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STUDIES IN THE ANIONIC POLYMERIZATION OF METHYL METHACRYLATE

COLIN JAMES CROOK

Doctor of Philosophy

ASTON UNIVERSITY

October 1999

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SUMMARY

A study has been made of the anionic polymerization of methyl methacrylate using butyllithium and polystyryl lithium as initiators and using aluminium triisobutyl as a cocatalyst. The aspects of the polymerization that were examined were the effect of changing the order of addition of reagents, the temperature at which polymerization takes place and the polarity of the solvent. Trends were assessed in terms of molecular weight, molecular weight distribution and tacticity. In addition, a second monomer addition test was carried out to verify that the polymerization was truly a living one, and a kinetic study was attempted.

Studies to investigate the effect of changing the order of addition of reagents showed that polymer with similar polydispersities and tacticities are produced whether the pre-mixing (mixing initiator and cocatalyst before addition of monomer) or the post-mixing (mixing monomer and cocatalyst before addition of initiator) method were used. However, polymerizations using the post-mixing method demonstrated lower initiator efficiencies, possibly indicating a different initiating species. Investigations into the effect of changing the polymerization temperature show the molecular weight distribution to narrow as the temperature decreases, although a small amount of low molecular weight tailing was also observed at low temperature. A clear relationship between tacticity and temperature was observed with syndiotacticity increasing with decreasing temperature. Changes in solvent polarity were achieved by using mixtures of the standard solvent, toluene, with varying amounts of cyclohexane, tetrahydrofuran or dichloromethane. Experiments at low solvent polarity (using toluene/cyclohexane mixtures) showed problems with initiator solubility but produced polymer with lower polydispersity and higher syndiotacticity than in toluene alone. Experiments using toluene/THF mixtures yielded no polymer, thought to be owing to a side reaction between THF and aluminium triisobutyl. Increased solvent polarity, achieved using toluene/dichloromethane mixtures produced polymer with higher polydispersity and at lower yields than the conventional system, but also with higher syndiotacticity.

Second monomer addition reactions demonstrated that the polymerization was 'living' since an increase in molecular weight was observed with no increase in polydispersity.

Kinetic studies demonstrated the high speed of the polymerization but yielded no useful data.

Key words: Lithium alkyls, Aluminium Alkyls, Tacticity, Quench Flow Reactor, Living.

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CHAPTER ONE

INTRODUCTION

1.1 Scope of the work

Anionic polymerization has, in the latter half of the century, become an extremely useful and widely implemented technique¹⁻¹². The reason for this intense interest is the ability of anionic systems, like few others, to polymerize without transfer or termination steps under suitable conditions. This can lead to the production of polymers with well-defined architectures and with narrow molecular weight distributions. Polymerizations which behave in this manner are known as 'living' systems and were first described as such by Szwarc.

Aside from the ability to control molecular weight and molecular weight distribution that anionic polymerization gives, many other benefits stem from the fact that the reactive end of the 'living' polymer remains active after the polymerization is finished. This enables the polymer to then undergo subsequent reactions to produce functionally terminated polymers or block copolymers. The ability to synthesise block copolymers is of particular importance, and is the main commercial use for anionic polymerization. Block copolymers are widely used as thermoplastic elastomers by virtue of their ability to 'microphase separate', i.e. the incompatible blocks of the copolymer try to separate and can form microstructures of varying morphologies. These types of material can be used in such diverse applications as the production of adhesives, paints, sponges, films, surgical sutures, dialysis membranes and prosthetic materials. Amphiphilic block

copolymers, i.e. containing both hydrophilic and hydrophobic blocks, have commercial application as solubilisers, dispersants, compatibilisers and emulsifying agents.

Poly(methyl methacrylate) is of enormous commercial importance by virtue of its transparency and optical clarity, particularly useful in the contact lens industry, and also its cost. It is generally made commercially by a conventional free-radical process, as this is the cheapest and easiest method available. However, this process leads to polymers with broad molecular weight distributions, and does not make possible the synthesis of well-defined block copolymers. The anionic polymerization of methyl methacrylate would be seen as the obvious path to block copolymers, yet the innate chemistry of the monomer leads to intrinsic side reactions, making true 'living' polymerization problematic.

This chapter serves as an introduction to anionic polymerization, and also outlines some of the work that has been carried out regarding the anionic polymerization of methyl methacrylate.

1.2 General principles of polymerization

The concept of the polymer chain was first introduced by Staudinger in 1920¹³. It was a concept which met with a great deal of disfavour at the time but eventually earned the Nobel Prize in 1953. He proposed long chain structures for polystyrene, natural rubber, and polyoxymethylene.

Staudinger's macromolecular viewpoint was given quantitative support by a series of experiments conducted in 1929 by Caruthers¹⁴ who suggested classification of polymers into two groups, *condensation* and *addition* polymers. A condensation polymer was

defined as one which eliminates a small molecule, such as water, as it forms. In the formulation of addition polymers, this loss of a small molecule does not take place.

These distinctions were amended by Flory who placed more emphasis on the actual mechanism of the reaction. He redefined condensation polymers, or step growth polymers, as usually being formed by the stepwise intermolecular condensation of reactive groups, and addition polymers, or chain growth polymers, as ordinarily resulting from chain reactions involving some sort of active centre. The piece of research described in this thesis is concerned primarily with addition polymers.

The majority of addition polymers are generated from monomers of the general structure $\text{CH}_2=\text{CR}_1\text{R}_2$. The nature of the π -bonds of these compounds make them susceptible to attack and rearrangement by free radical or ionic initiators. The resulting polymerization can be viewed as a three-stage process.

(i) Initiation

In this stage the active centre responsible for polymerization is produced, usually by the reaction with monomer with an initiating species.

(ii) Propagation

The active centre forms a polymer chain by repeatedly adding further monomer units by a kinetic chain mechanism.

(iii) Termination

The active species is neutralised, resulting in the growth of the polymer chain being halted. Transfer reactions may also take place where the active species can go on to initiate a new polymer chain.

1.2.1 Choice of initiator

Although others exist, there are three main categories of addition polymerization: free radical; cationic; and anionic. The nature of the monomer and the initiator involved in the polymerization largely determines which mechanism takes place. The choice as to which is most suitable mechanism for polymerization depends largely on the nature of the substituents, R_1 and R_2 , in the monomer, and their ability to polarise the π -bond. Electron withdrawing substituents such as $-\text{COOR}$, $-\text{CN}$, and $-\text{CONH}_2$ reduce the electron density of the double bond and therefore favour propagation by an anionic species. Electron donating species such as alkenyl, alkoxy, and phenyl groups, increase the double bond nucleophilicity and encourage attack by cationic initiators.

The ability of the substituents to stabilise the active species through resonance and inductive effects can also be an important factor in determining which mechanisms of polymerization are possible. For example, monomers such as styrene and 1,3-butadiene can undergo polymerization by both ionic mechanisms because of their ability to stabilise both positive and negative charges. Free radical polymerization is an electronically neutral process and so most substituents can provide some stabilisation of the propagating species. Free radical polymerization is therefore very useful since it is possible to polymerize a much greater variety of monomers by this mechanism than by ionic means; however, it tends to be a more uncontrolled process and does not yield a pure linear polymer. Anionic polymerization also holds other significant advantages over free radical polymerization as will be discussed later.

1.3 Anionic polymerization

The polymerization of monomers with strongly electronegative groups – acrylonitrile, vinyl chloride, styrene, and methyl methacrylate, can be initiated either:

- (a), by the addition of an anionic species to monomer to create a carbanion, or
- (b), by the transfer of an electron to monomer to produce an intermediate radical anion.

Mechanism (a) requires an ionic or ionogenic molecule, consisting of an anionic part capable of adding to the carbon-carbon double bond to create a carbanion, and a counterion, or gegen-ion, which may be organic or, more normally, inorganic. Typical initiators include butyllithium, KNH_2 , and Grignard reagents (alkyl magnesium bromides). If the monomer has a strongly electron-withdrawing group, only a weakly electropositive initiator such as a Grignard is required for polymerization, but when the side group is phenyl, or the electronegativity is low, a highly positive metal initiator such as a lithium alkyl compound is needed.

An example of mechanism (a) is the initiation of styrene using butyllithium, which takes place with simple addition of an anion to the monomer, as shown in scheme 1.1.

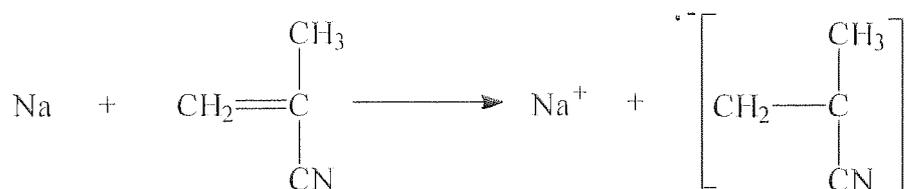
Scheme 1.1 Initiation of Styrene Polymerization by Butyllithium



delocalisation of negative charge
around benzene ring

In mechanism (b), an electron is transferred directly from a donor to the monomer to produce a radical anion. This may be achieved by the use of an alkali metal; for instance Na or K can initiate the polymerization of methacrylonitrile in liquid ammonia at 198K as shown in scheme 1.2.

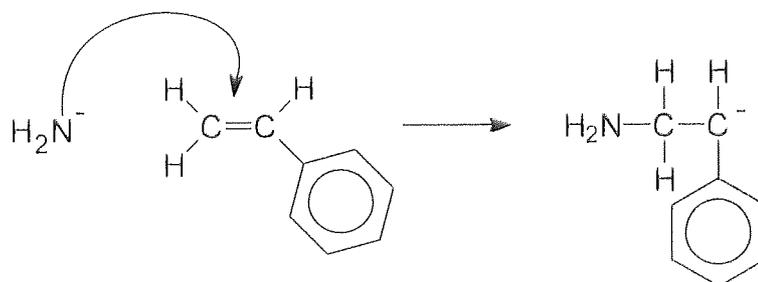
Scheme 1.2 Initiation of Methacrylonitrile Polymerization by Sodium



The resulting radical anion generally dimerises to form a dianion.

One of the first anionic reactions to be studied in detail was the polymerization of styrene in liquid ammonia, with potassium amide as the initiator. The mechanism of initiation is shown in scheme 1.3¹⁴. Potassium amide dissociates into its constituent ions, followed by the addition of the resulting anion to the monomer to create the propagating species.

Scheme 1.3 Initiation of Styrene Polymerization by Potassium Amide.



Anionic polymerizations generally proceed rapidly at low temperatures. Reaction rates depend on the dielectric constant of the solvent, the stability of the carbanion, the electronegativity of the initiator and the degree of solvation of the counterion.

1.4 'Living' polymerization systems

As early as 1936, Ziegler¹⁵ first identified that anionic polymerizations are devoid of intrinsic termination reactions. The absence of this stage in a polymerization mechanism holds significant implications for the way that these reactions are used. Polymerization is, however, sensitive to traces of impurities of water, alcohol, carbon dioxide and oxygen, which are effective terminating agents. Termination can also occur by transfer of a positive fragment, usually a proton from the solvent or some other transfer agent. Exclusion of these impurities from the system imposes the need for rigorous experimental conditions. In 1956, Szwarc⁴ conclusively demonstrated the lack of a termination step in anionic polymerization of vinyl monomers in the absence of impurities. The term 'living polymers' was proposed for those macromolecules since they may spontaneously resume their growth whenever fresh monomer is supplied to the system.

