

Atom Transfer Radical Polymerisation of Unusual Monomers

by

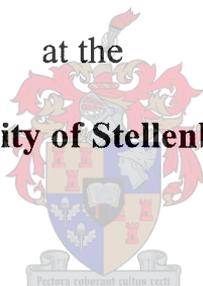
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DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not previously, in its entirety or in part, been submitted at any university for a degree.

ABSTRACT

Controlled free radical polymerisation techniques offer several practical and theoretical advantages compared to many other polymerisation techniques. Living polymerisation techniques such as anionic polymerisations require the total exclusion of impurities such as oxygen and moisture. Controlled free radical polymerisations, however, do not require such stringent methods of practice. This is very advantageous for industrial purposes.

Atom Transfer Radical Polymerisation (ATRP) is a form of a controlled/living free radical polymerisation technique by which one is able to synthesize controlled architectural structures and predetermine the molecular weights of macromolecules.

The monomers that were investigated for this research project include methyl methacrylate (MMA), 4-vinylpyridine (4VP) and lauryl methacrylate (LMA). The latter two monomers (4VP and LMA) are not commonly used in ATRP-mediated reactions. The synthesis of block copolymers of MMA and LMA were attempted. The homopolymerisation of 4VP did not give the control expected when polymerising by means of ATRP. This prompted an investigation into possible side reactions that could take place with 4VP in this specific ATRP system. This included possible quaternization of 4VP with the alkyl halide initiator species.

OPSOMMING

Beheerde vrye-radikaalpolimerisasietegnieke bied verskeie praktiese en teoretiese voordele bo verskeie ander vrye-radikaalpolimerisasietegnieke. Lewende polimerisasietegnieke soos anioniese polimerisasie, vereis die totale uitsluiting van onsuiverhede soos suurstof en water. Beheerde vrye-radikaalpolimerisasies vereis egter nie sulke streng reaksiekondisies nie. Hierdie is baie voordelig vir industriële doeleindes.

Atoomoordragradikaalpolimerisasie (ATRP) is 'n tipe beheerde/lewendende vrye-radikaalpolimerisasietegniek wat dit moontlik maak om die samestelling en struktuur van makromolekules asook die molekulêre massa presies te beheer.

In hierdie studie is die monomere metielmetakrilaat (MMA), 4-vinielpiridien (4VP) en laurielmetakrilaat (LMA) bestudeer. Laasgenoemde twee monomere (4VP en LMA) word beskou as ongewone monomere om in ATRP-sisteme te gebruik. Daar is gepoog om blok kopolimere van MMA en LMA te sintetiseer. Die homopolimerisasie van 4VP het minder beheer gelewer as wat by beheerde vrye-radikaal sisteme soos hierdie verwag word. Na aanleiding van hierdie resultate is 'n ondersoek geloods om die moontlike newereaksies van 4VP in hierdie spesifieke ATRP-sisteme te ondersoek. Daar is gepoog om te bewys dat die alkielchloriediniseerder verdwyn deur kwaternisasie met 4VP.

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LIST OF ABBREVIATIONS

ABS	Acrylonitrile-butadiene-styrene
ATRP	Atom Transfer Radical Polymerisation
BPO	Benzyl peroxide
BPY	2,2'-bipyridine
CRP	Controlled radical polymerisation
D ₂ O	Deuterium oxide
DP	Degree of polymerisation
2-EBP	Ethyl 2-bromopropionate
CuBr	Copper bromide
CuCl	Copper chloride
[D]	Deactivator concentration
GPC	Gel Permeation Chromatography
HCl	Hydrochloric acid
[In]	Initiator concentration
[In] ₀	Initiator concentration at start of reaction
iPrOH	Isopropyl alcohol
k _{act}	Activation rate constant
k _{app}	Apparent rate constant
k _{deact}	Deactivation rate constant
k _{eq}	Equilibrium rate constant
K _{eq}	Equilibrium constant
k _p	Propagation rate constant
KOH	Potassium hydroxide
LMA	Lauryl methacrylate
[m]	Monomer concentration
[m] ₀	Monomer concentration at start of reaction
MA	Methyl acrylate
Me ₆ TREN	hexamethyl tris(2-(dimethylamino)ethyl)
MMA	Methyl methacrylate
MM _{Initiator}	Molecular mass of initiator
MM _{monomer}	Molecular mass of monomer
\bar{M}_n	Number-average molecular weight
$\bar{M}_{n,cal}$	Calculated Number-average molecular weight
\bar{M}_p	Peak-average molecular weight
\bar{M}_w	Weight-average molecular weight
MVTR	Moisture vapour transmission rate
MWD	Molecular weight distribution
\bar{M}_w / \bar{M}_n	Molecular weight distribution
MX(I/II)	Metal halide concentration
NaOH	Sodium hydroxide
NMP	<i>n</i> -methyl-2-pyrrolidone
<i>P</i>	Conversion
[P*]	Polymeric radical concentration
PDI	Polydispersity index

1-PECl	1-chloro-1-phenylethane
PMDETA	<i>N,N,N',N',N''</i> - Pentamethyldiethylenetriamine
P4VP	Poly 4-vinylpyridine
RAFT	Reversible Addition-Fragmentation Chain Transfer
R_p	Rate of propagation
$[RX]_0$	concentration of the propagating species at the start of reaction
$[RX]_t$	concentration of the propagating species at a specific reaction time t
SAN	Styrene-acrylonitrile
SFRP	Stable Free Radical Polymerisation
TEMPO	2,2,6,6-tetramethylpiperidin-1-oxyl
T_g	Glass transition temperature
TsCl	Toluene-4-sulfonyl chloride
4VP	4-Vinylpyridine

1. INTRODUCTION AND OBJECTIVES

1.1 INTRODUCTION

Free radical polymerisation is a very important mechanism for producing a wide variety of polymers of different molecular weights, under solution, emulsion, suspension or bulk conditions. In 1995, free radical polymerisations accounted for approximately half of the total polymer production in the United States ^[1]. The disadvantage of this process is the lack of control over the macromolecular structure due to diffusion-controlled termination reactions by radical coupling and disproportionation. For this reason, the development of controlled free radical polymerisations techniques such as Atom Transfer Radical Polymerisation (ATRP) and Reversible Addition-Fragmentation Chain Transfer (RAFT) has had a phenomenal impact upon the synthesis of tailored polymers for specific architectures.

ATRP is a relatively new controlled free radical polymerisation technique in which one is able to prepare new well-defined block- and graft copolymers, stars, combs and networks that could not previously be prepared using ionic living polymerisation. The need for extremely rigorous conditions, as applied in ionic polymerisations, is not necessary with ATRP. Many monomers have been polymerised in a controlled manner such as styrenics ^[2,3,4,5], methacrylates ^[2,3,5], acrylates ^[2,5], acrylonitriles ^[6,7], and 4-vinylpyridine ^[8]. The ATRP process was developed independently by Matyjaszewski ^[1-19] and Sawamoto ^[20-23].

ATRP differs from conventional radical polymerisation in that it allows the synthesis of controlled polymeric structures with narrow molecular weight distributions of polydispersities less than 1.5. An advantage of ATRP is that the transferring group is a simple halogen atom, which becomes incorporated into the end of the dormant chain, giving the polymer a functional end-group. This is useful, for example, for low molar mass chains that have a high proportion of halide end groups that can act as macro initiators. A disadvantage of ATRP is the metal (usually Cu) catalyst, which must usually be removed from the final product for the product to be used in industry. Systems employing copper ^[2,8,10,11,26] as catalyst seem to be the most reactive catalytic

systems ^[2] compared with those using metals such as iron ^[3,11], nickel ^[20,25] or ruthenium ^[21,24].

1.2 OBJECTIVES

The overall objective of this work was the attempted polymerisation of

- Methyl methacrylate (MMA)
- 4-Vinylpyridine (4VP)
- Lauryl methacrylate (LMA)

by ATRP. The last two monomers are considered to be unusual monomers with regards to their structure. With these monomers I attempted the:

- 1) ATRP of methyl methacrylate and lauryl methacrylate
- 2) ATRP of 4-vinylpyridine. An investigation into the effect of the quaternization of the initiator and monomer on reaction performance, such as molecular weight distributions, was also carried out.

Subsequently, the synthesis of controlled block copolymers of methyl methacrylate and lauryl methacrylate by ATRP was also carried out.

1.3 SPECIFIC OBJECTIVES

The individual objectives for each section of the work were as follows:

1.3.1 SECTION 1: ATRP OF METHYL METHACRYLATE

The preparation of methyl methacrylate by ATRP has also been reported in the literature ^[1]. The objective here was to obtain polymers of MMA with good characteristics, such as high molecular weight and narrow polydispersities, in order to be used as a macro initiator in the presence of LMA monomer to produce block copolymers.

1.3.2 SECTION 2: ATRP OF 4-VINYLPYRIDINE

The initial objective here was to obtain polymers of 4-vinylpyridine (4VP) that have narrow molecular weight distributions, via Atom Transfer Radical Polymerisation (ATRP), and copolymerise 4VP with styrene in a controlled manner to form a star-like structure by using a multifunctional initiator. To date, little ATRP work has been done on 4-vinylpyridine^[8]; the suspected reason for this being that it is difficult to obtain a controlled system with low polydispersities. Polyvinylpyridine readily quaternizes with acids or alkyl halides^[26]. In the ATRP reactions that were performed here, 1-chloro-1-phenyl ethane was used as the initiator. The reason for using this initiator is because it has a similar chemical structure to that of 4-vinylpyridine. The chlorine atom is a better leaving group than the bromine compound. It is suspected that a quaternary complex is formed with this initiator. Suitable conditions for the formation of the complex were not known at the start, but proposals have been formed from the results.

As it was difficult to achieve good control with 4-vinylpyridine, an investigation into the possible effect of a quaternary structure being formed, which would disrupt the process of ATRP from continuing in its predicted manner, to produce narrow molecular weight polymers, was conducted.

- NMR was used to determine the chemical shifts of individual atoms. The formation of a quaternary complex would allow one to see a difference in the chemical shifts of participating and neighbouring atoms. This, in turn, would affect the reactivities of the various compounds and they would not participate in the polymerisation in the exact same manner.
- The determination of possible variables that might contribute to the formation of a quaternary complex were also investigated.

1.3.3 SECTION 3: ATRP OF LAURYL METHACRYLATE

According to literature, the polymerisation of this monomer by ATRP has not been done before. My objective was to use this polymer as a macro initiator in the presence of MMA monomer to produce block copolymers.

1.3.4 SECTION 4: SYNTHESIS OF BLOCK COPOLYMERS OF METHYL AND LAURYL METHACRYLATE

According to the literature, copolymers of methyl- and lauryl methacrylate have also not yet been synthesized by means of ATRP. It has however been done by other methods such as Group Transfer Polymerisation ^[27]. It is thought that these copolymers may provide extra strength to polymeric materials. My objective was subsequently to determine if it was possible to synthesize block copolymers of these two monomers, with narrow polydispersities, by ATRP.

¹ Patten, T. E.; Matyjaszewski, K. *Advanced Materials*, **1998**, *10*(12), 901

² Queffelec, J.; Gaynor, S.G.; Matyjaszewski, K. *Macromolecules*, **2000**, *33*, 8629

³ Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules*, **1997**, *30*, 8161

⁴ Patten, T. E.; Matyjaszewski, K. *Advanced Materials*, **1998**, *10*(12), 905

⁵ Coca, S.; Jasieczek, C. B.; Beers, K. L.; Matyjaszewski, K. *J. Polm. Sci., Part A: Polym. Chem.*, **1998**, *36*, 1417

⁶ Greszta, D.; Matyjaszewski, K. *Polymer Preprints*, **1997**, *38*(1), 709

⁷ Matyjaszewski, K.; Jo, S. M.; Paik, H. J.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 6398

⁸ Xia, J.; Zhang, X.; Matyjaszewski, K. *Polymer Preprints*, **1999**, *39*, 562

⁹ Patten, T. E.; Matyjaszewski, K. *Accounts of Chemical Research*, **1999**, *32*, 895

¹⁰ Wang, J. S.; Matyjaszewski, K. *Journal of the American Chemical Society*, **1995**, *117*, 5614

¹¹ Matyjaszewski, K. *Polymer Preprints*, **2000**, *41*(1), 411

¹² Matyjaszewski, K. *Accounts of Chemical Research Symp. Series*, **1998**, *685*, 258

- ¹³ Patten, T. E.; Matyjaszewski, K.; Xia, J. *Journal of the American Chemical Society*, **1997**, *119*, 674
- ¹⁴ Wang, J.; Matyjaszewski, K. *Macromolecules*, **1995**, *28*, 7572
- ¹⁵ Patten, T. E.; Matyjaszewski, K.; Xia, J.; Abernathy, T. *Science*, **1996**, *272*, 866
- ¹⁶ Patten, T. E.; Matyjaszewski, K.; Xia, J. *Journal of the American Chemical Society*, **1997**, *119*, 674
- ¹⁷ Matyjaszewski, K.; Xia, J. *Macromolecules*, **1999**, *32*, 5199
- ¹⁸ Matyjaszewski, K.; Xia, J. *Macromolecules*, **1997**, *30*, 7697
- ¹⁹ Shipp, D. A.; Wang, J.; Grimaud, T.; Matyjaszewski, K. *Polymer Preprints*, **1998**, *39(2)*, 504
- ²⁰ Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, **1997**, *30*, 2249
- ²¹ Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules*, **1995**, *28*, 1721
- ²² Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, **1996**, *29*, 1070
- ²³ Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, **1997**, *30*, 4507
- ²⁴ Haddleton, D. M.; Jasieczek, C. B.; Hannon, M. J.; Shooter, A. J. *Macromolecules*, **1997**, *30*, 2190
- ²⁵ Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules*, **1996**, *29*, 8576
- ²⁶ Mark, H. F.; Gaylord, N. G.; Bikales, N. M. *Encyclopaedia of Polymer Science and Technology*, **1968**, *8*, 656
- ²⁷ Sannigrahi, B.; Wadgaonkar, P. P.; Sehra, J. C.; Sivaram, S. *J. Polm. Sci., Part A: Polym Chem.*, **1997**, *35*, 1999

2. HISTORICAL AND THEORETICAL BACKGROUND

2.1 RADICAL POLYMERISATIONS

Free radical polymerisation reactions are tolerant to many impurities, such as oxygen. Initiation is relatively slow, and propagating species react with each other, leading to termination reactions during the polymerisations. These termination reactions lead to loss of radical activity of the growing chains, and result in broadening of the distribution of chain lengths. Examples of controlled living polymerisations include Atom Transfer Radical Polymerisations (ATRP) ^[1], Reversible Addition-Fragmentation Chain Transfer (RAFT) ^[2] and Stable Free Radical Polymerisation (SFRP) ^[3,4]. An example of SFRP is nitroxide-mediated polymerisations.

There are several differences between conventional free radical polymerisations and controlled radical polymerisations (see table 2.1). The fundamental difference between these techniques is that with the conventional systems, due to irreversible termination reactions, one has no control over the macromolecular structure obtained. Conventional techniques are considered to be non-living. This means that once radicals have terminated with each other, they have no means of being reinitiated to further chain growth. Depending on the system, with conventional techniques the polydispersity of the molecular weight distribution increases over time and usually the number-average molecular weight (\bar{M}_n) is approximately constant. Polymerisations with conventional systems can be completed within a few hours. The reason for this is that the radical concentration is very high, and therefore polymerisation is very fast. Also, since it is active and does not have to be “reactivated” such as the controlled radical system, polymerisation times are reduced.

With the controlled methods, functionality is introduced into the polymer chains and various structures can be synthesized e.g. stars, networks, graft, block, and comb structures. These structures can also be synthesized with conventional reactions, but not with the same degree of control or functionality as can be achieved with the controlled techniques. Carboxyls, amines, double bonds and halogens are examples of functional groups which can be incorporated into the polymer either at the beginning,

in the middle, or at the end(s) of the chain, between blocks, or evenly spaced along the polymer backbone. The description of controlled systems as living implies that termination is minimal, thus allowing the growing chain ends to remain active after polymerisation is complete. This allows one to synthesize structures such as block copolymers. The advantage of this is that these products may be further polymerised or otherwise functionalised by re-initiation. With living systems, a narrow molecular weight distribution can be obtained and the number-average molecular weight, which increases in reaction time, can be predetermined. However, for these systems, more than 72 hours are often necessary to complete a reaction. This is due to the usually very low propagating radical concentration. Due to this low active radical concentration in controlled radical polymerisation systems, control is achieved mainly because all chains are growing at the same rate.

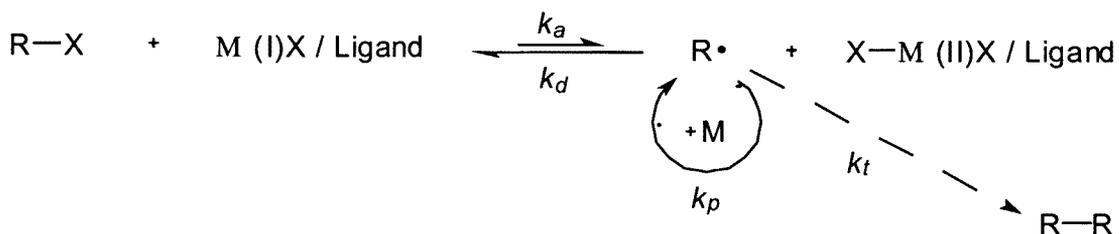
Table 2.1 Differences between conventional and controlled free radical polymerisations

	Conventional Free Radical	Controlled Free Radical
1	No control over structure	Controlled topologies and i.e. stars, graft, block, combs, networks
2	Non-living	Termination minimal - controlled/living
3	Polydispersity of MWD increases and is high	MWD narrow
4	M_n remains approximately constant	M_n increases linearly with conversion
5	Lower [initiator] than CRP	Higher [initiator] than conventional
6	Very fast polymerisation - minutes to hours	Usually very slow polymerisation - days
7	No chain-end control	Functional end group available for reinitiation / further reaction

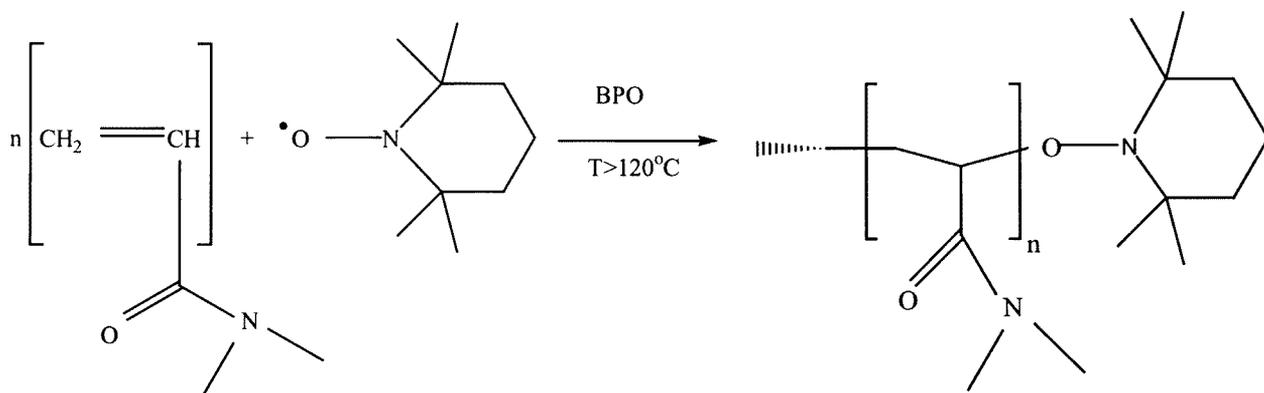
As mentioned in the beginning of the chapter, ATRP, SFRP and RAFT are examples of controlled/living polymerisations.

The reaction schemes for ATRP (X= halogen) and SFRP (X= nitroxide) are given in schemes 2.1 and 2.2, and for RAFT in scheme 2.3. It must be stated that in the reaction schemes below, when the symbol M is used, this is referring to the metal species used. For the purpose of my investigation, Cu metal was used as the catalyst for the ATRP reactions. The metal undergoes oxidation when a halogen atom is abstracted from the growing polymer chain. Cu^{I} was oxidised to Cu^{II} . For various

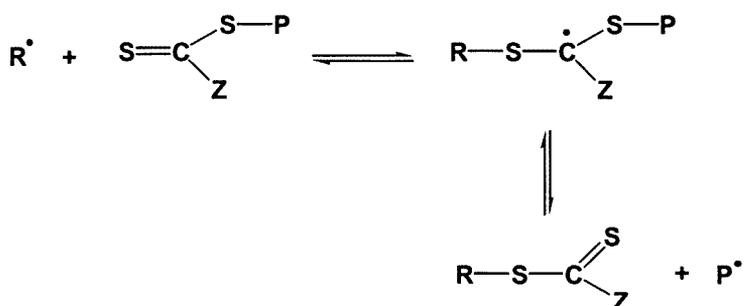
other metals which have been used, the oxidation states may vary, eg. Ni^{II} is oxidised to Ni^{IV}, and Fe^{II} is oxidised to Fe^{III}.



Scheme 2.1 ATRP mechanism. (M = transition metal, X = halogen)



Scheme 2.2 Nitroxide-mediated polymerisation using TEMPO as capping agent and BPO as an initiator.



Scheme 2.3 RAFT mechanism. (Z = stabilising group, P = leaving group)

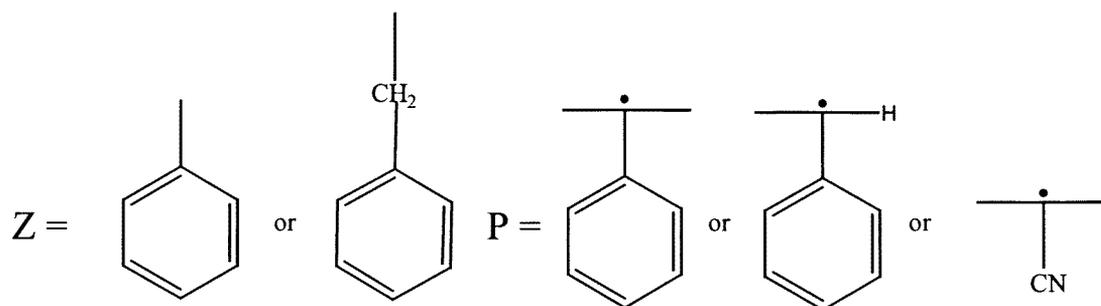


Figure 2.1 Examples of possible structures of the stabilising (Z) and leaving group (P), which are part of the RAFT scheme.

SFRP (scheme 2.2) ^[3] uses TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl), a nitroxide, a stable free radical, plus other nitroxides as its counter radical, and therefore has the advantage of being free of any metal compounds ^[5]. Rizzardo ^[4] did the pioneering work using TEMPO as a nitroxide. Initiation reactions in SFRP are slower than for ATRP and RAFT reactions. This leads to higher molecular weights than the expected theoretical molecular weights at lower conversions ^[5]. To date, this system is very limited in successfully polymerising monomers in a controlled fashion. In many cases, high temperatures ($T > 100\text{ }^\circ\text{C}$) are required for polymerisation to take place. Styrene homopolymers and copolymers, as well as methacrylic derivatives and 4-vinylpyridine, have shown living polymerisation features ^[3]. Various other compounds such as nitrones ^[6,7,8] and nitroso compounds ^[7,9] have been investigated as possible reagents in controlled nitroxide-mediated polymerisations.

RAFT (scheme 2.3) ^[2] involves the addition of a polymeric radical to a RAFT species already attached to the polymeric chain, followed by fragmentation to give a polymeric radical ^[5]. This allows exchange of radical activity between the two polymer chains. Examples of possible stabilising (Z) and leaving groups (P) can be seen in figure 2.1. The RAFT species is usually a dithio-compound. With RAFT, the RAFT: monomer ratio is the main controlling factor, and so the initiator concentration may be low. \bar{M}_n is primarily dependent on the ratio concentration of RAFT species to monomer. An advantage is that no metal catalyst is required. There is always a low concentration of low molecular weight radicals present in this system, which is a

disadvantage, since this enhances the probability of termination, due to their greater mobility. A wide range of monomers, such as styrenes, acrylates, methacrylates, and acrylonitrile, have been successfully polymerised by this technique.

For the reaction mechanism of ATRP, see section 2.1.

2.2 MECHANISM OF ATRP

As with conventional radical polymerisations, there are three stages in ATRP:

- 1) Initiation
- 2) Propagation
- 3) Termination

ATRP (scheme 2.1) ^[1] is defined as the reversible abstraction of a halogen atom between the active (radical) and dormant (temporarily halogen end-capped) functional chain ends ^[5]. Initiation may be thermal, chemical or photochemical stimuli of the dormant species. Generally, a transition metal catalyst is used, which abstracts the halogen atom from the initiator. The catalyst is then oxidized when the halogen is transferred and a radical generated, hereby allowing the polymer chain to grow.

To achieve controlled polymers, the process of deactivation must be fast to keep the polydispersity low. For this to happen there must be a drastic reduction in the concentration of the active radicals at any given moment. Choosing conditions enabling a fast exchange of the halogen to take place between the active and dormant species can do this. Equilibrium conditions must be strongly shifted to favour the dormant species. This would then cause the concentration of the active radicals to be very low and short lived, hereby decreasing the probability of collisions of radicals. As the number of radicals in the system increases, so the concentration of the deactivator increases, the equilibrium is shifted to the dormant side and the catalyst is regenerated by reduction of the oxidized transition metal complex. This activation/deactivation cycle is reversible.

During propagation, monomer units are added to the radical species. The number of monomer units which are added during each cycle must be kept as constant as possible if narrow polydispersities are desired. Fortunately, the equilibrium between active and dormant states usually favours the dormant species under the correct conditions, and in this way adds control to the mechanism by keeping a low radical concentration at all times and limiting irreversible termination. The fewer the number of propagation steps that take place, the greater the chances of all the chains growing at roughly the same rate. This is the main characteristic that makes ATRP different from conventional radical polymerisations.

The initiator (an alkyl halide with a labile halide group) is activated by the transition metal complex, which rapidly forms a significant number of radicals that can undergo polymerisation in the presence of the monomer. \bar{M}_n is dependent on the ratio of initiator to monomer concentration as determined by equation 2.4. The metal in the higher oxidation state then donates a halogen atom to the radical chain, thereby deactivating the chain. Generally, $\bar{M}_w / \bar{M}_n < 1.5$ for ATRP processes ^[1,10], due to the rapid deactivation and short initiation period, i.e. all chains grow at the same rate. \bar{M}_w / \bar{M}_n is a measure of polydispersity.

Compared to conventional radical polymerisations a higher initiator concentration is usually used for ATRP. ATRP is tolerant of many functional groups, which is not the case with techniques such as ionic polymerisations. Compared to other controlled radical polymerisation techniques, ATRP can be used for the synthesis of a broad range of monomers, as well as for preparing tailor-made polymers ^[11]. A disadvantage of the ATRP system is that a metal catalyst is used in the polymerisation process. It is often essential that this metallic species be removed from the final product for end-use in consumer products.

As previously mentioned (section 2.1), there are several transition metal catalysts that may be used in ATRP reactions. Several criteria need to be fulfilled for a catalyst to be seen as suitable for ATRP reactions: the catalyst must be selective, efficient, dynamically changing between two oxidation states, robust and inexpensive ^[12]. The

dynamically changing between two oxidation states, robust and inexpensive^[12]. The ATRP catalyst should only be involved in the extraction of halogen atoms between active and dormant chains, and not participate in any side reactions. Other important factors are the stability and cost of the catalyst and the ease with which the metal can be converted to its higher oxidation state. The equilibrium constant is the determining factor of how many radicals are present. Optimum conditions should be met for having a low enough radical concentration present in order to minimise irreversible termination between radical species and keep polydispersities as narrow as possible.

There are several transition metals that have been used for ATRP. The earlier used transition metals such as Ni^[13,14] and Pd are generally now avoided, unless the ligands would force them into an atom transfer process, as they tend to participate in side reactions. Fe, as catalyst^[12,14], has not been extensively studied, but research with a variety of coordinating ligands for MMA and styrene polymerisations have been successfully performed^[15].

In order to produce well-controlled polymer chains, the following conditions must be satisfied^[16]:

- 1) $k_p < k_{\text{deact}}$ (eq. 2.1)^[1]

k_p is the polymerisation rate constant and k_{deact} is the deactivation rate constant.

- 2) The activation constant must be significantly lower than the deactivation constant in order to obtain a low concentration of radicals and minimise termination reactions.
- 3) The rate of initiation must be fast with respect to the rate of polymerisation to ensure that all chains will start growing at the same time.

$$\frac{\bar{M}_w}{\bar{M}_n} = 1 + \left(\frac{2}{p} - 1 \right) \left(\frac{([RX]_0 - [RX]_t) k_p}{k_{\text{deact}}[D]} \right) \quad (2.1)$$

Here \bar{M}_w is the weight-average molecular weight distribution, whereas \bar{M}_n is the number-average molecular weight, $[RX]_0$ and $[RX]_t$ are the concentrations of the propagating species at the starting and current reaction times, respectively.

There are many precautions one has to take in order to produce polymers of uniform molecular weight. Elimination of impurities in the system is by no means an easy process. The presence of 0.1 mol % water in the system is sufficient to destroy uniformity of molecular weight, forming a product with $\bar{M}_w / \bar{M}_n = 2$ ^[17]. On the other hand, there are some catalysts that work very well in aqueous environments. Poor mixing is another factor which can lead to broad polydispersities. This problem is more prominent in reactions that have fast propagation rates.

It is of importance to note that by increasing the concentration of the deactivator [D], $M^{II}X_2$ /ligand, the equilibrium is shifted towards the dormant species, and radical production and termination is decreased. Hence, the rates of deactivation and propagation depend on the concentration of the deactivator. The rate of propagation (eq. 2.2) ^[1] is largely influenced by the persistent radical effect ^[1]. This effect is defined as the build up of the $M^{II}X_2$ /ligand species due to the irreversible termination of the active radical species through coupling or chain transfer reactions, shifting the equilibrium to the dormant side. As the concentration of the $M^{II}X_2$ /ligand increases, the amount of active radicals that react with the persistent radicals, rather than with each other, increases. Thus, the rate of deactivation soon becomes larger than the rate of termination. This effect is more pronounced during the initiation stages, as a large number of radicals are formed in the presence of very few deactivators. These can then react with one another, thereby decreasing the concentration of active radicals and consequently increasing the persistent radical concentration. If a large number of radicals are formed during the initiation stages, instead of allowing them to inevitably react with each other and form dead polymer chains, it is favourable to add extra Cu^{II} to the solution.

$$R_p = k_p[m] = k_p[P^*][m] = k_p k_{eq}[In] \frac{([M^I])}{[M^{II}X]}[m] \quad (2.2)$$

Here R_p is defined as the rate of propagation and $[m]$ refers to the monomer concentration. The latter is not the conventional notation but is used as above to distinguish it from the $[M]$, which is defined as the metal species concentration. $[m]$, $[P^*]$ and $[In]$ refer to the concentrations of monomer, polymeric radical and initiator, respectively. k_p , k_{app} and k_{eq} are the propagation, apparent and equilibrium rate constants, respectively. $[M^{II}X]$ refers to the metal halide concentration in the various oxidation states.

In ATRP the concentration of deactivator continuously increases logarithmically with time, in an ideal case, due to the persistent radical effect. The final molecular weights do not depend on the concentration of deactivator, but the polymerisation rate will decrease with higher deactivator concentration, due to the lower $[P^*]$.

During each activation/deactivation cycle, monomer is consumed (eq. 2.3).

$$-\frac{d[m]}{dt} = k_p[P^*][m] \quad (2.3)$$

The rate at which monomer is consumed is directly proportional to the rate coefficient for propagation, the radical and monomer concentrations. The rate of polymerisation can be increased by increasing the catalyst or initiator concentration, but this may affect the polydispersity, since more radicals will then be active, which would then lead to more termination. When the initiator concentration is increased the molecular weight of the obtained polymer decreases, as predicted by the equation 2.4^[18] for the number average degree of polymerisation.

$$DP = \frac{[m]}{[I]} \times \text{conversion} \quad (2.4)$$

Here DP is the degree of polymerisation which relates to the polymer length. This equation implies that if every single initiator successfully initiates the start of a growing polymer chain, then the fraction of the initial amount of monomer present over the initial amount of initiator present multiplied by the conversion is equal to the degree of polymerisation.

