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The Synthesis and Polymerization of Methacrylate Macromonomers.

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A thesis submitted for the Degree of Doctor of Philosophy

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C ACKNOWLEDGMENTS

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I suppose at this point I should mention Jayne Whittingham for her friendship over three years, but mainly for keeping me entertained during our horse riding lessons, although not acknowledging her would probably be more amusing.

Finally, but most importantly, I would like to thank all of my family, particularly my mum and dad for all their support throughout my seven years as a student. Last, but certainly not least, I would like to thank James for all of his encouragement and support (financial and emotional) during particularly during the last two years.

D. DECLARATION

All experimental work contained in this thesis is original research that was carried out by the author in the Department of Chemistry, University of Warwick, between October 1994 and October 1997. No material contained herein has been submitted for any other degree to this, or any other, institution. Results from other authors are referenced in the usual manner throughout the text.

Signed Date

E. SUMMARY

The use of macromonomers in free radical polymerizations has received much research interest in the past decade due to recognition of their utility as intermediates in the formation of well-defined graft copolymers. This thesis examines the behaviour of methacrylate macromonomers with a low degree of polymerization, e.g. dimer, trimer, prepared by catalytic chain transfer polymerization, in free radical systems; bulk, solution and emulsion polymerizations, in addition to their behaviour in a more controlled polymerization system, group transfer polymerization.

Macromonomers of a range of functional methacrylate monomers are prepared using a catalytic chain transfer agent. The lower molecular weight oligomers, e.g. dimer, trimer, are isolated by reduced pressure distillation and characterised by IR and ^{1}H and ^{13}C NMR spectroscopy.

It has previously been established in the published literature that methacrylate macromonomers can undergo three different types of reaction when added to radical polymerizations. They can copolymerize or undergo an addition-fragmentation reaction (β-scission) or they can undergo a depropagation mechanism along the backbone to yield the starting materials. This β-scission mechanism is utilised to prepare a range of telechelic methacrylate polymers using functional dimers, some of which have been shown to undergo further reactions.

The chain transfer constants of MMA dimer, MMA trimer and BMA trimer in bulk polymerizations of MMA and BMA are determined using an integrated form of the Mayo equation. The trends seen in these values are related to differences in structure between the macromonomers.

The BMA and MMA dimers and trimers are added to group transfer polymerizations of MMA and BMA and the resulting polymers analysed by SEC and MALDI-TOF mass spectrometry. The dimers copolymerize with one or two dimer units adding to each chain whereas trimers undergo a chain transfer reaction to form a new initiating species. The addition of dimer, trimer and tetramer all lead to a reduction in molecular weight.

F. ABBREVIATIONS

AIBME	Dimethyl 2,2'-azobisiobutyrate
AIBN	2,2'-azobisisobutyronitrile
amu	atomic mass unit
BA	n-butyl acrylate
BMA	n-butyl methacrylate
BzMA	benzyl methacrylate
CCT	catalytic chain transfer
CCTA	catalytic chain transfer agent
CCTP	catalytic chain transfer polymerization
CoBF	[bis{μ-[(2,3-butanedione dioximato)(2-)O:O']} tetrafluorodiborato(2-)N,N',N'',N''']cobalt
Cs	chain transfer coefficient
CTA	chain transfer agent
CVA	4,4'-azobis(4-cyanopentanoic acid)
Da	dalton
DHB	2,5-dihydroxy benzoic acid
DMF	dimethylformamide
dmg	dimethyl glyoxime
DP	number average degree of polymerization
f	initiator efficiency
Fc	fraction of radicals that terminate by combination
FT-IR	Fourier transform infra-red spectroscopy

GMA	glycidyl methacrylate
GTP	group transfer polymerization
HDI	hexamethylene diisocyanate
HEMA	hydroxyethyl methacrylate
HPLC	high performance chromatography
k_d	rate constant for dissociation of initiator
k_i	rate constant for initiation
k_p	rate constant for propagation
k_{tc}	rate constant for termination by combination
k_{td}	rate constant for termination by disproportionation
k_{tr}	rate constant for chain transfer
LMA	lauryl methacrylate
MALDI-TOF MS	matrix assisted laser desorption ionization mass spectrometry
MDI	methylene diphenylene diisocyanate
mL	millilitres
MMA	methyl methacrylate
Mn	number average molecular weight
MTS	1-methoxy-2-methyl-1-trimethyl siloxypropene
NMR	nuclear magnetic resonance specroscopy
PBMA	polybutyl methacrylate
PDi	polydispersity index
PHEMA	polyhydroxyethyl methacrylate
PLMA	polylauryl methacrylate

PMMA	polymethyl methacrylate
ppm	parts per million
R_i	rate of initiation
R_p	rate of propagation
R_t	rate of termination
SEC	size exclusion chromatography
$TASHF_2$	trisdimethylaminosulphonium bifluoride
TBAmCB	tetrabutylammonium metachlorobenzoate
TFA	trifluoroacetic acid
THF	tetrahydrofuran

Chapter

1.

Introduction

1.1 General Introduction

In recent years, when synthesizing polymers for specific applications, emphasis has shifted from the design and use of new monomers to the use of existing monomers put together in different ways and modification of existing polymers and polymerization processes, the latter in an attempt to obtain greater control of the reaction. Among the factors that can be controlled to some extent and that have been investigated in this thesis are :

- molecular weight and molecular weight distribution
- molecular architecture e.g. block and graft copolymers
- the rate of polymerization
- the introduction of functional groups at specific locations within the molecule
- macromolecular composition e.g. copolymers

In the past decade a number of living polymerization techniques have been developed which allow greater control over the polymer product. These include Group Transfer Polymerization (GTP) (see Section 1.2.2)[1], Screened Anionic Polymerization (SAP)[2] and Living Free Radical Polymerization[3,4]. These types of polymerization are generally referred to as living polymerizations and allow control over the polymer product because they involve the sequential addition of monomer units to the polymer chain and termination reactions are reduced, often by reversible protection of the propagating chain end. Living polymerization systems provide polymers with a narrow molecular weight distribution, molecular weight (Mn) that increases linearly with conversion and Mn that is directly

proportional to the monomer to initiator ratio. Living polymerizations find one of their main uses in the preparation of block copolymers. The propagating end remains active when all of the monomer is consumed and is capable of initiating a second monomer to form a block copolymer (sequential addition).

Free radical polymerization techniques offer the least expensive way to produce commercially useful acrylic polymers (see Section 1.2.1), however, these processes generally afford very little control over the polymer product. Methods that increase the flexibility of free radical polymerizations are therefore of great interest. One area that has recently received a great deal of attention has been the use of macromonomers to form well-defined graft copolymers and to introduce controlled amounts of functionality into the polymer chain, Section 1.4.

1.2 Polymerization Systems.

A number of polymerization techniques, free radical and group transfer polymerization systems, were employed for the work presented in this thesis. An outline of each of the methods used is presented below.

1.2.1 Free Radical Polymerizations.

Free radical polymerizations are industrially the most widely used and most cost effective method of producing polymers. The low cost is a result of the tolerance of radical systems to protic and other impurities, unlike ionic systems that require rigorous exclusion of all protic species, i.e. dry and pure reagents. The

widespread use of radical polymerizations stems from the wide variety of monomers that can be polymerized by this technique. This includes functional monomers, e.g. monomers containing hydroxy and amino functionalities that in an ionic polymerization would have to be protected and deprotected before and after reaction. This is not necessary in a radical polymerization and these monomers can be used to produce polymers that find diverse applications including use as chain extenders, crosslinking agents and compatibilizers.

A free radical polymerization consists of four main reactions.

1. Initiation. This consists of two stages, firstly the decomposition of a radical initiator by application of heat or ultra violet light to form primary radicals, this is the rate determining step of the initiation reaction.

$$I \xrightarrow{k_d} 2R\bullet$$

$$\text{Rate} = 2fk_d[I] \qquad (1.1)$$

where 'f' is the initiator efficiency since not all radicals go on to initiate a polymerization, side reactions may occur such as primary radical combination which result in the loss of some of the active radicals.

These primary radicals may then react with monomer to form a propagating centre.

$$R\bullet + M \xrightarrow{k_i} R_1\bullet$$

$$\text{Rate} = k_i[R\bullet][M] \qquad (1.2)$$

2. Propagation. The propagating chain will continue to grow by the addition of monomer until a termination or transfer reaction occurs.

$$R_n\bullet + M \xrightarrow{k_p} R_{n+1}\bullet$$

$$\text{Rate} = k_p[R_n\bullet][M] \qquad (1.3)$$

3. Termination. Termination in radical reactions can occur by two bimolecular pathways. Two propagating centres can combine in a head to head linkage to form one longer dead polymer chain. Alternatively, two polymer chains can terminate by a disproportionation reaction. This involves the abstraction of hydrogen from one propagating centre by the other. This results in the termination of one chain with a vinyl group and the formation of a dead polymer chain with a saturated end group.

$$R_n\bullet + R_m\bullet \xrightarrow{k_{tc}} P_{n+m}$$

$$R_n\bullet + R_m\bullet \xrightarrow{k_{td}} P_n + P_mH$$

$$\text{Rate} = k_t[R\bullet]^2 \quad \text{where } k_t = k_{tc} + k_{td} \qquad (1.4)$$

4. Transfer. A fourth, but equally important, component of a free radical polymerization is a transfer reaction. This involves the transfer of an atom or group from some other constituent of the reaction. This results in the termination of the polymer chain and the formation of a new propagating centre that can reinitiate polymerization. The propagating centre can be transferred to monomer, initiator, solvent, polymer or a specifically added chain transfer agent.

$$R\bullet + SH \xrightarrow{k_{trs}} RH + S\bullet$$

$$\text{Rate} = k_{trs}[R\bullet][SH] \qquad (1.5)$$

1.2.1.1 Chain Transfer

In many applications it is necessary to control the molecular weight of the polymer product as higher molecular weight polymers are more difficult to process. In living systems this is easily achieved by adjustment of the monomer to initiator ratio. In radical polymerizations, although it is possible to use low monomer to initiator ratios to reduce molecular weight this is not done in practice as the initiator is the most expensive component of the reaction and hence this method is more costly. An alternative method to lower molecular weights is to increase the reaction temperature thus increasing the rate of decomposition of the initiator and producing more primary radicals at the start of the reaction. However, this may lead to undesirable depropagation, thermal initiation and secondary reactions. Instead, reduction in molecular weight in radical polymerizations is accomplished more effectively by the addition of chain transfer agents. Chain transfer usually involves the abstraction of hydrogen or a labile group from another component in the system, this may be monomer, polymer, initiator, solvent or specifically added chain transfer agents. This results in a dead polymer chain and a free radical that can reinitiate polymerization.

$$R\bullet + SH \xrightarrow{k_{tra}} RH + S\bullet$$

Most conventional chain transfer agents used are mercaptans, disulfides or organic halides. However, these have inherent disadvantages in that the quantities required to effect a reduction in molecular weight result in toxicity, odour and colour problems, in addition to the incorporation of a "foreign" group and hence

possible site of chemical weakness. These transfer agents have the advantage however that they can be used to introduce functionality into the polymer chain. Another commonly used form of molecular weight control is catalytic chain transfer using a cobalt (II) macrocycle, which acts by way of hydrogen abstraction from the propagating chain end to form an unsaturated chain end (forming a macromonomer) and a cobalt (III) hydride. The cobalt (III) hydride can then reinitiate polymerization by donation of the hydrogen to a monomer molecule, reforming the cobalt (II) species and a propagating radical, section 1.2.1.1. Although this is a catalytic cycle it can be poisoned by the presence of acidic species such as monomer. It does, however, require the addition of only parts per million quantities to bring about significant reductions in molecular weight.[5]

It has also been shown, as discussed in section 1.3.2, that methacrylate macromonomers can themselves behave as chain transfer agents when added to methacrylate polymerizations. In terms of chain transfer, these act in a similar way to conventional chain transfer agents and are known as addition-fragmentation chain transfer agents. Addition of the methacrylate macromonomer to the propagating chain end forms a sterically hindered radical adduct. This then fragments (β-scission) to terminate the polymer chain with one unit from the macromonomer and a double bond, and to form a radical with one monomer unit less than the original starting macromonomer. The newly formed radical can then reinitiate polymerization by addition to monomer. A recent paper by Rizzardo et al[6] described the polymerization behaviour of methacrylate macromonomers and has calculated the chain transfer constants for MMA dimer, trimer, tetramer and macromonomer (DP = 24) with MMA by analysis of the natural logarithm of chain length distributions, this paper is discussed in more detail in Chapter 3.

The advantage of utilising macromonomers as chain transfer agents is that they add a species to the chain that is identical in nature to the polymer backbone, hence no cleavable weak links or toxicity, colour or odour problems, and that it can be used to add controlled amounts of functionality to the chain end, this will be discussed in more detail in Chapter 4.

The efficacy of an added chain transfer agent is usually reported in terms of its chain transfer constant C_s. This is a measure of the rate of chain transfer relative to the rate of propagation:

$$C_s = \frac{k_{trs}}{k_p} \tag{1.6}$$

An ideal chain transfer agent will have a C_s value close to unity as this means that the ratio of transfer agent to monomer will remain constant throughout the reaction and that the number average degree of polymerization will also remain constant with conversion, resulting in a narrow polydispersity. If C_s is much greater than one (i.e. ktrs>>kp) then there will be a rapid consumption of transfer agent at low conversion and the reaction will be unregulated at higher conversions. Conversely, a low Cs value (i.e. kp>>ktrs) results in an increase in the ratio of the concentrations of chain transfer agent to monomer as the polymerization proceeds and hence a parallel reduction in the number average degree of polymerization. Both these scenarios will result in a broadening of the polydispersity.[7]

The usual way of measuring a chain transfer constant is by use of the Mayo equation. (Equation 1.7)

$$\frac{1}{DP} = \frac{1}{DP_0} + \frac{[S]}{[M]} \qquad (1.7)$$

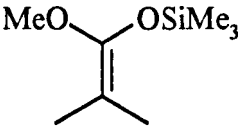
Hence a plot of 1/DP vs [S]/[M] will yield a straight line of gradient Cs. However, the Mayo equation assumes that the chain transfer agent does not alter the rate of polymerization. Macromonomers do not behave as conventional chain transfer agents and, as can be seen from Figure 1.3, upon addition of the macromonomer to the propagating chain end they can undergo a reversible depropagation step which alters the overall rate of polymerization. Therefore the conversion is dependent upon the concentration of macromonomer in the feed. If a Mayo plot is used in such cases a curve is obtained rather than a straight line, hence no gradient may be measured. A new equation (equation 1.8) has been derived which incorporates the conversion as one of the components, and hence may be used for such chain transfer agents.[8]

$$DP_n = \frac{[M]_0 p}{(2 - F_c) f [I]_0 (1 - \exp(-k_d t) + C_s [S]_0 \ln(1 - p)} \qquad (1.8)$$

1.2.2 Group Transfer Polymerization

Group Transfer Polymerization (GTP) is a living polymerization system for use with acrylic monomers that was first reported by Owen Webster and his coworkers at Du Pont in 1983.[1] One of the major practical differences between GTP and classical anionic polymerization is the tolerance of GTP to reaction

temperatures at or above room temperature whilst still retaining the features of a living polymerization, i.e. controlled molecular weight, narrow molecular weight distribution and quantitative conversion.[9] The polymerization is initiated by a silicon based initiator, most commonly a silyl ketene acetal, 1-methoxy-2-methyl-1-trimethyl siloxypropene (MTS), **1.1**, the model compound for the chain end in the polymerization of MMA[10].



1.1

MTS is unreactive with respect to monomer except in the presence of a nucleophilic or Lewis acid catalyst. The degree of polymerization is governed by the ratio of monomer to initiator[1] and is independent of catalyst concentration, although this does affect the rate of polymerization.[11,12]

A variety of anionic species have been found to catalyze GTP including bifluoride, acetate and benzoate ions. They are introduced as a salt of a cation such as the tetrabutylammonium ion. Only a small amount of catalyst relative to initiator is required, typically 1 mole %. Polymerizations are usually carried out in a polar solvent, commonly THF. The mechanism of GTP has been debated since the technique was first established with a number of associative and dissociative mechanisms being postulated. However, one single mechanism has not been generally accepted, and it is now thought possible that the mechanism may depend on the catalyst employed. A generalised mechanism for the group transfer polymerization of BMA using MTS as initiator is shown in Figure 1.1.

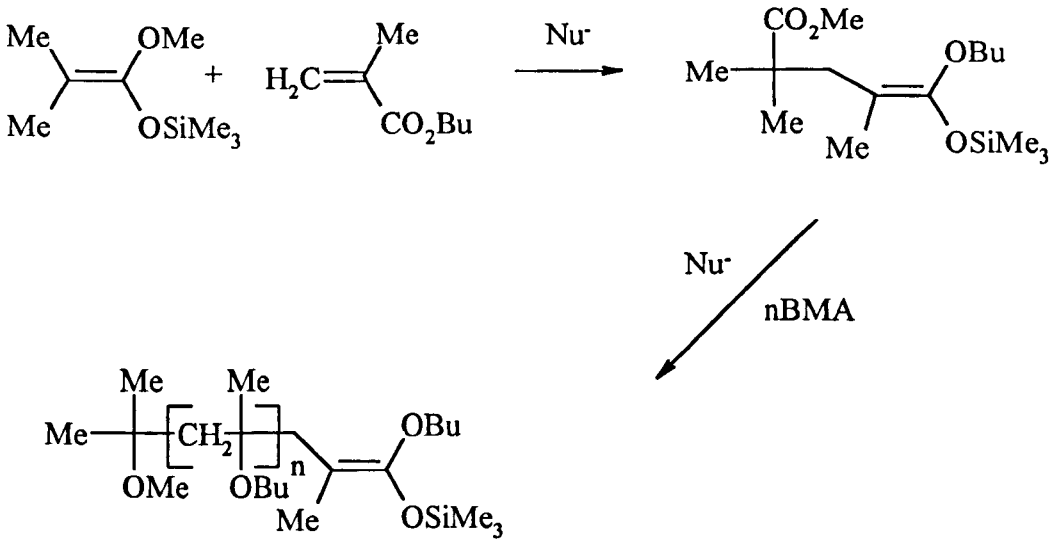


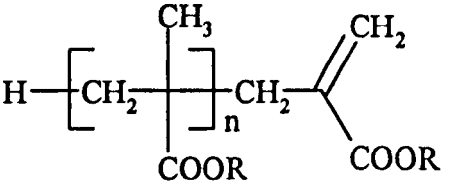
Figure 1.1 Generalized mechanism of group transfer polymerization

The initial mechanism proposed by Webster et al[1] is an associative one that involves the coordination of catalyst to the silicon, followed by the addition of a monomer unit. This leads to the formation of a hypervalent silicon atom, however, these species are well known. Experiments carried out by Quirk[13] have led to the proposal of a non-reversible dissociative mechanism, whereby the trimethylsilyl group is abstracted by the nucleophile to form an enol anion prior to the addition of monomer. A third mechanism that has been proposed is a reversible dissociative mechanism which again involves the abstraction of the trimethylsilyl group by the nucleophile, but the silyl group returns to the chain end after the addition of each monomer unit. The debate is further complicated by the apparently conflicting results obtained by different research groups. Attempts to trap the nucleophile-silicon complex that would be present in a dissociative mechanism, e.g. fluorosilane intermediates in the case of $TASHF_2$ catalysis, were unsuccessful. Experiments where a mixture of living PMMA and living PBMA with different silyl end groups were used to initiate the polymerization of BMA

resulted in polymers which showed no exchange of silyl groups that would be indicative of a dissociative mechanism. However, research by Quirk and coworkers[14] showed that exchange of silyl groups occurs when the polymerization of MMA is initiated by living PMMA of two different molecular weights catalysed by $TASHF_2$, one PMMA had a trimethylsilyl end group, the other a phenyldimethylsilyl end group. Hence evidence exists that supports all three proposed mechanisms.

1.3 Macromonomers

Macromonomers are defined as linear polymers with a molecular weight ranging from several hundreds to tens of thousands with a functional group at the chain end that can undergo further polymerization.[15,16] The macromonomers used in this thesis have the general structure shown below, **1.2**.



1.2

They differ from normal methacrylate macromonomer in that the polymer is substituted on the methylene group and not the ester group.

In the mid 1970s Milkovich of CPC International Inc. presented the concept of a "macromer". He synthesized various macromonomers by the end capping of anionic living polymers with electrophiles possessing a polymerizable end

group.[17] However, Bamford and coworkers had demonstrated as early as 1958 that graft copolymers were formed when a small monomer was copolymerized with poly(methyl methacrylate) containing terminal vinyl groups produced by disproportionation from a free radical polymerization.[18,19]

1.3.1 The Preparation of Macromonomers.

Macromonomers have been prepared by a number of methods, both ionic and radical. They can be prepared using a functional initiator, although this requires the absence of side reactions with the functional group. This method is mainly used in ionic polymerizations. It is restricted by the limited number of monomers that can be polymerized ionically, in addition to the inherent stringent purity requirements associated with anionic and cationic polymerizations. For this method to be useful in a radical polymerization, termination must be exclusively by disproportionation and not by combination, and transfer reactions must be zero or insignificant. Other methods used to prepare macromonomers include the use of functional chain terminators, which again require the absence of chain transfer events, and functional chain transfer agents in free radical polymerizations. However, this may lead to inappropriate functional groups and may entail the conversion of the functional group to that required for further reactions.
The macromonomers used throughout this thesis have been prepared using catalytic chain transfer. This free radical method was first developed by Enikolopyan and his coworkers in 1981[20] and employs a cobalt (II) macrocycle as chain transfer agent. The cobalt (II) species works by abstracting a hydrogen atom from the propagating polymer to form an unsaturated chain end (a

macromonomer) and a cobalt (III) hydride species. The cobalt (III) hydride can then reinitiate polymerization by donation of the hydrogen to a monomer unit to form a new propagating centre and regenerate the cobalt (II) species,[21] see Figure 1.2.

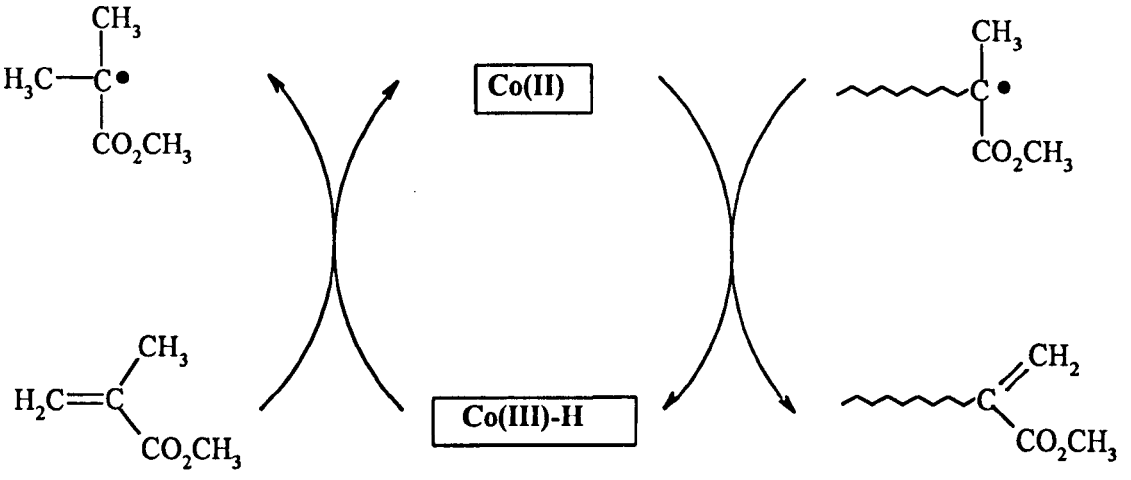
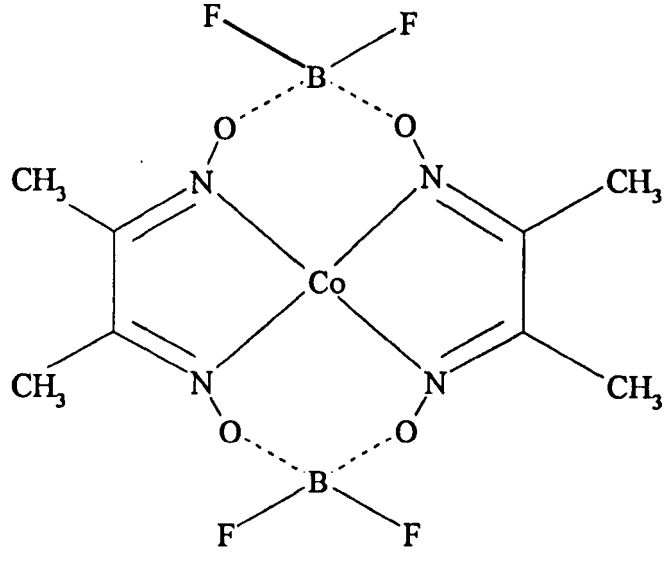


Figure 1.2 Catalytic chain transfer cycle for a cobalt (II) macrocycle with MMA.

This mechanism has been fully investigated in recent years[5,22] by analysis of the products of CCTP using MALDI-TOF coupled with a Fourier transform ion cyclotron resonance detector (FTICR) which gives isotopic resolution and can therefore distinguish between saturated and unsaturated chain ends. The spectra obtained showed a predominance of peaks initiated by hydrogen and with a vinylic end group. Peaks were also detected that showed initiation by AIBN, with a small number of saturated end groups detected for both forms of initiation, but with no evidence for any radical-radical termination. Thus it was concluded that the predominant form of termination in the presence of cobalt macrocycles is chain transfer to give a high proportion of unsaturated chains. If sufficient cobalt (II) species is used low molecular weight oligomers can be formed which can then

be isolated by reduced pressure distillation. The synthesis of methacrylate macromonomers by CCTP has been scaled up to kilogram quantities using a tubular reactor in a continuous process, with isolation from monomer using an extruder.[23] The main advantages of using cobalt macrocycles in the preparation of methacrylate macromonomers arises from their relatively low cost, as only small amounts of the cobalt macrocycle are needed to produce low molecular weight polymers due to the catalytic nature of the reaction. Their tolerance to functional groups allows, for exmple, macromonomers with hydroxy and amino functionalities to be prepared. For experimental details of the preparation of macromonomers using catalytic chain transfer polymerization see section 7.3. One commonly used catalytic chain transfer agent, and the one employed in this work, is CoBF, bis(boron difluorodimethylglyoximate)cobaltate (II)[24] pictured below, **1.3**.



1.3

Details of the preparation of CoBF are given in section 7.2.

1.3.2 β-Scission Chain Transfer of Methacrylate Macromonomers.

When added to a polymerization a methacrylate macromonomer can follow a number of possible pathways, see Figure 1.3. This scheme was first proposed in 1987 by Rizzardo and co-workers,[25] who used GC-MS and NMR spectroscopy to analyse products from the reaction of high concentrations of AIBN with MMA trimer at 60 °C. Addition of cyanopropyl radicals to the double bond of the trimer occurs but does not result in products that could be attributed to a propagation step or the self-combination of the primary-trimer radical adducts or their combination with the less sterically hindered cyanopropyl radicals. Instead of being ascribed to products from propagation reactions the major products were assigned structures that could all be derived from the β-scission of the initial radical adduct formed by the addition of the macromonomer to a growing polymer chain.

The addition of macromonomer to the polymer radical forms a new propagating centre which is sterically hindered. Thus the rate of termination is sufficiently reduced relative to reactions without added macromonomer that it can follow one of three possible pathways other than termination. Firstly, it can propagate, i.e. copolymerize, resulting in the formation of a graft copolymer (pathway 1, Figure 1.3), see section 1.4 for the formation of graft copolymers. This was not observed in the original work involving the homopolymerization of MMA trimer. The highly hindered radical is sufficiently stable that the rate of propagation is reduced enough to enable β-scission to take place, as shown in pathway 2, Figure 1.3. In this pathway the macromonomer section of the radical adduct fragments to leave one unit terminating the propagating chain with a vinylic group and a new

radical with one unit less than the original starting macromonomer is formed. This new radical can reinitiate polymerization by reaction with monomer. This chain transfer mechanism results in lower molecular weight polymers than would have been obtained in the absence of macromonomers, see Chapter 3 for a discussion of the chain transfer properties of macromonomers. As can be seen from Figure 1.3, if the starting macromonomer is a dimer with functional groups β-scission will result in the placement of one unit and hence one functional group on each chain end to form telechelic polymers, see section 1.6. If the starting macromonomer is of a higher degree of polymerization, reinitiation after β-scission will place a block of macromonomer on the chain end, thus representing a pathway to block copolymers.

Pathways 1 and 2 are in competition and a mixture of block and graft copolymers is usually formed. However, for polymerizations of methacrylate monomers with methacrylate macromonomers copolymerization does not occur unless forced under harsh conditions with high concentrations of macromonomer in the feed. The product of the addition of 75 mole/mole per cent of MMA dimer (FW = 200.24) to a radical polymerization of d^8-MMA (FW = 108.17) has been analysed by MALDI-TOF mass spectrometry.[5] This showed two series of peaks, the main series corresponded to the incorporation of one dimer unit into each d^8-MMA chain, but the smaller series of peaks showed the incorporation of two dimer units. This shows, albeit under forcing conditions, that methacrylate macromonomers can copolymerize with methacrylate monomers, contrary to claims made by Berge et al.[26] An alternative β-scission mechanism that could also occur is pathway 3. This is a depropagation step along the backbone to yield

the starting materials. The effect of this is to reduce the overall rate of polymerization, but it does not affect the molecular weight of the final product. For further discussion of this topic see Chapter 3.

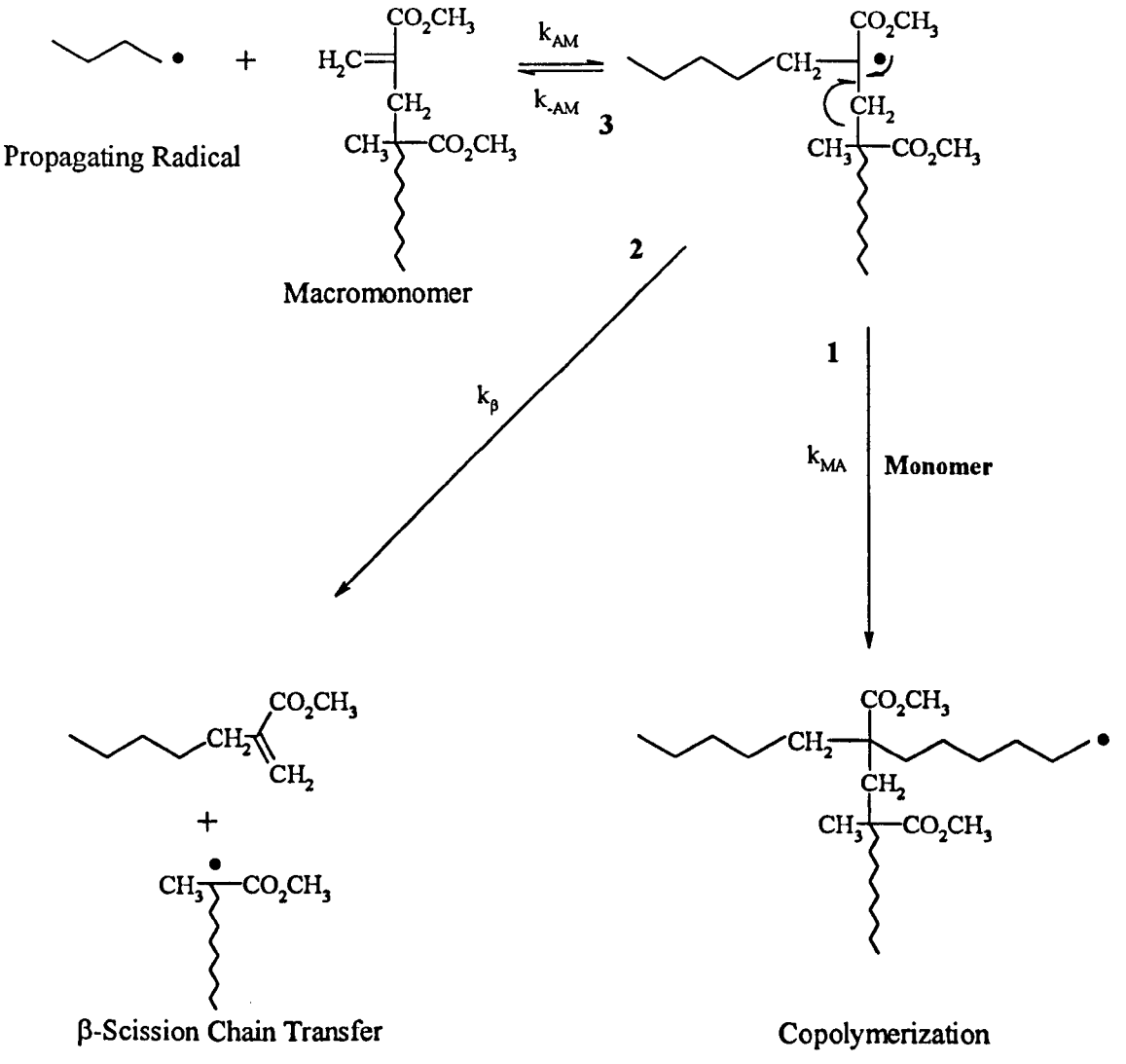


Figure 1.3 β-scission (addition-fragmentation) mechanism for MMA macromonomer with MMA.

1.3.3 Earlier Research Concerning The Polymerization of ω-Unsaturated Methyl Methacrylate Oligomers.

There are a number of papers in the literature describing the homopolymerization and copolymerization of macromonomers, including a comprehensive review by Meijs and Rizzardo. [27] Tsukahara et al have published a number of papers in which they highlight numerous features of reactions involving macromonomers which differ from polymerizations of small monomers in ways which point to a high sensitivity to the diffusion controlled step in macromonomer systems[28-30]. One of the most important characteristics is the higher molecular weight of a macromonomer compared with monomer, which results in a low molar concentration of reactive end groups in addition to higher viscosity of the polymerization solution.[31] Hence the viscosity is highly dependent on the concentration of macromonomer in the feed. This has consequences for both the homo and copolymerizations of macromonomers. The work presented by Tsukahara and co-workers demonstrated that in the homopolymerization of methacrylate terminated styrene macromonomer, both the degree of polymerization and the rate of polymerization were dependent on the macromonomer concentration in the feed. This dependence was attributed to the presence of the gel effect from the start of the reaction due to the higher viscosity imparted by the macromonomers. In a recent paper by Rizzardo et al[6] a series of MMA polymerizations with and without macromonomer were performed. The polymerizations were carried out at 60 °C with the same initial macromonomer concentration, but with different reaction times. The control experiments showed a conversion time plot that was typical of bulk polymerizations, i.e. with a sharp

increase in the rate of polymerization at about 10-15 % conversion at the onset of the gel effect. With the addition of macromonomer a linear polymerization rate was observed, with no acceleration over the conversion rate studied. In a bulk polymerization involving small monomers the onset of autoacceleration occurs due to an increase in viscosity of the reaction mixture. This is caused by an increase in molecular weight and hence a reduction in the mobility of the chains which results in a decrease in termination events and an acceleration in polymerization rate.

The work by Tsukahara's group also showed that the macromonomer adduct is sufficiently stable at 60 °C as to be detectable by ESR spectroscopy. Similar findings were made by Harrison.[32] This is confirmation of the hypothesis that the radical adduct formed is sufficiently stabilised so as to allow fragmentation to occur.

Although homopolymerization of macromonomers usually results in low yields of polymers with low degrees of polymerization, the fact that chain growth occurs at all indicates that macromonomer addition is not precluded by the high peripheral segment density around the active centre (arising from the multibranched structure of the growing chain).

The reactivity of macromonomers in copolymerizations is thought to be influenced by a number of parameters, including macromonomer chain length, the total molar ratio of the comonomers and the nature of the solvent.[33] In a system designed to remove the effects of incompatibility, Radke and co-workers carried out a number of polymerizations of ω-methacroyl-PMMA and methyl methacrylate (MMA).[33] From this work three major conclusions were drawn. First, the reactivity of the macromonomer strongly decreases as its weight

concentration increases (due to the increased viscosity and hence reduced mobility of the macromonomer). Second, the reactivity decreases with decreasing molar ratios of monomer to macromonomer (due to the increased segment density in the vicinity of the propagating centre). Third, at low polymer concentrations and high molar ratios of monomer to macromonomer the reactivity is independent of macromonomer chain length.

Cacioli et al[25] have copolymerized MMA macromonomers with a number of monomers, ethyl acrylate, styrene, methyl methacrylate, acrylonitrile and vinyl acetate, to prepare graft copolymers. In each case a substantial reduction in molecular weight compared with the homopolymer prepared in the absence of macromonomer was observed.[25] This was attributed to the highly hindered radical formed by the addition of macromonomer, which slows the rate of propagation sufficiently to allow chain transfer by the β-scission mechanism described earlier in addition to copolymerization in experiments involving monomers other than MMA.

Yamada et al[34] prepared a number of dimers and cross-dimers from methyl methacrylate, ethyl methacrylate, methacrylonitrile and α-methylstyrene using a cobalt (III) complex as catalytic chain transfer agent. Polymerization of these dimers with MMA and styrene at 80 °C resulted in chain transfer by addition-fragmentation. Both the dimers and resulting polymers were characterized by NMR but only the chain transfer constants for the cross-dimers were calculated.

1.4 Graft Copolymers

The past two decades have seen a marked increase in macromonomer research resulting from the recognition of their utility as intermediates in the production of well-defined graft copolymers. A graft copolymer has a branched structure, with a main chain (backbone) which has pendant polymeric chains attached to it.[35] If these polymer chains are of the same chemical nature as the backbone they are usually termed branched or comb polymers. If the backbone and side chains are chemically different then the copolymer will have a number of properties that differ from those expected from a blend of the two homopolymers. Amphiphilic graft copolymers which contain hydrophobic and hydrophilic polymers in the same chain will have some solubility in both aqueous and organic media which can result in the polymer having components in two different phases with covalent bonds crossing the phase boundaries. These graft copolymers find applications as emulsifiers, other applications include use as surface-modifying agents, coating materials and compatibilizers in polymer blends. The controlled architecture of a graft copolymer also presents the possibility of different physical properties, e.g. lower density and melt viscosity properties that cannot be obtained using linear block copolymers.

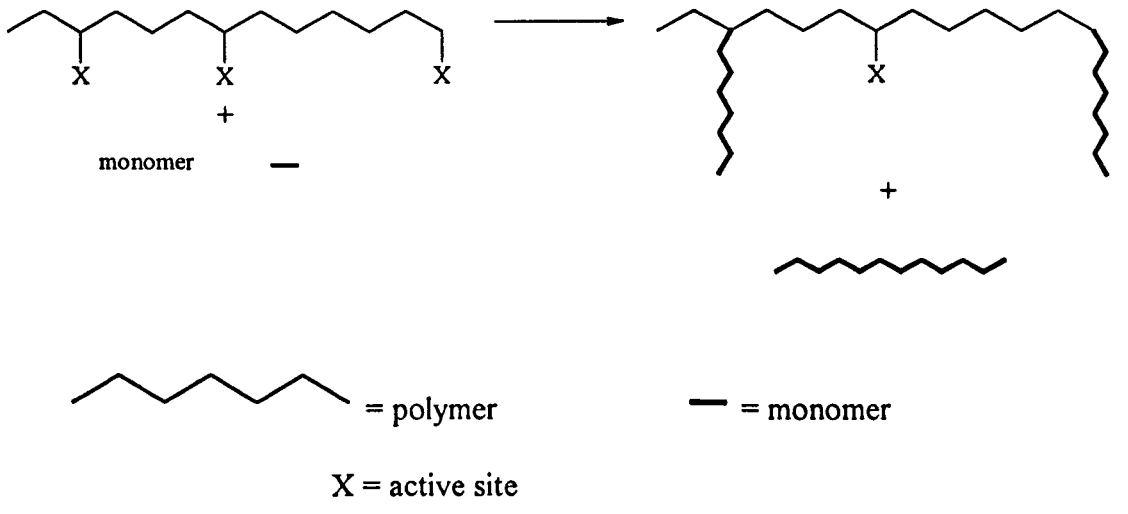
1.4.1 Graft copolymer synthesis

The macromonomer technique presents significant advantages over traditional methods of graft copolymer synthesis, since traditional 'grafting from' and

'grafting to' techniques often yield mixtures of homopolymers, gels and graft copolymers with irregular and poorly defined grafts.

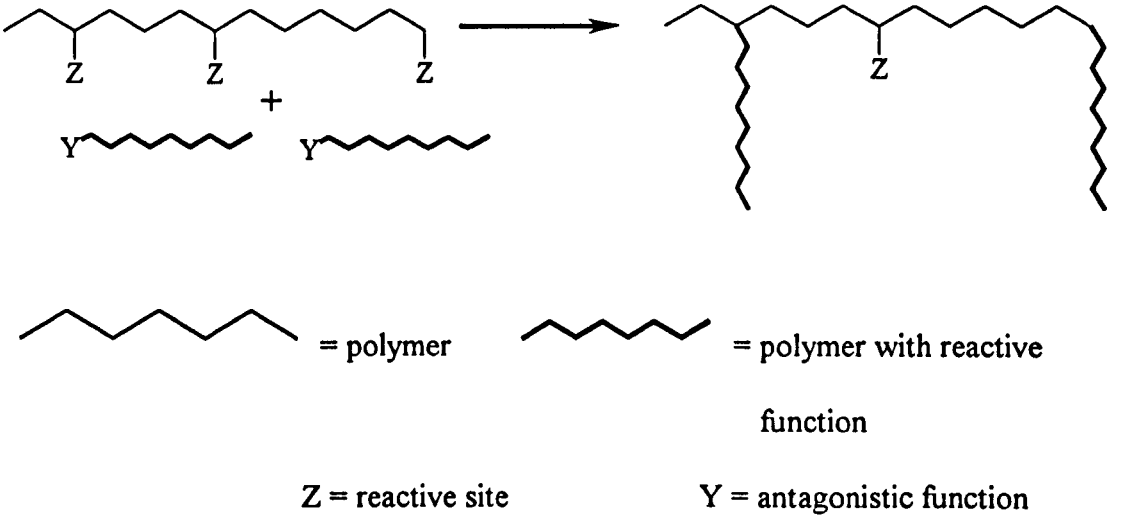
1.4.1.1 'Grafting From' Processes

In this method a polymer backbone is fitted with initiating sites that can be activated. A second polymer can then be grown from these sites to form the grafts of the polymer. However, this method gives no accurate knowledge of the number of grafts per chain, the length of the graft cannot be controlled and there may be homopolymers formed from both monomers. The length of each graft depends on the rate of initiation and the monomer concentration, but the mechanism by which the propagating radical terminates determines the ratio of grafts to crosslinks in the system.[36] A polymer that terminates by combination leads to a high degree of crosslinking.



1.4.1.2 'Grafting To' Processes

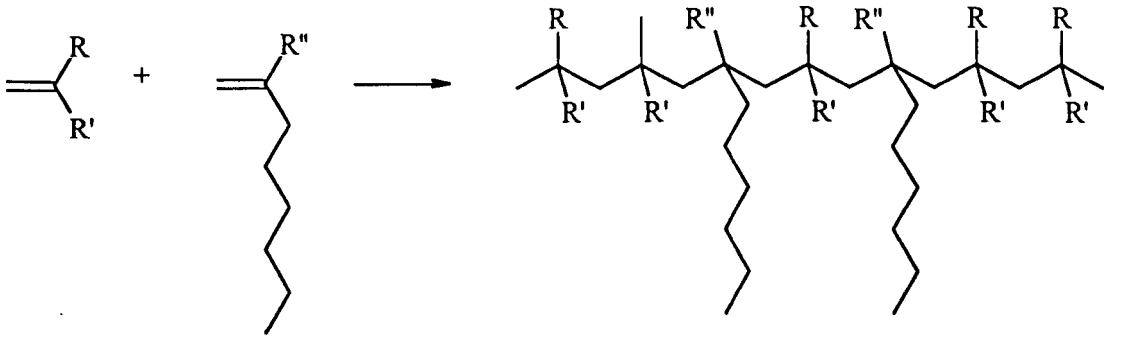
This method involves fitting a polymer chain (backbone) with functional groups and attaching a second polymer (graft) that has an antagonistic functional group at the chain end. The advantage of this method is that as the backbone and grafts are prepared separately they can be fully characterized individually, hence, as the molecular weight of each is known and the overall composition of the graft copolymer can be determined it should be possible to obtain a value for the number of grafts per polymer chain. However, this method requires that the active sites are accessible to the chain ends, for polymers of different chemical structure this is not always possible.



1.4.1.3 The Macromonomer Technique.

This method offers full control over graft length by preselection of the molecular weight of the starting macromonomer, and, in theory, the number of grafts per

chain can be regulated by adjusting the molar ratio of the monomer to macromonomer in the feed.[27]



Also, as the macromonomer technique may be carried out using free radical methods, a large number of monomers may be polymerized in this way in order to confer the polymer with the desired properties. However, knowledge of the polymerization behaviour of macromonomers is essential to controlling the graft copolymers which can be derived from them. (This is often difficult to obtain due to the complexity of the products from macromonomer polymerizations.)

1.5 Analytical Techniques

A number of analytical techniques were employed in this work to characterize both the macromonomers and the polymers prepared from them. These techniques include nuclear magnetic resonance and infra red spectroscopy, size exclusion chromatography and matrix assisted laser desorption ionization time of flight mass spectrometry, the two latter techniques are described in more detail below.

1.5.1 Measurement of Molecular Weight by Size Exclusion Chromatography (SEC).

The molecular weights of polymers prepared in this work were determined by size exclusion chromatography, also known as gel permeation chromatography (GPC). SEC is the most powerful technique for the molecular weight characterization of polymers since it yields the entire molecular weight distribution of the polymer, enabling all useful molecular weight averages to be determined. SEC uses columns containing highly crosslinked gels, swollen by solvent, with a distribution of pore sizes. A solvent, e.g. tetrahydrofuran (THF), is pumped at a constant rate through the column. A solution containing the analyte is injected into the solvent stream and the polymer molecules are separated according to their hydrodynamic volume. The larger molecules are excluded from the smaller pores in the gel and pass quickly through the larger channels between the gel particles, and, as a result, are eluted from the column first. As the size of the polymer molecule decreases, the number of pores into which the molecule can diffuse increases, resulting in a longer path length and hence longer elution time. Therefore, by appropriate choice of pore size, separation of molecular weights can be effected. The eluted fractions then pass into the detector.

There are various types of detector, one of the most commonly used being a differential refractometer. This makes use of the difference in refractive index between solvent and polymer.

Unfortunately, SEC is not an absolute method for molecular weight determination and must be calibrated with samples of known molecular weight and narrow

molecular weight distribution of the same type of polymer as that which is to be analyzed.

1.5.2 Matrix Assisted Laser Desorption Ionization Time of Flight Mass Spectrometry. (MALDI-TOF MS)

MALDI - TOF mass spectrometry is a soft ionization technique that has been used throughout this thesis to determine the number of macromonomer units that are present in a polymerization product. Traditional forms of analysis of polymer molecules by mass spectrometry have been unsuccessful since the large amount of energy required to produce gas-phase polymer ions usually results in fragmentation of the chain prior to detection. MALDI-TOF MS differs from other forms of mass spectrometry in that the parent ion is seen by the detector and fragmentation does not take place. This is because instead of energy from the laser pulse being transferred to the analyte molecules which then ionize and vaporize, the energy is transferred to a UV-light absorbing matrix onto which the analyte is deposited. It is thought that some of the matrix material vaporizes, carrying intact analyte molecules into the gaseous phase and transferring a charge to the unfragmented chains. Cations are added to the matrix as a salt solution, e.g. sodium chloride, and hence the polymers are detected as a distribution of singly charged molecular ions. The polymer chains of different molecular weight are detected by a time of flight detector. The ions are accelerated by a fixed potential and separated into m/z fractions as they drift down a field free tube. As all ions should possess the same initial kinetic energy, those with the lowest mass will have the highest velocity and so will reach the detector first. Any variation in

initial kinetic energy can be compensated for by use of an ion reflectron prior to detection. The resolution obtained using a MALDI-TOF mass spectrometer is in the order of 5 daltons. A typical setup for a MALDI TOF mass spectrometer is shown in Figure 1.4.

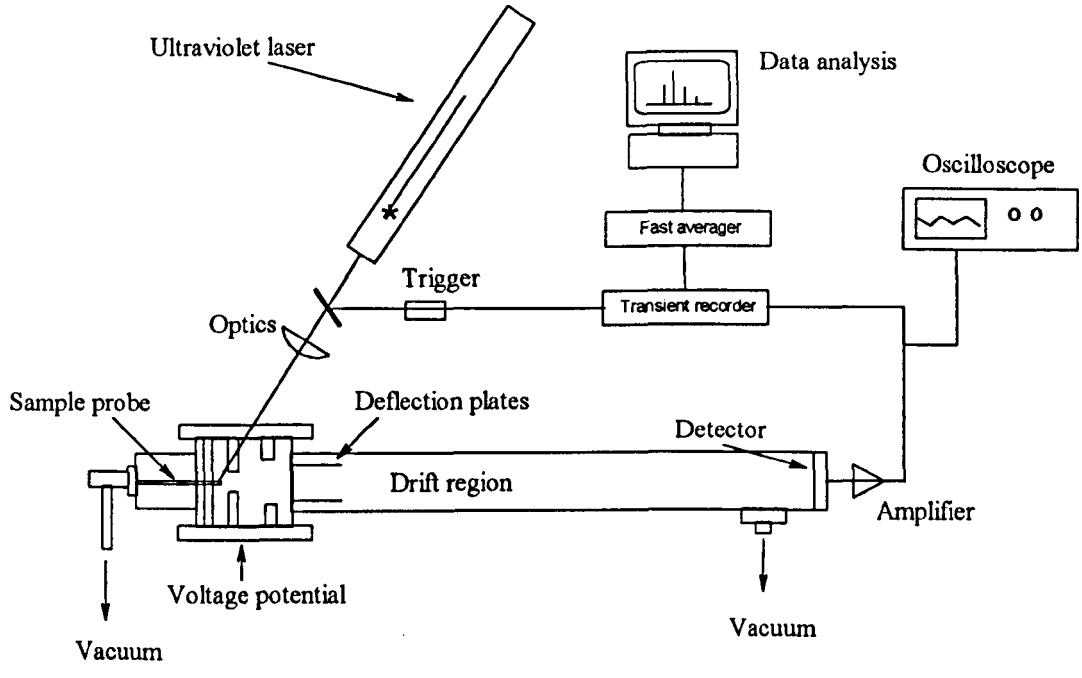


Figure 1.4 Typical MALDI-TOF mass spectrometry setup[37]

In a typical experiment polymer sample (~1 mg ml^{-1}) is dissolved in acetone, precipitated from water and redissolved in acetone to give the analyte in a 50:50 acetone:water mix. A 0.1 M solution of matrix in 50:50 acetone:water was used in this work. The matrix was usually 2,5-dihydroxybenzoic acid doped with sodium or potassium chloride; it is spotted onto a slide and the solvent allowed to evaporate. The polymer solution is then spotted on top of the matrix, before insertion of the slide into the spectrometer where it is irradiated by the laser.

1.6 Telechelic Polymers.

As has previously been noted, the use of functional macromonomers in methacrylate polymerizations can result in the formation of polymers with controlled amounts of functionality. In the case of methacrylate dimers a telechelic polymer is produced, with higher molecular weight macromonomers the product is a block copolymer.[38]

A telechelic polymer is one containing a reactive functional group at each chain end that can further polymerize or chain extend. The term telechelic originates from the Greek from tele meaning at a distance and chelos meaning claw. The term was first applied to polymers by Uranek[39] in 1960 to describe relatively low molecular weight polymers with a reactive functional group at each chain end[40]. The interest in telechelic polymers has stemmed from their use as prepolymers, usually with suitable linking agents, to perform three main types of reaction:[41]

1. chain extension of short chains to longer ones using bifunctional linking agents.
2. network formation using multifunctional linking agents.
3. formation of block copolymers by combination of telechelics containing different backbones and end groups.

One of the main uses of telechelic polymers is in the use of high solids coatings. The drive towards environmentally friendly systems and the increasing costs of the solvents that evaporate from coatings have encouraged research into the development of high solids coatings.[42] One of the prime components for high solids coatings is a liquid polymer with a functionality of at least two. The most

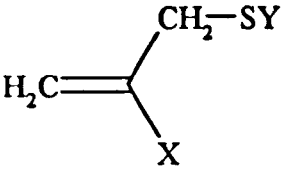
widespread use of telechelic polymers is in the synthesis of polyurethane materials where both termini usually contain hydroxyl functionality. The most common telechelic materials used in polyurethane synthesis are based on polyethers, with a smaller number using polyesters.

Telechelic polymers have been synthesized by a number of methods, both radical and ionic. Ionic preparations have all the inherent disadvantages associated with this class of reaction, i.e. high purity and dryness of reagents, intolerance towards protic functionalities in the monomers which would mean protection and deprotection steps if, for example, hydroxy or amino functional monomers were used and low polymerization temperatures, all of which results in increased processing and equipment costs. One method of preparing telechelic polymers by radical methods involves the use of functional initiators and monomers that terminate predominantly by combination rather than disproportionation. Unfortunately this completely rules out an entire class of monomers, methacrylates. However, even for monomers such as styrene that have approximately 85 % of termination occurring by combination this would still result in a large number of chains with a functionality of less than two.

A chain transfer agent can be used to prepare telechelic polymers provided that both the terminating and reinitiating species contain functional groups.

In recent years a number of research workers have reported the use of addition fragmentation agents in the preparation of telechelic polymers.[43-45] An addition-fragmentation process is said to occur in a free radical polymerization when a growing polymer chain reacts with a compound that contains both an activated site of unsaturation and a weak bond located elsewhere in the molecule. The intermediate radical formed by the addition of the compound to the propagating

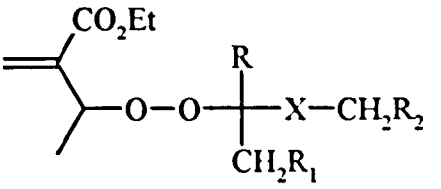
radical undergoes fragmentation involving the weak bond. This generates another radical that can enter the polymerization, usually by the initiation of monomer.[43] If the addition-fragmentation chain transfer agent contains functionality the resulting polymer has terminal functionality. If the radical formed by fragmentation is also functional and reinitiates polymerization then the polymer so formed will be telechelic. The current trends in research follow one of two routes, either the development of previously established addition-fragmentation agents, or the design of new, specific addition-fragmentation chain transfer agents, the latter generally with the goal of producing telechelic polymers. Rizzardo et al have developed a number of allylic compounds that act as addition-fragmentation chain transfer agents.[44-45] By the incorporation of functional groups in X and/or Y end-functional polymers have been prepared by free radical polymerizations with MMA and styrene. They have calculated the chain transfer constants for a number of allylic sulfides based on structure **1.4**.



1.4

These compounds exhibited Cs values of between 0.3 and 1.4 for polymerizations with MMA.

Colombani and Chaumont[46] have also synthesised a number of addition fragmentation agents to prepare telechelic polymers. These are based on the structure **1.5** below where R_1 and R_2 form a cyclic structure:



1.5

These compounds function by homolytic dissociation of the peroxide bond after addition of the chain transfer agent to the propagating chain and subsequent β-scission of the expelled ring to form a radical that can reinitiate polymerization.

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Chapter

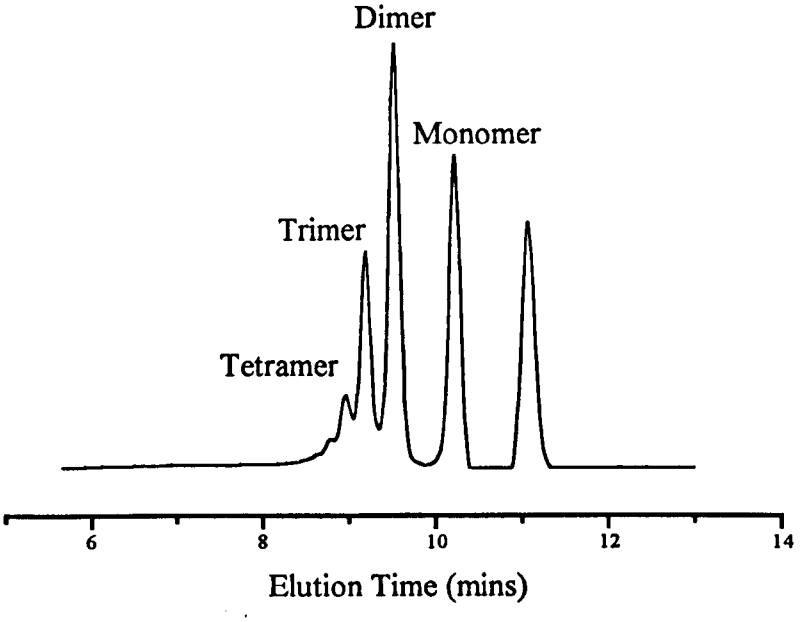
2.

Synthesis, Isolation and Characterization of Methacrylate Macromonomers

2.1 Introduction

All of the macromonomers used in this thesis were prepared by catalytic chain transfer polymerization using CoBF as chain transfer agent, as detailed in section 7.3. Catalytic chain transfer of methacrylates leads to a complex mixture of oligomers as observed by SEC, as shown in Figure 2.1a. Sufficient CoBF was added to polymerizations such that low molecular weight oligomers were prepared. Dimer and trimer macromonomers were isolated by reduced pressure distillation using a kugelrohr apparatus. The purity of the separated components was verified by SEC, see Figure 2.1b, and ^{1}H and ^{13}C NMR.