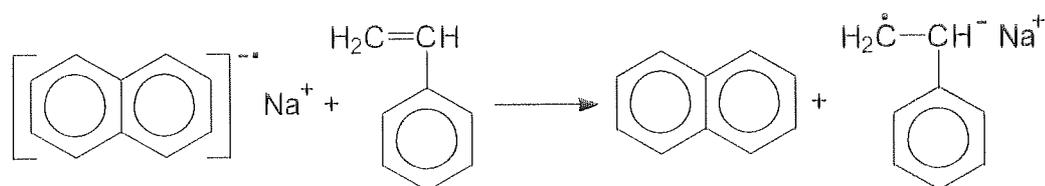
The initial system used by Szwarc was the polymerization of styrene initiated by sodium naphthalide. The initiator was formed by the addition of sodium to naphthalene in 50cm³ of tetrahydrofuran (scheme 1.4).

Scheme 1.4 Formation of Sodium Naphthalide Initiator



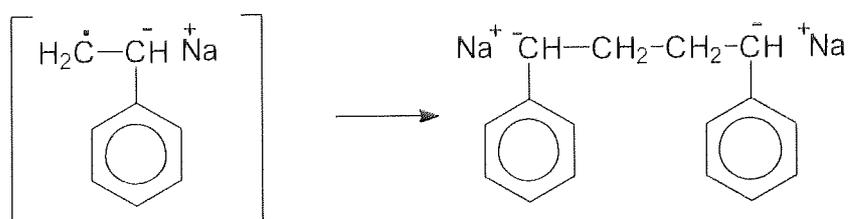
The sodium dissolves in the THF to form a charge transfer complex, which then goes on to form the highly delocalised naphthalide radical anion which has a distinctive green colour. Initiation then occurs by electron transfer to styrene monomer (scheme 1.5). The styryl radical anion produced is red in colour owing to delocalisation of π electrons around the benzene ring of the styryl anion, which absorb electromagnetic radiation in the visible range of the spectrum.

Scheme 1.5 Initiation of Styrene Polymerization by Sodium Naphthalide



A further reaction then occurs where two styryl radical anions combine to form one dianion, which can propagate from both ends (scheme 1.6).

Scheme 1.6 Propagation of Styrene Polymerization Initiated by Sodium Naphthalide



Propagation continues until the monomer concentration reaches its equilibrium value. Since there is no formal termination step, the carbanions are left intact, providing that all impurities that can react with carbanions are removed from the system. This is borne out by the fact that the distinctive red colour of the styryl anion is still present, and also

that the polymerization resumes when fresh monomer is added. Szwarc conclusively demonstrated this, as well as the ability of living polymers to produce block copolymers. He achieved this by the addition of isoprene to living polystyryl ends, resulting in the formation of poly(styrene)-*b*-poly(isoprene).

Although the absence of termination and transfer means that the chains will remain active indefinitely, providing that no terminating impurity is present, living polymers do not become infinitely long. This is because the system contains only a certain number of active centres, and therefore available monomer is distributed among them. Hence, for a perfectly living polymerization, the number average degree of polymerization (\overline{DP}_n) is given by the ratio:

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

where

$[M]_0$ = initial concentration of monomer

$[M]_t$ = concentration of monomer at time t

and

$[I]_0$ = initial concentration of initiator

The resulting polymers ideally have a Poisson molecular weight distribution, provided that propagation is irreversible, the polymerized solution, or melt, remains homogeneous during the whole course of the polymerization, termination and transfer reactions are rigorously excluded, and that the rate of initiation is faster than, or at least equal to, the rate of propagation. Although all these conditions are generally desirable, they are not necessarily defining of a living system.

The lack of a spontaneous termination step does not mean that a living polymer is immortal since the reactive living end of a polymer can be destroyed by certain species. When this occurs, the living chain is said to have been 'killed'. This can be useful as the deliberate introduction of a suitable reagent can yield polymer with a particular functional end group, e.g. $-OH$ or $-COOH$. These polymers, especially difunctional polymers which are known as *telechelic* polymers, can then be used in further reactions and have a wide range of applications.

In theory, a living polymer should retain its activity indefinitely, providing that no terminating reagent is added to the system. However, in practice this is not the case since some feasible slow side reactions are unavoidable. In spite of this, the shelf life of a living polymer is generally believed to be very long, and providing the rates of these side reactions are sufficiently slow to allow the successful completion of the desired task, the system may be defined as a living system.

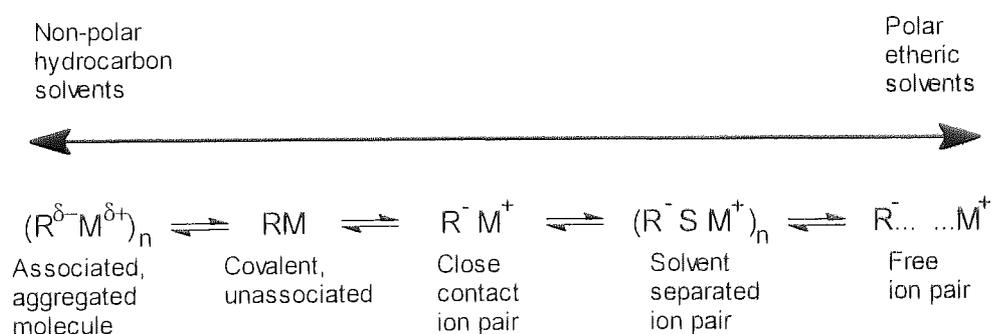
It can be seen, therefore, that the lifetime of a living polymer depends on the nature of the monomer, the conditions prevailing in the polymerization system and the presence of impurities¹⁶. Living polymers tend to decay more slowly at lower temperatures. Indeed, some living polymers have to be kept at low temperature at all times to prevent decomposition during preparation and storage. For most systems, dilution of living polymers is detrimental to their stability, because the ratio of the concentration of the damaging impurities present in the solvent, to the concentration of living polymer ends increases with dilution¹¹. Dilution also affects the degree of aggregation of active species; at lower degrees of aggregation the reactive species are more reactive and therefore more susceptible to destruction by solvent, impurities or side reactions.

In the past, the proportionality of the number-average molecular weight, M_n , to the degree of conversion was generally thought of as sufficient evidence for the ‘livingness’ of a polymerization. However, Penczek *et al*¹⁷ stated that this, whilst proving the absence of transfer during propagation, does not exclude the occurrence of termination. Nevertheless, if a system exhibits such behaviour, and produces polymer with a narrow molecular weight distribution, then this is generally regarded as satisfactory evidence for the living character of a polymerization, especially when the polydispersity decreases with conversion.

1.5 Solvent and counterion effects

Unlike free radical polymerization, where the structure of the chain end is largely independent of the dielectric constant (polarity) of the solvent, and hence the rate is relatively unaffected, the situation of anionic polymerization is more complex. The propagating chain end may exist in a number of forms of varying reactivity (Fig. 1.1).

Figure 1.1 Effect of Solvent Polarity on Nature of Propagating Species



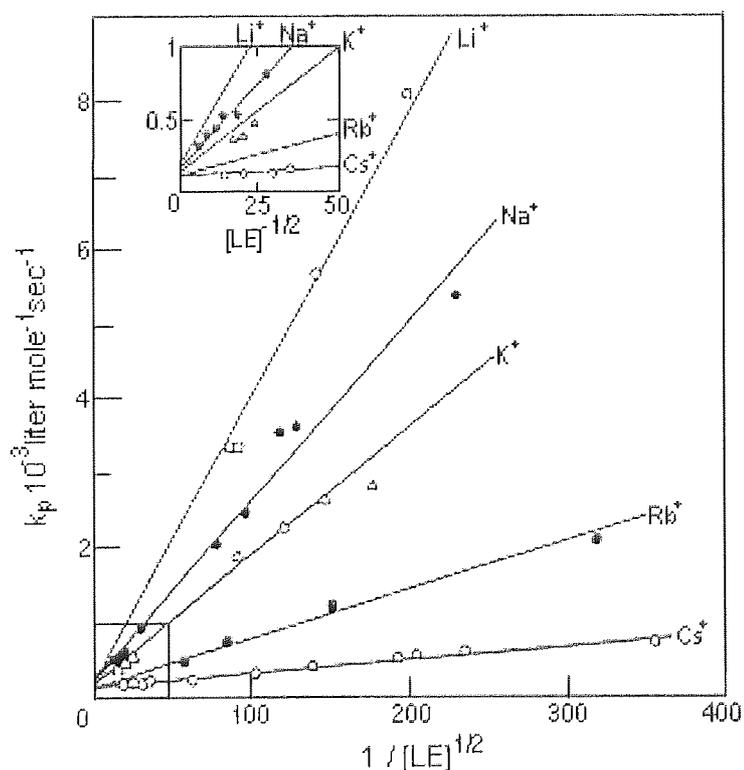
where R denotes the propagating polymer chain, and M denotes the counterion.

For instance, in a polar solvent such as tetrahydrofuran (THF), which has a dielectric constant of 7.6, the equilibrium is shifted towards the right, i.e. favouring dissociated species. In a non-polar solvent such as hexane, which has a dielectric constant of 1.9, the formation of close contact pairs and aggregates of covalent structures is favoured. Evidence suggests that free ions tend to undergo propagation reactions much faster than their relative ion pairs and covalent counterparts. Hence, the rate of polymerization is very much dependent on the solvent used. When interconversion between the various species, i.e. free ions, ion pairs etc., is very rapid, propagating ends have identical probabilities of being found in any of the forms present, which results in an 'averaging-out' of the rate of propagation and allows the production of polymers with narrow molecular weight distributions.

In general, if non-polar solvents are used, solvation hardly occurs and the equilibrium tends towards contact ion pairs or even covalent bonding. Initiators and propagating ends tend to exist as aggregates which can lead to very slow initiation. The steady increase in concentration of propagating living ends may give rise to a broad molecular weight distribution. When low polarity solvents containing electron donor groups, for example ethers and amines, are used, the position of equilibrium tends to favour solvent separated ion pairs, i.e. the ions are solvated but still in close proximity to each other. In this case the activity of the propagating and initiating species is greater than in hydrocarbon solvents, which leads to faster initiation and therefore narrower molecular weight distributions. When polar solvents containing donor groups, for example THF, the equilibrium lies between solvent separated ion pairs and free ions. Initiation is rapid in this case and narrow molecular weight distributions are achieved.

Another factor affecting the position of the equilibrium is the nature of the counterion. Smaller ions such as Li^+ can be solvated more easily than larger ions such as K^+ and Cs^+ , owing their higher charge density. The influence of the counterion on the polymerization of styrene in THF at 298K^{1,2} is shown in figure 1.2. There is an observed decrease in rate associated with an increase in counterion size. This reflects a shift from free ions to ion pairs being the active species, as the ability of the counterion to be solvated decreases.