ATRP is a form of a controlled/“living” polymerisation technique^[18]. Because of the dynamic equilibrium in the reaction (scheme 2.1) and the large rate coefficient for k_{deact} , only a limited number of monomer units are inserted into the backbone in one activation/deactivation cycle. This is because $k_{\text{deact}} > k_p$. Thus, the molar mass of the polymer can be controlled. The addition of M(II) at the beginning of the reaction is an important factor in forcing the equilibrium to favour the dormant species, and thus lowering the radical concentration. Termination reactions cannot be disregarded, since there will always be an equilibrium concentration of radicals present at a given time, although the lifetime of any given radical is short for an activation/deactivation cycle. These termination reactions are however minimised by reducing the equilibrium concentration of radicals, by shifting the equilibrium to favour the dormant species. The rate of deactivation will change in these reactions due to the higher $[\text{Cu}^{\text{II}}\text{X}_2]$, but the equilibrium constant will not shift, only the position of the equilibrium will shift (eq. 2.5). These reactions are therefore called controlled/living polymerisations due to the reversible activation/deactivation cycles that allow the chains to have a living character (minimal termination, and thus preservation of activity) while molecular weight and polydispersity are well controlled (eq. 2.5)^[19].

$$K_{\text{eq}} = \frac{k_{\text{act}}}{k_{\text{deact}}} = \frac{[\text{P}^{\bullet}][\text{Cu}^{\text{II}}\text{X}_2]}{[\text{RX}][\text{Cu}^{\text{I}}\text{X}]} \quad (2.5)$$

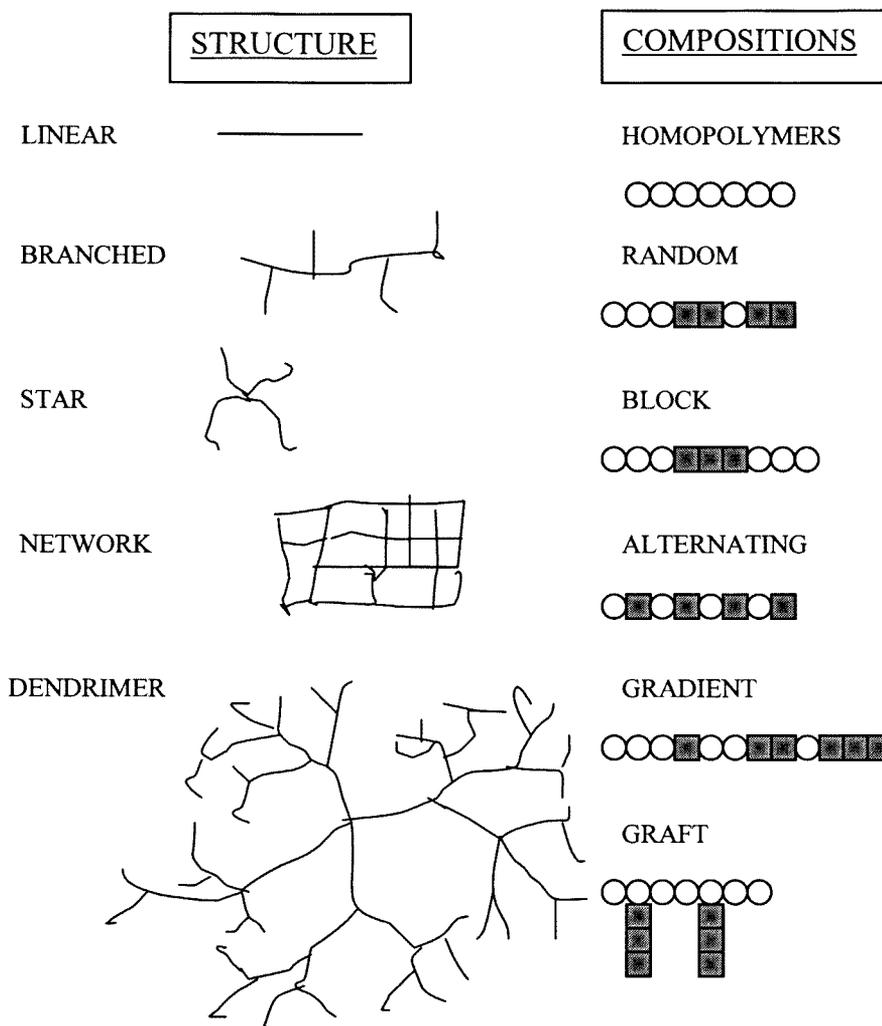
Here $[\text{Cu}^{\text{III}}\text{X}_n]$ refers to the concentration of the metal halide species in the various oxidation states.

2.3 BLOCK COPOLYMERS

A copolymer is defined as a polymer derived from more than one species of monomer [20]. Copolymers are in block form if each of the monomers forms a continuous homopolymer block in the chain sequence.

Block copolymers differ from blends, which are defined as homogenous mixtures of two or more different species of polymer [20]. In general, block copolymers offer several advantages over blends. Because the individual blocks are covalently bonded to one another, materials with high strength can be produced. And because the two phases are chemically bonded to each other, they cannot separate. Thermoplastic elastomers have been prepared by this method in which the central blocks are soft polymers with low T_g values, and the outer blocks are hard polymers with high T_g values. An example is a diblock copolymer consisting of the low T_g *n*-butyl acrylate and the high T_g methyl methacrylate [21].

The architecture of the copolymers can be accurately controlled using controlled radical polymerisations (or ionic techniques) to produce novel materials with interesting properties. Elastomeric behaviour, melt rheology and toughness are properties that are directly affected by architecture. There are many different types of architectures of blocks, which can readily be synthesized using controlled radical polymerisations (scheme 2.4).



Scheme 2.4 Type of copolymers that can be polymerised with controlled radical polymerisation techniques.

It has often been found that the synthesis of block copolymers by conventional free radical polymerisations is extremely difficult, or even impossible [22-21]. Ionic polymerisation methods, using either n-butyl lithium or a Ziegler-type catalyst, have made the synthesis of controlled polymer blocks a lot easier compared to the conventional free radical methods. However, these latter techniques are available for a limited choice of monomers and functionalities that may be incorporated. The development of ATRP (and controlled / living free radical polymerisation methods in general) have allowed the production of functional block copolymers with a variety of monomers [22-31].

2.3.1 STEPS IN THE SYNTHESIS OF BLOCK COPOLYMERS

In this thesis, the synthesis of a controlled block copolymer of MMA and LMA, using ATRP as choice of method for polymerisation, was attempted. It was approached as follows.

2.3.1.1 Homopolymerisations of MMA and LMA

This involved determining the ideal polymerisation conditions for ATRP of the individual monomers. The final products should have adequately high molar masses and sufficient end-functionalised chains in order for them to be re-activated for the second monomer.

2.3.1.2 Formation of diblocks

Once the reaction conditions for the homopolymerisations have been determined, one of the polymers synthesized in section 2.3.1.1 that meets the above criteria may then act as a macro-initiator for the synthesis of a second block, under conditions appropriate for the preparation of a second controlled block.

2.3.1.3 Approaches for making controlled triblock copolymers

If triblock copolymers are desired, the homopolymerisations of the individual monomers have to be optimised (section 2.3.1.1), and a difunctional macro-initiator made and used.

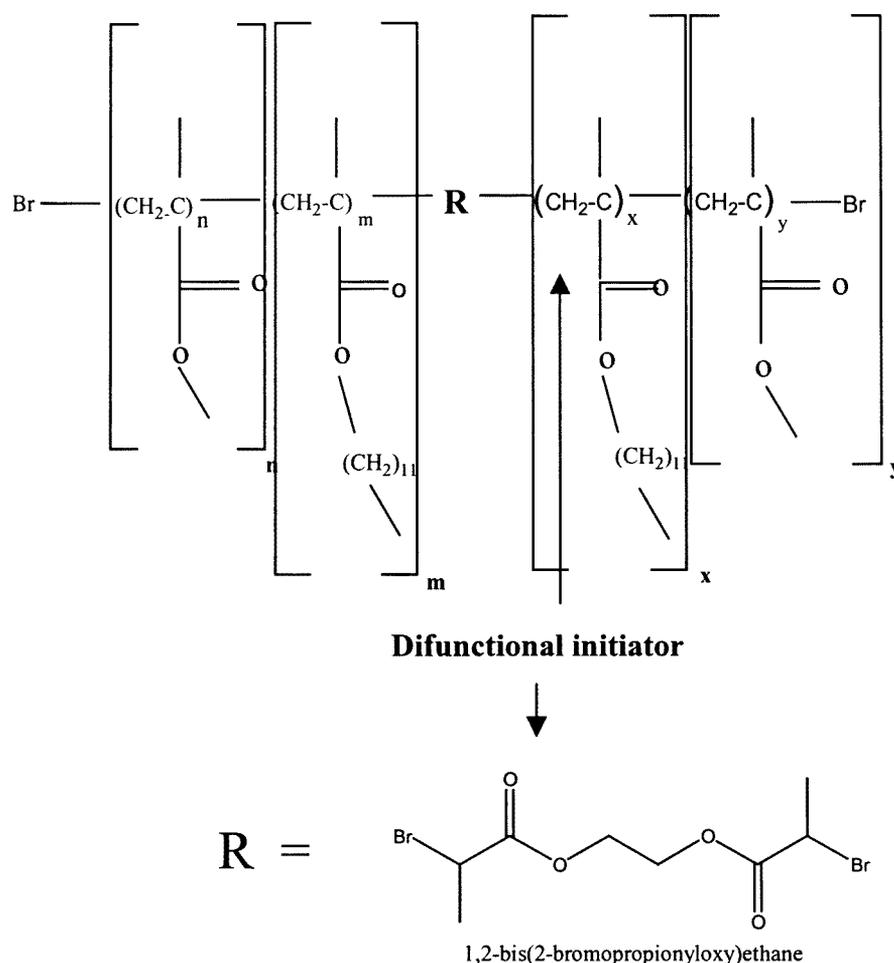
2.3.2 TECHNIQUES BY WHICH BLOCK COPOLYMERS CAN BE SYNTHESIZED VIA ATRP

There are various techniques by which one can synthesize block copolymers via ATRP:

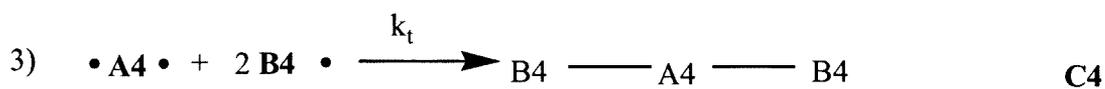
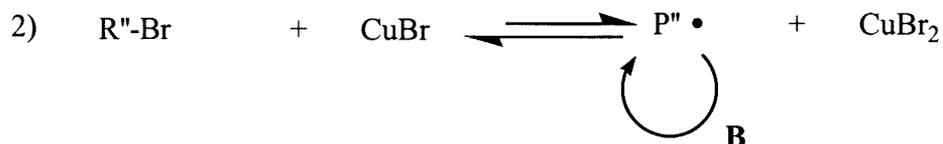
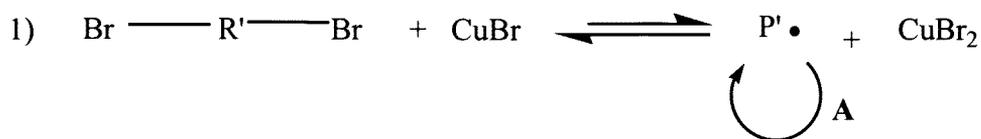
- a) Use of a macro-initiator ^[23,27-31]
- b) Sequential addition of second monomer to reaction mixture ^[23,25,26]
- c) Coupling reactions.

An advantage of making triblocks with a difunctional macro-initiator (scheme 2.5) is that a triblock copolymer is very likely to be produced on addition and reaction of a second monomer. A disadvantage of this technique is that accurate measurement of the molecular weights of the outer blocks is difficult. The centre block can be analysed accurately by, say, GPC, but analysis of the final triblock by GPC may not give accurate results due to the different properties in solution of either homopolymer.

The following scheme (scheme 2.6) shows the structure of a proposed triblock structure between LMA and MMA, prepared using a macro-initiator, LMA ATRP as first step, and MMA ATRP as second step, using the synthesized difunctional LMA block as a macro-initiator.



Scheme 2.6 Triblock copolymer of methyl and lauryl methacrylate showing an example of a difunctional initiator that may be used for such a reaction by ATRP.



TRIBLOCK

Scheme 2.9 Coupling reactions through combination of activated macro-initiator and polymeric species leading to the formation of a triblock copolymer.

Species **A4** was formed from an ATRP reaction of MMA (**A**) using a difunctional initiator, Br-R'-Br. Species **B4** is a polymer chain of LMA (**B**) capped with a bromine atom. This species is then used in another reaction in which species **A4** and **B4** are used in an ATRP reaction in which combination of active radicals results in species **C4**, which is a triblock. Because species **A4** has twice as many radicals as that of species **B4**, two moles of species **B4** are used relative to species **A4**.

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- ¹ Patten, T. E.; Matyjaszewski, K. *Accounts of Chemical Research*, **1999**, *32*, 895
- ² Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, G.; Moad, C. L.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559
- ³ Fischer, A.; Brembilla, A.; Lochon, P. *European Polymer Journal*, **2000**, *1*
- ⁴ Rizzardo, E. *Chem. Austr.* **1987**, *54*, 32
- ⁵ Shipp, D. A.; Matyjaszewski, K. *Polymer Preprints*, **1999**, *40(2)*, 450
- ⁶ Janzen, E. G. *Acc. Chem. Res.* **1971**, *4*, 3126
- ⁷ Nesvadba, P.; Kramer, A.; Steinmann, A.; Stauffer, W. US Patent US 6,-262, 206, 2001
- ⁸ Detrembleur, C.; Sciannamea, V.; Koulic, C.; Claes, M.; Hoebeke, M.; Jérôme, R. *Macromolecules*, **2002**, *35(19)*, 7214
- ⁹ Chalfont, G. R.; Perkins, M. J. *J. Am. Chem. Soc.* **1971**, *75*, 3467
- ¹⁰ Matyjaszewski, K. *J. Macromol. Sci. Pure Appl. Chem.* **1997**; A34: 1785
- ¹¹ Wang, J. S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7572
- ¹² Matyjaszewski, K. *Polymer Preprints*, **2000**, *41(1)*, 411
- ¹³ Uegaki, H.; Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, **1997**, *30*, 2249
- ¹⁴ Granel, C.; Dubois, Ph.; Jérôme, R.; Teyssié, Ph. *Macromolecules*, **1996**, *29*, 8576
- ¹⁵ Matyjaszewski, K.; Wei, M.; Xia, J.; McDermott, N. E. *Macromolecules*, **1997**, *30*, 8161
- ¹⁶ Chambard, G. "Control of Monomer Sequence Distribution", *Ph.D thesis*, Eindhoven University of Technology, **2000**
- ¹⁷ Mark, H. F; Gaylord, N. G.; Bikales, N. M. *Encyclopaedia of Polymer Science and Technology*, **1968**, *8*, 309
- ¹⁸ Matyjaszewski, K.; Patten, T. E.; Xia, J. *J. Am. Chem. Soc.*, **1997**, *119*, 674
- ¹⁹ Patten, T. E.; Matyjaszewski, K. *Advanced Materials*, **1998**, *10(12)*, 901
- ²⁰ <http://www.iupac.org>
- ²¹ Matyjaszewski, K. *Polymer Preprints*, **1997**, *38(2)*, 383
- ²² Jagur-Grodzinski, J. *Reactive and Functional Polymers*, **2001**, *49*, 1

- ²³ Mühlebach, A.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules*, **1998**, *31*, 6046
- ²⁴ Fukuda, T.; Terauchi, T.; Goto, A.; Tsujii, Y.; Miyamoto, T. *Macromolecules*, **1996**, *29*, 3050
- ²⁵ Greszta, D.; Matyjaszewski, K. *Polymer Preprints*, **1996**, *37*, 569
- ²⁶ Greszta, D.; Matyjaszewski, K. *Polymer Preprints*, **1997**, *38(1)*, 709
- ²⁷ Moineau, C.; Minet, M.; Teyssié Ph; Jérôme, R. *Macromolecules*, **1999**, *32*, 8277
- ²⁸ Davis, K. A.; Matyjaszewski, K. *Macromolecules*, **2001**, *34*, 2101
- ²⁹ Roos, S. G.; Müller, A. H. E. *Macromolecules*, **1999**, *32*, 8331
- ³⁰ Tong, J. D.; Moineau, G.; Leclère, Ph.; Brédas, J. L.; Lazzaroni, R.; Jérôme, R. *Macromolecules*, **2000**, *33*, 470
- ³¹ Davis, K. A.; Matyjaszewski, K. *Macromolecules*, **2000**, *33*, 4039
- ³² Davis, T. P. *J. Polym. Sci., Part A: Polym. Chem*, **2001**, *39*, 597
- ³³ Rudin, A. *The Elements of Polymer Science and Engineering*, 2nd edition, **1998**, 241

3. ATRP OF METHYL METHACRYLATE (MMA)

3.1 ABSTRACT

MMA (figure 3.1) was polymerised by means of ATRP. The aim was to produce polymers of high molecular weight and narrow polydispersity, which could then be used as macro-initiators in the presence of LMA monomer to produce block copolymers.

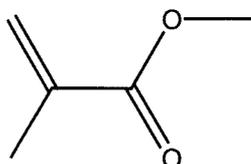


Figure 3.1 Structure of methyl methacrylate.

3.2 EXPERIMENTAL

3.2.1 General

Materials. MMA (Chemicals and Polymers, 99.9 %) was purified by extraction with aqueous 0.03 % KOH solution, followed by distillation under vacuum at a temperature below 40 °C, after which it was stored at 4 °C.

CuBr (Aldrich, 99.9 %), CuBr₂ (Aldrich, 99 %), CuCl (Fluka, > 97%), toluene-4-sulfonyl chloride (TsCl) (Fluka, ≥ 99 %), 2,2-bipyridine (BPY) (Aldrich, 99 %), *N,N,N',N',N''*- Pentamethyldiethylenetriamine (PMDETA) (Aldrich, 99%) and 2-butanone (Acros, 99 + %) were all used as received.

Analytical methods. Gravimetry was used in the case of MMA to determine conversion. Gel permeation chromatography was used to determine the molecular weights and polydispersities of both MMA and LMA. The theoretical molecular weights were calculated assuming a final conversion of 100%. The following equation (3.1) is that used to determine the theoretical number-average molecular weight at a 100 % conversion for ATRP reactions.

$$\bar{M}_{n\text{cal}} = \frac{[m]_0}{[I]_0} \times MM_{\text{monomer}} \times \text{conversion} + MM_{\text{initiator}} \quad (3.1)$$

Here, $[m]_0$ and $[I]_0$ refer to the monomer and initiator concentrations at the start of the reaction, whilst MM_{monomer} and $MM_{\text{initiator}}$ refer to the molar masses of the monomer and initiator, respectively.

In the results that follow in this chapter, the \bar{M}_n and \bar{M}_p versus % conversion plots have both been included. Differences in these values may arise due to the manner in which the GPC calculates them. The reason for sometimes rather using the peak mass as an indication of molecular weight is because the number-average molecular weights is a lot more sensitive to low molecular weight species, and there is a significant fraction of low molecular species present, which would affect \bar{M}_n calculations. \bar{M}_p values can be used as a guideline if \bar{M}_n is very stable. \bar{M}_n calculations are very sensitive to short chains and it is important that these fractions are taken into account when it comes to calculating the molecular weights. The detector does not sense the presence of very short chains, therefore the peak heights of longer chains are greater than those of their shorter counterparts. Also, the baseline becomes difficult to calibrate when there is a significant amount of low molecular weight species present, which is the real problem, as this would lead to tailing of the chromatographs. Unless the system is accurately calibrated, homotermination, or termination with impurities, could lead to low molecular weight species being formed, which would reduce the \bar{M}_n values.

A problem with the reactions that were carried out is the fact that they are heterogeneous. The copper does not completely dissolve in the mixture. For this reason, an excess of Cu^{I} is added. The polydispersity shows constant control (does not show large scatter distributions) during the polymerisation process, apart from the first sample. The reason for the latter (higher value) might be attributed to the partial insolubility of the $\text{Cu}^{\text{I}}\text{Br}$. Although the polydispersities are not as low as desired, the polymer might contain enough living chains to act as a macro initiator in order to reinitiate further monomers. Water did not enhance or contribute to better results for

the system in which copper was used as catalyst and 2,2'-bipyridine as ligand. The total exclusion of water was necessary as it is seen as an impurity to the system. The metal catalyst used for the purposes of this project was generally copper bromide ($\text{Cu}^{\text{I}}\text{Br}$), although ($\text{Cu}^{\text{I}}\text{Cl}$) was also used.

3.3 ATRP HOMOPOLYMERISATIONS OF MMA

ATRP reactions were carried out with MMA, with varying molar ratios of reactants, to determine the optimum conditions for obtaining a controlled polymerisation system.

The experimental conditions for the MMA reactions that were carried out are shown in table 3.1. The molar ratios and GPC results of a few of the MMA ATRP reactions that were performed are shown in table 3.2.

Table 3.1 Experimental conditions for MMA ATRP reactions. Reaction temperature 70 °C

Reaction	Masses (g)								Reaction time (h)
	MMA	$\text{Cu}^{\text{I}}\text{Br}$	$\text{Cu}^{\text{I}}\text{Cl}$	$\text{Cu}^{\text{I}}\text{Br}_2$	TsCl	BPY	PMDETA	2-butanone	
1	20.00	0.29			0.19	0.68		20.00	11.3
2	25.00	0.36			0.24	0.86		25.00	7
3	20.00	0.26			0.1	0.68		20.00	5.5
4	20.00		0.08		0.38		0.14	40.00	24.5
5	25.00	0.36		0.11	0.10	0.86		25.00	21.8
6	25.00	0.07		0.02	0.10	0.17		25.00	23.5

Table 3.2. Ratios of reactants used as well as molecular weight data for MMA ATRP reactions

Reaction	Ratios						\bar{M}_n	\bar{M}_p	PDI
	MMA	Cu ^I Br	Cu ^{II} Cl	TsCl	BPY	PMDETA			
1	100	1		0.5	2.2		10 290	28 333	2.19
2	100	1		0.5	2.2		11 221	19 681	1.75
3	100	1		0.25	2.2		13 776	23 783	1.69
4	100		0.4	1		0.4	6269	9384	1.28
		MMA	Cu^IBr / Cu^{II}Br₂	TsCl		BPY			
5	100		1 / 0.2	0.2		2.2	15 835	31 397	1.74
6	100		0.2 / 0.04	0.2		0.44	18 735	34 738	1.70

Reactions 1 and 2 showed high conversion and linear logarithmic plots of time (see sections 3.4.1 and 3.4.2, respectively). Reaction 1 displayed much scatter in the molecular weight and polydispersity graphs and was used for further re-initiation with MMA monomer to determine if the chains were living. Results hereof can be seen in section 7.6.

Reaction 2 displayed better molecular weight and polydispersity results than reaction 1. This polymer was then used as a macro-initiator in the presence of MMA (section 7.7).

Reaction 3 displayed high conversion and good molecular weight and polydispersity results, but the logarithmic plot was not very linear, indicating that a fair amount of termination had taken place. This would also have contributed to the short reaction time (5.5 h).

Reaction 4 showed high conversion, which did not seem to die off drastically towards the end of the reaction period. The logarithmic plots showed a linear region in the middle stages of the reaction, indicating that termination of radicals was minimal. The molecular weights increased linearly with time and the molecular weight distribution remained low throughout the entire reaction.

Reaction 5 showed high conversion, linear logarithmic plots, high molecular weights and fair polydispersities.

Reaction 6 also showed high conversion and good molecular weight plots, but the logarithmic plots of time were not very linear and the polydispersity index was fairly broad.

Use of the following molar ratio (as for reaction 1) was decided upon for further investigations as it showed results that indicated that it could possibly display living character.

100 : 1 : 0.5 : 2.2

MMA Cu^I TsCl BPY

In a typical reaction based on this ratio, TsCl (0.19 g, 0.99 mmol), Cu^IBr (0.29 g, 2.02 mmol), BPY (0.68 g, 4.4 mmol), MMA (20.00 g, 200 mmol) and 2-butanone (20.00g, 277 mmol) were added to a 150 mL schlenk tube. All reactants were weighed and the tube sealed in a glove box. Three freeze-thaw cycles were performed on the contents of the tube. The mixture was stirred overnight to ensure complete dissolution of the reactants. The schlenk tube was then immersed in an oil bath that was maintained at 70 °C. Samples were taken at regular time intervals for gravimetric and GPC analyses. The polymer was slowly precipitated in a 10-fold excess of methanol. Traces of copper could be detected from the green colour of the polymer. The polymer was therefore washed several times with methanol to reduce the concentration of the remaining copper, and dried in a vacuum oven overnight. This produced an off-white polymeric product, which was analysed by gravimetry and GPC.

Another polymerisation of MMA via ATRP (reaction 2) was carried out with slightly different amounts of reactants compared to those used in reaction 1. The same molar ratios were used for the reactants, but the amounts of MMA and 2-butanone used differed from reaction 1. See table 3.1 for reaction conditions and section 3.4.2 for results hereof. The reason for performing another reaction was to determine if results were reproducible or if results could be improved.

100 : 1 : 0.5 : 2.2

MMA Cu^I TsCl BPY

In this reaction, TsCl (0.24 g, 1.25 mmol), Cu^IBr (0.36 g, 2.5 mmol), BPY (0.86 g, 5.49 mmol), MMA (25.00 g, 249 mmol) and 2-butanone (25.00 g, 347 mmol) were added to a 150 mL schlenk tube. The same procedure was followed as for reaction 1.

A third polymerisation of MMA via ATRP (reaction 4) was further investigated. The difference between this reaction and the previous two (reactions 1 and 2) is the catalyst and ligand which was used. Cu^ICl was used as catalyst in this reaction compared to Cu^IBr, and PMDETA compared to BPY. The molar ratios of the reactants, as well as the temperature, were also different to those used in reactions 1 and 2. See table 3.1 for reaction conditions and section 3.4.2 for results hereof.

100 : 0.4 : 1 : 0.4

MMA Cu^I TsCl PMDETA

In this reaction, TsCl (0.38 g, 1.99 mmol), Cu^ICl (0.08 g, 0.8 mmol), PMDETA (0.14 g, 0.8 mmol), MMA (20.00 g, 199 mmol) and 2-butanone (40.00 g, 556 mmol) were added to a 150 mL schlenk tube. All reactants were weighed off and the sealed in the schlenk tube, after which the mixture was degassed for 1 hour with nitrogen gas before immersion in an oil bath maintained at 60°C. The mixture was degassed over the entire duration of the reaction. Samples were taken at regular time intervals over a period of 24.5 hours for gravimetric and GPC analyses. The polymer was slowly precipitated in a 10-fold excess of methanol. Traces of copper could be detected from the blue colour of the polymer. The polymer was therefore washed several times with methanol to reduce the concentration of the remaining copper, and dried in a vacuum oven overnight. This yielded an off-white polymeric product, which was analysed by gravimetry and GPC.

3.4 RESULTS AND ANALYSIS

3.4.1 MMA polymerisations (reaction 1)

The following data refer to the polymerisation reaction 1 (table 3.2). Refer to table 3.1 for reaction conditions.

Results showed that conversion of MMA was high (figure 3.2) and that the slope of the logarithmic graph (figure 3.3) of relative monomer concentration versus time was good. A linear trend of $\ln([M]_0/[M]_t)$ versus time indicates that the number of radical species remains constant during the reaction and that termination of radicals was absent or minimal. Figure 3.3 shows the entire range of data samples, including the inhibition stage and the last point. This graph shows a good linear relationship during the polymerisation period of 3 – 7.5 h, indicating that the number of radicals remained approximately constant during that part of the reaction. Because gravimetry is not an absolute method by which to determine very accurate and reliable conversion data, the possibility does exist that error may have been encountered. Therefore, absolute errors of 3 % have been calculated for each of the samples, and have been plotted as the upper and lower limits of error on the logarithmic graph (figure 3.3). It can be seen from this graph that for some points a better fit is suggested through the error bars rather than the original sample points.

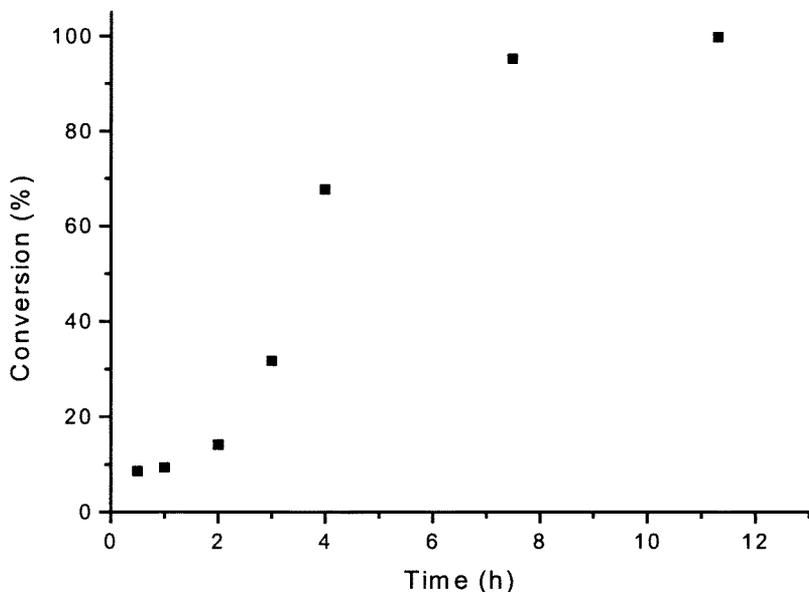


Figure 3.2 Graph of conversion versus time for MMA polymerisation via ATRP for reaction 1.

Polymerisation of 20.00 g MMA in 20.00 g 2-butanone at 70 °C.

Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

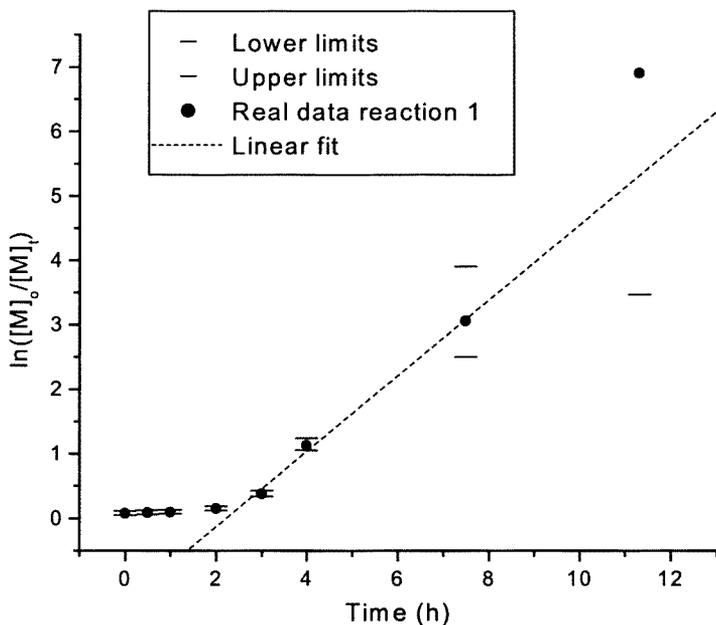


Figure 3.3 Logarithmic graph of reaction 1. ATRP polymerisation of MMA.

Polymerisation of 20.00 g MMA in 20.00 g 2-butanone at 70 °C.

Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

The number-average molecular weights (\bar{M}_n) of PMMA, as determined by GPC, did not show a linear increase with time, indicating that there was no control in the system. The measured values were significantly lower than the theoretical values ($20\,200\text{ gmol}^{-1}$) according to equation 3.1. The measured \bar{M}_n value of the final precipitated sample was $10\,300\text{ gmol}^{-1}$, the \bar{M}_p was $28\,300\text{ gmol}^{-1}$ and the polydispersity was 2.18. Figure 3.4 shows the plot of \bar{M}_p versus conversion for reaction 1 and it appears to be increasing linearly. The evolution of the corresponding peak masses (\bar{M}_p) have been included in further reactions for comparison of results; these are much closer to the theoretical \bar{M}_{ncal} . Refer to section 3.2.1 for explanations as to why the inclusion of peak mass is sometimes favourable for indications of molecular weight.

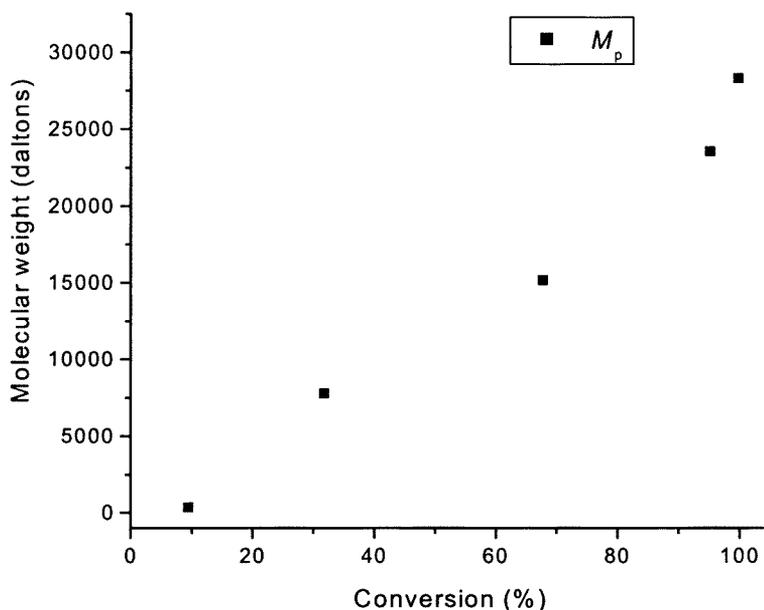


Figure 3.4 Peak-average molecular weight (\bar{M}_p) graph for reaction 1.