(a)



(b)

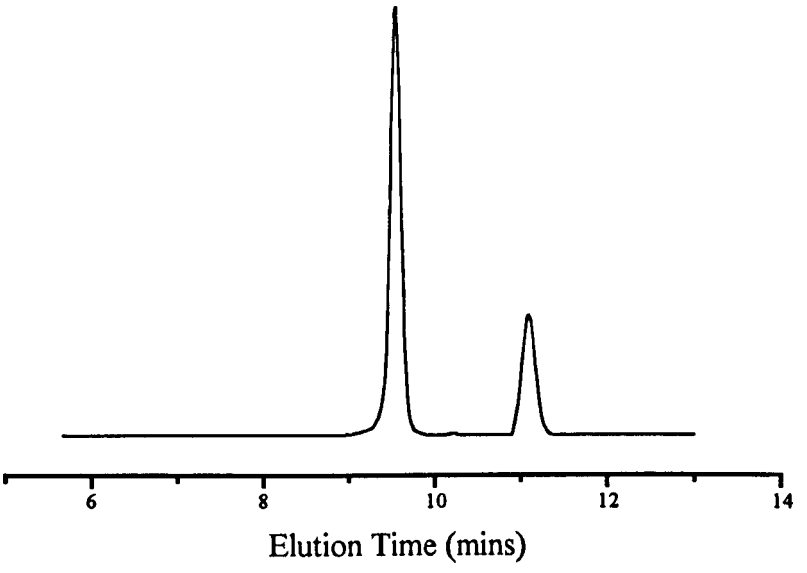


Figure 2.1 SEC trace of a) benzyl methacrylate macromonomers prepared by CCT polymerization and b) isolated benzyl methacrylate dimer. (The peak at t > 11 minutes is due to the internal toluene flow marker.)

Macromonomers prepared in this work had two main uses. Firstly, they were added to bulk methacrylate polymerizations in order to calculate their chain transfer activity. Since the chain transfer activity of trimer is typically an order of magnitude greater than dimer,[1] all higher molecular weight oligomers must be removed so that accurate values for chain transfer coefficients, Cs, are obtained. Also the monomer must be removed so that the exact composition of the feed was known, essential for the determination of Cs. Secondly, the dimers were used to produce telechelic polymers via radical addition-fragmentation. In order to reduce the production of polymers with a functionality greater than 2.0, it is

important to obtain the dimer with as little contamination from trimer and higher molecular weight oligomers as possible.

2.2 Experimental

The conditions required for separation of the oligomers used in this thesis from higher molecular weight macromonomers are shown in Table 2.1.

Table 2.1 Temperature and pressure conditions for separation of methacrylate macromonomers.

Macromonomer	Temperature (°C)	Pressure (mbar)
BMA dimer	125	0.2
BMA trimer	220	0.07
BzMA dimer	244	0.3
GMA dimer	115	0.1
HEMA dimer	156	0.8
MMA dimer	130	0.12
MMA trimer	170	0.12
MMA tetramer	150	0.06

^{1}H and ^{13}C NMR spectra of MMA dimer, trimer and tetramer have been recorded previously in the literature.[2] They are shown here only for comparison for work presented later in the chapter where mixed macromonomers of HEMA and MMA have been prepared and, in the case of a mixed MMA-HEMA dimer, isolated.

The IR spectra of the dimers were recorded using NaCl plates with the liquid dimer deposited as a thin film.

2.3 Characterization of Isolated Macromonomers.

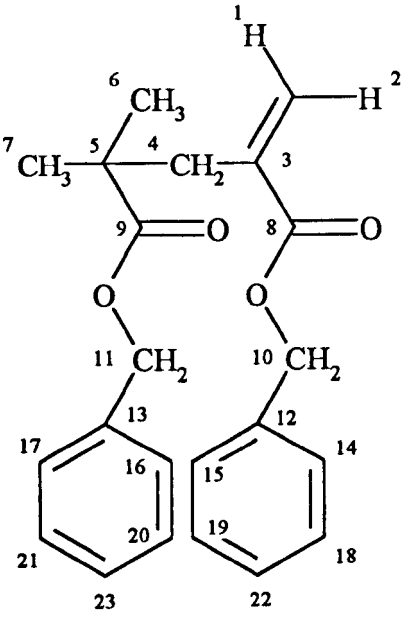
The dimers and trimers were isolated and analysed by ^{1}H and ^{13}C NMR at 400 MHz or 250 MHz using either 1,1,2,2-tetrachloroethane (TCE) $C_2D_2Cl_4$ or chloroform, $CDCl_3$. TCE was used in some of the initial analysis to allow comparison with published work[2] which had used this solvent. ^{1}H NMR and ^{13}C NMR spectra of BzMA, BMA, GMA and HEMA dimer and BMA trimer are presented in sections 2.3.1 to 2.3.5 together with the ^{1}H- NMR spectra of MMA dimer, trimer and tetramer. The data from the IR spectra of HEMA, GMA and BzMA dimer are also presented.

2.3.1 Benzyl Methacrylate Dimer

Analysis of the carbon and hydrogen content of BzMA dimer gave the results shown below.

$C_{22}H_{24}O_4$	calculated	C 74.98	H 6.86
	found	C 75.09	H 6.98

The structure of BzMA dimer is shown below, **2.1**. The ^{1}H NMR and ^{13}C NMR spectra are shown in Figure 2.2 and Figure 2.3 and assignments of the peaks are given in Table 2.2 and Table 2.3 respectively.



2.1

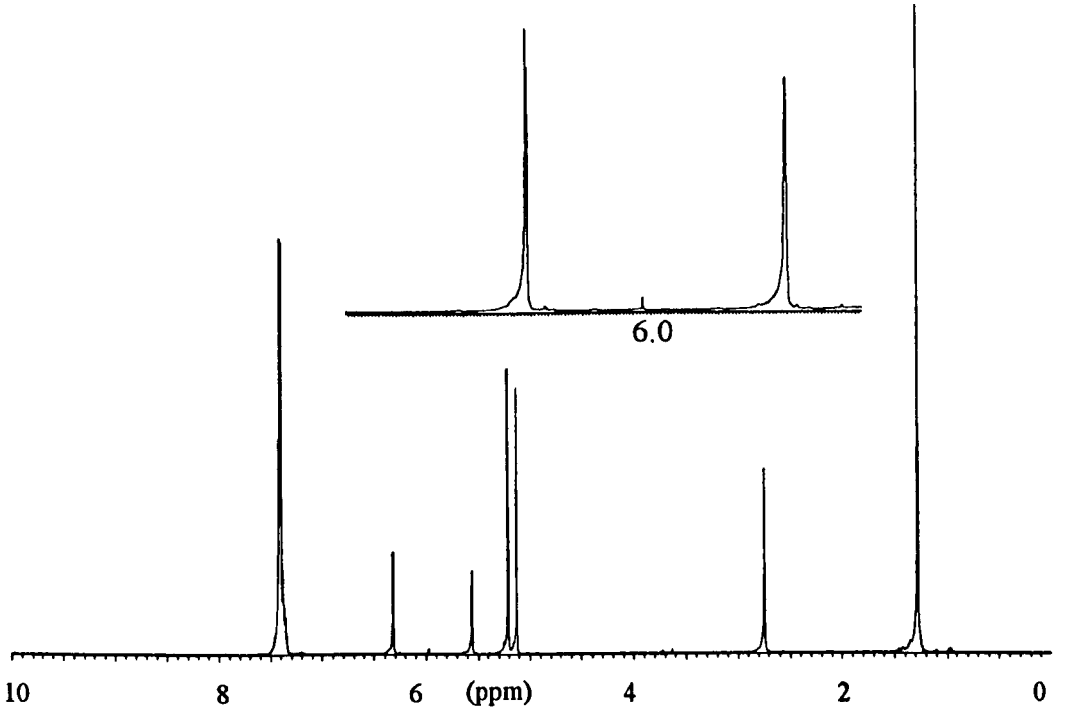


Figure 2.2 ^{1}H NMR spectrum (TCE, 298 K, 400 MHz) of benzyl methacrylate dimer, inset shows the expanded vinylic region.

Table 2.2 ^{1}H NMR (TCE, 298 K) data for benzyl methacrylate dimer.

Chemical Shift (ppm)	Multiplicity	Assignment
7.41-7.35	multiplet	H^{14}-H^{23}
6.31	singlet	H^{1}
5.55	singlet	H^{2}
5.20	singlet	H^{11}
5.12	singlet	H^{10}
2.74	singlet	H^{4}
1.26	singlet	H^{6}
1.26	singlet	H^{7}

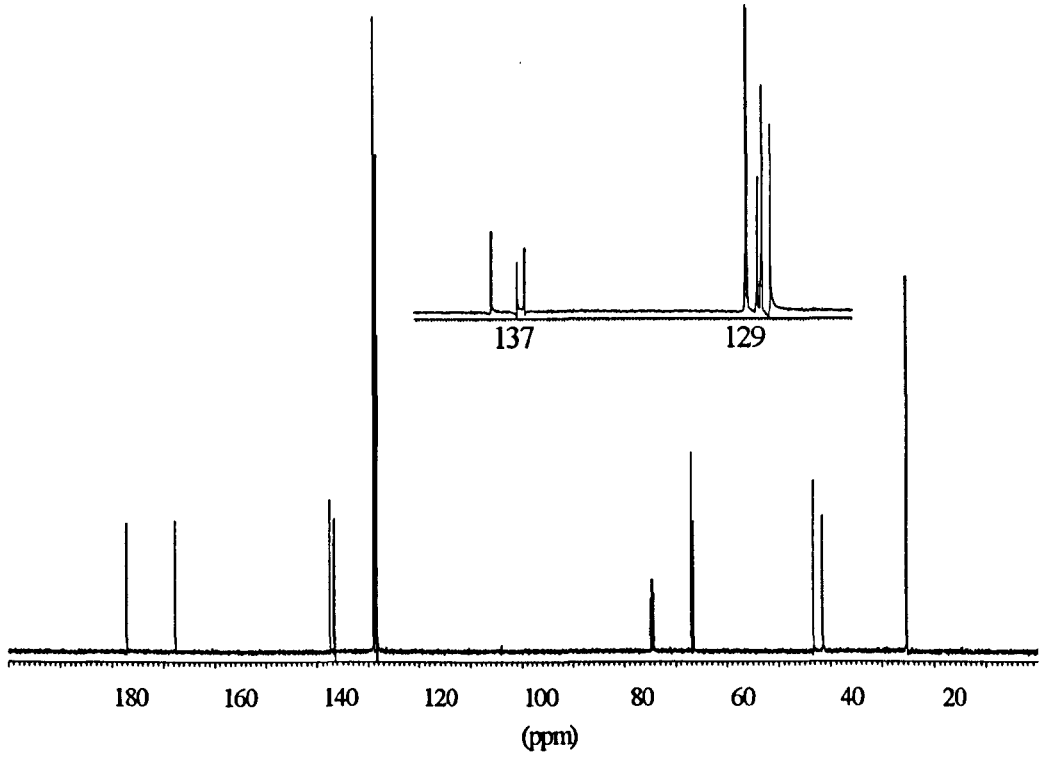


Figure 2.3 ^{13}C NMR spectrum (TCE, 298 K, 400 MHz) of benzyl methacrylate dimer, inset shows the expanded vinylic and aromatic region.

Table 2.3 ^{13}C NMR data (TCE, 298 K) for benzyl methacrylate dimer

Chemical Shift (ppm)	Assignment
176.26	C^9
166.75	C^8
136.73	C^3
135.88	C^{13}
135.62	C^{12}
128.18	C^1
127.81, 127.65, 127.36	C^{14}-C^{23}
66.12, 65.71	C^{10}, C^{11}
42.46	C^5
40.57	C^4
24.50	C^6, C^7

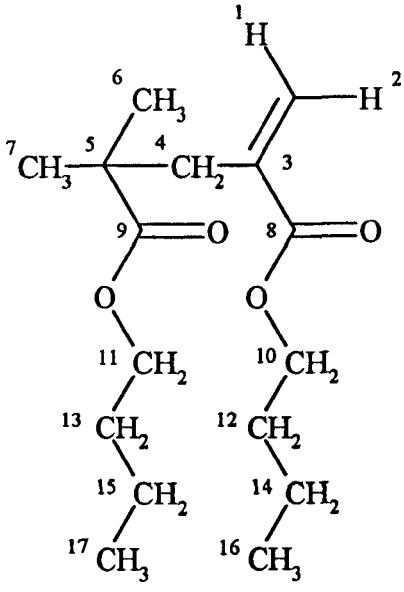
BzMA dimer was analysed by FT-IR, using NaCl plates with the liquid dimer deposited as a thin film, the data are shown below.

IR: 3090, 3065, 3033 (s, aromatic C-H), 2973, 2873 (vs, aliphatic C-H), 1721(vs, C=O), 1627 (s, C=C), 1498, 1472 (aliphatic C-H), 1456 (aromatic C=C), 1390 (aliphatic CH_3), 1375, 1338, 1289 (C-O), 1197, 1145, 1081, 1020, 957, 916, 818, 751 and 697 cm^{-1}.

2.3.2 Butyl Methacrylate Dimer

The structure of BMA dimer is shown below, **2.2**, with the ^1H NMR and ^{13}C NMR spectra shown in Figure 2.4 and Figure 2.5 respectively. Assignment of the

peaks, using the numbering shown in **2.2**, is given in Table 2.4 and Table 2.5. The expanded region of the ^{1}H NMR spectrum clearly illustrates the presence of two different O-CH_2- groups.



2.2

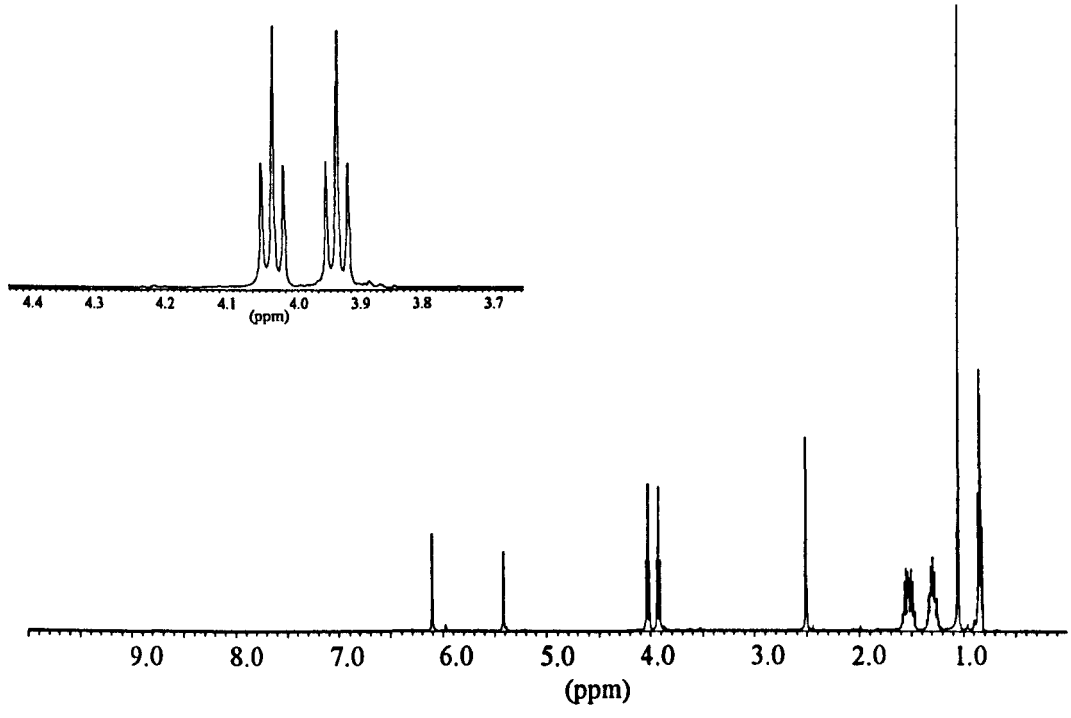


Figure 2.4 ^{1}H NMR (TCE, 298 K, 400 MHz) spectrum of n-butyl methacrylate dimer, inset shows the expanded O-CH_2- region.

Table 2.4 Assignment of peaks from the ^{1}H NMR spectrum of n-butyl methacrylate dimer

Chemical Shift (ppm)	Multiplicity	Assignment
6.12	singlet	H^{1}
5.43	singlet	H^{2}
4.07 - 4.03	triplet	H^{10}
3.97 - 3.94	triplet	H^{11}
2.54	singlet	H^{4}
1.61 - 1.49	multiplet	H^{12}, H^{13}
1.37 - 1.26	multiplet	H^{14}, H^{15}
1.08	singlet	H^{6}, H^{7}
0.88 - 0.84	multiplet	H^{16}, H^{17}

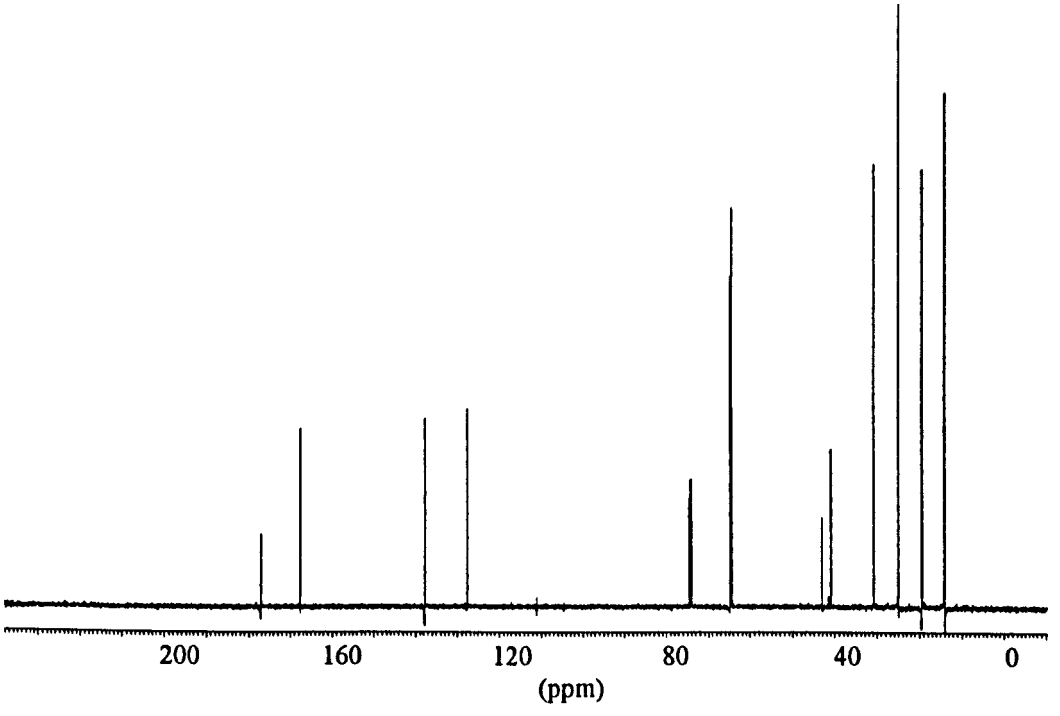


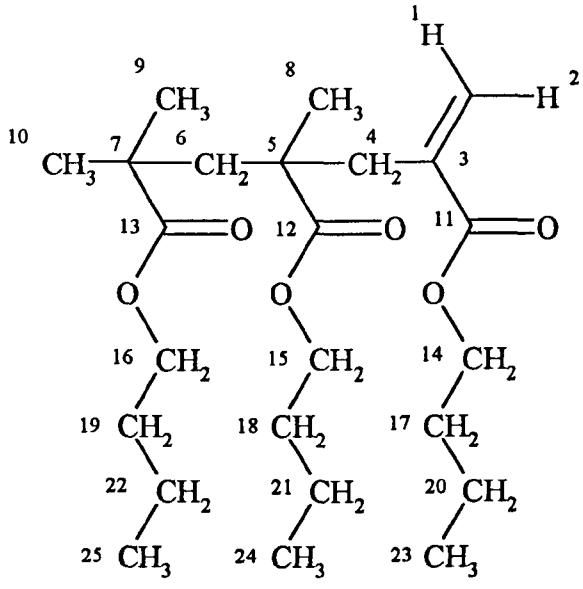
Figure 2.5 ^{13}C NMR spectrum (TCE, 298 K, 400 MHz) of n-butyl methacrylate dimer.

Table 2.5 Assignment of the peaks from the ^{13}C NMR spectrum of n-butyl methacrylate dimer.

Chemical Shift (ppm)	Assignment
177.00	C^9
167.47	C^8
137.71	C^3
127.34	C^1
64.58	C^{10}
64.23	C^{11}
42.94	C^5
40.66	C^4
30.59	C^{12}, C^{13}
24.76	C^6, C^7
19.14	C^{14}, C^{15}
13.64	C^{16}, C^{17}

2.3.3 n-Butyl Methacrylate Trimer

The structure of n-butyl methacrylate trimer is shown below, **2.3**. The ^1H NMR and ^{13}C NMR spectra are shown in Figure 2.6 and Figure 2.7 respectively, with peak assignments in Table 2.6 and Table 2.7. The expanded region in Figure 2.6 shows the presence of three different O-CH_2- groups.



2.3

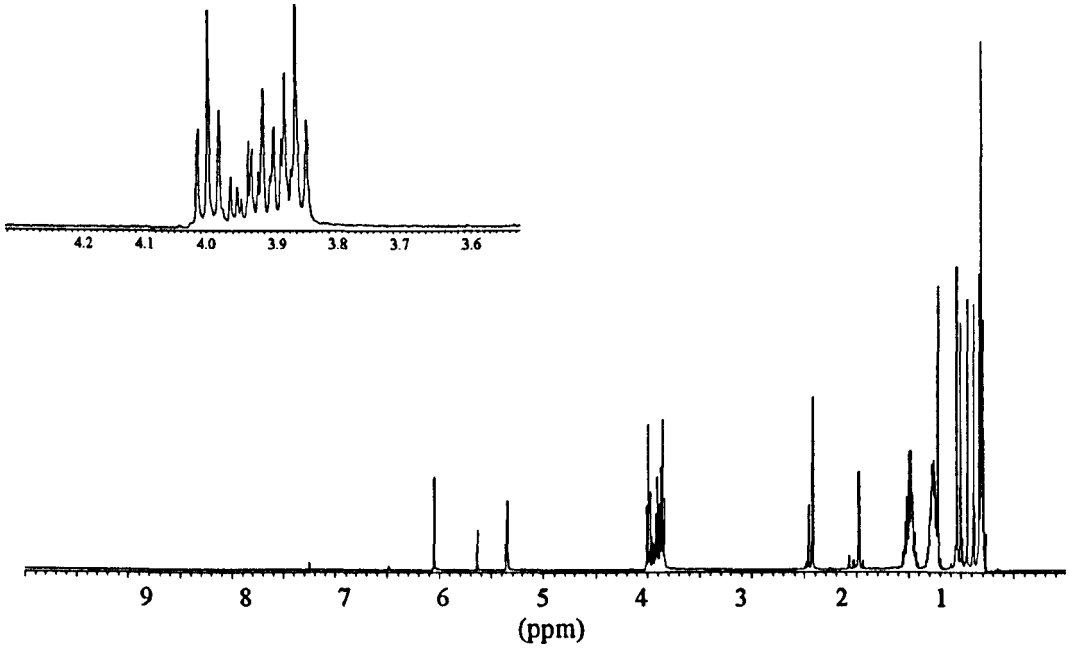


Figure 2.6 ^{1}H NMR spectrum (TCE, 298 K, 400 MHz) of n-butyl methacrylate trimer. The inset shows the expanded O-CH_2- region.

Table 2.6 Peak assignment of ^{1}H NMR spectrum of n-butyl methacrylate trimer.

Chemical Shift (ppm)	Multiplicity	Assignment
6.05	singlet	H^{2}
5.35	singlet	H^{1}
4.00 - 3.84	multiplet	H^{14} - H^{16}
2.46 - 2.42	multiplet	H^{4}
1.98	singlet	H^{6}
1.53 - 1.44	multiplet	H^{17} - H^{19}
1.30 - 1.22	multiplet	H^{20} - H^{22}
1.04 - 0.94	multiplet	H^{8} - H^{10}
0.88 - 0.77	multiplet	H^{23} - H^{25}

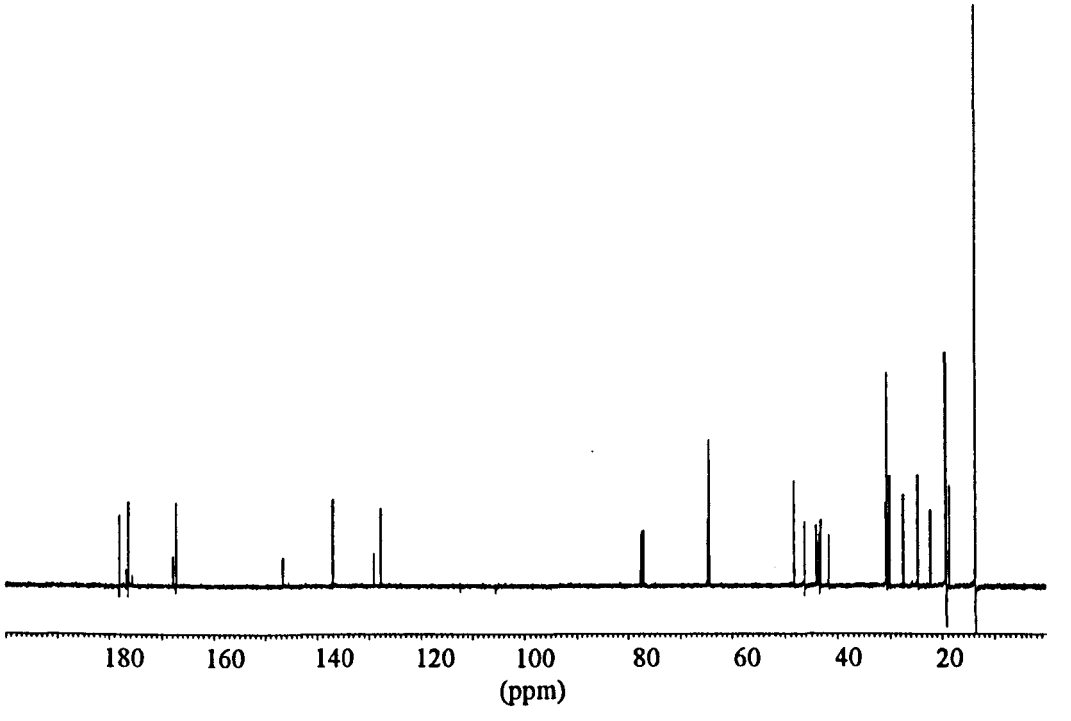


Figure 2.7 ^{13}C NMR spectrum (TCE, 298 K, 400 MHz) of n-butyl methacrylate trimer.

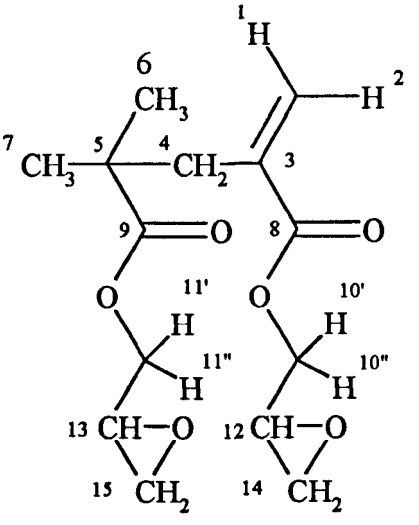
Table 2.7 Peak assignment of the ^{13}C NMR spectrum of n-butyl methacrylate trimer.

Chemical Shift (ppm)	Assignment
178.04	C^{13}
176.32	C^{12}
167.19	C^{11}
136.91	C^{3}
127.70	C^{1}
64.51 - 64.12	C^{14} - C^{16}
48.06 - 46.18	C^{7}
43.89 - 42.93	C^{5}
41.37	C^{4}
30.54 - 29.82	C^{17} - C^{19}
27.20	C^{6}
24.44 - 22.05	C^{8} - C^{10}
19.19 - 18.45	C^{20} - C^{22}
13.58	C^{23} - C^{25}

2.3.4 Glycidyl Methacrylate Dimer

The structure of glycidyl methacrylate (GMA) dimer is shown below, **2.4**. The ^{1}H and ^{13}C NMR spectra are shown in Figure 2.8 and Figure 2.9 respectively, with assignment of the peaks using the numbering system shown in **2.4** presented in Table 2.8 and Table 2.9. The expanded region in Figure 2.8 clearly shows the

doublet of doublets for each of the protons in the O-CH_2- groups of the dimer caused by the presence of the epoxy ring in the molecule.



2.4

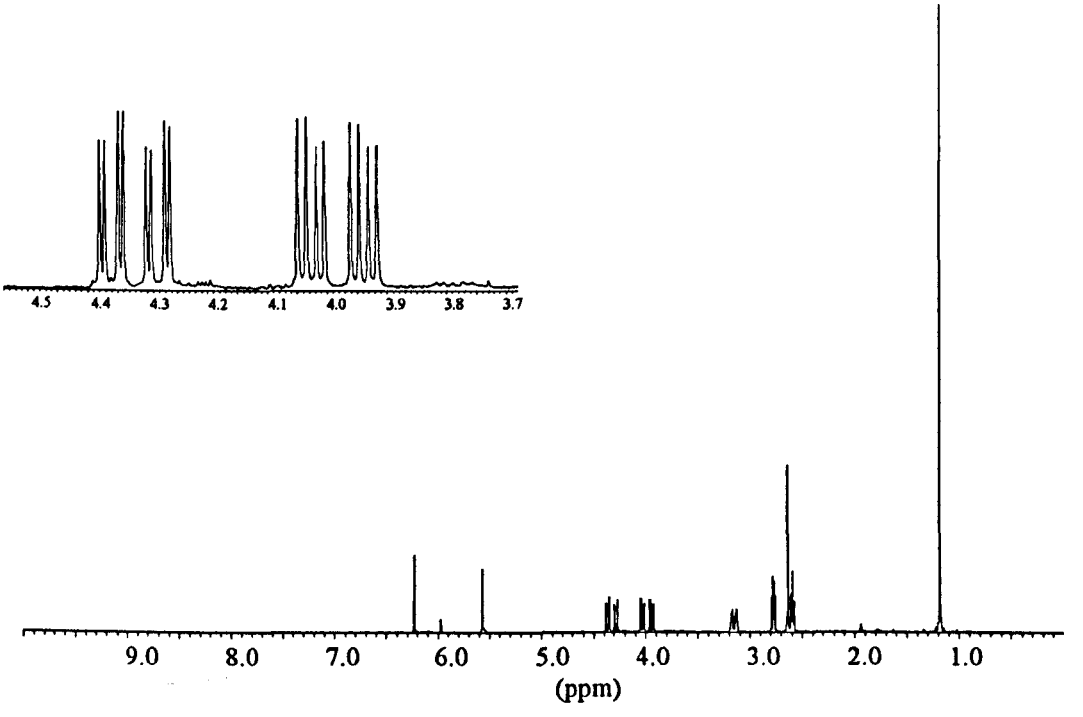


Figure 2.8 ^{1}H NMR spectrum (TCE, 298 K, 400 MHz) of glycidyl methacrylate dimer. The inset shows the expanded O-CH_2- region.

Table 2.8 Peak assignment for the ^{1}H NMR spectrum of glycidyl methacrylate dimer.

Chemical Shift (ppm)	Multiplicity	Assignment
6.23	singlet	H^{2}
5.57	singlet	H^{1}
4.38 - 4.34	doublet of doublets	$H^{10'}$
4.30 - 4.26	doublet of doublets	$H^{11'}$
4.05 - 4.00	doublet of doublets	$H^{10''}$
3.96 - 3.92	doublet of doublets	$H^{11''}$
3.19 - 3.15	multiplet	H^{12}
3.15 - 3.11	multiplet	H^{13}
2.79 - 2.75	multiplet	H^{14a}, H^{15a}
2.63	singlet	H^{4}
2.61 - 2.57	multiplet	H^{14b}, H^{15b}
1.18	singlet	H^{6}, H^{7}

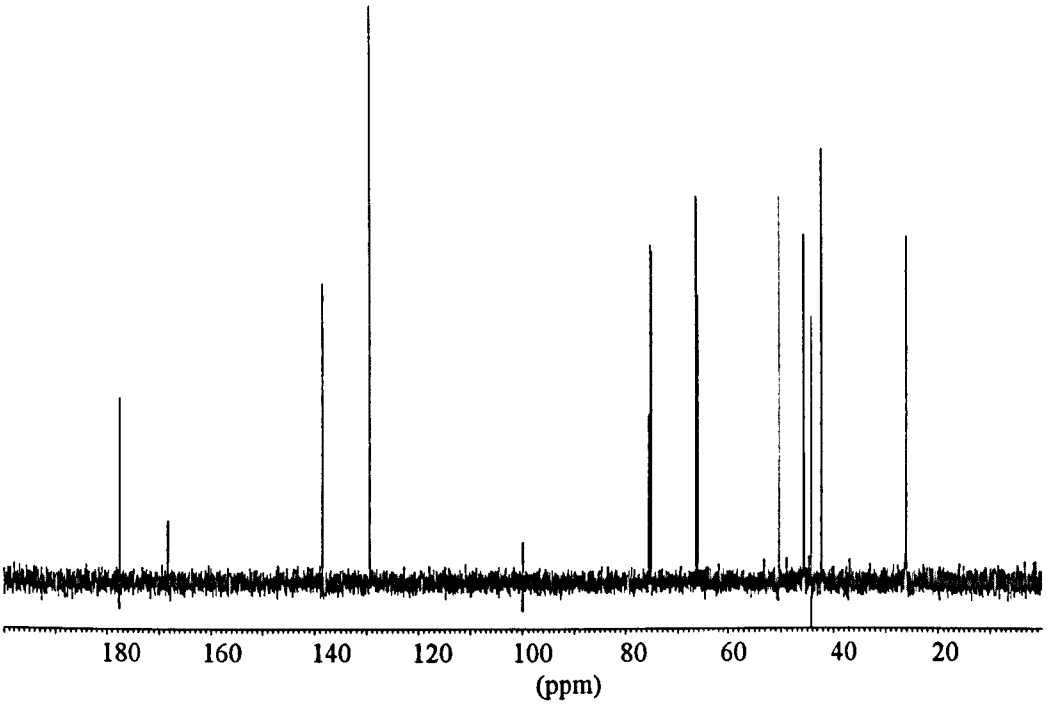


Figure 2.9 ^{13}C NMR spectrum (TCE, 298 K, 400 MHz) of glycidyl methacrylate dimer.

Table 2.9 Peak assignment for ^{13}C NMR spectrum of glycidyl methacrylate dimer.

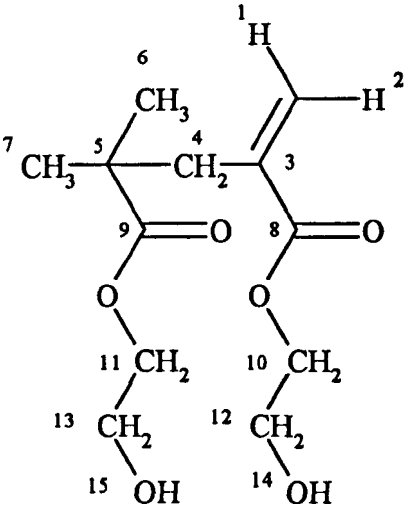
Chemical Shift (ppm)	Assignment
176.61	C^9
167.17	C^8
137.46	C^3
128.38	C^1
64.40	C^{10}
65.00	C^{11}
49.43	C^{12}, C^{13}

44.67	C^{14}, C^{15}
43.12	C^{5}
41.17	C^{4}
25.10	C^{6}, C^{7}

IR: 3527 (br; water or H-bonding), 3060 (epoxide C-H), 2977 (vs; aliphatic C-H), 1723 (vs; C=O), 1628 (s; C=C), 1474 (aliphatic C-H), 1451 (aliphatic C-H), 1391 (aliphatic CH_3) , 1354, 1290 (C-O), 1254 (epoxide ring), 1171, 1078, 1021, 998, 958, 910 (epoxide ring), 847 (unsaturated C-H), 819 (epoxide ring) cm^{-1}.

2.3.5 Hydroxyethyl Methacrylate Dimer

The structure of hydroxyethyl methacrylate dimer (HEMA) is shown below, **2.5**.



2.5

Analysis of the carbon and hydrogen content of HEMA dimer gave the results shown below.

$C_{12}H_{20}O_6$	calculated	C 55.37	H 7.74
	found	C 54.68	H 7.73

The ^{1}H and ^{13}C NMR spectra are shown in Figure 2.10 and Figure 2.11 respectively, with assignment of the peaks using the numbering system shown in **2.5** presented in Table 2.10 and Table 2.11. The expanded region in Figure 2.10 clearly shows the presence of two different O-CH_2-CH_2- groups in the dimer, due to the presence of the vinylic end group, in addition to a signal from the OH group.

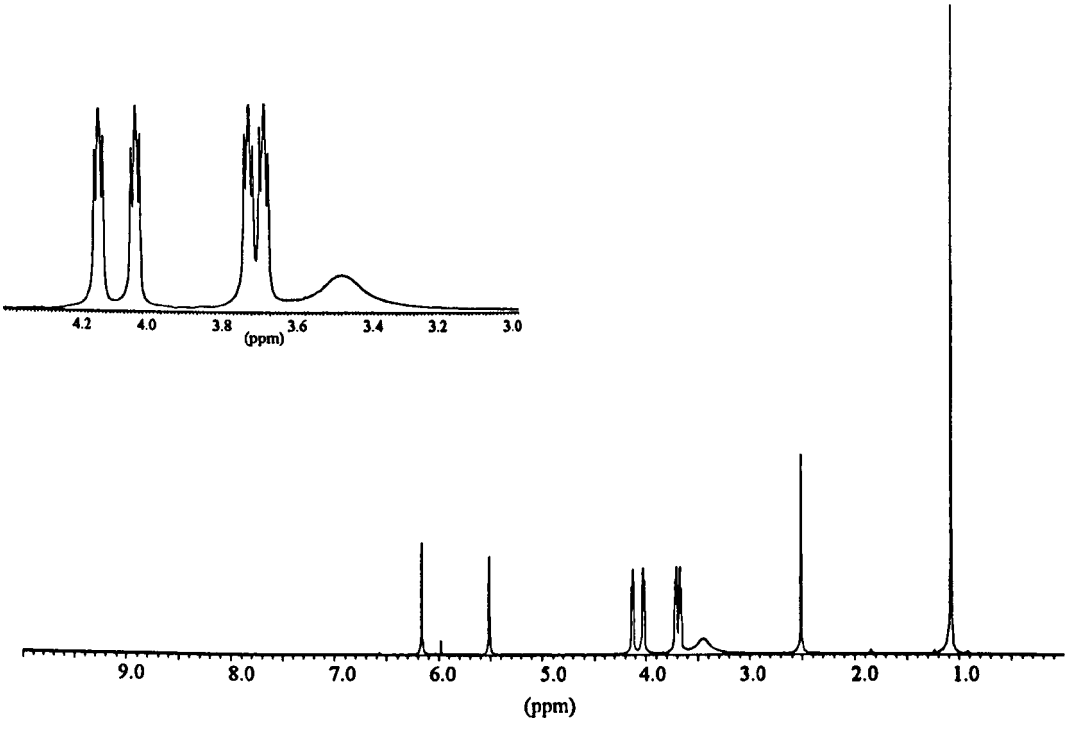


Figure 2.10 ^{1}H NMR spectrum (TCE, 373 K, 400 MHz) of hydroxyethyl methacrylate dimer. The inset shows the expanded region of the O-CH_2-CH_2- and OH groups.

Table 2.10 ^{1}H NMR data (TCE, 373 K) for hydroxyethyl methacrylate dimer.

Chemical Shift (ppm)	Multiplicity	Assignment
6.17	doublet	H^{1}
5.52	doublet	H^{2}
4.20	multiplet	H^{11}
4.10	multiplet	H^{10}
3.76	multiplet	H^{13}
3.72	multiplet	H^{12}
3.51	broad singlet	OH
2.59	singlet	H^{4}
1.15	singlet	H^{6}
1.15	singlet	H^{7}

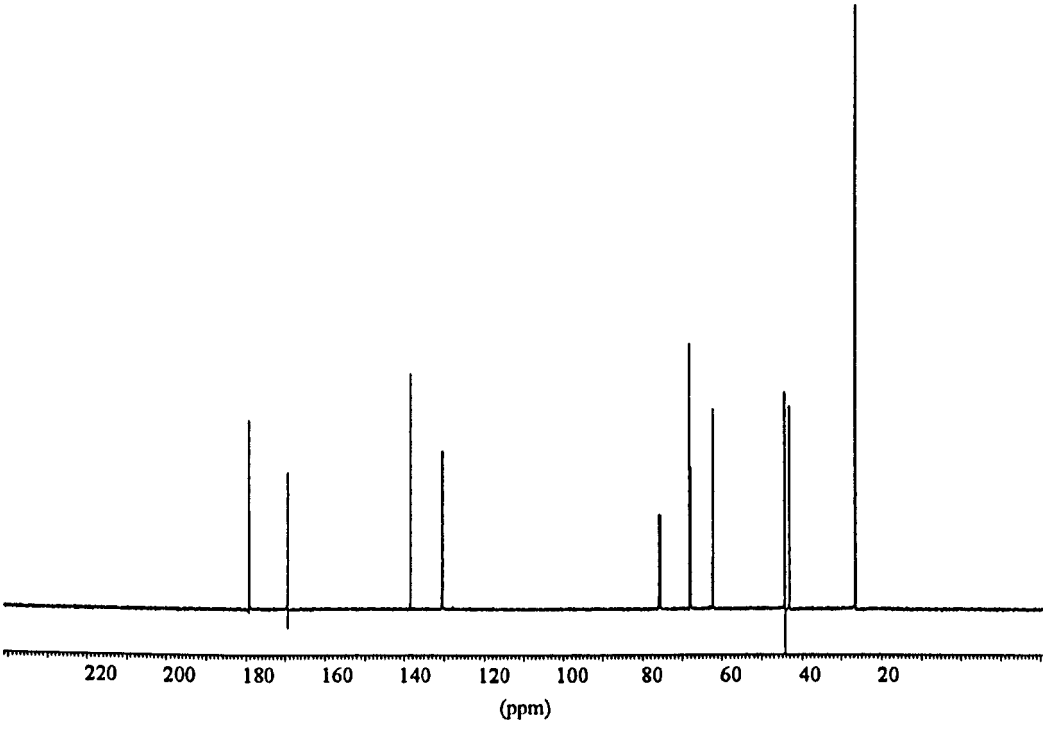


Figure 2.11 ^{13}C NMR spectrum (TCE, 373 K, 400 MHz) of hydroxyethyl methacrylate dimer.

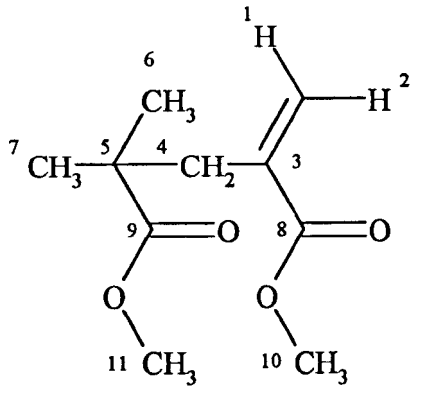
Table 2.11 ^{13}C NMR data (TCE, 373 K) for hydroxyethyl methacrylate dimer

Chemical Shift (ppm)	Assignment
177.45	C^9
167.97	C^8
137.77	C3
128.11	C^1
66.71, 66.43	C^{12}, ^{C13}
42.94	C^5
41.57	C^4
25.22	C^6, C^7

IR: 3436(vs, br; OH), 2972(s; aliphatic C-H), 1718 (vs; C=O) 1627 (vs, C=C), 1474, 1455 (aliphatic C-H), 1393 (aliphatic CH_3), 1370, 1338, 1294(s; C-O), 1170(vs), 1124 (s), 1079, 1029, 960, 920, 849 and 821 cm^{-1}.

2.3.6 Methyl Methacrylate Dimer

The structure of MMA dimer is shown below, **2.6.** The ^1H NMR spectrum is shown in Figure 2.12, with assignment of peaks, made with reference to the numbering shown in structure **2.6**, being presented in Table 2.12. The expanded region in Figure 2.12 clearly illustrates the presence of two different methoxy groups due to the presence of the vinylic end group of the dimer.



2.6

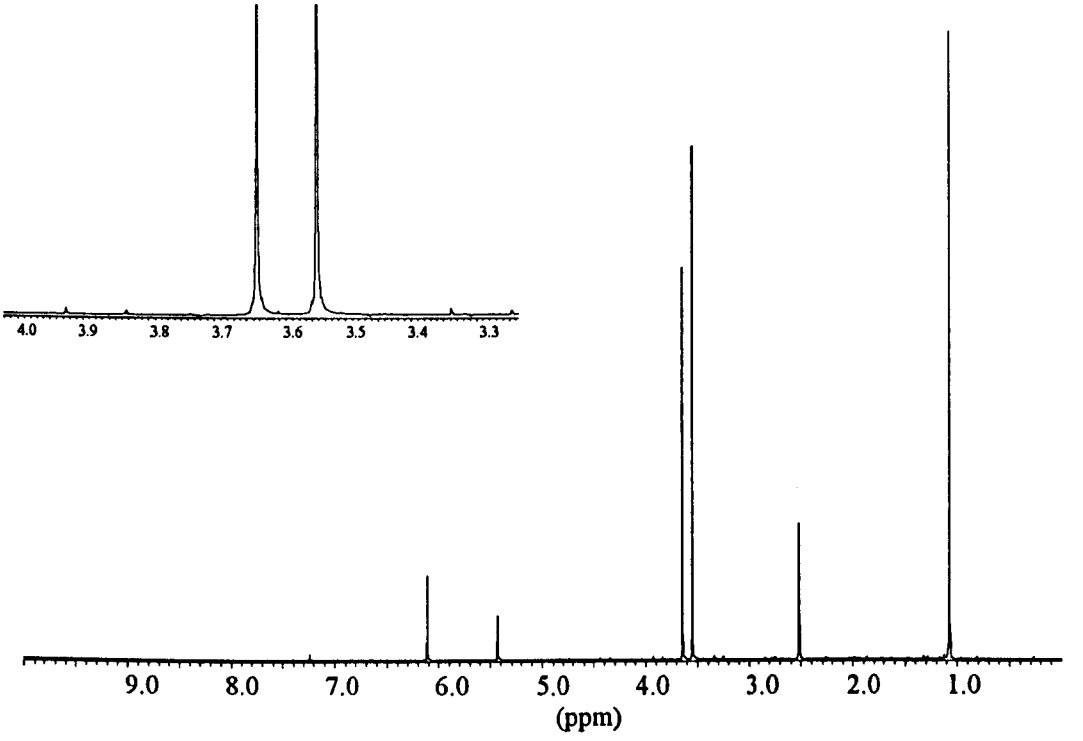


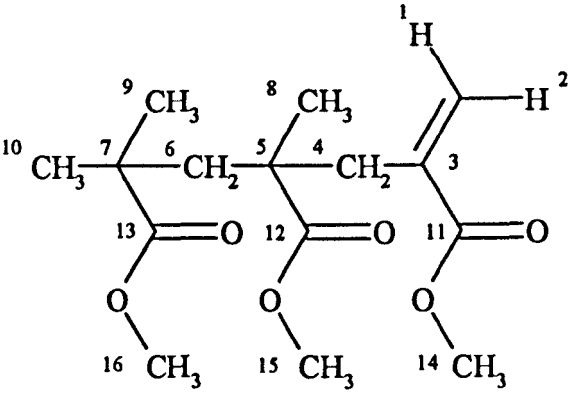
Figure 2.12 ^{1}H NMR spectrum ($CDCl_3$, 298 K, 250 MHz) of methyl methacrylate dimer. The inset shows the expanded O-CH_3 region.

Table 2.12 Assignment of the peaks in the ^{1}H NMR spectrum of methyl methacrylate dimer.

Chemical Shift (ppm)	Multiplicity	Assignment
6.12	singlet	H^2
5.44	singlet	H^1
3.64	singlet	H^{10}
3.55	singlet	H^{11}
2.52	singlet	H^4
1.08	singlet	H^6, H^7

2.3.7 Methyl Methacrylate Trimer

The structure of MMA trimer is shown below, **2.7**. The ^{1}H NMR spectrum is shown in Figure 2.13, with assignment of peaks, made with reference to the numbering shown in structure **2.7**, being presented in Table 2.13. The expanded region clearly shows the presence of three different methoxy groups, with the methoxy group nearest to the vinylic end group giving a distinct signal separated from the signals from the other methoxy groups.



2.7

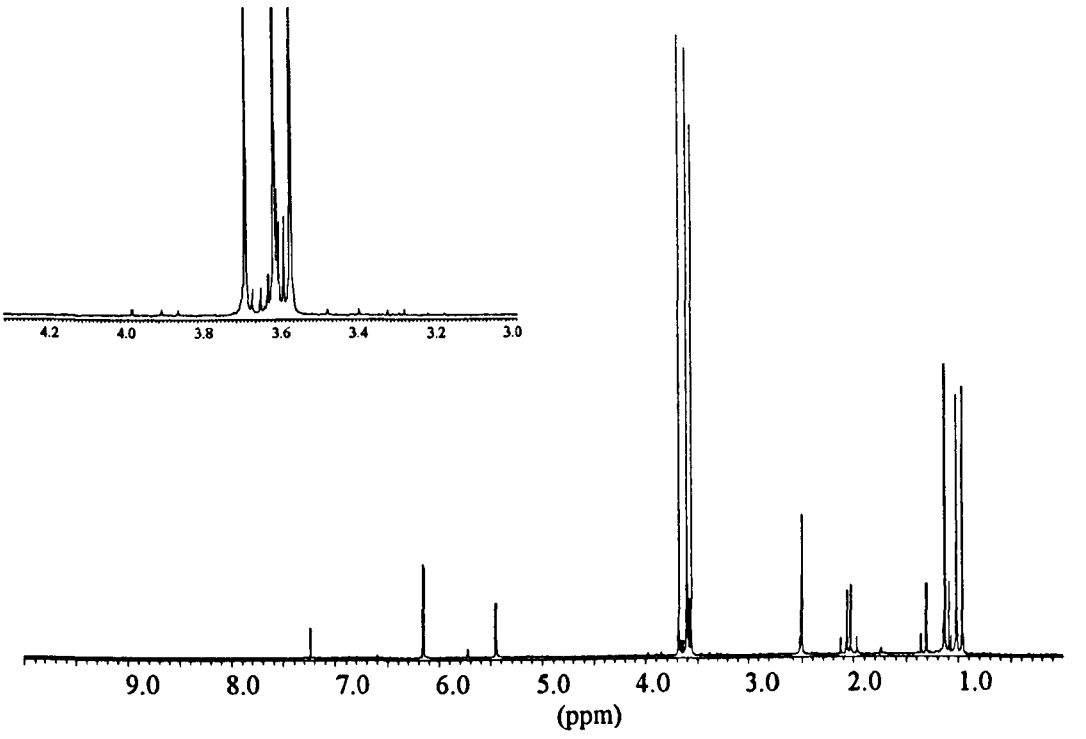


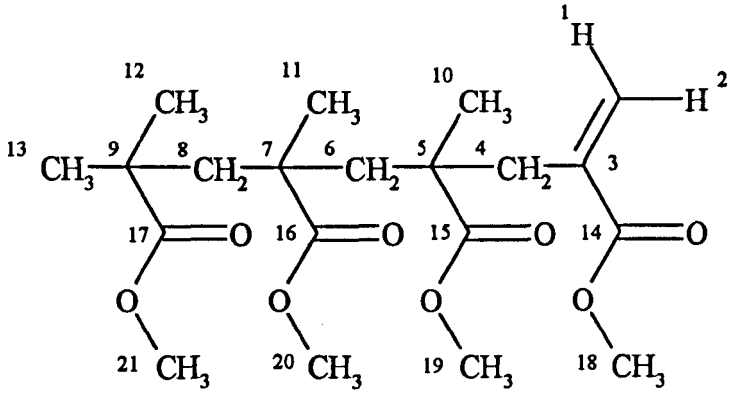
Figure 2.13 ^{1}H NMR spectrum ($CDCl_3$, 298 K, 250 MHz) of methyl methacrylate trimer. The inset shows the expanded O-CH_3 region.

Table 2.13 Assignment of the peaks from the ^{1}H- NMR spectrum of methyl methacrylate trimer.

Chemical Shift (ppm)	Multiplicity	Assignment
6.16	singlet	H^{2}
5.46	singlet	H^{1}
3.69	singlet	H^{14}
3.61 - 3.57	multiplet	H^{15}, H^{16}
2.52	singlet	H^{4}
2.13 - 1.98	multiplet	H^{6}
1.31	singlet	H^{9}
1.14 - 0.97	multiplet	H^{10}, H^{8}

2.3.8 Methyl Methacrylate Tetramer

The structure of MMA tetramer is shown below, **2.8**. The ^{1}H NMR spectrum is shown in Figure 2.14, with assignment of peaks, made with reference to the numbering shown in structure **2.8**, being presented in Table 2.14. The expanded region in Figure 2.14 again clearly shows the presence of multiple different methoxy groups, with the methoxy group closest to the vinylic end group giving a distinct, separated signal.



2.8

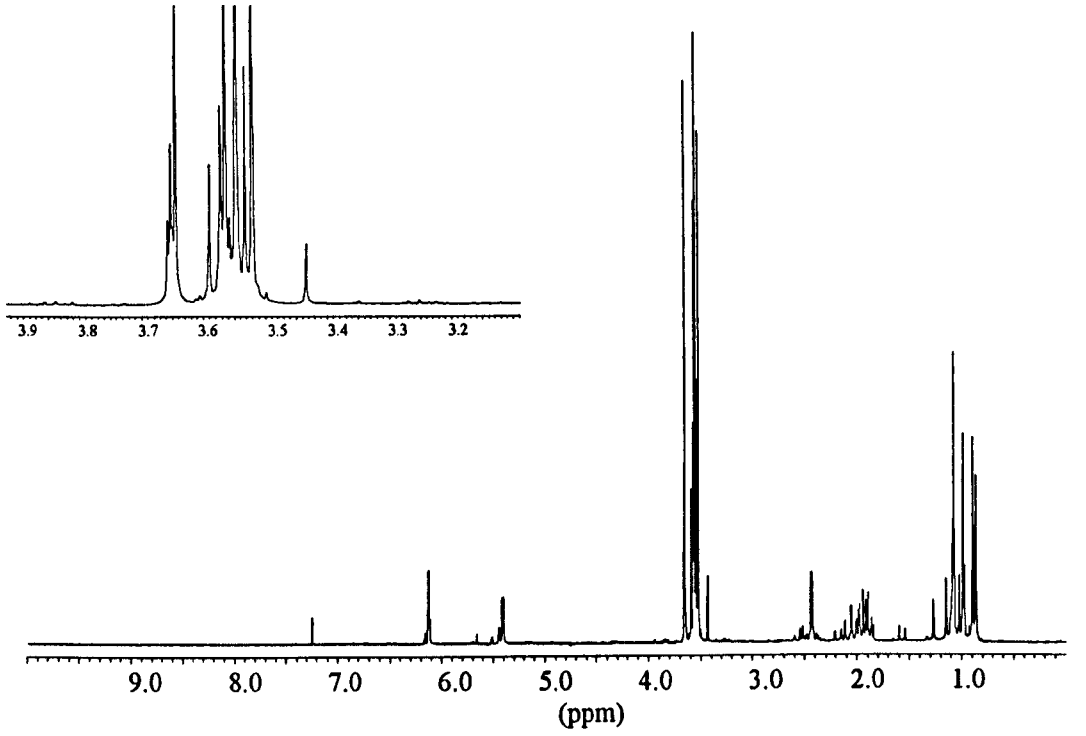


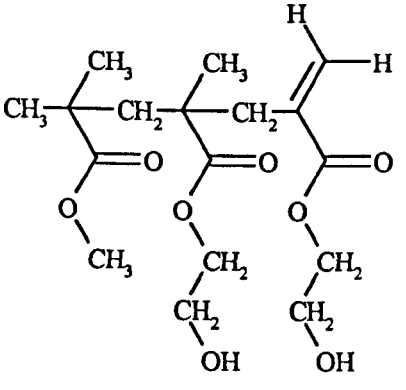
Figure 2.14 ^{1}H NMR spectrum ($CDCl_3$, 298 K, 250 MHz)) of methyl methacrylate tetramer. The inset shows the expanded O-CH_3 region.

Table 2.14 Assignment of the peaks in the ^{1}H NMR spectrum of methyl methacrylate tetramer.

