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*Cationic Ring Opening
Polymerisation (CROP) of oxetane
and its derivatives using oxonium
derived initiators.*

By

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A Thesis Submitted for Degree

Of

Doctor of Philosophy

Of

The University of Aston in Birmingham

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The University of Aston in Birmingham
The Cationic Ring Opening Polymerisation (CROP) of oxetane and its derivatives
using oxonium ion initiators
David Bray
PhD 2009

Summary

Several cationic initiator systems were developed and used to polymerise oxetane with two oxonium ion initiator systems being investigated in depth. The first initiator system was generated by the elimination of a chloride group from a chloro methyl ethyl ether. Adding a carbonyl co-catalyst to a carbocationic centre generated the second initiator system. It was found that the anion used to stabilise the initiator was critical to the initial rate of polymerisation of oxetane with hexafluoroantimonate resulting in the fastest polymerisations. Both initiator systems could be used at varying monomer to initiator concentrations to control the molecular number average, \overline{M}_n , of the resultant polymer.

Both initiator systems showed 'living' characteristics and were used to polymerise further monomers and generate higher molecular weight material and block copolymers.

Oxetane and 3,3-dimethyl oxetane can both be polymerised using either oxonium ion initiator system in a variety of DCM or DCM/1,4-dioxane solvent mixtures. The level of 1,4-dioxane does have an impact on the initial rate of polymerisation with higher levels resulting in lower initial rates of polymerisation but do tend to result in higher polydispersities. The level of oligomer formation is also reduced as the level of 1,4-dioxane is increased.

3,3-bis-bromomethyl oxetane was also polymerised but a large amount of hyperbranching was seen at the bromide site resulting in a difficult to solvate polymer system.

Multifunctional initiator systems were also generated using the halide elimination reactions with some success being achieved with 1,3,5-tris-bromomethyl-2,4,6-tris-methyl-benzene derived initiator system. This offered some control over the molecular number average of the resultant polymer system.

Keywords; Oxetane, Cationic-Ring-Opening-Polymerisation (CROP), 3,3-dimethyl oxetane, 3,3-bis-bromomethyl oxetane, block copolymers, multifunctional initiators

I dedicate this work to my wife Annmarie

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I would like to express my sincere gratitude to my supervisor Dr Allan Amass who has helped me and guided me through this work. I would also like to thank Dr Mike Wilson and Dr Dave Walton for their patience in teaching me how to run NMR and MALDI-TOF samples.

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Chapter 1

Aims and Objectives

1.1 Aims.

The aim for the project is to synthesise a new binder system that is stable for an extended period of time and that are completely stable with plasticizers such as nitroesters^[1-3].

1.2. Objectives.

To produce new routes to synthesise oxetane-based polymers, for use in high energy binder systems. The new system must be able to bind the explosive without impairing the energy release when the explosive is used. The polymer must not contain volatile components or be too 'soft'.

1.3. Project Brief.

Polymer bonded explosives currently have three main components^[4], these being the granular explosives, binder and additive (typically plasticizers). The resultant composition gives rise to good overall properties but there are still a few drawbacks with the system.

Currently, the binder used is based on a hydroxyl terminated polybutadiene crosslinked with isocyanate and has good binding properties. This system however, needs to be plasticized to improve its rheological properties. As with most plasticizers, the ones used tend to migrate out of the matrix over a period of years leaving the composition prone to cracking. These cracks, once formed, can result in a possible interface where an energy discharge can be released causing unpredictability and reduced reliability in the resulting composition.

Oxetane-based polymers have an intrinsically low glass transition temperature and are compatible with plasticizers that are commonly used^[5-14]. This has a two-fold effect; the first is that less plasticizer is needed and the second that less will migrate from the system. By investigating the polymerisation of oxetane and its derivatives, it is hoped that a good replacement binder system can be found increasing the lifetime of the explosive material.

1.4. Project Background.

Polymer bonded explosives (PBX) are more complex systems than the traditional explosives such as trinitrotoluene (TNT). They have several key advantages and are now used in most high performance applications such as missile warheads, bombs, underwater mines, shaped charges and shells.

The main reasons why PBX are so widely used is due to their better performance in terms of reduced threat (burn in a uniform and smooth way), increased life time of product, improved and more controlled processing and enhanced reliability of the system.

PBX is produced by the incorporation of granules of explosive such as 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) or 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) into a plasticised polymeric material. There are several preferred materials used to produce the PBX. Currently a system that uses polybutadiene crosslinked with isocyanate as a binder is used. This binder has rubber-type properties and is plasticised with nitroester-type compounds to modify its properties. This system has a good overall performance but the inclusion of the plasticiser does cause several problems such as reduced performance due to migration of the plasticiser for example.

Current work in the area of energetic polymers is directed towards producing PBX, which contains polymer binder systems that add to the explosive effect of the system. This means that research has been directed towards polymer systems that are energetic, requiring the polymers to have the following properties: low polydispersity (PD), bifunctionality and low glass transition temperatures (T_g 's).

Owing to these requirements, oxetane and its derivatives have been used as starting materials as they tend to exhibit most of these properties once they have been polymerised. In order to improve the system, copolymers have been synthesised to increase the energetic component whilst still maintaining a low T_g . Varying copolymer structures have been studied, such as random, di and tri block as well as hyper-branched systems. The tri-block system ABA shows good promise, as

sequential addition of 'hard' (high energy, high T_g) ends to a 'soft' (low T_g) section can potentially produce the desired properties^[15-16]. A major problem with producing these copolymers is that the polydispersity of the resultant polymer tends to be larger. Due to this increase, the performance and processability of the polymer is reduced.

One of the most effective ways of producing multifunctional polymers is by using a living polymerisation pathway as the polymer structure can be easily controlled. Living polymerisations^[17-22] have been used to produce polymers of varying physical structure, improve the variety of functionality and retain low PD of the polymers synthesised. The main feature of a living polymerisation is that there are no termination or transfer steps.

Chapter 2

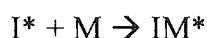
Background Information

2.1. Polymerisations.

Polymers are long chain molecules made up of small chemical units (monomers)^[23-24]. Copolymers^[25] are polymers that contain more than one type of monomer unit. The reactions in which the monomer or monomers combine are either polymerisation or a copolymerisation respectively.

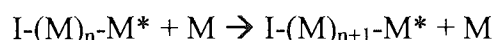
Since the first polymerisation, many techniques have been developed to produce new types of polymers. Although there are many methods of production, they can all be broken down into two classes. This was first done by Carothers who classified the polymers into either addition or condensation types. Flory^[24] who noted the difference in the mechanism in which the polymers were formed then modified these distinctions. These two mechanisms are now described as either step or chain polymerisations.

Chain polymerisation proceeds by a large number of monomer units adding sequentially to the growing active centre via a chain reaction. For a successful chain polymerisation to occur, several steps have to take place and are normally as follows;
Initiation The active centre (which acts as the chain carrier) is activated.



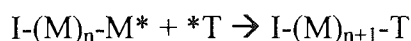
Where I^* is activated initiator and M is the monomer and $-M^*$ is the active chain end of the polymerisation

Propagation The addition of the monomer to the active centre.



Where $(M)_n$ represents many repeating monomer units in a chain $(M)_{n+1}$ denotes the chain gaining one more monomer or repeat unit.

Termination The active chain is terminated.



Where T is the terminating group.

Many types of chain polymerisation have been devised and include free radical^[26], ionic (cationic and anionic)^[27-28], ring opening^[29], co-ordination (Ziegler-Natta)^[30], ring opening metathesis^[31] and group transfer mechanisms. Polymers such as

polyethylene, polypropylene, PVC, PVA and polystyrene can be synthesised by chain polymerisation.

Step-growth polymerisations unlike chain polymerisations proceed by reactions in which each bond in the polymer is formed independently of the others. The step-growth of polymers is normally via a chemical reaction between two difunctional reactants. Step-growth polymerisations are used for the synthesis of some common materials such as polyesters, polyamides and polyurethanes.

2.2. Ring Opening Polymerisations

Ring opening polymerisations usually proceed via an ionic polymerisation mechanism such as cationic^[32], anionic or a co-ordinate anionic. The most common of these mechanisms is via cationic polymerisation and will be discussed later. There are many factors to consider when performing a ring opening polymerisation. These specifically include the degree of ring strain^[33] in the starting monomer, nucleophilicity of monomer^[34], solvent effects, counter-ion interactions, initiation mechanism, temperature, electronic and steric effects on the monomer^[25].

2.2.1 Ring Strain

The total ring strain and conformation of a cyclic molecule is determined by several factors such as angle strain, torsional strain and steric strain.



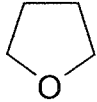
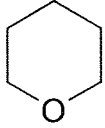
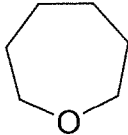
Molecules will adopt their lowest energy conformation taking into account the following^[35].

- Angle Strain; caused by the expansion or compression of angles.
- Torsional Strain; caused by eclipsing of orbitals of neighbouring atoms.
- Steric strain; caused by repulsive interaction when atoms are too close to each other.

By comparing the following series of cyclic ethers, it can be understood that ring strain is an important factor for the degree of polymerisation and rate at which a polymerisation will occur as shown in figure 2.1.

Fig 2.1

Ring strain and calculated enthalpies of reaction with various cyclic ethers^[25]

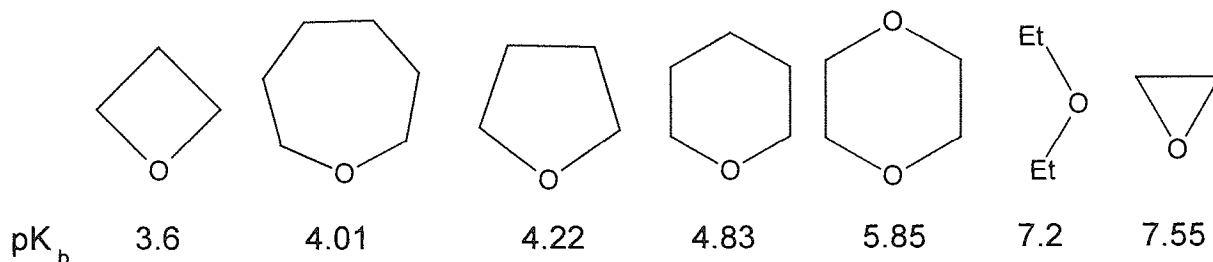
Structure					
Ring strain kJ/mol	114	107	23	5	42
Enthalpy of polymerisation $-\Delta H_p^\circ$ kJ/mol	95	81	15	0	34

The ring strains for the oxirane and oxetane monomers are very similar but the enthalpy of polymerisation is significantly lower for the former.

2.2.2 Basicity of Monomer

When considering if a monomer can be polymerised cationically, the reaction site on the monomer must be the most basic point on the molecule. For cyclic ethers such as oxetane the reaction site is at the carbon-oxygen bond. The oxygen atom in molecules such as oxetane and its derivatives is the most basic point in the monomer. The nucleophilicity of the monomer can have an effect on its polymerisability with competitive reactions occurring through other nucleophilic centres in the reaction. These centres can be from the polymer chain itself in the form of linear ether groups or side groups as well as end groups. Due to these competing centres of nucleophilicity, transfer and side reactions occur, generating cyclic oligomers and other products. The nucleophilicity of the monomer can be estimated by measuring its pK_b value with the lower value representing greater basicity. From fig 2.2 it can be seen that the basicity of oxetane (pK_b 3.6) is greater than that of oxirane (pK_b 7.6) and of linear ethers such as ethyl ether (pK_b 7.2). This indicates that oxetane will preferentially undergo chain growth resulting in high molecular weight polymer systems with some formation of cyclic ethers^[36].

Fig 2.2
pK_b of various cyclic and linear ethers



In comparison to the polymerisation of oxetane, oxirane has a substantially lower basicity and as such can generate high levels of side products such as 1,4-dioxane resulting in lower molecular weight polymers.

2.2.3 The Solvent

The solvent plays an important role in the process, because it determines to a large extent the separation of the counterion from the chain carrier^[25, 37]. One of the main properties that determine the rate of propagation is the solvent dielectric constant, which is related to the solvent polarity. Due to the large ionic character of the chain carrier and the counterion, the more polar the solvent the faster the rate of polymerisation. This can be shown effectively by studying solvent systems with varying dielectric constants shown in table 2.1 for the polymerisation of styrene initiated using HClO₄.

Table 2.1

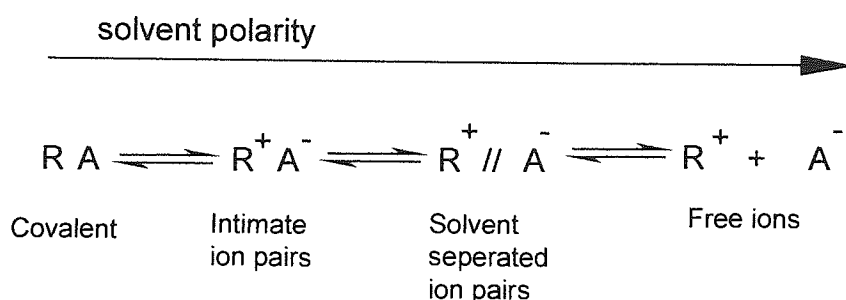
Rate of propagation for the polymerisation of styrene using solvent systems of varying dielectric constants.

Solvent System	Dielectric constant	$\frac{k_p}{\text{dm}^{-3} \text{ mol}^{-1} \text{ s}^{-1}}$
CCl ₄	2.3	0.0012
CCl ₄ + CH ₂ Cl ₂ (40/60)	5.2	0.4
CCl ₄ + CH ₂ Cl ₂ (20/80)	7.0	3.2
CH ₂ Cl ₂	9.72	17.0

From table 2.1, it is evident that the choice of solvent system has a profound effect on the polymerisation. The propagation of polymerisations largely depends on the association of the counterion to the chain carrier. By increasing the polarity of the solvent, the separation of the two ions also increases, allowing for a more rapid propagation to take place as shown by figure 2.3.

Fig 2.3

Solvent polarity effect on ion pair association



As the separation increases between the ions, then the ion's characteristics change. In a low polar solvent, they are intimate ion pairs and associated to each other closely. These are more stable and therefore the rate of propagation is slower. When they are separated by the effect of a polar solvent, they adopt a stronger free ion characteristic and are more reactive. By increasing the separation of the ions, steric effects (from the counterion) are reduced, contributing to the increased rate of propagation.

2.2.4 Counterions

Many cationic polymerisations are initiated by using one or more species illustrated in figure 2.3, where R^+ is the chain carrier and A^- is the counterion. The counterion is of critical importance and if the wrong one is used, then the rate of polymerisation and the yield of the resulting polymer can be very low^[25, 38]. The counterion must be mobile and follow the active end. It must also be stable so as not to cause any side reactions. Counterions that are used regularly are BF_3OH^- , SbF_6^- , PF_6^- in addition to many others^[39-43]. The size of the ions and their charge density are important for if they have a high charge density, it is more difficult to separate them from the chain

carrier. Therefore, the polymerisation rate is too low. Contrastingly, if they are too large, there is no stabilisation and a highly polydisperse polymer is generated.

2.3 Cationic Initiators Used for the Polymerisation of Cyclic Ethers

There have been many cationic initiators reported that have been used to polymerise various monomers containing vinyl^[44] or cyclic ether^[45-51] functional groups. There have been many different mechanisms that have been used to initiate the polymerisation of cyclic ethers with some of them discussed below.

- Systems include Friedel-Crafts initiators such as BF_3 , AlBr_3 , SbF_5 , SnCl_4 and FeCl_3 have been used but require trace co-initiators such as H_2O or HX in order to work^[52-54]. The system then forms an oxonium ion with the monomer that can then lead to propagation and high molecular weight products.

One common example of this is the addition of boron trifluoride to water to a cyclic monomer solution as shown in fig 2.4.

Fig 2.4

Formation of oxonium ion with BF_3

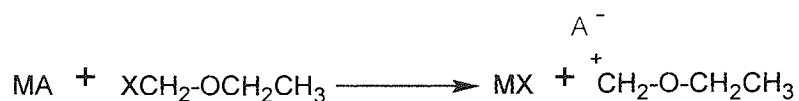


- Other systems that have been used to polymerise cyclic ethers include protonic acids or their derivatives, oxonium salts and oxycarbonium systems.
- Aluminium alkyls (AlR_3)^[55] which are Lewis acids have been used to polymerise oxetane based systems and normally require the presence of water to be active.

Another system that has been used recently is the formation of the oxonium ion by adding the product from the elimination of a halide ion from a halogenated methyl ethyl ether compound as shown in figures 2.5 and 2.6.

Fig 2.5

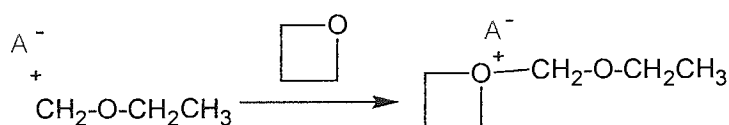
Formation of a cation using elimination of halogenated methyl ethyl ether compound.



By adding the product from figure 2.5 to a cyclic ether an oxonium ion is formed which can then lead to the initiation of the polymerisation

Fig 2.6

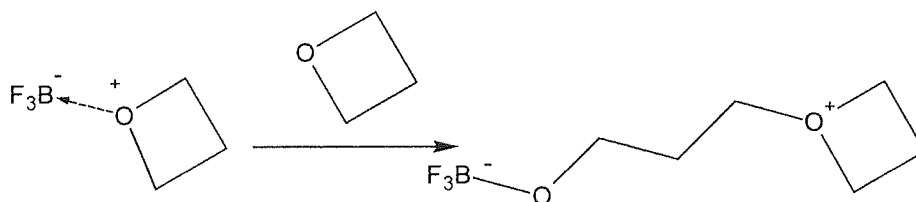
Formation of an oxonium ion initiator.



- It has been seen from fig 2.4-2.6 that an anion is needed to stabilise the charge of the oxonium ion but by using zwitterionic initiation mechanism none is required, as shown in figure 2.7.

Fig 2.7

Initiation of oxetane involving a zwitterion

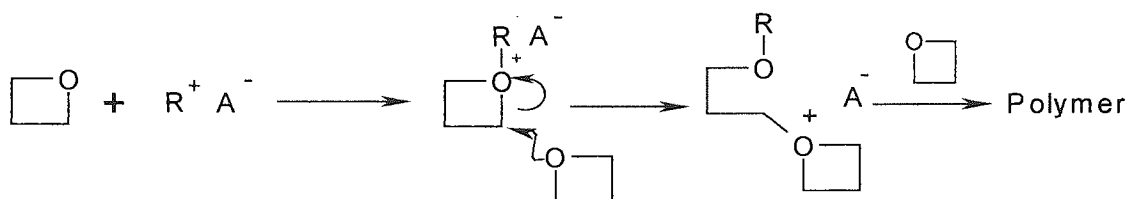


2.3.1 Mechanisms for CROP Polymerisations of Oxetane

There have been many reported reactions for the polymerisation of oxetane. These can be broken down into two main classes of mechanism. These mechanisms are either a $\text{S}_{\text{N}}1$ type, through a α -cleavage or an $\text{S}_{\text{N}}2$ type through a β -cleavage.

The $\text{S}_{\text{N}}2$ substitution type ring opening mechanism involves the interaction of the catalyst system with the monomer to form an oxonium ion. This then acts as an initiating species. Propagation then occurs via a $\text{S}_{\text{N}}2$ type reaction as shown in figure 2.8.

Fig 2.8
S_N2 scheme for the propagation of oxetane.



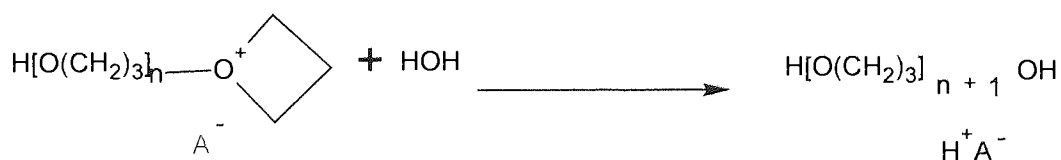
2.3.2 Termination of CROP systems

There are several possible reactions that have been reported^[27, 34, 57, 61], which act as termination reactions during the polymerisation of oxetane. These mechanisms can be divided into the following;

- Transfer reactions with contaminants

A major contaminant in many polymerisation reactions is water and is used in some systems as a co-catalyst such as BF₃ initiated systems as shown in figure 2.9.

Fig 2.9
Chain transfer termination reaction with water



When the concentration of water or alcohol is increased, a reduction in the molecular weight is observed.

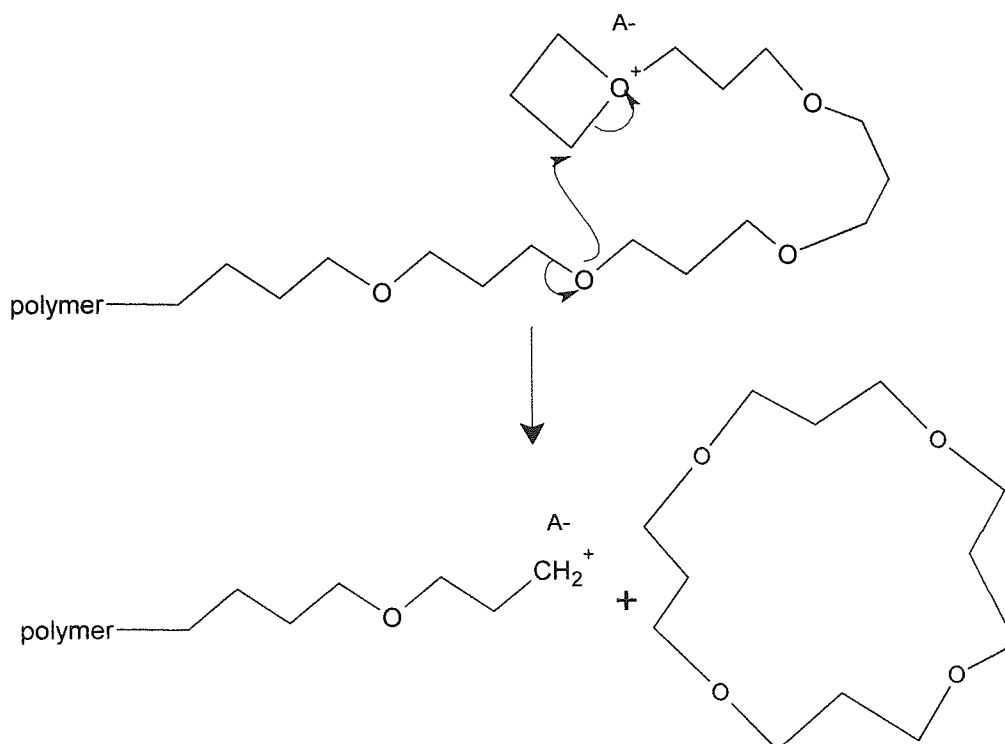
- Intramolecular transfer

The polymer chain propagates via an active chain end mechanism where the growth occurs at the cationic end. This active chain end can also undergo transfer mechanisms with itself, for example, of backbiting reactions. The backbiting reaction shown in figure 2.10, generates cyclic oligomers which are characterised as low

molecular weight fragments. In addition to the cyclic oligomers that are formed during this process, a new initiation centre is generated in the form of a carbonium ion which can go on to form a new oxonium ion by coupling with another oxetane molecule.

Fig 2.10

Intramolecular transfer of a cationic oxetane polymerisation generating a cyclic oligomer and new active chain end



2.4 Controlled and Living Polymerisations

2.4.1 Living Polymerisations

There have been many reported polymerisations of various monomers that have synthesised using a living system. There have also been copious definitions of the terms ‘living’ polymerisation systems. This resulted in a paper being published in 2000 by T. Darling et al, which attempted to address the issue^[56], focusing on living radical polymerisations.

Szwarc^[57] made the distinction between dead and living systems (due to them being) “able to grow whenever additional monomer is supplied”. This definition allows for various interpretations of polymer systems that could be considered living or non-

living. Typically, living systems have fast rates of initiation, which in turn results in narrow polydispersities of such systems. There are however, several reported systems such as that of the polymerisation of butadiene initiated by *n*-butyl lithium, which has a slow rate of initiation and as such; a high polydispersity but has other attributes that are living in characteristic.

2.4. Controlled Polymerisations

There are polymerisations that can be carried out which generate polymer systems with a high polydispersities. These systems are generally classed, as uncontrolled polymerisations with the molecular number average, \bar{M}_n , of the polymer chain not growing linearly as the monomer is consumed. This uncontrolled growth leads to polymer chains with a wide variety of molecular weights and a high polydispersity. Controlled polymerisations can be identified as systems that have a \bar{M}_n growth consistent with that of monomer conversion resulting in low polydispersities.

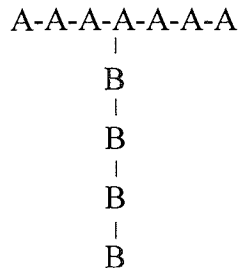
The use of various counterions can have a significant impact on the transfer reactions during the course of polymerisation of cyclic ethers and influences the control of the system. The use of counterions such as SbF_6^- may reduce the transfer reactions but have little control over the, \bar{M}_n , or PD of the system. The uses of additives have been used to reversibly end-cap the growing chains and offer control over the polymerisations. It has been proven previously^[34] that the use of 1,4-dioxane can be used to slow the rate of propagation and generate polymers with low polydispersities and lower levels of cyclic ether compounds.

2.5. Copolymers

Copolymers^[58] are polymers that are made from more than one type of monomer unit (represented as A and B) and can yield several types of polymeric structure depending on the method used to produce them. These polymeric structures can be classed as;

- Random copolymers have a structure with a random arrangement of monomer positioning such as ABAAABBABABBABBA

- Block copolymers have a structure where a sequence of one monomer type occurs followed by a sequence of the other monomer such as AAAABBBBBAAAA
- Graft copolymers have a structure where a chain is made up from one monomer with a side chain made up of the other monomer.



- Alternating copolymers have a structure of regular repeating structure such as ABABABABAB.
- Dendrimers are polymer and copolymer systems that have a novel architecture where the chains are arranged in branched configuration.

Copolymers are normally produced to offer enhanced properties than their respective component homopolymers. Common examples are; styrene copolymerised with methyl methacrylate resulting in better heat resistance. Vinyl acetate is copolymerised with polyethene for enhanced flexibility. Vinyl acetate is copolymerised with vinyl chloride resulting in a copolymer that has enhanced processability.

Copolymers are used in wide variety of products as they exhibit a combination of their components better properties. Simple blending of the materials often result in less beneficial properties due to the potential phase separation and incompatibility of the polymer constituents.

2.5.1. Random Copolymers

Random copolymers can be made via various mechanisms such as free radical or CROP. The properties of random copolymers are varied by the ratio of the component monomers such as vinyl acetate and vinyl chloride. Vinyl acetate homopolymers are used in adhesives where vinyl chloride homopolymers are used as rubber substitutes (with plastisizer addition). When a copolymer comprising of 10% vinyl acetate and

90% vinyl chloride is prepared, a system with good strength and solvent resistance is made.

The monomers used in random copolymerisations rarely have the same reactivity and as such, the resultant system can vary from the initial ratio fed into the reaction.

Random copolymers can be made via CROP mechanism. This can be done by introducing a mixed feed of monomer solution to a reaction vessel followed by the initiator. The resultant composition will be dependent on the reactivity ratios of the monomers used and the molar ratio added.

2.5.2. Block Copolymers

Block copolymers consist of two or more long linear sequences of different monomers. They can be prepared from living chain polymerisation, step growth or from macro-initiator systems. Typically diblock, triblock and sandwich systems are used to generate unique properties. A common diblock system that is prepared is that comprising of polyurethane and polyether components. This diblock results in a hard crystalline segment (from polyurethane) and a soft rubber segment (from the polyether), and is used in products such as 'Spandex'. A common triblock copolymer ABS (acrylonitrile, butadiene, and styrene) has very good mechanical properties and chemical resistance. Effective examples of sandwich polymers are those comprising of styrene and butadiene components.

Block copolymers can be prepared via a CROP mechanism by relying on the living characteristics of the system. The initial monomer can be polymerised and an additional second monomer added after the initial monomer is consumed.

2.5.3 Graft Copolymers

Graft copolymers tend to be made of blocks of polymers grafted onto a backbone of another polymer and can have similar properties to those of block copolymers.

2.5.4 Alternating Copolymers

Alternating copolymers are completely regular in structure and in general are difficult to produce via addition and ring opening mechanisms.

2.5.5 Dendrimer Systems

Dendrimers are polymers of novel architecture that can be made up of several short chains linked together in an array. They differ from conventional linear polymers as they have more terminal groups and vary in physical structure. These methods can be grouped into two classes, branching from a central core or coupling short chains with multifunctional coupling agents. Mathias et al ^[59] reported that dendrimers have different physical properties from their corresponding linear relatives. The main differences, which have been noted, are the solvation and rheological properties of dendrimers compared to linear systems and the effects of temperature. These differences have been attributed to hyperbranching, a second functional group resulting in branching and resulting in differing properties. During the anionic polymerisation of 3-ethyl-3-hydroxymethyl oxetane, the pendant hydroxyl groups were a source of multiple, branching resulting in the type dendrimer system.

Chapter 3

Experimental Procedures

3.1 Purification Techniques of Raw Materials

3.1.1 Vacuum Line Distillation and De-aeration

This technique was used to purify liquids with boiling points up to around 180°C at atmospheric pressure (figure 3.1). The technique works by using lowered pressure to vaporise a dried liquid and then condensing it into another clean vessel, being cooled with liquid nitrogen^[33,34, 60]. Owing to the low pressures, no heating was required. Separation occurred between the liquid and any drying agents that have been used. Typically, calcium hydride, anhydrous magnesium sulphate or molecular sieves are used as drying agents. The technique is particularly suited for solvents and monomers but for some particularly high boiling point materials vacuum distillation is required. Once the materials were purified they were stored in Schlenk flasks under a dry and inert atmosphere such as argon filled glove box as shown in figure 3.3.

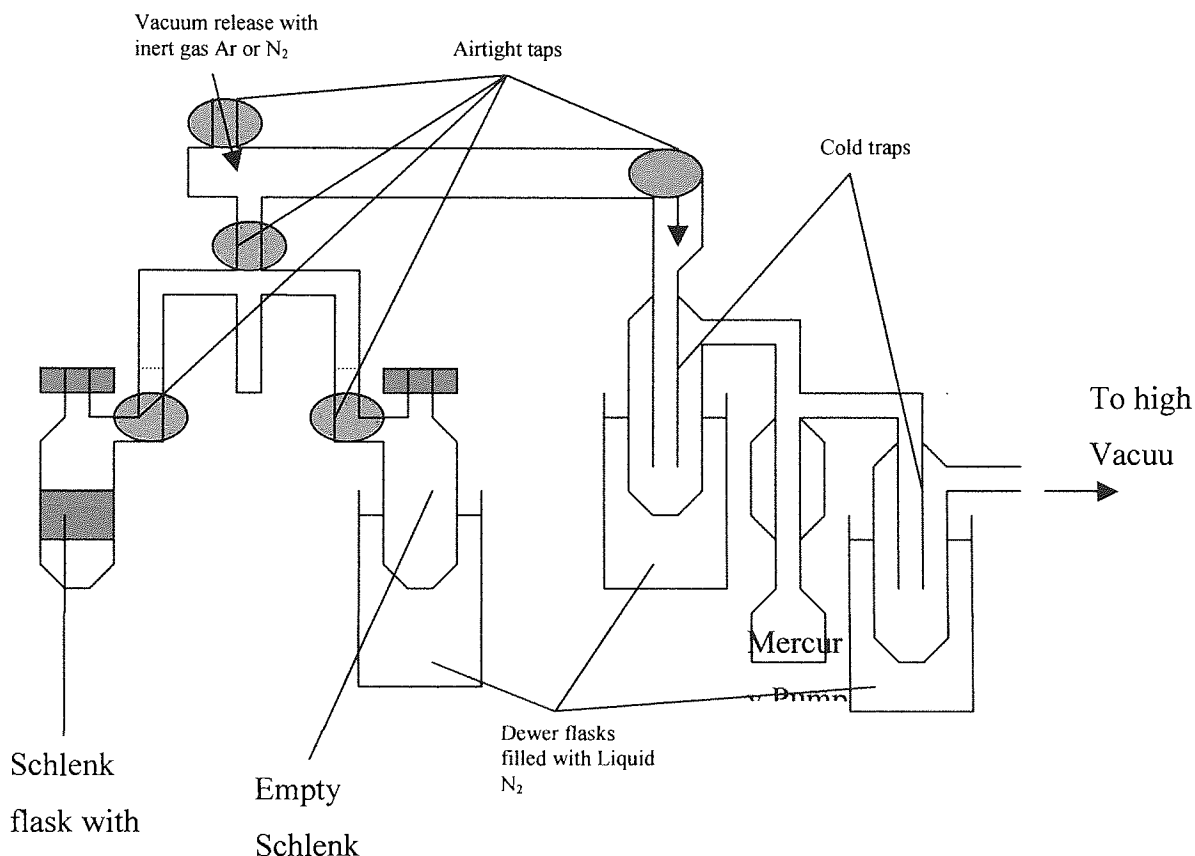
Initiators that were made for the project were sensitive to both moisture and air. The drying agents were used to remove the moisture from the starting materials, which were then purified by distillation. The distillation process did not remove the dissolved oxygen from the liquids. The dissolved oxygen can potentially react with the initiator, reducing its efficiency to eliminate the dissolved oxygen from the reaction, de-aeration was carried out on the solvents and monomers. The Schlenk flask containing the dried liquid was attached to the vacuum line and cooled using liquid nitrogen. Whilst the liquid was freezing, an inert gas was fed into the Schlenk flask. Once the liquid was frozen, the inert gas flow was turned off and the vacuum line opened to the liquid. After 10 minutes, the vacuum tap was closed and the inert gas tap re-opened. The liquid nitrogen dewer was removed and the liquid left to thaw. Once the liquid had melted, the nitrogen dewer was reapplied to refreeze the liquid. The flask was then evacuated again by closing the inert gas tap and opening the vacuum tap. This process was repeated several times ensuring that there was no dissolved oxygen in the liquid.

Solids could also be degassed using the vacuum line^[33,34, 60]. The solid (such as AgSbF₆) to be degassed was placed in a Schlenk flask (in a glove box) and transferred to the line. The vacuum tap was then opened and allowed to degas the solid for

several minutes. The inert gas line was then opened allowing an inert gas flow for several minutes. The gas was then evacuated and the process repeated several times.

Fig 3.1

The vacuum line used to degas, purify and transfer liquids under an inert atmosphere.



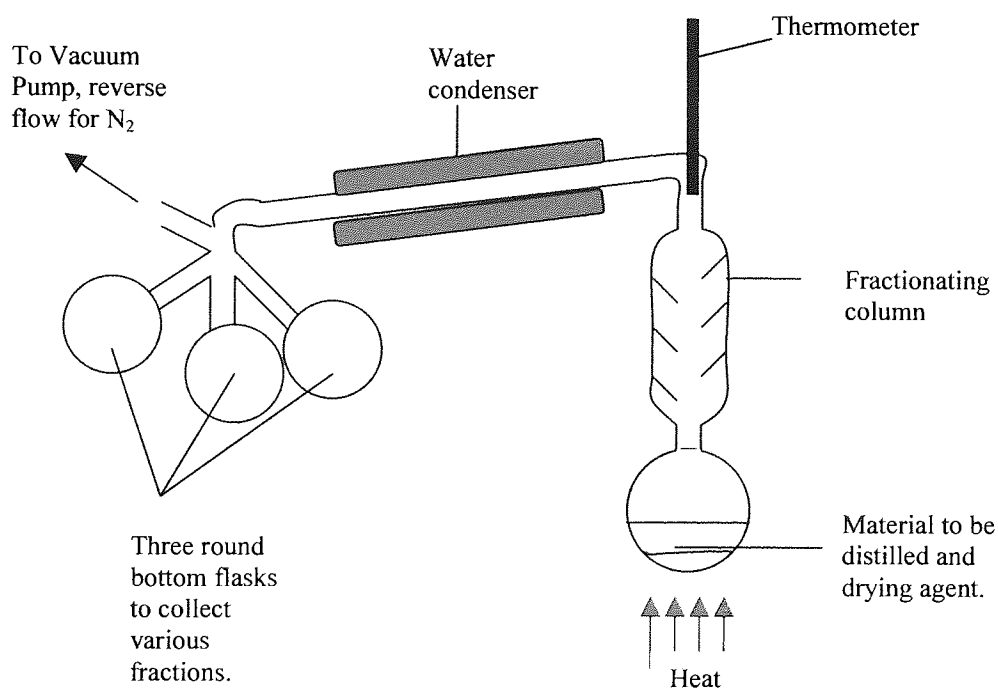
3.1.2 Vacuum Distillation

Vacuum distillation (figure 3.2) was used to purify materials that have high boiling points. The material (such as monomers) to be purified was placed in a clean dry conical flask and connected to a fractionation column, condenser, pig (three-way separator) and three conical flasks^[33,34, 60]. These conical flasks were used to collect the distillate fractions and stoppered as soon as the distillation was complete. The pig had an airline attached to it with two separate lines attached. The first line attached was connected to a vacuum pump. The second line was connected to a dry nitrogen gas feed, to allow for an inert gas to be introduced at the end of the distillation.

The vacuum distillation line was evacuated using a pump, whilst being heated to remove any remaining moisture. Heat was applied to the stock solution (such as monomer and drying agent) using an electric heating element and allowed to reach boiling temperature. The distillates were collected into their respective conical flasks, using changes in temperature to determine when to change collection flask. Once the distillation was complete, the vacuum tap was turned off and an inert gas stream applied to the system. When a positive pressure was obtained, the distillate fraction needed was disconnected and stopped with an appropriate stopper immediately. The flask was then made secure and placed into an argon atmosphere glove box. The distillate was then transferred to a clean dry Schlenk flask and transferred to the vacuum line for degassing.

Fig 3.2

Diagram of vacuum distillation for the purification of liquid materials

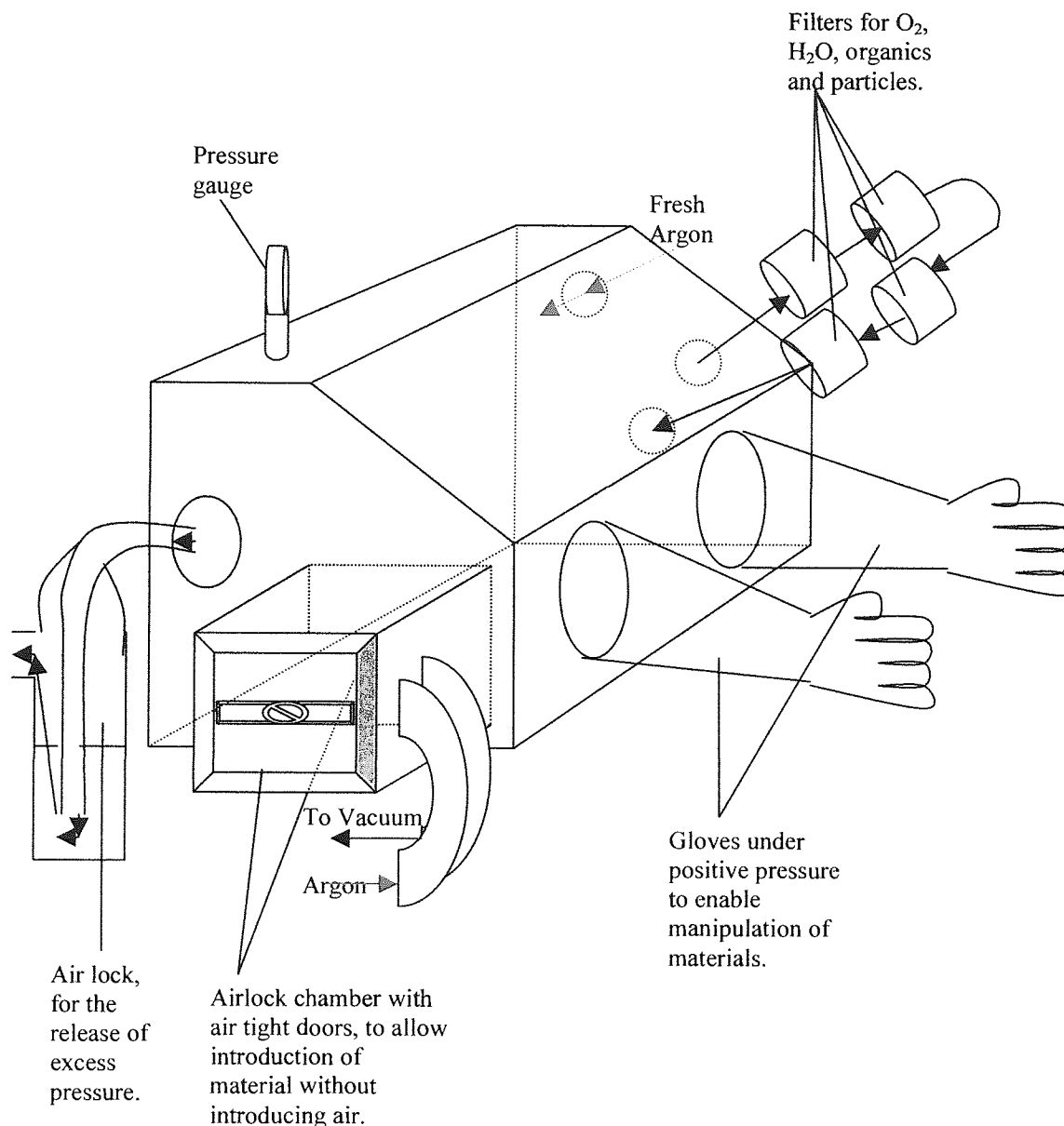


3.1.3 Argon Glove Box

The argon glove box shown in figure 3.3 provided an inert environment where oxygen and moisture sensitive materials could be handled safely. The glove is filled with an inert gas such as argon and is free from residual amounts of moisture and oxygen. The glove box reduces the risk of the reactants being contaminated. Materials are introduced into the glove box via an air lock, which is evacuated and filled with argon several times before being opened to the main chamber. The materials are handled through thick gloves inside of the box. Inert argon gas was used to provide a positive pressure inside of the box, which was recycled through a series of filter columns to remove any remaining oxygen, moisture, VOC's (volatile organic compounds) or particulates. Once the materials had been manipulated weighed or mixed for example, the Schlenk flask was removed via the air lock. Generally, most of the purified materials are stored in the glove box for future use.

Fig 3.3

Diagram of argon glove box used to manipulate sensitive materials in an inert atmosphere.

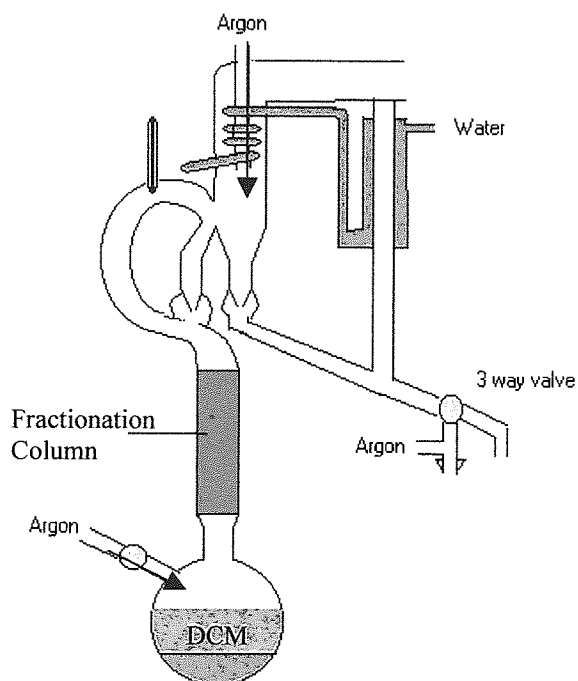


3.1.4 DCM (dichloro methane) Still

One of the main solvents used for the experiments, detailed in later chapters, was DCM. Due to the volumes of DCM required during this work, a dedicated still^[60] as shown in figure 3.4 was used. The still was used at atmospheric pressure with an inert gas flow (nitrogen). Heat was applied to the stock solution of DCM and calcium hydride (drying agent). The purified DCM fractions were collected in a Schlenk flask.

The purified DCM was then degassed on the vacuum line and stored in the argon glove box.

