium) are contained, thus giving end-capped products, as shown in Scheme 1.14.



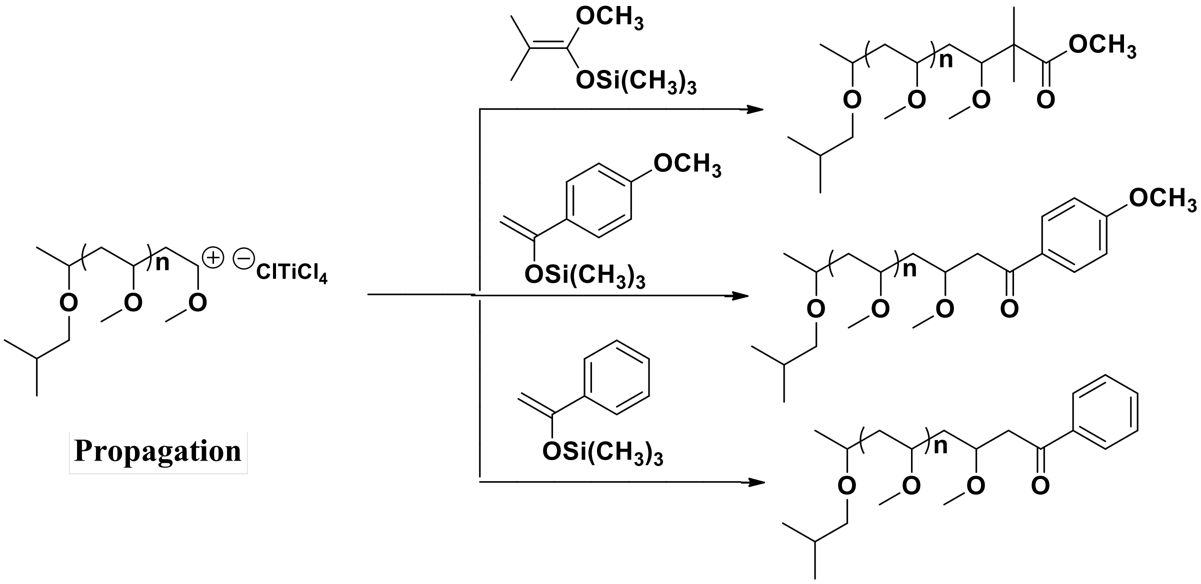
Scheme 1.14: Silyl enol ethers react with growing carbon radicals in the present of Ruthenium.

Based on the observation of the reactivity of SEEs and vinyl ethers, in 2001, W. Lang and S. Rimmer reported that mono-functional silyl enol ethers are effective as *ab initio* end capping agents in cationic polymerisation, as shown in Scheme 1.15.[70]



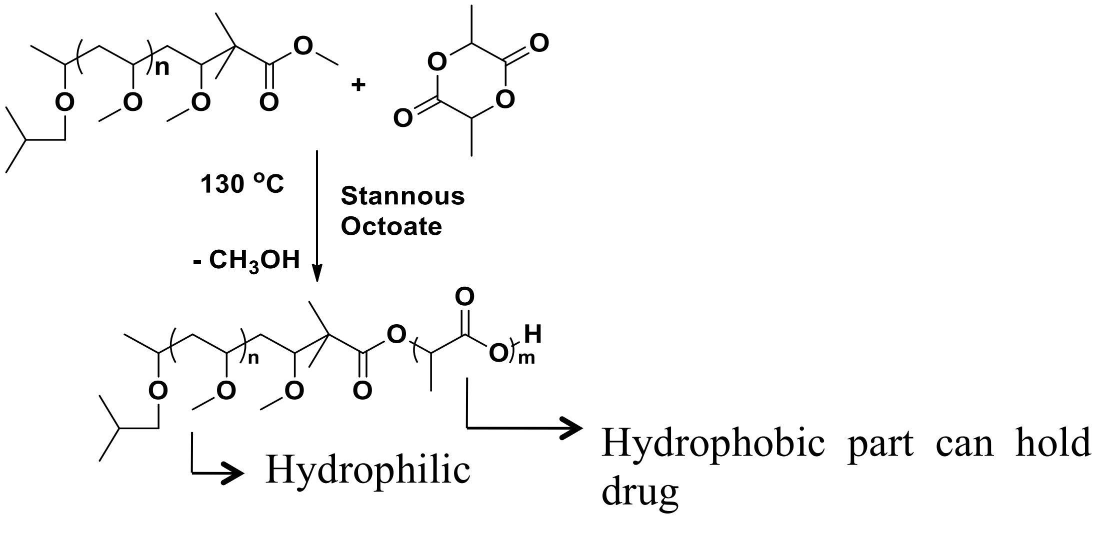
Scheme 1.15: Silyl enol ethers are effective as *ab initio* end-capping agents in cationic polymerisation.

P. Sarker and S. Rimmer have reported many experiments using *ab* initio technique.[71, 72] They successfully produced a series of end groups, using three different mono-functional silyl enol ethers (1-methoxy-2-methyl-1-(trimethylsilyloxy)propene **1**, 1-methoxyphenyl-1-(trimethylsilyloxy)ethylene **2**, 1-phenyl-1-(trimethylsilyloxy)ethylene **3**), as shown in Scheme 1.16. The polymerisations were carried out using methyl vinyl ether as a monomer and HCl-IBVE/$TiCl_4$ as an initiator/co-initiator. Their study concluded that silyl enol ethers **1** and **2** give high average degrees of functionality, due to the strong electron donating substituent on the silyloxy group. Correspondingly, the silyl enol ethers **3** gave low end-group functionality, due to the lower electron donating capacity of the attached groups.



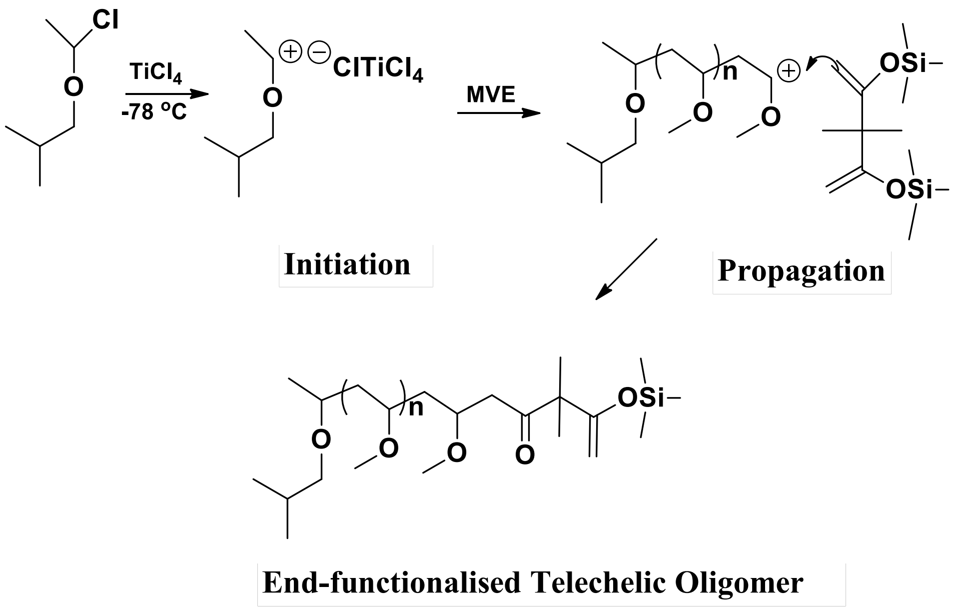
Scheme 1.16: A series of end-capping reactions were carried out using *ab initio* cationic polymerisation of MVE.

After the oligo(methyl vinyl ether) with ester group was prepared, they created a reaction of this polymer with lactide, to obtain a PMVE-*block*-PLA copolymer. This block can be used for drug delivery because it contains two phases hydrophobic, which can hold a drug, and hydrophilic, as denoted in Scheme 1.17.



Scheme 1.17: The mechanism of poly(MVE-*block*-LA) copolymer.

In addition, they used 3,3-dimethylpent-2,4-(trimethylsilyloxy)-1,4-diene as a difunctional silyl enol ether for the polymerisation of isobutyl vinyl ether (*i*BVE). Silyl enol ether end groups were produced in this case. These groups were then reacted with benzaldehyde to receive ketones at the chain ends, as shown in 1.18.



Scheme 1.18: Mechanism of *ab initio* cationic polymerisation, using difunctional SEEs.

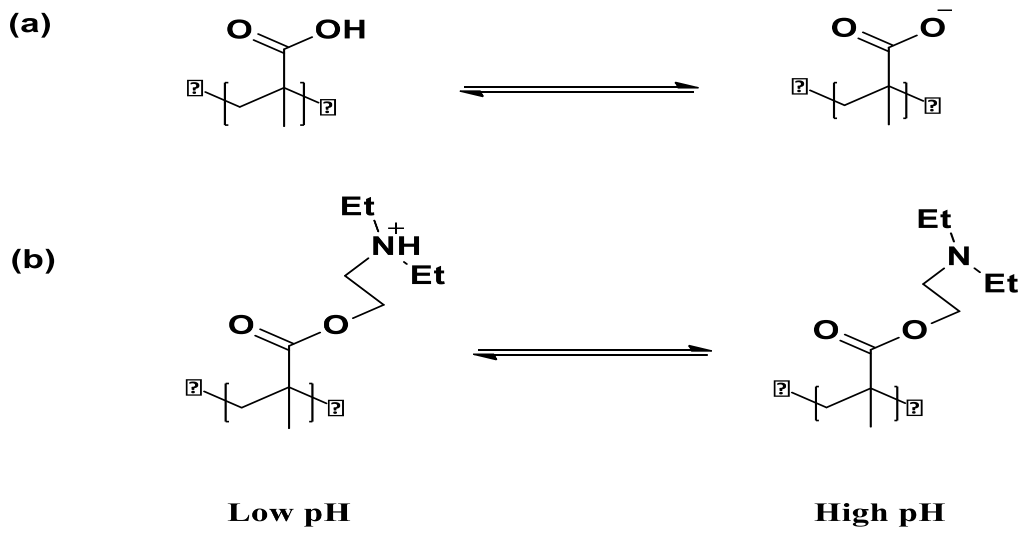
1.2 Synthesis of Highly Branched Functional Polymers

1.2.1 Stimuli Responsive Polymers

Stimuli responsive polymers are becoming popular for their potential applications in biotechnology, particularly in the fields of enzyme and cell immobilisation, controlled gene and drug delivery, the protein dewatering process, biosensors and in molecular motors.[73] Stimuli can be defined as chemical or physical. Chemical stimuli can be due to general environmental changes such as pH or ionic strength, whereas physical stimuli includes temperature, magnetic fields, electricity or UV.[74] However, the most widely investigated stimuli are pH and temperature, both of which have been employed in biomedical applications. Rimmer *et al*[75] introduced new biological stimuli that actually mimic the natural chain refolding process. This new approach involves first binding, followed by a desolvation induced conformational change.

1.2.3 pH Responsive Polymers

Two types of pH responsive polymer can be prepared, the ones with acidic groups (polyacid), like poly(methacrylic acid), and the ones with basic groups (polybase), like poly(diethyl aminoethyl methacrylate), as in Scheme 1.19.



Scheme 1.19: Structures of (a) poly(methacrylic acid) and (b) poly(diethyl aminoethyl methacrylate).

Acidic polymers release their protons at a high pH. The solubility of the polymer in polar solvents such as water can be increased by the buildup of a strong negative charge. This is due to polymer chains being extended, from a globular structure to a random coil formation. The same principle applies to basic polymers ionised at low pH.

1.2.4 Temperature Responsive Polymers

Temperature responsive polymers undergo a transition at the Lower Critical Solution Temperature (LCST). The LCST occurs because the balance between hydrogen bonding (hydrophilic) groups and hydrophobic aggregation is perturbed. When the temperature of the polymer system is below the LCST, the polymer is hydrophilic and exists simply as individual random coils in water. In contrast, when the temperature is higher than the LCST, the hydrogen bonds are broken and the polymer becomes hydrophobic, collapsing into globules, which aggregate, as presented in Figure 1.1.

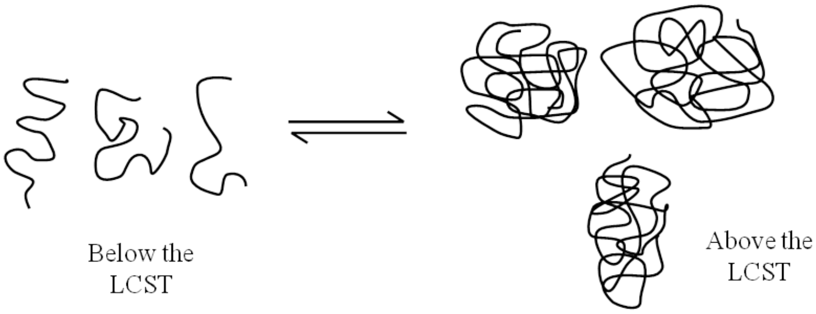


Figure 1.1: Reversible collapse of linear polymer (random coil) into globule and aggregates at the LCST.

The most important polymer studied in this field is the thermo-responsive polymer poly(N-isopropylacrylamide), abbreviated as (PNIPAM). It has a well-known LCST at 32 °C. PNIPAM and its copolymers have the ability to exhibit thermo-responsive behavior, which is known as 'smart' behavior, in aqueous solutions. PNIPAM is a thermoresponsive polymer and thus it has very useful applications for controlled drug delivery systems. Thermoresponsive polymers, such as linear PNIPAM, have initiated great interest because of the transition between an expanded to a collapsed form, at the LCST. However, linear chains have only small amounts of chain end functionality compared with other architectures, such as the comb, star, graft and branched.

Branched polymers, a very common type of architecture, get used in generating a large number of chain end groups. The large number of chain end groups can be employed to add suitable chemical functional groups that may not be available on the main chain.[76] Highly branched PNIPAM copolymers can be used with imidazole groups at the chain ends, as ligands for protein purification and other potential uses in drug and gene delivery systems.[77]

1.2.5 Hyperbranched Polymer Synthesis

1.2.5.1 The History of Hyperbranched Polymers

In the last 15 years, polymer chemists have introduced new dendritic macromolecules, which can be further divided into two groups, dendrimers and hyperbranched polymers. Hyperbranched polymers are usually not as aesthetically pleasing as dendrimers, as branching does not emanate from a central core. Yet they are composed of more random, highly branched and linear segments dispersed throughout the structure, as shown in Figure 1.2.

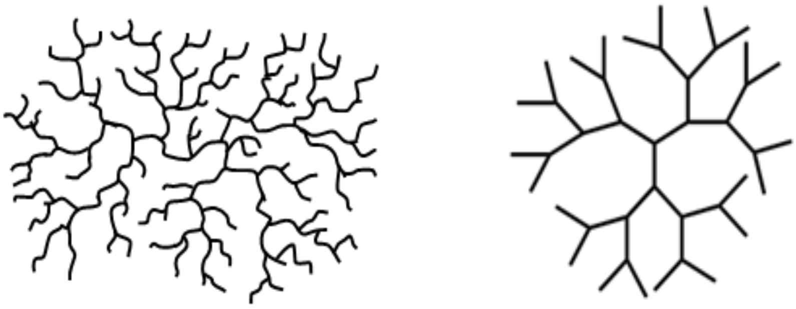


Figure 1.2: The description of dendritic polymers, comprising dendrimers (right) and hyper-branched polymers (left).[78]

Hyperbranched polymers contain highly branched macromolecules, included within, with a three-dimensional dentritic structure. The hyper-branched polymers' history begins as the 19th century was ending, with the work of Berzelius[79], who reported the formation of a resin out of tartaric acid, which is A_2 - B_2 monomer, and glycerol, a B_3 monomer. In 1909, Baekeland prepared the first commercial synthetic plastics and phenolic polymers. These polymers had random hyperbranched structures.[80] Sometime in the 1940s, Flory *et al* calculated the molecular weight distributions of three-dimensional polymers, with tri- and tetra-functional branching units, by using statistical methods.[81] The first experimentally verified hyperbranched polymers were found by Kim and Webster, in 1988, when they prepared soluble hyperbranched polyphenylene. After that, hyperbranched polymers have had growing attention owing to their unique synthesis and properties, which can be compared with dendrimers although they are altogether easier to prepare.[82]

1.2.5.2 Synthesis of Hyperbranched Polymers

1.2.5.2.1 Polymerisation of AB_x Type Branched Polymers

Hyperbranched polymers can be prepared with techniques that are faster and easier than those for the dendrimers, while the resulting material has commercial importance. The synthesis of hyperbranched polymers can be divided into two major categories. The first method involves step growth polycondensation of AB_x type monomers, where $x \geq 2$, as depicted in Figure 1.3.

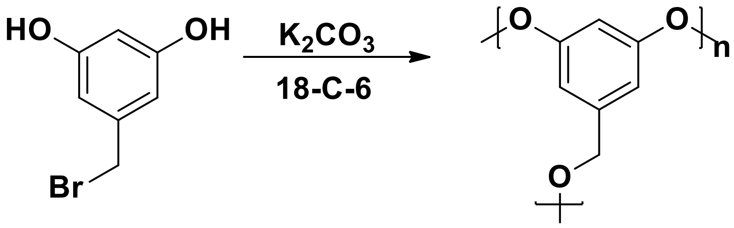


Figure 1.3: AB_2 type monomer for branched polymerisation.

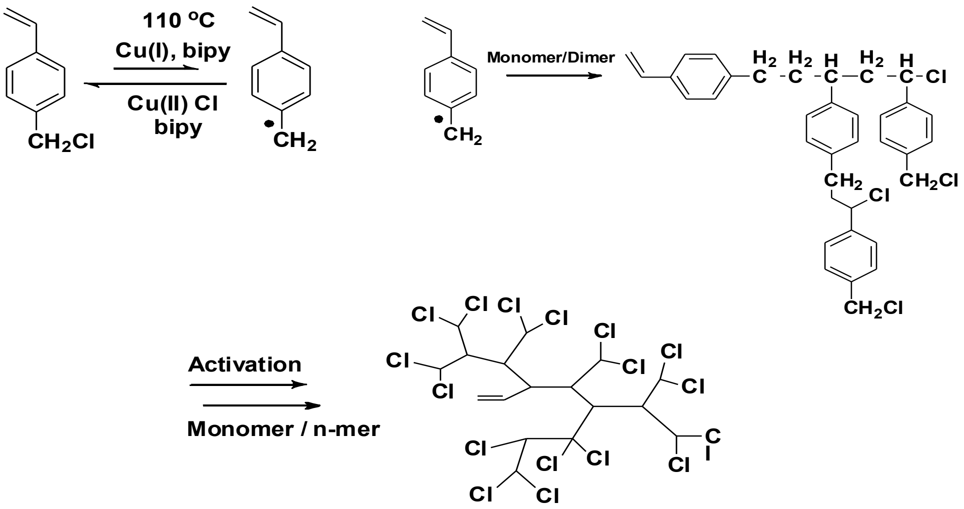
The most common examples of hyperbranched polymers are prepared by step-growth polymerisation, using polycondensation of AB_x type monomers. A and B are two functional groups that can react with each other, but not with themselves. This AB_2 describes a monomer with three sites of functionality, one of A and the other two of B. In this method, there is a lack of control over the size of the polymer and thus broad molecular weight distributions are produced.

1.2.5.2.1 Self Condensing Vinyl Polymerisation

The second method was discovered by Frechet in 1995 and is called self-condensing vinyl polymerisation (SCVP).[83] There are a large number of examples of highly or hyperbranched polymers that have been prepared successfully in this way. The Frechet method includes the polymerisation of 3-(1-chloroethyl)ethenyl benzene, in the presence of a Lewis acid ($SnCl_4$), to produce hyperbranched polystyrene and this polymerisation progresses cationically.

An example of anionic SCVP was reported from the creation of a vinyl monomer carrying an active anion by the reaction of 1,3-diisopropenylbenzene and butyl lithium.[84] The living nature of the reaction allows for additional styrene to be used, to build up the architecture to many generations.

In 1996, Matyjaszewski *et al* first reported a route to obtaining hyperbranched polystyrene, using ATRP in the presence of Cu(I) involving the monomer, p-(chloromethyl) styrene and normal ATRP conditions (Cu(I) and 2,2’-bipyridyl). The p-(chloromethyl) styrene was used as an initiator. The result was that a chain with a double bond at one chain end and a chlorine atom at the other was produced. The double bond acted as a branch point by incorporating it into the growing polymer, as shown in Scheme 1.20.



Scheme 1.20: The homopolymerisation of p-(chloromethyl) styrene via ATRP to produce hyperbranched polymer.

Yang *et al* used reversible addition-fragmentation chain transfer (RAFT) to control an SCVP polymerisation, in 2003. They prepared branched polymers, by using a dithioate easter as a RAFT agent, containing a styrene group.[85] However, hyperbranched polymers produced in this way often led to polymers with very broad molecular weight distributions (MWD) and lower degrees of branching than their dendrimer counterparts. In addition, the Rimmer group was the first to produce highly branched polymers with functionality at the chain ends for binding to cells. The synthetic route to highly branched polymers uses RAFT monomers that contain also dithionate ester functionality.[86, 87]

1.2.6 Branching and Gelation Theory

The functionalities of comonomers present in branching polymerisation are ≥ 2 and 0 to 2 bonds are formed by the unit monomer, with its adjacent molecules if the value of *f* becomes 2. Thus, it helps to develop a macromolecule. In a specific condition, an infinite cluster is formed and the connection of material moves from one terminal to the other, giving the whole group of molecules a shape called a gel.

Gel point is defined as the condition that supports the transformation of a reaction mixture, present in the form of viscous liquid, into an elastic semi-solid material, exhibiting infinite viscosity. Flory first presented theories gel-forming processes and he described, in his research, how sol and gel formation can be differentiated. After acquiring the gel point, two different types of polymers exist, a soluble *sol* and an insoluble *gel*, with the latter making up the infinite network structure.[88] Further gelation occurs as time progresses. This process consumes all the sol present in the solution, to develop an insoluble cross-linked network. Stockmayer outlined statistical problems relating to the cluster size, which he described as a function of monomer conversion, following the determination of molar mass distribution and then the relationship between the weight and the average degree of polymerisation.[88]

$$(X_{T,g}/N_o)(Mw_{,o}/Mn_{,o}) = \tfrac{1}{2}$$

N_o and X_T represent the concentration of prepolymer and crosslinks respectively, whereas *o* and *g* symbolise the prepolymer and gel point. About ½ the value is reported, as a critical number of cross-links perpolymer exhibit a polydispersity effect, as depicted by this equation.

The suggestion of Flory-Stockmayer's (FS) model fails to provide information about intermolecular cross-links and cyclisation.[90] A high fraction of cross-links were found to be wasted, once a gel point was reached in the co-polymerisation process of N-butylmethacrylamide and methylenebisacrylamide, as mentioned in the study of Ulbrich *et al.*[91] During the cyclisation process, 30% of the pendant vinyl was utilised, as reported in the study of Okay *et al.*[92]

By using silyl enol ethers, added to cationic polymerisation as chain terminating agents to produce chain end functionality in branching polymerisations, it is possible to gain control over intermolecular reactions and also the number of branch points per chain, thus preventing gelation.

1.3 Mass Spectrometric analysis of Oligomers/ Polymers

The chain end functionalism of oligomers is studied through the Matrix Assisted Laser Desorption Ionisation Time-of-Flight Mass Spectrometer, also known as MALDI-

TOF MS. Molecular ions are produced from large non-volatile molecules through this method, which involves minimum fragmentation.[93] Biomolecular analyses are performed via this, including peptides, oligonucleotides, polysaccharides, proteins and synthetic polymers. It can derive information about molecular structure as well as molecular weight.

Molecular weight obtained through MALDI-TOF MS is accurate in comparison with that estimated through chromatographic techniques, such as size exclusion chromatography (SEC). Molecular weights that are determined by the latter technique are relative values that employ polymer standards and do not yield information about polymer composition and chain end structure. A series of different polymer chains that have a similar chain size can be easily separated, using MALDI-TOF MS. This is impossible with traditional chromatographic techniques. A detailed analysis of the polymerisation method and side reactions can also be performed through MALDI-TOF MS.

A comparative analysis of MALDI-TOF MS with other traditional polymer characterisation methods has been made in Table 1.4 and it is mentioned that the sample amounts required for processing are significantly smaller than those required for other techniques, while only a few picomoles and femtomoles are required, to generate a well-resolved mass spectrum. This is a fast and efficient means of determining molecular weight, with high precision of given samples obtainable, within minutes. It is, unlike the SEC, not independent of a polymer structure.

Technique	**Absolute M_n**	**Relative M_n**	**Absolute M_w**	**Relative M_w**	**End-group**	**Structure**	**Purity**	***D***
MALDI-MS					+	+	+	
SEC		+		+			(+)	+
NMR	+				+	+	+	
IR	(+)				(+)	+	+	
Elemen. analysis	(+)				(+)	+	+	
Light Scattering			+					
Osmometry	+							
Titration	+				+			

Table 1.4: Comparison between MALDI-TOF MS and conventional polymer characterisation.

However, there are some limitations in terms of molecular weight resolution with high molecular weight polymers in MALDI-TOF MS. On the contrary, SEC works very well for the high molecular weight polymers. In MALDI-TOF MS, the molecular weight resolution increases for very low molecular weight polymers, whereas it does not work very well for a high molecular mass. The reason for this limitation on MALDI samples is that the solid samples are not always homogeneous and the small sized molecules are comparatively easier to desorb, than from larger molecules. SEC is preferred over MALDI for the determination of polymer sample distribution, due to its accuracy and efficiency, in providing the molecular weight distribution. Besides this, successful sample preparations plays a critical role in producing a MALDI-TOF MS spectrum with a good resolution and the chemical structure of a polymer also has a significant impact on this.

In 1988, Tanaka *et al*[94] enacted the laser desorption of intact polymers and this process was used to determine of sodium cationised oligo(propylene glycol) and oligo(ethylene glycol) distribution. A number of categories of polymers have been reportedly analysed by MALDI.[95] Key polymers include, poly(acrylic acid), poly(ethylene glycol), polar organic-soluble polymers like poly(methyl methacrylate), nonpolar organic-soluble polymers, including polystyrene and poly (vinyl chloride), polyethylene and low solubility polymers, such as cured polyimide. Studies show that a decreased solubility of polymers poses difficulties. An analysis of low soluble polymers was quite difficult and the completely insoluble polymers cannot be analysed by MALDI-TOF MS, as a preparation of analyse and matrix is unachievable, if not completely dissolved.[96]

The steps involved in a typical MALDI-TOF MS analysis are summarised as follows, one prepares sample mixtures, with a molar excess of matrix material and then an evaporation process on a flat stainless steel plate follows. The sample first enters a vacuum system and then it is pumped downwards. A burst of ions is generated when a fast laser pulse hits the sample. These ions are then accelerated in an electric field and forced to down to a detector. Ions that are lighter, due to their low molecular weight, reach the detector earlier, while heavier ions approach it later. Then the molecular weight of a specific ion can be computed, after a measurement is obtained of its time of flight, along with proper calibration.

A few of the ionisation methods commonly employed in organic and biological applications are Chemical Ionisation (CI), Spray Ionisation (SI), Desorption Ionisation (DI) and Electron Ionisation (EI). All of these methods have been derived from the concepts of ion chemistry and they provide complementary information regarding the species under study, as well as the use of multiple spectra that are suggested for unknown compounds.

The MALDI process is the latest DI technique that offers greater sensitivity, while it yields single charged ions. The analysis of the ion plume is mainly provided in the Time of Flight (TOF) for MALDI. An electrical field produces the acceleration of ions, before the ions move towards a detector. Lighter ions are first detected, due to their low mass and so they travel fast, reaching the detector before any heavier ones. The m/z ratio of any ion can be obtained from its time, of light measured from its arrival after detection. The mass spectrum is developed after the conversion and registration of the flight time and intensity of all the available ion packs.

There are limitations on resolution and the accuracy of mass spectra, as not all the participating ions exhibit significant differences in their velocities. To counter this short coming, the reflectron mode technique was introduced for the compensation of initial velocity distribution possessed by ions, so that the MS resolution could be enhanced. Figure 1.4 shows the diagram of MALDI-TOF MS analysis.

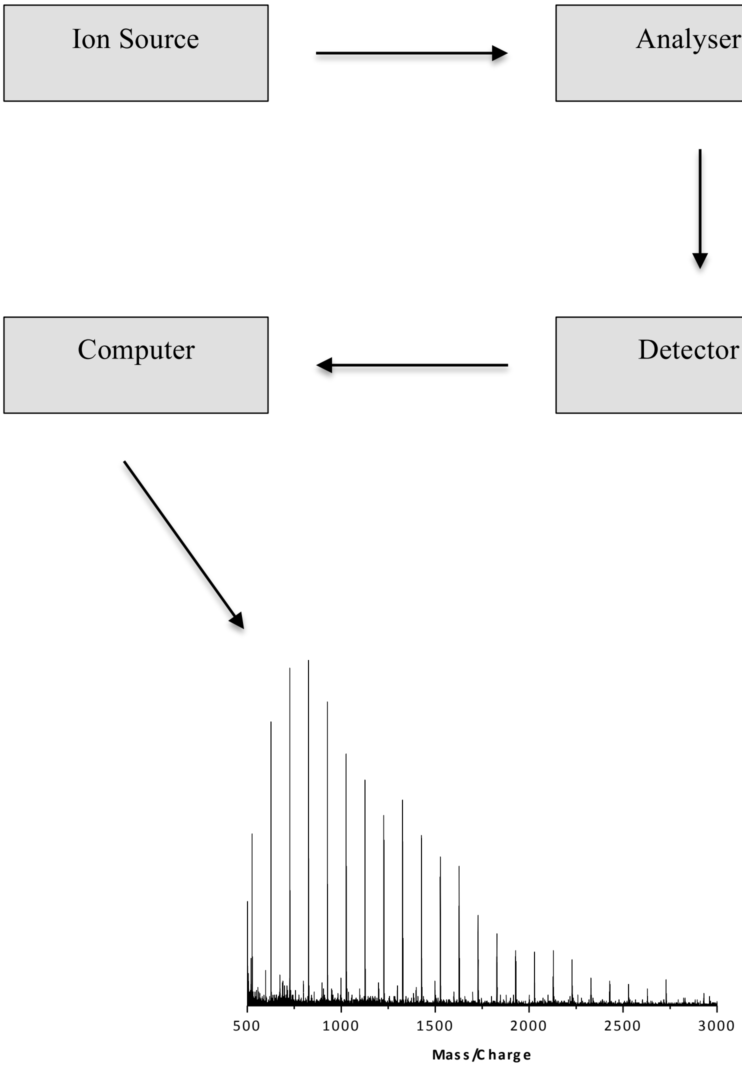


Figure 1.4: The MALDI-TOF MS analysis.

1.4 Aim of this Project

In previous research, the Rimmer group was the first group to produce highly branched polymers with functionality at the chain ends for binding to cells.[97-105] These polymers can be driven through a phase transition in water, when they bind to cells, and they use these systems to attack some major global issues such as the need to detect pathogens and transport human cells. The synthetic routes to these branched polymers[106, 107], as well as other stimulus responsive oligomers, can be derived from cationic polymerisation.[109, 110] The general synthetic route to highly branched polymers in our laboratories, is the use of RAFT monomers, in other words, monomers that also contain dithionate ester functionality.[106, 107] This is shown, in Figure 1.5.

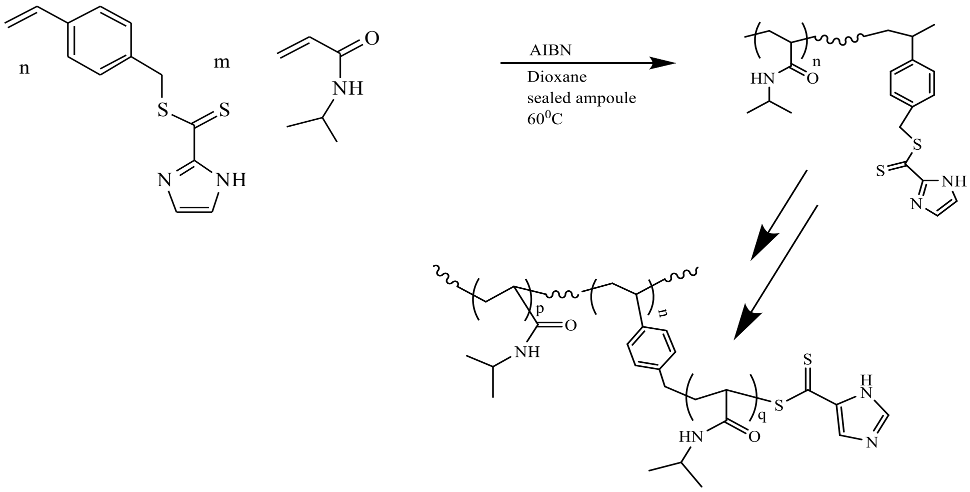


Figure 1.5: A controlled radical polymerisation, using RAFT copolymerisation with a monomer containing the dithionate ester group. The synthesis produces highly branched polymers via a branch-on-branch formation (self-condensing vinyl polymerisation).

However, living/ controlled polymerisations are limited in utility, because the degree of branching is limited by the continuous growth of the chain. For this reason, R. England, in 2010, used radical polymerisation in the presence of silyl enol ethers to produce telechlic oligomers with end groups.[111] A series of monomers were applied, such as styrene, methyl methacrylate and N-isopropyl acrylamide. This study proved that gelation could be halted in radical polymerisation. A difunctional comonomer could be polymerised by gelation could be prevented through the addition of a chain-terminating agent, such as silyl enol ether.

The work of this project has concentrated on the synthesis of short chain polymers with a high degree of functionality at the end chains and then in the synthesis of highly branched polymers. It includes several unique synthetic methodologies, including *ab* initio cationic polymerisations. Silyl enol ethers will be typically used in this area, as the chain-capping agents. The synthetic strategy is the use of the addition of silyl enol ethers to cationic polymerisations, to produce chain end functionality oligomers and reduce the chain length, as shown in Figure 1.6.[108-110] These syntheses involve the capping of the chain end during propagation and the application of this reaction to cationic polymerisations can be used to produce branched polymers.

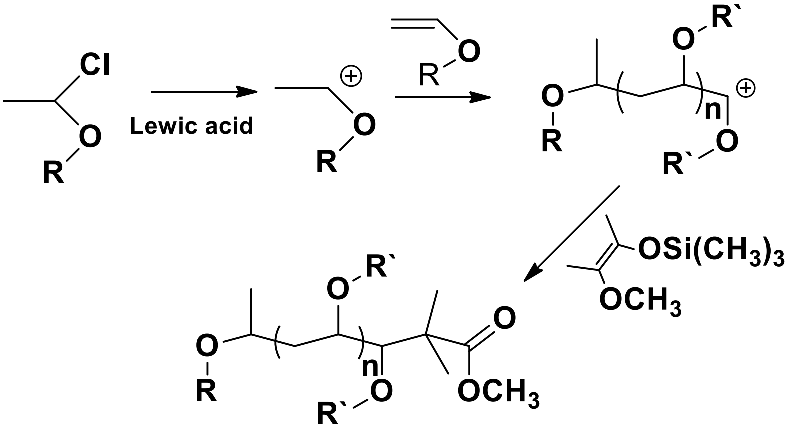


Figure 1.6: An example of a cationic polymerisation carried out in the presence of a silyl enol ether. The capping of the chain and termination both occur simultaneously, with propagation.

The capping reaction, along with silyl enol ether, reduces the degree of polymerisation and with careful optimisation, highly branched polymers can be produced. Already, this can be achieved with radical co-polymerisations of NIPAM and a di-functional monomer.[111] This new approach has many advantages over our RAFT procedure. For example, the RAFT process allows the primary chain to continue growing and this, as well as bimolecular termination, leads to gelation even in systems that are not predicted, by theory, to gel. The project will initially explore this new synthetic route and then the polymers will be fully characterised and their properties examined. Furthermore, continuous processes in the presence of silyl enol ethers aimed at the synthesis of highly branched polymers, using *ab initio* cationic polymerisation, will be investigated.

The programme will examine also the synthesis of a functional chain end-capping agent, as seen in Figure 1.7.

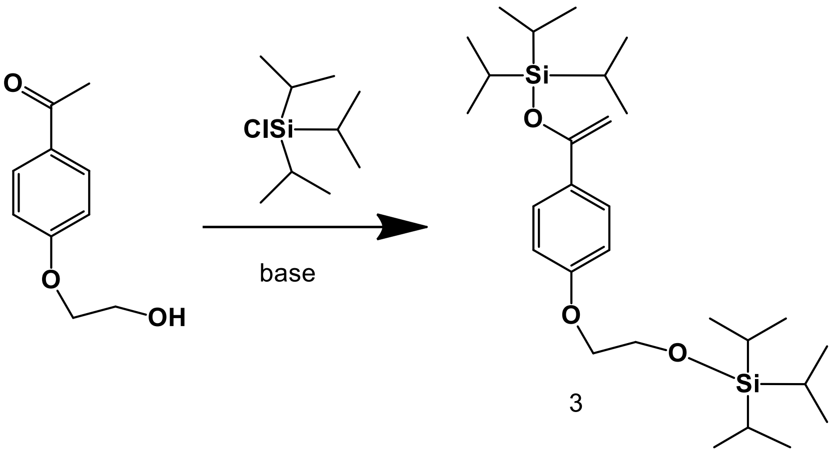


Figure 1.7: Synthesis of a functional chain end capping agent.

The incorporation of **3** into the polymerisations described in ref [111] could be used to produce branched polymers, with the silyloxy chain end group functionality. If these polymerisations were carried out using branching monomers, then it would be possible to prepare the highly branched polymers with the chain end functionality shown in Figure 1.8.

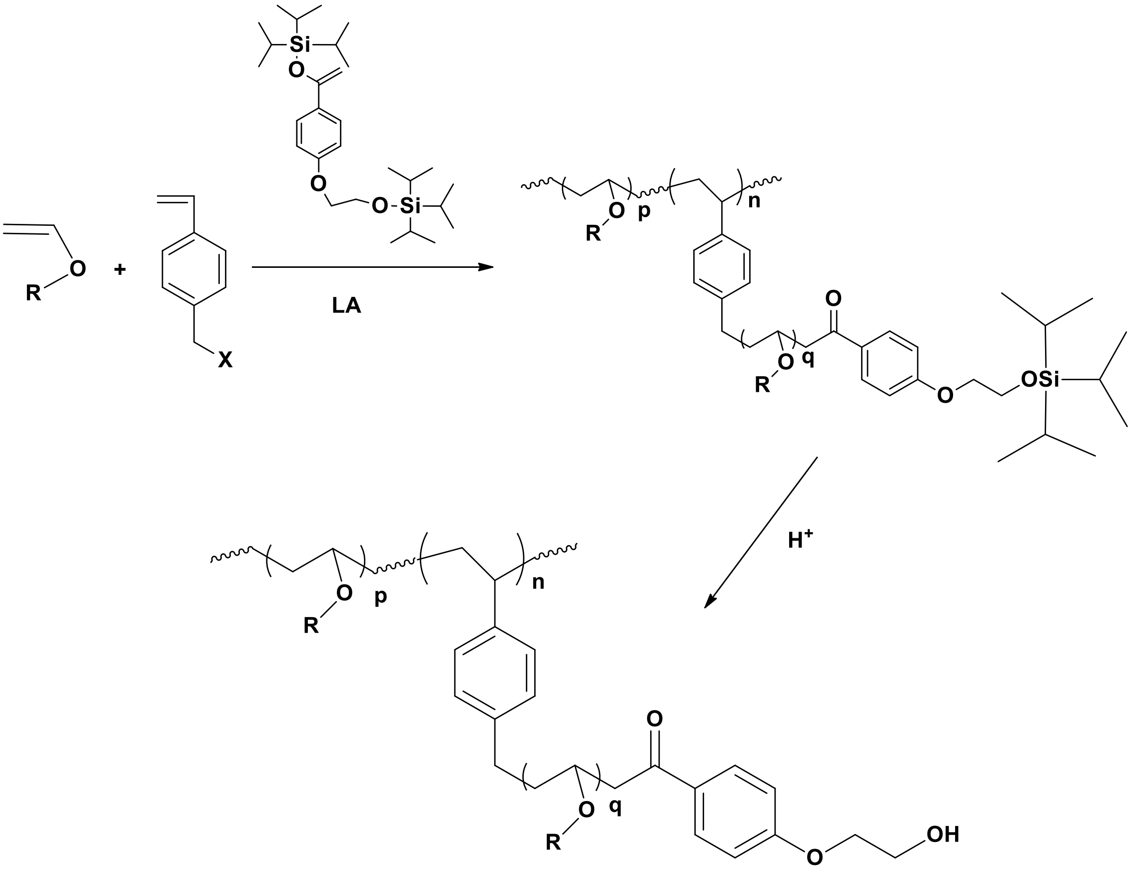


Figure 1.8: Synthesis of highly branched functional polymers using the new route.

In addition, other silyl chain capping agents can be used, such as (1-methoxy-2-methyl-propenyloxy)-trimethyl silane as mono-functional silyl enol ether, to produce highly branched polymers with ester groups as chain end-functionalities, as seen in Figure 1.9.

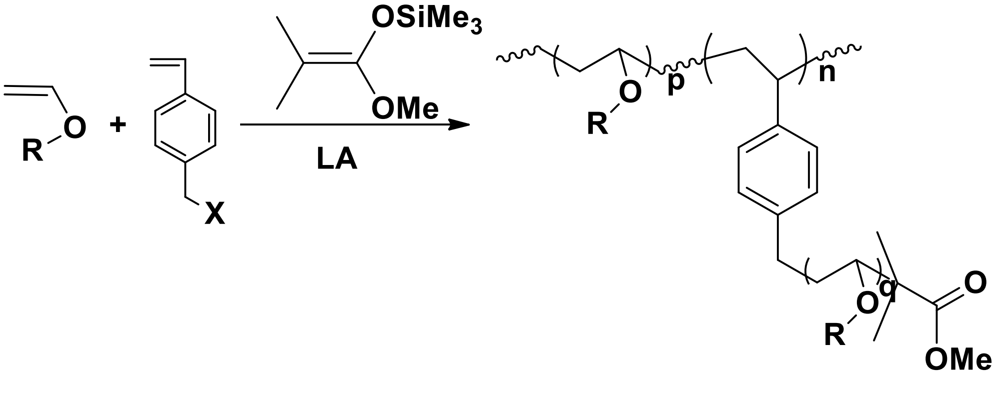


Figure 1.9: Synthesis of highly branched polymers with ester group.

Chapter 2

2. *Ab* initio cationic polymerisation of MVE and *i*BVE using Batch system

2.1 Introduction

High molecular weight polymers can be prepared easily at low temperature with cationic polymerisation.[112] However, the reaction conditions can be difficult to reproduce.[113] Cationic polymerisation reactions can be quenched by adding useful end-capping agents such as silyl enol ether.[61,62] Until recently, end-capping agents in cationic polymerisations have generally required a living polymerisation system in which the chain grows without termination then chain end functionality is added by reacting the chain ends with nucleophilic agents. These agents are known as end-capping agents because they facilitate chain termination by capping the living carbocation chain ends and form terminal functionalities. However, adding chain end functionality in this way entails having to wait until the monomer is consumed before adding a capping agent and this allows time for other termination reactions to occur. Consequently it is important to rigorously exclude any impurities in living cationic polymerisations that are laboratory based in order to restrict the application of living cationic polymerisation in industrial large-scale production processes. Therefore, commercially cationic polymerisation is dependent on the usual termination reactions (elimination reactions) in order to acquire chain end functionalities.

The method adopted (*ab initio* cationic polymerisation) in this study is preferable to living systems in that during capping a terminating compound competes with the fast propagation processes and reaction of the chain end with this compound becomes the dominant termination reaction. In ideal conditions, the capping agent should interact with the carbocationic chain in competition with the propagation reaction and the rate constant for this interaction is proposed to be equal to or less than the rate constant of propagation reaction. In this method, reacting agents are introduced into the polymerisation mixture and these participate in capping of chain ends at a rate that lies between the termination and propagation rates. Ideally, because the normal termination reactions are much slower than propagation (this must be the case for polymerisation to be observed), termination becomes dominated by reactions to the added capping agent. It would be useful here to have the absolute values of the rate constants, however, the high propagation rates and perceived change in the rate constants as an element of conversion means that it is in fact very difficult to measure these parameters. Variation in rate constants is often suggested to be the result of changes in the ion pairing of the propagating chain during the progress of conversion.

As was mentioned in chapter one, the main objective of molecular engineering is to devise methods for controlled polymerisation for the production of a well-defined polymer. This process includes production of polymer using control of the molecular weight and its distribution. If living polymerisation can be performed, in ideal conditions it will provide a narrower molecular weight distribution; a great deal of work has focused on this aspect using anionic, radical and cationic methods. However, useful functional polymers require control of other parameters such as: degree of pendant group or end group functionality, sequence of constitutional repeat units, stereochemistry structure, spatial shape and 3-D structure.[32, 107, 108] In fact, in many applications obtaining narrow molecular distribution is of secondary importance to obtaining maximum degree of functionality, although obtaining narrow molecular weight distribution (usually defined by size exclusion chromatography) is often a more achievable goal.

Sawamoto and Higashimura conducted intensive studies on cationic polymerisation of vinyl ether monomers[114] and were able to successfully establish a well-controlled polymerisation system. Tin tetrachloride ($SnCl_4$), Lewis Acid has been used in cationic polymerisation reactions since 1979 and numerous living cationic process have been produced.[115, 116] In the current study, we employed it and titanium tetrachloride ($TiCl_4$) as Lewis Acids in *ab initio* methods for a variety of purposes. Initially, we were curious to see if a cationic polymerisation reaction mediated by $SnCl_4$ and $TiCl_4$ was capable of generating chain end functionalisation or not. We were interested in developing a novel cationic method in which we could combine all the following aspects: oligomer molecular weight, control molecular weight dispersity and control degree of chain end functionality. The temperature of a polymerisation reaction is a crucial parameter that has a significant effect on the cationic polymerisation process. In this chapter, the considerable impact of temperature on chain end functionality will be reported.

2.2 Experimental

2.2.1 Materials

*i*BVE, 99% Aldrich product was washed with 10% aqueous NaOH solution and then with water three times to be free from inhibitor, dried overnight with anhydrous sodium sulphate and distilled before use.[117] MVE, (98% Aldrich) was purified by passing the gaseous monomer through a calcium hydride column and condensed at –80 ^{o}C.[118] n-Hexane, (99% Aldrich) was refluxed over CaH_2 for two hours and distilled over molecular sieve. o-Xylene, (99 % Aldrich) was used as received. Sulphuric acid (concentrated) and sodium chloride (99 %), BDH (AR grade) products were used as received. Charcoal was dried over three days at 120 ^{o}C. DCM, (99.6% Aldrich) was refluxed over CaH_2 and then distilled just before use. $SnCl_4$, (1.0 M) solution in DCM (Aldrich) was used as received. $TiCl_4$, (1.0 M) solution in DCM, (Aldrich) was used as received. 1-methoxy-2-methyl-1-(trimethylsilyloxy)propene, **SEE 1**, (95 %, Aldrich) was purified by fractional distillation under reduced pressure.

2.2.2 Synthesis of HCl-*i*BVE adduct

The HCl-*i*sobutyl vinyl ether adduct was generated by bubbling dry HCl gas into the solution of *i*sobutyl vinyl ether (in n-hexane, 1.0 M) at 0 °C for one hour under magnetic stirring. Dropping concentrated sulphuric acid into powdery sodium chloride produced the HCl gas. Then, the product was purified and dried by passing through concentrated sulphuric acid, activated charcoal and finally dry silica gel respectively. The unreacted HCl in the reaction mixture was removed by bubbling dry nitrogen gas through the vessel. The pure adduct was confirmed by using ^{1}H NMR. In addition, the concentration of HCl-*i*BVE adduct was measured by the Volhard method.[119] The solution was sealed into a brown bottle and stored in a freezer.

2.2.3 Determination of HCl-*i*BVE adduct concentration by Volhard method

The general protocol used to determine HCl-*i*BVE adduct was as follows. HCl-*i*BVE (2 ml) in n-hexane solution, nitric acid solution (6.3 M) and slight excess of standard (0.1 M) silver nitrate solution (35 ml) were added in a 250 ml conical flask. Tartazine (0.5%) was used as an indicator (about 4 drops). The suspension was shaken for two minutes in order to ensure that the indicator was absorbed on the precipitate as much as possible. The residual silver nitrate was titrated with standard potassium thiocyanate (0.1014 M) until the very pale yellow supernatant liquid assumed a rich lemon-yellow colour. The titration was repeated with two other portions of the solution.

Calculations:

Concentration of HCl-*i*BVE adducts:

$$\frac{(Vol.of AgNO_3 x Concentration of AgNO_3) - (Vol.of KSCN x Concentration of KSCN)}{Vol.of Solution(taken)}$$

$$= \frac{(35x10^{-3}x0.1) - (2.5x10^{-3}x0.1014)}{2x10^{-3}}$$

$$= \frac{3.3025}{2}$$

$$= 1.65 mol.cm^{-3}$$

2.2.4 *Ab* initio cationic polymerisation of MVE with Lewis acids

2.2.4.1 Cationic polymerisation of MVE without end-capping agent

Cationic polymerisation reaction was performed in a pre-sealed three neck round bottom flask placed under dry nitrogen. The MVE gas cylinder as well as the reaction flask was attached to the T-glass tube through an air tight syringe. The MVE entered the reaction flask when connection of flask was blocked and cylinder was connected to it. Subsequently, MVE cylinder connection was opened to let it fill inside the syringe up to a volume of 100 ml and the cylinder connection was closed. Reaction flask was connected to it so that the whole volume present in the flask was occupied by the MVE. The MVE settled in flask and condensed there by cooling. Using the atmospheric pressure and volume of gas, the amount of deposited MVE was computed using the ideal gas law. Upon addition of a solution of Lewis acids ($SnCl_4$ or $TiCl_4$), MVE polymerisation began. In this reaction HCl-*i*BVE was used as an initiator and DCM solvent maintained at -26 or -76 °C for 45 minutes. (2 M) methanol/ammonia solution was used to terminate the reaction. Washing was performed with 2 % HCl_{aq} and then with warm deionised water for the elimination of tin residues. In the end the solution was kept overnight so that undesirable solvents evaporated to yield the polymer.

2.2.4.2 Cationic polymerisation of MVE in the presentce of monofunctional silyl enol ethers as an end-capping agent

The polymerisation of MVE was initiated by adding of a solution of Lewis acid ($SnCl_4$ or $TiCl_4$) to the solution containing MVE, HCl-*i*BVE adduct as an initiator, DCM as a solvent and three different concentrations of silyl enol ethers as end capping agent (0.05, 0.10 and 0.15 M) at -76 °C for 1.5 hours. The reaction was terminated with ammonia solution (2.0 M) in methanol. The resultant solution was washed with HCl (2%) and warm deionised water three times (both below 10 °C) to remove the Tin containing residues. Finally, the solvent was evaporated and dried over night to give the polymer.

2.2.5 *Ab* initio cationic polymerisation of *i*BVE with Lewis acids

2.2.5.1 Cationic polymerisation of iBVE without end-capping agent

The polymerisation of *i*BVE was carried out at -26 and -78 °C placed in a three-neck round flask under dry nitrogen and DCM as a solvent. The polymerisation was initiated by the addition of a solution of Lewis acids ($SnCl_4$ or $TiCl_4$) to a cold solution including *i*BVE and initiator. The polymerisation was generally run for 1.5 hours. The product was washed with 2 % of HCl_{aq} then followed with warm deionised water three times. After that, the solution of the oligomer was left in a vacuum oven overnight to isolate the oligomer.

2.2.5.2 Cationic polymerisation of iBVE with end-capping agent

O*i*BVE were synthesised using a three neck round bottom flask with DCM under dry nitrogen at -26 and -78 °C. The polymerisation was initiated by the addition of a solution of Lewis acids ($SnCl_4$ or $TiCl_4$) to a cold solution including *i*BVE, initiator silyl enol ether as end capping agent. The reaction was terminated with ammonia solution (2.0 M) in methanol. The resultant solution was washed with HCl_{aq} (2%) and warm deionised water three times (both below 10 °C) to remove the Tin containing residues. The solvent was evaporated and the residue dried over night to give the polymer.

2.3 Organic and Polymer characterisation

2.3.1 ^{1}H and ^{13}C NMR

^{1}H NMR spectra were recorded on a Bruker 250 MHz instrument at ambient temperature. Chemical shifts are reported in part per million (δ). In general, approximately 30mg of the compound were dissolved in deuterated chloroform, filtered and placed in a 7mm NMR tube.

^{13}C NMR spectra were obtained on a Bruker 400 MHz instrument at ambient temperature operating at 100.5 MHz. The parameters employed in each case:
Number of transients (NS): 25499, acquisition time (AQ): 1.3 sec, line broadening (LB): 2.00Hz. In general, 100 mg of sample were dissolved in deuterated chloroform, filtered it and placed in a 7mm NMR tube.

2.3.2 SEC measurements

Size exclusion chromatography (SEC) measurements were carried out using combined RI and UV (260 nm) detectors at ambient temperature using THF as the solvent and toluene as a flow marker. Polymer laboratories gel 2 x 60 cm low molecular weight columns were used for *i*BVE and MVE polymers. Sample concentration was 2.5 mg cm^{-3}. SEC measurements were calibrated against polystyrene standards. OMVE and O*i*BVE SEC fractions were collected using a Gilson FC 205 fraction collector, under the same SEC conditions.

2.3.3 FT-IR

All samples were analysised at room temperature using FT-IR spectroscopy, recorded from 500-4000 cm^{-1} using a Perkin- Elmer spectra software 100 FT-IR. All spectra were compiled from 4 scans. A universal diamond (Perkin-Elmer) was used to measure all samples directly.

2.3.4 MALDI-TOF MS analysis

Equipment

MALDI-TOF mass spectra were obtained using a TofSpec 2E instrument from Micromass, using dithranol as the matrix with a quadrupole detector. The following parameters were used to analyse the polymer samples: Instrument voltage 20 KV;

sampling rate 500 MHz; pluse time 39 pluse voltage 2471 V, detector voltage 1689 V and cationic agent: NaI.

Sample preparation

Polymer samples (10 mg) were dissolved in 0.5 ml of THF, dithranol (10 mg) was also dissolved in 0.5 ml of THF and sodium iodide (5 mg) was dissolved in 0.5 ml of THF. 20 μl of the polymer solution, 20 μl of matrix solution and 5 μl of NaI solution were mixed together. 1 μl of the mixed sample solution was applied on the target plate and allowed to dry fully before being loaded into the MALDI-TOF mass spectrometer.