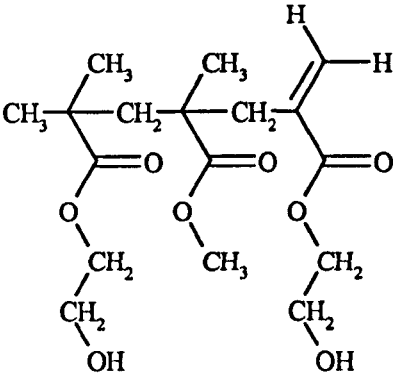
Chemical Shift (ppm)	Multiplicity	Assignment
6.13	singlet	H^{2}
5.41	singlet	H^{1}
3.66	singlet	H^{18}
3.60 - 3.53	multiplet	H^{19} - H^{21}
2.44	singlet	H^{4}
2.21 - 1.85	multiplet	H^{6}, H^{8}
1.11 - 0.87	multiplet	H^{10} - H^{13}

2.4 Mixed Macromonomers.

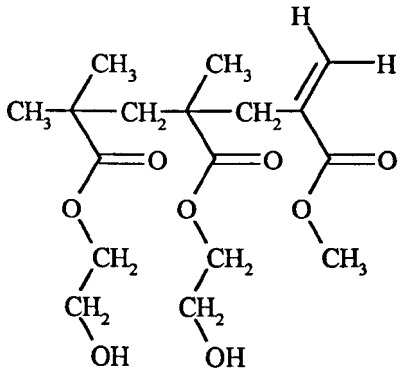
The work presented in Chapter 4 concerning the formation of telechelic polymers using HEMA dimer shows that there is a limit to the reduction in molecular weight that can be achieved using methacrylate dimers. In order to achieve lower molecular weight polymers two approaches may be taken. Firstly, trimer may be used instead of dimer. Trimers have a higher chain transfer constant than dimers and hence a lower molecular weight polymer is obtained[1]. However, this method results in reinitiation with two HEMA units which, upon chain extension reactions, could lead to the formation of networks rather than linear polymers. A second associated problem lies in the isolation of HEMA trimer. HEMA macromonomers have higher boiling points than MMA macromonomers and the higher molecular weight oligomers are difficult to isolate without crosslinking or degradation occurring. A second possible approach lies in the formation of mixed macromonomers by copolymerization of MMA and HEMA in the presence of CoBF. This would result in the formation of three trimer macromonomers containing two HEMA units., **A**, **B**, and **C**.



A



B



C

One of these three isomers, **B**, could be used to form hydroxy telechelic PMMA, and, as trimer would be used instead of dimer, a lower molecular weight polymer would be produced. It was surmised that, as the trimers contain one MMA unit, they should boil at a lower temperature than pure HEMA trimers and therefore might be easier to isolate.

2.4.1 Preparation and analysis of mixed macromonomers.

A number of polymerizations were carried out in which the ratio of MMA to HEMA and the amount of CoBF in the reaction mixture were varied. This resulted in low molecular weight oligomers which were distilled using a kugelrohr apparatus. The isolated fractions were analysed by SEC and the fractions that seemed to contain only one species were analysed by NMR. Two fractions showed only one *size* of species by SEC, but analysis by NMR showed more than one species to be present, Figure 2.15.

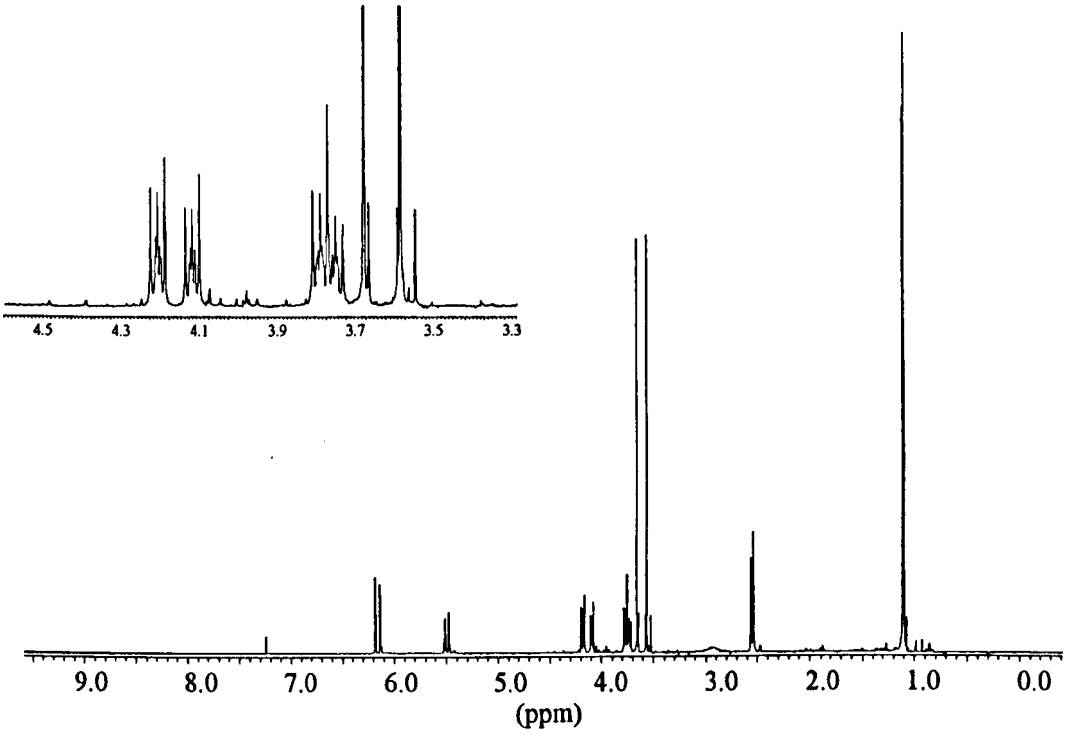
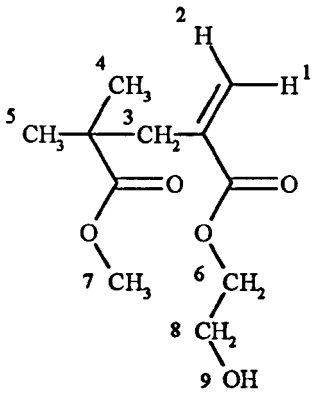


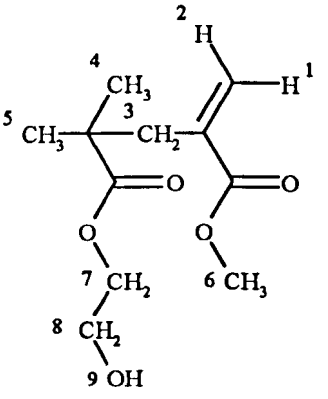
Figure 2.15 ^{1}H NMR spectrum ($CDCl_3$, 298 K, 250 MHz) of mixed macromonomer fraction collected at 125 °C and 0.02 mbar. The inset shows the expanded region of the O-CH_2-CH_2- and O-CH_3 groups of HEMA and MMA respectively.

Inspection of the ^{1}H NMR spectrum of the fraction collected at 125 °C, 0.02 mbar reveals the presence of two bridging methylene groups at 2.55 ppm and 2.53 ppm, indicating two different dimer units or one trimer unit. As the fraction was collected at a relatively low temperature it is thought likely to be a mixture of two dimers. Four peaks are seen in the vinyl region 6.18 to 5.47 ppm, which confirms the presence of two different dimer units rather than a trimer unit. The expanded region shown in Figure 2.15 from 3.3 ppm to 4.5 ppm also shows the presence of two different HEMA and two different MMA units. Integration of the two sets of peaks reveals that there are indeed two distinct arrangements, the multiplet at

4.20 to 4.16 ppm and that at 3.57 to 3.52 ppm being from one structure, those at 4.11 to 4.07 ppm and 3.65 to 3.56 from a different structure Two possible structures are shown below, **9** and **10**. Integration of the appropriate signals in the ^{1}H NMR spectrum reveal an approximate ratio of **9** : **10** of 55 : 45.



2.9



2.10

Assignment of the peaks in the ^{1}H-NMR spectrum of the mixed dimer, Figure 2.15, is given in Table 2.15 for peaks from structure **2.9** and Table 2.16 for peaks from structure **2.10**.

Table 2.15 Peak assignment for the ^{1}H NMR spectrum of mixed macromonomers collected at 125 °C, 0.02 mbar, peaks from structure **2.9**.

Chemical Shift (ppm)	Multiplicity	Assignment
6.18	singlet	H^1
5.47	singlet	H^2
4.20 - 4.16	multiplet	H^6
3.78 - 3.71	multiplet	H^8
3.57 - 3.52	multiplet	H^7
2.93	broad singlet	H^9
2.53	singlet	H^3
1.11	multiplet	H^4, H^5

Table 2.16 Peak assignment for the ^{1}H NMR spectrum of mixed macromonomers collected at 125 °C, 0.02 mbar, peaks from structure **2.10**.

Chemical Shift (ppm)	Multiplicity	Assignment
6.14	singlet	H^1
5.51	singlet	H^2
4.11 - 4.07	multiplet	H^7
3.78 - 3.71	multiplet	H^8
3.65 - 3.64	multiplet	H^6
2.93	broad singlet	H^9
2.56	singlet	H^3
1.11	multiplet	H^4, H^5

2.4.2 Analysis of Mixed Macromonomers by HPLC.

The separation of the mixed macromonomers by reduced pressure distillation did not result in the isolation of the required trimer. An alternative method of isolation for mixed macromonomers, and indeed the MMA and HEMA macromonomers, is High Performance Liquid Chromatography (HPLC). HPLC utilises differences in the polarity of various species. As with any liquid chromatography technique, HPLC involves the use of a mobile phase which is pumped over a stationary phase held in a tightly packed column. The analyte is dissolved in a solvent (usually the same as the mobile phase) and injected into the mobile phase. The analyte is separated into its components as a result of different interactions with the stationary phase, and the separated components are sensed by an on-line detector, often a UV-detector. The majority of stationary phases used in HPLC consist of uniform, porous silica particles. The silica particles have different chemical groups bonded to their surface (bonded phases) which allow the separation of various different species to be achieved. The column employed in this work contained silica particles with C-18 alkyl groups attached to their surface.

In the case of the mixed macromonomers, all macromonomers that are homopolymers of HEMA should have approximately the same polarity and thus elute from the column first. Whilst HPLC does not allow the separation of individual HEMA macromonomers, it does allow a mechanism for their isolation from mixed macromonomers and MMA macromonomers. Similarly, the MMA macromonomers all have a similar polarity and will therefore have approximately the same retention time; since they are less polar than HEMA macromonomers they will have longer retention times. Hence, HPLC should provide a mechanism

to separate the macromonomers according to the relative numbers of HEMA and MMA groups.

The work presented in this chapter was carried out using a mobile phase comprising of 70 % vol/vol water and 30 % vol/vol acetonitrile with 0.1 % vol/vol of trifluoroacetic acid (TFA), pumped at a rate of 0.5 mL min^{-1} through a C-18 5 μm column. The separated components were detected by UV at 235 nm and retention times were recorded relative to the injection time.

Analysis of a mixture of MMA dimer and HEMA monomer in acetonitrile under the conditions described above showed a clear separation of 3.5 mL between the two types of species, elution volumes of 8.25 and 3.25 mL respectively, Figure 2.16a. Analysis of a mixture of HEMA monomer, dimer and trimer showed one peak with two shoulders. The shoulders were due to the trimer species, eluted first, the dimer eluted slightly later. Analysis of a fraction of the mixed macromonomers containing structures **9** and **10** by HPLC gives a peak between the HEMA monomer and MMA dimer with an elution volume of 7 mL, all of the mixed dimer has eluted before the MMA dimer is eluted, Figure 2.16b. Hence it contains a species more polar than MMA dimer, but less polar than HEMA monomer. The peak shows a slight separation with two maxima, this is probably due to the two isomeric species present within the sample which may have slightly different polarities. Analysis of fractions collected at higher temperatures by HPLC shows the presence of a number of species in each fraction. However isocratic elution fails to give a clear separation between the fractions. This may be overcome by the use of gradient elution and a lower flow rate or smaller particle column packing. All of the fractions collected at higher temperatures also

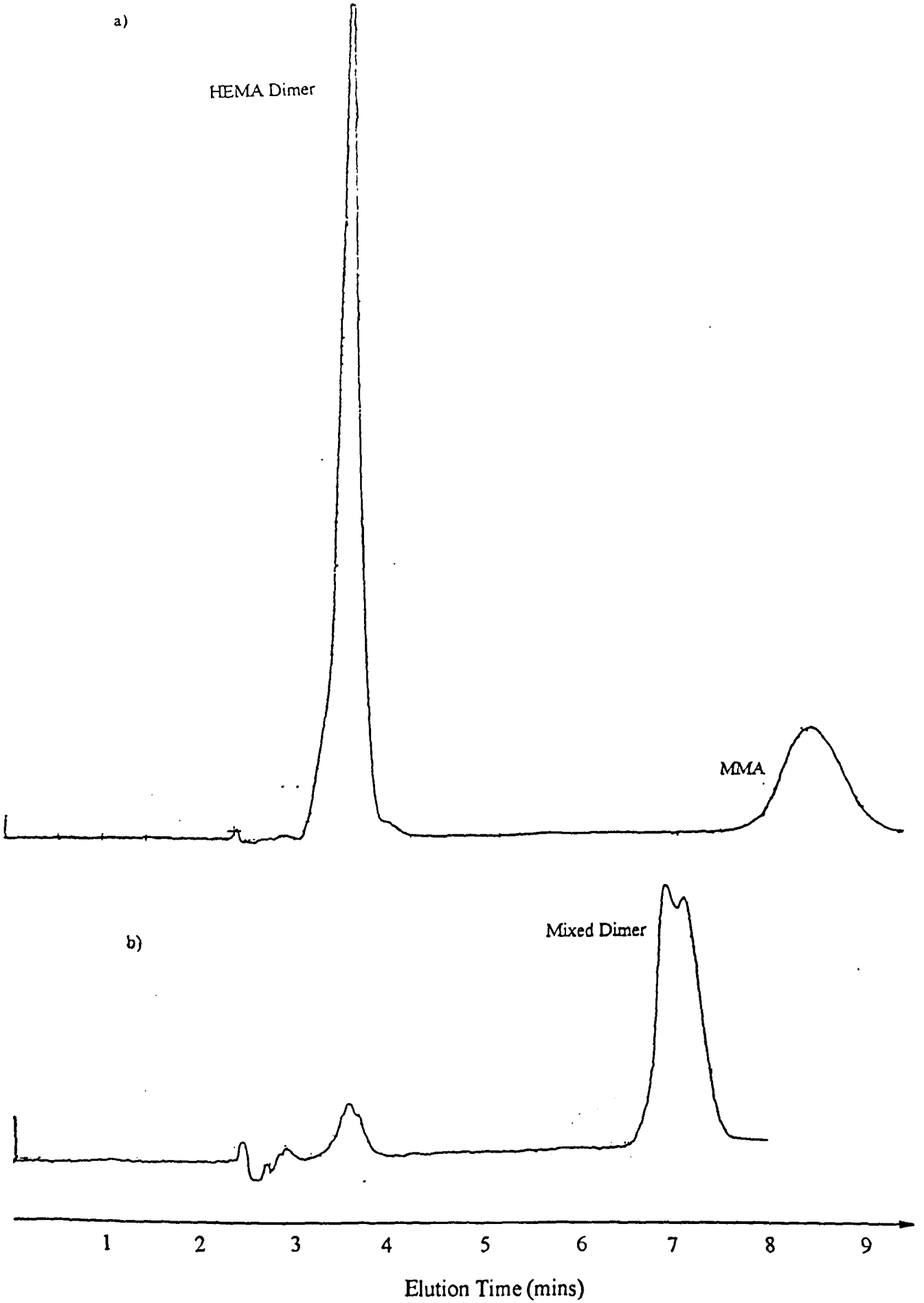


Figure 2.16 HPLC traces of a) HEMA dimer and MMA monomer and b) mixed MMA-HEMA dimer collected at 125 °C and 0.02 mbar.

contained HEMA homomacromonomers, indicating that the high temperatures lead to some degradation of the mixed macromonomers.

2.5 Conclusions

The use of reduced pressure distillation to separate mixed MMA-HEMA macromonomers resulted in the isolation of a number of isomeric species. Analysis by SEC revealed only one size of species, analysis by NMR showed more than one species to be present. These included a mixed MMA-HEMA dimer, both isomers of which were in an approximate ratio of 55:45.

The use of HPLC to separate the macromonomers made from the CCT copolymerization of MMA and HEMA has potential for future work. However, under the conditions used in this work, i.e. isocratic elution and a flow rate of 0.5 mL min^{-1} only some of the species were separable. These included the MMA and HEMA homomacromonomers and a mixed HEMA-MMA dimer. Under suitable conditions it may be possible to separate the two isomers of this mixed dimer.

2.6 References

1. Harrison, D. S. *The Chemistry of ω-unsaturated Oligomers and Polymers*; MSc. Thesis; Swimburne Institute of Technology, 1988.
2. McCord, E. F., Anton, W.L., Wilczek, L., Ittel, S.D., Nelson, L.T.J., Raffell, K.D., Hansen, J.E., Berge, C. *Macromol. Symp.* **1994**, *86*, 47.

Chapter

3.

Determination of the Chain Transfer Constants of Some Low Molecular Weight ω-Unsaturated Methacrylate Macromonomers

3.1 Introduction

The role of chain transfer agents in reducing the molecular weight of polymers and the chain transfer action of macromonomers have both been previously discussed in an earlier chapter, sections 1.2.1 and 1.3.2 respectively.

Although the chain transfer activity of methacrylate macromonomers has been recognised for a number of years, very little quantitative data concerning the chain transfer constants of these macromonomers or their molecular weight dependence has been published in the literature[1-3]. The traditional method for calculating chain transfer constants has been through the use of the Mayo equation, equation 3.1.

$$\frac{1}{DP} = \frac{1}{DP_0} + \frac{[S]}{[M]} \qquad (3.1)$$

where DP and DP_0 are the number average degrees of polymerization with and without chain transfer agent respectively, and [S] and [M] are the concentrations of chain transfer agent and monomer respectively.

However, as described in the introduction, macromonomers do not behave as conventional chain transfer agents and the possibility of a depropagation step along the polymer backbone alters the polymerization rate. The Mayo equation does not have any components that take this into account. Instead, a new equation has been derived[1] that allows for any variation in conversion with the amount of macromonomer in the feed, equation 3.2.

$$DP = \frac{[M]_o p}{(2 - F_c) f [I]_o (1 - \exp(-k_d t) + C_s [S]_o \ln(1 - p)} \qquad (3.2)$$

where DP is the number average degree of polymerization,

$[M]_0$, $[I]_0$, $[S]_0$ are the initial concentrations of monomer, initiator and chain transfer agent,

p is the conversion,

f is the initiator efficiency, (the value of 'f' for AIBN in the polymerization of MMA is typically around 0.6 - 0.7 so a value of 0.6 is assumed),[4]

Fc is the fraction of termination that occurs by combination (a value of 0.25 is used) and

k_d is the rate constant for decomposition of initiator (a value equated using the formula $k_d = 1.34 \times 10^{15} \exp(-15500/T)$ is used[5])

For the derivation of this equation see Appendix 1.

In order to use macromonomers to control polymerizations it is necessary to understand their polymerization behaviour. It was for this reason that the chain transfer constants of methyl methacrylate dimer and trimer with methyl methacrylate monomer at molar concentrations of 0 to100 % and for MMA trimer with BMA monomer and BMA trimer with MMA monomer at molar concentrations of macromonomer 0 to 10 % were determined using equation 2. As it is apparent that the macromonomer concentration in the feed affects the polymerization rate and hence the chain transfer activity, a range of Cs values will be reported for each combination of monomer and macromonomer.

It has been postulated that a number of factors can affect the chain transfer activity of macromonomers. These include steric effects, chain length, partitioning of the radical intermediates between products and starting materials and the amount of macromonomer in the feed. This chapter aims to investigate

these hypotheses in addition to providing a comparison between published literature values and values calculated using different methods.[1-3] The majority of the work in the literature involves the determination of Cs values for low concentrations of MMA dimer and trimer with MMA, this present work investigates these effects more comprehensively by providing a comparison with other macromonomers (BMA trimer) and by calculating Cs values across the entire concentration range for MMA dimer and trimer.

3.2 Experimental

Methacrylate macromonomers were prepared by the catalytic chain transfer polymerization of the appropriate monomer employing CoBF as chain transfer agent. Dimer and trimer were isolated by reduced pressure distillation using a kugelrohr apparatus under the conditions shown in Chapter 2, Table 2.1.
The purity of the macromonomers was verified by SEC and ^{1}H-NMR. (See Section 2.1.)
Bulk polymerizations were carried out in sealed ampoules containing various mixtures of stock solutions in order to give molar concentrations of macromonomer varying from 0-100 % or 0-10 %. Reactions were stopped after 2 hours in order to keep conversions below approximately 10 % to ensure that the composition of the solution did not change significantly and that secondary reaction of the macromonomer formed by the chain transfer reactions does not play a significant role. Number average molecular weights were obtained by SEC and conversions by precipitation of the products into hexanes. Chain transfer

constants were calculated using equation 3.2. For full experimental details see section 7.4.

3.3 Results

Reaction conditions and polymerization data are given in Tables 3.1, 3.2, 3.3, and 3.4 for MMA dimer with MMA (0 - 100 % mole/mole), MMA trimer with MMA (0 - 100 % mole/mole), MMA trimer with BMA (0 - 10 % mole/mole) and BMA trimer with MMA (0 - 10 % mole/mole) respectively.

As described previously, a number of chain transfer constants in the literature have been calculated using the Mayo equation. However, as shown in Figure 3.1, a Mayo plot of the results obtained from methacrylate macromonomers, Table 3.2 yields a curve as opposed to a straight line.

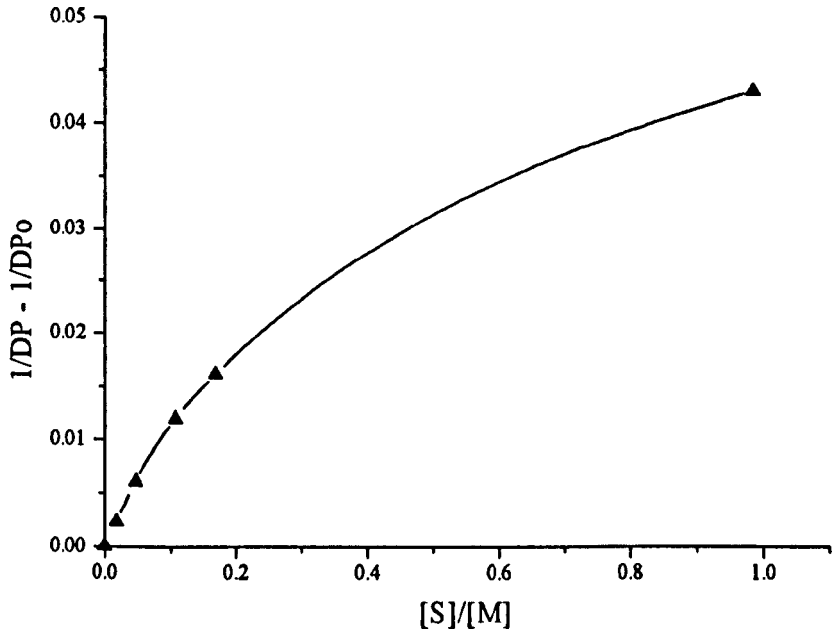


Figure 3.1 Mayo plot for bulk polymerizations of MMA trimer with MMA plotted using data from Table 3.2.

3.3.1 Chain transfer activity of MMA dimer in bulk MMA polymerizations.

Table 3.1 below shows the reaction conditions and polymerization data for MMA polymerizations with MMA dimer at 0 - 100 mole %.

Table 3.1 Polymerization Data for MMA dimer with MMA.

Mole Fraction MMA Dimer	Conc. AIBN (mol dm^{-3})	Conversion[a]	Mn	PDi	Cs[b]
0	0.0027	5.07	516600	2.30	-
0	0.0027	8.49	460800	2.37	-
0	0.0027	7.07	885400		-
0.0189	0.0027	7.63	224900	2.97	0.0104
0.0190	0.0027	9.36	305300	1.76	0.0066
0.0191	0.0027	7.89	250600	2.28	0.0083
0.0484	0.0027	6.49	176100	1.83	0.0052
0.0484	0.0027	5.67	147900	1.88	0.0065
0.0484	0.0027	9.10	159500	2.22	0.0078
0.1008	0.0027	2.84	83600	2.18	0.0039
0.1007	0.0027	3.82	67800	2.19	0.0081
0.1007	0.0027	5.46	80800	2.35	0.0074

0.1936	0.0027	5.58	37800	2.41	0.0089
0.1936	0.0027	5.52	36400	2.36	0.0093
0.1936	0.0027	6.57	44800	2.13	0.0074
0.5292	0.0027	2.17	11100	1.93	0.0057
0.5291	0.0027	3.46	10200	1.77	0.0072
0.5290	0.0027	4.36	8120	2.20	0.0096
0.6920	0.0027	1.68	6000	1.59	0.0050
0.6927	0.0027	1.82	6150	1.77	0.0050
0.9054	0.0027	1.47	-	-	-
0.9054	0.0027	0	-	-	-
1	0.0027	-	-	-	-

a conversion based on MMA monomer in feed

b calculated using equation 3.2

Figures 3.2 to 3.4 show the effect of changing the amount of macromonomer in the feed on molecular weight, conversion and chain transfer coefficient, respectively. Due to the large amount of data generated, average values only are presented in the graph.

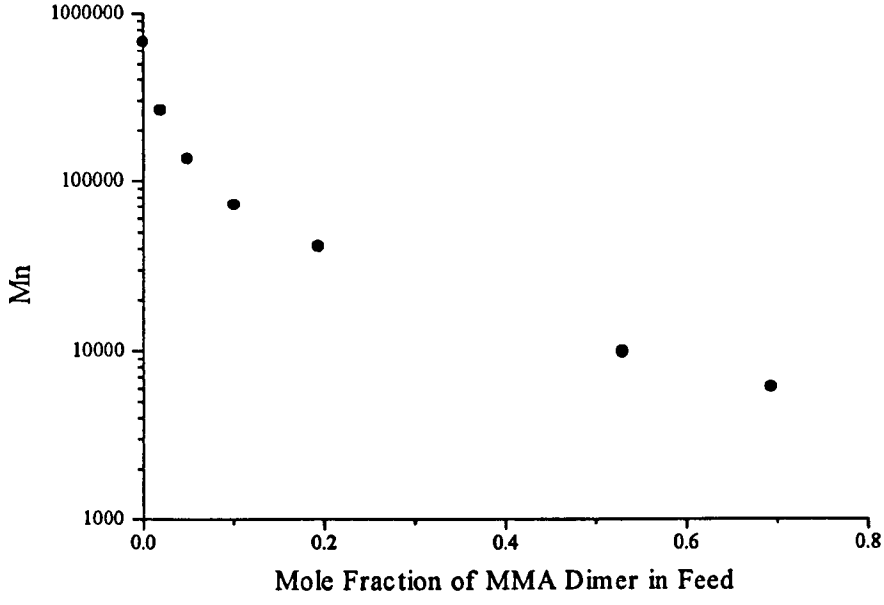


Figure 3.2 The dependence of molecular weight on feed composition for MMA with MMA dimer (average values).

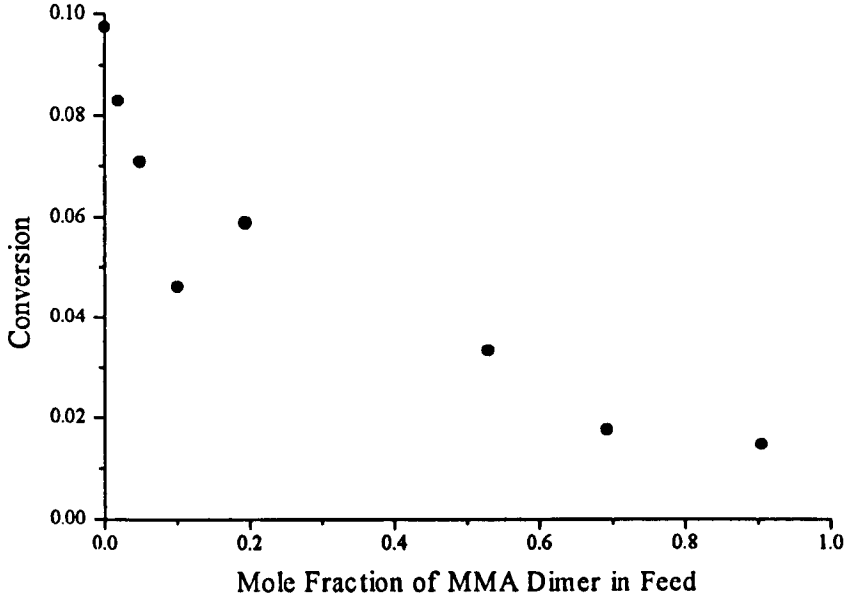


Figure 3.3 Reduction in conversion with increasing amounts of MMA dimer in feed (average values).

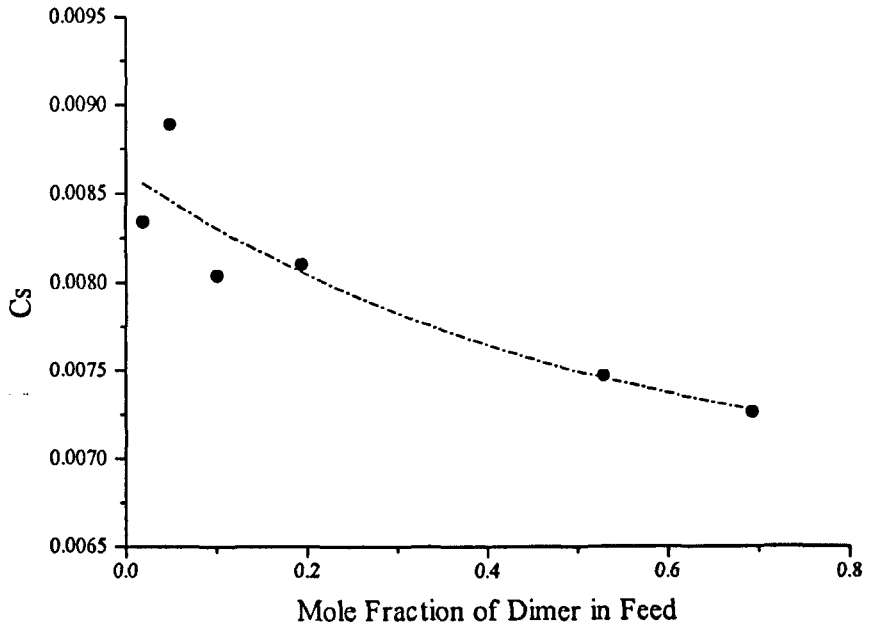


Figure 3.4 Average Cs values for MMA dimer with MMA

3.3.2 Chain Transfer Activity of MMA Trimer in Bulk Polymerizations of MMA

The reaction conditions and molecular weight data for polymerizations of MMA with MMA trimer (0 - 100 mole %) are shown below in Table 3.2.

Table 3.2 Polymerization data for MMA with MMA trimer

Mole Fraction MMA Trimer	Conc. AIBN (mol dm^{-3})	Conversion[a]	Mn	PDi	Cs[b]
0	0.0027	9.74	678700	2.18	-
0.0174	0.0027	10.16	40900	2.09	0.1219
0.0174	0.0027	10.80	40900	2.13	0.1217
0.0451	0.0027	9.22	16100	2.17	0.1212
0.0971	0.0027	9.29	8100	1.87	0.1078
0.0971	0.0027	9.57	8500	1.84	0.1025
0.1446	0.0027	8.27	6200	1.79	0.0903
0.4966	0.0027	3.65	2400	1.20	0.0400
0.4966	0.0027	3.09	2350	1.21	0.0403
0.5650	0.0027	1.91	-		-
0.9081	0.0027	0.69	-		-
1	0.0027	0	-		-

a conversion based on MMA in feed

b calculated using equation 3.2

Figures 3.5 to 3.7 show the variation in molecular weight, conversion and chain transfer activity respectively with increasing amounts of MMA trimer in the feed. Due to the large amount of data generated only average values are shown.

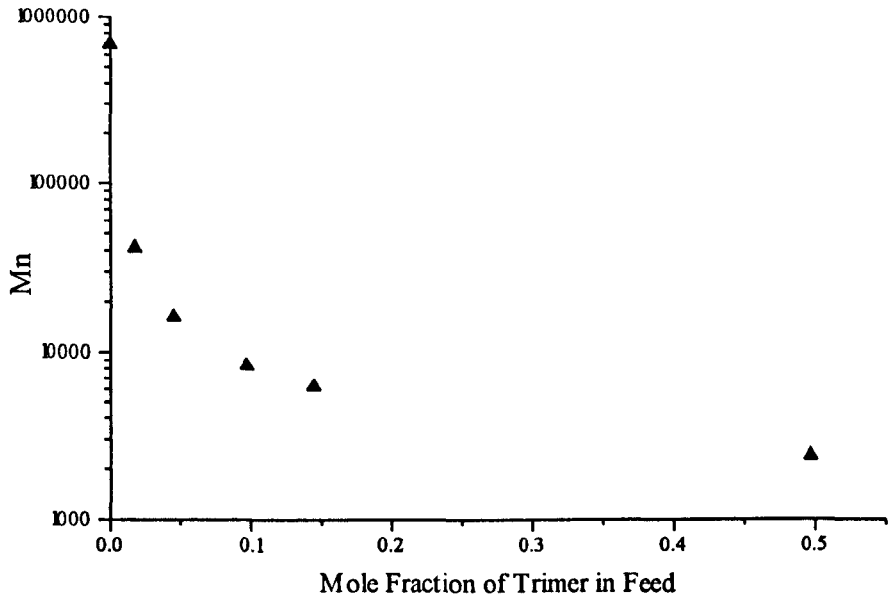


Figure 3.5 The dependence of molecular weight on macromonomer concentration for MMA with MMA trimer (average values).

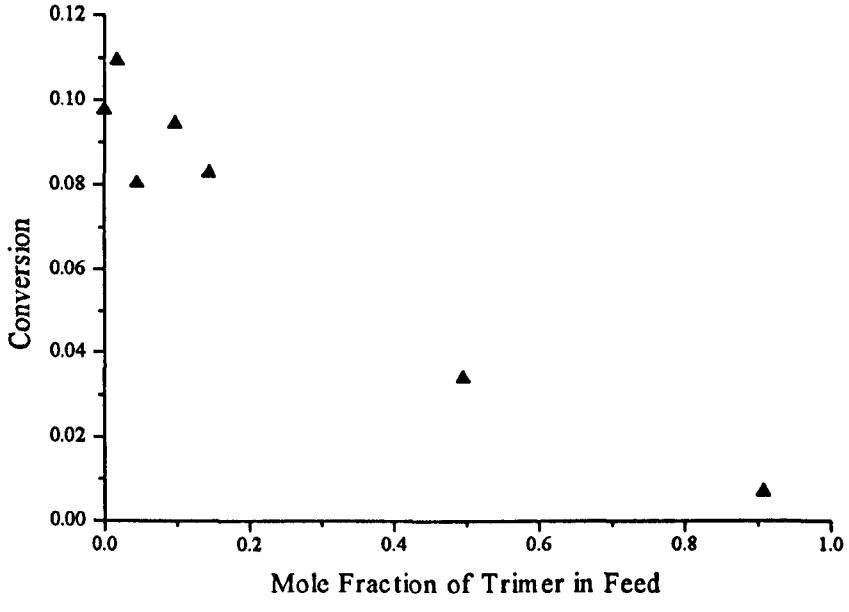


Figure 3.6 Variation in conversion with increasing amounts of MMA trimer in the feed for bulk polymerizations of MMA.

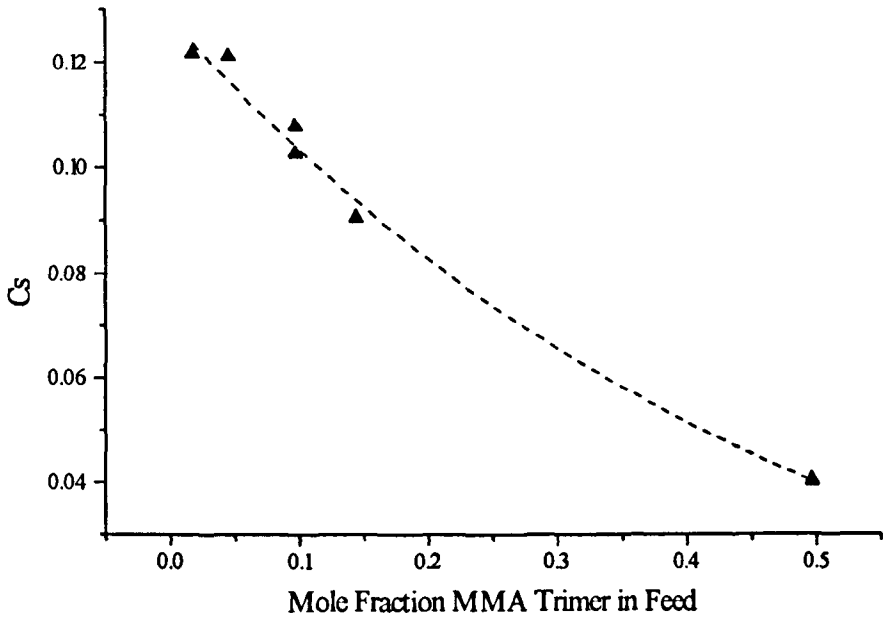


Figure 3.7 Average Cs values for MMA trimer with MMA

3.3.3 Chain Transfer Activity of MMA Trimer with BMA

Table 3.3 below shows reaction conditions and molecular weight data obtained for the polymerization of BMA in the presence of MMA trimer (0-10 mole %). Variation in molecular weight, conversion and chain transfer activity for bulk polymerizations of BMA with varying amounts of MMA trimer are shown in Figures 3.8, 3.9 and 3.10, respectively.

Table 3.3 Polymerization Data for BMA with MMA trimer

Mole Fraction MMA Trimer	Conc. AIBN (mol dm^{-3})	Conversion[a]	Mn	PDi	Cs[b]
0	0.0027	3.74	627800	1.85	-
0	0.0027	13.38	220600	3.43	-
0.0207	0.0027	14.15	49300	1.69	0.1184
0.0207	0.0027	3.01	51000	1.69	0.0881
0.0529	0.0027	12.39	24500	1.53	0.0935
0.0529	0.0027	12.47	23900	1.55	0.0958
0.1098	0.0027	8.17	15400	1.35	0.0686
0.1098	0.0027	7.86	15000	1.36	0.0704

a conversion based on BMA in feed

b calculated using equation 3.2

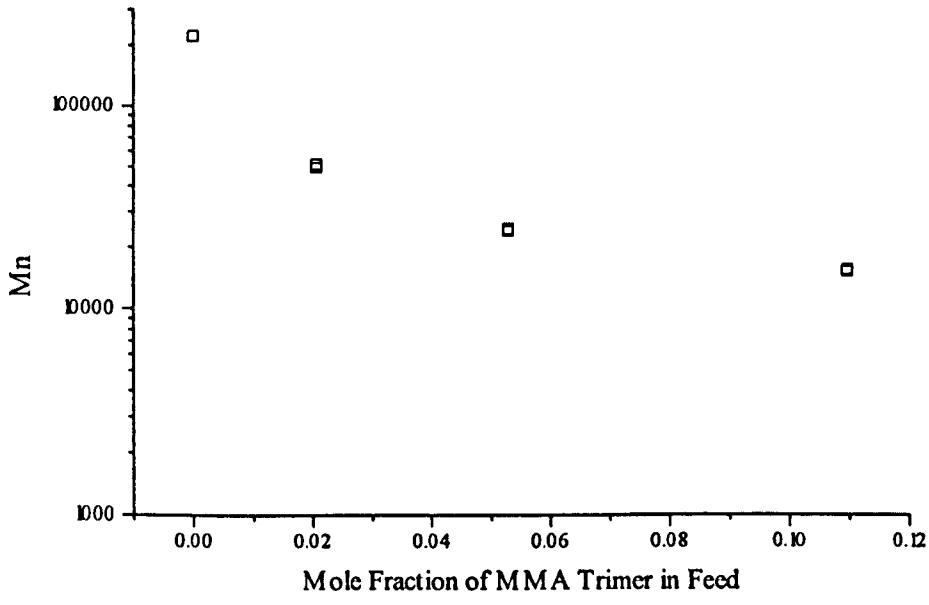


Figure 3.8 Dependence of Molecular Weight on Trimer Concentration.

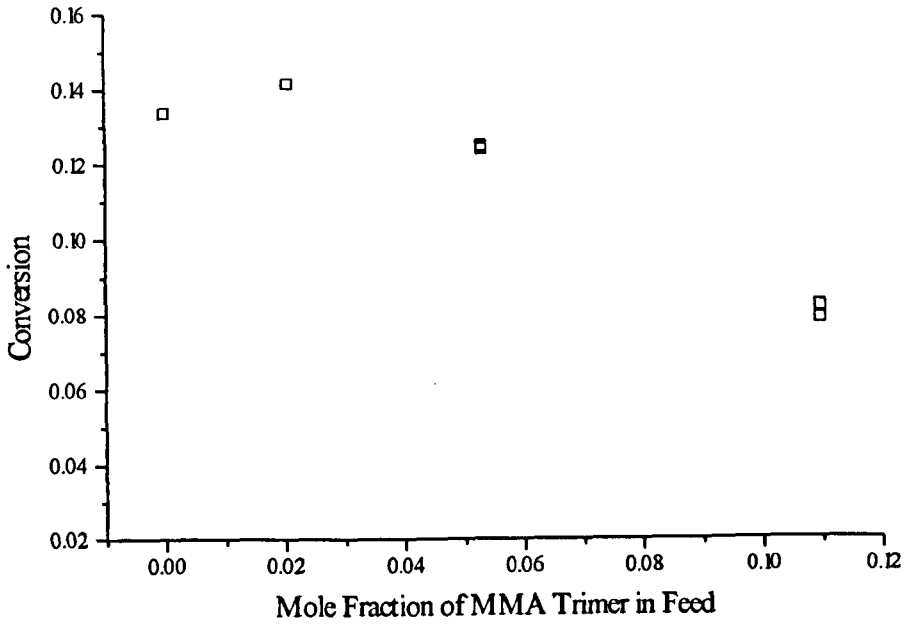


Figure 3.9 Variation in conversion for the polymerization of MMA trimer with BMA

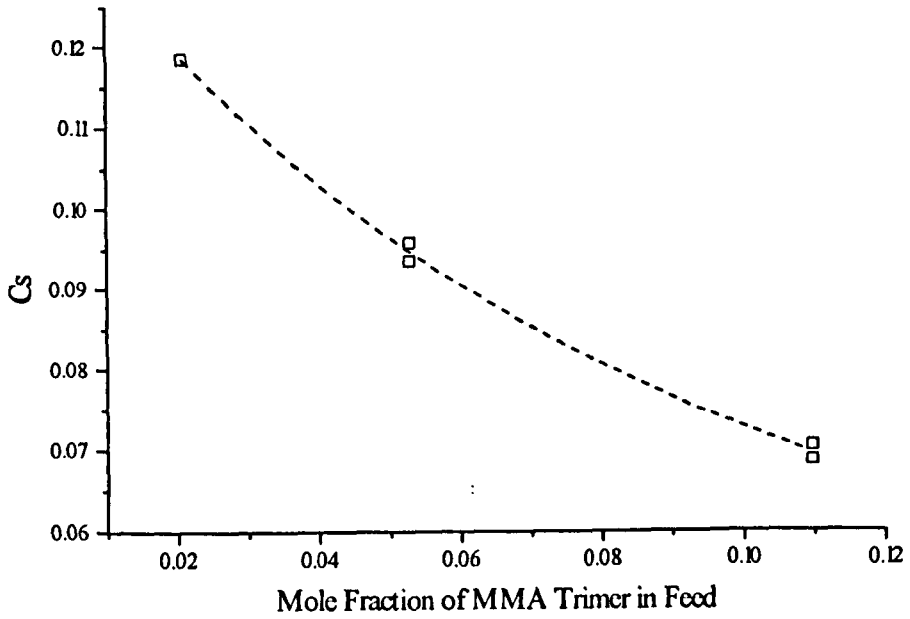


Figure 3.10 Dependence of chain transfer activity of MMA trimer with increasing mole fraction in feed.

3.3.4 Chain Transfer Activity of BMA Trimer with MMA

The chain transfer coefficient of BMA trimer with MMA monomer was measured for feeds with 0 - 10 % mole/mole, results and reaction conditions are shown in Table 3.4. Figures 3.11 to 3.13 show the effect of altering the BMA trimer content of the feed on the molecular weight of the final polymer, the conversion and the chain transfer activity of the macromonomer.

Table 3.4 Polymerization data for MMA with BMA trimer

Mole Fraction BMA Trimer	Conc. AIBN (mol dm^{-3})	Conversion[a]	Mn	PDi	Cs[b]
0	0.0028	25.30	553000	1.95	-
0.0120	0.0028	8.38	46700	1.66	0.1514
0.0120	0.0028	13.20	42800	2.03	0.1687
0.0320	0.0028	9.64	19800	1.72	0.1400
0.0719	0.0028	9.06	9110	1.64	0.1320
0.0719	0.0028	9.29	9240	1.63	0.1301

a based on MMA in feed

b calculated using equation 3.2

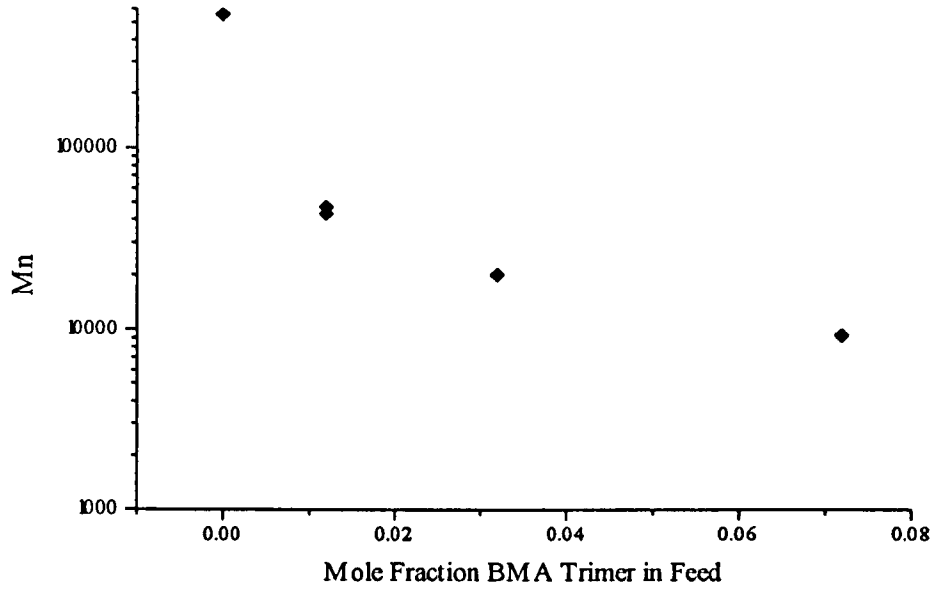


Figure 3.11 Dependence of molecular weight on amount of BMA trimer in feed

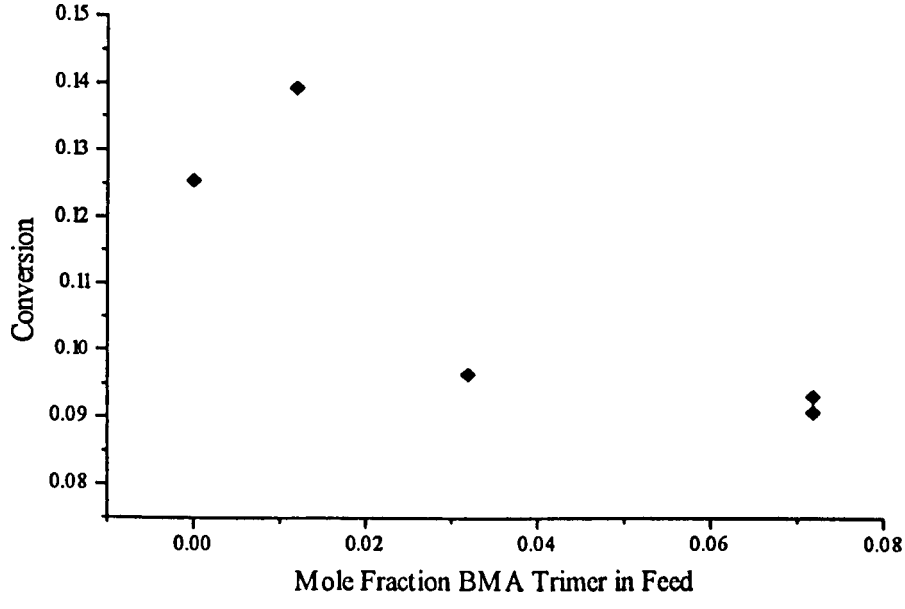


Figure 3.12 Dependence of conversion on amount of BMA trimer in feed

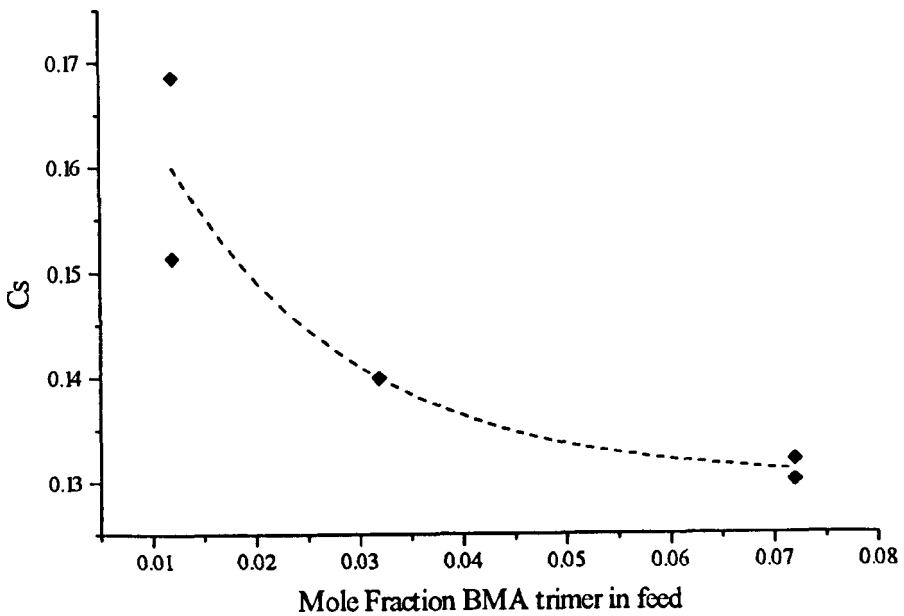


Figure 3.13 Dependence of Cs value on the mole fraction of BMA trimer in the feed.

3.4 Discussion:

The addition of MMA and BMA macromonomers to free radical bulk polymerizations of MMA and BMA has shown that, unless forcing conditions are used, macromonomers act only as chain transfer agents and do not copolymerize.[6,7] Figures 3.2, 3.5, 3.8 and 3.11 show that the addition of even small amounts of methacrylate macromonomer to methacrylate polymerizations brings about a significant reduction in molecular weight, i.e. they act as chain transfer agents. Molecular weights of approximately 700000 for methacrylate polymerizations without macromonomer are reduced to approximately 80000 with only 10 mole % MMA dimer and approximately 9000 with less than 10 mole

% MMA or BMA trimer with MMA and approximately 15000 for 10 mole % MMA timer with BMA, a reduction of one or two orders of magnitude. This can be ascribed to the entropically favorable β-scission chain transfer mechanism shown in Figure 3.14, which for these systems is the predominant reaction pathway for the radical adduct.

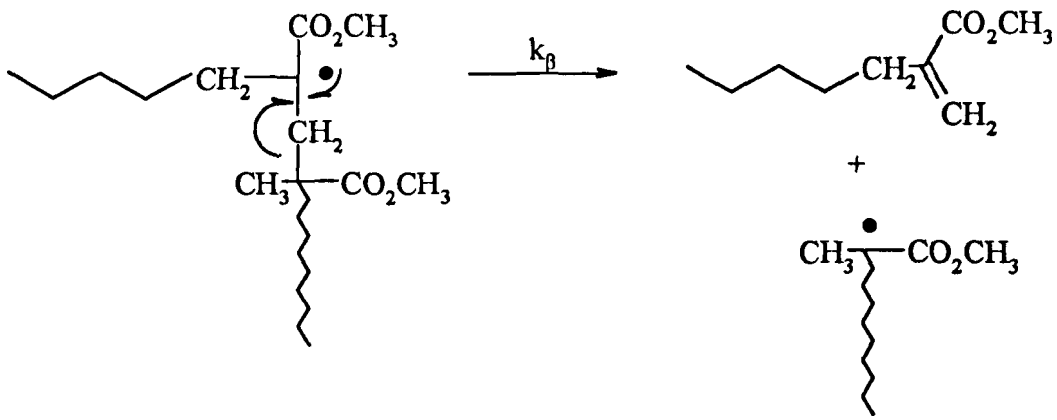


Figure 3.14 β-scission (radical-addition-fragmentation) chain transfer mechanism for methacrylate macromonomers

Figures 3.3, 3.6, 3.9 and 3.12 show that conversion decreases with increasing macromonomer concentration for all the systems investigated. The reduction in Mn observed for MMA dimer reactions, Figure 3.2, has been confirmed by the work conducted by other researchers.[1,2] This could be due to a number of reasons. Firstly, the new macroradical formed by the transfer reaction could be slow to reinitiate. However this is unlikely since, in the case of the dimer, β-scission results in a monomeric radical; other macromonomers produce a radical identical to a propagating PMMA radical. A second reason could be the absence of the gel effect, which is caused by the higher viscosity of the macromonomers compared to small monomers. In free radical reactions an acceleration in the rate

of polymerization is observed at a conversion around 10 - 15 %. This is caused by the increase in viscosity of the reaction solution brought about by the increasing molecular weight of the polymer chains. This leads to a reduction in the mobility of the chain ends, and hence a reduction in radical-radical termination reactions, which leads to a rapid increase in polymerization rate. Since the predominant mode of termination in reactions involving methacrylate macromonomers and monomers is chain transfer, more mobile, lower molecular weight chains are produced. The absence of the gel effect means that there is no acceleration in the rate of polymerization and hence a lower conversion will be obtained for a given reaction time. This has also been observed by other workers[1,2]. Suddaby[1] conducted a number of conversion-time experiments for MMA dimer at concentrations of 2, 5 and 10 mole % with MMA. The reaction at 10 mole % showed no autoacceleration but the autoacceleration became more apparent at lower macromonomer concentrations, i.e. increased macromonomer concentration leads to increased suppression of the gel effect. This was also observed by Rizzardo and co-workers[2] who compared bulk polymerizations with and without added macromonomer (MMA dimer and MMA trimer). Again, no acceleration in conversion for reactions involving macromonomer was observed. The reduction in conversion in those polymerizations involving MMA dimer was attributed to a third possibility, the preferential partitioning of intermediates towards the starting materials. Thus the number of depropagation events in this system is significant, Figure 3.15.

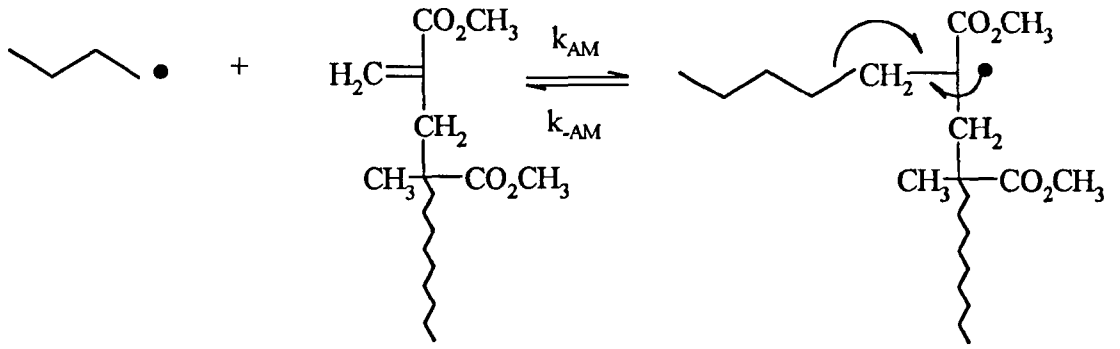


Figure 3.15 Depropagation mechanism for methacrylate macromonomers.

The radical intermediate formed by addition of macromonomer to propagating polymer chain could undergo two possible fragmentation mechanisms. In the case of dimer, β-scission results in the formation of an unstable monomer radical while the alternative pathway leads to the formation of starting materials. This proposal is also consistent with the observation made by Tanaka et al[8] that the radical formed by the addition of MMA dimer to 2-carbomethoxy-2-propyl radicals is persistent, hence the 2-carboalkoxy-2-propyl radical would appear to be a poor radical leaving group. The reactions involving MMA and BMA trimer also show a slight reduction in conversion, e.g. from 25.3 % without trimer to 9.2 % with 10 mole % BMA trimer added, although it is not as dramatic as the effect seen with dimer. Figure 3.9 and Figure 3.12 indicate only a small reduction in conversion over the range of feed composition shown. However, Figure 3.6 shows a greater decrease in conversion at higher molar concentrations of macromonomer. This would seem to indicate that the suppression of the gel effect caused by the increased viscosity of the starting mixture (compared with that for a polymerization in the absence of macromonomer) plays a significant role. Retardation caused by slower initiation by the dimer radical species formed by

chain transfer (although this would be expected to be negligible since it is analogous to the propagating polymer chain), slow β-scission and the partitioning of the intermediate towards the starting materials could also be partly responsible for the differences seen in conversion. Rizzardo et al[2] state that no retardation in bulk polymerizations of MMA with MMA macromonomers occurs and that the addition of MMA trimer and tetramer to polymerizations does not alter the conversion seen for a given reaction time. They ascribe this to the absence of partitioning towards starting materials with higher molecular weight macromonomers, since increasing the molecular weight of the macromonomer reduces the difference in the bulkiness between the starting and product radicals. Both are MMA propagating species, and for chain lengths greater or equal to tetramer the partitioning would be expected to be equal.