Polymerisation of 20.00 g MMA in 20.00 g 2-butanone at 70 °C.

Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

Although the polydispersity values were not as low as expected (using the technique of ATRP), this polymer may contain enough living chains to reinitiate further monomers.

3.4.2 MMA polymerisations (reaction 2)

The following data refer to the polymerisation reaction 2 (table 3.2). Refer to table 3.1 for reaction conditions.

Results from figure 3.5 show that the conversion of MMA is high. The slope of the logarithmic graph is almost completely linear (figure 3.6). Figure 3.6 shows the logarithmic plot across the entire polymerisation time. The approximately constant slope indicates that the number of radicals remained approximately constant during the intermediate stages of the reaction. Once again, absolute errors of 3 % have been calculated for each of the points, and in some cases seem to fit the linear trend more appropriately.

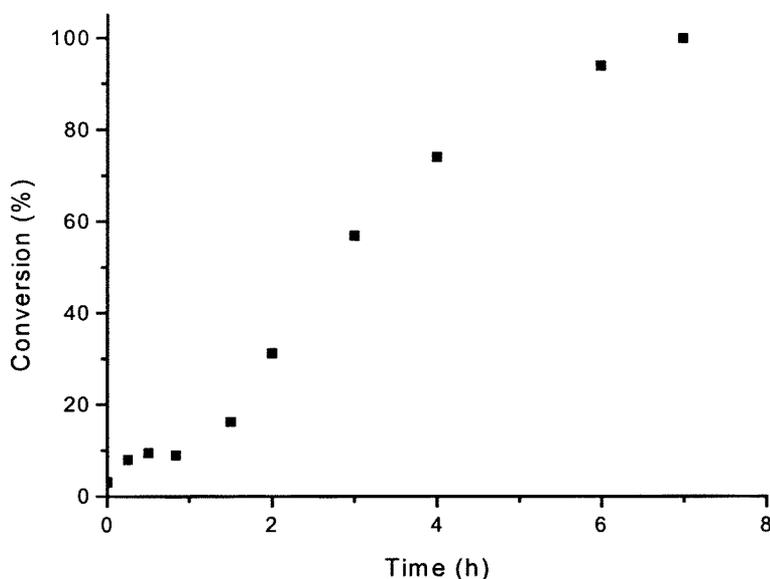


Figure 3.5 Graph of conversion versus time for MMA polymerisation via ATRP for reaction 2.

Polymerisation of 25.00 g MMA in 25.00 g 2-butanone at 70 °C.

Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

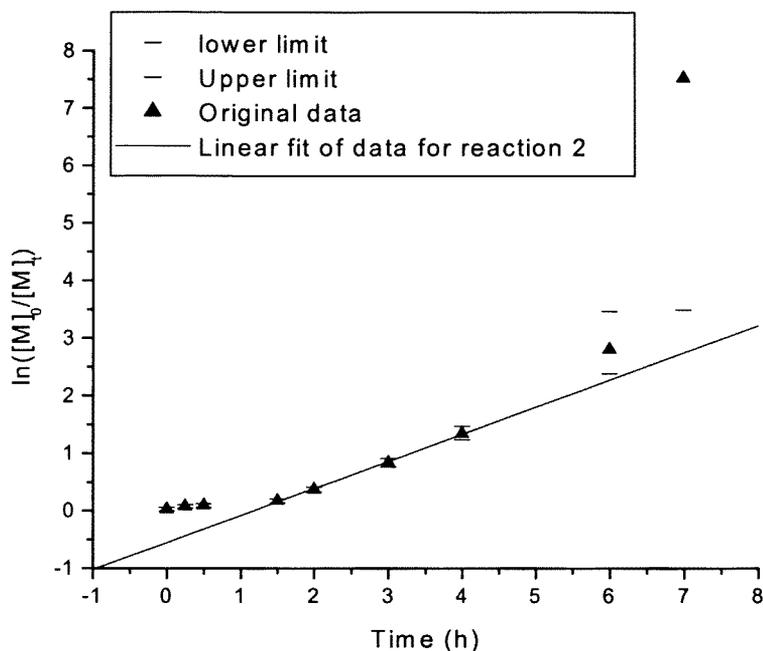


Figure 3.6 Logarithmic graph of MMA polymerisation for reaction 2 done via ATRP.

Polymerisation of 25.00 g MMA in 25.00 g 2-butanone at 70 °C.

Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

The number-average molecular weights (\bar{M}_n) increased with conversion (figure 3.7), indicating that molecular weight is controlled. The polydispersity index is fairly low, indicating constant control during the polymerisation process, apart from the first sample. The reason for this latter higher value might be attributed to the partial insolubility of the Cu^IBr. Although the polydispersity values are not as low as would have been expected (by the technique of ATRP), this polymer may contain enough living chains to reinitiate further monomers.

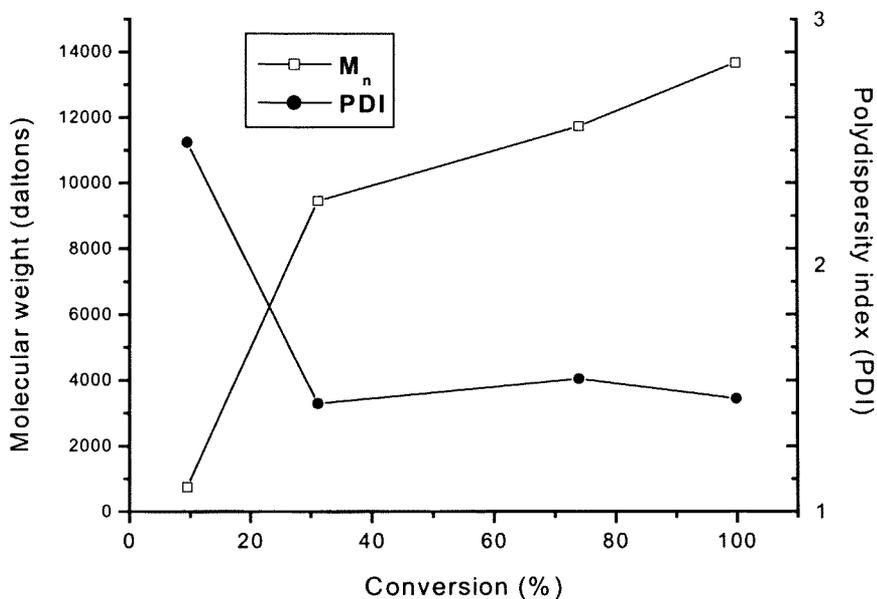


Figure 3.7 Graph of molecular weight and polydispersity index versus % conversion for reaction 2. Polymerisation of 25.00 g MMA in 25.00 g 2-butanone at 70 °C. Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

According to equation 3.1, for 100 % conversion, the calculated molecular weight for the above reaction is 20 200 gmol^{-1} . The measured \bar{M}_n values are significantly lower than the theoretical values (20 200 gmol^{-1}). It must be stated that the \bar{M}_n value of the final sample in solution (13 600 gmol^{-1}) differed from that of the precipitated sample (11 200 gmol^{-1}) even though both samples were terminated at the same time. The reason for this is not known. The evolution of the corresponding peak masses (\bar{M}_p) (figure 3.8) has been included; these are much closer to the theoretical $\bar{M}_{n\text{cal}}$ than the \bar{M}_n values. The manner in which the GPC calculates these values causes differences to be there between them, which can sometimes be rather large. Refer to section 3.2.1 for explanations as to why the inclusion of peak mass is sometimes favourable for indications of molecular weight.

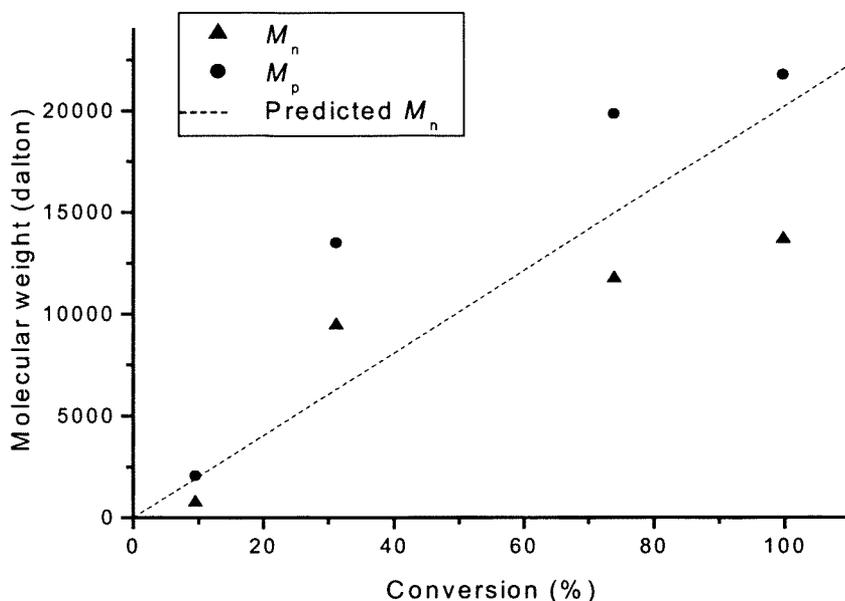


Figure 3.8 Molecular weight graphs of peak molecular weight (\bar{M}_p) compared to number-average molecular weight (\bar{M}_n) for reaction 2.

Polymerisation of 25.00 g MMA in 25.00 g 2-butanone at 70 °C.

Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

3.4.3 MMA polymerisation (reaction 4)

The following data refer to the polymerisation reaction 4 (table 3.2). Refer to table 3.1 for reaction conditions.

Results in figure 3.9 show that the conversion of MMA is high. The slope of the logarithmic graph is almost completely linear during the middle stage of the reaction (figure 3.10). The approximately constant slope indicates that the number of radicals remained almost constant during the intermediate stage of the reaction, hence termination of the active radicals did not play a major role in this reaction. Once again, absolute errors of 3 % were calculated for each of the points, and in some cases these error values seem to fit the linear trend more appropriately.

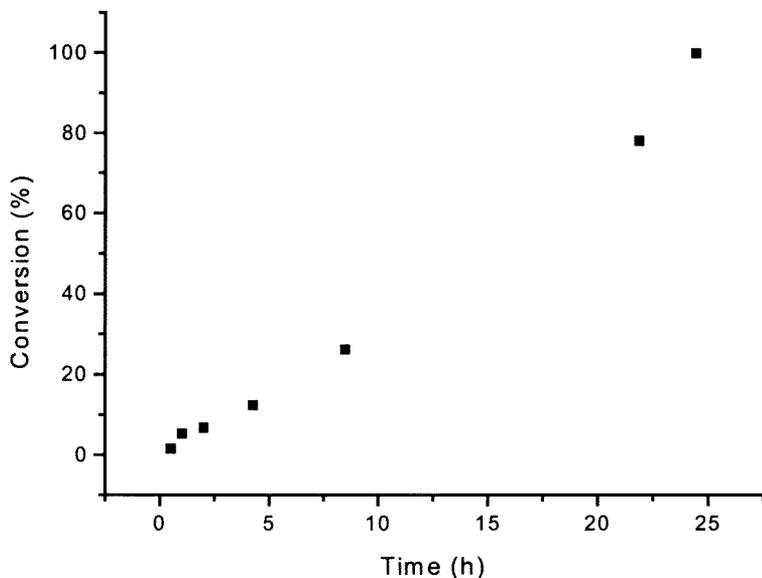


Figure 3.9 Graph of conversion versus time for MMA polymerisation via ATRP for reaction 4.

Polymerisation of 20.00 g MMA in 40.00 g 2-butanone at 60 °C.

Monomer / CuCl / TsCl / PMDETA = 100 / 0.4 / 1 / 0.4

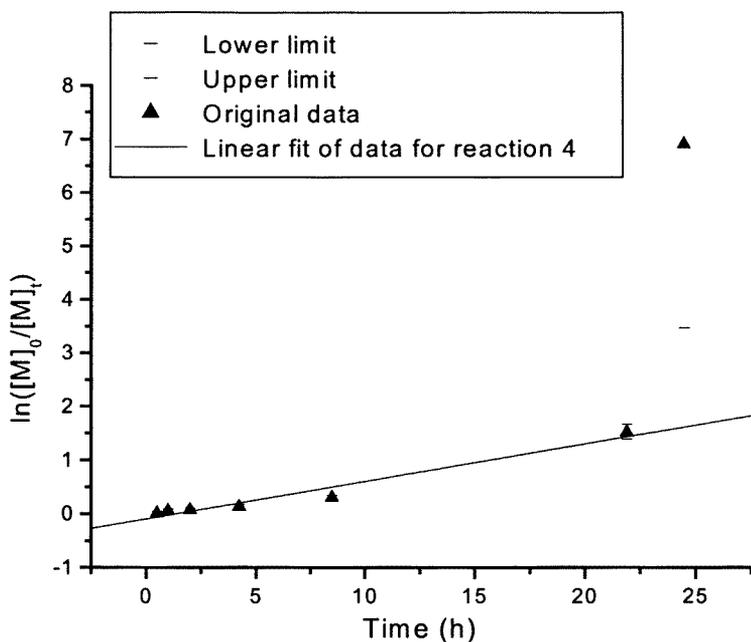


Figure 3.10 Logarithmic graph of MMA polymerisation for reaction 4 done via ATRP.

Polymerisation of 25.00 g MMA in 40.00 g 2-butanone at 60 °C.

Monomer / CuCl / TsCl / PMDETA = 100 / 0.4 / 1 / 0.4

The number-average molecular weights (\bar{M}_n) increased with conversion (figure 3.11), indicating that molecular weight is controlled. The polydispersity index of the polymer is below 1.3 and shows constant control during the latter part of the reaction. Results of the first few samples have not been included in figure 3.11 as the peaks seem to be overlapping with another peak, quite possibly the ligand complex which may be emerging through at this point.

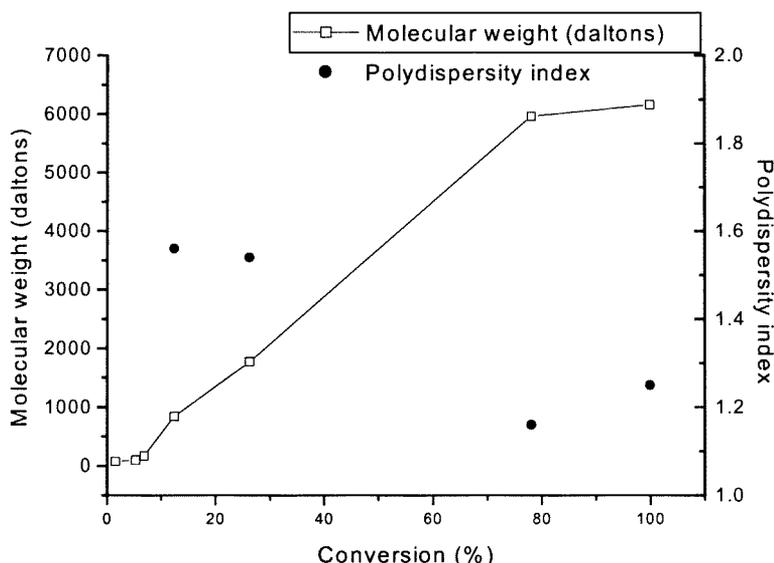


Figure 3.11 Graph of molecular weight and polydispersity index versus % conversion for reaction 4. Polymerisation of 20.00 g MMA in 40.00 g 2-butanone at 60 °C.
Monomer / CuCl / TsCl / PMDETA = 100 / 0.4 / 1 / 0.4

The calculated molecular weight for the above reaction is 10 200 gmol^{-1} , according to equation 3.1, for 100 % conversion. The measured \bar{M}_n values are lower than the theoretical values (10 200 gmol^{-1}). The reason for this is not known. The evolution of the corresponding peak masses (\bar{M}_p) (figure 3.12) has been included; these are much closer to the theoretical $\bar{M}_{n\text{cal}}$. The manner in which the GPC calculates these values causes there to be differences between them, which can sometimes be rather large. Refer to section 3.2.1 for explanations as to why the inclusion of peak mass is sometimes favourable for indications of molecular weight.

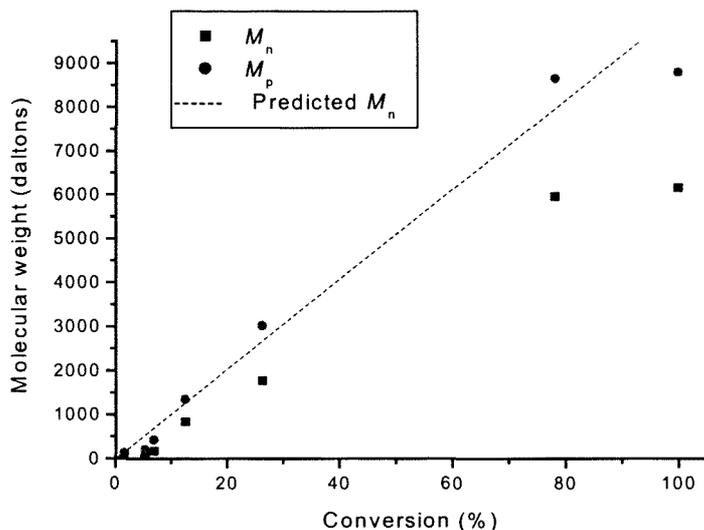


Figure 3.12 Molecular weight graphs of peak molecular weight (\bar{M}_p) compared to number-average molecular weight (\bar{M}_n) for reaction 4.

Polymerisation of 20.00 g MMA in 40.00 g 2-butanone at 60 °C.

Monomer / CuCl / TsCl / PMDETA = 100 / 0.4 / 1 / 0.4

3.5 SUMMARY OF RESULTS OF MMA ATRP REACTIONS

MMA polymerised by ATRP techniques (reaction 1, section 3.4.1) did show high conversion and an approximately constant slope in the rate plot, but the molecular weights were scattered and a plot of the molecular weight was therefore considered to be inconclusive in terms of reliable results. Another ATRP polymerisation of MMA (reaction 2, section 3.4.2) did display high conversion, good linear rate plots, an increase in molecular weight and a fairly narrow polydispersity range. Both these polymers will be used as macro-initiators to determine if they contain active chain ends, which will allow the growth of another polymeric block (see chapter 7). Reaction 4 differed from reactions 1 and 2 with respect to the nature of the halogen on the metal catalyst, as well as the temperature at which the reaction was carried out (60 °C). Much lower polydispersities (1.28) were obtained when the chlorinated catalyst was used instead of the brominated one (2.19 and 1.75 for reactions 1 and 2, respectively). The only possible explanation for this at this point seems to be a preference for same halogen transfer between the catalyst and initiator in this

particular polymerisation of MMA monomer. It has been found in the literature that certain monomers display better control of the polymerisation if there is halogen transfer, whereas others may not ^[1]. Because the bromine atom has a lower activation energy than the chlorine atom, it would mean that the carbon bromine bond would form active radicals more quickly. An alkylbromide would therefore be more suitable as an initiator for ATRP processes ^[2]. When it comes to determining which halogen to use with the metal catalyst it would appear that a cuprous chloride would be more favourable because the higher activation energy that is required would imply that the reversible transfer process between the two states of the metal would take place more slowly. The slower the transfer process, the greater the probability of lower polydispersity indexes.

3.6 INVESTIGATION OF THE EFFECT OF Cu^{II} ADDITION TO A REACTION MIXTURE

Reactions were carried out with MMA to determine whether or not the addition of extra Cu^{II} at the start of the reaction would improve the characteristics of the polymer formed, such as faster reaction times accompanied by narrow polydispersities.

According to literature ^[3], the “persistent radical effect”, which is the build up of the Cu^{II} species, decreases radical-radical termination, and consequently leads to a decrease in polydispersity. During the initiation step, the halogen atoms of the initiators are abstracted to produce radical species. During this step the transition metal complex is oxidized, and a deactivator species is produced. The function of the deactivator is to shift the equilibrium back to the dormant species when the concentration of the free radicals becomes high. By allowing this shift to take place, the radical will remain active for a shorter period of time, the collision of free radicals is minimised and termination does not have a profound effect, hence better control over the system is maintained. Because the deactivator species first has to be generated, it is thought that if this generating process takes very long during the initiation step, one can already be heading for uncontrolled growth as there is not enough deactivator present to shift the equilibrium.

Depending on the amount of Cu^{II} used, the polymerisation rate will follow different equations ^[39]:

If $\frac{[\text{Cu}^{\text{II}}]_0}{[\text{Cu}^{\text{I}}]_0} \leq 10$ % by weight, then Fischer's equation applies (3.2)

$$\ln\left(\frac{[m]_0}{[m]}\right) = \frac{3}{2}k_p([\text{RX}]_0[\text{Cu}^{\text{I}}]_0)^{1/3}\left(\frac{k_{\text{eq}}}{3k_t}\right)^{1/3}t^{2/3} \quad (3.3)$$

If $\frac{[\text{Cu}^{\text{II}}]_0}{[\text{Cu}^{\text{I}}]_0} \geq 10$ % by weight, then Matyjaszewski's equation applies (3.4)

$$\ln\left(\frac{[m]_0}{[m]}\right) = k_p k_{\text{eq}} \frac{[\text{RX}][\text{Cu}^{\text{I}}]}{[\text{Cu}^{\text{II}}]}t = K_{\text{app}}t \quad (3.5)$$

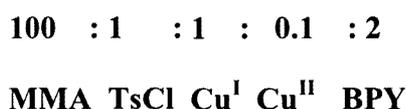
3.6.1 Experimental

In two similar reactions, 10 and 20 % Cu^{II}Br₂ by weight, with respect to Cu^I, (0.18 mmol and 0.36 mmol) were added to the rest of the reaction mixture, respectively, in order to determine the effect that Cu^{II} had on the control of the reactions.

To a 100 mL three-necked flask, Cu^IBr (0.36 mol), Cu^{II}Br₂, BPY (0.78 mol) and 2-butanone (50.00 g) were added and the solution degassed with UHP nitrogen for 30 minutes. Addition of degassed TsCl (0.48 mol) and MMA (25.00 g) to the contents in the flask before the start of the reaction was followed by immersion of the flask into an oil bath maintained at 70 °C. Samples were taken at regular intervals for gravimetric and GPC analyses to determine conversion and molecular weights, respectively.

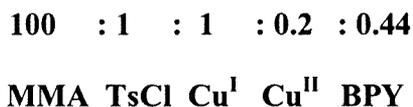
3.6.2 ATRP MMA with 10 % Cu^{II} added relative to Cu^I (Reaction 5)

The following molar ratios were used for this reaction:



3.6.3 ATRP MMA with 20% Cu^{II} added relative to Cu^I (Reaction 6)

The following molar ratios were used for this reaction:



3.6.4 Results and Discussion

The following graphs of conversion/time (figure 3.13), \bar{M}_n /conversion (figure 3.14), \bar{M}_p /conversion (figure 3.15), PDI/conversion (figure 3.16) and the rate plots (figure 3.17) were plotted for the two reactions (sections 3.6.2 and 3.6.3), with their respective percentages of added Cu^{II}.

The $\bar{M}_{n\text{cal}}$ for these reactions is 10 200 gmol⁻¹ (eq. 3.1).

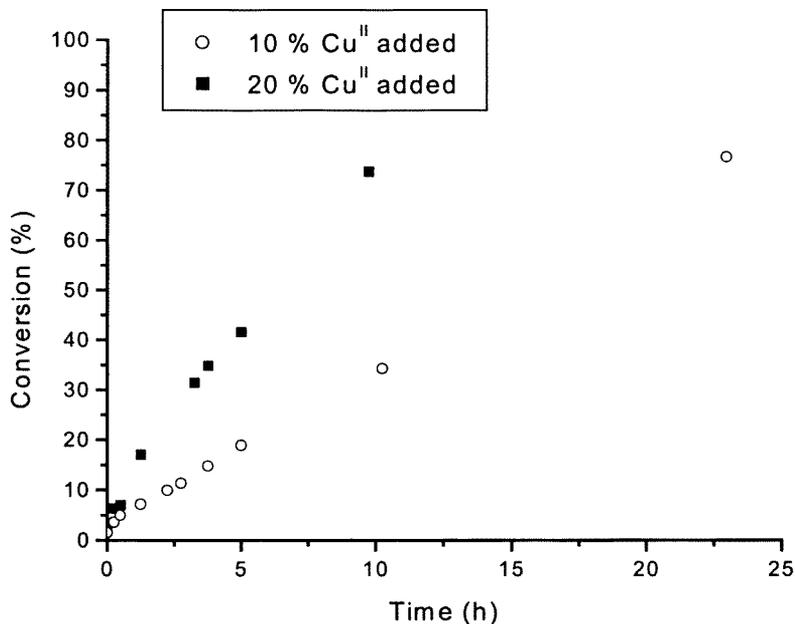


Figure 3.13 Conversion versus time graph for MMA ATRP reactions with 10 and 20 % Cu^{II} added relative to Cu^I.

Polymerisation of 25.00 g MMA in 50.00 g 2-butanone at 70 °C.

MMA/ TsCl/ Cu^I/ Cu^{II}/ BPY = 100 / 1 / 1 / 0.1 or 0.2 / 2

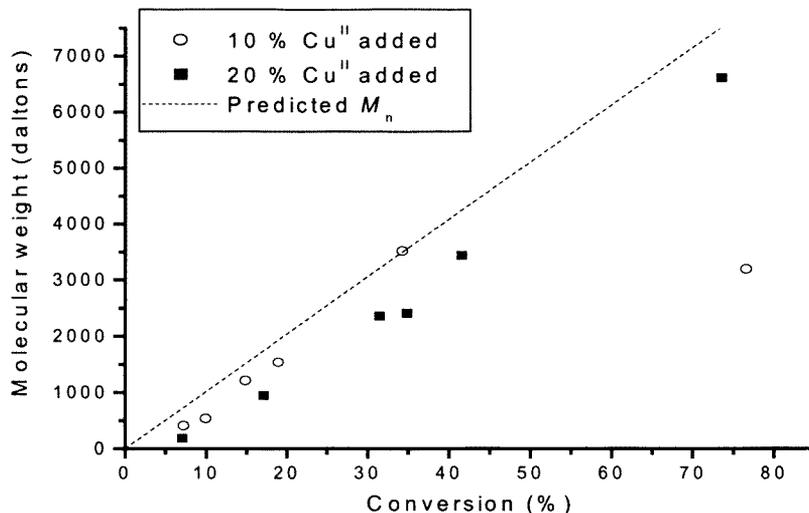


Figure 3.14 Molecular weight graph of number-average molecular weight (\bar{M}_n) versus conversion for MMA ATRP reactions with 10 and 20 % Cu^{II} added relative to Cu^I.
 Polymerisation of 25.00 g MMA in 50.00 g 2-butanone at 70 °C.
 MMA/ TsCl/ Cu^I/ Cu^{II}/ BPY = 100 / 1/ 1 or 0.2/ 0.2 or 0.04/ 2.2 or 0.44

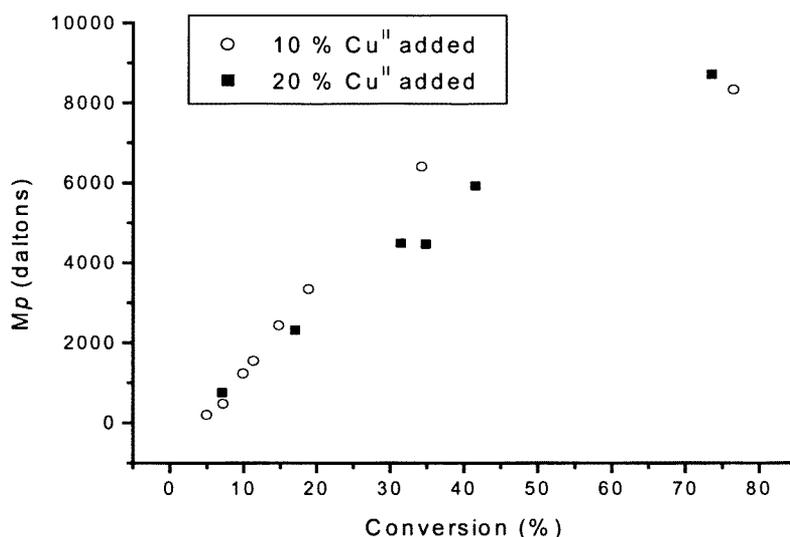


Figure 3.15 Molecular weight graph of peak molecular weight (\bar{M}_p) versus conversion graph for MMA ATRP reactions with 10 and 20 % Cu^{II} added relative to Cu^I.
 Polymerisation of 27.00 g MMA in 50.00 g 2-butanone at 70 °C.
 MMA/ TsCl/ Cu^I/ Cu^{II}/ BPY = 100 / 1/ 1 or 0.2/ 0.2 or 0.04/ 2.2 or 0.44

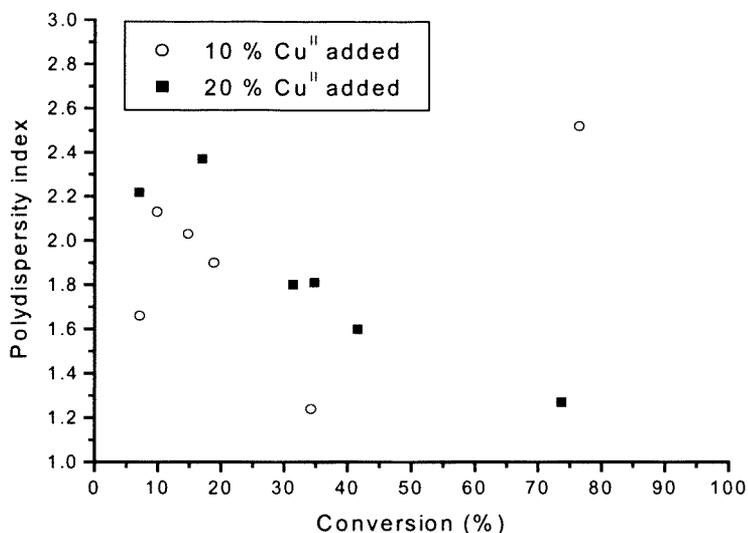


Figure 3.16 Polydispersity versus conversion graph for MMA ATRP reactions with 10 and 20 % Cu^{II} added relative to Cu^I.

Polymerisation of 27.00 g MMA in 50.00 g 2-butanone at 70 °C.

MMA/ TsCl/ Cu^I/ Cu^{II}/ BPY = 100 / 1/ 1/ 0.1 or 0.2/ 2

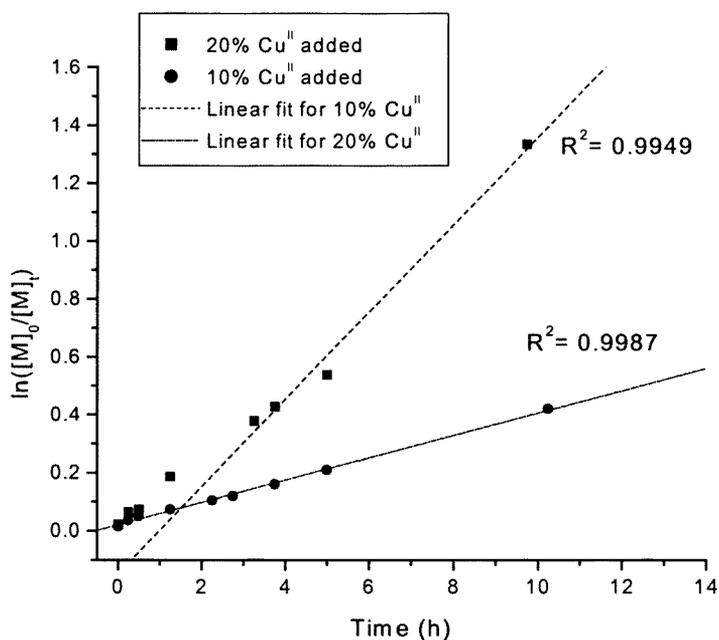


Figure 3.17 Logarithmic graph for MMA ATRP reactions with 10 and 20 % Cu^{II} added relative to Cu^I. Polymerisation of 27.00 g MMA in 50.00 g 2-butanone at 70 °C.