Calibration

Each standard peptide was dissolved in 0.1% trifluoroacetic acid (TFA) aqueous solution (1 mg cm^{-3}), stored in sealed amber sample tube in a freezer and thawed as required. Matrix solution was prepared by dissolving 10 mg of dithranol in 1 ml 60 % of 0.1 % TFA aqueous solution and 40 % acetonitrile. Due to the variable quality of this matrix the dithranol was recrystallised from a MeOH/pentane mixture.

External calibration was applied to each sample plate. Bradykinin (M_w= 1060.2), Angiotensin (M_w= 1296.5), Substance P (M_w= 1347.6), Renin (M_w= 1759.0), ACTH (M_w= 2465.7), and Insulin (M_w= 5733.5) were used as calibration standards. At least 100 shots were combined to produce each spectrum. Calibrated combined spectra were preferred to examine the detailed polymer ion spectra. Calibration solution was prepared by mixing of 3 μl Bradykinin solution, 2 μl Angiotensin solution, 4 μl Insulin solution, 1 μl Substance P solution, 1 μl ACTH solution, 150 μl 0.1% TFA/water solution and 160 μl dithranol in 40:60 acetonitrile: water solution.

Average functionality calculation of silyl enol ethers from MALDI-TOF mass spectra

Functionality of each oligomer of repeat number, I (f_i) was calculated using the following equation:

$$f_i = \frac{I_{i,Alk}}{I_{i,Alk} + \sum I_{i_{nf}}}$$

Where, I_{alk} = intensity of the alkylated peak of repeat number, i

Ii_{nf} = intensity of other peaks with repeat number, i and end groups after than that derived from alkylation.

The repeat number were selected across the whole distribution and mass number. Then, $\sum M_i f_i$ and mass of main peaks' intensities were calculated.

Average functionality of silyl enol ethers were calculated using the following equation:

$$\bar{F} = \frac{\sum M_i f_i}{\sum M_i}$$

Combination of SEC and MALDI-TOF MS

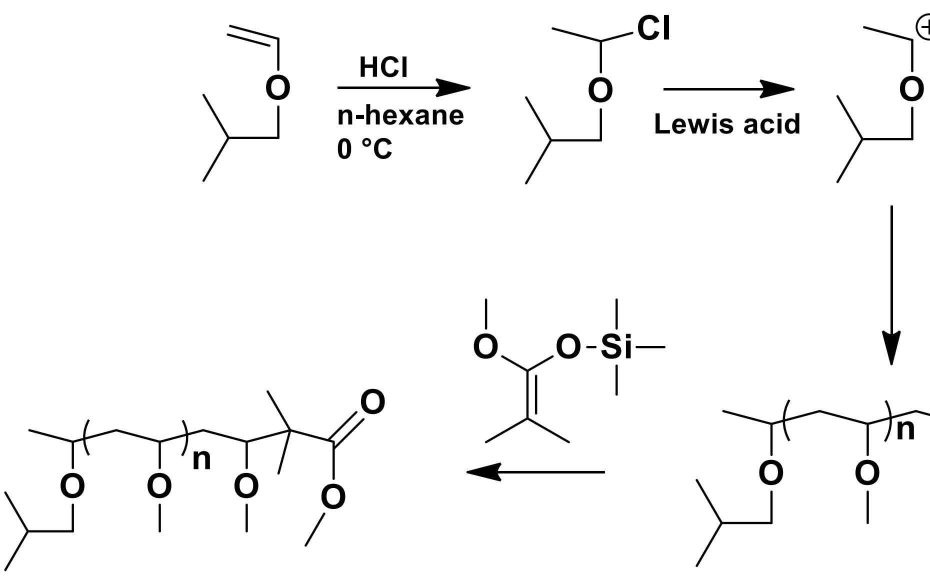
SEC fractionation was performed by the connection of 3×30cm low molecular weight Styragel™ 5 mm mixed gel columns (Polymer Labs.) with Gilson FC 205 fraction collector. After the polymer sample had flowed through the SEC column and had been separated by molecule size, it was collected at the fraction collector. Various fractions were collected from 11 to 16 minutes elution time. The collected SEC fractions were left to evaporate to condense to 10 times higher concentration, to give about 2 mg ml^{-1} solution in THF. This was used as polymer solution to prepare the MALDI-TOF MS samples. THF was applied as the solvent for SEC and MALDI sample preparation. The final MALDI-TOF MS sample contains about 1 mg ml^{-1} OMVE or O*i*BVE and 5 mg ml^{-1} dithranol and clear MALDI-TOF mass spectra were produced.

2.4 Results and discussion

2.4.1 *Ab intion* cationic polymerisation of MVE in the presence of $SnCl_4$ as a Lewis acid

2.4.1.1 Polymerisation of MVE at -26 °C

This research has chosen to study the polymerisation of MVE catalysed by tin tetrachloride and HCl-*i*BVE adduct at -26 ℃ using DCM as a solvent. The results of a series of polymerisations carried out in the presence of 1-methoxy-2-methyl-1(trimethylsilyloxy)propene, **SEE 1** are shown in Scheme 2.1.



Scheme 2.1: General mechanism of *ab initio* chain end functionality in cationic polymerisation of methyl vinyl ether.

In the case of the use of **SEE 1,** the alkylation of silyl ketene acetals with carbocations produces esters that would be of general utility in the production of polymers with a wide variety of useful end groups. Further, silyl ketene acetals are highly nucleophilic and the reactivity scales produced by Mayer indicate that they would have suitable rate constants for use as terminating agents during *ab initio* cationic polymerisation. The rate constants for addition to vinyl or silyl enol ethers were compared using the results of Mayr et al. on the reaction of carbocations with nucleophiles. The researchers compared the reactivities of alkyl vinyl ethers and silyl enol ethers in similar model reactions with electrophiles. Although silylated enol ethers rapidly desilyate and the carbonyl bond is formed after the electrophilic addition, silyl enol ethers can in this way prevent further polymerisation and thus may be applied as end-capping agents in our *ab initio* cationic polymerisation. Consequently, it is suggested in this work that modification of cationic polymerisations of vinyl ethers, such as MVE, with **SEE 1**, produces oligomers with useful ester groups; this was also demonstrated in the previous scheme. $SnCl_4$ has been used for the polymerisation of MVE and it can also be used as a Lewis Acid. This strong Lewis Acid often produces very fast rates of polymerisation. However, chain capping with agents added at the start of the polymerisation can be used to alleviate this problem because the rate of chain capping is similar to the rate of propagation and this minimises the lifetime requirement for the carbocationic chain end. Table 2.1 shows the polymerisation conditions and SEC analysis results as well as end functionality data carried out in the presence of **SEE 1** for 1.5 hours at -26℃.

ID Sample	$[M]^a$ mol L^{-1}	$[SEE]^b$ mol L^{-1}	$[I]^c$ mol L^{-1}	Conversion (%)	Mn g mol^{-1}	*D*	$[F]^d$ (%)	Type of modal
RO 09	0.6	0	0.05	99.41	7,800	1.14	0	Monomodal
RO 10	0.6	0.05	0.05	97.76	4,800	1.93	24	Bimodal
RO 11	0.6	0.1	0.05	98.07	7,300	2.00	40	Bimodal
RO 12	0.6	0.15	0.05	96.42	10,900	1.10	20	Monomodal

Table 2.1: Results of the polymerisation of MVE. (a) [M] = Monomer concentration. (b) [SEE] = Concentration of **SEE 1**. (c) [I] = Initiating concentration system = HCl-*i*BVE/$SnCl_4$ in DCM. (d) [F] = Average functionality measured by MALDI-TOF analysis.

The molecular weight distributions of these polymerisations are shown in Figure 2.1. It can clearly be seen that at high temperature (-26℃) the silyl enol ether reacted with the carbocationic chain end during the propagation process of MVE, but only to a limited extent, and broad molecular weight distributions with functionalities of 40 % or less were obtained. This occurred because at high temperature the polymerisation was very fast and this lead to producing oligomers with unwanted end groups by side reactions.

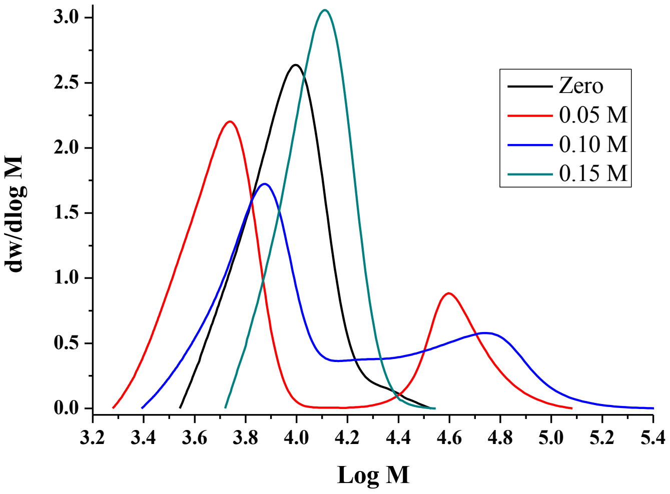


Figure 2.1: Molecular weight distributions of OMVE derived at -26 ℃.

It can be seen from Table 2.1 that higher concentrations of silyl enol ether in this system produced larger molecular weights of the polymer. Thus, the rates of propagation in these reactions were significantly higher compared with the rates of termination. This result is surprising when considered against previous studies on the same subject and it may be due to the fact that $SnCl_4$ is a very strong Lewis Acid. The rate of termination was also still too high compared to the rate of end-capping and functionalities were low. The data indicates that the rapid reaction of **SEE 1** with the initiator occurs in competition with initiation. The dominance of this process would decrease the concentration of the initiator so that once the concentration of **SEE 1** decreases to a point where initiation becomes feasible, the concentration of the initiator has been reduced substantially and this leads to increasing molecular weight as the concentration of **SEE 1** increases. Thus the system requires using a lower temperature to decrease the rate of termination. These results are shown graphically in Figure 2.2.

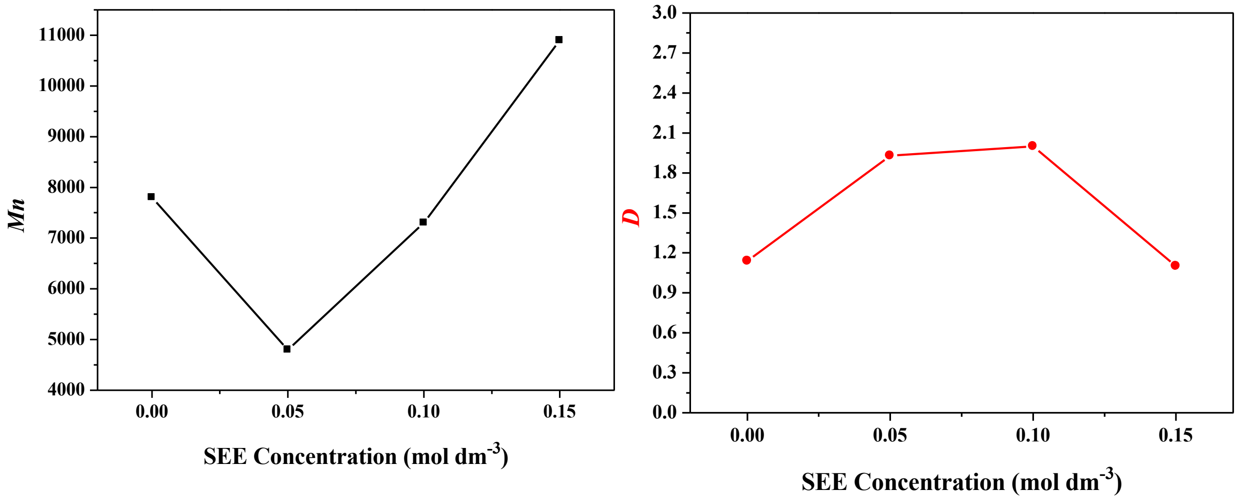


Figure 2.2: Molecular weight (left), dispersity (right) via different concentrations of **SEE 1** at -26 °C.

The monomer conversions and average functionalities are plotted with concentration of **SEE 1** in Figure 2.3. The data showed that all monomer conversions were very high even when different concentrations of **SEE 1** were used. The average functionality increased with concentration of **SEE 1** until 0.10 M and then decreased directly. The data thus show that *ab initio* polymerisations of MVE at -26℃ using SnCl$_4$ were unsuccessful and useful OMVE with reasonable end group functionality were not obtained. A lower temperature in this case would probably help to reduce the side reactions. Therefore, in next section, lower reaction temperatures such as -78℃ are considered.

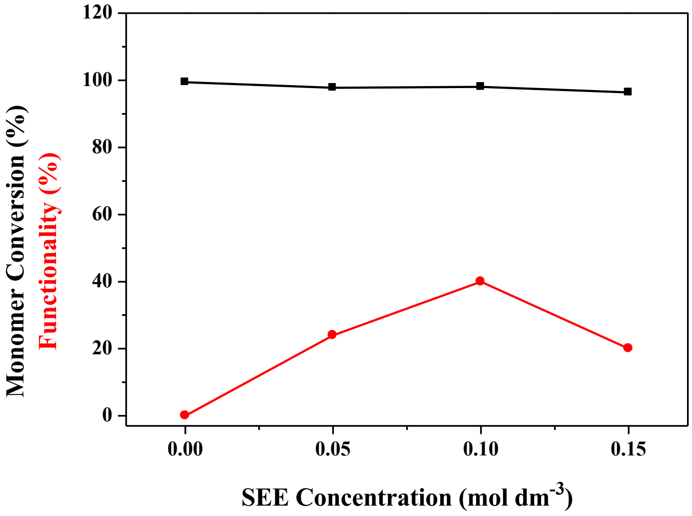


Figure 2.3: The monomer conversion (black) and the average functionality (red) of PMVE derived from different concentration of **SEE 1** at -26 °C.

In the previous study, $TiCl_4$ was used for the polymerisation of MVE under the same conditions that were used in this section. However, it was reported that the products were less dispersed in molecular weight when **SEE 1** was added.[120] Furthermore, the average chain-end functionality increased as the concentration of **SEE 1** increased.

2.4.1.2 Polymerisation of MVE at -78 ℃

Ab initio polymerisations of MVE were performed at -78 °C. The functionality, monomer conversion and molecular weight data of the polymers obtained in the presence of **SEE 1** are listed in Table 2.2.

ID Sample	**[M]^a mol L^{-1}**	**[SEE]^b mol L^{-1}**	**[I]^c mol L^{-1}**	**Conversion (%)**	**Mn g mol^{-1}**	***D***	**[F]^d (%)**
RO 08	0.6	0	0.05	99.00	5,600	1.81	0
RO 05	0.6	0.05	0.05	98.00	2,800	1.26	48.27
RO 06	0.6	0.1	0.05	100.00	2,600	1.22	63.20
RO 07	0.6	0.15	0.05	99.00	4,200	1.33	22.05

Table 2.2: Results of the polymerisation of MVE at -78 °C. (a) [M] = Monomer concentration. (b) [SEE] = Concentration of **SEE 1**. (c) [I] = Initiating concentration system = HCl-*i*BVE/$SnCl_4$ in DCM. (d) [F] = Average functionality measured by MALDI-TOF analysis.

Figure 2.4 shows that the use of a lower temperature led to the production of a well-defined oligomer. Cationic polymerisation of MVE that was carried out in the absence of silyl enol ether led to the production of higher molecular weight material with the broadest dispersity. Cationic polymerisation of MVE in the presence of various concentrations of **SEE1** enabled the production of oligomers with a narrower dispersity and lower molecular weight. Thus, it was possible to control the cationic polymerisation to some extent and Mn, *D* and chain end functionality could be regulated.

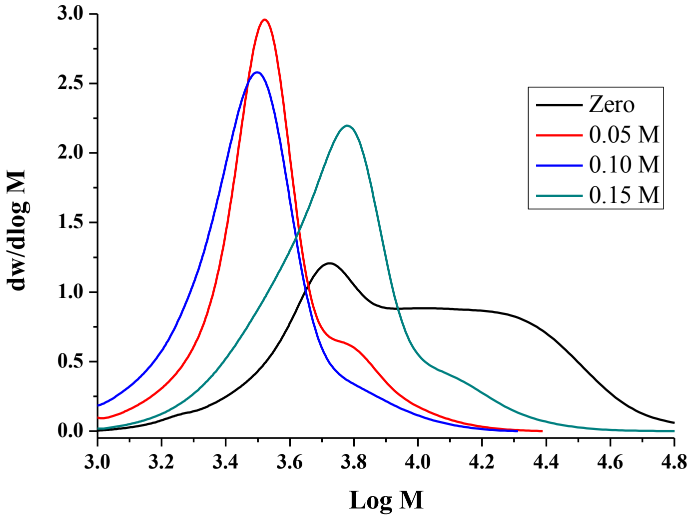


Figure 2.4: Figure 2.1: Molecular weight distributions of PMVE derived at -78 ℃.

In Figure 2.5 the highest molecular weight is shown was produced in the absence of **SEE 1**. On adding **SEE 1**, the molecular weight decreased and the termination reactions was observed with a decrease in dispersity. However, further increases in **SEE 1** (0.15 M) lead to increased the molecular weight with a broad dispersity was obtained.

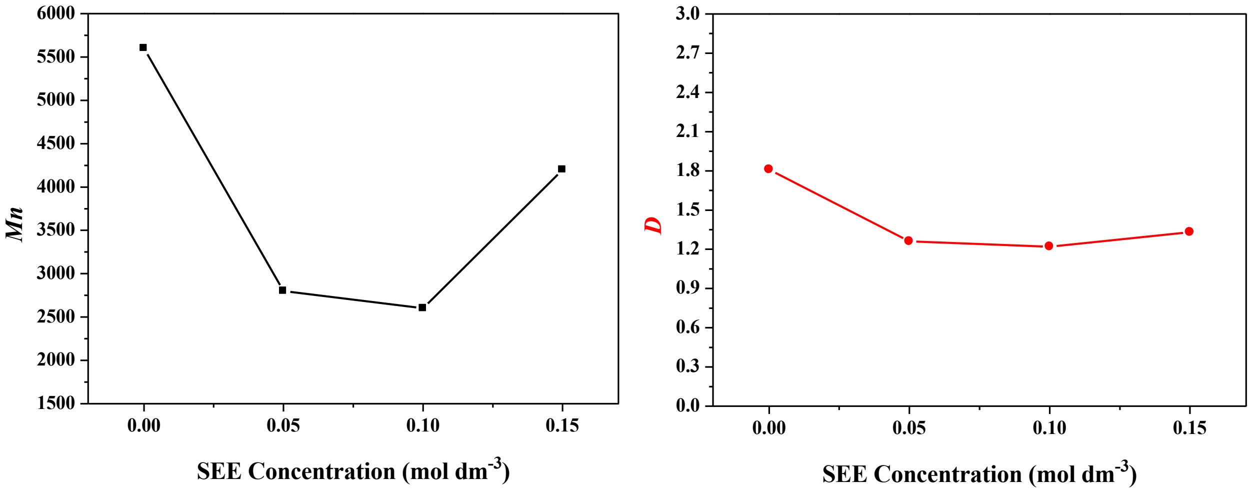


Figure 2.5: Molecular weight (left), dispersity (right) via different **SEE 1** concentration at -78 °C.

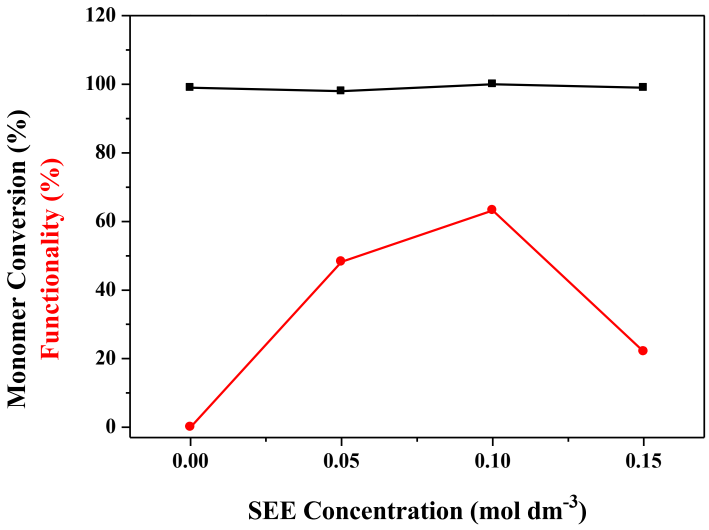


Figure 2.6: The monomer conversion (black) and the average functionality (red) of OMVE derived from different concentration of **SEE 1** at -78 °C.

The data are shown graphically in Figure 2.6. The chain end group functionalities increased as **SEE 1** concentration increased. However, the functionalities decreased at a **SEE 1** concentration of 0.15 M. The data indicates that carrying out the polymerisations at -78°C provided some improvements in the system, but the polymerisation was far from optimum; the functionalities were moderate and the M_n varied in a more complex manner than expected. In general, when $SnCL_4$ (rather than $TiCl_4$) was used for the polymerisation, the polymers produced had higher molecular weight averages and lower functionality. The data imply that the Lewis acid $TiCl_4$ produced higher rates of alkylation relative to the rates of termination and was better suited to the control of this polymerisation.

Figure 2.7, also shows ^{1}H NMR spectra of the polymers produced without and with **SEE 1**. At 1.1 to 1.2 ppm, the spectra provided evidence for the methyl groups from the ω-methyl-(2, 2dimethyl); ethanonate was observed at position **a**. Methoxy from the ester end group was also observed at 3.70 ppm in position **b** in the presence of **SEE 1**. The peaks at **a** and **b** were both absent from polymerisation carried out in the absence of **SEE 1**.

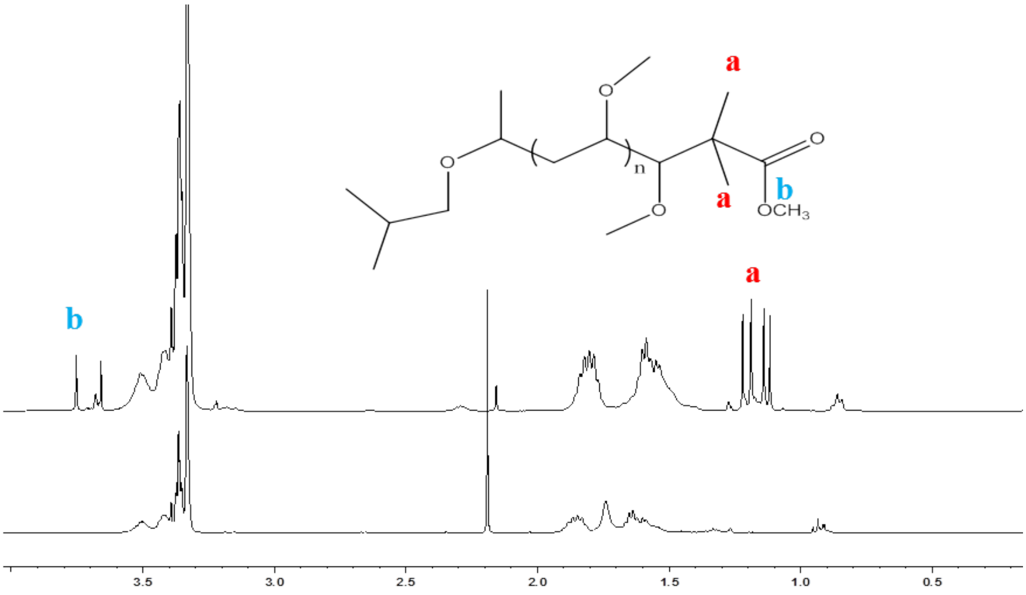


Figure 2.7: ^{1}H NMR spectrum of OMVE prepared at -78 °C in the absence (below) and presence (top) of **SEE 1**.

The ^{13}C NMR spectra showed resonances at 178 ppm due to the ester carbonyl group (Figure 2.8).

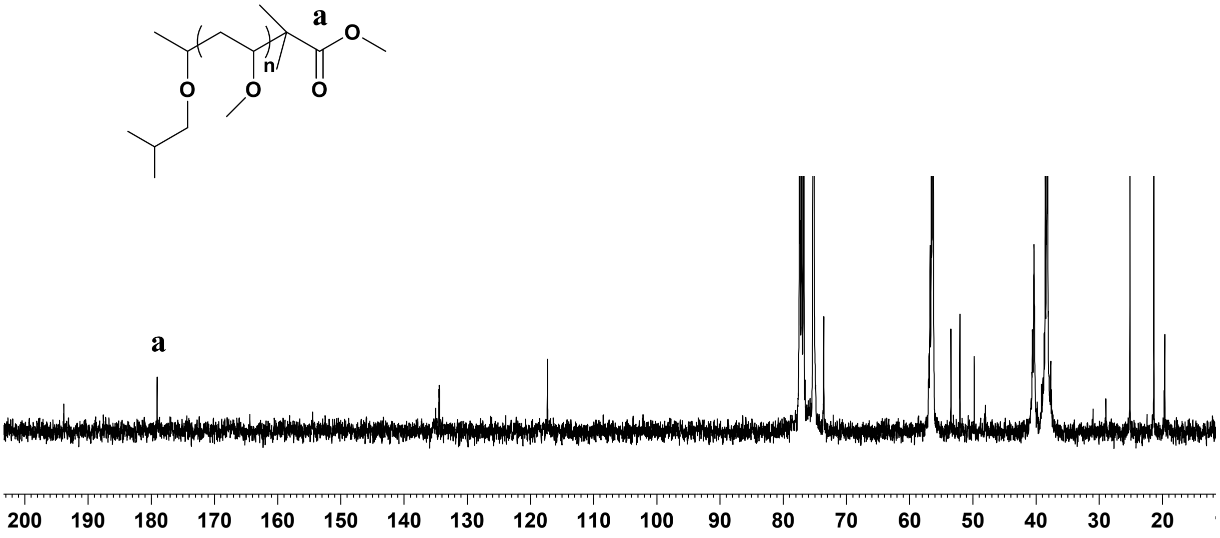


Figure 2.8: ^{13}C NMR spectrum of OMVE with ester group functionality.

Fourier Transform Infrared (FT-IR) spectroscopy of the OMVE (Figure 2.9) show peaks around 1700 and 1490 cm^{-1} corresponding to the C=O and C-O bonds of ester groups.

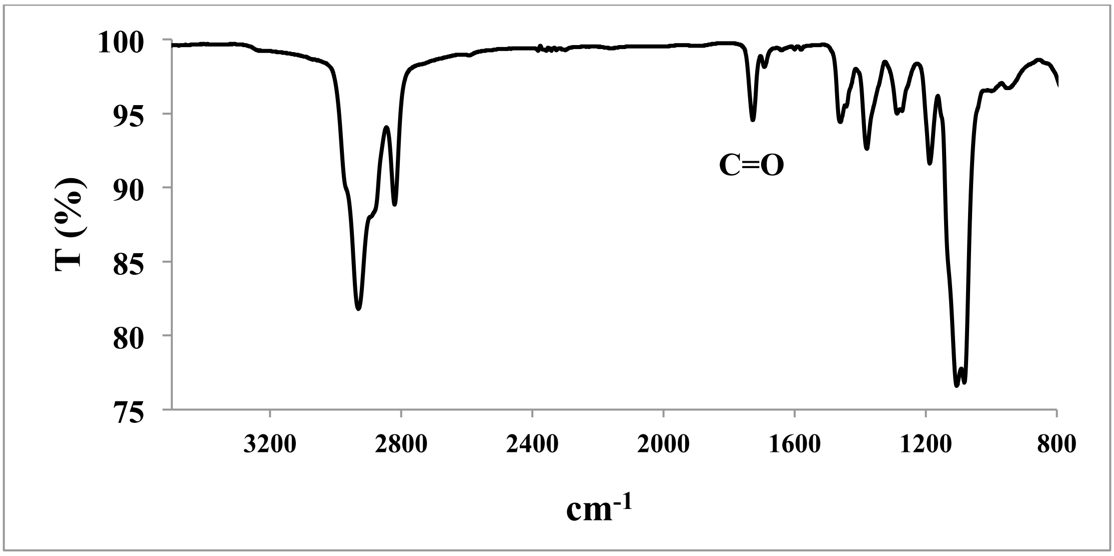


Figure 2.9: FT-IR spectrum of PMVE in the presence of **SEE 1**.

Thus, it can be reported that at -78℃ the polymerisation MVE produced some of the target oligomers. However, as the concentration of **SEE 1** reached 0.15 M the molar mass and dispersity increased. These data suggest that a substantial amount of initiator is being used in reactions before propagation takes place. In the absence of **SEE 1**, the dispersity was very broad and multi-modal. In contrast, in the presence of **SEE 1**, there was a general decrease in dispersity. Thus, to sum up, at -78℃ in the absence of **SEE 1** the termination process created a high dispersity; this effect decreased with the addition of **SEE 1**. However, the relationship between molar mass and concentration of **SEE 1** was not as predicted for an *ab initio* cationic polymerisation (decreasing M_n with increasing concentration of **SEE 1**). Instead, as the concentration of **SEE 1** increased, M_n decreased but at higher concentrations there was an increase in $M_{n.}$

2.4.2 MALDI-TOF mass spectrometric analysis of OMVE end-capped by SEE 1

Polymerisation carried out in the presence of **SEE 1** produced material with different degrees of functionality, as determined by NMR spectroscopy, at different concentrations of silyl enol ether. MALDI-TOF mass spectrometry was further used to examine the chain end functionalities of these polymers. Figure 2.10 shows the

MALDI-TOF mass spectra derived from polymerisations conducted at -78°C. When the polymerisation was carried out at 0.05 and 0.10 M concentrations of silyl enol ether, the MALDI-TOF mass spectra consisted of two series of polymer ions. **SEE 1** typically capped the oligomer chain end and produced the oligomer series labelled as A, which can be assigned to oligomers with ester end groups m/z = (58.08n + 23 + 202), due to the repeat number. The other series labelled B is from oligomers with the alcohol chain end group derived from the quenching process with methanol added m/z = (58.08n + 23 + 174). However, when polymerisation was carried out at a concentration of 0.15 M of silyl enol ether, the MALDI-TOF mass spectra consisted of three series of polymer ions (Figure 2.11). As was noted above, these two series suggested the presence of ester and alcohol groups. The other peak, which was observed only at 0.15 M of **SEE 1**, can be assigned to the methoxy chain end group, which was also present following the quenching reaction with methanol and could be described by m/z = (58.08n + 23 + 187).

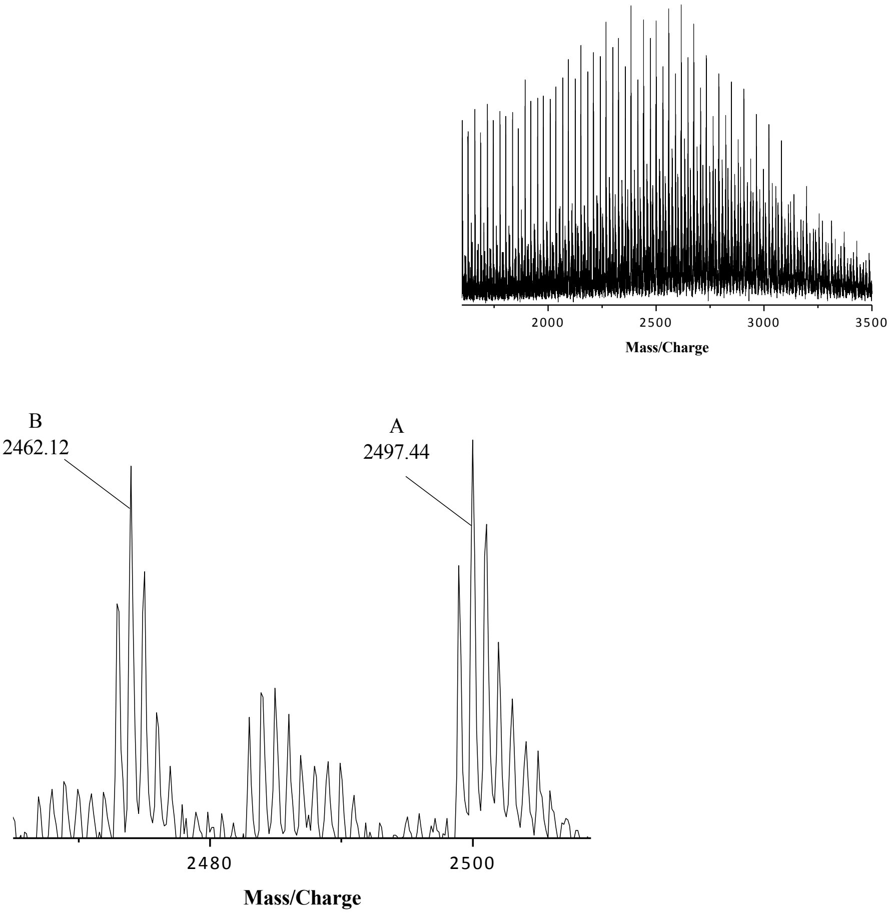


Figure 2.10: MALDI-TOF-MS spectrum with the determined chain end groups for OMVE (0.05 M of **SEE 1**) obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

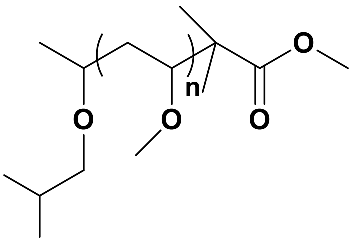
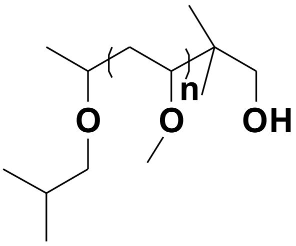
	A	***B***
Structure		
End group mass	202	174
m/z	202 + 58.08 n (Na^+)	174 + 58.08 n (Na^+)
Proportion (%)	48.27	51.73

Figure 2.10: Continued.

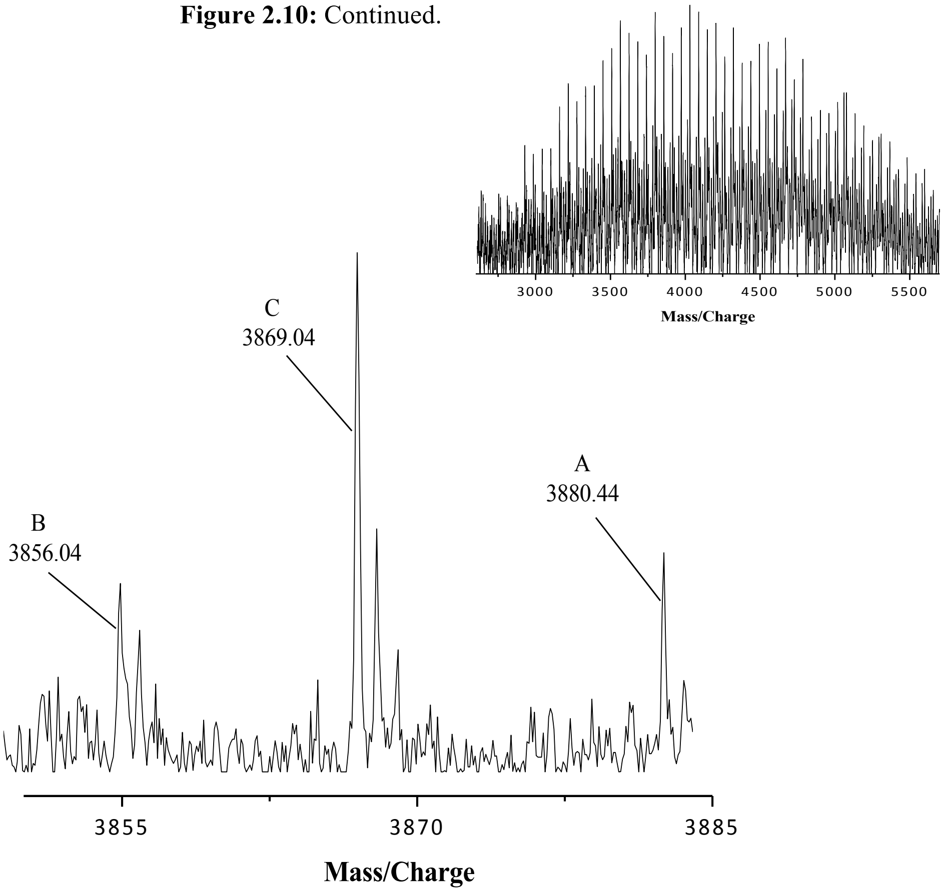


Figure 2.11: MALDI-TOF-MS spectrum with the determined chain end groups for OMVE (0.15 M of **SEE 1**). obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

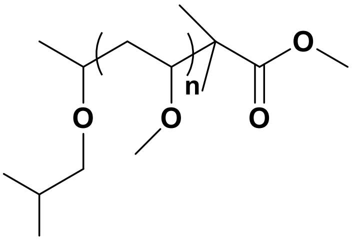
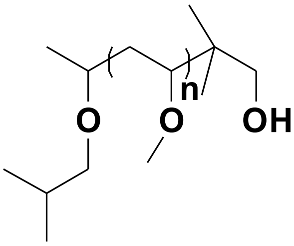
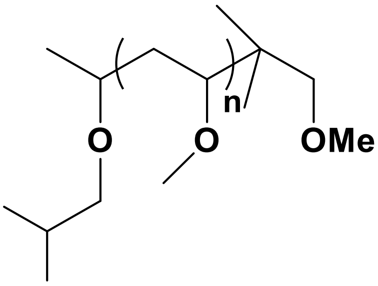
	Structure	***End group mass***	***m/z***	***Proportion (%)***
A		202	202 + 58.08 n (Na$^+$)	22.05
B		174	174 + 58.08 n (Na$^+$)	16.17
C		187	187 + 58.08 n (Na$^+$)	61.78

Figure 2.11: Continued.

Analysis of side reactions

Several oligomer chain end functionalities were observed in the MALDI-TOF mass spectra. Analysis of these side reactions in order to attain the fullest information about the polymerisation process is very important. Different chain end formations (B and C) were obtained in MALDI-TOF MS. These formations were produced from reduction occurring in the presence of the Lewis Acid.

2.4.3 Measurement of molecular weight from SEC and MALDI-TOF

SEC provides separation of polymer samples according to hydrodynamic volume. However, converting these chromatograms into absolute molecular weight distributions requires knowledge of the relationship between retention time and log molar mass in specific solvents for specific polymer types. For a low molar mass sample, MALDI-TOF mass spectra of the fraction derived from SEC separations can provide the required calibration. Figure 2.12 shows the molecular weight distributions from SEC and MALDI-TOF MS of the same polymer sample. In SEC without molar mass sensitive detectors, the molecular weight distribution of the polymer is calculated as a relative value of molecular weight based on calibration, such as with polystyrene standards. MALDI-TOF MS can be used to calculate the molecular weight according to the absolute values of polymer ions.

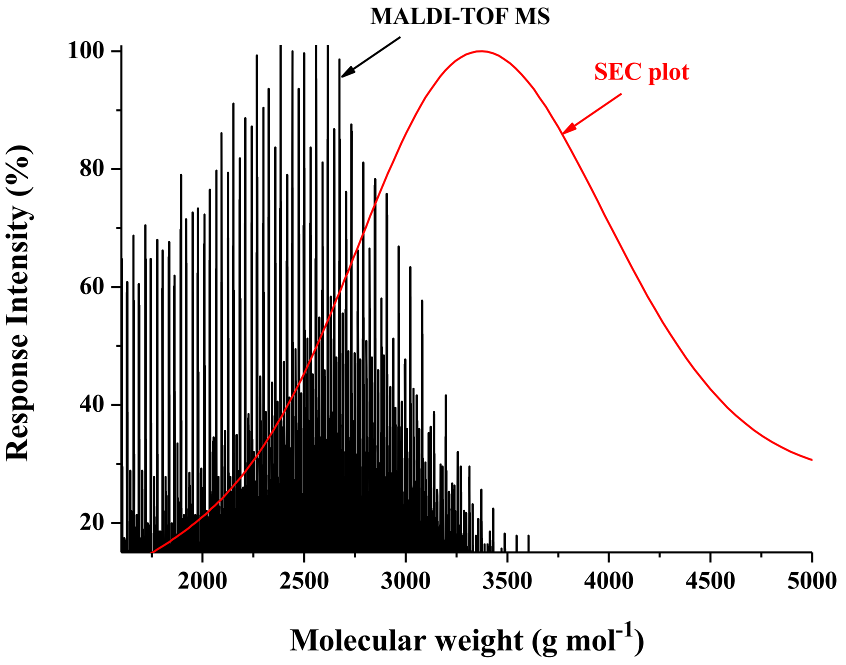


Figure 2.12: Molecular weight distribution of OMVE from SEC and MALDI-TOF MS.

SEC result :(*Mn* = 2760, *D* = 1.26.

End group mass averaged from several peaks taken from the MALDI-TOF mass spectrum can be given by plotting repeat units with different molecular weights. This demonstrates that, according to the end group mass outlined in Figure 2.13, the intercept was 202.

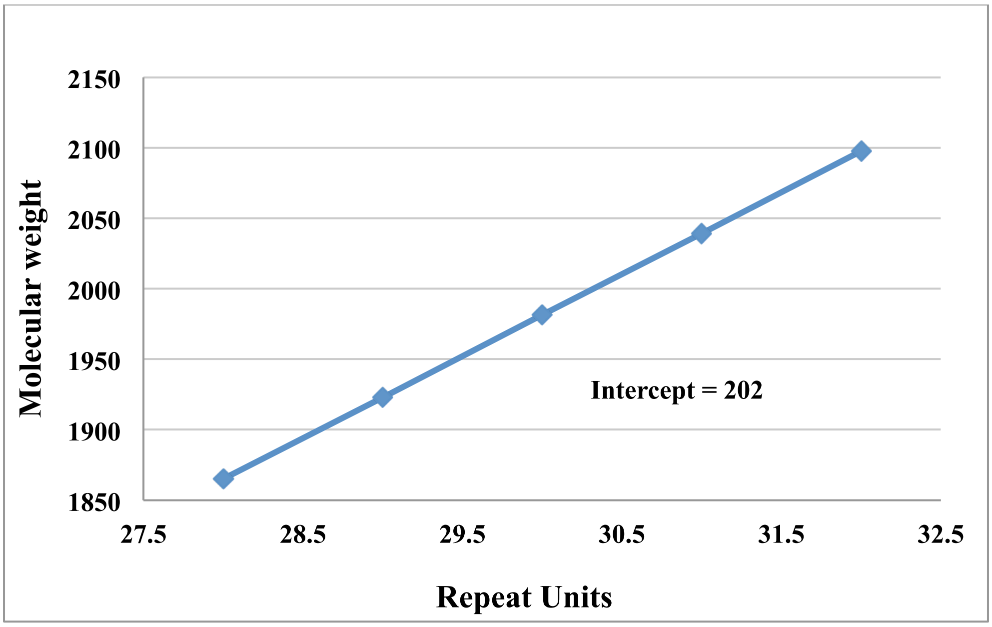


Figure 2.13: Regression plot (calculated from MALDI-TOF MS) for 0.10 M concentration of **SEE 1** at - 78 °C. The intercept shows the end group mass.

2.4.4 The Kuhn-Mark-Houwink relation for PMVE

2.4.4.1 Viscosity Theory

Linear polymer solutions have a relatively large viscosity, even in the very dilute situation. This viscosity of a polymer solution depends on the size (molecular weight) of the dissolved polymer and the polymer concentration. Therefore, this relationship is used to measure the intrinsic viscosity and the molecular weight of dilute polymer solutions. It can be used to obtain the molecular weight provided the relationship between viscosity and molecular weight is known. Furthermore, viscosity systems are very common because the equipment of the experiment is simple and easy to operate. The molecular weight applies to a wide range and also there is a high experimental accuracy.

The most important experimental property is intrinsic viscosity $[\eta]$. It can be measured by measuring the specific viscosity $[\eta_{sp}]$ at many different concentrations and extrapolating to zero concentration. In addition, the efflux time dependence of the specific viscosity of a dilute polymer solution flowing through a capillary is shown in the equation below:

$$\eta_{sp} = \frac{(t - t_0)}{t_0} \qquad (1)$$

t_0: efflux time of solvent. t: efflux time of dilute polymer solution.

Dilute polymer solutions generally conform to the relations defined in the Huggins equation (2) and Kreamer equation (3):

$$\frac{\eta_{sp}}{C} = [\eta] + k_1[\eta]^2 C \qquad (2)$$

$$In\frac{\eta_r}{C} = [\eta] + K_2\,[\eta]^2\,C \qquad (3)$$

In these two equations, $\eta_r = \eta/\eta_0$ is the relative viscosity of the polymer solution. η_{sp} is the specific viscosity of the polymer solution. *C* is the concentration of the solution. $[\eta]$ is the viscosity of the polymer solution and η_0 is the viscosity of the pure solvent.

The relationship between the polymer molecular weight and polymer intrinsic viscosity can be given by using Mark-Houwink equation:

$$[\eta] = K\,M^{\alpha} \qquad (4)$$

In this equation, [η] is polymer intrinsic viscosity. K and α are constants, which are related to the type of polymer, temperature, solvent interaction and molecular weight range. When, K and α are known, the polymer intrinsic viscosity [η] can be established. The α is a constant that depends on the polymer, solvent and temperature. Values of α for a linear flexible polymer chain typically lie between 0.5 and 0.8. The polymer can be dissolved in a theta solvent, if the value of alpha close to 0.5. Linear, randomly coiling vinyl polymers is very good solvents give values of alpha near to 0.8. In addition, when the solvent becomes a theta solvent, α is equal to 0.5. However, when the solvent becomes thermodynamically better than the theta conditioned, then the α increases directly.

2.4.4.2 Viscosity Experimental

In this case, MALDI-TOF mass spectrometry was use to obtain reaction conditions were the dominate termination reaction was alkylation of the silyl ketene acetal. In addition, a size exclusion chromatograph (SEC) was calibrated using MALDI-TOF MS to obtain molecular weights of narrow fractions (SEC-MALDI-TOF MS). After that, the Kuhn-Mark-Houwink relation for poly(methyl vinyl ether) was established.

Polystyrene standards with polydispersity index (PDI) of less than 1.2, has been typically used to calibrate the SEC. Polystyrene is a linear polymer and therefore it is only suitable to compare it to other polymers, which are linear and with the same solubility characteristics. However, polystyrene standards in THF solvent are often used as a calibration for other polymers in SEC. This calibration can be obtained by plotting the retention time versus the logarithm of the polystyrene molecular weight, as shown in for this analyses in Figure 2.14.

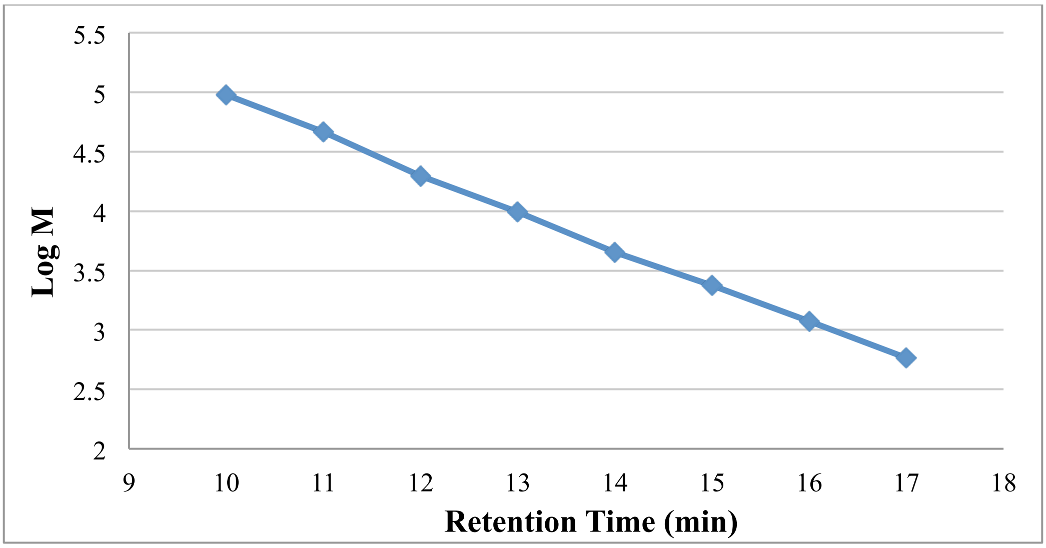


Figure 2.14: The relationship between retention time via log M of polystyrene standard.

Polymerisation of MVE with end capped agent

SEC fractionation was used to collect several molecular sizes of OMVE in the presence of (0.05 M) **SEE 1** at -78°C. Once the polymers had been separated they were collected in a fraction collector at between 14 and 16 minutes. Several fractions were collected for each OMVE sample. Each fraction contains 0.16 minute of eluent. Following this, the collected SEC fractions were analysed using MALDI-TOF MS, as shown in Figure 2.15.

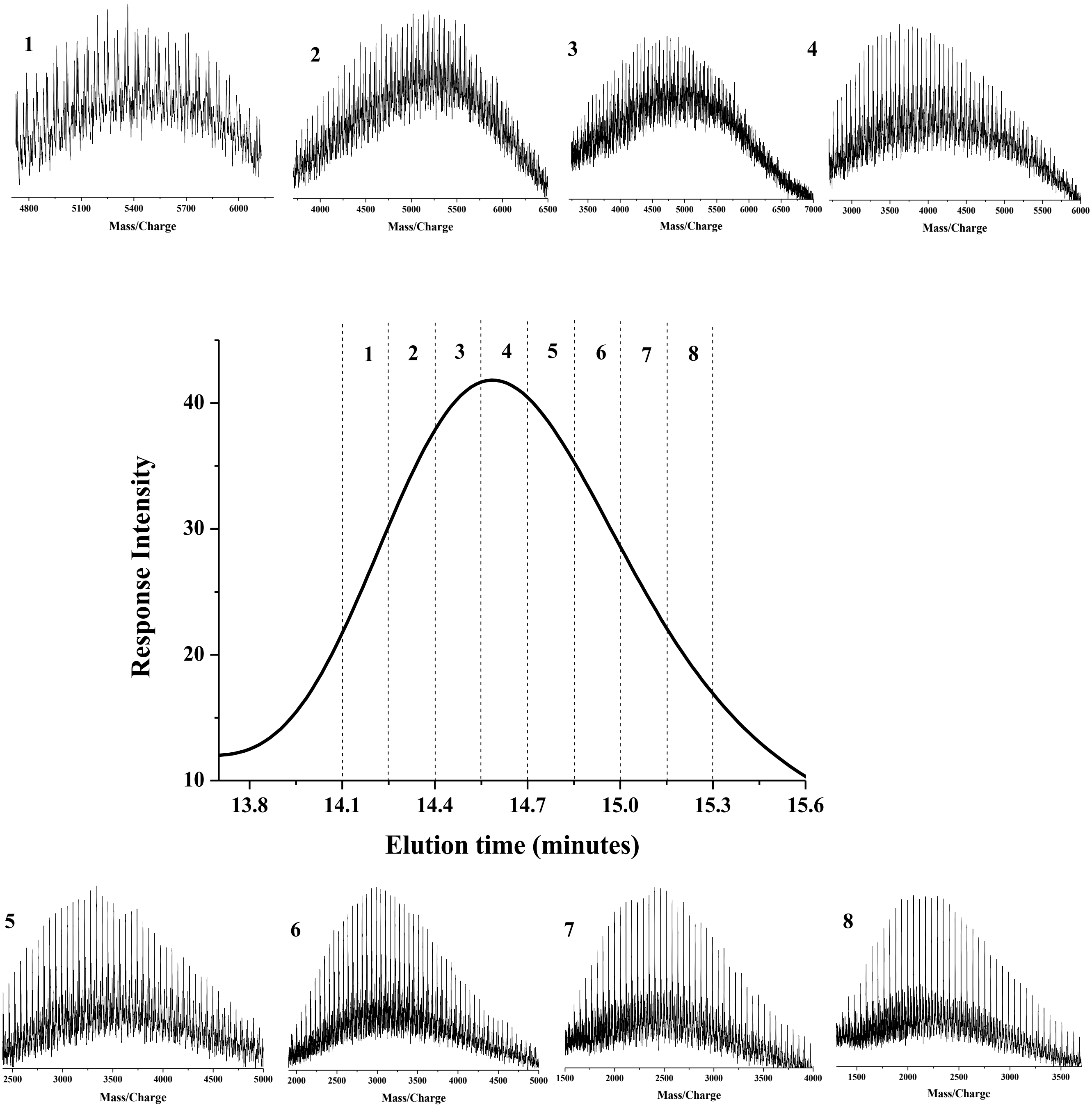


Figure 2.15: Combination of SEC and MALDI-TOF MS for OMVE with end groups.

The average molecular weight of each SEC fraction was measured according to MALDI-TOF mass spectral data. The plot of the average molecular weight (Mn) was calculated from the respective MALDI-TOF mass spectrum to show SEC elution time; the data are shown in Figure 2.16.

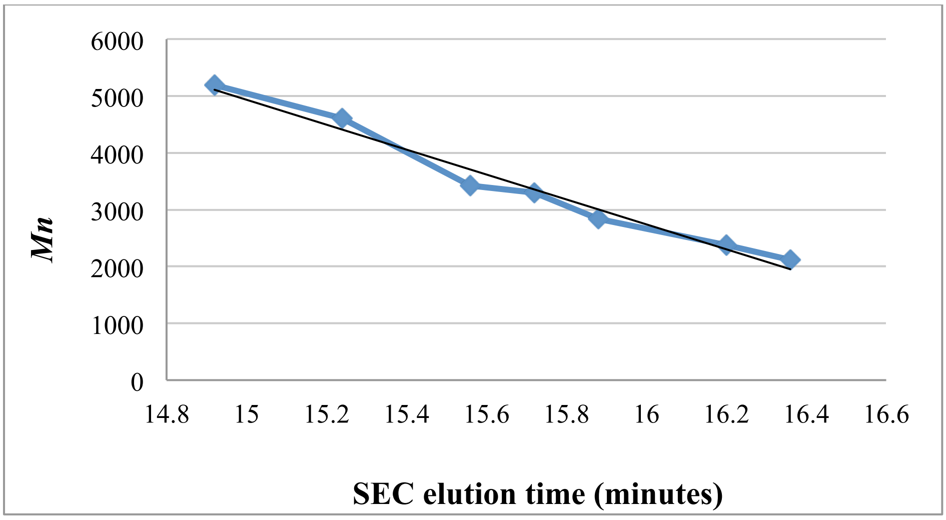


Figure 2.16: Calibration of SEC column by the combination of SEC-MALDI.