Figure 1.2 Effect of Change in Counterion on the Polymerization of Styrene in THF at 298K



The effect that solvent polarity has on the structure of the propagating chain end can also be seen in the change of rate of propagation, and hence k_p , the rate constant of

propagation. The rate of propagation of anionic polymerization increases with increasing solvent polarity, e.g. $k_p = 2.0 \text{ liter mol}^{-1}\text{s}^{-1}$ for the anionic polymerization of styrene in benzene, but $k_p = 3800 \text{ liter mol}^{-1}\text{s}^{-1}$ in 1,2-dimethoxyethane. Another effect seen in solvents of higher dielectric constant is that only a complex propagation constant (k_p^{app}) can be obtained, which increases with decreasing concentration of active centres. The existence of an equilibrium involving propagating species also explains this effect because the position of the equilibrium is pushed towards a higher proportion of free ions at higher dilution. The apparent k_p for low degrees of ionisation can be expressed as:

$$k_p^{\text{app}} = k_p^{\pm} + \frac{k_p^{-} K_{\text{diss}}^{1/2}}{[\text{active centres}]^{1/2}}$$

Where k_p^{\pm} = propagation rate constant of ion pairs

k_p^{-} = propagation rate constant of free ions

And K_{diss} = ionic dissociation constant

If k_p^{app} is plotted against $[\text{active centres}]^{1/2}$ the intercept gives k_p^{\pm} directly and the slope gives $k_p^{-} K_{\text{diss}}^{1/2}$. If the ionic dissociation constant (K_{diss}) is known, then k_p^{-} can be evaluated. Some typical values of k_p^{\pm} and k_p^{-} are shown in table 1.1^{1,18}. Although the degree of ionisation is very low in all cases, the presence of very small quantities of free anions is very important because of their extremely high reactivity compared to other structures. However, a high rate of polymerization is not only caused by the presence of free anions. In solvents such as THF, k_p^{\pm} is much higher than the corresponding rate constant in dioxane, because a fraction of the ion pairs (at least for Li^+ and Na^+) is converted into solvent separated ion pairs, which have a reactivity approaching that of

the related free ions. Curious dependencies of rate of polymerization on temperature can occur under certain conditions. These changes result from a dependence of K_{diss} on temperature and the proportions of active species changing accordingly.

Table 1.1 Typical Ion Pair (k_p^+) and Free Anion (k_p^-) Propagation Constants of Some Vinyl Monomers

Monomer-Solvent	k_p^+ For Counter-ion				k_p^-
	Li^+	Na^+	K^+	Cs^+	Free Anion
Styrene-THF, 25°C	160	180	~60	22	6.5×10^4
Styrene-dioxane, 25°C	0.9	3.4	20	24.5	
2-vinylpyridine-THF, 25°C		2.1×10^3		1.5×10^3 (15°C)	10^5
Methyl methacrylate- THF, 98°C	~1	32	~30	33	2×10^3

1.6 The polymerization of styrene initiated by lithium alkyls

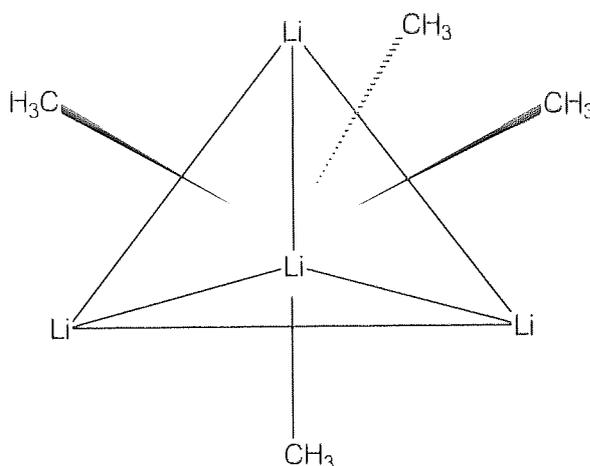
The simplest and most widely used initiators of anionic polymerization are the alkali-metal alkyls. The behaviour of this class of initiators has been studied extensively and indicates a rather complex behaviour¹. Most significant of the alkali-metal alkyls are the lithium alkyls which exhibit some unusual features owing to the small size of the lithium cation, its high electronegativity, and the availability of empty, low-energy *p*-orbitals². Lithium alkyls are soluble in hydrocarbon solvents as associated forms, mostly tetramers or hexamers, and form reversed micelles, i.e. the lithium atoms are in the aggregate centre surrounded by the alkyl groups, each of which appears to be bonded to more than one lithium. These aggregates persist in the most dilute solutions and even in the gas phase. These structures account for their solubility and also their high volatility, e.g. the vapour pressure of butyl lithium is 10^{-4} Torr at 60°C.

Studies of the colligative properties of solutions of alkyl lithiums show that the degree of aggregation is dependent on the nature of the alkyl group and the solvent. Butyllithium and ethyllithium have been shown to be hexameric in hydrocarbons, but tetrameric in diethyl ether¹⁹⁻²¹, whereas a mixture of dimers and trimers of butyllithium is formed in THF. In hydrocarbon solvents and ethers, both *sec*-BuLi and *tert*-BuLi are found to be tetrameric^{22,23}. As a general rule, the degree of aggregation appears to decrease with increasing bulkiness of the alkyl group and increasing polarity of the solvent. Dilution of hydrocarbon solutions of alkyl lithiums has no effect on the degree of aggregation, implying that each alkyl lithium will form only one kind of aggregate in a particular solvent.

Arylmethyl lithiums, such as polystyryl lithium, exhibit lower degrees of aggregation and are usually dimeric in hydrocarbons. It would appear that the C-Li bond in arylmethyl lithiums is more ionic than that of the alkyl lithiums, although the ^{13}C NMR spectrum seems to contradict this, indicating sp^3 hybridisation of the benzylic carbon atom.

X-ray crystallography studies of methyllithium tetramers show the structure to be tetrahedral in shape (see figure 1.3)²⁴. The four lithium atoms form a tight tetrahedral core with the methyl groups placed above each face.

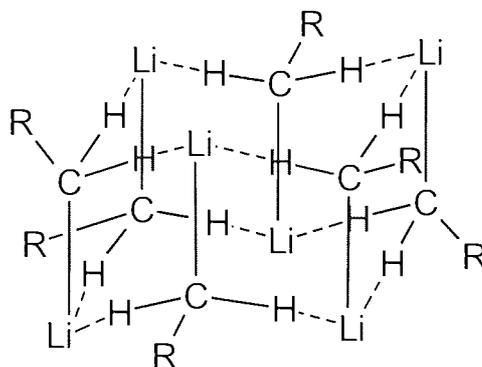
Figure 1.3 Tetrahedral Structure of Methyllithium



The Li-Li bond length of 2.5 Å, is shorter than the length of the Li-Li bond of the Li₂ molecule (2.67 Å). Each lithium atom donates 3 *p*-orbitals to the binding of the aggregate and is associated with the carbon atoms of three methyl groups; each methyl group contributes a single sp^3 orbital, and is linked to three Li atoms. A similar structure is attributed to tetrameric ethyllithium and *t*-butyllithium, whereas a more

complex structure involving Li-C bonds as well as hydrogen bridges was proposed for the hexamers (see figure 1.4).

Figure 1.4 Hexameric Structure of Butyllithium

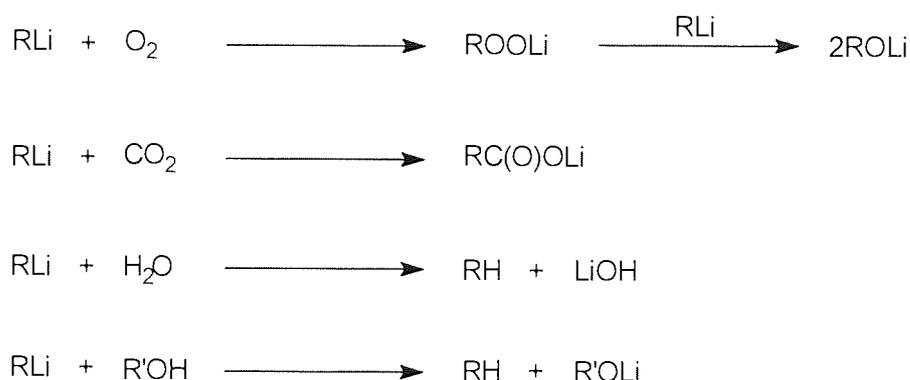


The higher aggregates of lithium alkyls can dissociate in certain solvents to form mixed aggregates.

1.6.1 Initiation

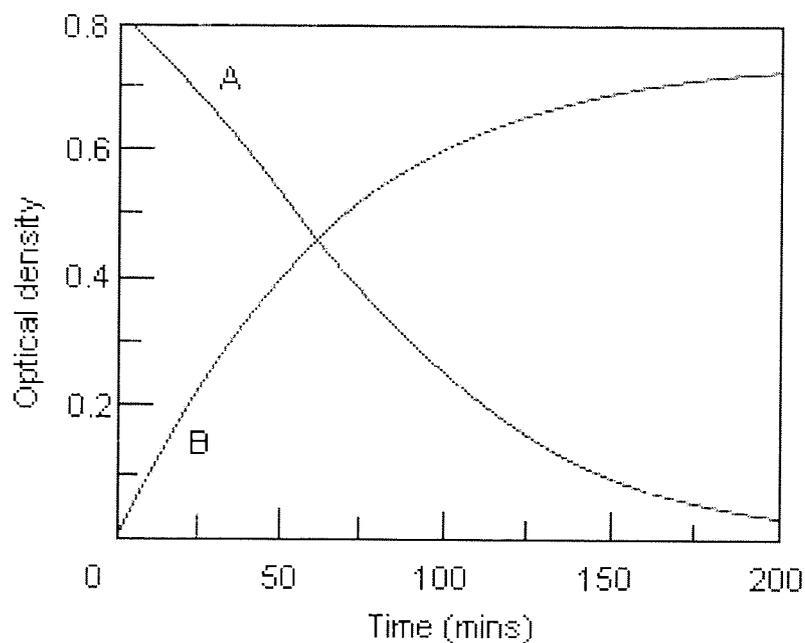
Alkyl lithiums act as initiators for anionic polymerization because they readily react with carbon-carbon double bonds, including those of styrene. However, they also react rapidly with oxygen, carbon dioxide, water, alcohols, etc. (scheme 1.7). Unfortunately, these unwanted reactions tend to occur more rapidly than the desired initiation reaction and so monomers and solvents have to be purged of all traces of impurities before these initiators can be used.

Scheme 1.7 Some Reactions of Lithium Alkyls



Ziegler carried out the first studies into the anionic polymerization of styrene initiated by alkyl lithiums in hydrocarbon solvents¹⁵, and a great volume of research has been carried out since²⁵. Worsfold and Bywater investigated the initiation and propagation of styrene initiated by butyllithium in benzene by following the reaction spectroscopically²³. Initiation produces the lithium salt of polystyryl carbanions that adsorb light at $\lambda_{\text{max}} = 334 \text{ nm}$. The absorbance increased in intensity as the reaction proceeded until it reached a constant value. This is shown by curve B in figure 1.5. The persistence of the absorbance at 334 nm indicates that the polymerization is living. The concentration of styrene, monitored by its absorbance at 291 nm, decays continuously to zero, as shown by curve A in figure 1.5.