Fig 3.4
Diagram of DCM still



3.2 Monomer Synthesis

Most monomers such as oxetane, 3,3-dimethyl oxetane (DMO) and 3-methyl oxetane-3-metanol (MOM) were purchased directly from suppliers who are listed in section 3.5. The 3,3-bis-bromomethyl-oxetane monomer could not be purchased, and as such, needed to be synthesised prior to purification and polymerisation.

3.2.1 BBMO Synthesis by Phase Transfer.

3,3-bisbromomethyloxetane (BBMO) was synthesised using a phase transfer reagent [47, 60-64]. The reaction involves the ring closure of a brominated alcohol and was achieved as follows;

Into a 1000ml conical flask, containing a large magnetic flea, 75g of 2,2-dibromomethyl bromopropan-3-ol was dissolved, using 375ml of toluene. Once dissolved 22.5g of tributyl propyl ammonium chloride was added.

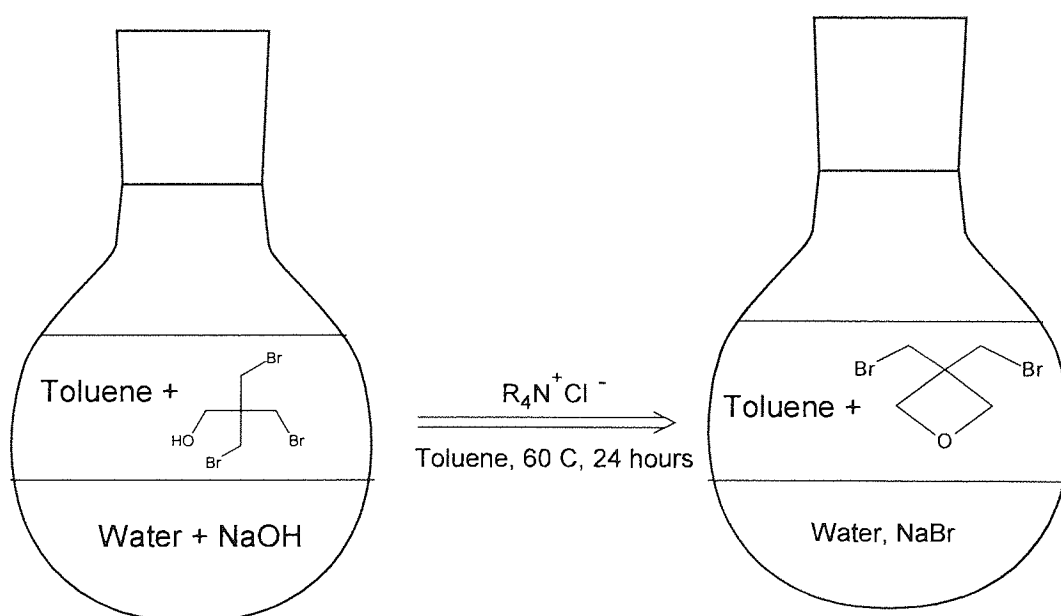
In a separate 500ml conical flask, 185ml of distilled water were added, followed by 94g of sodium hydroxide. The sodium hydroxide was allowed to dissolve releasing a large amount of heat and left to cool.

Once both sets of solids were completely dissolved, they were mixed together (Figure 3.5) in the larger flask. This was placed onto a magnetic stirrer and hot plate and stirred whilst being heated to 60°C. The reaction was stirred for eighteen hours before being turned off and cooled. The mixture was separated using a separating funnel and the toluene solution was washed twice with 2 lots of 200ml of warm distilled water.

The toluene solution was transferred to a rotary evaporator where 90-95% of the toluene was removed. The remaining solution was transferred to the vacuum distillation apparatus as described in figure 3.2. The BBMO was collected from the third fraction (1st being remaining toluene) and flushed through with an inert gas. It was then stored in the argon glove box until required.

Fig 3.5

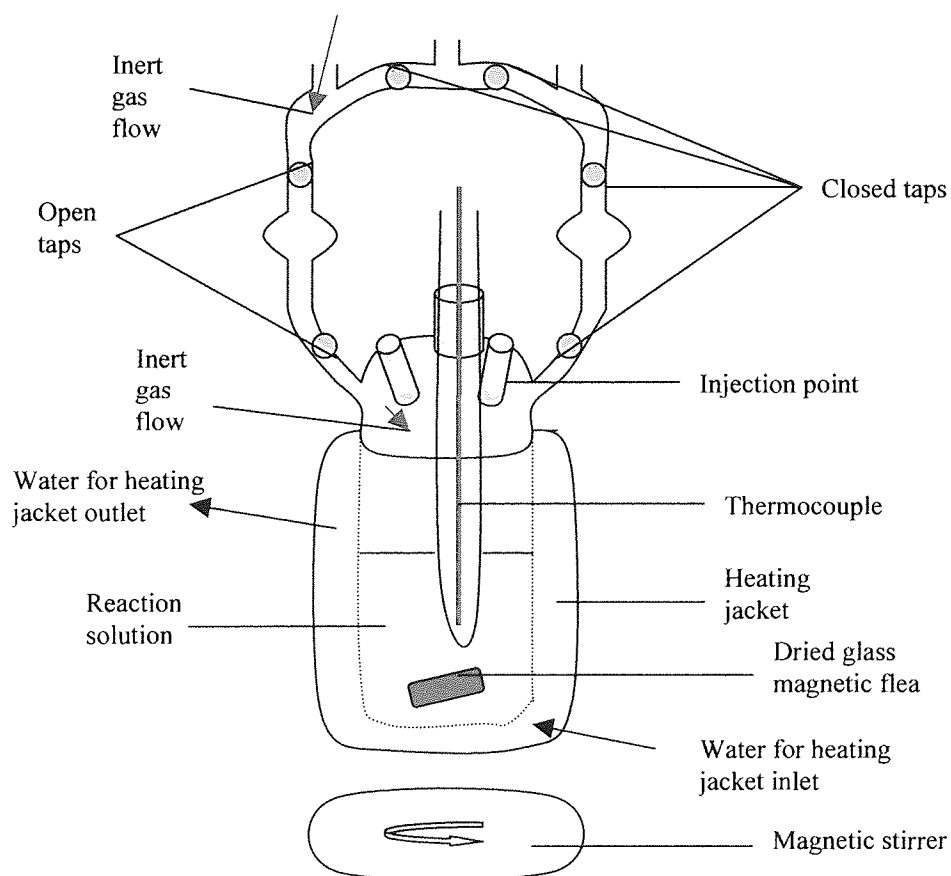
Synthesis of 3,3-bisbromomethyloxetane (BBMO) via a phase transfer mechanism.



3.3 Polymerisation vessel

The solutions were prepared in the argon glove box and sealed using Schlenk flasks [33,34,60]. They were transferred to the reaction vessel using clean, dry and airtight syringes with luer lock fittings, under a nitrogen or argon atmosphere. The solutions were transferred to the polymerisation vessel (figure 3.6) using the positive pressure technique described in section 3.4.

Fig 3.6
Polymerisation reaction vessel with thermocouple attachment.



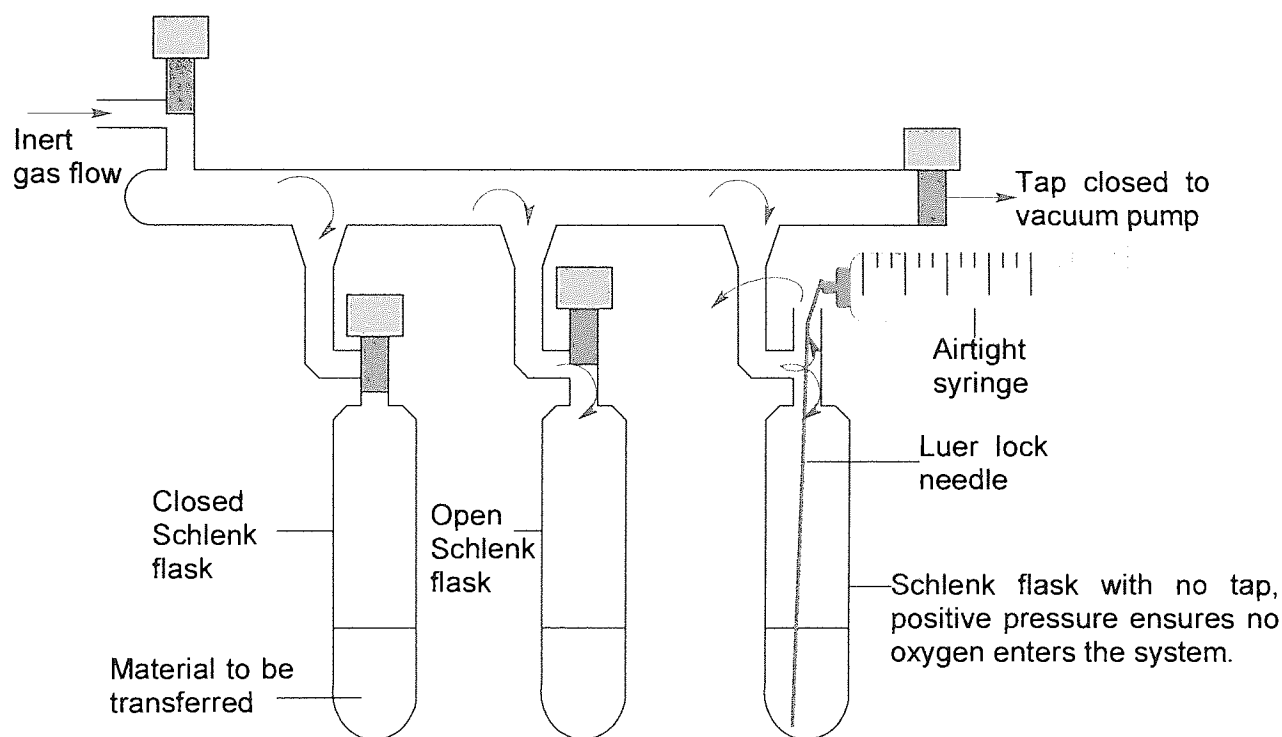
3.4 Transfer of Mixtures Using the Schlenk Technique

There were several techniques that were used for the transfer of air and moisture sensitive materials [60]. One of which was the Schlenk positive pressure technique (figure 3.7). The material was transferred to a reaction vessel by using an airtight syringe, purged and filled with an inert gas. The vessel was attached to a vacuum line

and the line evacuated using vacuum pumps. The line was heated to remove any oxygen or water whilst still under vacuum. A positive pressure gradient was applied to the system by filling the system with an inert gas. Once the positive pressure gradient had been established, the cap containing the material to be transferred was opened. The cap was removed from the flask under a positive flow of pressure and parafilm™ stretched over the open hole. A clean, dry and airtight syringe with a tight fitting luer lock needle was purged with an inert gas, which was used to transfer the required volume of liquid to the appropriate vessel also under positive pressure. This technique was used to transfer solvents and solutions to various vessels to either; prepare reagents prior to the polymerisation or to transfer the reagents to the polymerisation vessel.

Fig 3.7

Transfer of air sensitive material using the Schlenk technique.



3.5 Material Preparation

The materials used for the project were supplied and purified using a combination of techniques previously described in this chapter.

3.5.1 Monomers

Oxetane (trimethylene oxide): was supplied by Lancaster chemicals (99%) and dried over calcium hydride, distilled on the vacuum line into a clean Schlenk flask and stored in the argon box.

3,3-Dimethyl oxetane (DMO): was supplied by Sigam-Aldrich (99%) and dried over calcium hydride, distilled on the vacuum line into a clean Schlenk flask and stored in the argon box.

3,3-Bisbromomethyl oxetane (BBMO): was synthesised as described in 3.2.1, the raw materials were supplied by QuinetiQ, purified by recrystallisation and placed in the vacuum oven. The resultant product was dried over molecular sieves for over 24 hours and vacuum distilled. The purified product was then stored in the argon glove box until required.

Methyl oxetane methanol (MOM): was purchased from Sigma-Aldrich (96%) and dried over magnesium sulphate for over 24 hours, it was then distilled using vacuum distillation.

3.5.2 Initiator Starting Compounds

Chloromethyl ethyl ether: was supplied by Sigma-Aldrich and dried over calcium hydride and was then distilled using the Vacuum line and stored in the argon box.

Silver hexafluoroantimonate: was supplied by Sigma-Aldrich and used as supplied, being handled under an inert atmosphere.

Silver hexafluorophosphate: was supplied by Sigma-Aldrich and used as supplied, being handled under an inert atmosphere.

Silver heptafluorobutyrate: was supplied by Sigma-Aldrich and used as supplied, being handled under an inert atmosphere.

Potassium hexafluoroantimonate: was supplied by Sigma-Aldrich and used as supplied, being handled under an inert atmosphere.

Potassium hexafluorophosphate: was supplied by Sigma-Aldrich and used as supplied, being handled under an inert atmosphere.

Bromoxylenes: were supplied by Sigma-Aldrich (GC purified) and used as supplied, being handled under an inert atmosphere.

Bromomethyl toluenes: were supplied by Sigma-Aldrich (GC purified) and used as supplied, being handled under an inert atmosphere.

Benzyl bromide: was supplied by Sigma-Aldrich and used as supplied, being handled under an inert atmosphere.

Benzyl aldehyde: was supplied by Sigma-Aldrich and dried over magnesium sulphate for 24 hours, then purified using the Vacuum line.

3.5.3 Solvents

DCM (dichloromethane) (HPLC grade): was supplied by Fisher chemicals and dried over calcium hydride and distilled under a nitrogen (oxygen free) atmosphere.

THF (tetrahydrofuran) (HPLC grade): was supplied by Fisher chemicals and used as supplied.

Toluene (HPLC): was supplied from Fisher chemicals and distilled on the vacuum line for use in polymerisations and as a marker. Toluene was used as supplied for other preparatory work.

Methanol: was supplied by Fisher chemicals and used as supplied.

3.5.4 Additives

1,4-Dioxane: was supplied by Sigma-Aldrich chemicals and dried over calcium hydride and distilled using the vacuum line.

Ditertbutyl pyridine (DTBP): was supplied by Sigma-Aldrich and dried over molecular sieves and separated using the vacuum line.

Chapter 4

Analytical Techniques

4.1 Analytical Techniques

Once the polymers had been synthesised, various techniques were employed in order to evaluate the efficiency of the polymerisation system. The techniques used; ranged from gravimetric percentage yields, chromatography and NMR studies. This chapter gives a brief description and main points of each technique used and how they helped in the elucidation of the efficiency of the polymerisation system.

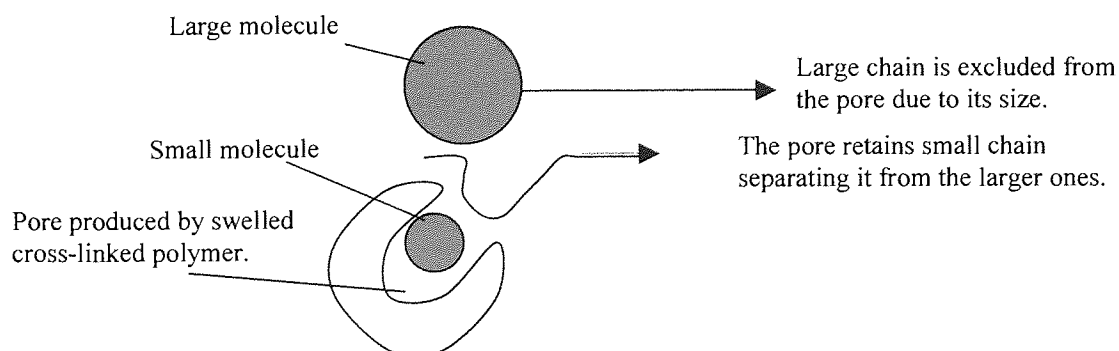
4.1.1 Background Theory of Gel Permeation Chromatography

The separation of the polymer chains by gel permeation chromatography^[25] was carried out using a column packed with a porous gel medium, such as polystyrene cross-linked with divinyl benzene.

Swollen with a suitable solvent, the swelling of the polymer created pores in its structure with which the solute chains could interact (shown in figure 4.1). The pores generated from this system had a distribution of pore sizes depending on how the gel medium was made. The smaller molecules fitted into more of the pores and thus spent more time in the column. The larger molecules spent only a short time in the few pores, which they fitted into, thus eluting faster. The difference in the time it took for the chains to elute from the column was related to the distribution of the chain sizes. When the chains became so small that they fitted into every pore, no separation was seen between them, irrespective of their size; this is referred to as the permeation limit. When the chains were so large that they did not fit into any pore, no separation of chains occurred; this is known as the exclusion limit.

Fig 4.1.

Small molecule permeating into pore of swollen crosslinked polystyrene packing with large molecule is eluted more quickly.

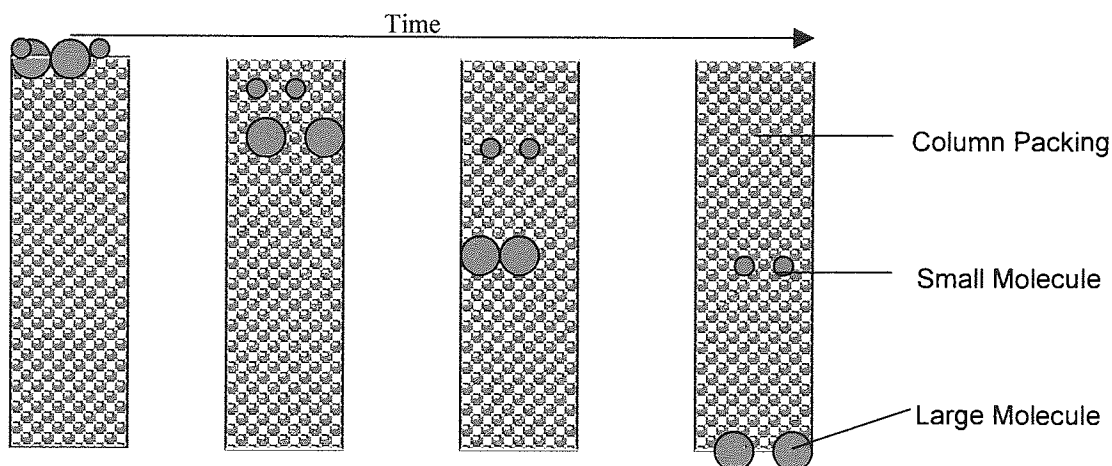


4.1.2 Gel Permeation Chromatography (GPC) Experimental Description.

The polymer solute was injected into the column via a valve and loop type injector and pumped through at a fixed flow rate (1 ml/min) with the solvent (THF). The solute passed through the stationary phase (in the column) causing separation of the various size molecules (fig 4.2.).

Fig 4.2

Separation of a polydisperse polymer through a column with a porous gel packing.

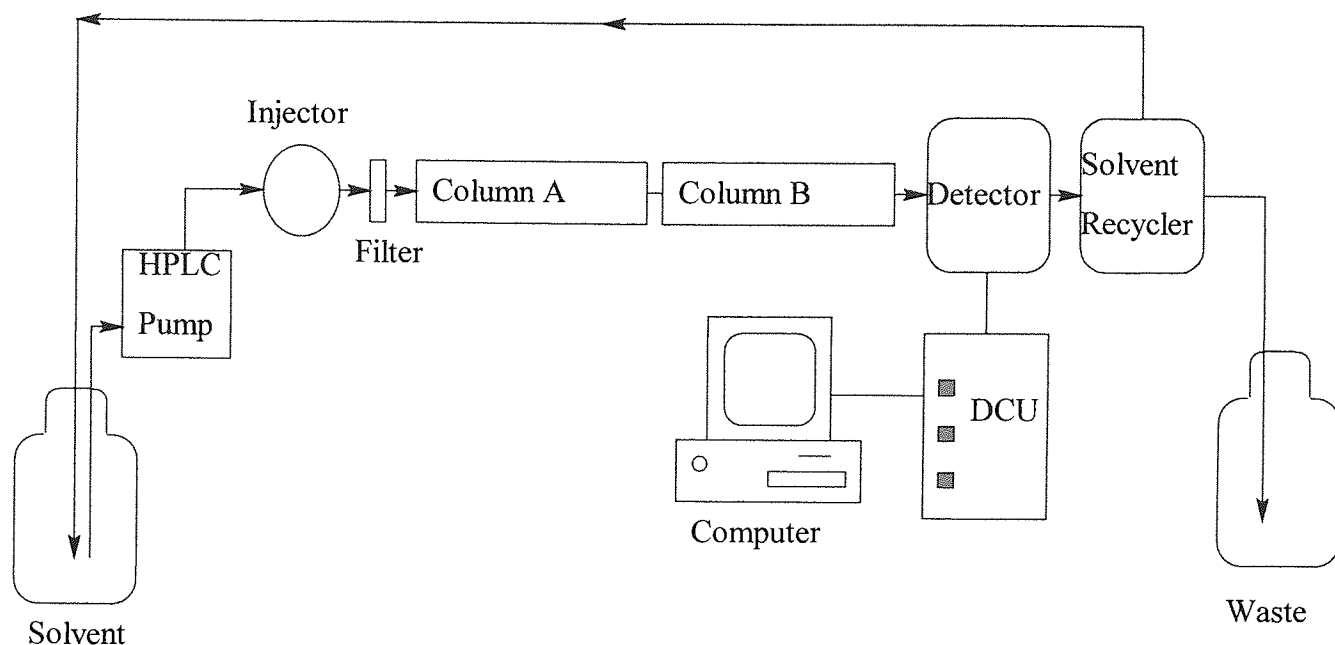


The larger molecules were 'held' by fewer pores, as they could not fit into the smaller pores, thus elute fastest. The smallest molecules were 'held' by more pores, delaying their elution through the column.

The solute was detected at the end of elution by techniques such as a differential refractometry, UV, IR, viscometer and light scattering. The signal from the detector/s was continuously recorded using a data collection unit and sent to a PC for analysis. Once the solute had left the detector, it either went to a waste or clean solvent reservoir via a recycling system (flow diagram of the GPC process is shown in figure 4.3). Once the solute has been eluted, another could be introduced via the injection loop

Fig 4.3

Schematic of gel permeation chromatography (GPC) apparatus.

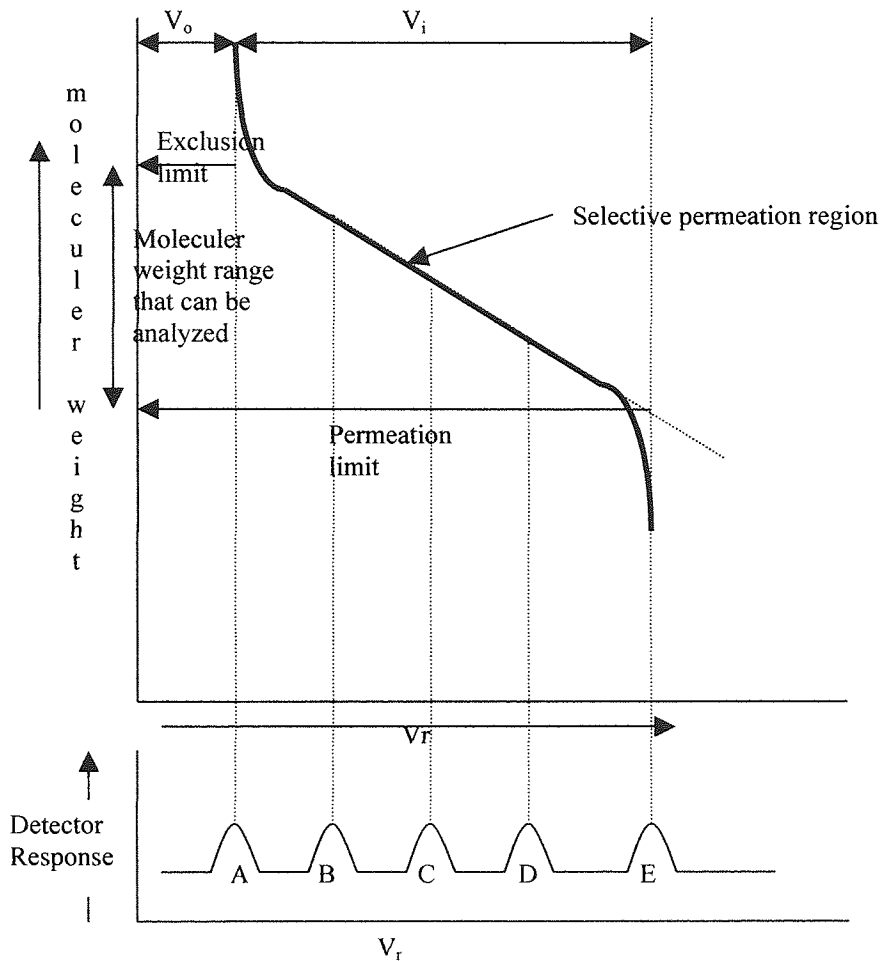


4.1.3 Calibration of a Gel Permeation Chromatogram.

GPC is not a primary technique for measurement of molecular weights; a calibration of the columns has to be performed. The calibration allows the molecular weight to be calculated by relating the size of the solute molecules to the retention volume, V_r , this is volume of solvent that has to be pumped through the system to cause the polymer of a particular molecular weight to elute.

Fig 4.4

The curve generated when several polymers of known molecular weight and polydispersity are used to generate a calibration.



The diagram in figure 4.4 depicts a calibration curve for a GPC column. Peak A shows all of the components that had molecular weights greater than the exclusion limit and therefore were not separated. Peak E illustrates all of the components smaller than the permeation limit and could not be analysed. Peaks B, C and D are components within the selective permeation region that could be analysed.

4.1.4 Column Selection.

The column packing is very important when considering GPC analysis. There are several available, which offer advantages and disadvantages. There are two main classes of packing for the GPC column that can be used:

- i) Crosslinked swollen polymer gel, or
- ii) Silica based beads.

Both packing types have particle sizes typically around 5-10 μm .

Polymeric based packings are normally based on crosslinked styrene-divinyl benzene copolymers. The pore size generated in the gel is dependent on the amount of crosslinking present. When these polymer-based packings were first sold, only hydrophobic packings were available, but, with the use of surface modification, hydrophilic packings are now in widespread use.

The effective separation range of the polymer chains is directly related to the distribution of the pore sizes. For columns with narrow pore size distribution, very good resolving power of the column is achieved, but only for a very limited range of chain size. If the size distribution of the pores is very broad, then the range of chain sizes that can be separated is wide, however the resolving power is reduced. The resolving power is reduced for higher distribution of pore sizes because there is less of a specific size to effectively separate the polymer chains. This means that the residence time of the polymer chains is shorter for a particular size. Therefore they are not separated from the rest of the solute as effectively.

It has been common practice to have several columns placed in series with each other, each with a well-defined pore volume distribution, giving good resolving power and chain size within a range. This is an effective system, however it did pose problems when using a calibration curve, as it had to accommodate several column separations in one curve. Furthermore, this led to significant errors in the calibration curve, which was then used to calculate molecular weights of an unknown sample. Recently, there have been significant developments in mixed columns which offer good resolving power and good separation range whilst reducing the error of using a calibration from several columns.

4.1.5 Evaluation of Average Molecular Weights by Gel Permeation Chromatography.

The main use of GPC in polymer characterisation is to determine the average molecular weights and polydispersity of the polymer^[25,58,65-69]. Polymers are made up

of many repeat units and not all of the chains have the same number of units. This therefore, leads to the polymer being polydisperse with different a range of chain lengths.

By using an analytical treatment of the chromatogram obtained from GPC, it is possible to determine the molecular weights and polydispersity of the polymer. The two main averages that are used are the weight average, \overline{M}_w , and number average, \overline{M}_n . The polydispersity, (PD), is also derived from these averages. The molecular weight gives an idea of the number of molecules in the chain whilst the polydispersity gives an indication of the breadth of the distribution. The values are therefore important in predicting the properties of the polymer.

If N_i is the number of molecules with a molecular weight, M_i , then the following averages may be defined as follows:

$$\overline{M}_n = \frac{\sum(N_i \cdot M_i)}{\sum(N_i)} \quad \text{Eq 4.1}$$

$$\overline{M}_w = \frac{\sum(N_i \cdot M_i^2)}{\sum(N_i \cdot M_i)} \quad \text{Eq 4.2}$$

Polydispersity index (PD) is a ratio calculated by dividing the average molecular weight, (\overline{M}_w), by the molecular number average weight, (\overline{M}_n), and is an indication of how dispersed the polymer molecules are.

$$PD = \frac{\overline{M}_w}{\overline{M}_n} \quad \text{Eq 4.3}$$

Typically, during a gel permeation chromatography experiment N_i cannot be determined easily. The height (h_i) of the peak at a given time is known and is proportional to the weight fraction (w_i). By substitution with equation 4.1 and 4.2, the number (\overline{M}_n) and molecular weight (\overline{M}_w) averages can be rewritten as follows:

$$\bar{M}_n = \frac{\sum w_i}{\sum (w_i / M_i)} \quad \text{Eq 4.4}$$

$$\bar{M}_w = \frac{\sum (w_i \cdot M_i)}{\sum w_i} \quad \text{Eq 4.5}$$

4.1.6 Interpretation of a Typical GPC Chromatogram

The eluted polymer solution was passed through a differential refractometer (DRI) detector where the response was proportional to the concentration of eluted material, except in the case of low molecular weight materials. The response from the detector was then sent to a data collection unit (DCU), which was then sent to a computer for processing where the \bar{M}_n , \bar{M}_w and PD were calculated. In order to convert the volume eluted, (V_e), into useful values such as \bar{M}_n and \bar{M}_w then equation 4.6 needs to be applied.

$$V_e = V_i + kV_p \quad \text{Eq 4.6.}$$

Where V_i is the interstitial volume and V_p is the volume of the solvent in pores, $0 < k < 1$, k is dependant on the molecular weight of the polymer.

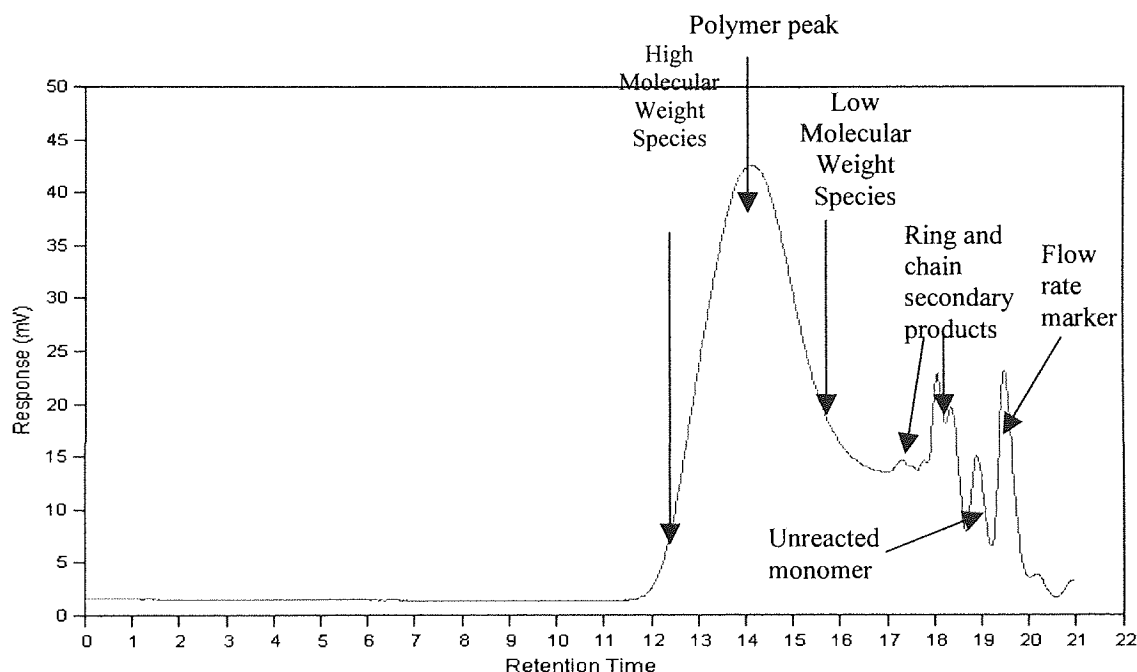
The calibration curve shown in figure 4.4, which was used to determine the retention weight dependence on the retention volume of various polymers, was created using polymer standards. The polymer standards that were used were based on polystyrene polymer systems with low polydispersities. The solvent used for the calibration was tetrahydrofuran (THF) which was also used for the analysis of the experimental systems. The value k from equation 4.6 was dependent on the polymer type and as such, the experimental polymer systems will have a differing k value to those from the polymer standard. Owing to these differing k values of the experimental systems, the GPC data obtained could not give absolute values, but did give useful indicators to molecular weight properties.

For low molecular weight fractions and by-products, the sensitivity of the DRI was determined by the dn/dc of the component which is dependent on its molecular weight at low molecular weights.

Despite the limitations of gel permeation chromatography, it was a very useful technique in rapidly determining the molecular weight distribution characteristics of polymeric systems. A typical chromatogram as shown in figure 4.5 shows how the molecules in the system differed in terms of molecular weight, with the presence of some by-products in the form of cyclic and linear oligomers.

Fig 4.5

Typical GPC trace of polyoxetane with no additives polymerised using an oxonium ion initiator at 35°C in DCM.



4.2 Nuclear Magnetic Resonance (NMR).

There are two main types of NMR^[70-73] in use today, which are based on either pulsed or continuous wave experiments. In recent years, the pulsed technique has proven to be more efficient and generates better-resolved spectra, making it the preferred method.

4.2.1 Description of NMR.

The principle of NMR relies on the fact that the nuclei of certain atoms spin and this spin has associated with it, a spin angular momentum, p . It's maximum observable angular momentum is a half multiple of $h/2\pi$ where h is the Planck's constant. The

nucleus has associated with it, a spin quantum number, I , which can take values $1/2$, $3/2$, $5/2$... or $0, 1, 2, 3$... depending on the ratio of protons to neutrons in the nucleus. The nucleus has $(2I + 1)$ discrete states that have components of angular momentum in any chosen direction when it spins in a magnetic field. If there is no magnetic field experienced by the nucleus these states have equal energies, or are said to be degenerate.

If a magnetic field is applied to the nucleus, the $(2I+1)$ states will differ in energy, the difference in energy between the states depending on the environment of the nucleus.

The three nuclei that are of interest in this project are ^1H , ^{13}C and ^{31}P , all of which have the spin quantum number $1/2$. Therefore each of the nuclei mentioned has two spin states where either $I = +1/2$ or $I = -1/2$. This eases their analysis of these nuclei because there is only one transition, $I = -1/2$ to $I = +1/2$, that can occur when the nuclei are placed in a strong magnetic field. Comparatively a spinning charged nucleus creates a magnetic field in a similar way as electricity from a magnetic field when it flows through a coil of wire. The magnetic field produced has associated with it, a magnetic moment, μ , which is directly proportional to the spin angular momentum, p . The proportionality constant γ , is known as the magnetogyric ratio.

$$\mu = \lambda p \quad \text{Eq 4.7}$$

The magnetogyric ratio is different for each nucleus and is also dependent on the frequency of the absorbed energy and the strength of the magnetic field.

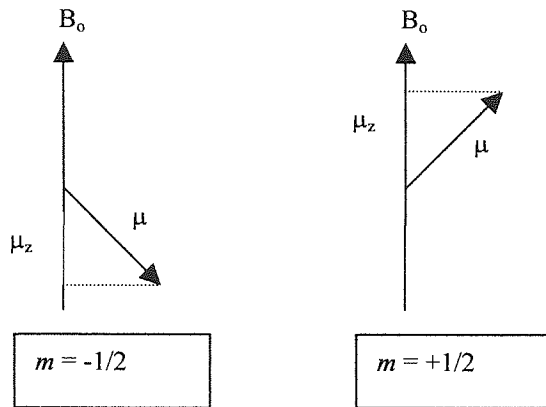
Owing to the relationship between the nuclear spin and the magnetic moment, a magnetic quantum state m can be observed, which can take values $m = I, I-1, I-2, \dots, -(I-1), -I$. For the nuclei considered in this project, the magnetic quantum numbers are $m = \pm 1/2$

4.2.2 The Effect of an External Magnetic Field.

When a nucleus with a spin quantum number of $1/2$ is subjected to an external magnetic field of strength, B_0 , the magnetic moment of the nucleus becomes orientated with respect to the field in one of two directions, as shown in figure 4.6.

Fig 4.6

Orientation of spins of a nucleus with spin $\frac{1}{2}$, when an external magnetic field with strength B_0 is applied.



There will be a difference in the energy between the two orientations, the $m = +\frac{1}{2}$ state having the lower energy. The potential energy E of an orientation is obtained from equation 4.8.

$$E = -\frac{\gamma\hbar B_0}{2\pi} \quad \text{Eq 4.8.}$$

The magnitude of the energy in the lower energy state, $m = +\frac{1}{2}$, is given by:

$$E_{+1/2} = -\frac{\gamma\hbar B_0}{4\pi} \quad \text{Eq 4.9.}$$

and in the higher energy state, $m = -\frac{1}{2}$:

$$E_{-1/2} = \frac{\gamma\hbar B_0}{4\pi} \quad \text{Eq 4.10.}$$

The difference in energy, ΔE , between the two states is then:

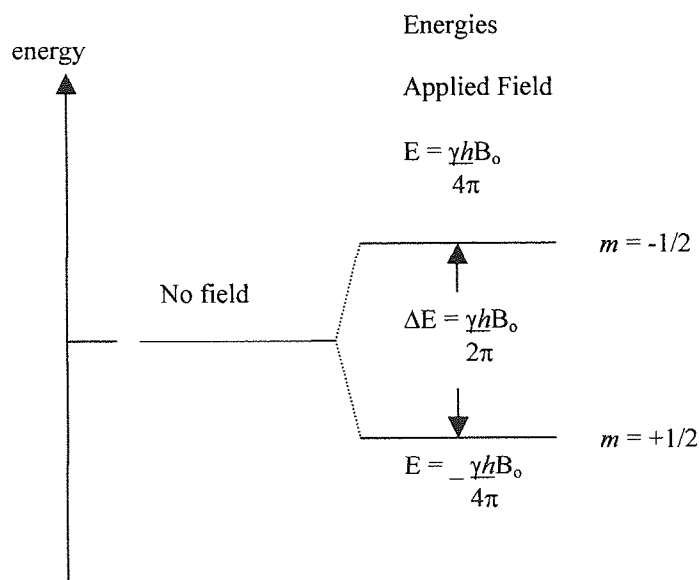
$$\Delta E = \frac{\gamma\hbar B_0}{4\pi} - \left(-\frac{\gamma\hbar B_0}{4\pi}\right) = \frac{\gamma\hbar B_0}{2\pi} \quad \text{Eq 4.11.}$$

A transition between these two energy states may be brought about by the absorption or emission of electromagnetic radiation at a defined resonant frequency ν_0 . The frequency of the absorbed radiation corresponds to the energy difference between the two states according to the equation as shown in figure 4.7.

$$\text{Accordingly } h\nu_0 = \frac{\gamma\hbar B_0}{2\pi} \text{ and } \nu_0 = \frac{\gamma B_0}{2\pi} \quad \text{Eq 4.12.}$$

Fig 4.7

The effect of applying a magnetic field to energy levels of a nucleus with a spin quantum number of $\pm 1/2$.



The relative populations of the two states that differ in energy may be determined from the Boltzman equation 4.13.

$$\frac{N_j}{N_o} = \frac{P_j}{P_o} \exp\left(-\frac{E_j}{kT}\right) \quad \text{Eq 4.13.}$$

N_j = number of atoms in excited state.

N_o = number of atoms in ground state.

P_j and P_o are statistical factors related to the number degeneracy of the states. In this case $P_j = P_o$.

E_j = The difference (Jmol^{-1}) in energy between the two states.

k = Boltzman constant ($1.28 \times 10^{-23} \text{Jmol}^{-1}\text{K}^{-1}$).

T = Absolute temperature (K).

Since the degeneracy of each state for the spinning nucleus is one, the ratio of numbers of nuclei in the excited state to ground state is given by equation 4.14.

$$\frac{N_j}{N_o} = \exp\left(-\frac{\Delta E}{kT}\right) \quad \text{Eq 4.14.}$$

Accordingly, substitution for ΔE leads to:

$$\frac{N_j}{N_o} = \exp\left(-\frac{\gamma\hbar B_o}{2\pi kT}\right) \quad \text{Eq 4.15.}$$

Equation 4.15. can be approximated to:

$$\frac{N_j}{N_o} = 1 - \left(-\frac{vhB_o}{2\pi kT} \right) \quad \text{Eq 4.16.}$$

The difference between the numbers of spins in the higher and lower states is very small and dependent on field strength. Typically, there are only 33 more lower energy spins per million under the influence of a 4.7T magnet but this difference is sufficient to be used in the NMR experiment.

It can be determined from Eq 4.16 that by increasing the field strength, the fraction of species in the lower energy state will increase. This factor will lead a more intense signal when high magnetic fields are used.

4.2.3 Precession of a Nucleus in a Magnetic Field.

By considering the nucleus to be in a fixed position and rotating it around a fixed position, the nucleus precesses around a vector represented by the magnetic field, B_o (figure 4.8). Owing to the movement of the spinning particle, it is said to have an angular velocity, ω_o , described by equation 4.17.

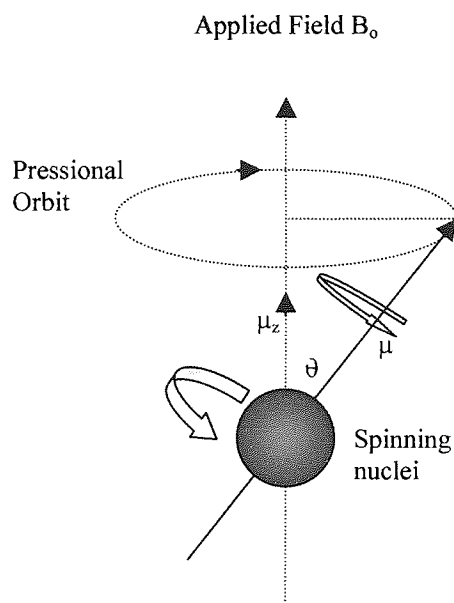
$$\omega_o = \gamma B_o \quad \text{Eq 4.17.}$$

The angular velocity can be converted easily to give the frequency of precession by dividing by 2π . This frequency is also known as the Larmor frequency (ν_o) and is given by equation 4.18.

$$\nu_o = \frac{\gamma B_o}{2\pi} \quad \text{Eq 4.18.}$$

Fig 4.8

Precession of a rotating particle around a magnetic field.



4.2.4 NMR Experiments

In the early examples of NMR spectroscopy, most experiments were performed using the continuous wave technique. The spectrum was obtained by varying the frequency of electromagnetic radiation or the strength of the magnetic field. As the field or frequency was varied, spins displaying different chemical shifts were brought into resonance. The NMR signal was recorded during the process of such experiments. One major drawback with the technique was that the time of the sweep had to be very long. In order to achieve good spectra, the spins had to reach their equilibrium state, the time that a particular frequency of field strength must therefore be greater than the spin lattice relaxation time, T_1 , and the spin-spin relaxation time, T_2 , of the nucleus. This therefore was to ensure that there was no distortion of the signals from spins not reaching their equilibrium state. As the T_1 and T_2 can be of the order of seconds or minutes then, to achieve a good scan of the entire electromagnetic frequency or magnetic field range, very long scan times were needed.

4.2.5 Pulsed NMR Techniques

In order to obtain high resolution pulsed NMR spectra several pieces of equipment are needed. These are the magnet, radiofrequency transmitter, NMR probe, radiofrequency receiver and a computer.

1. Magnet;

The magnet must generate a strong field that is, homogeneous and stable. By using the strongest magnetic field available, several advantages can be seen. These include

- (I) Optimum sensitivity.
- (II) Greater multiplet separation.
- (III) Reduction of any strong coupling effects.

In addition to its strength, the field must also be uniform, as any variation in the field will result in line broadening of the spectrum. NMR experiments can last for several days and as such, the magnet construction is of crucial importance.

Presently, only magnets of superconducting solenoid construction are used for high-resolution applications. Other conventional magnets are restricted to 2.3T (100 MHz) whilst solenoid types can have magnetic fields in excess of 17.5T (750 MHz).

2. Radiofrequency transmitter;

The radiofrequency generator is a waveform generator that produces a continuous sinusoidal by varying voltage of the desired frequency. This sine wave is broken up into smaller segments to form pulses by a switch or gate mechanism known as the pulse generator. The pulses are then amplified and sent to the NMR probe.