These data can be used to calculate the constants α and K by plotting log molecular weight of polystyrene standard from SEC to log the molecular weight of oligo(methyl vinyl ether) regarding the data taken from the MALDI-TOF mass spectra as shown in Figure 2.17.

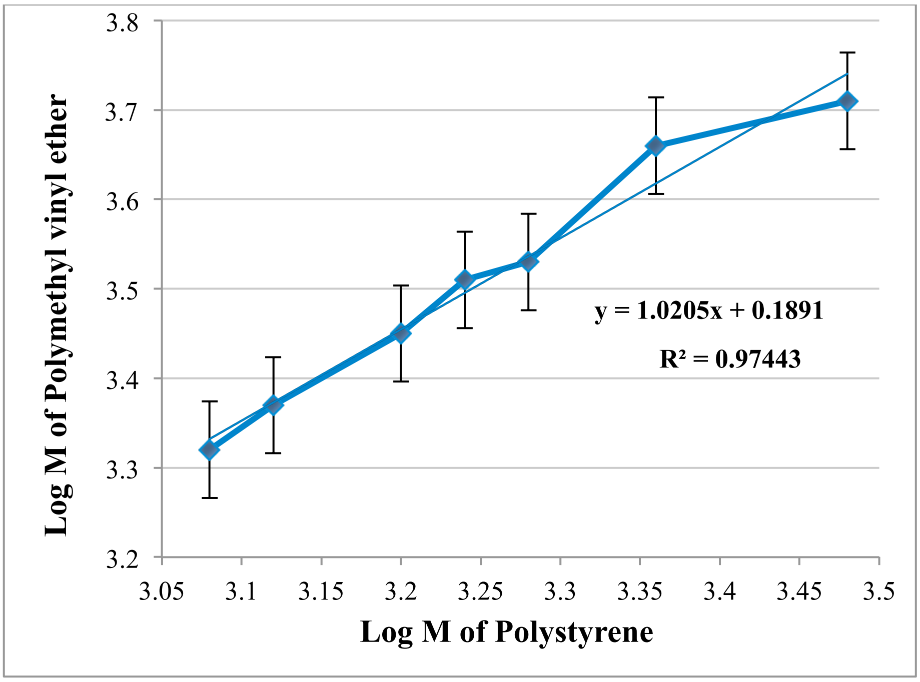


Figure 2.17: Plot of log molecular weight of polystyrene versus log molecular weight of OMVE with end group.

Regarding to the previous Figure, it is possible to calculate α and k constants of oligo(methyl vinyl ether) by using these equations:

Mark-Houwink:

$$[\eta] = K\, M^{\alpha}$$

Flory-Fox (universal):

$$[\eta]_1\, M_1 = [\eta]_2\, M_2$$

$$[\eta]_1\, M_1 = K_1\, M_1^{\alpha+1}$$

$$[\eta]_2\, M_2 = K_2\, M_2^{\alpha+1}$$

$$K_1\, M_1^{\alpha+1} = K_2\, M_2^{\alpha+1}$$

$$\log K_1 + (\alpha_1+1) \log M_1 = \log K_2 + (\alpha_2+1) \log M_2$$

$$(\alpha_1+1) \log M_1 = \log \left(\frac{K2}{K1}\right) + (\alpha_2+1) \log M_2$$

$$\log M_1 = \underbrace{\frac{\log \left(\frac{K2}{K1}\right)}{\alpha 1+1}}_{} + \frac{(\alpha 2+1)}{(\alpha 1+1)} \log M_2$$

→ Intrtcept so can set α_2 as well as k_2

If the α constant of polystyrene is known then m_{PMVE} can be calculated from Figure 2.17, then

$$m_{PMVE} = \frac{(\alpha_{PS}+1)}{(\alpha_{PMVE}+1)}$$

$$1.0205 = \frac{(0.768+1)}{(\alpha_{PMVE}+1)}$$

$$\boldsymbol{\alpha_{PMVE} = 0.73}$$

According to the value of alpha, it can be seen that THF is a good solvent for oligo(methyl vinyl ether) at -78 °C. The alpha values are particularly important because they depend on the polymer architecture and therefore demonstrate how linear the material is as well as provide an indication of solvency. Table 2.3 shows how the polymer architecture can be inferred from the value of alpha.

α constant	**Interpretation**
0 – 0.5	Spheres
0.5 – 0.8	Random coils
1.0	Stiff coils
2.0	Rods

Table 2.3: The intercept of polymer dependent on alpha values.[121]

The alpha value for the OMVE with end group functionality was between 0.5 and 0.8. As was predicted, this result demonstrates that the polymer has a random coil conformation, as illustrated in Figure 2.18.

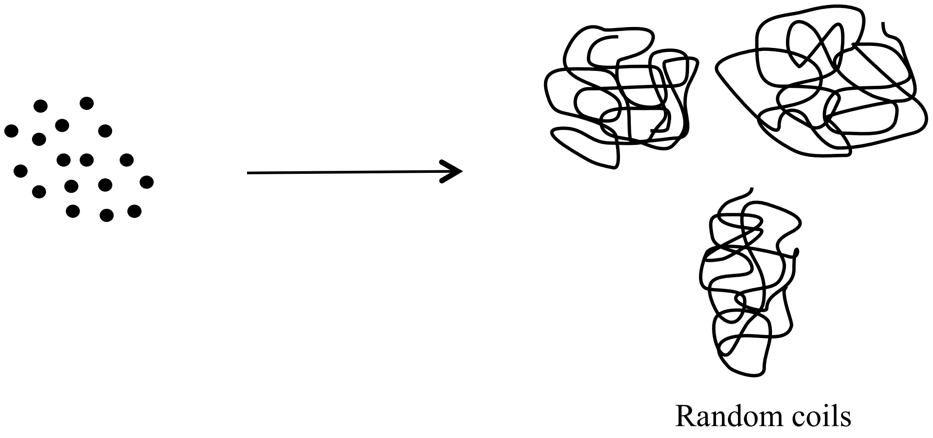


Figure 2.18: The linear OMVE architecture with end group were produced after polymerisation at -78 °C.

The K constant of OMVE was then calculated according to this equation below:

$$C = \frac{\log(\frac{K_{PS}}{K_{PMVE}})}{(\alpha_{PMVE} + 1)}$$

If is C known by calculating the intercept in Figure 2.17, K constant of OMVE can be then calculated.

$$0.1891 = \frac{log(\frac{0.609\times10^4}{K_{PMVE}})}{(0.73 + 1)}$$

$$K_{PMVE} = 2864.53 \text{ ml/g}$$

Therefore,

$$[\eta] = 2864.5 \text{ x } M^{0.73}$$

Polymerisation of MVE without end capping agent

SEC fractionation was also used to collect several molecular sizes of OMVE in the absence of **SEE 1** at -78°C. Once the molecular sizes of the polymer had been separated, they were collected in a fraction collector at between 11 and 16 minutes. Several fractions were collected for each OMVE sample. Each fraction contains a 1 minute eluent. Following this, the collected SEC fractions were analysed using the MALDI-TOF mass spectrum as shown in Figure 2.19.

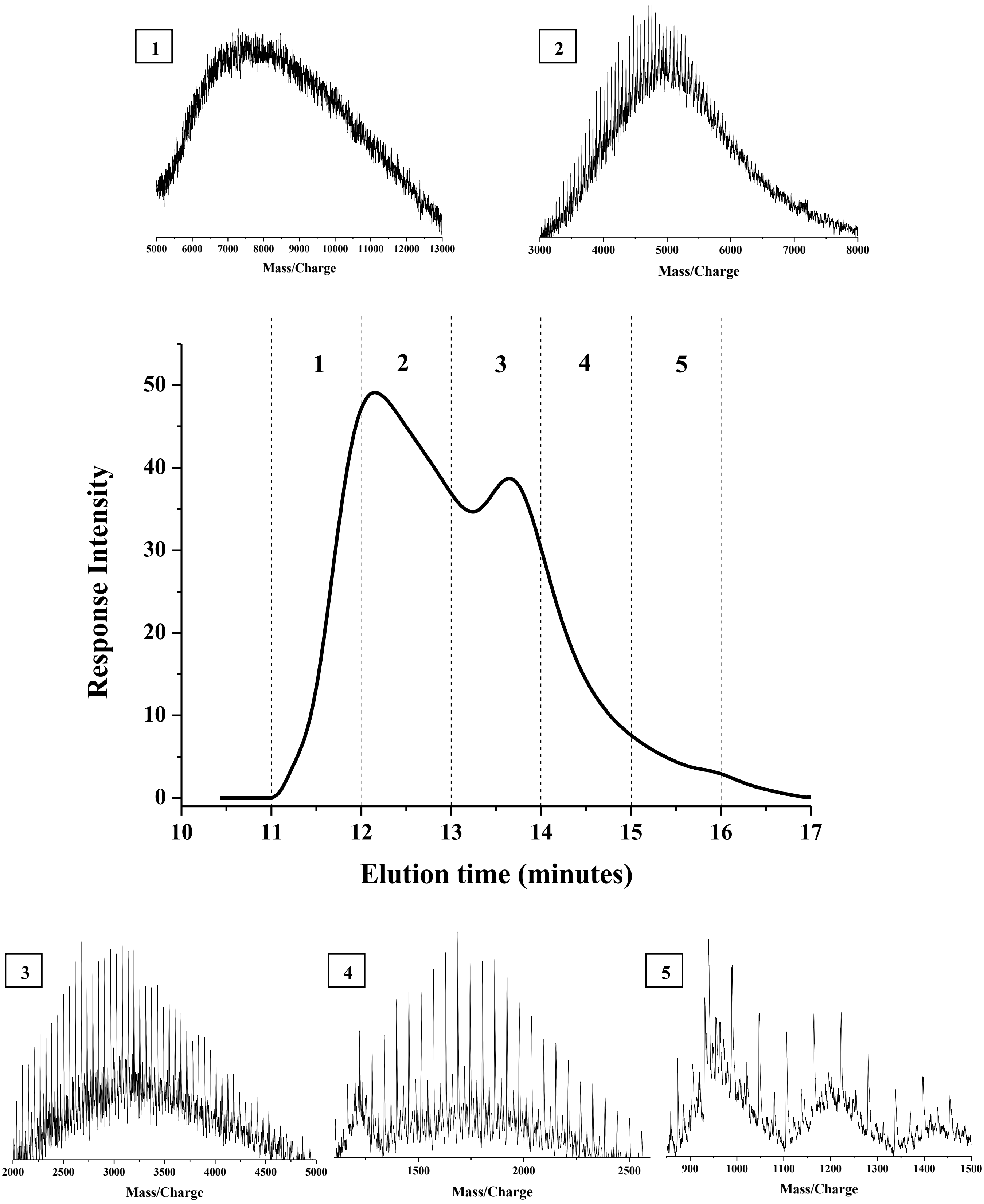


Figure 2.19: Combination of SEC and MALDI-TOF MS for OMVE without end groups.

The relationship between log molecular weight of polystyrene standard from SEC with a log molecular weight of oligomethyl vinyl ether without end-capped agent and derived at -78°C is shown in Figure 2.20.

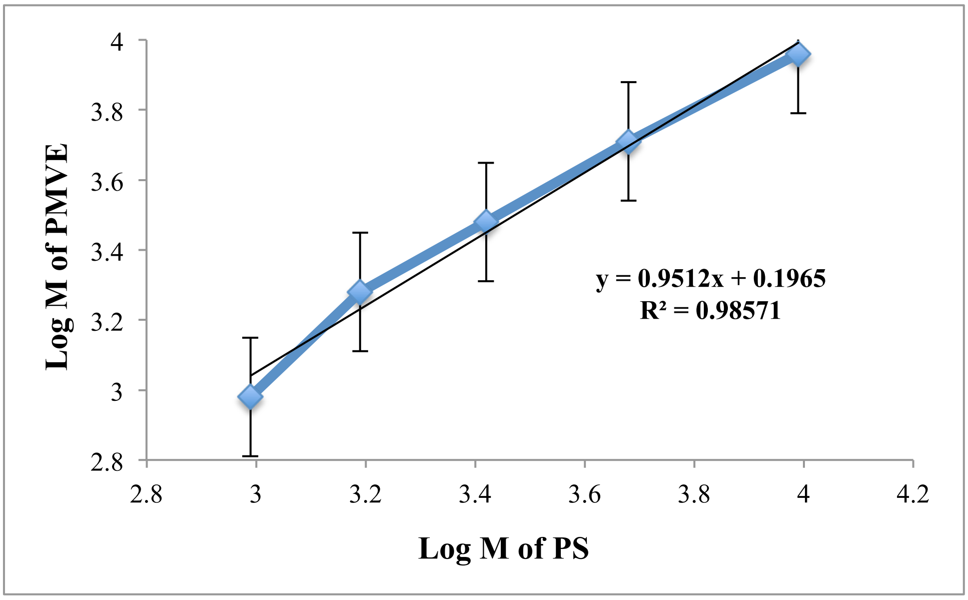


Figure 2.20: Plot of log molecular weight of Polystyrene with log molecular weight of OMVE without end group.

Then from previous treatment, the alpha constant of OMVE can easily be calculated as below:

$$0.9512 = \frac{(0.768+1)}{(\alpha_{PMVE}+1)}$$

$$\boldsymbol{\alpha_{PMVE} = 0.86}$$

The K constant of OMVE was then calculated according to this equation below:

$$C = \frac{\log(\frac{K_{PS}}{K_{PMVE}})}{(\alpha_{PMVE} + 1)}$$

If is C known by Calculating the intercept in Figure 2.20, K constant of OMVE can be then calculated.

$$0.1965 = \frac{log(\frac{0.609\times10^{4}}{K_{PMVE}})}{(0.86 + 1)}$$

$$K_{PMVE} \ = 2626.33 \text{ ml/g}$$

Therefore,

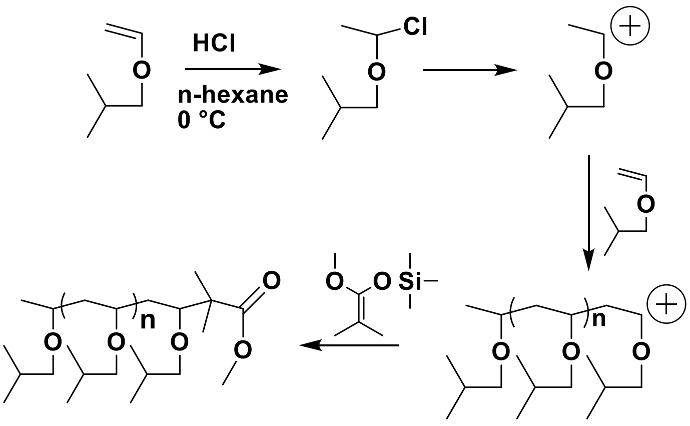
$$[\eta] = 2626.33 \text{ x } M^{0.86}$$

It can be clearly indicated that, the solution coil conformation is dependant on the end group structure.

2.4.5 *Ab initio* cationic polymerisation of *i*BVE in the presence of $TiCl_4$ as a Lewis acid

2.4.5.1 Polymerisation of iBVE at -26 °C

At this stage the same PMVE conditions as before were used in the experiments, except that $TiCl_4$ was used instead of $SnCl_4$ as the Lewis Acid. Scheme 2.4 shows the mechanism of *iso*butyl vinyl ether polymerisation using *ab initio* cationic polymerisation under batch process.



Scheme 2.4: General mechanism of *ab initio* chain end functionality in cationic polymerisation of *iso*butyl vinyl ether.

The summary of the results for the *iso*butyl vinyl ether polymerisation using $TiCl_4$ at -26 °C in the absence and presence of **SEE 1** are shown in Table 2.4.

ID Sample	**[M][a] mol L^{-1}**	**[SEE][b] mol L^{-1}**	**[I][c] mol L^{-1}**	**Conversion (%)**	**Mn g mol^{-1}**	***D***	**[F][d] (%)**
RO 47	1.0	0	0.01	81.72	7,700	1.76	0
RO 48	1.0	0.05	0.01	64.78	6,100	1.55	0
RO 49	1.0	0.1	0.01	60.76	6,000	1.52	0
RO 50	1.0	0.15	0.01	35.54	5,000	1.38	41.90

Table 2.4: Results of the polymerisation of O*i*BVE samples. (a) [M] = Monomer concentration. (b) [SEE] = Concentration of **SEE 1**. (c) [I] = Initiating concentration system = HCl-*i*BVE/$TiCl_4$ in DCM. (d) [F] = Average functionality measured by MALDI-TOF analysis.

From the previous table it is clear that different concentrations of **SEE 1** (such as 0.05 or 0.10 M) had no affect on the polymerisation. Therefore, the molecular weights of these polymers were not very different from polymerisation in the absence of **SEE 1.** Clearly the polymers were not produced with the required end group functionalisation. However, at a 0.15 M concentration of **SEE 1**, lower molecular weight was obtained with some of the chains containing the target functional group.

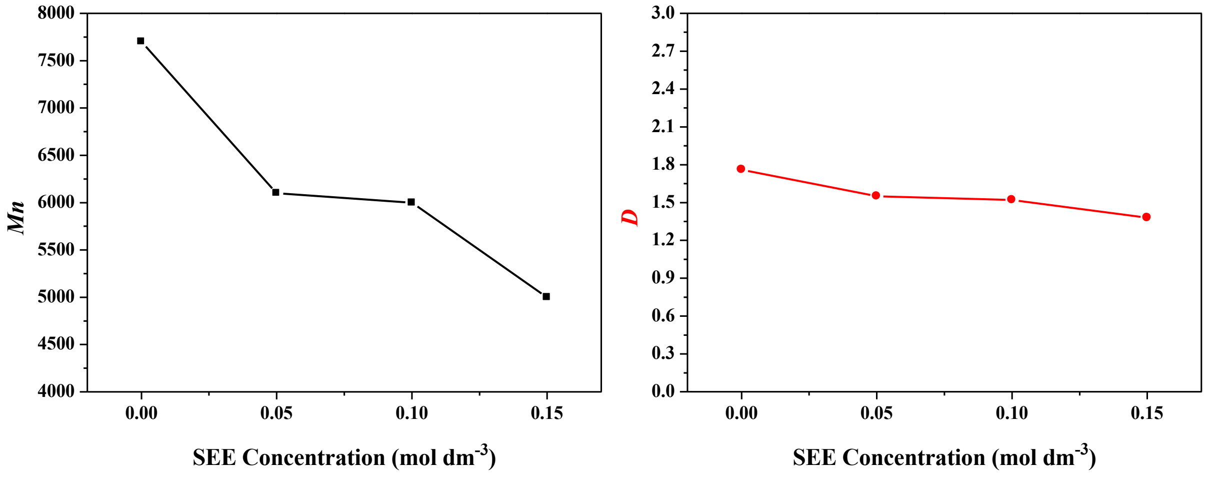


Figure 2.21: The molecular weight (left), dipersity (right) of O*i*BVE with **SEE 1** concentration at -26 °C.

The data from these experiments, which were obtained at -26°C, are presented in Figure 2.21. The molecular weights decreased sharply when the **SEE 1** concentration increased. As expected, **SEE 1** increased as the Mw/Mn decreased.

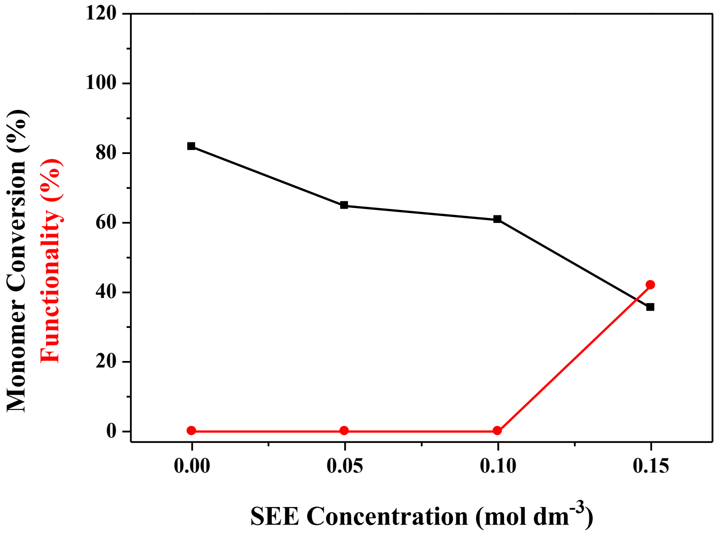


Figure 2.23: Monomer conversion (black), average functionality (red) via **SEE 1** concentration at -26 °C.

The final monomer conversions are shown in Figure 2.22. The monomer conversions decreased when the concentration of **SEE 1** increased. The average chain ends that are capped are shown in the same figure. At 0.05 and 0.10 M the ester group functionalities were not produced. This means that the polymerisations were very fast under these conditions, which is obviously a disadvantage in attempting to produce highly molecular weight with a broad dispersity. However, at a higher concentration of **SEE 1** (0.15 M), the final monomer conversion decreased and the frequency of chain end-capping increased sharply.

The relationship between the number of molecules and their molecular weight is defined as the molar mass. Adding **SEE 1** provided polymer with decreased molecular weight and interestingly the distribution became Gaussian in appearance at a **SEE 1** concentration of 0.15 M, as is shown in Figure 2.24.

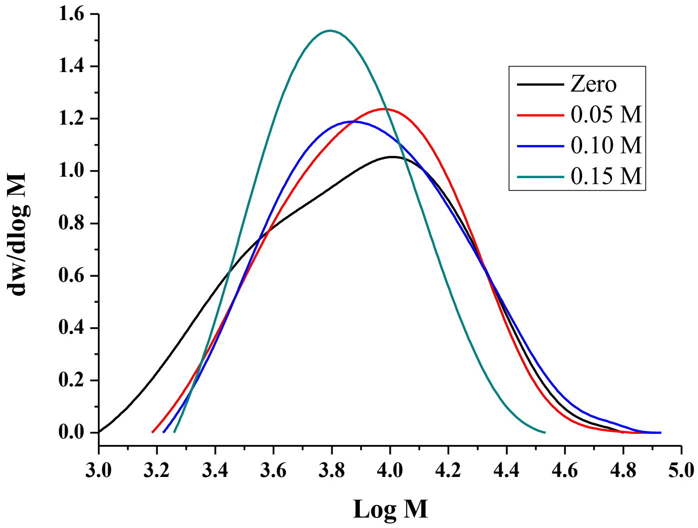


Figure 2.24: Molecular weight distributions of oligo*iso*buty vinyl ether derived at -26 °C.

MALDI-TOF MS analysis

In the MALDI-TOF mass spectra there were two different chain end groups and the ratio of each end group to the other was differed as the **SEE 1** concentration changed (Figure 2.25). The target product was end group with ester group functionality but this was only observed at higher concentrations (0.15 M). The ester end group accounted for under this condition was approximately 41.90%. The other major product was from the methoxy end group; this group was obtained in each different concentration of **SEE 1** and accounted fully for 100% of the end group functionality at the **SEE 1** concentration of 0.05 and 0.10 M.

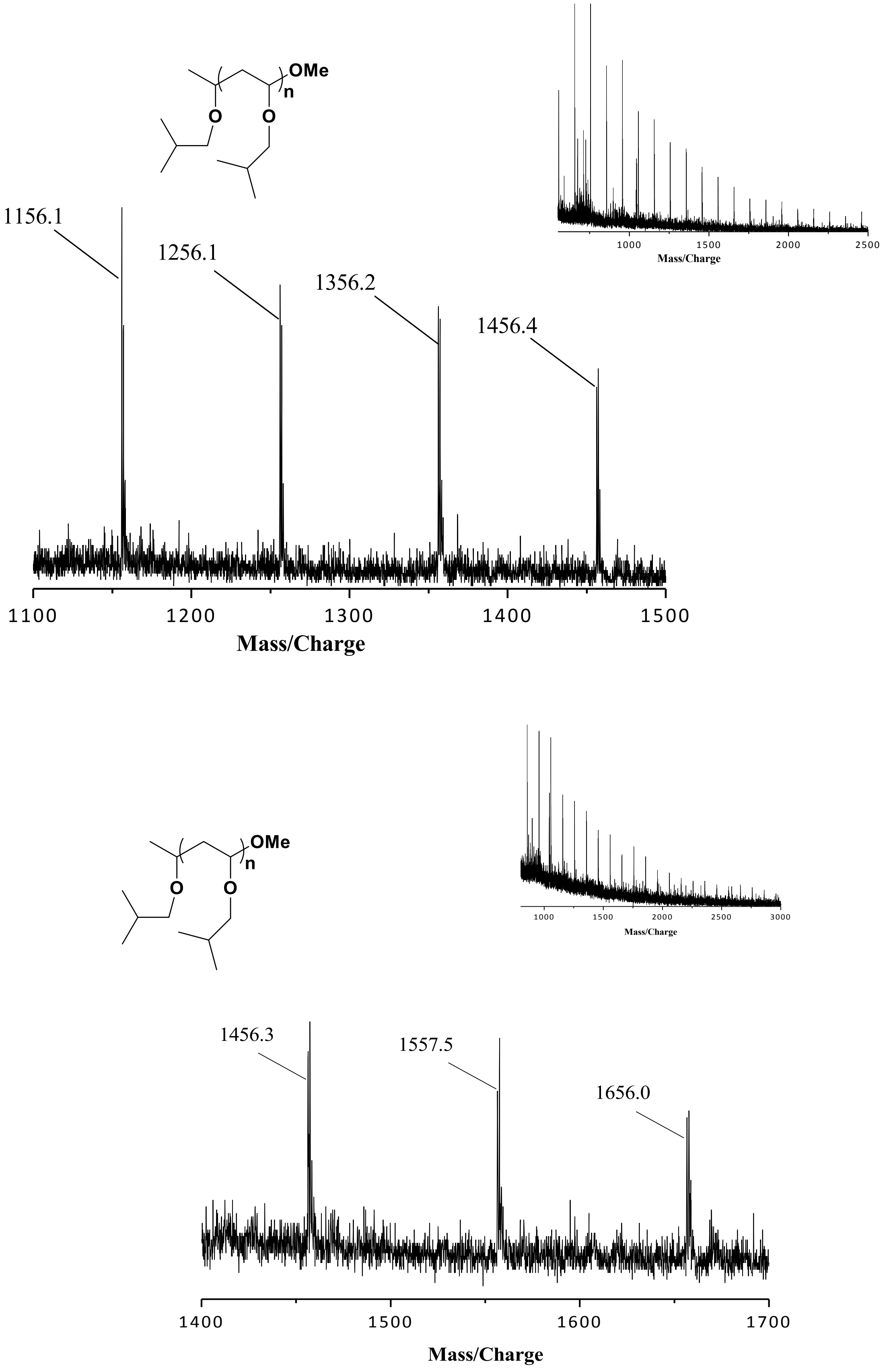


Figure 2.25: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.05 and 0.10 M respectively)

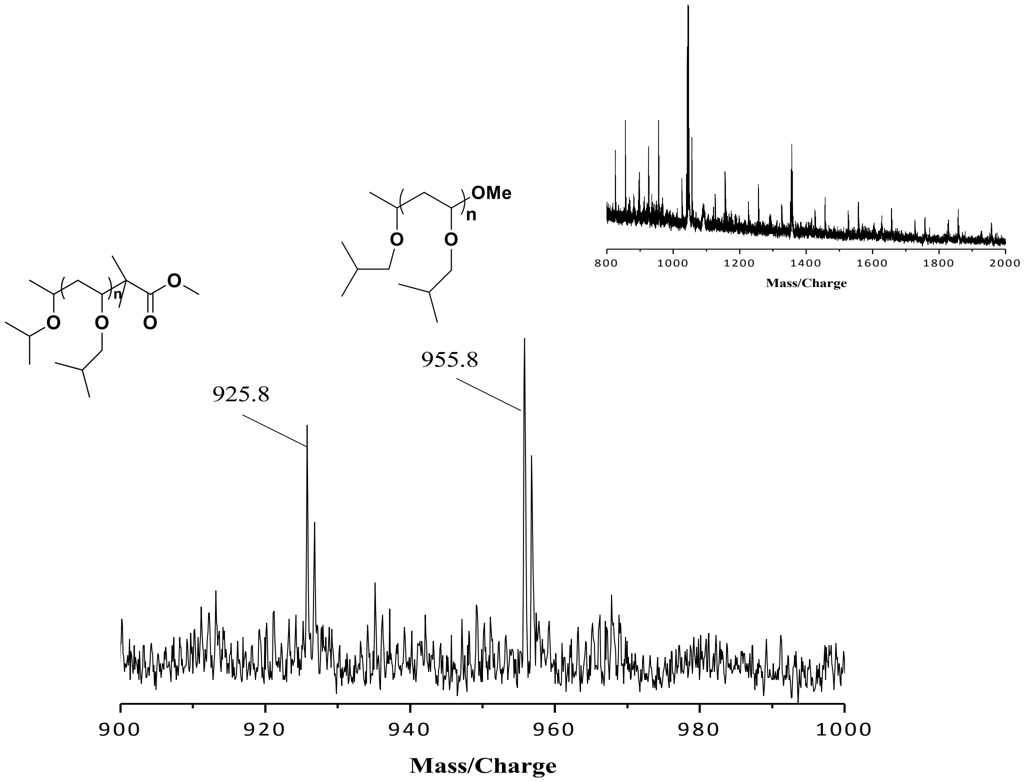
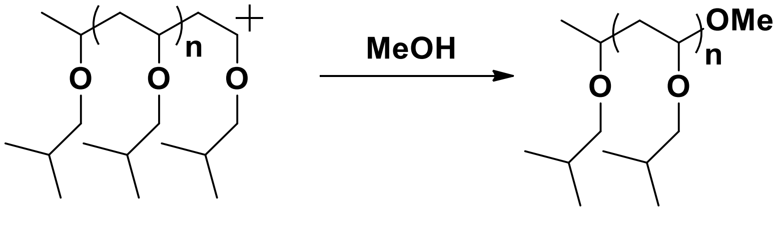


Figure 2.25: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE 0.15 M obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

Formation of methoxy end group

Scheme 2.5, shows the mechanism of formation methoxy end group. This functionality is produced from the quench process so that methoxy end groups reflect carbocation end groups that were still active at the end of the polymerisation.



Scheme 2.5: The mechanism of methoxy end group.

2.4.5.2 Polymerisation of iBVE at -78 ˚C

A brief summary of results for *iso*butyl vinyl ether polymerisation is shown in Table 2.5. The polymerisations were carried out at -78 °C with different concentrations of **SEE 1**. The results suggest that, so long as the concentration of **SEE 1** is high enough, a lower temperature can produce polyisobutyl vinyl ether which has a well controlled and high degree of ester end group functionality.

ID Sample	**[M]^a mol L^{-1}**	**[SEE]^b mol L^{-1}**	**[I]^c mol L^{-1}**	**Conversion (%)**	**Mn g mol^{-1}**	***D***	**[F]^d (%)**
RO 43	1.0	0	0.01	100	7,400	1.55	0
RO 44	1.0	0.05	0.01	87.76	9,800	1.35	31.27
RO 45	1.0	0.1	0.01	79.77	5,400	1.32	33.95
RO 46	1.0	0.15	0.01	54.13	4,700	1.20	100

Table 2.5: Results of the polymerisation of O*i*BVE samples. (a) [M] = Monomer concentration. (b) [SEE] = Concentration of **SEE 1**. (c) [I] = Initiating concentration system = HCl-*i*BVE/$TiCl_4$ in DCM. (d) [F] = Average functionality measured by MALDI-TOF analysis.

The relationship between molecular weight and different concentrations of **SEE 1** are plotted in Figure 2.26 where it is shown that higher concentrations of silyl enol ether produce polymers with decreasing molecular weight. The same figure also shows dispersity (*D*) plotted against different concentrations of **SEE 1**. These polymers were produced successfully with high end group functionality when the high concentration of silyl enol ether increased significantly.

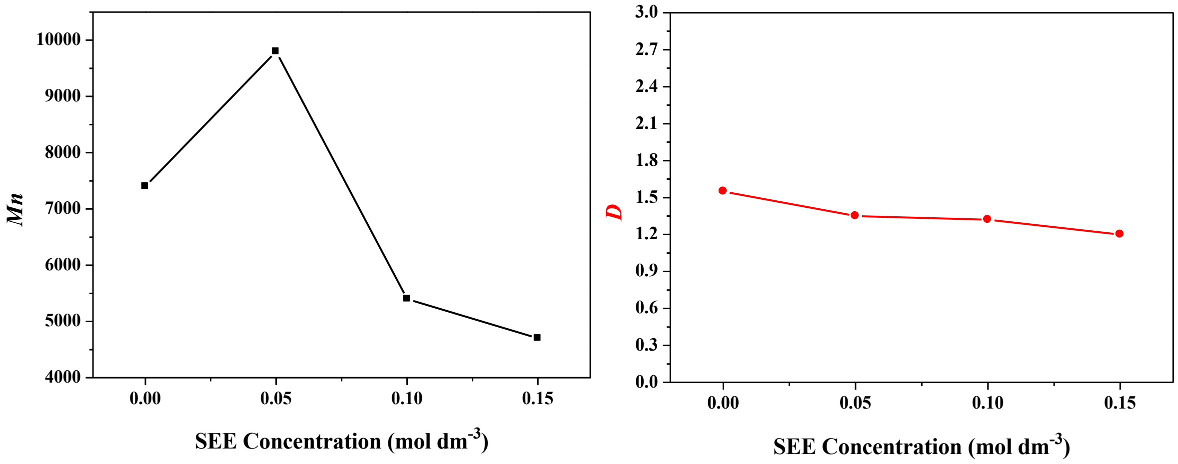


Figure 2.26: The molecular weight (left), dipersity (right) of O*i*BVE with **SEE 1** concentration at -78 °C.

Figure 2.27 shows the monomer conversion with several concentrations of **SEE 1**. The final monomer conversion decreased linearly as the concentration of silyl enol ether increased. At low concentration of **SEE 1** (0.05 M), the ester group functionality was achieved vey low, as was determined by using MALDI-TOF MS. By increasing the concentration of **SEE 1**, the ester end group functionality increased directly. Full functionalisation with the ester group was observed at a 0.15 M concentration of silyl enol ether.

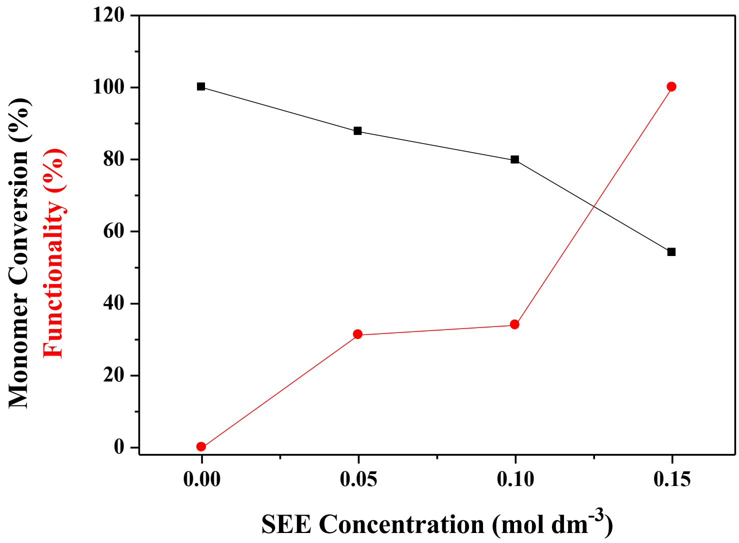


Figure 2.27: Monomer conversion (black), average functionality (red) of O*i*BVE with **SEE 1** concentration at -78 °C.

Figure 2.28 shows a ^{1}H NMR spectrum of polyisobutyl vinyl ether in the presence of **SEE 1**. The methyl groups were observed at 1.10 ppm. The methoxy group from ester end functionality was also observed at 3.70 ppm.

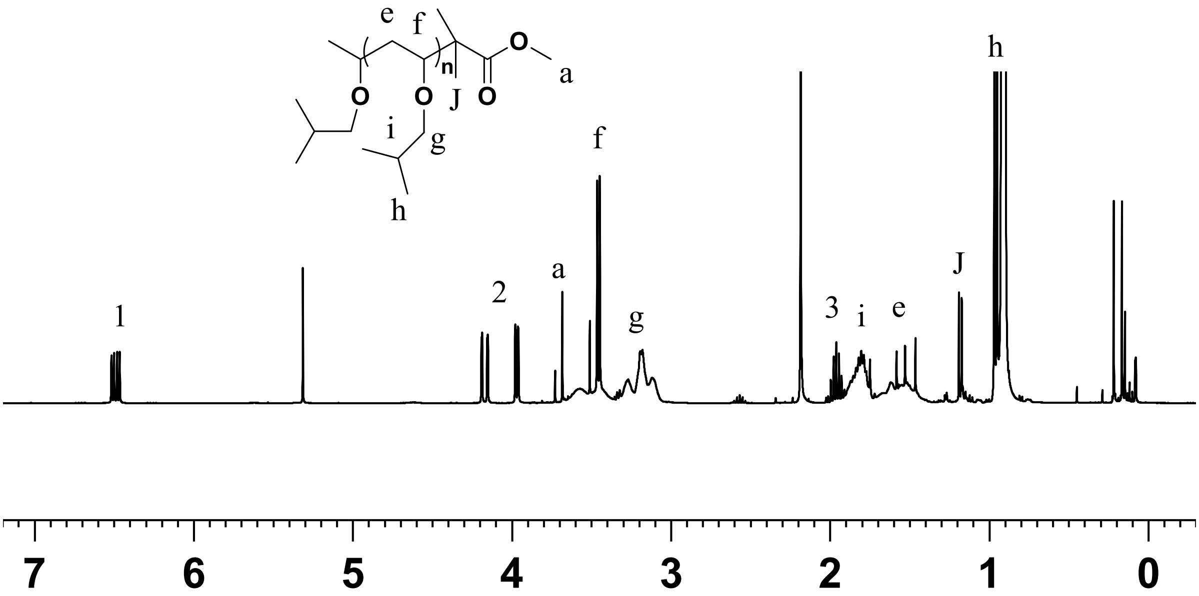


Figure 2.28: ^{1}H NMR spectra of poly*iso*butyl vinyl ether in the presence of **SEE 1**. Protons from *i*BVE monomer were labeled as 1, 2 and 3.

As outlined above, a broad molecular weight distribution with a large molecular weight was achieved when concentrations of **SEE 1** were low or zero. On the other hand, narrower molecular weight distributions with low molecular weight were obtained at high concentrations of **SEE 1**, such as 0.10 and 0.15 M (Figure 2.29).

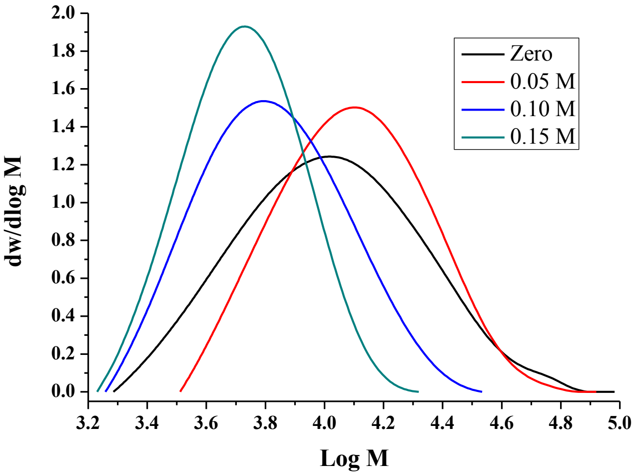


Figure 2.29: The molar mass distributions of poly*iso*butyl vinyl ether were derived at -78 °C.

MALDI-TOF MS analysis

The MALDI-TOF mass spectra showed that there were three different chain end groups resulting from incorporation of **SEE 1** at different concentrations. Using a concentration of **SEE 1** of 0.05 M three products were discerned; the ester group, the methoxy end group and another unknown end group. Three series of polymer ions were obtained at 0.10 M concentration of **SEE 1**. The major product was assigned to the ester group and accounted for 33.95 mol%. The full (100 mol%) functionalisation of the end groups with ester functionality was achieved at high concentration of silyl enol ether (0.15 M) (Figure 2.30).

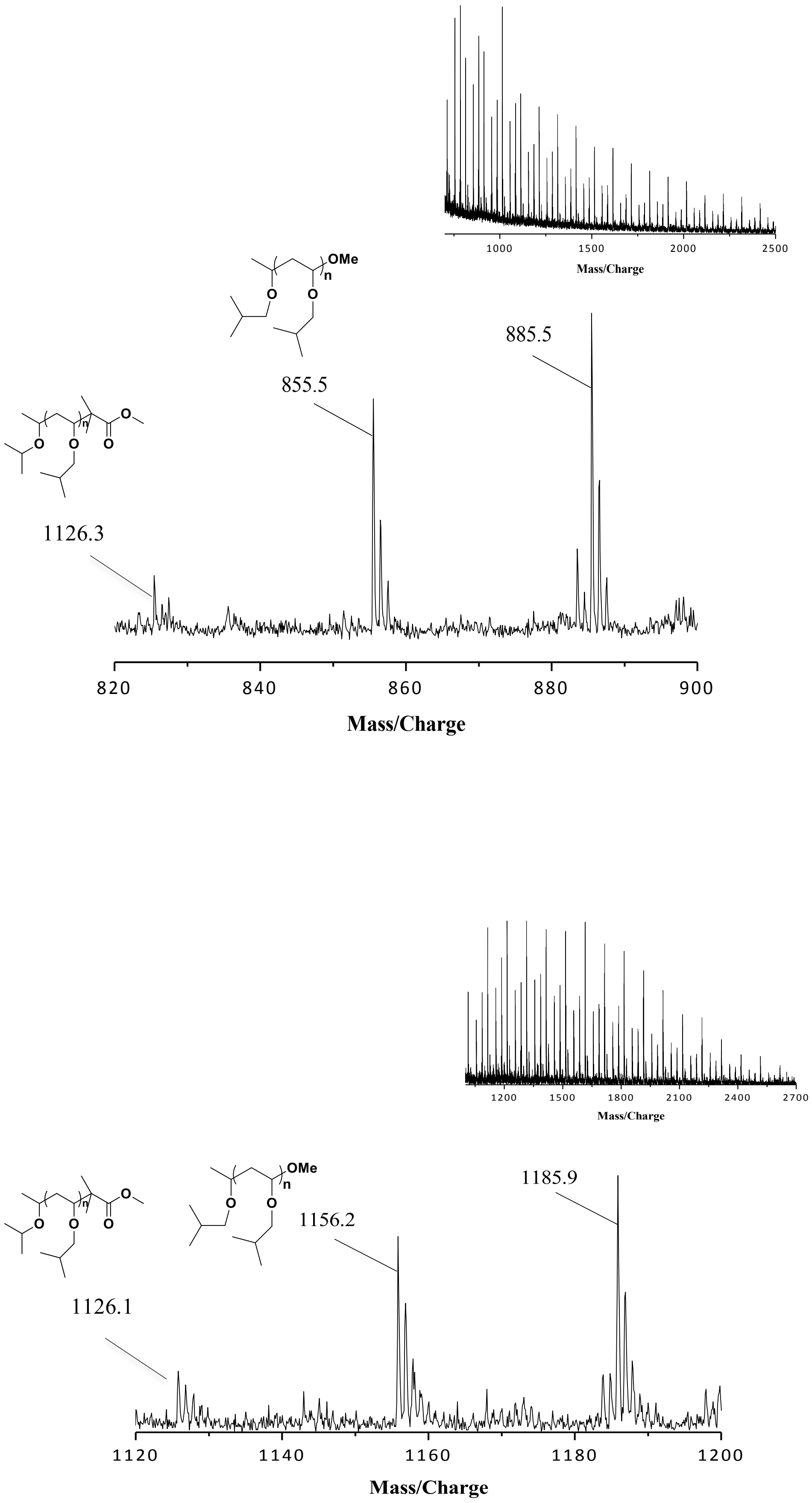


Figure 2.30: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.05 and 0.10 M respectively).

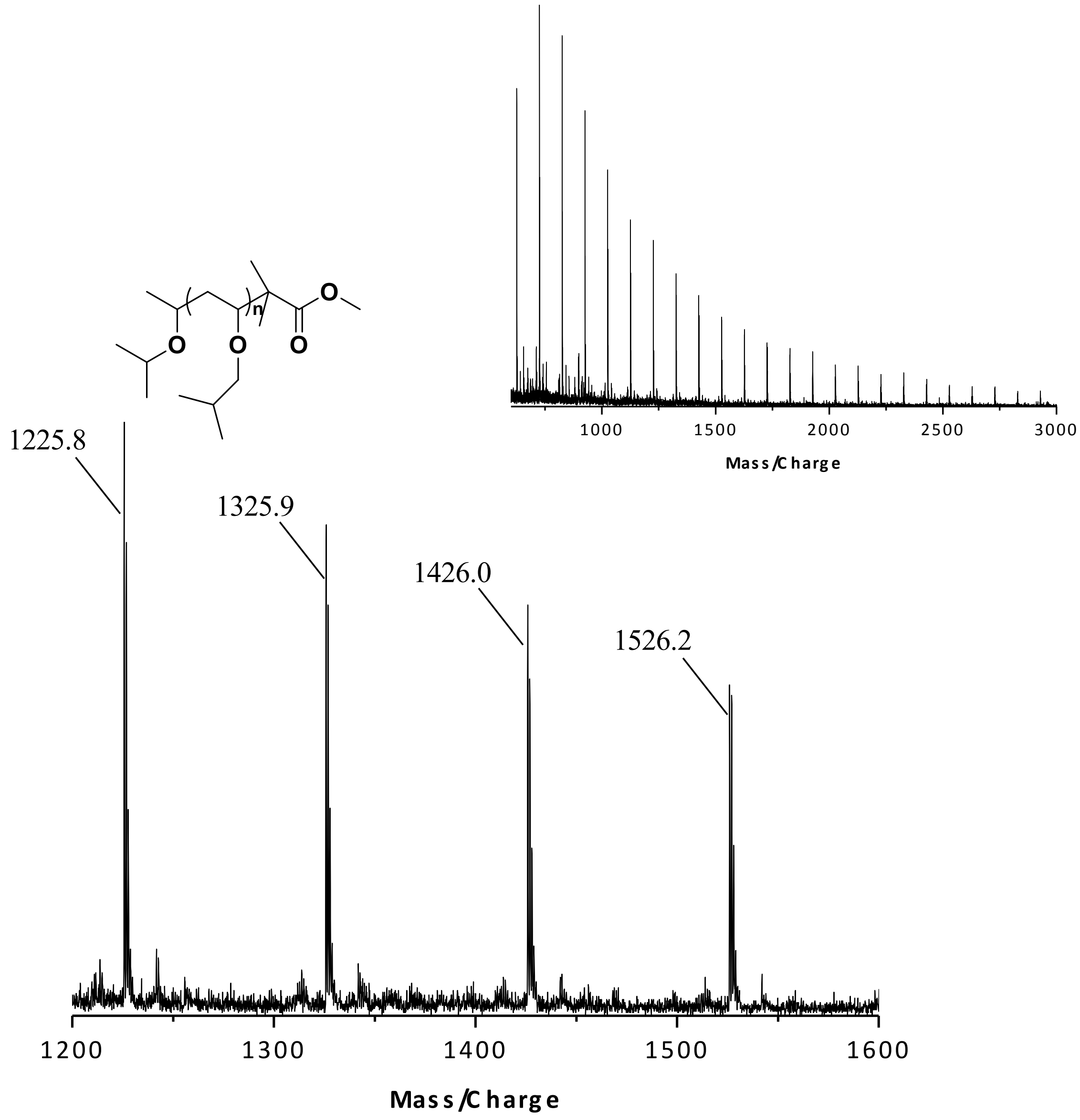


Figure 2.30: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE 0.15 M obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

In a previous study, Lang and Rimmer was used $SnCl_4$ as a Lewis acid to produce O*i*BVE with high ester-end-group functionality under the same conditions that were used in this section.[122] It was demonstrated that it was possible to obtain O*i*BVE with a narrow molecular weight distribution and high functionality when $SnCl_4$ was applied under a high temperature (-26 °C) rather than under a low temperature (-78 °C).

Therefore, it can be concluded that the polymerisation of iBVE with SnCl4, used as a Lewis acid, at relatively high temperatures (-26 °C) favours narrow molecular weight distribution with high chain-end group functionality. Constant, low temperature environments (-78 °C) were found to produce a narrow molecular weight distribution with a high mean functionality when TiCl4 was applied as a Lewis acid.

2.5 Conclusions

The focus of this chapter was on producing materials with high end group functionality by controlling the monomer concentration, reaction temperature and concentration of silyl enol ether. A silyl ketal enol ether was used as a nucleophilic capping agent; this reacts with carbocations at similar rates to the propagation of vinyl ethers. The ester end groups were then produced by rapid desilation of the primary adducts.

Oligomethyl vinyl ethers were polymerised successfully at -26 and -78°C using $SnCl_4$ as a Lewis Acid. Low polymerisation temperature produced high end group functionality, probably because decreasing the temperature reduces the side reactions. The best chain end capping was found at a 0.10 M concentration of **SEE 1**. MALDI-TOF mass spectrometry was used to obtain reaction conditions where the dominant termination reaction was alkylation of the silyl ketene acetal. A size exclusion chromatograph (SEC) was calibrated using MALDI-TOF MS to obtain molar mass of narrow fractions (SEC-MALDI-TOF MS). The Kuhn-Mark-Houwink relationship for oligo(methyl vinyl ether) was then established. The data indicate that the solution coil conformation is dependant on the end group structure, which means that application of a Universal calibration to mixtures of polymers with different end groups is difficult. For this reason molecular weights have been reported compared to polystyrene standards.

Oligo*iso*butyl vinyl ether was also prepared successfully at different temperatures using $TiCl_4$ as a Lewis Acid. It was demonstrated that a low temperature and high concentration of **SEE 1** are both necessary in order to produce high degrees of chain end functionality. Full functionalisation of the chains with ester end groups was found at 0.15 M, which is a molar ratio of **SEE 1** to an initiator of 3:1 and -78 °C. Successful ester end group functionalisation of the polymers (OMVE and O*i*BVE) was shown using MALDI-TOF MS, ^{1}H, ^{13}C NMR and FT-IR spectres.

Chapter 3

3. Polymerisation of *i*sobutyl vinyl ether using continuous processes

3.1 Introduction

In recent years, significant efforts and resources have been allocated to the development of mild, alternative, and environmentally friendly polymerisation conditions for the cationic polymerisation of vinyl monomers. A variety of reaction media have been used, including n-hexane, toluene, xylene and DCM.

Vinyl ethers are the most reactive monomers in cationic polymerisation. The first polyvinyl ethers were made in Germany in 1940. They have been widely used in the adhesive industry. Poly(*iso*butyl vinyl ethers) (PIBVE) is one of the most popular poly(vinyl ethers) that has been discovered to have very important applications as impregnating agents for textiles and coatings. The polymerisation of IBVE can be readily accomplished with cationic initiators to obtain polymer by chain growth polymerisation mechanisms.[123]

Several of the initiators such as $HCl/SnCl_4/nBu_4NCl$, $Yb(OSO_2CF_3)_3$ and many others have been reported as catalyst systems to produce better control of molecular weight and to form isotactic rich PIBVE. Generally, the development of a polymerisation technique to produce polymers with high molecular weight (Mn), narrow dispersity (*D*) and high steroregularity has posed challenges for polymer synthesis. In many cases, a very low temperature (-78 °C) should be applied to achieve isotactic O*i*BVE with narrow dispersity.[124]

Therefore, in this chapter, the polymerisations of *i*sobutyl vinyl ether were studied using cationic polymerisations, but a continuous polymerisation methodology was used for the first time. The process involved an *in situ* chain end capping during propagation but monomer and other ingredients were continuously fed into the reactor. In this method, we refrain from using the *ab initio* to avoid confusion with the use of this term in emulsion polymerisation technology in order to denote batch polymerisation processes rather than continuous processes. The chapter describes the cationic polymerisation of isobutyl ether (*i*BVE) with a silyl enol ketal, 1-methoxy-2-mehyl-1-(trimethylsiloxy)-propene, **SEE 1**, to produce oligomers with ester end groups. $TiCl_4$ and $SnCl_4$ were both utilised as Lewis acids involving HCl-*i*BVE as an initiator for the polymerisation of *i*BVE at -15 °C. Most importantly, a continuous process has been applied.

During the batch manufacturing processes, the materials are all charged at the start of the reaction, and discharged at the end of the process. However, in the continuous manufacturing processes, materials are added during processing and discharged from the process continuously. The fast polymerisation rates observed in the batch *ab initio* polymerisations make them ideal to use for a continuous process because only short residence times are required for successful reaction.

Continuous manufacturing has some advantages over batch processing. For instance, it offers integrated processing with fewer steps, no manual handling, increased safety, more flexible operations, lower capital costs, less work-in-progress materials, rapid development screening over many conditions, on-line monitoring and control for increased product quality assurance in real time. Figure 3.1 demonstrates the technique's route with two feeds. Feed A including monomer and the silyl enol ether (**SEE 1)** delivered in 1 L of DCM as a solvent. Feed B including the initiator (HCl-*i*BVE) and Lewis acid ($SnCl_4$ or $TiCl_4$) was also delivered in 1 L of DCM. The two separate feeds were connected together with a peristaltic pump to control the flow time of the solution through the reaction vessel. The reaction vessel was cooled with a dry ice/methanol bath. Allowing the reaction mixture to overflow through a side arm allowed for continuous removal of the reaction mixture. The overflowing mixture was then quenched adding the mixture to methanol. Over time, different samples were collected in separate flasks that contained methanol. The set up is shown in Figure 3.1.

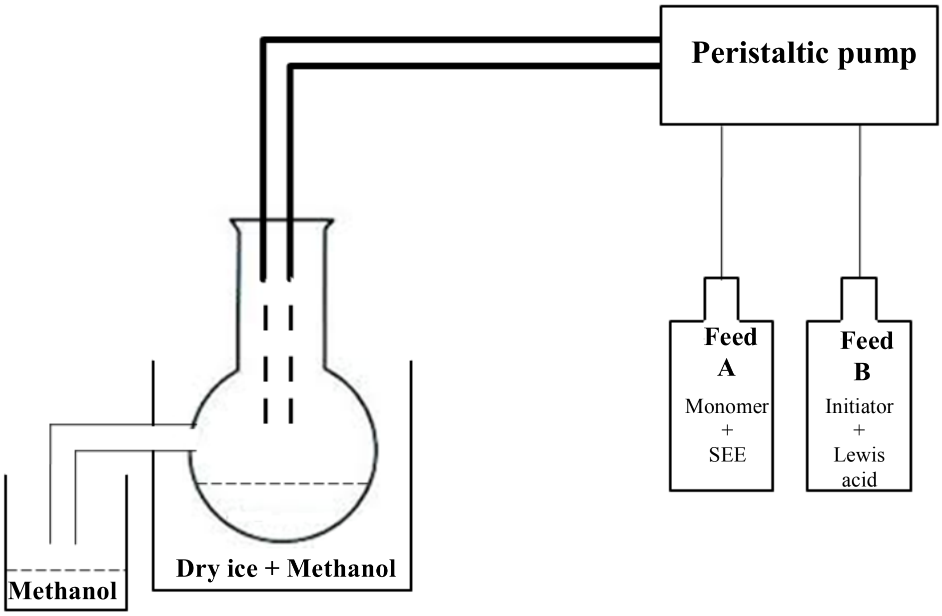


Figure 3.1: Continuous process.