Figure 3.16 shows the variation in Cs values determined for all reaction systems with between 0 - 10 mole % macromonomer in the feed. The values obtained for trimers are an order of magnitude higher than those for dimers. A variety of factors are thought to influence the specificity of addition-fragmentation reactions. In this work many of these factors are the same for all the chain transfer agents studied and hence steric factors are thought to be the main influence in determining the preferred fragmentation pathway. The intermediate species formed by the addition of macromonomer to the growing polymer chain can follow one of three pathways. From the β-scission scheme shown in Figure 3.14 it can be seen that in the case of dimer, β-scission results in the formation of a monomeric radical, whereas trimer forms a dimer radical which is sterically more

stable, hence the driving force for β-scission is greater for trimer than for dimer. As discussed earlier, Rizzardo et al[2] also claim that the difference in chain transfer activity is due to preferential partitioning of the dimer reaction towards the starting materials thus resulting in a reduction in conversion for reactions involving dimer that is not seen with trimer reactions. However, as the data collected in this thesis shows, there is a slight reduction in conversion for reactions involving trimers, although it is not as pronounced as for dimer. This could explain the lower chain transfer activity of methacrylate dimer but probably only plays a small part in the difference in chain transfer activity observed between MMA dimer and higher oligomers, e.g. trimer, tetramer.

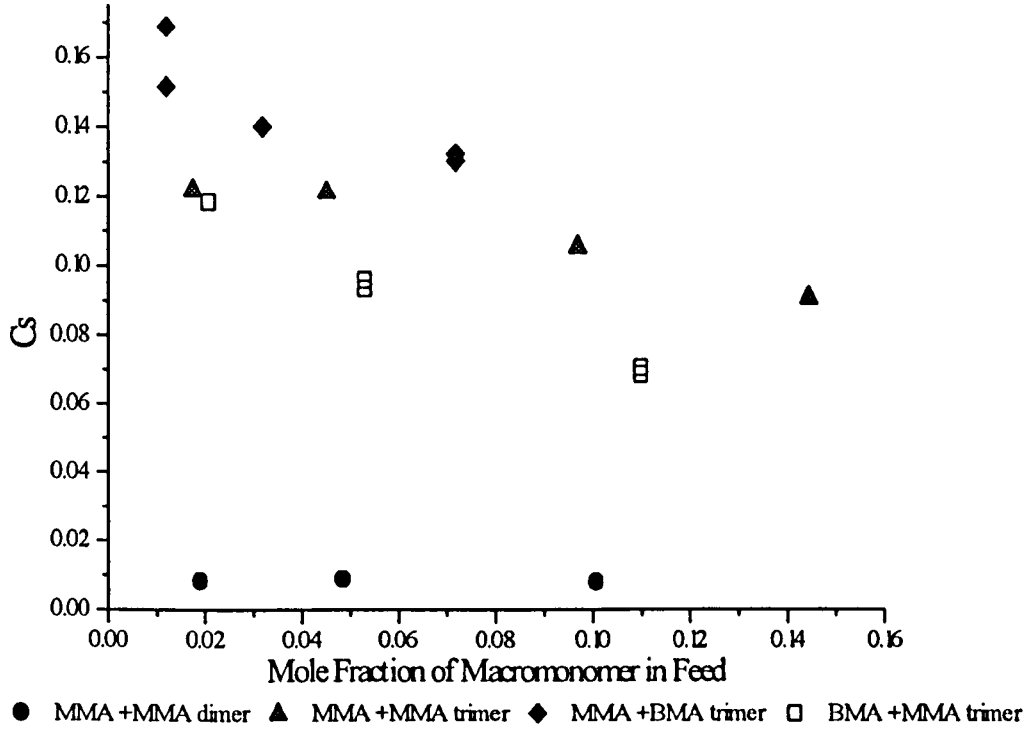


Figure 3.16 Variation in chain transfer efficiency with macromonomer concentration.

Although the chain transfer constants determined for MMA and BMA trimer are of a similar order of magnitude and are both an order of magnitude higher than those calculated for dimer, slight variations in value are seen, Figure 3.16. For a given concentration of macromonomer BMA trimer has a higher Cs value than MMA trimer. This would seem to reinforce the view that steric factors play the major role in determining the chain transfer activity of a macromonomer, since the product of β-scission would be more sterically hindered and hence slightly more stable than that formed from MMA trimer.

Conversely, the reaction of BMA with MMA trimer yields lower chain transfer constants than the reaction of MMA with MMA trimer. This could be due to the slightly lower conversions obtained with BMA which could be attributed to increased partitioning towards the starting materials as a BMA terminated radical would be more sterically stable than the MMA terminated radical intermediate.

The plot of Cs versus macromonomer feed concentration, Figure 3.16, demonstrates that the chain transfer activity appears to decrease as the amount of macromonomer is increased, for all the systems studied. This has been observed by other workers[1] and has been attributed to an effect similar to the 'bootstrap effect' suggested by Harwood[9] to explain the apparent differences between monomer reactivity ratios determined in different solvents. It was proposed that the composition of the medium around the propagating polymer chain is different to that in the bulk of the solution and that there is a partitioning of the macromonomer between the free solvent and the microdomains around the propagating radicals. Thus the different properties of the environment surrounding a polymer chain compared to those of a monomer solution e.g.

increased viscosity, will affect the distribution of species throughout the solution. The increase in chain transfer coefficient with decreasing macromonomer concentration would seem to suggest that the macromonomer is found preferentially around the propagating radicals. If the macromonomer was located preferentially in the bulk of the solution, or if it was distributed evenly, then altering the concentration would not be expected to alter the chain transfer activity. However, if the macromonomer were preferentially found in the vicinity of the propagating centres then the enrichment of the macromonomer relative to the bulk of the solution would be more significant at lower macromonomer concentrations. At higher concentrations the composition of the solution around the polymer chain is more similar to the bulk of the solution, so the effect of the enrichment is diminished. This effect is greater for reactions involving trimers, as would be expected since trimers are closer in structure to the propagating radicals than dimers. Hence, trimers would be more likely to be found in the environment of the propagating chain than dimers.

One effect that is also quite noticeable, particularly in the case of the methacrylate trimers, is the low polydispersity of the polymers made with higher concentrations of macromonomer. This effect has also been observed by other workers, who have used this form of controlled growth polymerization in order to form narrow polydispersity polymers and block copolymers.[10] The low polydispersity is a result of the "livingness" of the macromonomers formed by the β-scission reaction. The macromonomer that is formed by β-scission can add to a growing polymer chain, where it will undergo further β-scission and the resulting macromonomer radical can reinitiate polymerization by addition of monomer. In

this way the macromonomer formed by β-scission will undergo some chain extension. Radical-radical termination results in the formation of non-macromonomer, i.e. dead chains, but the presence of the macromonomer lowers the proportion of termination that occurs in this way in comparison with conventional free radical polymerizations. This is because the β-scission provides a pathway for the conversion of mobile short chains to longer, less mobile, chains. Hence, as the reaction proceeds the polydispersity will decrease and the more chain transfer events that take place the lower the probability of radical-radical termination.

3.5 Conclusions

The results obtained in this work indicate that methacrylate dimers and trimers behave as chain transfer agents in methacrylate polymerizations. Table 3.5 overleaf shows the chain transfer constants for various chain transfer agents with MMA at 60 °C including a catalytic chain transfer agent, CoBF, conventional chain transfer agents, alkyl halides and mercaptans, and methyl methacrylate dimer and trimer macromonomers with methyl methacrylate.

Table 3.5 Chain transfer constants for some commonly used chain transfer agents.

Chain transfer agent	C_s
CoBF	~40 000[6]
CCl_4	2.4[11]
EtSSEt	0.00013[11]
MMA Dimer	~0.01
MMA Trimer	~0.1

Although methacrylate dimers and trimers are less efficient chain transfer agents than catalytic chain transfer agents, e.g. CoBF, by several orders of magnitude they exhibit chain transfer activity that is comparable to many commonly used chain transfer agents, e.g. disulfides and organohalides.

The results obtained in this work are comparable to those already available in the literature which appeared after this work had been completed.[1-3] Table 3.6 shows values of chain transfer coefficients for bulk MMA polymerizations with added macromonomer obtained from the literature.

Table 3.6 Comparison of chain transfer constants for MMA macromonomers with MMA at 60 °C from the literature.

Macromonomer	Cs	Reference
MMA Dimer	0.0075[a]	This thesis
MMA Trimer	0.1[a]	This thesis
MMA Dimer	0.0049[a]	1
MMA Trimer	0.12	3
MMA Tetramer	0.21	3
MMA Dimer	0.013	2
MMA Trimer	0.19	2
MMA Tetramer	0.29	2

a calculated for 10 % mole/mole dimer

The value presented in Table 3.6 from reference 1 was calculated for 10 mole % MMA dimer using a similar equation to equation 2 and is similar to the value obtained in this work. The values published in reference 2 were calculated by analysis of the natural logarithm of the chain length distributions. As in reference 3, only one value of chain transfer constant is given for each macromonomer, both dimer and trimer chain transfer constants being of a similar order of magnitude to those presented in this thesis. The values presented in reference 3 were calculated using a Mayo plot, hence only one value is given for each macromonomer species and can only be an approximate value due to the curvature of the graph demonstrated at the beginning of Section 3.3. However, the value of 0.12 obtained for MMA trimer is similar to that obtained in this work.

All of the results obtained can be explained in terms of the addition-fragmentation mechanism outlined in Chapter 1. They support the view that it is the reactivity of the double bond and the partitioning of the intermediate radical formed by the addition of a macromonomer to a propagating centre that determine the chain transfer activity of the macromonomer. The chain transfer constant obtained for trimer is an order of magnitude higher than that obtained for dimer. This is due to steric effects and the preferential partitioning of the dimer towards the starting materials resulting in a reduction in polymerization rate. Although an increase is seen in the literature values when the chain length is increased from trimer to tetramer[2], this is not as great an increase as that seen on going from dimer to trimer since the difference in bulkiness between the two species is not as great. Changes in the monomer to be polymerized or the chain length of the macromonomer do not have as large an effect as changing from dimer to trimer or from trimer to tetramer. Addition of macromonomer to a reaction substantially suppresses or eliminates the gel effect, leading to a reduction in the observed conversion compared to that seen in a bulk polymerization carried out in the absence of chain transfer agent.

3.6 References

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Chapter

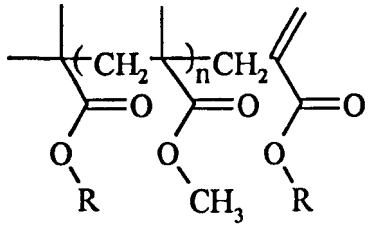
4.

Telechelic Polymers by Addition-Fragmentation Chain Transfer.

4.1 Introduction.

The formation and uses of telechelic polymers have been reviewed in an earlier chapter, section 1.6. Addition-fragmentation chain transfer offers a viable route to telechelic polymers via a free radical process, with all of the associated advantages that radical polymerization offers.[1,2,3] The use of addition-fragmentation chain transfer agents in the formation of telechelic polymers has received considerable interest in recent years.[4] However, most of these involve the use of sulfur or oxygen containing compounds which introduce possible sites of chemical weakness into the polymer. Although the use of methacrylate macromonomers has been mentioned in patents published by workers at Du Pont,[5] no work has been published in the literature concerning the specific use of functional methacrylate dimers to form telechelic polymers.

This present work aims to show the necessary reaction conditions for the formation of telechelic polymers by the addition fragmentation chain transfer of methacrylate dimers. The macromonomers employed in this work are HEMA, GMA and BzMA dimer which were added to polymerizations of MMA in order to determine whether or not functionality or size had any effect on the chain transfer activity of the macromonomer. Addition-fragmentation of the dimer in polymerizations with MMA results in a polymer with structure **4.1**,

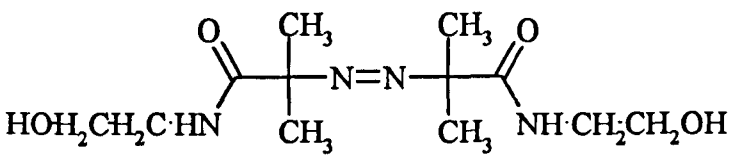


4.1

where R is CH_2CH_2OH, and either an epoxy ring or an aromatic ring.

HEMA dimer was also added to BMA and LMA polymerizations in order to confirm that the chain transfer mechanism is applicable to other monomers, with the further aim of forming polymers with a different backbone that can be further reacted to form block copolymers containing segments with different glass transition temperatures.

The polymerizations were initiated using a hydroxyl containing azo initiator, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] (VA-086), **4.2**, which has a half life of 1020 minutes at 80 °C, to ensure that all polymer chains contained an α-functionality.

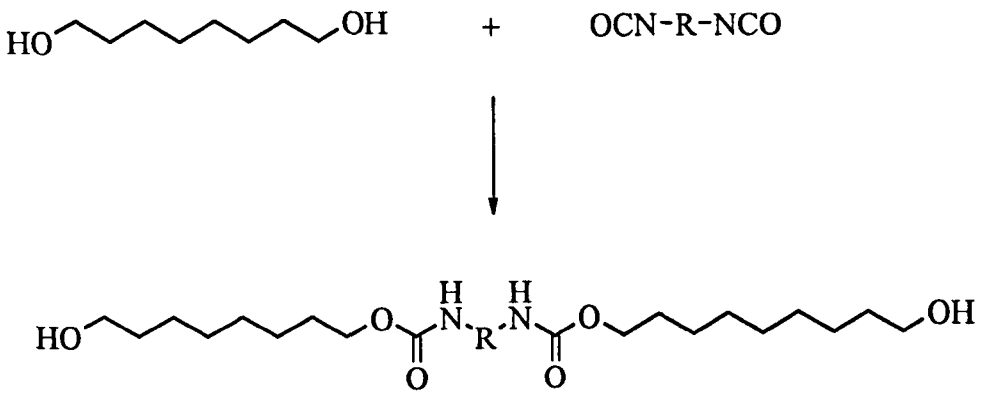


4.2

The telechelic nature of the final product was verified by analysis of the polymer by a combination of NMR and MALDI-TOF mass spectrometry. The molecular weights were determined by SEC and approximate conversions for polymers were obtained by precipitation.

The hydroxy telechelic polymers formed in these polymerizations were further reacted with isocyanates and diisocyanates. This is the most common reaction carried out using hydroxy telechelic polymers, Scheme 4.1.

Scheme 4.1:



The benzyl methacrylate terminated PMMA was hydrogenolysed to remove the benzyl group and form methacrylic acid end groups. No reactions were carried out on the polymer formed from GMA dimer as the NMR revealed that it was not entirely telechelic. However, it is believed that the functional groups in this polymer would be available to undergo the normal reactions of epoxides, i.e. ring opening by reaction with acid or base.

4.1.1 Emulsion Polymerization

The essential components of an emulsion polymerization are water, a monomer that is immiscible with water, an emulsifying agent and a water soluble initiator. The emulsifier forms micelles in the water creating a hydrophobic interior. The majority of the monomer exists as droplets in the aqueous phase, but some dissolves in the micelles. Free radicals are generated from the initiator and diffuse through the aqueous phase to penetrate both the micelles and droplets. However, since the surface area and concentration of the micelles is greater than the droplets

most initiation occurs within the micelles. The polymer chain continues to grow until another radical diffuses into the micelle to cause termination when it encounters the propagating chain end. The micelle remains dormant until another radical enters. Monomer in the micelles is consumed by polymerization but this is replenished by diffusion from the monomer droplets. The polymerization continues until all of the monomer droplets have been exhausted and the monomer in the micelles has been consumed.[6] The theory that each micelle contains only one active radical species at any given time is known as the Smith-Ewart model. This describes the rate of initiation and termination in the micelles as being controlled by both the rate of radical production and the number of micelles in the system. The consequences of this are that increasing the initiator concentration reduces the chain length but does not alter the rate of polymerization and that for a fixed initiator concentration both the rate of polymerization and the chain length are dependent on the number of micelles in the system. As a result of this the rate of polymerization and the molecular weight can be increased by increasing the concentration of surfactant. Emulsion polymerization has advantages over other types of polymerization in that there is no problem with heat transfer and viscosity, hence a reaction can be taken to high conversion and that as the medium is water it is seen as environmentally friendly.

4.2 Experimental

Macromonomers used in this work were prepared by catalytic chain transfer polymerization and isolated by reduced pressure distillation as outlined in section 7.3. The isolated dimers were characterized by ^{1}H and ^{13}C NMR and infra red spectroscopy and elemental analysis. For the characterization of the dimers used see section 2.3.

Polymerization mixtures containing varying amounts of degassed monomer, dimer, initiator and solvent were reacted in ampoules at 80 °C for varying times. For full experimental procedures see section 7.5.

4.3 Results and discussion

4.3.1 Polymerizations of MMA with MMA dimer.

The chain transfer coefficient of MMA dimer, **2.6**, is approximately 0.01, see section 3.3.1. Although the aim of this work is to prepare α,ω-difunctional telechelics, a series of control experiments were carried out with MMA dimer so as to establish reaction conditions for functional dimers as MMA dimer is readily available. Reaction conditions and experimental data for the polymer products are given in Table 4.1 and Table 4.2.

Table 4.1 Reaction conditions for the polymerization of MMA in the presence of MMA dimer, **2.6**.

	Amount of MMA (g)	Amount of **2.6** (g)	Amount of VA-086 (g)	Amount of DMF (g)	Reaction Time (mins)
MM.A	1.016	0	0.005	3.12	11520
MM.B	1.059	1.013	0.005	2.13	11520
MM.C	1.010	2.003	0.005	1.01	11520

Table 4.2 Molecular weight data for products of reactions MM.A-MM.C

	mol% **2.6**	Reaction Time (mins)	Mn	Mw/Mn
MM.A	0	11520	66500	4.99
MM.B	32.5	11520	9300	2.27
MM.C	49.7	11520	7100	1.74

These reactions also enabled NMR analysis of MMA terminated with a vinylic end group for comparison with telechelic polymers prepared for this work.

4.3.2 Polymerization of MMA with HEMA dimer

The reaction conditions and molecular weight data for a number of MMA polymerizations with HEMA dimer, **2.5**, are shown in Table 4.3 and Table 4.4 respectively. Reactions were carried out in which both the amount of dimer and the polymerization time were varied.

Table 4.3 Reaction conditions for polymerizations of MMA in the presence of HEMA dimer, **2.5**.

	Amount of MMA (g)	Amount of **2.5** (g)	Amount of Initiator (g)	Amount of DMF (g)	Reaction Time (mins)
MH.A	0.785	0.782	0.004	2.34	1020
MH.B	0.782	0.779	0.004	2.33	2460
MH.C	0.786	0.783	0.004	2.34	2460
MH.D	0.759	3.013	0.005	2.02	2880
MH.E	0.769	3.014	0.005	2.00	7200
MH.F	0.784	0.782	0.004	2.34	11520
MH.G	1.004	1.006	0.005	3.01	11520
MH.H	1.002	2.008	0.005	2.01	11520

Table 4.4 Molecular weight data for products of reactions MH.A-MH.H

	mol% **2.5**	Reaction Time (mins)	Mn	Mw/Mn	Conversion based on MMA in feed
MH.A	27.8	1020	16400	2.20	60.2
MH.B	27.8	2460	9600	2.91	
MH.C	27.8	2460	10600	2.71	83.4
MH.D	60.4	2880	6600	1.88	
MH.E	60.1	7200	6100	1.98	
MH.F	27.8	11520	8400	3.22	95.2
MH.G	28	11520	9200	3.01	
MH.H	41.8	11520	7000	2.57	

The effects of polymerization time are seen in experiments A, B, C and F where the polymerization has been terminated after approximately 1, 2.5, 2.5 and 11 half lives respectively. Reactions B and C are duplicates to examine the reproducibility which is seen to be good. As would be expected, the conversion increases with time. The molecular weight decreases and the PDi increases with conversion which is what would be predicted for a chain transfer agent with a Cs value below one. The fact that the chain transfer constant of dimer is less than one means that propagation is faster than transfer and so the monomer is consumed at a faster rate than the dimer. As a result, there is an increase in the ratio of the concentration of dimer to monomer as the reaction proceeds, and hence an increase in the number of chain transfer events occurring. There is also a corresponding increase in polydispersity as a result of the polymer being formed at a lower molecular weight, thus increasing the distribution of chain lengths. As the amount of dimer is increased, at a given reaction time the polydispersity decreases because the polymer is already at a lower molecular weight. Therefore as the conversion increases, the molecular weight drops but the dispersity is not broadened to the same extent.

The MALDI-TOF mass spectrum obtained from reaction MH.H, Figure 4.1, shows the predominant macromolecular species to have the overall composition $HEMA_2MMA_x$. This spectrum was obtained using a matrix of DHB doped with KCl. Hence two series of peaks are obtained, both with a separation of approximately 100 Da between the individual peaks. The first series of peaks corresponds to the Na^+ adduct; the second, 16 Da higher, to the K^+ adduct, the sodium has been picked up from the glass vial containing the matrix solution. The peak at *m/z* 1182.8 corresponds to $HEMA_2MMA_9Na$, which has a calculated

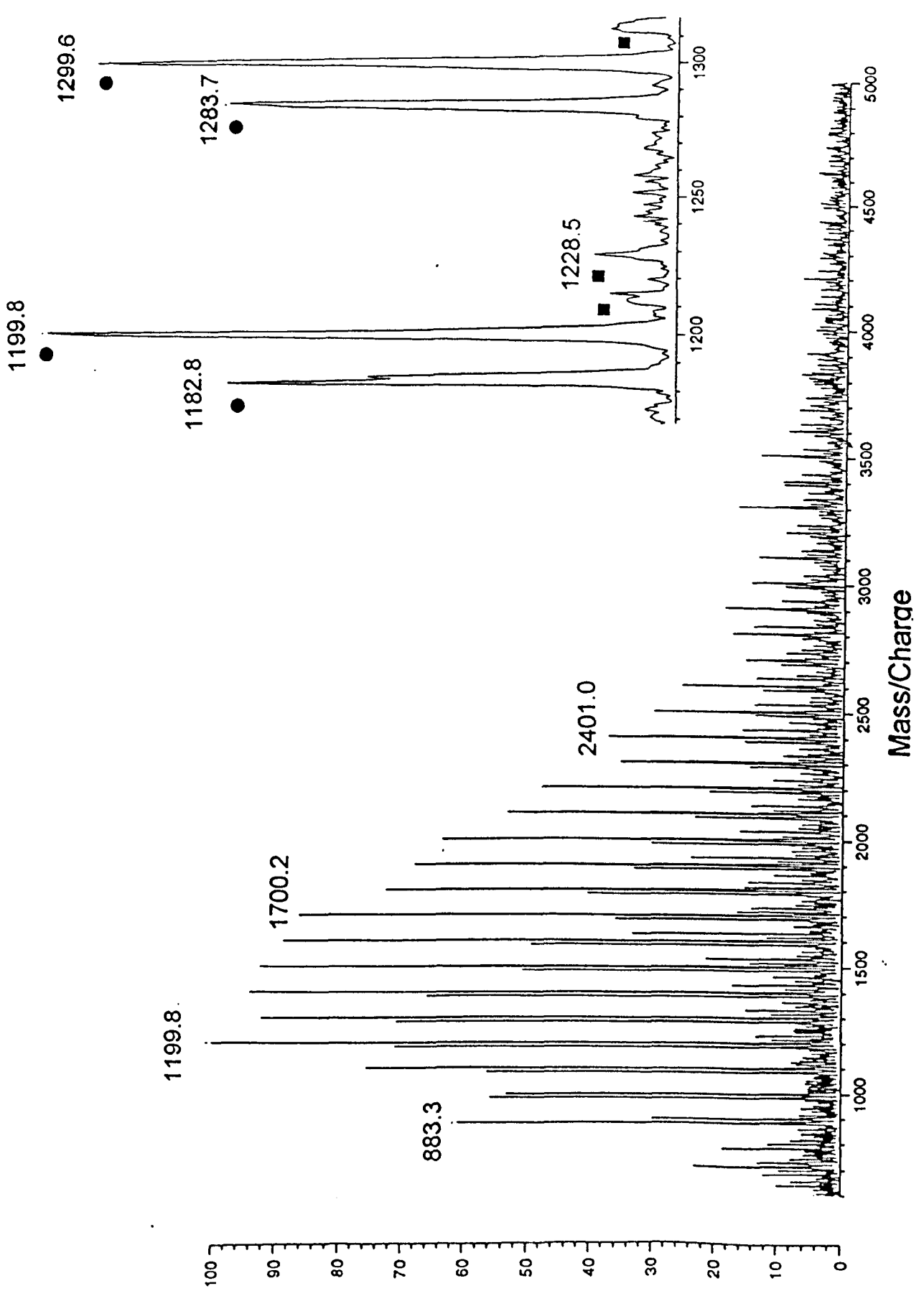


Figure 4.1 MALDI-TOF Mass Spectrum of Hydroxy Telechelic PMMA

mass of 1184.4 Da, and the peak at *m/z* 1283.7 to $HEMA_2MMA_{10}Na$ which has a calculated mass of 1284.5 Da.

A small amount of $HEMA_3MMA_x$ seems to be present in the sample as indicated by the peak at *m/z* 1228.5 for the potassium adduct. This may be due to contamination of the dimer by small amounts of trimer. However this was not detected by SEC or ^1H NMR, see section 2.3.5. An alternative explanation is the occurrence of normal termination of the polymer by HEMA dimer which would result in three HEMA units on a chain, one from initiation and two from the termination. It must be noted here that no similar peaks are seen in other MALDI-TOF spectra obtained in this work and all previous work, as outlined in Section 1.3.3 of the introduction, has pointed to β-scission being the only reaction pathway for these systems except under the forcing conditions described. No evidence is seen for PMMA homopolymer, which would be expected at *m/z* x(100.12) + 130 (initiator) + 22.99, e.g. 1154 Da for a degree of polymerization of eleven. MALDI-TOF mass spectrometry has been shown to be mass-sensitive under the conditions used here. This can be seen as the envelope of peaks from MALDI-TOF-MS has a maximum at *m/z* 1199.8 with few peaks being observed above *m/z* 2600. However, SEC with refractive index detector shows the number average molecular weight to be 7010 Da with the weight average molecular weight greater than 18000 Da. Unfortunately at 130 Da the formula weight of a unit of HEMA monomer corresponds to that of the initiator fragment. This means that they cannot be distinguished by MALDI-TOF-MS and hence further reactions with GMA dimer were carried out.

MALDI-TOF mass spectrometry is an excellent tool for verifying the number of different monomer units in the polymer. However, it does not indicate the

position of the units in the chain. For this purpose ^{1}H NMR analysis of the hydroxy telechelic polymer was compared to PMMA obtained under similar conditions but using MMA dimer, Figure 4.3 and Figure 4.2 respectively. From this latter spectrum it was discovered that the terminal methoxy group nearest to the vinylic unsaturation gave a signal at approximately 3.71 ppm, the penultimate unit is at 3.62 ppm and the remaining methoxy groups are at 3.59 ppm. Comparison of the NMR spectrum from the hydroxy telechelic polymer shows an absence of a peak at 3.71 ppm indicating that none of the terminal units in the polymer contain a methoxy group. Furthermore the position of the peaks from the ester groups of the incorporated HEMA clearly shows two different types of HEMA unit, with one α to the vinylic end group by comparison with the spectrum obtained from HEMA dimer, Figure 2.10, section 2.3.5.

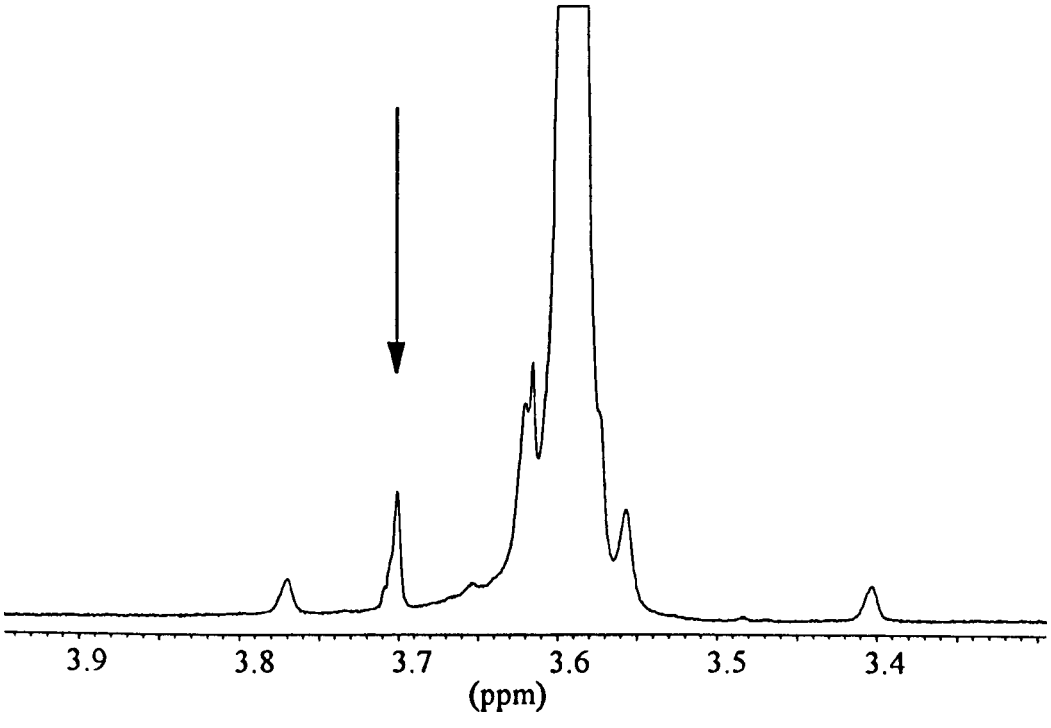


Figure 4.2 Expanded region of the ^{1}H-NMR spectrum of PMMA formed by reaction of MMA and MMA dimer.

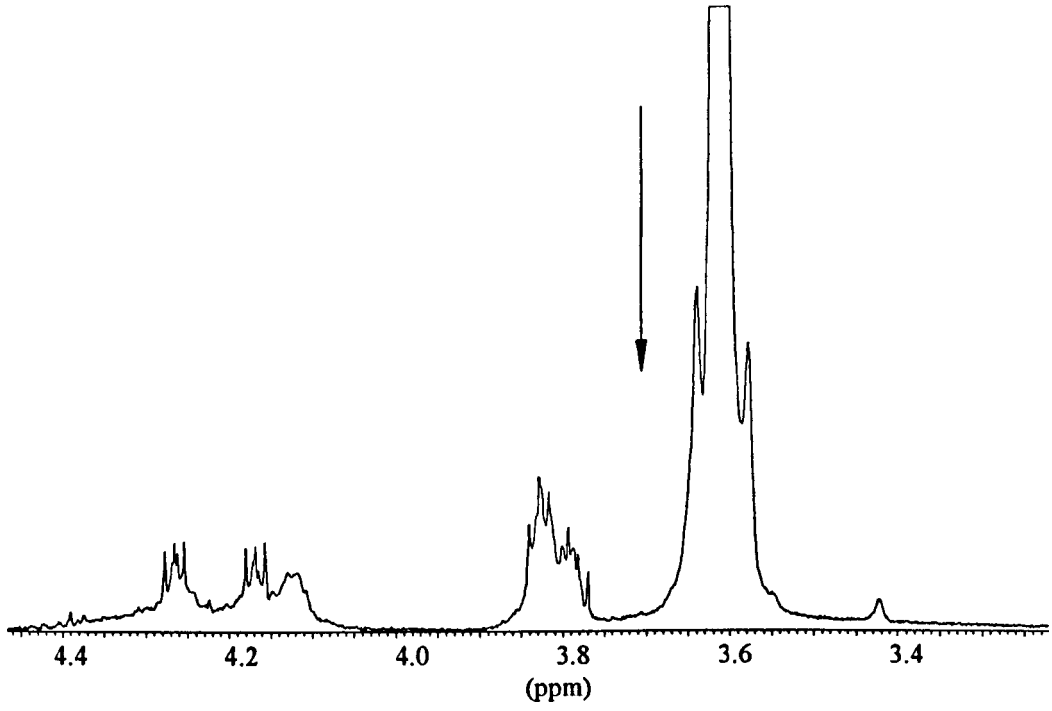


Figure 4.3 Expanded region of the ^{1}H-NMR spectrum of hydroxy telechelic PMMA. The arrow indicates the position that a peak from a terminal methoxy group would be expected.

The potential exists, although it is unlikely, for the dimer or the macromonomer prepared during the reaction to copolymerize and form graft copolymers. The weight average molecular weight obtained using the differential refractometer detector was compared to that obtained using light scattering which gives a response based on the amount of electromagnetic radiation transmitted by polymers of different sizes. The differential refractometer will not give accurate molecular weight data for polymers with any degree of branching as the hydrodynamic volume of a graft copolymer is different to that of a linear polymer of the same molecular weight.

The results of this analysis are shown in Table 4.5 below.

Table 4.5 Comparison of molecular weight data obtained using refractive index and light scattering detectors.

Reaction	mole % **2.5**	Mw (refractive index)	Mw (LALLS)
MM.A	0	332200	331500
MM.B	32.5	21100	23200
MM.C	49.7	12300	14100
MH.A	27.8	36200	43000
MH.B	27.8	27900	26900
MH.C	27.8	28600	32800
MH.D	60.4	12500	14700
MH.E	60.1	12100	14900
MH.F	27.8	27200	28100
MH.H	41.8	18000	20900

There is good agreement between the molecular weight data obtained using both methods despite the molecular weights of most of the polymers being at the lower limits of the LALLS useful range. This indicates that the polymers formed are linear and not branched.

4.3.3 Polymerization of MMA with GMA dimer

As the initiator fragment from the VA-086 has a formula weight that does not allow it to be distinguished from a unit of HEMA in the MALDI-TOF spectrum, a similar series of experiments were carried out, this time using GMA dimer, **2.4**, the data for which are given in Table 4.6 and Table 4.7.

Table 4.6 Reaction conditions for the polymerization of MMA in the presence of GMA dimer, **2.4**.

	Amount of MMA (g)	Amount of **2.4** (g)	Amount of Initiator (g)	Amount of DMF (g)	Time (mins)
MG.A	0.978	0.979	0.005	0.98	1020
MG.B	0.978	0.980	0.005	0.98	2460
MG.C	0.979	0.981	0.005	0.98	2460
MG.D	0.977	0.978	0.005	0.98	12960
MG.E	0.962	0.963	0.005	0.97	12960
MG.F	1.015	2.004	0.005	0	12960

Table 4.7 Molecular weight data obtained for products of reactions A-F

	mol% **2.4**	Reaction Time (mins)	Mn	Mw/Mn	Conversion based on MMA in feed
MG.A	26.1	1020	17900	2.13	57.5
MG.B	26.1	2460	17000	2.16	76.0
MG.C	26.1	2460	19000	2.03	61.0
MG.D	26.1	12960	14800	2.36	84.9
MG.E	26.1	12960	13900	2.61	79.1
MG.F	41.0	12960	11600	1.95	76.1

The MALDI-TOF spectrum obtained for reaction F, shown in Figure 4.4 would seem to indicate that the major species present corresponds to MMA_xGMA_2K, and hence would be thought to be telechelic, the peak at *m/z* 1625.7 corresponding to $MMA_{13}GMA_2K$, the calculated molecular weight being 1625.0 Da [13(100.12) + 2(142.16) + 39.10]. The smaller series of peaks at 16 Da lower than the major series arises from the sodium adduct.

However, analysis of the product by NMR reveals the presence of terminal methoxy groups, Figure 4.5, Figure 4.6, Figure 4.7 and Figure 4.8. The relative amount of these groups decreases with increasing dimer content in the feed and decreasing molecular weight.

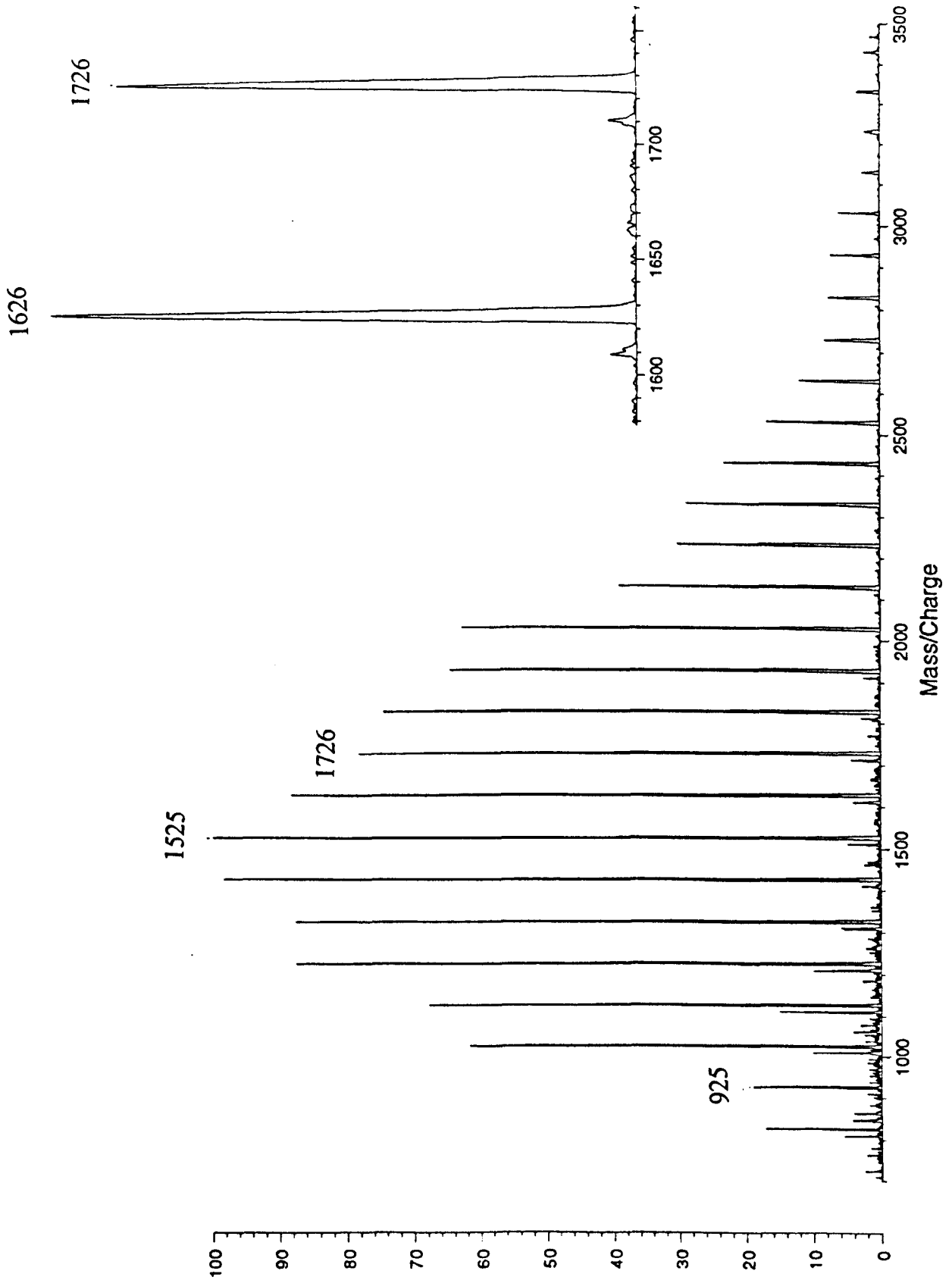


Figure 4.4 MALDI-TOF Mass Spectrum of GMA Terminated PMMA

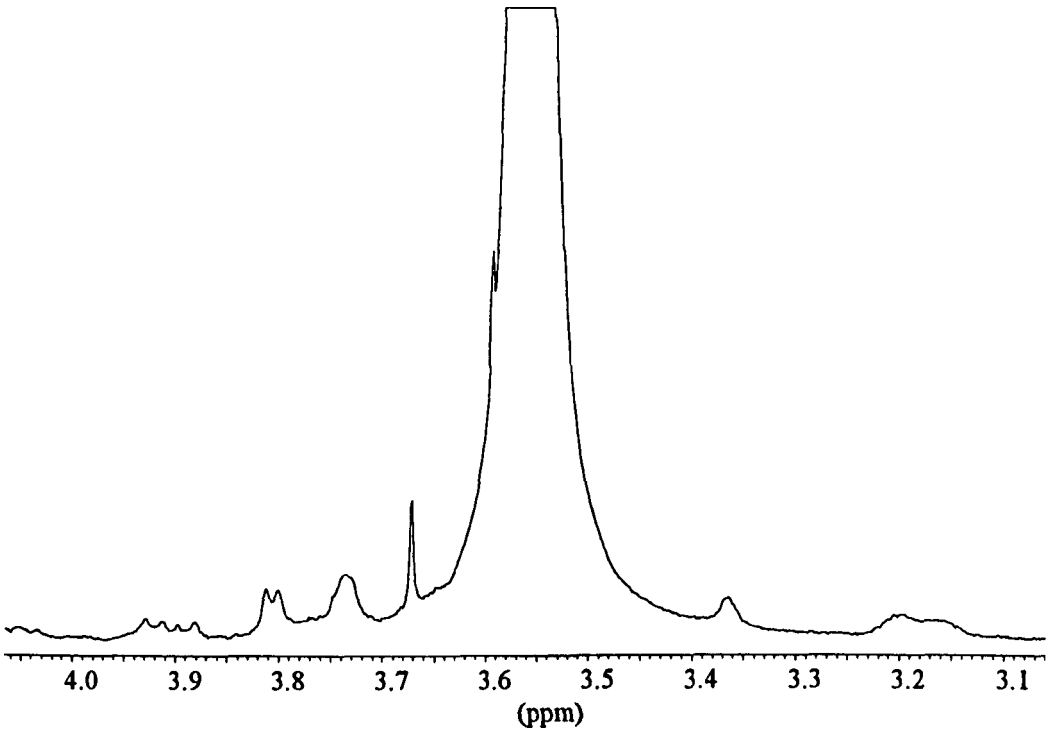


Figure 4.5 Expanded region of ^{1}H-NMR spectrum from reaction MG.A

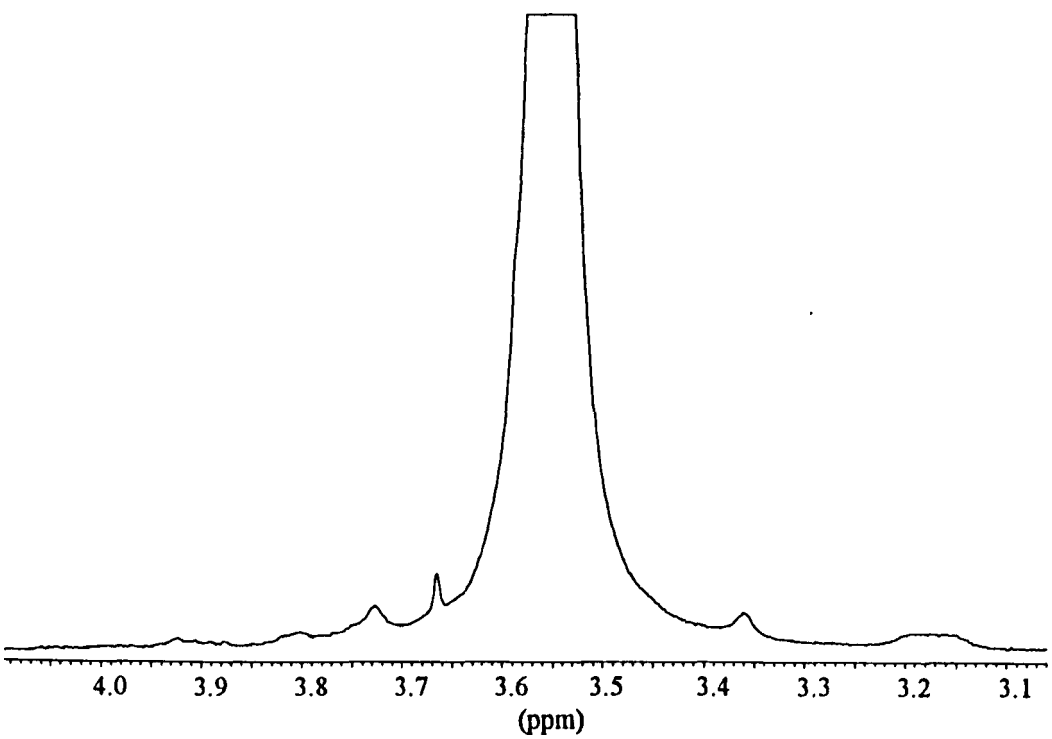


Figure 4.6 Expanded region of ^{1}H-NMR spectrum from reaction MG.B

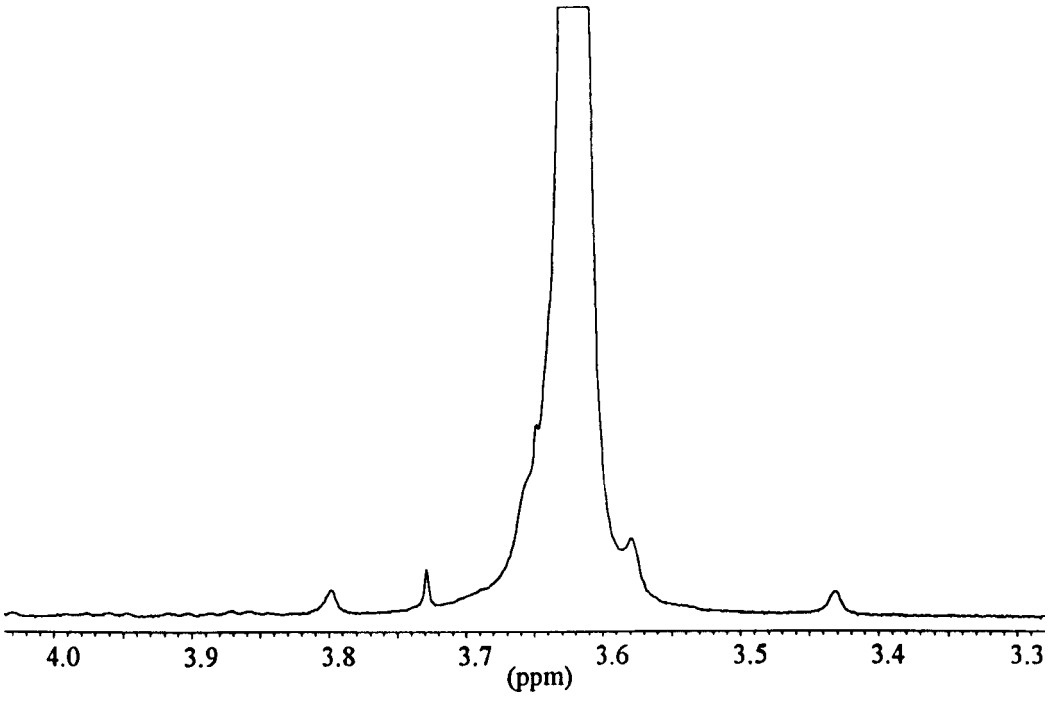


Figure 4.7 Expanded region of ^{1}H-NMR spectrum from reaction MG.E

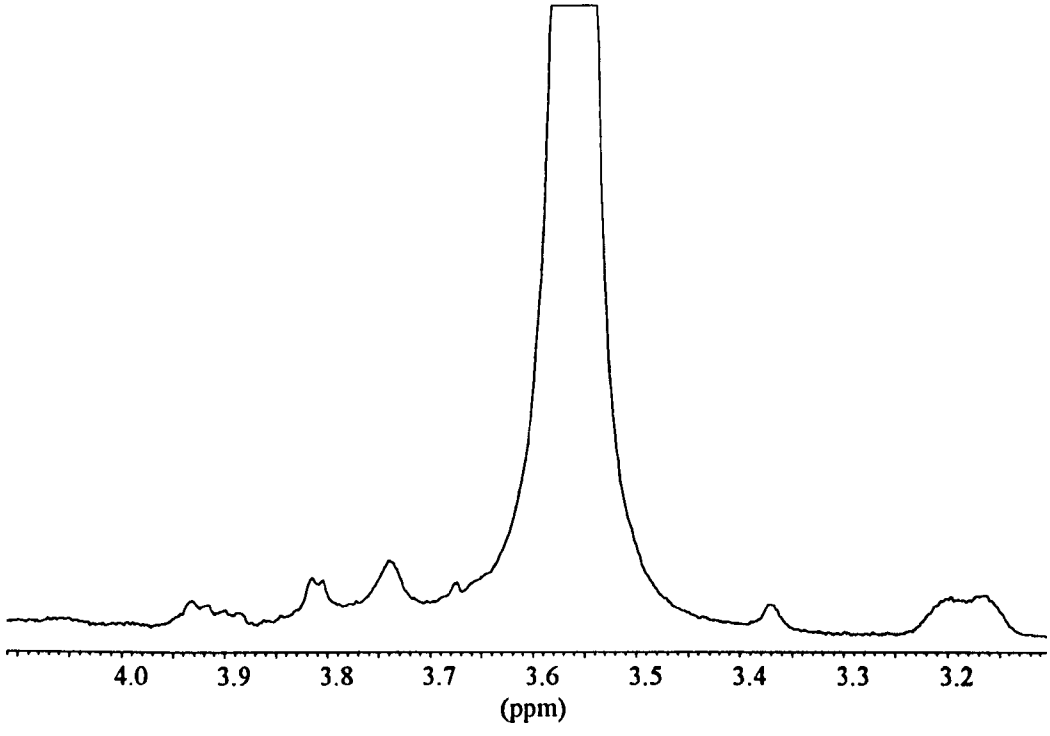


Figure 4.8 Expanded region of ^{1}H-NMR spectrum from reaction MG.F

This could be due to a number of reasons. Firstly, the dimer could be less efficient as a chain transfer reagent as indicated by the slightly higher molecular weights obtained compared to the results from the polymerizations involving HEMA dimer. The dimer could be less reactive than other dimers, and the PMMA could terminate normally by disproportionation without reaction with GMA dimer. Alternatively, some of the GMA dimer could undergo a side reaction rather than undergo β-scission and so copolymerization could occur. Although this is not seen in the MALDI spectrum it has earlier been pointed out that the MALDI technique is mass-sensitive, and thus the non-telechelic polymers may only occur in the higher mass region.

The MALDI-TOF-MS of GMA terminated PMMA shows that there are no peaks due to the initiator fragment.

4.3.4 Polymerization of MMA with BzMA dimer.

To gauge the effect of the size of the dimer on its reactivity and chain transfer activity, and to attempt to explain the anomalies seen in the results from the work using GMA dimer, a series of reactions involving the bulkier BzMA dimer, **2.1**, were conducted, data for which are presented in Table 4.16 and Table 4.17.

Table 4.8 Reaction conditions for polymerizations of MMA in the presence of BzMA dimer.

	Amount of MMA (g)	Amount of **2.1** (g)	Amount of VA-086 (g)	Amount of DMF (g)	Time (min.)
MBz.A	1.016	1.005	0.005	2.99	11520
MBz.B	1.021	1.009	0.005	3.00	1020
MBz.C	1.018	1.009	0.005	3.00	11520
MBz.D	0.508	1.020	0.003	3.54	11520

Table 4.9 Molecular weight data for products from reactions A-D

	Conc. of **2.1** in mol-%	Reaction Time (mins)	Mn	Mw/Mn	Conversion based on MMA in feed
MBz.A	21.9	11520	8000	3.46	62.0
MBz.B	21.9	1020	18400	1.93	51.3
MBz.C	22.0	11520	8400	3.41	62.2
MBz.D	56.4	11520	6100	2.66	72.9

The molecular weight data shown in the above table indicate that the size of the benzyl methacrylate group does not affect the chain transfer activity of the macromonomer, with molecular weight reductions comparable to those of MMA dimer. The MALDI-TOF mass spectrum, Figure 4.9, again indicates the presence of two BzMA units per chain, and there is no evidence for the presence of initiator derived fragments. This again supports the belief that chain transfer is the predominant mode of termination and hence initiation.

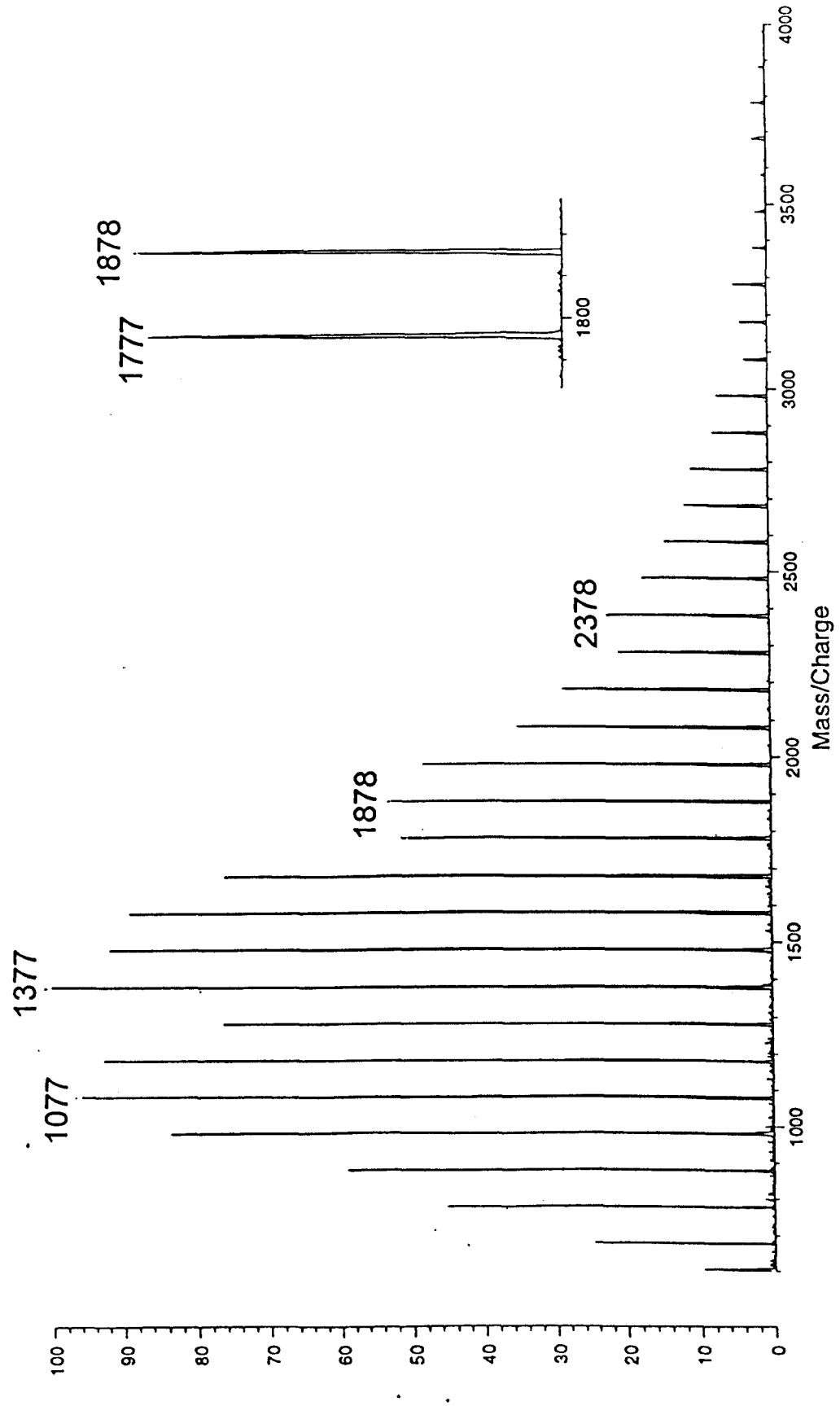


Figure 4.9 MALDI-TOF Mass Spectrum of BzMA Terminated PMMA

The ^{1}H-NMR spectrum, Figure 4.10, again clearly shows an absence of any terminal methyl methacrylate groups as there are no peaks in the region of 3.73 ppm.

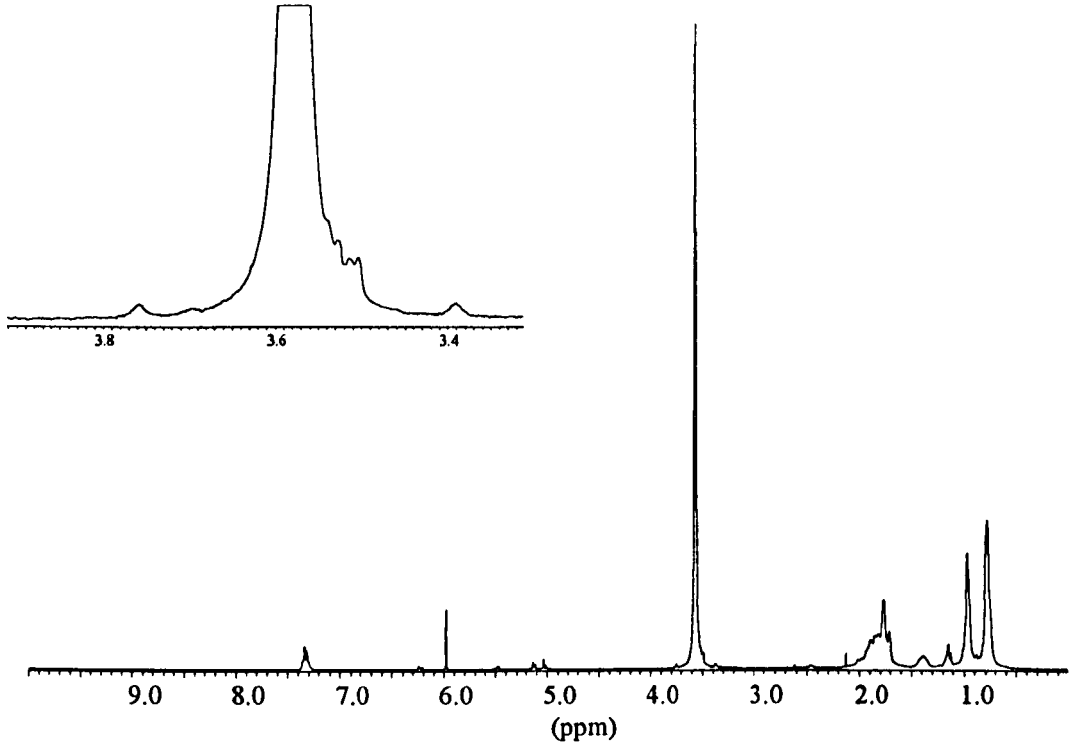


Figure 4.10 ^{1}H-NMR spectrum of BzMA terminated PMMA (reaction MBz.D). The inset shows the expanded region where a peak from a terminal O-CH_3 group would be expected.