3. NMR probe;

The NMR probe holds the sample in place and spins it in the strong continuous magnetic field to overcome unhomogeneity in the liquid phase. The probe both transmits the pulses of radiofrequency to the sample and receives the subsequent signal. The main component in the probe is a wire coil that is placed around the sample to which the pulses are applied. An alternating current in the coil generates a magnetic field, which is the same as the transmitted frequency. The nuclear magnetisation of the sample is excited by the radiofrequency and induces an

oscillating voltage. The oscillating voltage is the NMR signal and is amplified and passed onto the receiver.

4. NMR receiver;

Once the signal has been amplified, the NMR receiver mixes the signal from the NMR probe with a reference voltage. By this process, the reference voltage is eliminated and generates a voltage that is only due to the sample and not the other types of magnetisation. This is then sent to the computer where the spectrum is stored for processing.

In pulsed experiments, many pulses can be applied in a relatively short period of time and information gathered enables the spectrum to be built up. This has several benefits including improved resolution and improved peak to noise ratio. It also allows nuclei with a low natural abundance such as ^{13}C to be analysed quickly.

4.2.6 Analysis of the NMR Spectrum.

Much information can be deduced from NMR spectroscopy and its usefulness is increasing all the time, as new techniques are developed [74-77]. However, in the context of this work, the discussion will be limited to chemical shifts, spin-spin splitting and the integration of peaks. There are several considerations that must be made when performing experiments and in some cases limitations of the technique.

4.2.6.1. Chemical Shifts.

The overriding factor that determines a resonance frequency of a molecule is its gyrometric ratio and the magnetic field it experiences (eqn 4.12). If all of the nuclei were to resonate at the same frequency, then NMR would be of little use. However, the gyrometric ratio depends very slightly on the position of the nucleus in respect to the molecule. It is this slight difference that is of the most interest as it enables the user to differentiate between two nuclei of the same type in different positions. This slight difference arises because the local electron distributions in the molecule are usually different for reasonably complex structures. Typically, the ^1H nuclei in a molecule has different chemical environments, which cause them to come into

resonance at different frequencies. These differences in resonance frequency give rise to the chemical shift.

4.2.6.2. Nuclear Shielding.

The field (B) that a nucleus experiences is different from the applied external field (B_o). Typically, the field the nucleus experiences is slightly smaller than the applied field because of the shielding of the electrons surrounding the nucleus. This occurs as the electrons present in the external field circulate in their orbitals and produce an opposing magnetic field (B') to the applied field. This effect shields the nuclei from the applied field by as much as the opposing magnetic field and the field (B) the nucleus experiences is given by equation 4.19.

$$B = B_o - B' \quad \text{Eq 4.19.}$$

The magnitude of the opposing magnetic field is proportional to the applied field. Therefore, if a stronger magnetic field (B_o) is applied, a stronger opposing field (B') counteracts it. It is then possible to replace equation 4.19 with 4.20.

$$B = B_o(1 - \sigma) \quad \text{Eq 4.20.}$$

The shielding constant, σ , describes the proportionality between the opposing field (B') and the applied field (B_o). Modification can then be made to equation 4.12 into equation 4.21, which describes the frequency at which a nucleus comes into resonance.

$$\nu = \frac{\gamma B_o(1 - \sigma)}{2\pi} \quad \text{Eq 4.21.}$$

4.2.6.3. Recording the Chemical Shift.

It is difficult to measure the absolute shielding constant and indeed, this is not normally needed. A more convenient system is used to compare resonance frequencies between a reference nucleus (ν_{ref}) and that of interest (ν). By dividing the difference between these resonances, by the reference resonance value, a dimensionless parameter (δ) is obtained as shown in equation 4.22.

$$\delta = 10^6 \frac{(\nu - \nu_{ref})}{\nu_{ref}} \quad \text{Eq 4.22.}$$

One main advantage of using such a system is that the parameter becomes a molecular property and is independent of the strength of the magnetic field. Very small numbers are involved; a factor of a million is used to make the parameter easy to use.

Typically δ , the chemical shift, is quoted in terms of parts per million (ppm).

Historically, tetramethyl silane (TMS) was used as the reference resonance and is still used today. TMS has highly shielded carbon and hydrogen atoms so that σ is large.

Due to this large value of σ , the resonances for both nuclei are at the low frequency end of the spectrum. This is advantageous, as most other frequencies are higher and so are seen as positive values of δ .

4.2.6.4 Spin-Spin Coupling.

Apart from the chemical shift, another important source of information can be found from NMR spectra, this being the magnetic interactions between nuclei. This gives important information about the environment next to the atom of interest.

Spin-spin couplings cause NMR lines to split. Usually, the more couplings there are, the more complex the spectrum is. There are several forms of coupling, this section will focus on two types; hetero and homonuclear. Consider a system A-X with A and X being nuclei with spin of $\frac{1}{2}$. Both A and X will, as a result of their spins, act as a small source of magnetisation. In consequence, the field generated by the spin of A will affect the field acting on X and vice versa. For systems comprising of the nuclei interactions of ^{13}C - ^1H , the number of interactions caused by the spin from ^{13}C is low, due to its low natural abundance. For ^1H NMR experiments, the coupling caused by ^{13}C is very low and does not need to be decoupled. For ^{13}C experiments, the interaction of the ^1H spin does affect the coupling, meaning that decoupling is required to allow useful spectra to be obtained.

4.2.6.5 Multiplet Patterns.

Although it is not necessary to decouple the ^{13}C spin from a ^1H , NMR spectra, coupling does occur between neighbouring hydrogen atoms. This coupling occurs through:

H_A -C-C- H_B where H_A and H_B are both a ^1H nucleus.

As coupling of the nuclear spins affects the NMR spectrum, a way of determining and predicting what the peaks will look like is of great importance. Several rules of multiplicity have been developed that enable the prediction of structure-spectra to be determined more easily and expressed by equation 4.23.

$$M = 2nI + 1 \quad \text{Eq 4.23.}$$

M = multiplicity, n = number of equivalent neighbouring nuclei, I = spin number.

For ^{13}C , ^1H and ^{31}P the spin is $\frac{1}{2}$ and so the equation 4.23 can be simplified to equation 4.24.

$$M = n + 1 \quad \text{Eq 4.24.}$$

Therefore, by taking one from the multiplet peak, a number of neighbouring hydrogen atoms can be determined easily. The heights (summation of same energy peaks) following a pascal formation are shown in figure 4.9.

Fig 4.9

Pascal triangle showing number of peaks and relative intensities observed for a hydrogen with n number of neighbouring hydrogen atoms.

	Relative intensity of peaks			
$n = 1$	1			
2	1 2 1			
3	1 3 3 1			
4	1 4 6 4 1			

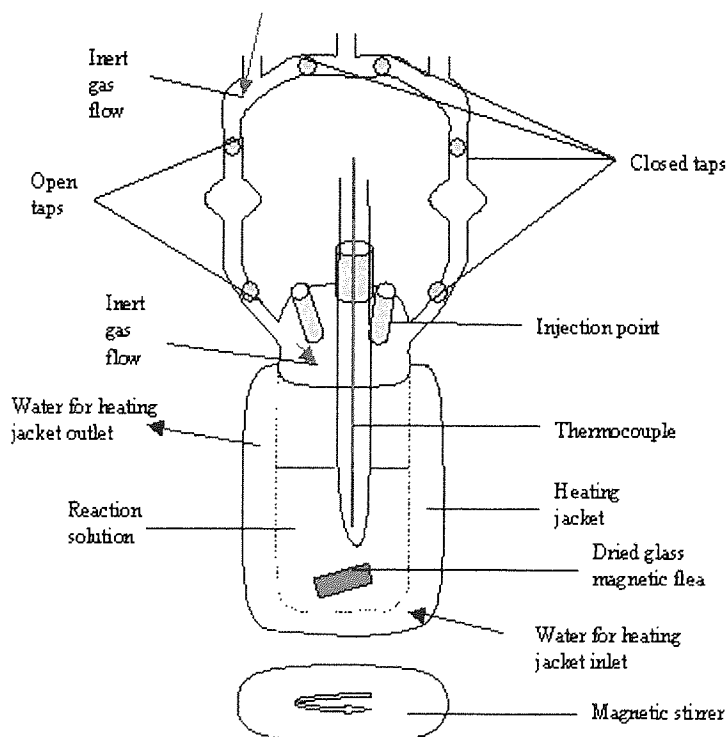
4.3 Calorimetric Analysis.

The measurement of rate of polymerisations was considered to be an important aspect of the comparison of the activities of the catalyst systems generated in this project.

The most convenient technique available in this project made use of the fact that oxetane, a four membered ring, is a highly strained monomer and that polymerisation to the linear polymer results in the release of that strain energy. The calorimetric technique developed in the laboratories^[33,34,60] over many years, uses a piece of apparatus designed to measure the rate of increase of the temperature of the polymerising solution as shown in figure 4.10.

Fig 4.10

Polymer reaction with thermocouple attached.



The information gathered, can be used to give an indication of the rate of polymerisation. The rate at which the reaction evolves heat dQ/dt ($J.s^{-1}$) can be considered a function of rate of polymerisation, R_p , which under adiabatic conditions as expressed by equation 4.25.

$$\frac{dQ}{dt} = \Delta H_p \cdot V \cdot R_p \quad \text{Eq 4.25}$$

ΔH_p is enthalpy of polymerisation, V is the volume reacted and R_p is the rate of polymerisation.

The first law of thermodynamics states that heat release at constant volume is proportional to the change in temperature then.

$$dQ = C_v \cdot dT \quad \text{Eq 4.26}$$

Where C_v is the constant volume heat capacity of the system and dT the temperature change in $^{\circ}K$.

By substituting equation 4.26 into 4.25 it can be rewritten as equation 4.27

$$\frac{C_v \cdot dT}{dt} = \Delta H_p \cdot V \cdot R_p \quad \text{Eq 4.27}$$

by rearranging equation 4.27 to give equation 4.28 to give an expression for R_p

$$\frac{C_v \cdot dT}{dt \cdot V \cdot \Delta H_p} = R_p \quad \text{Eq 4.28}$$

For any given system ΔH_p , C_v and V are constant values so that, R_p , can be described as proportional to the initial rate of temperature increase shown by equation 4.29.

$$R_p \propto \frac{dT}{dt} \quad \text{Eq 4.29}$$

Chapter 5

Development of Oxonium Ion Initiator Systems

5.1 Current Initiator System.

Recent studies by Bouchekief (2002)^[34] involved the generation of an oxonium ion species using chloromethyl ethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$) reacted with silver hexafluoroantimonate (AgSbF_6). The initiator system developed by Bouchekief was reproduced during an exercise to assess the reproducibility of the system. It was found during the experiment, that the system gave effective control of molecular weights and narrow polydispersities for the polymerisation of oxetane. The system also showed 'living' characteristics with monomer being polymerised when added after the initial polymerisation had taken place. Due to the fact that the initiator system was effective and showed living characteristics, an interest for the possible generation of block copolymers was found. The conditions used in the control experiment are discussed in detail in 5.1.3.

5.1.1 Generation of Oxonium Ion Catalysts.

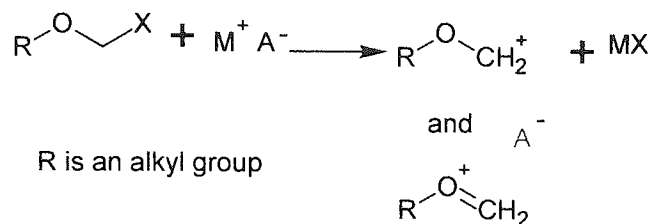
The initiator system discussed in 5.1 has been useful in the synthesis of homopolymers with potential to be used in the synthesis of statistical and block copolymers. There was however, a potential drawback in that the halogenated methyl ether group is quite difficult to synthesise on a multifunctionalised core molecule. Owing to the difficulty of synthesis of a multifunctional halogenated methyl ethers, the numbers of available compounds were low. The restriction of the number of multifunctional molecules with several halogenated alkyl ether groups has led to an investigation into other routes of producing oxonium ions.

5.1.2. Halide Elimination from a Halogenoalkyl Ether.

Oxonium ions can be generated by reacting an halomethyl ether with a silver salt consisting of a stable anion such as SbF_6^- . The elimination of the halide as a precipitate of a metal salt occurs along with the formation of the oxonium ion, which must be resonance, stabilised. The anion of the original complex then acts as a stable counterion to the cationic oxonium ion, this therefore associates with the growing active chain end (ACE).

The reaction can be represented in the general form shown by figure 5.1.

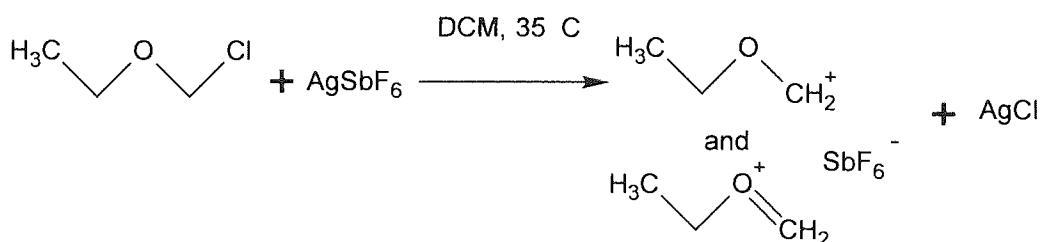
Fig 5.1
Scheme of oxonium ion generation using halogenomethyl ethers.



This reaction was investigated in detail with the majority of the work focused towards which type of stable anion salt would be used. The work was carried out using chloromethyl ethyl ether, with silver hexafluoroantimonate being used as a standard reaction with which variations were compared. The reaction shown in figure 5.2 shows the route of how the oxonium ion standard was generated.

Fig. 5.2

Reaction scheme showing the generation of the oxonium ion initiator used as a standard.



5.1.3 Control Experiment.

Work reported by H. Boucekief (2002)^[34] found oxetane could be polymerised using an $[\text{CH}_3\text{CH}_2\text{OCH}_2]^+$ cationic initiator system stabilised with either a BF_4^- or SbF_6^- counter ion. It was found that the use of the different anions resulted in a difference in the polymerisation of the oxetane, with the BF_4^- counterion yielding a polymerisation system where some control over the polymerisation was seen but with the generation of cyclic oligomers. When SbF_6^- was used as a counterion, less control of the polymerisation was seen with the degree of polymerisation (\overline{DP}_n), differing greatly from the % conversion of the polymer. The SbF_6^- anion initiator generated a polymer

system with less cyclic oligomer formation but had a relatively high polydispersity of 3.8 (after 17h) compared to 2.0 (after 26 h) for the BF_4^- anion system.

A control experiment was performed by preparing an initiator, reacting 2.0×10^{-3} mol of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ with 2.0×10^{-3} mol of AgSbF_6 in 20ml of dried dichloromethane (DCM) under an inert atmosphere and agitated for 24 hours in a foil coated Schlenk flask. After 24 hours, decanting separated the oxonium ion solution from the silver bromide precipitate and was stored under an inert atmosphere. Prior to the polymerisation, 1 ml of the initiator solution was transferred to a clean dry Schlenk flask and a further 32ml of dried DCM added to the solution. The solution was mixed thoroughly, made airtight and transferred to the vacuum line. In a separate Schlenk flask, a 1M solution of oxetane was prepared by mixing 4×10^{-2} mol with dried DCM solvent. 30 ml of monomer solution was transferred to the polymerisation vessel by using the Schlenk positive pressure technique as described in chapter 3.4. 3 ml of the diluted initiator solution was transferred to the monomer solution using the Schlenk positive pressure technique, the initial rate of reaction was followed by calorimetric and GPC analysis.

The \overline{M}_n and PD results of the control experiment along with those obtained by H. Bouchekief are shown in table 5.1

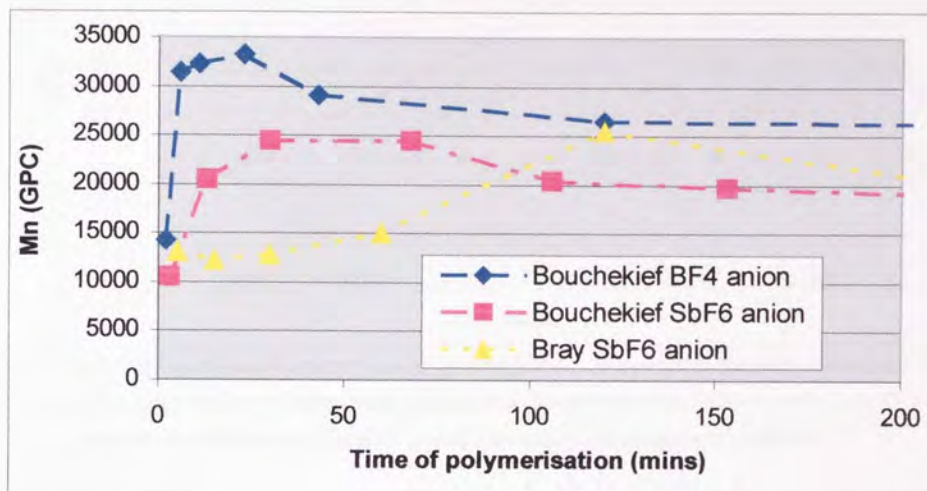
Table 5.1
Results of polymerisation of oxetane using $[\text{CH}_3\text{CH}_2\text{OCH}_2]^+[\text{M}_i\text{X}_n]^-$ system.

Sample	Anion	Time (min)	\overline{M}_n (GPC) ($\text{g}\cdot\text{mol}^{-1}$)	PDI
Bouchekief	BF_4^-	2	14250	1.72
Bouchekief	BF_4^-	6	31370	1.76
Bouchekief	BF_4^-	11	32300	1.9
Bouchekief	BF_4^-	23	33230	1.9
Bouchekief	BF_4^-	43	29120	2
Bouchekief	BF_4^-	120	26500	2
Bouchekief	BF_4^-	1560	22950	2.05
Bouchekief	BF_4^-	5760	18690	2.1
Bouchekief	SbF_6^-	3	10500	1.72
Bouchekief	SbF_6^-	13	20420	1.89
Bouchekief	SbF_6^-	30	24450	2.02
Bouchekief	SbF_6^-	68	24450	2.06
Bouchekief	SbF_6^-	106	20370	2.1
Bouchekief	SbF_6^-	153	19700	2.14
Bouchekief	SbF_6^-	1020	10360	3.8
Bray	SbF_6^-	5	13088	1.86
Bray	SbF_6^-	15	12209	1.85
Bray	SbF_6^-	30	12751	2.09
Bray	SbF_6^-	60	15045	1.66
Bray	SbF_6^-	120	25471	1.71
Bray	SbF_6^-	300	15343	1.64
Bray	SbF_6^-	360	13473	1.69

The results for the systems synthesised all generated similar molecular weight polymers although there was a slight difference in time when the molecular weight was at its highest as shown by graph 5.1.

Graph 5.1

\overline{M}_n progression of polymerisation of oxetane in DCM using $[\text{CH}_3\text{CH}_2\text{OCH}_2]^+$ with various $[\text{M}_i\text{X}_n]^-$



From graph 5.1, it can be concluded that the majority of the polymerisation is completed for all of the systems before the first sample could be taken. The newly synthesised system made does differ slightly but does yield similar molecular weight polymer systems to those previously synthesised.

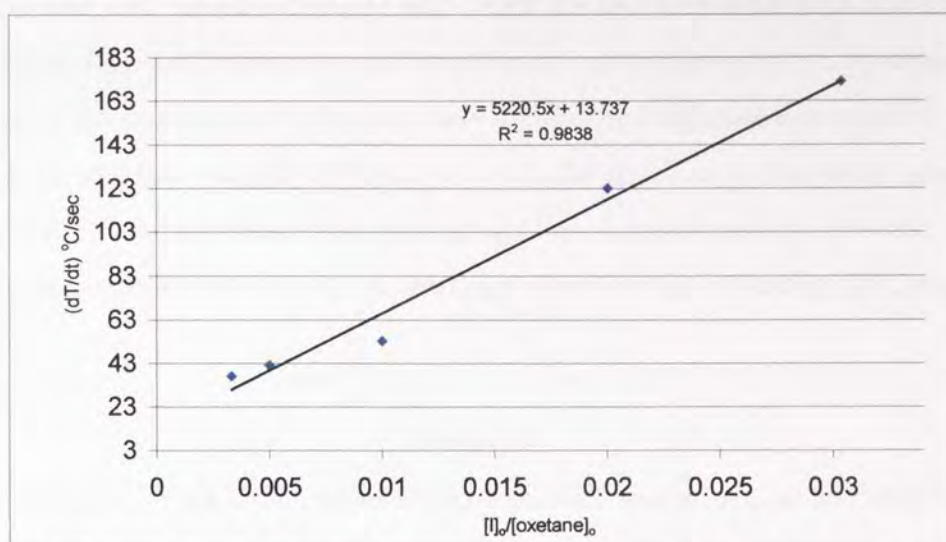
5.1.4 Control Experiment Effectiveness and Errors

It was found in 5.1.3 that the polymerisation of oxetane in DCM could be achieved by using an initiator prepared by reacting AgSbF_6 with $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$.

Polymerisations were performed using the initiator system at various initiators to monomer ratios. The polymerisations were followed by measuring maximum rate of temperature change using the calorimetric method, described in chapter 4.3 and highlighted in graph 5.2.

Graph 5.2

Initial rate temperature increase (dT/dt) of oxetane at various monomer to initiator ratios.



Where $[I]_0$ is the initial initiator molar ratio and $[\text{oxetane}]_0$ is the initial monomer molar ratio, the concentration of the monomer solution was 1M the initiator solution concentration was 0.1M the solvent used of both systems was DCM. The polymerisations were carried out at 35°C using chloromethyl ethyl ether derived initiator.

From graph 5.2 it can be seen that by increasing the ratio of initiator to monomer the initial temperature increases proportionally. From equation 4.29 where $R_p \propto \frac{dT}{dt}$ the rate of polymerisation was proven to be proportional to the rate of temperature increase, during the polymerisation of oxetane under adiabatic conditions. It can be seen from graph 5.2 that by increasing the initiator to monomer ratio, an increase in the rate of polymerisation is seen but at the expense of lower molecular weight (\bar{M}_n) averages (determined by GPC) and degrees of polymerisation (\bar{DP}_n) as shown by the table 5.2.

Table 5.2

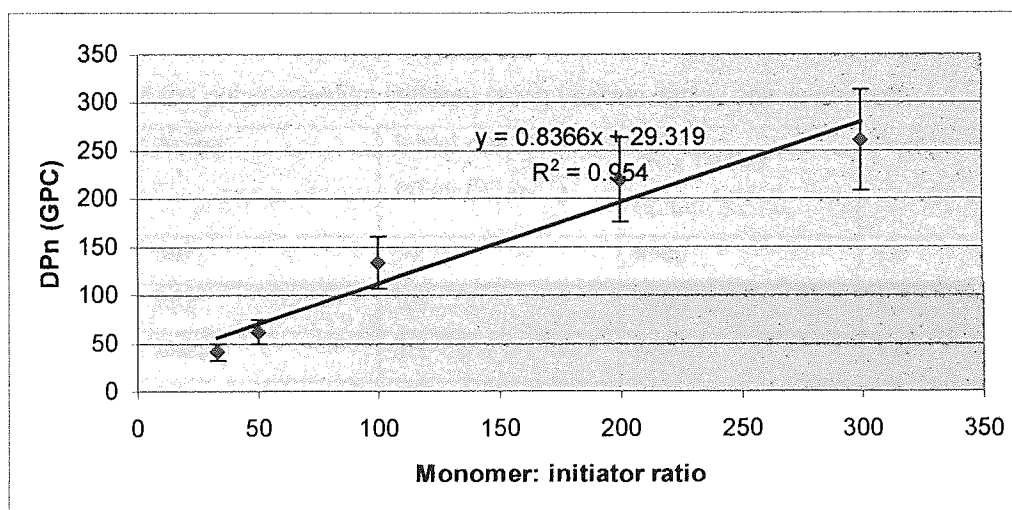
Molecular weight \bar{M}_n averages and \bar{DP}_n of various monomer to initiator ratios using chloromethyl ethyl ether derived initiator system.

Monomer: initiator ratio	'dT/dt °C/sec	\bar{M}_n after 60min	\bar{DP}_n after 60min
33	172	2400	41
50	123	3600	62
100	53	7800	134
200	42	12800	220
300	37	15100	261

From table 5.2 and graph 5.3 it can be seen that the monomer to initiator ratio does not match the \overline{DP}_n measured using GPC. There are several possibilities why this could occur. The possibilities are that the polymer systems have not polymerised as expected or that the resultant polymers have a differing k value as expressed in equation 4.6 and have slightly differing values to the standard (polystyrene) used. From graph 5.3, the deviation from the average line is approximately 20% and these were typical experimental errors that were considered when evaluating GPC derived data.

Graph 5.3

Measured \overline{DP}_n to known monomer to initiator ratio feed polymerisation system



5.2 Effect of the Counterion on the Polymerisation of Oxetane.

It was thought that the type of anion used to stabilise the positive charge of the oxonium ion would affect the rate of polymerisation of oxetane. In a series of experiments, the salt used was varied to see if the polymerisation could be controlled or improved with a particular combination of anion and cation. In this way, it was thought that the degree of separation of the ion pairs could be varied and the consequent effect on the polymerisation measured. Table 5.3 highlights the results of this series of experiments.

A series of experiments were performed by preparing an initiator and reacting 2.0×10^{-3} mol of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ with 2.0×10^{-3} mol of AgSbF_6 , AgPF_6 , KSbF_6 , KPF_6 or $\text{Ag}(\text{C}_4\text{H}_9\text{O}_2)$ in 20ml of dried DCM under an inert atmosphere and agitation for 24 hours in a foil coated Schlenk flask. After 24 hours, the oxonium ion solution was separated from the silver bromide precipitate and stored under an inert atmosphere. The solution was mixed thoroughly, made airtight and transferred to the vacuum line. In a separate Schlenk flask, a 1M solution of oxetane was prepared by mixing 4×10^{-2} mol with dried DCM solvent. 30 ml of monomer solution was transferred to the polymerisation vessel by using the Schlenk positive pressure technique as described in chapter 3.4. 3 ml of the initiator solution was transferred to the monomer solution using the Schlenk positive pressure technique, the initial rate of reaction was followed by calorimetric and GPC analysis.

Table 5.3

Results of the polymerisation initiated using various cation and anion salts.

Metal	Anion	Initial rate DT/dt ($^{\circ}\text{C} \cdot \text{sec}^{-1}$)	\overline{M}_n (GPC) ($\text{g} \cdot \text{mol}^{-1}$)	Polydispersity
Ag^+	SbF_6^-	50	8900	1.6
Ag^+	PF_6^-	3.6	5000	1.7
K^+	SbF_6^-	2.9	500	1.0
K^+	PF_6^-	0.0	500	1.0
Ag^+	$\text{C}_4\text{H}_9\text{COO}^-$	2.6	500	1.0

It can be seen that catalyst systems derived from silver salts are more effective than those derived from potassium salts. This can be seen in table 5.1 with higher degrees of polymerisation being obtained with catalyst systems based on silver salts. It is also possible that the products derived from the potassium compounds are mainly cyclic oligomers rather than linear polymer chains. The solubility of potassium chloride in the solvent used was greater than that of silver chloride. The K^+ ions can form a complex with the propagating chain and promote cyclic oligomer formation.

5.2.1 Addition of Cyclic Ether to KPF_6 Derived Initiator System.

Due to the poor polymerisation of oxetane with KPF_6 and that the residual potassium halide was present in the initiator system, 18-crown-6 ether was added to the initiator system to see if the efficiency could be improved.

A series of experiments were performed by preparing an initiator and reacting 2.0×10^{-3} mol of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ with 2.0×10^{-3} mol of KPF_6 in 20ml of dried DCM under an inert atmosphere and agitation for 24 hours in a foil coated Schlenk flask. After 24 hours, 4.0×10^{-3} or 2.0×10^{-2} mol of 18-crown-6 was added to the initiator solution. After a further 24 hours, the oxonium ion solution was separated from the silver bromide precipitate and stored under an inert atmosphere. The solution was mixed thoroughly, made airtight and transferred to the vacuum line. In a separate Schlenk flask, a 1M solution of oxetane was prepared by mixing 4×10^{-2} mol with dried DCM solvent. 30 ml of monomer solution was transferred to the polymerisation vessel by using the Schlenk positive pressure technique as described in chapter 3.4. 3 ml of the initiator solution was transferred to the monomer solution also using the Schlenk positive pressure technique, the initial rate of reaction was followed by calorimetric and GPC analysis with the results shown in table 5.4.

Table 5.4

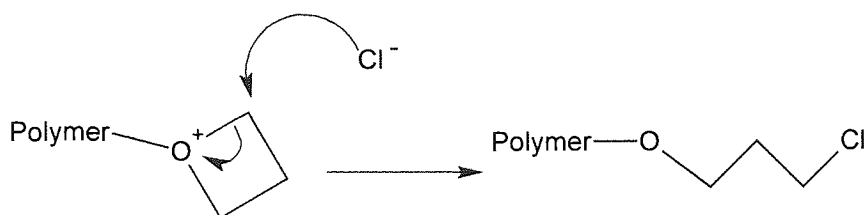
Results of the polymerisation of oxetane initiated using KPF_6 salt derived initiator with and without 18-crown-6 added.

Metal salt relative ratio	18-C-6 relative ratio	Initial rate DT/dt ($^{\circ}\text{C} \cdot \text{sec}^{-1}$)	\bar{M}_n (GPC) ($\text{g} \cdot \text{mol}^{-1}$)	Polydispersity
1	0	0	540	1.0
1	2	0	530	1.0
1	10	0	550	1.0

The silver ion was important although it did not play any direct role in the propagation of the polymer. The main reason for this is likely to be that the silver halide salt is insoluble in the solvent, this leads to a low concentration of chloride ions, which can readily terminate the polymerisation shown in figure 5.3. The addition of a crown ether had no effect on the efficiency of a KPF_6 derived initiated polymerisation of oxetane.

Fig 5.3

Termination of ACE by chloride ions remaining from the generation of the oxonium ion.



5.3 Resonance Stabilisation of Carbocation Derivatives.

Although the resonance structure of the oxonium ion detailed previously showed good promise as an initiator, it did have several drawbacks. The main drawback in the use of ethers such as chloromethyl ethyl ether, is that there are limited number of such halogenated methyl ethers available. This restricts the polymer architectures of such systems; alternative ways of generating such stabilised oxonium ions were therefore investigated. Generating an oxonium ion by way of coupling of a carbonyl ($\text{C}=\text{O}$) group such as benzaldehyde to a carbocation centre (fig 5.6) was considered as an alternative. The resulting coupling was expected to generate an oxonium ion similar to that obtained by the resonance technique using chloromethyl ethers.

In the design of suitable oxonium ions, it was necessary to generate the corresponding stable carbocation with which the carbonyl group could react. The selection of suitable precursors for these ions required judicious design in order that the resulting ion could be stabilised by effects such as resonance. In addition to the source of the carbocation having a structure that could lead to stabilisation of the positive charge, it was also necessary for the molecule to have a good leaving group^[35], such as a halide ion. Alkyl chains with conjugated unsaturation could be used but those with suitable leaving groups were also relatively rare. Stabilisation of charges around aromatic rings is well-documented^[35] and by choosing an appropriate starting material, systems can be generated with varying stabilities. A balance had to be struck between stability and reactivity as very stable systems may pose a problem, and they may not initiate the polymerisation reaction. Compounds that were initially investigated were halogenated xylenes and their derivatives.

Halogenated xylenes lend themselves to the generation of carbocations in the presence of a suitable counterion. By adding silver hexafluoroantimonate to a brominated xylene, silver bromide is produced, leaving hexafluoroantimonate as a stable anion and a cationic xylene ion. A series of experiments was undertaken, using various halogenated xylenes as initiators for the polymerisation of oxetane. These xylenes were reacted with $\text{Ag}^+\text{SbF}_6^-$ detailed in 5.3.1. Initially, experiments were performed without the addition of benzaldehyde to assess the effectiveness of carbocation generation.

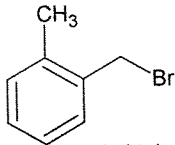
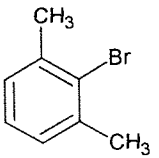
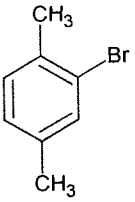
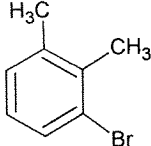
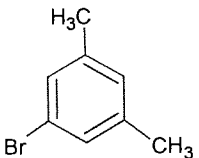
5.3.1 Halogenated Aromatic Compound Derived Initiators

A series of experiments were performed by preparing an initiator and reacting 2.0×10^{-3} mol of brominated aromatic compound (shown in table 5.5) with 2.0×10^{-3} mol of AgSbF_6 . 20ml of dried DCM was added to the mixture under an inert atmosphere and agitated for 24 hours in a foil coated Schlenk flask. After a further 24 hours, the oxonium ion solution was separated from the silver bromide precipitate and stored under an inert atmosphere. The solution was mixed thoroughly, made airtight and transferred to the vacuum line. In a separate Schlenk flask, a 1M solution of oxetane was prepared by mixing 4×10^{-2} mol with dried DCM solvent. 30 ml of the monomer solution was transferred to the polymerisation vessel by using the Schlenk positive pressure technique as described in chapter 3.4. 3 ml of the initiator solution was transferred to the monomer solution using the Schlenk positive pressure technique, the initial rate of reaction was followed by calorimetric, gravimetric and GPC analysis with the results shown in table 5.4.

Certain types of halogenated aromatic compounds are more effective than others as initiators, for the polymerisation of oxetane. The efficiency was dependent on what their electronic resonance configurations were. Table 5.5 shows the initial rates of polymerisation and resultant molecular weight with various halogenated aromatic derivatives.

Table 5.5

Reactivity of various initiators based on brominated xylene derivatives for the polymerisation

Brominated compound	Initial rate of temperature change dT/dt *	Mn (GPC) after 4h	% Yield
 2-bromomethyl toluene	62	7900 PD= 1.6	57
 2-bromo-meta-xylene	4.3	3500 PD= 3.5	53
 2-bromo-para-xylene	0	14000 PD= 2.2	28
 3-bromo-ortho-xylene	0	15000 PD= 2.0	68
 5-bromo-meta xylene	1.5	4000 PD= 3.9	30

From table 5.5, it can be seen that the molecular weight achieved depends on the type of halogenated aromatic compound used. The polymerisation showing the fastest initial rate of polymerisation was 2-bromomethyl toluene indicating that it is an effective catalyst. The other catalyst systems gave much slower initial rates of polymerisation, although their effectiveness varied.

The 2-bromo-para-xylene and 3-bromo-ortho-xylene derived initiator systems both had low initial rates of polymerisations, but generated high molecular weight systems after 4 hours of polymerisation with moderate polydispersities of ~2. For both systems

the bromide group was positioned in an ortho and meta position to the respective methyl groups on the benzene ring. The systems may perform similarly due to them both sharing similar resonance structures.

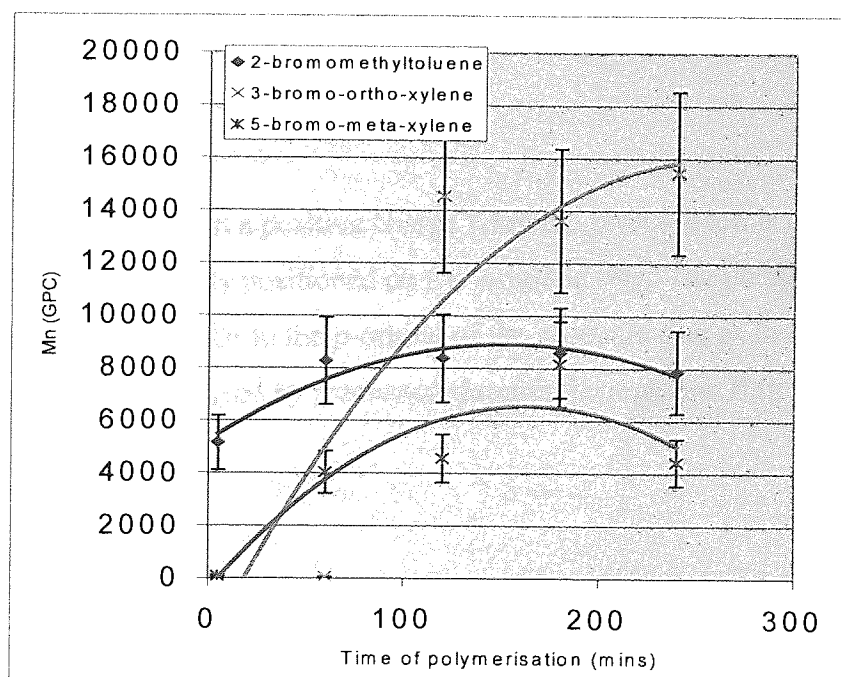
The 2-bromo-meta-xylene and 5-bromo-meta-xylene systems also gave similar results of slow initial rates of polymerisation. They also had significantly lower molecular weights and high polydispersities of 3.5 and 3.9 respectively.

5.3.2 Development of Molecular Weight During Course of Polymerisation.

During the series of experiments detailed in 5.2.1, samples were taken at regular intervals and quenched in methanol. The samples were dried in a vacuum oven at 30°C for several days until the solvent and methanol was drawn off. The samples were dissolved in HPLC grade THF and analyzed using GPC. The \overline{M}_n progression was followed for several of the polymerisations and is shown in graph 5.4.

Graph 5.4

Polymerisation of oxetane using various aromatic brominated derived initiator systems reacted with AgSbF_6 in DCM at 35°C



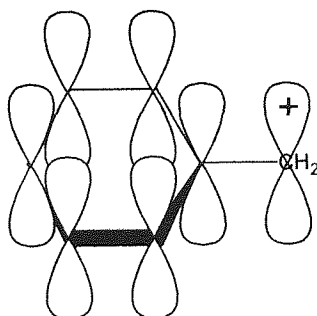
The \overline{M}_n progression of the xylene based systems was initially very slow and was shown by low initial molecular weights. The bromomethyl toluene system had a

higher initial rate of monomer conversion seen by higher \overline{M}_n values. The low rates of polymerisation for the xylene systems led to highly disperse polymer systems and these were characterised with high PD values as illustrated in table 5.5.

5.3.3 Carbocation Ring Stabilisation

In order for a positive charge to be delocalised around an aromatic system, it must have the potential (steric alignment) to be part of the conjugated system. For bromomethyl benzene, it will form the structure seen in figure 5.4 with the p orbitals of the ring and those of the $-\text{CH}_2^+$ being co-linear giving rise to stabilisation by resonance around the aromatic ring.

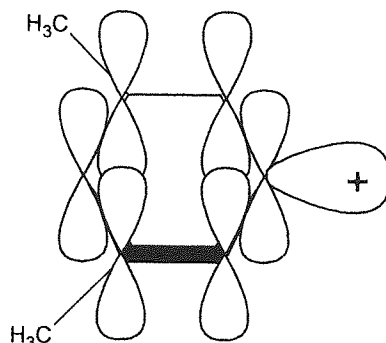
Fig 5.4
Stabilisation of bromomethyl benzene due to alignment of the p-orbitals.



Brominated xylenes form a positive charge when the bromide ion is eliminated. The positive charge is directly positioned on the aromatic ring. The positive charge will be in an orbital perpendicular to the p-orbital of the aromatic ring as in figure 5.5, which cannot be directly stabilised by resonance through the aromatic ring.

Fig 5.5

Inductive effect of the resonance stabilisation due to perpendicular alignment of the positive charge to the p-orbitals of the aromatic ring of 5-bromo-meta-xylene.



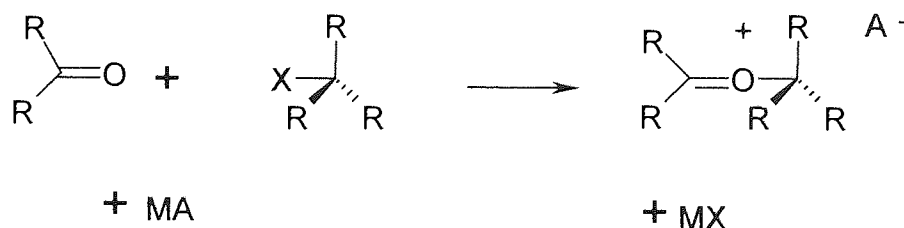
Although the xylene-derived initiators could not be stabilised directly, a hydride rearrangement within the molecule could lead to a system similar to that described by figure 5.4 resulting in a resonance stabilisation.

5.4 Carbonyl Co-Initiator

Although an oxonium ion may be obtained by elimination of the halide from the halogenated ether, the mechanism did have several disadvantages. The most major of these was the restricted number of halogenated ethers available as the starting materials limited their use to linear polymer systems. Another possible method for generating the initiator was by a reaction of a carbonyl compound with a carbocation centre as shown in the general reaction scheme figure 5.6. This coupling had the potential to create a more efficient initiator system compared to those generated in section 5.3 as the number of starting compounds was much greater. This could allow for extra stabilisation from other substituents incorporated into the initiator molecule.

Fig 5.6

Proposed reaction scheme for generation of oxonium ion.



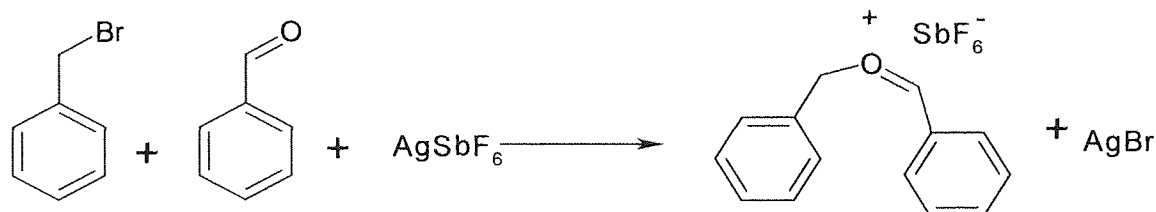
This approach could open up a novel synthetic route making use of compounds of a greater variation through the two substituent (R) groups. There are many types of halogenated materials and aldehydes and ketones available and therefore the potential number of corresponding catalysts is very large. Using 'core' molecules with several reactive sites could also generate multifunctional initiators.

5.4.1 Benzaldehyde as a Co-Initiator.

From the experiments carried out in section 5.2, one of the most effective initiators was based on a 2-bromomethyl-toluene derivative. Bromomethyl-benzene is a similar compound and was used with and without the addition of a benzaldehyde to assess its effectiveness. After the generation of the carbocation by halide elimination (with the AgSbF_6), the carbonyl oxygen on the benzaldehyde, was attracted to it forming an oxonium ion as shown in figure 5.7.

Fig 5.7

Generation of stable oxonium ion by the addition of a benzaldehyde to a carbocation derived from bromomethyl-benzene.



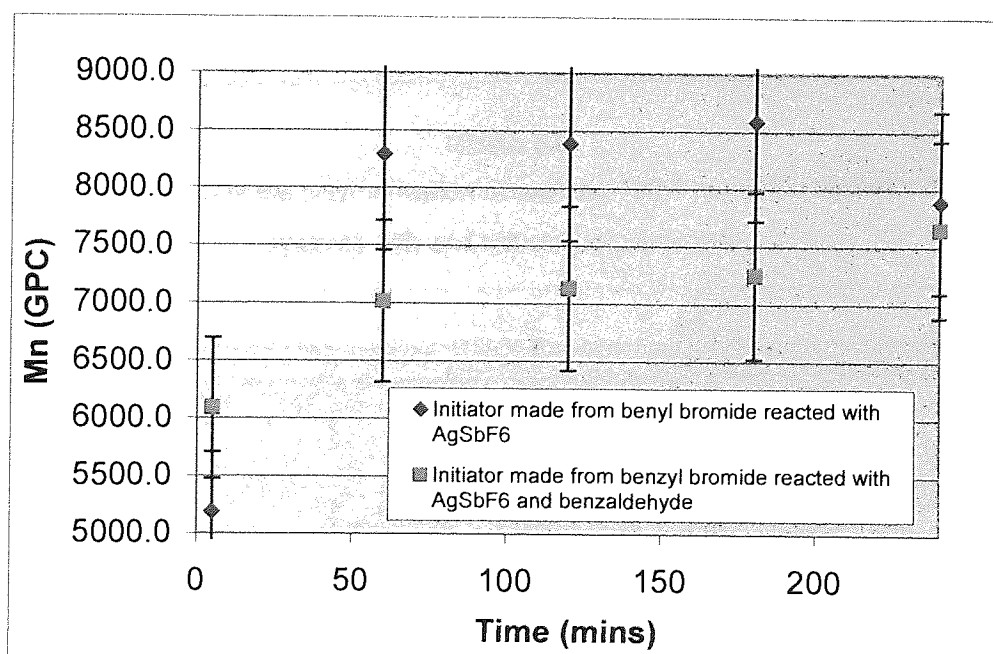
Two initiator systems were prepared to assess the effect of adding benzaldehyde to a carbocation. The first system was used as a control and was made by reacting molar equivalents of bromomethyl benzene with AgSbF_6 in a 0.1M solution with DCM as a solvent. The materials were added to a Schlenk flask in argon filled glove box. The reaction vessel was covered with aluminium foil prior to any chemical additions to prevent any decomposition of the silver precipitate and left for 24 hours prior to use. The supernatant solution was decanted from the silver halide precipitate and used as an initiator for the polymerisation of oxetane (in 1M DCM solution). The molar ratio of initiator to monomer was set at 1: 100. The initiator was added to the polymerisation vessel with an inert gas flow having a positive pressure difference using dried glass syringes.