3.2 Experimental

3.2.1 Materials

*i*BVE, 99% Aldrich product. *i*BVE was washed with 10 % aqueous NaOH solution and then with water three times to be free from inhibitor, dried overnight with anhydrous sodium sulphate and distilled before use. N-hexane, (99% Aldrich) was refluxed over calcium hydride for two hours and distilled over A4 molecular sieves. $SnCl_4$ and $TiCl_4$, 1.0 M solution in DCM (Aldrich) were used as received. 1-methoxy-2-methyl-1-(trimethylsilyloxy)propene, **SEE 1**, (95 %, Aldrich) was purified by fractional distillation under reduced pressure.

3.2.2 Preparation of Oligo(*i*sobutyl vinyl ether) with an ester group

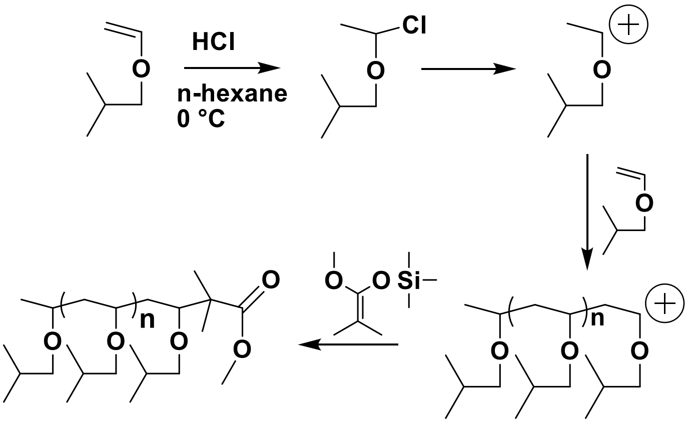
The continuous polymerisation of *i*BVE was carried out by using two separate feeds. Feed A contains (2 M) of *i*BVE as a monomer and **SEE 1** (0.04, 0.05, 0.06 and 0.08 M) as an end-capping agent in DCM. Feed B included (0.04 M) of both HCl-*i*BVE adduct and $TiCl_4$, $SnCl_4$ as an initiator and Lewis acids, respectively in DCM. A peristaltic pump was used to establish the flow time of the reactions (5, 3 and 2 ml min^{-1}). It was cooled in cardice/methanol to a temperature of -15 °C and DCM used as a solvent. The polymerisation, which was carried out at 5 ml min^{-1} was sampled every 30 minutes. At 3 ml min^{-1}, the samples were collected every 50 minutes. In addition, the samples were collected every 1.5 hours for the polymerisation carried out at 2 ml min^{-1}. Methanol was added in each sample to stop the polymerisation. Finally, the solvent was evaporated and dried overnight to receive the polymer product.

All polymer characterisations were as reported in Chapter 2.

3.3 Results and discussion

3.3.1 Polymerisations of *i*BVE using $SnCl_4$

In this study, the polymerisation of *i*BVE was selected and catalysed by tin tetrachloride and HCl-*i*BVE adduct at -15 °C using DCM as a solvent through a continuous process carried out in the presence of **SEE 1**. The general mechanism is shown in Scheme 3.1.



Scheme 3.1: General conditions used to produce poly(*i*sobutyl viyl ether) in DCM at -15 °C.

3.3.1.1 Polymerisation of iBVE at 5 ml min^{-1}

The polymerisation of *i*BVE at flow rate of 5 ml min^{-1} in the presence of **SEE 1** (0.04 M) was examined. Scheme 1 outlines the route of this reaction. The polymerisation took place over the course of 4.5 hours, and 12 samples were collected at different times throughout the reaction. Figure 3.2 (black), shows the molecular weights and dispersities of all the polymerisations that were carried out at a 5 ml min^{-1} flow time. The molecular weight became constant between 3,400 to 3,900 g mol^{-1}, 40 minutes after the beginning of the reaction. This is evidence that the polymerisation was in a steady state under continuous processing. However, the high molecular weight product was only achieved at the beginning of the reaction. In the same figure, the termination reactions were also indicated by the decreasing dispersity (M_w/M_n).

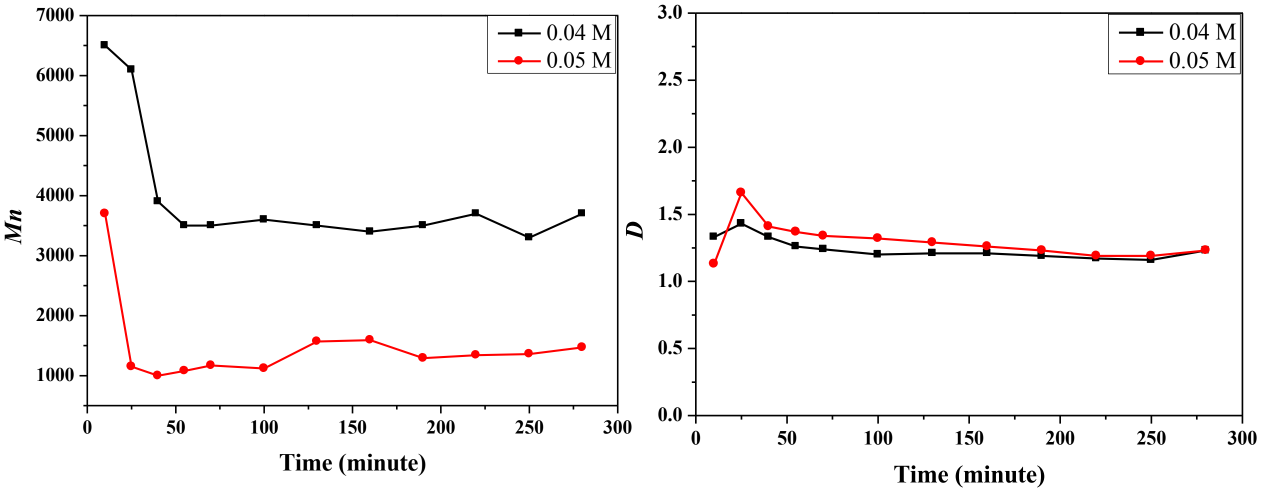


Figure 3.2: Molar mass data (left) and dispersities (right) for polymerisation of *i*BVE (2 mol dm^{-3}) in the presence of **SEE 1** initiated by *i*BVE:HCl:SnCl$_4$ (0.02:0.04 mol dm^{-3}) at 5 ml min^{-1}.

In the next reaction, the modification of the cationic polymerisations of *i*sobutyl vinyl ethers and **SEE 1** was utilised to produce oligomers with useful ester groups and attempts to increase the yield of this product by increasing the concentration of silyl enol ether were made. Therefore, a 0.05 M concentration of **SEE 1** at same flow time was used in the next reaction. Figure 3.2 (red), shows the molecular weight of O*i*BVE that was produced over time.

On first examination, it appears that the molecular weight was very high at the start of the reaction, rather than at the end. The polymerisation became constant and a steady state was achieved after 100 minutes and remained for the rest of the reaction. Generally, the range of molecular weights was between 1,500 to 1,400 g mol^{-1}. Furthermore, the dispersities remained below 1.5 during the polymerisation. This indicates that the polymerisation was giving low molecular weight polymers with very narrow dispersities.

The polymer weights were calculated several times for each sample (Figure 3.3). The total weight of all the samples was about 40 g and one of the main advantages of this technique is its ability to produce a very large amount of the polymer in a short amount of time. Therefore, it can be widely used in industrial applications.

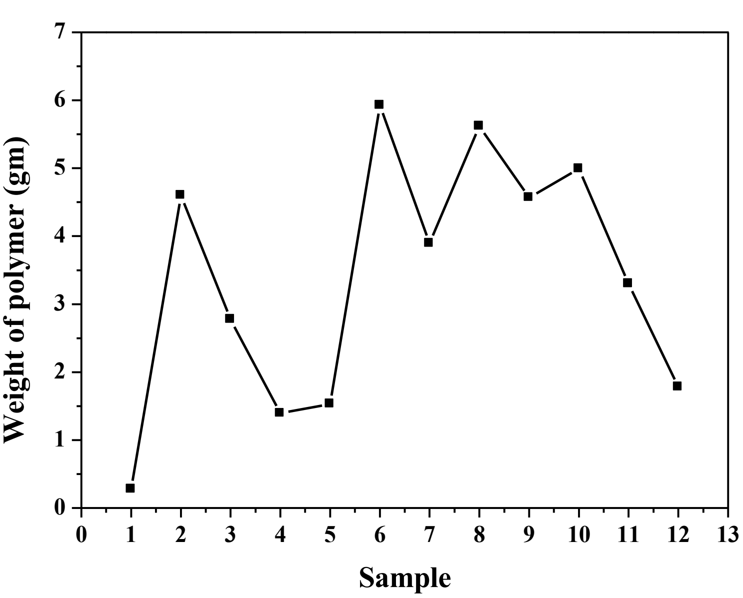


Figure 3.3: Weight of oligo(*iso*butyl vinyl ether) via volume of sample.

^{1}H NMR spectroscopy (Figure 3.4) showed the presence of the proton from the ester methoxy group at 3.70 ppm which is labelled as **a**. Thus, the polymerisation of *i*sobutyl vinyl ether produced oligomers with the ester end group as desired. Monomer conversions have been calculated, from ^{1}H NMR spectra and are outlined in Figure 3.4. The data clearly shows the presence of more than 99 % conversion in each of the samples.

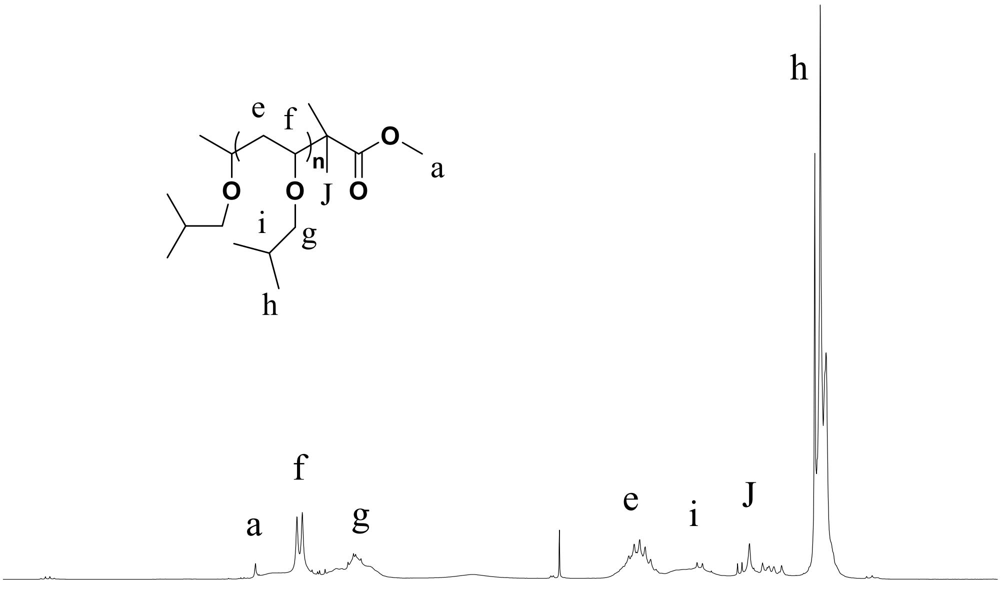


Figure 3.4: ^{1}H NMR spectrum of oligo(*iso*butyl vinyl ether) prepared at -15 °C in present of **SEE 1**.

Figure 3.5 provides the Fourier Transform Infrared (FT-IR) spectrum of the oligo(*i*sobutyl vinyl ether) prepared in the presence of **SEE 1**. The spectrum include peaks around 1700 and 1490 cm^{-1} corresponding to the C=O and C-O bonds of the ester end groups.

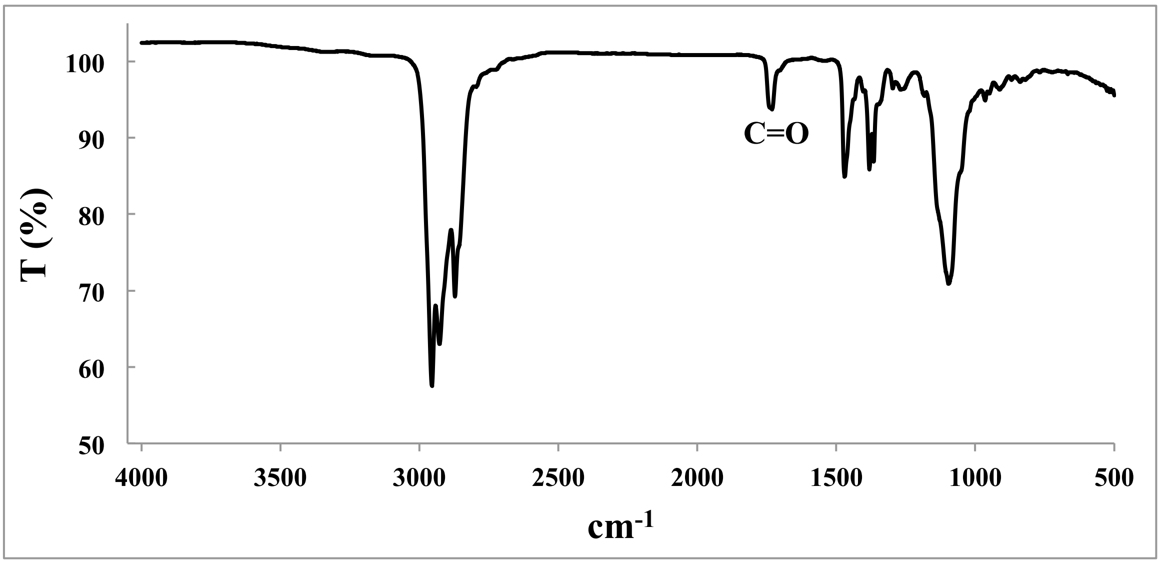


Figure 3.5: FT-IR spectrum of oligo(*i*sobutyl vinyl ether) when **SEE 1** is present.

MALDI-TOF analysis of the oligomers at 5 ml min^{-1}

Figure 3.6, shows all of the MALDI-TOF mass spectra of oligo(*i*sobutyl vinyl ether)s prepared at 5 ml min^{-1} with 0.04 M of **SEE 1**. The data were obtained through the dried droplet method using dithranol as the matrix, sodium iodide as cationisation agent and THF as the carrier solvent.

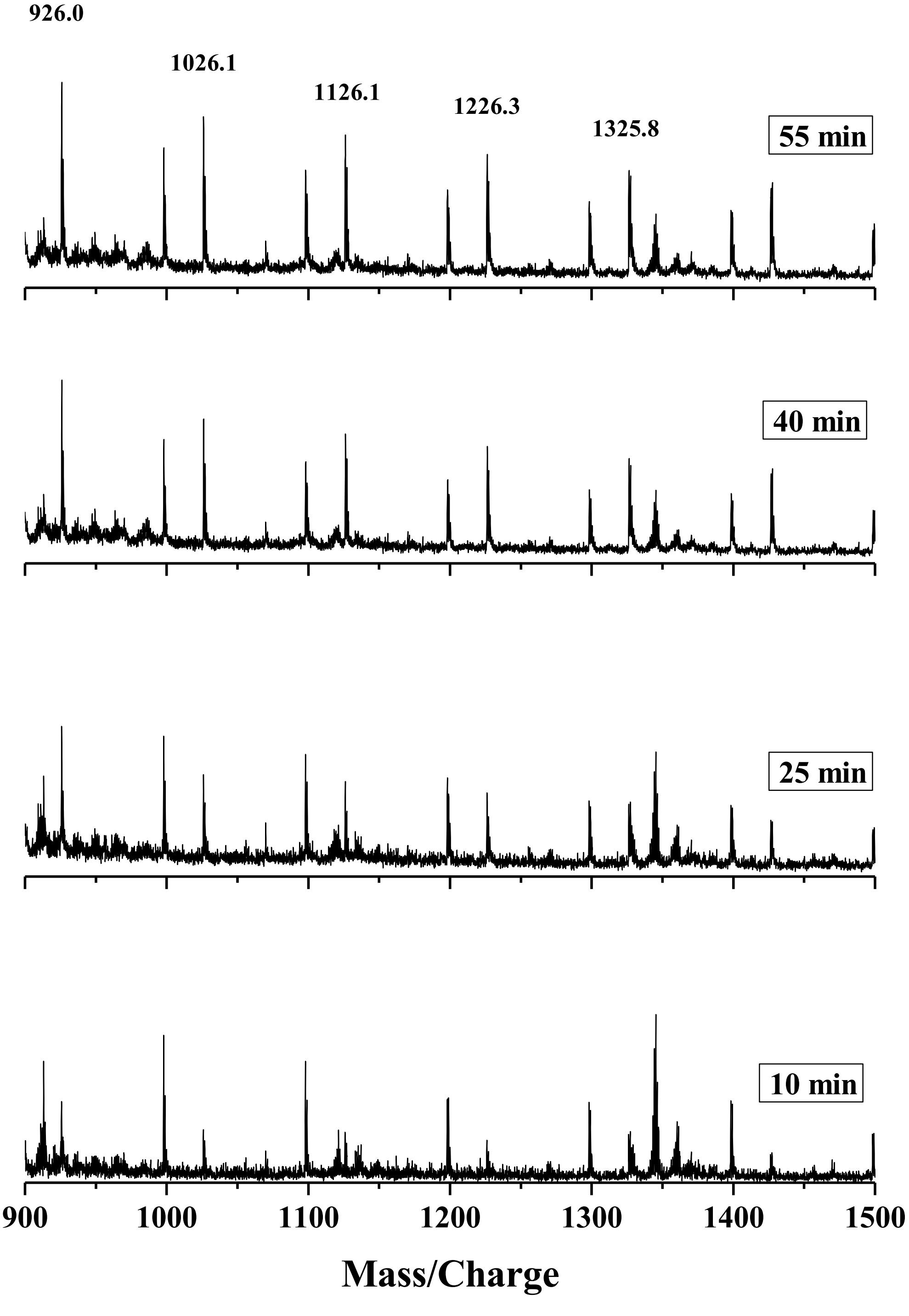


Figure 3.6: MALDI-TOF mass spectra of O*i*BVE end-capped by 0.04 M of **SEE 1**, 5 ml min^{-1} at different times.

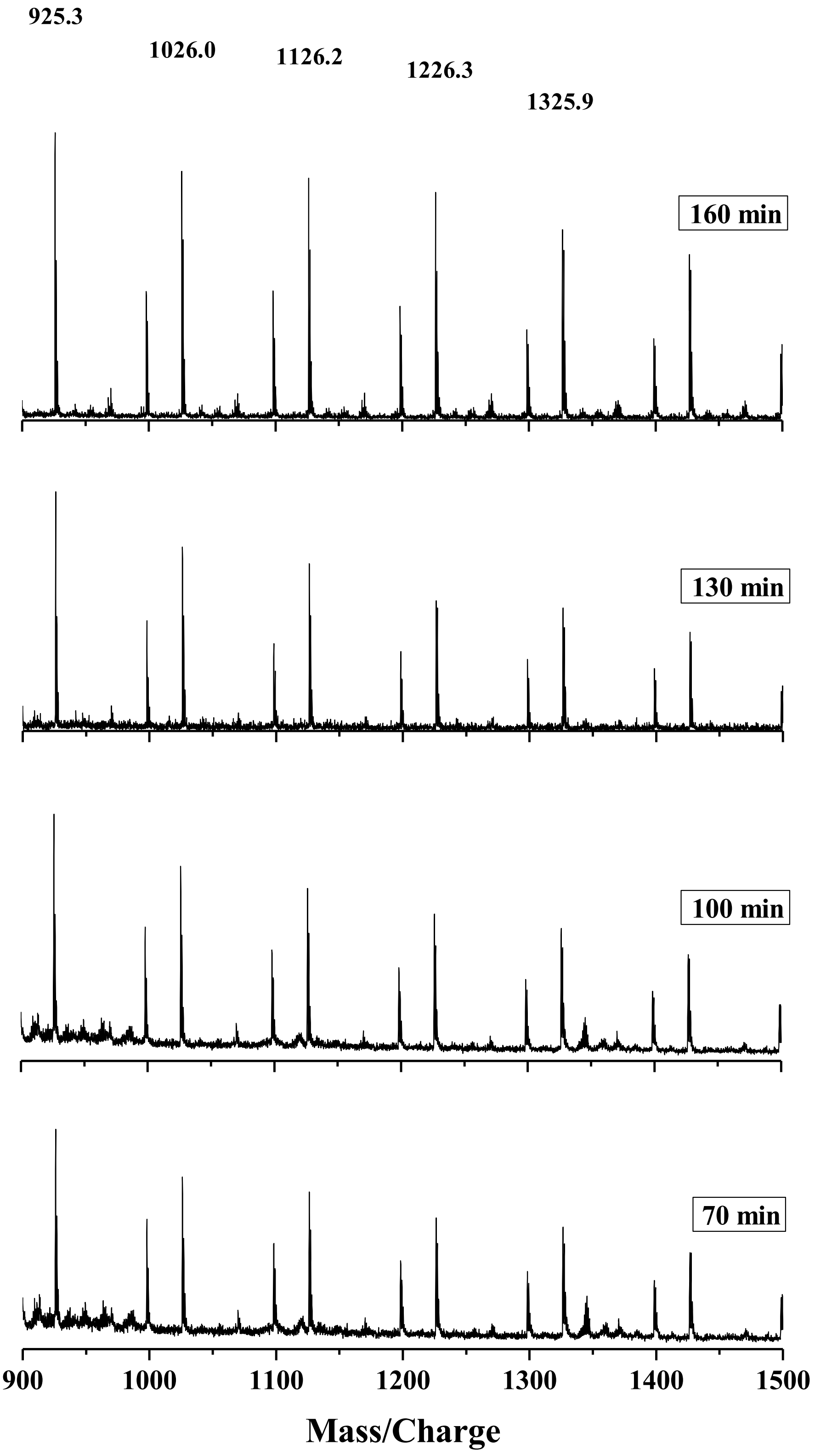


Figure 3.6: Continued.

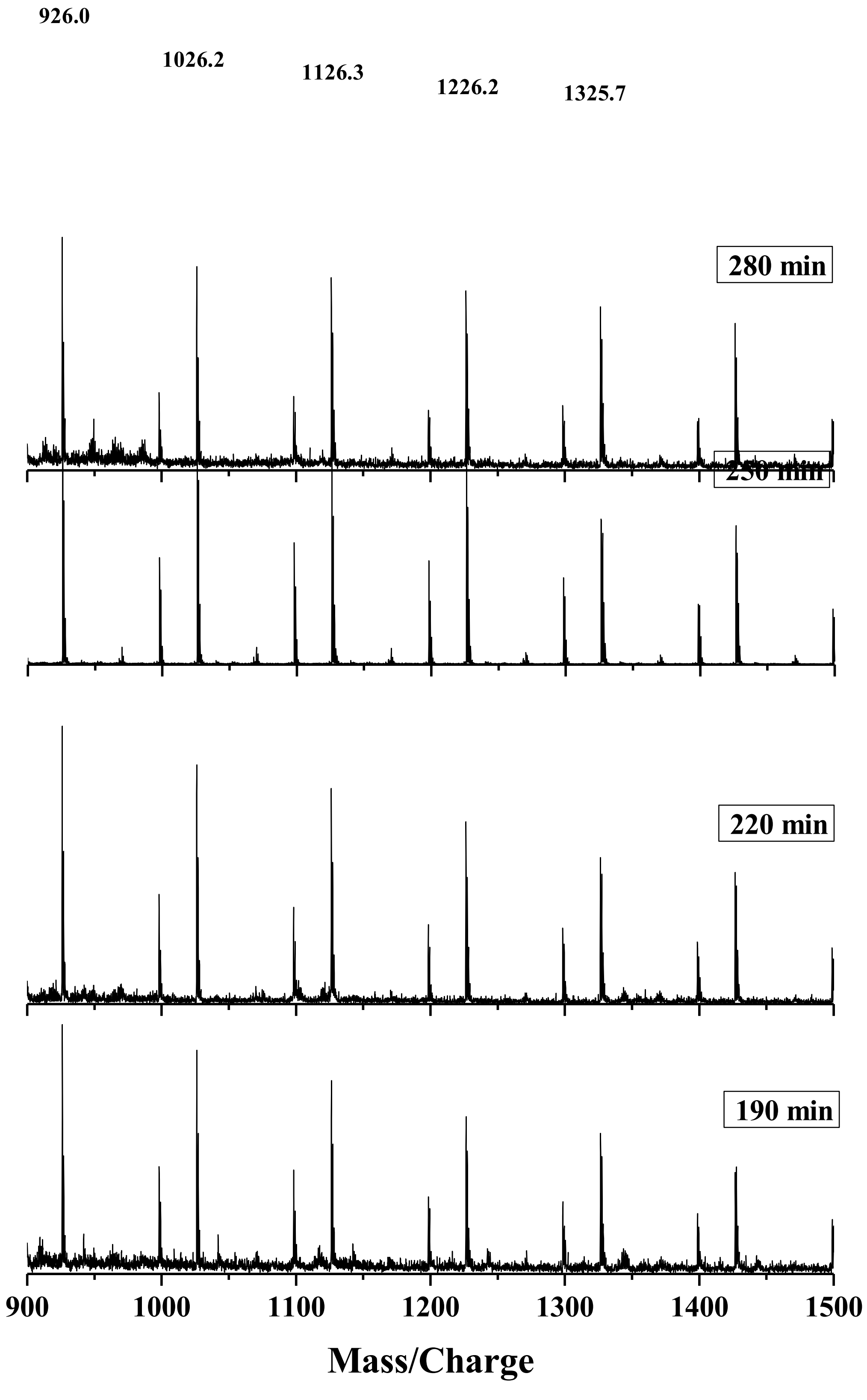


Figure 3.6: Continued.

The MALDI-TOF mass spectrum of polymerisation including 0.04 M of **SEE 1** consists of two series of polymer ions as shown in Figure 3.7. Silyl enol ether typically capped the oligomer chain end and produced the oligomer series labelled A, which can be assigned to oligomer with ester end groups. The other series labelled B, is from the oligomer with the alcohol chain end group, derived from the quenching process reaction with methanol.

However, the average functionality of the ester group was 64.49. In next section, the concentration of **SEE 1** was increased from 0.04 to 0.05 M to improve the average functionality of these polymers.

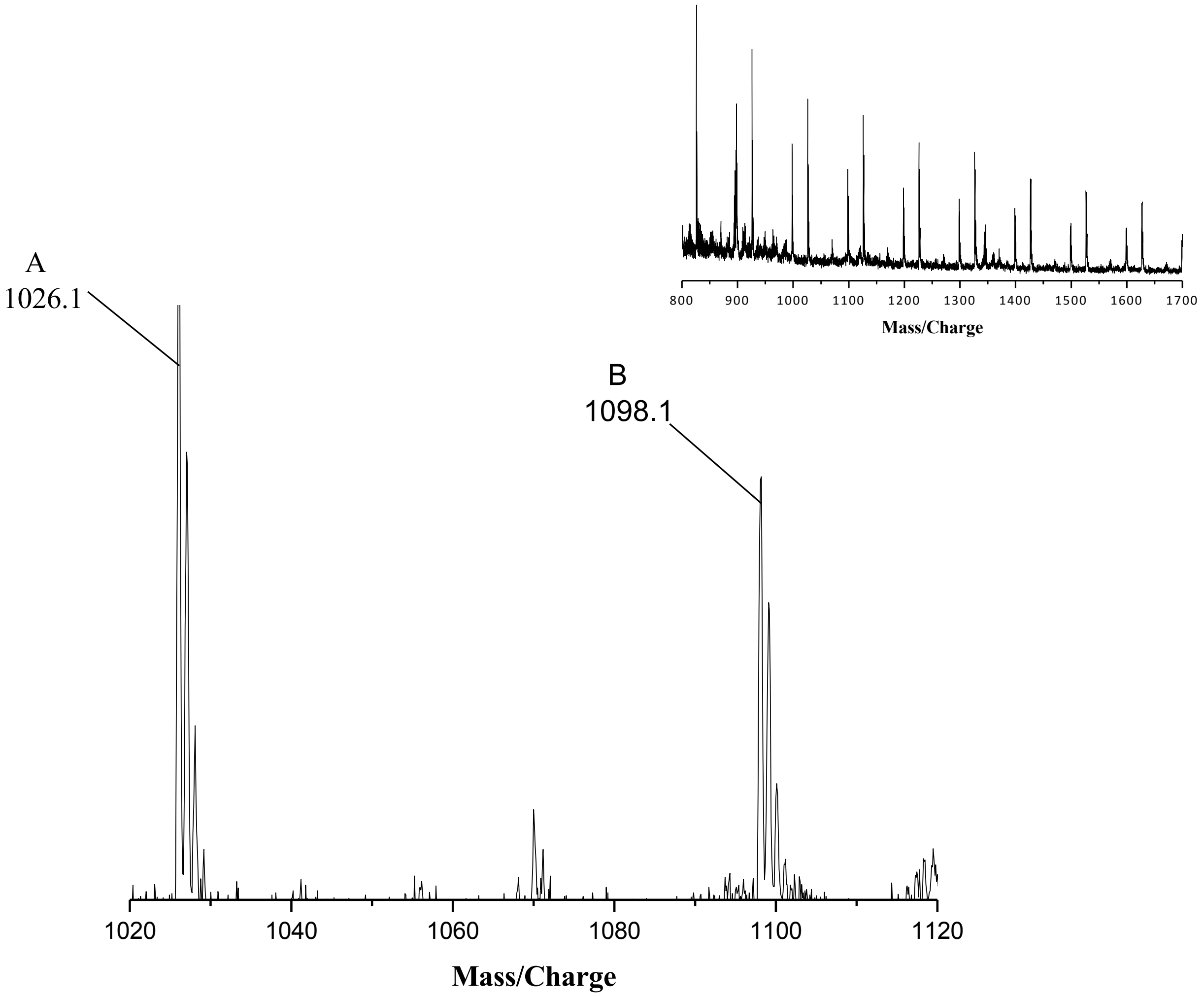
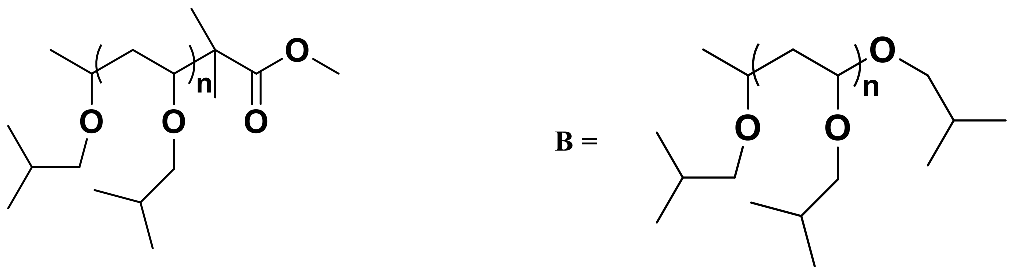


Figure 3.7: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.04 M of **SEE 1**) at 5 ml min^{-1} obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.



A =

B =

End group mass = 202

End group mass = 174

m/z = 202 + 100.16 n (Na^+)

m/z = 174 + 100.16 n (Na^+)

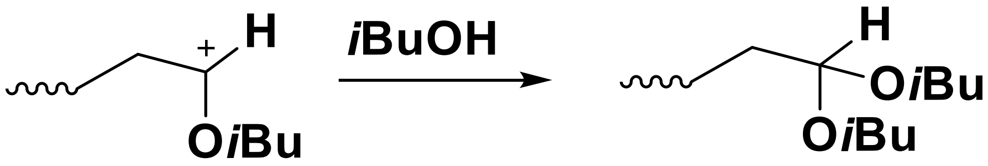
Proportion (%) = 64.49

Proportion (%) = 35.51

Figure 3.7: Continued.

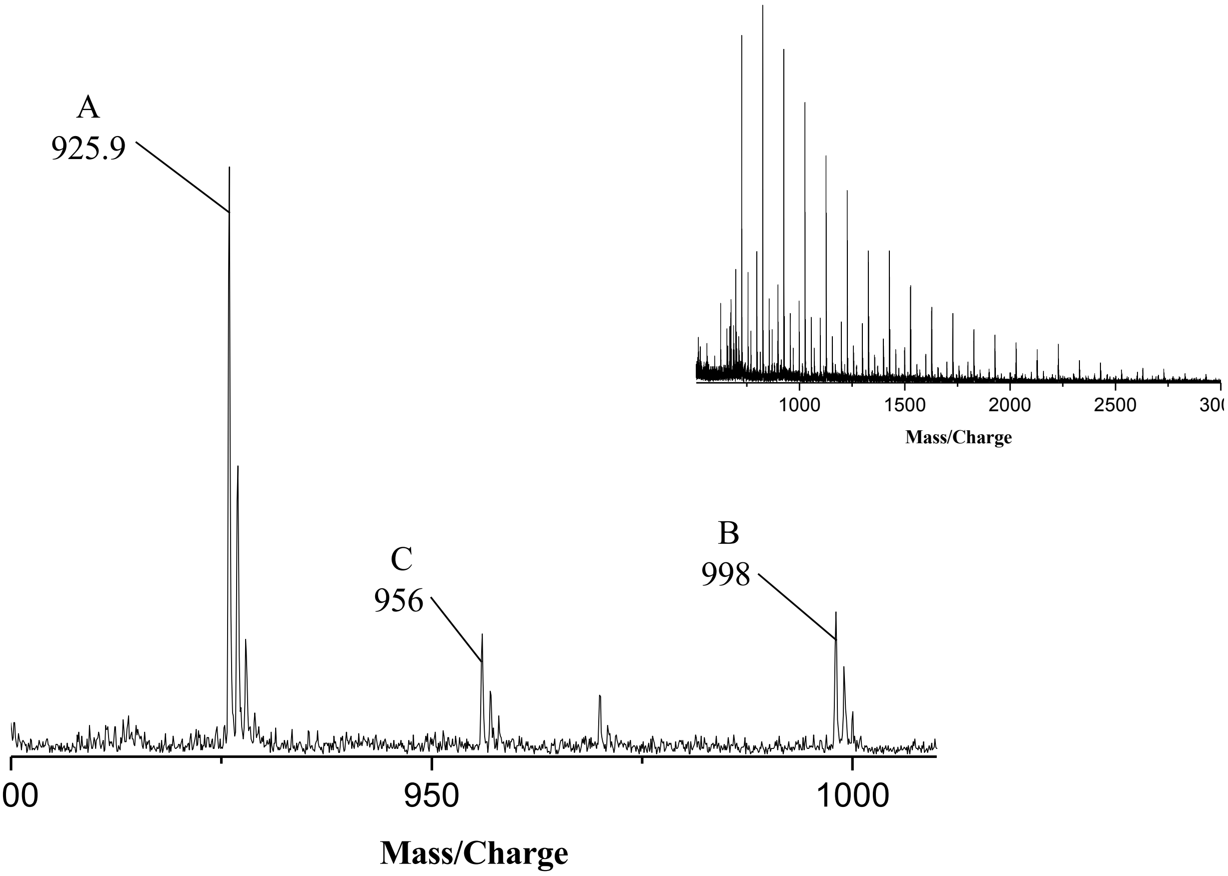
Analysis of side reaction (formation of B)

Scheme 3.2 shows the formation mechanism of the acetal chain end. However, other side reactions were previously explained in Chapter 2.



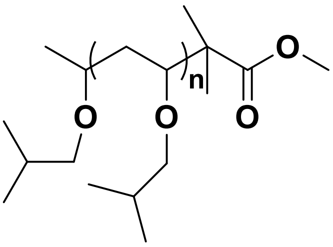
Scheme 3.2: Formation of acetal end group.

The MALDI-TOF mass spectrum of the product from the polymerisation involving 0.05 M concentration of **SEE 1** consists of three series of polymer ions as shown in Figure 3.8. Silyl enol ether typically capped the oligomer chain end and produced the oligomer series labelled A, which can be assigned to the oligomer with ester end groups. The two other series labelled B and C were from oligomers with acetal and alcohol chain end groups, derived from the quenching process reaction with methanol. The average ester group functionality of the oligomer products was 52.38, which showed no improvement on the previous system. This means the balance between the rate of propagation and the rate of termination was not perfect in this system. In the following section, the flow times will be varied under the same conditions to improve the average functionality of polymers.



Fiure 3.8: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.05 M of **SEE 1**) at 5 ml min^{-1} obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

A =

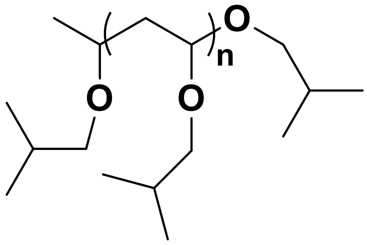


End group mass = 202

m/z = 202 + 100.16 n (Na^+)

Proportion (%) = 52.38

B =

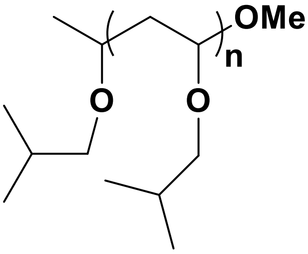


End group mass = 174

m/z = 174 + 100.16 n (Na^+)

Proportion (%) = 26.02

C =



End group mass = 132

m/z = 132 + 100.16 n (Na^+)

Proportion (%) = 21.60

Figure 3.8: Continued.

Comparing the monomer conversion and the average ester group functionality between 0.04 and 0.05 M of **SEE 1** at 5 ml min^{-1}

The monomer conversion was measured using ^{1}H NMR spectroscopy. It can be seen clearly in Figure 3.9 that all of the monomer was consumed in these polymerisations over the reaction time. The average chain end functionality was calculated by MALDI-TOF mass spectrometry, which resulted in well-resolved spectra. Figure 3.9 compares the average chain end functionality produced by reactions fed at 5 ml min^{-1} with two different concentrations of **SEE 1** (0.04 and 0.05 M respectively). The polymerisations conducted at 5 ml min^{-1} with various concentrations of **SEE 1** showed lower than average functionality. Then, the functionality increased steadily throughout the polymerisation time. The highest level of average functionality achieved in these conditions was 76 % after 4.5 hours.

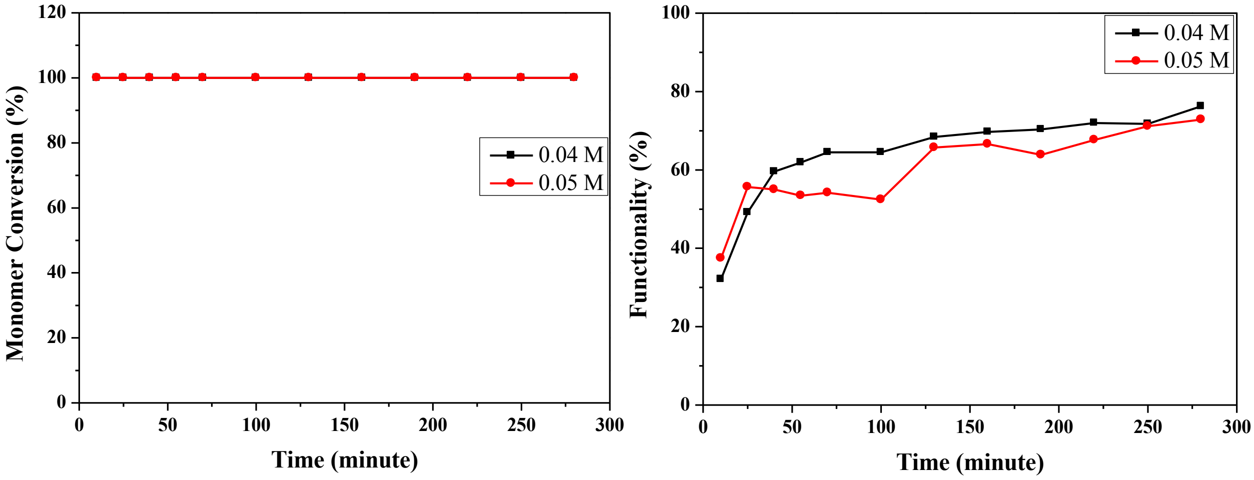


Figure 3.9: The monomer conversion (left) and the average chain end functionality (right) at 5 ml min^{-1} in 0.04 and 0.05 M concentrations of **SEE 1** observed by ^{1}H NMR MALDI-TOF spectrum, respectively.

3.3.1.2 Polymerisation of iBVE at 3 ml min^{-1}

A series of polymerisations were optimised at the 3 ml min^{-1} flow time with various concentrations of **SEE 1** (0.04, 0.05, 0.06 and 0.08 M). In this case, several experiments were run to discover the reaction conditions that produced the polymer with a high degree of chain end functionality. Figure 3.10, shows the average molecular weights and dispersities of these different polymers over time. The highest molecular weights were reached with 0.04 and 0.05 M concentrations of **SEE 1,** whereas 0.06 and 0.08 M provided low molecular weights. That is because when the polymer chain starts growing, the high concentration of silyl enol ether (end capping agent) will stop the growth from proceeding very rapidly. The dispersity of all the polymers over time remained low, at about 1.5, during the polymerisation reaction, demonstrating good control under continuous processes.

The monomer conversion and the average functionality derived from different concentrations of **SEE 1** at 3 ml min^{-1} are shown in Figure 3.11. All monomers were consumed under these conditions. Generally, the best average functionality that was recorded was 75 % after 2.5 hours, using 0.05 M of **SEE 1**.

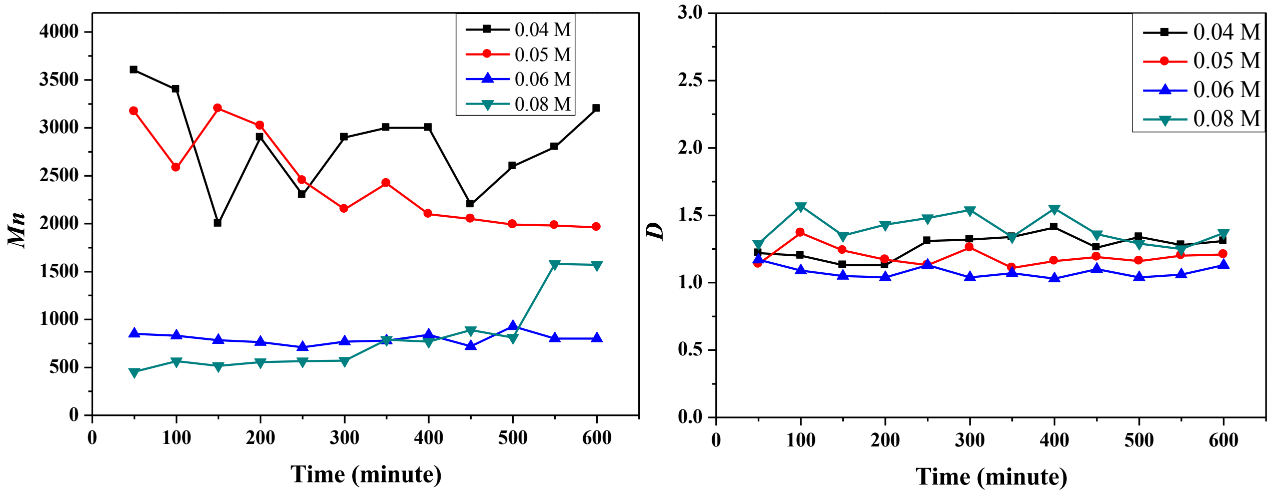


Figure 3.10: The plot of molecular weight (left) and dispersity (right) against time in 0.04, 0.05, 0.06 and 0.08 M of **SEE 1** concentration.

The monomer conversion and the average functionality derived from different concentrations of **SEE 1** at 3 ml min^{-1} are shown in Figure 3.11. All of the monomer was consumed in these polymerisations. Generally, the best average of functionality measured was 75 % after 2.5 hours using 0.05 M of **SEE 1**.

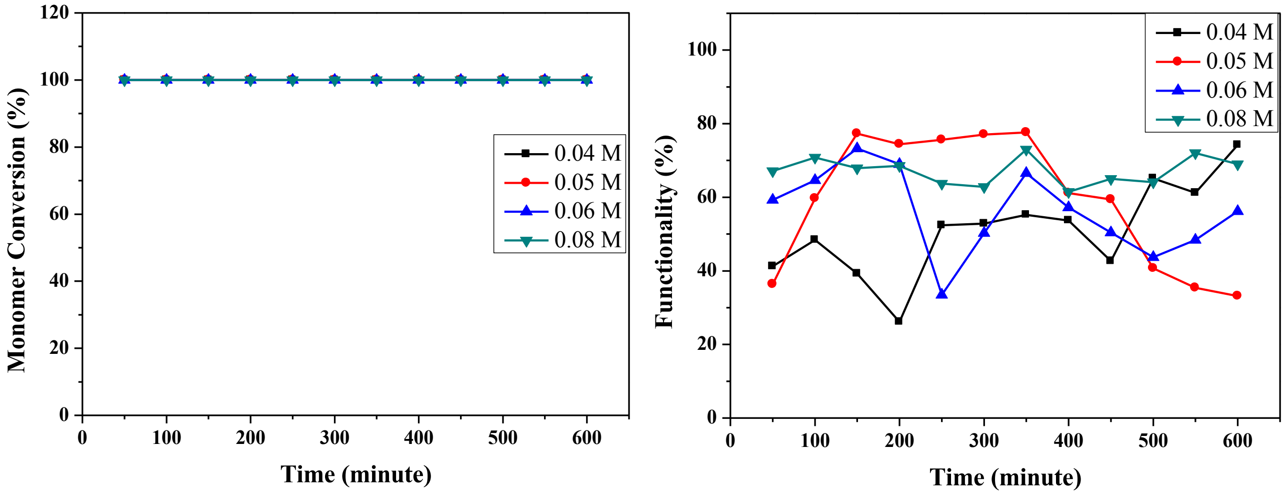


Figure 3.11: The monomer conversion (left) and the average chain end functionality (right) at 3 ml min^{-1} with various (0.04, 0.05, 0.06 and 0.08 M) concentrations of **SEE 1** observed by MALDI-TOF spectroscopy.

MALDI-TOF analysis of the oligomers

Figure 3.12 shows the MALDI-TOF mass spectra of O*i*BVE that have been observed in each of the separate samples. These samples were produced using 0.05 M of **SEE 1** and gave the best average chain end functionality at 3 ml min^{-1} flow time.

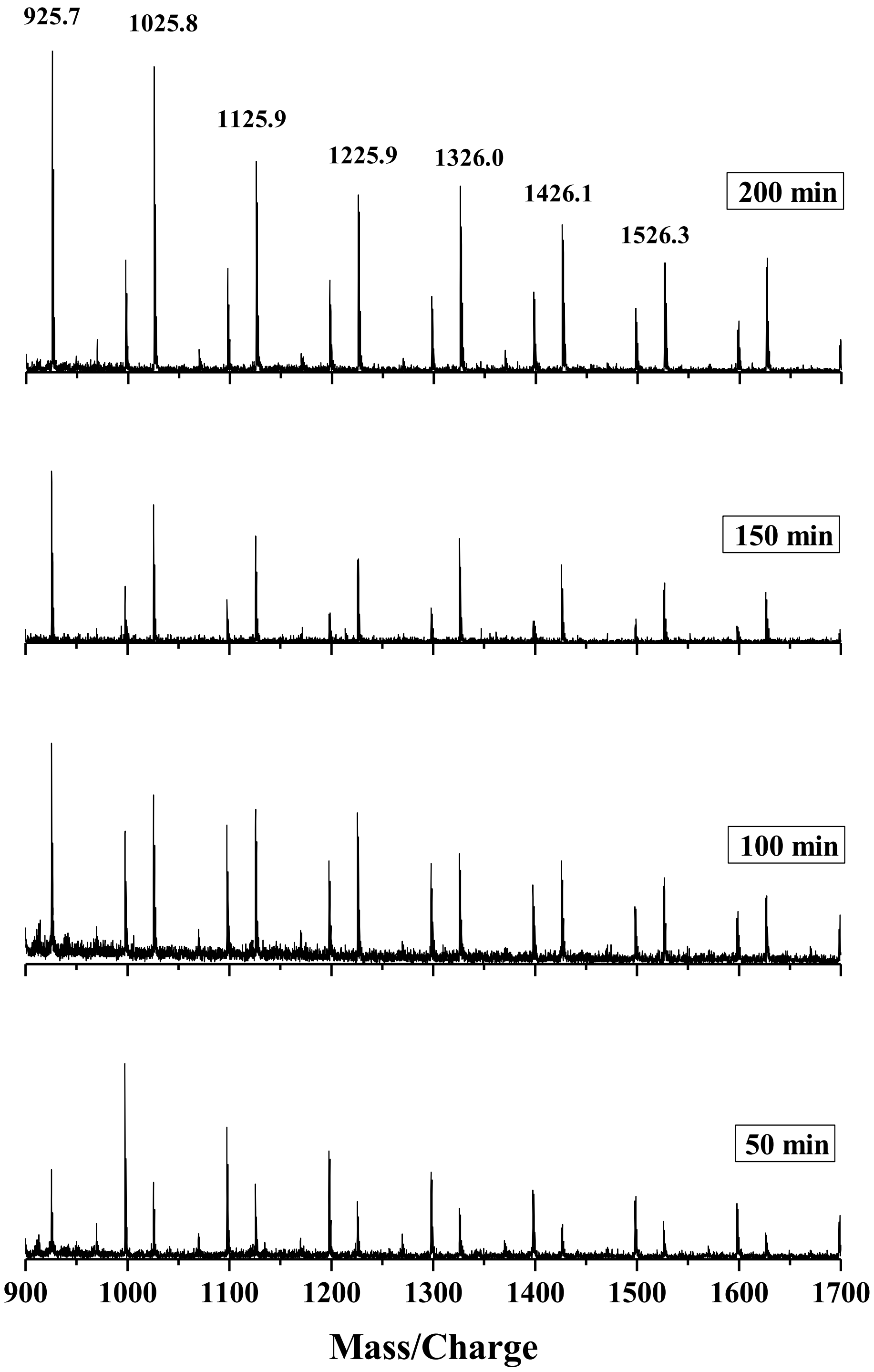


Figure 3.12: MALDI-TOF mass spectra of O*i*BVE end-capped by 0.05 M of **SEE 1**, 3 ml min^{-1} at different times.

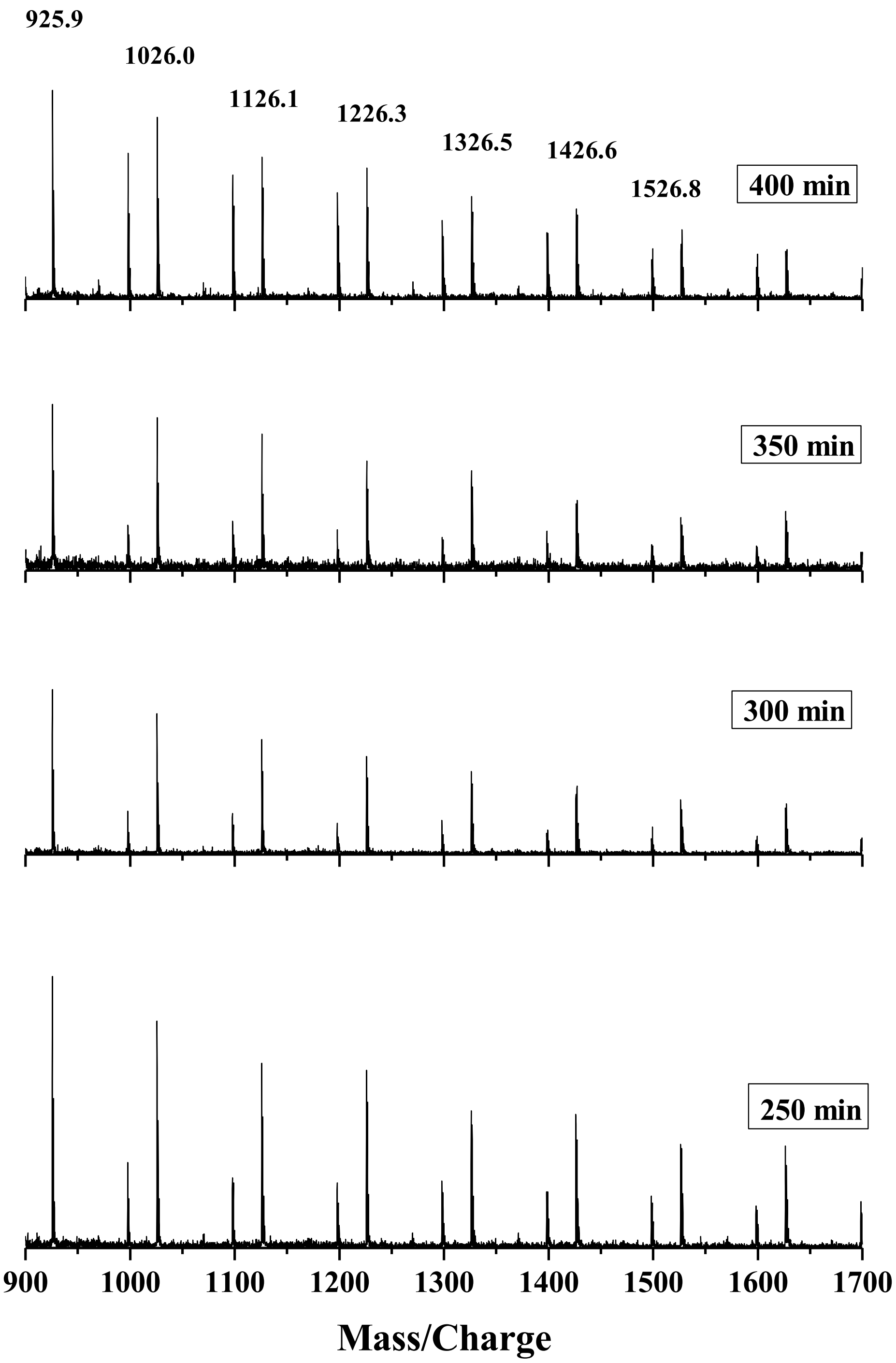


Figure 3.12: Continued.