Figure 1.5 Conversion Curves Recorded Spectrophotometrically for the
Initiation of Styrene Polymerization in Benzene by Butyllithium



$$[\text{styrene}] = 1.4 \times 10^{-2} \text{M} \quad [\text{BuLi}] = 1.1 \times 10^{-3} \text{M}$$

The initial slope of curve B shown in figure 1.5 may be used to measure the early rate of initiation (R_i). The plot of $\log(R_i/[\text{styrene}]_0)$ as a function of $\log[\text{BuLi}]_0$, given in figure 1.6, is linear for $[\text{BuLi}]_0 > \sim 10^{-4} \text{M}$, implying that the concentration of active species in the early stages of the reaction is proportional to $[\text{BuLi}]^\alpha$, α being the slope of the line shown in figure 1.6. α was found to be $1/6$ and, since BuLi was found to be hexameric in benzene, it was proposed that monomeric BuLi, present in dynamic equilibrium with the hexamers, was the initiating species. The rate of polymerization was then given by:

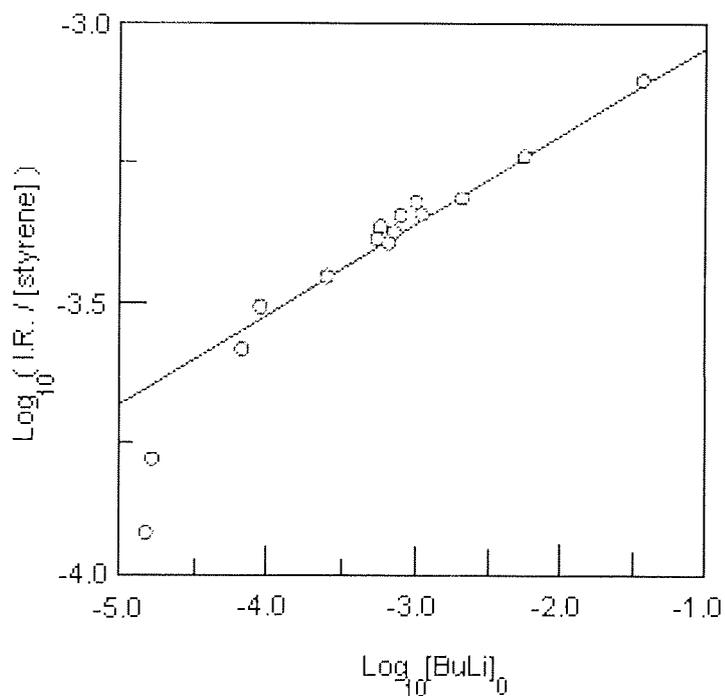
$$\frac{-d[\text{styrene}]}{dt} = k_p \cdot \left(\frac{K_{\text{diss}}}{6} \right)^{1/6} [\text{styrene}] \cdot [\text{BuLi}]^{1/6}$$

where k_p = rate constant of addition of monomeric BuLi to styrene

K_{diss} = equilibrium constant of dissociation of hexamers into monomers

Figure 1.6 The Dependence of the Initial Rate of Styrene Polymerization in Benzene.

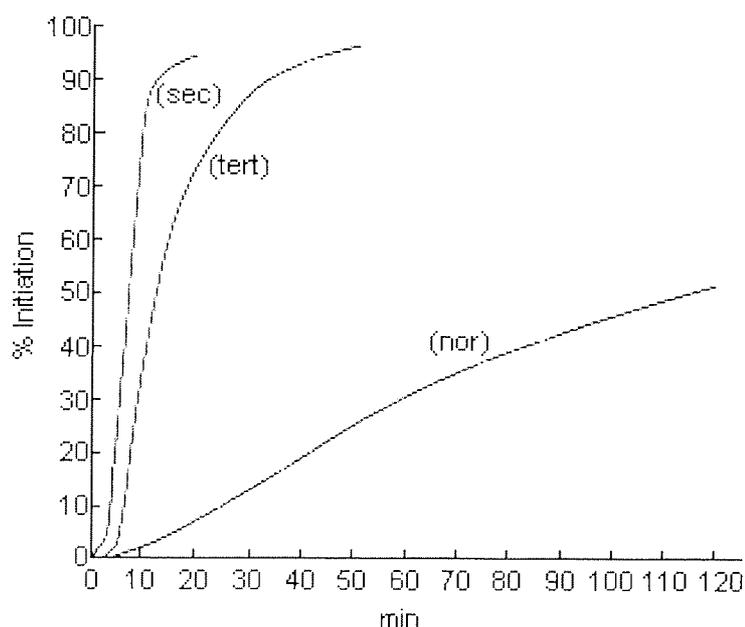
Plot of $\log(R_i/[\text{styrene}]_0)$ as a Function of $\log([\text{BuLi}]_0)$



The experimental results provide the constant $k_p \cdot K_{\text{diss}}^{1/6}$. The proposed mechanism gains support from the results obtained with other alkyl lithium initiators. For example, the polymerization of styrene or isoprene initiated by *sec*-butyllithium in benzene, proceeds at a rate ten times greater than that of the equivalent polymerization initiated by BuLi^{26,27}. The initial rates of polymerization of styrene initiated by *sec*-butyllithium

are proportional to $\sim 1/4$ power of the initiator concentration, which can be attributed, in turn, to the tetrameric aggregation of *sec*-butyllithium. Secondary or tertiary butyllithiums are used in preference to butyllithium or ethyllithium to achieve rapid initiation, and hence to narrow the molecular weight distribution of the resultant polymer.

Figure 1.7 Percentage Conversion of the Different Structural Isomers of Butyllithium in the Initiation of Styrene Polymerization in Cyclohexane at 40°C



An additional effect is that straight-chain lithium alkyls tend to be poor initiators in aliphatic solvents such as cyclohexane, leaving appreciable quantities of initiator unreacted after all the monomer has been consumed (figure 1.7). Although there may be some contribution from intrinsic differences in reactivity, this is most likely due to steric factors; as secondary and tertiary butyl groups are more bulky than the straight chain isomer, the aggregation of initiator is inhibited and the equilibrium is shifted to increase the concentration of monomeric initiator. Straight chain alkyls can be made

more efficient initiators by the presence of small amounts of polar materials, e.g. ethers or lithium alkoxides²⁸. This is because mixed aggregates formed in the presence of lithium alkoxides are more readily dissociated than the homoaggregates.

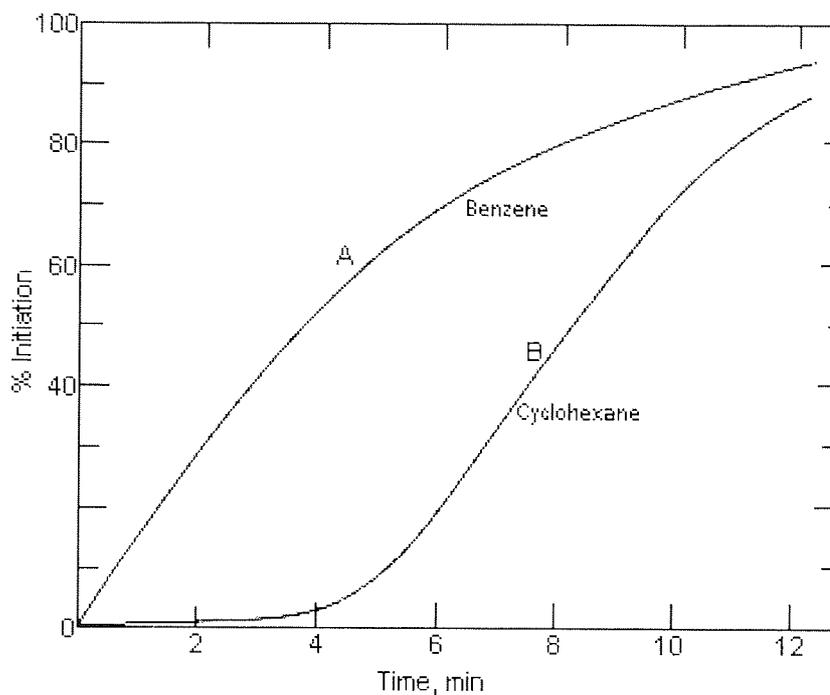
An investigation by Bywater found the initiation of styrene polymerization in benzene using *tert*-butyllithium to be unconventional²⁹. The rate was found to be proportional to the first power of *tert*-BuLi but independent of monomer concentration. An explanation was proposed involving the rapid formation of a monomer-BuLi complex [(*t*-BuLi)₄•M], which then undergoes a slower intramolecular rearrangement resulting in the formation of *t*-Bu•M⁻Li⁺ adduct :



Hence the most convenient, least complex, and therefore preferred initiator for the polymerization of styrene and the dienes is *sec*-BuLi.

As can be seen in figure 1.8, the rate of polymerization in benzene decreases as the reactants are consumed. In cyclohexane or hexane, however, the rate is initially slow and then rapidly accelerates before slowing again as the reactants are consumed. Both situations appear to be connected to the fact that both the initiator and the growing chains are aggregated in hydrocarbon solvents.

Figure 1.8 Rate of Formation of Polystyryl Anions as a Function of Time, Initiated by *sec*-Butyllithium



Curve A: $[s\text{-BuLi}] = 1.1 \times 10^{-3}\text{M}$ $[\text{styrene}] = 5.3 \times 10^{-4}\text{M}$ solvent benzene at 30°C
 Curve B: $[s\text{-BuLi}] = 1.3 \times 10^{-3}\text{M}$ $[\text{styrene}] = 8.7 \times 10^{-2}\text{M}$ solvent cyclohexane at 40°C

This leads to a complex kinetic situation, as at various times mixed aggregates containing initiator and polymeric-lithium species exist, and the composition of these change as the initiator is gradually depleted. These miscellaneous aggregated species can produce different initiation rates, and it can be shown by adding some preformed polymeric-initiator species to a monomer initiating system in cyclohexane that mixed aggregates are responsible for the acceleration in rate after a period of time has elapsed. Whereas lithium alkyls $(\text{RLi})_n$ on their own are thought not to be very reactive, their solvation in benzene causes an increase in reactivity possibly because of the following dissociative mechanism:



Where, M = monomer

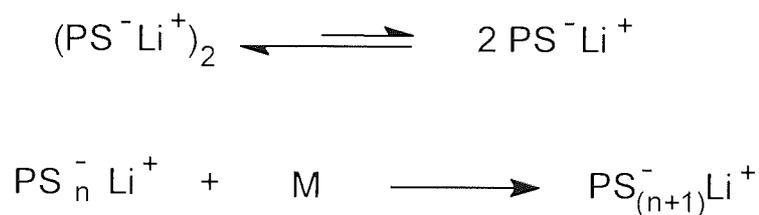
Hence, the negligible dependence of the rate of polymerization on the concentration of initiator, i.e. $[\text{RLi}]^{1/n}$, is in agreement with the hypothesis that aromatic solvents promote the dissociation process to more reactive forms by solvation.

At the beginning of the polymerization, both initiation of new chains, and their propagation occur simultaneously. For a system that exhibits efficient initiation, initiation is complete at about 10-15% conversion of monomer to polymer. At this point the polymerization rate is equal to the rate of propagation. The chain propagation process is also dominated by the association phenomenon; the dependence of rate is quite insensitive to the concentration of growing chains, which itself is proportional to the concentration of initiator added.