The second initiator system was made by reacting equimolar quantities of bromomethyl-benzene with AgSbF_6 in a 0.1M solution using dried DCM as a solvent. After 30 mins the solution changed to yellow and a molar equivalent of benzaldehyde was added to the reaction vessel creating a vivid orange solution. Prior to the chemical additions the reaction vessel was covered with aluminium foil. The reaction solution was left for 24 hours prior to use. The initiator solution was decanted from the silver halide precipitate and used as an initiator for the polymerisation of oxetane (in 1M DCM solution). 3 ml of the initiator solution was added to 30ml of the monomer solution in the polymerisation reactor under an inert gas flow with a positive pressure using dried glass syringes.

Samples were taken from both polymerisations using dried glass syringes. The samples were quenched immediately in methanol. The methanol was then evaporated and the resultant polymers analysed using GPC with the results shown in graph 5.5. The progressions of the polymerisations were also monitored calorimetrically and gravimetrically highlighted in table 5.6.

Graph 5.5.

The effect of the addition of benzaldehyde to the initiator on the progression of polymerisation of oxetane



By comparing the progression of \overline{M}_n for the polymerisation (graph 5.6) of oxetane with and without benzaldehyde, it can be seen that the addition of benzaldehyde increased the initial rate of polymerisation which was confirmed by the calorimeter results in table 5.6. The conversion of monomer when benzaldehyde was used was very high after 5 minutes and remained constant throughout the polymerisation as seen from graph 5.5. It is likely that the rate of polymerisation was so fast for the benzaldehyde system that all of the monomer was used up in the first stages of the polymerisation.

The polymerisation rate was also fast for the initiator not containing the benzaldehyde additive and a high initial \overline{M}_n was obtained after five minutes of polymerisation. The % conversion of the monomer grew more slowly than the benzaldehyde system but with a slightly narrower polydispersity.

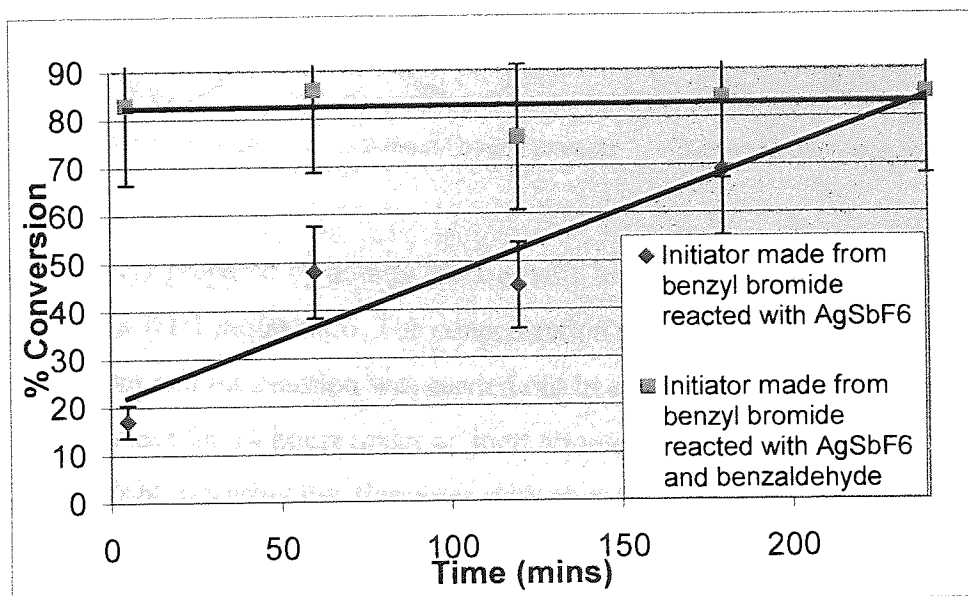
Table 5.6

Effect of the addition of Benzaldehyde on the polymerisation of oxetane. When added to the initiator generated using benzyl bromide and AgSbF_6 .

Initiator system	Initial rate of polymerisation DT/dt ($^{\circ}\text{C}\cdot\text{sec}^{-1}$)	% yield after 4 hours	Mn (GPC) after 4 hours
Benzyl bromide and AgSbF_6	71	84	7900 PD= 1.6
Benyl bromide, AgSbF_6 and Benzaldehyde	105	86	7700 PD= 1.8

Graph 5.6

% Conversion (GPC) of the polymerisation of oxetane 100:1 monomer : initiator for initiator systems with and without benzaldehyde.



From graph 5.6, it can be seen that the addition of benzaldehyde does increase the rate at which the polymerisation occurs, but does not significantly alter the resultant polymer system with similar molecular weights and polydispersities being observed for the systems with and without benzaldehyde.

5.5 Benzylic Bromide Initiators.

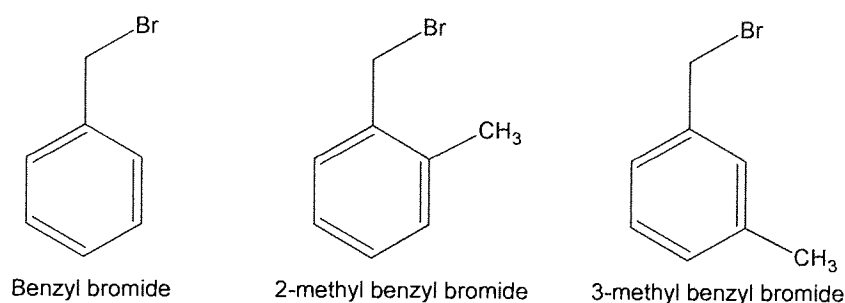
Experiments carried out so far, indicate that initiation of polymerisation of oxetane is achieved with aromatic (benzylic) bromides. By changing the type of brominated compounds used, it was thought to be possible to vary the reaction, and this would lead to an enhanced functionality and possibly the generation of advanced structures such as multifunctional initiator systems.

5.5.1 Polymerisations Using Substituted Benzyl Bromides.

The benzyl bromide derived initiator system had been found to be effective at polymerising oxetane. It was not known what the effect of an additional methyl group on the benzylic ring would have on the efficiency of the polymerisation. A series of methyl substituted benzyl bromides were used to generate oxonium ion initiators as shown in figure 5.8.

Fig 5.8

Methyl substituted benzyl bromides used to generate initiator systems.

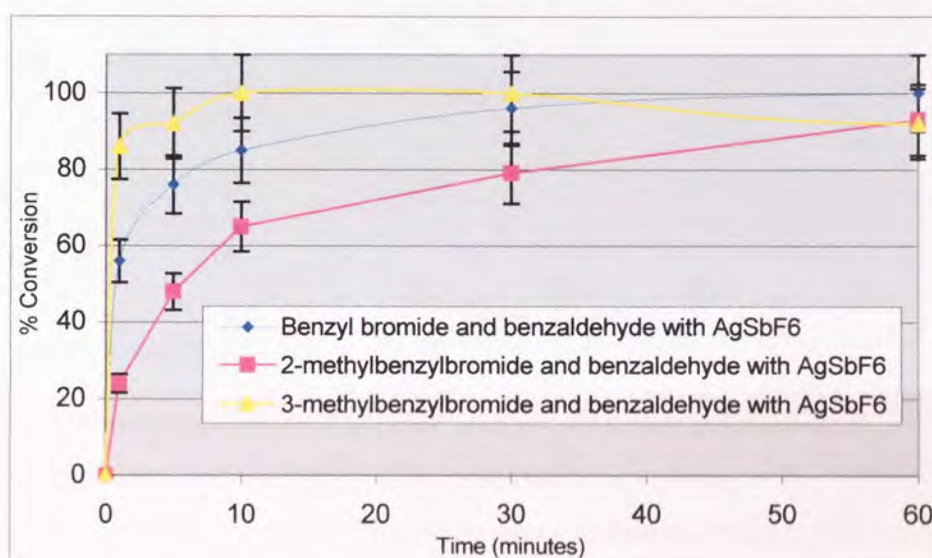


The initiators were prepared by adding the aromatic bromide to AgSbF_6 and benzaldehyde in a 1:1:1 molar ratio. The concentration of the reactants was 0.1M in DCM as a solvent and the reaction was carried out in a Schlenk flask. The initiator was allowed to react for 24 hours under an inert atmosphere in an argon glove box, in the absence of light, covering the glassware with aluminium foil. 3ml of the initiator

was then added to 30 ml of the 1M monomer solution of oxetane (in DCM as a solvent) by the Schlenk technique under a flow of oxygen free nitrogen as described in section 3.4. The ratio of monomer to initiator was 100:1. The initial rate of polymerisation was recorded by measuring the rise in temperature of the reaction mixture resulting from the exotherm during the initial stages of polymerisation. The % conversion was measured by taking samples at set times and recording the yield and shown in graph 5.7.

Graph 5.7

% Conversion (GPC) of polymerisation of oxetane at 100:1 with various substituted benzyl bromides.



By comparing the rates of conversion in graph 5.7, 3-methylbenzyl bromide led to the fastest polymerisation of oxetane. The slowest polymerisation observed was with the 2-methylbenzyl bromide. This suggests that the position of the methyl group have a significant effect upon the stability and reactivity of the cation formed.

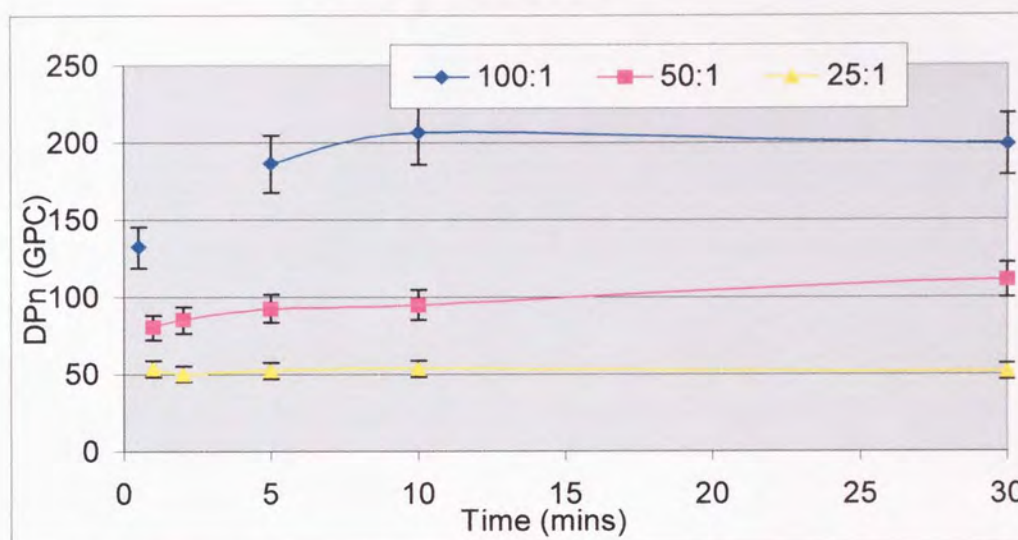
5.5.2 Polymerisations using 3-Methyl Benzyl Bromide.

From graph 5.7 it was found that the methyl group in the meta position increased the rate of conversion of the oxetane monomer. The rate of polymerisation of oxetane using 3-methylbenzyl bromide reacted with silver hexafluoroantimonate and benzaldehyde was studied at various monomer to initiator ratios. Three reactions were performed with the initiator being made by addition of a 1:1:1 of 3-methylbenzyl bromide, AgSbF₆ and benzaldehyde in DCM at a concentration of 0.1M. A 1M

solution of oxetane in DCM was used for all three polymerisations. The ratios of monomer to initiator were set at 25, 50 and 100 to 1.

Graph 5.8

Progression of the polymerisation of oxetane with various monomer: initiator ratios using a initiator derived from 3-methylbenzyl bromide.



Fast initial rates of polymerisation were seen for all of the polymerisations with the molecular weights of the completed polymerisation increasing with increased levels of monomer addition. By adjusting the monomer to initiator ratio it was possible to control the resultant molecular weight of the polymer.

Chapter 6

Synthesis of Novel Shaped Polymer Systems

6.1 Dendrimers and Star Shaped Polymer Systems.

Dendrimers^[79-83] are polymers of novel architecture that can be made up of several short chains linked together in a starburst array. They differ from conventional linear polymers as they have more terminal groups and vary in physical structure. These methods can be grouped into two classes, branching from a central core or coupling short chains with multifunctional coupling agents. Mathias et al^[59] reported that dendrimers have different physical properties from their corresponding linear relatives. The main differences that have been noted are the solvation and rheological properties of dendrimers^[81] compared to linear systems and the effects of temperature. These differences have been attributed to hyperbranching a second functional group resulting in branching and resulting in differing properties. During the anionic polymerisation of 3-ethyl-3-hydroxymethyl oxetane, the pendant hydroxyl groups were a source of multiple branching, resulting in the dendrimer system^[59].

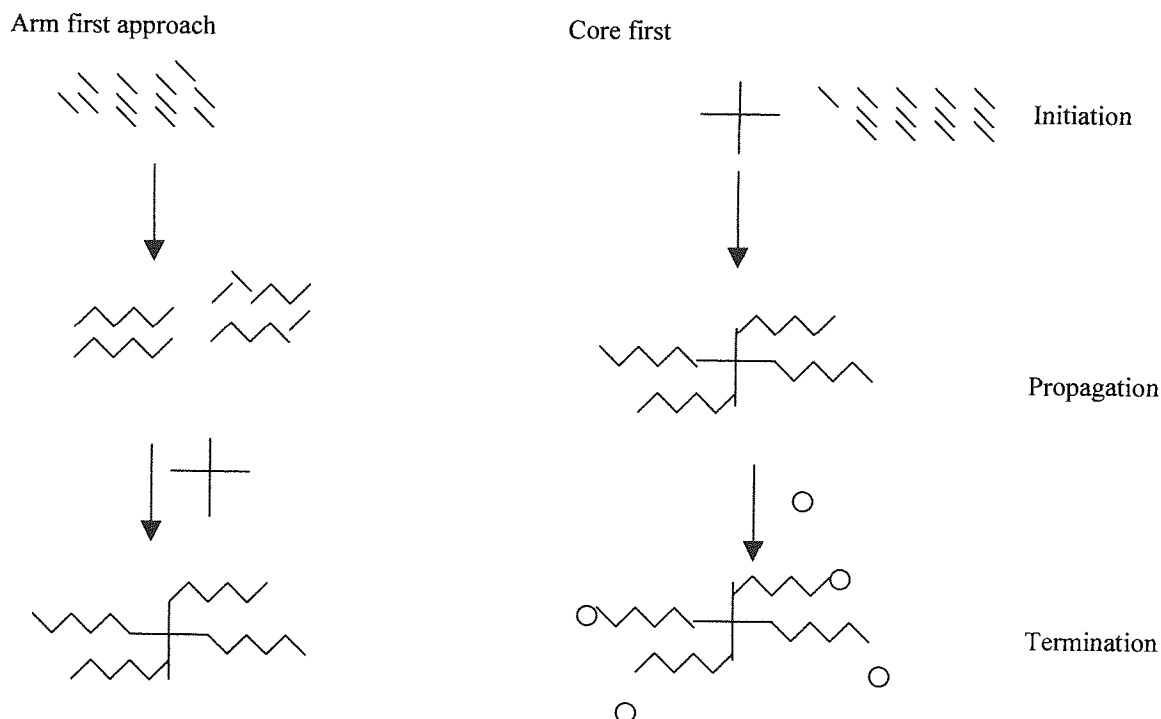
6.2 Synthetic Routes For “Star” Shaped Polymers

There have been many reports of the synthesis of star shaped polymers in literature (Trollsas et al^[80]). These syntheses can be classified into two main categories. The first of these is the core first approach strategy, which involves building up several polymer chains simultaneously from a multifunctional initiator molecule. Multifunctional initiators, based on the dextrin-type system, offer an effective nucleus by which to build up the polymer chain. The main difficulty of using this type of core molecule, is that the size of the centre of the molecule is very large.

The second method of synthesis is the arm (chain) first approach. Such an approach is normally performed using a condensation type mechanism where a chain is built up and then terminated at the end by the addition of the multifunctional core molecule. Both the centre first and arm first approaches are shown schematically in figure 6.1.

Figure 6.1

General approaches used for the generation of 'star' shaped polymer systems.



6.3. 'Star' Shaped Polymers Using the Core Approach.

Star shaped polymers can be synthesised by cationic ring opening polymerisation using either the core first or arm first approaches. In order to perform a core approach polymerisation, the synthesis of a multifunctional initiator is vital. The results from chapter 5 suggest that there are several effective initiator systems that can be used to develop a multifunctional initiator. The central molecule must have several reactive functional groups that can act as initiation sites.

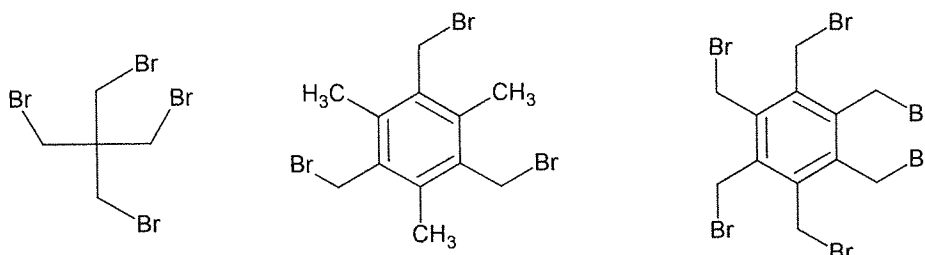
There are a number of multiple brominated compounds, however this study was focused on multifunctional aliphatic and aromatic compounds. By utilising difunctional core compounds, only a simple telechelic chain could be made, therefore these were excluded from the study. This then, limited the study to the use of molecules with three or more reactive sites on the molecule.

Three compounds of interest were based on systems similar to those studied in chapter five. These could be divided into two main groups; aromatic and alkyl based systems. Hexakis bromomethyl benzene and 1,3,5-tris-bromomethyl-2,4,6-trimethyl benzene

are both derivatives of the benzyl bromide system. 2,2-bis(dibromomethyl)-1,3-dibromopropane are based on the alkyl system. The structures of these compounds are shown in figure 6.2.

Figure 6.2

Structures of potential halogenated core molecules to be used as a starting material for the generation of multifunctional initiators.



1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene

2,2-bis(dibromomethyl)-1,3-dibromopropane

Hexakis(bromomethyl)benzene

6.4. Preparation of Multifunctional Initiators

The synthesis of star polyoxetane using the core approach, was restricted because the number of oxonium ions that could be synthesised using the chloromethyl ethyl ether mechanism was very limited. Few multifunctional compounds were available with the chloromethyl ether groups. In order to generate multifunctional cores, an alternative way of generating oxonium ions was needed. It was shown in Chapter 5 that by adding benzaldehyde to the benzyl bromide and silver hexafluoroantimonate initiator system, control of the polymerisation could be achieved. The initiators were prepared by reacting equivalent ratios of benzaldehyde and brominated methyl groups in the presence of the molar equivalent of silver hexafluoroantimonate. The following initiators were prepared using the molar ratios of materials shown in table 6.1.

Table 6.1

Molar ratios of materials used in preparation of multifunctional initiators.

Brominated compound	Ratio of Brominated Compound	Ratio of Benzaldehyde	Ratio of AgSbF ₆	Solvent 0.1M Solution
Pentaerythryl tetrabromide	1	4	4	DCM
1,3,5-trisbromomethyl mestyline	1	3	3	DCM
Hexakis bromomethyl benzene	1	6	6	DCM

All initiator systems were prepared at 0.1M concentration using DCM as a solvent and prepared using Schlenk technique described in chapter 3. Once prepared the initiators were stored prior to use in an airtight vessel under an inert atmosphere.

6.5. Kinetic Studies of Multifunctional Initiators Polymerisations.

In order to study the kinetics^[60] of polymerisations at 35°C, the initiator solution was added to the monomer solution in the polymerisation vessel and samples taken and quenched in methanol at timed intervals. The initial plan was to take a sample of known size and calculate a yield of the monomer conversion. It was found at this time that an unknown amount of monomer would become trapped within the polymer network making gravimetric analysis difficult. Therefore, a new methodology was used to study the kinetics of polymerisation using the number average degree of polymerisation after different time periods.

For rapid initiated living polymerisations, the number average degree of polymerisation could be given by equation 6.1, if all the initiator molecules led to a growing molecular chain.

$$\overline{DP}_n = \frac{[M]_0 - [M]_t}{[I]_0} \quad \text{Eq 6.1}$$

\overline{DP}_n = number average degree of polymerisation, $[M]_0$ = initial concentration of monomer, $[M]_t$ = concentration of monomer after time t, $[I]_0$ = initial concentration of initiator.

The concentration of the monomer at time t , $[M]_t$ could be calculated by equation 6.2 where k = apparent first order rate constant.

$$[M]_t = [M]_0 e^{-kt} \quad \text{Eq 6.2}$$

By substituting equation 6.2 into 6.1, then the degree of polymerisation could be obtained from equation 6.3.

$$\overline{DP}_n = \frac{[M]_0 (1 - e^{-kt})}{[I]_0} \quad \text{Eq 6.3}$$

Assuming that after some time, all of the monomer is consumed, then the final degree of polymerisation ($\overline{DP}_{n\infty}$) can be obtained from equation 6.4.

$$\overline{DP}_{n\infty} = \frac{[M]_0}{[I]_0} \quad \text{Eq 6.4}$$

Substituting equation 6.4 into equation 6.3 gives equation 6.5.

$$\overline{DP}_n = \overline{DP}_{n\infty} (1 - e^{-kt}) \quad \text{Eq 6.5}$$

Rearranging equation 6.5 and taking the natural logarithm gives equation 6.6.

$$\ln \left(1 - \frac{\overline{DP}_n}{\overline{DP}_{n\infty}} \right) = -kt \quad \text{Eq 6.6}$$

For living polymerisations, a plot of $\ln \left(1 - \frac{\overline{DP}_n}{\overline{DP}_{n\infty}} \right)$ against time

gives a straight line with the gradient equal to the apparent first order rate of polymerisation. This treatment of the average degree of polymerisation was most useful for early on in the polymerisation as when \overline{DP}_n tends to $\overline{DP}_{n\infty}$, small inaccuracies lead to large errors. For molecules with large initiator molecules and low molecular weight polymers such as at the start of a polymerisation, the value of \overline{DP}_n was higher than expected, as the initiator molecular weight was included in the analysis. The effect of using multifunctional core molecules resulted in relatively high molecular weight core molecules. By substituting \overline{DP}_n by equation 6.8 this effect was minimised.

$$\overline{DP}_n = \frac{(\overline{M}_n + M_{\text{int}})}{M_{\text{mon}}} \quad \text{Eq 6.7}$$

Where M_{int} is the molecular weight component of the initiator system and M_{mon} is the molecular weight of unreacted monomer.

6.6. Four Armed Initiators.

Prior to the synthesis of the initiator and monomer solutions, all glassware and chemicals were treated as described in chapter three so to prevent contamination. The initiator molecule was prepared by the addition of 6.4×10^{-3} mol of silver hexafluoroantimonate to 1.6×10^{-3} mol of 2,2-bis-bromomethyl-1,3-dibromopropane in 8ml of dried DCM. The solution was allowed to react for 2 hours and then 6.4×10^{-3} mol of benzaldehyde was added to the reaction vessel. The Schlenk vessel was sealed and wrapped in aluminium foil and left for 24 hours under an oxygen free argon atmosphere. After 24 hours, the reaction solution was decanted into a freshly dried and de-aerated Schlenk flask (coated in aluminium foil), removing the silver halide precipitate. The flask was stored in an inert atmosphere until required.

The monomer solution was prepared by mixing 0.05mol of purified oxetane with 48ml of dried DCM. The solution was stored under an inert atmosphere until required.

For the polymerisation reaction, 30ml of monomer solution was added to the polymerisation vessel under a flow of oxygen free nitrogen and allowed to reach 35°C . Once the monomer solution had reached a constant temperature 7.5ml of the initiator solution was added to the polymerisation vessel using an oxygen free nitrogen gas filled syringe. The initial rate of polymerisation was followed using a thermocouple attached to the polymerisation vessel shown in chapter 3.3.

Samples were taken at timed intervals and quenched in methanol. The methanol and unreacted monomer were removed by placing the quenched samples in a vacuum oven set to 40°C and left for over 72 hours. The dried samples were then analysed using GPC and NMR with the molecular weight and average degree of polymerisation shown in table 6.2 and graph 6.1.

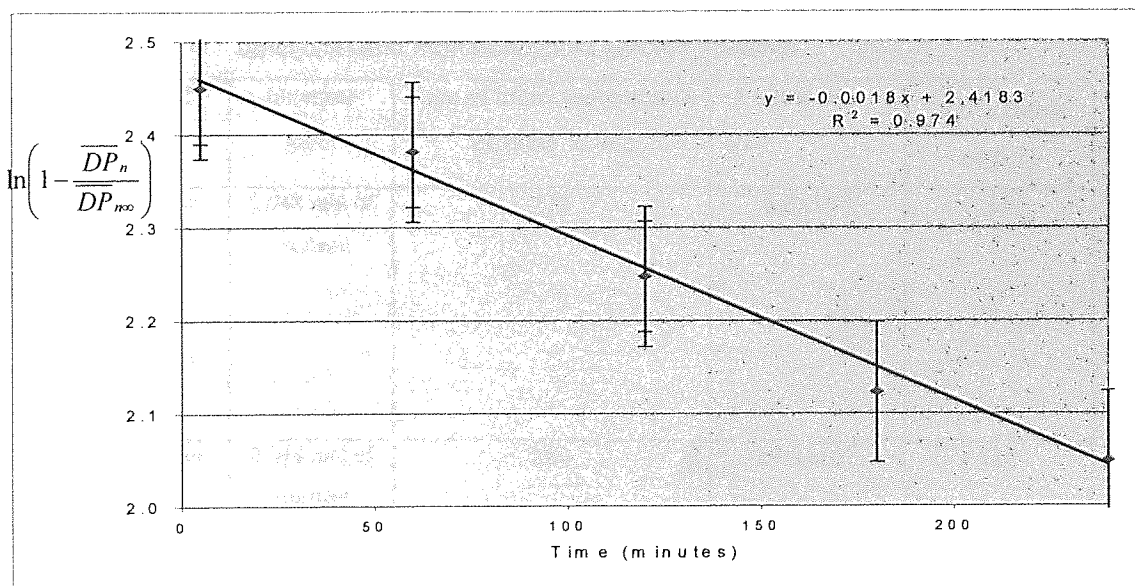
Table 6.2

GPC results for polymerisation of oxetane using a initiator derived from 2,2-bis-bromomethyl-1,3-dibromopropane.

Time (minutes)	\overline{M}_n (GPC)	PDI	\overline{DP}_n	$\ln\left(1 - \frac{\overline{DP}_n}{\overline{DP}_{\infty}}\right)$
5	1269	1.5	14	-1.34
60	1311	1.6	16	-1.85
120	1386	1.7	17	-2.25
180	1447	1.8	18	-2.94
240	1480	2.0	19	

Graph 6.1

$\ln\left(1 - \frac{\overline{DP}_n}{\overline{DP}_{\infty}}\right)$ against time for the polymerisation of oxetane using an initiator derived from 2,2-bis-bromomethyl-1,3-dibromopropane.



From table 6.2 and graph 6.1 it can be seen that there is a linear correlation in accordance with equation 6.6. The gradient of the plot is proportional to the apparent first order rate constant, k , for the polymerisation of oxetane.

6.6.1. Short Chain Linear Polymerisations.

In order to compare the rate of polymerisation of multifunctional initiated systems a series of polymerisations were carried out using a monofunctional initiator with various low ratios of monomer to initiator being used.

Two initiator systems were prepared and their methods of manufacture are described in 5.4 and 6.5. Both systems had methyl bromide groups reacted with AgSbF_6 and benzaldehyde in DCM at 0.1M. The initiators were allowed to react for 24 hours and the silver halide precipitate was removed by decantation. The first initiator system is based on mono-functional initiator with 1 reactive site per initiator molecule with the second initiator system being based on a tetra functional core initiator with four reactive centres per molecule. For the tetra-functional molecule four molar equivalents of AgSbF_6 and benzaldehyde were reacted.

The initiators were added to a 1M solution of oxetane in DCM at various ratios into a polymerisation vessel and the ensuing reaction followed using thermo-kinetic data and reaction sampling.

Table 6.3.

Molar ratios and results for polymerisations of oxetane at various initiator ratios using tetra functional and monofunctional initiator systems

Initiator system and level	Oxetane level	Rate of initial temperature increase °C/sec	$-k$ (from eq 6.6)	\overline{DP}_n (from eq 6.7)
Tetra-functional initiator system 1.2×10^{-3} mol of pentaerythrityl tetrabromide, 4.8×10^{-3} mol of AgSbF_6 , 4.8×10^{-3} mol of Benzaldehyde	0.048 mol of oxetane	233	6.0×10^{-3}	11
Mono-functional initiator system 1.2×10^{-3} mol of benzyl bromide, 1.2×10^{-3} mol of AgSbF_6 , 1.2×10^{-3} mol of Benzaldehyde	0.048 mol of oxetane	280	29.8×10^{-3}	121
Mono-functional initiator system 4.8×10^{-3} mol of benzyl bromide, 4.8×10^{-3} mol of AgSbF_6 , 4.8×10^{-3} mol of Benzaldehyde	0.048 mol of oxetane	260	6.9×10^{-3}	8

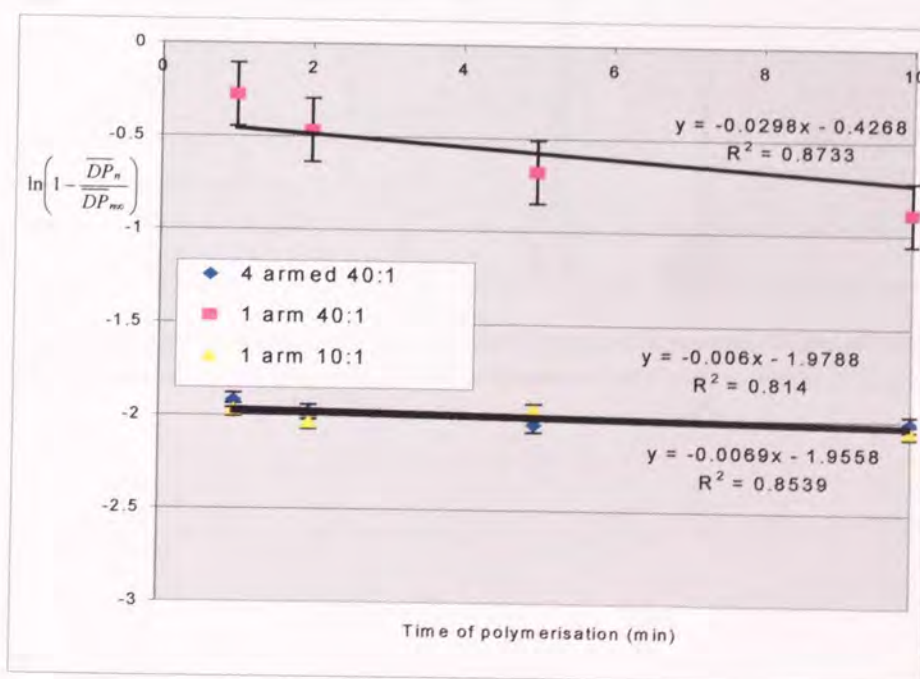
All of the initial rates of polymerisation determined by calorimetric analysis were similar for all initiation systems shown in table 6.3. The rates for all three of the polymerisation systems were fast. Owing to the systems having similar initiator systems, this similarity in initial polymerisation suggests that the tetra functional system did not reduce the efficiency of polymerisation.

The apparent first order rate constants of polymerisation, k , were determined by using equation 6.7 and calculated from the gradients shown in graph 6.2. It was found that, k , for the tetrafunctional initiator was similar to that of the short chain polymerisation and significantly lower than that of the longer polymerisation. The similarity suggests that the tetra-functional initiator behaved similarly to that of the short chain, implying that several chains are being initiated from the chain rather than just one. The apparent rate constants for the tetra functional initiator system and short chain system were very low, suggesting that the polymerisation was very fast and was complete prior to the first sample being taken.

If the polymerisation only initiated from one active site on the multifunctional initiator large \overline{DP}_n values (table 6.3) would be expected, but these however are similar to that of the short chain polymer system.

Graph 6.2

Rate of polymerisation for various initiator systems. Rates following the polymerisation of oxetane with multi and monofunctional initiator systems



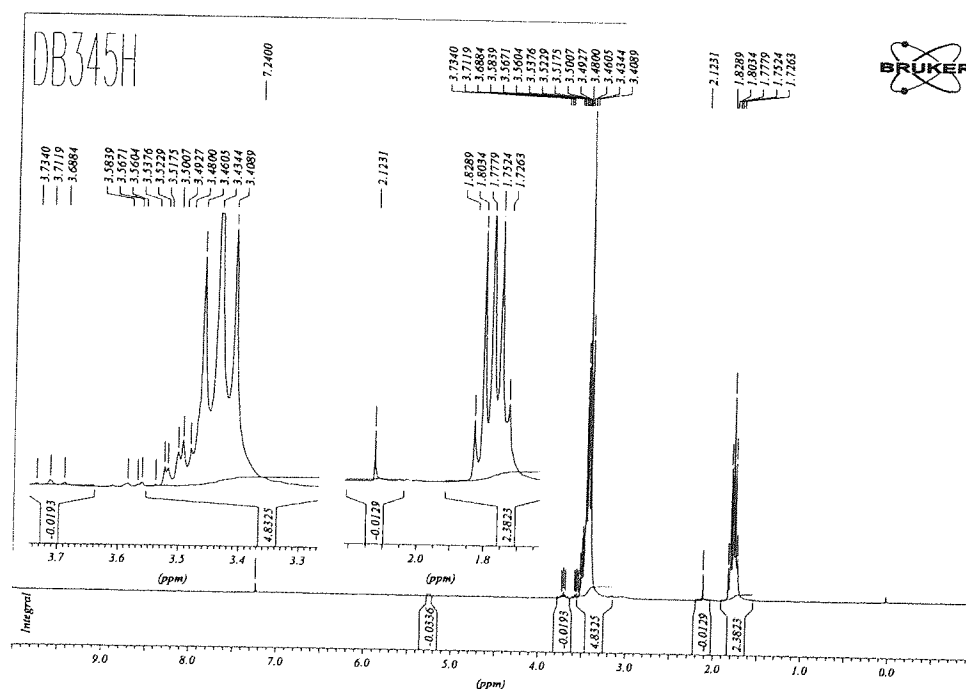
6.6.2. NMR Analysis of Tetrafunctional Core First Polymer System.

A ^1H NMR experiment was performed on the resulting polymers synthesised in 6.5. The dry polymers were transferred to a NMR tube using a clean spatula and dissolved in deuterated chloroform CDCl_3 .

The chemical shifts associated with the $\text{CH}_2\text{-O}$ hydrogens had a very similar chemical shift (3.46 ppm) to that of the $\text{CH}_2\text{-Br}$ hydrogens (3.52 ppm). This formed the residual unreacted initiator. This makes finding the lack of linkage peaks more difficult to find as any remaining $\text{CH}_2\text{-Br}$ peaks that are present due to not reacting were overlapped by the higher number of and more prominent $\text{CH}_2\text{-O}$ peaks.

Fig 6.3.

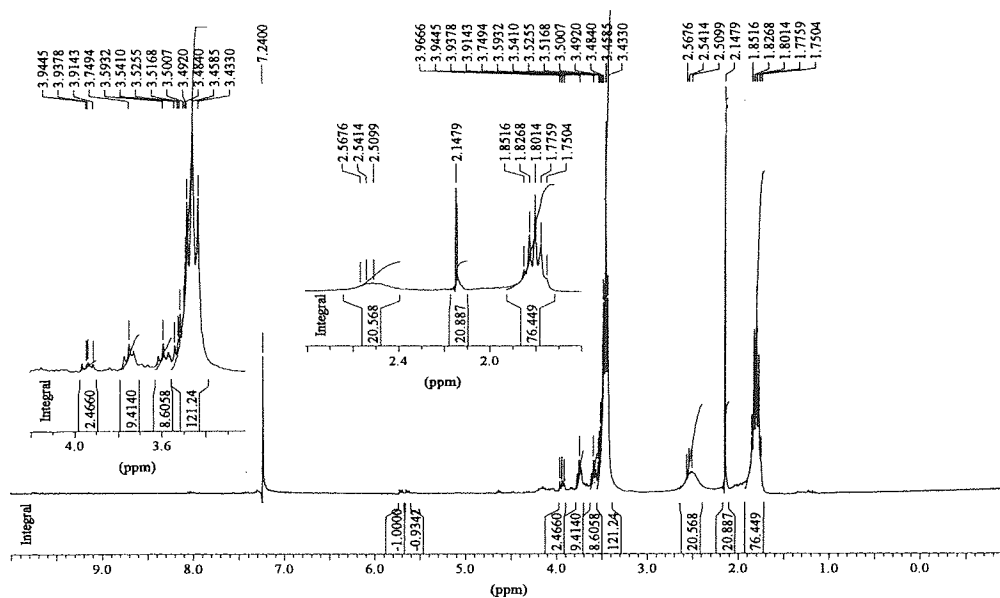
^1H NMR of polyoxetane using a monofunctional initiator system.



Polymerised under the following conditions; Initiator 2-bromo-2-methylpropane reacted with silver hexafluoroantimonate and benzaldehyde. Conditions; oxetane: initiator= 40:1 in DCM at 35 °C after 4h.

Fig 6.4.

^1H NMR of polyoxetane polymerised using a tetrafunctional initiator system.



Initiator 2,2-bis-bromomethyl-1,3-dibromopropane reacted with silver hexafluoroantimonate and benzaldehyde.

Conditions; oxetane: initiator = 40:1 in DCM at 35 °C after 4h.

The ^1H NMR spectra shown in figures 6.3 and 6.4 show the resultant polymers initiated using a monofunctional and tetrafunctional initiator system respectively.

There are characteristic polyoxetane peaks present with the central CH_2 (at 1.83ppm) and the $\text{CH}_2\text{-O}$ (at 3.52ppm) peaks. The ratio between these two peaks were around 2:4 respectively, which is typical to that seen for the mono-functional initiator in fig 6.3. The multifunctional initiated core polymer NMR also had extra peaks appearing at 2.5ppm.

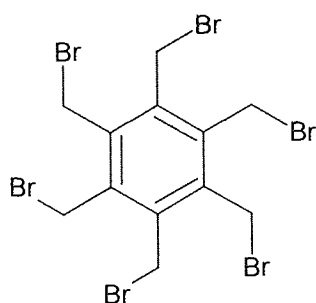
The mono-functional initiated polymer ^1H NMR shown in figure 6.3 had a multiplet at 1.8 ppm, a singlet at 2.1ppm and a major triplet at 3.5ppm. A small peak was observed at 2.1ppm and was attributed to the 2-methyl propane hydrogens CH_2 -from the monofunctional initiator. A linkage from the initiator to the polymer chain could not be seen but the expected $\text{CH}_2\text{-O}$ linkage was likely to be hidden by the 3.5ppm peak on the spectrum. Typically, the oxetane peak area ratios would correspond to 4:2 with respect to the peaks found at 3.5ppm and 1.8ppm respectively, which is what was observed.

The ^1H NMR for the tetra-functional initiated polymer system, was more difficult to analyse as several extra peaks were present. The typical oxetane peaks were present at 1.8ppm and 3.4ppm with respective ratios close to 4:2. There were two extra peaks, one narrow peak at 2.14ppm and another broad peak at 2.56ppm with very similar ratios. The peak at 2.14ppm could be attributed to the CH_2 groups from the initiator

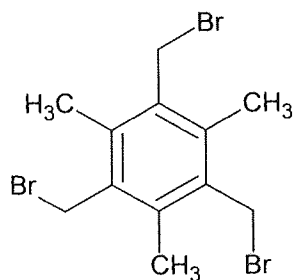
molecule. The peak found at 2.56ppm could be attributed to residual methanol used to quench the reaction. The peak found at 2.14ppm represents eight hydrogen atoms from the initiator molecule and the peak at 1.8ppm represents two hydrogen atoms from the polymer chain. The peak height for the initiator hydrogens was twenty which have eight hydrogen atoms and four initiator sites. The peak height for the polymer was seventy-six for two hydrogen atoms. For the whole polymer system, there were 15 units of oxetane polymerised with an average length of ~4 units per arm. The experiment was designed to incorporate 10 units per arm resulting in an efficiency of ~40% conversion of monomer.

6.7 Benzyl Bromide Derivatives (3 and 6 armed).

Initiators for the polymerisation of oxetane, were synthesised in chapter five, based on mono substituted benzyl bromide systems. In order to synthesise novel star shaped initiators more effective than those in the previous section 6.6, multifunctional bromomethyl benzene compounds were selected. These compounds were hexakisbromomethyl benzene and 1,3,5-tris-bromomethyl-2,4,6-trimethylbenzene.



hexakis(bromomethyl)benzene



1,3,5-tris(bromomethyl)-2,4,6-trimethylbenzene

6.7.1 Multifunctional Initiators Generated Using Tri and Hexa Functional Bromomethylbenzene.

There were two systems generated using hexakis (bromomethyl) benzene as the core molecule. Six molar equivalents of both AgSbF₆ and benzaldehyde were reacted with hexakis (bromomethyl) benzene in DCM as a solvent. The silver halide precipitate was removed by decantation and the resulting initiator stored under an inert atmosphere using a Schlenk flask and protected from sunlight. The initiator

concentration was made up at 0.1M and added to a 1M-oxetane solution using DCM as a solvent. The system was also generated using three molar equivalents of AgSbF₆ and benzaldehyde to the hexakis bromomethylbenzene molecule.

The second system was based on a 1,3,5-tribromomethyl-2,4,6-trimethyl benzene core molecule reacted with three molar equivalents of AgSbF₆ and benzaldehyde. The quantities of reagents used are detailed in table 6.4 along with the calorimetric data/

Table 6.4.