Figure 4.11 shows a comparison of the molecular weights obtained using the different dimers with reactions taken to high conversion. Similar molecular weights are obtained from all of the dimers, indicating similar chain transfer activity regardless of the functionality on the dimer. A slight exception to this is GMA dimer which gave higher molecular weights than were obtained with the other dimers. This could be due to the size of the functional group or, more probably, due to side reactions that occur with epoxy functional groups. As has

already been noted, the NMR spectra obtained from these materials show a difference when compared to those obtained from the analysis of the other polymers.

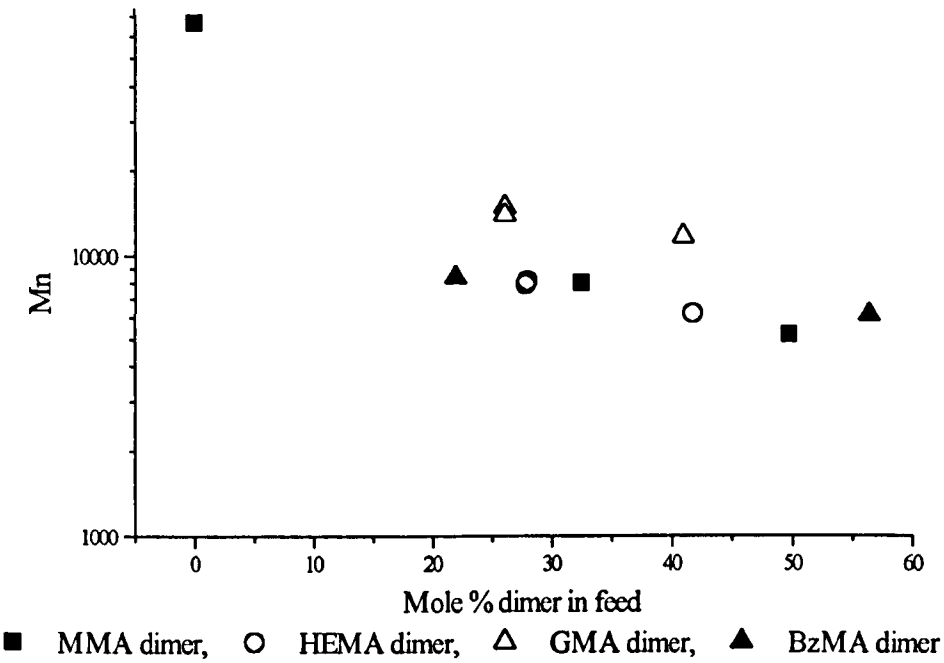


Figure 4.11 Comparison of the molecular weights obtained using different functional dimers in the polymerization of MMA at 11520 minutes.

As was also seen in the work concerning the calculation of chain transfer constants, there is a limit to the molecular weight reduction that can be obtained using a methacrylate dimer, i.e. as the level of dimer relative to monomer is increased the effect on the molecular weight becomes less apparent. That is, the Cs value is concentration dependent and changes during the course of the reaction. This was ascribed to an effect similar to Harwood's bootstrap effect described in the previous chapter. Hence low molecular weight telechelic polymers cannot be obtained using dimer macromonomers. This problem could

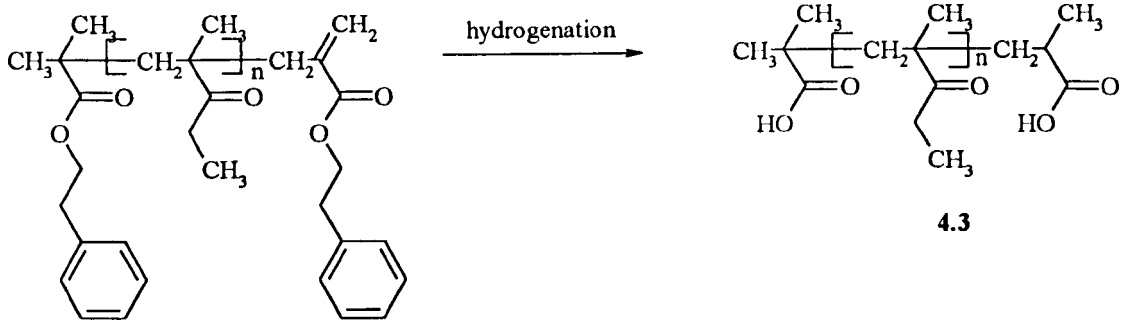
be alleviated using higher molecular weight macromonomers which have a chain transfer constant an order of magnitude higher than dimer. This would, however, lead to multifunctional, as opposed to telechelic, polymers.

4.3.5 Hydrogenolysis of BzMA terminated PMMA.

The benzyl methacrylate terminated PMMA produced in reaction MBz.D was hydrogenolysed using a palladium on carbon catalyst. Full experimental details are given in section 7.8. The product of the hydrogenolysis reaction was analysed by SEC, NMR and MALDI-TOF mass spectrometry. A qualitative yield of hydrogenolysed product was obtained with a number average molecular weight of 4470 and polydispersity of 6.43. This substantial broadening of the polydispersity upon hydrogenolysis of the benzyl methacrylate group has been noted by other workers[7] who ascribed it to non-size exclusion effects, ie adsorption to the column.

The catalytic hydrogenolysis of the BzMA terminated PMMA leads to the evolution of toluene leaving α,ω-dicarboxyl functionality, Scheme 4.2. This is observed by ^{1}H-NMR, Figure 4.12, which shows the absence of any signal in the aromatic region. The vinylic unsaturation is also hydrogenated; this is also seen in the ^{1}H-NMR spectrum which shows the loss of the peaks between 5.5 and 6.5 ppm.

Scheme 4.2:



4.3

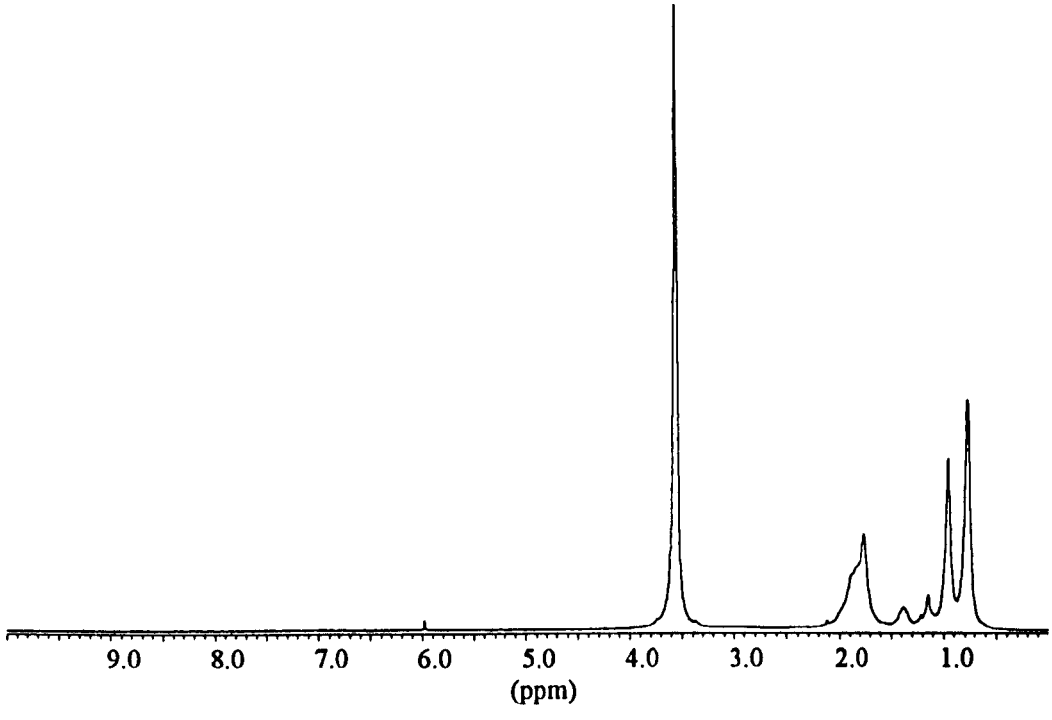


Figure 4.12 ^{1}H-NMR of the product of the hydrogenolysed polymer.

Analysis of the hydrogenolysis product by dual detector SEC at 254 nm shows the loss of the UV signal when compared to that of the BzMA telechelic polymer, confirming the loss of the aromatic groups from the polymer, see Figure 4.13.

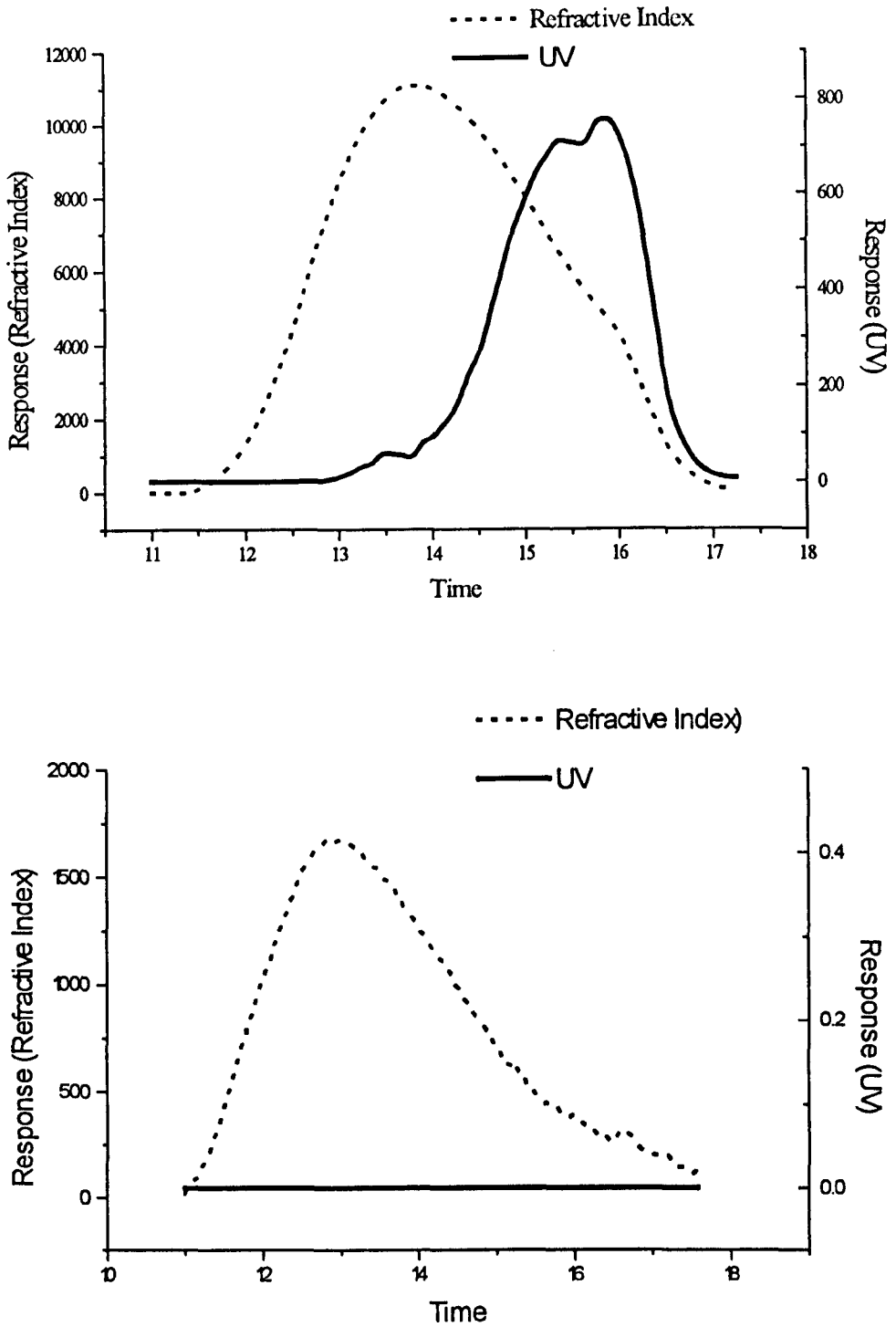


Figure 4.13 Dual detector SEC of BzMA terminated PMMA (upper trace) and hydrogenolysed product (lower trace).

Although the UV SEC trace of the BzMA terminated PMMA would seem to give virtually no signal at higher molecular weights this is due to the concentration

dependence of the UV detector. As there are only two aromatic groups per chain, as Mn increases, the concentration of aromatic groups decreases. If the chromatogram is replotted as a number distribution, Figure 4.14, the signals from the UV and refractive index detectors correspond.

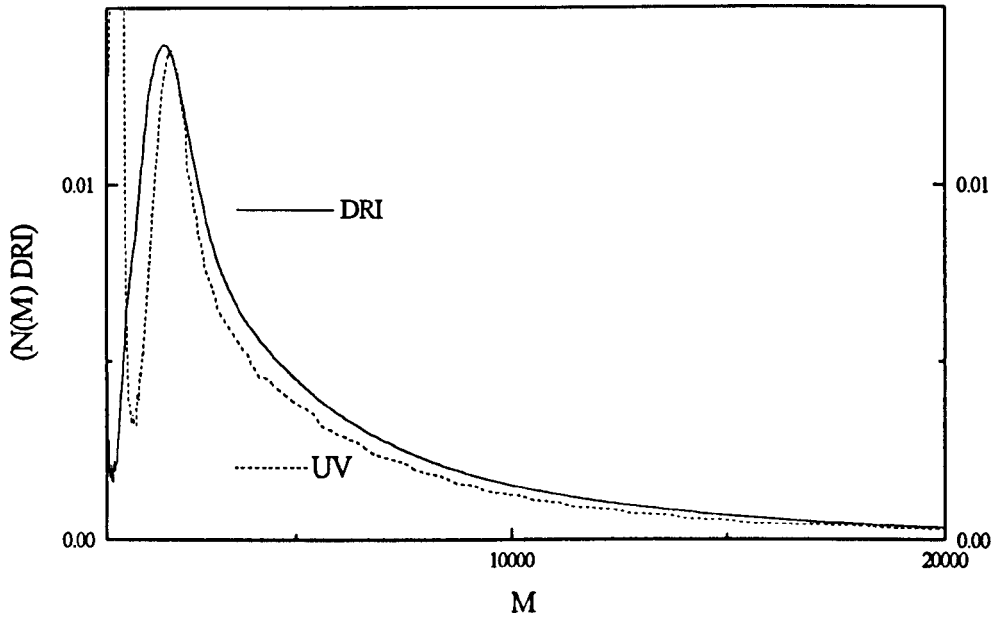


Figure 4.14 Number average distribution of benzyl methacrylate terminated PMMA.

The MALDI-TOF mass spectrum is shown in Figure 4.15 and shows no evidence for the presence of any starting material, note the lack of a peak at *m/z* 1777. The MALDI-TOF spectrum supports **4.3** as the main product where the peak at *m/z* 1597 corresponds to $MAAMMA_nMAANa$ with n=14, calculated *m/z* 1596.85, i.e. the hydrogenolysis product from the peak at *m/z* 1777 from $BzMAMMA_{14}BzMANa$.

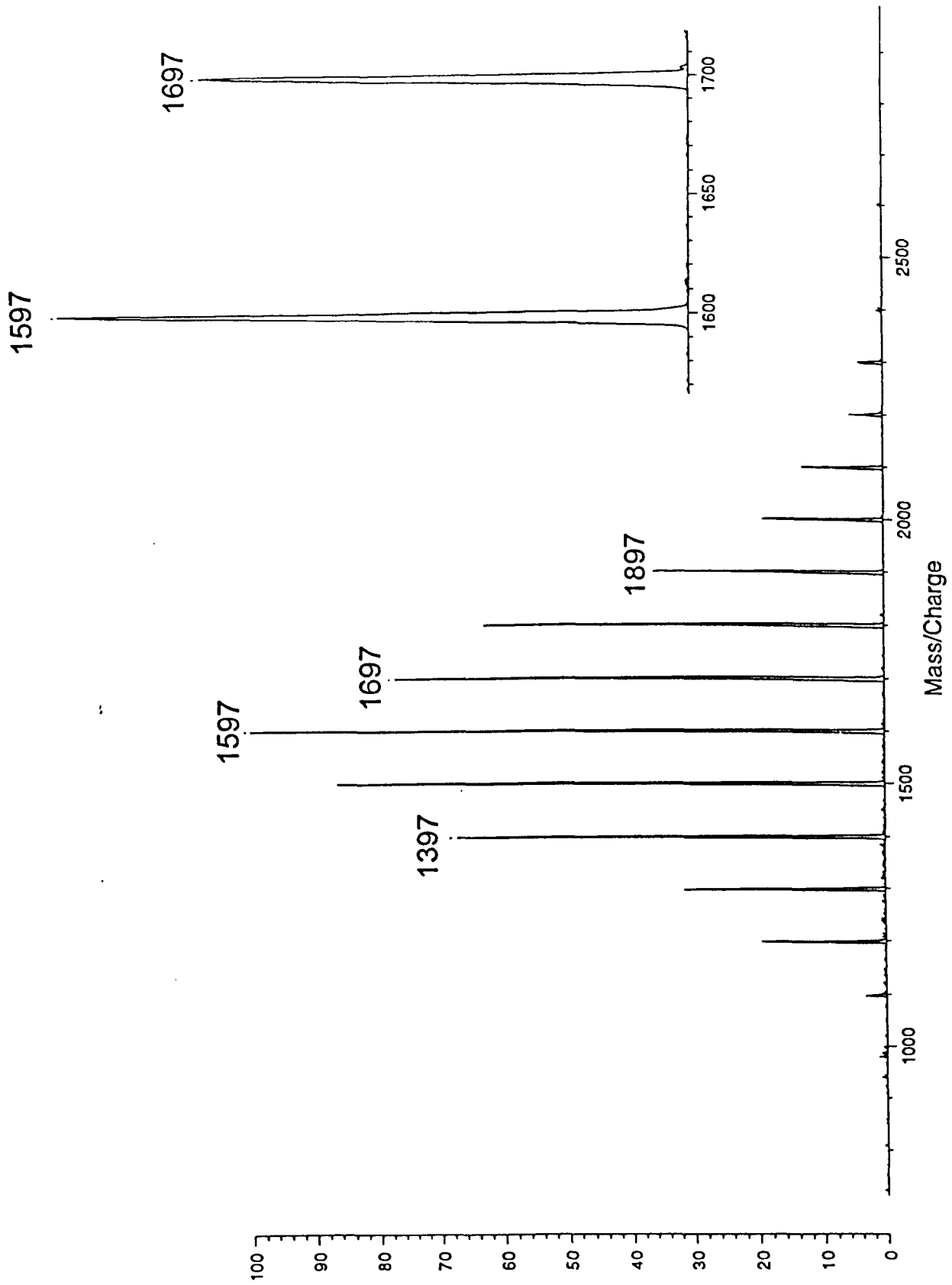


Figure 4.15 MALDI-TOF mass spectrum of the hydrogenolysed polymer.

4.3.6 Polymerizations of BMA with HEMA dimer

As a comparison with work carried out using MMA, similar reactions were carried out using BMA. As earlier work, presented in Chapter 3, has shown that changing the monomer had little effect on the chain transfer efficiency of the dimer, this work sought to qualitatively confirm this. Polymerization data for the reactions of BMA with HEMA dimer, **2.5**, is shown in Table 4.10 and Table 4.11.

Table 4.10 Reaction conditions for polymerizations of BMA in the presence of HEMA dimer

	Amount of BMA (g)	Amount of **2.5** (g)	Amount of Initiator (g)	Amount of DMF (g)	Time (mins)
BH.A	1.003	0	0.005	2.01	11520
BH.B	1.003	0	0.005	2.02	11520
BH.C	0.964	0.964	0.005	0.97	1200
BH.D	0.962	0.962	0.005	0.96	2940
BH.E	0.961	0.962	0.005	0.96	11520
BH.F	0.965	0.966	0.005	0.96	11520
BH.G	0.507	1.039	0.003	2.77	11520

Table 4.11 Molecular weight data for products of reactions BH.A-BH.G.

	mol% HEMA dimer	Reaction Time (mins)	Mn	Mw/Mn	Conversion based on BMA in feed
BH.A	0	11520	103200	3.74	92.7
BH.B	0	11520	140100	2.76	89.2
BH.C	35.37	1200	27600	1.54	53.2
BH.D	35.37	2940	11200	2.80	79.6
BH.E	35.37	11520	9550	3.20	94.0
BH.F	35.37	11520	9000	3.36	91.8
BH.G	52.87*	11520	-	-	-

* no precipitate was formed.

The MALDI-TOF mass spectrum of the hydroxy telechelic PBMA is shown in Figure 4.16. The matrix used was DHB doped with NaCl, hence only one series of peaks, separated by 142 Da, corresponding to BMA_xHEMA_2Na are seen. For example, the peak at 1707 Da corresponds to $BMA_{10}HEMA_2Na$, calculated mass 1705.3 Da.

Examination of the ^{1}H-NMR spectrum of BMA trimer, Figure 2.6, would lead to the expectation of a peak from the terminal O-CH_2 group at approximately 4.05 ppm. The ^{1}H-NMR spectrum in Figure 4.17 for hydroxy telechelic PBMA shows an absence of peaks in this area, leading to the assumption that the product is telechelic. Again, as seen in the earlier reactions with MMA, two different types of HEMA groups are present, as indicated by the different resonances.

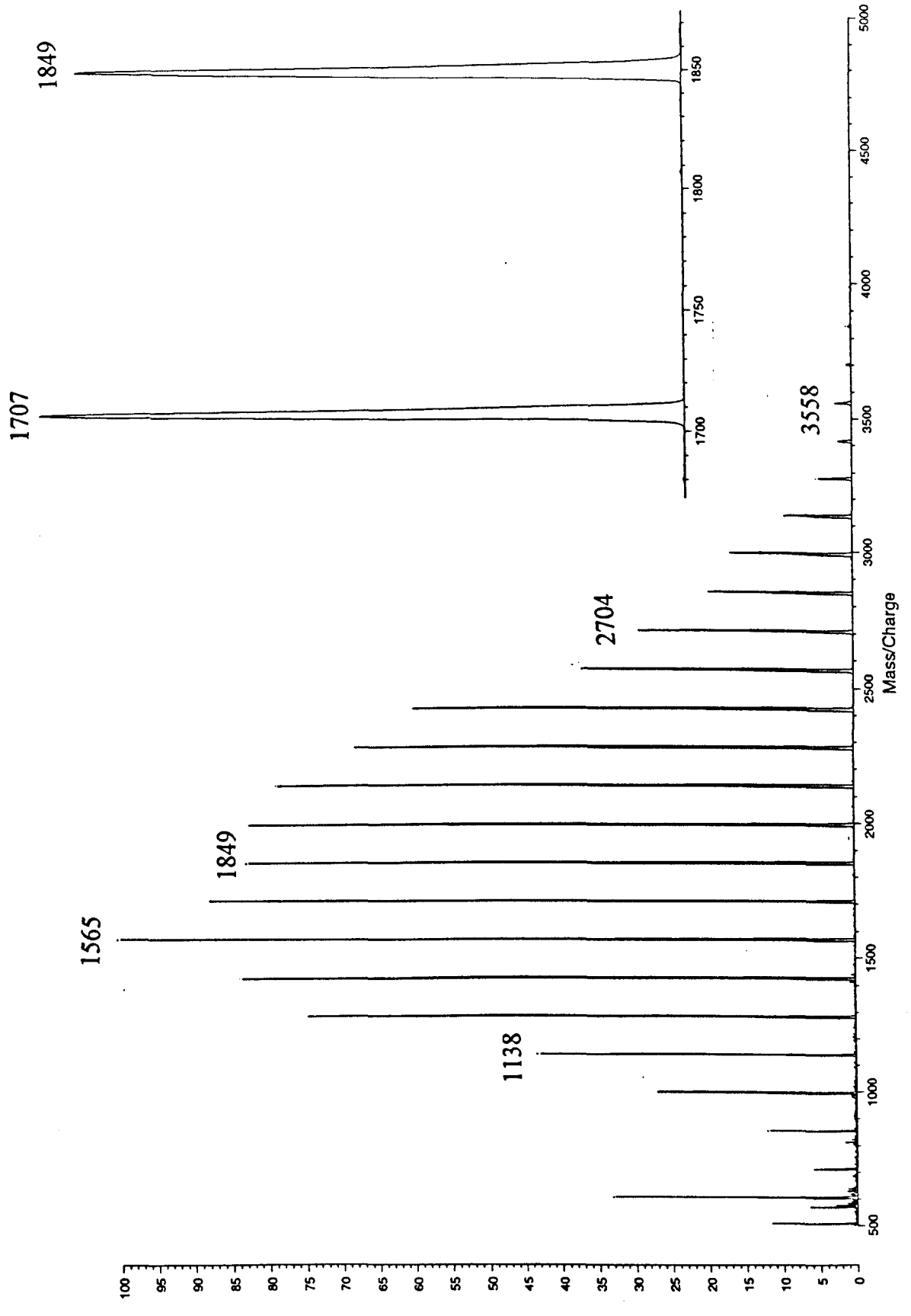


Figure 4.16 MALDI-TOF Mass Spectrum of Hydroxy Telechelic PBMA

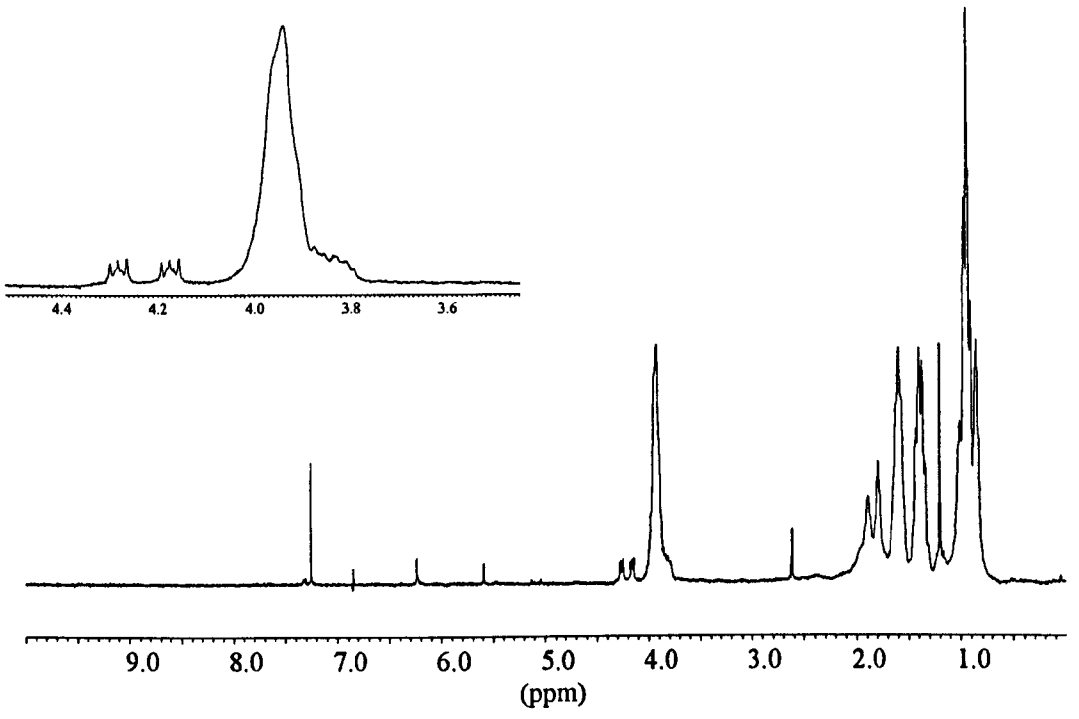


Figure 4.17 ^{1}H-NMR spectrum of hydroxy telechelic PBMA (reaction BH.E)

4.3.7 Polymerization of BMA with MMA dimer

Reactions were carried out using MMA dimer, **2.6**,. in order to aid NMR analysis, which is complicated for HEMA dimer by the presence of O-CH_2 groups in both the monomer and dimer. It was assumed that HEMA and MMA dimer would behave in a similar fashion. Polymerization data for these reactions are shown in Table 4.12 and Table 4.13.

Table 4.12 Reaction conditions for polymerization of BMA in the presence of MMA dimer.

	Amount of BMA(g)	Amount of **2.6** (g)	Amount of initiator (g)	Amount of DMF (g)	Reaction Time (mins)
BM.A	1.000	0.800	0.006	1.00	11520
BM.B	1.000	0.799	0.006	1.00	1200
BM.C	1.001	0.800	0.006	1.00	11520
BM.D	0.491	0.831	0.003	2.73	11520

Table 4.13 Molecular weight data for products of reactions BM.A-BM.D

	mole % **2.6**	Reaction Time (min.)	Mn	Mw/Mn	Conversion
BM.A	36.21	11520	12600	2.41	77.4
BM.B	36.21	1200	19000	1.74	52.3
BM.C	36.21	11520	13100	2.26	72.4
BM.D	54.57	11520	10100	1.78	67.7

Polymerizations involving BMA with both MMA and HEMA dimer give similar results to those carried out with MMA: the degrees of polymerization being similar, as are the trends in molecular weight and polydispersity.

The MALDI-TOF spectrum for BMA with MMA dimer is shown in Figure 4.18 and, as would be expected, the peaks are separated by 142 Da, indicating a predominant species of BMA_xMMA_2Na. The peak at 1357 is from a chain with the structure BMA_8MMA_2Na.

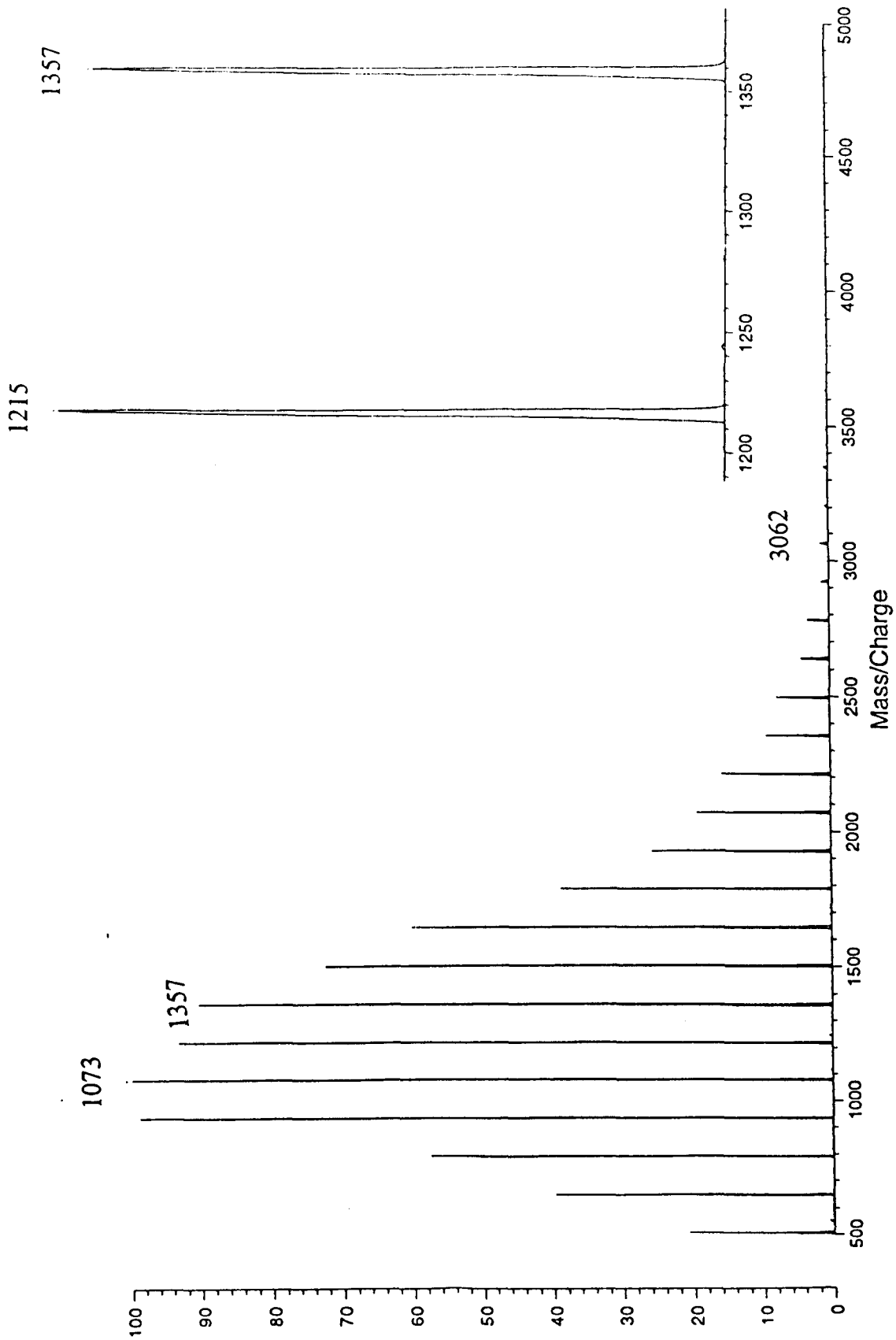


Figure 4.18 MALDI-TOF Mass Spectrum of MMA Terminated PBMA

The NMR spectra obtained, Figure 4.19, also showed the lack of terminal O-CH_2 groups in the product in the region of 4.05 ppm. Two resonances from the methoxy groups of the MMA are observed in the spectrum between 3.6 and 3.8 ppm, indicating that the MMA groups are in two different environments.

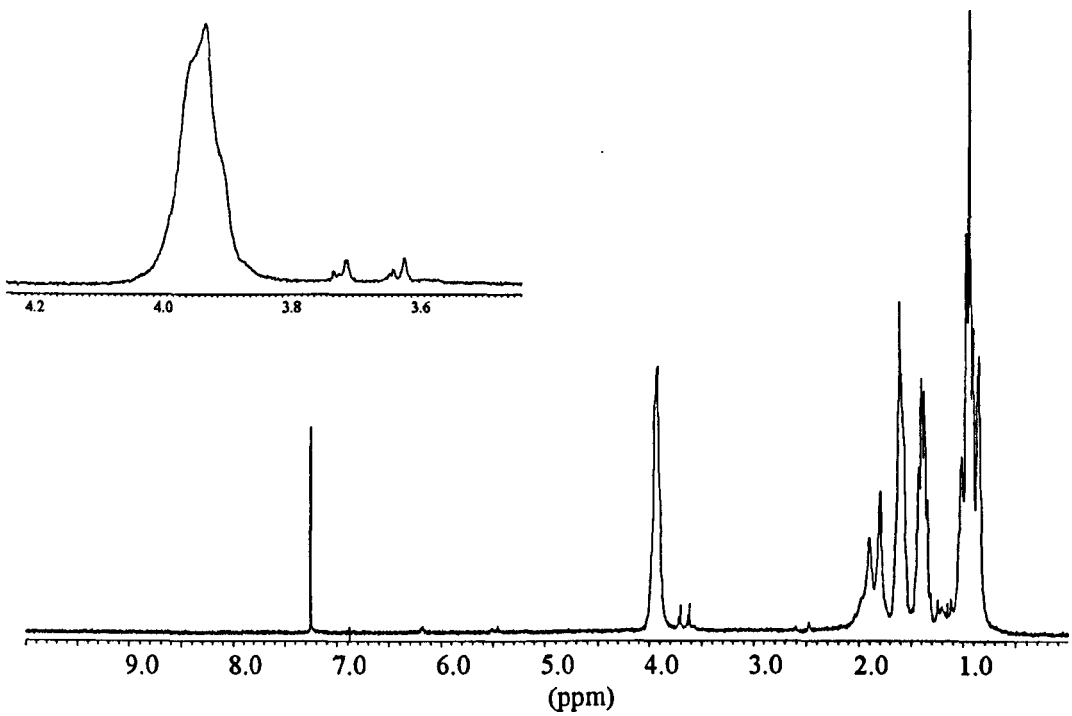


Figure 4.19 ^{1}H-NMR spectrum of MMA terminated PBMA (reaction BM.D)

4.3.8 Polymerizations of LMA in the presence of HEMA dimer.

In order to compare earlier results with a much more bulky monomer with a very low Tg a series of polymerizations of LMA were carried out in the presence of HEMA dimer, **2.5**, the polymerization data for which are contained in Table 4.14 and Table 4.15.

Table 4.14 Reaction conditions for polymerizations of LMA in the presence of HEMA dimer.

	Amount of LMA (g)	Amount of **2.5** (g)	Amount of initiator (g)	Amount of DMF (g)	Reaction Time (min.)
LH.A	0.998	0.992	0.005	1.43	11520
LH.B	1.109	0.559	0.006	1.11	11520
LH.C	1.109	0.559	0.006	1.11	11520
LH.D	1.109	0.559	0.006	1.11	1020
LH.E	0.515	1.031	0.003	2.52	11520
LH.F	1.391	0	0.007	1.39	11520

Table 4.15 Molecular weight data for products of reactions LH.A-LH.F

	mole% **2.5**	Reaction time (min.)	Mn	Mw/Mn	Conversion based on LMA in Feed
LH.A	49.30	11520	20700	3.53	
LH.B	33.00	11520	24600	4.90	96.7 %
LH.C	33.00	11520	27000	4.49	
LH.D	33.00	1020	63300	2.98	31.1 %
LH.E	66.16	11520	12000	2.80	84.5 %
LH.F	0	11520	*	*	

* The polymer formed was too high a molecular weight to fit through the SEC filter.

At first glance, the presence of the bulky group on the monomer would seem to greatly diminish the effectiveness of the dimer as a chain transfer agent. However, when the molecular weight data are considered in terms of the degrees of polymerization obtained, there is a closer match to the data obtained using smaller monomers. The MALDI-TOF mass spectrum was obtained using 9-nitroanthracene doped with silver ions, as the polymer is less polar than PBMA and PMMA and no spectra were obtained using DHB, Figure 4.21. The peaks are separated by 254 amu, the molecular weight of LMA. The ^{1}H-NMR spectrum of the telechelic PLMA is shown in Figure 4.20. Again, the presence of more than one signal from the HEMA groups indicates that it is in more than one environment. There are no shoulders on the main PLMA peak in the region of 4.0 ppm, which is where a signal from the terminal O-CH_2 group would be expected.

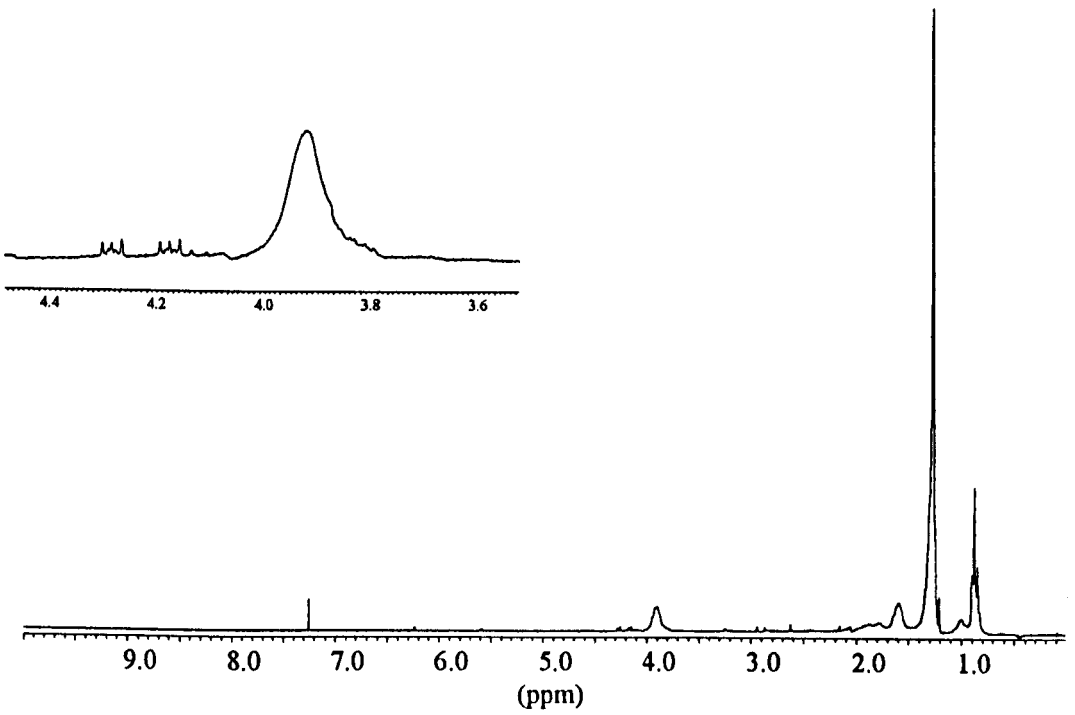


Figure 4.20 ^{1}H-NMR of hydroxy telechelic LMA (reaction LH.C)

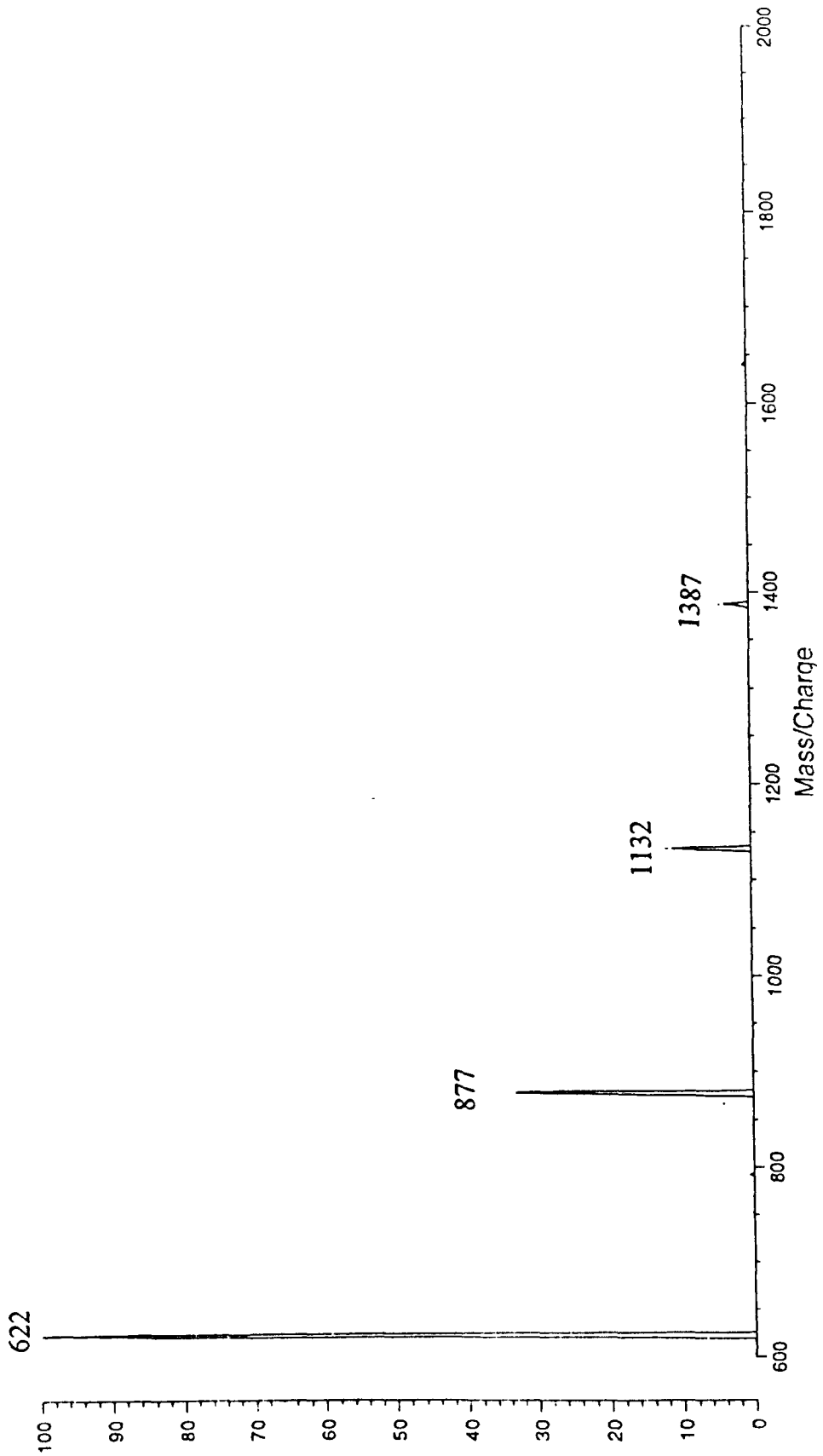
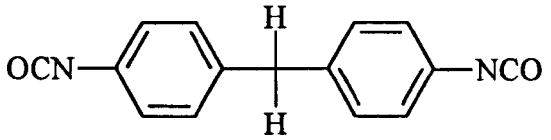


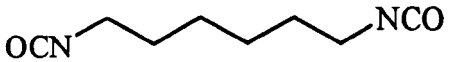
Figure 4.21 MALDI-TOF Mass Spectrum of Hydroxy Telechelic PLMA

4.3.9 Reactions of hydroxy telechelic polymers with isocyanates.

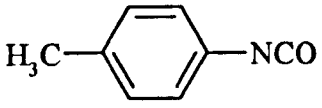
A common reaction employed to chain extend hydroxy telechelic polymers is a polyurethane reaction which is the basis of the polyurethane industry. It was for this reason that the polymers prepared using HEMA dimer were reacted with methylene diphenylene diisocyanate (MDI), hexamethylene diisocyanate (HDI) or p-tolyl isocyanate.



Methylene Diphenylene Diisocyanate



Hexamethylene Diisocyanate



p-Tolyl Isocyanate

The reactions were carried out by refluxing in toluene overnight with a 1:1 molar ratio of hydroxyl to isocyanate groups, experimental details are given in section 7.7.

The reactions involving aromatic groups were analysed by dual detector SEC equipped with a UV detector in addition to a differential refractometer. Where possible, a MALDI-TOF spectrum of the resulting polymer was obtained.

The end-capping reactions of hydroxy telechelic PMMA and PBMA with p-tolyl isocyanate were analysed using dual detector SEC. The chromatograms obtained are shown in Figure 4.22 and Figure 4.23 and indicate the presence of aromatic groups throughout the polymer.

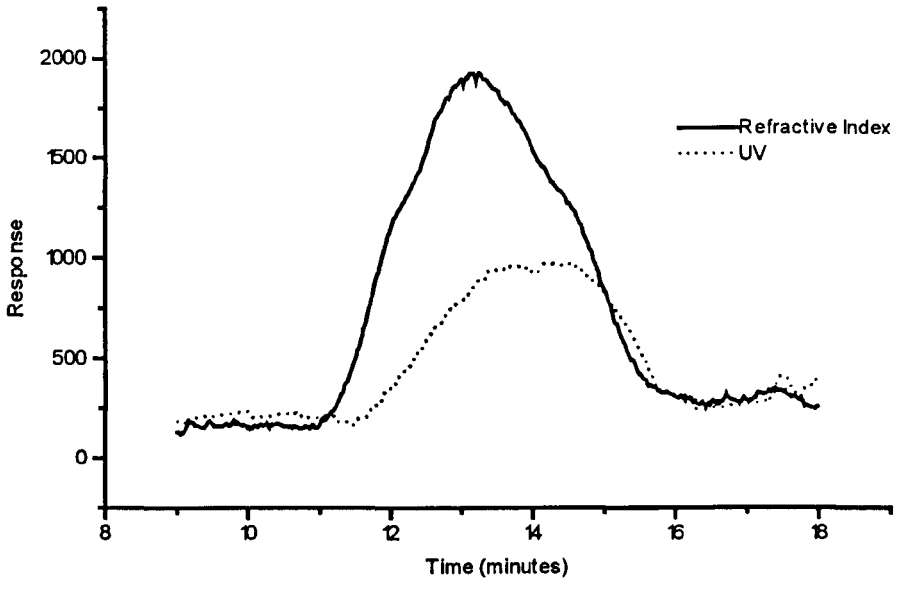


Figure 4.22 Dual detector SEC for the reaction of hydroxy telechelic PMMA with p-tolyl isocyanate

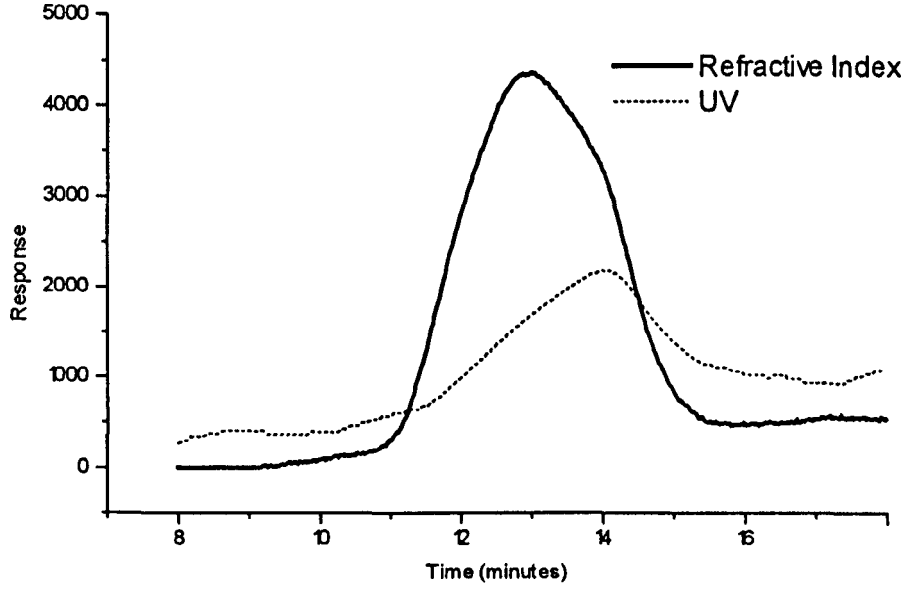


Figure 4.23 Dual detector SEC for the reaction of hydroxy telechelic PBMA with p-tolyl isocyanate

An attempt was made to chain extend the hydroxy telechelic PMMA using MDI. This was only partially successful, the molecular weight increasing from 6030 Da (PDi = 4.26) to 10560 (PDi = 3.16). The dual detector SEC from this reaction shows a strong signal in the UV trace, Figure 4.24. The presence of peaks in the aromatic region of the ^{1}H-NMR, Figure 4.25, indicates a reaction, although not complete chain extension, i.e. the molecular weight did not double.

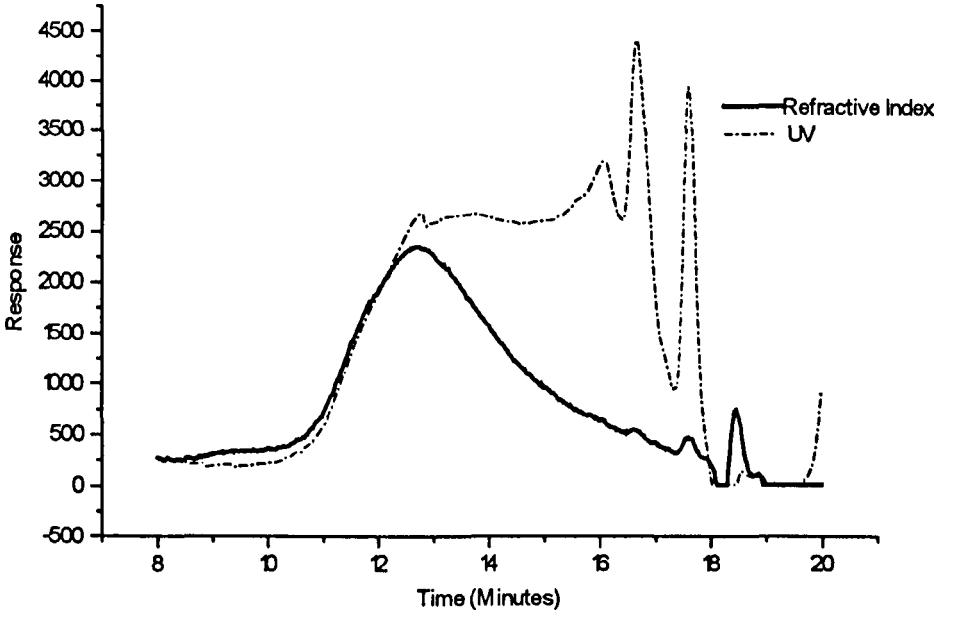


Figure 4.24 Dual Detector SEC of hydroxy telechelic PMMA after reaction with MDI.

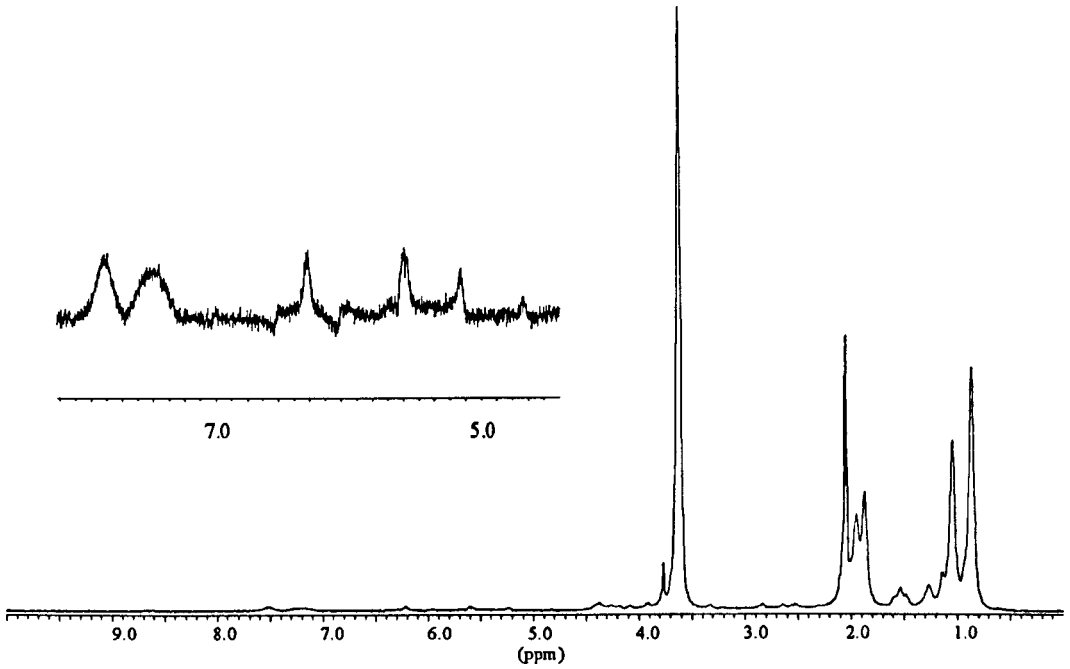


Figure 4.25 ^{1}H-NMR spectrum of hydroxy telechelic PMMA after reaction with MDI.

A MALDI spectrum was obtained for the chain extension reaction with MDI, Figure 4.26, but is complicated by the fact that two MDI units have a formula weight of 500 while MMA has a formula weight of 100.12. However, the presence of peaks with a mass of XX35, indicates addition of an odd number of MDI units to the polymer chains.