MMA/ TsCl/ Cu^I/ Cu^{II}/ BPY = 100 / 1/ 1 or 0.2/ 0.2 or 0.04/ 2.2 or 0.44

From the conversion graph (figure 3.13), it is clearly seen that the polymerisation rate of the reaction is much faster when 20 % Cu^{II} is added, instead of 10 % Cu^{II}. The reason for this is explained through the persistent radical effect, which has less of an effect when more Cu^{II} is added, because the equilibrium is forced to the dormant side sooner. This will ensure that the radical concentration is very low and that the radicals are short lived, which, in turn, will lead to less irreversible termination from taking place and consequently narrower polydispersities.

The \bar{M}_n values for the 20% Cu^{II} reaction increase with conversion and are higher than when 10 % Cu^{II} is added. The molecular weight values when 20 % Cu^{II} is added are closer to the $\bar{M}_{n,cal}$ values than when 10 % Cu^{II} is added, as seen from figure 3.14. The reason for this is most probably attributed to the prevention of the initial radical loss during the initiation stage as the presence of the extra Cu^{II} facilitates the deactivation cycle to take place and the radical concentration remains low. Due to practical problems experienced with calibrating the baseline on the GPC instrument, the peak mass (\bar{M}_p) has been included for an indication of molecular weights. As previously mentioned, \bar{M}_p can sometimes be used as a guideline for molecular weights. These values are higher for the 20 % Cu^{II} reaction (figure 3.15) than for the 10 % Cu^{II} reaction. \bar{M}_n is sensitive to the baseline for broader distributions, which would allow for greater chance of error in calculating values.

The polydispersities \bar{M}_p (figure 3.16) are relatively broad for these reactions, but they do seem to be generally narrower for the 20 % Cu^{II} reaction, especially towards the end of the reaction.

Figure 3.17 is indicative of the concentration of radical species present. According to these graphs, the trend tends to be more linear when 20 % Cu^{II} is added. Both reactions are quite linear, but when 20 % Cu^{II} is added, the trend is linear for a longer

reaction time, indicating that the number of radical species remained constant throughout that time period.

3.6.5 Conclusions

The conclusions that can be made are that the results show more control being achieved in the system when 20 % Cu^{II} is added than when 10 % Cu^{II} is added. In theory, it is important to add extra Cu^{II} if the initiation period is quite long as the role of the Cu^{II} is to force the equilibrium back to the dormant side and decrease the active radical concentration, hereby decreasing collisions of free radicals and minimising the probability of termination taking place.

In the MMA ATRP reactions that were carried out (table 3.2), there was not a significant difference in the polydispersities when extra Cu^{II} was added. It is thought that extra Cu^{II} may have an additional effect in that it may cause deactivation to take place too quickly and provide less control in certain cases.

¹ Shipp, D. A.; Wang, J.; Grimaud T.; Matyjaszewski, K. *Polymer Preprints*, **1998**, 39 (2), 504

² Tang, C.; Kowaleski, T.; Matyjaszewski, K. *Macromolecules*, to be published

³ Zhang, H.; Klumperman, B.; Ming, W.; Fischer, H.; van der Linde, R. *Macromolecules*, **2001**, 34(18), 6169

4. ATRP OF 4-VINYLPYRIDINE

4.1. ABSTRACT

Consideration was given to the preparation of star copolymers of 4-vinylpyridine (4VP) and styrene by means of ATRP. Firstly, the ATRP conditions suitable for the living, controlled polymerisation of 4VP needed to be determined. A number of problems were encountered during attempts to produce 4VP polymer. Broad polydispersities were obtained, showing little control over molecular weight (these results will be looked at in greater detail in the next chapter). Therefore, investigations into the various factors which could be the cause of these poor results were initiated. These included: the type of ligand, type of catalyst, the potential for complexation of the catalyst by monomer, etc. Still, the polydispersity index ranged between 2-3. A further possible reason for these poor results that was investigated was the possibility of quaternization of the pyridine ring with the alkyl halide initiator. Results of experiments with these two compounds and the polar solvent (isopropyl alcohol) showed significant changes in chemical shifts, leading us to initially believe that quaternization has an influence on increasing the polydispersity index of this system.

4.2. APPLICATIONS OF 4-VINYLPYRIDINE

The 4VP monomer, the initiator, and ligand that were used here are shown schematically in figures 4.1 – 4.3.

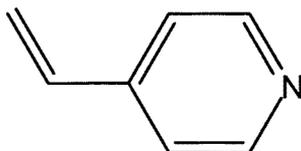


Figure 4.1 Structure of 4-vinylpyridine

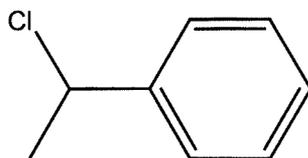


Figure 4.2 Structure of 1-chloro-1-phenylethane initiator

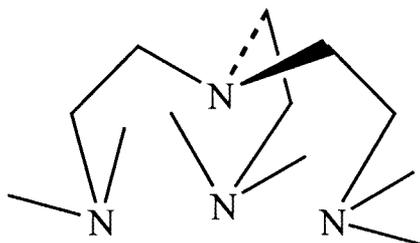


Figure 4.3 Structure of hexamethyl tris(2-(dimethylamino)ethyl (Me₆TREN) ligand

As a copolymer with butadiene, vinylpyridine has found use as a synthetic rubber which provides better properties than styrene-butadiene rubber ^[1]. This monomer has also found applications in the textile industry, as a comonomer with acrylics, to improve the dye ability of fibres.

Vinylpyridine polymers have also found applications as polyelectrolytes, flocculants, ion exchangers, emulsifiers, and in electrical applications ^[1].

These polymers have been used as polymer supports in reaction catalysis.

4.3. EXPERIMENTAL

4.3.1. General

Materials. Dichloromethane and ethanol (Biosolve Ltd.), HCl (Merck), NaOH (Fluka), diethyl ether (Lamers & Pleuger), 2-propanol (SASOL), Cu^{II}Cl (Janssen), 1-chloro-1-phenylethane (Acros) and Cu^ICl (99.995+ %), Cu^IBr (98 %), (1-bromoethyl)benzene (97 %), tris(2-aminoethyl)amine (96 %), formic acid (88 %) and formaldehyde (37 wt. % solution in water) (Aldrich) were used as purchased. 4-vinylpyridine (Aldrich) was distilled and purified through an alumina column (Aldrich).

Analytical methods. NMR spectra were recorded on VARIAN VXR 300 MHz and VARIAN INOVA 600 MHz instruments. Molecular weights and molecular weight

distributions were measured by gel permeation chromatography (GPC) using *n*-methyl-2-pyrrolidone (NMP) as eluent and narrow molecular weight polystyrene standards (Polymer Labs) for calibration. 2 Plgel columns were used at 30 °C and a flow rate of 1 mL/min in THF. The GPC samples were filtered using a 1 micron Teflon filter. A Waters 150 GPC instrument, with a Waters 410 differential refractometer and Millenium software (version 3), was used. Conversion was determined gravimetrically.

4.3.2. Synthesis of hexamethyl tris(2-(dimethylamino)ethyl) (Me₆TREN):

This ligand was synthesized as described in the literature ^[2].

A 32 wt. % solution of HCl (83.00 g, 0.73 mol) was dissolved in water (200 mL) at 0 °C. Tris(2-aminoethyl)amine (35.47 g, 0.24 mol) was added dropwise and the mixture stirred vigorously. The latter was then added dropwise to a 35 wt. % solution of formic acid (220.00 g, 1.64 mol) at 0 °C. 10 minutes after complete addition of formic acid, a 35wt. % solution of formaldehyde (210.00 g, 2.45 mol) was added dropwise. A light yellow solution resulted. The reaction mixture was refluxed at 100 °C for 24 hours and the colour changed to deep orange. A 10M aqueous NaOH solution (500 mL) was added at 0 °C to change the pH to 13-14. The reaction mixture was extracted twice with diethyl ether (500 mL), the combined organic fractions washed twice with a saturated solution of NaCl (500 mL) and dried over MgSO₄. After filtering and removing the solvent under vacuum, pure Me₆TREN (15.22 g, 0.07 mol) was obtained as a dark yellow oil in 25 % yield.

¹H NMR (CDCl₃, 25 °C): δ 2.58 (m, 6H, CH₂), 2.35 (m, 6H, CH₂), 2.21 (s, 18H, CH₃)

¹³C NMR (CDCl₃, 25 °C): δ 57.33 (CH₂), 53.0 (CH₂), 45.78 (CH₃)

4.3.3. Polymerisations

For the polymerisations of 4VP under ATRP conditions, all glassware was dried at 60 °C in an oven. The glassware was assembled immediately upon removal from the oven and purged with inert gas to eliminate condensed water and oxygen. The polymerisations were carried out according to a standard procedure, but the reactants varied from experiment to experiment. The procedure is given below.

In a three-necked flask, equipped with a reflux condenser, a dropping funnel and an argon inlet, Cu^IBr (37.6 mg, 0.26 mmol) and Me₆TREN (134.0 mg, 0.59 mmol) were dissolved in

isopropyl alcohol (50 mL) and degassed with argon for 30 minutes. A mixture of 4-vinylpyridine (25 mL, 0.23 mol) and (1-bromoethyl)benzene (48.0 mg, 0.26 mmol) was degassed with argon for 30 minutes and added dropwise to the rest of the reaction contents. The reaction mixture was heated to 60 °C for 24 hours. Samples were drawn at intervals to determine molecular weight distributions and conversions.

Molecular weights are predicted according to the following equation (4.1).

$$\bar{M}_{n\text{cal}} = \frac{[m]_0}{[I]_0} \times MM_{\text{monomer}} \times \text{conversion} + MM_{\text{initiator}} \quad (4.1)$$

Here, $[m]_0$ and $[I]_0$ refer to the monomer and initiator concentrations at the start of the reaction, whilst MM_{monomer} and $MM_{\text{initiator}}$ refer to the molar masses of the monomer and initiator, respectively.

4.4. Results and Discussion

4.4.1. The effect of monomer and initiator addition to the reaction flask, prior to start of reaction

Two reactions were performed under identical conditions to determine if significant polymerisation would take place irrespective of whether or not all compounds were added at the start of the reaction. Results are given in figures 4.4 - 4.6. In experiment 1, the monomer and initiator were only added to the rest of the contents in the flask when it was immersed in the oil bath at 60 °C. In experiment 2, all reactants were stirred at room temperature for 30 minutes prior to immersion in the oil bath at 60 °C. The initiator that was used was (1-bromoethyl)benzene (1-PEBr). The first samples were taken when the flasks were immersed in the oil bath.

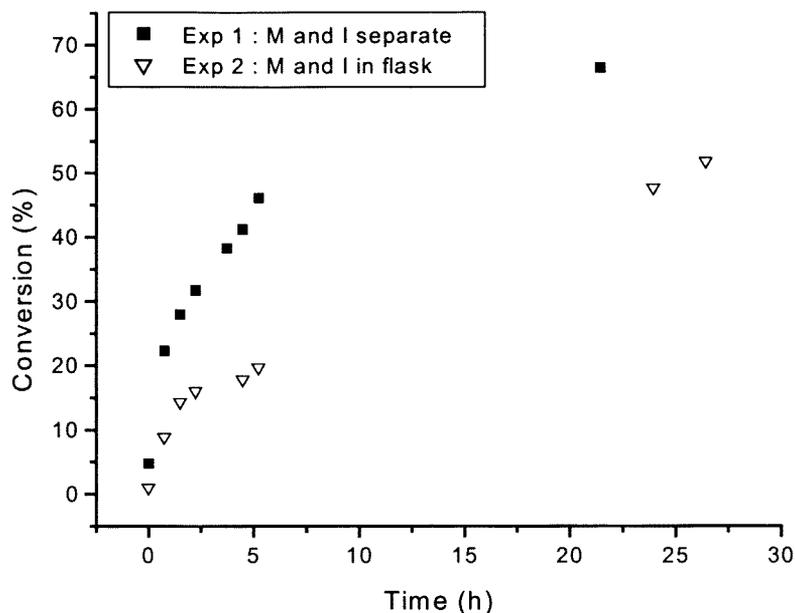


Figure 4.4 Effect of monomer (M) and initiator (I) addition, prior to start of reaction, on conversion. Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropanol at 60 °C. Monomer / CuBr / 1-PEBr / Me₆TREN = 1000 / 1 / 1 / 2

Surprisingly, the rate of the reaction in which monomer and initiator were kept separate was higher than when they were initially added (figure 4.4). It is believed that this is the result of possible termination occurring while oxygen was still present, thus reducing the radical flux that is in the reaction.

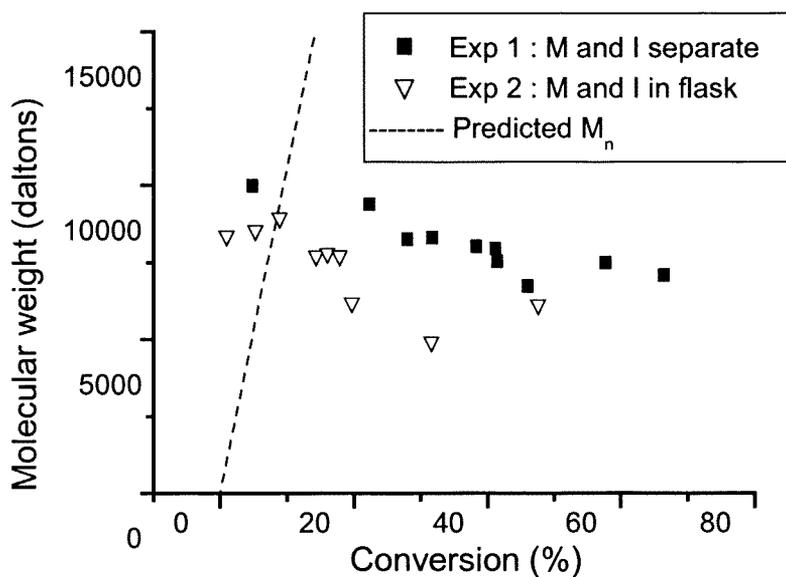


Figure 4.5 Effect of monomer (M) and initiator (I) addition, prior to start of reaction, on number-average molecular weight (\bar{M}_n). $\bar{M}_{n,cal} = 105\,280\text{ gmol}^{-1}$ at 100 % conversion (eq. 4.1). Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C. Monomer / CuBr / 1-PEBr / Me₆TREN = 1000 / 1 / 1 / 2

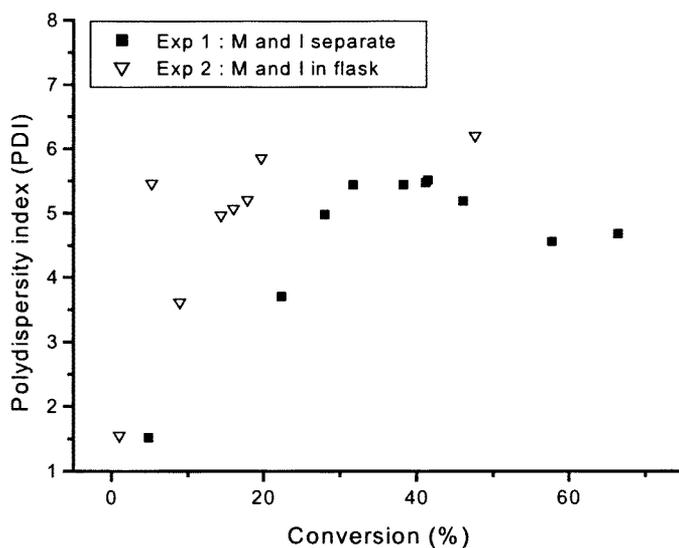


Figure 4.6 Effect of monomer (M) and initiator (I) addition, prior to start of reaction, on the polydispersity index (\bar{M}_w / \bar{M}_n). Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C. Monomer / CuBr / 1-PEBr / Me₆TREN = 1000 / 1 / 1 / 2

There is no control of molecular weight as seen from figure 4.5, and the polydispersities are broad (figure 4.6).

4.4.2. The effect of initiator addition on reaction conversion

The results of two experiments were compared to determine the possible effect of the monomer forming a complex with the catalyst prior to forming a complex with the ligand. Results are given in figures 4.7- 4.9. In experiment 3, only the monomer was kept apart from all the reactants, whereas in experiment 4, both the initiator and monomer were kept apart from the other reactants. Experimental procedure was similar to the standard polymerisation procedure given in section 4.3.3.

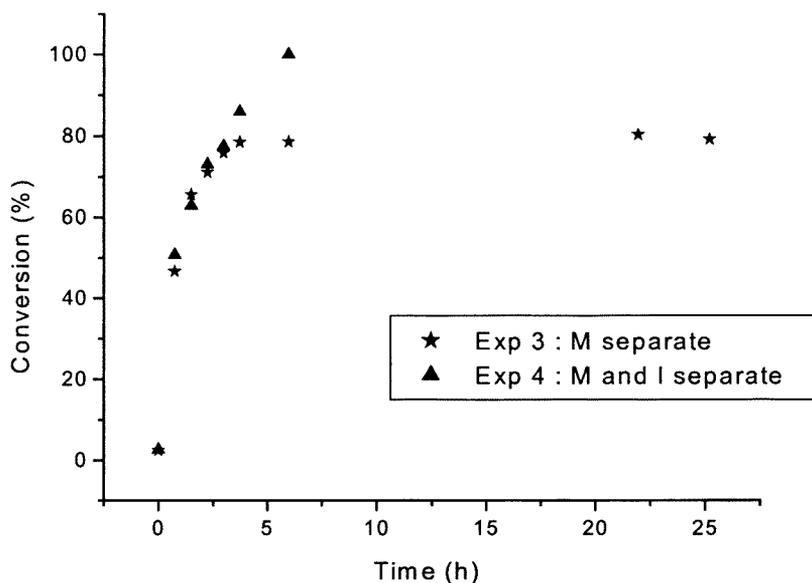


Figure 4.7 Effect of initiator (I) addition, prior to start of reaction, on conversion with time. Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C. Monomer / CuCl / 1-PECl / Me₆TREN = 100 / 1.5 / 1 / 2

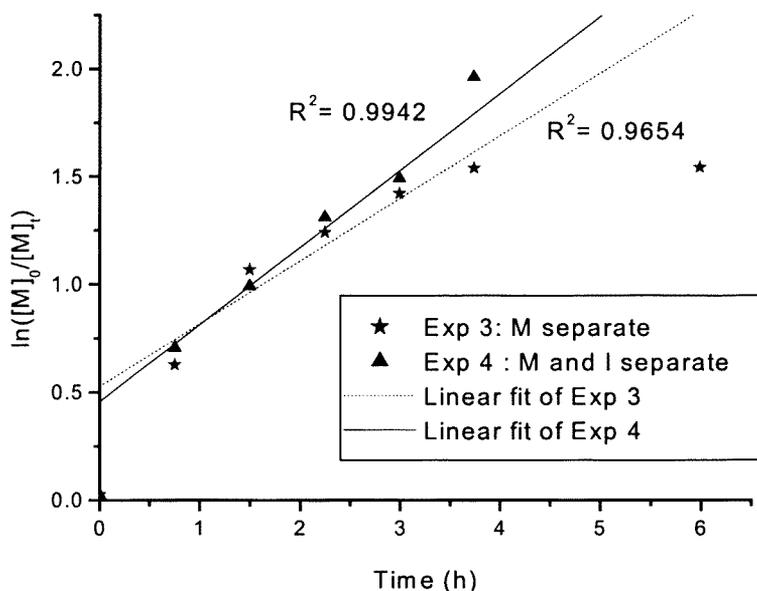


Figure 4.8 Effect of initiator addition, prior to start of reaction, on the logarithmic graph of time. Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C. Monomer / CuCl / 1-PECl / Me₆TREN = 100 / 1.5 / 1 / 2

From figure 4.7 it is clear that up to 5 hours, the rate of both reactions are the same. It is therefore unlikely that the initial results were a result of premature addition of the initiator. The discrepancy in the graphs at longer times may be due to oxygen entering the reactor and terminating the polymerisation. Figure 4.8 is the logarithmic plot, which is representative of the concentration of radical species. If there is a linear increasing trend through the points, then that indicates that the number of radical species remained constant throughout the reaction. The plot for experiment 4 displays a very good linear trend compared to that for experiment 3.

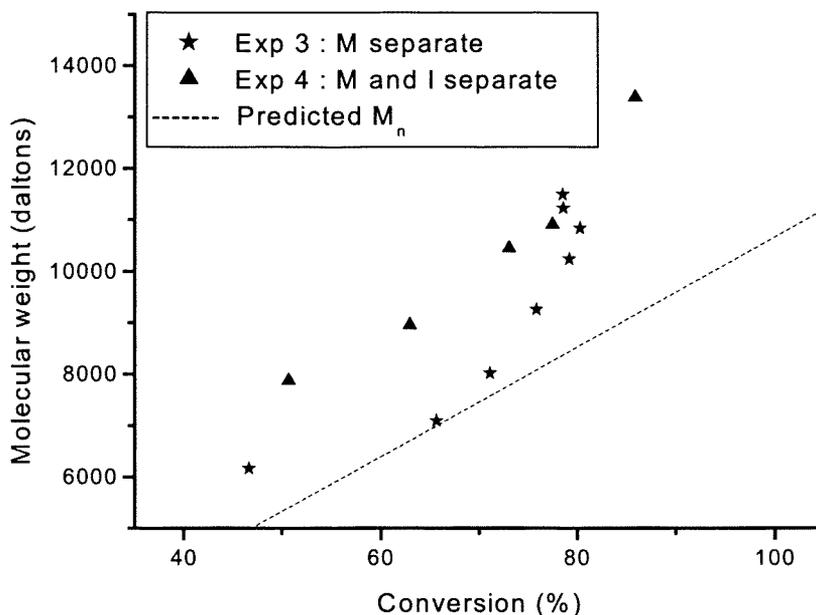


Figure 4.9 Effect of initiator addition, prior to start of reaction, on the change in number-average molecular weight (\bar{M}_n) with conversion. $\bar{M}_{n,cal} = 10\,654\text{ gmol}^{-1}$ at 100 % conversion (eq. 4.1). Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C. Monomer / CuCl / 1-PECl / Me₆TREN = 100 / 1.5 / 1 / 2

In both experiments, \bar{M}_n increased with conversion (figure 4.9).

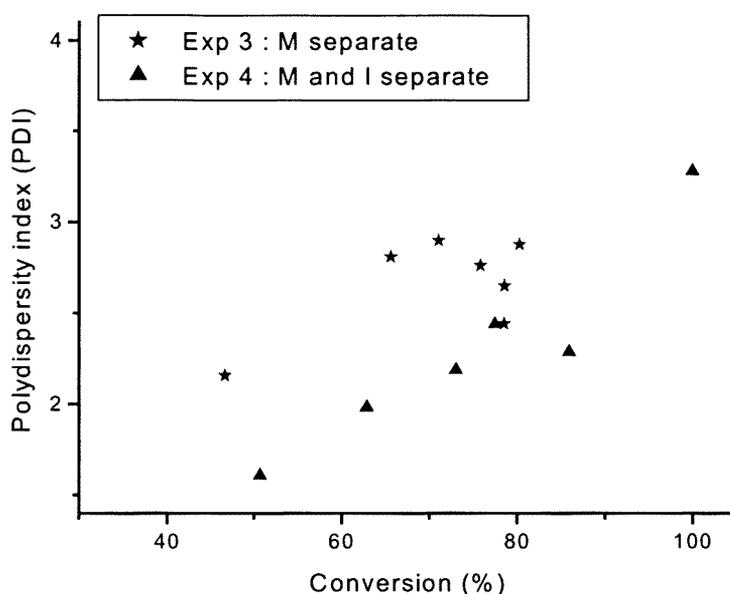


Figure 4.10 Effect of initiator addition, prior to start of reaction, on (\bar{M}_w / \bar{M}_n) .

Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C.

Monomer / CuCl / 1-PECl / Me₆TREN = 100 / 1.5 / 1 / 2

It is encouraging to note that although the polydispersities were broad (figure 4.10), the molecular weights increased with conversion (figure 4.9).

4.4.3. The effect of the catalyst on the conversion and polydispersity

Two similar experiments were performed, differing only in the choice of catalyst used. In experiment 5, CuCl was used as catalyst, and in experiment 6, CuBr. The fact that there is a difference between the bond strengths of the Cu-Cl and Cu-Br suggested that changing the catalyst could lead to narrower polydispersities.

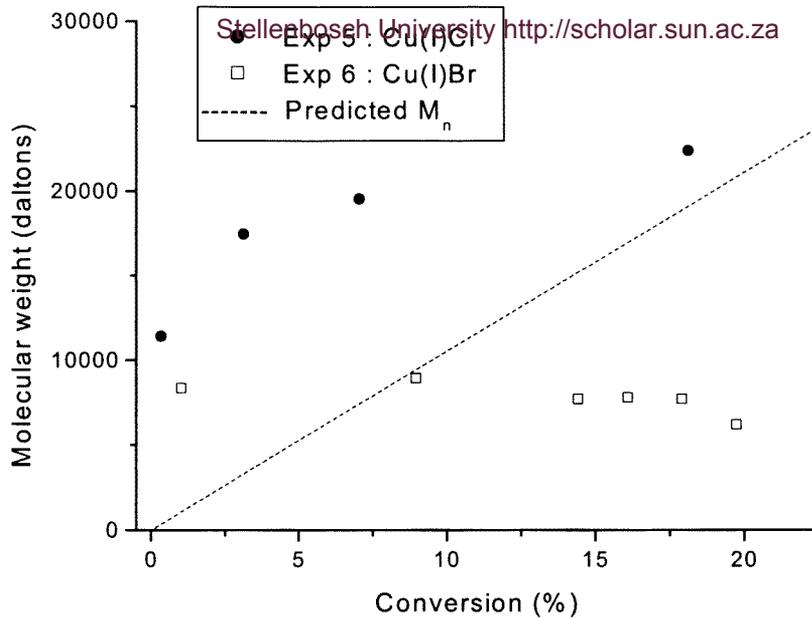


Figure 4.11 Effect of type of catalyst on number-average molecular weight (\bar{M}_n).

$$\bar{M}_{n,cal} = 105\,320 \text{ gmol}^{-1} \text{ at } 100\% \text{ conversion (eq. 4.1).}$$

Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C.

Monomer / Catalyst / 1-PEBr / Me₆TREN = 1000 / 1 / 1 / 2

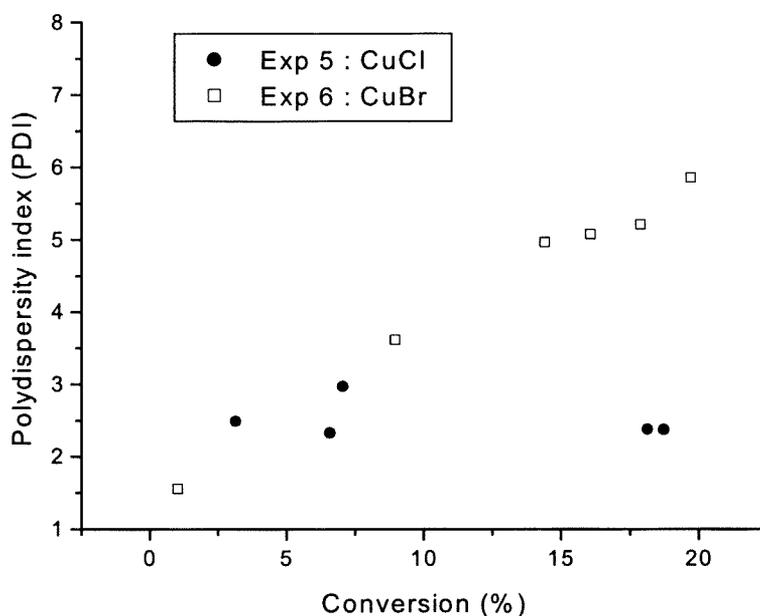


Figure 4.12 Effect of type of catalyst on polydispersity index (\bar{M}_w / \bar{M}_n).

Polymerisation of 25 mL 4-vinylpyridine in 50 mL isopropyl alcohol at 60 °C.

Monomer / catalyst / 1-PEBr / Me₆TREN = 1000 / 1 / 1 / 2

Figure 4.11 shows a gradual increase in \bar{M}_n for the CuCl catalyst and a decrease in \bar{M}_n for the CuBr, showing a living character in the case of CuCl. From figure 4.12 it can be seen that lower polydispersities were obtained for the CuCl catalyst than for the CuBr one. The C-Cl bond is stronger than the C-Br bond, therefore, transfer of the halide to the catalyst is slower, resulting in a lower radical flux, leading to less bi-molecular termination and thus lower polydispersities.

4.4.4. The effect of different ligands on ATRP polymerisations

4.4.4.1. *Efficiency of Me₆TREN on methyl acrylate polymerisation*

A bulk polymerisation was done to determine if the ligand was synthesized correctly. The monomer used to test this was methyl acrylate (MA) ^[3].

Cu^ICl, initiator (ethyl 2-bromopropionate – [2-EBP]), ligand (Me₆TREN) and monomer were placed in a round-neck flask, in an ice bath, and degassed for 30 minutes. Experimental conditions were as follows:

$$[\text{MA}]_0 = 10.8\text{M}$$

$$[\text{2-EBP}]_0 = 0.047\text{M}$$

$$[\text{Cu}^{\text{I}}\text{Cl}] = [\text{Me}_6\text{TREN}] = 0.0094\text{M}$$

Temperature 25 °C

In the case of the ATRP polymerisation of MA, a polydispersity of 1.1 was obtained after 24 hours. This value is lower than the results obtained by Matyjaszewski ^[3], showing a high efficiency of the ligand. Experiments performed with other ligands (see section 4.4.4.2) showed that the Me₆TREN ligand gave significantly higher conversions.

4.4.4.2. *Efficiency of different ligands on 4-vinylpyridine polymerisation*

Various ligands were tested upon the 4-vinylpyridine systems to determine the efficiency of these ligands in complexing the catalyst, while competing with possible complexation by the monomer. From the following figure (figure 4.13) it can be concluded that Me₆TREN is the most suitable ligand as it gave the highest rate of conversion.

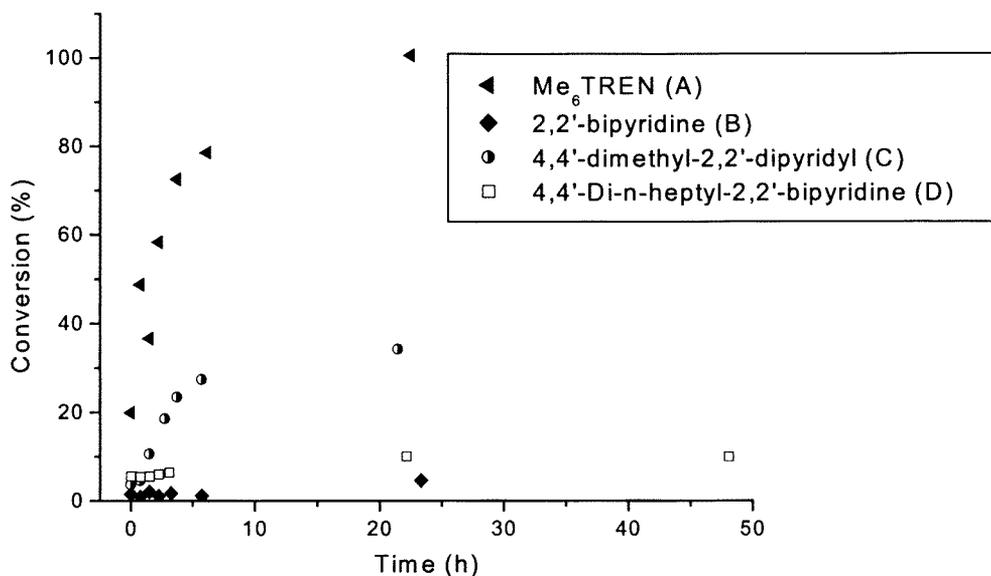


Figure 4.13 Effect of different ligands on conversion versus time.

Monomer / CuCl / 1-PECl / ligand = 100 / 1.5 / 1 / 2

4.4.5. The effect of the metal catalyst on conversion

The possibility that some metals catalyse self-initiation, hereby contributing to broadening the polydispersities, was investigated. Initiator was omitted to determine whether induced initiation occurred. The reactions were run over a 24 hour period.