Molar ratios and results for polymerisations of oxetane at various initiator ratios using aromatic multifunctional and monofunctional initiator systems

Initiator system and composition	Oxetane level	Rate of initial temperature increase °C/sec	-k (from eq 6.6)	DPn (from eq 6.7)
Hexafunctional initiator system 5.4x10 ⁻⁴ mol of hexakisbromomethyl benene, 3.2x10 ⁻³ mol of AgSbF ₆ , 3.2x10 ⁻³ mol of Benzaldehyde	0.033 mol of oxetane	9	-0.02	41
Hexafunctional initiator system 1.1x10 ⁻³ mol of hexakis bromomethyl benzene, 3.3x10 ⁻³ mol of AgSbF ₆ , 3.3x10 ⁻³ mol of Benzaldehyde	0.033mol of oxetane + 0.033mol after 1 h	63	-0.05 1 st addition 2 nd addition after 1 hour rate 0.05	76
Hexafunctional initiator system 5.4x10 ⁻⁴ mol of hexakis bromomethyl benzene, 1.7x10 ⁻³ mol of AgSbF ₆ , 1.7x10 ⁻³ mol of Benzaldehyde	0.033mol of oxetane	1.0	-0.09	146
Trifunctional initiator system 1.1x10 ⁻³ mol of tribromomethyl trimethyl benzene, 3.3x10 ⁻³ mol of AgSbF ₆ , 3.3x10 ⁻³ mol of benzaldehyde.	0.033 mol of oxetane	240	-0.040	39
Trifunctional initiator system 1.1x10 ⁻³ mol of tribromomethyl trimethyl benzene, 3.3x10 ⁻³ mol of AgSbF ₆ , 3.3x10 ⁻³ mol of benzaldehyde.	0.11 mol of oxetane	166	-0.022	81
Trifunctional initiator system 1.1x10 ⁻³ mol of tribromomethyl trimethyl benzene, 3.3x10 ⁻³ mol of AgSbF ₆ , 3.3x10 ⁻³ mol of benzaldehyde.	0.22mol of oxetane	107	-0.029	82
Mono-functional initiator system 1.2x10 ⁻³ mol of benzyl bromide, 1.2x10 ⁻³ mol of AgSbF ₆ , 1.2x10 ⁻³ mol of Benzaldehyde	0.048 mol of oxetane	280		121
Mono-functional initiator system 4.8x10 ⁻³ mol of benzyl bromide, 4.8x10 ⁻³ mol of AgSbF ₆ , 4.8x10 ⁻³ mol of Benzaldehyde	0.048 mol of oxetane	260		8

The apparent first order rate constant, *k*, shown in table 6.4 for the hexakis

bromomethyl benzene initiators were calculated by plotting $\ln\left(1 - \frac{\overline{DP}_n}{\overline{DP}_{n0}}\right)$ against time,

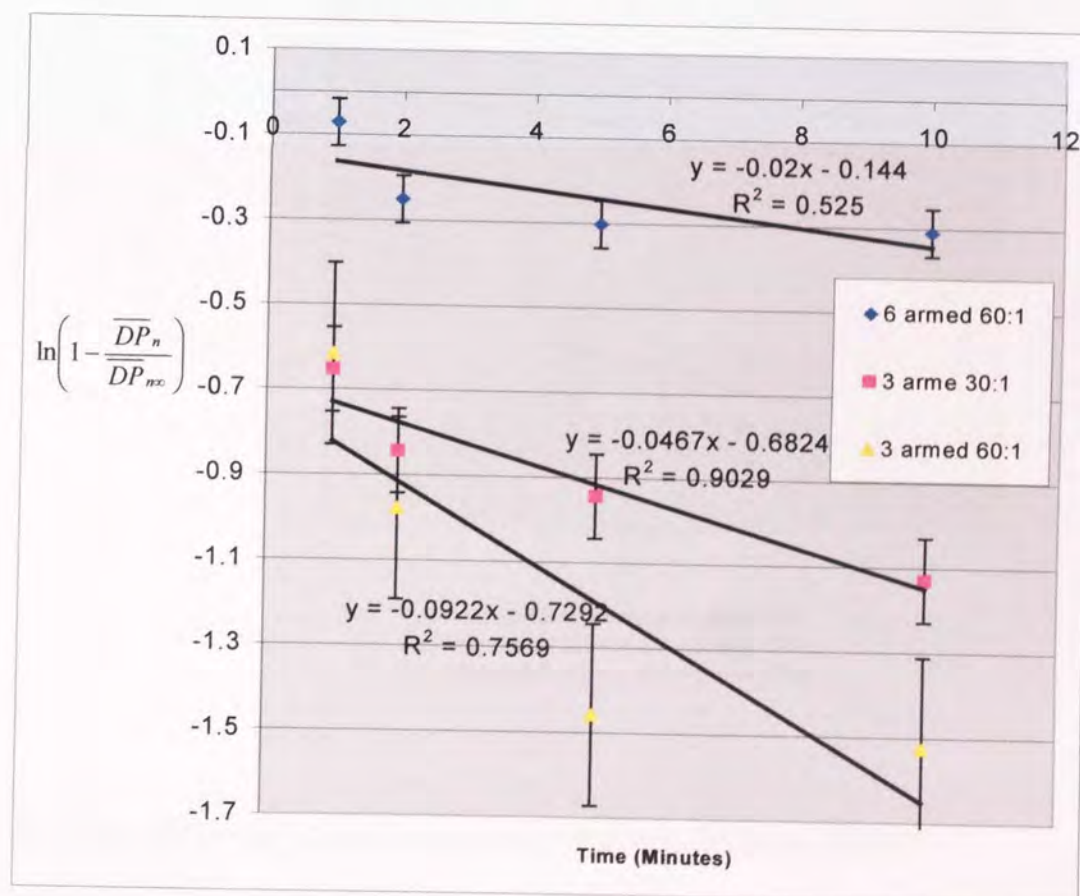
interpreting the gradients from graph 6.4. It was found that the hexafunctional initiator

core molecule with potentially six reactive sites produced an initial polymer system that increased in molecular weight slowly. The system also exhibited a slow initial rate of polymerisation when tracked using temperature increases.

By reducing the level of AgSbF_6 and benzaldehyde to the hexakis bromomethyl benzene to 3:3:1 respectively, it was found that the system polymerised steadily. This initiator system showed living characteristics, as when more monomer was added, the same rate of polymerisation was observed for both the first and second additions of the monomer solution to the polymerisation vessel. When the level of oxetane was doubled, the initial rate of polymerisation was also seen to increase by a factor of two.

Graph 6.4

$\ln\left(1 - \frac{\overline{DP}_n}{\overline{DP}_{\infty}}\right)$ against time for the polymerisation of oxetane using a initiator derived from hexakis bromomethyl benzene.

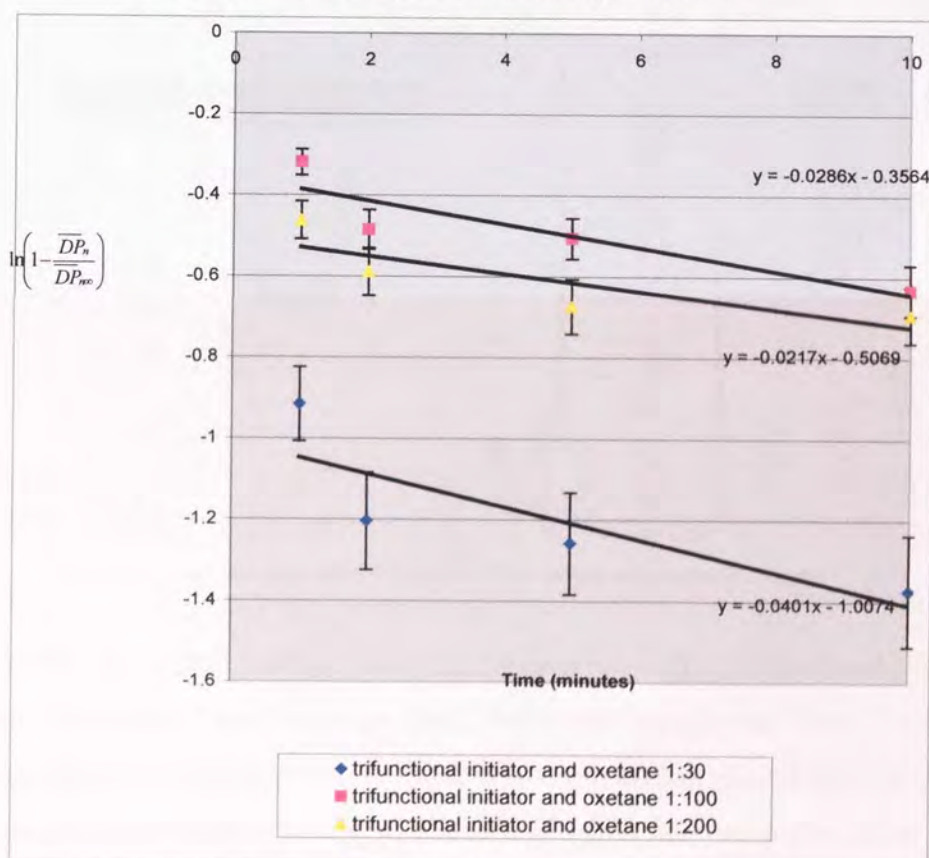


The apparent rate constants, k_{app} , shown in table 6.4 were for the 1,3,5-tris-bromomethyl-2,4,6-tris-methyl benzene initiators calculated by plotting

$\ln\left(1 - \frac{\overline{DP}_n}{\overline{DP}_{n\infty}}\right)$ against time, interpreting the gradient from graph 6.5. The rate of polymerisation for the low monomer to initiator ratio (30:1) showed that there was a slow reduction in molecular weight. This was due to an initial rapid polymerisation of the monomer, shown with a fast temperature increase. For the higher monomer to initiator ratio's, the polymerisation rates were similar for both reactions as seen in graph 6.5.

Graph 6.5

$\ln\left(1 - \frac{\overline{DP}_n}{\overline{DP}_{n\infty}}\right)$ against time for the polymerisation of oxetane using initiators derived from 1,3,5-trisubstituted benzene.



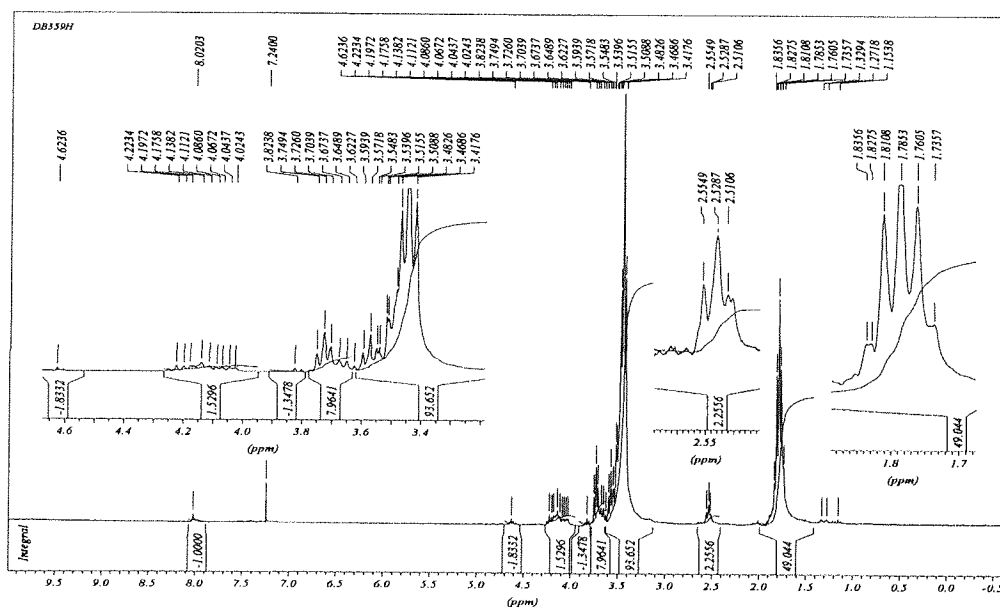
6.7.2 NMR Analysis of hexakisbromomethylbenzene Initiator System

After 4 hours of polymerisation, the reaction was quenched using methanol. The polymer solution was then dried in a vacuum oven for 48 hours and the polymer solution dissolved in THF (tetrahydrofuran) and then filtered through a nylon film

filter, to remove any particulate from the system. The THF was removed in a vacuum oven. A ^1H NMR was performed on the resulting polymer and was dissolved in CDCl_3 solvent and performed on a Bruker aspect 3000 NMR spectrometer. The chemical shifts associated with the $\text{CH}_2\text{-CH}_2\text{-O}$ hydrogens had the same chemical shift (1.5ppm) to those of the $\text{CH}_2\text{-Br}$ hydrogens (1.5ppm) from the initiator core molecule. This made finding the lack of linkage peaks more difficult to ascertain as any remaining $\text{CH}_2\text{-Br}$ peaks that were present were overlapped by the larger $\text{CH}_2\text{-CH}_2\text{-O}$ peaks. The distinct peak at 2.5 ppm was due to a carbonyl $\text{CH}_2\text{-CH=O}$ group.

Fig 6.5

^1H NMR of polyoxetane initiated using Hexakis bromomethyl benzene reacted with AgSbF_6 and benzaldehyde at a ratio of 1:6:6 respectively using DCM as solvent.



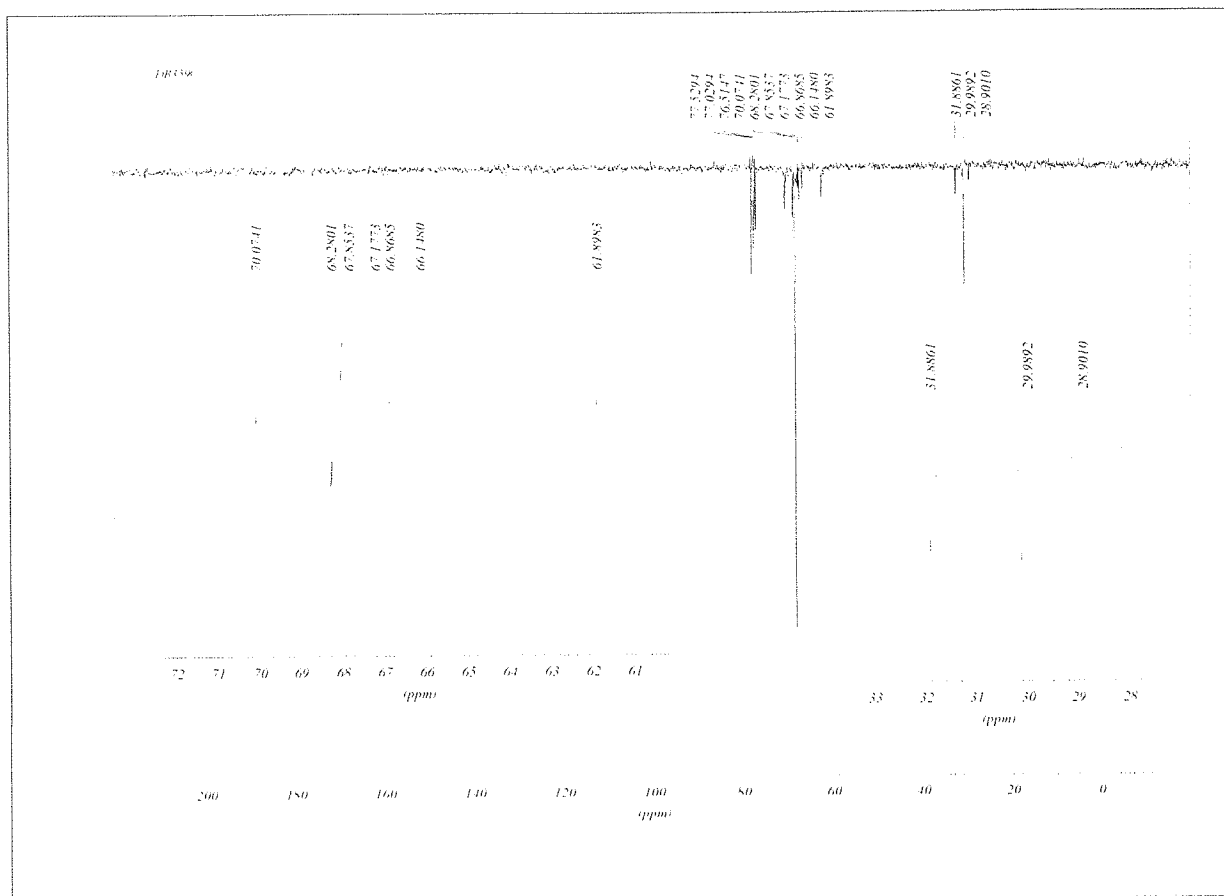
The polymer was analysed using CDCl_3 as a NMR solvent and marker (7.24ppm)

From figure 6.5, the typical oxetane peaks can be seen at ($-\text{CH}_2-$) 1.8ppm and ($-\text{CH}_2\text{-O-}$) 3.4ppm. The integral ratios between these peaks were also typical for a polyoxetane system at 2:4 respectively. There was a non-typical quartet peak at 2.5ppm, owing to the presence of $-\text{CH}_2\text{-Aromatic}$ groups. There were also minor peaks seen at 8.0ppm due to aromatic components from the initiator compound and at 4.6ppm. There were major shoulders of peaks at 3.5-4.2ppm and were due to various linkages of the oxetane compound and of oligomers that are formed during the polymerisation.

In addition to the ^1H NMR experiment, a ^{13}C NMR experiment was performed using a PENDANT pulse sequence on the polymer system and illustrated in figure 6.6.

Fig 6.6

^{13}C NMR using Hexakis bromomethyl benzene reacted with AgSbF_6 and benzaldehyde at a ratio of 1:6:6 respectively as an initiator in DCM as solvent.



Typical CDCl_3 marker peaks can be seen as a triplet at 77ppm. The typical $-\underline{\text{C}}\text{H}_2\text{-O}-$ peaks are seen as a major peak at 67.8ppm and the central $-\underline{\text{C}}\text{H}_2-$ peaks can be seen at 30ppm. There are 4 distinct peaks in addition and close to that at 77ppm and can be attributed to various linkages from the polymer to the initiator molecule and cyclic oligomers formed during the polymerisation. There were two distinct peaks in addition and close to the peak seen at 30ppm.

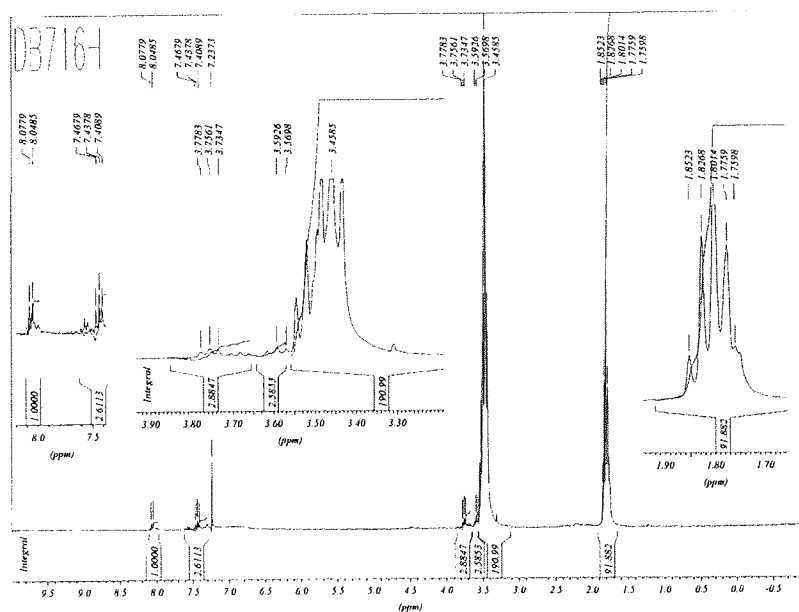
From ^{13}C NMR spectra there appears to be little evidence of the core initiator being present in the end system. For benzyl carbons, peaks would normally be apparent at around 130 ppm but cannot be identified on the spectra.

6.7.3 NMR Analysis of 1,3,5-trisbromomethyl-2,4,6-trimethyl-benzene Initiator System.

The NMR results of the 1,3,5-trisbromomethyl 2,4,6-trimethyl benzene derived initiator system were similar to that of the monofunctional initiated polymers generated. The highlighted hydrogens $(-\underline{\text{CH}}_2\text{CH}_2\underline{\text{CH}}_2\text{O}-)$ had a chemical shift of 3.5ppm and formed a triplet. The highlighted hydrogens $(-\text{CH}_2\underline{\text{CH}}_2\text{CH}_2\text{O}-)$ have a chemical shift of 1.8ppm and formed a quintet pattern. Typically, aromatic peaks associated with the initiator were seen at chemical shifts of 7.5-8.5ppm and were seen as minor peaks in figure 6.7.

Fig 6.7.

^1H NMR 1,3,5tris-bromomethyl-2,4,6-tris-methyl benzene derived initiator polymerised with 30 equivalents of oxetane.

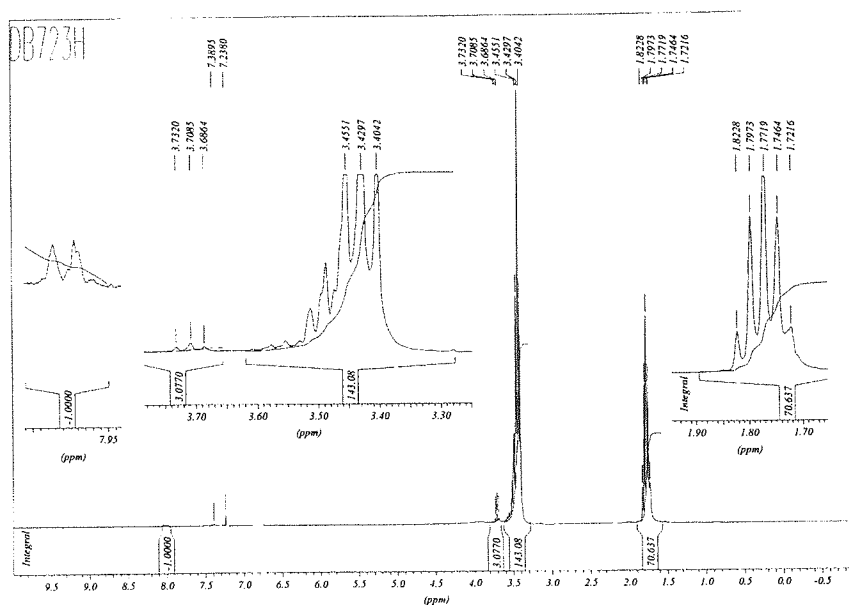


For most of the initiator systems, small peaks were seen close to the 3.5ppm peak and were attributed to the cyclic formation, of crown ether type compounds. The small peaks found at 3.5ppm were reduced for this system compared to those of the monofunctional initiators. It was noticed that the polymerisation had a reduction in side peaks at 3.5ppm, arising from reduced oligomer formation when compared to the hexakis-bromomethyl benzene system.

For larger monomer: initiator ratios, the peaks seen at 7.5-8.5 become very small and can not be easily detected as shown in figure 6.8.

Fig 6.8

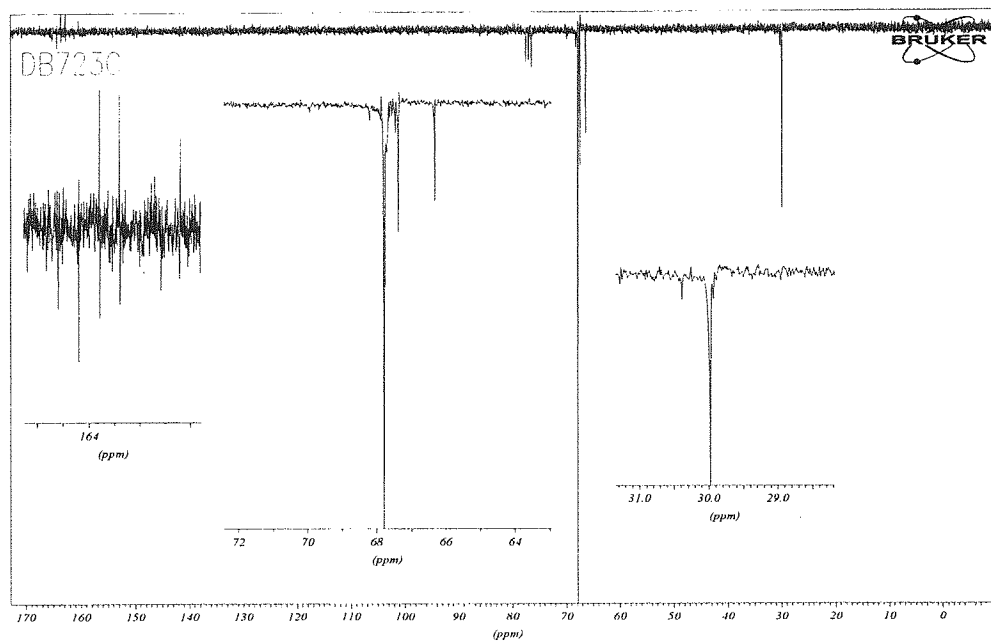
^1H NMR of polyoxetane polymerised using 1,3,5-trisubstituted benzene derived initiator with a ratio of monomer: initiator ratio of 100:1.



The low levels of cyclic oligomer formation was also seen in the ^{13}C NMR with a low number of peaks being seen as shown in figure 6.9. The peaks at 30 and 68ppm were attributed to those of the polyoxetane. There are also some minor peaks with a chemical shift of 164ppm in the positive direction. These peaks were in the region of aromatic carbon peaks, arising from the initiator molecule.

Fig 6.9

^{13}C NMR polyoxetane initiated using a 1,3,5-trisbromomethyl 2,4,6-trimethyl benzene derivative at monomer : initiator ratio of 100:1.



Chapter 7

Additives

7.1. The Role of Additives.

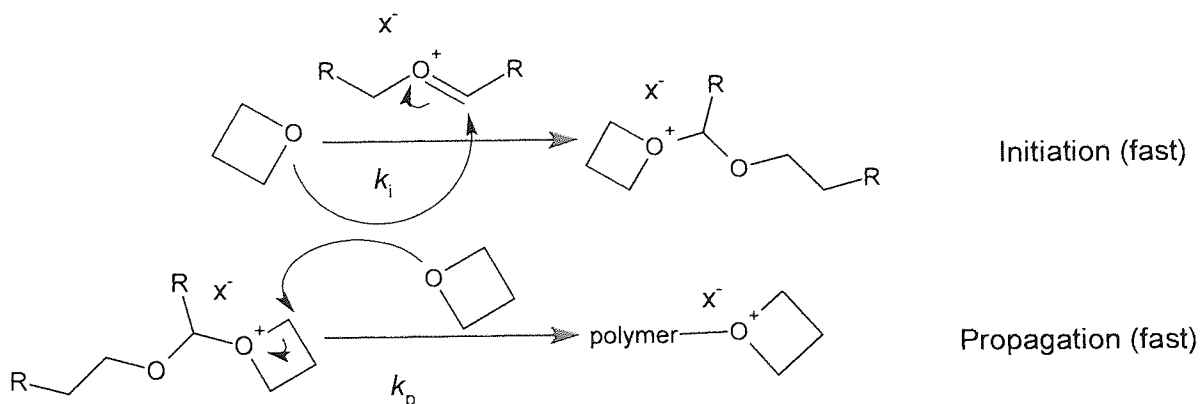
Additives have been used in reactions for numerous reasons and work in a variety of ways. It has been reported that the use of proton sponges can be used to absorb free acid particles, which improves the propagation of the polymerisation as less transfer and side reactions occur.

When undertaking CROP reactions using oxetane as a monomer, backbiting transfer reactions regularly occur resulting in unwanted by-products such as cyclic oligomers for example. There have been reported instances of ‘capping’, the active chain end (ACE) of the propagating chain species reducing the level of backbiting reactions^[34].

7.2. Oligomer Formation.

Oligomers have been found to form during all the polymerisations undertaken thus far with the exception of some low molecular weight dendrimer species. The oligomers form during the polymerisation of the oxetane through a backbiting reaction as proposed in figure 7.2. The oligomers were identified due to separate peaks eluting before the marker and unreacted monomer peaks from GPC analysis.

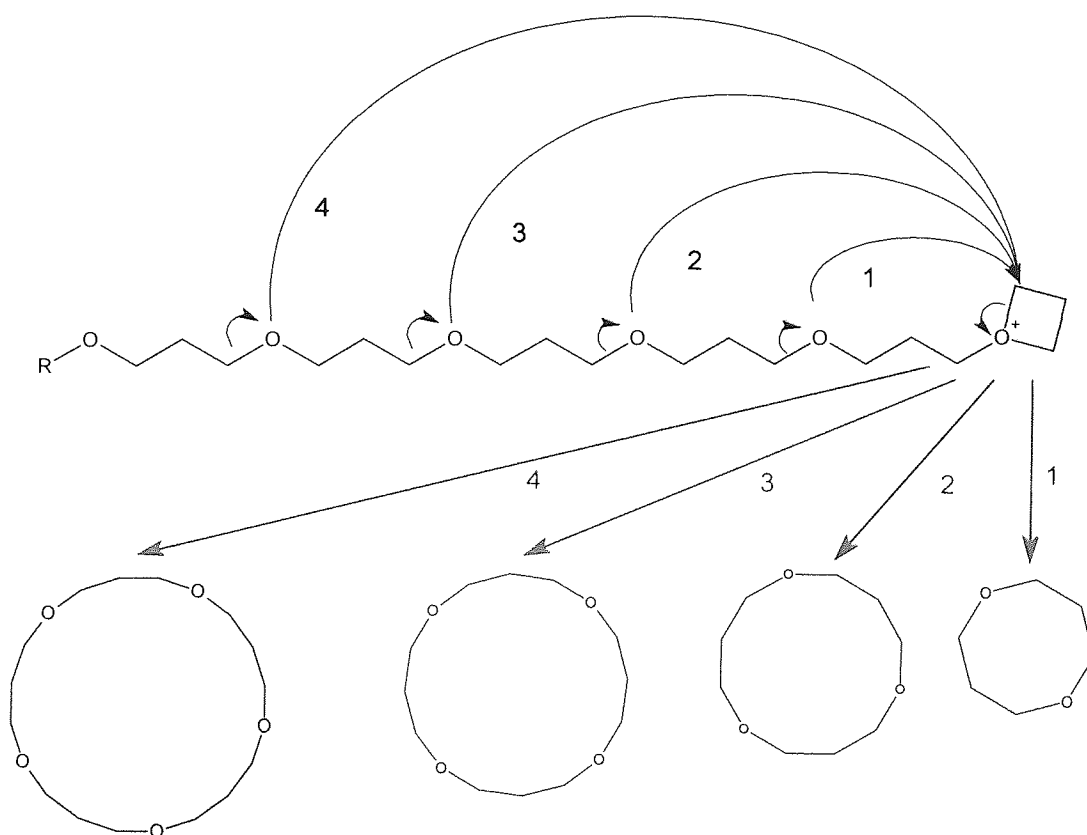
Fig 7.1
Initiation and propagation mechanism of polymerisation of oxetane



Once the polymerisation was started, the propagation of the monomer occurred and resulted in chain growth of the polymer as illustrated in figure 7.1. During the propagation stage of the polymerisation, competing side reactions took place at the ACE, reducing the efficiency of the system. The ACE had positively charged species. This was attracted to the lone pairs of electrons on the oxygen atoms. These oxygen atoms were found in the backbone of the polymer system. This attraction led to the ACE bonding onto the polymer backbone releasing a cyclic oligomer and regenerated a carbonium ion, which continued to polymerise the available monomer.

Fig 7.2

Backbiting of the active chain end of polyoxetane polymerisation forming cyclic oligomers.



The formation of oligomers had several effects on the polymerisation such as a reduction in the number average of molecular weight \overline{M}_n . The second and more significant effect was that the formation of the oligomer was slower than the propagation of the monomer resulting in a slower growing chain in relation to the

others. As the polymerisation and propagation rate were very fast using the CROP system, then an increased polydispersity was likely to be formed from such systems.

7.3. Oligomer Formation with Current Initiator Systems.

From chapter 5, two main initiator systems were found to be effective for the polymerisation of oxetane. The first system was based on the elimination of a chloride ion from a halogenated methyl ethyl ether. The second system was generated via the addition of carbonyl oxygen to a carbonium ion. Both systems were studied to assess the affects of oligomer formation during the polymerisations.

7.3.1. Oligomer Formation using Chloromethyl Ethyl Ether Reacted with Silver Hexafluoroantimonate.

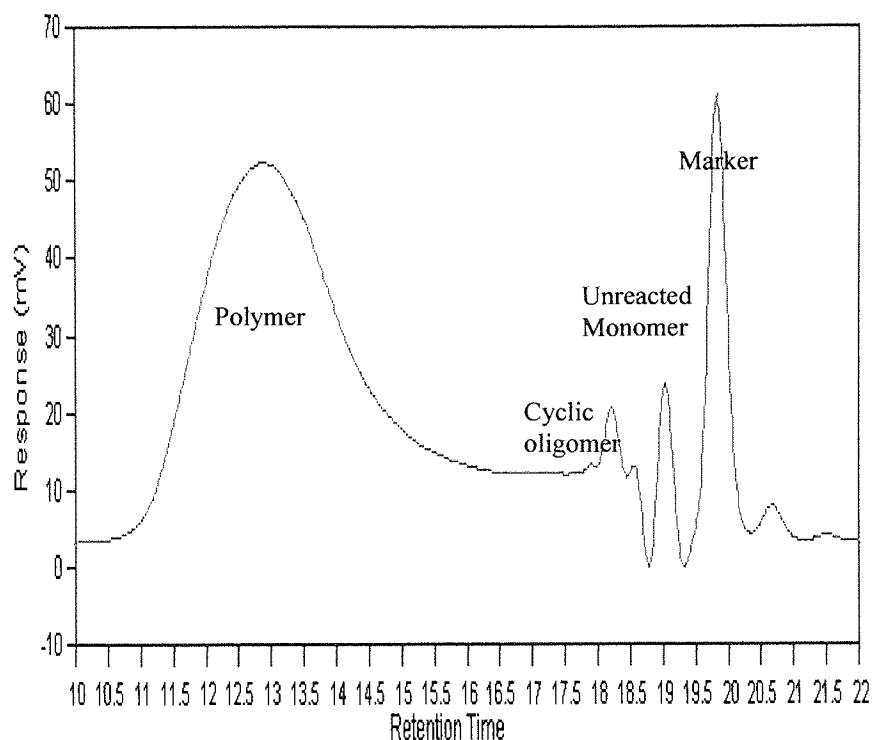
Reacting 1.5×10^{-3} mol of $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ with 1.5×10^{-3} mol AgSbF_6 in 15ml of dried DCM made the initiator. The reaction was left for 24 hours in an aluminium foil covered Schlenk flask filled with argon. After 24 hours, the solution was decanted, removing the silver halide precipitate and the solution stored under an inert atmosphere.

The monomer solution was prepared in an inert atmosphere at a concentration of 1M in dried DCM. The solution added to the reaction vessel under a positive pressure inert gas flow. Various volumes of initiator solution were added to 30 ml of the monomer solution using positive pressure techniques.

The polymerisations were followed using calorimetric analysis to measure the initial temperature increase. Samples were taken at regular intervals during the polymerisation and quenched in methanol dried in a vacuum oven re-dissolved in THF (tetrahydrofuran), filtered and analysed using GPC. Chromatograms such as that seen in figure 7.3, were used to characterise the molecular number, \overline{M}_n , and molecular weight, \overline{M}_w , averages along with the polydispersity and level of oligomer formation. The results from this series of experiments are highlighted in table 7.1.

Figure 7.3.

Typical gel permeation chromatogram of polyoxetane with cyclic oligomer formation.



By comparing the area ratios between the polymer and oligomer peaks, an approximate ratio between the two was found. This ratio indicates how much oligomer is formed during the polymerisation as highlighted in table 7.1.

Table 7.1.

% ratios of polymer to cyclic oligomer at various times during the polymerisation . Peaks at various molar Oxetane: Initiator ratios

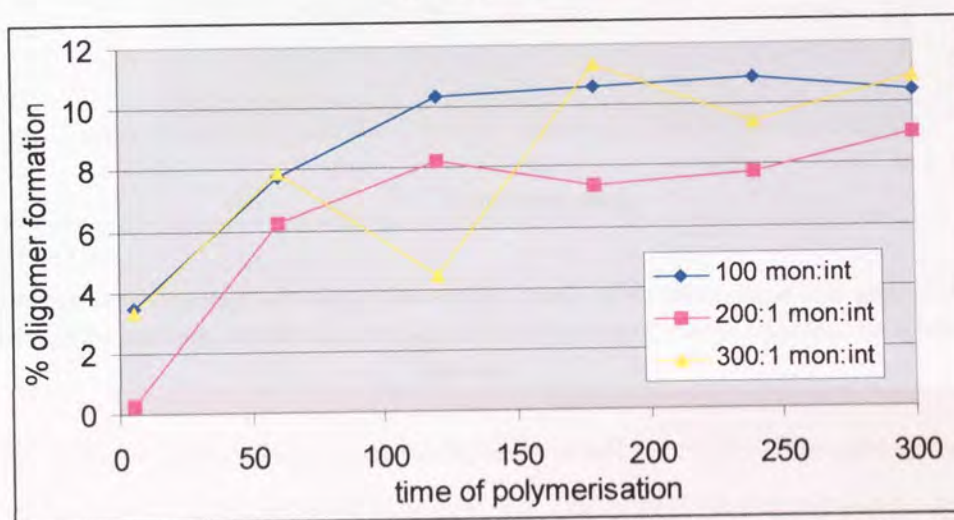
Time Minutes	3×10^{-2} mol Oxetane	3×10^{-4} mol initiator	3×10^{-2} mol Oxetane	1.5×10^{-4} mol initiator	3×10^{-2} mol Oxetane	1×10^{-4} mol initiator
	% PolyOx	% Cyclic	% PolyOx	% Cyclic	% PolyOx	% Cyclic
5	96.54	3.46	99.75	0.25	96.66	3.34
60	92.21	7.79	93.80	6.20	92.08	7.92
120	89.68	10.32	91.76	8.24	95.55	4.45
180	89.39	10.61	92.64	7.36	88.67	11.33
240	89.13	10.87	92.24	7.76	90.59	9.41
300	89.60	10.40	90.96	9.04	89.15	10.85

(initiator made by $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl} + \text{AgSbF}_6$) in DCM solution at 35°C

The formation of the oligomers was slow at the start of the polymerisation owing to the propagation of the monomer dominating the reaction. As the amount of free monomer decreased, the backbiting reaction started to form oligomers. The rate of oligomer formation slowed down as the reaction proceeded with a maximum of oligomer formation reaching around 11% as determined by GPC and depicted by graph 7.1.

Graph 7.1

% ratio of oligomer formation during polymerisation of oxetane at various monomer : initiator molar ratios

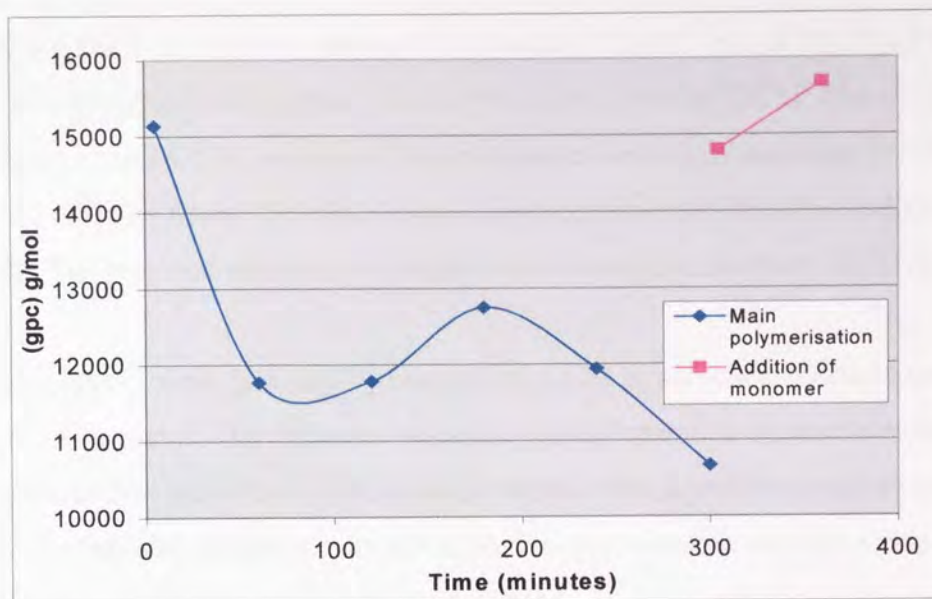


Initiator made using $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ reacted with AgSbF_6 . Carried out in DCM at [1M] solvent at 35°C under an inert atmosphere at various monomer: initiator ratios.

When the cyclic oligomer was formed, a non-reactive species was generated, but a new carbocation capable of propagating further monomer additions was also generated (figure 7.4). Due to the reactive species being transferred, the reaction continued when more monomer was added. Extra monomer was added to the polymerisation of oxetane to see if the polymerisation exhibited 'living' characteristics as seen in other cationic systems. It was found (graph 7.3.) that the polymerisation system did increase in \overline{M}_n as more monomer was added exhibiting 'living' characteristics.

Graph 7.2

Effect of adding a second portion of oxetane to a polymerisation after 5 hours.

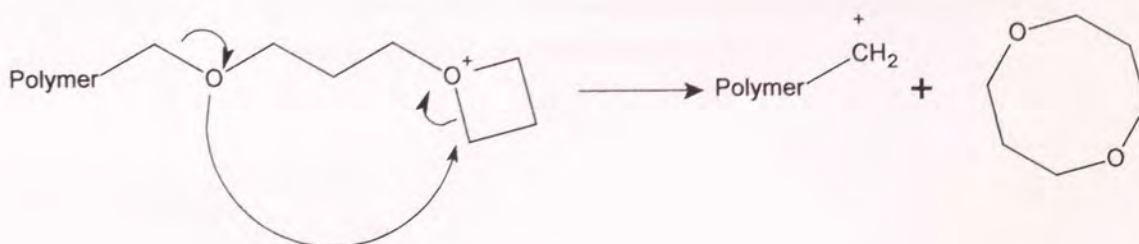


Initiator made using $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ reacted with AgSbF_6 . Carried out in DCM at [1M] at 35°C under an inert atmosphere the initial monomer: initiator molar ratio was 200:1 with a further 200 molar equivalents being added after 300 mins.

The effect of the oligomer formation can be seen to reduce the average molecular weight of polymerisation as shown by graph 7.2. Many transfer reactions resulted in non-reactive species being formed that resulted in the termination of the polymerisation. It was discovered that this did not occur when oligomers were formed as more monomer was propagated when added to the system. Owing to this result, when cyclic oligomer was formed, more reactive species were generated, that could either carry on to form more cyclic oligomers or react with available monomers to continue propagation of the polymer chain as seen by fig 7.4.

Fig 7.4

Scheme showing generation of new active species and cyclic oligomer through intramolecular transfer



7.3.2. Oligomer Formation using Bromomethyl Benzene Reacted with Silver Hexafluoroantimonate and Benzaldehyde.

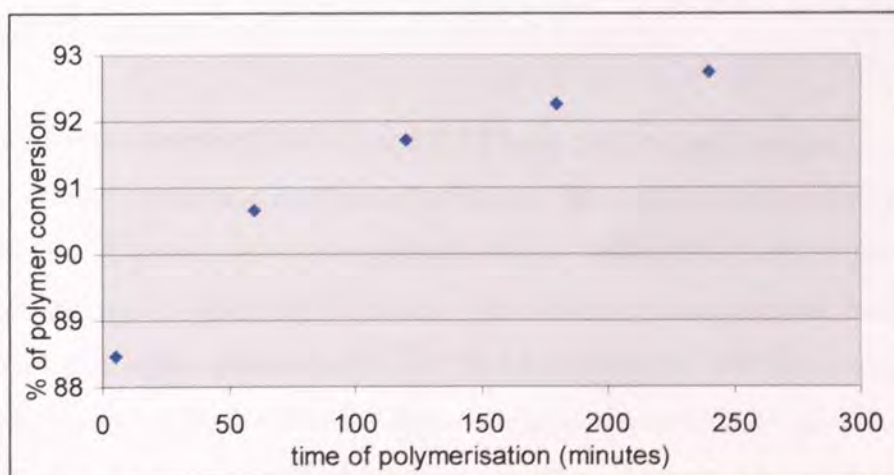
The second initiator system was prepared by reacting 1.5×10^{-3} mol of PhCH_2Cl with 1.5×10^{-3} mol of AgSbF_6 and 1.5×10^{-3} mol of PhCHO in 15ml of DCM. The mixture was allowed to react for 24 hours in a Schlenk flask covered in aluminium foil, filled with argon. After 24 hours, the solution was decanted removing the silver halide precipitate. The resultant solution was stored under an inert atmosphere until required.

Monomer solutions were prepared by using dried DCM as solvent and dried oxetane as detailed in chapter 3. The monomer solutions were prepared in an inert atmosphere at 1M concentration and added to the reaction vessel under a positive pressure inert gas flow. The initiator solutions were also added to the monomer solution using positive pressure techniques at various molar ratios.

For the control experiment, 30ml of monomer solution was transferred to the reaction vessel followed by 3ml of initiator solution. Samples were taken at regular intervals and quenched in methanol. The samples were then dried in a vacuum oven and re-dissolved in THF, which was then filtered and analysed using gravimetric, GPC and NMR techniques.

Graph 7.3

% conversion of oxetane with time using benzyl bromide derived initiator system.