Reactions were also carried out using the more reactive hexamethylene diisocyanate, again with the intention of chain extension of the hydroxy telechelic PMMA, i.e. doubling the molecular weight. However, this was again only partially successful, the MALDI spectrum, Figure 4.27, shows:

a large number of unreacted polymer chains, indicated by the series of peaks at XX83:

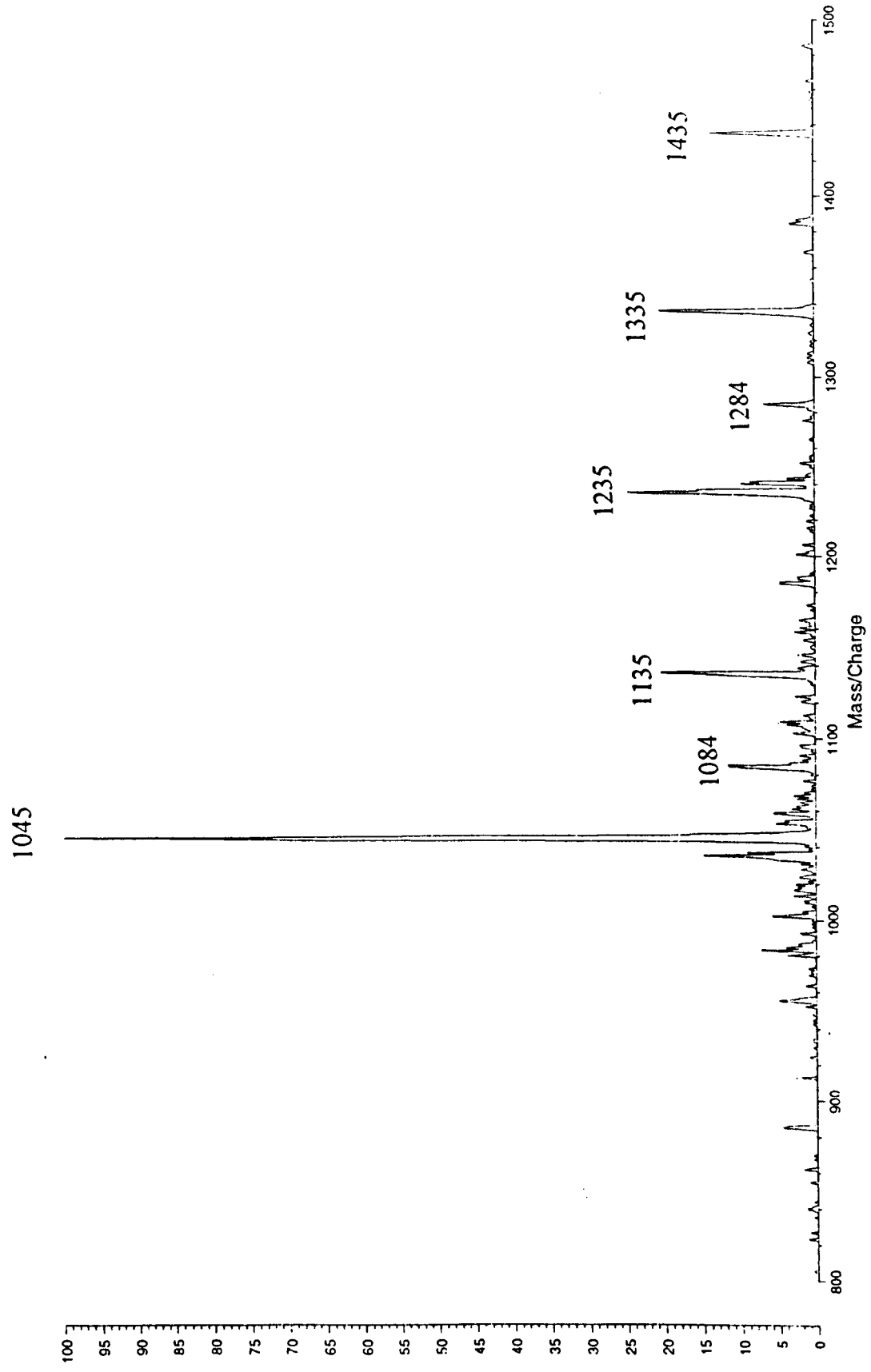


Figure 4.26 MALDI-TOF Mass Spectrum of Hydroxy Telechelic PMMA After Reaction with MDI

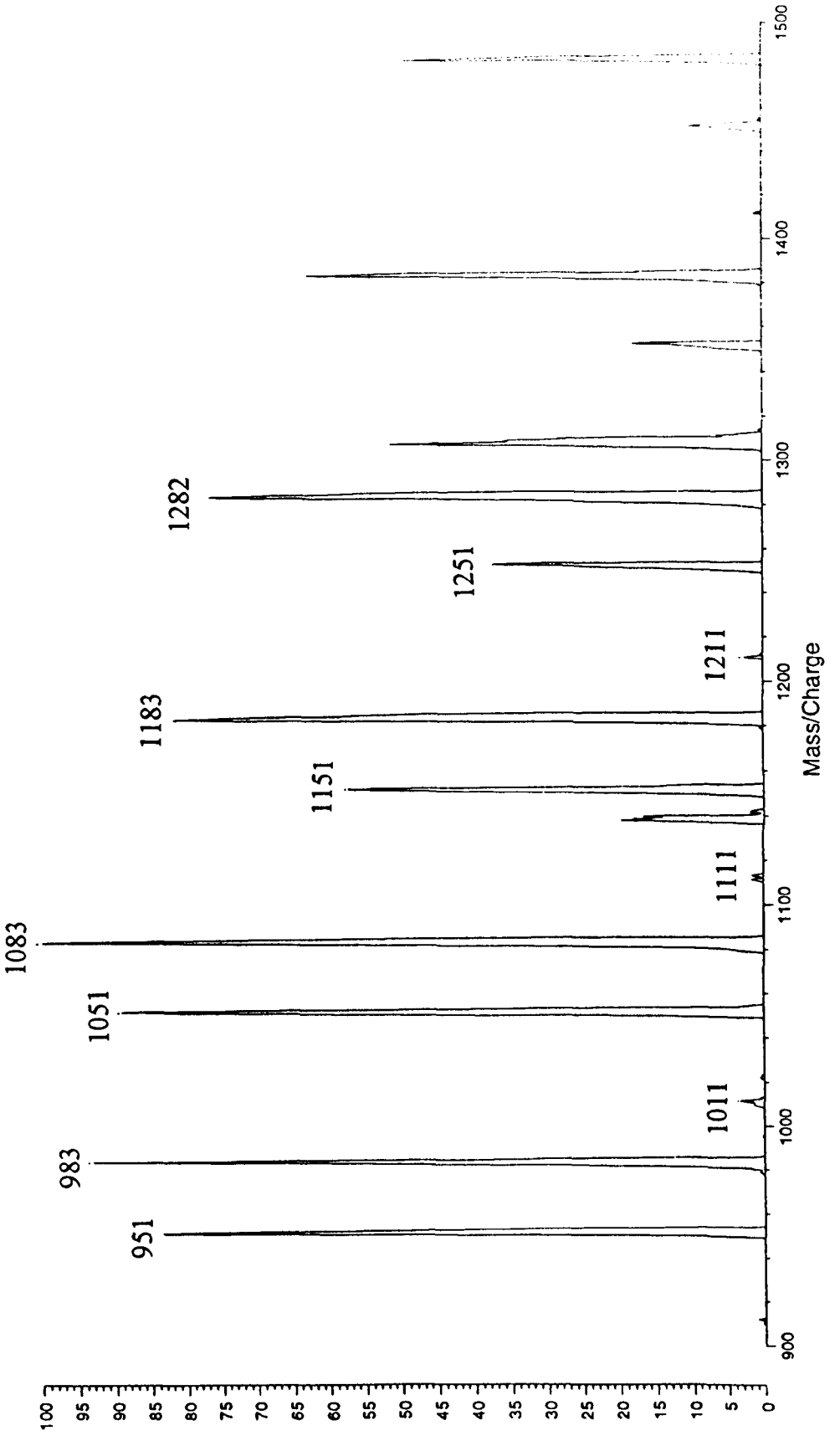
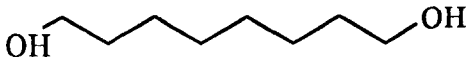
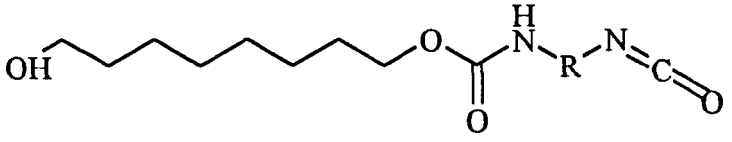


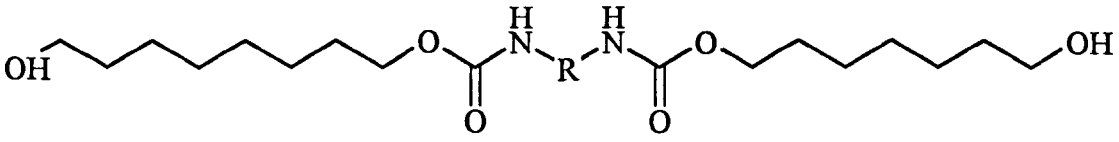
Figure 4.27 MALDI-TOF Mass Spectrum of Hydroxy Telechelic PMMA After Reaction with HDI



some peaks at XX51 indicating one diisocyanate end group on one chain end



and some peaks at XX11 showing one diisocyanate linking two telechelic polymers.



The molecular weight for this polymer used in this reaction also increased from 7570 to 10620 Da.

4.3.10 The preparation of PMMA with more than two HEMA groups per chain

The chain extension of dihydroxy telechelic polymers with diisocyanates has previously been investigated, section 4.3.9. However, if network formation is required, rather than chain extension, then the possibility arises of utilising mixed MMA-HEMA macromonomers in their impure state. Since the purpose of the polymer is to have random placement of HEMA groups on the polymer chain, the removal of HEMA monomer is not required and, as the macromonomers are polymerized with MMA, it is unnecessary to remove the unreacted MMA before

reaction. The use of higher molecular weight macromonomers opens up the possibility of obtaining lower molecular weight polymers containing hydroxy functionality since they have higher chain transfer coefficients than pure dimer. Four experiments were carried out to prepare polymers by the addition of mixed HEMA/MMA macromonomers (Mn = 563, PDi = 2.13) to polymerizations of MMA; reaction conditions are given in Table 4.16. This resulted in the formation of PMMA with a small number of hydroxy groups near to the chain end via β-scission. Molecular weight data and the average number of HEMA groups per chain, calculated by a combination of NMR spectroscopy and SEC, are given in Table 4.17.

Table 4.16 Reaction conditions for the preparation of PMMA with more than two HEMA groups per chain.

	mass of MMA (g)	mass of mixed macromonomers (g)	mass of VA-086 (g)	mass of DMF (g)
A	1.002 (10.0 mmol)	0.110 (0.2 mmol)	0.005	3.908
B	1.001 (10.0 mmol)	0.500 (0.9 mmol)	0.005	3.557
C	1.004 (10.0 mmol)	0.517 (0.9 mmol)	0.005	3.571
D	1.000 (10.0 mmol)	1.012 (1.8 mmol)	0.005	3.025

Table 4.17 Molecular weight data for reactions A-D.

	Mn	PDi	Conversion[a]	number of HEMA units per chain[b]
MM.A	27250	2.09	65.4	5.1
MM.B	6810	2.23	77.3	4.3
MM.C	6270	2.32	80.9	4.4
MM.D	3990	2.31	77.3	4.2

a based on MMA in feed

b calculated by combination of NMR spectroscopy and SEC.

The ^{1}H-NMR spectrum of MM.D is shown in Figure 4.28 below. The expanded region illustrates the presence of both MMA and HEMA groups in the polymer.

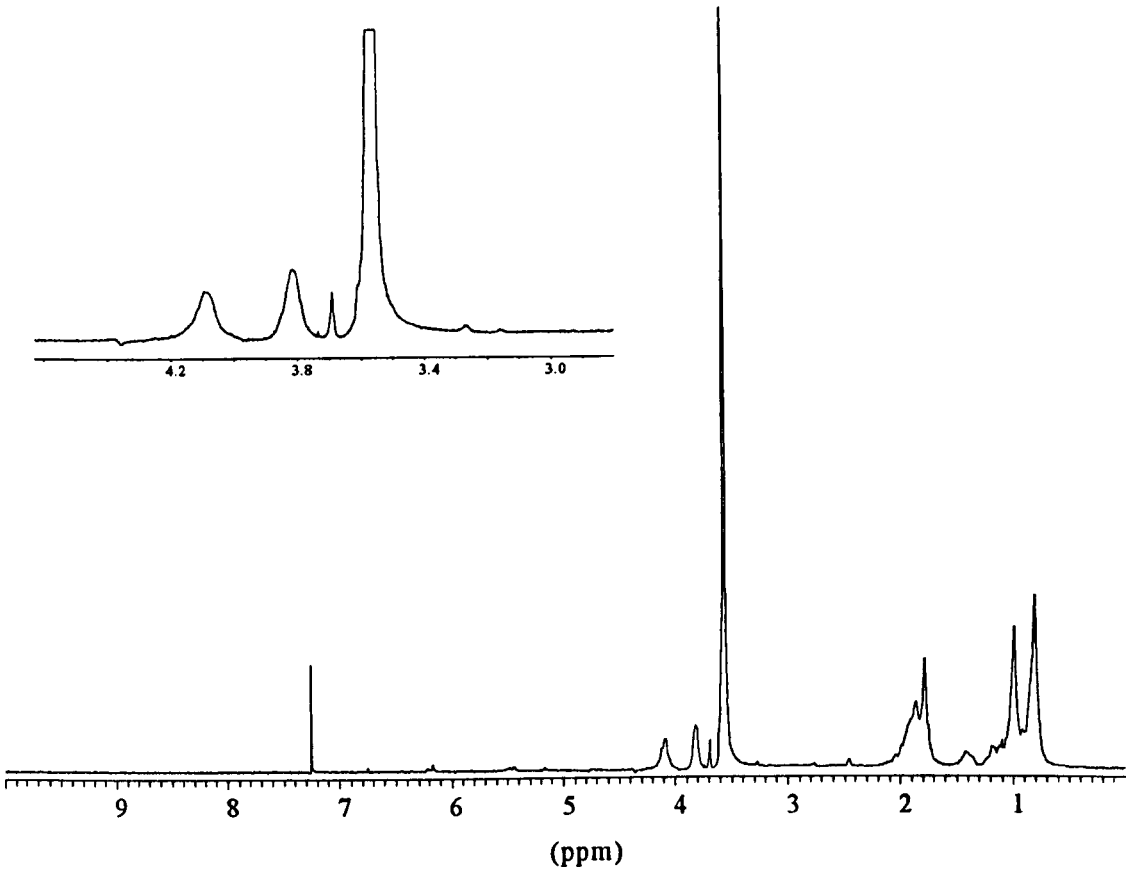


Figure 4.28 ^{1}H-NMR spectrum ($CDCl_3$, 298 K, 250 MHz) of the product of the polymerization of MMA and mixed MMA-HEMA macromonomers (reaction D). The inset shows the expanded region of the O-CH_3 groups of PMMA and O-CH_2 groups of PHEMA.

The addition of increasing amounts of macromonomer resulted in a decrease in the molecular weight of the final polymer, as expected. A comparison with the molecular weights obtained using HEMA dimer to form telechelic polymers under similar conditions shows that using higher molecular weight macromonomers allows a greater reduction in molecular weight than that afforded by the use of pure dimer. This leads to the possibility of producing multifunctional polymers in the liquid state, thus reducing the required amount of solvent in many reactions.

4.3.11 Addition of diisocyanate to PMMA with more than two HEMA units per chain

Since the aim of these experiments was to form a random network by the reaction of diisocyanate to hydroxyl groups it should be possible to carry out the reactions without removal of unreacted macromonomer. The macromonomer has a similar composition to the polymer but is likely to be more reactive. However, the macromonomer should still undergo chain extension and crosslinking reactions. It is possible to form higher molecular weight mixed macromonomers by the reaction of MMA and HEMA but with smaller amounts of CoBF than used for the macromonomers prepared in this work. It should be possible to use these macromonomers without further polymerization with monomer to form networks by reaction with diisocyanates.

Two reactions were carried out in order to form a network using polymer from reactions D and B with MDI and HDI respectively. In the first reaction a stock solution of 0.25 g of MDI in 20 mL of anhydrous toluene was prepared. 0.50 g of polymer D was dissolved in toluene (50 mL) and refluxed before addition of 1 ml of the MDI solution and four drops of dibutyltin dilaurate. A further 1 ml was added every 30 minutes for 2.5 hours to give an excess of MDI over calculated hydroxyl groups. A further 1 ml was added over a period of one hour with 1.5 ml added after 5 hours. After 6 hours the heat was removed and the solution stirred over the weekend. No network was formed, but analysis of the polymer by dual detector SEC showed the presence of aromatic groups throughout the polymer and an increase in molecular weight from 3990 to 8250 g mol^{-1}. The increase in

molecular weight after reaction with MDI is clearly illustrated in the SEC overlay, Figure 4.29.

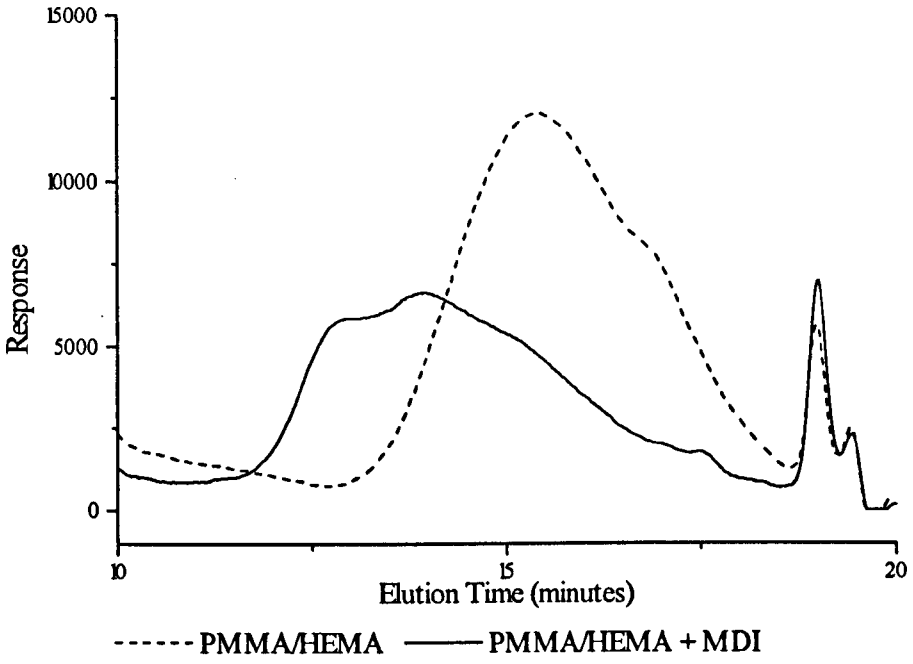


Figure 4.29 Overlay of the SEC traces for the polymer formed from mixed macromonomers before and after reaction with MDI.

A similar reaction, again with the aim of forming a network, was carried out using polymer B and HDI. 190 μL of HDI was added to 20 ml of toluene. 2 ml of this solution was added to the refluxing polymer (0.58 g in 50 ml toluene) in addition to four drops of catalyst. A further 1.5 ml of HDI solution was added after 2 hours (3.2 ml of HDI solution would give a 1:1 ratio of NCO:OH groups based on average of 4.3 hydroxyl groups per chain). The reaction was refluxed for 22 hours before being terminated with methanol. At the end of the reaction a gel was observed around the sides of the reaction flask which was found to be insoluble in

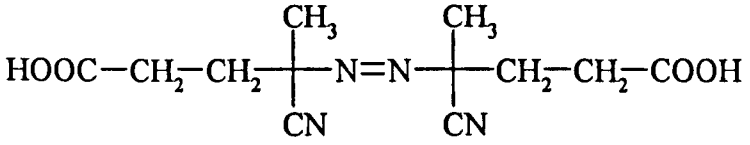
THF, acetone and chloroform. Hence it was assumed that a network had been formed.

4.4 Emulsion polymerizations.

It has already been demonstrated that the addition of macromonomers to solution polymerizations can result in the formation of telechelic polymers, Chapter 4. This work aims to repeat the addition-fragmentation reactions of methacrylate dimers already carried out in bulk and solution, but in emulsion polymerizations. The advantages of using emulsion techniques have already been briefly presented in the introduction, section 4.1.1.

Block copolymers of butyl methacrylate and methyl methacrylate with various higher molecular weight methacrylate macromonomers have previously been reported, [8, 9] but no papers have been published in the literature concerning the use of methacrylate dimers in emulsion polymerizations. The aim of this work was determine the effect of the addition of various amounts of MMA dimer (10 and 50 % vol/vol) to polymerizations of BMA on the molecular weight and architecture of the chain.

The polymerizations were initiated using a water soluble initiator, 4,4'-azobis(4-cyanopentanoic acid), (CVA), **4.4**:



4.4

Homopolymerizations of BMA and MMA were also carried out as a control to gauge the effect of the addition of the dimer on both the molecular weight and the rate of polymerization. The polymers obtained from the reactions with macromonomers were analysed by SEC and MALDI-TOF mass spectrometry. Table 4.18 shows the reaction conditions and molecular weight data obtained for all of the reactions carried out in emulsion.

Table 4.18 Reaction data for emulsion polymerizations.

	volume of monomer	volume of dimer	Conversion after 2 hours	Mn of final polymer	PDi of final polymer
EM.A	50 mL MMA (0.467 moles)	0	100%	339200	2.18
EM.B	50 mL MMA (0.467 moles)	0	96%	292500	2.23
EM.C	0	50 mL MMA (0.262 moles)	2%	-	-
EM.D	50 mL BMA (0.314 moles)	0	86%	109800	4.23
EM.E	45 mL BMA (0.283 moles)	5 mL MMA (0.026 moles)	67%	20400	3.32
EM.F	25 mL BMA (0.157 moles)	25 mL MMA (0.131 moles)	21%	5600	2.22
EM.G	45 mL BMA (0.283 moles)	5 mL HEMA (0.096 moles)	78%	63100	3.21

The control experiments conducted in the absence of dimer result in polymers of substantially higher molecular weights. This is evidence that, in an emulsion system containing methacrylate dimers, chain transfer is the predominant

mechanism for chain termination. For example, the emulsion polymerization of BMA in the absence of dimer has a molecular weight in excess of 100 000. Addition of 10 % vol/vol (8 mole %) reduces the molecular weight to approximately 20 000. Increasing the dimer content to 50 % vol/vol (45 mole %) further reduces the molecular weight, but only to 5 600.

Addition of 10 % vol/vol HEMA dimer also brings about a reduction in molecular weight, but only to 63 000. This is not unexpected as HEMA dimer is much more water soluble than MMA dimer. Thus despite being premixed with the BMA, a greater proportion of the dimer would be found in the aqueous phase rather than in the monomer droplets, leading to a reduction in the efficiency of the dimer as a chain transfer agent in emulsion systems.

The reduction in the rate of polymerization that occurs with the introduction of methacrylate dimers is also analogous to the reactions carried out in bulk and solution. This can again be attributed to the partitioning of the radical adduct intermediate towards the starting materials, as discussed in Chapter 3.

The apparent chain transfer constants for the reactions with dimers calculated using the Mayo equation are as follows:

E: $C_s = 0.0615$, F: $C_s = 0.0288$, G: $C_s = 0.0141$

Thus the chain transfer activity of the methacrylate dimers is of a similar order of magnitude to that observed in bulk polymerizations. It is also noticeable that the chain transfer activity is again dependent on the amount of dimer in the feed, experiments E and F. Increasing the amount of dimer in the feed results in a reduction in the apparent chain transfer activity, this can again be attributed to a phenomenon similar to the bootstrap effect discussed in Chapter 3. The lower chain transfer constant of HEMA dimer, experiment G, compared to MMA dimer

experiment E, is again a result of the water solubility of the HEMA dimer, which results in a reduced probability of finding the dimer in the monomer micelles and hence in the vicinity of the propagating chains. This is not seen in solution polymerizations carried out to form telechelic polymers where MMA dimer and HEMA dimer brought about similar reductions in the molecular weight of the BMA polymer.

Figure 4.30 shows a MALDI-TOF mass spectrum of the product of an emulsion polymerization between BMA and MMA dimer which was stopped at low conversion. The main series of peaks are 142 Da apart and correspond to BMA_x with one unit of MMA and one unit from the initiator fragment. For example, the peak at *m/z* 958 corresponds to $BMA_5MMA_1CVA_{0.5}Na$, for which the calculated molecular weight would be 960 Da. This shows that the reactions carried out in emulsion polymerization are analogous to free radical polymerizations carried out in bulk in that the added macromonomers undergo a β-scission mechanism. This is the only explanation for the presence of only one MMA unit in the chains. The second series of peaks corresponds to BMA_xMMA_2Na, i.e. the peak at *m/z* 933 is from a chain with the formula BMA_5MMA_2Na.

A MALDI-TOF mass spectrum of a similar reaction carried to a higher conversion (F), Figure 4.31, shows a main series of peaks corresponding to the presence of two MMA units per chain, and no initiator fragments. The peaks are separated by 142 Da, e.g. the peak at *m/z* 1219 matches the structure BMA_7MMA_2Na. This shows that the main termination and initiation mechanisms involve the addition-fragmentation chain transfer action of the MMA dimer.

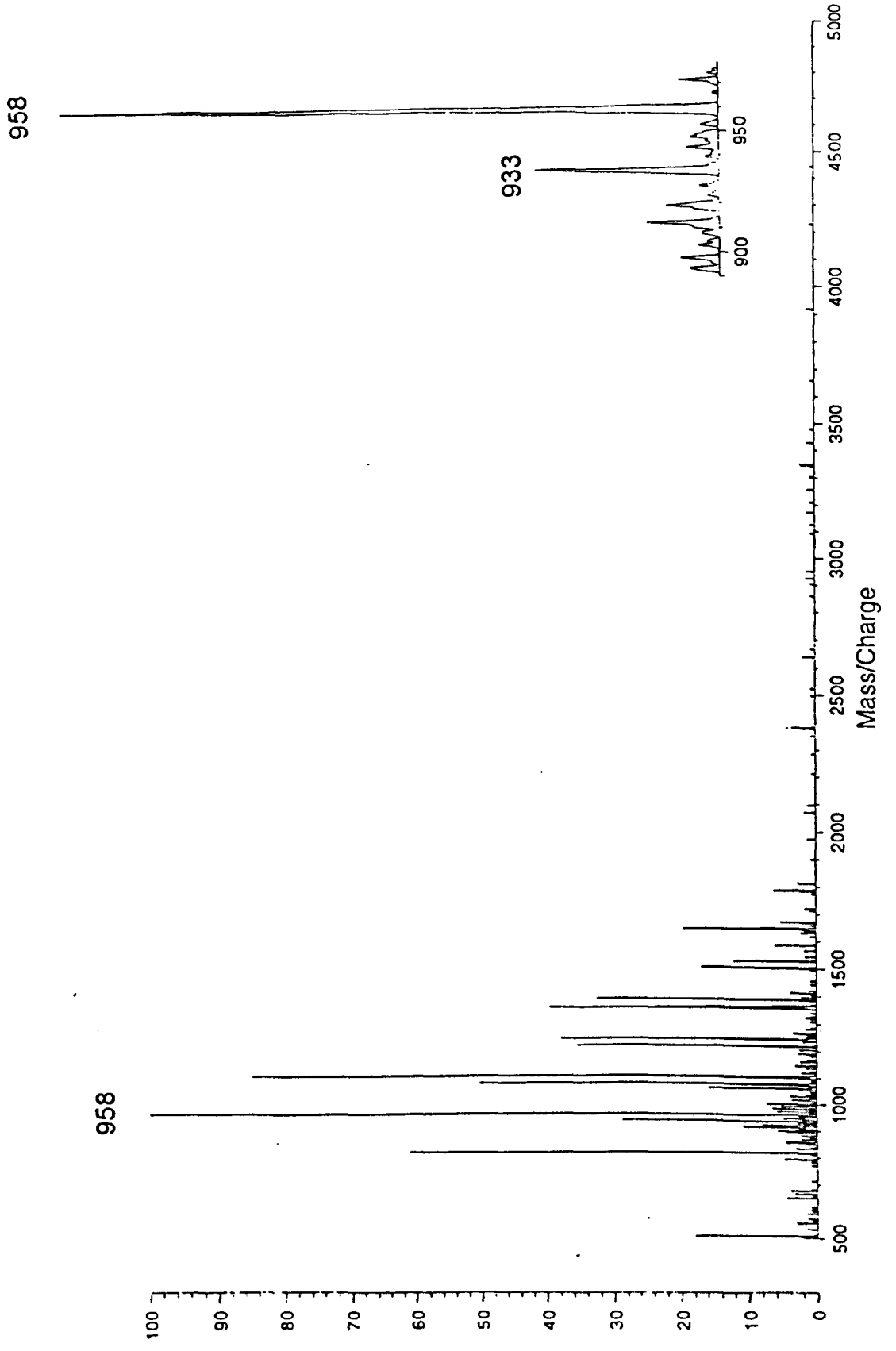


Figure 4.30 MALDI-TOF Mass Spectrum of the Product of the Emulsion Polymerization of BMA and MMA Dimer at Low Conversion

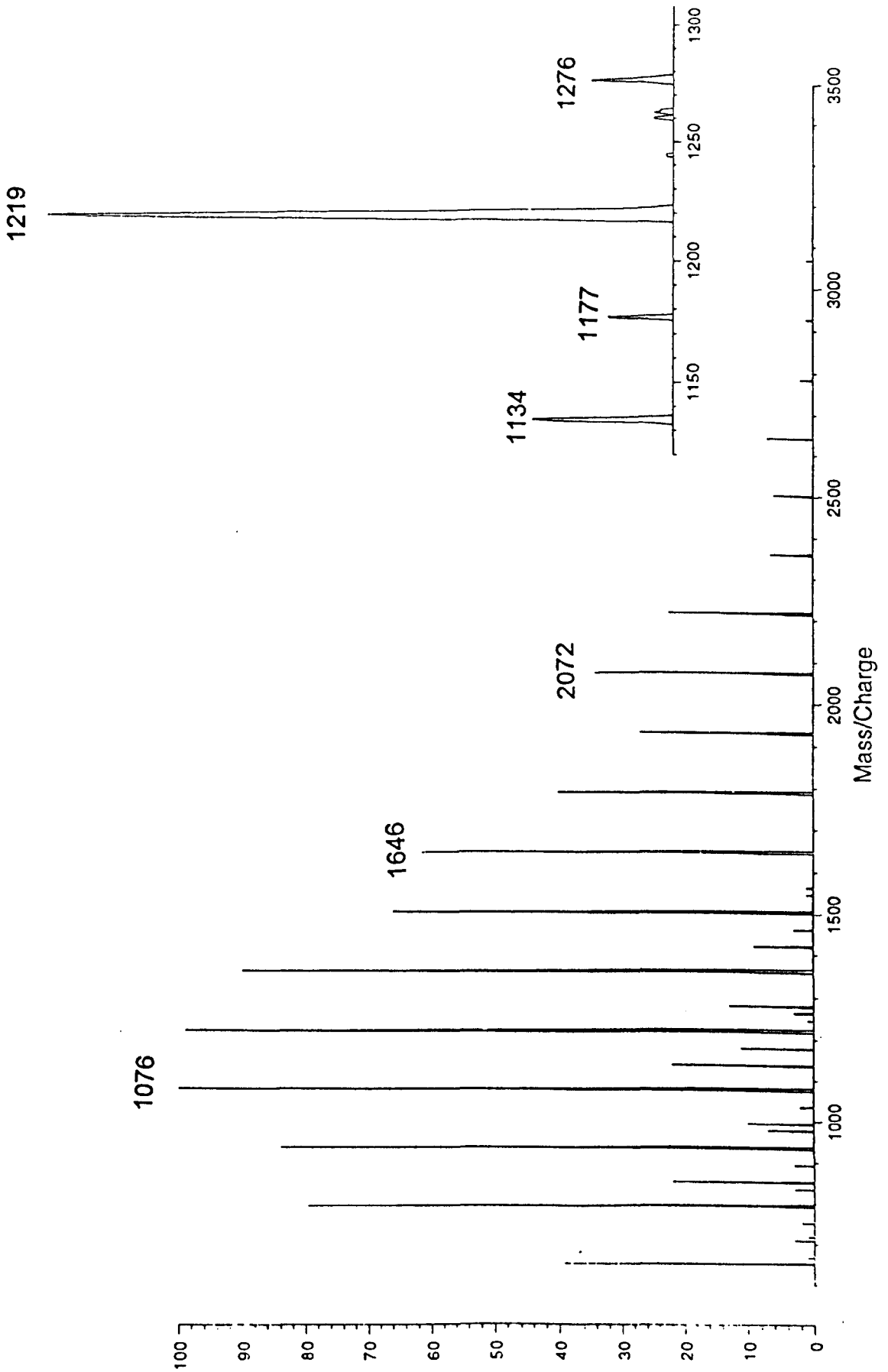


Figure 4.31 MALDI-TOF Mass Spectrum of the Product of the Emulsion Polymerization of BMA and MMA Dimer at High Conversion

There are also two minor series of peaks, one corresponding to the presence of four MMA units, e.g. *m/z* 1134 BMA_5MMA_4Na, and the other to three MMA units, e.g. *m/z* 1177 BMA_7MMA_3Na. One possible explanation is that the peak corresponding to the presence of four MMA units could arise from some copolymerization of MMA dimer with BMA, with β-scission also occurring giving an MMA unit on each end of the chain and a dimer unit within the chain. The three MMA units would arise from copolymerization, followed by normal termination by disproportionation.

From these results it would seem that polymerizations of methacrylate monomers and macromonomers predominantly undergo β-scission type reactions analogous to those seen in bulk polymerizations. However, the emulsion system apparently allows a small amount of copolymerization to take place.

Figure 4.32 shows the ^{1}H-NMR spectrum of the polymer formed in reaction EM.F. Comparison of this spectrum with that formed in the solution polymerization, Figure 4.19, shows that a similar product is formed, but with larger relative amounts of MMA in the polymer as a result of the lower Mn (5630 compared with 10050). This spectrum shows the absence of terminal butoxy units, and the presence of vinyl groups in the polymer.

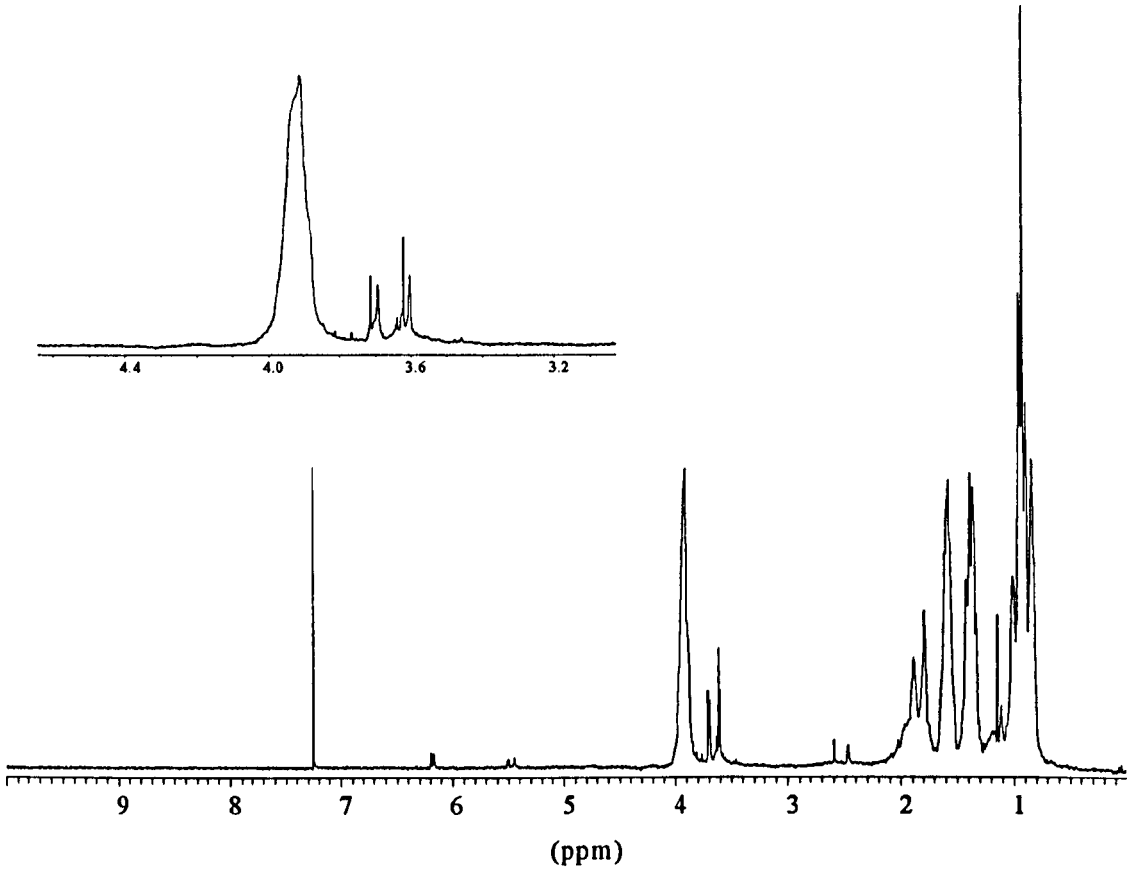


Figure 4.32 ^{1}H- NMR spectrum ($CDCl_3$, 298 K, 250 MHz) of the polymer produced by the emulsion polymerization of BMA with MMA dimer. The inset shows the expanded region around the PBMA O-CH_2 and PMMA O-CH_3 peaks.

The ^{1}H-NMR spectrum presented in Figure 4.33 is obtained from the polymer formed in reaction EM.G between BMA and HEMA dimer. Again, comparison with the spectrum of the polymer formed in the analogous solution reaction, Figure 4.17, shows that a similar product is formed. Again, the presence of vinyl groups in the region 5.5 to 6.5 ppm is noted, along with the absence of terminal butoxy groups.

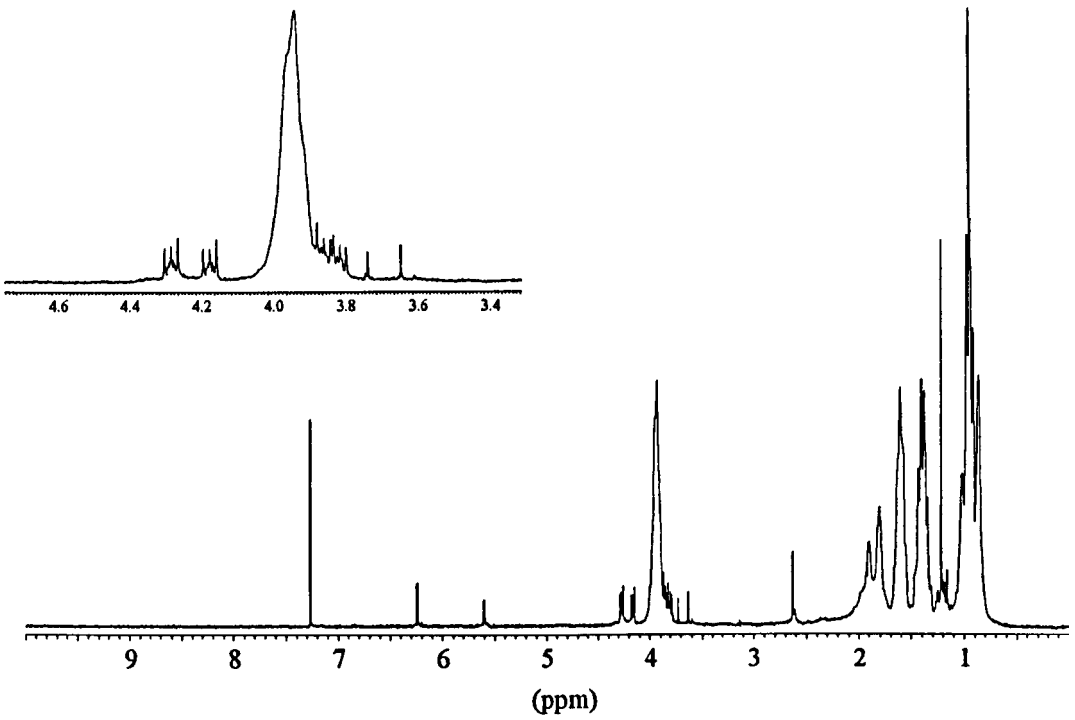


Figure 4.33 ^{1}H-NMR spectrum ($CDCl_3$, 298 K, 250 MHz) of the product of the emulsion polymerization of BMA and HEMA dimer. The inset shows the expanded region of the O-CH_2 groups of PBMA and PHEMA.

4.5 Conclusions

The use of macromonomers as addition fragmentation chain transfer agents results in a reduction in the molecular weight of the final polymer. Moreover, the use of functional methacrylate dimers allows the introduction of controlled amounts of functionality to the polymer chain and the production of telechelic polymers without diminishing the chain transfer activity of the dimer.

A combination of SEC and NMR data shows a functionality for the hydroxy telechelic PMMA of 2.05.

MALDI-TOF mass spectrometry has been shown to be a useful tool in the characterization of telechelic polymers as it indicates the number of functional monomer units per chain. The absence of peaks from initiator fragments in both the MALDI-TOF and NMR spectra confirms the β-scission chain transfer mechanism to be the predominant form of initiation and termination in these systems.

Different results were obtained with GMA dimer which according to NMR analysis, does not give completely telechelic polymers. However, as this is not seen with BzMA dimer, it is not believed to be due to the size of the functional group. It is more probable that it is a feature of the ring opening chemistry of the epoxy functionality.

The polymers produced in these reactions undergo further reactions typical of the functional groups present at the chain ends. Hydrogenolysis of BzMA terminated PMMA forms methacrylic acid terminated polymer in 100% yield. The hydroxy telechelic polymers will end cap and chain extend to some extent with the addition of methylene diphenylene diisocyanate and hexamethylene diisocyanate under the reaction conditions described. It is thought that a longer reaction time would lead to more chain extension.

4.6 References

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Chapter

5.

Group Transfer Polymerization and Copolymerization of Methacrylate Macromonomers.

5.1 Introduction

Group Transfer Polymerization (GTP) of methacrylates was first discovered by Webster et al in 1983.[1] An overview of the published literature concerning GTP and mechanistic aspects is presented in the introduction to this thesis, section 1.2.2. Although a large number of monomers have been homopolymerized and copolymerized by GTP there is very little work published in the literature concerning the copolymerization of methacrylate monomers and macromonomers using this technique.

This work aims to address this issue by presenting the results of numerous copolymerizations of BMA with MMA macromonomers and MMA with BMA macromonomers. From these results it is hoped to present a comparison with analogous reactions carried out using free radical techniques using analysis by MALDI-TOF mass spectrometry and size exclusion chromatography.

5.2 Experimental

Reactions were carried out in THF and in bulk using the experimental conditions given in section 7.10. Reactions were carried out at room temperature and in some cases further additions of catalyst solution were made.

The resulting polymers were analysed by SEC after removal of solvent and unreacted monomer. MALDI-TOF mass spectra were obtained using DHB matrix doped with NaCl.

5.3 Homopolymerization of methacrylate macromonomers by GTP

A number of reactions were carried out in an attempt to homopolymerize MMA dimer, MMA trimer and BMA dimer by GTP. Previous work has shown that whilst MMA macromonomers will undergo an initiation step they do not homopolymerize under free radical conditions.[2] It was thought that the β-scission mechanism which is largely responsible for the absence of homopolymerization in free radical systems may be absent in GTP and so the macromonomers may undergo some homopolymerization.

Reaction conditions and molecular weight data for polymerizations of MMA dimer are given in Table 5.1. Molecular weight data was obtained by SEC, in some cases after the removal of part of the dimer using a kugelrohr apparatus to simplify analysis of the chromatogram.

Table 5.1 Reaction conditions and polymerization data for homopolymerization of MMA dimer by GTP.

	mL of MMA dimer	Mn	PDi	moles MTS	moles TBAmCB	Comments
M2.A	6.0 (3.14×10^{-2} moles)	400	1.50	6.40×10^{-4}	6.28×10^{-6}	a
M2.B	10.0 (5.24×10^{-2} moles)	550[b,c]	1.20	5.41×10^{-4}	5.24×10^{-6}	-
M2.C	10.0 (5.24×10^{-2} moles)	423[b,c]	1.11	5.41×10^{-4}	5.20×10^{-6}	a

a molecular weight data obtained after removal of unreacted monomer and dimer by reduced pressure distillation

b further aliquots of catalyst solution added every 30 minutes for 2 hours

c reaction carried out in bulk

The molecular weight obtained from these reactions suggests that although the macromonomer undergoes initiation, there is little or no propagation. Analysis of the MALDI-TOF mass spectra, Figure 5.1,obtained shows some evidence to suggest that propagation has occurred. Most of the spectra obtained contain a peak at *m/z* 492. This is consistent with cyclization of a species containing five MMA units, i.e. $MTSMMA_4Na$, with the evolution of a methoxy group, Figure 5.2. In spectra where this is not seen a peak at *m/z* 692.0 is observed, due to cyclization of a chain containing seven MMA units.

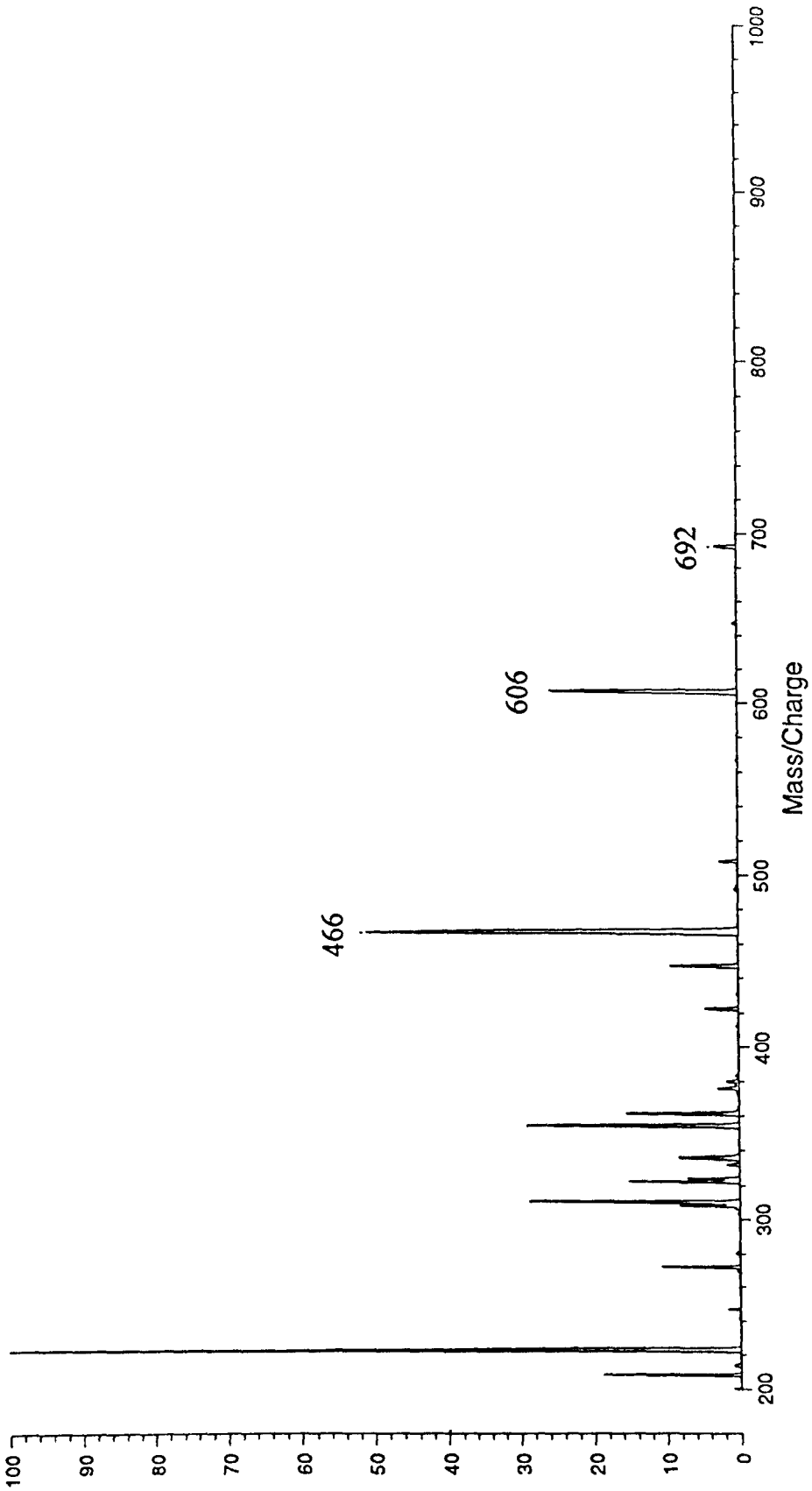

Figure 5.1 MALDI-TOF Mass Spectrum of the GTP Reaction of MMA Dimer

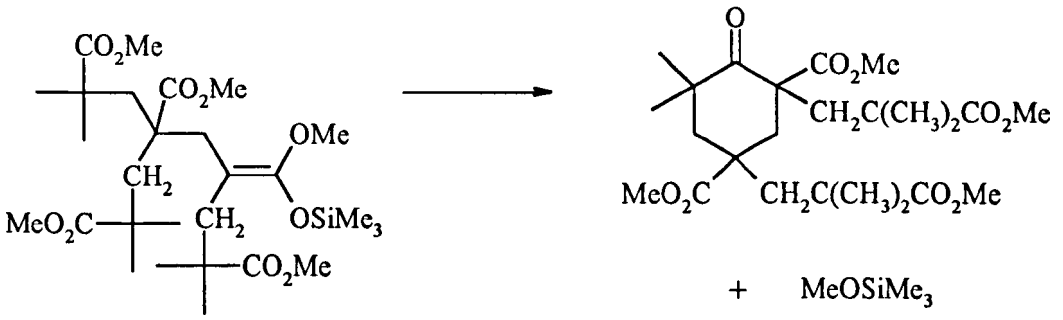

Figure 5.2 Cyclization mechanism for homopolymerization of MMA dimer.

Further homopolymerizations were also attempted using BMA dimer and MMA trimer. The reaction conditions and molecular weight data for these reactions are given in Table 5.2.

Table 5.2 Polymerization data for homopolymerization reactions of BMA dimer and MMA trimer by GTP.

	mL Macromonomer	Mn	PDi	Comments
BMA Dimer	2 (6.26×10^{-3} moles)	472	1.02	a
MMA Trimer	2 (7.37×10^{-3} moles)	420	1.05	b

a moles MTS = 3.20×10^{-6}, moles TBAmCB = 3.16×10^{-6}

b moles MTS = 3.69×10^{-4}, moles TBAmCB = 3.68×10^{-6}

Both these reactions were analysed by MALDI-TOF mass spectrometry in order to gain some information regarding the polymerization mechanism. Although the MALDI-TOF spectra contain a number of peaks that cannot be explained, there are also some peaks that point to a propagation reaction of the macromonomers

by GTP. The MALDI-TOF mass spectrum for the reaction of BMA dimer, Figure 5.3, contains a peak at *m/z* 593 which indicates the presence of a species with the formula BMA_4Na, i.e. no MTS contained in the molecule. The most probable explanation for this is chain transfer to leave a BMA initiating species followed by the addition of two dimer units, one of which again undergoes chain transfer to give four BMA units in the chain. Peaks are also seen at *m/z* 409 from MTS-BMA_2Na, and *m/z* 619 and 661 from cyclization products of MTS-BMA_4Na with the elimination of butoxy and methoxy anions respectively.
The MALDI-TOF mass spectrum from the products of the reaction of MMA trimer, Figure 5.4, contains peaks at *m/z* 423, 525 and 625. These indicate that a propagation reaction is occurring, although it is not possible to ascertain whether or not chain transfer has occurred. A peak is also seen at *m/z* 592 from the cyclization product of MMA_6, with elimination of a methoxide anion.

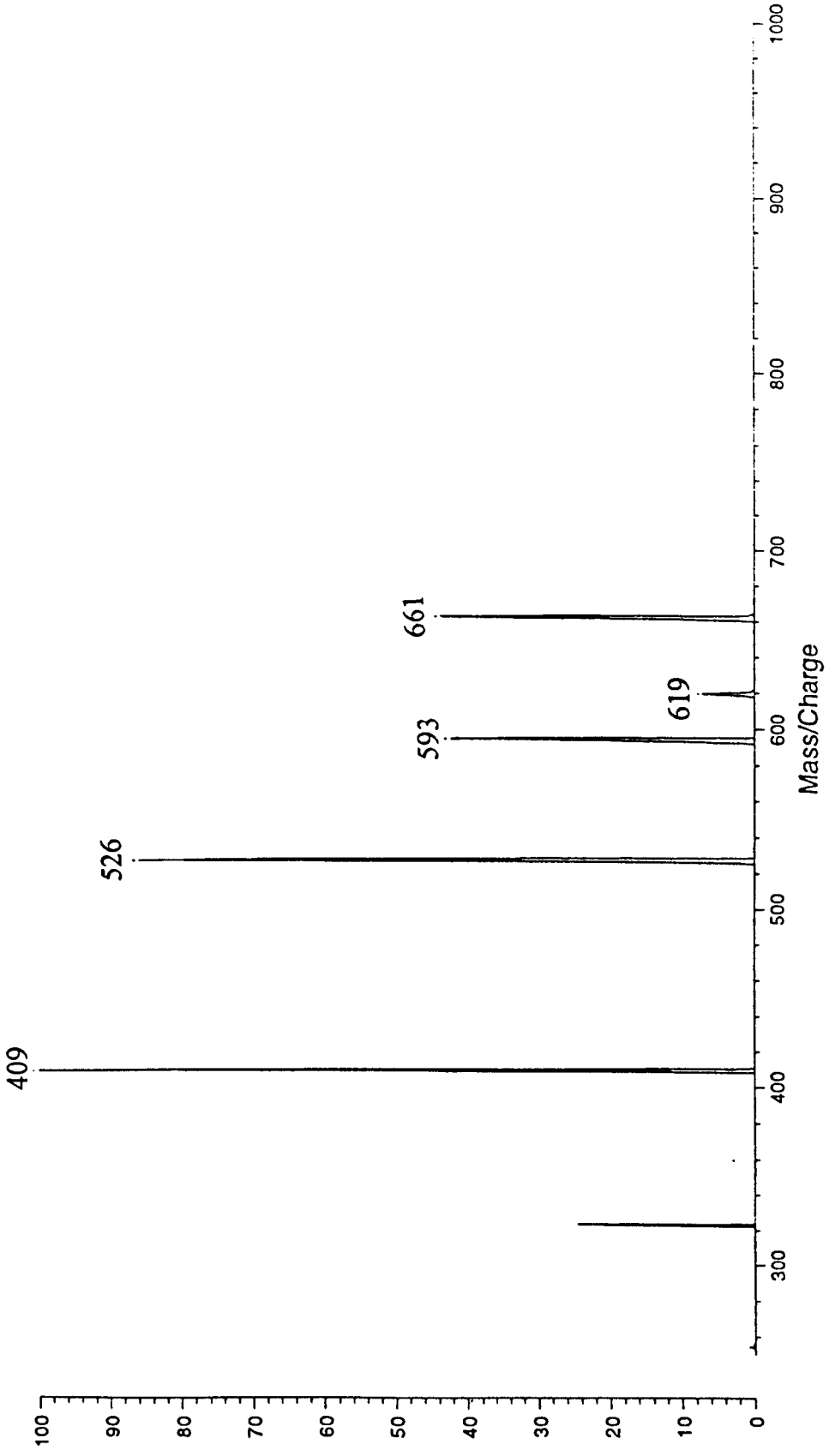

Figure 5.3 MALDI-TOF Mass Spectrum of the GTP Reaction of BMA Dimer

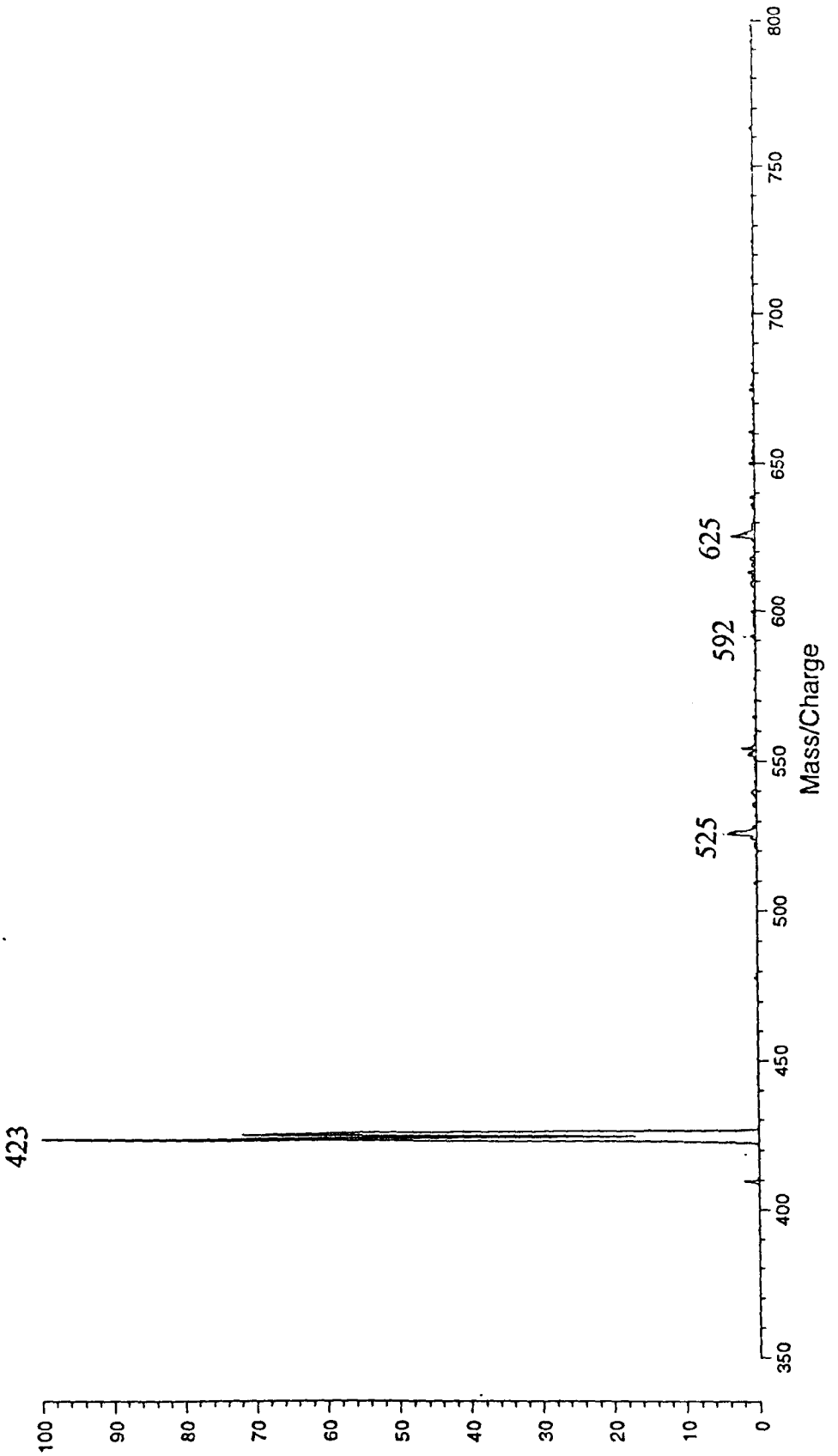

Figure 5.4 MALDI-TOF Mass Spectrum of the GTP Reaction of MMA Trimer

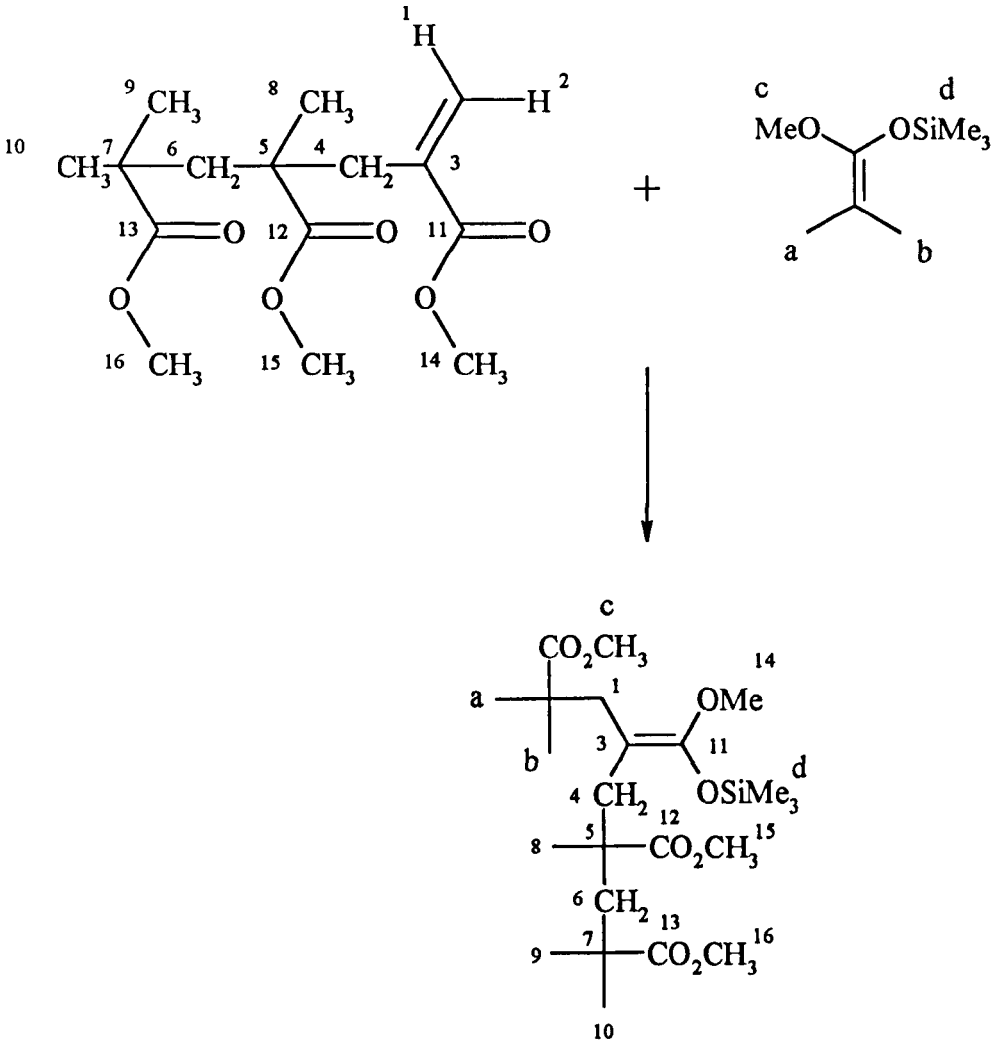

Figure 5.5 Initiation step in GTP of MMA trimer with MTS.