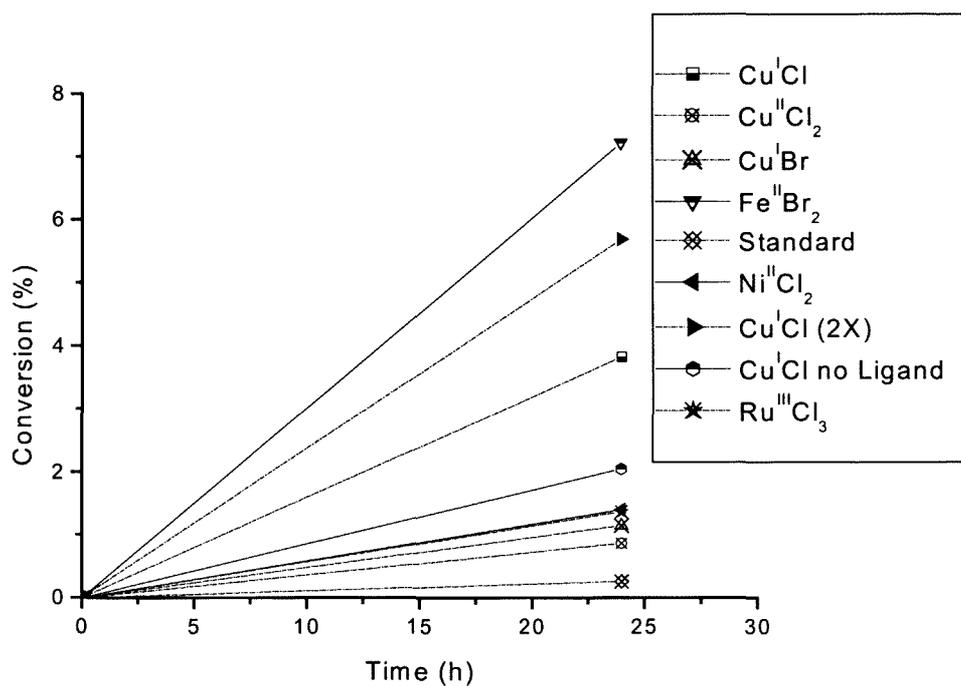
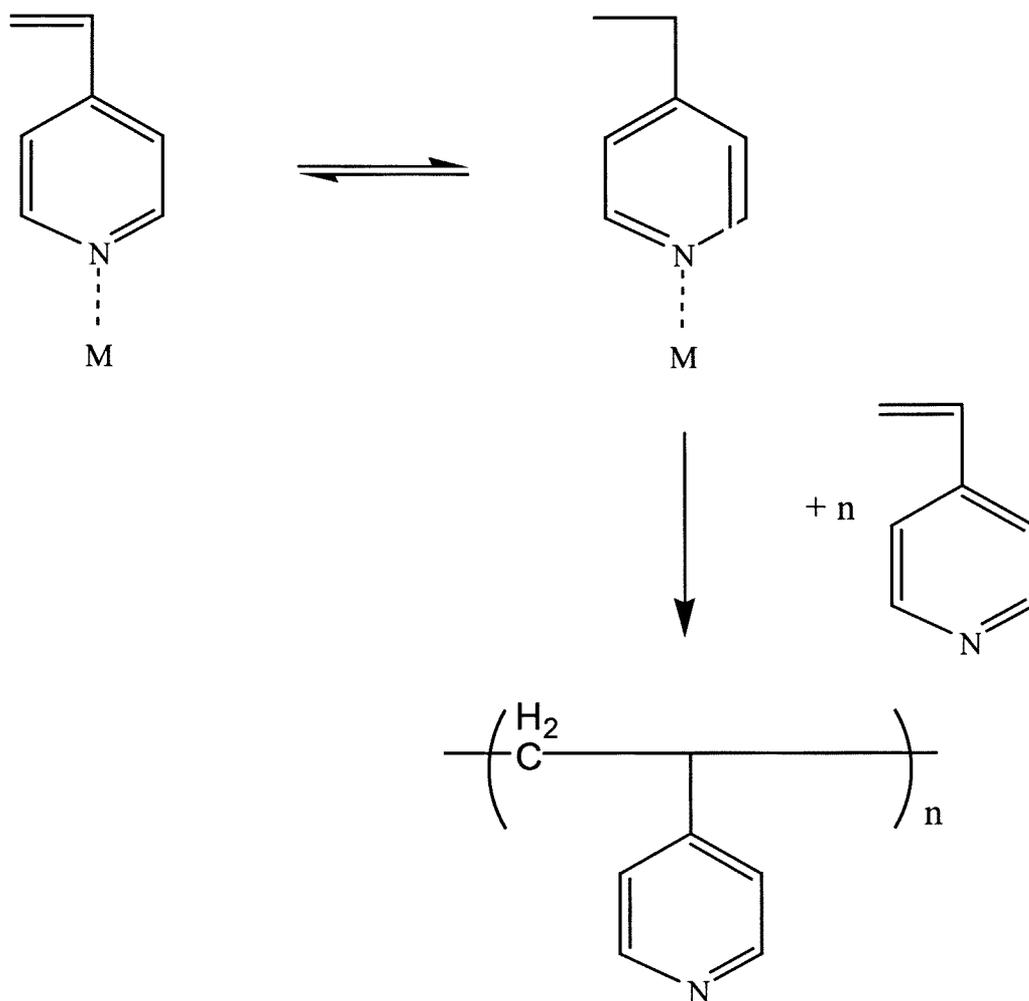


Figure 4.14 Effect of different metals on conversion
Catalyst / Me₆TREN = 1 / 2 ; Standard – no catalyst used

The Fe^{II} metal gave the highest conversion (figure 4.14), followed by Cu^I. This is a clear indication that the copper (Cu) metal does catalyse self-initiation of 4VP.

The following mechanism for the ATRP of 4VP is proposed:



Scheme 4.9 Proposed mechanism for ATRP of 4-vinylpyridine

4.4.6. The effect of solvent and temperature on the reaction

The effects of solvent [methanol (MeOH) and isopropyl alcohol (iPrOH)] and temperature on conversion, the MeOH at 25 °C and 60 °C, and iPrOH at 75 °C, were compared.

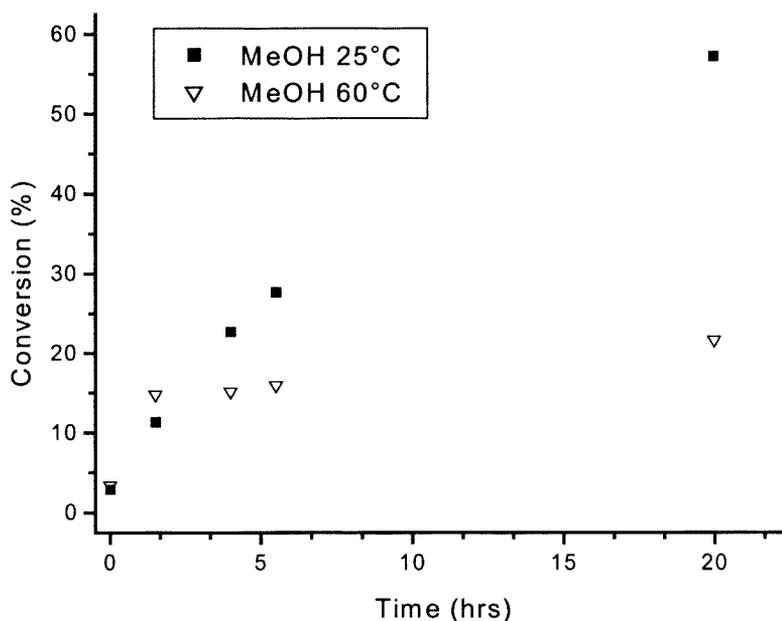


Figure 4.15 Effect of temperature on conversion versus time, in methanol.

Polymerisation of 25 mL 4-vinylpyridine in 50 mL methanol.

Monomer / CuBr / 1-PEBr / Me₆TREN = 100 / 0.2 / 0.4 / 0.5

The ATRP of 4-vinylpyridine has a higher rate at lower temperatures (figure 4.15). This is very probable because the proportion of free radicals increases as temperature decreases, due to a shift in the equilibrium brought about by a change in the $k_{\text{act}} / k_{\text{deact}}$ ratio, as seen in cationic polymerisation reactions. This could also be the reason why the polydispersity index at the lower temperature is slightly broader than that at the higher temperature.

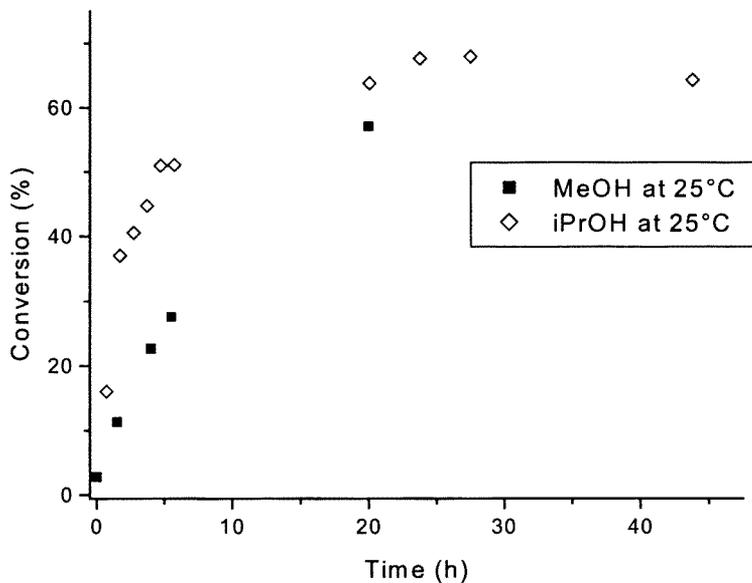


Figure 4.16 Effect of methanol (MeOH) and isopropyl alcohol (iPrOH) on the reaction at room temperature. Monomer / CuBr / 1-PEBr / Me₆TREN = 100 / 0.2 / 0.4 / 0.5 for isopropyl alcohol reactions.

Changing the polarity of the solvent resulted in a change in the rate of the polymerisation (figure 4.16). This is probably due to the oxidation state of the catalyst, which in turn influences the bond strength of the catalyst towards the halogen atom, resulting in differences in the radical flux.

4.5. CONCLUSIONS

- From the results of experiments 1 and 2 we can conclude that in the ATRP of 4VP it is better to initially keep the monomer and initiator separate from the rest of the contents in the reaction flask.
- It is also more suitable to keep the initiator separate from the reaction solution to prevent premature initiation while purging with argon, which seemed to lead to higher polydispersities.
- Comparing catalysts showed that Cu^ICl is the preferred catalyst to Cu^IBr in the ATRP of 4-vinylpyridine; Cu^ICl gave a narrower polydispersity and the \bar{M}_n increased with conversion.
- The ligand Me₆TREN performed better for the ATRP of 4VP than the bipyridines and the substituted bipyridines did.
- The ATRP of 4-vinylpyridine is complicated by the fact that the copper catalyst and other metal catalysts catalyse the self-initiation of this monomer, giving a secondary initiating process that leads to a broader polydispersity.
- The solvent choice seems to have a large influence on the bond strength of the halogen atom towards the catalyst.

Due to the broad polydispersities of the 4VP ATRP reactions that resulted on a regular basis, further investigations were carried out regarding the possible effects that would contribute to broaden the polydispersity index. Results hereof can be seen in chapter 5.

¹ Mark, H. F.; Gaylord, N. G.; Bikales, N. M. *Encyclopaedia of Polymer Science and Technology*, **1968**, 8, 309

² Queffelec, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules*, **2000**, 33, 8629

³ Xia, J.; Gaynor, S. G.; Matyjaszewski, K. *Macromolecules*, **1998**, 31, 5958

5. INVESTIGATION OF THE POSSIBLE SIDE REACTIONS TAKING PLACE DURING THE ATRP OF 4VP

5.1 ABSTRACT

Results obtained thus far for the polymerisation of 4VP by ATRP were considered inadequate; polydispersity results of the polymerisations of 4VP via ATRP that were carried out (chapter 4) were as high as 6 in some cases. Polydispersities of 1.2 should easily be achieved with the methods used ^[1]. It is thought that 4VP could have difficulty in maintaining a low polydispersity throughout the reaction due to side reactions, which may occur with the nitrogen atom on the pyridine ring. It is also possible that the nitrogen based ligand that was used (Me₆TREN), as well as the initiator species (1-chloro-1-phenylethane or 1-bromoethylbenzene) may be involved in some kind of side reactions taking place. Many possible side reactions were then investigated in order to determine whether significant deviations of chemical shifts could be found that would characterise side reactions that may be associated with broadened polydispersities.

When a proton spectrum of a mixture of 4-vinylpyridine (4VP), 1-chloro-1-phenylethane (1-PECl) and isopropyl alcohol (iPrOH) was compared against the individual spectra of these reactants, there were slight chemical shift differences to be seen. It was not known whether these slight chemical shifts were due to scatter or whether or not one or more of the components had an influence towards causing these slight shifts.

In a series of cases, it was always found that there is a slight shift in the individual peaks. Results of the following reactions show slight chemical shift differences between the pure compounds alone and the compounds when they are in a mixture with the other compounds.

5.2 EXPERIMENTAL

Materials and techniques. CDCl₃ (Merck- 0.03 vol % TMS deuteration degree min 99.8 %), iPrOH (Aldrich, 99.5+ %), 4VP (ACROS, 95 % stabilized), 1-chloro-1-phenylethane (ACROS, 97 %), Deuterium oxide (D₂O) (Aldrich, 99.9 atom % D), NaCl (Saarchem, 99.5 %).

300 MHz Varian VXR spectrometer equipped with a Varian magnet (7.0 T) and a 5 mm switchable probe, or a 600 MHz Varian Unity Inova spectrometer equipped with an Oxford magnet (14.09 T) and a 5 mm inverse detection probe, were used to analyse the spectra in this chapter.

Figure 5.1 depicts the different types of carbons found in the proposed quaternary structure formed during polymerisation of 4VP by ATRP. Chemical shift values for the specific peaks are shown in table 5.1 [values in δ (chemical shift downfield in ppm from TMS)].

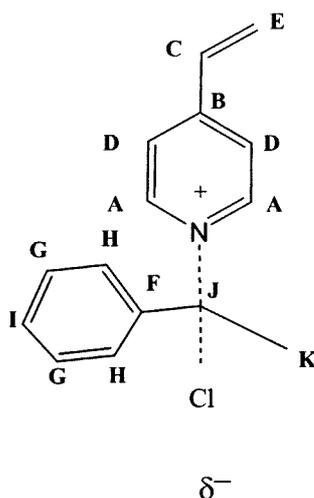


Figure 5.1 Proposed structure of quaternization effect between 4-vinylpyridine and 1-chloro-1-phenylethane

Table 5.1 ¹³C chemical shift values for figure 5.1. Deuterated chloroform used as solvent

Peak	A	B	C	D	E	F	G	H	I	J	K
ppm	150.1	144.3	135.5	120.7	118.9	140.2	128.2	126.3	125.7	56.5	22.1

Table 5.2 Experimental conditions for all NMR investigation reactions in this chapter

Section	Molar ratios			Masses (g)			Reaction time (h)	Temperature (°C)
	4VP	1-PECl	iPrOH	4VP	1-PECl	iPrOH		
5.3	5	1	8	3.74	1.00	7.68	24	60
	6	1	21	4.49	1.00	8.95	24	60
	7	1	24	5.23	1.00	10.20	24	60
	8	1	27	5.98	1.00	11.50	24	60
	10	1	33	7.48	1.00	14.10	24	60
5.4	4VP	1-PECl	iPrOH	4VP	1-PECl	iPrOH	0.17	25
	1		1	1.00		0.57		
	1		6	1.00		3.42		
	1		100	1.00		57.00	0.17	25
5.5	4VP	1-PECl	MeOH	4VP	1-PECl	MeOH	0.17	25
	1		1	1.00		0.30		
	1		6	1.00		1.82	0.17	25
5.6	4VP	1-PECl	iPrOH	4VP	1-PECl	iPrOH	24	60
	3	1	24	2.00	0.89	9.05		
	6.6	1	24	10.10	2.03	20.80		
	8	1	24	10.10	1.67	16.90	24	60
5.7	4VP	1-PECl	iPrOH	4VP	1-PECl	iPrOH	0.17	25
	3	1	24	2.00	0.89	9.06		
	3	1.5	24	2.00	1.33	9.06		
	3		24	2.00	1.77	9.06		
	3	2.5	24	2.00	2.22	9.06		
	3	3	24	2.00	2.67	9.06		
	3	6	24	2.00	5.34	9.06	0.17	25
5.8	4VP	1-PECl	iPrOH	4VP	1-PECl	iPrOH	16	25
	3	3	24	2.00	2.67	9.06		

5.3 THE COMPARISON OF DIFFERENT RATIOS OF 4VP TO ISOPROPYL ALCOHOL IN THE REACTION MIXTURE

Five experiments were performed, with each consecutive reaction differing in the ratio of 4VP to isopropyl alcohol. The total mole ratio of 4VP and 1-chloro-1-phenylethane, the initiator, to isopropyl alcohol was kept constant for each reaction. All reactions were run for 24 hours at 60 °C before NMR analysis. Deuterated chloroform (CDCl_3) was used as the solvent for NMR analysis and TMS as internal standard. ^{13}C NMR results (figure 5.2) of the five reactions are as follows.

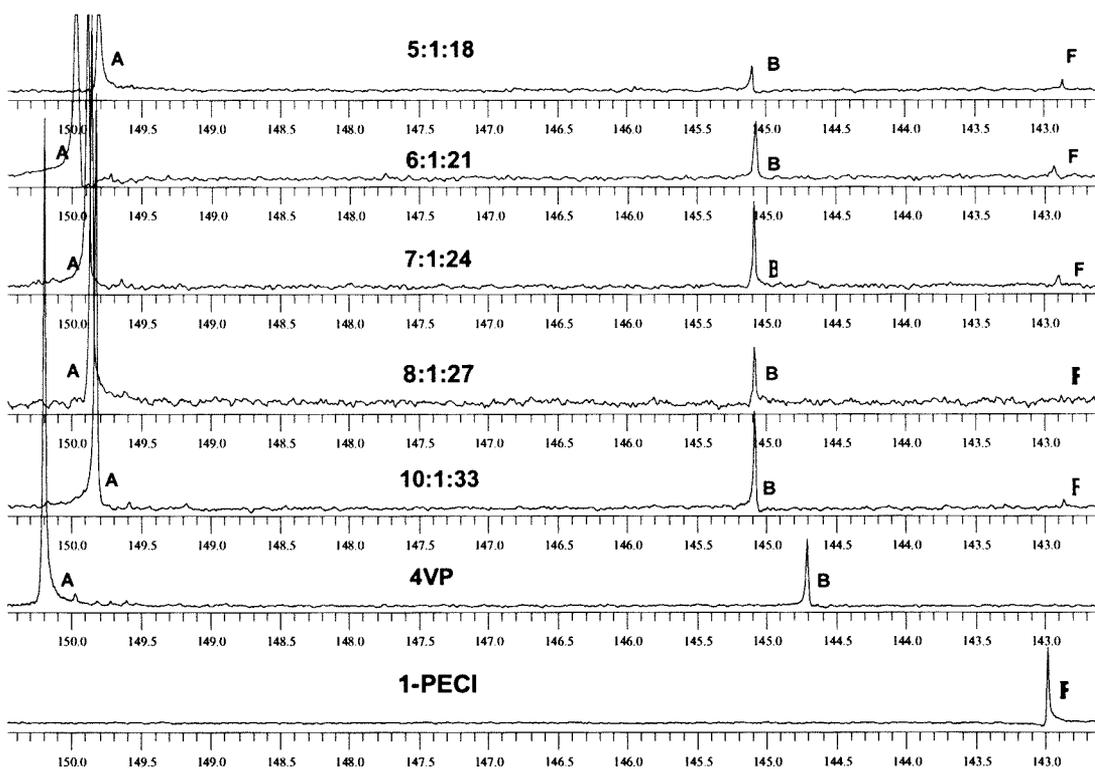
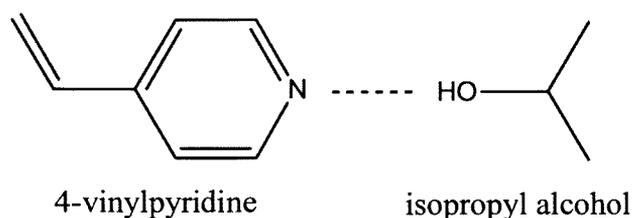


Figure 5.2 ^{13}C spectra, in CDCl_3 , across the 142.0 – 151.0 δ (ppm) region for mixtures of varying ratios of 4VP:1-PECl:iPrOH. (Refer to figure 5.1 for peak assignment and table 5.2 for reaction conditions.)

Table 5.3 Chemical shift changes for the individual peaks as a function of 4VP and iPrOH concentrations. $X \delta$ (ppm) = Difference in chemical shift values between the pure spectra of 4VP and 1-PECl, and the mixture spectra with reference to the same carbon peaks

Ratio of 4VP:1-PECl:iPrOH	Peak	A	B	F
5:1:18	X	0.39	0.36	0.07
6:1:21	X	0.24	0.33	0.05
7:1:24	X	0.33	0.37	0.03
8:1:27	X	0.33	0.33	0.05
10:1:33	X	0.37	0.37	0.07

Peaks A and B are for the monomer 4VP, and peak F is with respect to the initiator 1-PECl. There is a significant difference between the chemical shifts of the pure 4VP in solution and 4VP in the mixtures. It is thought that these shifts can be attributed to bonding with the isopropyl alcohol or the initiator, 1-PECl. With the solvent isopropyl alcohol, it is possible that there is hydrogen bonding taking place between the lone pair of electrons on the pyridine N-atom and the polar -OH bond of the isopropyl alcohol (scheme 5.1).



Scheme 5.1 Hydrogen bonding between 4VP and iPrOH

It is thought that this solvent effect has an influence on the differences in the observed chemical shifts in figure 5.2. Based on this hypothesis, it might be expected that chemical shift differences would increase with increasing solvent concentration, which was investigated in the next section. Another factor that may cause shifts is π -stacking of the aromatic components.

5.4 THE EFFECT OF DIFFERENT AMOUNTS OF THE SOLVENT ISOPROPYL ALCOHOL ON THE CHEMICAL SHIFTS

Three reactions with different molar ratios of the solvent, isopropyl alcohol, were performed to determine if the chemical shift differences between specific peaks would be greater with a greater amount of isopropyl alcohol present in the solution. Samples containing 1:1, 1:6 and 1:100 mole ratios of 4VP:iPrOH were prepared and analysed by ^{13}C NMR. Deuterated chloroform was used as the solvent for NMR analysis and TMS as internal standard. ^{13}C NMR results of the experiments are shown in figure 5.3:

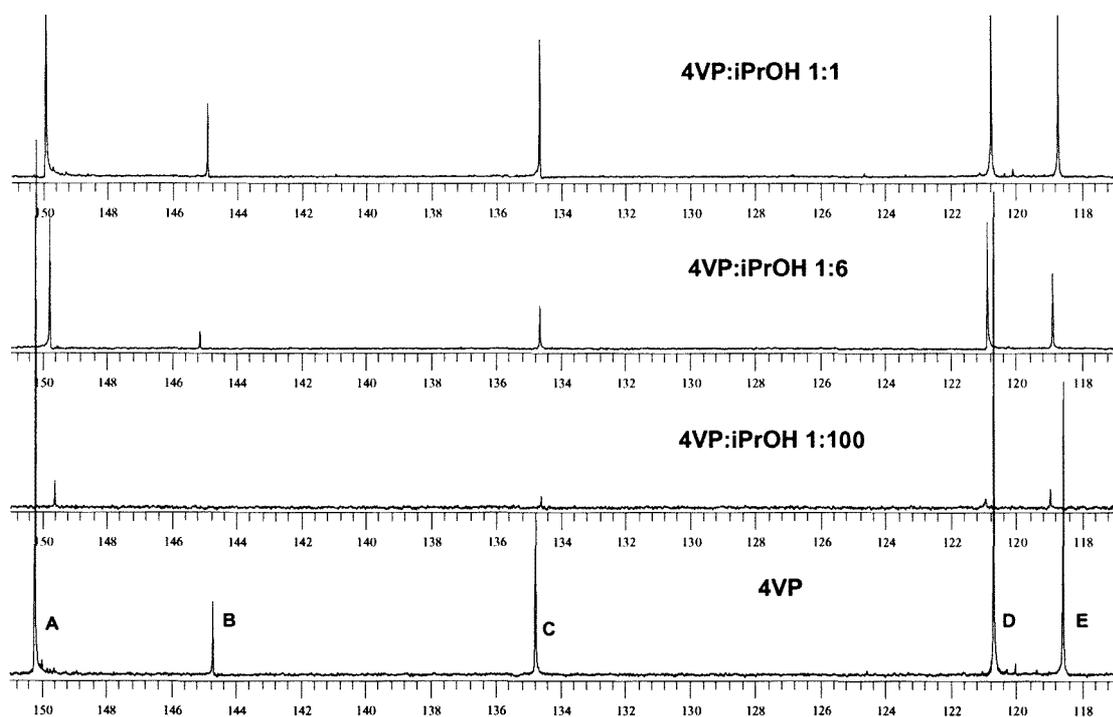


Figure 5.3 ^{13}C spectra, in CDCl_3 , across the 117.0 – 151.0 δ (ppm) region for mixtures of 1:1, 1:6 and 1:100 ratios of 4VP:iPrOH. (Refer to figure 5.1 for peak assignment and table 5.2 for reaction conditions.)

For this series of experiments, there was a significant difference in the chemical shift values of the 4VP peaks. This difference increased when the concentration of solvent was increased (table 5.4).

Table 5.4 Chemical shift changes for the individual peaks as a function of the presence of iPrOH concentration. $X \delta$ (ppm) = Difference in chemical shift values between the pure 4VP spectrum and the spectrum of the mixture with reference to the same carbon peaks

Ratio of 4VP:iPrOH	Peak	A	B	C	D	E
1:1	X	0.35	0.17	0.09	0.07	0.15
1:6	X	0.43	0.39	0.13	0.17	0.31
1:100	X	0.61	0.44	0.16	0.25	0.41

Two more experiments were run; both contained the same molar ratio of reactants, but in the second experiment the isopropyl alcohol was evaporated off before NMR analysis.

Table 5.5 Chemical shift changes for the individual peaks as a function the presence of iPrOH. X (ppm) = Difference in chemical shift values between the pure 4VP spectrum and the spectrum of the mixture with reference to the same carbon peaks

Ratio of 4VP:1PECl:iPrOH	Peak	A	B	C	D	E	F	G	H	I	J	K
3:1:24	X	0.98	0.25	0.42	0.03	0.21	0.41	0.37	0.37	0.38	0.15	0.04
3:1:24(iPrOH evaporated)	X	0.01	0.02	0.19	0.01	0.01	0.16	0.15	0.15	0.15	0.15	0.16

The results in table 5.5 show that the presence of solvent does have a significant effect on increasing the chemical shift differences. These results reinforce the previous experiment's results (table 5.4). They indicate a solvent effect rather than a quantitative effect.

Since a larger amount of solvent resulted in larger chemical shift differences, a more polar solvent might also be expected to increase the chemical shift differences. This was tested and the results discussed in the following section.

5.5 THE EFFECT OF REACTION TIME ON CHEMICAL SHIFT DIFFERENCES

The idea that a chemical reaction could be taking place in the NMR tube before the analysis is very possible. A mixture was therefore prepared to be analysed by ^{13}C NMR over a period of time, recording spectra at regular intervals.

One sample of a mixture of 4VP, 1-PECl and iPrOH was prepared and immediately analysed by ^{13}C NMR in order to see if there were significant changes in the chemical shifts of the individual peaks as well as the appearance of new peaks. Deuterated chloroform was used as the solvent for the NMR analysis and TMS as internal standard. ^{13}C results of the sample are shown in figure 5.4.

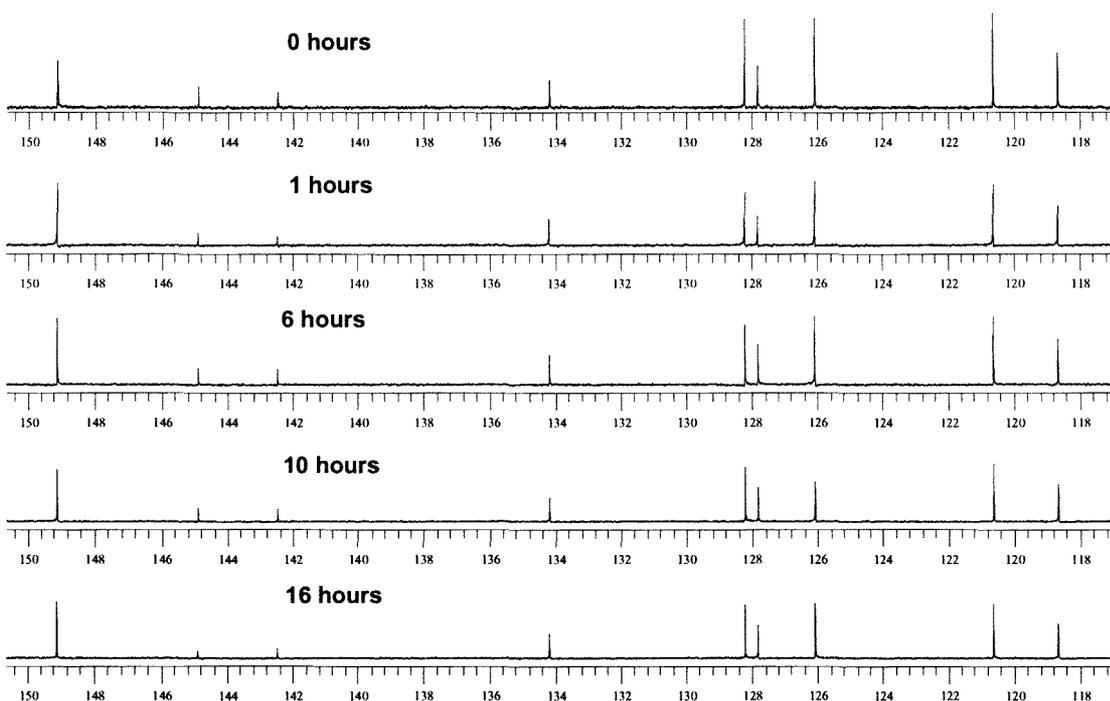


Figure 5.4 ^{13}C spectra, in CDCl_3 , across the 150.2 – 117.0 δ (ppm) region of a mixture of 4VP, 1-PECl and iPrOH to determine the effect that time has on the chemical shifts. (Refer to figure 5.1 for peak assignment and table 5.2 for reaction conditions.)

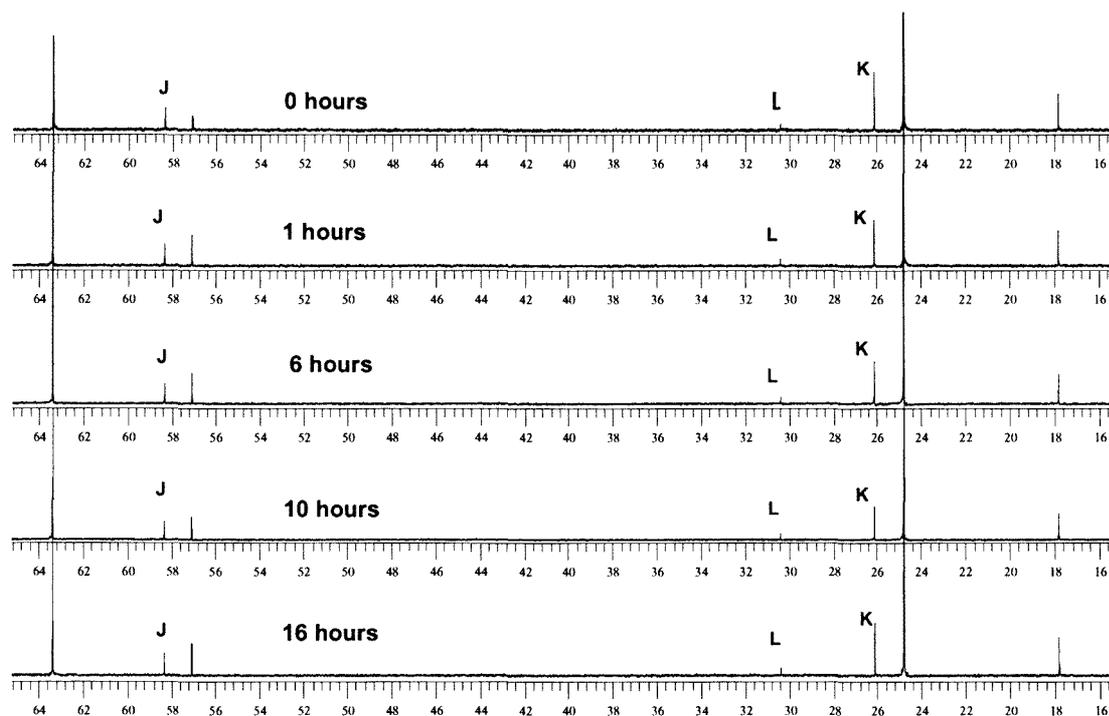


Figure 5.5 ^{13}C spectra, in CDCl_3 , across the $65.0 - 15.8 \delta$ (ppm) region of a mixture of 4VP, 1-PECl and iPrOH to determine the effect that time has on the chemical shifts. Chemical shifts for iPrOH are at 64.0 and 25.0δ (ppm). Impurities in the iPrOH occur at 57.8 and 18.0δ (ppm). (Refer to figure 5.1 for peak assignment and table 5.2 for reaction conditions.)