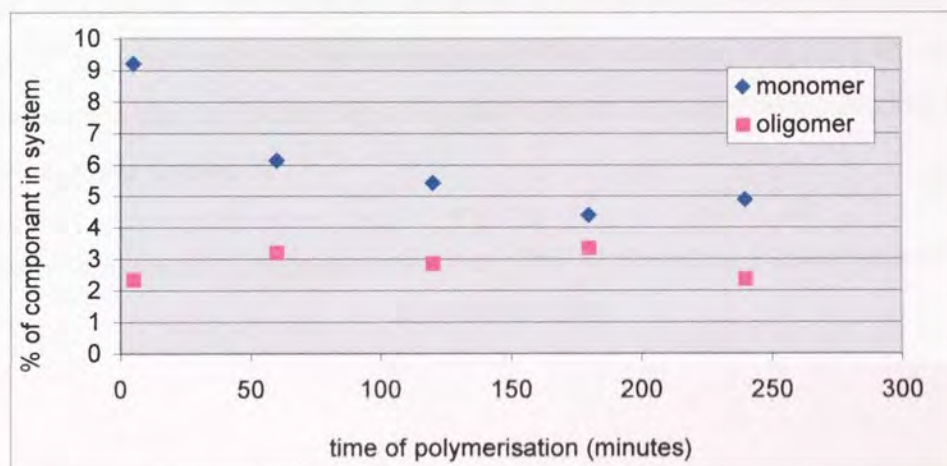


For the polymerisation of oxetane initiated using PhCH_2Cl reacted with PhCHO and AgSbF_6 in DCM at 35°C . starting monomer: initiator molar ratio of 100:1.

For the benzyl bromide derived initiator system, there was a steady progression of polymer conversion as shown in graph 7.3. Previously for the chloromethyl ethyl ether derived initiator system, as the polymerisation progressed the level of oligomer formation increased (graph 7.1). From graph 7.4 it is shown that the levels of oligomer formation with the benzyl bromide derived initiator system were relatively constant for the duration of the polymerisation. This implied that active chain end was more stable than for the chloromethyl ethyl ether derived initiator system.

Graph 7.4.

% area of monomer and oligomer peaks during the polymerisation of oxetane using the benzyl bromide derived initiator system.



7.3.3. Oligomer Formation using Various Initiator Systems.

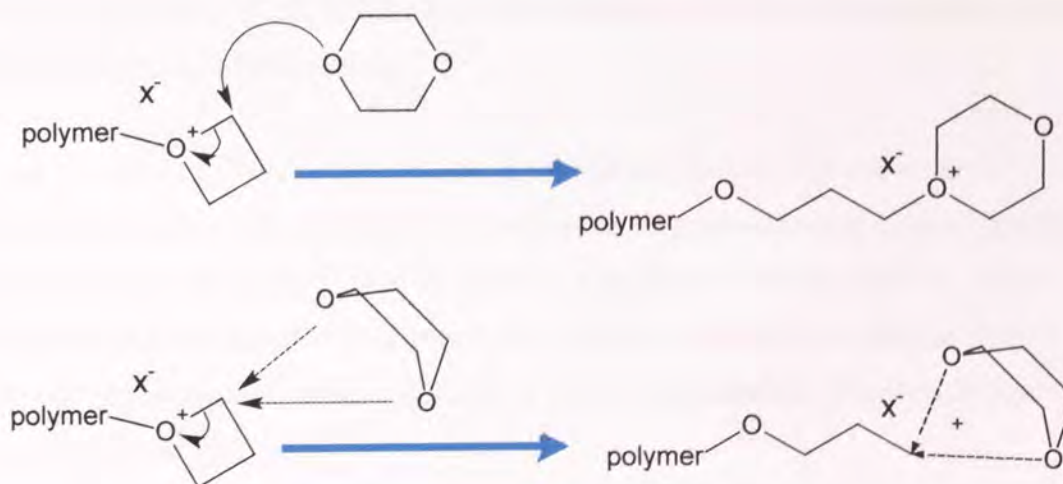
Both initiator systems described in 7.3.1 and 7.3.2 both polymerised oxetane effectively with high conversion rates being achieved. The initiator system derived from $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ produced narrow polydisperse polymers (PD 1.4-1.5), but with relatively high amounts of oligomer formation. The initiator system derived, from PhCH_2Cl produced a higher polydisperse (PD 1.6-1.8) system but with less oligomer formation. The benzyl bromide derived initiator contains a benzaldehyde co-catalyst, which was found to improve control of the polymerisation. It is possible that the benzaldehyde also acted as a pseudo 'capping' agent reducing the backbiting reactions that resulted in cyclic oligomer formation.

7.4. 1,4-Dioxane.

It has been reported by Bouchekief^[34] that by using 1,4-dioxane in systems initiated by oxonium ions stabilised by $[\text{BF}_4]^-$ regions, more control over the polymerisation could be obtained. There were two possible mechanisms (fig 7.5) by which 1,4-dioxane could induce control over the polymerisation of oxetane. The first was that the 1,4-dioxane reacted with the oxonium ion creating a stable “dormant” species. The dormant species then reactivated, allowing for more propagation to occur. Another explanation was that a boat type structure was adopted, which in turn co-ordinated to the active chain end. Both of these mechanisms introduced a slower rate determining intermediate, which reduced the propagation of the monomer. The main advantage of this addition is that the backbiting of the polymerisation was reduced, leading to less cyclic oligomer formation.

Fig. 7.5

Proposed scheme of 1,4-dioxane stabilisation of the ACE resulting in lower amount of cyclic oligomer formation.



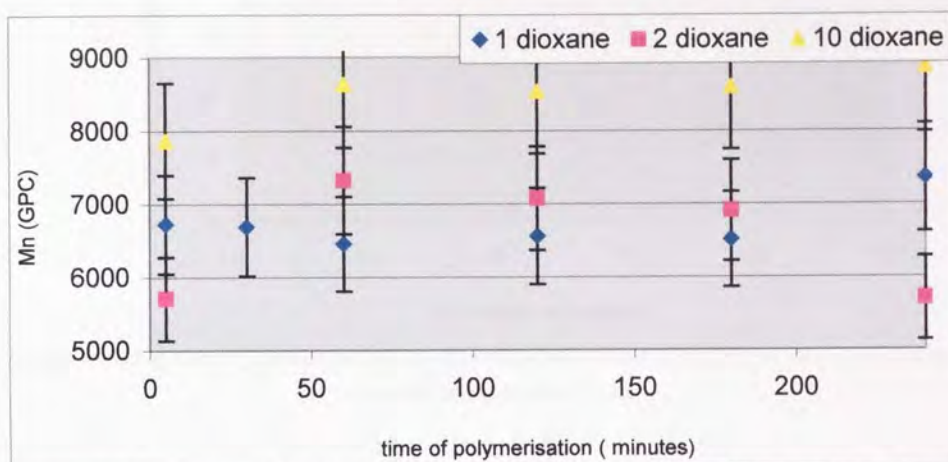
7.4.1. 1,4-Dioxane Added to the Chloro methyl Ethyl Ether Derived Initiator System.

Polymerisations of oxetane were performed with 1,4-dioxane being used as a major component in the solvent system, but not as an additive to the initiator system. The initiator was made as described in 7.3.1 but with various levels of 1,4-dioxane being

added to the initiator system. The molar equivalent amounts of 1,4-dioxane added to the initiator were; 1.5×10^{-3} , 3.0×10^{-3} and 1.5×10^{-2} mol of to 1.5×10^{-3} mol of initiator. There was little control over the progression \overline{M}_n gained by adding small amounts of 1,4-dioxane to the initiator (graph 7.5) but some improvement was seen when the level of 1,4-dioxane addition was increased significantly.

Graph 7.5.

Polymerisation of oxetane with 1,4-dioxane added to the initiator systems at various levels.



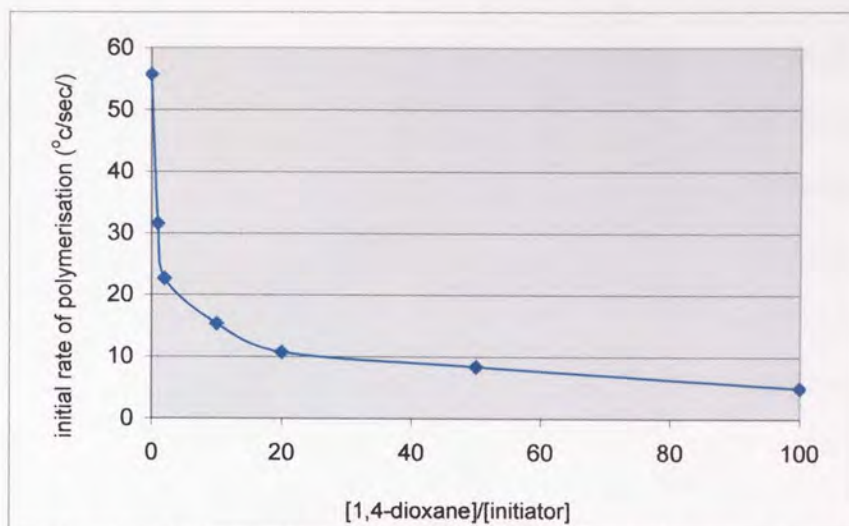
Initiator generated by reacting $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ reacted with AgSbF_6 doped with either 1,2 or 10 equivalents of 1,4-dioxane in DCM solvent at 0.1M. Initiator added to a 1M oxetane solution in DCM at a molar ratio of 1:100 respectively.

7.4.1.1 Initial Rate of Polymerisation with Dioxane Added to Chloromethyl Ethyl Ether Derived Initiator System.

It was found that by adding 1,4-dioxane to the initiator system, the initial rate of polymerisation could be controlled. The initial rate of polymerisation reduced rapidly as more 1,4-dioxane was added to the initiator system as shown in graph 7.6. This reduction in the initial rate of polymerisation confirmed that the 1,4-dioxane slowed down the rate of polymerisation by either of the two mechanisms described in figure 7.4 as it caps the ACE of the polymerisation.

Graph 7.6.

Initial rate of polymerisation (calorimetric analysis) of oxetane initiated with chloromethyl ethyl ether derivative doped with various levels of 1,4-dioxane.



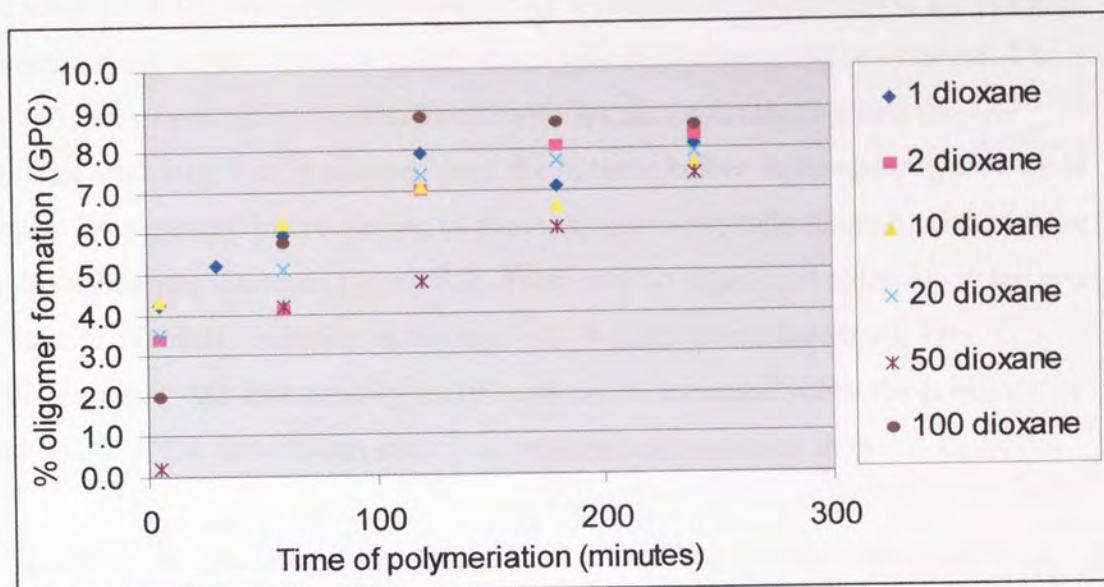
Initiator generated by reacting $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ reacted with AgSbF_6 doped with either various equivalents of 1,4-dioxane as described in 7.4.1.

7.4.1.2. Oligomer Formation with 1,4-dioxane added Chloromethyl Ethyl Ether derived Initiator System.

When 1,4-dioxane was used as an additive in the initiator system, the initial rate of polymerisation was reduced as seen in graph 7.6. This allowed for control of the initial rate of polymerisation with respect to the monomer, adding to the propagating species. The principle reason for adding the 1,4-dioxane was to reduce the amount of cyclic oligomer formed, by decreasing the level of unwanted side reactions. Graph 7.7 shows that by adding the 1,4-dioxane to the initiator system, no significant reduction of cyclic oligomer formation was achieved. There was however, an increase in the polydispersity of the systems as more 1,4-dioxane was added (graph 7.8). As the addition of the 1,4-dioxane was increased a rise in the polydispersity was measured, implying that the ACE was hindered. Oligomer formation still occurred suggesting that the coupling to the ACE was only temporary.

Graph 7.7.

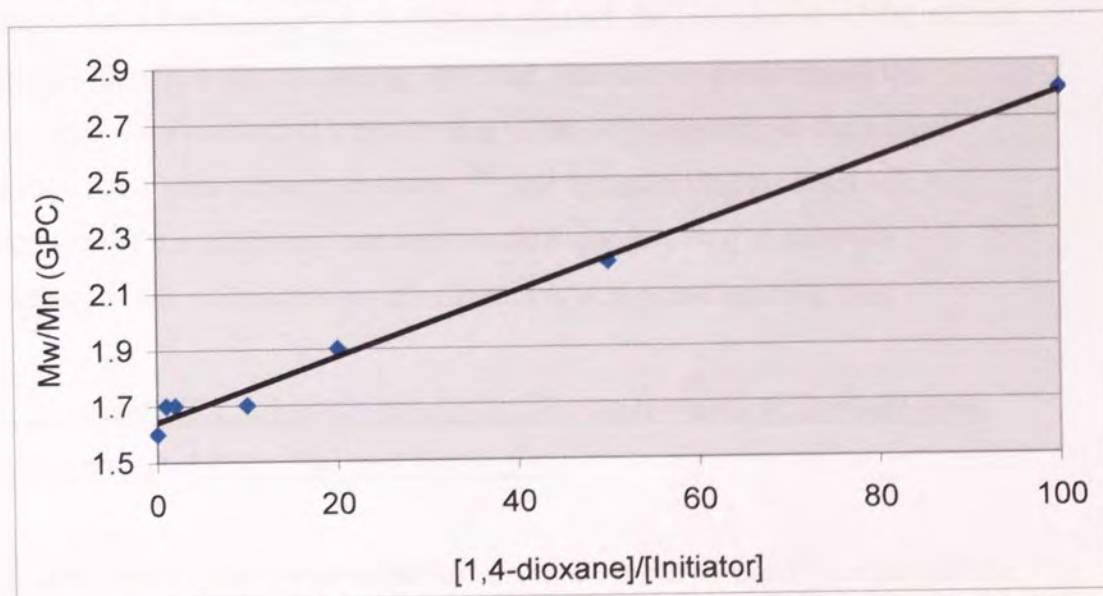
% oligomer formation for polymerisation of oxetane initiated using chloromethyl ethyl ether derivative with various levels of 1,4-dioxane added to initiator system.



3×10^{-4} mol of initiator solution at 0.1M added to 3×10^{-2} monomer solution at 1M in DCM reacted for 4h at 35°C under nitrogen (oxygen free) gas flow.

Graph 7.8.

Effect on polydispersity of polymerisation of oxetane initiated using chloromethyl ethyl ether derivative with various levels of 1,4-dioxane added to initiator system.



3×10^{-4} mol of initiator solution at 0.1M added to 3×10^{-2} monomer solution at 1M in DCM reacted for 4h at 35°C under nitrogen (oxygen free) gas flow.

7.4.2. Dioxane and DCM solvent mixtures for polymerisations of oxetane initiated using chloromethyl ether derivative.

In section 7.4.1, it was seen that by adding 1,4-dioxane as an additive to the initiator system, some control over the initial rate of polymerisation could be obtained. The initial rate was controlled due to the initiator system co-ordinating with the 1,4-dioxane requiring it to be released from the initiator before further propagation could occur. This resulted in broadening of the molecular weight distribution, as the level of 1,4-dioxane was increased (graph 7.8). There was no significant reduction in the level of cyclic oligomer formation as the level of 1,4-dioxane was increased. The polydispersity was increased by the reduced rate of initiation whilst the 1,4-dioxane did not 'cap' the active chain end of the propagating species as shown in figure 7.4.

In order for the 1,4-dioxane to be effective at controlling the rate of propagation, a uniform distribution of capped ends had to be obtained throughout the system, during initiation and propagation of the monomer. Bouchekief found that by using a high proportion of 1,4-dioxane in a solvent system, good control over the propagation of oxetane could be achieved using systems stabilised with BF_4^- regions.

When there was a low amount of 1,4-dioxane present, the propagation of the oxetane dominated with only a few sites being inhibited. The uneven hindering of the propagating centres resulted in a broadening of the polydispersity of the system (graph 7.8). It has been shown previously^[34] that by increasing the level of 1,4-dioxane, more of the inhibiting reactions would occur resulting in narrower polydispersities due to a more even distribution of active and inactive sites.

7.4.2.1. Dioxane/DCM Solvent Mixtures for Polymerisations of Oxetane using Chloromethyl Ethyl Ether Derived Initiators.

The initiator systems were prepared as in 7.3.1 and were used to polymerise oxetane using various mixtures of 1,4-dioxane/DCM as a solvent system (table 7.2). The polymerisations were followed by calorimetric analysis and by GPC. Samples were taken at regular intervals and quenched in methanol, dried and re-dissolved in THF and filtered. The samples were tested for molecular weight averages and

polydispersity using GPC. Selected samples were also analysed using NMR techniques to assess the chemical composition of the polymers formed.

Table 7.2

GPC results for polymerisations of oxetane initiated with $\text{CH}_3\text{CH}_2\text{O}^+\text{CH}_2\text{SbF}_6^-$ in various 1,4-dioxane/DCM solvent mixtures.

Sample	% 1,4-dioxane : DCM (vol: vol)	Time of polymerisation (minutes)	Mn	PD	% Oligomer
7.1	0: 100	5	4265	1.45	21.1
7.2	0: 100	60	3986	1.47	24.2
7.3	0: 100	120	3883	1.46	24.6
7.4	0: 100	180	4006	1.44	25.2
7.5	0: 100	240	4190	1.44	21.6
7.6	10: 90	1	4526	1.80	4.5
7.7	10: 90	2	4908	1.62	5.1
7.8	10: 90	5	4908	1.74	3.4
7.9	10: 90	10	5439	1.59	3.6
7.10	10: 90	30	5459	1.60	4.0
7.11	10: 90	60	5109	1.73	3.5
7.12	10: 90	120	4680	1.64	3.7
7.13	10: 90	240	5491	1.73	3.6
7.14	10: 90	360	5270	1.68	3.5
7.15	50: 50	1	4188	2.01	16.8
7.16	50: 50	2	6939	1.74	11.9
7.17	50: 50	5	7014	2.12	4.4
7.18	50: 50	10	5414	2.37	2.0
7.19	50: 50	30	3540	3.20	3.2
7.20	50: 50	60	3449	3.09	3.2
7.21	50: 50	120	5155	2.66	4.8
7.22	50: 50	240	7765	2.01	
7.23	75: 25	1	1837	2.01	2.0
7.24	75: 25	2	4989	1.55	5.1
7.25	75: 25	5	7543	1.59	2.0
7.26	75: 25	60	6966	1.93	3.6
7.27	75: 25	120	6281	2.03	3.6
7.28	75: 25	240	6616	1.99	7.0

All reactions carried out at 35°C with a monomer: initiator molar ratio of 3×10^{-2} to 3×10^{-4} mol respectively.

Adding 1,4-dioxane to the solvent system rather than as an additive to the initiator system resulted in a reduction in the rate of propagation as seen in graph 7.6. The

reduction in the rate of propagation led to improved control over the polymerisation. In the absence of 1,4-dioxane, the level of oligomer formation was high at around 20%. By incorporating the 1,4-dioxane to the solvent system, varied results were obtained. When the level of 1,4-dioxane inclusion was at 10% of the solvent volume, low polydispersity (PD ~ 1.6) and reduced cyclic oligomer formation (~4%) systems were obtained. At high levels of 1,4-dioxane incorporation (75% 1,4-dioxane), low levels of oligomer formation and controlled rates of propagation were achieved. For the higher level of 1,4-dioxane addition, there was a broadening of the polydispersity of the polymer systems.

Both the 10% and 75% levels of 1,4-dioxane added to the solvent system resulted in reducing the oligomer formation. There was a broadening in the polydispersity for all the systems containing 1,4-dioxane compared to the control. The broadening was brought about by the slower propagation rate of polymerisation resulting in uneven growth of the polymer chains.

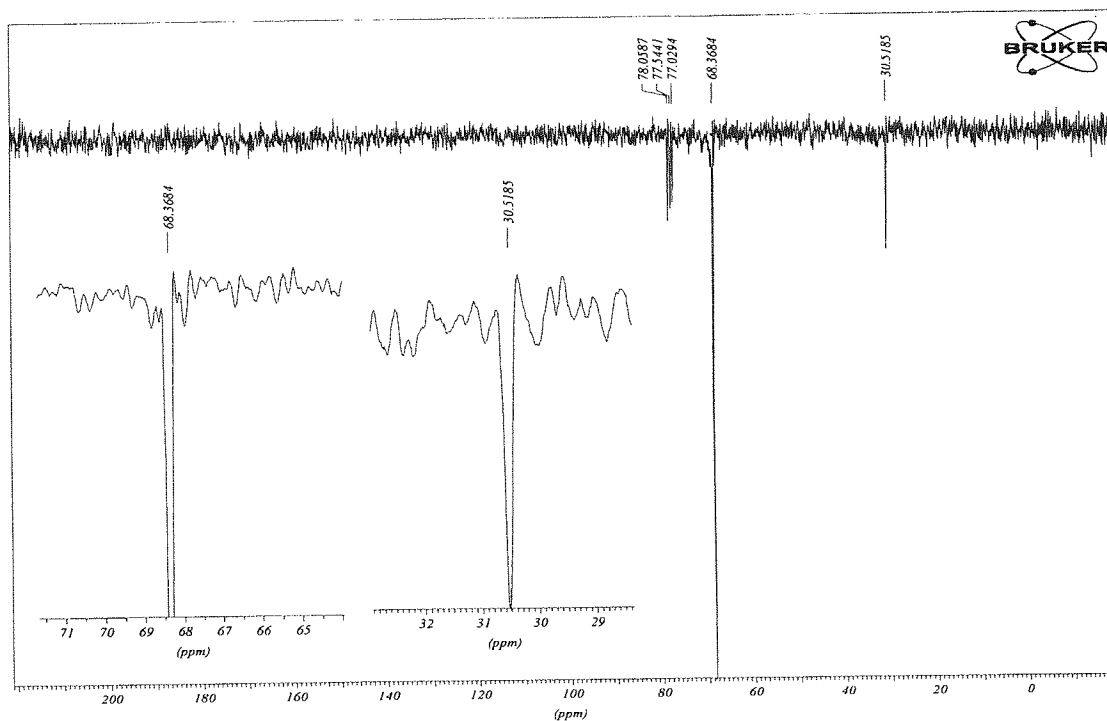
7.4.2.2. ¹³C NMR Studies of Polyoxetane Initiated using Chloromethyl Ethyl Ether Derivative and 1,4-Dioxane Solvent System

In section 7.4.1 it was found that 1,4-dioxane could be added to the polymerisation of oxetane to reduce the amount of oligomer formation. One proposed mechanism of the 1,4-dioxane interaction with the propagating chain was to react with the active chain end of propagating species. This prevented the site from propagating further until it was released, slowing down the rate of monomer consumption.

From ¹³C NMR studies of the system, there was evidence of a PEG type $-(O-CH_2-CH_2-O)-$ linkage. By comparing the polymers synthesised using 1,4-dioxane containing solvent systems with those prepared in DCM solvent it was observed that a significant peak appeared at a similar shift to that of PEG type linkage typically signified as a peak with a chemical shift of 66.3ppm.

Fig. 7.6

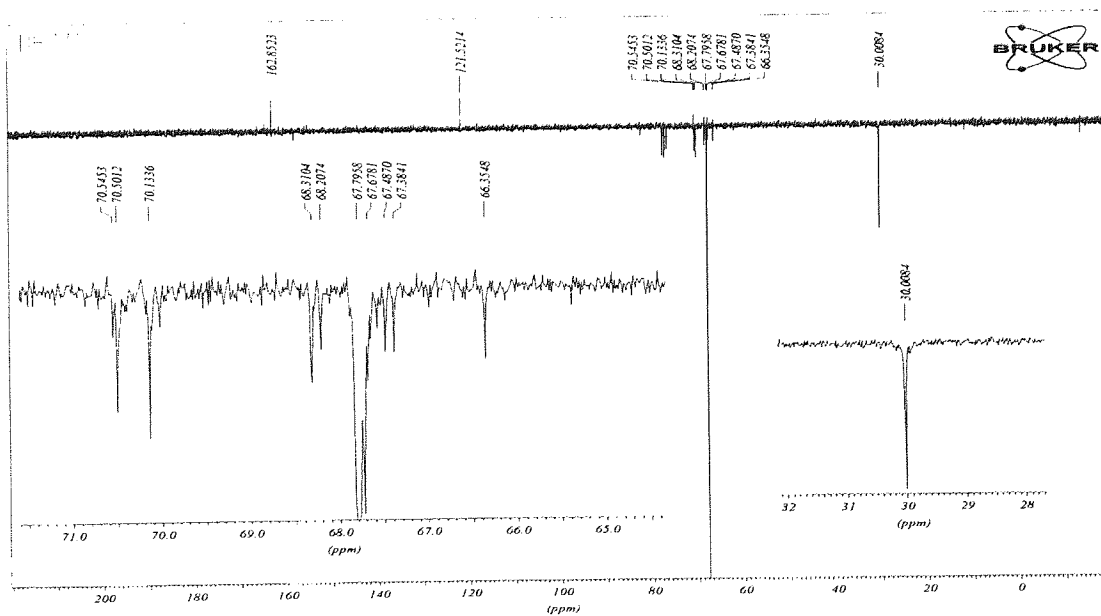
^{13}C NMR of polyoxetane initiated using chloromethyl ethyl ether derivative in 100%DCM solvent system.



Monomer and initiator solutions made in DCM solvent reacted at 35°C and reacted for four hours. Molar ratio of monomer: initiator was 100:1 respectively.

Fig. 7.7

^{13}C NMR of polyoxetane initiated using chloromethyl ethyl ether derivative in a solvent system containing 75% 1,4-dioxane and 25% DCM (vol/vol).

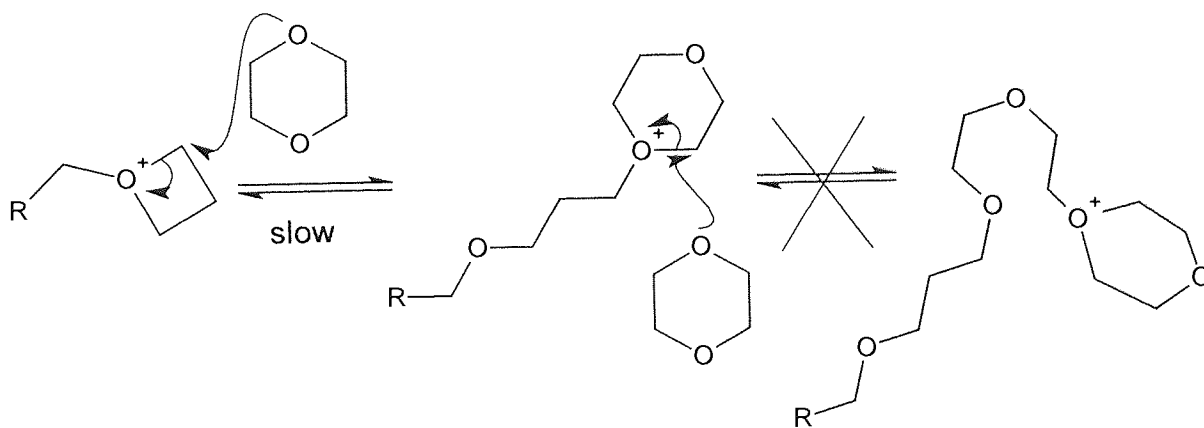


Monomer solution made in DCM / 1,4-dioxane solvent system reacted at 35°C and reacted for four hours. Ratio of monomer: initiator was 100:1.

From figures 7.6 and 7.7, which were ^{13}C NMR spectra of equivalent polymer systems synthesised without and with 1,4-dioxane being used as a solvent respectively, two sets of peaks were found. These peaks at 30.5ppm and 67.5ppm are those of the $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})-$ and $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})-$ carbon atoms respectively. The peak found at 66.3ppm on figure 7.7 corresponds to the linkage of the oxetane to the opened 1,4-dioxane molecule. The peaks found at 70.1ppm and 70.5ppm on figure 7.7 are singlets and appear to be similar in size, therefore showing that the carbons in the 1,4-dioxane are approximately equivalent. The presence of opened 1,4-dioxane joined to another of the same type would bring about extra peaks at around the 70ppm region but are not present. The presence of the approximately equal peaks also indicates that there are no back to back 1,4-dioxane linkages. As there are no back to back 1,4-dioxane linkages in the system, 1,4-dioxane does not react with the capped end. It indicates that once the end of the propagating species has been capped with a 1,4-dioxane molecule it can only be reactivated or reacted with an oxetane monomer, as shown in figure 7.8.

Fig 7.8

Proposed scheme of low reactivity between 1,4-dioxane on an already capped propagating active chain end with 1,4-dioxane added as a component of the solvent system.



7.4.3 Dioxane/DCM Solvent Mixtures for Polymerisations Initiated using Benzyl Bromide derivative

An alternative initiator system was developed and prepared as in 7.3.2 when benzyl bromide was reacted with silver hexafluoroantimonate and benzaldehyde to generate the initial cationic centre.

The monomer solutions were prepared by adding the solvent mixtures to the monomer in Schlenk flasks to make 1M-monomer solutions. The monomer solutions were transferred to the reaction vessel using Schlenk techniques on the vacuum line. The initiator solution was added to the monomer solution in the reaction vessel using the Schlenk technique. The initial temperature increases were measured using calorimetric analysis. Samples were taken at regular intervals during the polymerisation and quenched in methanol and dried using a vacuum oven, redissolved in THF and filtered prior to testing for molecular weight averages using GPC.

The molar ratio of monomer to initiator was set a 100: 1 respectively with 0.00048mol of initiator being added to 0.048mol of oxetane. The solvent mixtures were prepared using a varying percentage volume ratios of dried DCM and 1,4-dioxane. The DCM, 1,4-dioxane solvent systems used, consisted of 100:0, 95:5, 90:10, 50:50 and 25:75 percent volume ratios respectively. The polymerisations were carried out at 35°C under an inert nitrogen gas flow with the results shown in table 7.3.

Table 7.3
 GPC results for polymerisations of oxetane in various 1,4-dioxane, DCM solvent compositions.

Sample	% 1,4-dioxane : DCM (vol: vol)	Time of polymerisation (minutes)	\overline{M}_n	PD	% Oligomer
7.29	0: 100	5	5123	1.75	10.3
7.30	0: 100	60	5084	1.69	9.3
7.31	0: 100	120	5344	1.70	8.2
7.32	0: 100	180	6167	1.65	7.7
7.33	0: 100	240	5410	1.73	7.3
7.34	5: 95	1	923	1.2	3.1
7.35	5: 95	2	-	-	-
7.36	5: 95	5	-	-	-
7.37	5: 95	10	9245	1.92	2.9
7.38	5: 95	30	8797	1.98	3.6
7.39	5: 95	60	9158	1.82	3.7
7.40	5: 95	120	9329	1.86	2.9
7.41	5: 95	240	8039	1.84	3.1
7.42	10: 90	1	7029	1.50	5.6
7.43	10: 90	2	11845	1.52	4.8
7.44	10: 90	5	12884	1.52	5.4
7.45	10: 90	10	14946	1.38	3.5
7.46	10: 90	30	12075	1.54	1.8
7.47	10: 90	60	11728	1.54	1.1
7.48	10: 90	120	10849	1.57	3.6
7.49	10: 90	240	8832	1.67	6.6
7.50	50: 50	1	2876	1.70	0
7.51	50: 50	2	4863	2.07	0
7.52	50: 50	5	8866	2.47	0
7.53	50: 50	10	9012	2.69	0
7.54	50: 50	30	9732	2.33	0
7.55	50: 50	60	9733	2.34	0
7.56	50: 50	120	8468	2.38	0
7.57	50: 50	240	15119	1.67	0
7.58	75: 25	1	1147	1.89	0
7.59	75: 25	2	2280	1.51	0
7.60	75: 25	5	3475	1.38	0
7.61	75: 25	10	2355	1.72	0
7.62	75: 25	30	1881	2.18	0
7.63	75: 25	60	1805	1.87	0
7.64	75: 25	120	1906	1.84	0
7.65	75: 25	240	1631	1.95	0

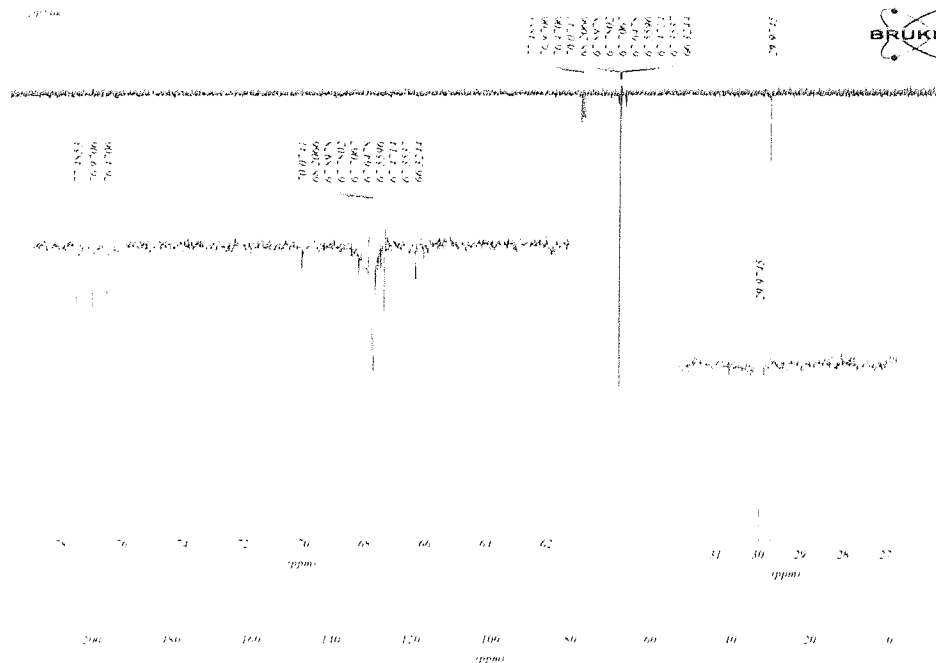
When low levels of 1,4-dioxane as part of the solvent system were used (0-10%), cyclic oligomer formation was evident from GPC analysis. At higher levels (50-75%), oligomer formation was not observed. For very high levels of 1,4-dioxane, low molecular weight systems were generated indicating that the propagation of the monomer was hindered by the modified solvent system. When a solvent system of 50% DCM and 50% 1,4-dioxane was used, oligomer formation was not seen and a high \overline{M}_n was achieved. With the 50% 1,4-dioxane system there was a general broadening in PD compared to 100% DCM solvent system.

7.4.3.1. ^{13}C NMR Analysis of Polyoxetane Initiated using Benzyl Bromide Derived Initiator using 1,4-dioxane and DCM Solvent Systems.

^{13}C NMR experiments were performed on the polymers generated from oxetane initiated using the PhCH_2Br derived system. The spectra were analysed to assess if there was any 1,4-dioxane inclusion into the polymer backbone. The presence was previously observed in figure 7.7 as extra peaks at 70.1 and 70.5 ppm on the ^{13}C NMR spectrum. By comparing the spectra of the polymers generated without (figure 7.9) and with (figure 7.10) 1,4-dioxane, differences in the composition could be seen. For the 1,4-dioxane solvent system, additional peaks at 70.1 and 70.5 ppm appear were present. When 1,4-dioxane was used there was incorporation of it into the polymer backbone. This was also found for the initiator system based on chloromethyl ethyl ether system. Also present in the 1,4-dioxane solvent system spectrum are several small peaks with chemical shifts at 108, 132 and 155 ppm. The peaks are consistent with aromatic carbons and can be attributed to the initiator system.

Fig 7.9

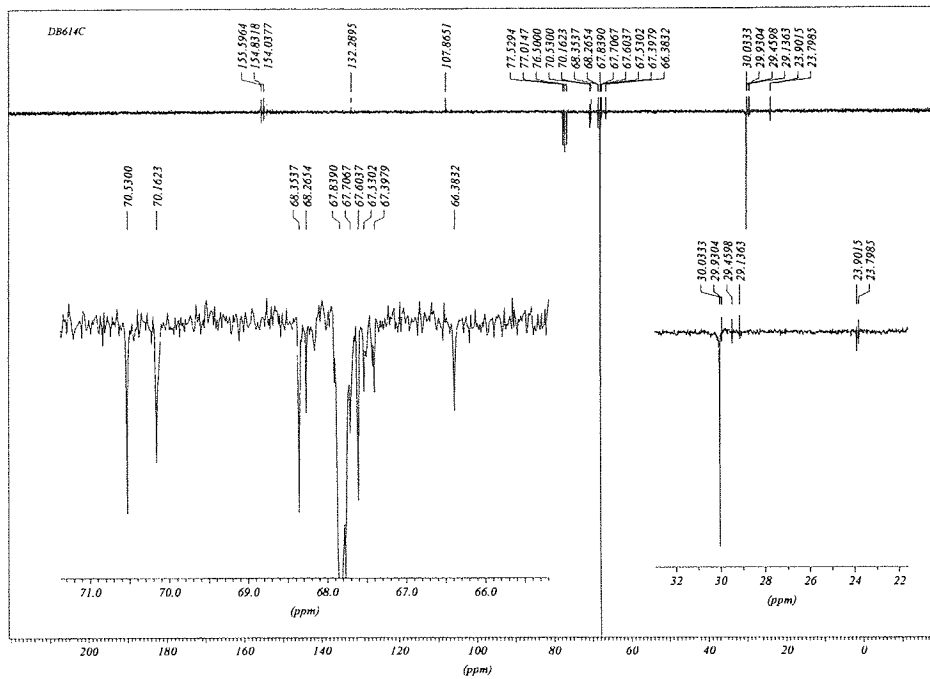
^{13}C NMR spectrum of polyoxetane polymerised with 100% DCM solvent system



PhCH_2Cl reacted with AgSbF_6 and PhCHO as an initiator. Polymerised using DCM as a solvent at 35°C with an inert atmosphere with a monomer: initiator molar ratio of 100:1.

Fig 7.10

^{13}C NMR spectrum of polyoxetane polymerised with 50% DCM and 50% 1,4-dioxane solvent system, initiated using bromomethyl benzene derivative.



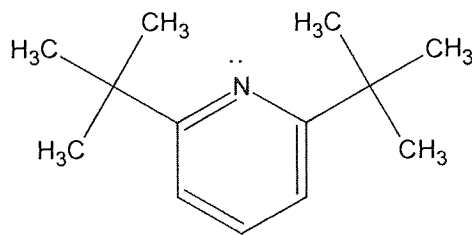
PhCH_2Cl reacted with AgSbF_6 and PhCHO as an initiator. Polymerised using DCM as a solvent at 35°C under an inert atmosphere with a monomer: initiator ratio of 100:1.

7.5. Addition of 2,6-Ditert-Butyl Pyridine (DTBP) to Initiators.

Another additive that was used to improve the control CROP reactions in the past was 2,6-ditert butyl pyridine (DTBP) figure 7.11. DTBP can improve the control of the polymerisation by absorbing any excess cationic species or free acid particles in the system.

Fig 7.11

Structure of 2,6-ditertbutyl pyridine



2,6-di-tert-butylpyridine

The initiators were prepared as described in 7.3.1 and 7.4.3 but using DCM as the only component in the solvent system with the incorporation of 1.5×10^{-3} mol of DTBP to 1.5×10^{-3} mol of initiator solutions prior to polymerisation.

3×10^{-4} mol of the DTBP doped initiator solutions were added to 3×10^{-2} mol of oxetane monomer solutions using positive pressure techniques. Samples were taken at regular intervals and quenched in methanol, dried, re-dissolved in THF, filtered and analysed using GPC. The results from both polymerisations are summarised in table 7.4.

Table 7.4

GPC results for polymerisations of oxetane with DTBP added to the initiator systems.

Sample	Initiator system	Time of polymerisation (minutes)	\overline{M}_n	PD	% Oligomer
7.66	PhCH ₂ Br + AgSbF ₆	1	4082	2.63	4.0
7.67	+ PhCHO in DCM	2	4594	2.59	2.4
7.68	With 1 equivalent	5	5537	2.19	4.7
7.69	DTBP	30	5014	2.13	5.4
7.70		60	5386	2.28	3.8
7.71		240	5232	2.06	6.2
7.72	CH ₃ CH ₂ OCH ₂ Cl +	1	2475	7.70	0
7.73	AgSbF ₆ in DCM	2	3200	4.90	0
7.74	With 1 equivalent	5	2182	4.70	0
7.75	DTBP	30	1863	5.50	0
7.76		60	5800	2.88	1.3
7.77		240	2757	3.45	0.3

Reacted at 35°C and samples taken and quenched at regular intervals with methanol. (100:1 monomer: initiator).

When DTBP was added to the chloromethyl ethyl ether derived initiator system low levels of cyclic oligomer formation was observed. The PD of the polymer system was broadened drastically and the, \overline{M}_n , of the system was relatively low compared to when no DTBP was added. These effects can be attributed to the ACE being stabilised by the DTBP, thus reducing the rate of initiation and propagation of the polymerisation. This stabilisation of the ACE also slowed the backbiting reactions of the polymer chain resulting in low levels of cyclic oligomer formation.

Table 7.6.

Exothermal results generated with various initiator systems with and without DTBP added for the polymerisation of oxetane.

Initiator system	Initial rate of polymerisation. °c/sec
CH ₃ CH ₂ OCH ₂ Cl reacted with AgSbF ₆	50
CH ₃ CH ₂ OCH ₂ Cl reacted with AgSbF ₆ with DTBP.	0.16
PhCH ₂ Br reacted with AgSbF ₆ and PhCHO	117
PhCH ₂ Br reacted with AgSbF ₆ , PhCHO and DTBP.	108

Reacted in DCM at 1M monomer solution, 0.1M initiator solution at 35°. The monomer: initiator ratio was 100:1.

The addition of DTBP to the chloromethyl ethyl ether derived initiator, significantly reduced the rates of initiation and propagation resulting in a high polydispersity. Little control of polymerisation was achieved when DTBP was added to the initiator.

When DTBP was added to the benzyl bromide derived initiator no significant change was seen in terms of initial rate of polymerisation. This maybe due to the fact that the initiator is already stabilised with the benzaldehyde co-initiator, preventing the DTBP from associating with the ACE.

Of the two-initiator systems tested, it was found that DTBP had a greater affect on the chloromethyl ethyl ether derived system. For the benzyl bromide derived initiator system benzaldehyde was added as in chapter 5 because it improved the control of the system.

Chapter 8

Derivatives of oxetane

8.1. Oxetane and its Derivatives

Oxetane is a simple heterocycle with a high level of ring strain as previously discussed in chapter 2. It is this ring strain that enables oxetane to be polymerised readily by means of cationic ring opening polymerisation (CROP). By attaching substituents to the heterocycle, the properties of the polymer can potentially be drastically altered. In the literature, there are many examples of oxetane based monomers with various functionalities. These, can range from difunctional oxetane based systems to produce branching, or nitrated systems as used in explosives^[1,47,50]. The polymerisation propagation of oxetane involves an S_N2 attack at either the 2 or 4 positions on the oxetane ring. By substituting hydrogen atoms at the 2 or 4 positions with a larger group, potentially resulting in a reduction in the rate of polymerisation. Therefore, by using oxetane derivatives with substituents on the 3,3 positions of the ring, omittance in reduction of potential attack sites can be observed. Any changes brought about by substituents on the 3,3 positions will be either due to steric or electronic effects.

There are many polymers that have been produced using derivatives of oxetane via CROP. Perhaps the most relevant to this project, was the monomer 3,3-bis-bromomethyl oxetane (BBMO) which has been prepared by QinetiQ^[84]. The BBMO was prepared using a phase transfer reaction as detailed in chapter 3.2.1. BBMO has potential reactive functional groups to allow further chemical modification of the polymer system. Subsequent chemical reactions that can be performed include nitration of the bromide group, which can be undertaken to generate higher energy systems for use in explosives.