Comparison of the ^{1}H-NMR spectrum of MMA trimer before, Figure 5.6, and after reaction with MTS, Figure 5.7, shows a shift in the position of the peaks from the trimer. However, the ^{13}C NMR spectrum shows no change. The expected initiation step of MMA trimer with MTS is shown in Figure 5.5. From this it would be expected that the main changes in the ^{1}H-NMR spectrum of the MMA trimer would be in the position of the peaks associated with H^{14}. In the case of the spectrum of MTS peaks from H^{c} and H^{d} would be expected to shift.

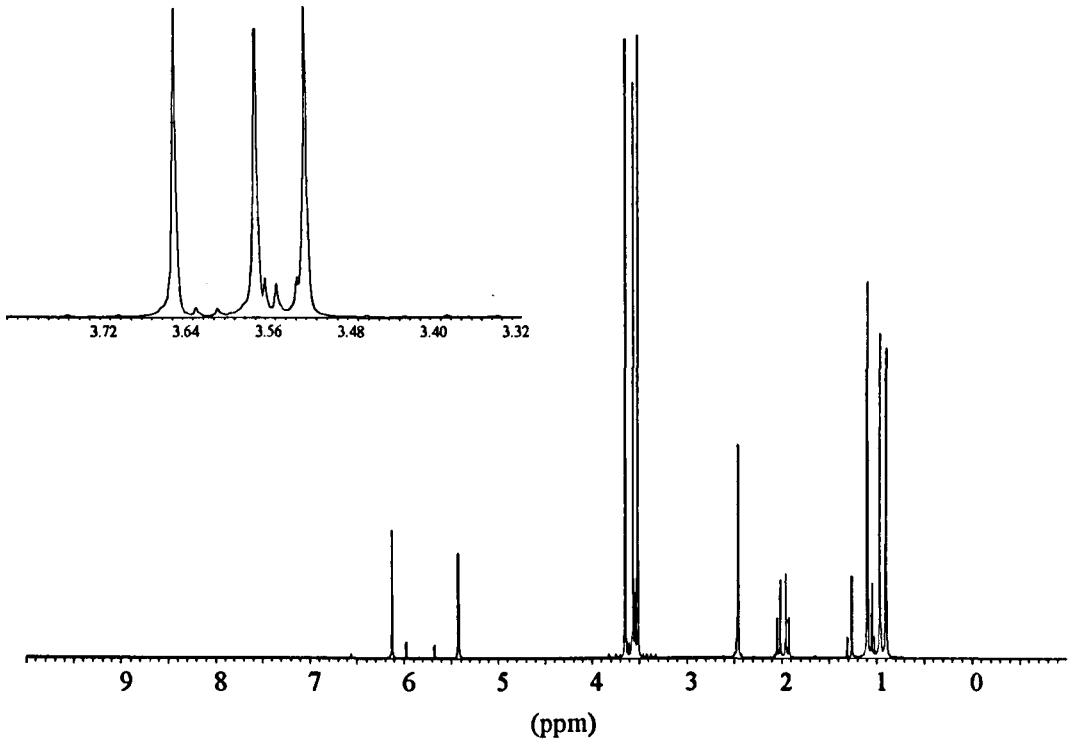

Figure 5.6 ^{1}H NMR spectrum (TCE, 298 K, 400 MHz) of MMA trimer. The inset shows the expanded region of the O-CH_3 groups.

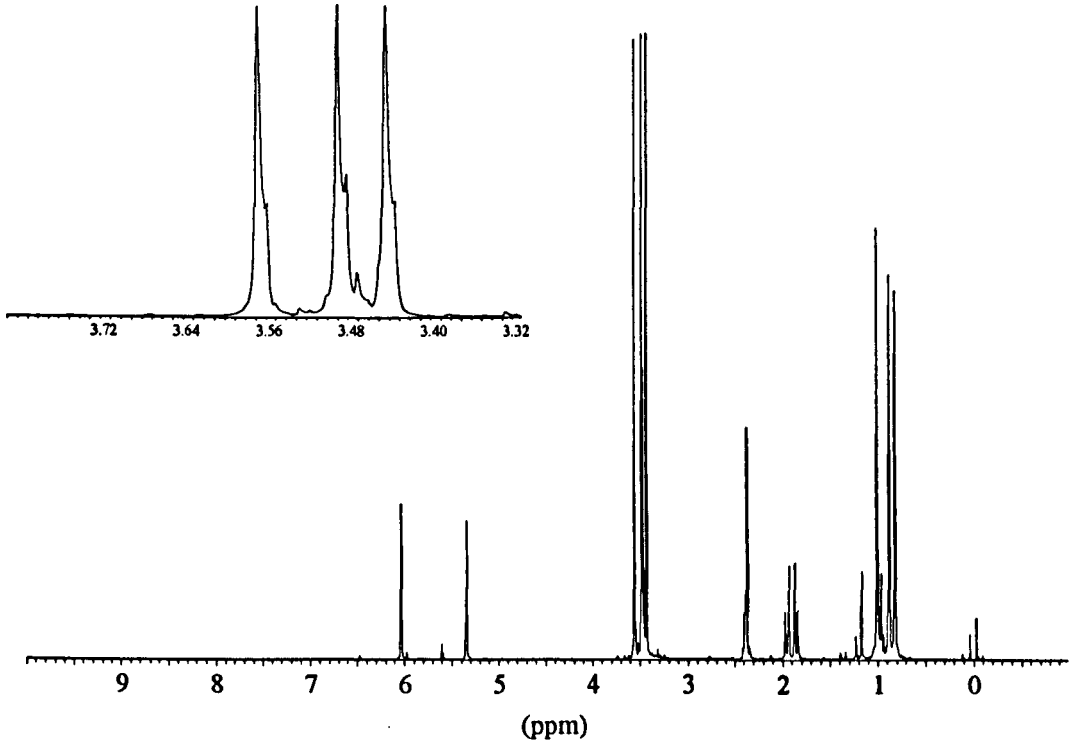

Figure 5.7 ^{1}H NMR spectrum (TCE, 298 K, 400 MHz) of MMA trimer after reaction with MTS. The inset shows the expanded region of the O-CH_3 groups.

Comparison of the relevant spectra shows a shift of the trimer O-CH_3 groups from 3.64 - 3.51 ppm before addition of MTS to 3.56 - 3.43 ppm after addition of MTS. The bridging CH_2 groups have also shifted after the addition of MTS. The singlet has shifted from 2.45 to 2.37 ppm and the multiplet from 2.05 - 1.92 to 1.97 - 1.84 ppm after the addition of MTS. A multiplet is also seen in the trimer + MTS spectrum in the region 0.11 to -0.10 ppm. A peak is seen in this region in the MTS spectrum at 0.18 to 0.15 ppm, i.e. all peaks were above 0 ppm. The relative positions of the trimer peaks remain virtually unchanged.

5.4 GTP of BMA with MMA macromonomers

In order to evaluate the effect of the addition of MMA macromonomers to a GTP reaction a number of reactions were carried out using BMA as monomer in order to allow analysis by MALDI-TOF MS and NMR spectroscopy. Reactions were carried out with the addition of various amounts MMA dimer, trimer and tetramer to the monomer feed.

5.4.1 GTP of BMA with MMA Dimer.

The first experiments carried out involved copolymerization of BMA with MMA dimer, in addition to the homopolymerization of BMA as a control reaction. The resulting polymers were analysed by NMR spectroscopy and MALDI-TOF mass spectrometry with molecular weight data obtained using SEC. Varying molar ratios of MMA dimer were added to the polymerization of BMA, reaction conditions and molecular weight data are shown in Table 5.3.

Table 5.3 Reaction conditions and molecular weight data for GTP copolymerization of BMA with MMA dimer, **2.6**.

	mole fraction BMA	mole fraction MMA Dimer	Mn	PDi
BM2.A	1[a] (3.14×10^{-2} moles)	0	17700	1.35
BM2.B	0.50[b] (3.14×10^{-2} moles)	0.50 (3.14×10^{-2} moles)	190	1.04[c]
BM2.C	0.50[b] (3.14×10^{-2} moles)	0.50 (3.14×10^{-2} moles)	350	1.04[c]
BM2.D	0.90[b] (5.66×10^{-2} moles)	0.10 (6.28×10^{-3} moles)	8330	1.38
BM2.E	0.90[b] (5.66×10^{-2} moles)	0.10 (6.28×10^{-3} moles)	8390	1.44
BM2.F	0.80[b] (5.03×10^{-2} moles)	0.20 (1.26×10^{-2} moles)	6440	1.47
BM2.G	0.70[b] (4.40×10^{-2} moles)	0.30 (1.89×10^{-2} moles)	1900	1.18
BM2.H	0.60[b] (3.77×10^{-2} moles)	0.40 (2.51×10^{-2} moles)	1410	1.17

a moles MTS = 3.20×10^{-4}, moles TBAmCB = 3.16×10^{-6}

b moles MTS = 6.4×10^{-4}, moles TBAmCB = 6.28×10^{-6}

c molecular weight data after 2 hours, low PDi results from complication of chromatogram by unreacted monomer and dimer

The molecular weights of the resulting polymers show a significant decrease as the amount of dimer in the feed is increased. This is illustrated in Figure 5.8 which also shows the molecular weight that would be expected if the dimer did not participate in the reaction and acted only as a diluent, i.e. the theoretical molecular weights for monomer:initiator ratios based on monomer only, not the total amount of monomer and macromonomer. This indicates that it is not a decrease in the monomer to initiator ratio that is responsible for the reduction in molecular weight.

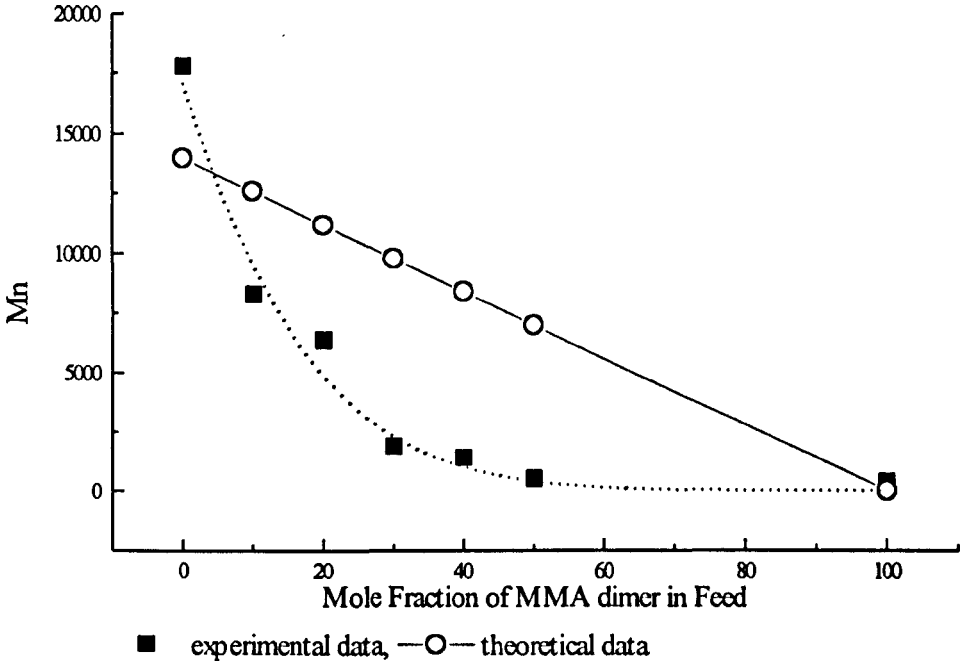

Figure 5.8 Molecular weight data for GTP of BMA with MMA dimer.

The MALDI-TOF mass spectra obtained for the products of these reactions show two main series of peaks, this is illustrated in Figure 5.9 for reaction I. The MALDI-TOF mass spectrum shows no evidence for any homopolymerization of BMA without MMA dimer. A peak for BMA homopolymer would be expected

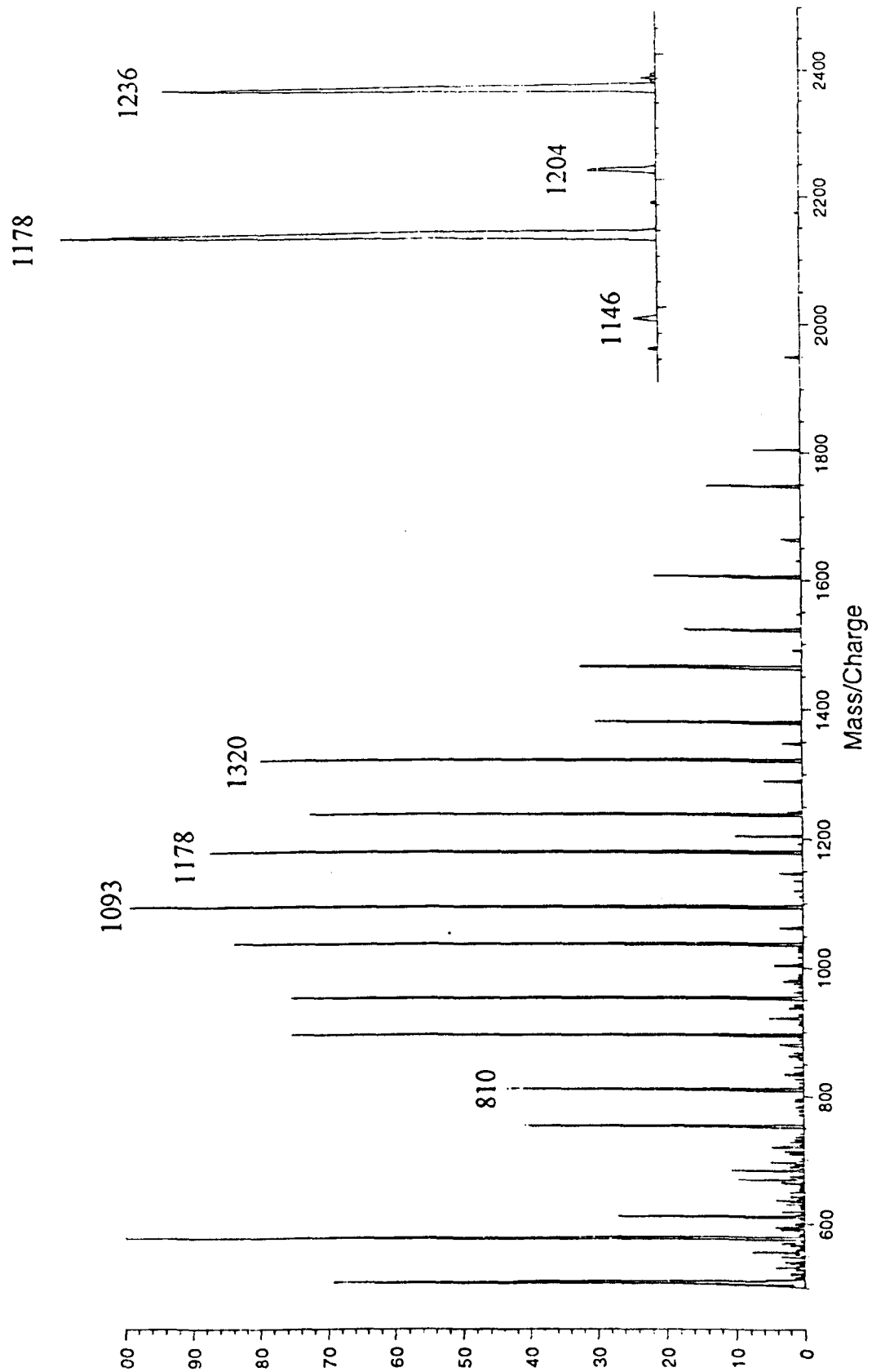

Figure 5.9 MALDI-TOF Mass Spectrum of the GTP Reaction of BMA with MMA Dimer

at e.g. *m/z* 1262, BMA_8Na. One set of the series of peaks corresponds to macromolecules containing two MMA groups in addition to xBMA units and one unit originating from the initiator (this group could be from either initiator (MTS) or MMA as both have similar molecular weights). For example, the peak at *m/z* 1178 corresponds to $MMABMA_6MMA_2Na$ (101.1 + 6(142.2) + 2(100.1) + 23.0), the initial MMA unit is derived from the MTS initiator. The second set of peaks at 58 amu higher than series one is from macromolecules with two dimer units per chain i.e. copolymerization has occurred, for example the peak at *m/z* 1236 is assigned to $MMABMA_5MMA_4Na$, (101.1 + 4(142.2) + 4(100.1) + 23.0). A possible explanation for this is that the addition of the dimer to the propagating chain end slows the reaction down to such an extent that in the time period of the reaction not all chains will continue to propagate and only a small number will add further BMA monomer. Once another BMA unit has added it propagates rapidly until it adds a second dimer. The slow rate of the polymerization results in a slow rate of propagation which means that no more than two dimer units add to any one chain before the reaction dies and could also explain the low molecular weight of the product. An alternative explanation, which is consistent with both the incorporation of one or two dimer units and the reduction in molecular weight, is that the silyl group from the MTS exchanges with the dimer to form a new species which is more stable with a slower rate of initiation than MTS. Slower initiation would explain the reduction in polymerization rate when compared to the homopolymerization of BMA, and, if only some of the propagating chains encountered dimer, only some would contain two dimer units. The silyl exchange would also result in the formation of monomeric MMA which could copolymerize with BMA and explain the presence of a group with a

molecular weight of around 100 Da in addition to the dimer units in the MALDI spectra. However, if this were the case some chains with more than one free MMA unit incorporated would be expected.

A similar chain transfer mechanism has been reported by Hertler[3] to explain the reduction in molecular weight that is observed in GTP reactions conducted in the presence some carbon acids, e.g. α-phenylpropionate. He states that silylation of the chain transfer agent by the silyl ketene acetal group of the living polymer to form a new initiating species is the mechanism by which chain occurs. This would seem to be in agreement with Quirk and Ren[4] who published data indicated that the living ends of two samples of PMMA of different molecular weight can exchange. However, silylation of the MMA dimer would not explain the presence of more than one dimer unit in some chains unless some copolymerization had occurred. Nor would it explain the presence of an odd number of MMA units in each chain (MTS fragment plus dimer) or the evolution of a methoxy group from the polymer chain end outlined below.

There are two series of smaller peaks in the MALDI-TOF mass spectrum, the peaks within each series are separated by 142 Da, and are found 32 mass units lower than the two major series, e.g. *m/z* 1146 assigned to the cyclization product of a chain containing one dimer unit and *m/z* 1204 from cyclization of chains containing two dimer units. This corresponds to termination by cyclization of the terminal MMA unit which would result in the loss of MeOH. However, the normal form of termination by cyclization results in the formation of a six membered ring with the loss of the alkoxy group adjacent to the carbonyl group three monomer units from the propagating end. In the case of reaction with

dimer, where the dimer unit is at the chain end, this would correspond to the loss of a butoxy group from the BMA unit three units back, Figure 5.10.

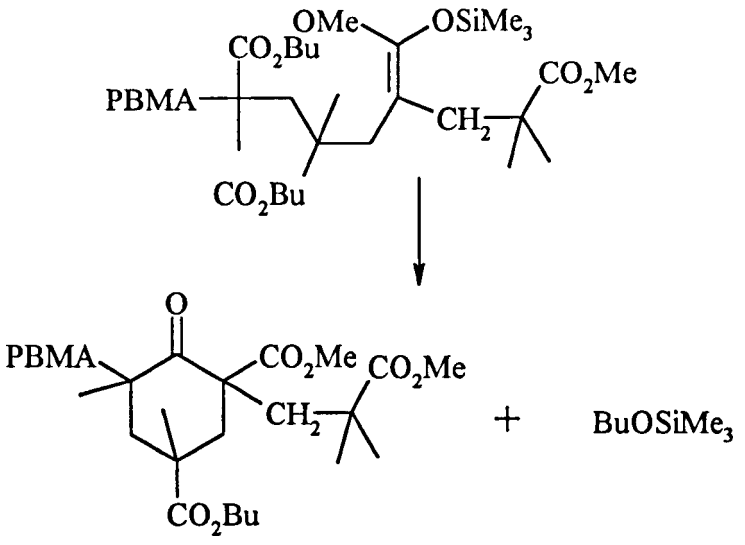

Figure 5.10 Cyclization termination mechanism for GTP of BMA and MMA dimer

This is not observed in the MALDI-TOF mass spectrum, which implies that termination via the formation of a six membered ring from a chain with a terminal dimer unit is not occurring. The fact that methanol groups are lost suggests either that the dimer is not randomly located within the polymer chain but is found quantitatively at the chain end (otherwise the loss of a butoxy group would also be expected) or that the presence of dimer at the chain end causes termination. The presence of more than one dimer unit in some chains indicates that it is the former and not the latter that is the case. An alternative explanation for the loss of methanol is termination by cyclization after a BMA unit has added to the end dimer unit. This leads to the loss of a methoxy group and is illustrated in Figure 5.11.

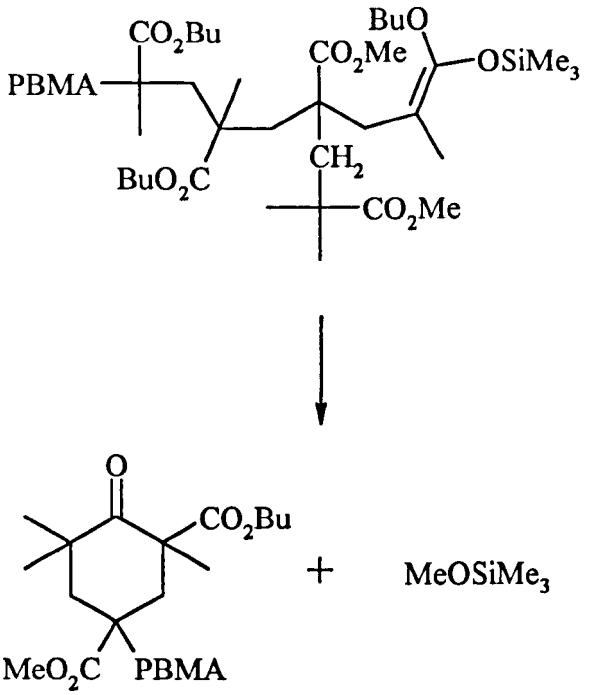

Figure 5.11 Termination by cyclization with the evolution of a methoxy group.

It is hypothesised that addition of MMA dimer to the growing chain end results in the formation of a stable adduct and significantly slows the reaction. As a consequence only some of the chains will continue to propagate during the time period of the reaction, resulting in only a fraction of chains containing two dimer units. As the reaction proceeds by the sequential addition of monomer units, a slower reaction will result in a lower molecular weight in a given period of time. The homopolymerization reaction of BMA carried out in the absence of macromonomer is complete within an hour. Further evidence for the reduction in the rate of the reaction is presented in Section 5.5.

The ^{1}H NMR spectrum of the product of reaction BM2.D is shown in Figure 5.12. This shows the presence of more than one type of MMA unit in the polymer.

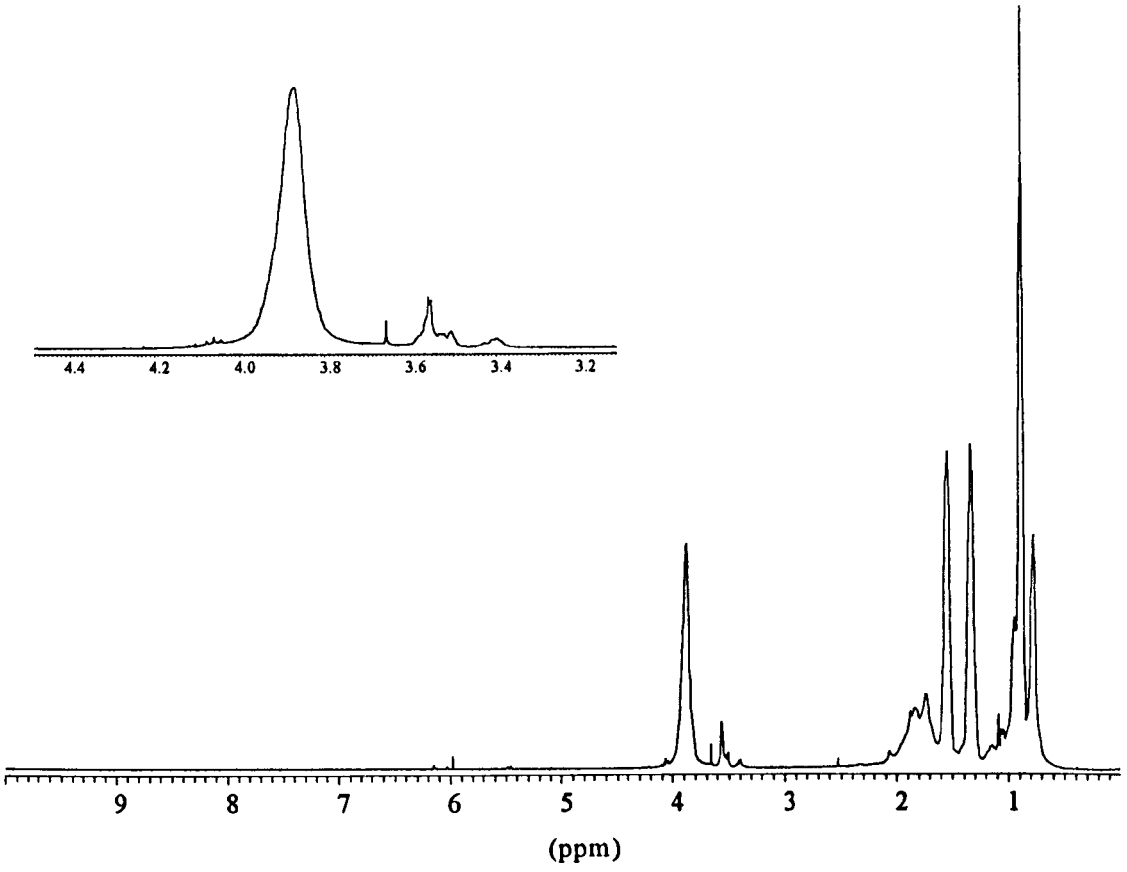

Figure 5.12 ^{1}H NMR spectrum (TCE, 298 K 400 MHz) of the product of the GTP of BMA and MMA dimer. The inset shows the expanded region of the BMA O-CH_2- and MMA O-CH_3.

5.4.2 GTP of BMA with MMA Trimer.

In order to investigate whether or not increasing the degree of polymerization of the macromonomer would affect the GTP of BMA, further copolymerizations were conducted using MMA trimer with BMA. The resulting copolymers were again analysed by SEC and MALDI-TOF mass spectrometry. The reaction conditions and molecular weight data for these reactions are shown in Table 5.4.

Table 5.4 Reaction conditions and polymerization data for GTP of BMA with MMA trimer.

	mole fraction BMA	mole fraction MMA trimer	Mn	PDi
BM3.A	0.90[a] (6.61 x 10^{-2} moles)	0.10 (7.35 x 10^{-3} moles)	1760	2.11
BM3.B	0.90[b] (5.23 x 10^{-2} moles)	0.10 (5.87 x 10^{-3} moles)	803[d]	2.13
BM3.C	0.80[a] (5.90 x 10^{-2} moles)	0.20 (1.48 x 10^{-2} moles)	1710	2.84
BM3.D	0.80[c] (4.41 x 10^{-2} moles)	0.20 (1.10 x 10^{-2} moles)	1030	1.17

a moles MTS = 7.38 x 10^{-4}, moles TBAmCB = 7.36 x 10^{-6}

b moles MTS = 5.91 x 10^{-4}, moles TBAmCB = 5.84 x 10^{-6}

c moles MTS = 5.41 x 10^{-4}, moles TBAmCB = 5.52 x 10^{-6}

d low Mn and high PDi due to complication of unreacted trimer in SEC trace

The addition of MMA trimer to a GTP reaction of BMA results in a greater reduction in molecular weight than is observed with the addition of MMA dimer. This means that either the reaction is slowed down to a greater extent with the addition of trimer or that a chain transfer mechanism is occurring. The MALDI-TOF mass spectrum obtained from the product of reaction A, Figure 5.13, shows one major series of peaks, separated by 142 Da indicating a difference of one BMA unit. However, the mass of the peaks correspond to either two MMA units

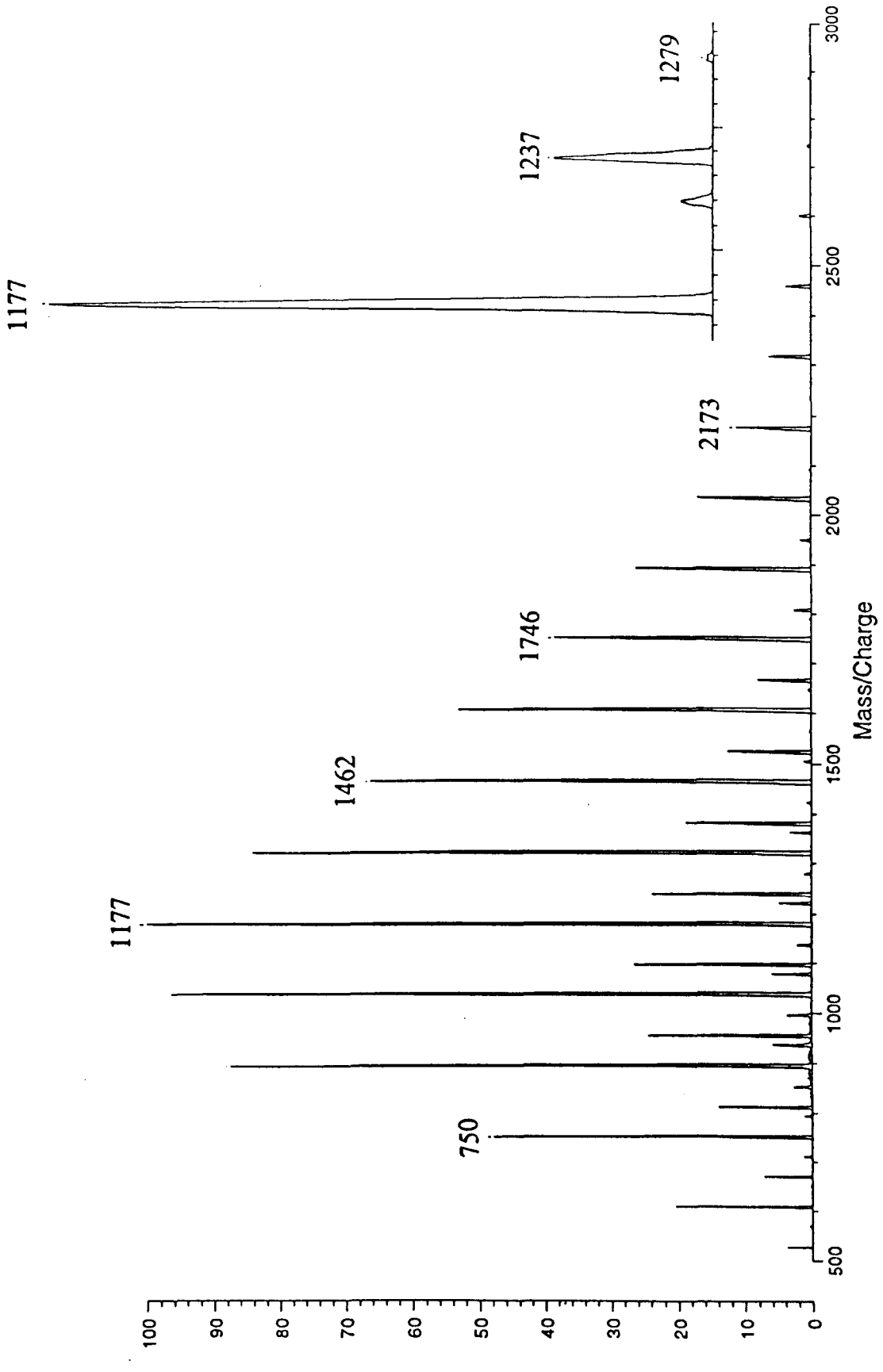

Figure 5.13 MALDI-TOF Mass Spectrum of the GTP Reaction of BMA with MMA Trimer

and one MTS fragment, or three MMA units. Again, there is a peak at *m/z* 1177 from the species $MTSBMA_6MMA_2Na$, calculated mass 1177.5 Da. The smaller series of peaks at e.g. *m/z* 1237 are also seen in the spectrum obtained from the reactions with MMA dimer, and correspond to the presence of four MMA units and one MTS fragment. Some of the spectra also contain peaks that correspond to chains containing an MTS fragment and one or three MMA units. The reactions were duplicated in order to confirm these findings. (The spectra from the duplicate reactions (B and D) show the major series of peaks and those corresponding to the presence of four MMA units, but not the peaks from chains containing one and three MMA units.) Analysis of the reactions carried out with 20 mole % trimer results in a similar mass spectrum, but without the smaller series of peaks corresponding to one and three MMA units in a chain.

These results indicate a difference in the behaviour of the species formed by reaction with dimer and trimer. The results obtained in these reactions can be explained in two ways. Firstly, as postulated previously, there may be a silyl exchange between initiator and macromonomer to form a trimer initiator species. A more likely explanation is that the species formed by the addition of the trimer is sufficiently stable that it undergoes an anionic scission mechanism that results in chain transfer, similar to that previously seen for radical reactions involving methacrylate macromonomers. However, if it were a β-scission-type mechanism analogous to those seen in radical reaction then the major series of peaks would have one MTS and one MMA unit. There would then be a further series expected, containing one MMA dimer initiating unit and one MMA monomer unit resulting from chain scission, Figure 5.14.

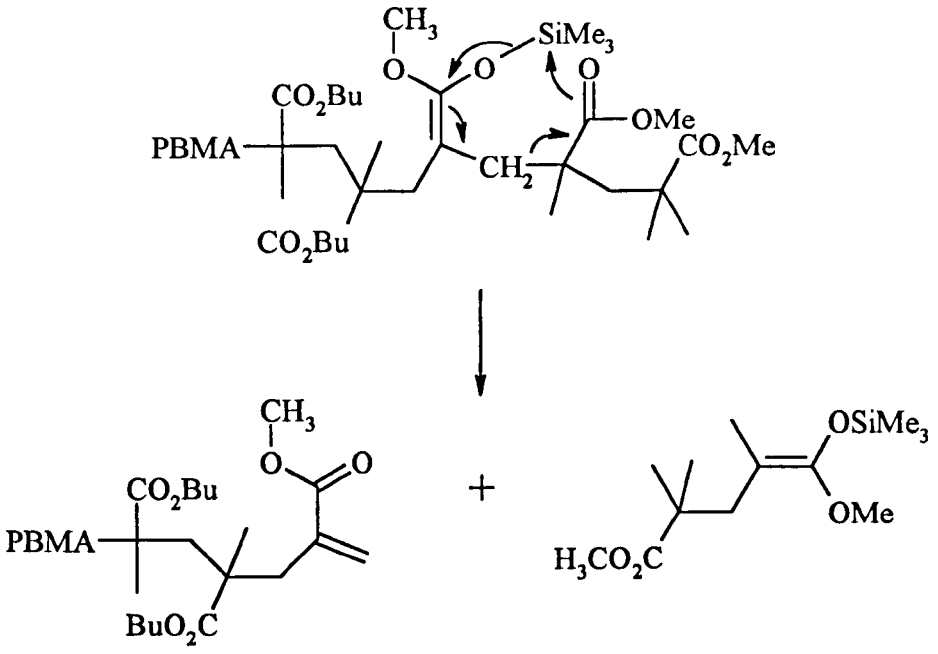

Figure 5.14 Chain transfer mechanism by β-scission in GTP of BMA and MMA Trimer.

This first series that would be expected from a β-scission type reaction is seen only as a minor set of peaks in the MALDI-TOF mass spectra of the reactions carried out in THF and is not seen in bulk polymerizations, see section 5.5. The series of peaks corresponding to one MTS and three MMA units e.g. the peak at *m/z* 1279, is from chains initiated by MTS that have added MMA trimer but not undergone any chain scission. The MALDI-TOF mass spectra would seem to indicate that if a chain transfer reaction is occurring on addition of MMA trimer then a new initiating species that is identical to the MTS is formed. The fact that there is a series corresponding to chains containing four MMA and one MTS unit observed in the MALDI-TOF mass spectrum indicates that, in some cases, both copolymerization and chain transfer occurs.

5.4.3 GTP of BMA with MMA Tetramer.

As an extension of the reactions carried out using MMA trimer, a similar reaction was carried out using the higher molecular weight MMA tetramer. The reaction conditions and molecular weight data for this reaction is presented in Table 5.5.

Table 5.5 Polymerization data for GTP of BMA with MMA tetramer.

	mole fraction BMA	mole fraction MMA tetramer	Mn	PDi
BM4.A	0.91 (5.05×10^{-2} moles)	0.09 (5.61×10^{-3} moles)	1460	1.25

moles MTS = 4.68×10^{-4}, moles TBAmCB = 4.56×10^{-6}

The reduction in molecular weight observed for MMA tetramer, when compared to the homopolymerization of BMA, is of a similar order of magnitude to that seen with the addition of MMA trimer. This indicates a similar chain transfer activity and effect on the rate of polymerization by the two macromonomer species.

The MALDI-TOF spectrum for this reaction, Figure 5.15, is similar to that found for the reactions involving MMA trimer. The major set of peaks are 142 Da apart and have either one MTS fragment and three MMA units or four MMA units. The structural elucidation is again complicated by the similarity in formula weight of MMA and the initiating fragment of MTS. For example, the peak at *m/z* 850

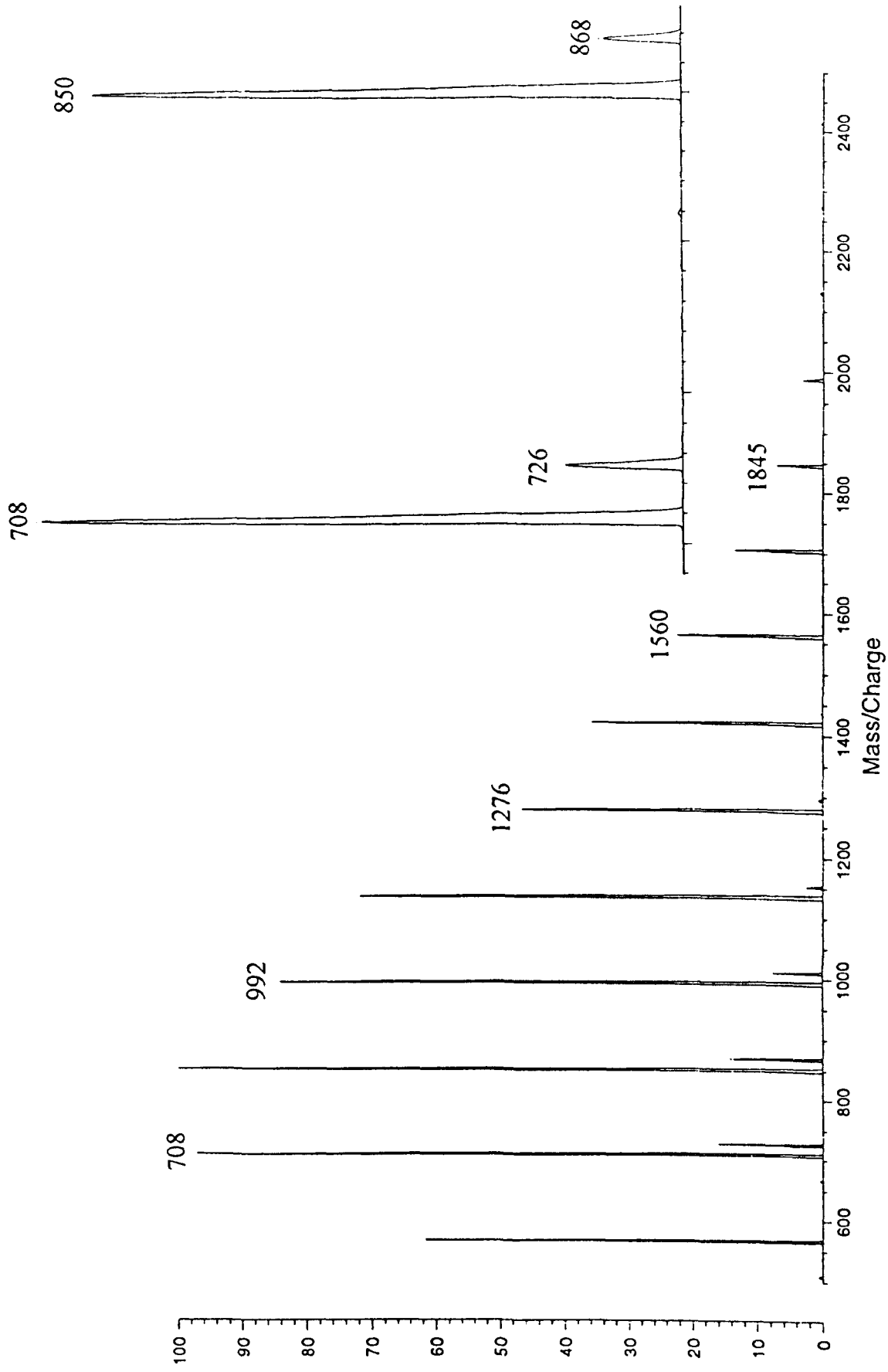

Figure 5.15 MALDI-TOF Mass Spectrum of the GTP Reaction of BMA with MMA Tetramer

is from chains with the formula $MMABMA_4MMA_3Na$, calculated mass 851 Da (101.1 + 3(142.2) + 3(100.1) + 23). A smaller set of peaks at the low molecular weight end of the spectrum are seen, with a possible structure corresponding to $MTSBMA_xMMA_6Na$. For example, the peak at *m/z* 868 corresponds to the formula $MTSBMA_2MMA_6Na$, calculated mass 866.9 Da (101.1 + 142.2 + 6(100.1) + 23). The origin of chains with this formula is uncertain but their presence implies that both copolymerization and chain transfer occur.

Again, if chain transfer occurred via a β-scission type mechanism, Figure 5.16, then a different series of peaks would be expected than is observed in the MALDI-TOF mass spectrum. A series of peaks corresponding to MTS initiation and termination by monomeric MMA from the tetramer, i.e. two MMA units per chain, would be expected in addition to chains initiated by a trimer species and terminated by MMA, i.e. four MMA units per chain. This latter series is seen, but it could also correspond to initiation by MTS and termination by a trimer species.

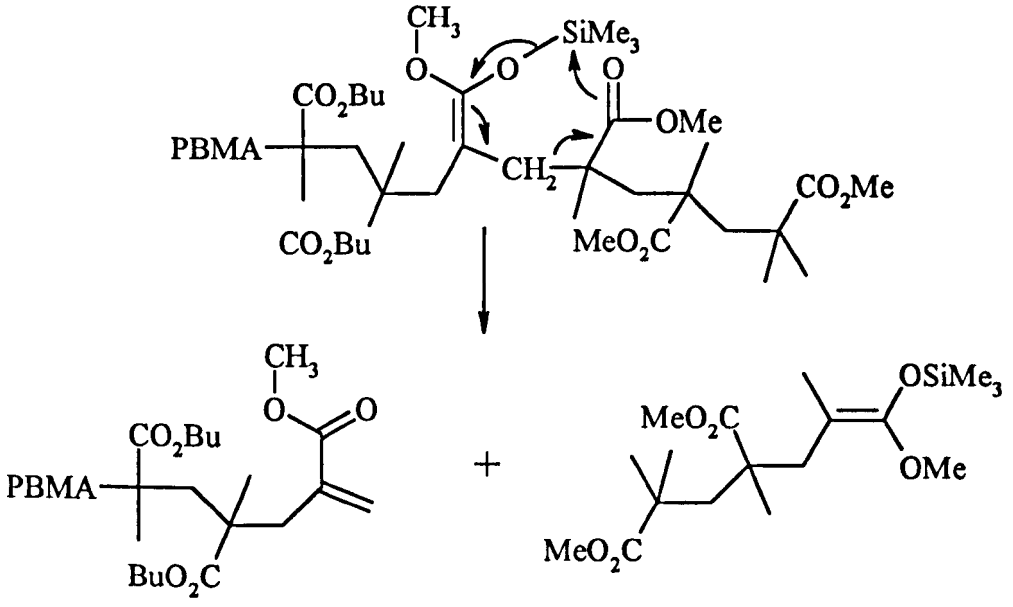

Figure 5.16 Chain transfer by β-scission in GTP of BMA and MMA tetramer.

5.5 Bulk GTP reactions of BMA and MMA macromonomers

A number of reactions were carried out in which the bulk polymerization of BMA with MMA dimer, trimer and tetramer were compared to the bulk homopolymerization of BMA monomer. The initial ratios of monomer to initiator and initiator to catalyst were identical for all of the experiments. The composition of each of the monomer mixtures for reactions containing macromonomers were determined by NMR spectroscopy. In the reactions involving macromonomers further additions of catalyst solution were made every hour over seven hours. The temperatures of the reactions were monitored using a thermocouple as it is known that after a short period of time the temperature of a bulk GTP reaction accelerates rapidly. This occurs because there is no solvent to transfer the heat from the exotherm that occurs as the reaction proceeds. As a result of this the thermal polymerization mechanism becomes dominant and control over the reaction is lost. This loss of control is seen as an increase in the polydispersity of the final polymer. The reaction conditions and polymerization data for all of the reactions carried out in bulk are shown in Table 5.6.

Table 5.6 Polymerization data for bulk GTP reactions

	mole fraction BMA	mole fraction macromonomer	Mn	PDi
monomer	1	0	18370	2.36
dimer	0.900	0.100	8550	1.53
trimer	0.903	0.097	2350	1.39
tetramer	0.898	0.102	1640	1.30

The molecular weight data obtained from the bulk reactions show a reduction in molecular weight with the addition of macromonomer. These results also indicate larger reductions in molecular weight with increasing molecular weights of macromonomer. The reduction in molecular weight is of a similar order of magnitude to that observed for reactions carried out in THF.

Figure 5.17 shows the variation in temperature with time for the bulk GTP reaction of BMA monomer. After approximately 40 - 50 seconds there is a large exotherm to give a maximum temperature of 144 °C. This corresponds to the loss of control where the monomer is seen to boil, leading to a conversion of one hundred per cent. The PDi of the resulting polymer increased from 1.35 for a reaction carried out in THF to 2.36 for the bulk polymeriztion, indicating a loss of control of the polymerization.

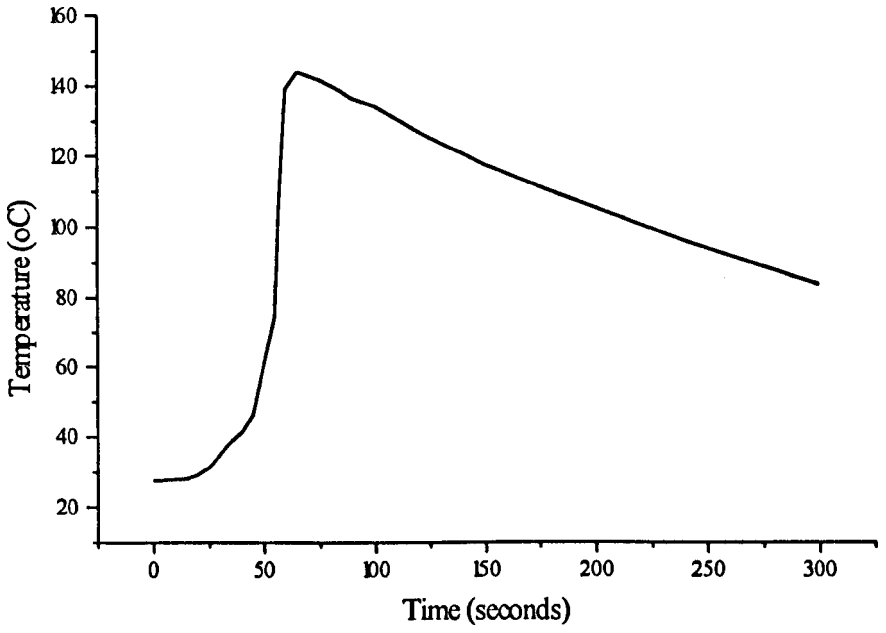

Figure 5.17 Temperature change during a bulk GTP reaction of BMA monomer.

In the corresponding reactions carried out with the addition of 10 mole % MMA dimer, trimer and tetramer to the BMA no rise in temperature from the polymerization was observed. This is illustrated in Figure 5.18 which shows the change in temperature for the three GTP reactions involving macromonomers in addition to the variation in room temperature over the time period during which the reaction was monitored.

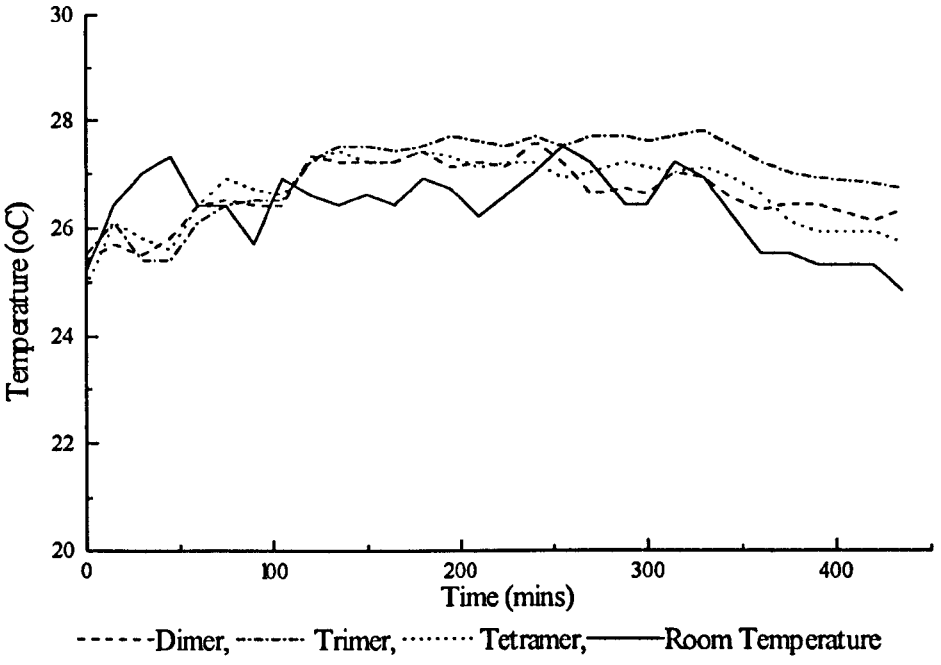

Figure 5.18 Variation in temperature for bulk GTP reactions involving MMA macromonomers.

The reactions involving MMA macromonomers were left overnight during which time the viscosity increased to the point of gelation. However, no bubbles trapped in the reaction products that would have indicated if a significant exotherm had occurred were observed. In addition, the polydispersity of the

products did not increase relative to the reactions carried out in THF which indicates that control of the reaction is not lost.

Thus it can be concluded that the addition of methacrylate macromonomers either slows down the reaction sufficiently that no exotherm occurs and thermal polymerization does not become dominant or increases the induction period from approximately 25 seconds to more than 7 hours.

The polymers obtained in these reactions were analysed by MALDI-TOF mass spectrometry which showed the same major series of peaks that had already been observed for the analogous reactions carried out in THF, but the smaller series e.g. for MMA trimer, the peaks indicating the presence of MTS and either one or three MMA units, are missing.

5.6 Reactivity Ratios for BMA and MMA dimer in GTP reactions.

A reactivity ratio gives a measure of the preference of a propagating centre for cross propagation and hence is important in the study of copolymerization reactions. They are usually determined by establishing a relationship between the feed composition of monomer and the resulting copolymer composition, measured e.g. by ^{1}H NMR. The reactivity ratios are defined in equations 5.1 and 5.2 where k is the rate constant for cross-propagation and homopropagation.

$$r_1 = \frac{k_{11}}{k_{22}} \tag{5.1}$$

$$r_2 = \frac{k_{22}}{k_{21}} \tag{5.2}$$

If two monomers have a similar reactivity towards a propagating centre then the values for reactivity ratios should be close to unity. The reactivity ratios for BMA and MMA monomers in GTP reactions have been previously determined to be 0.67 and 1.76 respectively.[5] This work aims to give an approximate value for the reactivity ratios of BMA and MMA dimer in a GTP reaction. The calculation of reacyivityratios requires a conversion of approximately 5 % in order to prevent changes in the feed composition. However, in this work this was difficult to achieve for all systems due to the retardation of the reaction by the addition of increasing amounts of MMA dimer, hence the values calculated in this work are only approximate. The reaction mixtures were prepared in the ratios 90:10, 80:20 and 70:30 BMA:MMA dimer. Experimental details for this work are given in section 7.10. It would be preferable to have a mixture containing a large amount of dimer, but due to the limited availability of the dimer this was not possible. The composition of each mixture was verified by NMR. The reactivity ratios were calculated using the error-in-variables model (EVM) used previously in the published literature [5] which uses the Mayo-Lewis copolymer composition equation. For this method the compositions of the starting mixtures and the polymers obtained at low conversion were determined using NMR spectroscopy. The reactions were carried out with sufficient initiator to give a molecular weight of 20000 so that a low conversion would result in a polymer of molecular weight in the region of 1000 - 2000 in order to aid analysis by NMR. The reaction conditions and polymerization data are given in Table 5.7.

Table 5.7 Reaction conditions for the determination of reactivity ratios.