1.6.2 Propagation

Early studies of the propagation step of styrene polymerization were confused by the lack of differentiation between initiation and propagation. Since mixed alkyl lithium-polystyryl lithium aggregates are present in the early stages of the reaction, the kinetics of propagation are distorted and effective measurement of true rates of propagation can only be made after the initiator has been depleted.

The kinetics of polymerization were first reported by Bywater and Worsfold^{23,26}. The rate of propagation was found to be first order in monomer, but $\frac{1}{2}$ order with respect to active centres. This seems to be in agreement with the fact that in hydrocarbon solvents polystyryl lithium is present as inactive dormant dimers in equilibrium with a very low concentration of unassociated species, believed to be the active form:



When the equilibrium above is rapid, the concentration of the active form, i.e. unassociated polystyryl lithium, is proportional to the square root of the concentration of dimeric species. The supposition that virtually all the polymer chains are associated into dimers has been confirmed by viscosity measurements³⁰. The viscosity of a solution of living polystyryl lithium was found to decrease by a factor of ~ 10 on addition of a drop of methanol, which converts the dimeric living polymer into 'dead' unassociated polymer. This decrease in viscosity corresponded to a decrease in molecular weight, confirming the dimeric nature of polystyryl lithium in hydrocarbons.

The rate equation for propagation can be expressed as follows:

$$-\frac{d[\text{Styrene}]}{dt} = k_p[\text{Styrene}][\text{Active centres}]^{1/2}$$

This can be rearranged to give the following:

$$-\left(\frac{1}{[\text{Styrene}]} \cdot \frac{d[\text{Styrene}]}{dt}\right) = k_p \left(\frac{K_{\text{diss}}}{2}\right)^{1/2} \cdot [\text{LP}]^{1/2}$$

Where [Styrene] = concentration of styrene at time t

[Active centres] = concentration of active polystyryl lithium

[LP] = total concentration of living polystyryl lithium

k_p = propagation rate constant of the unassociated LP

K_{diss} = dissociation constant of dimeric polymers into monomeric

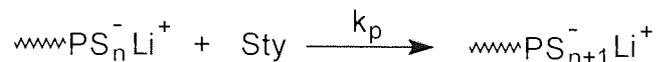
i.e. the plot of

$$\ln \left[- \left(\frac{1}{[\text{Styrene}]} \cdot \frac{d[\text{Styrene}]}{dt} \right) \right] \text{ vs } \ln[\text{LP}]$$

is linear with a slope of $\frac{1}{2}$. The value of $k_p K_{\text{diss}}^{1/2}$ in benzene or toluene was found to be $0.93 \times 10^{-2} \text{ M}^{1/2} \text{ s}^{-1}$ at ambient temperatures. In cyclohexane the value is lower but only by a factor of three. The comparability of rates in aromatic and aliphatic solvents is in marked contrast to the effect on rates of initiation.

The exact nature of the C-Li bond of polystyryl lithium in hydrocarbon solvents is a matter of some dispute². However, since the electronic spectrum of its solution in hydrocarbons or in THF is similar to that of polystyryl sodium in THF, the bond is thought to be most probably ionic rather than covalent.

Polymerization in polar solvents with high dielectric constant is simpler to study as the rates of initiation are so fast that the measured rates of polymerization are those of propagation. The dimeric polystyryl lithium dissociates in solvents such as THF. The kinetics of the anionic propagation of styrene in THF were first carried out using polystyryl sodium by Geacentov *et al*^{31,32}. They made use of a capillary flow technique to demonstrate that the consumption of styrene exhibited first order kinetics. Subsequent research^{33,34} using polystyryl lithium has confirmed that, and also shows a linear dependence of k_p on the reciprocal of the square root of the concentration of living polymer, which was explained by the presence of free polystyryl anions in equilibrium with their ion pairs as the species responsible for propagation. In dioxane, however, the rates of polymerization are linearly proportional to both the active centre and monomer concentrations and increase in the series $Li^+ < Na^+ < K^+ < Cs^+$ ³⁵⁻³⁹. These observations indicate that a simple contact ion-pair is the propagating species:



So that:

$$\frac{-d[Sty]}{dt} = k_p [Sty] [\sim PS_n^- Li^+]$$

From which k_p can be determined experimentally.

The polymerization rate increases with an increase in dielectric constant of the solvent in the series dioxane < oxepane < tetrahydropyran < tetrahydrofuran. The activity of the propagating free anion (k_p^-) has been shown to be greater than that of the ion pair ($k_p^{+/-}$).

1.7 The Anionic Polymerization of Methyl Methacrylate

1.7.1 Termination and Transfer Reactions

The polymerization of polar vinyl monomers by living systems poses numerous challenges, and a great deal of research has been undertaken, particularly using the monomer, methyl methacrylate. The ester functionality of methyl methacrylate leads to a number of complications as it can result in both physical interactions, as well as chemical side reactions such as termination and transfer, which occur particularly in non-polar solvents, at temperatures higher than -75°C and at very low concentrations of living ends^{7,12}.

These side reactions give rise to:

- (i) a non-linear first-order plot of monomer concentration as a function of time, i.e. $\ln([M]_0/[M])$ against time, indicating a decrease in the concentration of living ends caused by disappearance of propagating chains, and
- (ii) a broadening of molecular weight distribution. This can be seen as a low molecular weight tail on the SEC chromatograms. The number average degree of polymerization, however, is still proportional to the percentage conversion, since the total number of chains is determined by the initial concentration of initiator, and since all the initiator has reacted to produce growing chains, the total number of chains is as expected.

Polymerizations involving *tert*-butyl methacrylate were found to exhibit no termination reactions, even at ambient temperatures⁴⁰. This is thought to be due to the inductive

effect of the *tert*-butyl group overcoming the carbonyl activity, and hence decreasing the rate of termination.

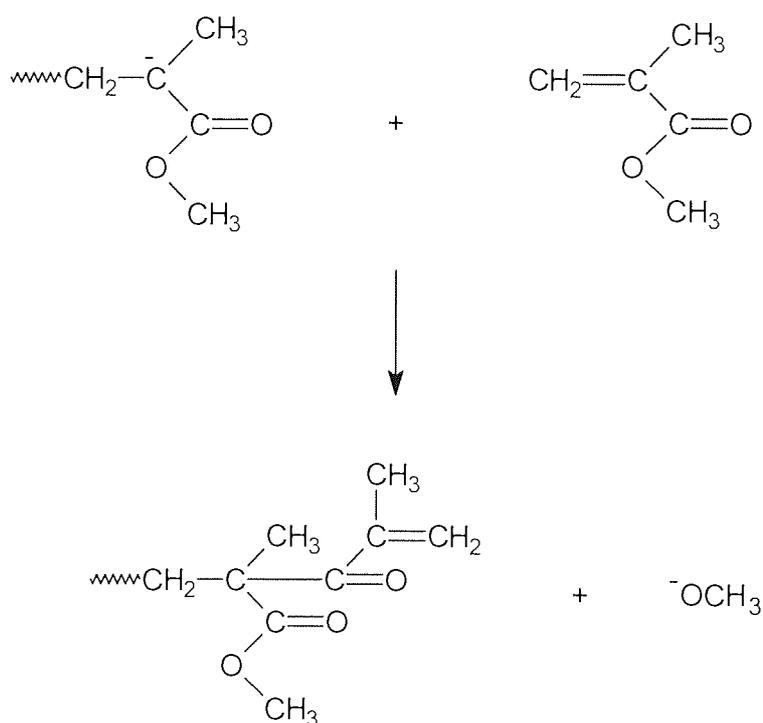
The polymerization of methyl methacrylate initiated by butyllithium in toluene has been studied and it has been found that, despite the numerous side reactions, some active centres persist during polymerization since a new batch of monomer, added after the completion of the initial polymerization, will still polymerize. However only a small fraction of the initiator produces growing chains, most being destroyed by side reactions. The high molecular weight polymer produced was found to have a broad molecular weight distribution and a large fraction of low molecular weight (oligomeric) product was also formed. Schreiber identified three different termination reactions involving attack by either initiator or living ends on the carbonyl group of either monomer or polymer⁴¹. These were:

- (i) Reaction of the living end with the carbonyl group of the monomer resulting in the formation of a vinyl ketone, 'monomer termination', as shown in scheme 1.8.
- (ii) Reaction of the living end with the ester group from a different polymer chain, resulting in chain coupling, 'intermolecular polymer termination', as shown in scheme 1.9.
- (iii) Reaction of the living end with the antepenultimate ester group of its own polymer chain resulting in a cyclic- β -keto ester structure, 'intramolecular polymer termination' or 'backbiting', as shown in scheme 1.10.

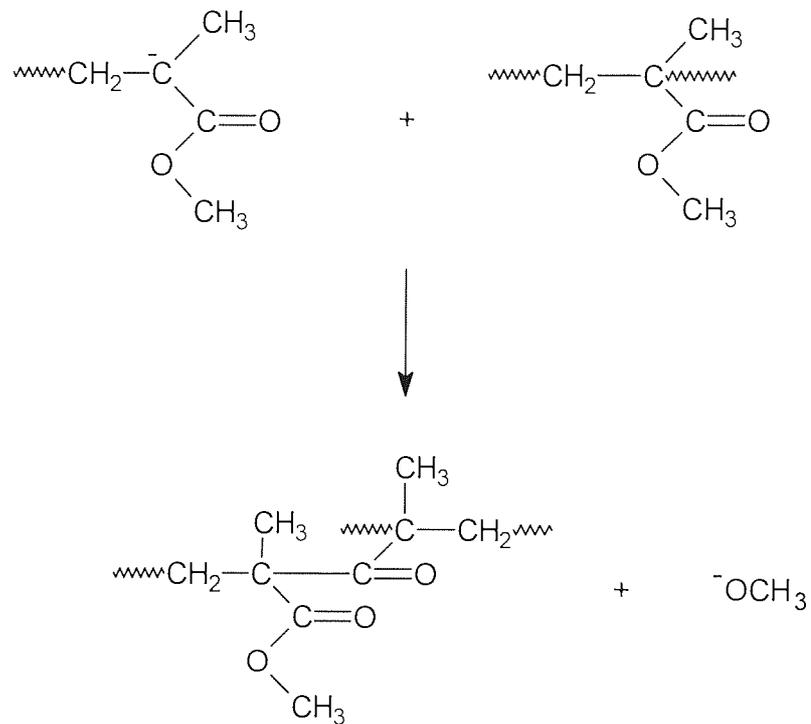
A further method of intramolecular termination has been postulated involving ketene formation⁴⁴ (see scheme 1.11).

All of these reactions produce methoxide as a by-product. Both Wiles and Bywater⁴², and Mita *et al*⁴³ showed that nearly all methoxide is produced in the very early stages of the reaction. As there is no polymer present at this point in the reaction, the methoxide must be generated by the attack of the initiator on the carbonyl group of the monomer, as shown in scheme 1.12.