Other monomers that have been studied are 3,3-dimethyl oxetane (DMO) with two methyl groups on the 3,3 positions and 3-methyl oxetane methanol (MOM).

The derivatives of oxetane that were, studied all had substituents at the 3,3 position on the oxetane ring. These were selected so that none of the potential S_N2 sites of attack were hindered. The monomers were polymerised using the two types of initiator system reported in chapter 5 and developed further in chapter 7. The monomers were polymerised using either DCM (dichloromethane) or a DCM/1,4-dioxane solvent system, using SbF_6^- as a counter ion. The substituents selected were, hydroxyl,

bromomethyl and methyl groups. The hydroxyl and bromide substituted monomers were selected as these functional groups can be used for subsequent reactions. The methyl substituents were studied to show if the presence of the methyl group at the 3,3 position affected the polymerisability of the monomer.

There were several techniques used to follow the progress of the reaction. These were by calorimetric, GPC and gravimetric analysis. ^1H and ^{13}C NMR were performed on a selection of the resultant polymers to elucidate the structure and the possible presence of any side reactions or cross-linking that occurred.

8.2. 3,3-Bis-Bromomethyl Oxetane (BBMO).

BBMO was a monomer made at a pilot plant level by QinetiQ^[84]; it was produced via a phase transfer reaction discussed in chapter 3. The structure of BBMO was similar to that of oxetane but with two bromomethyl groups at the 3,3 position on the heterocyclic ring. Bromides are effective leaving groups and other reactions can be performed easily to produce other novel materials.

8.2.1. BBMO Polymerisation Initiated with Chloromethyl Ethyl Ether Derivative.

A 0.1M initiator solution was prepared by reacting 1.5×10^{-3} mol of chloromethyl ethyl ether with 1.5×10^{-3} mol of silver hexafluoroantimonate in 15ml of DCM for 24 hours. The solution was decanted, removing the silver halide precipitate, retaining the oxonium ion initiator. A 1M solution of dried BBMO and DCM was prepared in an argon glove box, by mixing 4×10^{-2} mol of BBMO made up to 40ml with DCM. 30ml of the monomer solution was transferred to the 35°C reaction vessel as in chapter 3, using the Schlenk positive pressure technique. 3ml of the initiator solution was added to the monomer solution whilst being agitated using a magnetic flea. Samples were taken at regular intervals, quenched in methanol and dried in a vacuum oven. The progress of the polymerisation was monitored by calorimetric, GPC and NMR analysis.

It was found by calorimetric analysis that the initial rate of polymerisation of BBMO was very fast (322°C/sec) and much more exothermic than the oxetane control

(50°C/sec) polymerisation under the same conditions. It was also found that the temperature increase was such that some of the solvent was lost through boiling. Due to the rapid increase in temperature, the pressure increased to such an extent as to force the unfastened stoppers out with force.

8.2.2. Analysis of the Polymerisation of BBMO Initiated with Chloromethyl Ethyl Ether Derivative.

During the research, it was found that the PolyBBMO generated in 8.2.1 was largely insoluble in all common organic solvents in addition to concentrated nitric and sulphuric acids. The results obtained were used with caution, as a large proportion of the product could not be easily analysed due to its low solubility. The GPC results indicate that there was a polymerisation, but the amount of polymer that was taken up in the solvent (THF) was very low and may be of only the low molecular weight fragments of the polymer system. The \overline{M}_n obtained was 8700 after 30 seconds of polymerisation, with a polydispersity of 1.7.

The resultant polymer was dissolved in deuterated chloroform (CDCl_3) and ^1H NMR results were summarised and are shown in table 8.1. The solubility of the resultant polymer was low in the deuterated solvent resulting in weak signals and poor signal to noise ratios.

During the polymerisation, it was also observed that a precipitate formed after several seconds. This precipitate was also very difficult to re-dissolve using common organic solvents.

Table 8.1.

^1H NMR summary of PolyBBMO initiated using $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ derivative

Chemical shift δ (ppm)	Relative intensity	Number of peaks	Chemical group
1.52	5.6	1	$-\text{CH}_2-$
3.39	0.58	2	$-\text{CH}_2\text{-Br}$
3.47	1.0	1	$-\text{CH}_2\text{-O}$
4.14	0.08	1	

During the polymerisation of BBMO as shown in figure 8.1, the CH₂-Br and CH₂-O should have been equivalent for a linear polymer system. From the above table it can be concluded that the amount of CH₂-O groups outnumber those of the CH₂-Br groups by approximately 2 to 1 respectively. The disparity between the quantities of the functional groups, coupled with the fact that the polyBBMO was difficult to dissolve, suggests that there was a cross-linking side reaction occurring, as proposed in figure 8.2.

Fig 8.1

Proposed initiation and propagation steps of polymerisation of BBMO initiated using chloromethyl ethyl ether reacted with silver hexafluoroantimonate.

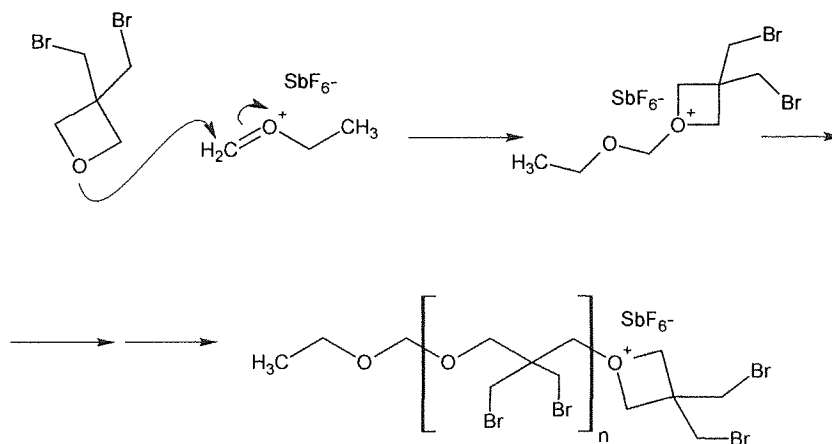
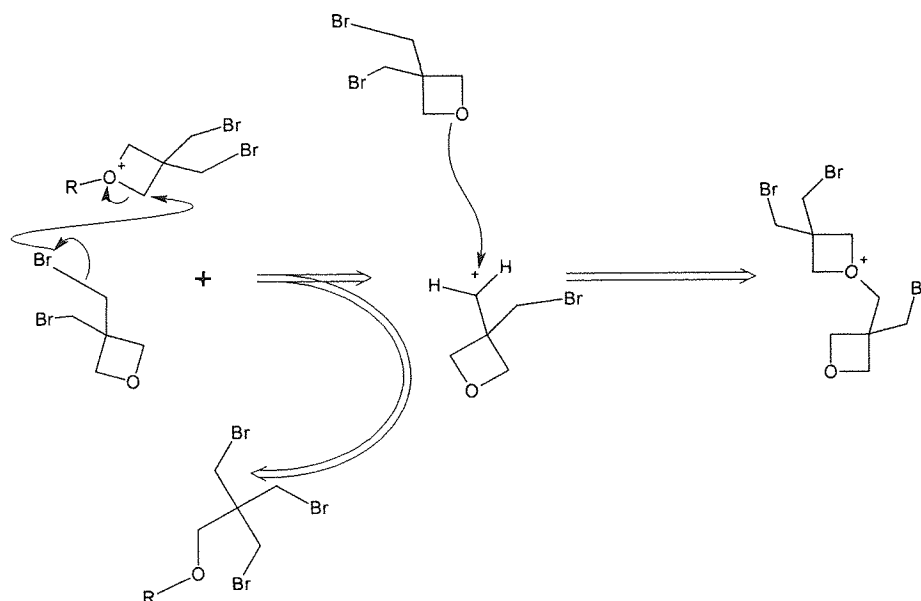


Fig 8.2

Cross-linking reaction during the polymerisation of BBMO reducing its ability to solvate in various solvents.



8.2.3. BBMO Polymerization Initiated with Chloromethyl Ethyl Ether Derivative with 1,4-dioxane Incorporated into Solvent Mixture.

It was discussed in chapter 7 that 1,4-dioxane was effective at controlling the rate of propagation of oxetane when added as a component of the solvent system. The initiator was prepared as in 8.2.1. 3ml of the initiator solution was added to 30ml of a 1M solution of BBMO using a solvent made up of 90% DCM; 10% 1,4-dioxane (vol%). The reaction solutions were added to the polymerisation vessel using the Schlenk positive pressure techniques. The initial stages of the polymerisation were followed using calorimetric methods.

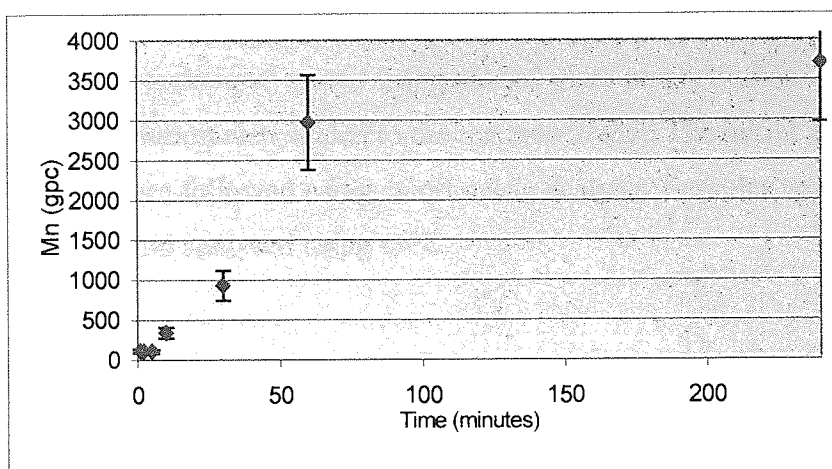
Samples were taken at regular intervals, quenched in methanol and dried in a vacuum oven. The resultant polymer systems were re-dissolved in THF, filtered and analysed using GPC. Selected samples were also analysed using ¹H NMR techniques.

The calorimetric results indicated that the initial rate of polymerisation was either very slow or non-existent with no change in temperature being observed. From the GPC results, the initiation of the BBMO appeared to be very slow with no increase in

\overline{M}_n for 10 minutes. After 30 minutes, the rate of propagation was steady and a moderate molecular weight was achieved after 4 hours of polymerisation (graph 8.1).

Graph 8.1.

Polymerisation of BBMO initiated using a $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ derivative in a 90% DCM and 10% 1,4-dioxane solvent mixture.



The addition of 1,4-dioxane to the solvent system significantly reduced the initial rate of polymerisation by “capping” the ACE of the polymer system. Although the rate of initiation was significantly slowed, only a low rate of monomer conversion was achieved of around 10%.

8.2.4. BBMO Polymerization Initiated with Chloromethyl Ethyl Ether Derivative with DTBP Added to the Initiator System.

Di-tertbutyl pyridine (DTBP) was used in chapter 7 and found to significantly reduce the initial rate of polymerisation of oxetane. The addition of DTBP to the polymerisation of oxetane also significantly increased the polydispersity of the system. The rate of polymerisation of the BBMO without additives was significantly faster than that of the oxetane. The BBMO polymerisation also generated side reactions that reduced the solvating and binding properties of the polymer system. DTBP was added to the system to assess whether it allowed the polymerisation to proceed without the presence of side reactions.

The initiator solution was prepared as in 8.2.1 with 1.5×10^{-3} mol of chloromethyl ethyl ether and AgSbF_6 being reacted in 15ml of DCM. After 24 hours of preparation, 1.5×10^{-3} mol of DTBP was added to the initiator solution and left for a further 24 hours. The initiator solution was decanted and stored in an inert atmosphere.

In a Schlenk flask 4×10^{-2} mol of dried BBMO was added to DCM to make up a 40ml, 1M solution. 30ml of the monomer solution was transferred to the reaction vessel using the Schlenk technique, stirred using a dried glass magnetic flea. 3ml of the initiator/DTBP solution were added to the reaction vessel. The initial stages of the polymerisation were followed using calorimetric analysis. Samples were taken at regular intervals and analysed using GPC.

There was no change in temperature and no progression of \overline{M}_n after 4 hours of polymerisation. These results show that DTBP stopped the polymerisation of BBMO when it was added to the initiator.

8.2.5. BBMO Polymerisation with Benzyl Bromide, Silver Hexafluoroantimonate and Benzaldehyde.

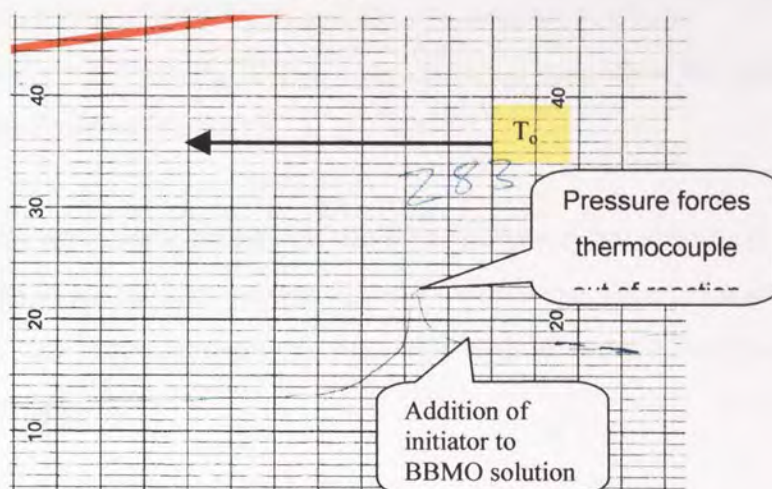
A 0.1M initiator solution was prepared by reacting 1.5×10^{-3} mol of each of the following; benzaldehyde, benzyl bromide and silver hexafluoroantimonate in 15ml of dried DCM, for 24 hours. The solution was decanted, removing the silver halide precipitate, whilst retaining the oxonium ion initiator solution. A 1M-monomer solution was prepared by mixing 4×10^{-2} mol of dried BBMO and added to make up a 40ml solution with dried DCM in an argon glove box. 30ml of the monomer solution was transferred to the reaction vessel using the Schlenk positive pressure technique. 3ml of the initiator solution was added to the monomer solution whilst being agitated using a glass magnetic flea. Samples were taken at regular intervals and quenched in methanol and then dried in a vacuum oven. Progress of the polymerisation was monitored by calorimetric, GPC and NMR analysis.

From the calorimetric analysis, it was seen that the initial rate of polymerisation was extremely rapid ($360^\circ\text{C}/\text{sec}$). The exothermic reaction caused the solvent to boil off in

less than 20 seconds and sufficient pressure was generated to cause the thermocouple to be pushed out of the reaction vessel as seen from fig 8.3.

Fig 8.3

Calorimetric profile of the polymerisation of BBMO initiated using benzyl bromide derived initiator.



The polyBBMO was difficult to dissolve in any solvent as in 8.2.1, making it difficult to analyse using GPC. The results are similar to that of the polymerisation of BBMO using chloromethyl ethyl ether derivative. Hyper-branching occurs when the oxonium ion initiators are used, via a similar mechanism as proposed in figure 8.2.

8.2.5.1. BBMO Polymerisation with Benzyl Bromide, Silver

Hexafluoroantimonate and Benzaldehyde with 1,4-dioxane Added to the Solvent.

A 0.1M initiator solution was prepared as in 8.2.5, a DCM and 1,4-dioxane solvent mixture of 90; 10 (volume %) was used. The solution was decanted, removing the silver halide precipitate, whilst retaining the oxonium ion initiator solution.

In a Schlenk flask 40ml of a 1M solution of dried BBMO was prepared in a DCM/ 1,4-dioxane solvent mixture (90;10 vol % respectively). 30ml of the monomer solution was transferred to the reaction vessel using the Schlenk positive pressure technique. 3ml of the initiator solution was added to the monomer solution whilst being agitated using a glass magnetic flea. Samples were taken at regular intervals and

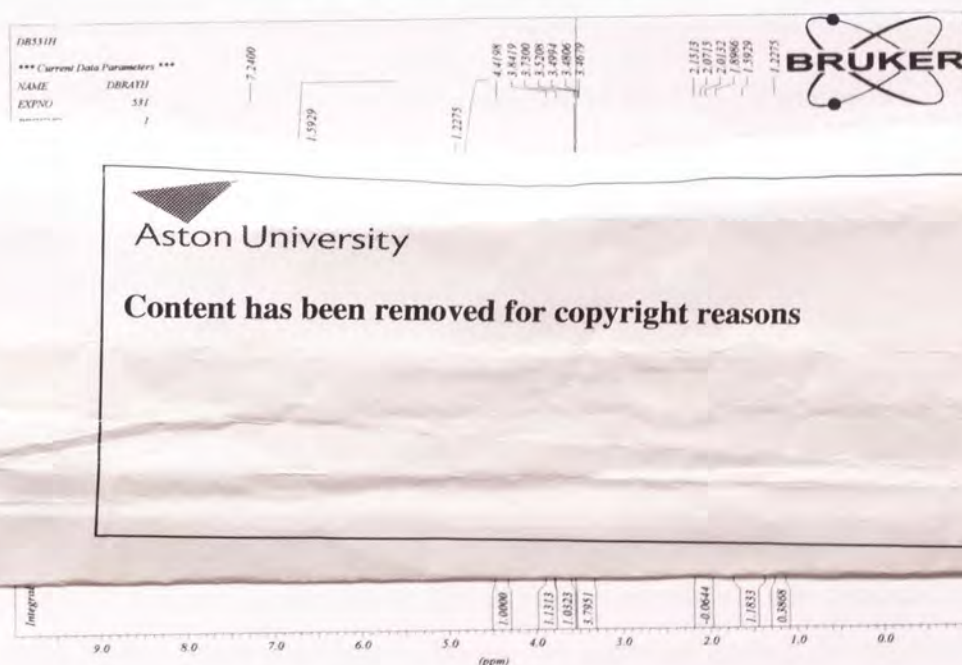
quenched in methanol and dried in a vacuum oven. Progress of the polymerisation was monitored by calorimetric, GPC and NMR analysis.

The experiment was repeated as previously described with the exception of using a solvent system comprising of 95% DCM and 5% 1,4-dioxane. For both polymerisations, there was no initial change in temperature seen when the initiator was added to the monomer solution.

During the polymerisation some precipitate did form, however, but at a much slower rate when compared to the initiator system without 1,4-dioxane. When characterised using GPC, only a small polymer peak was seen with large amounts of residual monomer left in the system.

Fig 8.4

^1H NMR spectrum of polyBBMO initiated using benzyl bromide derived initiator in a DCM: 1,4-dioxane solvent mixture at 90:10% ratio.



A ^1H NMR analysis was performed on the resultant polymer, as shown in figure 8.4 and summarised in table 8.2. From the ^1H NMR, it can be seen that there were a number of impurities in the system such as unreacted BBMO monomer (peaks at 3.8 and 4.4ppm) and methanol (at 1.6ppm). The GPC showed signs of large amounts of

low molecular weight impurities close to the toluene marker peak. These peaks were out of the calibration range on the chromatogram but were likely to come from the unreacted BBMO monomer. The area of polymer $\text{CH}_2\text{-O-}$ (at 3.5ppm) linkage to $\text{CH}_2\text{-Br}$ (3.7ppm) peaks were 4 : 1 respectively. This discrepancy suggests that a cross-linking mechanism through the $\text{CH}_2\text{-Br}$ occurred with the active chain end. The monomer was difficult to remove from the polymer; so therefore, gravimetric analysis yielded high figures of 82% but included a significant proportion the unreacted monomer.

Table 8.2.

^1H NMR of polyBBMO initiated using benzyl bromide reacted with silver hexafluoroantimonate and benzaldehyde in a DCM: 1,4-dioxane solvent mixture at 90:10% ratio.

Chemical shift δ (ppm)	Relative intensity	Number of peaks	Chemical group
1.23	0.4	1	Residual methanol
1.59	1.2	1 broad	Residual methanol
3.47	3.8	1 major 3 shoulders	$-\text{CH}_2\text{-O-}$, -
3.73	1.0	1	$-\text{CH}_2\text{-Br-}$
3.84	1.1	1	BBMO monomer
4.42	1.0	1	BBMO monomer

From the ^1H NMR in fig 8.4 a significant reduction in the $\text{CH}_2\text{-Br}$ linkage was seen with an increased level of the CH-O groups. This reduction in the halide group was a result of a hyper-branching reaction as described in figure 8.2.

8.2.5.2. BBMO Polymerisation with Benzyl Bromide, Silver Hexafluoroantimonate and Benzaldehyde with 2,6-Ditert-Butyl Pyridine.

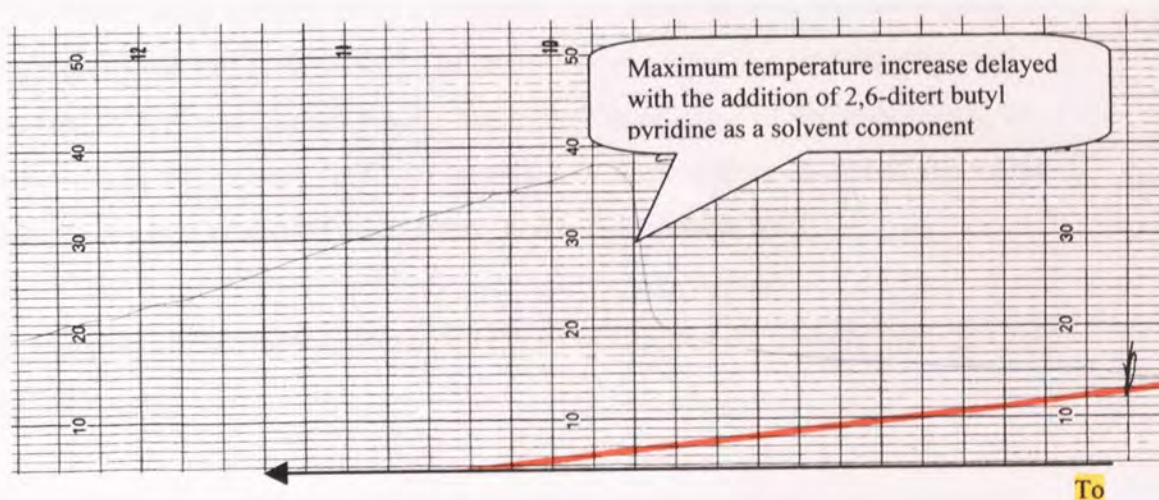
A 0.1M initiator solution was made as described in 8.2.5 using benzaldehyde, benzyl bromide and silver hexafluoroantimonate in DCM with the addition of 2 molar equivalents of 2,6-ditert butyl pyridine (3×10^{-3} mol). The solution was decanted, removing the silver halide precipitate retaining the oxonium ion initiator solution. 40ml of a 1M dried BBMO solution (in DCM) was prepared in an argon glove box. 30ml of the monomer solution was transferred to the reaction vessel using the Schlenk positive pressure technique. 3ml of the initiator solution was then added to the monomer solution whilst being agitated using a glass magnetic flea. Samples were

taken at regular intervals and quenched in methanol and dried in a vacuum oven. Progress of the polymerisation was monitored by calorimetric and GPC analysis.

When the initiator solution was added to the monomer solution, no initial temperature rise was observed, which indicates that the initial rate was slow. After 60 seconds of the initiator addition, the temperature increased rapidly as shown in figure 8.5. This observation has been made before for frontal approach polymerisations where an initial energy barrier has to be overcome before propagation can proceed. Owing to this, the 2,6-ditert-butyl pyridine initially inhibited the polymerisation but once the initiation energy was obtained, normal propagation occurred. BBMO and 2,6-ditert-butyl pyridine systems could potentially be used, where a delayed initiation is required such as in inkjet printing or blending materials for example.

Fig 8.5

Temperature profile of BBMO polymerised with benzyl bromide derived initiator doped with 2,6-ditertbutyl pyridine.



The resultant polymer of BBMO was again insoluble in common solvents making GPC and NMR analysis difficult. The 2,6-ditert-butyl pyridine slowed the initial rate of polymerisation down but did not prevent previously seen side reactions leading to cross-linking.

8.3. 3,3-Dimethyl Oxetane (DMO).

3,3-Dimethyl oxetane is the simplest of the derivatives of oxetane that was studied and has a similar structure and functionality to oxetane^[77, 85-87]. The monomer had two methyl substituents at the 3,3 positions, which do not add any significant reactive functionality to the monomer.

8.3.1. Polymerisation of DMO Initiated Using Chloromethyl Ethyl Ether Derivative.

A 0.1M initiator was prepared by reacting chloromethyl ethyl ether with silver hexafluoroantimonate as described in 8.2.1. The solution was decanted, removing the silver halide precipitate, retaining the oxonium ion initiator solution. 40ml of a 1M solution of dried DMO was prepared in an argon glove box using DCM as a solvent. 30ml of the monomer solution was transferred to the reaction vessel using the Schlenk positive pressure technique. 3ml of the initiator solution was added to the monomer solution whilst being agitated using a magnetic flea. Samples were taken at regular intervals and quenched in methanol. The samples were dried in a vacuum oven and redissolved in THF and filtered prior to analysis. The progress of the polymerisation was followed by calorimetric and GPC analysis. A NMR study was carried out on the resultant polymer to elucidate its structure, and is discussed in 8.3.2.

8.3.2. Analysis of the Polymerisation of DMO Initiated with Chloromethyl Ethyl Ether Derivative.

From the GPC analysis, it was seen that the initial rate of polymerisation was faster with a high initial molecular weight average, \overline{M}_n , being obtained. The initial rate of polymerisation was measured, using calorimetry, and compared to that of oxetane with DMO having a rate of over twice that of oxetane (50°C/Sec for oxetane and 109°C/Sec for DMO). The GPC and gravimetric results are shown in the table 8.3. Both the polydispersity and \overline{M}_n of the polymer were reasonably constant throughout the progress of the polymerisation, with a steady increase in the gravimetric % conversion of the monomer.

Owing to the increased initial rate of polymerisation of DMO compared to that of oxetane, the methyl groups on the 3,3 position of the oxetane ring do have an effect of the polymerisation of the monomer.

Table 8.3

GPC and gravimetric results for PolyDMO initiated using $\text{CH}_3\text{CH}_2\text{OCH}_2\text{Cl}$ reacted with AgSbF_6 . In DCM at 35°C .

Time (minutes)	\overline{M}_n	PD	% conversion
5	6500	1.6	34
60	6900	1.6	41
120	6900	1.6	47
180	7400	1.5	54
240	6300	1.7	58

The ^1H NMR of polyDMO which is summarised in table 8.4 indicates that linear polymer is formed in a similar way to oxetane.

Table 8.4

^1H NMR of DMO polymer initiated using chloromethyl ethyl ether reacted with silver hexafluoroantimonate in a DCM solution.

Chemical shift δ (ppm)	Relative intensity	Number of peaks	Chemical group
0.81	1.0	1	$-\text{CH}_3$ oligomer
0.85	3.6	1	$-\text{CH}_3$ polyDMO
0.90	0.3	1	$-\text{CH}_3$ oligomer
2.16	0.2	1	Initiator $\text{CH}_2\text{-O}$ linkage
3.05	0.8	1	$\text{CH}_2\text{-O}$ oligomer
3.09	2.1	1	$\text{CH}_2\text{-O}$ polyDMO
3.12	0.2	1	$\text{CH}_2\text{-O}$ oligomer
3.30	0.1	Multiplets	Oligomers

Due to the position of the $-\text{CH}_3$ groups, neighbouring protons are not present and therefore singlets would be expected on the ^1H NMR spectrum. There was however, secondary peaks were observed close to the major peaks with around 30% of the area of the main peaks. The conversion rate of the DMO ($\sim 60\%$) after 4 hours was

significantly lower than that of oxetane (~90%). The residual monomer was lost during the drying of the quenched polymer in the vacuum oven.

At 0.81ppm and 0.90ppm, two extra peaks to that of the main polymer peak was seen, these are present owing to the formation of cyclic oligomers, which was also seen during the polymerisation of oxetane.

8.3.3. Polymerisation of DMO Using a Benzyl Bromide Derived Initiator System.

A 0.1M-initiator solution of was prepared as in 8.2.5, The solution was decanted, removing the silver halide precipitate, retaining the oxonium ion initiator solution. 40ml of a 1M solution of dried DMO in DCM was prepared in an argon glove box. The monomer solution was transferred to the reaction vessel using the Schlenk positive pressure technique. 3ml of the initiator solution was then added to the monomer solution whilst being agitated using a glass magnetic flea. Samples were taken at regular intervals and quenched in methanol. Progress of the polymerisation was monitored using calorimetric and GPC analysis.

8.3.4. Analysis of the Polymerisation of DMO Using Benzyl Bromide derived Initiator System.

From the calorimetric analysis, it was concluded that the polymerisation using the benzyl bromide derived initiator was slower than that using a chloromethyl ethyl ether derivative. The rate was 47°C/Sec for benzyl bromide initiator compared to 109°C/Sec for the chloromethyl ethyl ether derivative. This result is the opposite of what was seen between the two initiators for the reaction with oxetane. This reduction in the initial rate of polymerisation could be due to the steric hindrance of the methyl groups attached at the 3,3, position on the oxetane ring, or electronic stabilisation of the propagating species due to the methyl groups.

The GPC results summarised in table 8.5, indicate that rapid polymerisation occurred within the first minute. The PD of the system was higher than that of the chloromethyl ethyl ether system but did decrease slightly during the course of the polymerisation. The percentage conversion of the polymerisation remained constant at around 60%

after 2 minutes, as did the molecular weight average, \overline{M}_n . This implied that the polymerisation was complete after 2 minutes, although free monomer was still available.

Table 8.5.

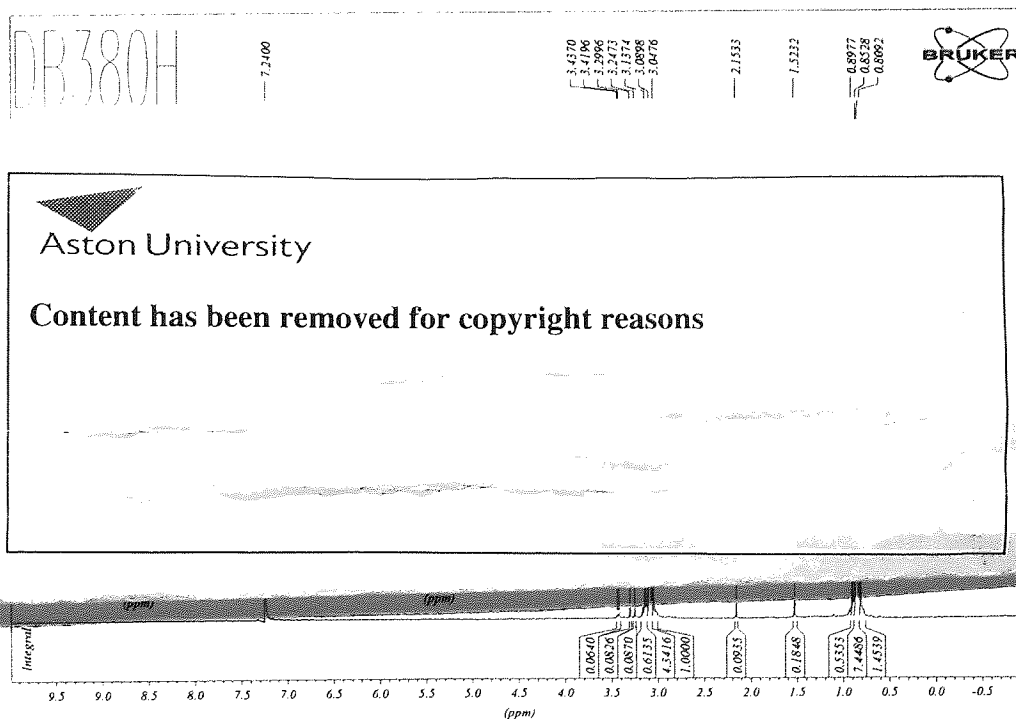
GPC and gravimetric results for PolyDMO initiated using benzyl bromide derivative.

Time (minutes)	Mn	PD	% conversion
1	3500	2.6	35
2	4300	2.1	62
5	5100	1.9	64
10	3900	2.2	55
30	4100	2.1	58
60	4000	2.1	62
240	3800	2.2	62

The ^1H NMR of the polymer (fig 8.6) show similar results to the polymer initiated with chloromethyl ethyl ether. The peaks of the NMR shown in figure 8.6 are summarised in table 8.6.

Fig 8.6.

^1H NMR of PolyDMO initiated using benzyl bromide, benzaldehyde reacted with silver hexafluoroantimonate in a DCM solution.



As with the chloromethyl ether derived initiator, ^1H NMR spectra there was a secondary small peak observed at 0.81 ppm. This was owing to the presence of a DMO cyclic oligomer coming from the $-\text{CH}_3$, alkyl group. At 3.05 ppm there was another peak, owing to the oligomers $\text{CH}_2\text{-O}$, ether group. The integer ratios between the two peaks were also consistent with the monomer at 3:2 respectively.

Table 8.6.

^1H NMR of DMO polymer initiated using benzyl bromide benzaldehyde reacted with silver hexafluoroantimonate in a DCM solution after 4h.

Chemical shift δ (ppm)	Relative intensity	Number of peaks	Chemical group
0.81	1.5	1	$-\text{CH}_3$ cyclic oligomer
0.85	7.4	1	$-\text{CH}_3$ polyDMO
0.90	0.5	1	$-\text{CH}_3$ polyDMO linkage
1.52	0.2	1	Initiator $\text{CH}_2\text{-O}$ linkage
2.16	0.1	1	Initiator $\text{CH}_2\text{-O}$ linkage
3.05	1.0	1	$\text{CH}_2\text{-O}$ cyclic oligomer
3.09	4.3	1	$\text{CH}_2\text{-O}$ polyDMO
3.12	0.6	1	$\text{CH}_2\text{-O}$ polyDMO linkage
3.30	0.1	Multiplets	Oligomers

By analysing the area of the peaks of the GPC chromatograms, it was seen that the amount of cyclic oligomer produced was similar to that measured, using ^1H NMR.

Chapter 9

Copolymerisations.

9.1. Copolymers.

There are two possible approaches that have been used to produce copolymers using oxetane based monomers^[88]. The first approach was to use a mixed monomer solution containing two or more monomer types. The second approach was to rely on the 'living' characteristics by adding a second monomer solution resulting in a block copolymer system.

The two main differences between the two techniques are that by adding the feed stock at the beginning of the polymerisation, a random or tapered type copolymer might be expected. By adding the monomer solutions sequentially, a block type system would be expected to form.

9.2. Initiator Systems.

In chapters 5 and 8 it was found that two initiator systems could be used to polymerise oxetane and its derivatives. The first initiator system was based on the halide (chloride) elimination from a halogenomethyl ethyl ether system. The resultant oxonium ion was stabilised using a hexafluoroantimonate counter ion. Although this system was effective, the limited number of materials with this functionality led to an investigation of other cationic initiator systems. It was found that by removing halide ions from aromatic systems and stabilising them with hexafluoroantimonate and carbonyl compounds, stable oxonium ions could be generated.

9.3. Mixed Feed Copolymerisations.

In chapters 5 and 8 it was found that oxetane and 3,3-dimethyl oxetane (DMO) could be polymerised easily using either initiator system. It was also found in chapter 8 that BBMO could be polymerised using either initiator system with hyperbranching reactions occurring. These monomers were copolymerised and various levels and techniques of addition were used with these monomers. The results of the mixed initial feed polymerisations are summarised in table 9.1.

Adding the initiator systems prepared as described in 8.2.1 and 8.2.5 to a mixed feed monomer solution, generated the copolymers. 3×10^{-4} mol of the initiator solution as a 0.1M solution (DCM as solvent) was added to 3×10^{-2} mol of the mixed monomer solutions. The monomer solutions either comprised of 3×10^{-2} mol of monomer in the case of homopolymer controls or 1.5×10^{-2} of each monomer. The monomer solutions were prepared by adding the dried monomers to dried DCM in a Schlenk flask under an argon atmosphere.

Where mixed monomer solutions were used, the appropriate proportion of that monomer was added to generate the systems detailed in table 9.1. The monomer solutions were added to the reaction vessel via positive pressure techniques. The copolymerisations were carried out with the addition of 3ml of initiator solution to the monomer solution heated at 35°C and kept under constant agitation. Samples were taken at regular intervals and quenched in methanol and dried in a vacuum oven. The samples were then redissolved in THF and filtered prior to analysis.

The progress of the polymerisations was followed by using calorimetric, GPC and NMR analysis.

Table 9.1

GPC and calorimetric results for copolymers of oxetane using a initial mixture of monomers.

Sample no	Initiator mol and type*	Oxetane mol	DMO mol	BBMO mol	Initial rate of polymerisation $^{\circ}\text{C}/\text{sec}$	\overline{M}_n after 4 hours g/mol	$\overline{M}_w / \overline{M}_n$ after 4 hours
9.1	$3 \times 10^{-4*}$	3×10^{-2}	0	0	50	6000	1.7
9.2	$3 \times 10^{-4*}$	0	3×10^{-2}	0	109	8700	1.7
9.3	$3 \times 10^{-4*}$	0	0	3×10^{-2}	150	6300	1.7
9.4	$3 \times 10^{-4**}$	3×10^{-2}	0	0	106	6300	1.7
9.5	$3 \times 10^{-4**}$	0	3×10^{-2}	0	94	3800	2.2
9.6	$3 \times 10^{-4*}$	1.5×10^{-2}	1.5×10^{-2}	0	137	8400	1.6
9.7	$3 \times 10^{-4*}$	1.5×10^{-2}	0	1.5×10^{-2}	57	6200	1.4
9.8	$3 \times 10^{-4**}$	1.5×10^{-2}	1.5×10^{-2}	0	172	3800	2.2

* Initiator based on chloride elimination of chloromethyl ethyl ether stabilised with hexafluoro antimonate counter ion. ** Initiator system generated by adding a carbonyl group to carbocation centre stabilised using hexafluoro antimonate counter ion.

9.3.1. Mixed Feed Polymerisation of Oxetane and DMO Using Chloromethyl Ethyl Ether Derived Initiator.

The NMR of the resultant copolymer of sample 9.6 from table 9.1 shown in figure 9.1 shows that both DMO and oxetane were present in the system. The $\text{CH}_2\text{-O}$ group from the oxetane was seen at δ 3.4ppm, which normally gives rise to a triplet for the homopolymer. For the copolymer, a quartet was seen with the extra peak arising from the linkage of the DMO to oxetane sections of the polymer system. The $\text{CH}_2\text{CH}_2\text{CH}_2$ group from oxetane seen at δ 1.8 ppm normally gives rise to a pentet but a complex multiplet is seen. The CH_3 group attributed to the DMO component is seen at δ 0.8 ppm and is a singlet with minor peaks at the base of the peak. For the DMO homopolymer significant cyclic oligomer formation was observed and appeared as a large secondary peak next to the main peak. The $\text{CH}_2\text{-O}$ group from the DMO component is seen at δ 3.1 ppm and would normally be observed as a singlet (as in figure 8.6) but appears as a doublet. The extra peaks seen from the ^1H NMR are attributed to the linkages between the DMO and oxetane polymers in a random fashion. From the GPC it was seen that a significantly lower level of oligomer formation was present. This in combination with the NMR data of extra peaks indicates that linkages between the various monomers suggest a random structure of copolymer.

By studying the respective ratio's of the DMO to oxetane peaks highlighted in table 9.2, an assessment of the reactivity ratios of the monomers can be ascertained. The ratio of DMO to oxetane was found by comparing the CH_2O hydrogens from both component of the copolymer with a ratio of DMO to oxetane being found to be 1: 1.7. The ratio was also calculated using the central 3 position CH_2 from the oxetane and CH_3 groups at the 3,3 position on the oxetane ring. It was found that by using this method a ratio of 1: 1.5 for DMO: oxetane was observed. By using these ratios, more oxetane was incorporated into the copolymer than DMO. From table 9.1 it was seen that the initial rate of copolymerisation was greater than that of either homopolymerisation.

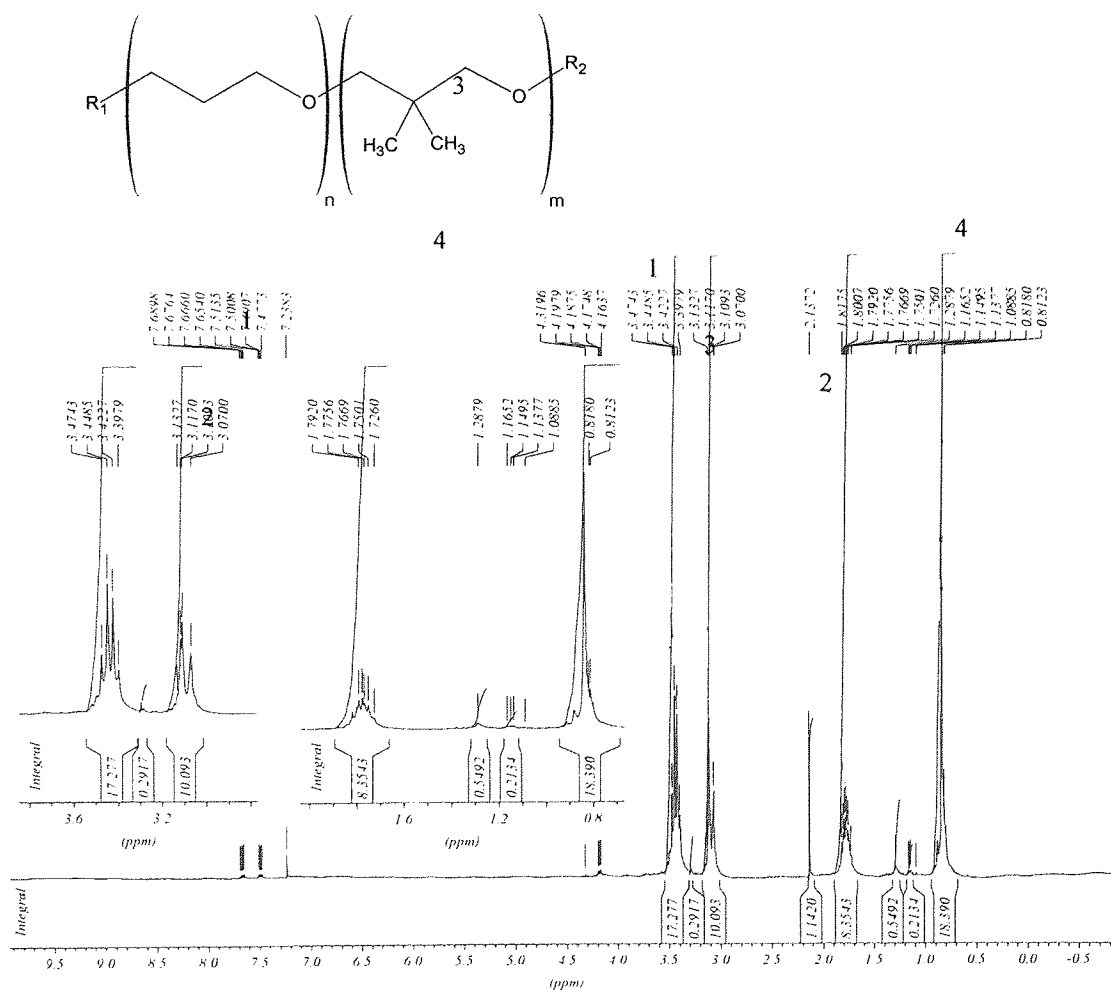
Table 9.2

Summary of ^1H NMR of DMO-oxetane random copolymer initiated using chloromethyl ethyl ether derivative.

δ Chemical shift	Ratio	Multiplicity	Chemical group
0.81	18.4	1	CH_3 from DMO polymer component
1.80	8.4	Multi	$\text{CH}_2\text{CH}_2\text{CH}_2\text{-O}$ from oxetane component
3.11	10.1	2	$\text{CH}_2\text{-O}$ from DMO component
3.43	17.3	4	$\text{CH}_2\text{-O}$ from oxetane component

Fig 9.1

^1H NMR of DMO-oxetane random copolymer initiated using chloromethyl ethyl ether derivative.



9.3.2. Mixed Feed Copolymerisation of Oxetane and BBMO Using Chloromethyl Ethyl Ether Derived Initiator.

The GPC data showed that the, \overline{M}_n , of the copolymer was similar to that of the BBMO homopolymer. There was a difficulty in the polymer to dissolving, meaning that the assessment of the molecular weight and chemical structure properties of the system were difficult.