Figure 5.4 shows the downfield shifts for the carbon atoms. There seems to be no apparent shifts, neither the appearance of new peaks over the time period of 16 hours. Figure 5.5 shows the upfield shifts for the carbon atoms. The shifts are relatively unchanged, and the impurity peak L at 30.4 ppm, from the initiator, is present in all the spectra. No reaction appears to take place.

5.6 IONIC CHLORINE ATOM VERSUS COVALENT CHLORINE ATOM

Up until this point, only the solvent has positively provided evidence of affecting the chemical shift values of the peaks of the reagents in a mixture with each other, compared to the pure reagents. It was not clear whether or not the chemical shift values that were obtained were significant enough to suggest the existence of a quaternary structure. Yet, it is published that a quaternary structure is expected ^[2]. For this reason, further investigations using ^{35}Cl NMR were run.

Chlorine NMR was used to analyse a mixture of 4VP:1-PECl:iPrOH (3:3:24 molar ratios). The reason for carrying out this analysis was to determine, by means of chlorine NMR, whether or not the chlorine atom is ionically associated with the structure or whether it is covalently attached to the initiator. The presence of an ionic chlorine atom could suggest the formation of a salt or the possibility of the chlorine containing initiator structure being disrupted. If a chlorine atom is covalently bonded, it will have a higher chemical shift value and the width of the peak in the spectrum will be much broader when compared to an ionically associated chlorine atom, which is found at around $\pm 0 \delta$ (ppm) ^[3] and is much narrower in width (10 δ (ppm)). All reactions were run for 24 hours before NMR analysis. Deuterium oxide (D₂O) was used as the solvent for NMR analysis and TMS as internal standard. Experimental conditions for the ³⁵Cl NMR reactions can be seen in table 5.6. ³⁵Cl NMR results of reactions A and B are shown in figures 5.6 and 5.7.

Table 5.6 Experimental conditions for the chlorine NMR reactions that were investigated in deuterated water

Reaction	Molar ratios			Masses (g)			Volume H ₂ O (ml)	Reaction time (h)	Temperature (°C)
	4VP	1-PECl	iPrOH	4VP	1-PECl	iPrOH			
A	3	3	24	2.00	2.66	9.12		24	25
B	3	3	24	2.00	2.66	9.12		24	60
C					1.33		10.00	24	25
D		1	8		1.33	3.56	10.00	24	25

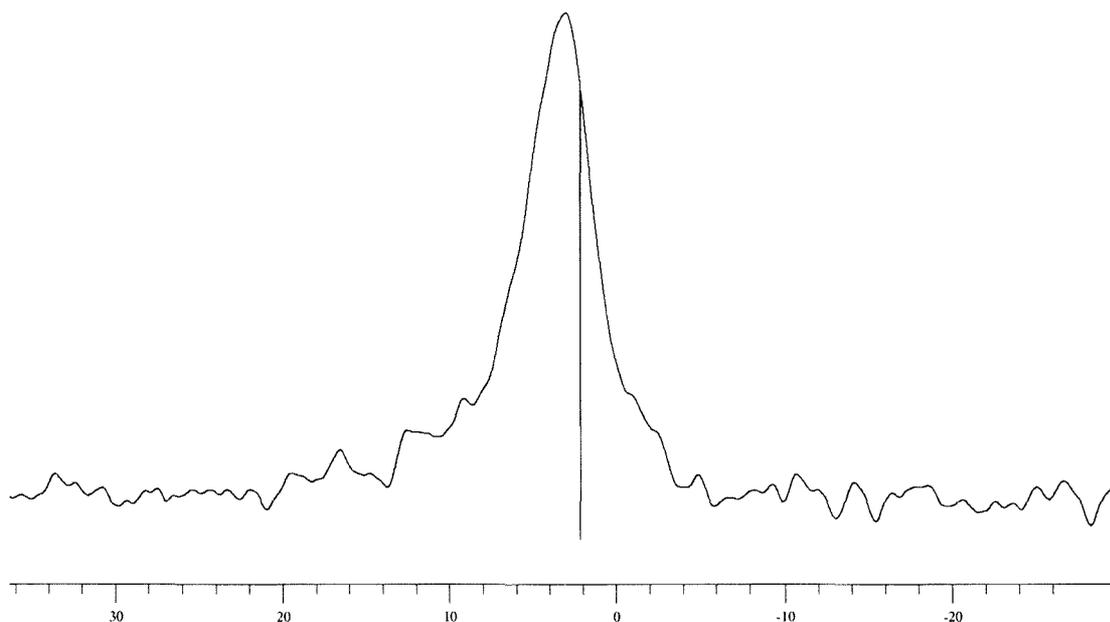


Figure 5.6 ^{35}Cl NMR, in D_2O , across the (-) 28 – 36 δ (ppm) region for a mixture of 4VP:1-PECl: iPrOH (3:3:24) at 25 °C. Refer to table 5.6 for experimental conditions

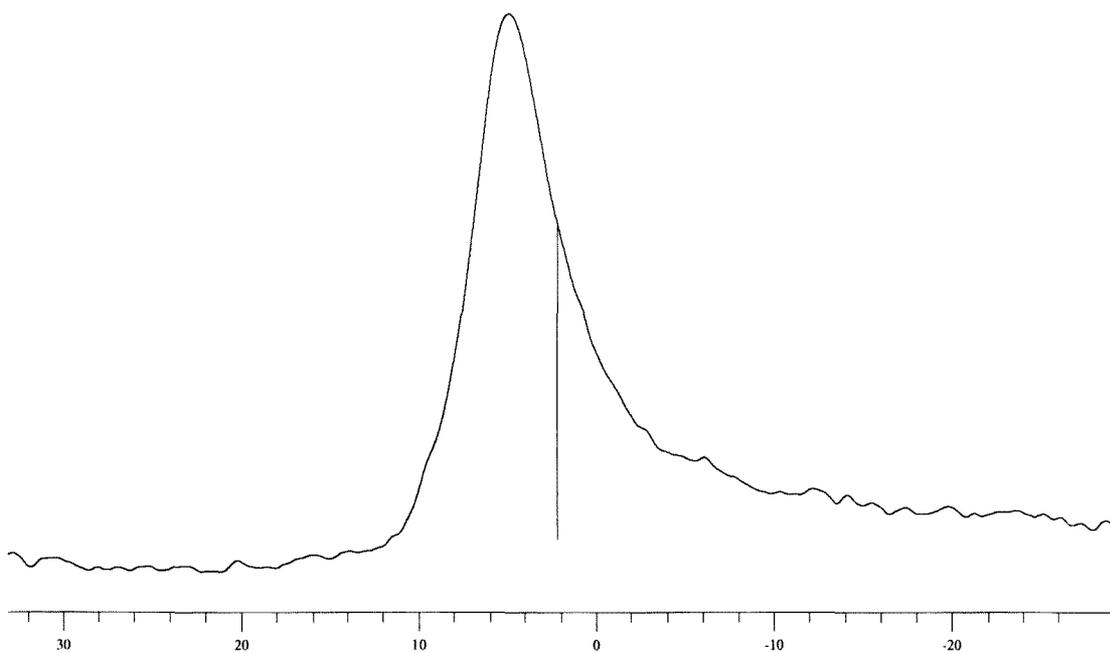


Figure 5.7 ^{35}Cl , in D_2O , across the (-)28 – 34 δ (ppm) region for a mixture of 4VP:1-PECl:iPrOH (3:3:24) at 60 °C. Refer to table 5.6 for experimental conditions

Figure 5.6 is the ^{35}Cl NMR spectrum of the 4VP:1-PECl:iPrOH (3:3:24 molar ratio) which was run for 24 hours at 25 °C. Figure 5.7 is the ^{35}Cl NMR spectrum of the

4VP:1-PECl:iPrOH (3:3:24 molar ratio) which was run for 24 hours at 60 °C. In both these spectra, the chlorine peak has a chemical shift of 2.88 δ (ppm), therefore temperature does not change the chemical structure. This shift is measured relative to 1M NaCl in D₂O. The source of the vertical line as seen in all the chlorine spectra is not known, but it is suspected that it serves as a calibration line. Ionic chlorine has a chemical shift at around ± 0 δ (ppm) [3]. The value found for the chlorine atom in the spectrum is highfield compared to the chemical shift of a covalently bonded chlorine atom, which is usually found much further downfield. Also, the width of the peak is narrow (10 δ (ppm)), compared to a covalently bonded chlorine atom. These spectra therefore indicate the presence of an ionic chlorine atom.

In reactions C and D, the monomer was excluded. From reactions A and B, the NMR analysis showed that the chlorine atom was ionically associated. Therefore, something is causing the chlorine atom to become labile. Reaction C only contained H₂O and the initiator itself, 1-chloro-1-phenylethane. Reaction D contained H₂O, iPrOH and the initiator, 1-chloro-1-phenylethane. Results of reactions C and D can be seen in figures 5.8 and 5.9, respectively.

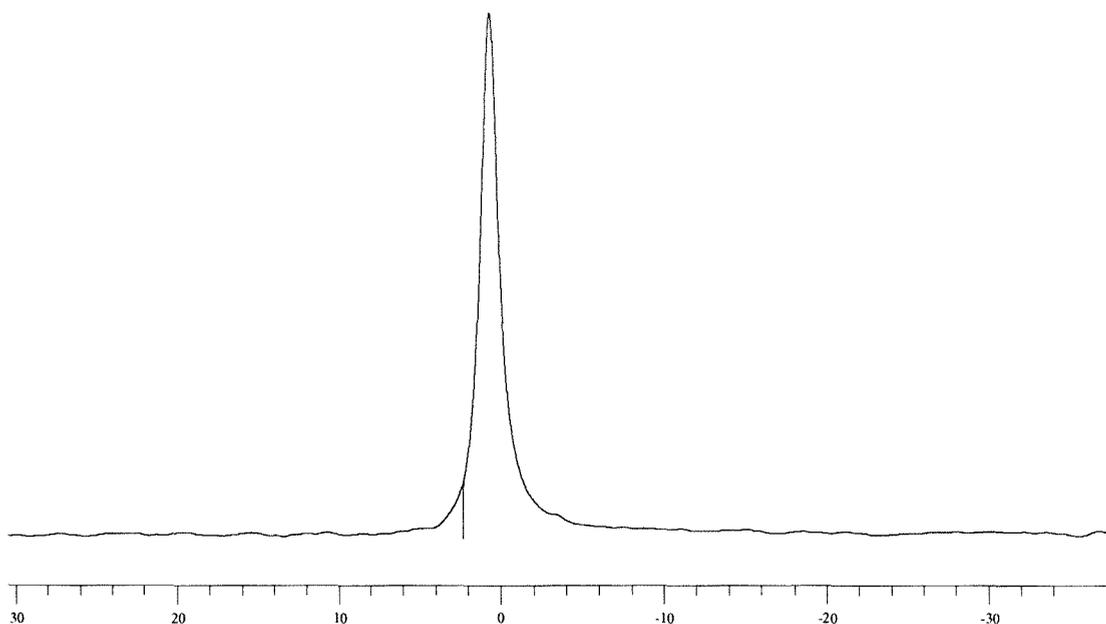


Figure 5.8 ³⁵Cl NMR, in D₂O, across the (-)36 – 30 δ (ppm) region for a mixture of 1-PECl and H₂O at 25 °C. Refer to table 5.6 for experimental conditions

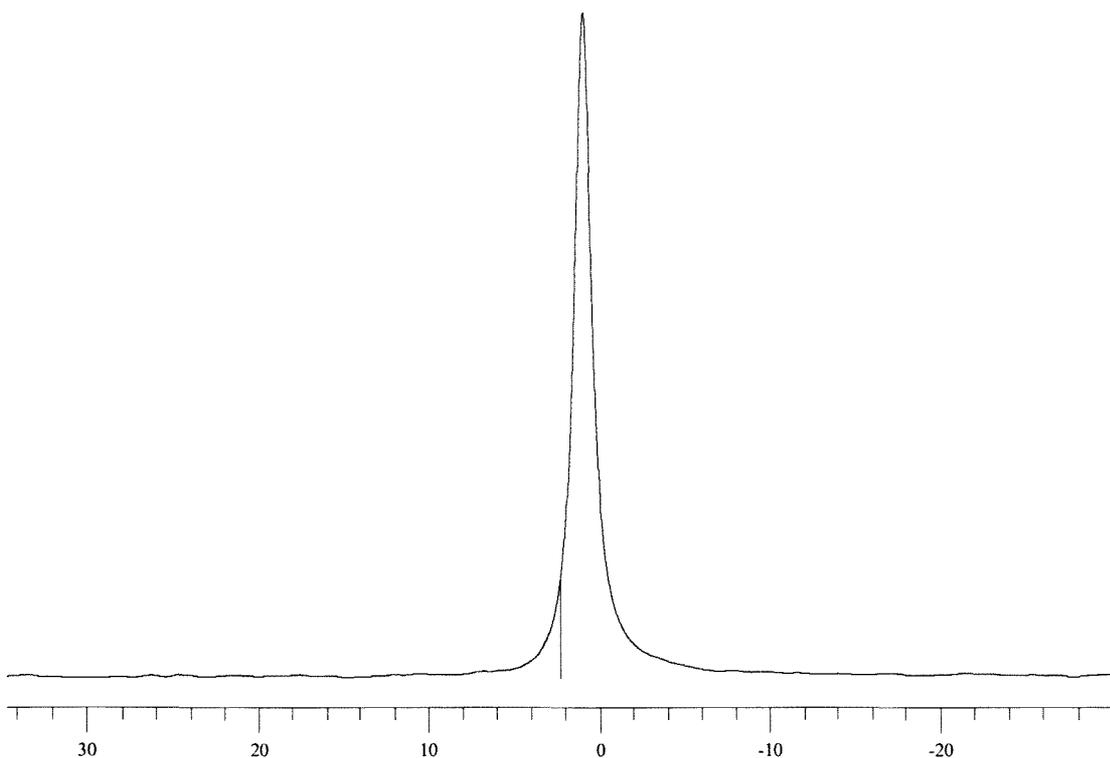


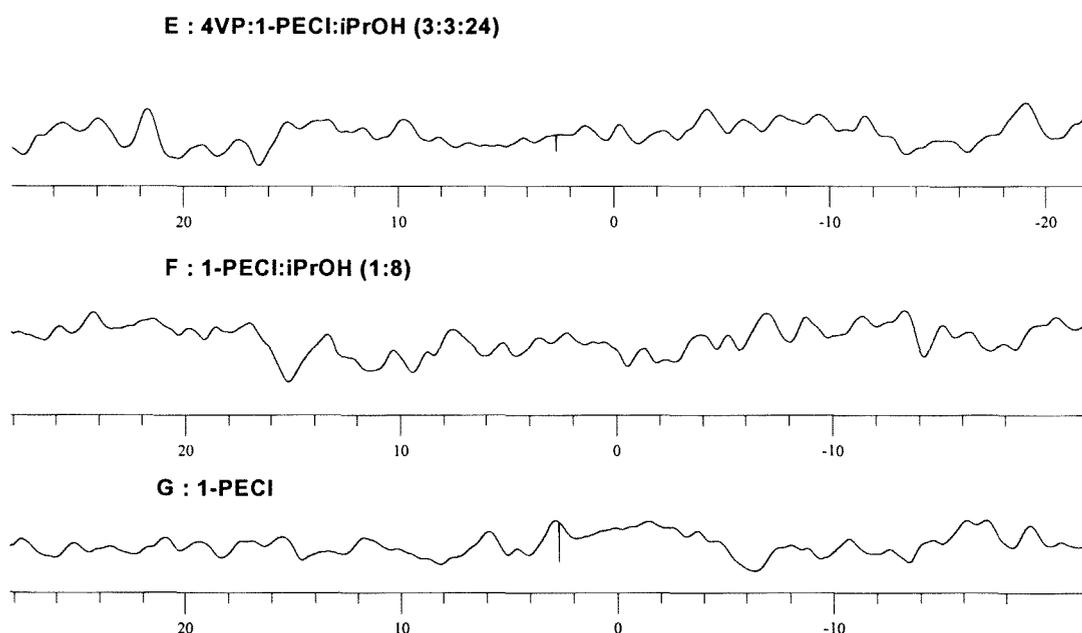
Figure 5.9 ³⁵Cl NMR, in D₂O, across the (-)28–34 δ (ppm) region for a mixture of 1-PECl:iPrOH (1:8) and H₂O at 25 °C. Refer to table 5.6 for experimental conditions

In figure 5.8 the chlorine atom has a chemical shift of 0.75 δ (ppm). This is an ionic chlorine atom, for the same reasons as mentioned for reactions A and B. Figure 5.9 also shows the chlorine atom to be ionically associated, and it has a chemical shift of 0.99 δ (ppm).

Further work included running the same samples that were run in section 5.8 with another deuterated solvent, namely dimethylsulphoxide (DMSO). The reason for this being that it is possible that the presence of water could disrupt the initiator structure. Experimental conditions are described in table 5.7 and the ³⁵Cl NMR results of these experiments are shown in figure 5.10.

Table 5.7 Experimental conditions for the chlorine NMR reactions that were investigated in deuterated DMSO

Reaction	Molar ratios			Masses (g)			Reaction time (h)	Temperature (°C)
	4VP	1-PECl	iPrOH	4VP	1-PECl	iPrOH		
E	3	3	24	2	2.66	9.12	24	25
F		1	8		1.33	4.56	24	25
G					1.33		24	25

**Figure 5.10** ^{35}Cl NMR spectra, in DMSO, across the (-) 20 – 28 δ (ppm) region for a combination of various mixtures of the reagents at 25 °C. Refer to table 5.7 for experimental conditions

The above figure indicates that in the presence of DMSO and, subsequently, in the absence of water, there is no indication of the presence of an ionic chlorine peak in the mixtures. Although it is not clear at this point, it has been shown that the initiator structure can be disrupted, whether it is by the presence of the water, or another compound present in the mixture.

Interestingly enough, evidence has been found in the literature that polyvinyl pyridines, and specifically poly(4-vinylpyridine) (P4VP), is involved in quaternization

reactions with ordinary alkyl halides ^[2]. The work investigated claimed to show an average of 65-70 % quaternization conversion to take place when polyvinyl pyridine and an alkyl halide were placed together. The same authors also claimed to have found quantitative quaternization of linear P4VP with active halogen compounds ^[4]. Although the above claims have been made for the polymers of 4VP, it is very likely that the same phenomenon could be found for the 4VP monomer and polymer as it is being formed in the polymerisation reaction.

For the work that was investigated for the purposes of my thesis, it seemed possible that quaternization of 4VP can occur for both the monomers and polymers.

These ³⁵Cl NMR experiments that were run (table 5.6) still did not justify nor prove the existence of a quaternary complex. Further experiments were therefore run which simulated the exact reaction conditions of the ATRP experiments that were performed with 4VP. In the following reaction mixtures no deuterated solvent was brought into direct contact with the solutions and they were submitted for ³⁵Cl NMR analysis in the original reaction conditions.

From figure 5.11 it can be seen that when the reaction mixture, which consisted of the monomer, initiator and solvent, was analysed by ³⁵Cl NMR, no ionic peak was observed. The normal broad chlorine peak, which is usually around 500 δ (ppm) for chloroform, now occurred at 42 δ (ppm) in the presence of the monomer, initiator and solvent (figure 5.11) and at 28 δ (ppm) in the presence of only the initiator and solvent (figure 5.12). This is indicative of the carbon chlorine bond still maintaining a sigma bond and becoming more electronegative whilst in the presence of only the solvent and initiator. It must be stressed that this is not evidence that a quaternary bond is formed.

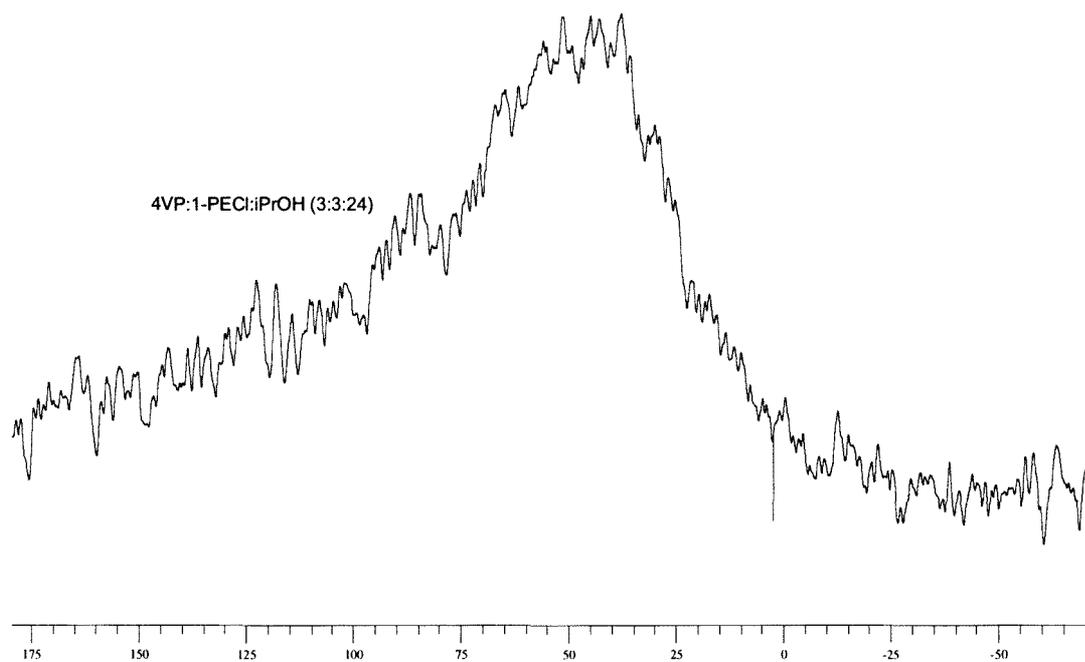


Figure 5.11 ^{35}Cl NMR spectrum, across the (-) 72 – 180 δ (ppm) region for a mixture of 4VP: 1-PECl:iPrOH (3:3:24) at 60 °C

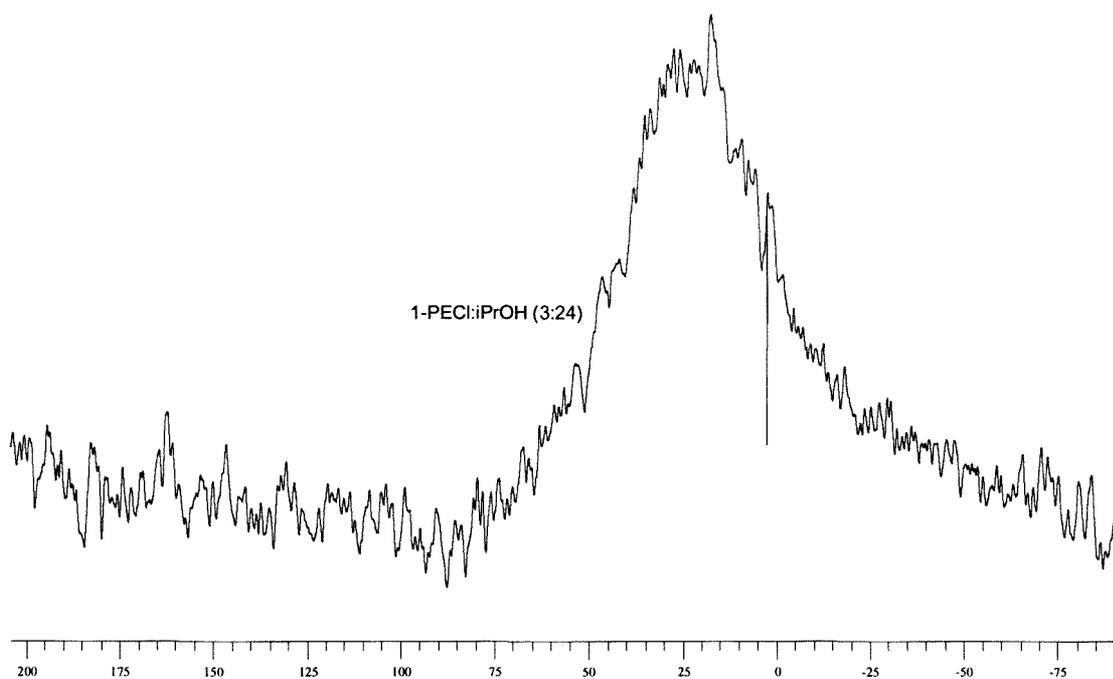


Figure 5.12 ^{35}Cl NMR spectrum, across the (-) 92 – 204 δ (ppm) region for a mixture of 1-PECl:iPrOH (3:24) at 60 °C.

Therefore, from this data, it was shown by NMR that the character of the carbon chlorine bond does change in the presence of the monomer. This is however not the reason why this particular reaction did not work. Other researchers who had also previously attempted the synthesis of P4VP by ATRP had experienced similar

difficulties with the polymerisations ^[5,6]. The reasons for this remains unknown. Unpublished work by a researcher in Japan ^[7] claims to have obtained P4VP via ATRP, with a polydispersity index of 1.16 and molecular mass of 5.43×10^4 . According to the information I received from him, they worked under ultra pure conditions and the reagents were purified.

Sonmez and Bicak ^[2] recently determined that quantitative conversions with polyvinyl pyridines were not possible when they were reacted with an alkyl halide species. I had expected a quaternary complex to be formed between the monomer and alkyl halide initiator that I had used, but, according to the techniques I had used to determine this, my results did not correlate with their results. They had however used a different analytical method to determine the formation of a quaternary complex; they used the mercuric thiocyanate method to analyse the content of chloride ions in solution, whereas I had used ¹H, ¹³C and ³⁵Cl NMR spectroscopy.

Following from this recent reference that had been found ^[2], another reaction was run which included the polymer in addition to a mixture of the monomer 4VP, the initiator and the solvent. The ³⁵Cl NMR spectrum thereof can be seen in figure 5.13. The chlorine peak was shifted slightly upfield (34.4 δ (ppm)) compared to the mixture alone (which did not contain any polymer in the sample (42 δ (ppm))). A small quantity of NaCl had been added to the mixture, which contained the polymer, and the ³⁵Cl NMR result of this is shown in figure 5.14. It is evident from figure 5.14 that there are now two chlorine peaks present. The peak at -47.3 δ (ppm) is that of the chlorine atom from the NaCl salt. The other chlorine peak is that of the initiator species which remains at the same chemical shift value as had been found in figure 5.13. The covalent nature of the initiator's carbon chlorine bond is not lost through quaternization, instead, the polarity of the sigma bond shifts the ³⁵Cl NMR signal to lower field.

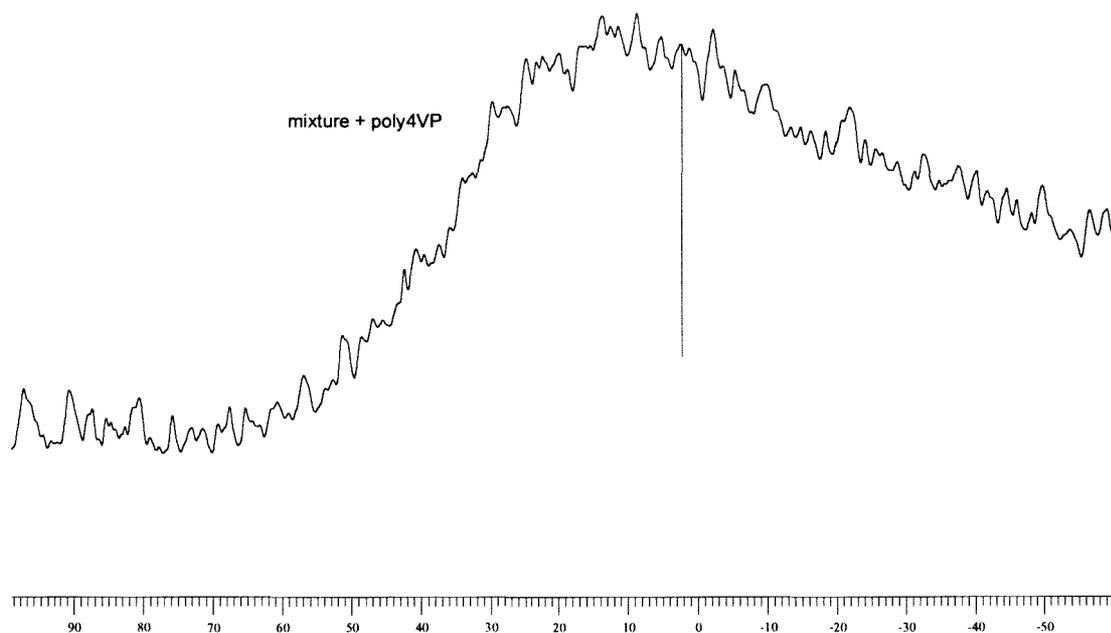


Figure 5.13 ^{35}Cl NMR spectrum, across the (-) 61 – 99 δ (ppm) region for a mixture of 4VP: poly4VP: 1-PECl:iPrOH (3:3:3:24) at 60 °C

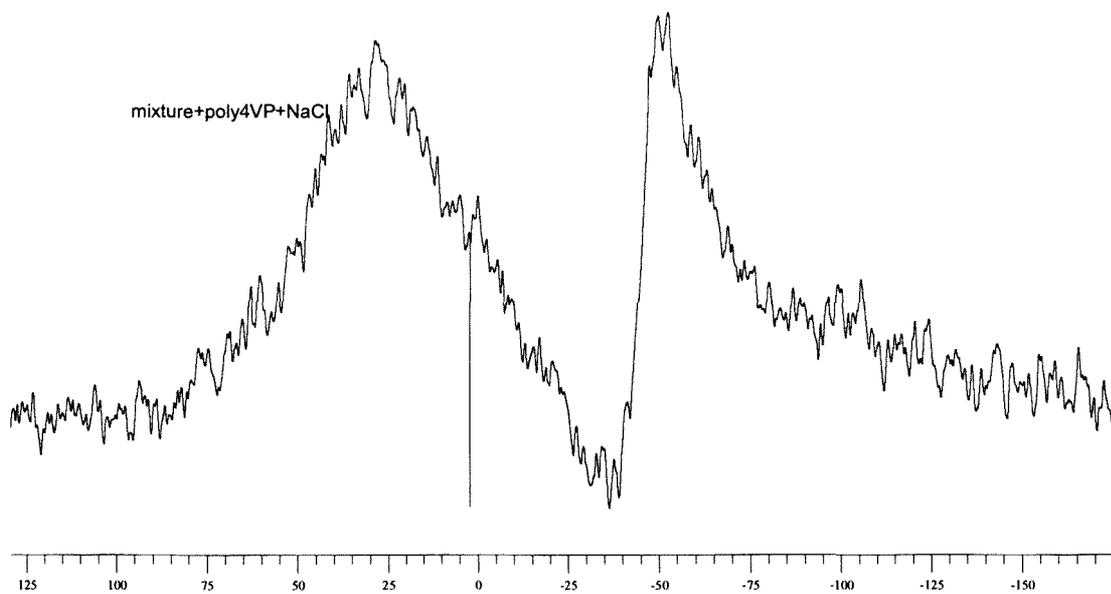


Figure 5.14 ^{35}Cl NMR spectrum, across the (-) 177 – 129 δ (ppm) region for a mixture of 4VP: poly4VP: 1-PECl:iPrOH and NaCl (3:3:3:24) at 60 °C

5.7 CONCLUSIONS

There are a number of possible reasons for why polydispersities of reactions of 4VP by ATRP remained very high. Requirements for good polydispersities are ^[8]:

- 1) Efficient initiation i.e. rate of initiation should be very high compared to rate of polymerisation
- 2) Fast activation-deactivation cycle i.e. k_{act} / k_{deact} should be low
- 3) k_p should be less than k_{deact}

In addition,

- 4) the initiator must be active to allow efficient initiation to take place
- 5) the monomer / ligand should not interact with other compounds.

¹³C NMR chemical shifts of the compounds used in the ATRP polymerisation process were carefully considered. Results have shown that there is always a change in the chemical shift values of compounds in mixtures compared to the pure compounds. This occurrence has led us to believe that interaction between the compounds affects the chemical shifts, and thus possibly changes the chemical behaviour of these compounds in some way.

Reagents used in the ATRP polymerisation reactions included solvent, monomer, initiator, catalyst and ligand. The first three were investigated as to whether they have an influence on causing differences in chemical shifts. Conclusions to the specific investigations are now given.