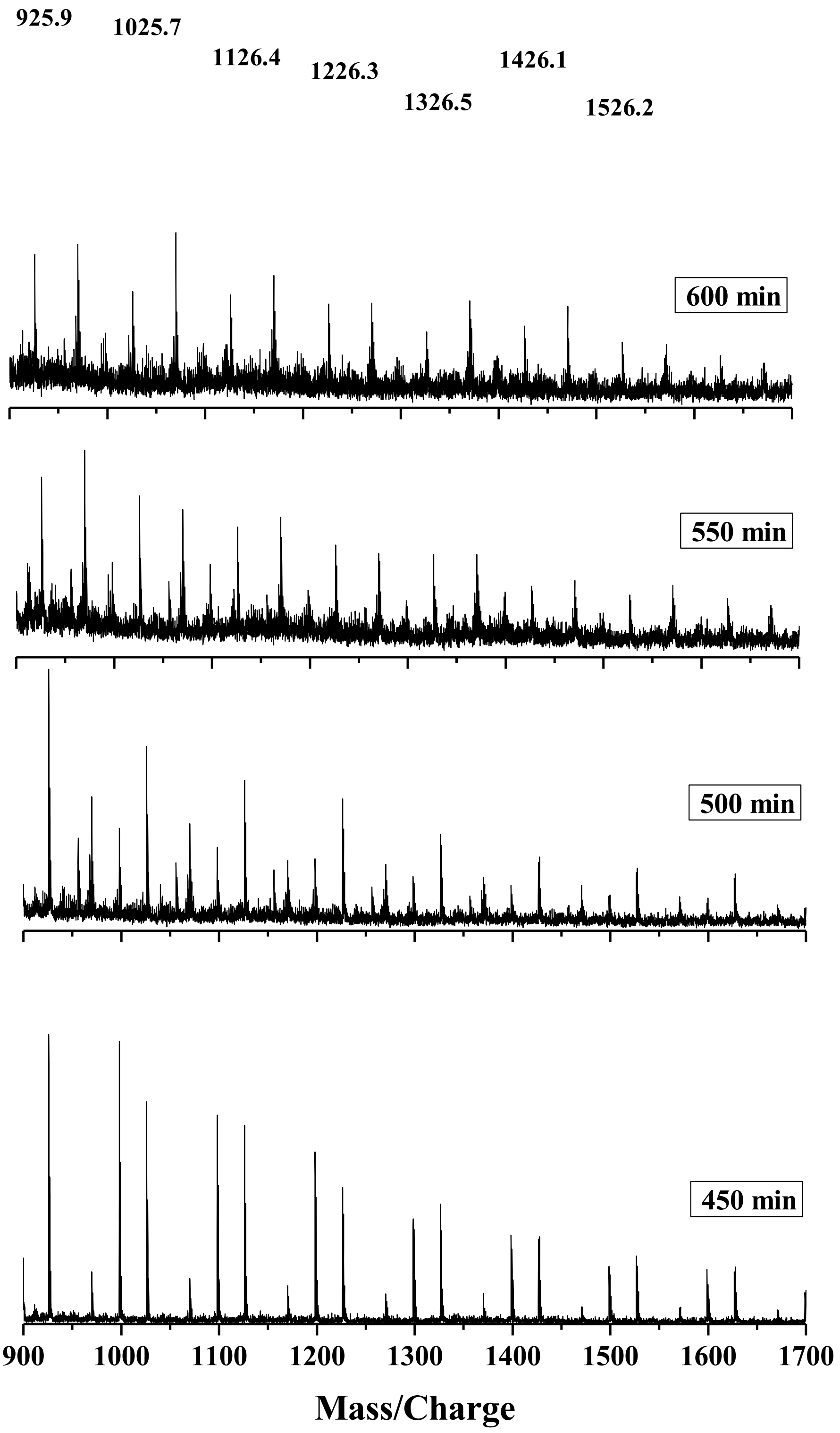


Figure 3.12: Continued.

Two series of polymer ions were measured from previous figures. Typically, the chain end group with the oligomer was achieved and labelled A. The other series was labelled B and is derived from the oligomer with the alcohol chain end that was derived from the quenching process. The average functionality of the ester group was 77.05 % (see Figure 3.13).

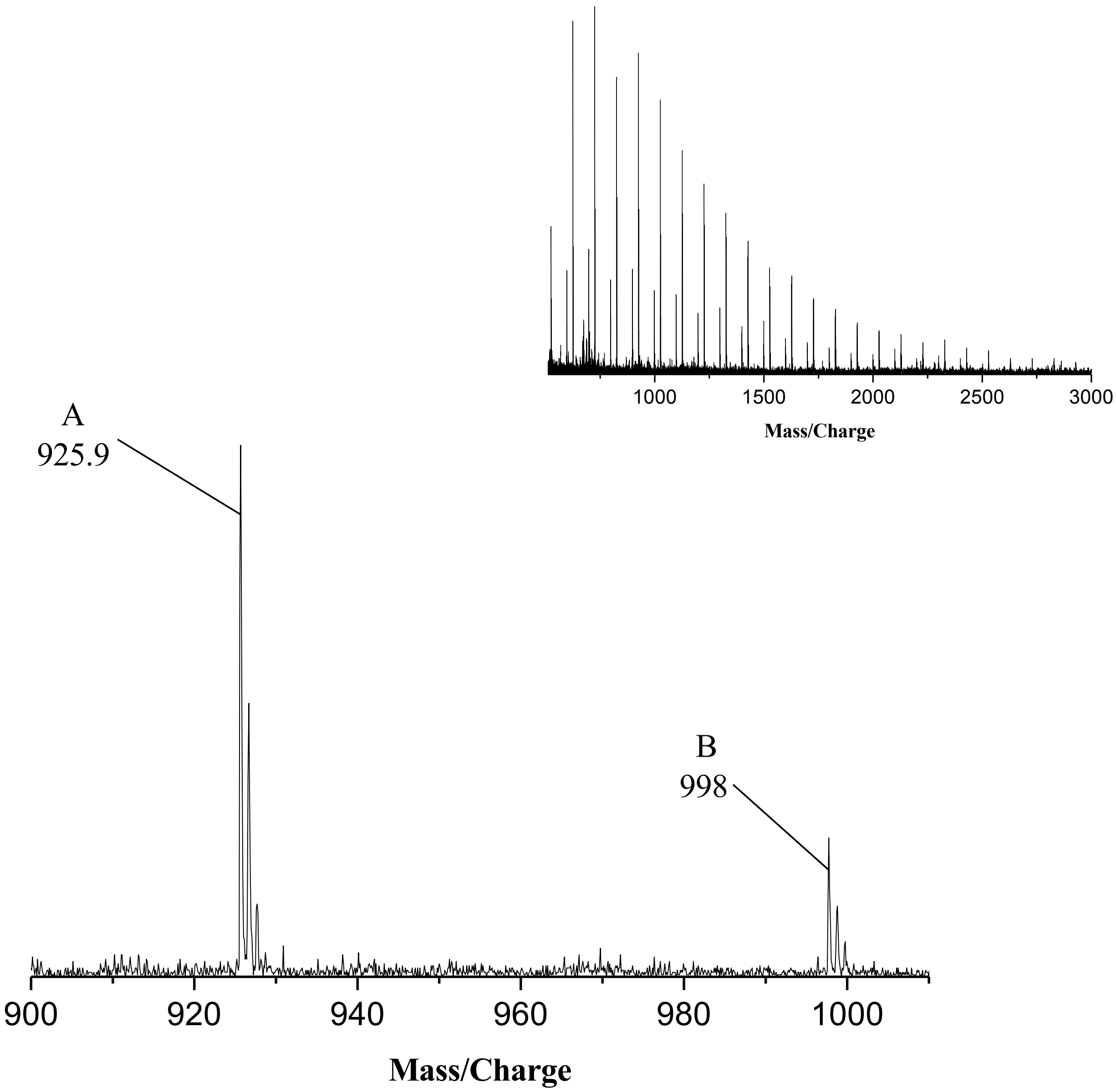


Figure 3.13: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.05 M) obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

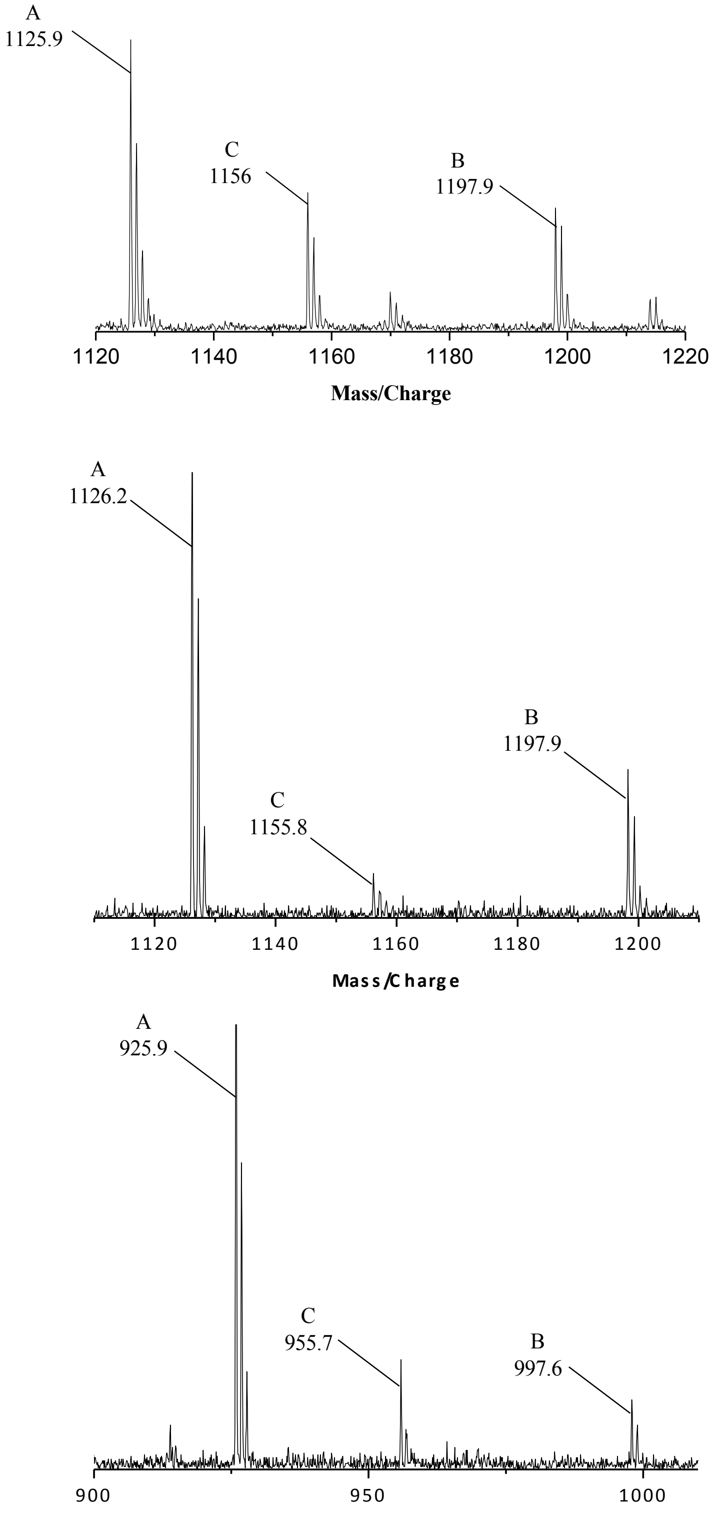


Figure 3.14: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.04, 0.06 and 0.08 M respectively) at 3 ml min^{-1} obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

Figure 3.14 shows one of the samples prepared at 3 ml min^{-1} flow time. At 0.04 M concentration of **SEE 1**, the best end-capping agent achieved was 65.7 %. On the other hand, the best average functionalities were measured at 79.31% and 73.01 % at 0.06 and 0.08 M of **SEE 1** respectively.

3.3.1.3 Polymerisation of iBVE at 2 ml min^{-1}

The polymerisation of *i*BVE was conducted in the presence of 0.06 and 0.08 M concentrations of **SEE 1** at 2 ml min^{-1} by using $SnCl_4$ as a Lewis acid. Figure 3.15, gave the highest molecular weight with 0.06 M of **SEE 1** concentration rather than at 0.08 M of **SEE 1**. Moreover, the two different polymerisations showed well-controlled molecular weights with narrow (remaining below 1.5) dispersities during the reaction time.

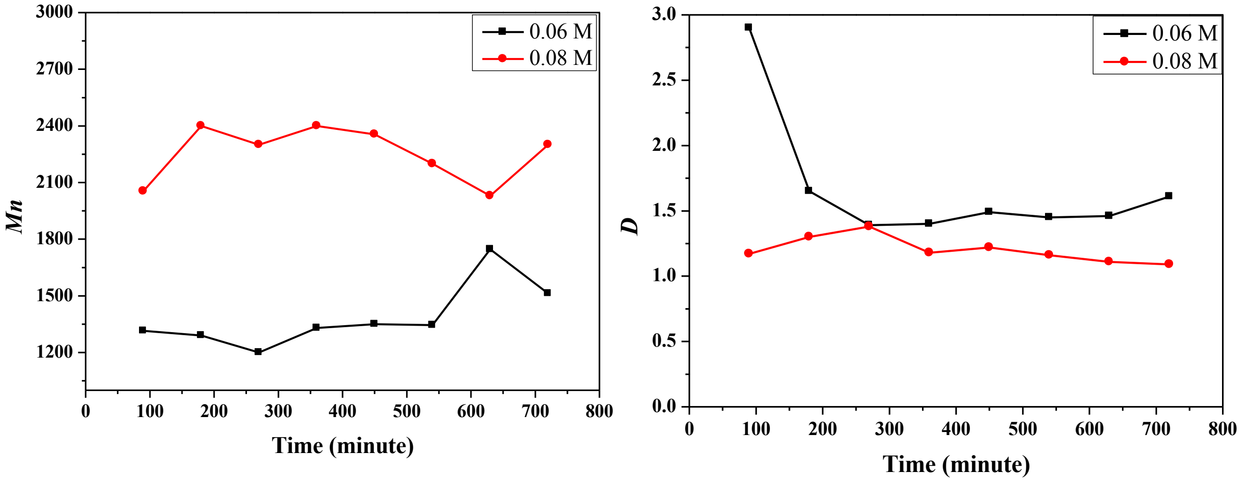


Figure 3.15: Molecular weight data (left) and dispersities (right) for polymerisation of *i*BVE (2 mol dm^{-3}) in the presence of **SEE 1** initiated by *i*BVE:HCl:$SnCl_4$ (0.02:0.04 mol dm^{-3}) at 2 ml min^{-1}.

Figure 3.16 shows that all of the monomer has been polymerised. The average functionality of the polymerisation run at 0.06 M increased over time. However, the functionality rose as the time increased to 3 hours since the beginning of the reaction. After that, it decreased continuously as the time frame increased when the polymerisation was carried out at 0.08 M of **SEE 1**. Therefore, the data provides indications that the highest average functionality of the ester group was measured using the 2 ml/min^{-1} flow time and 0.06 M concentration of **SEE 1**.

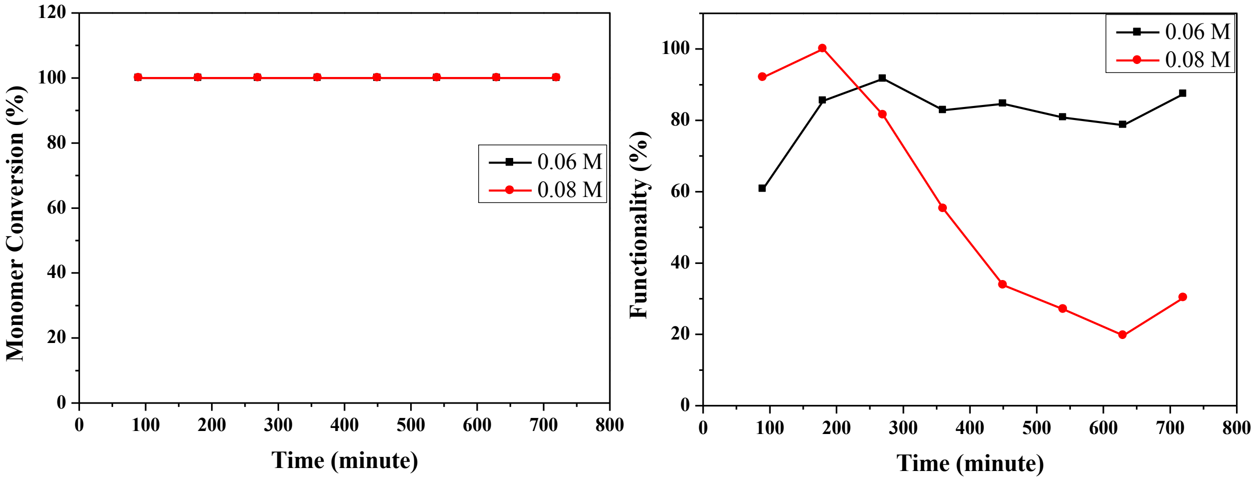


Figure 3.16: The monomer conversion (left) and the average chain end functionality (right) at 2 ml min^{-1} in 0.06 and 0.08 M concentrations of **SEE 1** observed by MALDI-TOF spectrum.

MALDI-TOF analysis of the oligomers

Figure 3.17 shows the MALDI-TOF mass spectra of O*i*BVE, which have been obtained from different samples. These samples were produced using 0.06 M of **SEE 1** and gave the best average chain end functionality at the 2 ml min^{-1} flow time.

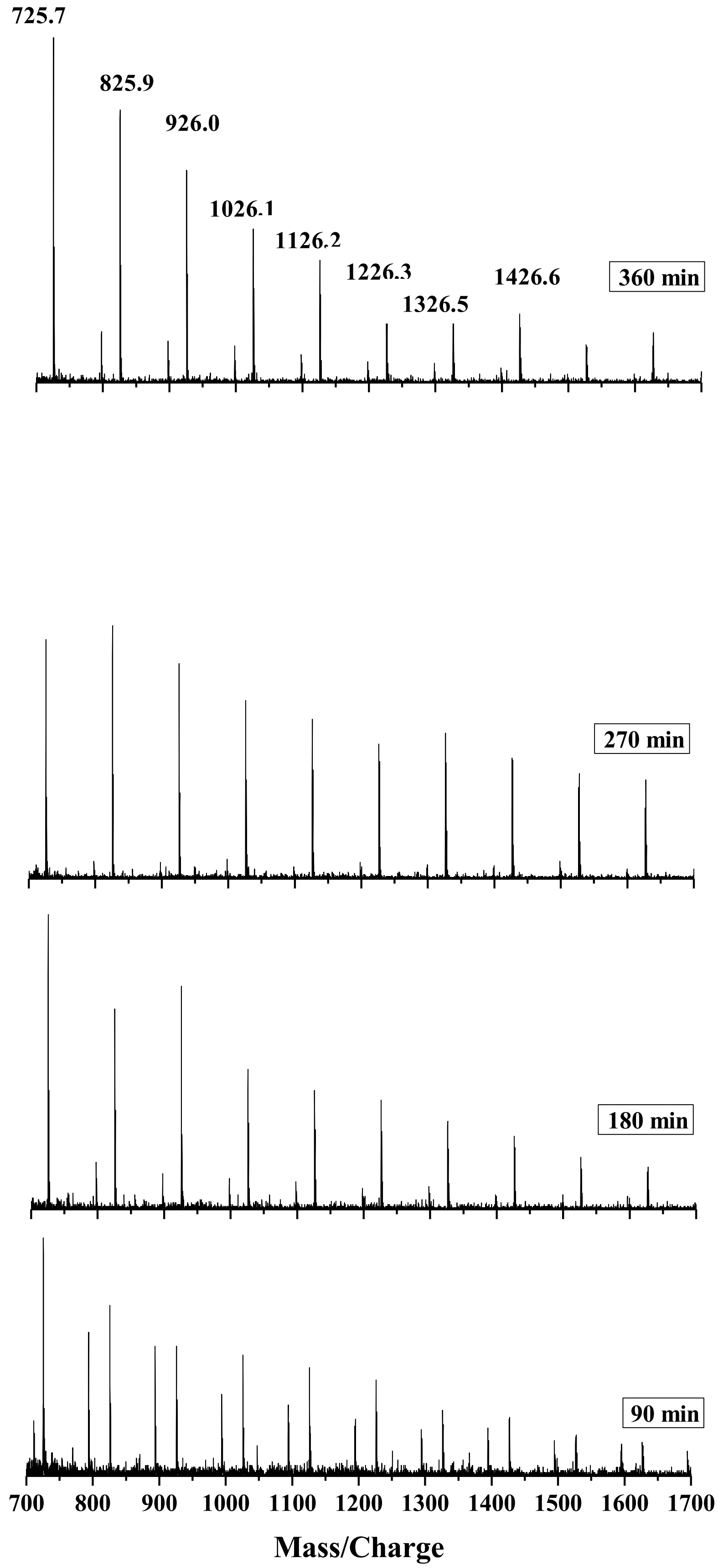


Figure 3.17: MALDI-TOF mass spectra of O*i*BVE end-capped by 0.06 M of **SEE 1**, 2 ml min^{-1} at different times.

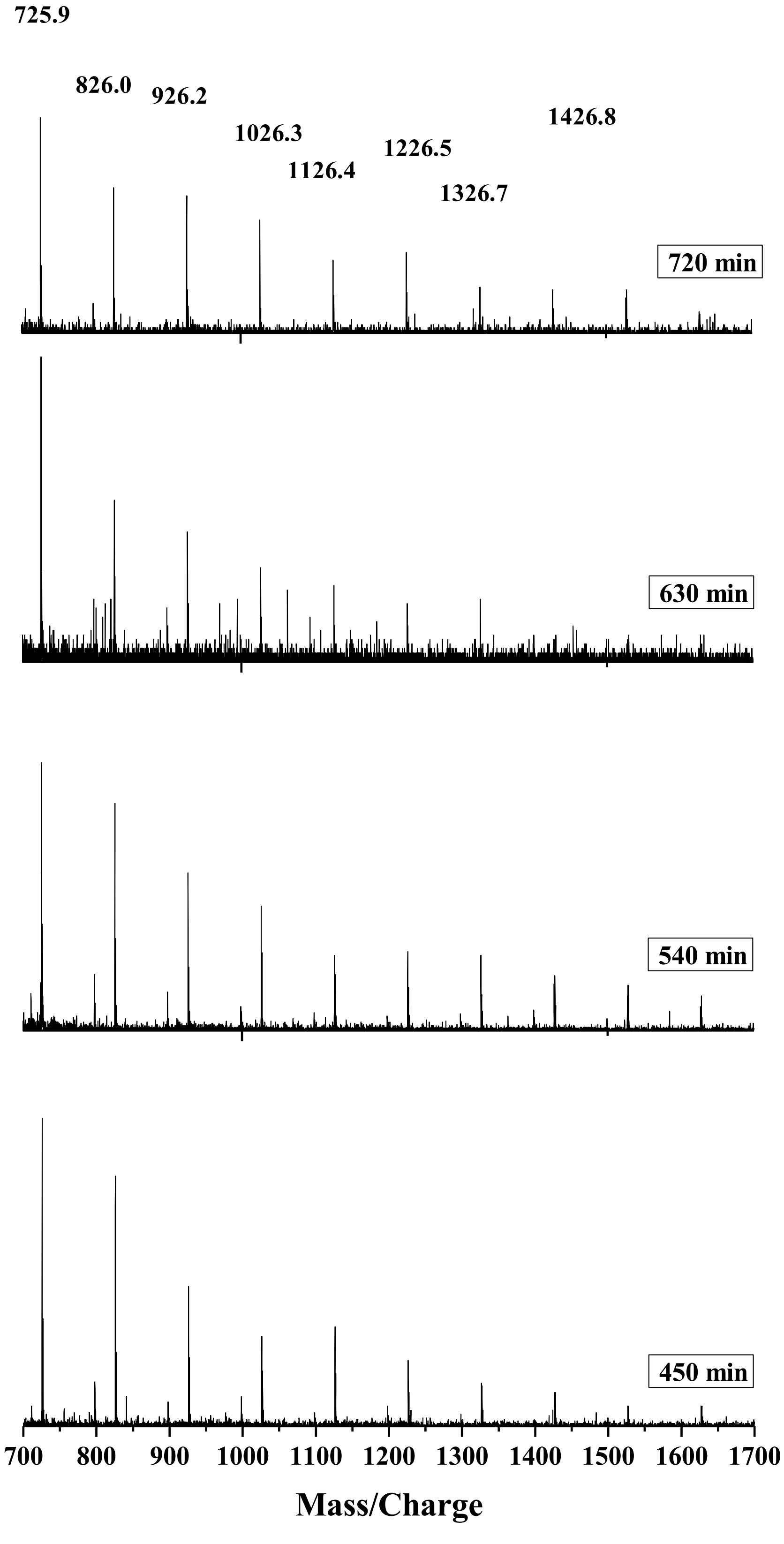


Figure 3.17: Continued.

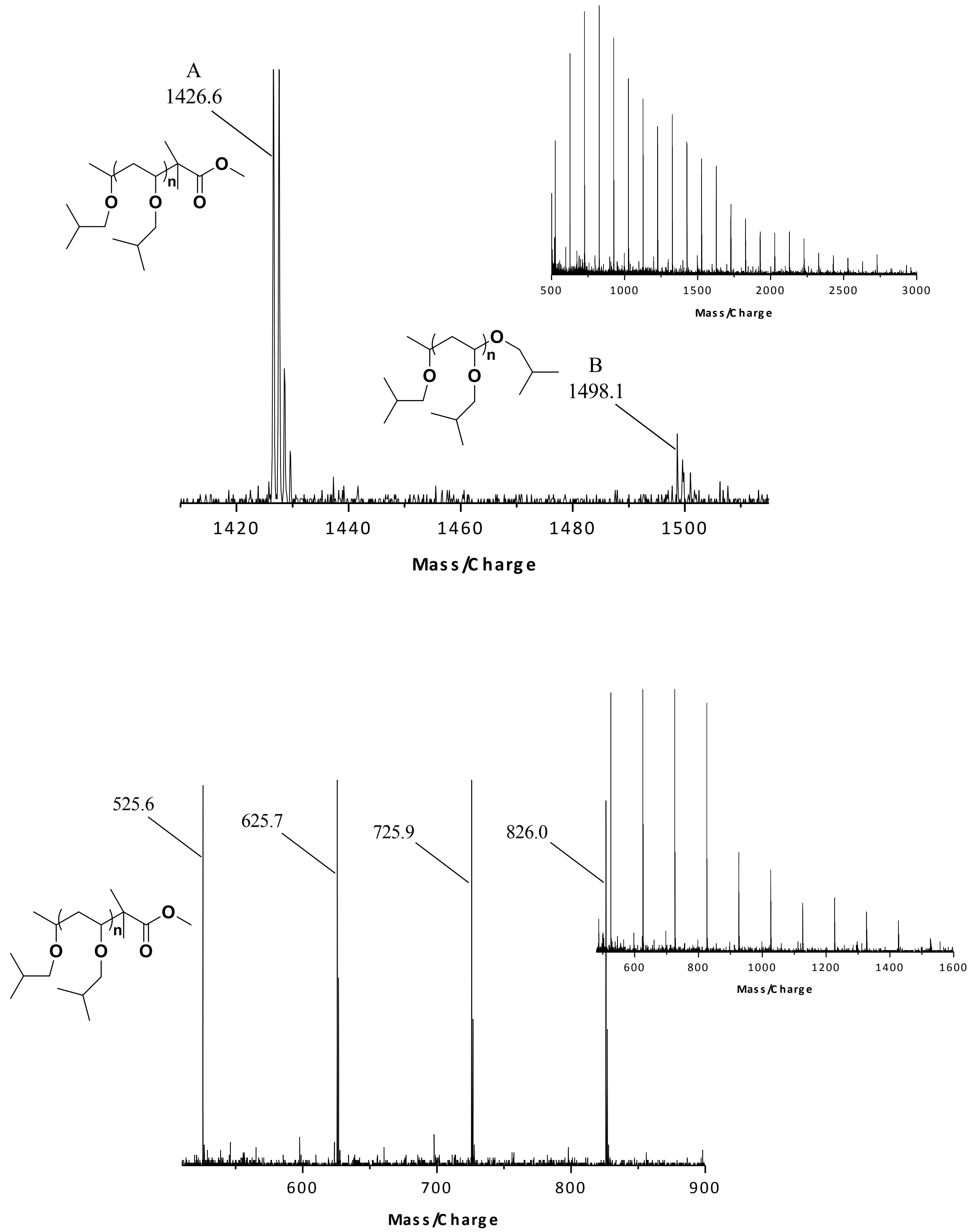


Figure 3.18: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.06 and 0.08 M respectively) at 2 ml min^{-1} obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent.

Figure 3.18 shows a mass spectrum produced from the polymerisation at 2 ml min^{-1} in 0.06 and 0.08 M of **SEE 1**. At 0.08 M, it contains one series of ions, m/z = n99.8 + (23 + 202), which was derived from cationisation by sodium. The average chain end functionality in this case was more than 99 %. This sample was collected after 3 hours of reaction time. Following this, the ester end group functionality decreased sharply as the time frame increased.

Molecular weight distributions measured from size exclusion chromatography (THF, low molecular weights of polystyrene as standards) are shown in Figure 3.19 for polymerisation at 2 ml min^{-1} and 0.06 M of **SEE 1.** At the start of the reaction, molecular weight fell before becoming constant over time. Therefore the polymerisation reached a steady state after 3 hours and many of the molecular weights were very similar to each other.

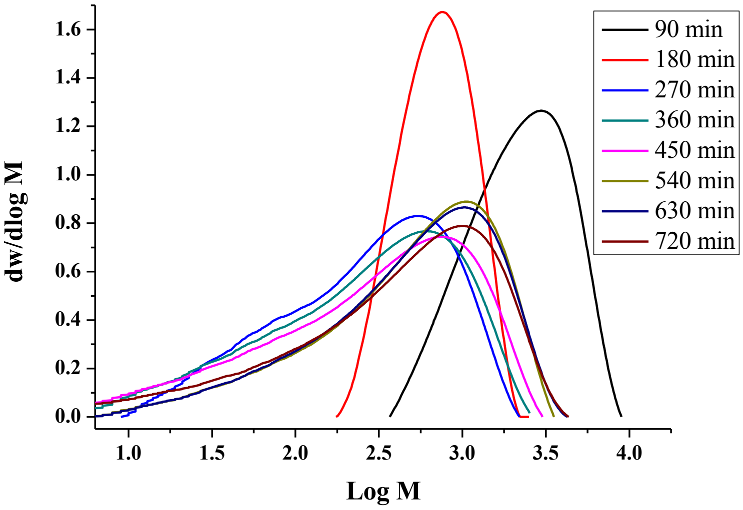


Figure 3.19: SEC of oligo*i*sobutyl vinyl ethers produced from 0.06 M of **SEE 1** at 2 ml min^{-1}.

All molecular weight distributions for poly*i*sobutyl vinyl ethers in the presence of 0.08 M of **SEE 1** at 2 ml min^{-1} are shown in Figure 3.20. The data shows clearly that the molecular weight distributions altered as the reaction progressed. Following this, the molecular weight decreased over time. The decrease in the molecular weight is probably due to the stability of the continuous process, especially when the time has been increased.

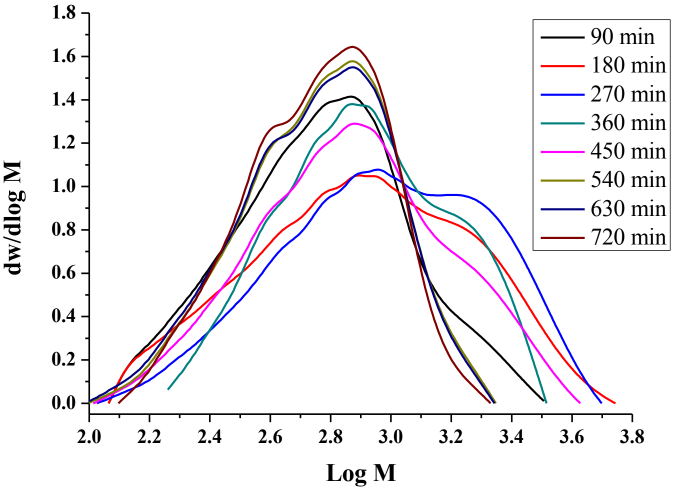


Figure 3.20: Molecular weight distributions for several oligo*i*sobutyl vinyl ethers synthesised in 0.08 M at 2 ml min^{-1}.

3.3.2 Polymerisations of *i*BVE using TiCl$_4$

3.3.2.1 Polymerisation of iBVE at 5 ml min^{-1}

In this case, a series of polymerisations were performed by using TiCl$_4$ as a Lewis acid in the presence of **SEE 1**. The molecular weights and dispersities data from these experiments are presented in Figure 3.21.

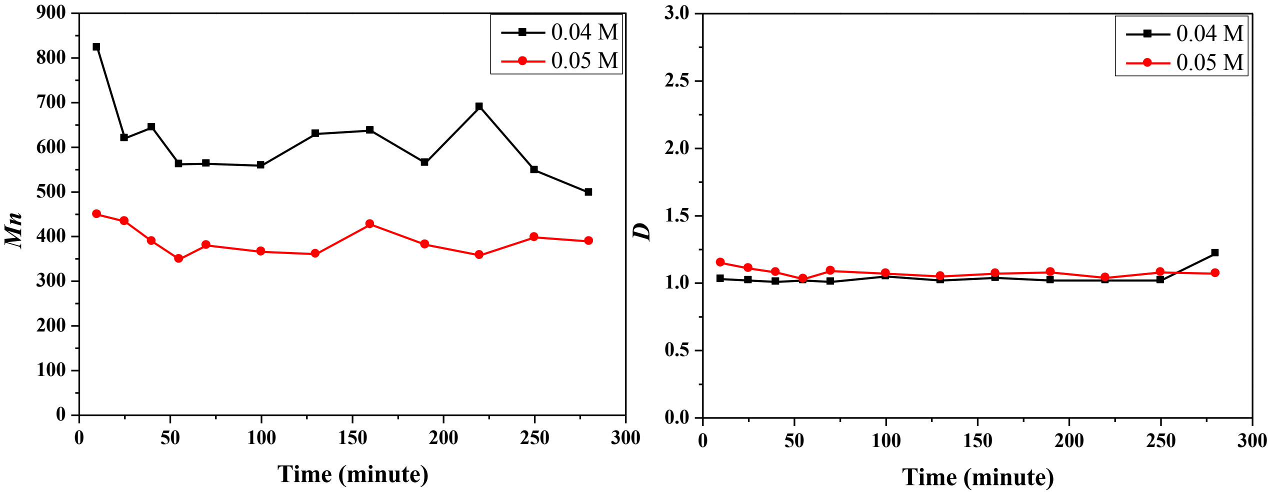


Figure 3.21: Molecular weight data (left) and dispersities (right) for polymerisation of *i*BVE (2 mol dm^{-3}) in the presence of **SEE 1** initiated by *i*BVE:HCl:TiCl$_4$ (0.02:0.04 mol dm^{-3}) at 5 ml min^{-1}.

In the previous Figure, the highest molecular weights were recorded using a low concentration of **SEE 1** (0.04 M). All of the polymerisations with different concentrations of **SEE 1** produced invariant material over time. The dispersities of these polymers were very narrow; below 1.5.

It is clear from Figure 3.22 that at a flow time of 5 ml min^{-1}, increasingly high degrees of chain-end functionality were obtained by increasing the concentration of **SEE 1** and continued over time. However, the general average end group functionalities were still very low when compared with previous Lewis acid ($SnCl_4$).

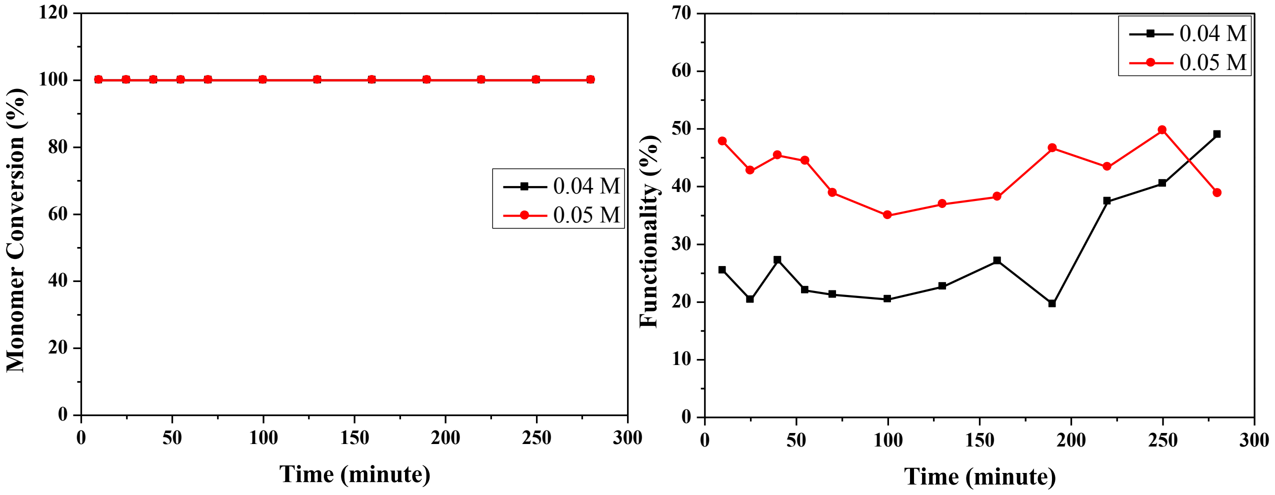
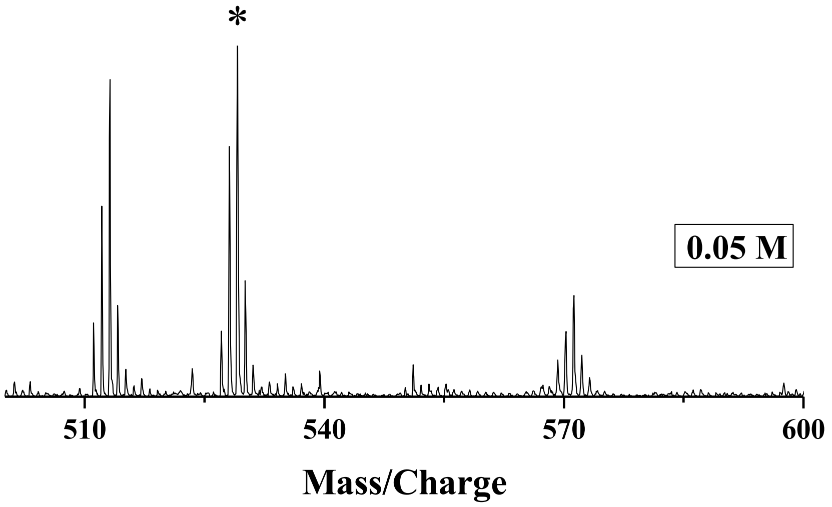


Figure 3.22: The monomer conversion (left) and the average chain end functionality (right) at 5 ml min^{-1} in 0.04 and 0.05 M concentrations of **SEE 1** observed by ^{1}H NMR and MALDI-TOF spectra.

MALDI-TOF analysis of the oligomers

Figure 3.23 shows the MALDI-TOF mass spectra of oligo(*iso*butyl vinyl ethers), which were studied under two different conditions. These samples were produced at 0.04 and 0.05 M of **SEE 1** at 5 ml min^{-1} flow time, using $TiCl_4$ as a Lewis acid.



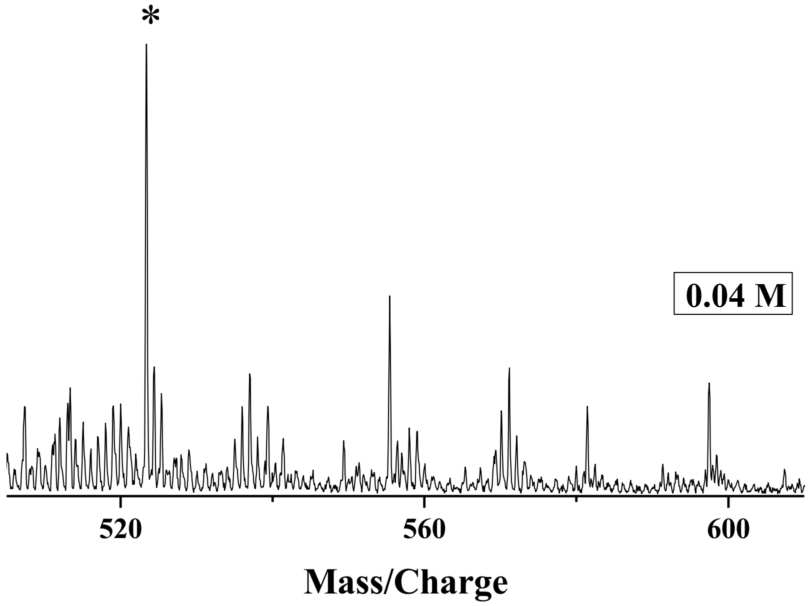


Figure 3.23: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.04 and 0.05 M) at 5 ml min^{-1} obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent. (*) refers to ester group.

3.3.2.2 Polymerisation of iBVE at 3 ml min^{-1}

Several experiments were optimised at a flow time of 3 ml min^{-1} with many different concentrations of **SEE 1** (0.04, 0.05, 0.06 and 0.08 M). Figure 3.24, shows all of the molecular weights and dispersities of these experiments. Generally, the molecular weights were very low, even with different concentrations of **SEE 1**. The reason for this was down to the nature of Lewis acid ($TiCl_4$). The Lewis acid did not support the production of polymer with a high molecular weight. All of these polymerisations showed well-controlled molecular weights, and dispersities remained under 1.5.

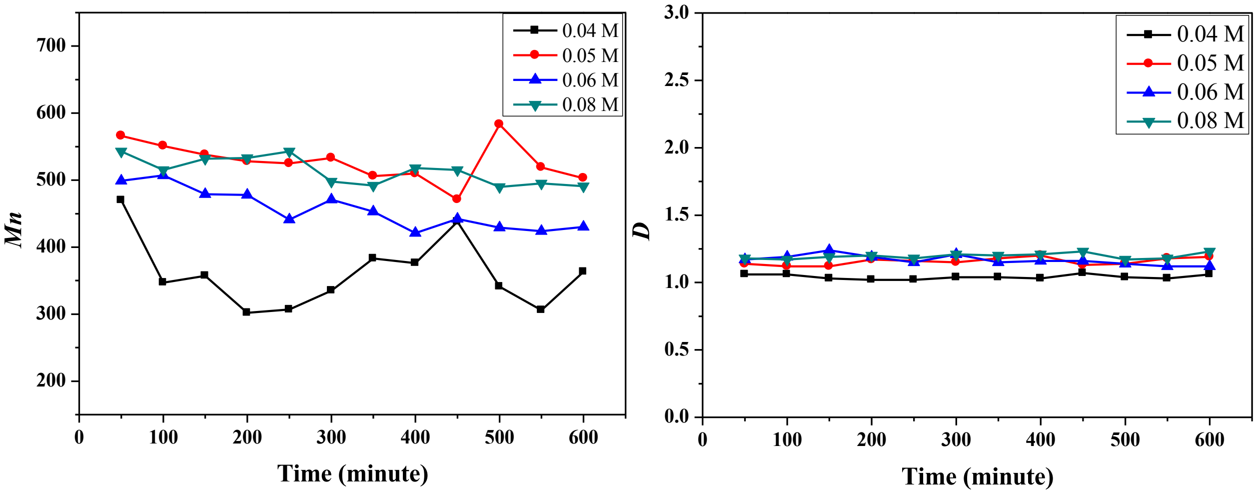


Figure 3.24: Molecular weight data (left) and dispersities (right) for polymerisation of *i*BVE (2 mol dm^{-3}) in the presence of **SEE 1** initiated by *i*BVE:HCl:$TiCl_4$ (0.02:0.04 mol dm^{-3}) at 3 ml min^{-1}.

All of the monomer conversions and the average ester group functionalities of these polymerisations are shown in Figure 3.25. All the monomer conversions were consumed during the polymerisation. The scale average chain end functionalities of all different concentrations ranged from 30 % to 50 %, which was very low when compared with the results of the polymerisations with $SnCl_4$ as Lewis acid test.

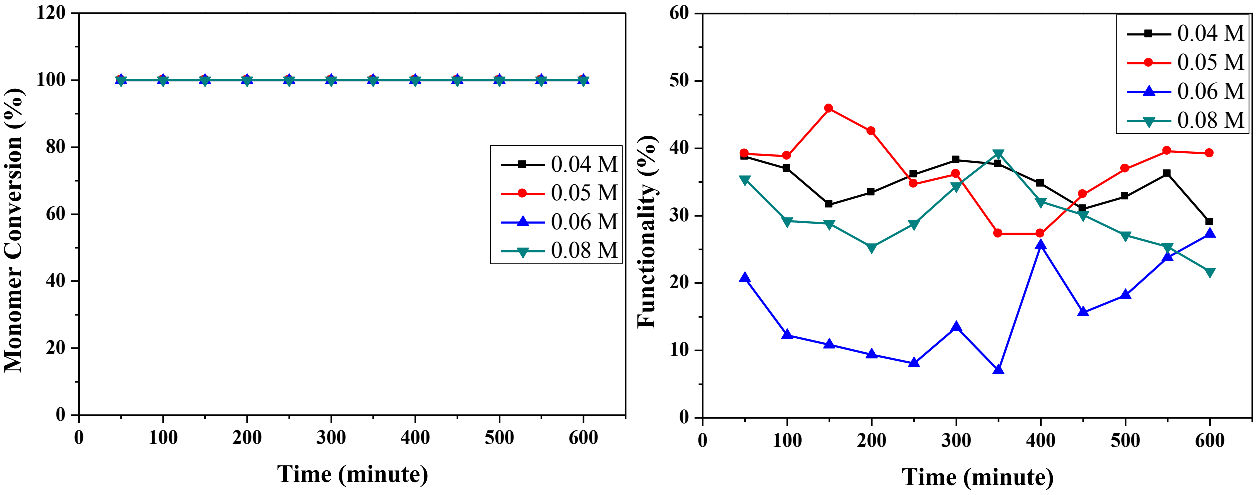


Figure 3.25: The monomer conversion (left) and the average chain end functionality (right) at 3 ml min^{-1} in 0.04, 0.05, 0.06 and 0.08 M concentrations of **SEE 1** observed by ^{1}H NMR and MALDI-TOF spectra.

MALDI-TOF analysis of the oligomers

MALDI-TOF mass spectres of oligo(*iso*butyl vinyl ethers) are shown in Figure 3.26. They were produced using in four different concentrations of 0.04, 0.05, 0.06 and 0.08 M of **SEE 1**. These samples were produced at a 3 ml min^{-1} flow time and used $TiCl_4$ as a Lewis acid.

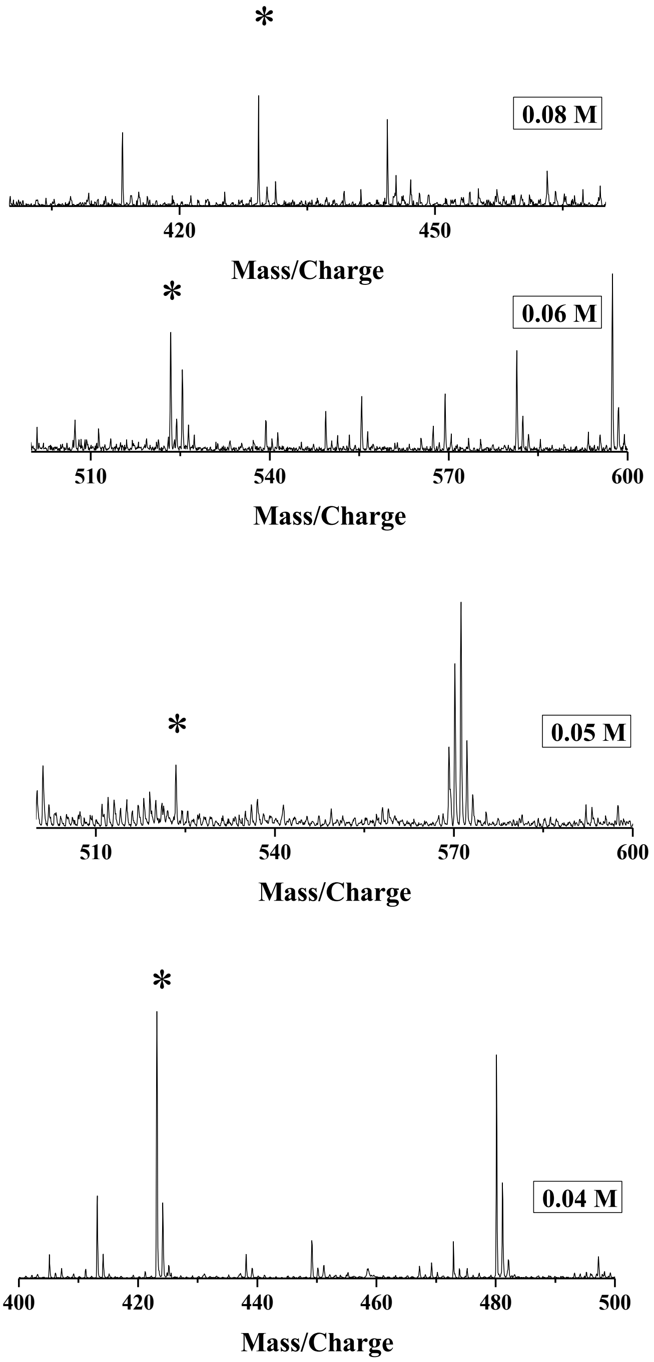


Figure 3.26: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.04, 0.05, 0.06 and 0.08 M respectively) at 3 ml min^{-1} obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent. (*) refers to ester group.

The molecular weight distribution became much narrower once the reaction time.. (Figure 3.27).

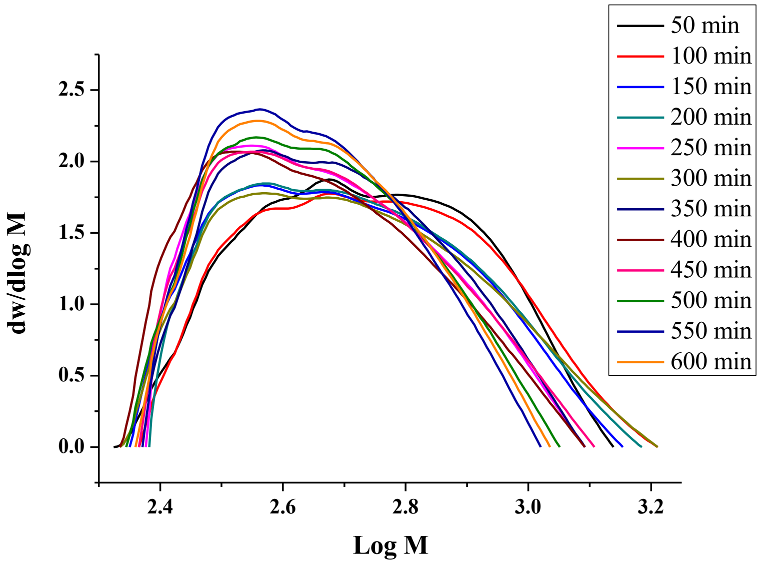


Figure 3.27: SEC of oligo*i*sobutyl vinyl ethers prepared from 0.06 M at 3 ml min^{-1}.

3.3.2.3 Polymerisation of iBVE at 2 ml min^{-1}

The polymerisation of *i*BVE was carried out in the presence of 0.06 and 0.08 M concentration of **SEE 1,** at 2 ml min^{-1} using $TiCl_4$ as a Lewis acid. Figure 3.28, shows the molecular weights were invariant over time with both **SEE 1** concentrations (0.06 and 0.08 M). In addition, the two different polymerisations provided narrow molecular weight distributions (remained below 1.5) and the distributions became narrower during the reaction time.

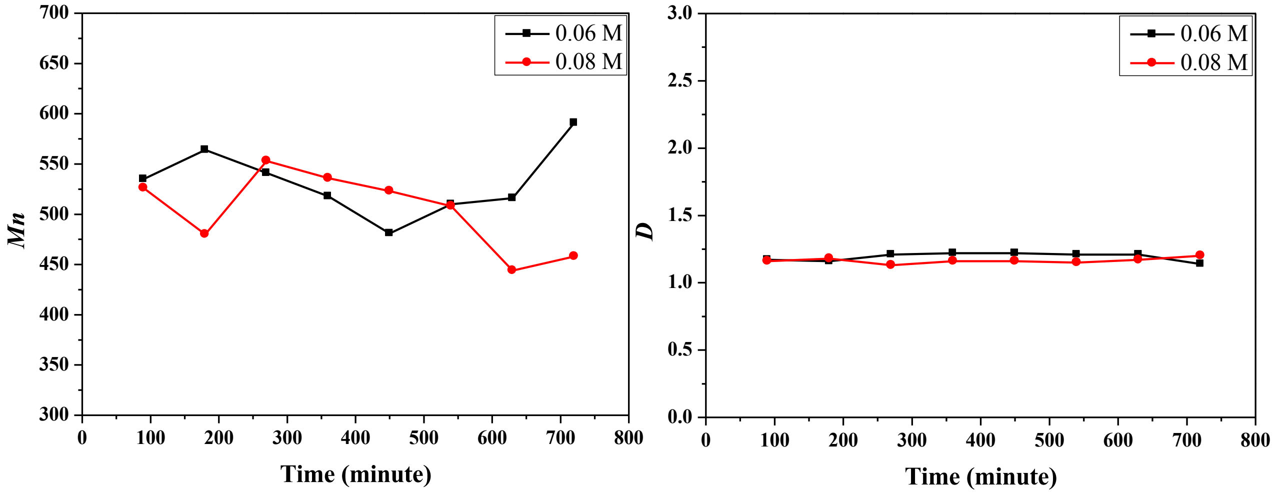


Figure 3.28: Molar mass data (left) and dispersities (right) for polymerisation of *i*BVE (2 mol dm^{-3}) in the presence of **SEE 1** initiated by *i*BVE:HCl:TiCl$_4$ (0.02:0.04 mol dm^{-3}) at 2 ml min^{-1}.