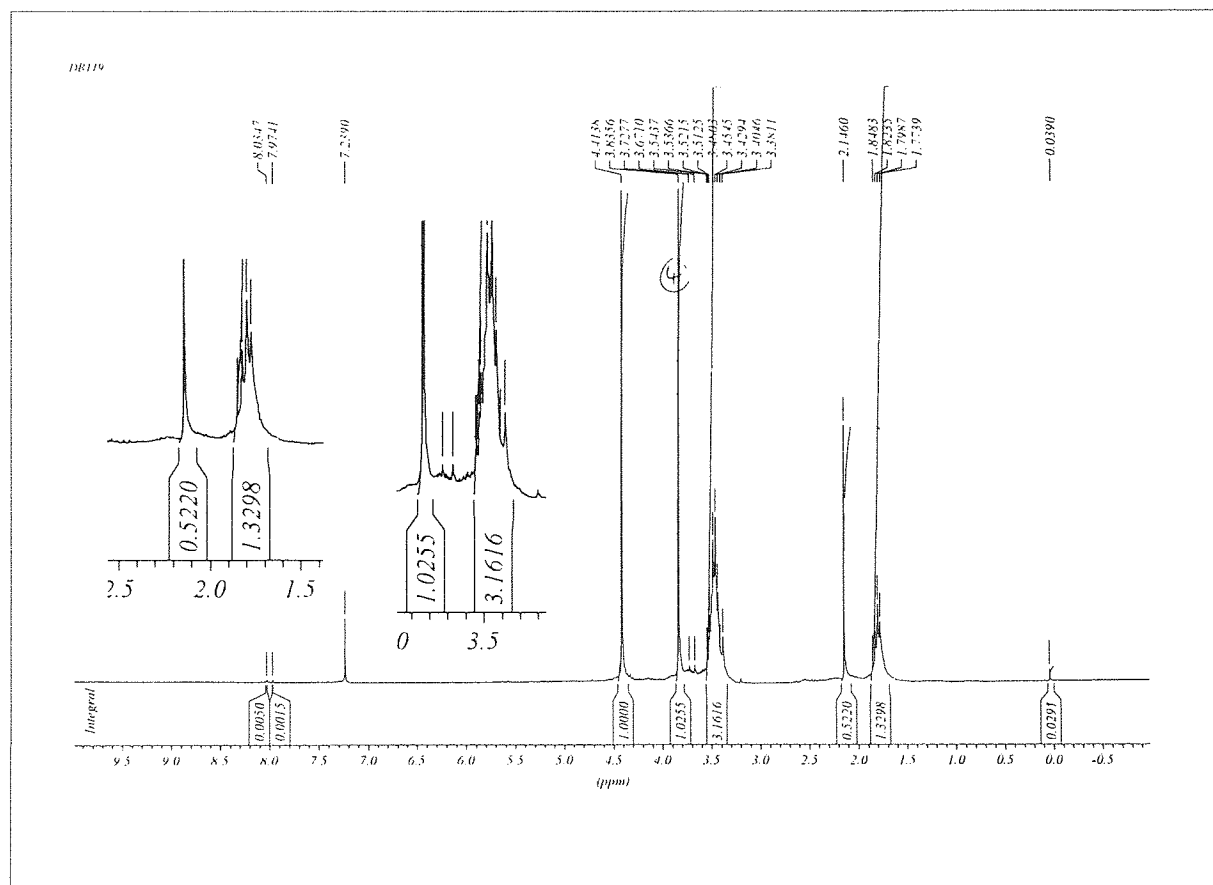
The ^1H NMR in figure 9.2 shows that a significant amount of BBMO monomer was still present in the system and appeared not to have been polymerised or been incorporated into the system (peaks at 3.8 and 4.4 ppm). Typically, when BBMO has been polymerised two main series of peaks were generated; the first was at $\sim 3.5\text{ppm}$ representing the ether linkage $\text{C}\underline{\text{H}}_2\text{-O-}$ group. The second main peak series that was observed on the homopolymer was at $\sim 3.8\text{ppm}$ and represented the $\text{C}\underline{\text{H}}_2\text{-Br}$ group. The homopolymer of polyoxetane also has 2 main sets of peaks; the first is normally observed at 1.8ppm as a pentet and is assigned to the saturated secondary hydrogen atoms in the centre of the repeat unit. The other main peaks present for polyoxetane were found at 3.5ppm and correspond to the ether linkage group. For the copolymer system, the typical oxetane peaks were seen at 1.8ppm , and at 3.5ppm . The typical respective ratios of 1 : 2 for the oxetane peaks were observed, meaning that the ether linkages from the BBMO were not present.

For the polyBBMO component the peaks should be seen at 3.5ppm and 3.8ppm and be equivalent to one another. Only the peaks corresponding to the unreacted BBMO (3.8ppm and 4.4ppm) were seen, suggesting that copolymerisation was not achieved. This result was confirmed by GPC, where a large single peak is eluted close to the marker peak confirming that unreacted BBMO monomer was present.

Due to the difficulty of dissolving the sample, the fraction analysed may have been one of low BBMO content. This would also explain the results that have been found from the NMR and GPC analysis.

Fig 9.2

^1H NMR of BBMO-oxetane random copolymer initiated using chloromethyl ethyl ether derivative.



The mixed feed copolymerisation of BBMO and oxetane using the chloromethyl ethyl ether derived initiator results, is a polymer system comprising mainly oxetane with unreacted BBMO monomer still present in the system.

9.3.3. Mixed Feed Polymerisation of Oxetane and DMO Using Carbonyl Addition Derived Initiator System.

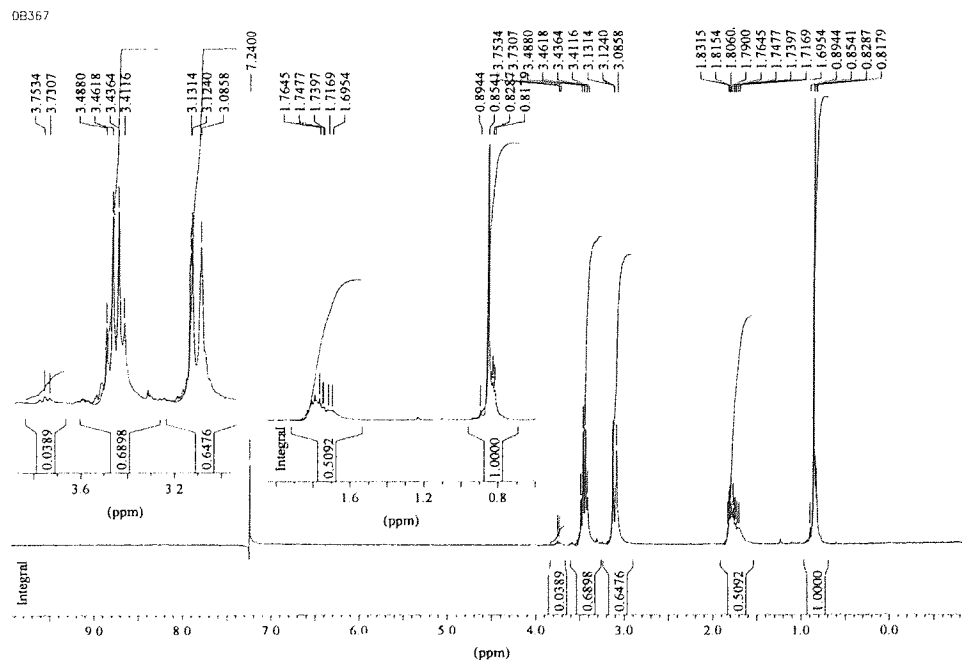
A copolymer was made as detailed in sample 9.8 in table 9.1. The resultant polymer system had a low \overline{M}_n value and a relatively broad PD of 2.2. From the ^1H NMR a complex spectrum was generated with four main series of peaks and shown in figure 9.3. The oxetane component peaks can be found at 1.8ppm and 3.7ppm. The peak at 1.8ppm which is from the saturated secondary hydrogen atoms have a significant shoulder that forms part of complex multiplet peak. The second peak that is attributed to the oxetane component of the copolymer has a quartet pattern. Typically, this peak

at 3.7ppm is a triplet for the homopolymer but the increase in the complexity strongly suggests that a random copolymer structure was achieved.

For the homopolymer of DMO, two main series of peaks were seen at 0.8ppm and at 3.1ppm. The peak at 0.8ppm was attributed to the saturated primary hydrogen atoms and the peaks at 3.1ppm were owing to the ether groups. The homopolymer had a secondary peak at 3.1ppm at around ~30% of the main peak height, this was owing to the cyclic oligomers that were present in the polymer system which was also seen from the GPC. The oligomer formation for the copolymers was significantly lower than compared to that of the homopolymer, determined again by GPC. Owing to the low oligomer formation, the secondary peak was attributed to the linkage of the DMO to oxetane unit.

Fig 9.3

¹H NMR spectra of mixed feed copolymerisation of oxetane and DMO using benzyl bromide derived initiator.



The mixed feed copolymerisation was successful in generating a copolymer of DMO and oxetane in a random configuration. This has been proven using NMR and GPC analysis.

9.4. Sequential Addition of Monomers.

In chapter 5, it was concluded that a second addition of a monomer solution after the initiator was added resulted in further propagation. This living characteristic was indicated with an increase in, \overline{M}_n , after the addition of extra monomer solution. This indicates that the polymerisation does not have major termination steps and can be considered 'living'. By reacting different monomers a block structure with varying backbone structures was possible.

9.4.1. Sequential Addition of Monomers Using Chloromethyl Ethyl Ether Derived Initiator System.

A series of experiments were performed with the initiator being made as described in 5.1.3 using various monomer addition sequences and are summarised in table 9.3. The first monomer was added to the reaction vessel followed by the initiator. The initial stages of the polymerisation were followed by calorimetric analysis. Samples were taken at regular intervals and quenched using methanol, dried in a vacuum oven and redissolved in THF for GPC analysis. The second monomer was added by using positive pressure techniques as described in chapter 3 and also followed using calorimetric techniques. After 4 hours from the first addition, the copolymerisations were quenched using methanol.

Table 9.3

Calorimetric and GPC results for block copolymer synthesis of oxetane base systems.

Sample no	Initiator Mol	Monomer and molar ratio of 1 st monomer	Monomer and molar ratio of 2 nd monomer	Initial rate of polymerisation after 1 st addition	Initial rate of polymerisation after 2 nd addition	\bar{M}_n (GPC) after 1h*	\bar{M}_n (GPC) after 4h	\bar{M}_w / \bar{M}_n (GPC) after 4h.
9.9	3×10^{-4}	Oxetane, 1.5×10^{-2}	BBMO, 1.5×10^{-2}	63 °C/sec	0 °C/sec	7000	9000	1.5
9.10	3×10^{-4}	Oxetane, 1.5×10^{-2}	DMO, 1.5×10^{-2}	60 °C/sec	82 °C/sec	11000	12000	1.6
9.11	3×10^{-4}	BBMO, 1.5×10^{-2}	Oxetane, 1.5×10^{-2}	173 °C/sec	35 °C/sec	Not soluble	Not soluble	Not soluble
9.12	3×10^{-4}	BBMO, 7.5×10^{-3}	Oxetane, 2.25×10^{-2}	188 °C/sec	28 °C/sec	Not soluble	10000	1.4
9.13	3×10^{-4}	BBMO, 3×10^{-3}	Oxetane, 2.7×10^{-2}	163 °C/sec	38 °C/sec	8000	12000	1.5

*After addition of 1st monomer before second monomer added. **after addition of both monomer solutions.

By increasing the level of oxetane incorporation into the BBMO-oxetane copolymer greater levels of solubility in THF are achieved as seen in table 9.3.

There was an increase in temperature when an oxetane solution was added to an initiated polyBBMO system (sample 9.11-9.13). An increase in temperature was also seen when DMO was added to an initiated oxetane polymerisation. These increases in temperature suggest that the second additions of monomers were polymerised, using the existing ACE of the previous part of the polymerisation.

9.4.2 ¹H NMR of Sequential Addition of Oxetane Based Copolymers Initiated Using Chloromethyl Ethyl Ether Derivative.

The copolymers were made as described in 9.4.1 and their molecular number averages and polydispersities were determined by GPC analysis. The copolymers were obtained when the oxetane solution was used as the initial monomer and showed that a regular polyoxetane ¹H NMR was obtained as displayed in figure 9.4. Two main peaks were observed; one at a chemical shift (δ) of 1.8 ppm with a quintet structure and a second

at 3.4 ppm with a triplet structure. There were several smaller peaks due to side reactions resulting in the formation of cyclic ethers.

After 1 hour of the polymerisation of oxetane, the second monomer solution of either DMO or BBMO was added. From the thermodynamic data it was found that the rate of polymerisation increased sharply with the addition of DMO solution but remained slow with the addition of BBMO.

9.4.2.1 ¹H NMR of Sequential Addition of Oxetane and DMO Based Copolymers Initiated Using Chloromethyl Ethyl Ether Derivative.

The ¹H NMR for the DMO sequentially added system shows that there are four main peaks seen from the co-polymerisation of oxetane and DMO as shown in figure 9.5. Two peaks with chemical shifts (δ) at 1.8 ppm and 3.4 ppm are attributed to oxetane component of the copolymer. The two peaks found at 0.8 ppm and 3.0 ppm belong to the DMO component. The chemical shifts, functionality and ratios are highlighted in table 9.3.

Fig 9.4

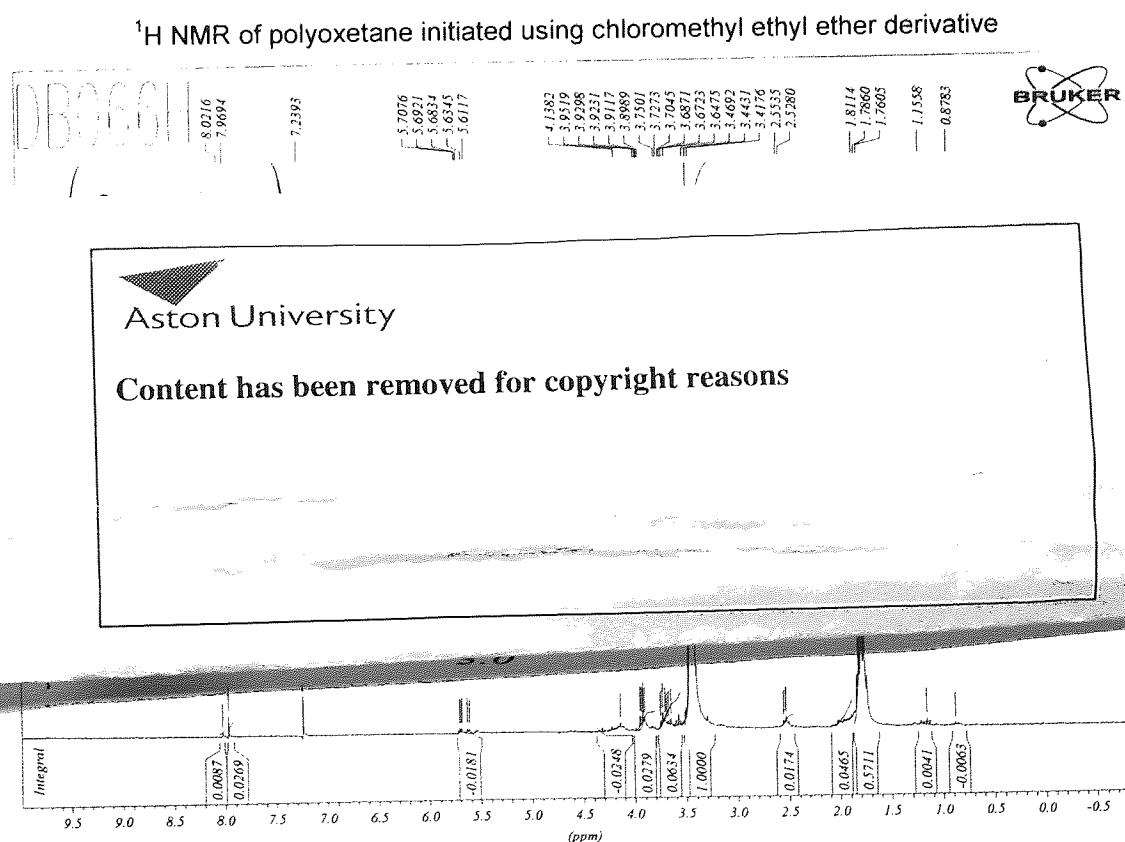
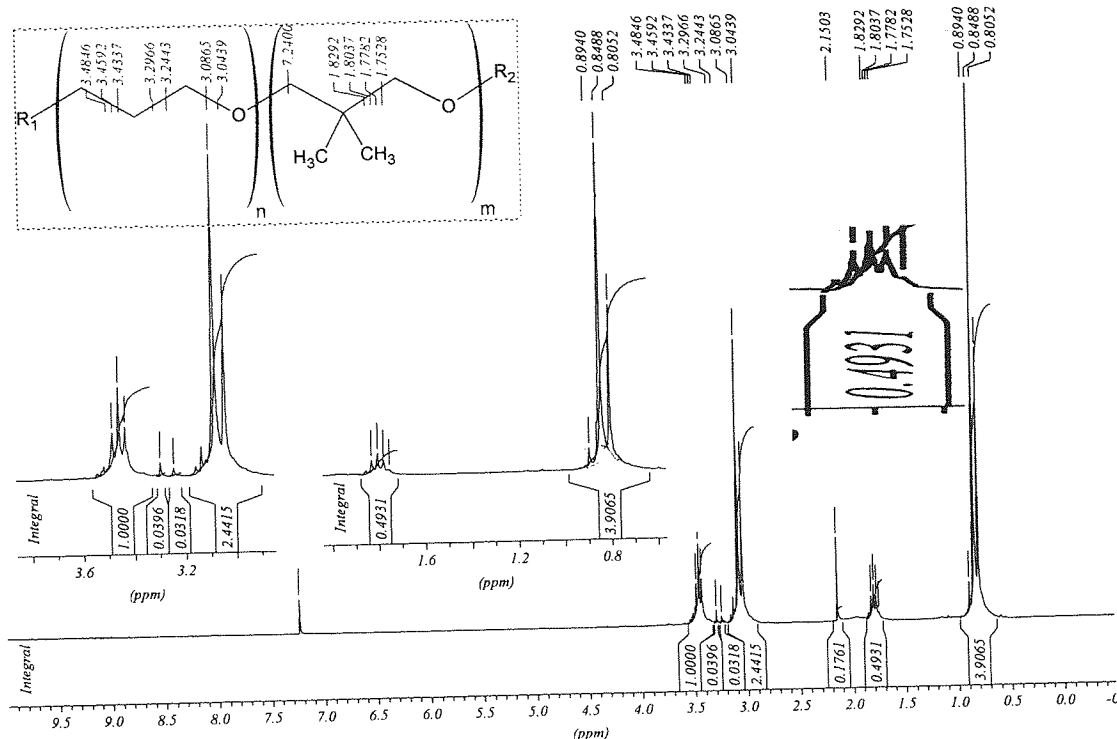


Fig 9.5

^1H NMR of block oxetane-DMO copolymer initiated chloromethyl ethyl ether derivative.



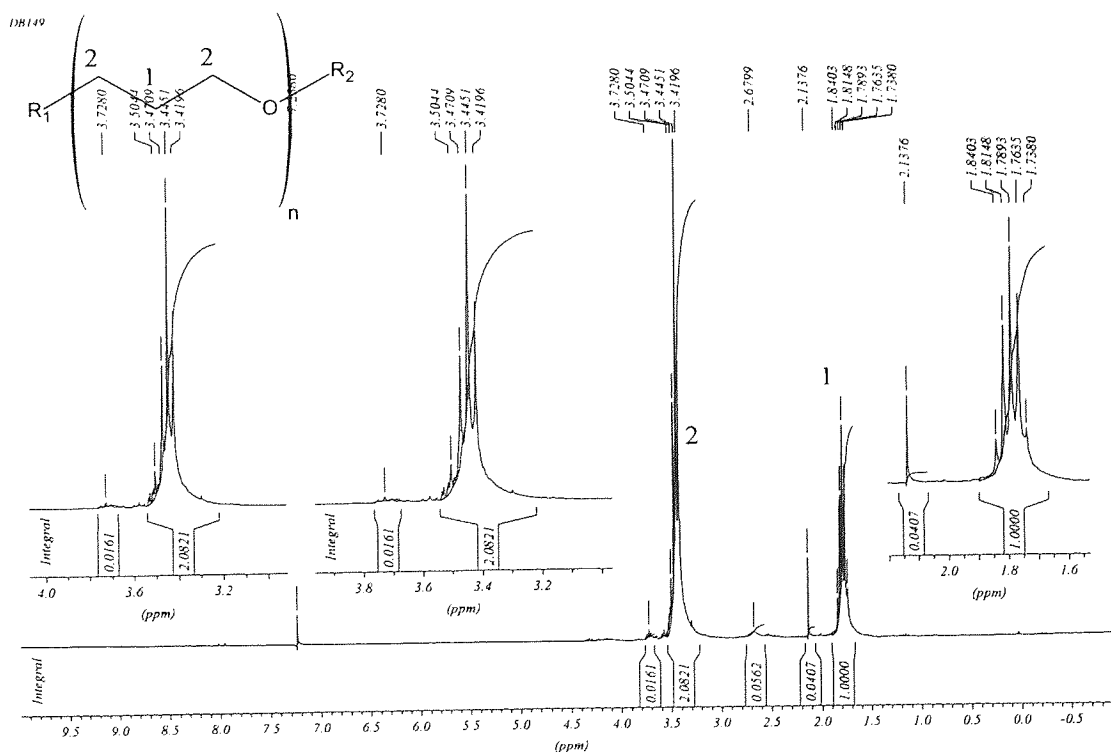
From figures 9.4 and 9.5, it was seen that the copolymer had both the oxetane and DMO components present in the system. By focusing on the DMO peaks present at 0.8ppm and 3.0ppm, it can be seen that doublets appear although the peak heights are not equivalent. For the ^1H NMR homopolymer of DMO shown in figure 8.6, there were also doublets present with the secondary peak being relatively minor in comparison to the main peak. For the random copolymer system shown in figure 9.3, the doublets at 3.0ppm were almost equivalent to one another. For the sequentially added DMO to oxetane system, a doublet in between that of the homopolymer and the random based system were achieved. In addition to the ^1H NMR findings, GPC analysis indicated that one polymer species was formed. A copolymer system was generated with a di-block (oxetane-DMO) structure, differing to the one formed when a mixed feed monomer system was used.

9.4.2.2 ¹H NMR of Sequential Addition of Oxetane and BBMO Based Copolymers Initiated Using Chloromethyl Ethyl Ether Derivative.

After 1 hour of the polymerisation of BBMO, the second solution of oxetane was added. From the thermodynamic data it was found that the initial rate of polymerisation was high for both monomer additions. As displayed in figure 9.6, the ¹H NMR had peaks at chemical shifts of 1.8 and 3.5ppm corresponding to those of polyoxetane and none from BBMO. From the thermodynamic and GPC analysis, there is an indication that the BBMO did initially polymerise but due to hyper-branching, precipitated out of the reaction solution prior to the addition of oxetane. This precipitation of the polyBBMO did not result in a termination of the initiator system as when the oxetane monomer was added, more polymerisation occurred. The second part of the polymerisation generated a soluble polymer of oxetane that is shown in figure 9.6. The GPC did not show any signs of two discrete polymer systems but this was due to polyBBMO not being soluble in the THF solvent system. The addition of oxetane to the polymerisation of BBMO did not improve its solvation properties.

Fig 9.6

¹H NMR of block BBMO-oxetane copolymers initiated chloromethyl ethyl ether derivative.



Chapter 10

Conclusions and further work

10.1 Overview.

The work presented in this thesis has investigated the development of a new oxonium ion initiator system for the polymerisation of oxetane and its derivatives. The initiator systems were generated and assessed to determine if novel polymeric structures could be obtained. Synthesis routes were developed including those resulting in linear, star shaped and hyperbranched homopolymer systems. Random and block copolymers were also synthesised utilising the 'living' properties of cationic ring opening polymerisation of oxetane and its derivatives.

10.2. Initiator Development.

The development an effective initiator was crucial to the investigation, as a system had to be developed to;

- Polymerise oxetane and its derivatives
- Generate controlled molecular number averages, \overline{M}_n , and narrow polydispersities (PD).
- Have low levels of secondary and side reactions resulting in high yields of monomer conversion
- Omit termination reactions allowing for further propagation of monomer

Several initiator systems were developed that could all be used to polymerise oxetane and DMO. BBMO could be polymerised but high levels of branching and crosslinking occurred.

10.2.1. Chloromethyl Ethyl Ether Derived Initiator Systems.

Previous work for the polymerisation of oxetane was focused on using chloromethyl ethyl ether, which was reacted with a potential counter ion such as BF_3 or AgSbF_6 . Larger selections of potential counter ions were studied to ensure that the most effective counter ion would be used for the investigation. It was found that the impact of the counter ion on the initial rate of polymerisation was crucially important. The use of smaller anions (counter ions) such as PF_6^- , slowed the initial rate of

polymerisation, as did small metal cations such as K^+ . This suggests that when the counter ion was too closely associated with the active chain end, hindrance of the initiation and propagation stages of the polymerisation occurred. In figure 10.1, the relative initial rate of polymerisation of oxetane showed that the fastest initial rate was achieved when $AgSbF_6$ was used.

Fig 10.1

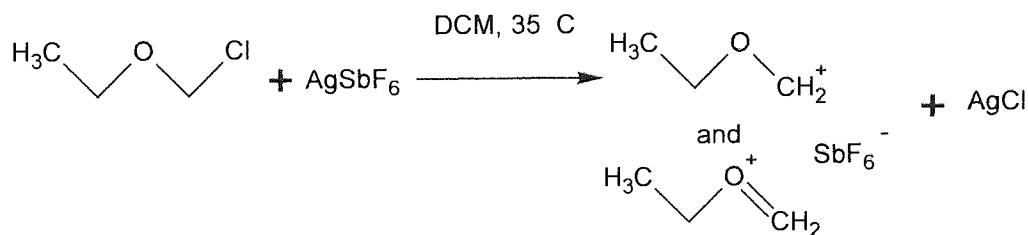
Relative Initial rates of polymerisation of oxetane using various $M_i^+A^-$ salts reacted with $CH_3CH_2OCH_2Cl$.

$M_i^+A^-$	$Ag^+SbF_6^-$	$Ag^+PF_6^-$	$K^+SbF_6^-$	$Ag^+C_4H_9COO^-$	$0 = K^+PF_6^-$
Relative rate	19.0	1.4	1.1	1.0	0

A chloromethyl ethyl ether derived initiator system using a wide range of counter ions can polymerise oxetane. The most effective counter ion used in this study was with SbF_6^- , generating the initiator system shown in figure 10.2.

Fig 10.2

Synthesis of chloromethyl ethyl ether derived initiator.



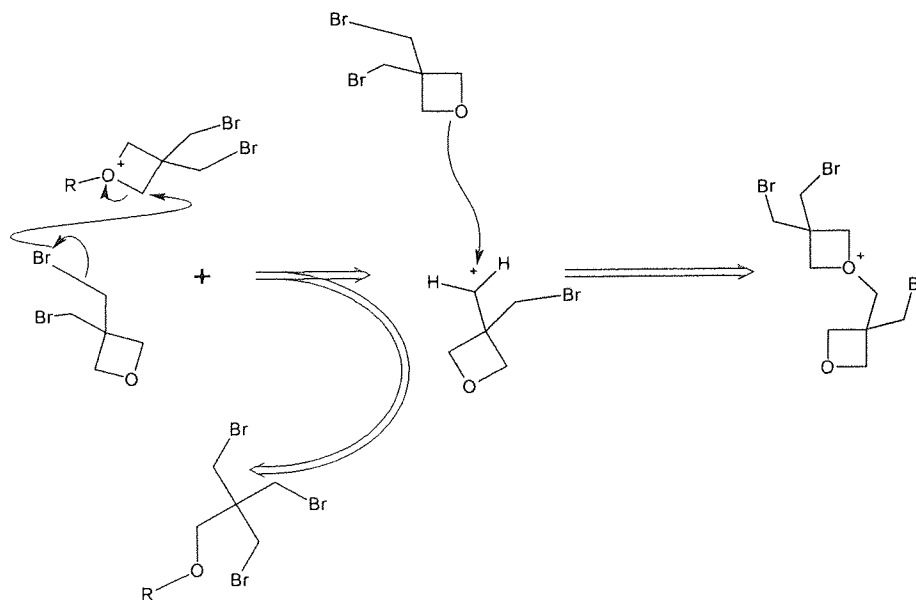
When this initiator was used; oxetane, BBMO and DMO could all be polymerised. For the polymerisations of DMO and oxetane, the formation of cyclic oligomers were present. Extra peaks being observed close to the marker peak on GPC determined the presence of oligomers. This was confirmed when extra peaks ~ 67 ppm were found on the ^{13}C NMR spectra. This suggests that there were backbiting reactions during the polymerisation. However, these did not result in the termination of the active chain end (ACE) of the propagating species, new ACE was generated along with the formation of the cyclic oligomer. When this initiator was used for oxetane and DMO, controlled molecular weights could be achieved with narrow polydispersities.

When BBMO was polymerised using this initiator system, polymer precipitates did occur but were difficult to analyse. PolyBBMO was difficult to analyse as the solubility of the polymer system was very poor and as such could not be analysed with conventional GPC or NMR analysis. These techniques had been used effectively to elucidate the polymer structures of the polyoxetane and polyDMO systems. Future investigations into the polymerisation of BBMO will need to use alternative methods of analysis. Such methods that could be used include solid state NMR spectroscopy, surface FTIR (golden gate) or dynamic scanning calorimetry (DSC).

From the limited studies that were carried out on the BBMO system it was found that hyperbranching occurred in a similar way to that shown in figure 10.3

Fig 10.3

Cross-linking reaction during the polymerisation of BBMO reducing its ability to solvate in various solvents.

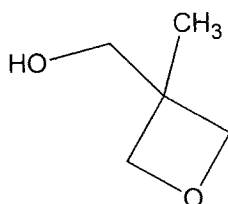


From ¹H NMR studies it was found that the CH₂-Br component was significantly lower than that of the CH₂-O component. For a linear polymer system, these two groups should be equivalent. The discrepancy between the theoretical and real samples can be explained by hyperbranching. The CH₂-Br group underwent a reaction with the ACE, resulting in the formation of an extra CH₂-O group and a branch in the polymer chain.

The difficulty in processing highly crosslinked polymers will mean that the polyBBMO system generated using these initiator systems will not be used without significant additives being used. Rather than trying to develop a polymer system based on BBMO, other derivatives could be used. One such derivative is methyl oxetane methanol (MOM) shown in figure 10.4, which has a hydroxyl, functional group.

Fig 10.4

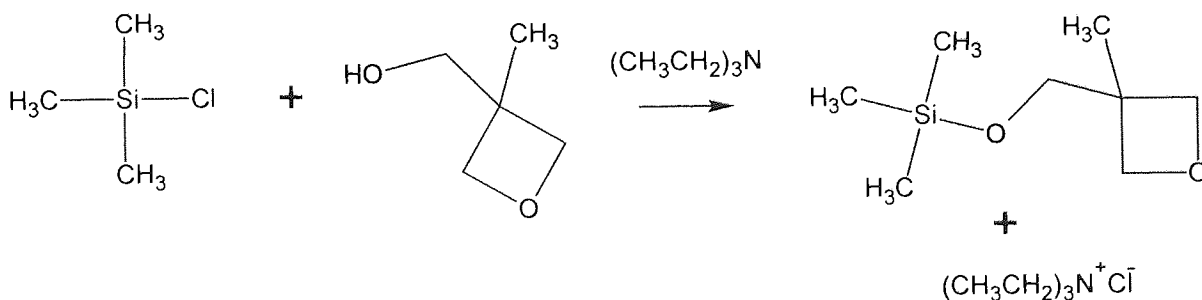
Structure of methyl oxetane methanol (MOM).



The hydroxyl group will be likely to cause branching to occur in a similar way to BBMO system. Prior to polymerisation, it would be possible to protect the hydroxyl group so that branching will not occur. In order to protect the hydroxyl group, the monomer could be reacted with chlorotrimethyl silane by the reaction scheme shown in figure 10.5.

Fig 10.5

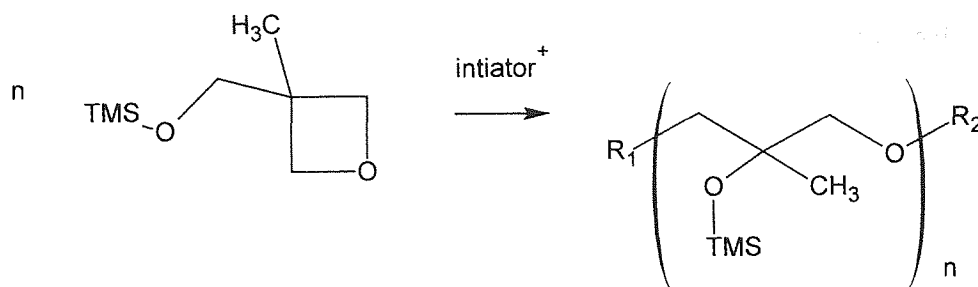
Protection of hydroxyl group on MOM.



The resultant protected monomer in figure 10.5 can then undergo polymerisation using any of the initiator systems developed to produce a polymer with protected side groups as shown in figure 10.6.

Fig 10.6

Polymerisation of protected MOM monomer.



Once the polymer has been polymerised, the TMS can be removed easily by reaction with an aqueous acid regenerating the hydroxyl group. Further reactions and functional groups interconversions can be performed using the hydroxyl group as a leaving group. Reactions that would be of particular interest would be those that generated nitrate or halogen functional groups.

10.2.2 Novel Initiator Systems.

Chloromethyl ethyl ether reacted with AgSbF_6 and was found to be a good initiator for oxetane and its derivatives. There are no multifunctional halogenomethyl ether compounds that are readily available implying that only a linear polymer system can be generated. Alternative systems were investigated that could potentially be used to make more novel architectures for oxetane based systems.

10.2.2.1. Halogenated Aromatic Initiator Systems.

Halogenated aromatic compounds were investigated as a potential source of multifunctional cationic materials. These were initially studied as it was thought that resonance stabilisation could assist in generating stable cationic initiators. AgSbF_6 was used as a source for the counterion, and formed the cation via a halide elimination reaction. Various brominated xylenes and bromomethyl toluene derivatives were used to assess what system would generate the most stable initiator. These were used to polymerise oxetane; it was found that the bromomethyl toluene based system polymerised oxetane with a controlled molecular number average, \overline{M}_n , and relatively narrow polydispersity.

The bromo xylene derived systems all had slow initial rates of polymerisation, owing to the fact that they had to rearrange prior to initiation of the polymerisation. This slow initial rate of polymerisation led to the xylene initiated polymer systems having broader polydispersities. The xylene based systems had the bromide attached directly onto the aromatic ring. When this was eliminated, a positive charge orbital that was perpendicular to the p-orbitals of the aromatic ring was generated. This alignment of the orbital made the direct stabilisation of the charge through the aromatic ring impossible.

For the bromomethyl aromatic system, the positive charge generated by the elimination of the bromide ion could be stabilised. This stabilisation occurred directly through the p-orbital of the aromatic ring.

It was found that when bromomethyl toluene was reacted with AgSbF_6 , an effective initiator for the polymerisation of oxetane could be generated. Derivatives of bromomethyl toluene were investigated to find the most suitable carbocation that could be used as an initiator. The initiator generated high yielding polymer systems with fast rates of monomer consumption. It was found that with the addition of a co-initiator of benzaldehyde the initial rate of polymerisation could be increased and the conversion of monomer increased.

The benzyl bromide/benzaldehyde derived initiator systems also generated polymer systems that had lower levels of cyclic oligomer formation than those produced using the chloromethyl ethyl ether systems. The reduction in the cyclic oligomer formation when the benzyl bromide initiator system was used was likely to arise from the benzaldehyde stabilising the ACE.

10.2.2.2 Multifunctional Initiator Systems.

Benzyl bromide and its derivatives have been used as a precursor to generate monofunctional initiators via a reaction with AgSbF_6 and benzaldehyde. These initiators have been found to successfully polymerise oxetane and DMO with

controlled, \overline{M}_n , and relatively narrow polydispersity (PD) values. These systems also generated less backbiting compared to previous initiator systems, resulting in less oligomer formation. The presence of the benzaldehyde as a co-initiator is thought to partially cap the ACE reducing the level of the backbiting reaction.

The systems generated thus far have produced either linear systems for oxetane and DMO, or hyperbranched systems in the case BBMO.

In order to produce novel architectures, multifunctional initiators were desired. It was hoped that if a novel architecture could be synthesised, more chemical functionality per unit volume could be achieved.

During the course of this study three system types were studied and the appropriate level of AgSbF_6 and benzaldehyde was added so that all of the potential reactive sites could have been used. The three systems used were 2,2-bis-bromomethyl-1,3-dibromopropane (4 sites), 1,3,5-tris-bromomethyl-2,4,6-trimethylbenzene (3 sites) and hexakisbromomethyl benzene (6 sites).

Plots of the polymerisations using the various multifunctional centres were made by plotting $\ln\left(1 - \frac{\overline{DP}_n}{\overline{DP}_{\infty}}\right)$ against time. The gradient of the plot is proportional to the apparent first order rate constant, k_{app} , and was used to assess which systems polymerised effectively. All of the systems initiated the polymerisation of oxetane, the hexakis bromomethylbenzene system polymerised the oxetane the fastest.

From the ^1H NMR spectra of the resultant polymer systems, the major peaks of polyoxetane were found for all of the polymer systems. Significant extra peaks were seen for the hexakisbromomethylbenzene and 2,2-bis-bromomethyl-1,3-dibromopropane systems, indicating that unreacted parts of the system remained. For the 1,3,5-tris-bromomethyl-2,4,6-trimethylbenzene system no other peaks were seen. It is likely that for the hexakisbromomethylbenzene and 2,2-bis-bromomethyl-1,3-dibromopropane systems the groups are too close to one another hindering the effectiveness of the site. The reactive groups on the 1,3,5-tris-bromomethyl-2,4,6-

trimethylbenzene system were well spaced allowing for the polymerisations to occur. The polymerisation of oxetane using the 1,3,5-tris-bromomethyl-2,4,6-trimethylbenzene derived initiator system generated a novel architecture for polyoxetane.

Further work should be directed at using the 1,3,5-tris-bromomethyl-2,4,6-trimethylbenzene initiator system with other oxetane derived monomers, assessing the physical properties of the resultant systems. It is possible to produce copolymers on each of the arms allowing for hard and soft components to be incorporated. These components could be altered to allow for improved processing performance whilst retaining chemical functionality.

10.3. 1,4-Dioxane.

The formation of oligomers has been seen for all polymerisations generated using the chloromethyl ethyl ether initiator system. The level of oligomer formation for the benzyl bromide derived initiator systems was significantly lower but is attributed to the use of benzaldehyde as a co-initiator, which associates at the ACE.

When oxetane was polymerised using the chloromethyl ethyl ether derived initiator, around 10% of the eluted volume (from GPC analysis) consisted of oligomer products. The benzyl bromide derived initiator system with benzaldehyde being added as a co-initiator, resulted in less oligomer formation at around 3%.

1,4-dioxane was incorporated into both types of initiator system as an additive or a component to the solvent system. When 1,4-dioxane was added to the chloromethyl ethyl ether derived initiator, little reduction in the oligomer formation was observed. When the levels of addition were increased, a steady broadening in the polydispersity was observed. A significant drop in the initial rate of polymerisation occurred as the level of 1,4-dioxane was increased. The 1,4-dioxane was associating with the ACE when added as part of the initiator system and hindered the propagation, increasing the polydispersity. The 1,4-dioxane then disassociated allowing for backbiting to occur, resulting in oligomer formation.

When 1,4-dioxane was added as a component to the solvent system for the chloromethyl ethyl ether derived initiator system, less oligomer formation occurred, with an increase in polydispersity. There was also some small inclusion of the 1,4-dioxane into the backbone of the polymer chain indicated by peaks appearing at ~67 ppm on the pendant ^{13}C NMR spectra.

When 1,4-dioxane was added as part of the solvent system, lots of 1,4-dioxane was available to cap the ACE of the system. Occasionally, the 1,4-dioxane was attacked by the oxetane monomer, generating a new oxetane ACE but with the ring opening of 1,4-dioxane, which was incorporated into the polymer chain. The level of inclusion was low, otherwise a disproportionate amount of $\text{CH}_2\text{-O}$ to $\text{-CH}_2\text{-}$ would have been observed on the ^1H NMR.

The level of oligomer formation was initially lower for the benzyl bromide and benzaldehyde initiator system compared with that for the chloromethyl ethyl ether derived system. When 1,4-dioxane was added to the system the level of oligomer formation could effectively be eliminated but did result in a worsening in the polydispersity. The rate of polymerisation could effectively be controlled when levels of 10-50% (v/v) of 1,4-dioxane to DCM, the rate of polymerisation then decreased. A similar mechanism exists as described with the chloromethyl ethyl ether derived system in capping the ACE. For the benzyl bromide and benzaldehyde initiator system, there was also an inclusion of the 1,4-dioxane into the backbone of the polymer system.

10.4. Copolymers of oxetane and its derivatives

Copolymers of oxetane, DMO and BBMO were synthesised using several different addition techniques using the benzyl bromide and chloromethyl ethyl ether derived initiator systems. Mixed feed and sequential addition of monomer experiments were conducted to assess the effectiveness of the initiator system for copolymerisations.

10.4.1. Mixed feed copolymer systems

The first form of synthesis used a mixed monomer feed at a 50:50 molar ratio and using the chloromethyl ethyl ether derived initiator system. The first system was of oxetane with DMO with the resultant copolymer comprising of a ratio of 1.3:1 (determined by ^1H NMR) into the polymer chain respectively. The second system was using the same initiator system with the molar ratio of the monomers being kept at 50:50 and using oxetane and BBMO as the monomer feed. Little BBMO inclusion occurred in the polymer system, although a polymer precipitate did form, that could not be analysed using GPC or standard NMR techniques. BBMO does not readily polymerise with oxetane due to the hyperbranching reactions that make the system drop out of the solution.

The experiment was repeated using the benzyl bromide and benzaldehyde derived initiator system. It was found that for the oxetane and DMO system, an inclusion ratio of around 1: 1.5 respectively was seen.

It is possible to copolymerise oxetane and DMO using the chloromethyl ethyl ether derived initiator system. From the ^1H NMR spectra for the polyoxetane-DMO, the $\text{CH}_2\text{-O}$ peak (3.1 ppm) associated with DMO component of the system appeared as a doublet. For the homopolymer, the peak appeared as a singlet with minor secondary peaks. The size of the second peak for the copolymer indicated that a random structure of oxetane and DMO was obtained. When the benzyl derived initiator system was used, similar results were seen for the mixed monomer feed of oxetane and DMO.

Both types of initiator systems can be used to copolymerise DMO and Oxetane. They can also be used to potentially copolymerise other oxetane-based systems including the monomer system of protected MOM. By controlling the input ratios of the starting monomers, controlled levels of functionality could be achieved.

10.4.2. Sequential Addition of Monomers.

A series of experiments were performed with one monomer initially being polymerised, followed by the addition of more monomer using the chloromethyl ethyl ether derived initiator system. When DMO was added to oxetane, a second exotherm was measured. This indicated that there was further polymerisation of the system when the second portion of monomer was added. In addition to this, a low polydisperse polymer system was created, seen as a single peak on the GPC. From the ^1H NMR spectra, both monomers were incorporated into the polymer structure. There was also a secondary peak seen on the DMO $-\text{CH}_2\text{-O}$ which was smaller than that seen for the mixed feed polymer system but larger than that seen for the homopolymer. This evidence suggests that a block copolymer system was generated, and could be used for other monomer types.

When BBMO was polymerised, a large exotherm was measured for the homopolymer, followed by precipitation of material from the reaction solution. The results of exotherm and precipitation suggest that the BBMO be initially polymerised. When Oxetane was added to the polymerisation, a second exotherm was seen with a resultant polymer forming, which did not contain any significant BBMO component, but a large proportion of oxetane units. The result of the sequential addition polymerisation of oxetane to a BBMO system was to generate two discrete homopolymer systems. It is likely that the BBMO polymer system underwent the crosslinking system, regenerating an initiator species but cross-linked and left the solution phase of the polymerisation. When the oxetane was added to the system, the monomer was polymerised by the remaining initiator but failed to polymerise with the BBMO as it was not in the reaction medium.

It is suggested that in order to build in functionality into the copolymer system that a protection stage of the functional groups taken place prior to the polymerisation and the functionality placed in after the polymerisation.

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