5.7.1 Ionic chlorine atom versus covalent chlorine atom

Analysis of the 4VP:1-PECl:iPrOH reaction mixture by ³⁵Cl NMR showed that an ionic chlorine atom occurred only in the presence of D₂O. It was not found under the ATRP reaction conditions used for mixtures of the monomer, polymer, initiator and solvent.

- ¹ Xia, J.; Zhang, X.; Matyjaszewski, K. *Polymer Preprints*, **1999**, *39*, 562
- ² Sonmez, H. B.; Bicak, N. *Reactive & Functional Polymers*, **2002**, *51*, 55
- ³ Brevard, C.; Granger, P. *Handbook of High Resolution Multinuclear NMR*, **1981**, 106-107
- ⁴ Bocak, N.; Gazi, M. *Polym. Bull.*, **2002** (submitted for publication)
- ⁵ C.P.Beyers, Eindhoven University of Technology, The Netherlands, email: C.P.Beyers@tue.nl
- ⁶ Hans Börner, Max Planck Institute of Colloids, Germany, email: Hans.Boerner@MPIKG-GOLM.MPG.DE
- ⁷ Mitsutoshi Jikei, Department of Organic and Polymeric Materials, Tokyo Institute of Technology, email: mjikei@o.cc.titech.ac.jp
- ⁸ Chambard, G. “*Control of Monomer sequence distribution*”, Ph.D thesis, Eindhoven University of Technology, **2000**

6. ATRP OF LAURYL METHACRYLATE (LMA)

6.1 ABSTRACT

The polymerisation of LMA (figure 6.1) by means of ATRP has not been described in the literature. ATRP of LMA was carried out to produce polymers of high molecular weight and narrow polydispersity, which can then be used as macro initiators in the presence of MMA monomer to produce block copolymers.

6.2 LMA MONOMER AND POLYMER

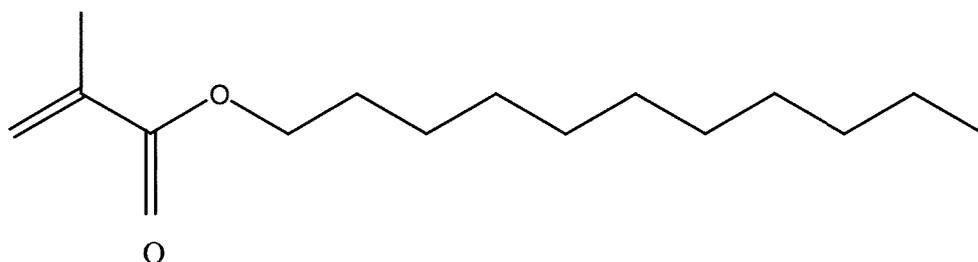


Figure 6.1 Structure of lauryl methacrylate: the backbone consists of a saturated hydrocarbon chain of 12 carbons.

LMA has $T_g = -65\text{ }^\circ\text{C}$ ^[1,2] and a boiling point in the range $272 - 343\text{ }^\circ\text{C}$ at 101 kPa ^[3]. The liquid monomer has a yellow tinge to it, and the polymer is a clear viscous product. Solvents in which both the monomer and polymer are both soluble include tetrahydrofuran, chloroform, 2-butanone and toluene. The molecular mass of LMA is 254 gmol^{-1} . K and α -values used in the Mark-Houwink equation for LMA are $5.18 \times 10^{-5}\text{ dLg}^{-1}$ and 0,720, respectively.

Table 6.1 Properties of the monomer lauryl methacrylate ^[3]

physical state	clear liquid
melting point	-7 °C
boiling point	142 °C at 4mm Hg ^[4]
specific gravity	0.871-0.876
solubility in water	Insoluble; 1.38 x 10 ⁻⁸ mL/mL ^[5]
pH	6.8-7.2
flash point	109 °C
refractive index	1.444-1.445

Polylauryl methacrylate has been produced commercially as a milk carton coating ^[6], to prevent moisture penetration and leakage of milk. It is possible that this hydrophobic polymer may mix with waxes, which could be applied to paper coatings to improve water resistance and decrease moisture vapour transmission rates (MVTR). The long hydrocarbon chains of LMA in such a mixture are expected to arrange themselves in a densely-packed, orderly structure, thereby decreasing the amount of available space between them for moisture to pass through. Also of interest is the non-polar nature of this polymer, which, if applied to paper as a coating, would give the surface (the exposed part) of the paper a non-polar nature.

6.3 EXPERIMENTAL

6.3.1 General

Materials. LMA (Bisomer LMA 97 (special)) was purified by extraction with an aqueous 0.03 % KOH solution. According to the literature, successful distillation of LMA had been performed under strong vacuum ^[4]. Attempts were made to repeat such distillations, but success was elusive, even using temperatures in excess of 100 °C and under the best vacuum available, due to the very difficult conditions that were required. Thus the monomer LMA was only extracted with 0.03 % KOH solution, washed with distilled water and then used as such for polymerisation.

CuBr (Aldrich, 99.9 %), CuBr₂ (Aldrich, 99 %), toluene-4-sulfonyl chloride (TsCl) (Fluka, ≥ 99 %), 2,2-bipyridine (BPY) (Aldrich, 99 %) and 2-butanone (Acros, 99 + %) were all used as received.

Analytical methods. The analytical method used to determine the conversion of LMA differed from that used for determining the conversion of MMA. It was not possible to use gravimetry to determine conversion for LMA because of the very high boiling point of the monomer ^[7] (272 – 343 °C at 101 kPa), which made evaporation of the monomer without distortion by further thermal polymerisation impossible with available equipment. Thus, ¹H NMR was used to determine the conversion of the LMA through analysis of the double bond.

6.4 ATRP POLYMERISATIONS OF LMA

ATRP reactions were done with LMA, with varying molar ratios of reactants, to determine the optimum conditions for obtaining a controlled polymerisation system. The experimental conditions for the LMA reactions that were carried out are shown in table 6.2. The molar ratios and GPC results of these LMA ATRP reactions are shown in table 6.3.

Table 6.2 Experimental conditions for LMA ATRP reactions. Reaction temperature 70 °C.

Reaction	Masses (g)							Reaction time (h)
	LMA	Cu ^I	Cu ^{II}	PMMA	TsCl	BPY	2-butanone	
6	20.00	0.11		0.15		0.27	20.00	27.25
7	15.00	0.09	0.03		0.22	0.11	30.00	21.08

It must be stated for the record that an ATRP experiment of LMA using Cu^ICl as catalyst had been attempted, but had failed to produce any polymer. The reason why very good molecular weight results had been produced using the particular reaction conditions that were used with MMA (Chapter 3, sections 3.3 and 3.4.3), and not with LMA, is not known at this point.

Table 6.3 Molar ratios of reactants and molecular weight results for LMA ATRP reactions

Reaction	Ratios				\bar{M}_n	\bar{M}_p	PDI
	LMA	Cu ^I	TsCl	BPY			
6	100	1	1	2.2	21 400	58 900	2.65
	LMA	Cu ^I / Cu ^{II}	TsCl	BPY			
7	100	1 / 0.2	1	2.4	1 842	6 400	3.00

Reaction 6 showed an increase in conversion according to ¹H NMR. GPC results showed an increase in molecular weight. Polydispersities were not as expected from ATRP reactions, nevertheless, this polymer was used as a macro-initiator for a reaction in the presence of MMA monomer (sections 7.8 and 7.9).

Reaction 7 did not yield a product with as high a molecular weight as that of reaction 6. The possibility that much termination took place therefore exists.

The following molar ratio was decided upon for further investigations.

100 : 1 : 1 : 2.2

LMA Cu^I TsCl BPY

In this reaction, TsCl (0.15 g, 0.78 mmol), Cu^IBr (0.11 g, 0.78 mmol), BPY (0.27 g, 1.73 mmol), LMA (20.00 g, 78.7 mmol) and 2-butanone (20.00 g, 277 mmol) were added to a 150 mL schlenk tube. All reactants were weighed and the tube sealed under a nitrogen atmosphere in a glove box. The same procedure was followed as described in section 3.3. This polymerisation resulted in a highly viscous, brown, polymeric product, which was analysed by ¹H NMR and GPC.

6.5 RESULTS AND ANALYSIS OF LMA

Due to the experimental limitation mentioned in section 6.2.1, the conversion of LMA to polymer was determined by use of ^1H NMR alone. Polymer peaks were identified and their integrals compared against the monomer peaks to determine conversion into polymer. The measured chemical shifts of pure lauryl methacrylate can be seen in figures 6.2 and 6.3, and predictions of these chemical shifts, according to Chemdraw version 5.0, can be seen in table 6.4.

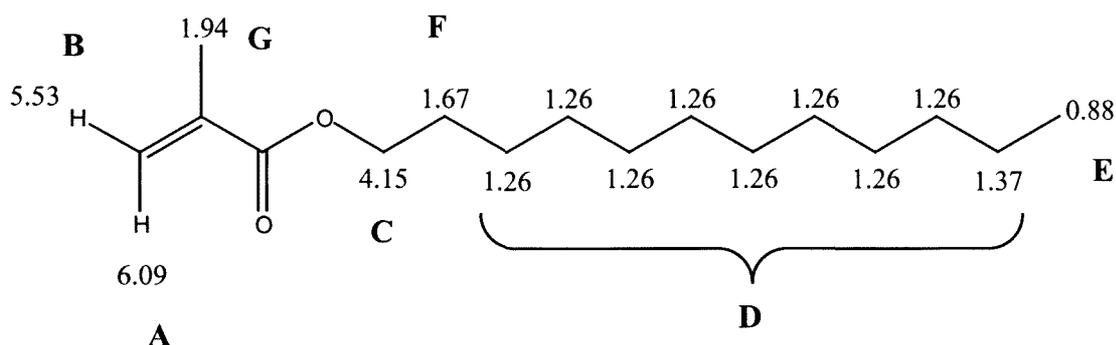


Figure 6.2 Measured ^1H NMR chemical shifts of pure lauryl methacrylate

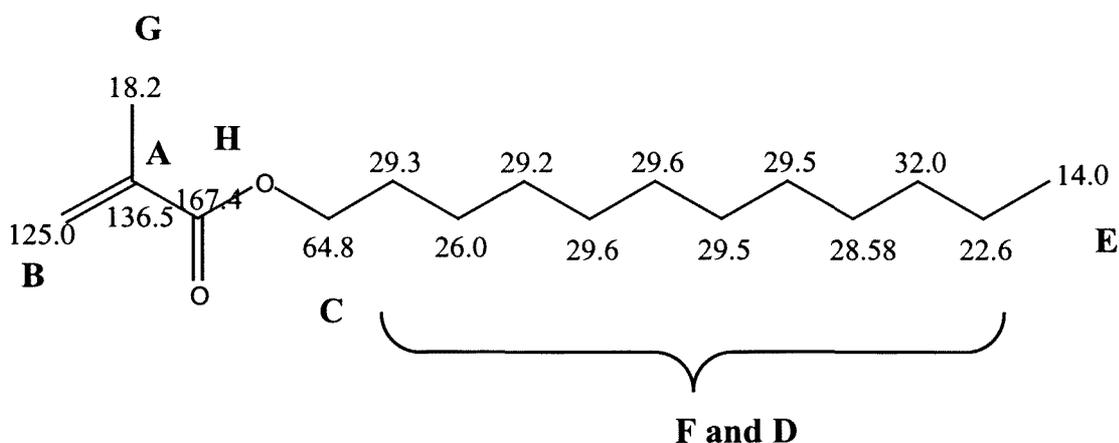


Figure 6.3 Measured ^{13}C NMR chemical shifts of pure lauryl methacrylate

Table 6.4 Predicted chemical shift values of lauryl methacrylate according to Chemdraw (version 5.0)

Peak	A	B	C	D	E	F	G	H
$^1\text{H } \delta$ (ppm)	6.15	5.58	4.15	1.29	0.96	1.57	1.93	
$^{13}\text{C } \delta$ (ppm)	138.00	122.90	67.10	23.10 – 32.50	14.00	30.00	18.40	165.00

Figures 6.4 and 6.5 show the ^1H NMR and ^{13}C NMR spectra of pure LMA respectively.

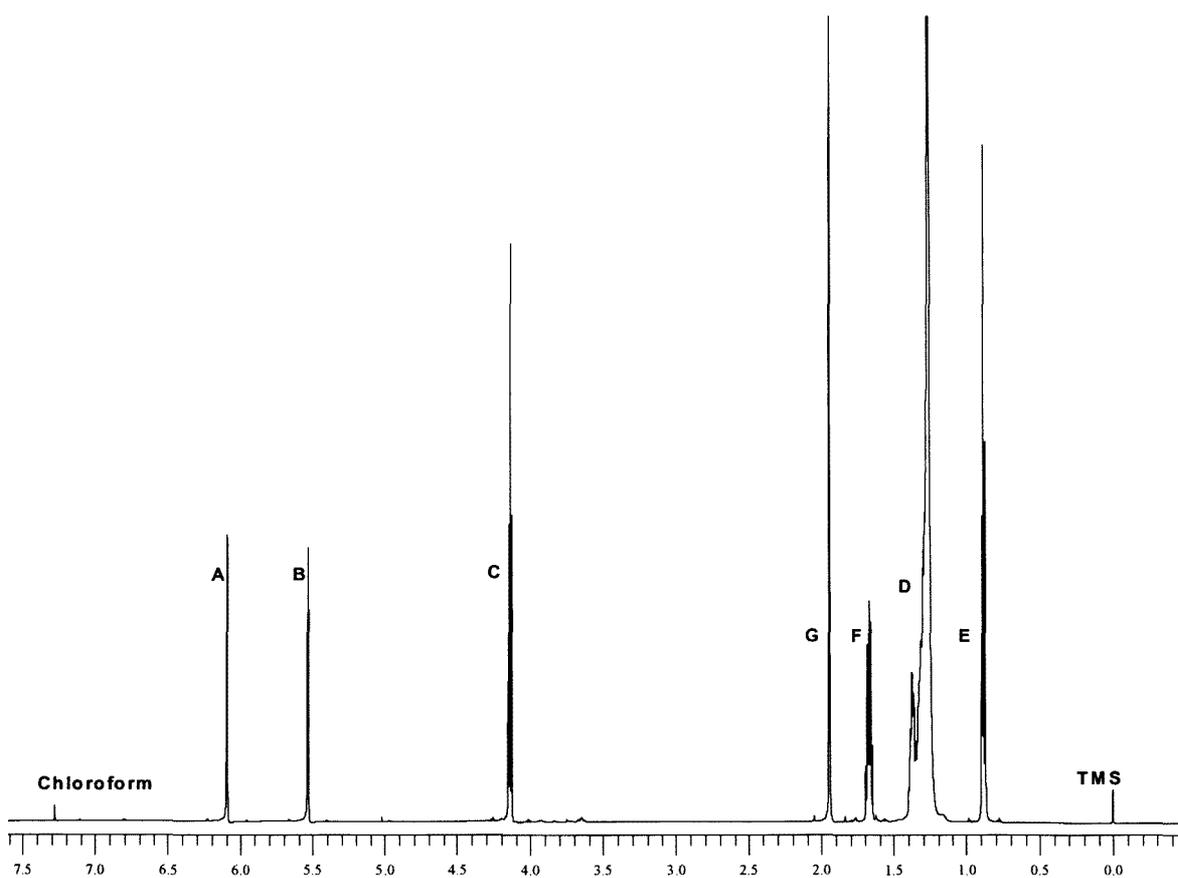


Figure 6.4 ^1H NMR spectrum, in CDCl_3 , across the 7.6 – 0 δ (ppm) region for pure LMA. Refer to figure 6.2 for peak assignments.

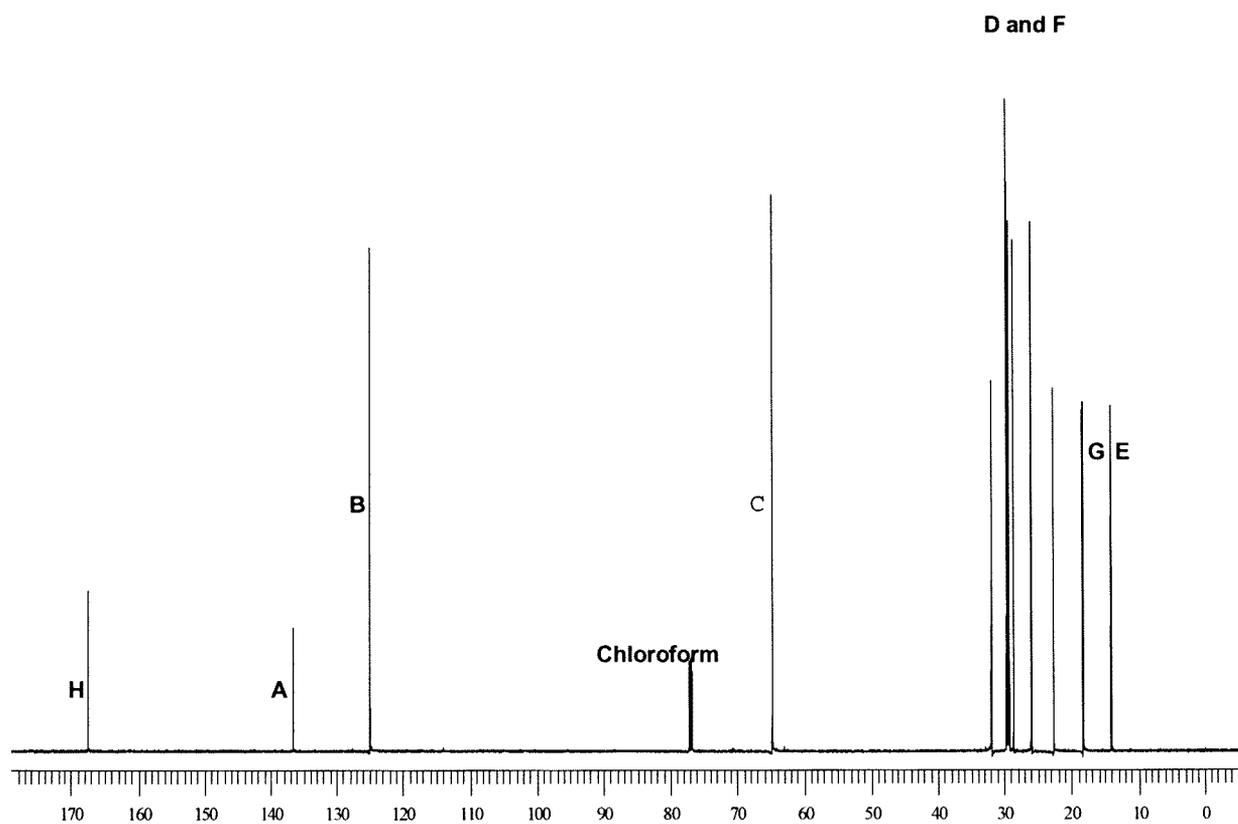


Figure 6.5 ^{13}C spectrum, in CDCl_3 , across the 180.0 – 0 δ (ppm) region for pure LMA. Refer to figure 6.3 for peak assignments.

Figures 6.6 and 6.7 show the ^1H NMR and ^{13}C NMR spectra obtained of the final solutions of the product of a polymerization of LMA and a pure polymer sample after precipitation in a 10-fold excess of methanol (figures 6.8 and 6.9).

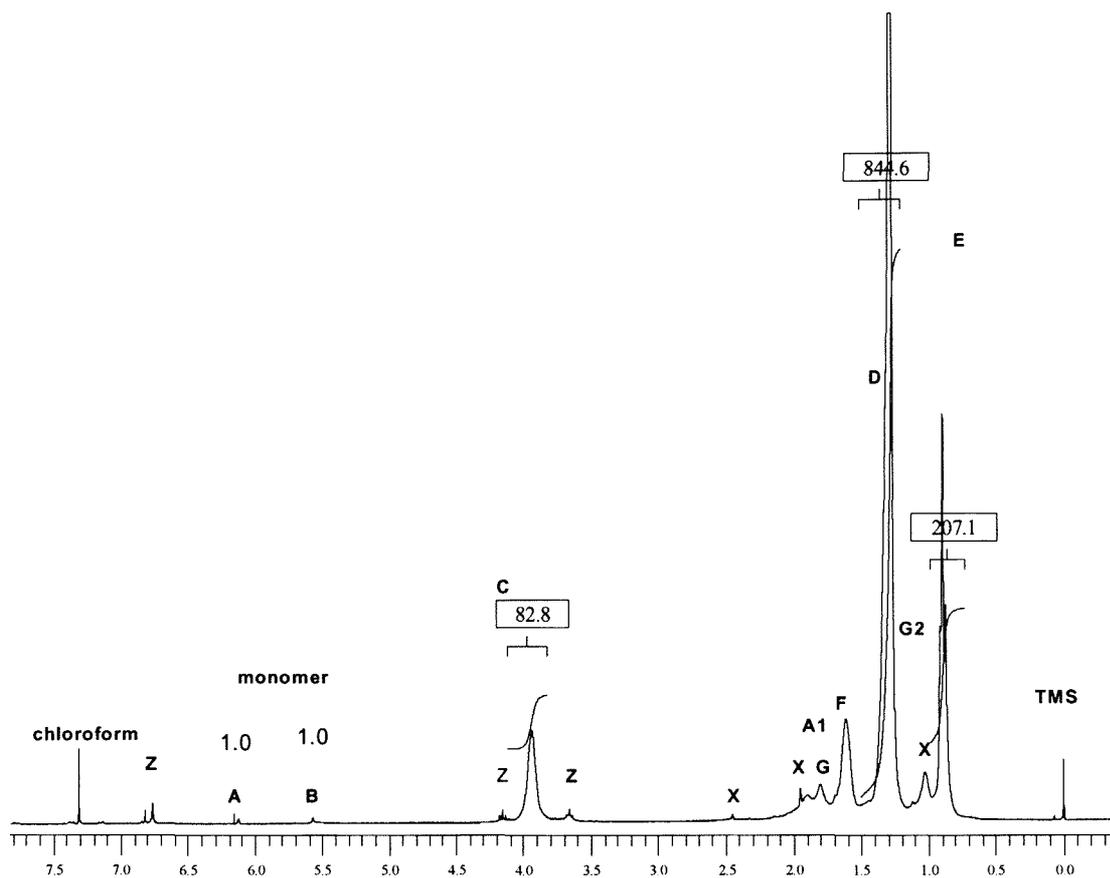


Figure 6.6 ^1H NMR spectrum, in CDCl_3 , across the 7.8 – 0 δ (ppm) region for the final LMA solution after 27.25 hours. X marks the chemical shifts for the solvent 2-butanone. Refer to figure 6.2 for peak assignments. Note: A and B are assigned to the presence of residual monomer.

The peaks marked Z are unidentified peaks. They may be due to the formation of side products that might have been formed during the polymerisation, or the development of impurities. When the polymer formed, the methyl peak (G) shifted upfield and is marked by peak G2 (which is overlapping the methylene peaks of the tail). When polymer forms, the double bond peaks disappear, and the backbone CH_2 group is formed, which has a chemical shift marked peak A1. Both peaks G2 and A1 are overlapping other peaks.

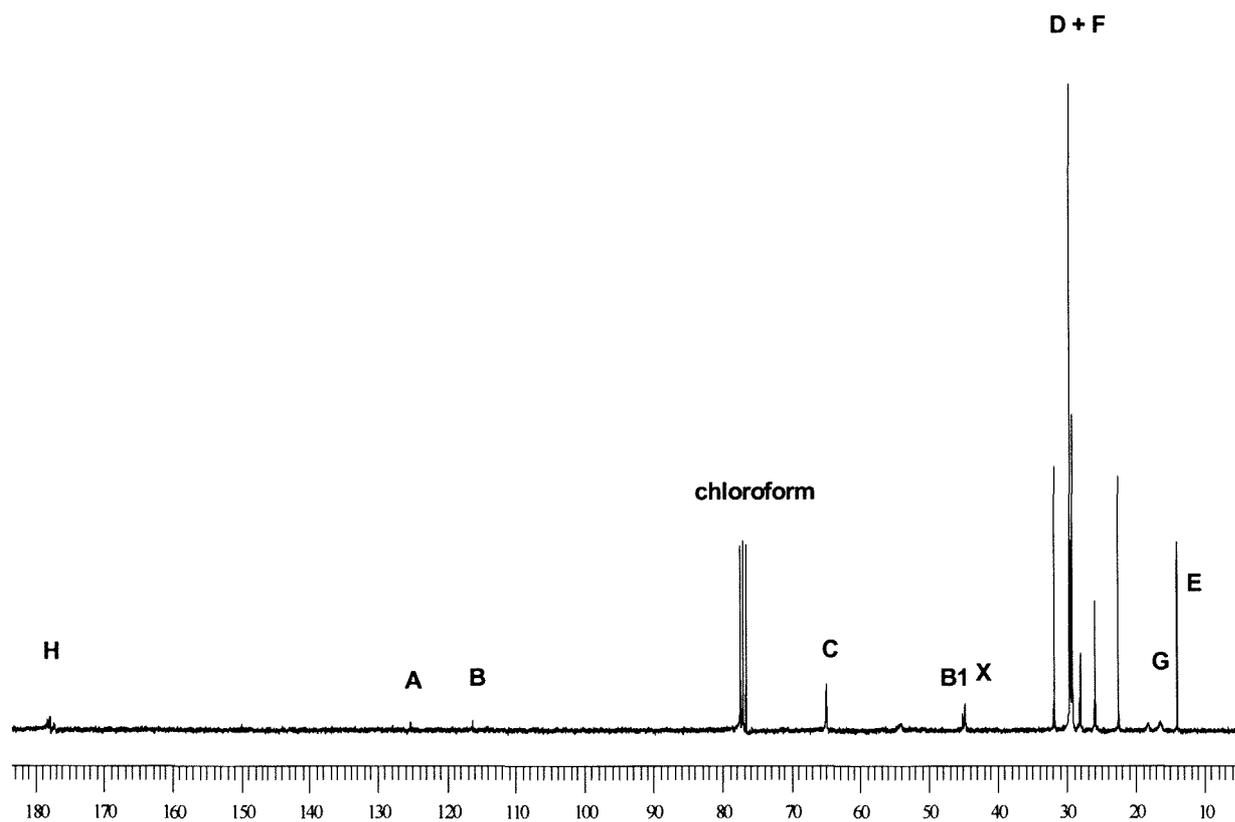


Figure 6.7 ^{13}C spectrum, in CDCl_3 , across the 183.0 – 6.2 δ (ppm) region for the final LMA solution after 27.25 hours. X marks the chemical shifts for the solvent 2-butanone. Refer to figure 6.3 for peak assignments. Note: peaks A and B are assigned to the presence of residual monomer.

The formation of the methylene polymer backbone peak is assigned B1 and has a chemical shift of 45.0 δ (ppm). When expanded, the solvent and the methylene peaks do appear as two separate peaks. The formation of the quaternary carbon of the backbone cannot clearly be seen. It may possibly have shifted to a lower chemical shift (perhaps in the region of the carbonyl group at 178.0 δ (ppm)).

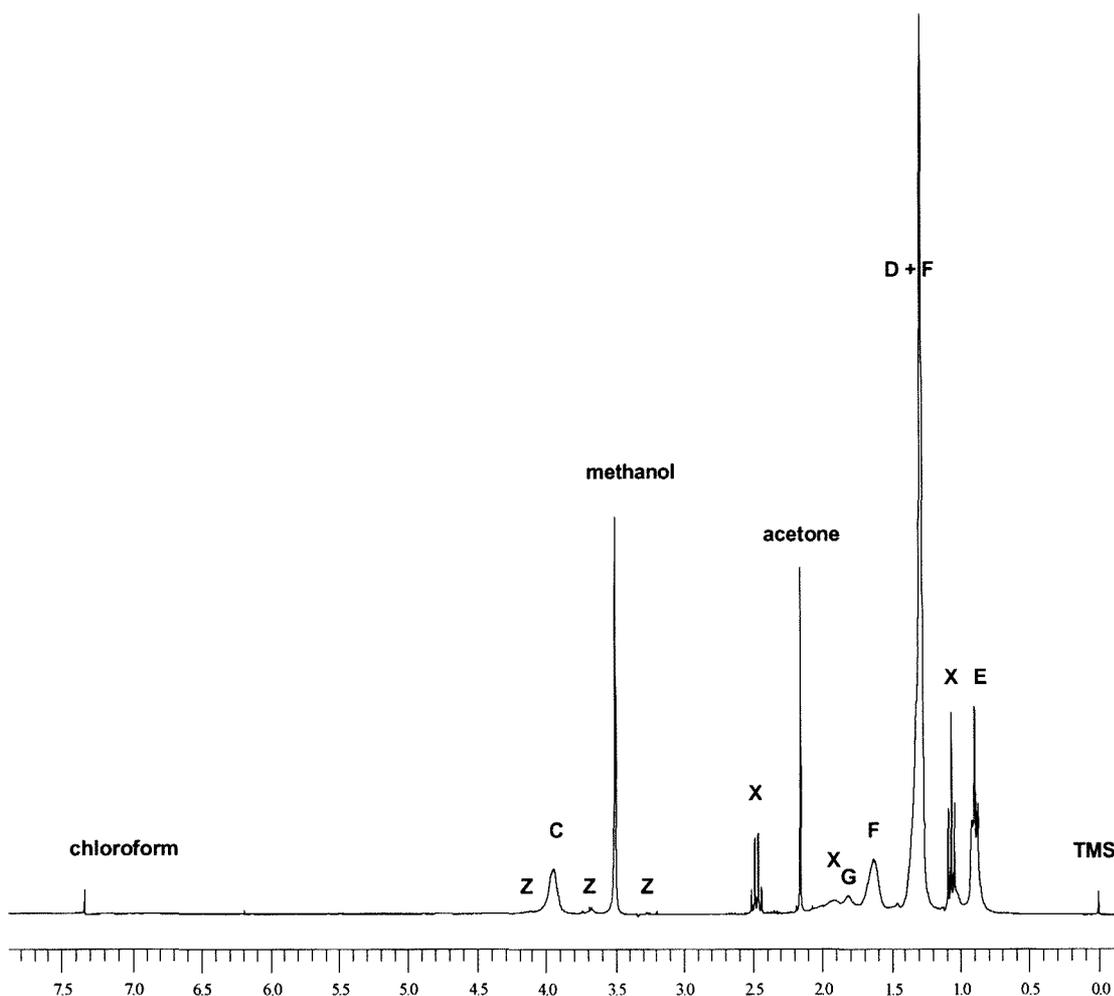


Figure 6.8 ^1H NMR spectrum, in CDCl_3 , across the 7.9 – 0 δ (ppm) region for poly(lauryl methacrylate) (PLMA). Refer to figure 6.2 for peak assignments. Note: peaks A and B are no longer present; they have been extracted during the precipitation process.

The solvent methanol had been used for precipitation purposes, and its presence can still be seen in the final polymer. It is likely that the large traces of acetone present are a result of cleaning the NMR tubes with it. The peaks marked Z are once again unidentified peaks, and may be due to impurities present or side products formed.

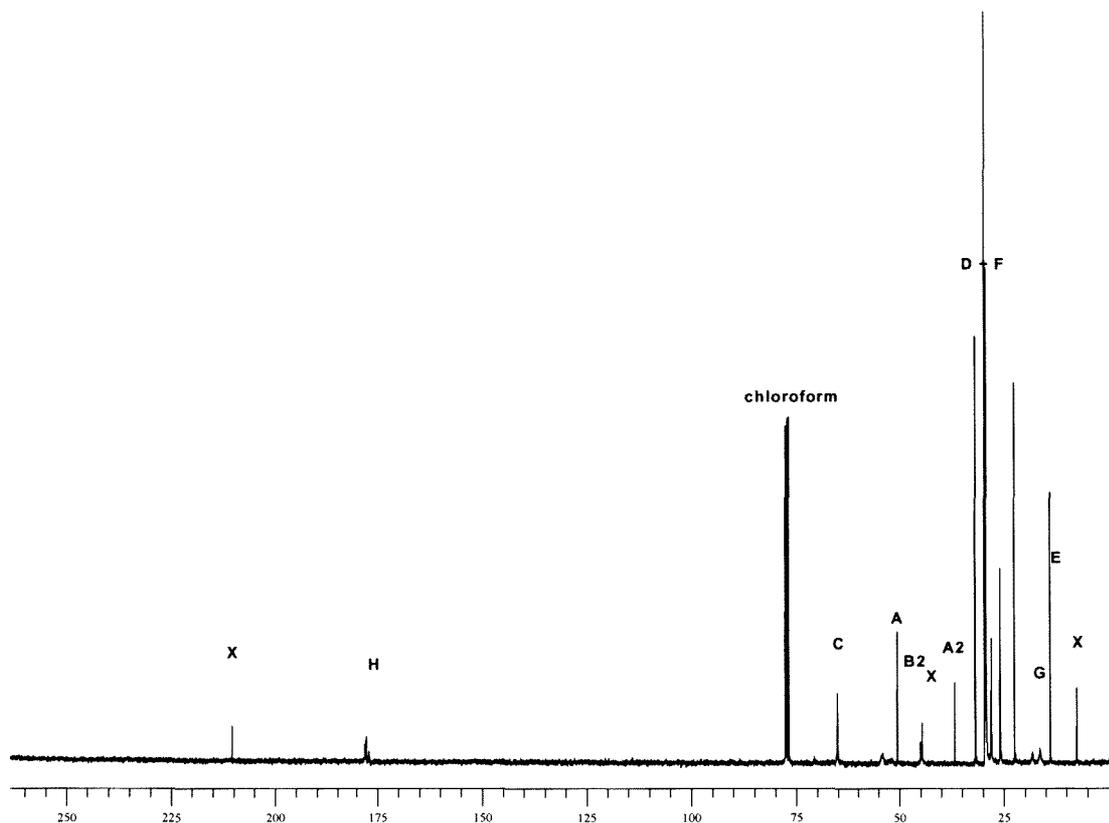


Figure 6.9 ^{13}C spectrum, in CDCl_3 , across the 222.0 – 0 δ (ppm) region for poly(1-lauryl methacrylate) (PLMA). Refer to figure 6.3 for peak assignments. Note: peaks A and B are no longer at the chemical shift values as found for the monomer (table 6.4), but have been shifted upfield when the double bonds are broken.