Figure 3.29 presents the monomer conversion and the average ester functionality. The data shows that all of the monomer was consumed. The degrees of chain end functionality at 2 ml min^{-1} using TiCl$_4$ with 0.06 and 0.08 M of **SEE 1** is shown in the same figure. It is clear that when the concentration of **SEE 1** was increased, the average end functionality also increased directly.

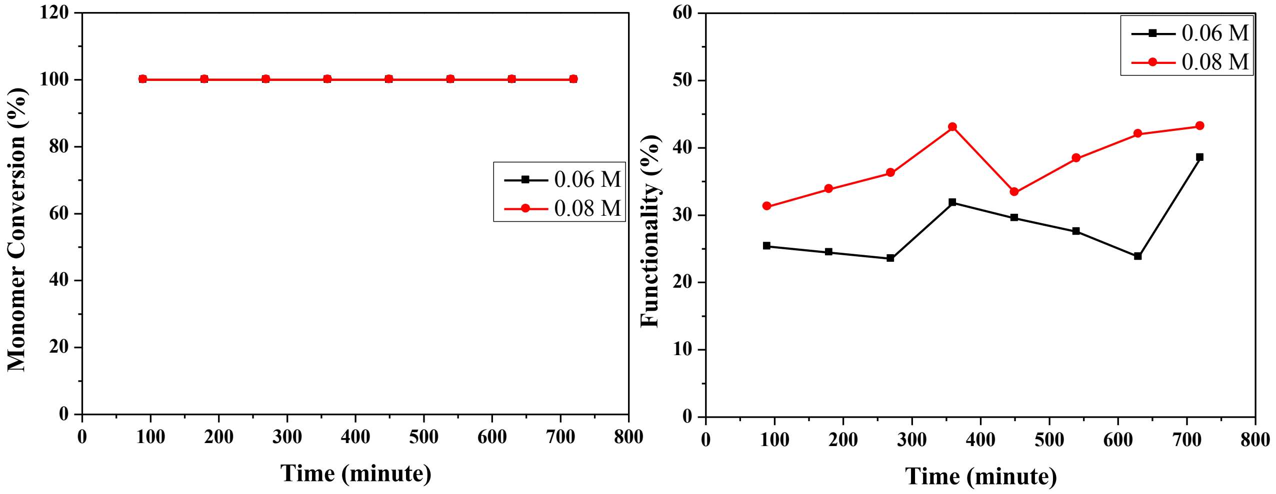


Figure 3.29: The monomer conversion (left) and the average chain end functionality (right) at 2 ml min^{-1} in 0.06 and 0.08 M concentrations of **SEE 1** observed by ^{1}H NMR and MALDI-TOF spectra.

MALDI-TOF analysis of the oligomers

MALDI-TOF mass spectres of oligo(*iso*butyl vinyl ethers) are shown in Figure 3.30. They were analysed under four different conditions, with 0.06 and 0.08 M of **SEE 1**. These samples were produced at 2 ml min^{-1} flow time, and used $TiCl_4$ as a Lewis acid.

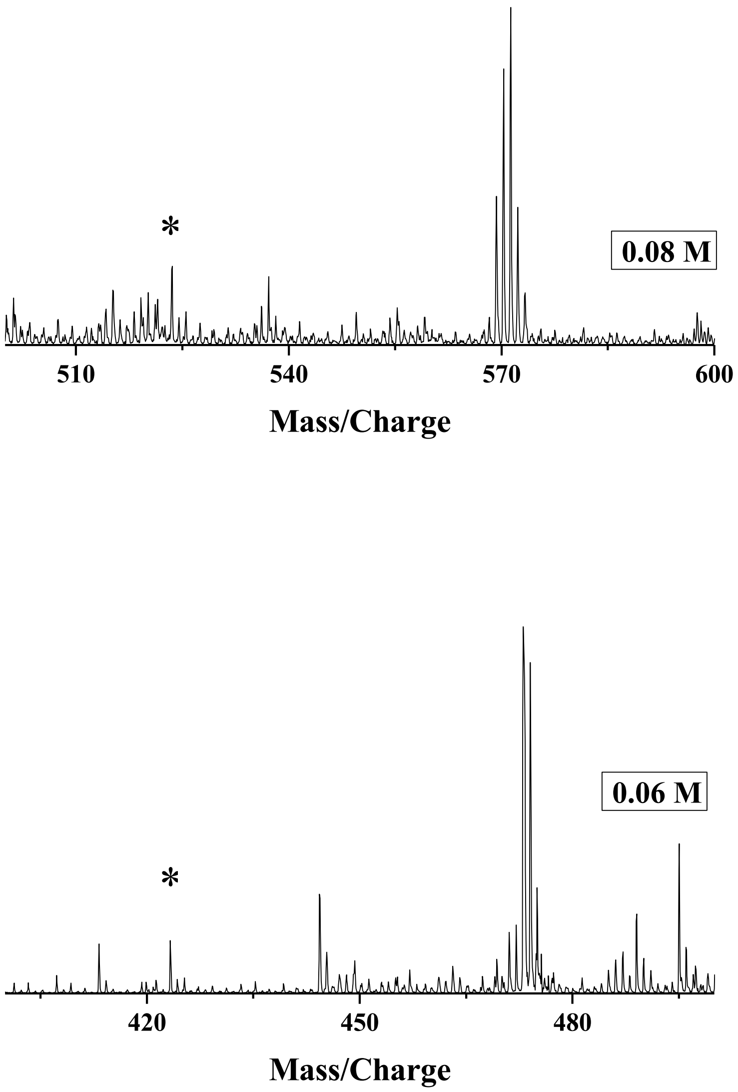


Figure 3.30: MALDI-TOF-MS spectrum with the determined chain end groups for O*i*BVE (0.06 and 0.08 M respectively) at 2 ml min^{-1} obtained by dried droplet method using Dithranol as a matrix, sodium iodide as salt and THF as the carrier solvent. (*) refers to ester group.

Figure 3.31 shows that all oligo*i*sobutyl vinyl ethers have approximately the same molecular weight distribution, even as the reaction time frame increased. The reaction conditions at this situation show increased concentration of **SEE 1** using $TiCl_4$ at 2 ml min^{-1} did not frequently develop modifications of the polymers and their molecular weight.

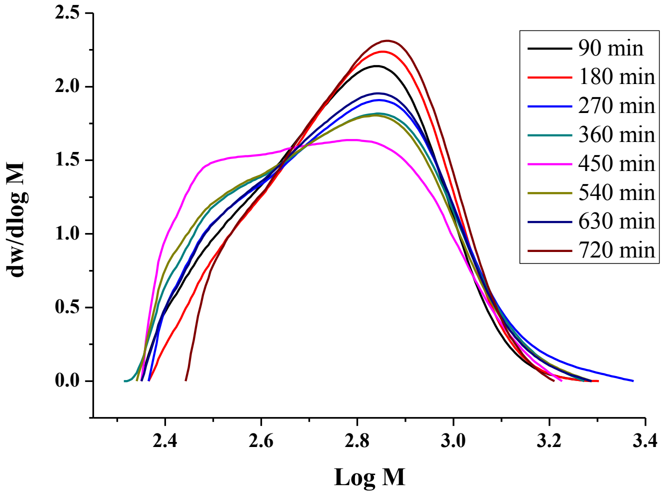


Figure 3.31: SEC of poly*i*sobutyl vinyl ethers prepared from 0.06 M at 2 ml min^{-1}.

3.4 Conclusions

Oligo*i*sobutyl vinyl ethers have been successfully prepared with ester end groups using non-living cationic polymerisations. This required using nucleophilic species such as silyl ketene actals, which react with carbocations with similar rates to vinyl ethers. Rapid reaction of the primary adduct produced the ester end groups. Careful choice of monomer concentration, the reaction temperature, Lewis acids and concentration of **SEE 1** were also required to obtain high degrees of chain end functionality. It has also been demonstrated that polymerisations can be run using continuous processes. The key advantage of this approach is the possibility to produce large amounts of polymer in a short space of time. Therefore, continuous processes can be used in many common industry applications. The production of oligomers with high degrees of ester end group functionality were obtained by decreasing the flow time and increasing the concentration of silyl ketene acetal. Importantly, polymerisations that have been carried out by using $SnCl_4$ (compared to $TiCl_4$) as Lewis acid produced oligomers with higher fractions of oligomers with chain ends with ester groups, especially when high concentration of **SEE 1** at slower flow time was applied. As indicated in Chapter 2, the polymerisation of *i*BVE using $SnCl_4$ showed better control at high temperature than $TiCl_4$.

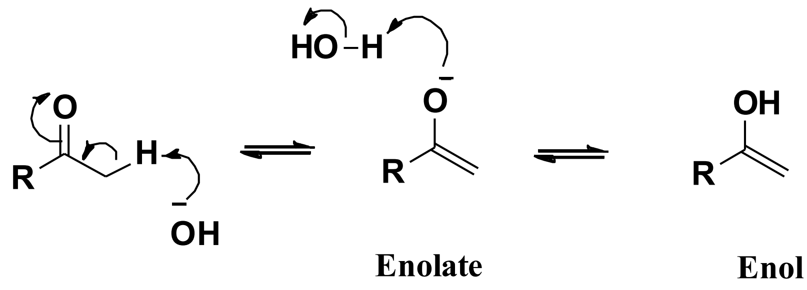
MALDI-TOF mass spectrometry was used to obtain the reaction conditions where the dominant termination reaction was alkylation of the silyl ketene acetal.

Chapter 4

4. Synthesis of difunctional chain end capping agent

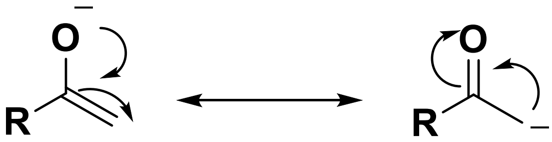
4.1 Introduction

Silyl enol ethers are equivalents of enols. They are intermediate in reactivity between enolates and enols but are stable enough to be produced in good yield from a carbonyl compound. They are particularly used to make and isolate a masked enolate ion. Enolates can be prepared during the base-catalysed enolisation of ketones or aldehydes occurring as an intermediate when α-hydrogen of the carbonyl is abstracted, Scheme 4.1.



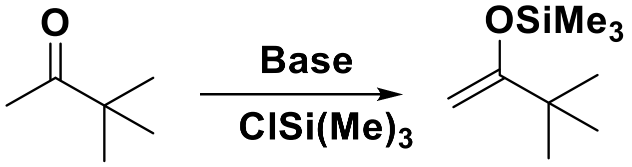
Scheme 4.1: Base catalysed enolisation of carbonyl.

As illustrated in Scheme 4.2, because of the resonance effects responsible for stabilising the resulting enolate ion, the α-hydrogen is more acidic than the analogous alkene protons. Therefore, the enolate is stabilised by resonance.



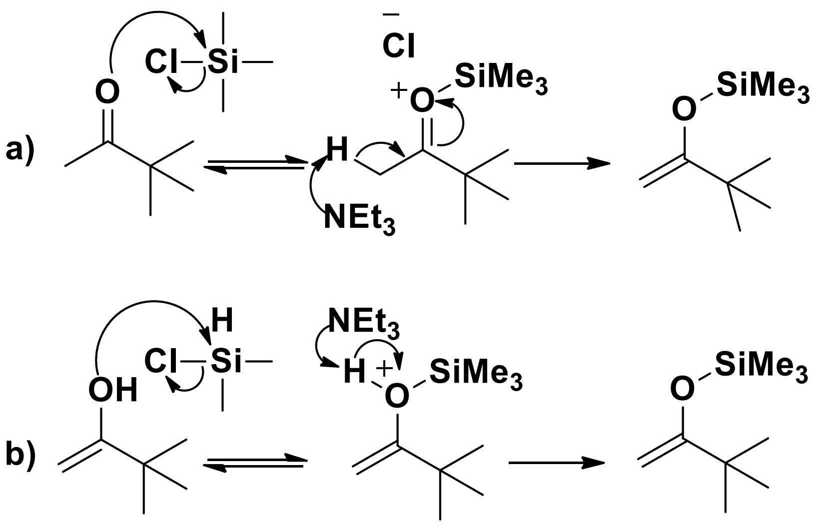
Scheme 4.2: The resonance of enolate ion.

The two non-equivalent forms, vinylic alkoxide and α-keto carbanion respectively, react with electrophiles at either the oxygen atom or the carbon. Therefore, enolate ions are known as ambident nucleophiles. These usually react with the oxygen atom, which is characterised by greater stability and electronegativity. However, the silyl enol ethers are generated by the trapping of the vinylic alkoxide with an electrophilic species. The quenching of an enolate ion with a silicon electrophile is generally used to prepare silyl enol ethers. The trimethylsilyl (TMS) group is the simplest one, as shown in Scheme 4.3. In addition, there are several often commonly used groups, such as tertiary-butyldimethylsilyl (TBDMS) and tertiary-butyldiphenylsilyl (TBDPS). The advantage of these alkyl-substituted silyl enol ethers is that they are often more stable to hydrolysis.



Scheme 4.3: The simplest reaction is using to produce silyl enol ether.

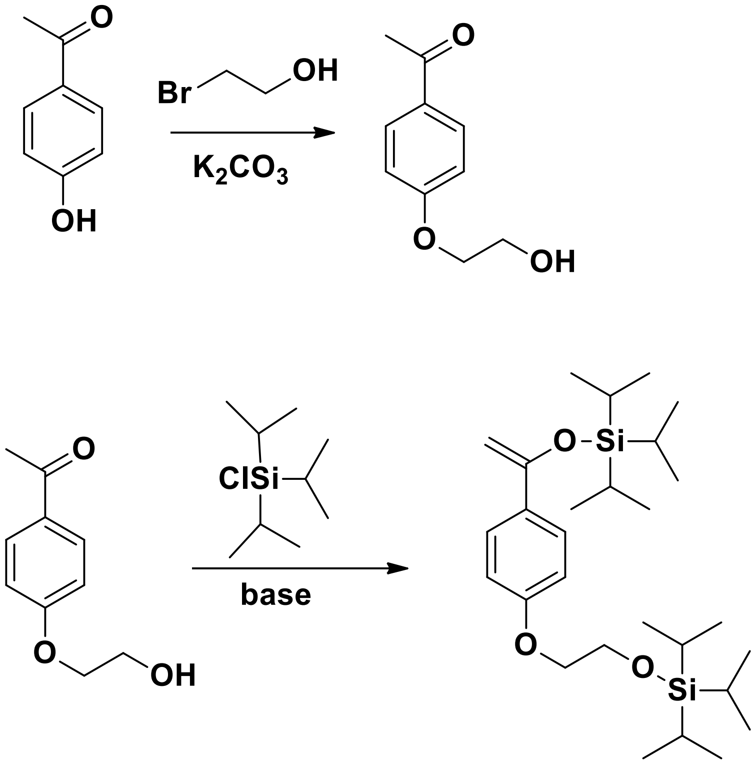
A strong Si-O bond is formed and only weak bases are needed in their synthesis. The silyloxy group has a bond energy of 368 KJ mol^{-1}.[125] Therefore, silicon elecrophiles are able to react with carbonyl oxygen even in the absence of a base to prepare enolate ion. There are two equally effective mechanisms through which this procedure can be undertaken.



Scheme 4.4: Routes to formation silyl enol ether mediated by a weak base.

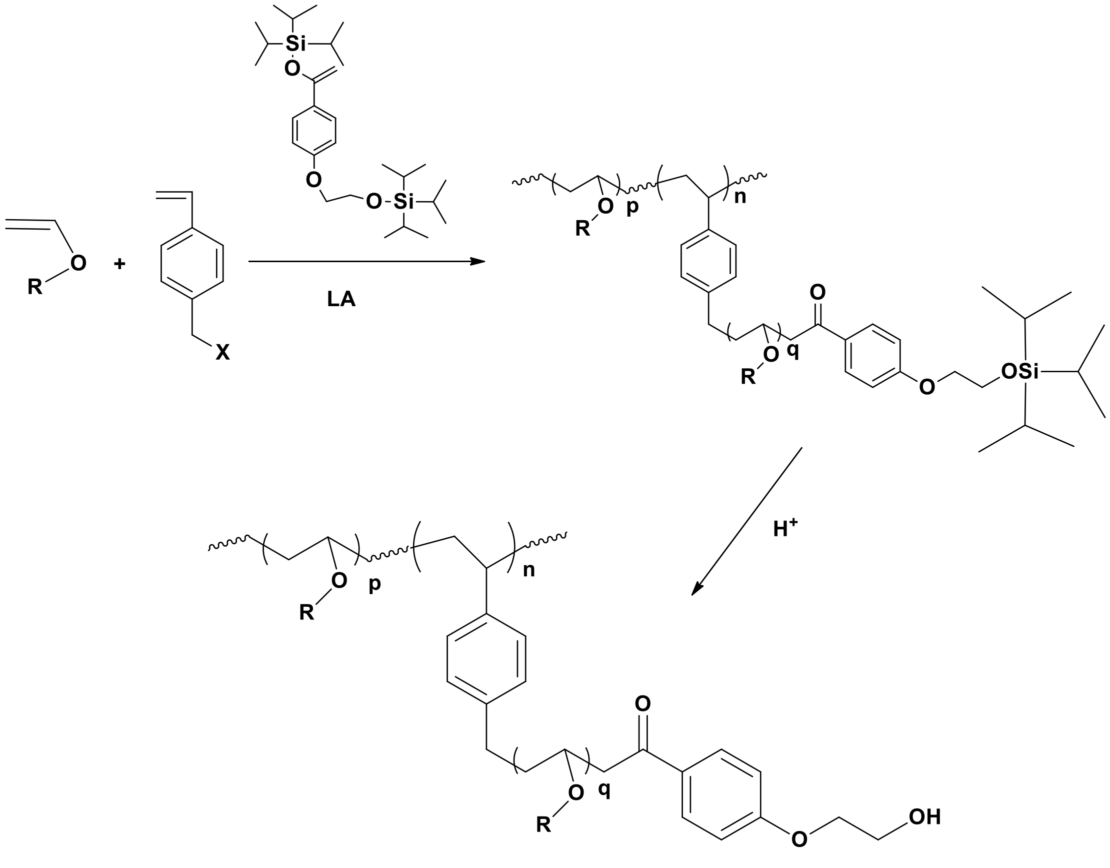
Scheme 4.4 shows the two possible ways in which silyl enol ethers can be produced. Mechanism **a** involves formation proceeding by attack of oxygen onto the silicon of the carbonyl group first and then subsequent removal of a proton by base to provide the silyl enol ether. Mechanism **b** entails formation via addition of the silicon electrophile onto an enol and then removal of a proton. However, it should be used stronger bases, as NaH, to give first enolate that then reacts at O^- with Si-Cl.

In this chapter, the synthesis of a difunctional silyl enol ether was attempted using several routes. Firstly, 1-(4-hydroxy phenyl) ethanone was reacted with 2-bromoethanol to give 4'-(2-hydroxyethoxy) acetophenone. Then, attempts to react this to form a silyl enol ether (eq. 2.1) were undertaken. Scheme 4.5 provides a summary of the synthesis of the difunctional silyl enol ether. If difunctional SEE is prepared well, it can be used in the preparation of functional polymers.



Scheme 4.5: The summary of synthesis difunctional SEE.

By incorporating a difunctional SEE into polymerisations, branched polymers with siloxy chain end group functionality could be created. If these polymerisations are carried out by using branching monomers, then it is possible to prepare highly branched polymers with chain-end functionality, as shown in Scheme 4.6.



Scheme 4.6: Synthesis of highly branched functional polymers using the new route.

4.2 Experimental

4.2.1 Materials

Acetone and potassium carbonate (AR grade) Aldrich products were used as received. 1-(4-hydroxy phenyl) ethanone, 99% Aldrich product, used as received. Chlorotrimethylsilane (98 %), triisopropylsilyl chloride (97 %) and trimethylsilyl trifluoromethanesulfonate (99%) Aldrich products were used as received. Triethyl amine, 99.5% Aldrich product was used as received. Lithium diisopropylamine, 97 % Aldrich product was used as received. Sodium hydride (60 % dispersion in mineral oil) was used as received.

4.2.2 Preparation of 4'-(2-hydroxyethoxy) acetophenone

1-(4-hydroxy phenyl) ethanone (5 g) was added to 2-bromoethanol (4.5860 g) in the present of potassium carbonate (7.75 g) and dimethyl sulfoxide (DMSO, 22.5 ml) as a solvent. The reaction mixture was stirred for 18 h and heated at 100 °C. After that, the reaction mixture was poured into 200 ml of water and extracted by using 200 ml of chloroform. The organic layers were combined to give a brown solution, which was dried with sodium sulfate to removed water. Then, the solvent was removed by evaporation the solution. Silica gel chromatography using hexane/ethyl acetate (1:1) mixture to give pure product as white solid, the yield was poor yield (28.6 %). ^{1}H NMR (400MHz, $CDCl_3$) δ_H / ppm: 2.6 (s,3H), 4.20 (s,2H), 4.35 (t, 2H), 7.15 (d,2H), 8.13 (d,2H). 4.2.3

Preparation of difunctional silyl enol ethers using chlorotrimethylsilane

Preparation at 50% solid concentration:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), lithium diisopropylamide (LDA; 0.6241 g), chlorotrimethylsilane (0.6330 g) and dichloromethane (50%; 1.7571 g) as a solvent were added to a 50 ml round bottom flask containing a magnetic stirrer at 0 °C for 1 hour.

Preparation at 10% solid concentration:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), lithium diisopropylamide (LDA; 0.6241 g), chlorotrimethylsilane (0.6330 g) and dichloromethane (90%; 15.8139 g) as a solvent were added to a 50 ml round bottom flask containing a magnetic stirrer bar at 0 °C for 1 hour.

4.2.4 Preparation of difunctional silyl enol ethers using triisopropylsilyl chloride

Preparation at 50% solid concentration:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), lithium diisopropylamide (LDA; 0.6241 g), Triisopropylsilyl chloride (1.1233 g) and dichloromethane (50 %; 2.2474 g) as a solvent were added to a 50 ml round bottom flask containing a magnetic stirrer at 0 °C for 1 hour.

Preparation at 10% solid concentration:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), lithium diisopropylamide (LDA; 0.6241 g), Triisopropylsilyl chloride (1.1233 g) and dichloromethane (90%; 20.2266 g) as a solvent were added to a 50 ml round bottom flask containing a magnetic stirrer at 0°C for 1 hour.

Preparation at 50% solid concentration using DCM as a solvent:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), lithium diisopropylamide (LDA; 0.8916 g), triisopropylsilyl chloride (1.1233 g) and dichloromethane (50%; 2.2474 g) were added in a 50 ml round bottom flask containing a magnetic stirrer at 0°C for 2 hours.

Preparation at 50% solid concentration using THF as a solvent:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), Lithium diisopropylamide (LDA; 0.8916 g), triisopropylsilyl chloride (1.1233 g) and tetrahydrofuran (50%; 2.2474 g) were added in a 50 ml round bottom flask containing a magnetic stirrer at 0°C for 2 hours.

Preparation at 50% solid concentration using DCM with increase both equivalent and time:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), lithium diisopropylamide (6 eq.;1.7832 g), triisopropylsilyl chloride (1.1233 g) and dichloromethane (50%; 2.2474 g) were added in a 50 ml round bottom flask containing a magnetic stirrer at 0°C for 4 hours.

Preparation at 50% solid concentration:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), lithium diisopropylamide (LDA; 0.6241 g), triisopropylsilyl chloride (1.1233 g) and dichloromethane (50%; 2.2474 g) as a solvent were added in a 50 ml round bottom flask containing a magnetic stirrer at -78 °C using a batch of dry ice with acetone. The reaction was carried out for one hour.

Preparation at 50 % solid concentration using triethylamine as a base:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), dry triethylamine (TEA; 2.1 eq.), and dichloromethane (50 %) were added in a 50 ml dried round bottom flask containing a magnetic stirrer then was cooled to0 °C with ice bath. Triisopropylsilyl chloride (2.1 eq.) was added via a 5 ml dropwise. The solution was allowed to warm to room temperature for 3 hours.

Preparation at 50% solid concentration using sodium hydride as a base:

4'-(2-hydroxyethoxy) acetophenone (0.5 g), sodium hydride in 60% dispersion oil (NaH; 0.3495 g), triisopropylsilyl chloride (1.1233 g) and dichloromethane (50%; 2.2474 g) as a solvent were added in a 50 ml round bottom flask containing a magnetic stirrer at 0°C for 1 hour.

4.2.5 Preparation of difunctional of silyl enol ethers using trimethylsilyltrifluoromethanesulfonate

- 4'-(2-hydroxyethoxy) acetophenone (0.5 g), Lithium diisopropylamide (LDA; 6 eq.), trimethylsilyltrifluoromethanesulfonate (2.1 eq.) and dichloromethane (50 %) as a solvent were added to a 50 ml round bottom flask containing a magnetic stirrer at 0 °C for 1 hour.
- 4'-(2-hydroxyethoxy) acetophenone (0.5 g), Lithium diisopropylamide (LDA; 6 eq.), trimethylsilyltrifluoromethanesulfonate (3 eq.) and dichloromethane (50 %) as a solvent were added to a 50 ml round bottom flask containing a magnetic stirrer at 0 °C for 1 hour.

4.3 Organic characterisation

4.3.1 Elemental analysis

The determination of the carbon and hydrogen content of a given sample of silyl enol ether was obtained using the Perkin-Elmer 2400 CHN Elemental analyser. About 2-4 mg of the sample was sealed in a tin capsule. This was in turn introduced into the analyser where it was combusted completely in the presence of excess oxygen and combustion reagent to form carbon dioxide and water. The gas mixture was carried in a flow of helium through a reducing agent. The gases were then separated before the level of each was determined using a thermal conductivity detector system. The percentage weight of each element was calculated automatically by a microprocessor contained in the analyser.

4.3.2 Mass spectrometry analysis

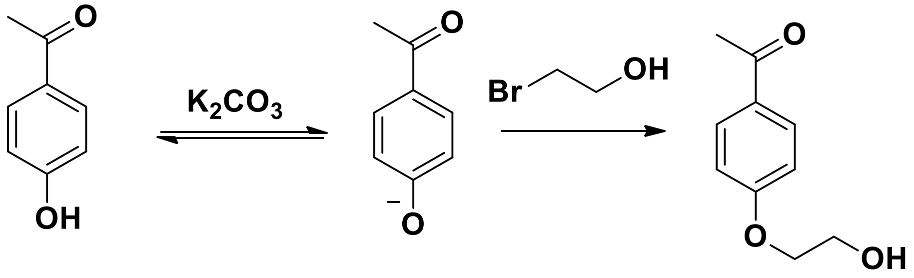
Mass spectrometry, Electron Ionisation (EI) MS was employed using a VG Autospec.

^{1}H NMR analysis was essentially the same as those described in chapter 2.

4.4 Results and discussion

4.4.1 Synthesis of 4'-(2-hydroxyethoxy) acetophenone

4'-(2-hydroxyethoxy) acetophenone has been successfully prepared on the basis of the reaction of 1-(4-hydroxy phenyl) ethanone with 2-bromoethanol in the presence of potassium carbonate and dimethyl sulfoxide as a solvent at 100 °C. The general mechanism of this reaction is explained in Scheme 4.7.



Scheme 4.7: Synthesis of 4'-(2-hydroxyethoxy) acetophenone.

Figure 4.1 depicts an expanded ^{1}H NMR spectrum of 4'-(2-hydroxyethoxy) acetophenone. The resonance at 2.6 ppm is due to a tertiary proton that is attached to the carbonyl group. The other resonances from 4 to 4.2 ppm are due to CH_2, which is next to the oxygen group. Moreover, two different resonances of CH groups were observed between 7 to 8 ppm in positions **b** and **c**, which are due to the aromatic protons.

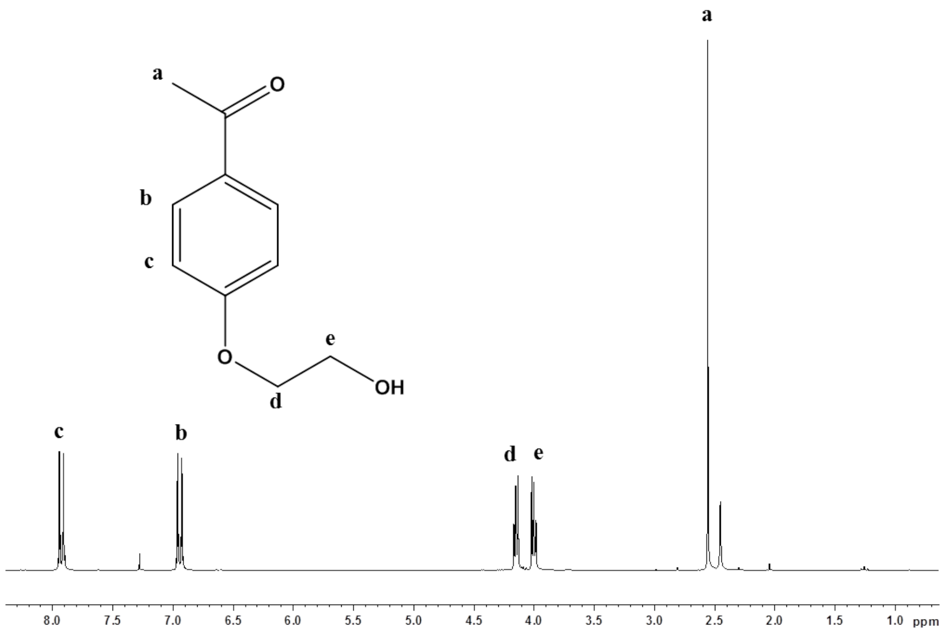


Figure 4.1:^{1}H NMR spectrum of 4'-(2-hydroxyethoxy) acetophenone.

4.4.2 Synthesis of difunctional silyl enol ether

4.4.2.1 Synthesis by using Chlorotrimethylsilane

Synthesis of difunctional silyl enol ether was attempted by reacting chlorotrimethylsilane in the presence of lithium diisopropylamine (LDA) as a base. Unfortunately, this reaction did not work even when the experiments were repeated many times with different solid concentrations (50 and 10%, respectively). The instability of the chlorotrimethylsilane structure is the likely motive for the failure of these reactions. For this reason, other more stable structures, such as triisopropylsilyl chloride and trimethylsilyl trifluoromethanesulfonate, were used in further experiments.

4.4.2.2 Synthesis by using triisopropylsilyl chloride

Several experiments have been carried out in this part. Two distinct mass spectra of silyl enol ether were obtained using either DCM or THF solvents (THF on the left and DCM on the right), in order to conduct a comparison of these two solvents. The spectra are shown in Figure 4.2. The values obtained confirmed the expected molecular ions m/z 181 and 337. The mass spectrum of 181 refers to the unreacted starting materials, 4'-(2-hydroxyethoxy) acetophenone. Thus, the other ion at m/z 337 signifies the product with the silyl group attached to only one side. This can be seen clearly in the previous figure. However, compared to THF, DCM provided a higher product yield.

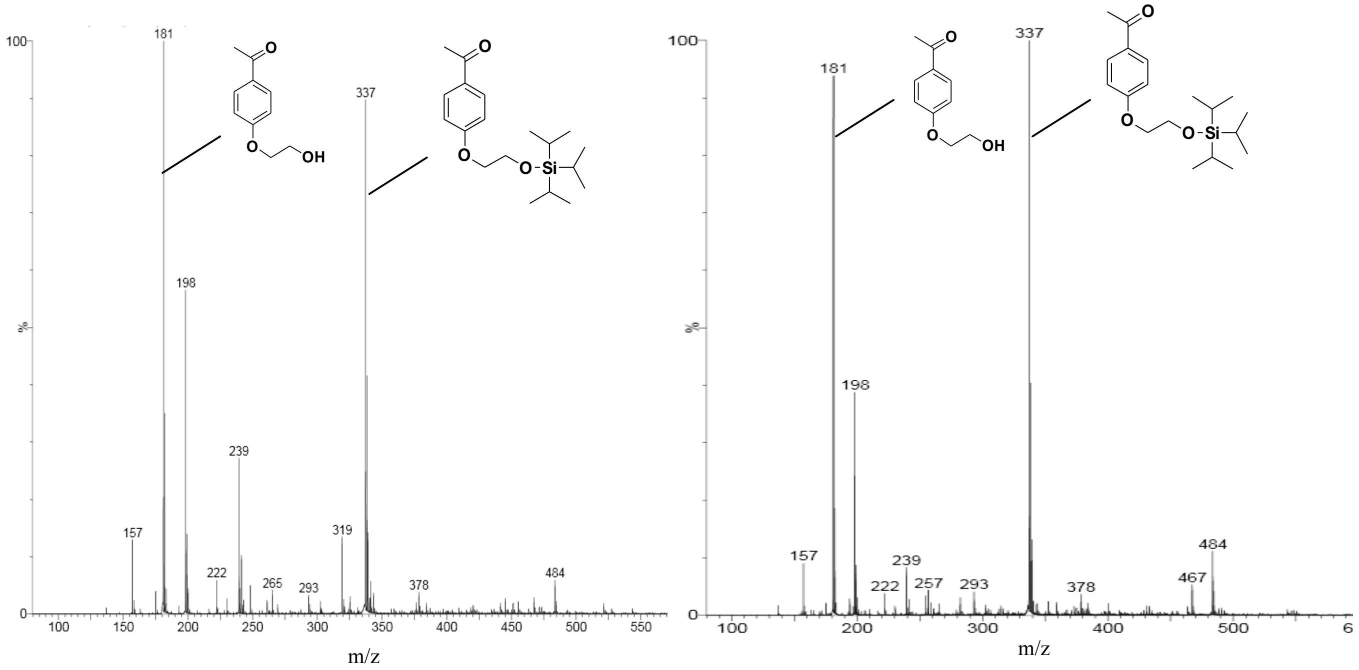


Figure 4.2: Mass spectrum of synthesis disilylenol ether in THF (left) and DCM (right).

Furthermore, a very strong base, NaH 2.1 eq., was used in order to attempt to prepare the target difunctional silyl compound. The ^{1}H NMR analysis demonstrated that the silyl group was attached to the starting material only at the ethoxy position, as shown in Figure 4.3.

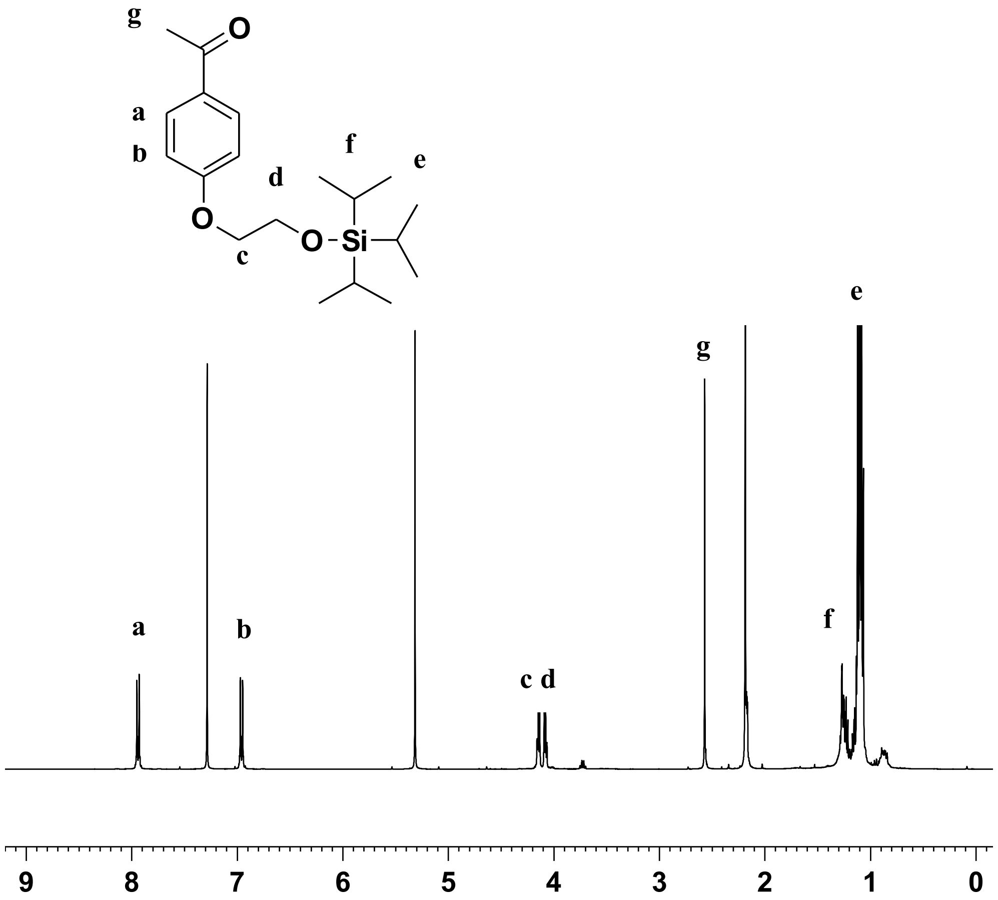


Figure 4.3:^{1}H NMR spectrum of synthesis difunctional SEE used NaH as a base.

4.4.2.3 Synthesis by using trimethylsilyltrifluoromethanesulfonate

In this case, a high equivalent of lithium diisopropylamide (6 eq.) was used with trimethylsilyltrifluoromethanesulfonate (2.1 and 3 eq.). Mass spectral analysis showed that this reaction mixture contained the largest yield of silylated material with lower amounts of starting materials than obtained in previous experiments. However, the starting compound still was only reacted at one side (at the ethoxy position), even though many equivalents of silyl chloride were used (Figure 4.4).

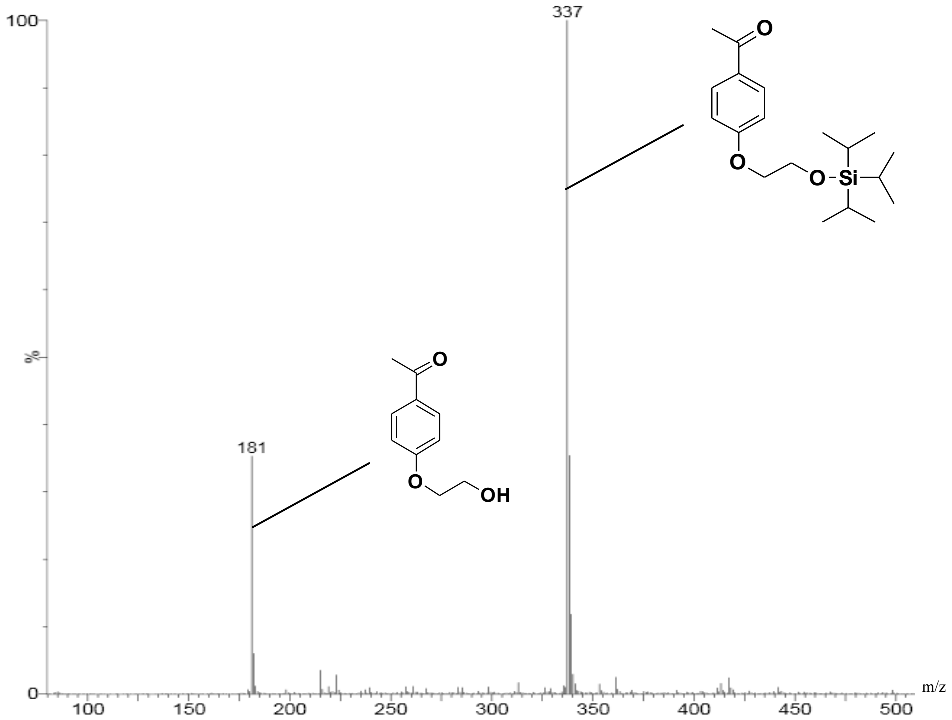


Figure 4.4: Mass spectrum of synthesis diSEE used LDA as a base.

Table 4.1 shows all experiments that were used in attempts to prepare the difunctional silyl enol ether using a range of different conditions.

	Base	Eq. of base	Temp. ©	Time (hour)	Solid conc.(%)	Solvent
TMSCl (2.1 eq.)	LDA	2.1	0	1	50	DCM
					10	
TIPSCl (2.1 eq.)	LDA	2.1	0	1	50	DCM
					10	
		3		2	50	
						THF
		6		4		DCM
		2.1	-78	1		
	TEA		0	3		
	NaH			1		
TMSOTf (2.1 eq.)	LDA	6				
TMSOTf (3 eq.)						

Table 4.1: The summary of all experiments that done to produce difunctional of silylenol ether in this chapter. TMSCl = chlorotrimethylsilane, TIPSCl = triisopropylsilyl chloride, TMSOTf = trimethylsilyltrifluoromethanesulfonate, LDA = lithium diisopropylamine, TEA = teriethylamine.

4.5 Conclusions

4'-(2-hydroxyethoxy) acetophenone has been successfully produced. However, the target difunctional silyl enol ether could not be prepared when using different silyl compounds. Triisopropylsilyl chloride was applied with different bases and solvents. The reactions produced a product silyated only at the ethoxy position in low yield. In addition, mass spectroscopy revealed that DCM gave a higher yield of the mono silyated compound by comparison with THF. Trimethylsilyltrifluoromethanesulfonate produced the highest product yield in the context of mass spectral analysis and this was the best compound. However, it was not possible to produce the target compound.

Chapter 5

5. Synthesis of highly branched functional polymers using a new route

5.1 Introduction

A silyl enol ether was used in this study as a means of ceasing the propagation of linear polymer chains, and therefore producing a functional ended polymer. This form of polymerisation offers a number of advantages, including: the ease of achieving the desired outcome; the simple nature of the purification; a product which is both highly functional and appropriate for various monomers and silyl enol ethers. The production of branched polymers which have high chain end functionality is currently a subject of particular interest as such polymers have very interesting properties. Most notably they possess: low solution and melt viscosities; superior solubility; considerable numbers of functional end groups. These properties make the utilisation of such polymers particularly useful, with a vast number of original and new uses presenting themselves, especially in terms of bio-applications.

Sherrington et al introduced the idea that adding transfer agents to limit chain growth can provide soluble highly branched polymers and that the gelation process can be limited. A number of theories can describe the gelation of chain growth polymers containing multi-functional polymers.[126] In general terms, one can consider that gelation occurs at critical points in the time-conversion plots. In the Carrothers approach this critical point is considered to be when the number of branches exceeds the number of chains. On the other hand, the Flory-Stockmayer approach considers the probability that segments are attached to crosslinks at both ends. In both approaches the limiting of chain growth can prevent the system from attaining the critical structural features that allow for gelation. In this project chain growth will be limited by adding a silyl enol ether, as demonstrated in the previous works,[63,75] This approach will be used in this chapter for the purposes of terminating polymer chain growth and producing branched polymers with end groups, at least in part, derived from the termination reaction.

The system relies on high rates of alkylation but the rates cannot be too high so that propagation is quenched.

Although the use of the agents that limit chain growth has been well-practised, it seems surprising that very few of the effects of such agents on systems with continuous monomer feeds had been studied. The results of this chapter will be compiled and analysed in order to properly optimise the process of preparing branched polymers from cationic polymerisations incorporating multi-functional monomers (under monomer-feeding conditions). The results allow for some reaction conditions to be discounted, but further study is required in order to produce a fully optimised system. Figure 5.1 illustrates the production of highly branched polymers by means of *ab initio* cationic polymerisation, making use of both **SEE 1** and Lewis acid.

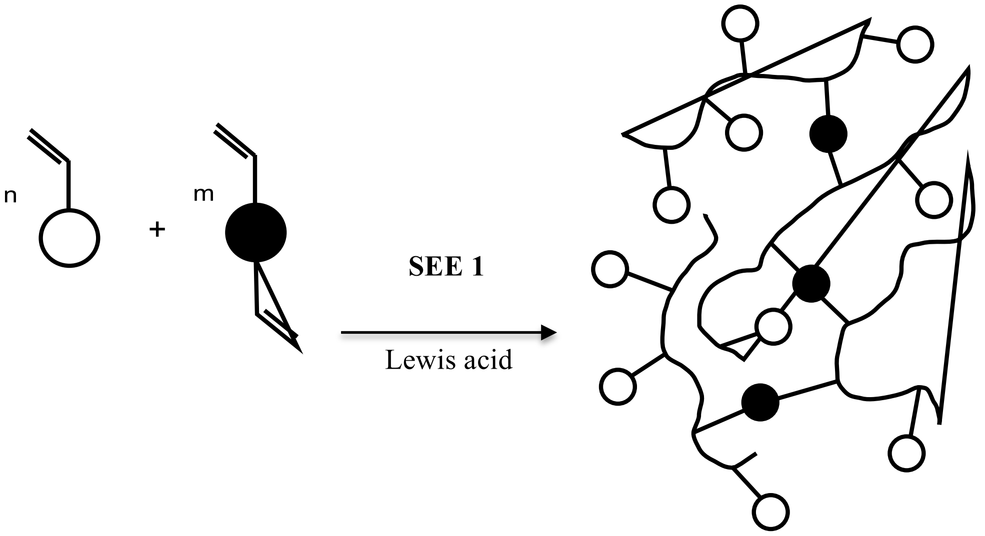


Figure 5.1: Synthesis of highly branched polymer using divinyl monomers. Redrawn from.[127]

5.2 Experimental

5.2.1 Materials

*i*BVE, (99 % Aldrich). *i*BVE was washed with 10% aqueous NaOH solution and then with water three times to be free from inhibitor, dried overnight with anhydrous sodium sulphate and distilled before use. N-hexane, (99% Aldrich) was refluxed over calcium hydride for two hours and distilled over molecular sieve. Di(ethylene glycol) divinyl ether (99 %, Aldrich) was used as received. Divinylbenzene, (80 % Aldrich) was used as received. Tin tetrachloride ($SnCl_4$) and titanium tetrachloride ($TiCl_4$), 1.0 M solution in DCM, Aldrich products were used as received. Zinc iodide (ZnI_2), > 98 % was used from Aldrich and dissolved in acetone before used. Hydriodic acid (HI) (puriss $\geq$ 67 %, Aldrich) was used as received. Ytterbium trifluoromethanesulfonate [$Yb(OTf)_3$], 99.99 % (Aldrich) was dissolved in THF before use. Scandium trifluoromethanesulfonate [$Sc(OTf)_3$], (99 %, Aldrich) was dissolved in THF before used. 1-methoxy-2-methyl-1-(trimethylsilyloxy)propene, **SEE 1**, (95 %, Aldrich) was purified by fraction distillation under reduced pressure.

5.2.2 Synthesis of highly branched functional polymers using di(ethylene glycol) divinyl ether (DEDVE) as a divinyl monomer

5.2.2.1 Synthesis of highly branched polymers using $SnCl_4$ as a Lewis acid

The syntheses of highly branched functional polymer using a continuous process were carried out using two different feeds. Feed A contains, (90 %) of *i*BVE as a first monomer, DEDVE (10 %) as a second monomer and (0.06 M) of **SEE 1** as an end-capping agent in 1 L of DCM as a solvent. Feed B involves, (0.04 M) of both HCl-*i*BVE adduct and $SnCl_4$ as an initiator and Lewis acids, respectively also in 1 L of DCM. The flow time of this reaction was set up using a peristaltic pump at 2 ml min^{-1}. The reaction vessel was cooled in cardice/methanol to -15 °C. Samples from the polymerisation were collected every 1.5 hours. Methanol was added in each sample to stop the polymerisation. Finally, the solvent was evaporated and dried over night to receive the polymer product.

5.2.2.2 Synthesis of highly branched polymers using $TiCl_4$ as a Lewis acid

The synthesis was repeated as explained above, but using 0.04 M of $TiCl_4$ as a Lewis acid.

5.2.2.3 Synthesis of highly branched polymers using ZnI_2 as a Lewis acid

Synthesised as explained previously, but 0.04 M of ZnI_2 as a Lewis acid used. The ZnI_2 was dissolved in acetone first and then the solution used in the reaction.

5.2.2.4 Synthesis of highly branched polymers using ZnI_2/HI as a Lewis acid and an initiator, respectively

Synthesised as explained before, but using the following quantities: 0.04 M of HI as an initiator and also 0.04 M of ZnI_2 solution after dissolved in acetone. These two compounds were placed together in feed B including DCM as a solvent.

5.2.2.5 Synthesis of highly branched polymers using $Yb(OTf)_3$ as a Lewis acid

Synthesised as above, but using $Yb(OTf)_3$ as a Lewis acid. It was dissolved in THF. Then, the solution used in the experiment.

5.2.2.6 Synthesis of highly branched polymers using $Sc(OTf)_3$ as a Lewis acid

Synthesised as before, but using $Sc(OTf)_3$ as a Lewis acid. The Lewis acid was dissolved in THF and then the solution used. The reaction was repeated as above but using different ratios of monomers such as: *i*BVE (80 %) with DEDVE (40 %) and also (60 %) of *i*BVE with (40 %) of DEDVE. Although, several reactions were replaced as previously but using different flow times. The flow time was 5 ml min^{-1}, the polymer was synthesised as above and also using different ratios of monomers as (90 and 80 %) of *i*BVE with (10 and 20 %) of DEDVE respectively. The flow time was 1 ml min^{-1} and the product was synthesised as above but with different ratios of *i*BVE (90 and 80 %) with DEDVE (10 and 20 %), respectively.

5.2.3 Synthesis of highly branched functional polymers using divinyl benzene (DVBz) as a divinyl monomer

5.2.3.1 Synthesis of highly branched polymers using $SnCl_4$ as a Lewis acid

Synthesised as explained above but using DVBz as a divinyl monomer.

5.2.3.2 Synthesis of highly branched polymers using $TiCl_4$ as a Lewis acid

Synthesised as explained above, but using 0.04 M of $TiCl_4$ as a Lewis acid.

5.2.3.3 Synthesis of highly branched polymers using ZnI_2 as a Lewis acid

Synthesised as explained previously but 0.04 M of ZnI_2 as a Lewis acid was used. The ZnI_2 was dissolved in acetone first and then the solution used in the reaction.

5.2.3.4 Synthesis of highly branched polymers using ZnI_2/HI as a Lewis acid and an initiator, respectively

Synthesised as explained before but using the following quantities: 0.04 M of HI as an initiator and also 0.04 M of ZnI_2 solution dissolved in acetone. These two compounds were placed together in feed B including DCM as a solvent.

The reaction was repeated using different flow time. At 5 ml min^{-1}, the synthesis was carried out as above but using 0.04 M of **SEE 1** and samples were collected every 30 minutes. At1 ml min^{-1}, the reaction was run as before but using 0.06 M concentration of **SEE 1** and samples were collected every 2 hours.

5.2.3.5 Synthesis of highly branched polymers using Yb(OTf)$_3$ as a Lewis acid

Synthesised as above, but using Yb(OTf)$_3$ as a Lewis acid. It was dissolved in THF. Then the solution was used in the experiment.

5.2.3.6 Synthesis of highly branched polymers using Sc(OTf)$_3$ as a Lewis acid

Synthesised as before, but using Sc(OTf)$_3$ as a Lewis acid. The Lewis acid was dissolved in THF and then the solution was used. The reaction was repeated as above but using different ratios of monomers such as: *i*BVE (80 %) with DVBz (40 %) and also (60 %) of *i*BVE with (40 %) of DVBz. Moreover, different flow times were applied such as 5 and 1 ml min^{-1} at (90 %) and (10 %) of *i*BVE and DVBz.

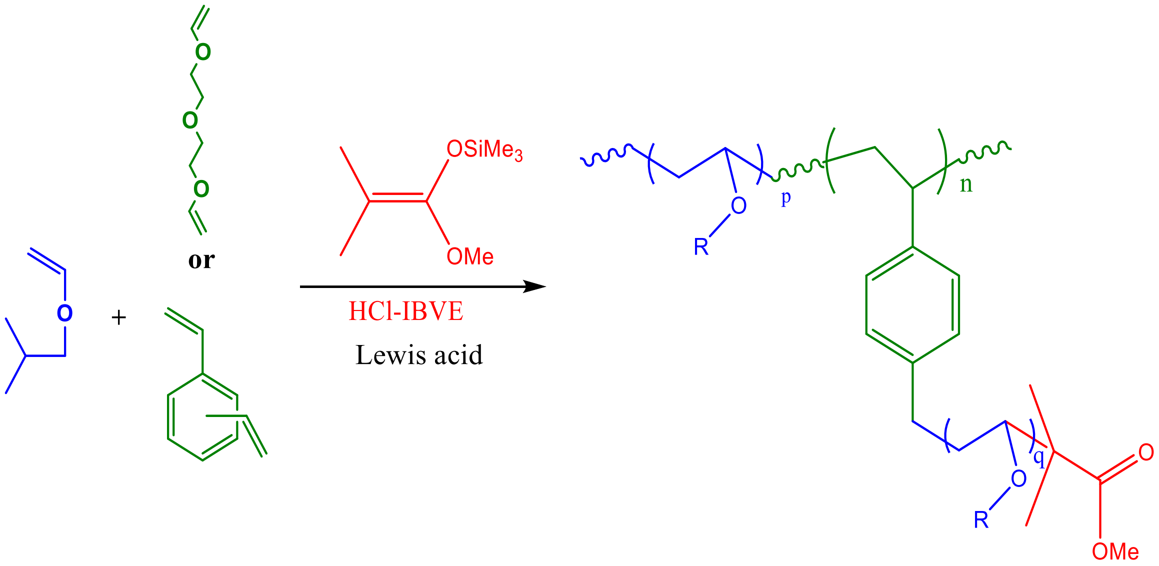
5.2.3 Polymer characterisation

SEC measurements

The number average molecular weight (M_n), weight average molecular weight (M_w) and their molecular weight distribution (M_w/M_n), also called the dispersity (*D*) of the highly branched functional polymers were estimated using size exclusion chromatography (SEC). Refractive index (RI) used to detect polymer at ambient temperature using tetrahydrofuran (THF) as the solvent and toluene as a flow marker. Polymer laboratories gel 2 x 60 cm high molecular weight column was used. Sample concentration was 2.5 mg cm^{-3}. SEC measurements were calibrated against polystyrene standards. The data were analysed using PL Cirrus SEC software. All other polymer characterisation methods were reported in Chapter 2.

5.3 Results and discussion

In this project the synthesis of highly branched functional polymers was carried out in a continuous process at -15 °C in the presence of **SEE 1** as an end-capping agent. These syntheses were applied with varying ratios of monomers, Lewis acids, flow times and concentrations of silyl enol ether. Such a technique may lead to the production of highly branched functional polymers with a high degree of ester group functionality, although these highly branched polymers may be unable to form gel. Scheme 5.1 details the general reaction occurring in the synthesis of highly branched functional polymers using DEDVE and DVBz as divinyl monomers with *i*BVE as a first monomer and including **SEE 1** and Lewis acid. A series of Lewis acids have been used in this chapter: $SnCl_4$, $TiCl_4$, ZnI_2, ZnI_2/I_2, $Yb(OTf)_3$ and $Sc(OTf)_3$.