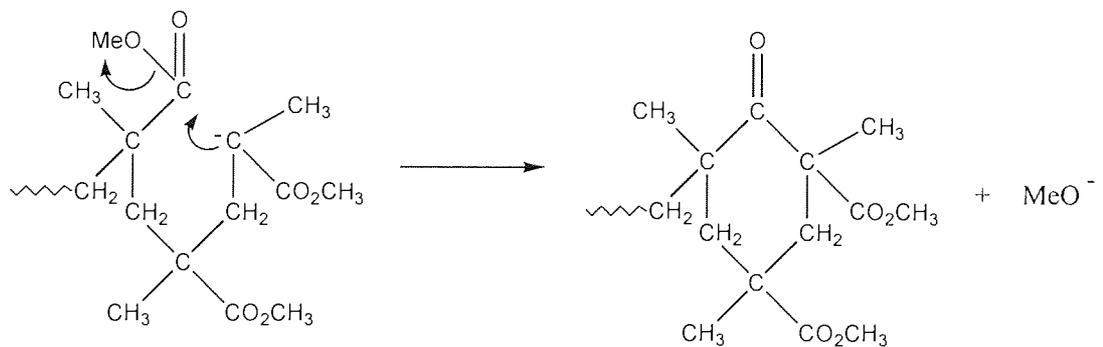
Scheme 1.8 'Monomer Termination' in the Anionic Polymerization of Methyl Methacrylate



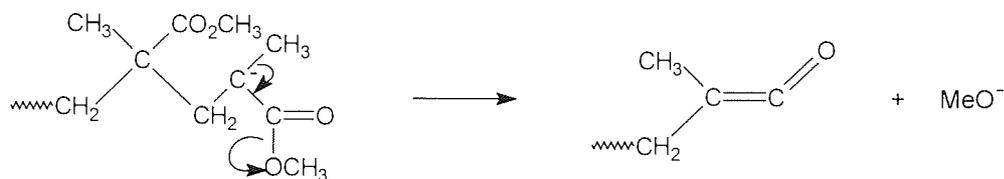
Scheme 1.9 'Intermolecular Polymer Termination' in the
Anionic Polymerization of Methyl Methacrylate



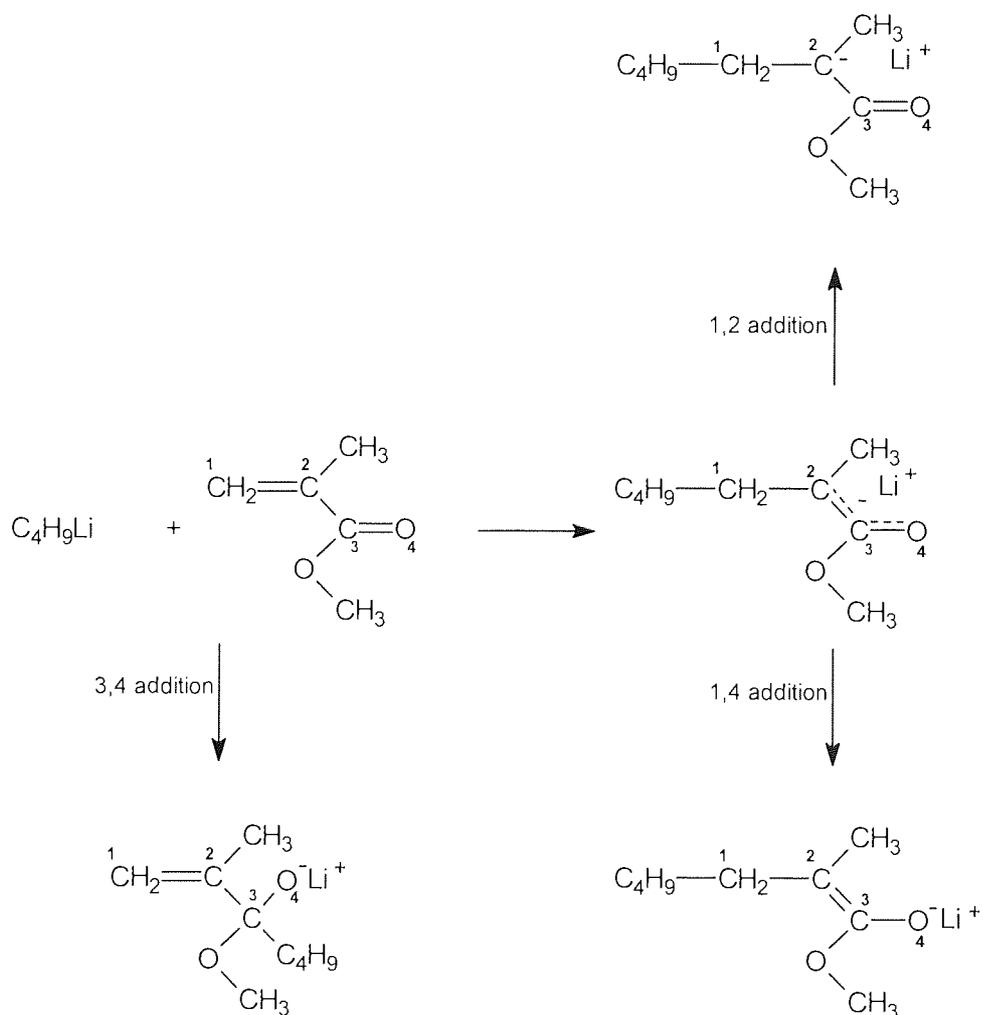
Scheme 1.10 'Intramolecular Polymer Termination' in the
Anionic Polymerization of Methyl Methacrylate



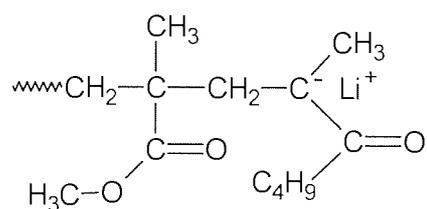
Scheme 1.11 Termination by Ketene Formation in the
Anionic Polymerization of Methyl Methacrylate



Scheme 1.12 Reactions of the Monomer with the Initiator Involved in the
Polymerization of Methyl Methacrylate



Only the reaction at the carbon-carbon double bond, i.e. the 1,2 addition reaction leads to chain growth. The product of reaction at the ester carbonyl group (1,4 addition) can eliminate lithium methoxide and form methyl pentyl ketene. Further complications arise from the addition of butyl isopropenyl ketone (the product of 3,4 addition) to the growing chains obtained from 1,2 addition at low temperatures. This is because the ketone is more reactive towards the propagating anions than MMA itself, and hence most of the chains become capped with the unreactive vinyl ketone ion pair, producing oligomers such as:

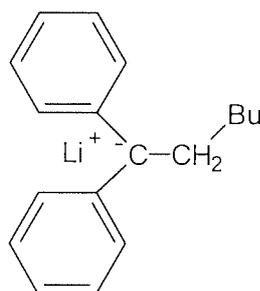


The vinyl ketone can also react with initiator molecules to form alcohols. The products of such additions have been studied using the initiators phenyllithium in diethyl ether⁴¹, butyllithium in hexane and THF⁴⁵ and butyllithium in toluene^{46,47}.

Although unreactive towards methyl methacrylate, these modified active centres have a small chance of adding a unit of methyl methacrylate very slowly and then propagating normally. Since some active centres may avoid reaction with the vinyl ketone altogether, the resulting distribution of molecular weights is broad. Hence butyllithium alone is not considered to be a suitable initiator for the polymerization of methyl methacrylate.

Poly(methyl methacrylate) with a narrow molecular weight distribution has been achieved by the use of less reactive or sterically hindered initiators, which, in addition to

suppressing propagation, also decreases reactivity towards the carbonyl group when used at low temperatures, in polar solvents and with ultrapure monomers. The polymerization of methyl methacrylate was studied in THF at -78°C by Rembaum and Szwarc⁴⁸, using sodium naphthalide or sodium polystyryl as initiators, and so provided the early evidence for the feasibility of methyl methacrylate polymerization. The polymerization was found to be quantitative, completed within seconds but the resulting polymer was not living and appeared to be terminated within half an hour. Similar success was also achieved by McGrath *et al*⁴⁹ using initiators such as 1,1-diphenylhexyl lithium.



1.7.2 Early kinetic studies

Until 1973 there were no reports of kinetic studies of the polymerization of methyl methacrylate in polar solvents, owing to the experimental difficulties associated with measuring the very high reaction rates involved¹²; when the concentration of living ends is 10^{-3} mol/L, the half-life for monomer addition to ion pairs is 5 seconds at -80°C and only 0.1 seconds at ambient temperatures. Lohr and Schulz^{50,51}, and Mita *et al*⁴³ investigated the kinetics of polymerization of MMA in THF, with Na^+ and Cs^+ as counterions, using flow tube techniques. Both groups showed that the reaction proceeds in an ideal way at low temperatures; initiation is fast compared to propagation, and propagation follows first order kinetics with respect to monomer concentration, and the rate studies indicated the absence of termination reactions. The number average degree of polymerization was found to be proportional to percentage conversion, consistent with the absence of transfer reactions. Lohr and Schulz obtained narrow molecular weight distribution polymers and demonstrated clearly that both free ions and ion-pairs participate in the propagation. These experiments were inadequate because, when using Na^+ as the counterion, only bifunctional initiators were used (i.e. sodium naphthalene and oligo- α -methylstyryl sodium), and it has been shown by Warzelhan *et al*^{52,53} that bifunctionally growing chains can form intramolecular associates, which differ from the multifunctionally growing species in rate of propagation as well as in the tacticity of the resulting polymer.

Schulz and coworkers⁵⁴⁻⁵⁶ investigated the propagation kinetics using cumylcaesium and monofunctional benzyl-oligo- α -methylstyryl sodium. In order to suppress the dissociation of propagating centres into free ions, $\text{Na}(\text{BPh})_4$ and $\text{Cs}(\text{Ph}_3\text{BCN})$ were added as common ion salts. Since free ions react faster than ion pairs, the effect of this

was to slow down the polymerization. As the flow tube reactor is difficult to use at low temperatures, reactions below -50°C were conducted in a stirred tank reactor, which allowed kinetic measurements of reactions with half-lives of 2 seconds and longer to be taken by extracting samples periodically⁵⁷. Polymerizations were rapid, even at -98°C . The monomer half-life was of the order of 10 minutes when lithium was used as counterion, and approximately 24 seconds using sodium and caesium. Although appreciable termination was observed at higher temperatures, the propagation rate constants could be measured from the initial slope of the first-order logarithmic conversion-time plot. The initial concentration of the living ends was determined from the reciprocal of the gradient in the plot of the number average degree of polymerization as a function of percentage conversion, which remains linear even when termination occurs. The Arrhenius plots for the propagating rate constants for ion pairs were found to be linear for both Na^+ and Cs^+ as the counterions, thus giving no evidence for the existence of more than one type of ion pair.

Only small differences in rate constant were observed among systems having Na^+ or Cs^+ as counterions, but the Li^+ system showed much slower rates. This behaviour is quite different from that observed in styrene polymerization, and appears to be characteristic of monomers in which intramolecular solvation of the counterion by polar groups, i.e. the penultimate ester group in the case of MMA, of the polymer chain can occur⁵⁶. Another possibility can be attributed to the active species existing in a special form of a contact ion pair, in which the counterion is less close to the α -carbon atom and exhibits less influence on its reactivity⁵⁸.