Mole Fraction BMA	Mole Fraction MMA Dimer	Conversion
0.900	0.100	0.203
0.844	0.156	0.077
0.721	0.279	0.032

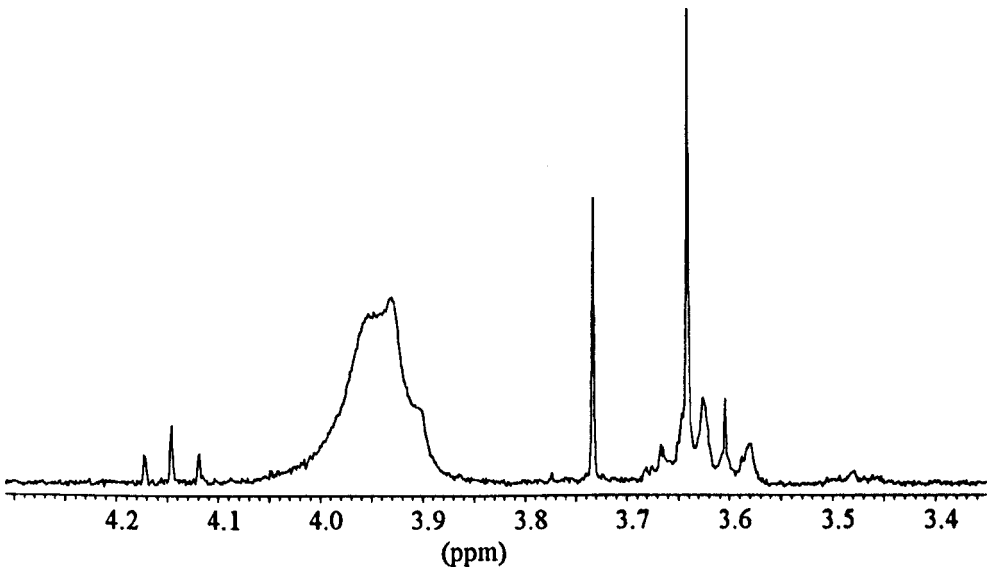

Figure 5.19 ^{1}H NMR spectrum ($CDCl_3$, 298 K, 250 MHz) used in the calculation of the reactivity ratios of BMA with MMA dimer.

Insertion of the area under the relevant peaks in the NMR spectrum, Figure 5.19, the peak at 3.95 ppm for PBMA and 3.65 ppm for PMMA, and the composition of the monomer feed into the reactivity ratio calculator program yielded values of $r_1 = 2.072$ and $r_2 = 0.0777$ where monomer 1 is BMA and monomer 2 is MMA

dimer. This shows, as expected given the increased bulkiness of the dimer, a greater preference of both BMA and MMA dimer propagating centres for BMA monomer. These results explain the presence of a maximum of two MMA dimer units per BMA chain. The BMA propagating polymer chain reacts much more rapidly with BMA monomer than with MMA dimer. If MMA dimer adds to the propagating chain then this will also react more rapidly with BMA monomer than with further MMA dimer. Hence the probability of observing more than one dimer per chain is low. Analysis by MALDI-TOF mass spectrometry indicates the probability of any chain containing more than two dimer units to be approximately zero.

5.7 GTP of MMA with BMA macromonomers

Analysis of the GTP reactions carried out using MMA macromonomers by MALDI-TOF MS showed the possibility of copolymerization or chain transfer reactions occurring. However, structural elucidation of the polymers using MALDI-TOF mass spectrometry was complicated by the similarity in molecular weight between MMA (100.1 Da) and the initiator fragment (101.1Da). In order to determine the number of units originating from the macromonomer that are present on the polymer chains a number of analogous reactions were carried out using BMA dimer and trimer.

5.7.1 GTP of MMA with BMA dimer

The reaction conditions and molecular weight data for the GTP of MMA with BMA dimer are shown in Table 5.8. Polymers were analysed by SEC and MALDI-TOF mass spectrometry.

Table 5.8 Polymerization data for GTP reactions of MMA with BMA dimer.

	mole fraction MMA	mole fraction BMA dimer	Mn	PDi
MB2.A	0.909[a] (4.67×10^{-2} moles)	0.091 (4.75×10^{-3} moles)	2650	1.51
MB2.B	0.901[b] (3.53×10^{-2} moles)	0.099 (3.87×10^{-3} moles)	1160	1.03
MB2C	0.794[c] (2.69×10^{-2} moles)	0.206 (6.67×10^{-3} moles)	1260	1.13[a]
MB2.D	0.668[d] (1.90×10^{-2} moles)	0.332 (9.41×10^{-3} moles)	1370	1.13[a]

a moles MTS = 5.17×10^{-4}, moles TBAmCB = 5.20×10^{-6}

b moles MTS = 2.85×10^{-4}, moles TBAmCB = 2.84×10^{-6}

c moles MTS = 2.61×10^{-4}, moles TBAmCB = 2.64×10^{-6}

d moles MTS = 2.61×10^{-4}, moles TBAmCB = 2.40×10^{-6}

The polymers formed in these reactions were analysed by MALDI-TOF mass spectrometry, the results of which are shown in Figure 5.20. The spectrum from

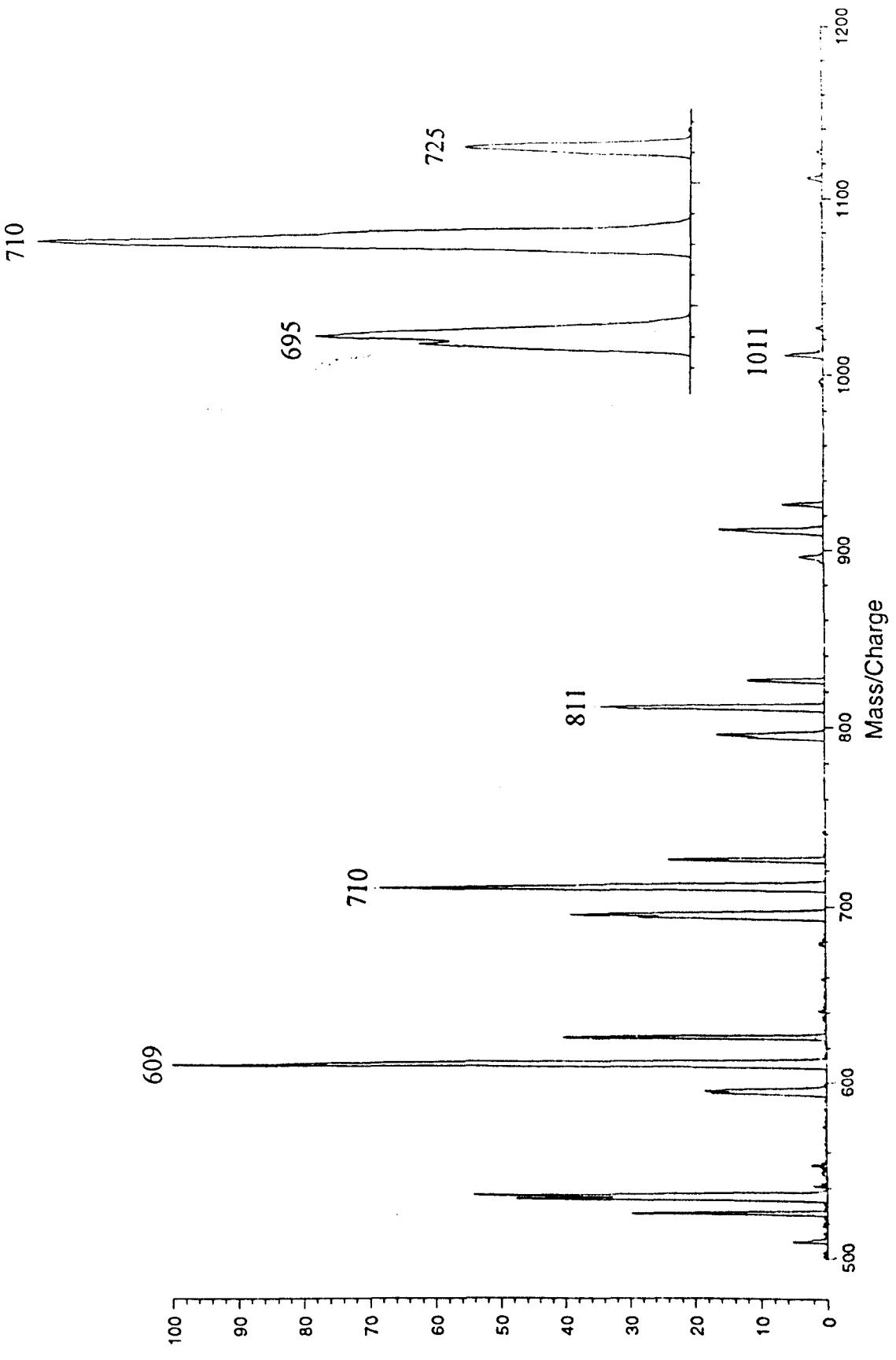

Figure 5.20 MALDI-TOF Mass Spectrum of the GTP Reaction of MMA with BMA Dimer

the addition of 20 mole % BMA dimer shows three series of peaks. These correspond to one BMA dimer unit, two BMA dimer units and no BMA dimer units on each chain. For example the peak at *m/z* 695 corresponds to MTS-BMA_4Na, *m/z* 710 corresponds to the formula MTS-MMA_3BMA_2Na and *m/z* 725 corresponds to MTS-MMA_6Na.

The homopolymerization of MMA in the presence of BMA dimer is not wholly unexpected as the reactivity ratios for MMA and BMA monomers in a GTP reaction point to a higher affinity of MMA propagating centres for MMA monomer than BMA monomer.[5] However, similar behaviour to MMA dimer is seen in that one or two dimer units are added to some of the chains.

5.7.2 GTP of MMA with BMA trimer

The reaction conditions and the molecular weight data for the GTP of MMA with BMA trimer are shown in Table 5.9.

Table 5.9 Polymerization data for GTP of MMA with BMA trimer

	mole fraction MMA	mole fraction BMA trimer	Mn	PDi
MB3.A	0.901[a] (3.14×10^{-2} moles)	0.099 (3.43×10^{-3} moles)	2690	1.47
MB3.B	0.799[b] (2.21×10^{-2} moles)	0.201 (5.56×10^{-3} moles)	1980	1.30

a moles MTS = 3.64×10^{-4}, moles TBAmCB = 3.62×10^{-6}

b moles MTS = 3.15×10^{-4}, moles TBAmCB = 3.14×10^{-6}

Addition of BMA trimer again results in a reduction in molecular weight compared to that expected for the homopolymerization of MMA. The MALDI-TOF mass spectrum of the polymer from reaction B is shown in Figure 5.21. Although the spectrum is of poor quality, peaks corresponding to the structure MMA_xBMA_3Na are present. For example, the peak at *m/z* 649 is from a chain with formula MMA_2BMA_3Na. Other peaks are observed in the spectrum, including a series of peaks 100 Da apart e.g. *m/z* 735 which may correspond to cyclization of a chain containing one BMA unit with the evolution of methanol. This would occur if chain transfer occurred to leave a new initiating species containing one BMA unit.

5.8 GTP of BMA with BMA macromonomers

Although the reactions of MMA and BMA macromonomers enabled the number of macromonomer units in the chain to be determined they did not provide any information regarding the presence of the MTS initiating fragment. Hence, a number of reactions were carried out to polymerize BMA macromonomers with BMA. Analysis of these products by MALDI-TOF mass spectrometry yields information regarding the presence of the MTS unit and hence the possible mechanism for the reaction.

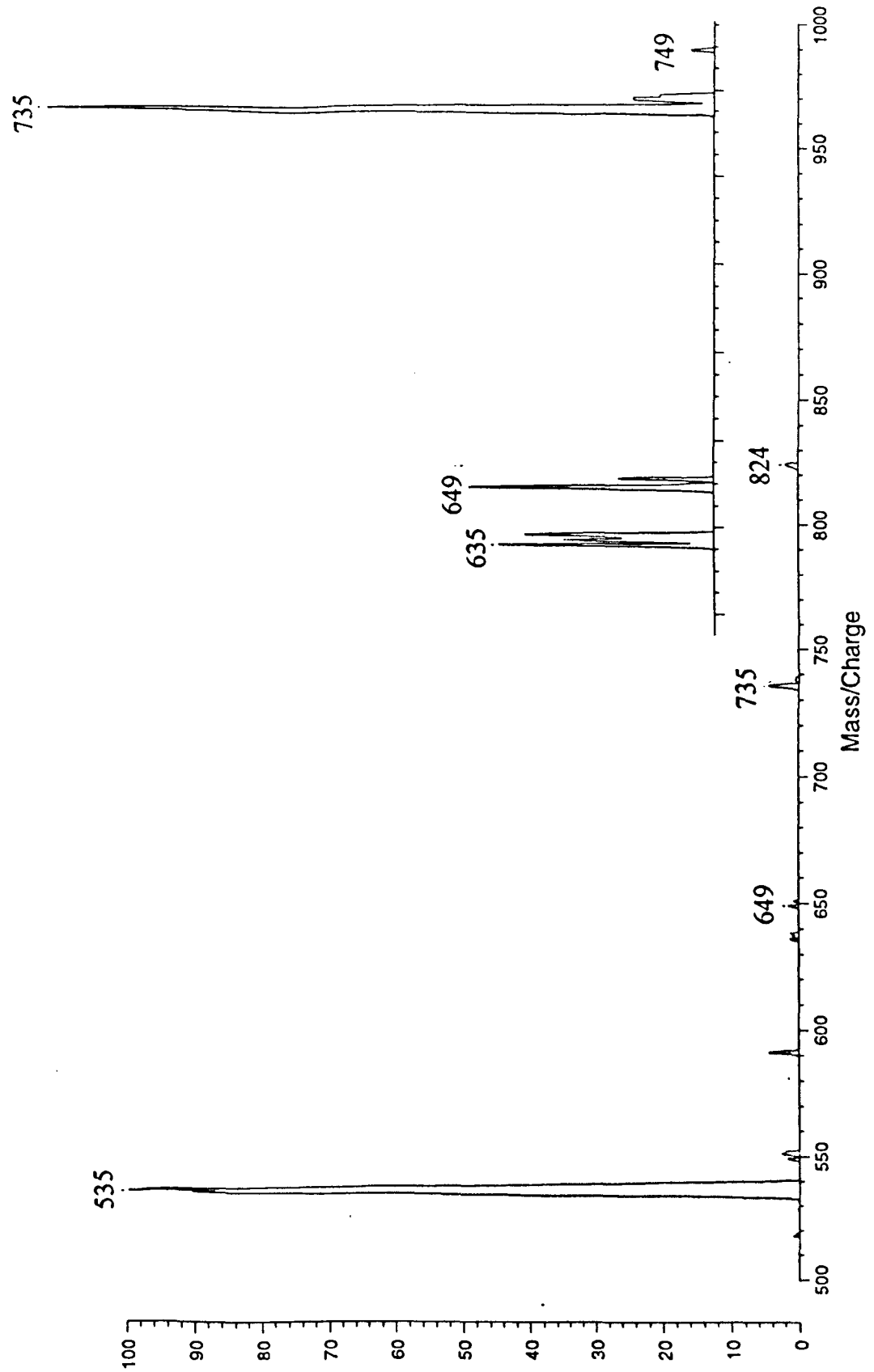

Figure 5.21 MALDI-TOF Mass Spectrum of the GTP Reaction of MMA with BMA Trimer

5.8.1 GTP of BMA with BMA dimer

It was thought that the addition of BMA dimer to BMA would show conclusively whether or not any chain transfer was occurring in GTP reactions involving methacrylate dimers. The reaction conditions and molecular weight data for the reactions carried out with BMA dimer are given in Table 5.10

Table 5.10 Polymerization data for GTP of BMA with BMA dimer

	mole fraction BMA	mole fraction BMA dimer	Mn	PDi
BB2.A	0.910[a] (3.14 x 10^{-2} moles)	0.090 (3.16 x 10^{-3} moles)	1530	1.08[a]
BB2.B	0.900[b] (2.57 x 10^{-2} moles)	0.100 (2.86 x 10^{-3} moles)	2240	1.35
BB2.C	0.800[c] (2.10 x 10^{-2} moles)	0.200 (5.24 x 10^{-3} moles)	1250	1.14

a moles MTS = 3.45 x 10^{-4}, moles TBAmCB = 3.52 x 10^{-6}

b moles MTS = 2.95 x 10^{-4}, moles TBAmCB = 2.92 x 10^{-6}

c moles MTS = 2.71 x 10^{-4}, moles TBAmCB = 2.72 x 10^{-6}

Analysis of the resulting polymers by MALDI-TOF mass spectrometry, Figure 5.22, shows the presence of two different polymer species. One was from normal initiation of BMA by MTS to give an MMA fragment, as illustrated by the peak at *m/z* 1119 from the polymer MTS-BMA_7-H Na. The other, minor, series of peaks

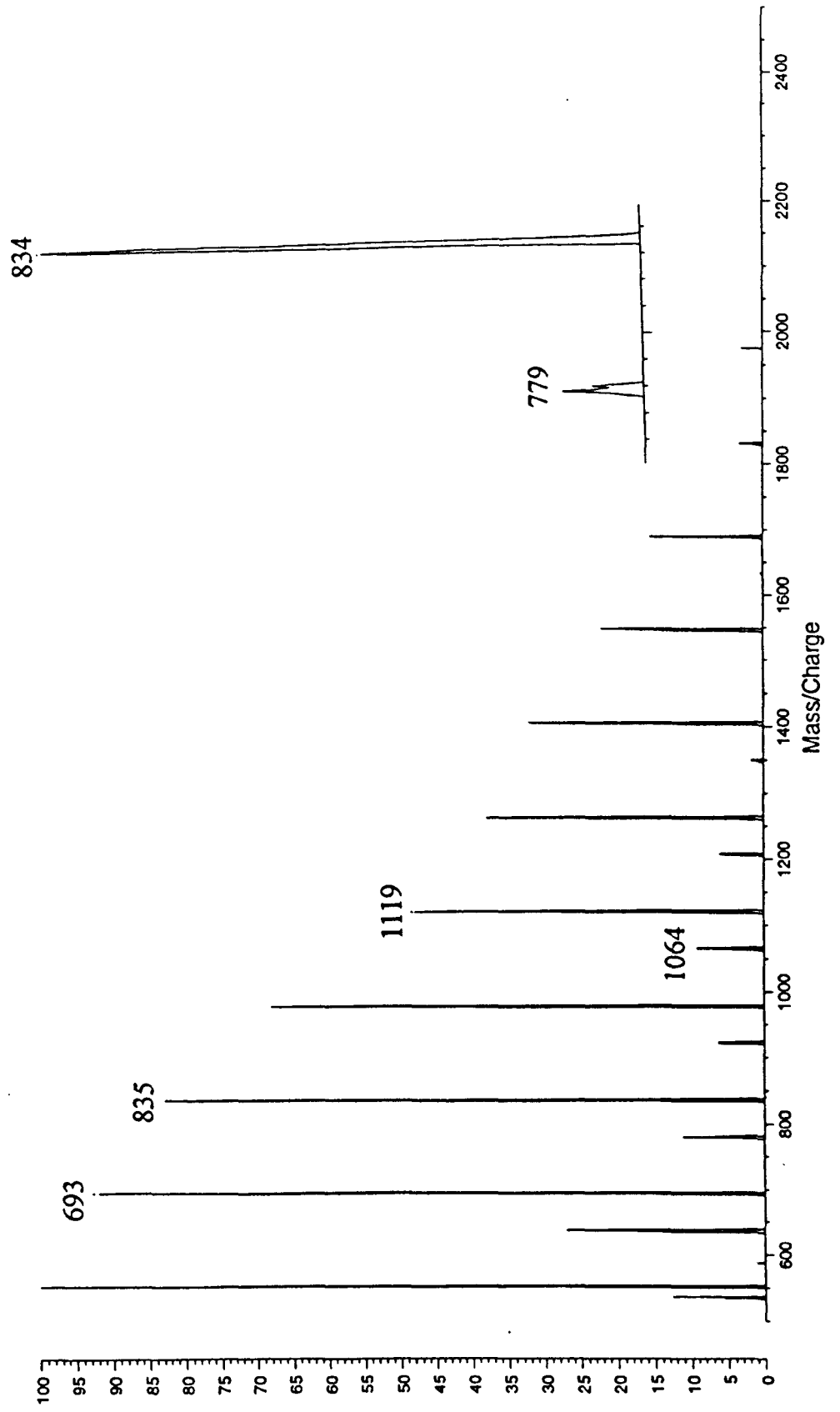

Figure 5.22 MALDI-TOF Mass Spectrum of the GTP Reaction of BMA with BMA Dimer

arises from another, as yet unidentified species, e.g. the peak at *m/z* 1063.5. This is observed in some of the spectra obtained from the reactions with both 10 and 20 mole % BMA dimer. However, the absence of peaks from initiation by a macromonomer derived species indicates that in dimer reactions no chain transfer occurs.

5.8.2 GTP of BMA with BMA trimer

Reaction conditions and molecular weight data for the polymerizations carried out with BMA trimer are given in Table 5.11.

Table 5.11 Polymerization data for GTP of BMA with BMA trimer

	mole fraction BMA	mole fraction BMA trimer	Mn	PDi
BB3.A	0.898[a] (2.35 x 10^{-2} moles)	0.102 (2.66 x 10^{-3} moles)	4950	2.26[b]
BB3.B	0.898[a] (2.35 x 10^{-2} moles)	0.102 (2.66 x 10^{-3} moles)	3240	1.44

a moles MTS = 2.71 x 10^{-4}, moles TBAmCB = 2.68 x 10^{-6}

b bimodal chromatogram

The polymers produced in these reactions were analysed by MALDI-TOF mass spectrometry, Figure 5.23. The spectrum shows two series of peaks with the peaks in each series are separated by 142 Da corresponding to a difference of one BMA unit in each chain. The first series of peaks represents chains with the general

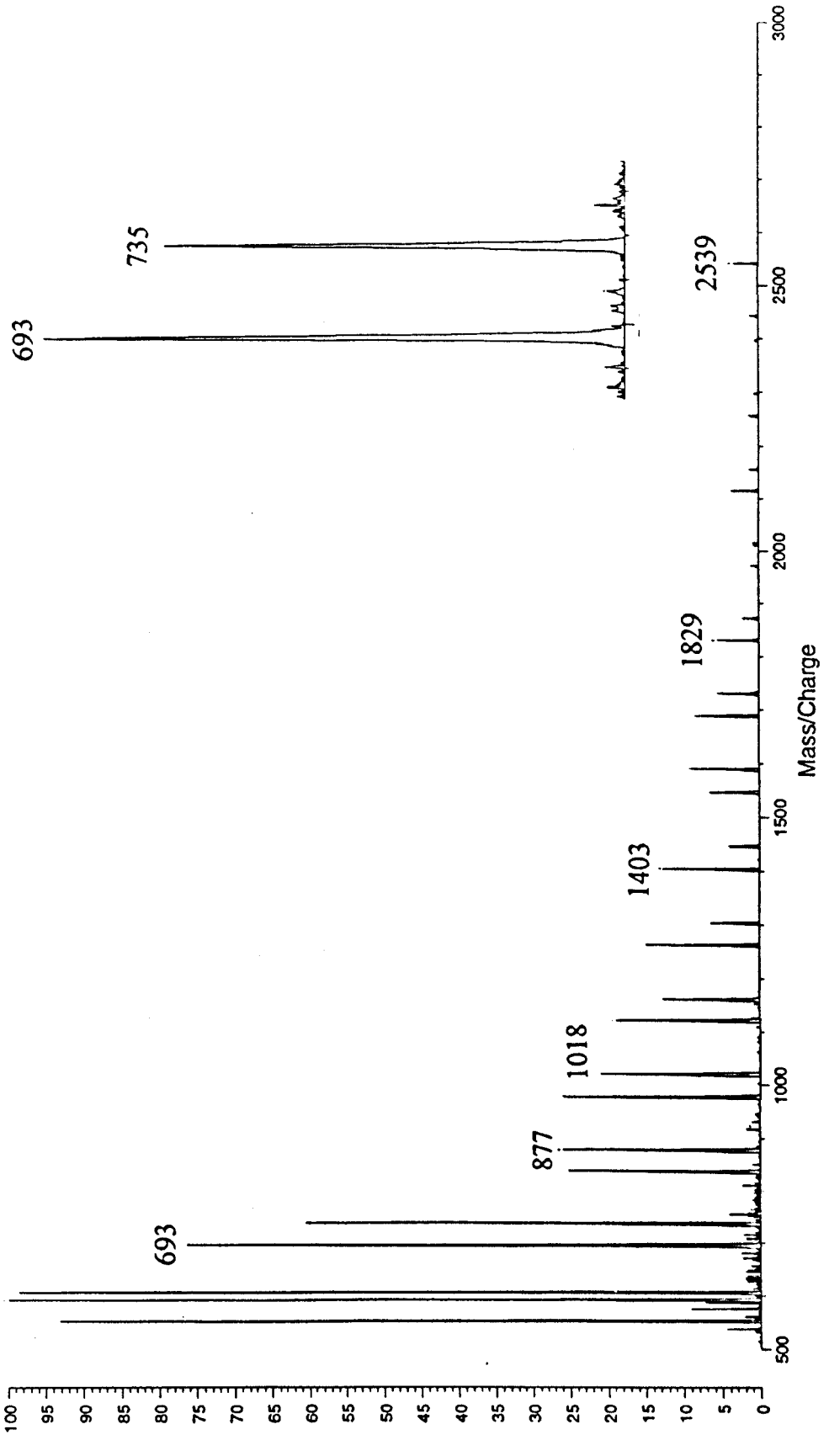

Figure 5.23 MALDI-TOF Mass Spectrum of the GTP Reaction of BMA with BMA Trimer

formula MMA-BMA_x-H Na which is expected from normal initiation using MTS, from which the MMA is derived, and termination by methanol, e.g. the peak at *m/z* 693 is due to a chain with a structure MMA-BMA_4-H Na. The second series of peaks are found 100 Da lower. These equate to chains with the general formula H-BMA_x-H Na, i.e. there is no MMA fragment from the MTS initiator. The peak at *m/z* 735 arises from a chain with the formula H-BMA_5-H.

This observation has two possible explanations. Firstly there could be some silyl exchange between the silicon initiator and the BMA trimer to form a new initiating species. If this new initiator is slower to initiate then the observed reduction in molecular weight and the bimodal nature of the SEC chromatogram is also explained. However, silyl exchange with initiator would lead to the formation of free MMA which would be available to polymerize in the usual way, which would mean that many of the chains would have one or possibly more than one MMA units in them. No peaks for chains containing more than one MMA unit are observed in the MALDI-TOF spectrum. Furthermore, recent studies regarding the reactivity ratios of MMA and BMA have pointed to the rate of reaction for MMA being faster than for BMA under conditions similar to those employed in this work. Hence it is probable that the presence of free MMA in the system would lead to some chains containing more than one MMA unit.[5] The spectrum obtained from the homopolymerization shows only the expected series of peaks from the initiation of BMA by MTS, i.e. all of the chains have the formula MMA-BMA_x-H Na. This means that there is also no evidence for any silyl exchange between the BMA and the MTS.

A second explanation is that a chain transfer mechanism occurs to leave a new BMA initiating species. This would mean that not all of the chains would be

initiated by MTS and hence some chains would have only BMA units in them. This would again account for the reduction in molecular weight and the bimodal distribution seen by SEC. Again, this points to a difference in behaviour for dimer and trimer. The chain transfer could occur by either of the two mechanisms discussed earlier in the chapter. The BMA trimer could be silylated by the living end of the polymer or the chain transfer could occur after the addition of the trimer to the propagating chain via a scission mechanism. The results obtained from these reactions cannot distinguish between the two mechanisms.

5.9 Conclusions

Analysis of the products of homopolymerization of methacrylate macromonomers by MALDI-TOF mass spectrometry leads to the conclusion that some initiation occurs. Although it is probable, the existence of propagation steps without chain transfer cannot be concluded with any degree of certainty without further research in this area.

Addition of methacrylate macromonomers prepared by CCT polymerization to the GTP of methacrylate monomers results in a reduction of molecular weight of the final polymer compared to homopolymerizations. This is thought to be due to an ionic chain transfer mechanism which results in the formation of a new initiating species. Analysis of the product of the GTP of BMA with BMA trimer initiated by MTS by MALDI-TOF mass spectrometry confirms this since a major series of peaks are observed which correspond to chains that do not contain an MTS fragment.

A difference in the behaviour of dimer and higher macromonomers is noted from the analysis of the relevant MALDI-TOF spectra. The addition of MMA dimer to BMA and BMA dimer to MMA polymerizations results in the addition of one or two dimer units. The addition of BMA dimer to BMA does not lead to initiation from a macromonomer derived species. These observations lead to the conclusion that chain transfer is not occurring and that the reduction in molecular weight is merely caused by a reduced rate of polymerization.

5.10 References

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Chapter

6.

Conclusions and Further Work

6.1 Conclusions

The addition of cobalt (II) macrocycle catalytic chain transfer agents to the polymerization of methacrylate monomers results in a reduction in the molecular weight of the resulting polymer and the formation of macromonomers with a vinylic end group as a result of the chain transfer mechanism. Addition of sufficient catalytic chain transfer agent results in the formation of macromonomers with a low degree of polymerization, e.g. dimer, trimer etc. The use of these chain transfer agents to form methacrylate macromonomers is applicable to most methacrylate monomers, including a range of functional methacrylates. The dimers and trimers produced in this way can be separated by reduced pressure distillation to produce pure macromonomers, e.g. dimer without contamination from monomer or higher molecular weight oligomers. Addition of such methacrylate macromonomers to the polymerization of methacrylate monomers results in a reduction in the molecular weight of the final polymer; the macromonomers are themselves effective chain transfer agents. This arises from a β-scission chain transfer mechanism that is the predominant mode of termination in polymerizations with methacrylic monomers and macromonomers. Radical addition-fragmentation results in fragmentation of the macromonomer after addition to the propagating centre to leave one unit on one chain end and evolution of a macroradical that has one unit less than the initial macromonomer. Evaluation of the chain transfer constants of MMA dimer and trimer show that trimer has a Cs value that is an order of magnitude higher than that of dimer. This is thought to be a result of steric factors, i.e. the radical formed by the β-scission of an adduct involving trimer is dimeric and therefore more stable than the monomeric radical formed from the dimer.

If a dimer containing a functional group, e.g. HEMA, is added to a methacrylate polymerization β-scission results in the placement of one functional group on each chain end and hence the formation of a telechelic polymer. The telechelic nature of the product is confirmed by analysis using a combination of MALDI-TOF mass spectrometry and NMR spectroscopy.

Addition of methacrylate macromonomers to GTP reactions of methacrylate monomers also results in a reduction in molecular weight. Analysis of the resulting polymers by MALDI-TOF mass spectrometry indicates a difference in behaviour between dimer and higher oligomers. Polymerizations involving dimer result in the addition of either one or two units per chain. Reactions involving trimer and tetramer lead to a chain transfer reaction that results in the formation of a new initiating species. The addition of dimer macromonomers to emulsion polymerization again results in a β-scission chain transfer reaction as seen in bulk and solution polymerizations. This leads to the possibility of preparing telechelic polymers by emulsion polymerization. Macromonomers with a higher degree of polymerization can be used to form block copolymers when added to methacrylate monomers. If added to acrylate polymerizations these macromonomers form a mixture of block and graft copolymers. Addition of a mixed macromonomer containing both MMA and HEMA with a range of degrees of polymerization to a radical polymerization of MMA leads to the formation of a polymer with more than two hydroxyl groups per chain. Reaction of this polymer with a diisocyanate leads to an increase in molecular weight and the formation of a polymer network.

6.2 Suggestions for Future Research

The use of functional methacrylate macromonomers has been shown to be a useful route to the formation of telechelic, block and graft copolymers by free radical techniques in both solution and emulsion polymerizations. However, further work is required to establish the necessary conditions for chain extension and network formation using these functional polymers.

Further studies in addition to those presented in this thesis concerning group transfer polymerizations involving methacrylate macromonomers are required in order to present a complete picture of the chain transfer mechanism occurring in these reactions. Further evidence as to the nature of the mechanism of chain transfer occurring in the reactions involving trimers and higher oligomers would be obtained using a different initiator. Careful choice of initiator, monomer and macromonomer should allow the determination of the number of macromonomer units per chain. The use of ^{29}Si NMR spectroscopy could also aid in the determination of the course of homopolymerization reactions of methacrylate macromonomers. It may also be of interest to study the effect of the addition of methacrylate macromonomers on the GTP of acrylates as these systems behave differently when polymerized by free radical methods.

The use of HPLC to separate mixed MMA-HEMA macromonomers was briefly explored in Chapter 2. However, it is suggested that better results may be obtained if a method was developed using gradient elution.

Chapter

7.

Experimental Section

7.1 General Procedures

All reactions were carried out using standard Schlenk line apparatus under an atmosphere of nitrogen. Reactions were carried out in round bottom flasks or Schlenk tubes fitted with rubber septa under nitrogen or in closed ampoules that were fitted with a Young's vacuum tap or ampoules that could be closed by flame sealing. All reagents were used as received unless otherwise stated. All solvents, monomers and macromonomers were degassed by purging with nitrogen for at least two hours or by four freeze pump thaw cycles. All liquid transfers were made by syringe unless otherwise stated.

7.1.1 Analysis.

Size exclusion chromatography was carried out using THF as an eluent at 1 mL min^{-1} with toluene (0.2 vol%) as an internal standard and flow marker in each sample. Two Polymer Laboratories PLgel 5 μm mixed-C columns (300 x 7.5 mm) and a PLgel 5 μm guard column (50 x 7.5 mm) were employed for high molecular weight polymers. Low molecular weight polymers were analysed using a system equipped with one pLgel 5 μm mixed-E column (300 x 7.5 mm) and a PLgel 5 μm guard column (50 x 7.5 mm). Both systems were equipped with a differential refractometer and calibrated with Polymer Laboratories PMMA standards from 200 - 1577000.

NMR was carried out at 400.135 MHz ^{1}H in TCE, $\delta = 5.97$ and 100.614 MHz ^{13}C in TCE $\delta = 74.2$ at 373K. Quantitative NMR was gated so as to remove NOE with a relaxation delay (RD) of 10 sec., ^{13}C and a RD of 30 sec., ^{1}H.

Matrix assisted laser desorption ionization time of flight mass spectrometry was carried out on a Kratos Kompact III spectrometer in reflectron mode. Samples were deposited in a 2,5-dihydroxybenzoic acid matrix from acetone and doped with NaCl or KCl which results in each species being observed as a Na^{+} or K^{+} adduct at molecular masses M+23 and M+39 respectively. The spectrometer was calibrated internally using bovine insulin (*m/z* 5734), Na (*m/z* 23.9898) and K (*m/z* 39.0983). The width of the peaks at approx. 4000 Da are approx. 10 Da at half peak height. These factors combine to allow an accuracy of to within 2-3 Da for each individual macromolecular species.[1]

Yields of polymerization were calculated either by drying the precipitate or a known mass of reaction mixture to constant weight in a vacuum maintained at 80 °C.

Infrared spectra of macromonomers were recorded as thin films on NaCl plates on a Unicam Mattson 1000 FT-IR spectrometer.

7.1.2 Reagents and sources.

- Cobalt (II) acetate, boron trifluoride etherate, MMA, BMA, BzMA, palladium on activated carbon (10% Pd), MTS, methylene diphenylene diisocyanate, p-tolyl isocyanate, hexamethlene diisocyanate, anhydrous toluene (ALDRICH)
- Dimethyl glyoxime, GMA (LANCASTER)
- Methanol, diethyl ether (FISONS)
- AIBN, THF (BDH)
- LMA (AVOCADO)
- VA-086 (WAKO)

7.2 Preparation of CoBF.

CoBF was prepared by a modified method of Espenson et al.[2,3]

7.5 g of cobalt (II) acetate tetrahydrate was placed in a Schlenk tube and the oxygen removed by pump-filling four times. Approximately 250 mL of degassed methanol was then added to form a purple solution. 7 g of dimethylglyoxime (dmg) was then added, this gave a 2:1 ratio of dmg:Co(II)Ac_2 with a slight excess of dmg. This turned the mixture a red/brown colour. The mixture was stirred overnight and was then filtered under nitrogen. The remaining solvent was removed under vacuum, before the crystals were washed with methanol, H_2O and methanol. About 250 mL of degassed diethyl ether was then added, followed by 37.5 mL of boron trifluoride etherate with the Schlenk tube cooled in ice. The mixture was left stirring for 24 hours, during which time the dark brown Co(dmg)

was replaced by lighter brown CoBF. The mixture was filtered under nitrogen and washed with two further aliquots of methanol, H_2O and methanol again. The solid was dried under vacuum before being recrystallised from hot methanol.

The chain transfer activity of the CoBF was evaluated by carrying out a series of reactions with various concentrations using MMA as monomer and AIBN as initiator. 4 mL of a stock solution containing 150 mg of AIBN in 24 mL of MMA was measured into each of five ampoules along with between 0 and 0.4 mL of containing 3.9×10^{-2} mg mL^{-1} of CoBF in MMA and between 1 and 0.6 mL MMA. The solutions were degassed by three freeze-pump thaw cycles and then sealed under vacuum. The solutions were thawed to room temperature and placed in a water bath at 60°C for 15 minutes. The number average molecular weights were determined by SEC and the data used to construct a Mayo plot.

Table 7.1 Polymerization data from reactions to determine chain transfer efficiency of CoBF

moles CoBF	moles MMA	Mn	PDi
0	4.69×10^{-2}	151850	1.97
1.67×10^{-9}	4.69×10^{-2}	58950	2.02
3.34×10^{-9}	4.69×10^{-2}	33870	2.06
6.68×10^{-9}	4.69×10^{-2}	18330	1.95
1.34×10^{-8}	4.69×10^{-2}	9560	2.00

A plot of $1/DP - 1/DP_o$ against [S]/[M] where DP and DP_o are the number average degree of polymerization with and without chain transfer agent and [S]

and [M] are the initial concentration of CoBF and MMA, results in a straight line, the gradient of which is equal to the chain transfer constant of the CoBF, Figure 7.1. From the gradient of the line in Figure 7.1 the Cs value for the CoBF was calculated to be 34 750.

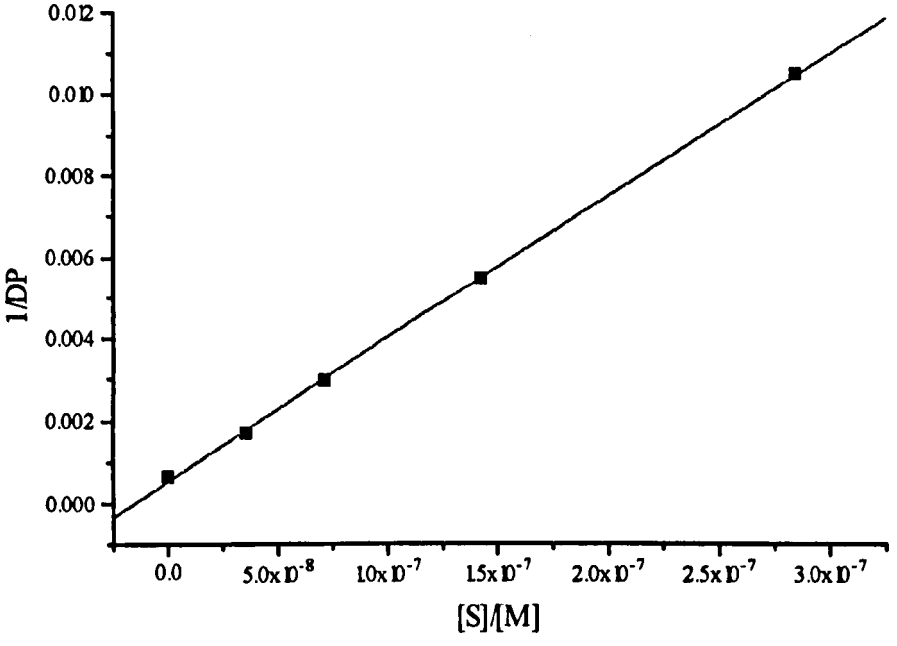

Figure 7.1 Mayo plot to calculate the chain transfer constant for CoBF

7.3 Preparation of Macromonomers

All methacrylate dimers and trimers were prepared by the same method. Methacrylate macromonomers were prepared by the bulk polymerization of monomer in the presence of CoBF initiated by AIBN. Monomer was used as supplied and degassed by bubbling through with nitrogen for at least two hours prior to use. The CoBF and AIBN were added to the reaction flask and pump-

filled with nitrogen prior to addition of the monomer. The reactions were carried out in a water bath at 60 °C for three days. In a typical reaction 250 mL of degassed monomer was added to 0.5 g of AIBN and 0.25 g of CoBF. Analysis of the reaction product showed a range of low molecular weight macromonomers that were separated by reduced pressure distillation on a kugelrohr apparatus. All low molecular weight macromonomers used in this work were collected under the conditions shown in section 2.2 and purity of dimer, trimer and tetramer was checked by NMR and SEC.

Mixed macromonomers were prepared by the bulk polymerization of MMA (65 mL, 0.61 moles) and HEMA (65 mL, 0.54 moles) in the presence of CoBF (0.22 g) initiated by AIBME (0.1615 g). Monomers and initiator were used as supplied. The CoBF and AIBME were pump-filled with nitrogen prior to addition of the monomers. The reaction mixture was deoxygenated by two freeze-pump-thaw cycles prior to being placed in a water bath for three days. This resulted in a range of low molecular weight oligomers as analysed by SEC which were separated under the conditions shown in Table 2.1.

7.4 Determination of Cs Values

All reactions were carried out in bulk in ampoules of size 120 mm by 20 mm with wall thickness 1 mm that could be flame sealed. Stock solutions containing varying amounts of monomer (purified by passing through a column of activated aluminium oxide and activated molecular sieves, 3Å, and stored under nitrogen

prior to use), macromonomer and initiator were prepared and transferred to ampoules using volumetric glassware in such quantities as to give a range of macromonomer concentrations between 0 and 100 % or 0 and 10 %. These solutions were degassed by freeze pump thaw cycles before being sealed under vacuum. After a reaction time of 2 hours at 60 °C reactions were quenched in liquid nitrogen. After opening reaction mixtures were diluted with dichloromethane and precipitated into hexanes before being dried to constant weight in vacuo. Molecular weight data was obtained by SEC analysis.
In a typical reaction stock solutions containing 0.045 g of AIBN in 46.807 g of MMA, 12.00 g of BMA trimer in 11.272 g of MMA were prepared. Eight reactions were prepared, each containing a total volume of 10 mL, 5 mL of initiator solution with the remainder from a combination of the macromonomer stock solution and MMA to give the required molar ratios of monomer and macromonomer. After being degassed and sealed all ampoules were immersed simultaneously in a water bath at 60 °C for 2 hours before being quenched in liquid nitrogen to stop the reaction.

7.5 Preparation of Telechelic Polymers

Reactions to prepare telechelic polymers were carried out in closed ampoules at 80 °C for various reaction times, typically 17 hours (one half life of the initiator), 41 hours and 8 days (to obtain a high conversion). Reactions were carried out in dimethyl formamide (DMF) in order to dissolve the hydroxy azo initiator (2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide]).

Telechelics were prepared using HEMA dimer with MMA, BMA and LMA, and BzMA dimer and GMA dimer with MMA. Reactions were also carried out with MMA dimer and BMA monomer. Products from reactions involving HEMA dimer and MMA were precipitated into water, redissolved in THF and reprecipitated into water, those with BMA as monomer were precipitated into cold water, redissolved in THF and reprecipitated into cold methanol. The polymer formed in reactions involving LMA precipitated from solution, therefore the polymer was isolated by decanting the unreacted liquid. The remaining polymers formed by reaction with MMA were isolated by precipitation into petroleum ether.

In a typical reaction 5 g of a stock solution containing 5 g MMA, 5 g BzMA dimer, 5 g DMF and 10 g of initiator stock solution (0.1 g VA-086 in 40 g DMF) was placed in an ampoule, degassed by four freeze pump thaw cycles, sealed under vacuum and heated for 8 days at 80 °C. The polymer was isolated by precipitation into petroleum ether and dried under vacuum.

7.6 Preparation of Hydroxy Functional PMMA

Four reactions were carried out with the aim of producing PMMA with various numbers of hydroxy groups per polymer chain by copolymerizing MMA with varying amounts of mixed MMA/HEMA macromonomer. A stock solution of VA-086 initiator in DMF (0.0507 g in 20.0027 g DMF) was prepared and 2 g added to each of four ampoules. To this was added 1 g of MMA and between 0.1 and 1.0 g of macromonomer and 1.9 and 1.0 g of DMF. Reaction mixtures were

degassed by three freeze-pump-thaw cycles, closed under vacuum and placed in a water bath at 80 °C for seven days. The polymers were isolated by precipitation into water, with reactions A and D redissolved in THF and reprecipitated into hexanes, and dried under vacuum.

7.7 Reaction of Hydroxy Functional Polymers with Isocyanates and Diisocyanates

Five reactions were carried out in which hydroxy telechelic polymers were end capped with p-tolyl isocyanate or chain extended using methylene diphenylene diisocyanate or hexamethylene diisocyanate. Reactions were also carried out using PMMA containing more than two hydroxyl groups per chain in order to form a network.

All reaction glassware was flame sealed prior to use and all transfers were made by syringe. Reactions were carried out in refluxing anhydrous toluene in a flask fitted with a condenser. For reactions involving telechelic polymers a 1:1 ratio of hydroxyl to isocyanate groups was used, those involving polymers with a functionality greater than two had an excess of hydroxyl groups. In a typical chain extension reaction 2 mL of a stock solution containing 0.35 g of MDI in 50 mL of toluene was added to a refluxing mixture of hydroxytelechelic PMMA (1.05 g in 60 mL toluene). Four drops of dibutyl tin dilaurate were then added. Further batches of 0.5 mL of MDI stock solution were added to the reaction every hour for four hours and the reaction was left refluxing overnight before

being killed with methanol. Products from reactions involving MDI were analysed using a dual detector SEC fitted with an RI and a UV detector.

7.8 Hydrogenolysis of Benzyl Methacrylate Terminated PMMA

0.3 g of BzMA terminated PMMA was dissolved in dichloromethane, precipitated using methanol and redissolved in dichloromethane in a Parr hydrogenation flask. 0.03 g of palladium on activated carbon (10% Pd) catalyst was added to the flask prior to being shaken under a hydrogen atmosphere for 4 days. The majority of the solvent was removed by rotary evaporation before the catalyst was removed by passing the solution through a column of Celite, acetone being used as eluent. The polymer was isolated by precipitation into hexanes.

7.9 Emulsion Polymerization with Macromonomers

All emulsion polymerizations were carried out in a one litre reaction flask fitted with a nitrogen inlet and condenser, at 80 °C with agitation from an overhead stirrer at 150 rpm.

The water (200 mL) was degassed by bubbling through with nitrogen overnight before being added to the flask by syringe and left to equilibrate to bath temperature for one hour. Surfactant, Aerosol OT-100 (0.5 g) was then added followed by the initiator, 4,4'-azobis(4-cyanopentanoic acid) (0.5 g). The monomer (50 mL) was degassed by two freeze pump thaw cycles, and was fed at approximately 3.3 mL min^{-1}. If macromonomer was used in the reaction it was

premixed with monomer in the required ratios to give 50 mL of solution before being degassed and fed into the reaction. Reactions were carried out for two hours, with sampling every twenty minutes in order to measure conversion by gravimetry, for reactions without added macromonomer, and for three days with sampling every 20 minutes for three hours with a further sample every hour for five hours followed by a sample after 24 hours and 48 hours for reactions with added macromonomer.

Molecular weights were measured by SEC and conversions by gravimetry.

7.10 Group Transfer Polymerization

Group transfer polymerizations of monomer (MMA and BMA) and macromonomer (MMA dimer, trimer and tetramer, and BMA dimer and trimer) were carried out in THF solution at room temperature for 24 hours. All transfers were made by syringe with all glassware flame dried under vacuum prior to use. Reaction mixtures containing the required quantities of monomer and macromonomer were prepared and degassed by three freeze pump thaw cycles and were dried in a closed ampoule over sieves overnight. THF was purified by distillation from sodium with benzophenone as indicator immediately prior to use. Methyltrimethylsilyl dimethylketene acetal (MTS) was obtained from Aldrich and stored over 4 Å molecular sieves in the bottle and used without further purification. Tetrabutyl ammonium m-chlorobenzoate (TBAmCB) was prepared by the method of Dicker and Sogah[4] and stored under nitrogen prior to use as ~ $8x10^{-3}$ molar stock solution in THF. Quantities of reactants were usually

calculated in order to give a [monomer]:[initiator] ratio of 100 and [initiator] to [catalyst] ratio of 100.

In the homopolymerization reaction 5 mL of MMA dimer was added to 5 mL of THF. To this was added 785 μl of TBAmCB stock solution (0.0165 g of TBAmCB in 4.9 mL of THF, 8.45 x 10^{-3} molar solution), 30 μl bis(dimethyl amine) methyl silane and 130 μl of MTS. A typical copolymerization reaction involved the addition of 6 mL of MMA dimer and 5 mL of BMA to 20 mL of THF. To this typically were added 785 μl of TBAmCB stock solution, 30 μl of bis(dimethyl amine) methyl silane and 130 μl of MTS. Further batches of 785 μl TBAmCB were added after one and two hours then the reactions were left stirring overnight. The majority of the solvent, monomer and dimer were removed using a kugelrohr apparatus in order for a sample to be obtained suitable for analysis by MALDI-TOF MS and higher molecular weight polymers were precipitated from acetone into cold methanol.

A number of bulk reactions of monomer and monomer plus macromonomer were carried out as described above, but without the THF in the reaction mixture. Temperature changes were monitored using a thermocouple.

Reactions to determine the reactivity ratio of BMA and MMA dimer were carried out in THF at room temperature with initial [monomer]:[MTS] ratios and [MTS]:[TBAmCB] ratios of 200:1 and 100:1 respectively. In a typical reaction a monomer solution was prepared to give BMA:MMA dimer 80:20 (40.014 g BMA and 14.073 g MMA dimer) and left to dry over 4 Å molecular sieves overnight. The composition of the monomer mixture was confirmed by ^{1}H NMR analysis. 10 mL of this mixture was added to 15 mL of THF. To this typically

were added 383 μl of TBAmCB stock solution (0.075 g TBAmCB in 23.5 mL THF, 8.02 x 10^{-3} M solution), 30 μl of bis(dimethyl amine) methyl silane and 62 μl of MTS. Further batches of 300 μl of TBAmCB solution were added every hour over four hours before the reaction was terminated with MeOH after 19 hours. 0.015 g of diphenylpicrylhydrazyl (DPPH) was then added to prevent UV-initiated polymerization before removal of volatiles from the reaction mixture under vacuum. The polymer product was removed from the reaction vessel using dichloromethane and then dried under vacuum at 60 °C until constant weight. Conversions were corrected using ^{1}H NMR analysis.

7.11 References

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Appendix 1

Derivation of Chain Transfer Equation

Cumulative number average degree of polymerization = the number of monomer molecules enchained divided by the number of polymer molecules formed

Number of monomer molecules enchained = conversion * initial monomer concentration

$$= [M]_o p$$

Number of polymer molecules formed = (number formed from initiator)*α + number formed from chain transfer events

<u>Number of polymer molecules formed from initiator:</u>

$$I \xrightarrow{k_d} 2I\bullet$$

$$R_i = \frac{-d[I]}{dt} = k_d[I]$$

$$\int_{[I]_o}^{[I]} \frac{-d[I]}{[I]} = k_d \int_0^t dt$$

$$-\ln \frac{[I]}{[I]_o} = -k_d t + C$$

t=0, $[I]=[I]_o$, C=0

$$\frac{[I]}{[I]_0} = \exp(-k_d t)$$

$$[I] = [I]_o \exp(-k_d t)$$

This is equal to the concentration of I left at time t

$\therefore$ amount consumed to form polymer = initial amount - amount left

$\therefore$ amount consumed:

$$= [I]_0 - [I]_0 \exp(-k_d t)$$
$$= [I]_0(1 - \exp(-k_d t))$$

but two radicals are formed from one initiator, and not all radicals initiate polymerization (f = initiator efficiency),

$\therefore$ number formed from initiator = $2f[I]_0(1 - \exp(-k_d t))$

some chains are terminated by combination, therefore less than one polymer chain formed per initiator fragment:

$$\alpha = \frac{2 - F_c}{2}$$

F_c = fraction of termination that occurs by combination

Number of chain transfer events

$$S + R\bullet \xrightarrow{k_{tr}} P + S\bullet$$

$$R_{tr} = \frac{-d[S]}{dt} = k_{trs}[S][R\bullet]$$

Steady state assumption $R_i = R_t$

$$2R\bullet \xrightarrow{k_t} P_n + P_m$$

$$R_t = [R\bullet]^2$$

$$k_t[R\bullet]^2 = 2fk_d[I]_0(\exp(-k_d t))$$

$$[R\bullet]^2 = \frac{2fk_d[I]_0}{k_t}(\exp(-k_d t))$$

$$[R\bullet] = \left(\frac{2fk_d[I]_0}{k_t}\right)^{1/2}(\exp -k_d t/2)$$

$$\frac{-d[S]}{dt} = k_{trs}[S]\left(\frac{2fk_d[I]_0}{k_t}\right)^{1/2}(\exp(-k_d t/2))$$

$$-\int_{[S]_0}^{[S]}\frac{d[S]}{[S]} = k_{tr}\left(\frac{2fk_d[I]_0}{k_t}\right)^{1/2}\frac{2}{k_d}(\exp(-k_d t/2)) + C$$

$$t = 0, [S] = [S]_0$$

$$-\ln\frac{[S]}{[S]_0} = -2k_{tr}\left(\frac{2f_d[I]_0}{k_t k_t}\right)^{1/2}(\exp(-k_d t/2)) + C$$

$$C = -2k_{tr}\left(\frac{2f_d[I]_0}{k_t k_t}\right)^{1/2}$$

$$\frac{[S]}{[S]_o} = \exp(-2k_{tr}\left(\frac{2f_d[I]_0}{k_t k_t}\right)^{1/2}(1-\exp(-k_d t/2))$$

Number of chain transfer events = initial concentration of chain transfer agent

- current concentration of chain transfer agent

$$= [S]_0 - [S]_0 \exp(-2k_{tr}\left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}(1-\exp(\frac{-k_d t}{2})))$$

$$= [S]_0(1-\exp(-2k_{trs}\left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}(1-\exp(\frac{-k_d t}{2}))))$$

$$\therefore DP = \frac{[M]_0 p}{(2-F_c)f[I]_0(1-\exp(-k_d t)+[S]_0((1-\exp(-2k_{trs}\left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}(1-\exp(\frac{-k_d t}{2}))))}$$

$$M + R\bullet \xrightarrow{k_p} M\bullet$$

$$\frac{-d[M]}{dt} = k_p[M][R\bullet]$$

$$[R\bullet] = \left(\frac{2fkd[I]_0}{k_t}\right)^{1/2}(\exp(\frac{-k_d t}{2}))$$

$$\frac{-d[M]}{dt} = k_p[M]\left(\frac{2fkd[I]_0}{k_t}\right)^{1/2}(\exp(\frac{-k_d t}{2}))$$

$$-\ln\frac{[M]}{[M]_0} = -2k_p\left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}(\exp(\frac{-k_d t}{2}))+C$$

$t = 0, [M] = [M]_0$

$$C = -2k_p\left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}$$

$$\frac{[M]}{[M]_0} = \exp(2k_p\left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}(1-\exp(\frac{-k_d t}{2})))$$

$$Conversion = \frac{[M]_0 - [M]}{[M]_0} = 1 - \frac{[M]}{[M]_0} = p$$

$$\ln(1-p) = -2k_p\left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}(1-\exp(\frac{-k_d t}{2}))$$

$$\text{let } A = \left(\frac{2f[I]_0}{k_d k_t}\right)^{1/2}(1-\exp(\frac{-k_d t}{2}))$$

$$A = -\frac{\ln(1-p)}{2k_p}$$

$$N_{CT} = [S]_0(1-\exp(\left(\frac{-2k_{trs}}{-2k_p}\right)\ln(1-p))$$

$$= [S]_0(1-\exp(\ln(1-p)^{C_s})$$

$$= [S]_0(1-(1-p)^{C_s})$$

$$\therefore DP = \frac{[M]_0 p}{(2-F_c)f[I]_0(1-\exp(-k_d t)+[S]_0(1-(1-p)^{C_s})}$$

Catalytic Chain Transfer

$[S] = [S]_0$

$$\frac{-d[S]}{dt} = k_{trs}[S]_0\left(\frac{2k_d f[I]_0}{k_t}\right)^{1/2}\exp(\frac{-k_d t}{2})$$

$$\int -d[S] = -2k_{trs}[S]_0\left(\frac{2f[I]_0}{k_t k_d}\right)^{1/2}\exp(\frac{-k_d t}{2}) + C$$

$$[S] - [S]_0 = 2k_{trs}[S]_0\left(\frac{2f[I]_0}{k_t k_d}\right)^{1/2}\exp(\frac{-k_d t}{2}) + C$$

$t = 0, [S] = [S]_0$

$$C = -2k_{trs}[S]_0\left(\frac{2f[I]_0}{k_t k_d}\right)^{1/2}$$

$$[S] - [S]_0 = -2k_{trs}[S]_0\left(\frac{2f[I]_0}{k_t k_d}\right)^{1/2}(1 - \exp(\frac{-k_d t}{2}))$$

$$[S] = [S]_0 - 2k_{trs}[S]_0\left(\frac{2f[I]_0}{k_t k_d}\right)^{1/2}\exp(\frac{-k_d t}{2})$$

$N_{CT} = [S] - [S]_0$

$$= [S] - [S]_0 + 2k_{trs}[S]_0\left(\frac{2f[I]_0}{k_t k_d}\right)^{1/2}\exp(\frac{-k_d t}{2})$$

$$= C_S[S]_0 \ln(1 - p)$$

$$\therefore DP = \frac{[M]_0 p}{(2 - Fc)f[I]_0(1 - \exp(-k_d t)) + C_S[S]_0 \ln(1 - p)}$$