Scheme 5.1: General synthesis of highly branched functional polymer.

5.3.1 Synthesis of highly branched functional polymers using di(ethylene glycol) divinyl ether (DEDVE) as a divinyl monomer

5.3.1.1 Synthesis of highly branched polymers using different of Lewis acids

A series of Lewis acids have been used to produce highly branched functional polymers with DEDVE as a divinyl monomer. The Lewis acids used included $SnCl_4$, $TiCl_4$, ZnI_2, ZnI_2/HI and $Yb(OTf)_3$; these acids were used in the presence and absence of **SEE 1** as an end capping agent.

When using $SnCl_4$ as a Lewis acid the polymerisation was carried out using 90 % of *i*BVE as a first monomer with 10 % of DEDVE as a second monomer, with 0.06 M of **SEE 1** used to form highly branched functional polymers at 2 ml min^{-1}. Table 5.1 provides a summary of this reaction; as the data demonstrates, highly branched polymers were not produced under the aforementioned conditions. The molecular weights of the polymers were particularly low, even when the time of reaction was increased. Moreover, the ester group functionality was not observed in the ^{1}H NMR spectra. It is therefore likely that these two monomers with $SnCl_4$ were not reactive to one other.

ID **Sample**	**Time** **(Minute)**	**Conversion** **(%)**	**Mn** **(g mol^{-1})**	***D***	**F** **(%)**
RO 60 (1)	90	100	500	1.31	0.00
RO 60 (2)	180	100	300	1.41	0.00
RO 60 (3)	270	100	600	1.13	0.00
RO 60 (4)	360	100	350	1.34	0.00
RO 60 (5)	450	100	400	1.44	0.00
RO 60 (6)	540	100	550	1.30	0.00
RO 60 (7)	630	100	580	1.33	0.00
RO 60 (8)	720	100	450	1.48	0.00

Table 5.1: Results of the highly branched polymer samples used (9 : 1 monomers ratio *i*BVE : DEDVE). Initiating concentration system = (0.02 / 0.02 M) of HCl-*i*BVE / $SnCl_4$ in DCM. The monomer conversion and average functionality were measured by ^{1}H NMR analysis.

Figure 5.2 shows two different ^{1}H NMR spectra; the first represents the sample before the reaction (ie. the starting materials), the second represents a sample after polymerisation has taken place. The spectra clearly demonstrate that all monomers reacted, as the peak of 6.5 ppm was absent. In addition to this signal, the peak of the methoxy group was not observed. This clearly confirms that the propagation chain end was not quenched with a silyl enol ether to give an ester end group, as was expected.

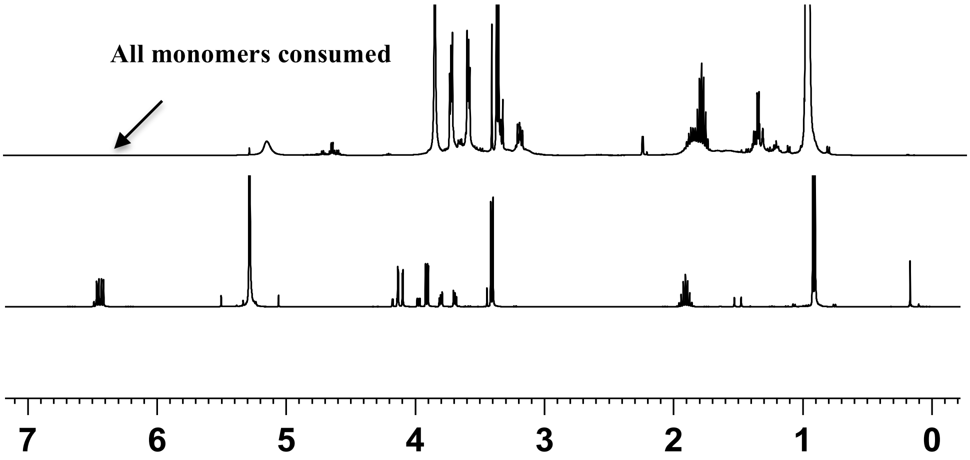


Figure 5.2: ^{1}H NMR spectra of starting materials (below) and the highly branched polymers used $SnCl_4$ in 0.06 M of **SEE 1** at 2 ml min^{-1} (top).

In Figure 5.3 the ^{1}H NMR spectrum of the previous reaction was repeated, but **SEE 1** was not used as a capping agent. As with above, all monomers conversions in all samples were at 100 %. This suggests that while silyl enol ether does not affect the polymerisation reaction as these reactions unexpectedly produced similar results, with or without **SEE 1**. High molecular weights should be generally obtained when the silyl enol ether is absent. However, it can be concluded that the polymerisation of *i*BVE does not react with DEDVE in the presences of $SnCl_4$ to produce highly branched polymers.

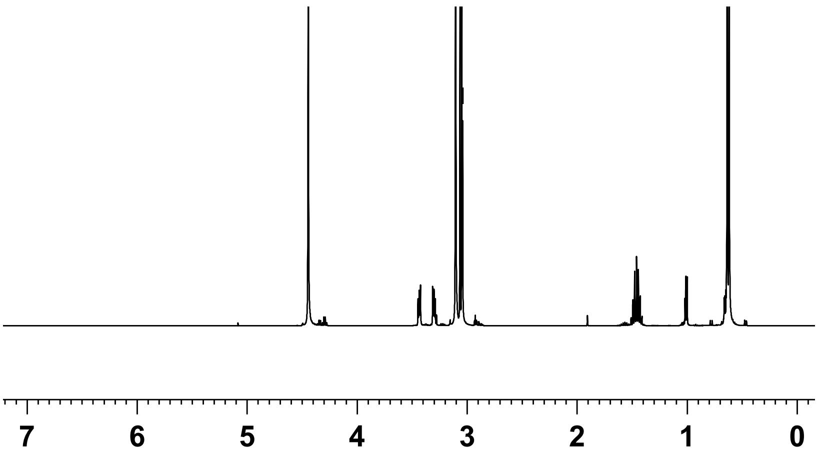


Figure 5.3: ^{1}H NMR spectrum of the highly branched polymers at 2 ml min^{-1} and without **SEE 1** used $SnCl_4$.

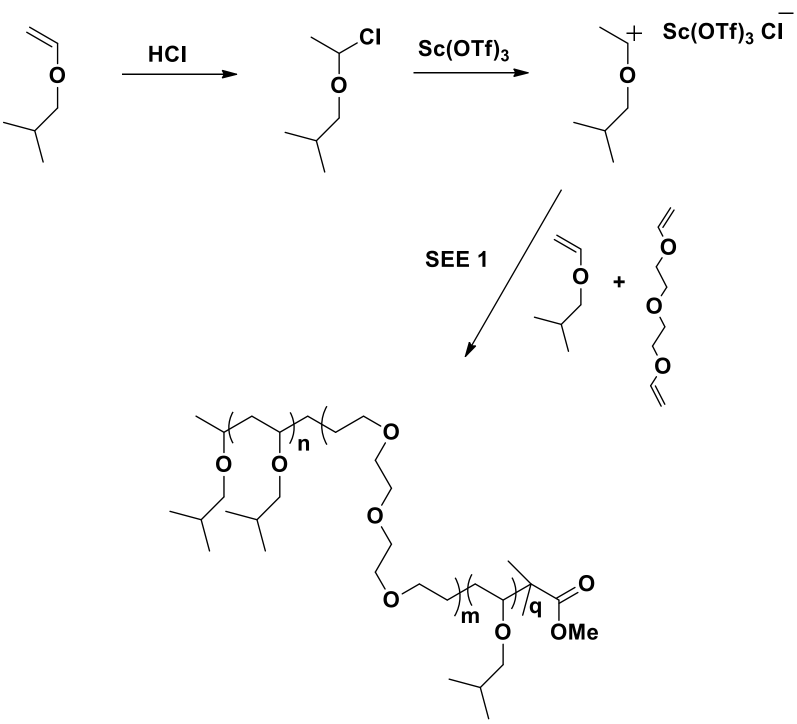
Many other different Lewis acids have been applied in this section; $TiCl_4$, ZnI_2, ZnI_2/HI and $Yb(OTf)_3$, including **SEE 1** at 2 ml min^{-1} flow time. The summaries of all experiments with the Lewis acids are presented in Table 5.2. It shows that, all of these polymerisations were not work well even when the duration was increased. This probably due to the fact that these varying Lewis acids were unable to react with the monomers (*i*BVE and DEDVE).

Lewis acid	***i*BVE (%)**	**DEDVE (%)**	**SEE 1**	**Initiator**
$SnCl_4$	90	10	0.06 M	HCl-*i*BVE
$SnCl_4$	90	10	None	HCl-*i*BVE
$TiCl_4$	90	10	0.06 M	HCl-*i*BVE
ZnI_2	90	10	0.06 M	HCl-*i*BVE
ZnI_2	90	10	0.06 M	HI
$Yb(OTf)_3$	90	10	0.06 M	HCl-*i*BVE

Table 5.2: The summary of all experiments applied at 2 ml min^{-1}.

5.3.1.2 Synthesis of highly branched polymers using $Sc(OTf)_3$ as a Lewis acid

This section will examine the polymerisation of *i*BVE as a first monomer with DEDVE as a second monomer, catalysed by a $Sc(OTf)_3$ and HCl-*i*BVE adduct at -15 °C using DCM as a solvent. The two monomers were used in differing ratios. This section will outline the results of a series of polymerisations using different concentrations of **SEE 1** as an end-group capping agent. The general mechanism of highly branched functional polymer production, using *ab initio* cationic polymerisation, is shown in Scheme 5.2.



Scheme 5.2: The general mechanism for pruction of highly branched polymers using Sc(OTf)$_3$.

Polymerisation of *i*BVE (90 %) with DEDVE (10 %)

The synthesis of highly branched functional polymers was performed with *i*BVE (90 %) as a first monomer and DEDVE (10 %) as a second monomer at flow rates of 1, 2 and 5 ml min^{-1}. **SEE 1** was applied in these polymerisations as a terminating agent, at concentrations of 0.04 M and 0.06 M. Figure 5.4 shows the molecular weight and dispersity of highly branched functional polymers derived from these polymerisations at different flow rates. At 1 ml min^{-1}, the variation in molecular weight plateaued after 200 minutes of reacting, while the dispersity slightly decreased over time. However, the polymerisation at 2 ml min^{-1} resulted in molecular weights that continued to increase with time, with the broadest dispersities being achieved at the beginning of the reaction. The flow rate of 5 ml min^{-1} also produced different results to the 1 and 2 ml min^{-1} experiments; this system produced large, highly branched polymers with a narrow dispersity, the molecular weight increased over time and the dispersity decreased over time. The data demonstrates that there is a strong relationship between feed rate and the distribution of molecular weight.

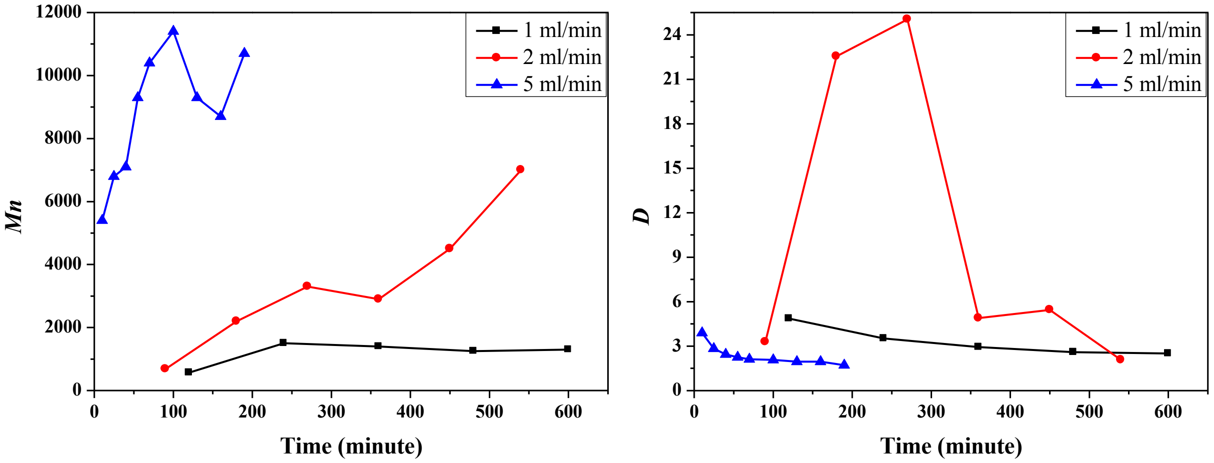


Figure 5.4: The number average molecular weight (left) and dispersity (right) for the highly branched functional polymers (9 : 1 monomer ratio of *i*BVE : DEDVE) derived by $Sc(OTf)_3$ at 1, 2 and 5 ml min^{-1}.

Figure 5.5 shows the progression of the overall conversion of vinyl monomer in regards to reaction time; it also shows the average end group functionality, which was calculated by ^1H NMR spectroscopy. All instantaneous monomer conversions reached 100 % in these polymerisations. The ratio of the integrations of the ester group resonance to the integrations of the proton from the polymer of *i*sobutyl vinyl ether resonance was used to calculate the average end group functionality. At flow rates of 1 and 2 ml min^{-1} the functionality fell with time, whilst the highest end group functionality was observed in the polymerisation prepared at 5 ml min^{-1}. In this reaction the functionality increased over time, presumably due to the increasing concentration of **SEE 1** in the reaction vessel. Therefore, it can be concluded that the feed rate had a substantial effect on the final chain end functionality, as all functionalities were low but the highest was achieved at a flow rate of 5 ml min^{-1}. This is most likely due to that at the lower feed rates the concentration of **SEE 1** is too low to ensure efficient chain end alkylation.

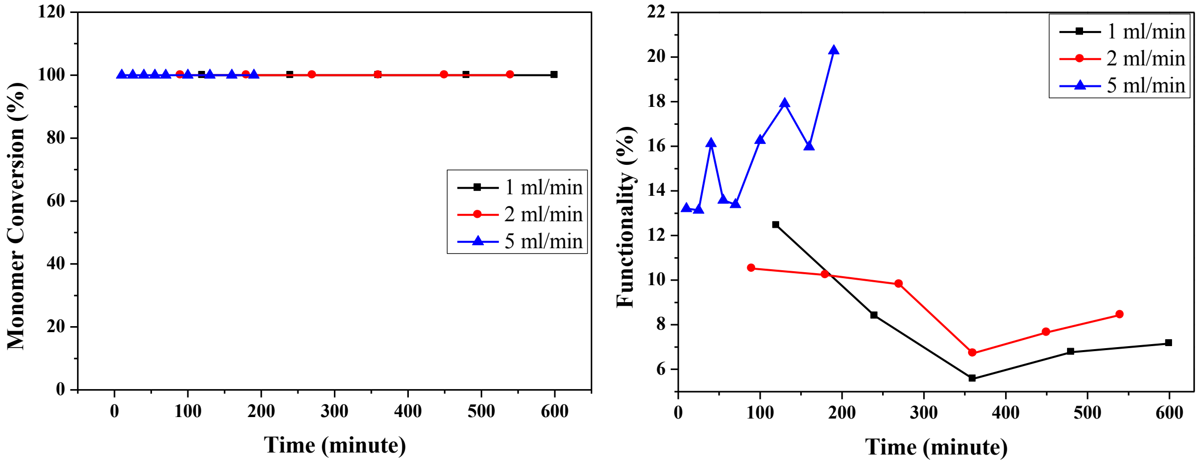


Figure 5.5: The monomer conversion (left) and the average functionality (right) fproduced in the synthesis of the highly branched functional polymers (9 : 1 monomer ratio of *i*BVE : DEDVE) obtained using Sc(OTf)$_3$ at 1, 2 and 5 ml min^{-1}.

Figure 5.6 details a ^{1}H NMR spectrum from highly branched functional polymer in the presence of **SEE 1** as an end-capping agent, with the spectrum showing the proton from the methoxy group at 3.70 ppm.

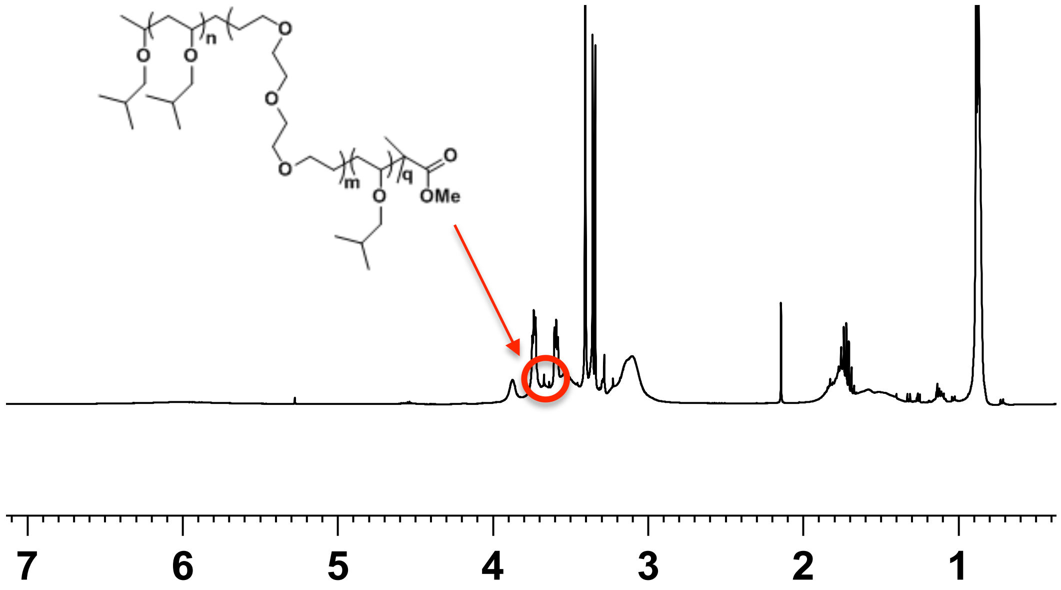


Figure 5.6: ^{1}H NMR spectrum of highly branched functional polymer prepared in the presence of 0.06 M concentration of **SEE 1** at 2 ml min^{-1}.

Figure 5.7 shows the molecular weight distributions measured from size exclusion chromatography (THF, high molecular weight of polystyrene as a standard) for polymerisation at 1 ml min^{-1} and 0.06 M of **SEE 1.** At the beginning of the reaction the molecular weight fell and then become constant over time. As such, the polymerisation reached a steady state after 4 hours and the molecular weight distributions were similar after this time.

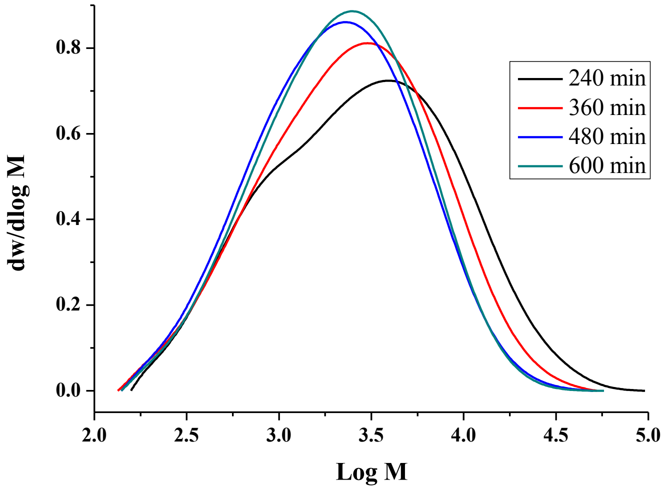


Figure 5.7: The molecular weight distributions of highly branched polymers (9 : 1 monomer ratio of *i*BVE : DEDVE) derived by Sc(OTf)$_3$ at 1 ml min^{-1}.

The molecular weight distributions of the polymerisation reaction at 2 ml min^{-1} and 0.06 M of **SEE 1** are detailed in Figure 5.8; it can be seen that the distribution is very broad at the beginning of the reaction, with the dispersities narrowing as the reaction progresses.

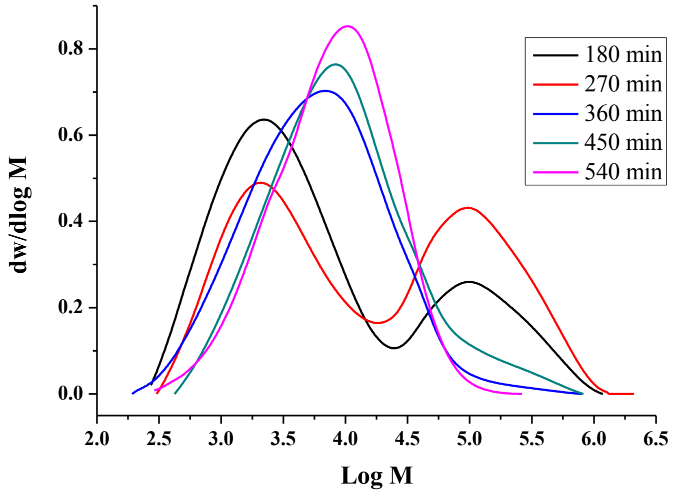


Figure 5.8: The molecular weight distributions of highly branched polymers (9 : 1 monomer ratio of *i*BVE : DEDVE) derived by $Sc(OTf)_3$ at 2 ml min^{-1}.

Figure 5.9 shows all molecular weight distributions of highly branched functional polymers produced in the presence of 0.04 M of **SEE 1** at 5 ml min^{-1}. As can be seen from the figure, the distributions were very similar to one another and dispersities narrowed as reaction time increased. This was an unexpected result, as usually the molecular weight distribution becomes broader over time if the polymerisation was carried out in a batch manner. The data demonstrates that the instantaneous conversion rate is particularly high at every time point in a continuous reaction, so that when the flow rate is optimised the cumulative conversion does not impact the weight distribution as it would in a batch reaction.

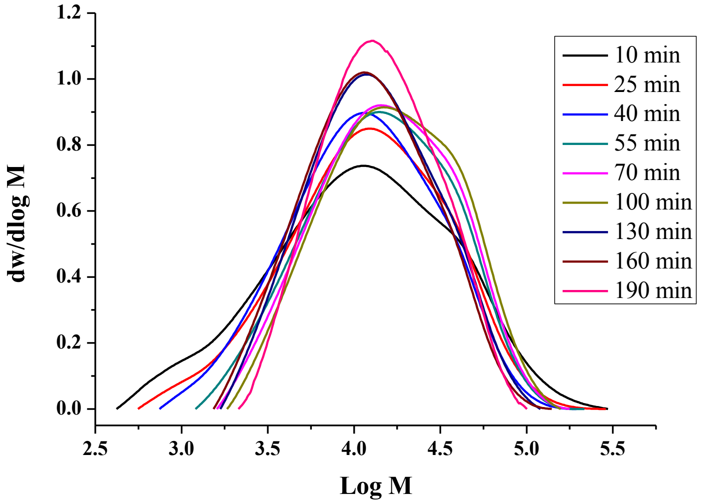


Figure 5.9: The molecular weight distributions of highly branched polymers (9 : 1 monomer ratio of *i*BVE : DEDVE) derived by $Sc(OTf)_3$ at 5 ml min^{-1}.

Polymerisation of *i*BVE (80 %) with DEDVE (20 %)

The copolymerisation of *i*BVE (80 %) with DEDVE (20 %) was conducted with 0.04 M of **SEE 1** at a feed rate of 5 ml min^{-1}, and 0.06 M of **SEE 1** at 1 and 2 ml min^{-1}. The relationship between molecular weight and time under different flow rates has been illustrated in Figure 5.10; it can be seen that molecular weight increased over time. Also, the same Figure shows the dispersity of the polymers plotted against time. These large molecular weight polymers were produced with broad molecular weight distribution and lacking control prior to gelation.

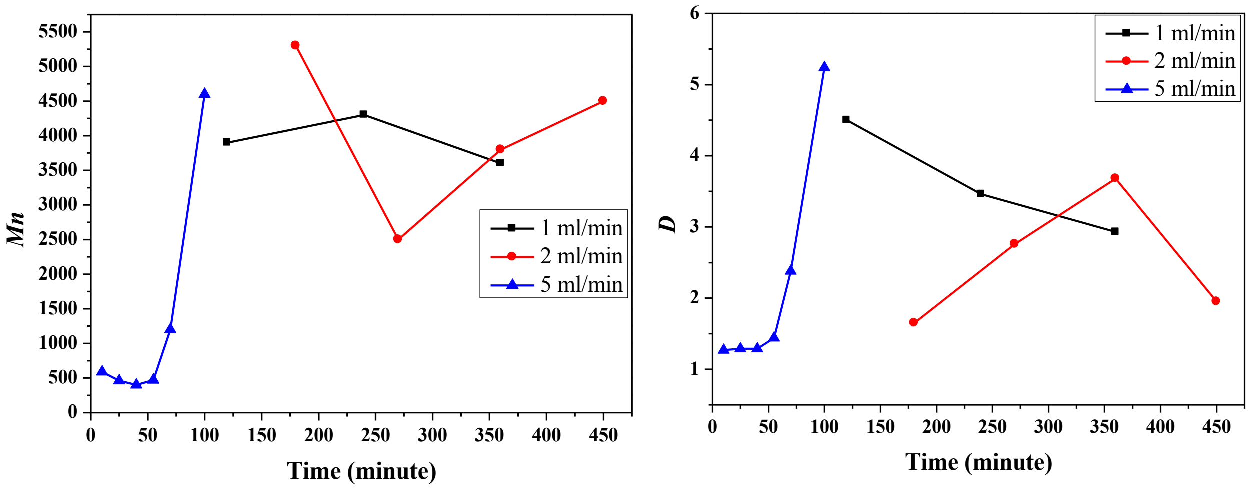


Figure 5.10: The number average molecular weight (left) and dispersity (right) for the highly branched functional polymers (8 : 2 monomer ratio of *i*BVE : DEDVE) derived using $Sc(OTf)_3$ at 1, 2 and 5 ml min^{-1}.

Figure 5.11 shows the monomer conversion and the average end group functionality for all polymers produced with different flow times. The instantaneous monomer conversions were 100% throughout but the functionality changed as the flow rate change and the polymers were not predominantly functionalised with the desired end groups. Therefore, it is clear that the system was dominated by terminations steps other than the target alkylation reactions. The average functionalities were calculated by using ^{1}H NMR spectroscopy. The best average functionality, 17 to 21 %, was obtained with polymers that were prepared using a flow rate of 2 ml min^{-1} with 0.06 M of **SEE 1**.

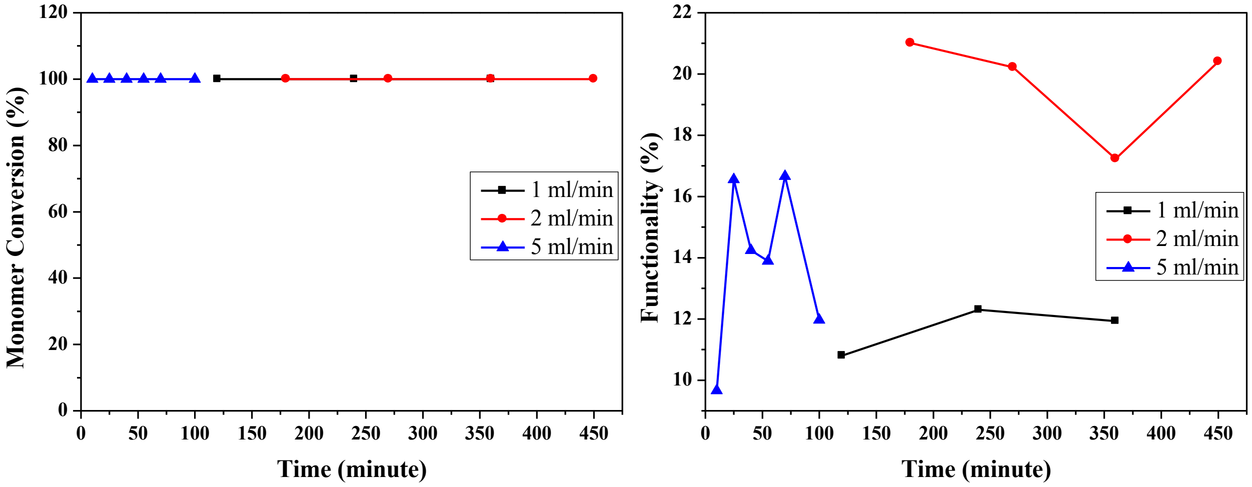


Figure 5.11: The monomer conversion (left) and the average functionality (right) for the highly branched functional polymers (8 : 2 monomer ratio of *i*BVE : DEDVE) derived by $Sc(OTf)_3$ at 1, 2 and 5 ml min^{-1}.

These polymerisations did not produce polymer with high degrees of functionalisation but they did provide high molecular weight material. The molecular weight distributions of highly branched functional polymers used 0.06 M of **SEE 1** at 1 ml min^{-1} shown in Figure 5.12. The high molecular weight of polymer with broad dispersity was determined after 120 minutes during reaction time until 360 minutes and after that time gelation was observed.

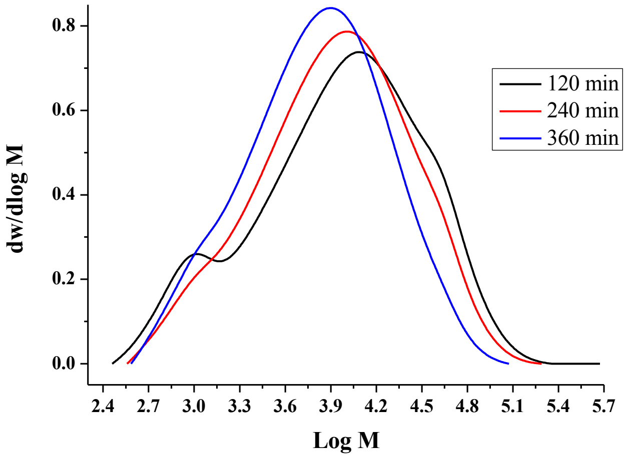


Figure 5.12: The molecular weight distributions of highly branched polymers (8 : 2 monomer ratio of *i*BVE : DEDVE) derived by $Sc(OTf)_3$ at 1 ml min^{-1}.

Figure 5.13 shows the molecular weight distributions of highly branched functional polymers produced at 2 ml min^{-1}. These data indicated that a large molecular weight of polymer was obtained from 180 minutes. It also shows these polymers have broad dispersities that changed with time. The last sample was collected at 450 minutes and after that gelation was observed.

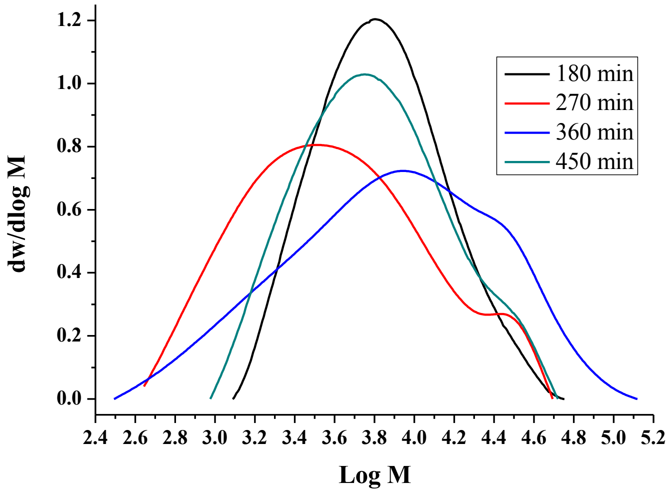


Figure 5.13: The molecular weight distributions of highly branched polymers (8 : 2 monomer ratio of *i*BVE : DEDVE) derived by Sc(OTf)$_3$ at 2 ml min^{-1}.

A photograph of highly branched functional polymer at 2 ml min^{-1} is shown in Figure 5.14. The sample was collected within 7.5 hours reaction time. It was the last sample collected under this condition because after that time gelation occurred.

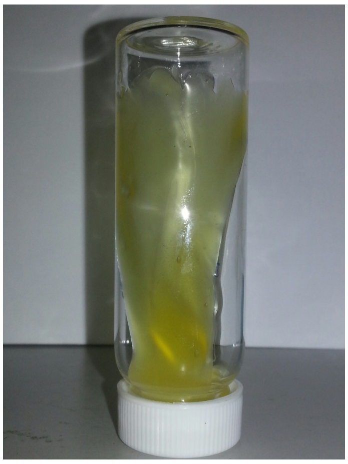


Figure 5.14: Digital photograph of highly branched functional polymer derived at 2 ml min^{-1} after 7.5 h and before gelation occurred.

The molecular weights of polymers produced at 5 ml min^{-1} are shown in Figure 5.15. It is clear that the polymers had high molecular weights, with a broad dispersity and that increased over time. However, gelation in this reaction was observed after 100 minutes.

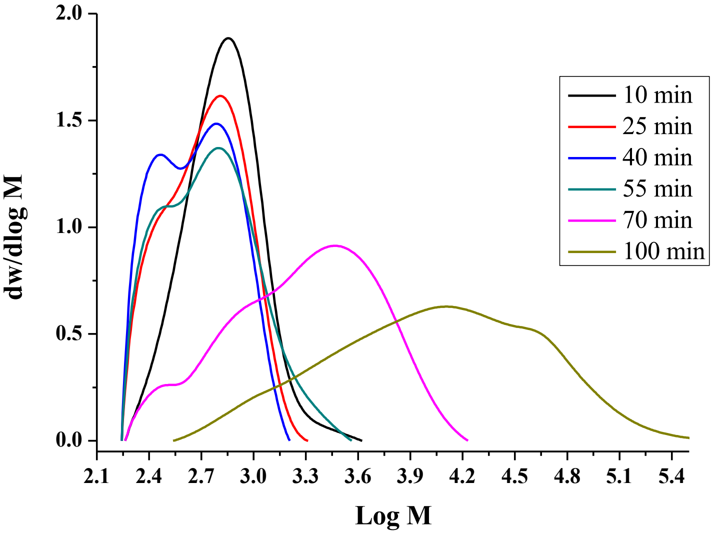


Figure 5.15: The molecular weight distributions of highly branched polymers (8 : 2 monomer ratio of *i*BVE : DEDVE) derived by $Sc(OTf)_3$ at 5 ml min^{-1}.

Polymerisation of *i*BVE (60 %) with DEDVE (40 %)

The highly branched polymers were prepared using 60 % of *i*BVE as a first monomer and 40 % of DEDVE as a second monomer in the presence of **SEE 1** (0.06 M). The polymerisation was run at 2 ml min^{-1}. There was only one sample measured in this reaction. This sample was collected after 60 minutes of reaction time; after that time gelation occurred (see Figure 5.17). The molecular weight distribution is shown in Figure 5.16.

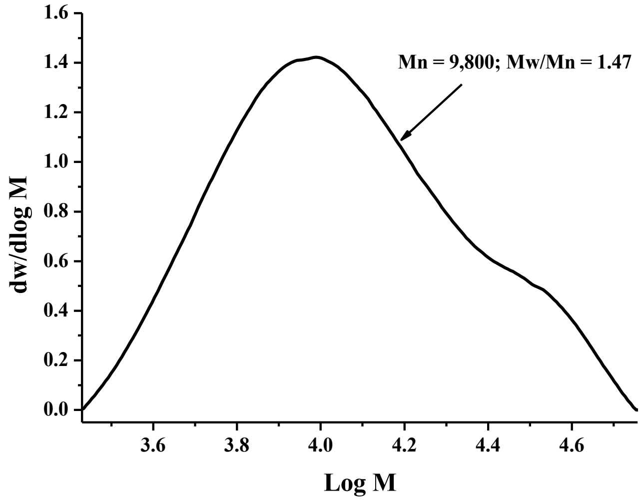


Figure 5.16: Molecular weight distribution plot for highly branched polymer (6 : 4 monomer ratio of *i*BVE : DEDVE) derived by $Sc(OTf)_3$ at 2 ml min^{-1}.

The monomer conversion and the average end group functionality were analysed through the use of ^1H NMR spectroscopy. The conversion in this polymerisation reaction was 100 %. Conversely, the ester group functionality was found to be very low in this polymerisation, at around 5.02 %; for these reasons the product gelled.

Figure 5.17: Digital photograph of gelation highly branched polymer occurred after 1 h.

5.3.2 Synthesis of highly branched functional polymers using divinyl benzene (DVBz) as a divinyl monomer

5.3.2.1 Synthesis of highly branched polymers using different of Lewis acids

The polymerisation of highly branched functional polymers has been attempted using divinyl benzene as a divinyl monomer and with *i*sobutyl vinyl ether as the main monomer in the presence of **SEE 1**. Various Lewis acids ($SnCl_4$, $TiCl_4$, ZnI_2 and $Yb(OTf)_3$) were applied and their varying effects on the polymerisation reactions were investigated. All of these reactions were carried out at a flow rate of 2 ml min^{-1} and at a temperature of -15 °C. These experiments were carried out with the aim to produce highly branched functional polymers through the use of varying ratios of the monomers.

The properties of the synthesised highly branched functional polymers, which were made with $SnCl_4$ as a Lewis acid, are detailed in Table 5.3. All samples produced polymers of particularly low molecular weights, so highly branched polymers were not observed even when the duration of the reaction increased.

ID Sample	Time (Minute)	Conversion (%)	Mn (g mol^{-1})	*D*	F (%)
RO 62 (1)	90	13.11	480	1.11	0.00
RO 62 (2)	180	12.94	580	1.07	0.00
RO 62 (3)	270	12.77	500	1.14	0.00
RO 62 (4)	360	12.46	570	1.06	0.00
RO 62 (5)	450	12.54	430	1.15	0.00
RO 62 (6)	540	12.58	500	1.17	0.00
RO 62 (7)	630	12.23	400	1.20	0.00
RO 62 (8)	720	12.07	450	1.19	0.00

Table 5.3: Results from the sythesis of the highly branched polymer samples using 9 : 1 monomers ratio (*i*BVE : DVBz). Initiating concentration system = (0.02 / 0.02 M) of HCl-*i*BVE / $SnCl_4$ in DCM. The monomer conversion and average functionality were measured by ^{1}H NMR analysis.

A ^{1}H NMR spectrum of the polymerisation is shown in Figure 5.18. The ratio of the integrations of the vinyl group resonance to the integrations of the protons from aromatic resonance was used to calculate the monomer conversion. It was found that all monomer conversions were very low under the reaction time applied. This clearly demonstrates that highly branched functional polymers were not produced in this set of experiments. Furthermore, the ester group functionality was not recorded in this spectrum. It should also be noted that terminations steps, other than the target alkylation reactions, dominated the system.

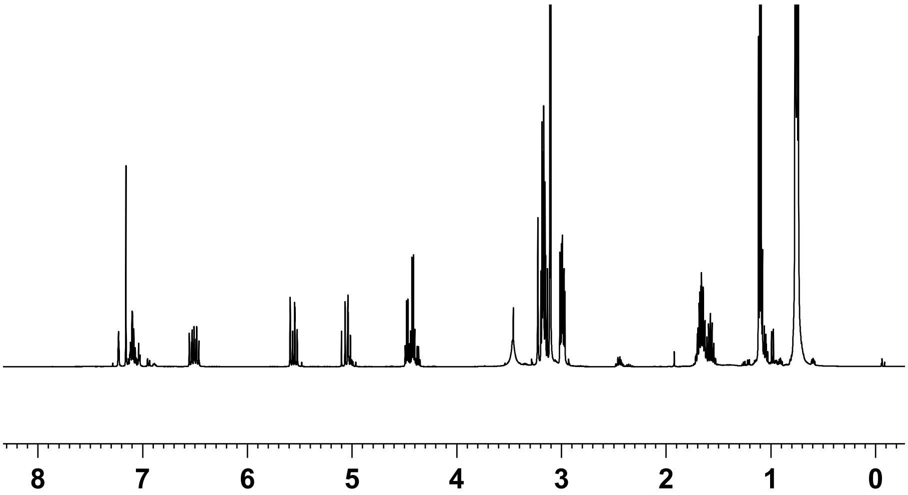


Figure 5.18: ^{1}H NMR spectrum of the highly branched polymers using $SnCl_4$ as Lewis acid.

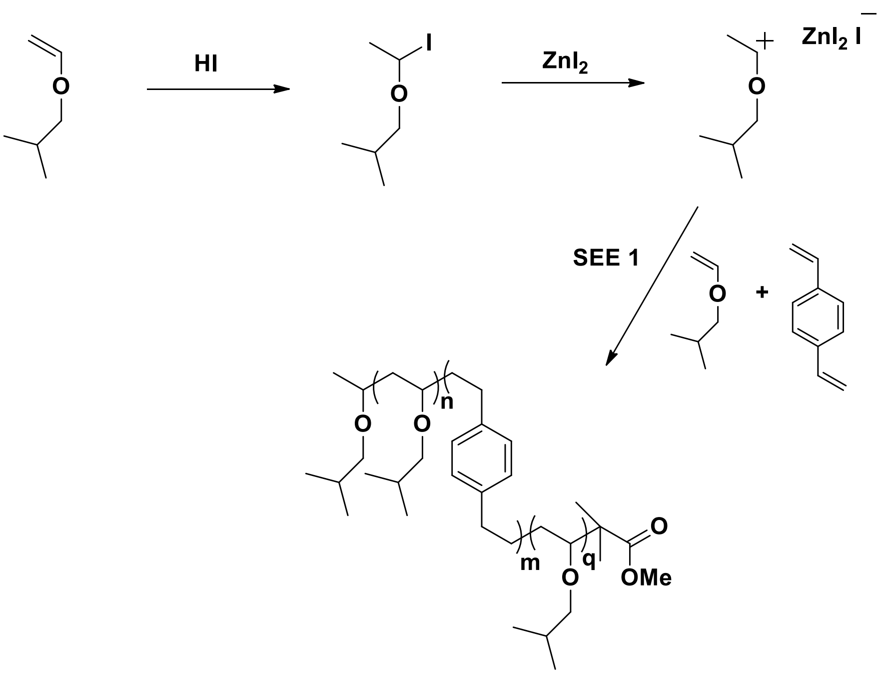
Table 5.4 (below) provides a summary of all experiments done using DVBz as a divinyl monomer in combination with various Lewis acids (such as $SnCl_4$, $TiCl_4$, ZnI_2 and $Yb(OTf)_3$, respectively) at a 2 ml min^{-1} flow rate. The low molecular weights of the products (determined using SEC) demonstrated that highly branched polymers did not form. In addition to this, the ester end group functionality was not recorded in ^{1}H NMR spectra. This may be due to the nature of the Lewis acid used or the inactivity of the two monomers used (*i*sobutyl vinyl ether with divinyl benzene).

Lewis acid	*i*BVE (%)	DVBz (%)	SEE 1	Initiator
$SnCl_4$	90	10	0.06 M	HCl-*i*BVE
$SnCl_4$	60	40	0.06 M	HCl-*i*BVE
$TiCl_4$	90	10	0.06 M	HCl-*i*BVE
ZnI_2	90	10	0.06 M	HCl-*i*BVE
$Yb(OTf)_3$	90	10	0.06 M	HCl-*i*BVE

Table 5.4: The summary of all experiments applied at flow rate of 2 ml min^{-1}.

5.3.2.2 Synthesis of highly branched polymers using ZnI_2/HI

The synthesis of highly branched functional polymers was optimised using hydriodic acid (HI) as an initiator, ZnI_2 as a Lewis acid and **SEE 1** as a terminating agent. Three different reaction conditions were examined in this set of experiments. The first reaction used 0.06 M of **SEE 1** at a flow rate of 1 ml min^{-1}. The second reaction used 0.06 M of **SEE 1** at 2 ml min^{-1}. The last reaction used 0.04 M of **SEE 1** at 5 ml min^{-1}. The monomer ratios for each experiment were 90 % of *i*BVE with 10 % of DVBz. The general mechanism of these reactions is detailed in Scheme 5.3.



Scheme 5.3: The general mechanism of polymerisation using ZnI_2/HI.

Figure 5.19 illustrates the relationship between the molecular weight (Mn) and time passed. At a flow rate of 1 ml min^{-1} all of the samples produced low molecular weight material; the highest molecular weight obtained was 1,100 g mol^{-1}, measured after 480 minutes of polymerisation. At 2 ml min^{-1}, the molecular weight increased as time increased; the highest molecular weight (3,900 g mol^{-1}) was obtained in the last sample after 540 minutes had elapsed. At a flow rate of 5 ml min^{-1}, large molecular weight polymers were produced, with the molecular weights decreasing over time; the molecular weights obtained lay between 1,700 to 4,500 g mol^{-1}, with SEC analysis demonstrating relatively broad dispersities. These results suggest that highly branched functional polymers have been produced, although the recorded molecular weights were still low.

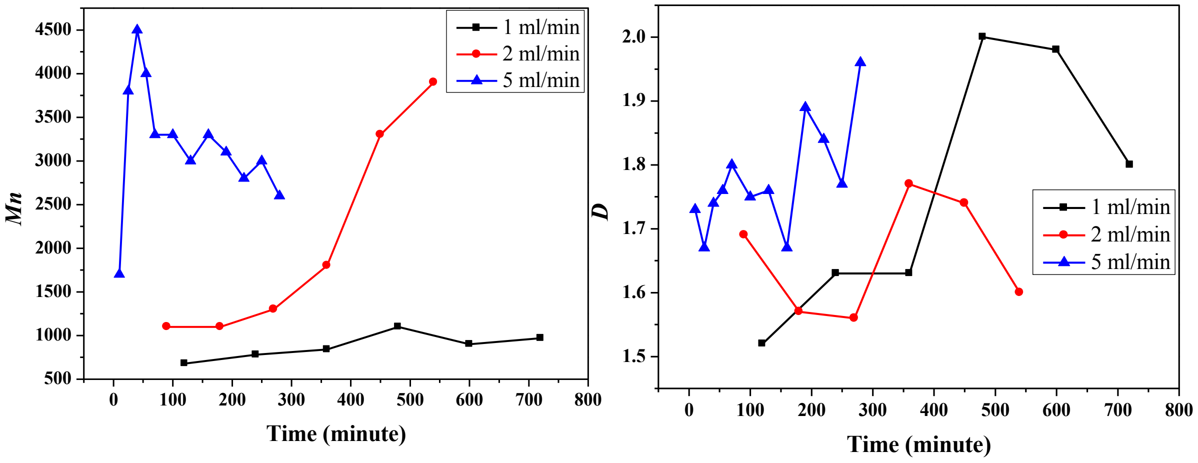


Figure 5.19: The number average molecular weight (left) and dispersity (right) for the highly branched functional polymers (9 : 1 monomer ratio of *i*BVE : DVBz) derived by ZnI_2/HI at 1, 2 and 5 ml min^{-1}.

The final monomer conversion and the average functionalities under the different flow rates are provided in Figure 5.20. As can be seen, the instantaneous monomer conversions were consistently lower than the previous reactions recorded in this study; the highest conversion rate, 23 %, was achieved at a flow rate 5 ml min^{-1}. This is due to the concentration of **SEE 1** being too high to ensure efficient chain end alkylation at the higher flow rates. The termination steps, as opposed to the target alkylation reactions, dominated in this system.

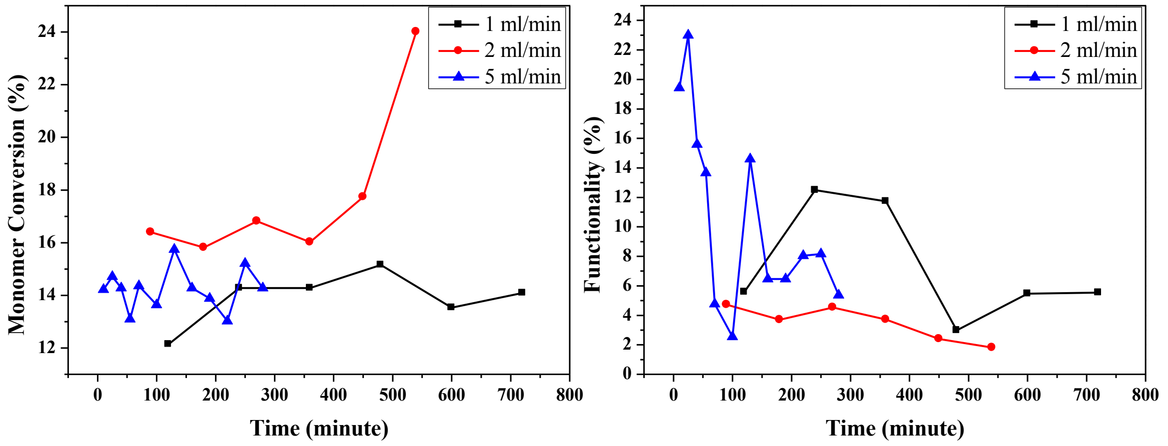


Figure 5.20: The monomer conversion (left) and the average functionality (right) for the highly branched functional polymers (9 : 1 monomer ratio of *i*BVE : DVBz) derived by ZnI_2/HI at 1, 2 and 5 ml min^{-1}.

The molecular weight distributions of the highly branched functional polymers produced at a flow rate of 1 ml min^{-1} are described in Figure 5.21. It can be seen that relatively low molecular weights were obtained with these polymerisation reactions. This is possibly because a higher rate of termination reduced the molecular weight of the polymers.

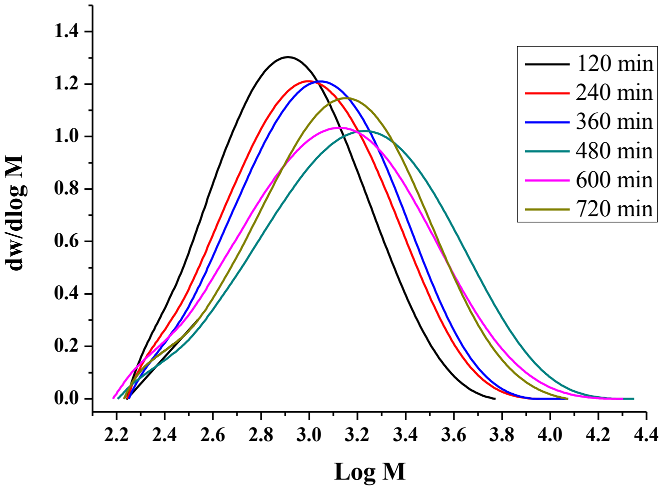


Figure 5.21: The molecular weight distributions of highly branched polymers at 1 ml min^{-1}.

The molecular weight distributions in Figure 5.22 also show the highly branched functional polymers were produced with a flow rate of 2 ml min^{-1}. The molecular weight distributions increased in comparison to those obtained at 1 ml min^{-1}; the molecular weight also increased over time.

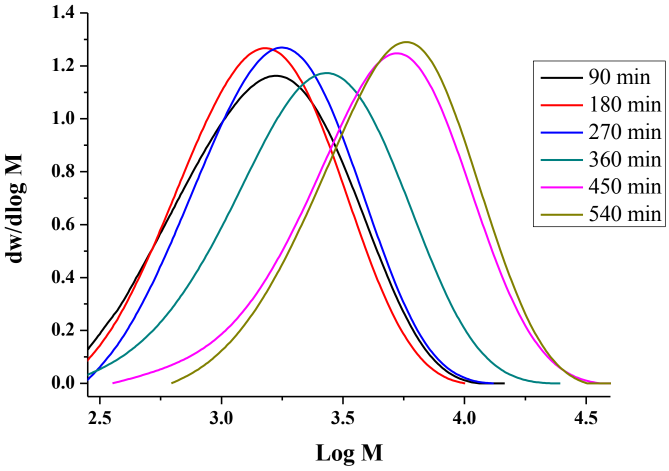


Figure 5.22: The molecular weight distributions of highly branched polymers at 2 ml min^{-1}.

Figure 5.23 details the molecular weight of highly branched polymers obtained using a feed rate of 5 ml min^{-1}, with higher molecular weight averages being obtained in these systems. Upon initiation of the reaction the molecular weight fell up until the 10 minute mark, at which point the decline troughed. This figure demonstrates that there is a strong relationship between the molecular weight and feed rate in this system.

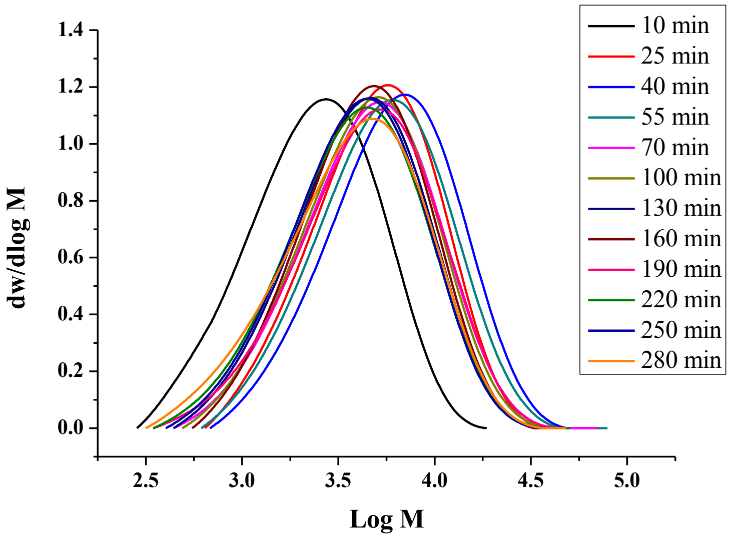


Figure 5.23: The molecular weight distributions of highly branched polymers at 5 ml min^{-1}.

The ^{1}H NMR spectra for each experiment are provided in Figure 5.24. All of the spectra demonstrated a peak from the methoxy groups at 3.70 ppm. This suggests the presence of ester groups derived from the alkylation of **SEE 1** following termination. Using this peak the average chain end functionality can then be calculated. The average functionalities lay between 4 % and 24 %; the best average functionality, 24 %, was obtained with polymers that were prepared using a flow time 5 ml min^{-1} with 0.04 M of **SEE 1**.