The kinetic results obtained by Kraft *et al*⁵⁹ from the anionic polymerization of methyl methacrylate using sodium and caesium as counterions in dimethylether (DME) confirmed that there was no dependence of the rate of polymerization on the nature of the counterion. The behaviour was similar to that in THF, in that the Arrhenius plots of the propagating rate constants were found to be linear and, within experimental error, identical for the two counterions used. The rate constants, however, were found to be higher when DME was used as the solvent compared with THF.

Further investigation was carried out by Muller and Jeuck¹⁸ using THF as the solvent in the presence of lithium and potassium counterions. They showed that the rate constant for Li^+ as the counterion was much lower, and hence the activation parameter higher than those for Na^+ and Cs^+ . When K^+ was used as the counterion, the propagation rate constant was almost identical, within experimental error, to those of Na^+ and Cs^+ . The activation energy using K^+ as the counterion was estimated to lie between those of Na^+ and Cs^+ . They concluded that there was a distinct dependence of the rate of polymerization of MMA on the counterion used, owing to the fact that a linear relationship existed between the logarithm of the propagation rate constant and the interionic distance.

The kinetics of the polymerization of *tert*-butyl methacrylate (TBMA) in THF were studied by Muller⁴⁰ using Na^+ and Cs^+ as the counterions. The rate constants for these systems were found to be considerably lower than the corresponding rate constants for methyl methacrylate polymerization because of the higher activation energy required for TBMA polymerization. This was in addition to the expectation of a higher steric factor caused by the bulkiness of the ester group. Moreover, rate constants for TBMA

polymerization in THF were found to be dependent on the counterion (Cs^+ producing values that were 4-10 times higher than the corresponding values for Na^+). It was believed that this effect was due to the counterion being closer to the carbanion because of the positive inductive effect of the *tert*-butyl group increasing the negative charge density.

1.7.3 Tacticity

The tacticities of PMMA prepared using a variety of solvents and counterions have been determined and a clear trend has been shown concerning the polarity of the solvent and the ability of the counterion to be solvated^{53,56,59}. Table 1.2 shows the tacticities of PMMA samples obtained in DME and THF, using Na^+ and Cs^+ as the counterions, with both mono- and bifunctional initiators.

Table 1.2 Tacticities of PMMA Samples Prepared in a Variety of Solvent/Counterion Systems in the Presence of a Common Ion Salt

Counterion/Solvent	Temperature/ $^{\circ}$ C	I	H	S	m	r
Na ⁺ /DME	-55	0.01	0.22	0.78	0.12	0.88
Cs ⁺ /DME	-65	0.02	0.37	0.60	0.21	0.79
Na ⁺ /THF	-61	0.04	0.36	0.58	0.23	0.77
Cs ⁺ /THF	-66	0.05	0.53	0.42	0.315	0.685
Na ⁺ /THF Bifunctional	-75	0.39	0.41	0.20	0.595	0.405

I, H, S: isotactic (mm), heterotactic (mr/rm), syndiotactic (rr) triads; m, r : meso and racemic dyads.

The table shows that the degree of isotacticity decreases with the solvating power of the solvent , exhibiting the following order:

$$\text{Na / DME} < \text{Cs / DME} \sim \text{Na / THF} < \text{Cs / THF}$$

This seems to indicate that a close contact between carbanion and counterion favours isotactic propagation. The tacticities of polymer produced using bifunctional initiators are significantly different from those produced from monofunctional initiators^{52,53}, which is thought to be due to intramolecular association of chain ends. The tacticities are intermediate between those produced in polar solvents by monofunctional initiators and those produced in non-polar solvents, where association of the growing ends with methoxide or with the monomer is possible. It is difficult to compare the results of different research groups regarding the tacticities of methyl and

alkyl methacrylates since, in many cases, anions were present at unknown concentrations, and often bifunctional initiators were used, which led to unknown degrees of intramolecular association. Intermolecular solvation may also occur in solvents of lower solvating power. Nevertheless Yuki and Hatada⁶⁰ have reviewed the tacticities of polymethacrylates obtained under different conditions.

1.7.4 The effect of lithium salts

The effect of lithium salts on the anionic polymerization of acrylates was first noted by Teyssie *et al*⁶¹⁻⁶⁶ during the synthesis of block copolymers by sequential addition of methyl methacrylate or *tert*-butyl acrylate to living polystyryl anions. The polymerization was carried out in a 50/50 (v/v) mixture of benzene and THF at -78°C with lithium as the counterion. The initial results were disappointing; more than half the polystyrene initiator was recovered as homopolymer and the molecular weight distribution of the block copolymer was found to be bimodal. The situation was improved when a molar excess of lithium acetate was added to polystyryl lithium before the addition of the methyl methacrylate monomer. The percentage of the homopolystyrene fell to 13% of the initial amount whereas the block copolymer exhibited a unimodal although still broad distribution.

A further improvement in the efficiencies of initiation and the molecular weight distribution was found when lithium acetate was replaced by lithium chloride, resulting in more than 98% polystyrene forming block copolymer and a polydispersity index between 1.2 and 1.3. An even narrower polydispersity was obtained when the polymerization was carried out in THF alone. Teyssie and co-workers concluded that LiCl had a dual favourable effect:

- (i) LiCl decreases the reactivity of polystyryl lithium towards methyl methacrylate resulting in a well-controlled initiation step free from side reactions on the monomer.

- (ii) The propagation of the anionic polymerization of methyl methacrylate occurred without transfer and termination reactions.

The effects of the LiCl on the molecular weight distributions of the copolymers of methyl methacrylate and *tert*-butyl acrylate are shown in figures 1.9 and 1.10 respectively. It is quite clear that the rate of initiation is fast enough, relative to the rate of propagation, to lead to a narrow molecular weight distribution.

Figure 1.9 Effect of LiCl on the Molecular Weight Distribution of PMMA – Size Exclusion Chromatograph of PMMA Synthesized in a 90/10 (v/v) Toluene/THF Mixture at -78°C with Polystyryllithium Initiator

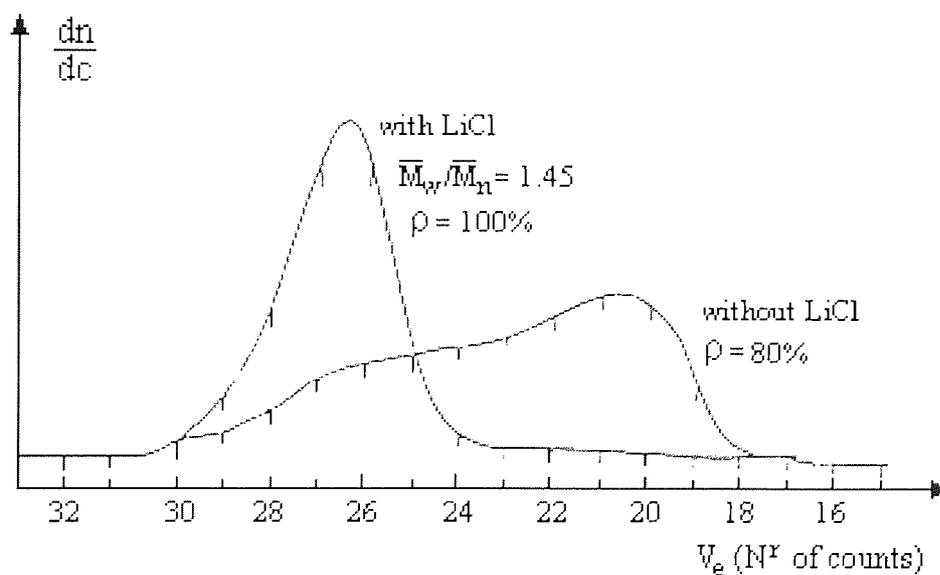
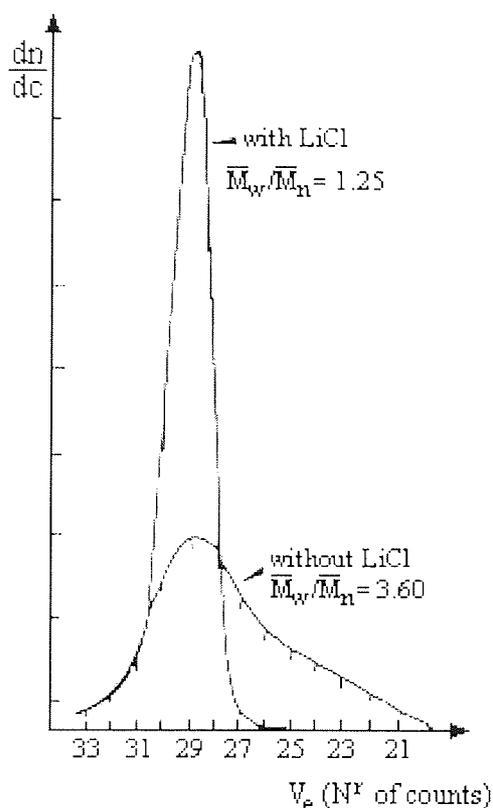


Figure 1.10 Effect of LiCl on the molecular weight distribution of *Pt*-BuMA – size exclusion chromatograph of *Pt*-BuMA synthesized at -78°C



A systematic change of the LiCl : initiator (polystyryllithium) ratio was found to result in a change in the molecular weight distribution of the poly(*tert*-butyl acrylate) synthesized in THF at -78°C ⁶¹. It was found that a 1:1 molar ratio or a slightly greater LiCl : ion pair adduct ratio had the most beneficial effect in successfully producing polymers of narrow molecular weight distributions.

In order to elucidate the possible interaction between the organolithium species and the LiCl, the ^7Li NMR spectra of PS^-Li^+ and PMMA^-Li^+ were recorded before and after the addition of various amounts of LiCl in THF at -60°C , as shown in table 1.3.

It is notable that when LiCl was added to PS^-Li^+ , a single line was observed, the chemical shift of which was not the weighted average of that for LiCl and PS^-Li^+ . This indicates that the observed resonance could not be attributed to a fast exchange of Li^+ between the salt and the organo compound but was most probably due to a complexed species in equilibrium with an excess of one or both of the starting lithium compounds.

Table 1.3 ^7Li Chemical shift in PS^-Li^+ and PMMA^-Li^+ in THF at -60°C , with and without added LiCl

Li^+ species	^7Li shift (ppm)	$[\text{Li}^+]$ (mM^{-1})
LiCl	0	0.02
PS^-Li^+	0.59	0.02
LiCl/ PS^-Li^+ (1/2)	0.19	0.06
LiCl/ PS^-Li^+ (1/1)	0.21	0.04
LiCl/ PS^-Li^+ (2/1)	0.06	0.06
PMMA^-Li^+	0.42	0.02
LiCl/ PMMA^-Li^+ (1/2)	0.42-0.11	0.06
LiCl/ PMMA^-Li^+ (1/1)	0.15	0.04
LiCl/ PMMA^-Li^+ (2/1)	0.06	0.06

It was concluded from this study that LiCl interacts as well with the initiating species (styryl type anion) as it does with the propagating carbanion derived from methyl methacrylate. It was also observed that, compared with the chemical shift reported for PS^-Li^+ and PMMA^-Li^+ alone, the value for the adduct was systematically smaller, in

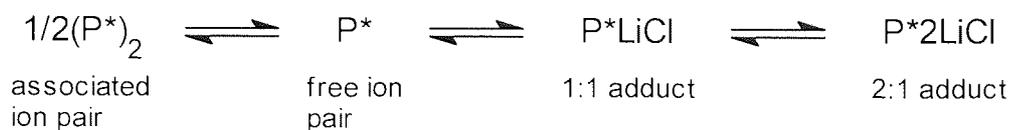
agreement with a loss of reactivity of the anionic species and making attack on the carbonyl function of the MMA less susceptible.