In the above spectrum, the backbone methylene and quaternary carbon peaks of the precipitated polymer may be seen at chemical shifts of 45.0 δ (ppm) (peak B2) and 36.7 δ (ppm) (peak A2), respectively.

6.5.1 Methods for determining conversion

Using, as an example, the sample referred to in figure 6.3, and the appropriate integral values, conversion was determined. Conversion was determined by comparison of the integrals of the monomer/polymer ^1H NMR peaks. The reference peaks given in table 6.5 were used.

Table 6.5 Conversion values of monomer into polymer according to calculations using certain peaks in the ^1H NMR spectrum of polylauryl methacrylate for reference. Refer to figure 6.3 for peak assignments.

Peak	A	B	C	D	E
Integral value	1.0	1.0	82.90	849.90	205.70
Conversion (%)			97.60	99.90	98.60
Average conversion (%)				98.70	

Peaks A and B are the monomer peaks, which were assigned a relative value of 1.0. Peaks C, D and E belong to the tail hanging off the backbone of LMA. These peaks will have the same chemical shifts for both the monomer and polymer. By assigning the monomer peaks an integral value of 1 in the ^1H NMR spectrum, the integral values of the peaks C, D and E will give an indication of the relative amounts of protons present in the polymer chain. Through comparison using the integral values of the monomer, polymer, and total peaks, the conversion of the polymer was determined.

6.5.2 Calculations used to determine the conversion

Peak C

This is the $-\text{CH}_2\text{-O}$ peak. The integral value was divided by 2, since this peak corresponds to two protons per monomer unit. This value is then divided by (itself +1). This group is present in both the monomer and polymer. Equation 6.1 shows an example calculation.

$$\begin{aligned} \text{Conversion (\%)} &= \frac{\frac{82.9}{2}}{\left(\frac{82.9}{2}\right)+1} \times 100 && (6.1) \\ &= 97.60\% \end{aligned}$$

Peak D

These peaks belong to the CH₂ peaks along the chain hanging off the polymer backbone. The first two CH₂ groups have a different chemical shift to the last nine. Peak D refers to the chemical shifts of the last nine. There are 18 protons present in this group. These 18 protons are subtracted from the integral value, and this value is then divided by (itself + 1). This group is present in both the monomer and polymer. Equation 6.2 shows an example calculation.

$$\begin{aligned}\text{Conversion (\%)} &= \frac{849.9-18}{(849.9-18)+1} \times 100 && (6.2) \\ &= 99.90\%\end{aligned}$$

Peak E

This peak refers to the methyl group hanging off the long alkyl side chain. It has three protons. These three protons are subtracted from the integral value, which is then divided by 3. This value is in turn divided by (itself + 1). This group is present in both the monomer and polymer. Equation 6.3 shows an example calculation.

$$\begin{aligned}\text{Conversion (\%)} &= \frac{\left(\frac{205.7-3}{3}\right)}{\left(\frac{205.7-3}{3}\right)+1} \times 100 && (6.3) \\ &= 98.60 \%\end{aligned}$$

The % conversions as determined from the integrals of each of these three peaks seem to show good correspondence with each other. By dividing the sum of the three conversion values by 3, we may then calculate the average conversion (eq. 6.4).

$$\begin{aligned}\text{Average \% conversion} &= \frac{(97.6+99.9+98.6)}{3} && (6.4) \\ &= 98.70 \%\end{aligned}$$

6.5.3 Molecular weights

Samples of PLMA were analysed by means of GPC. Due to the long inhibition period of the LMA monomer, associated with ATRP, earlier samples did not provide much useful GPC data. The signal corresponding to the ligand complex overpowers the signal due to the polymer peak at low conversions / \bar{M}_n . The later (higher conversion / \bar{M}_n) samples could provide information about molecular weights and molecular weight distributions. Table 6.6 shows some molar mass data and figure 6.9 shows the molecular weight distributions of the last two samples and the polymer (after precipitation).

Table 6.6 Molecular weight data for polylauryl methacrylate

	Time (h)	\bar{M}_n	\bar{M}_p	PDI
Entire reaction mixture	6.58	13 200	25 300	1.65
Entire reaction mixture	27.25	16 000	20 580	2.67
Purified polymer	27.25	21 400	58 900	2.65

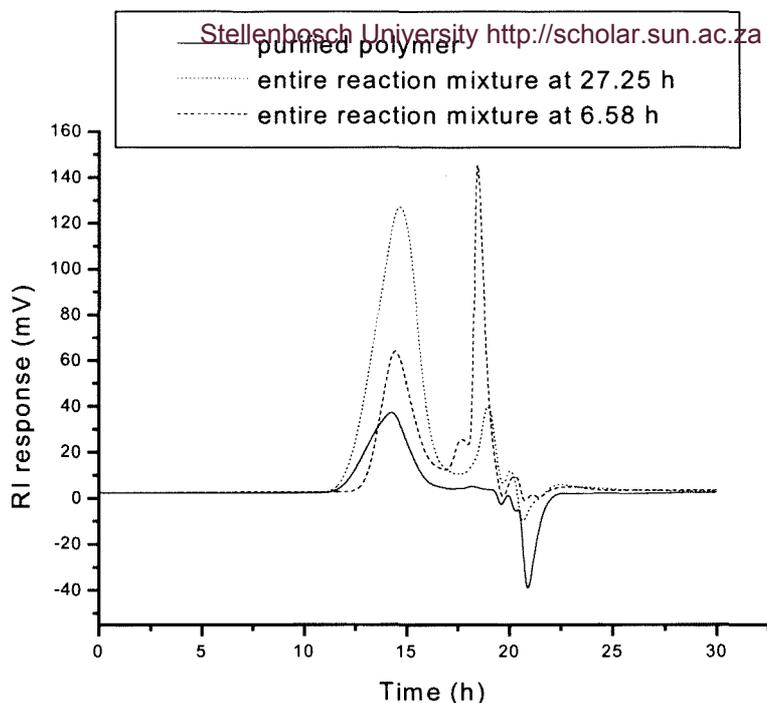


Figure 6.10 Overlay of the GPC chromatograms of the final two samples of the polymerisation of LMA as well as the purified polymer.

6.6 SUMMARY OF RESULTS OF LMA ATRP REACTIONS

The NMR spectra of polylauryl methacrylate indicate the presence of both the backbone and tail peaks (figures 6.8 and 6.9). These were used to obtain conversion data, which were calculated through the use of integration of monomer and polymer peaks as reference in the ^1H NMR spectra. Fairly consistent results were obtained (table 6.5). The GPC chromatograph shows that growth of the polymer took place (figure 6.10) and that the \bar{M}_n increased with time (table 6.6).

This polymer was used as a macro-initiator in the presence of MMA monomer to determine if it contains enough active chain ends to allow growth of a second block to take place (see sections 7.8 and 7.9).

¹http://sartomer.com/catalog_names.html

²<http://www.sartomer.com/wpapers%5C4115.pdf>

³<http://www.chemicalLAND21.com>

⁴ Sannigrahi, B.; Wadgaonkar, P. P.; Sehra, J. C.; Sivaram, S. *J. Polm. Sci., Part A: Polym Chem.*, **1997**, *35*, 1999

⁵ Chern, C. S.; Chen, T. *J. Colloids and Surfaces* **1998**, *138*, 65

⁶ personal communication with Dr. Kibret Mequanint. E-mail address: kibretmequanint@yahoo.com

⁷ Mark, H. F.; Gaylord, N. G.; Bikales, N. M. *Encyclopedia of Polymer Science and Technology*, **1969**, *8*, 309

7. SYNTHESIS OF BLOCK COPOLYMERS OF LAURYL- AND METHYL METHACRYLATE VIA ATRP

7.1 ABSTRACT

Attempts were made to form controlled block copolymers from methyl methacrylate (MMA), and lauryl methacrylate (LMA, or dodecyl methacrylate) as starting materials.

7.2 INTRODUCTION

Controlled polymers of the monomer lauryl methacrylate (LMA) have not, according to a literature study, been synthesized by ATRP. The first objective of the study involved the polymerisation of LMA by ATRP (chapter 6). The use of these polymers as macro initiators to form block copolymers has also not been previously described in the literature, and is the topic of the second objective, which is to form block copolymers of LMA and methyl methacrylate (MMA).

Through the copolymerisation of two or more monomers, new materials may be formed which have significantly better properties than those of the original components. An example is the incorporation of 20-35 % of acrylonitrile into a polystyrene backbone by copolymerisation, which produces a transparent copolymer with better oil and grease resistance, better impact resistance and a higher softening point than the corresponding polystyrene homopolymer. Styrene-acrylonitrile (SAN) ^[1] and acrylonitrile-butadiene-styrene (ABS) ^[2] copolymers are widely produced.

Similarly, it was thought that the addition of a small fraction of PMMA-*b*-PLMA-*b*-PMMA to Perspex (PMMA), or a similar material, might improve the impact resistance and physical properties.

7.3 APPLICATIONS

Lauryl methacrylate copolymers have been used in skin and hair care products. Styleze 2000 ^[3] is a copolymer derived from vinyl-pyrrolidone, acrylic acid, and lauryl methacrylate. This product forms clear gels, which can be applied to hair.

Other applications of LMA include use to form a copolymer with polyethylene oxide and methyl methacrylate. This copolymer can then be used as an electrolyte in lithium ion batteries ^[4]. Other uses include adhesives, binders and plasticized rubbers ^[5].

7.4 EXPERIMENTAL

Materials. Refer to sections 3.2.1 and 6.3.1 for materials used.

Analytical methods. Refer to sections 3.2.1 and 6.3.1 for a summary of the methods that were used to analyse the polymers.

7.5 RE-INITIATION OF METHYL METHACRYLATE

The polymers that were synthesized in section 3.3 were used in further reactions to determine if they were living by using them as macro-initiators in the presence of MMA monomer. A lower monomer to initiator molar ratio was used in these reactions compared to section 3.3 in order to produce fewer chains that were longer. See table 7.1 for reaction conditions of reactions 1.1 and 2.1.

Table 7.1 Experimental conditions for block copolymerisation reactions.
Reaction temperature 70 °C

Reaction	Masses (g)							Reaction time (h)
	MMA	LMA	Cu ^I	PMMA	PLMA	BPY	2-butanone	
1.1	10.00		0.14	1.00		0.24	10.00	6.5
2.1	25.00		0.36	2.50		0.86	25.00	6.5
8	20.00		0.17		0.22	0.37	20.00	6
9		20.00	0.29	0.19		0.68	20.00	11.3

Reaction 1.1

1337 : 13.4 : 1 : 30

MMA Cu^I PMMA BPY

In reaction 1.1 (using the polymer from section 3.3, reaction 1), PMMA (1.00 g, 0.074 mmol), Cu^IBr (0.14 g, 0.99 mmol), BPY (0.86 g, 2.18 mmol), MMA (10.00 g, 99.9 mmol) and 2-butanone (10.00 g, 138 mmol) were added to a 150 mL schlenk tube. The same experimental procedure was followed as described in section 3.3.

Reaction 2.1

1116 : 11 : 1 : 24.5

MMA Cu^I PMMA BPY

In reaction 2.1 (using polymer from section 3.3, reaction 2), PMMA (2.50 g, 0.22 mmol), Cu^IBr (0.36 g, 2.50 mmol), BPY (0.86 g, 5.47 mmol), MMA (25.00 g, 249 mmol) and 2-butanone (25.00 g, 347 mmol) were added to a 150 mL schlenk tube. The same procedure was followed as described in section 3.3.

The calculated molecular weight for the product to be formed is given by equation 7.1.

$$\bar{M}_{n\text{cal}} = \frac{m_{\text{monomer}} + m_{\text{initiator}}}{m_{\text{initiator}}} \times \bar{M}_{n\text{initiator}} \quad (7.1)$$

Here, m_{monomer} and $m_{\text{initiator}}$ refer to the individual masses of the monomer and initiator respectively. $\bar{M}_{n\text{initiator}}$ refers to the number-average molecular mass of the initiator.

7.6 RESULTS AND DISCUSSION FOR REACTION 1

Polymer from reaction 1 (section 3.3) was used as a macro-initiator in a further reaction (1.1, section 7.5) in the presence of MMA to determine if it could initiate the growth of a second block of MMA. This was a test of the livingness of the polymer. The GPC chromatogram (figure 7.1) of reaction 1.1 is shown below, and the molecular weight data of both the macro initiator and product it formed is shown in table 7.2.

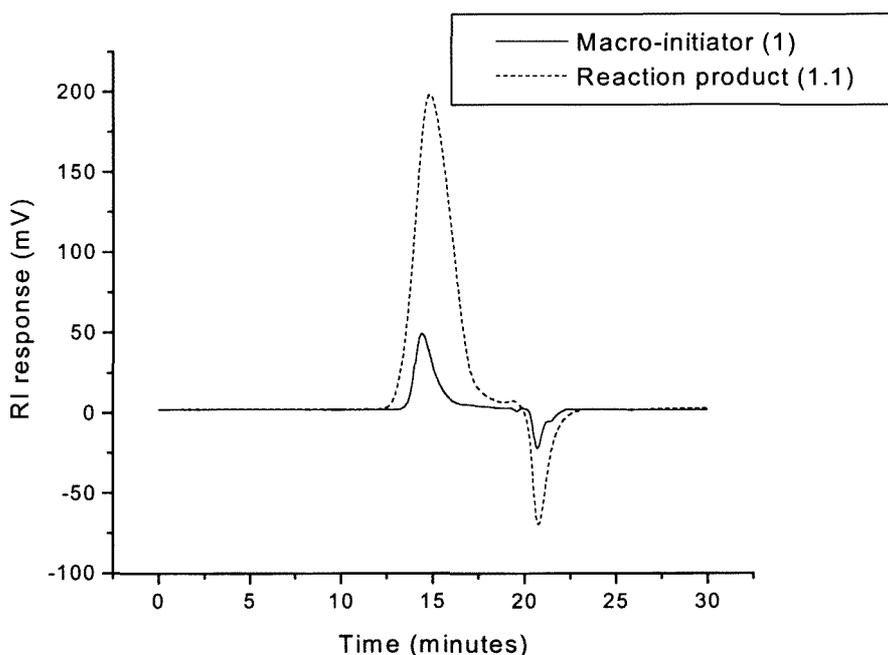


Figure 7.1 Overlay of the GPC chromatographs of the macro-initiator (reaction 1) and the product (reaction 1.1) after re-initiation of PMMA in the presence of MMA.

Polymerisation of 20.00 g MMA in 20.00 g 2-butanone at 70 °C.

Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

Table 7.2 Molecular weight data; comparison of the macro-initiator (reaction 1) and the product (reaction 1.1) after re-initiation of PMMA in the presence of MMA

	\bar{M}_n	\bar{M}_p	PDI
Macro-initiator 1	10 300	28 400	2.19
Reaction product 1.1	7000	17 000	2.74

This polymer (reaction 1) did not shift the molecular weight of the product it formed compared to its own molecular weight when polymerised again with MMA. The calculated molecular weight was $113\,300\text{ gmol}^{-1}$ (eq. 7.1). The polydispersity however did broaden (2.74) and the \bar{M}_n shifted to a lower molecular weight than that of the macro-initiator. There was considerable tailing of the product formed on the low molecular weight side. This is indicative of the presence of low molecular weight species. Therefore, it seems that new polymer chains were initiated and that when \bar{M}_n is calculated, it would take the presence of these short chains into account and cause this value to be smaller. There is also a slight tailing on the high molecular weight side. This implies that a small percentage of chains may have been re-initiated to increase in molecular weight. The chromatogram indicates that the possibility is strongly in favour of new homopolymer being formed instead of a block being formed.

When the PMMA from reaction 1 (section 3.3) was used to form a block with LMA (reaction 9) the polydispersity indexes are very broad (± 12) (figure 7.2 and table 7.3). See table 7.1 for reaction conditions.

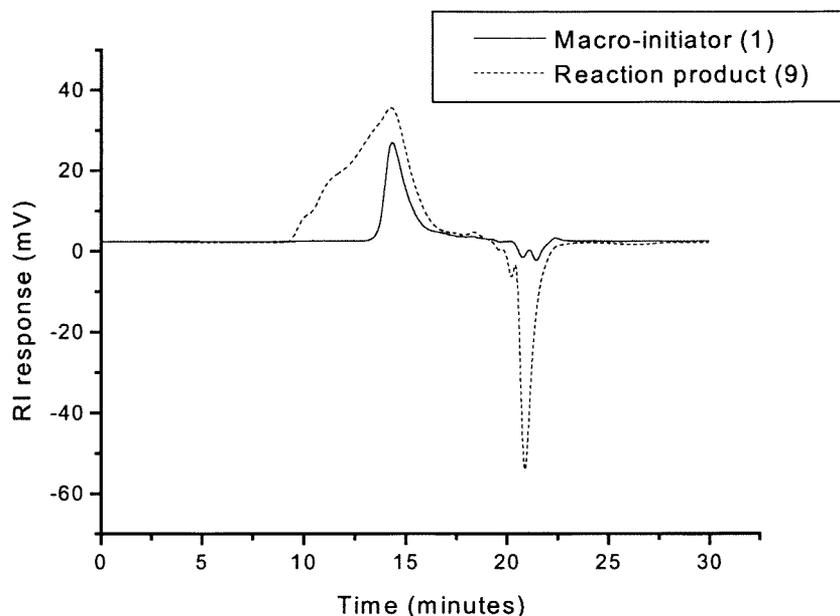


Figure 7.2 Overlay of the GPC chromatographs of the macro-initiator (reaction 1) and the product (reaction 9) after re-initiation of PMMA in the presence of LMA. Polymerisation of 20.00 g LMA in 20.00 g 2-butanone at 70 °C. Monomer / CuBr / PMMA / BPY = 531 / 26.5 / 1 / 80.5

Table 7.3 Molecular weight data; comparison of the macro-initiator (reaction 1) and the product (reaction 9) after re-initiation of PMMA in the presence of LMA

	\bar{M}_n	\bar{M}_p	PDI
Macro-initiator 1	10 300	28 400	2.19
Reaction product 9	26 200	30 000	12.83

From figure 7.2 one can clearly see that a shoulder has formed on the high molecular weight side of the distribution. This suggests the occurrence of a bimodal distribution, or even a multi modal distribution. They may be overlapping and masked by the higher molecular weight species. It is quite clear from figure 7.2 that there is a considerable amount of high molecular weight species present due to the broad shoulder and increase in molecular weight, as seen by the shift in the peak of the product formed compared to the macro-initiator. There is a small amount of low

molecular weight species which are present in the product formed from reaction 9. This is indicative of short new chains present. The results of this chromatogram suggest that a large number of chains of the macro-initiator were living and were able to allow LMA monomer to polymerise further and form a block product. Because the polydispersity is very broad, it seems as though extension of the macro-initiator was possible but the growth was uncontrolled.

7.7 RESULTS AND DISCUSSION FOR REACTION 2

Polymer from reaction 2 (section 3.3) was used as a macro-initiator in a further reaction (2.1, section 7.5) in the presence of MMA to determine if it could initiate the growth of a second block of MMA. This was a test of the livingness of the polymer. The GPC chromatogram (figure 7.3) of reaction 2.1 is shown below, and the molecular weight data of both the macro-initiator and product it formed are shown in table 7.4.

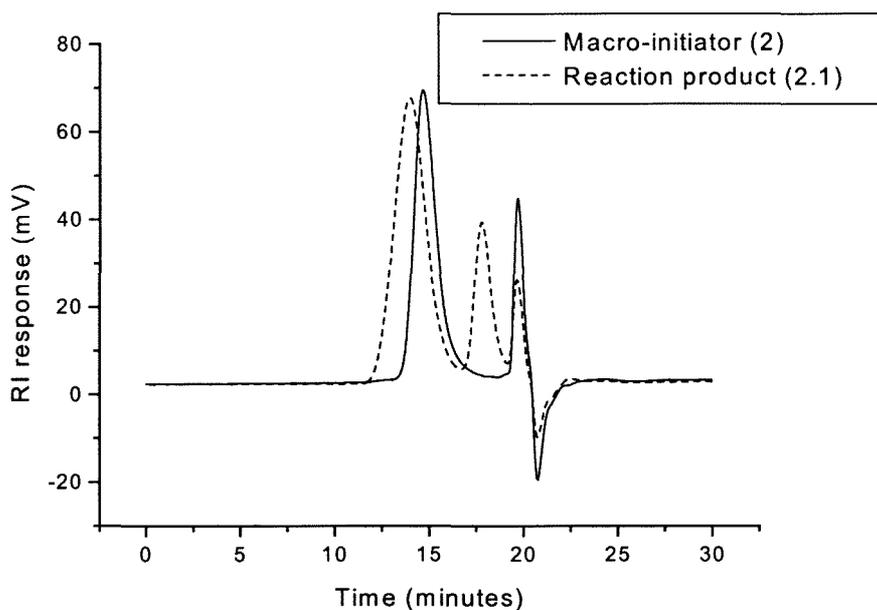


Figure 7.3 Overlay of the GPC chromatographs of the macro-initiator (reaction 2) and the product (reaction 2.1) after re-initiation of PMMA in the presence of MMA. Polymerisation of 25.00 g MMA in 25.00 g 2-butanone at 70 °C. Monomer / CuBr / TsCl / BPY = 100 / 1 / 0.5 / 2.2

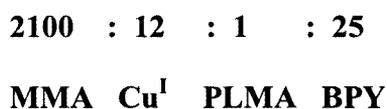
Table 7.4 Molecular weight data; comparison of the macro-initiator (reaction 2) and the product (reaction 2.1) after re-initiation of PMMA in the presence of MMA

	\bar{M}_n	\bar{M}_p	PDI
Macro-initiator	11 488	20 541	1.67
Reaction 2.1	25 771	40 429	2.01

Although the calculated molecular weight ($123\,000\text{ gmol}^{-1}$) (eq. 7.1) is much higher than the experimental molecular weight ($25\,771\text{ gmol}^{-1}$), there is an observable increase in molecular weight over that of the macro-initiator, as seen from figure 7.3 and table 7.4. From figure 7.3, it is quite clear that there is a bimodal distribution. The possibility exists that, because there was a clear increase in molecular weight, a fair percentage of chains from the macro-initiator were re-initiated. The lower molecular weight peak indicates that a number of new chains were initiated.

7.8 RE-INITIATION OF LAURYL METHACRYLATE

Polylauryl methacrylate from reaction 6 was used as the macro-initiator for the synthesis of a further block of methyl methacrylate (reaction 8). See table 7.1 for reaction conditions. The following ratios were used.



In this reaction, PLMA (2.00 g, 0.1 mmol), $\text{Cu}^{\text{I}}\text{Br}$ (0.17 g, 1.18 mmol), BPY (0.37 g, 2.36 mmol), MMA (20.00 g, 200 mmol) and 2-butanone (20.00 g, 277 mmol) were added to a 150 mL schlenk tube. The same experimental procedure was followed as described in section 3.3. A white / green polymeric product resulted from this polymerisation, which was analysed by GPC.

7.9 RESULTS AND DISCUSSION FOR REACTION 8

Polymer from reaction 6 (section 6.4) was used as a macro-initiator in a further reaction (reaction 8, section 7.8) in the presence of MMA to determine if it could initiate the growth of a second block of MMA. This was a test of the livingness of the polymer. The GPC chromatogram (figure 7.4) of reaction 8 is shown below, and the molecular weight data of both the macro-initiator and product it formed are shown in table 7.5.

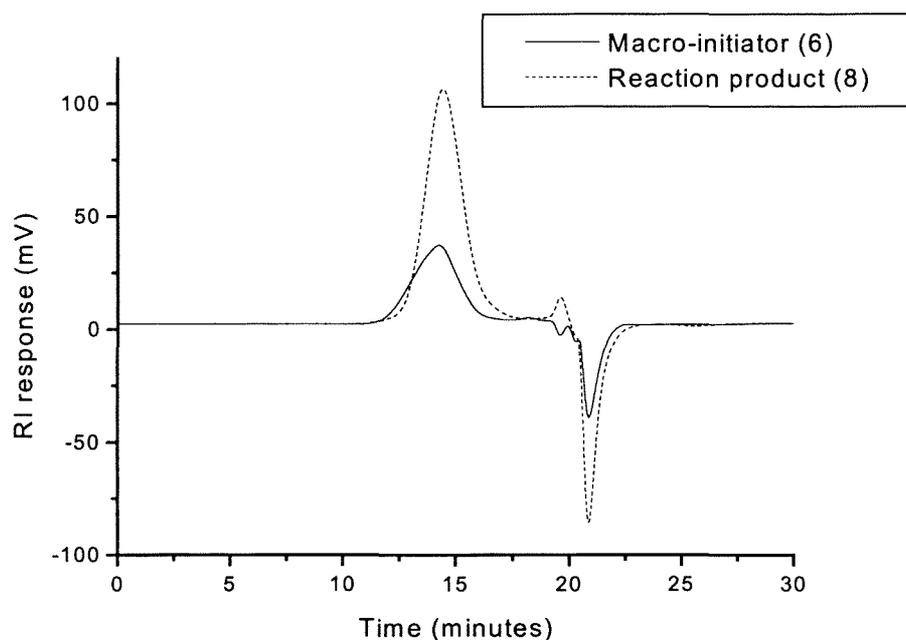


Figure 7.4 Overlay of the GPC chromatographs of the macro-initiator (reaction 6) and the product (reaction 8) after re-initiation of PLMA in the presence of MMA.

Polymerisation of 20.00 g MMA in 20.00 g 2-butanone at 70 °C.

Monomer / CuBr / PLMA / BPY = 2100 / 12 / 1 / 25

Table 7.5 Molecular weight data; comparison of the macro-initiator (reaction 6) and the product (reaction 8) after re-initiation of PLMA in the presence of MMA.

	\bar{M}_n	\bar{M}_p	PDI
Macro-initiator 6	21 400	58 900	2.65
Reaction product 8	15 400	25 500	2.19

The calculated molecular weight ($213\,000\text{ gmol}^{-1}$) (eq. 7.1) is much higher than the experimental molecular weight ($15\,400\text{ gmol}^{-1}$). There is a considerable amount of tailing towards the low molecular weight side (figure 7.4). This suggests that a large amount of new chains had started to grow instead of the chains of the macro-initiator, allowing a second block to grow. This is the reason for the \bar{M}_n shifting to a lower molecular weight, as the calculations take into consideration the formation of these new shorter chains.

7.10 SUMMARY OF RESULTS OF ATTEMPTS AT BLOCK COPOLYMERISATIONS

The product formed from reaction 1.1 (section 7.6) was not as desired, but when the same macro-initiator (reaction 1, section 3.3) was used in the presence of LMA monomer, the polymer did show the probable formation of a block copolymer (reaction 9, section 7.6), although the growth which took place proceeded in an uncontrolled manner. Refer to table 7.3 for molecular weight data.

The macro initiator from reaction 2 (section 3.3) showed desirable results when used in a further reaction with MMA monomer to test the livingness of the polymer (reaction 2.1, section 7.7). The product had shifted to higher molecular weight compared to the macro-initiator. Refer to table 7.4 for molecular weight data.

When polylauryl methacrylate from reaction 6 (section 6.3) was used as a macro-initiator in the presence of MMA monomer (reaction 8, section 7.9), the GPC did not display as good results as it had for MMA chain extensions.

No extra initiator was added to the reactions in which macro-initiators were used. Although growth seems to have been initiated, it cannot be said for certain how re-initiation takes place. There is the possibility that contaminants in one of the reactants used may have caused initiation, or there may be several initiator molecules still present in the macro-initiator that were not yet used, or even that the monomer undergoes chain transfer reactions.

Table 7.6 Molecular weight data for reactions 1, 1.1, 2, and 2.2 of MMA polymerisations done via ATRP.

	\bar{M}_n	\bar{M}_p	PDI
Macro-initiator 1	10 300	28 000	2.18
Reaction product 1.1	7000	17 000	2.74
Macro-initiator 2	11 200	20 000	1.75
Reaction product 2.1	25 771	40 000	2.01

¹ Haggard, K. W.; Paul, D. R. *Polymer*, **2002**, *43*, 3727

² Tiganis, B. E.; Burn, L. S.; Davis, P.; Hill, A. J. *Polymer Degradation and Stability*, **2002**, *76*, 425

³ [http://www.ispcorp.com/products/hairskin/prod cat/01 fix.html](http://www.ispcorp.com/products/hairskin/prod%20cat/01fix.html)

⁴ <http://flux.aps.org/meetings/YR97/BAPSMAR97/abs/S4080006.html>

⁵ <http://www.rohmmaas.com/monomers/products.html>

8. CONCLUSIONS

8.1 MMA ATRP REACTIONS

The objective was to obtain polymers of MMA with good characteristics, such as high molecular weight and narrow polydispersities, in order for it to be used as a macro-initiator in the presence of LMA monomer to produce block copolymers.

The MMA that was polymerised using $\text{Cu}^{\text{I}}\text{Br}$ as catalyst showed that almost complete conversion took place, good linear rate plots, an increase in the molecular weight and a fairly narrow polydispersity range. The final polydispersity of the polymer was below 1.5.

When $\text{Cu}^{\text{I}}\text{Cl}$ was used as a catalyst, the molecular weight data improved remarkably. The polydispersity of the final MMA polymer was 1.28, and the molecular weight was around 6000 gmol^{-1} .

8.2 4-VINYLPYRIDINE

The objective was to synthesize P4VP by ATRP. However, due to broad polydispersities occurring repeatedly, the focus of the work shifted to an investigation of the possible factors that could contribute to such a broad polydispersity index.

^{13}C NMR results of mixtures of 4VP, 1-PECl and iPrOH showed that the individual chemical shifts of the pure compounds differed to when the compounds were in a mixture. Results of experiments gave clear indications that the presence of the solvent can cause differences in the chemical shifts to occur. This would also affect the reactivity of the compounds and cause them to react differently in the ATRP reaction process.

^{35}Cl NMR results obtained indicated that a quaternary species was only formed in the presence of D_2O , and not under the reaction conditions that were used to synthesize 4VP via ATRP.

8.3 LMA ATRP REACTIONS

The objective was to synthesize LMA by ATRP and to then use this polymer as a macro-initiator in the presence of MMA monomer to produce block copolymers.

The ^1H NMR spectra showed that conversion took place with reaction time, and GPC results showed that growth of the polymer took place and that the \bar{M}_n increased with time.

When $\text{Cu}^{\text{I}}\text{Cl}$ was used as a metal catalyst instead of $\text{Cu}^{\text{I}}\text{Br}$, no polymer was obtained. The reason why the molecular weight data improved when $\text{Cu}^{\text{I}}\text{Cl}$ was used as catalyst for the MMA reactions, and why there was no significant effect when $\text{Cu}^{\text{I}}\text{Cl}$ was used for the LMA polymerisations, is not known.

8.4 BLOCK COPOLYMERS

The objective was to determine if it was possible to synthesize block copolymers of LMA and MMA with narrow polydispersities, by ATRP.

When MMA macro-initiator was used in the presence of MMA monomer, the resulting product showed a shift in the molecular weight compared to that of the macro initiator. When MMA macro-initiator was used in the presence of LMA monomer, the polymer did show the possible formation of a block copolymer, although the growth which took place proceeded in an uncontrolled manner.

When LMA macro-initiator was used in the presence of MMA monomer, the GPC did not display the good results as it had for MMA chain extensions.

Conclusions are that MMA would be preferable as a macro-initiator instead of LMA, but still, the growth is not controlled.