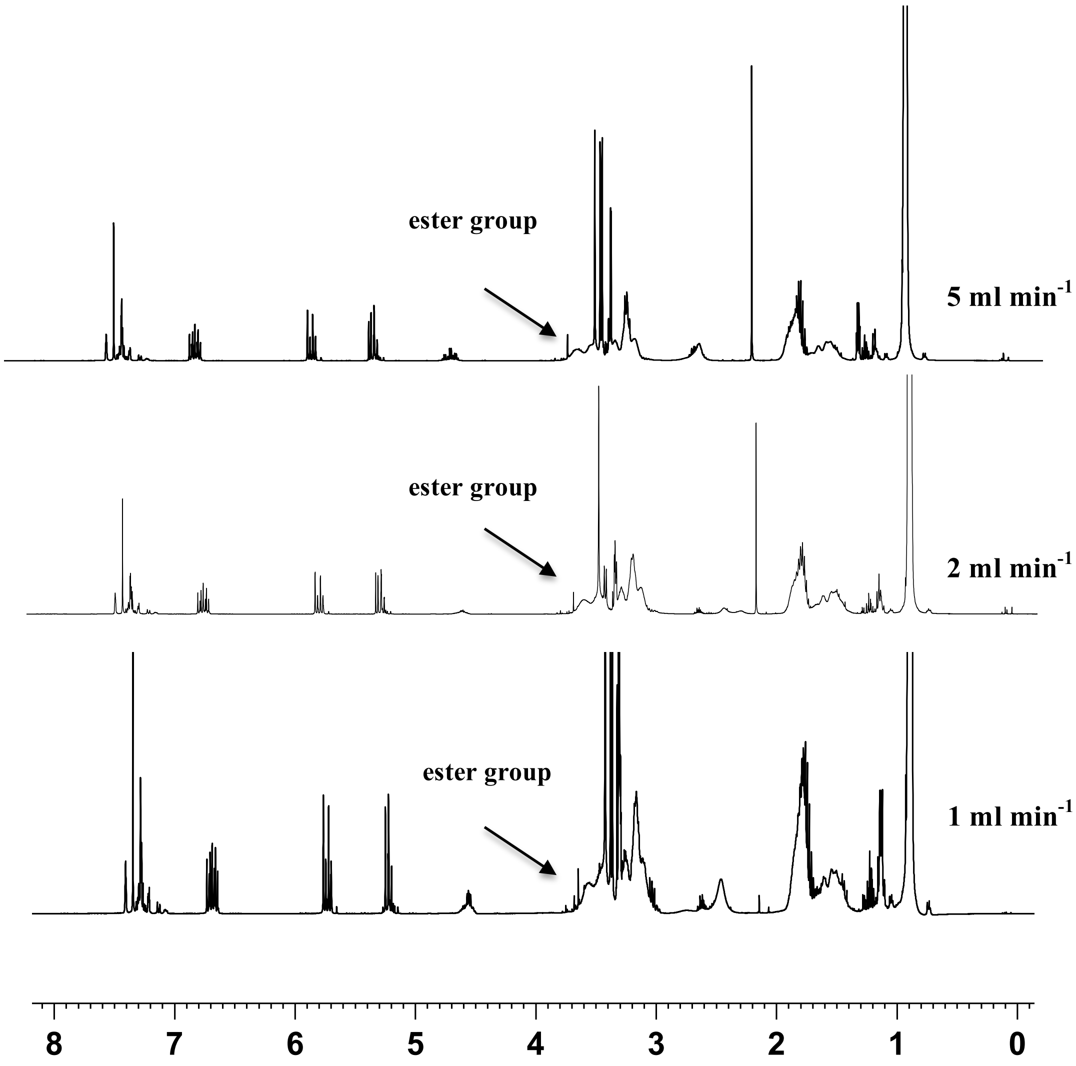


Figure 5.24: ^{1}H NMR spectrum for highly branched functional polymers produced from (9 : 1 monomer ration of *i*BVE : DVBz) with ZnI_2/HI at 1, 2 and 5 ml min^{-1} respectively.

5.3.2.3 Synthesis of highly branched polymers using Sc(OTf)$_3$ as a Lewis acid

In this set of experiments highly branched functional polymers were produced using *i*sobutyl vinyl ether as the main monomer, with divinyl benzene being used as a second monomer. All reactions were carried out using Sc(OTf)$_3$ as a Lewis acid. **SEE 1** was used at different concentrations, acting as an end capping agent. Several flow rates (1, 2 and 5 ml min^{-1}) were applied in these polymerisation reactions, and all of the reactions were cooled in cardice/methanol to a temperature of -15 °C.

Polymerisation of *i*BVE (90 %) with DVBz (10 %)

A monomer ratio of 90 % *i*BVE and 10 % DVBz was used to produce highly branched functional polymers with different concentrations of **SEE 1** and varying flow rates. Different parameters could be applied to produce highly branched polymers with high degrees of ester group functionality. These polymers have many potential uses in bio-applications.

The results of the experiments are provided in Figure 5.25. At a flow rate of 1 ml min^{-1} the molecular weight increased with time and the dispersity fell. The highest molecular weight was produced at 2 ml min^{-1}; early in the reaction broad dispersities were observed, dispersities that decreased over time. The molecular weights (M_n) from the polymerisation reaction at a flow rate of 5 ml min^{-1} were generally under 900 g mol^{-1}, which indicates that few highly branched polymers were produced. With this information it can be deduced that the best conditions for the production of highly branched polymers are as follows: a feed rate of 2 ml min^{-1}; polymerisation that used (9 : 1) monomer ratio of *i*BVE : DVBz; the use of Sc(OTf)$_3$ as a Lewis acid. The application of these conditions produced highly branched functional polymers of a quality better than those obtained using at 1 or 5 ml min^{-1} flow rates.

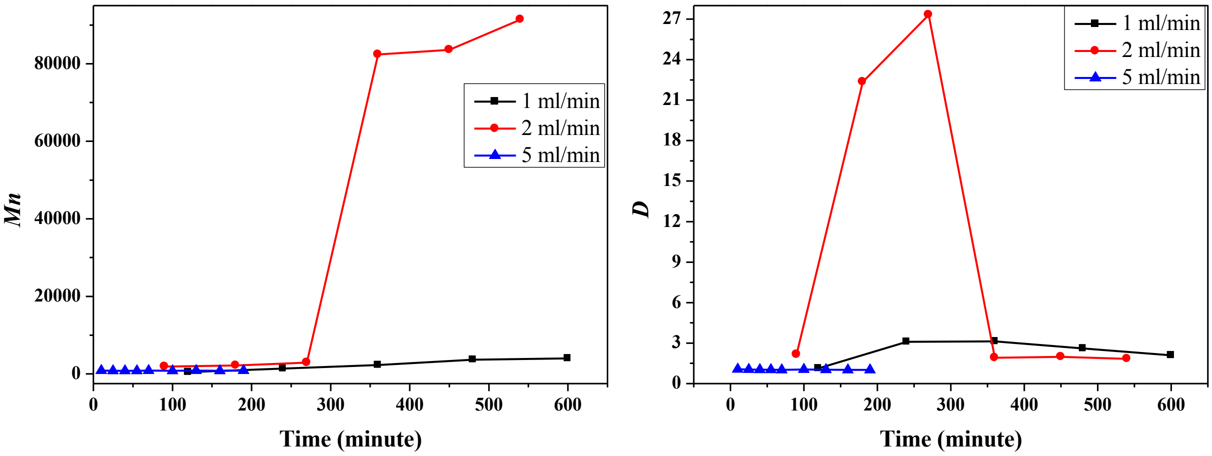


Figure 5.25: The number average molecular weight (left) and dispersity (right) for the highly branched functional polymers (9 : 1 monomer ratio of *i*BVE : DVBz) derived by Sc(OTf)$_3$ at 1,2 and 5 ml min^{-1}.

Figure 5.26 shows the monomer conversion rate and average functionality of the polymers produced. The monomer conversion was generally fairly low over the course of the polymerisations, indicating that the average rate of propagation is reduced in proportion to the level of alkylation. It can be seen that higher degrees of ester group functionality were obtained at low flow rates rather than higher ones. The synthesis of highly branched polymers at low flow rates (1 or 2 ml min^{-1}) is a requirement for the production of polymers with the highest functionality at the chain ends. Despite this chain end functionalities remained relatively low.

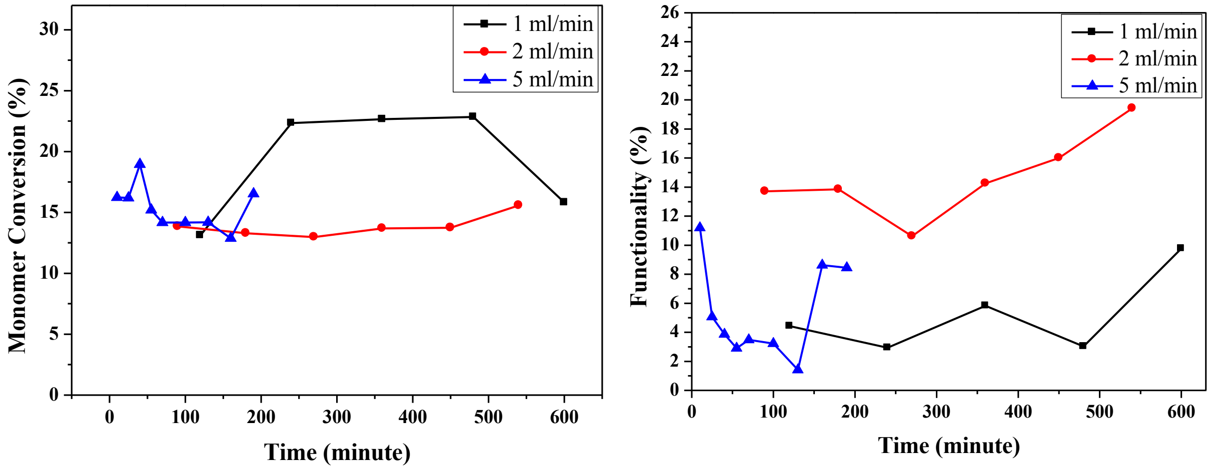


Figure 5.26: The monomer conversion (left) and the average functionality (right) for the highly branched functional polymers (9 : 1 monomer ratio of *i*BVE : DVBz) derived by Sc(OTf)$_3$ at 1, 2 and 5 ml min^{-1}.

The molecular weight distributions of highly branched functional polymers produced at a flow rate of 1 ml min^{-1} are detailed in Figure 5.27; it should be noted that polymers with large molecular weights and narrow dispersities were produced as time progressed. This type of result is usually observed in the synthesis of highly branched polymers during a continuous reaction, due to instability of the system at the beginning of the reaction. As such, the control of the polymerisation processes improved with time.

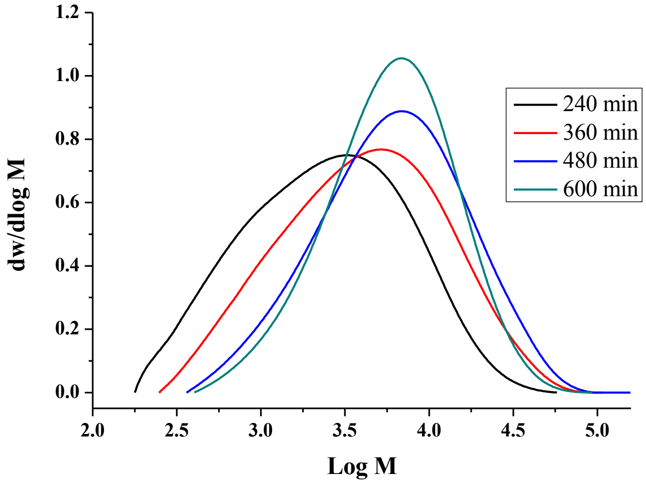


Figure 5.27: The molecular weight distributions of highly branched polymers (9 : 1 monomer ratio of *i*BVE : DVBz) derived by Sc(OTf)$_3$ at 1 ml min^{-1}.

Furthermore, Figure 5.28 details the molecular weight distributions of highly branched functional polymers at a flow rate of 2 ml min^{-1}. The data indicates that highly branched polymers were produced using this continuous reaction. The molecular weight distribution narrowed as the reaction went on.

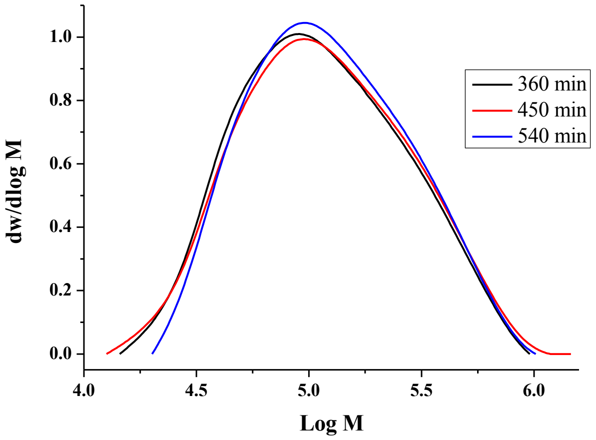


Figure 5.28: The molecular weight distributions of highly branched polymers (9 : 1 monomer ratio of *i*BVE : DVBz) derived by Sc(OTf)$_3$ at 2 ml min^{-1}.

Polymerisation of *i*BVE (80 %) with DVBz (20 %)

Highly branched functional polymers were synthesised using monomer ratios of 8 : 2 of *i*BVE : DVBz respectively. A flow rate of 2 ml min^{-1} was applied, along with 0.06 M of **SEE 1**. The Mn and the dispersity of these polymers are shown in Figure 5.29. The molecular weights remained consistently low until the 7.5 hour mark, from which time the molecular weights increased linearly with time. Broad dispersities of polymers were also observed after 7.5 hours. These results indicate that highly branched functional polymers were obtained extremely late in the polymerisation process, due to the high molecular weight material being produced late in the reaction.

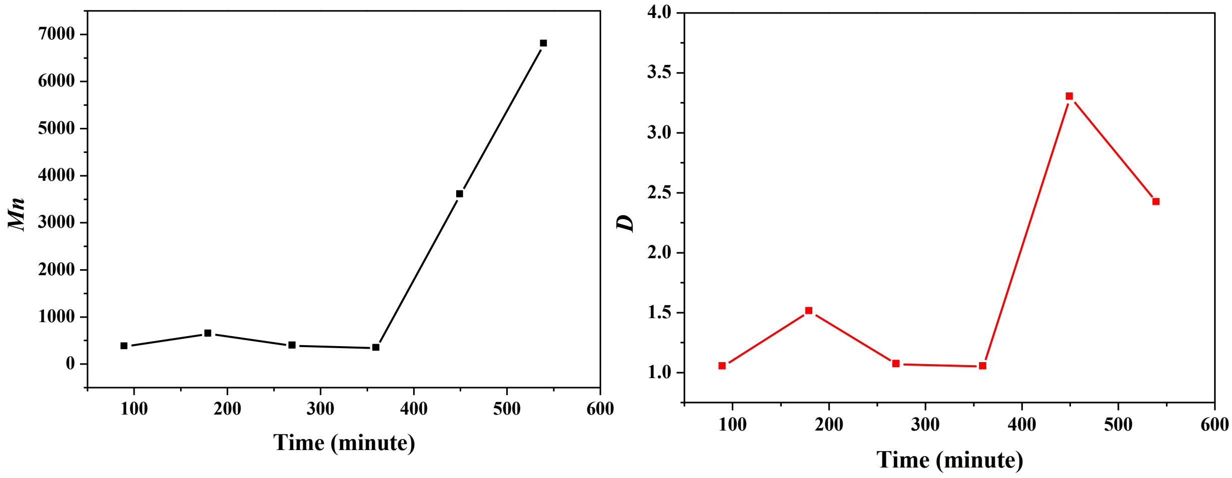


Figure 5.29: The number average molecular weight (left) and dispersity (right) for the highly branched functional polymers (8 : 2 monomer ratio of *i*BVE : DVBz) derived by Sc(OTf)$_3$ at 2 ml min^{-1}.

Figure 5.30 details the monomer conversion rate and the average chain end functionality of the highly branched functional polymers produced at a flow rate of 2 ml min^{-1}. The monomer conversion rates slightly decreased over time. The beginning of the reaction saw particularly low functionality of created polymers, with functionality only rising late in the course of the polymerisation in two samples.

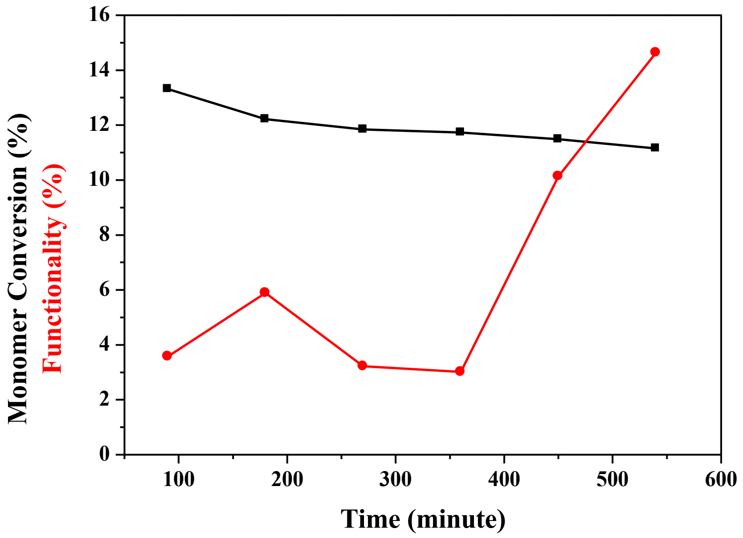


Figure 5.30: The monomer conversion (black) and the average functionality (red) for the highly branched functional polymers (8 : 2 monomer ratio of *i*BVE : DVBz) derived by Sc(OTf)$_3$ at 2 ml min^{-1}.

Figure 5.31 provides the molecular weight distributions of the two last samples from this set of polymerisation reactions. These samples produced polymers of large molecular weights with a broad dispersity; this indicates the presence of highly branched functional polymers.

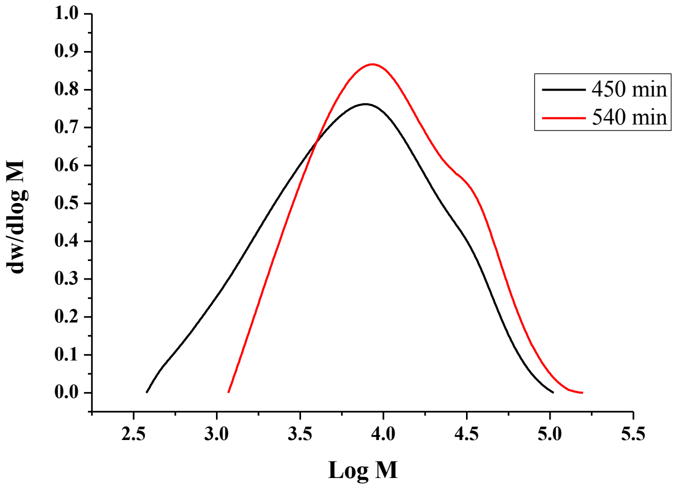


Figure 5.31: The molecular weight distributions of highly branched polymers (8 : 2 monomer ratio of *i*BVE : DVBz) derived by $Sc(OTf)_3$ at 2 ml min^{-1}.

Polymerisation of *i*BVE (60 %) with DVBz (40 %)

Figure 5.32 details the average molecular weight and dispersity for all samples at a flow rate of 2 ml min^{-1}. The monomer ratio was 60 % *i*BVE with 40 % DVBz, and the reaction took place in the presence of 0.06M of **SEE 1**. The molecular weights of the produced polymers increased slightly over time, as did the dispersities. This suggests that the polymerisation only truly began after 7.5 hours of reaction.

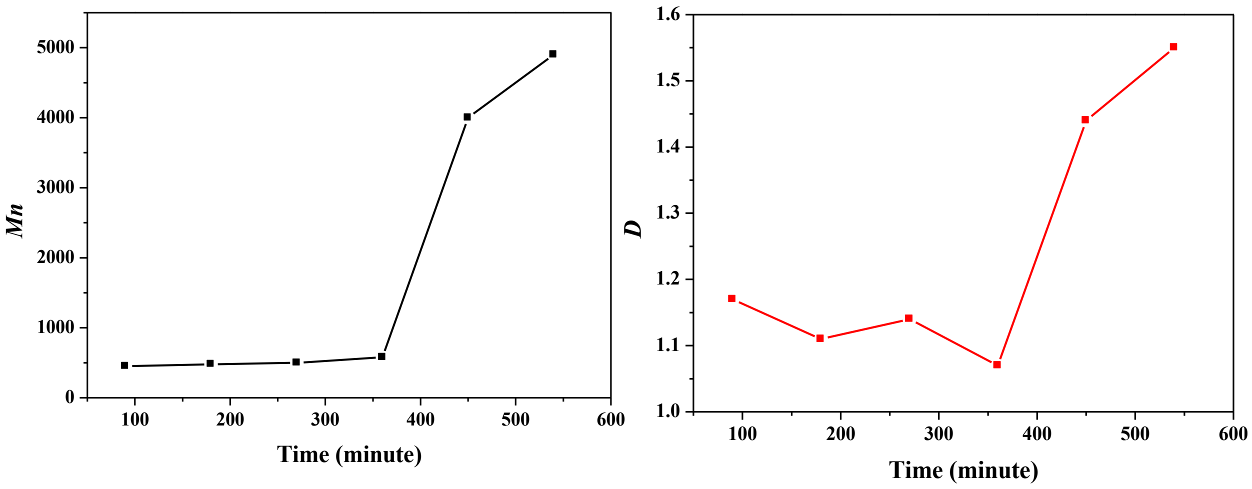


Figure 5.32: The number average molecular weight (left) and dispersity (right) for the highly branched functional polymers (6 : 4 monomer ratio of *i*BVE : DVBz) derived by $Sc(OTf)_3$ at 2 ml min^{-1}.

The monomer conversions and functionality are shown in Figure 5.33. The monomer conversions were constant but relatively low. The number of chain end ester groups observed increased significantly after the 7.5 hour mark. As such, it may make more sense to allow extra time for the reaction to begin producing highly branched polymers with ester groups.

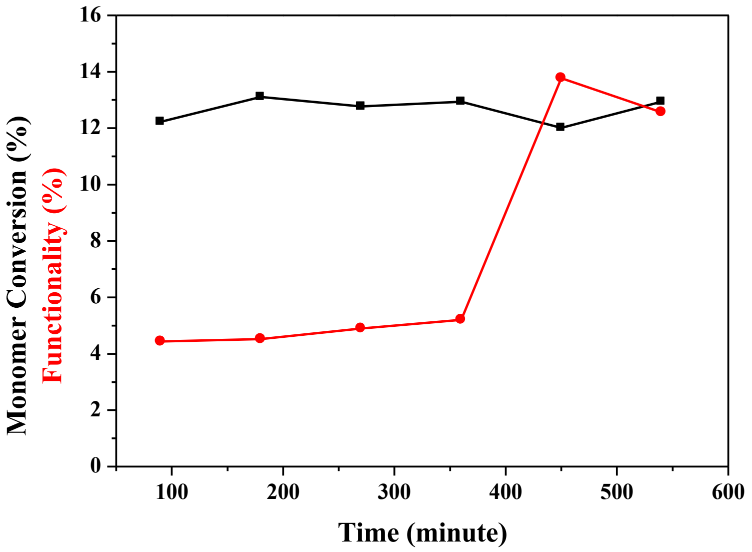


Figure 5.33: The monomer conversion (black) and the average functionality (red) for the highly branched functional polymers (6 : 4 monomer ratio of *i*BVE : DVBz) derived by $Sc(OTf)_3$ at 2 ml min^{-1}.

By examining the molecular weight distributions it can be seen that polymers with large molecular weights and broad dispersities were produced after 450 minutes, and it is further suggested that higher functionality could be obtained by allowing more time for the reaction (see Figure 5.34).

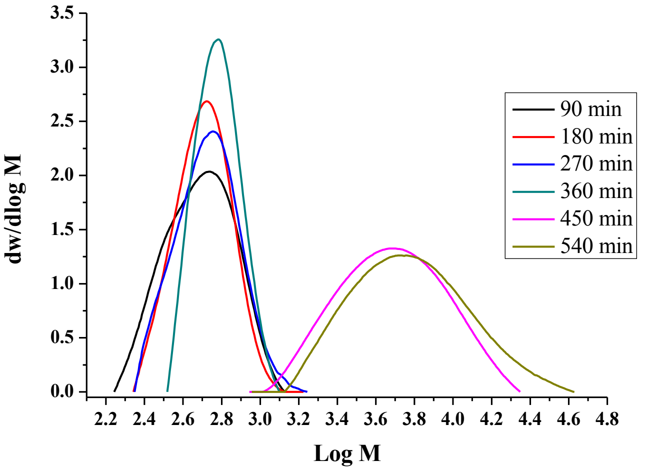


Figure 5.34: The molecular weight distributions of highly branched polymers (6 : 4 monomer ratio of *i*BVE : DVBz) derived by $Sc(OTf)_3$ at 2 ml min^{-1}.

5.4 Conclusions

The synthesis of highly branched functional polymers has been achieved through the use of a continuous reaction; the use of this method, as opposed to the batch technique, results in the production of a greater quantity of polymers in a shorter period of time. The preferred technique uses *i*sobutyl vinyl ether as the first monomer and DEDVE and DVBz as second monomers, with **SEE 1**also being present in the reaction vessel. A variety of Lewis acids were examined in this chapter: $SnCl_4$, $TiCl_4$, ZnI_2, ZnI_2/HI, $Yb(OTf)_3$ and $Sc(OTf)_3$. Side reactions and monomer conversions in these polymerisations were measured using ^1H NMR spectra. The molecular weights and dispersities were determined through the use of SEC analysis. The polymerisation of *i*BVE with DEDVE was only successful when $Sc(OTf)_3$ was used as the Lewis acid. Highly branched polymers with chain end group functionality were detected at a monomer ratio of 9 : 1 using low concentrations of **SEE 1** (0.04 M) and a high flow rate (5 ml min^{-1}). It was noted that increasing the monomer ratio of divinyl monomer (DEDVE) lead to gelation; in these reactions the instantaneous monomer conversions were 100 %. The polymerisation of *i*BVE with DVBz only worked with ZnI_2/HI and $Sc(OTf)_3$ being used as Lewis acids. When using ZnI_2/HI (as the Lewis acid/initiator), low concentrations of **SEE 1** (0.04M) and a flow rate of 5 ml min^{-1}, highly branched polymers with optimal end capping were detected. A setup consisting of another Lewis acid, ($Sc(OTf)_3$), a low flow rate (2 ml min^{-1}) and a high concentration of **SEE 1** (0.06 M) was found to be particularly effective at producing highly branched polymers with ester group functionality. These findings suggest that the feed rate has a substantial impact on the obtained chain end functionality; however low monomer conversions were obtained under these reaction conditions. Gelation did not occur in the polymerisation of DVBz as a second monomer. Generally, fewer average chain end groups were detected in highly branched polymers as compared with previous linear polymers, indicating that synthesis of highly branched polymers with high degrees of chain end functionality is still a hard to achieve aim.

Chapter 6

6. Conclusions and Future Work

6.1 Conclusions

Silyl enol ethers were alkylated in *ab initio* cationic polymerisations to generate oligo(vinyl ethers) with functionalised end-groups. The monomer concentration, reaction temperature, Lewis acids and silyl enol ether concentration were selected carefully to ensure a high level of chain-end functionality. Having a rate of reaction with carbocations comparable to vinyl ethers, highly nucleophilic species, such as silyl ketene actals, were also employed in the experiment. Meanwhile, the production of the ester end-groups was achieved by quickly eliminating the primary adducts. The analysis of the attained oligomers, as well as the evaluation of side reactions and chain-end functionalisation processes, was conducted via MALDI-TOF mass spectrometry.

6.1.1 *Ab* initio cationic polymerisation of MVE and *i*BVE using batch reaction system

The present chapter was concerned with the creation of materials characterised by high end-group functionality through the regulation of the reaction temperature and the concentrations of monomers and silyl enol ether. The nucleophilic capping agent that was employed was a silyl ketal enol, which possesses a rate of reaction with carbocations comparable to vinyl ether propagation. The primary adducts were subsequently eliminated rapidly, resulting in the production of the ester end-groups.

Tin tetrachloride ($SnCl_4$) was used as the Lewis acid in the polymerisation of oligomethyl vinyl ethers at -26°C and -78°C. The likely reason why high-end group functionality was achieved at low polymerisation temperature was that fewer side-reactions occur at a lower temperature. An **SEE 1** concentration of 0.10 M gave the optimal chain-end capping. In the case where alkylation of the silyl ketene acetal was the primary termination reaction, the reaction conditions were determined with the help of MALDI-TOF mass spectrometry. This technique was also employed to calculate the molecular weight of narrow fractions through the calibration of a size exclusion chromatograph (SEC). It was then possible to formulate the Kuhn-Mark-Houwink relationship for oligo(methyl vinyl ether). The data highlighted the end-group structure dependence of the solution coil conformation, making it challenging to apply a universal calibration to combinations of polymers with varying end-groups. Due to this, polystyrene standards were used as a reference point in determining the molecular weights.

Titanium tetrachloride ($TiCl_4$) was the Lewis acid used in the preparation of oligo*iso*butyl vinyl ether at different temperatures. The conditions found to be required to obtain a high level of chain-end functionality were a low temperature and high **SEE 1** concentration. The chains with ester end-groups attained full functionalisation at 0.15 M, representing **SEE 1** to initiator molar ratio of 3:1 and temperature of -78 °C. MALDI-TOF MS, ^{1}H, ^{13}C NMR and FT-IR spectres were employed to successfully accomplish ester end-group functionalisation of OMVE and O*i*BVE polymers.

6.1.2 Polymerisation of *i*sobutyl vinyl ether using continuous processes

Non-living cationic polymerisations were used in the successful preparation of oligoisobutyl vinyl ethers with ester end-groups. To this end, nucleophilic species, like silyl ketene actals, were employed, having a rate of reaction with carbocations comparable to vinyl ethers. The ester end-groups were obtained as a result of the fast reaction of the primary adducts. Furthermore, to ensure a high level of chain-end functionality, the reaction temperature, monomer concentration, Lewis acids and **SEE 1** concentration were selected with care. Additionally, continuous processes were found to facilitate the undertaking of polymerisations. This method is advantageous mainly because it allows the production of polymer in large quantities in a short time period. Hence, continuous processes are compatible with numerous industry applications. The flow time was reduced whilst the silyl ketene acetal concentration was increased in order to produce oligomers with high levels of ester end-group functionality. What was significant was that oligomers with greater proportions of oligomers with chain ends with ester groups were obtained, particularly at high **SEE 1** concentration and diminished flow time, when polymerisations were conducted with $SnCl_4$ as Lewis acid by comparison to $TiCl_4$. For instance, by contrast to $TiCl_4$, the use of $SnCl_4$ afforded *i*BVE polymerisation greater control at high temperature. In the case where alkylation of the silyl ketene acetal was the primary termination reaction, the reaction conditions were determined with the help of MALDI-TOF mass spectrometry.

6.2.3 Synthesis of difunctional chain end capping agent

The production of 4'-(2-hydroxyethoxy) acetophenone was successful, it was impossible to prepare the target difunctional silyl enol ether with the use of various silyl compounds. A range of bases and solvents were used in the application of triisopropylsilyl chloride. The reaction product was silated solely at the ethoxy position in low yield. Moreover, as shown by mass spectroscopy, a greater mono silated compound yield was obtained with DCM than with THF. The optimal compound was trimethylsilyltrifluoromethanesulfonate which was demonstrated through mass spectral analysis to have the greatest product yield. In spite of this, the target compound could not be produced.

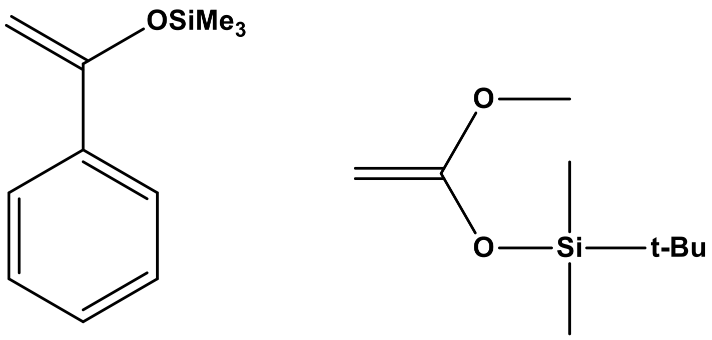
6.2.4 Synthesis of highly branched functional polymers using a new route

Due to the fact that it increases the amount of polymers produced and reduces production time, the continuous reaction was employed instead of the batch method to successfully obtain highly branched functional polymers. In this method, the first monomer is *iso*butyl vinyl ether while the second monomers are DEDVE and DVBz, the reaction occurring in the presence of **SEE 1**. Different Lewis acids were assessed, including $SnCl_4$, $TiCl_4$, ZnI_2, ZnI_2/HI, $Yb(OTf)_3$ and $Sc(OTf)_3$. Of these, only $Sc(OTf)_3$ enabled *i*BVE to be successfully polymerised with DEDVE. The ^1H NMR spectra were applied to the polymerisations to determine side-reactions and monomer conversions, whilst SEC analysis was conducted to calculate molecular weights and dispersities. Under conditions of low **SEE 1** concentration of 0.04 M and high flow rate of 5 ml min^{-1}, it was possible to identify highly branched polymers with chain end-group functionality at a 9:1 monomer ratio. Gelation was observed to occur when the monomer ratio of DEDVE was increased, leading to complete monomer conversions. On the other hand, only the use of ZnI_2/HI and $Sc(OTf)_3$ as Lewis acids allowed *i*BVE to be polymerised with DVBz. The identification of highly branched polymers with optimal end capping was possible under the conditions of low **SEE 1** concentration of 0.04M and 5 ml min^{-1} flow rate and with ZnI_2/HI serving as the Lewis acid. Furthermore, highly branched polymers with ester group functionality were obtained by using $Sc(OTf)_3$ as Lewis acid, high **SEE 1** concentration of 0.06 M and low flow rate of 2 ml min^{-1}. Based on such results, it can be implied that chain end functionality is significantly influenced by the feed rate. Nevertheless, the above-mentioned reaction conditions led to low monomer conversions. When DVBz was polymerised as a second monomer, no gelation took place. Overall, by comparison to previous linear polymers, highly branched polymers were associated with fewer average chain end-groups, emphasising the challenging nature of the task of producing highly branched polymers with high levels of chain end functionality.

6.2 Future work

Chapter 2, *ab initio* cationic polymerisation of methyl vinyl ether and *iso*butyl vinyl ether needs to focus on obtaining a controlled polymerisation in which molecular weight, dispersity and end group functionality are regulated at the same time. This could be further improved by using various Lewis Acids under different conditions. The polymerisation of MVE with $SnCl_4$ and *i*BVE with $TiCl_4$ were only used in this chapter. Looking for other parameters, *ab initio* cationic polymerisation of MVE and *i*BVE are still to be done in the future although all the reactions mentioned above could be repeated with the use of other silyl enol ethers and solvents.

Chapter 3, there is still a lot of work to be done in this area. The continuous process in this thesis describes the preparation of oligoisobutyl vinyl ethers using different Lewis acid, flow times and concentrations of **SEE 1**. The average chain end functionality may still need to be improved through acceptable modifications of the reaction conditions, as well as applying other commercially available silyl enol ethers. It is possible to suggest using Trimethyl-(1-phenyl-vinyloxy)-silane **SEE 2** or 1-(-tert-butyldimethylsiloxy)-1-methoxyethene **SEE 3** as chain end functional groups (see Figure 6.1). Doing this would increase the functionality and would produce polymers with high yield.



SEE 2 **SEE 3**

Figure 6.1: Other functional groups would be used in the future work.

Chapter 4, it is suggested that the alkylation of the ethoxy group may reduce the reactivity of the ketone, although no explanation can be given currently as to why this happens. Further research on a different group may shed new light on the findings obtained.

Chapter 5, this chapter provides evidence in the form of principle data, but much work needs to be done in order to produce an optimised system for the production of highly branched polymers with high end group functionality using silyl enol ethers. The method explained in this thesis for the synthesis of highly branched functional polymers uses a continuous process, as opposed to a batch process. Further analysis using SEC viscometetry is still required. The molecular weight, monomer conversion and average end group functionality still need to be improved; this can be done by trialling further experimental conditions, by using other commercially available silyl enol ethers (such as **SEE 2** and **SEE 3**) or by performing sets of experiments using the batch system at various temperatures. Undertaking such measures may help to prevent gelation and lead to the improved production of highly branched polymers with high degrees of functional end groups.

References

1. Merrifield, R. B.; *J. Am. Chem. Soc.*, **1963**, 85, p. 2149.

2. Cowie, J. M. G.; *Polymers:Chemistry & Physics of Modern Materials,* **1991**: Blackie Academic & Professional, p.436.

3. Thomas, R. M.; Sparks, W. J.; et al., *J. Am. Chem. Soc.*, **1940**, 62, p. 276.

4. Szwarc, M.; Levy, M.; and Milkovich, R.; *J. Am. Chem. Soc.,* **1956**b, 78, p. 2656.

5. Szwarc, M.; *Nature,* **1956**a, 178, p. 1168.

6. Kennedy, J. P.; Feinberg, S. C.; Huang, S. Y.; *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.* **1976**, p. 194

7. Kennedy, J, P.; Chou, R.; *Polym. Prep.* (*Am. Chem. Soc., Div. Polym. Chem.*), **1979**, p. 306.

8. Kennedy, J, P.; et al., *NATO ASI Ser.*, **1987**, p.133.

9. Cloutet, E.; Fillaut, J. L.; et al., *Macromolecules*, **1998**, 31, p. 6748.

10. Matyjaszewski, K.; *Cationic Polymerisations: Mechanisms, Synthesis, and Applications.* In: *Plast. Eng. (N. Y.),* **1996***,* 35.

11. Bui, L.; Nguyen, H. A.; Marechal, E.; *Polym. Bull.,* **1987**, 17, p. 157.

12. Pepper, D. C.; Reilly, P. J.; *J. Polym. Sci.*, **1962**, 58, p. 639.

13. Kennedy, J. P.; Carlson, G. M.; and Riebel, K.; *Polym. Bull. (Berlin)*, **1983**, p. 268.

14. Zsuga, M.; and Kennedy, J. P.; *J. Polym. Sci., Part A: Polym. Chem,* **1991**. p. 875.

15. Mah, H.; Faust, R.; and Zsuga, M.*; et. al.*, *Polym. Bull.,* **1987**, 18, p. 433.

16. Kunitake, T.; and Takarabe, K.; *Macromolecules*, **1979**, 12, p. 1067.

17. Varion, J. P.; Rives, A.; and Bunel, C.; *Macromol. Chem., Macromol. Symp*., **1992**, 60, p. 97.

18. Kennedy, J. P.; and Ivan, B.; *Designed Polymers by Carbocationic macromolecular Engineering: Theoty and Practice*, **1991**a: Hanser Publisher.

19. Lin, C. H.; and Matyjaszewski, K.; *Polym. Prepr. (Am. Chem. Soc.,* Div. *Polym. Chem.)*, **1990**, p. 599.

20. Si, J.; and Kennedy, J. P.; *Polym. Bull. (Berlin)*, **1994**, p. 651.

21. Aoshima, S.; and Kobayashi, E.; *Macromol. Symp*., **1995**, 95, p. 91.

22. Higashimura, T.; and Aoshima, S.; *Macromolecules*, **1989**, 22, p. 1009.

23. Matyjaszewski, K.; in *ACS Symp. Ser.* Cationic Polymerisation Fundamentals and Applications, **1997**, p. 12.

24. Corel, R.; Sauvet, G.; et al., *Macromolecules*, **1976**, 9, p. 931.

25. Evans, A. G.; and Polanyi, M.; *J. Chem. Soc*., **1947**, p. 252.

26. Deng, J. G.; and Peng, Y. X.*; Acta Polymerica Sinica*, **2001**, 3, p. 293.

27. Sawamoto, M.; and Kamigaito, M.; *Macromol. Symp,* **1995**, p. 153.

28. Faust, R.; Ivan, B.; and Kennedy, J. P.; *Journal of Macromolecular Science-Chemistry*, **1991**, 28, p. 1.

29. Deville, M.; *Ann. Chim. Phys.,* **1839**, 75, p. 66.

30. Lin, C. H.; Xiang, J. S.; and Matyjaszewski, K.; *Macromolecules*, **1993**, 26, p. 2785.

31. Katayama, H.; Kamigaito, M.; and Sawamoto, M.; *Macromolecules,* **1998**, 31,

p. 4703.

32. Kamigaito, M.; Maeda, Y.; Sawamoto, M.; Higashimura, T.; *Macromolecules,* **1993**, 26, p. 1643.

33. Hashimoto, T.; Iwata, T.; Minami, A.; Kodaira, T.; *J. Polym. Sci., Part A: Polym. Chem.,* **1998**, 36, p. 3173.

34. Yun, K.; *Organic Chemistry*, **1995**, China advanced education press.

35. Ledwith, A.; Lockett, E.; and Sherrington, D. C.; *Polymer*, **1975**, 16, p. 31.

36. Kwei, T. K.; Nishi, T.; and Roberts, R. F.; *Macromolecules*, **1974**, 7, p. 667.

37. Nishi, T.; Wang, T. T.; and Kwei, T. K.; *Macromolecules*, **1975**, 8, p. 227.

38. Pernecker, T.; Kennedy, J. P.; and Ivan, B.; *Macromolecules*, **1992**, 25, p. 1642.

39. Bae, Y. C.; and Faust, R.; *Macromolecules*, **1998**, 31, p. 2480.

40. Pernecker, T.; and Kennedy, J. P.; *Polymer Bulletin*, **1992**, 29, p. 15.

41. Ohmura, T.; Sawamoto, M.; and Higashimura, T.; *Macromolecules*. **1994**, p. 3714.

42. Hashimoto, T.; Hasegawa, H.; Hashimoto, T.; Katayama, H.; Kamigaito, M.; Sawamoto, M.; Imai, M.; *Macromolecules*, **1997**, p. 6819.

43. Forder, C.; Fatrickios, C.; Armes, S. P.; Billingham, N. C.; *Macromolecules*, **1996**, 29, p. 8160.

44. Vairon, J. P.; and Spassky, N.; *Cationic Polymerisations: Mechanisms, Synthesis and Applications,* 1996, p. 683.

45. Pazur, R. J.; and Greve, H. H.; *Ionic Polymerisations and Related Processes,* **1998**, p. 13.

46. Crivello, J. V.; and Lohden, G.; *Chem. Mater.,* **1996**, 8, p. 209.

47. Crivello, J. V.; and Lam, J. H. W.; *J. Polym. Sci., Polym. Symp.*, **1976**, 56, p. 383.

48. Goethals, E. J.; Reyntjens, W.; and Lievens, S.; *Macromol. Symp*, **1998**, 132, p. 57.

49. Lievens, S. S.; and Goethals, E. J.; *Polym. Int.,* **1996**, p. 277.

50. Tsubokawa, N.; Oyanagi, K.; and Yoshikawa, S.; *Journal of Macromolecular Science--Pure and Applied Chemistry*, **2000**, 37, p. 529.

51. Patrickios, C. S.; Forder, C.; Armes, S. P.; Billingham, N. C.; *J. Polym. Sci., Polym. Chem.*, **1996**, 34, p. 1529.

52. Forder, C.; Armes, S. P.; and Billingham, N. C.; *Polym. Bull.*, **1995**, 35, p. 291.

53. Ebdon, J. R.; *New Methods Polym. Synth.,* **1991**, p. 162.

54. Uraneck, C. A.; Hsieh, H. L.; Buck, O. G.; *J. Polymer Sci.,* **1960**, *46*, p. 535-9.

55. Matyjaszewski, K.; *Effect of Initiators, Lewis acid, Deactivators, Additives and Medium on Controlled/Living Carbocationic System, Huthig & Wepf Werlag, Jug*, **1996**.

56. Winstein, S.; Chlippinger, E.; et al., *J. Am. Chem. Soc.*, **1956**, 78, p.328.

57. Penczek, S.; *Comprehensive Polymer Science, Pergamon Press*, Oxford, **1989**, 3, p.719.

58. Nuyken, O.; Oh, S.; Ingrisch, S.; *ACS Symp. Ser.*, **1997**, 665, p.151.

59. Verma, A.; Nielsen, A.; McGrath, J. E.; Riffle, J. S.; Preparation of ester terminated poly(alkyl vinyl ether) oligomers and block copolymers using a combination of living cationic and group transfer polymerization Polymer *Bulletin,* **1990,** 23, p. 563-570.

60. Fukui, H.; Sawamoto, M.; Higashimura, T.; Multifunctional coupling agents for living cationic polymerization*. I. Sodiomalonate anions for vinyl ethers. Journal of Polymer Science,* **1993,** 31, p. 1531-1542.

61. Fukui, H.; Sawamoto, M.; Higashimura, T.; Multifunctional Coupling Agents for Living Cationic Polymerization.3.Synthesis of Tri- and Tetra-Armed Poly(vinyl ethers) with Tri- and Tetrafunctional Silyl Enol Ethers. *Macromolecules,* **1994,** 27, p. 1297-1302.

62. Fukui, H.; Yoshihashi, S.; Sawamoto, M.; Higashimura, T.; Multifunctional Coupling Agents for Living Cationic Polymerization. 7. Synthesis of Amphiphilic Tetraarmed Star Block Polymers with R-Methylstyrene and 2-Hydroxyethyl Vinyl Ether Segments by Coupling Reactions with Tetrafunctional Silyl Enol Ether. *Macromolecules,* **1996,** 29, p. 1862-1866.

63. Lang, W.; Sarker, P.; Rimmer, S.*;* Cationic polymerization of vinyl ethers in the presence of silyl enol ethers*, Macromolecular Chemistry and Physics,* **2004,** 205, p. 1011-1020.

64. Reetz, M. T.; *Angew. Chem., Int. Ed. Engl.*, **1982**, 21, p. 96.

65. Mukaiyama, T.; Banno, K.; Narasaka, K.; *J. Am. Chem. Soc.*, **1974**, 96, p.7503.

66. Mukaiyama, T.; Hayashi, M.; *Chem. Lett.*, **1974**, p.15.

67. Fukui, H.; Deguchi, T.; Sawamoto, M.; Higashimura, T.; *Macromolecules*, **1996**, p. 1131.

68. Bartl, J., S.; and Mayr, H.; *J. Am. Chem. Soc.*, **1991**, 113, p. 7710.

69. Mayr, H.; and Patz, M.; *Angew. Chem.*, **1994**, 106, p. 990.

70. Lang, W.; and Rimmer, S.; *Macro. Rapid Commun,* **2001**, 22, p. 194.

71. Sarker, P.; *Reactive Polymers by ab initio Cationic Polymerisation*, University of Sheffield, **2003**, p. 65.

72. Sarker, P.; *Reactive Polymers by ab initio Cationic Polymerisation*, University of Sheffield, **2003**, p. 147.

73. Langer, R.; Peppas, N. A.; Advances in biomaterials, drug delivery, and bionanotechnology. *AIChE Journal,* **2003,** 49, p. 2990-3006.

74. Szczubialka, K.; Nowakowska, M.; Response of micelles formed by smart terpolymers to stimuli studied by dynamic light scattering Polymer*,* **2003,** 44, p. 5269-5274.

75. Lang, W.; Sarker, P.; Rimmer, S.; *Macromol. Phys.*, **2004**, 205.

76.Carter, S.; Hunt, B.; Rimmer, S.; Highly branched poly(N-isopropylacrylamide)s with imidazole end groups prepared by radical polymerization in the presence of a styryl monomer containing a dithioester group*, Macromolecules,* **2005,** 38, p. 4595-4603.

77. Stayton, P. S.; Hoffman, A. S.; Murthy, N.; Lackey, C.; Cheung, C.; Tan, P.; Klumb, L. A.; Chilkoti, A.; Wilbur, F. S.; Press, O. W.; Molecular engineering of proteins and polymers for targeting and intracellular delivery of therapeutics. *Journal of Controlled Release,* **2000,** 65, p. 203-220.

78. Hult, A.; Johansson, M.; Malmstrom, E.; *Advances in Polymer Science*; **1999**, 143.

79. Kienle, R.; *J Am Chem Soc.*; **1929**, 51, p. 509–19.

80. Odian G.; *Principles of polymerization*, 3rd ed. New York: Wiley; **1991**, p. 125–132.

81.Flory, P.; Molecular size distribution in three dimensional polymers*. I. Gelation*, *J Am Chem Soc.*; **1941**, 63.

82. Kim, Y.; Webster, O.; *Hyperbranched polyphenylenes*, **1988**, 29.

83. Frechet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B.; Self-Condensing Vinyl Polymerization - *an Approach to Dendritic* Materials. *Science,* **1995,** 269, p. 1080-1083.

84. Baskaran, D.; *Synthesis of Hyperbranched Polymers by* Anionic Self-Condensing Vinyl Polymerisation. *Macromolecular Chemistry and Physics,* **2001,** 202, p. 1569-1575.

85. Wang, Z.; He, J.; Tao, Y.; Yang, L.; Jiang, H.; Yang, Y.; *Macromolecules*, **2003**, 36, p. 7446.

86. Carter, S.; Hunt, B.; Rimmer, S.; *Macromolecules,* **2005***,* 38.

87. Carter, S.; England, R.; Hunt, B.; Rimmer, S.; *MacromolBiosci,* **2007***,* 7.

88. Flory, P. J.; Principles of Condensation Polymerization*, Chemical Reviews,* **1946,** 39, p. 137-195.

89. Stockmayer, W. H.; *Journal of Physical Chemistry,* **1943,** 11, p. 45.

90. Gordon, M.; Roe, R. J.; *Journal of Polymer Science,* **1956,** 21, p. 27-75.

91. Ulbrich, K.; Dusek, K.; Ilavsky, M.; Kopecek, J.*;* Preparation and properties of poly(N-butylmethacrylamide) networks, *European Polymer Journal,* **1978,** 14, p. 45-49.

92. Okay, O.; Formation and structural characteristics of loosely crosslinked styrene-divinylbenzene networks*, Mackromolekulare Chemie,* **1988,** 189, p. 2201-2217.

93. Wu, K. J; and Odom, R. W.; *Anal. Chem.* **1998**, p. 456.

94. Tanaka, K.; Waki, H.; Ido, Y.; Akita, S.; Yoshida, Y.; Yoshida, T.; *Rapid Commun. Mass Spectrom.,* **1988**, 2, p. 151.

95. Danis, P. O.; Karr, D. E.; et al., *Rapid Commun. Mass Spectrom*., **1996**, 10, p. 82.

96. Wu, K. J.; and Odom, R. W.; *Anal. Chem.* **1998**, p. 456.

97. Carter, S.; Rimmer, S.; Sturdy, A.; Webb, M.; *Macromol. Biosci,* **2005**, 5, p. 373-378.

98. Carter, S.; Rimmer, S.; Rutkaite, R.; Swanson, L.; Fairclough, J.; Sturdy, A.; Webb, M.; *Biomacromolecules*, **2006**, 7, p. 1124-1130.

99. Collett, J.; Crawford, A.; Hatton, P, Geoghegan, M.; Rimmer, S.; *J. Roy. Soc.-Interface*, **2007**, 4.

100. Rimmer, S.; Carter, S.; Rutkaite, R.; Haycook, J.; Swanson, L.; *Soft Matter*, **2007**, 3.

101. Hopkins, S.; Carter, S.; Haycock, J.; MecNeil, S.; Fullwood, N.; Rimmer, S.; *Soft Matter*, *Chem*, **2007**, 17.

102. Hopkins, S.; Carter, S.; Haycock, J.; MecNeil, S.; Fullwood, N.; Rimmer, S.; *Soft Matter*, **2009**, 5.

103. Shepherd, J.; Sarker, P.; Swindells, K.; Douglas, I.; MacNeil, S.; Swanson, L.; Rimmer, S.; *J. Am. Chem. Soc.*, **2010**, 132.

104. Shepherd, J.; Sarker, P.; Swindells, K.; Douglas, I.; MacNeil, S.; Swanson, L.; Rimmer, S.; *Biomaterials*, **2011**, 32.

105. Shepherd, J.; Shepherd, J.; Swindells, K.; Douglas, I.; MacNeil, S.; Swanson, L.; Rimmer, S.; *Biomaterials*, **2011**, 12.

106. Carter, S.; Hunt, B.; Rimmer, S.; *Macromolecules,* **2005***,* 38.

107. Carter, S.; England, R.; Hunt, B.; Rimmer, S.; *MacromolBiosci,* **2007***,* 7.

108. Lang, W.; Rimmer, S.; *Macromol. Rap. Comm.*, **2001**, 22.

109. Lang, W.; Sarker, P.; Rimmer, S.; *Macromol. Phys.*, **2004**, 205.

110. Sarker, P.; Rimmer, S.; Macromol. *Chem. Phys.,* **2005**, 206.

111. England, R.; Rimmer, S.; *Chem. Commun.,* **2010***,* 46.

112. Misra, G. S.; *Introduction of Polymer Chemistry*, New Age Int. Ltd., New Delhi, **1997**, p. 48.

113. Ando, T.; Kamigaito, M.; Sawamoto, M.; *Macromolecules*, **1998**, 31, p. 6708.

114. Sawamoto, M.; Kanaoka, S.; Omura, T.; Higashimura, T.; *Polym. Prepr. (Am. Chem.Soc., Div. Polym. Chem.).* **1992**, p. 148.

115. Sawamoto, Mitsuo.; *Controlled polymer synthesis by cationic polymerization,* **1996**, 35, p. 381-436.

116. Higashimura, T.; Mitsuhashi, M.; Sawamoto, M.; *Macromolecules*, **1979**, p. 178.

117. Armarego, W. L. F.; *Purification of Laboratory Chemicals Book*, **1998**.

118. Bae, Y.C.; Faust, R.; *Macromolecules*, **1998**, 31, p. 2480.

119. Vogel, A. I.; *Text Book of Quantitative Inorganic Analysis*, Longman, 2nd Edn., 1972, p. 266.

120. Sarker, P.; *Reactive Polymers by ab initio Cationic Polymerisation*, University of Sheffield, **2003**.

121. Sperling, L. H., *Introduction to physical polymer science*. 4th ed.; Wiley Interscience: **2006**.

122. Lang, W.; Synthesis of Oligo(Vinyl Ether)s in ab initio cationic polymerisation, University of Sheffield, **2002**.

123. Alexei, R.; Sergei, K.; Francois, G.; *Polym. Chem.,* **2013**, 4, p.1883-1892.

124. Than, N.; Noh, S.; Lee, D.; *Polymer Science*, **2008**, 5, p. 611-620.

125. Clayden, J.; Greeves, N.; Warren, S.; *Organic Chemistry Book*; **2001**.

126. O'Brien, N.; McKee, A.; Sherrington, D. C.; Slark, A. T.; Titterton, A.; *Facile, versatile and cost effective route to branched vinyl polymers,* **2000,** 41, p. 6027-6031.

127. Frechet, J. M. J.; Henmi, M.; Gitsov, I.; Aoshima, S.; Leduc, M. R.; Grubbs, R. B.; Self-Condensing Vinyl Polymerization - *an Approach to Dendritic Materials Science,* **1995**, 269, p. 1080-1083.