The initiation efficiency, f , (given by the concentration of growing chains divided by the concentration of the initiator) was clearly improved⁶⁶ when the LiCl : initiator molar ratio was increased up to a value of 10.

A study of the effect of lithium chloride on the polymer microstructure in the polymerization of *tert*-butyl acrylate in THF at -78°C was carried out by Varshney and coworkers⁶⁷. It was found that the propagation rate constant was 20 times slower than when the polymerization was carried out in the absence of LiCl, and that the isotactic content of the polymers increased significantly when the [LiCl]/initiator ratio was greater than 2. The effect of LiCl on the rate constant and microstructure of the polymers was attributed to formation of a complex between the LiCl and the living polymer chains.

Muller has shown that the kinetics of propagation and termination, as well as the molecular weight distribution of methyl methacrylate polymers can be controlled by multiple equilibria between associated and non-associated ion pairs and ion pair ligand adducts. They showed that in the presence of LiCl, the formation of adducts of the active centres competes with association (as shown in figure 1.11).

Figure 1.11 The Active Centres Involved in the Anionic Polymerization of Methyl Methacrylate in the Presence of Lithium Chloride



The fraction of non-associated species increases on addition of LiCl. The effect of LiCl on the molecular weight distribution of poly(methyl methacrylate) was pronounced; M_w/M_n decreased from 1.3 to 1.04 in the presence of LiCl. This phenomenon was explained in terms of the equilibrium between free and LiCl complexed ion pairs being much faster than that between free and associated ion pairs. In the case of the former, a macromolecule is reacting with a small molecule, whereas in the latter, two macromolecules are reacting together. Hence the main function of LiCl was to deplete the system of slowly interconverting associates.

The existence of associated chain ends was demonstrated kinetically by the decrease of the apparent rate constant, k_p , with increasing concentration of active centres (P^*), even in the presence of common ion salt⁶⁹. The data clearly showed that the reactivity of the associates was much lower than that of free ion pairs; the dynamics of the association equilibrium having a significant influence on the molecular weight distribution of the polymers formed. A broadening of molecular weight distribution is therefore due to a rate of interconversion of associated and non-associated ion-pairs comparable to the rate of monomer addition. In the polymerization of *tert*-butyl acrylate, the effect of LiCl was found to be less pronounced, since molecular weight distributions are fairly narrow anyway. The fraction of associated forms in such

systems is believed to be low. The conclusion reached by Muller⁶⁸ was that the positions of the association/complexation equilibria strongly affect the kinetics of polymerization, whereas the dynamics are responsible for the molecular weight distributions of the polymers obtained.

Muller and Lochmann⁷⁰ also investigated the effect of lithium *tert*-butoxide (*t*-BuOLi) on the rate constants and equilibrium constants of reactions involved in the initial stage of anionic polymerization of methyl methacrylate. Reactions were carried out in THF, initiated by methyl 2-lithioisobutyrate at $23 \pm 3^\circ\text{C}$. They reported that addition of *t*-BuOLi decreased the rate constant of initiation and propagation by one order of magnitude; the rate constants of termination by cyclization decreased by two orders of magnitude. As a consequence, the probability of propagation relative to termination is ten times greater which explains the favourable effect of the alkoxide.

1.7.5 Aluminium alkyl enhanced polymerization

Living polymerization of methacrylates in THF is possible by the use of bulky initiators at low temperatures, as has been previously stated. Polymerizations carried out in this medium yield polymers that are predominantly syndiotactic. In relatively non-polar solvents such as toluene, the reaction proceeds in a non-living manner, resulting in isotactic polymer with a broad molecular weight distribution. However, it has been found that when MMA is polymerized in toluene in the presence of alkyl lithiums and trialkyl aluminiums (R_3Al), it is possible to produce living and highly syndiotactic PMMA with low polydispersity. This has proved to be an area of growing interest over the last few years⁷¹⁻⁷⁸, yet very little is known about the actual effect of the aluminium alkyl on the mechanism of polymerization.

Hatada *et al*⁷¹⁻⁷⁴, studied the polymerization of methyl methacrylate initiated by different butyllithium isomers in the presence of aluminium alkyls at -78°C in toluene. It was found that it was possible to produce highly syndiotactic polymers of narrow polydispersity index and in high yields only when *tert*-butyllithium was used to initiate the polymerization, as both butyllithium and *sec*-butyllithium gave very low yields of polymers with broad, multimodal molecular weight distributions. Increases in temperature were also found to lead to an increase in polydispersity and to decrease yields. The tacticity of the polymer produced was shown to be dependent on the ratio of AlR_3 to $\text{R}'\text{Li}$. Using triisobutyl aluminium (iBu_3Al) and *t*-BuLi, a 1:1 ratio of cocatalyst to initiator produced a stereoblend polymer, i.e. a mixture of syndiotactic and isotactic polymer, and a bimodal MWD indicating that more than one mechanism is taking place. When the ratio of cocatalyst to initiator was increased to 2:1 or higher, a highly syndiotactic polymer with a very narrow MWD was produced. Increasing the mole ratio of $[\text{Al}]/[\text{Li}]$ also appeared to increase the initiator efficiency.

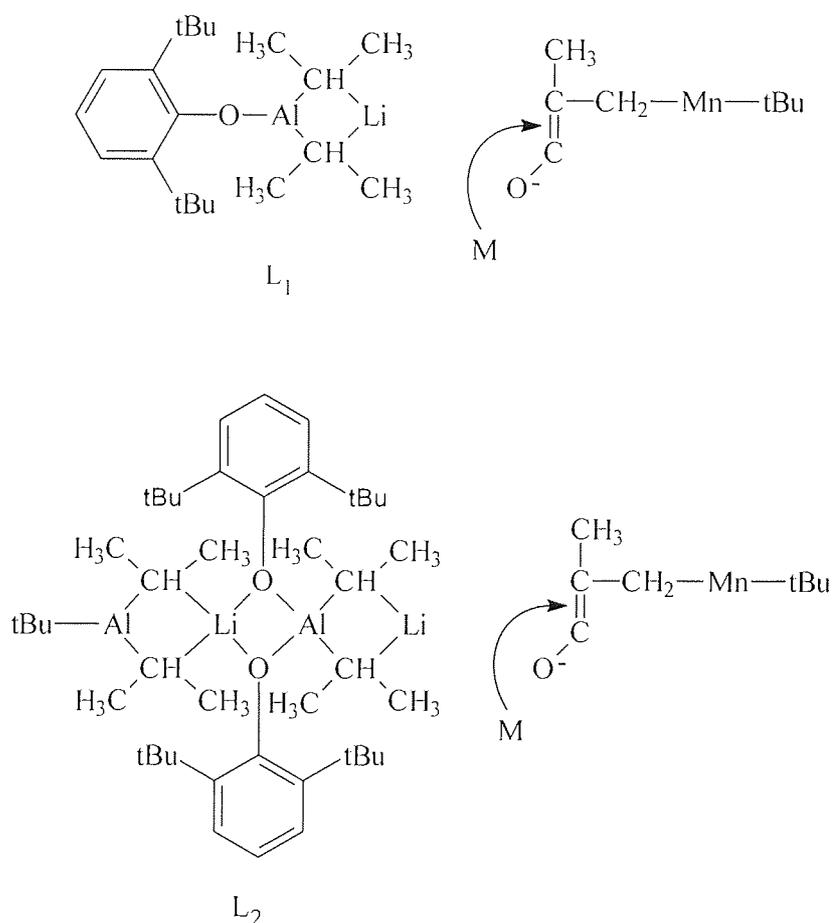
From these results it was suggested that the aluminium alkyl could cause the dissociation of the *tert*-butyl lithium aggregates into monomeric species, thus increasing the efficiency of the initiator. Alternatively, it was considered that coordination of the aluminium alkyl to the carbonyl group of the monomer suppressed the addition of alkyllithiums to the carbonyl group and favoured the conjugate addition across the carbon-carbon double bond to enable efficient propagation. The bulkier *tert*-butyl group of the alkyllithium sterically hindered termination reactions involving attack on the carbonyl group, *n*-butyl and *sec*-butyl lithium not being bulky enough. NMR investigations suggested that dimeric aluminium alkyl was co-

ordinated to both the metallated enolate structure of the living chain end and to the penultimate ester group of the polymer, favouring syndiotactic propagation.

Experiments were also carried out to investigate the effect of varying the nature of the alkyl group of the aluminium compound. It was found that increasing the size of R from C₂H₅ to nC₄H₉ significantly increased the syndiotacticity, although only a small further increase was found when the group was changed to nC₈H₁₇. However there was also a decrease in rate associated with the increase in size of the aluminium alkyl. These findings were verified by Ballard *et al*⁷⁵ who carried out polymerizations of methyl methacrylate initiated by *tert*-butyllithium in the presence of (2,6-di-*tert*-butyl-4-methylphenoxy)diisobutylaluminium conducted at temperatures as high as 40°C. Even at these high temperatures they obtained polymers with a polydispersity index as low as 1.05, leading Ballard to state that for best control both the alkyllithium and trialkyl aluminium should have as large a cross section as possible. The propagating species suggested by the group was an enolate bound to a mixed lithium/aluminium gegen-ion (counterion). The structures of these gegen-ions were based on the structure of solid state oligomeric LiAl(C₂H₅)₄ obtained from X-ray diffraction data. Two different possible active centres (L₁ and L₂ in scheme 1.13) are thought to be present which relate to the monomeric and dimeric species respectively. They proposed that these sorts of initiators are only effective in hydrocarbon solvents in which they are soluble; solvents that have been previously preferred for anionic polymerization such as THF cannot be used since they deactivate the initiator. In hydrocarbon solvents the separation between the anionic and cationic components is minimised, and the high cross-sectional area of the latter screens the propagating

terminus of the polymer chain from side reactions. This led Ballard to refer to the mechanism as ‘screened anionic polymerization’.

Scheme 1.13 Structures of Propagating Centres L_1 and L_2 in the ‘Screened Anionic Polymerization’ of Methyl Methacrylate in the presence of Aluminium Alkyls As Proposed by Ballard *et al*

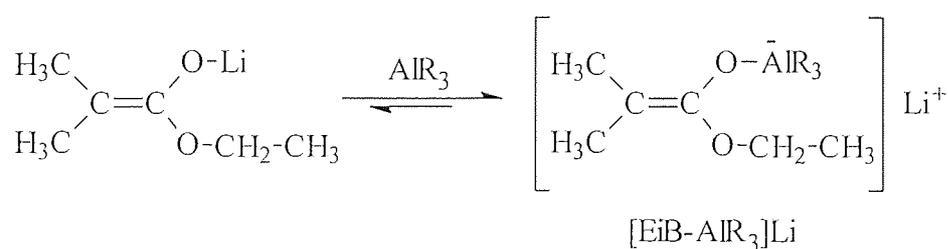


Haddleton *et al*⁷⁶ have carried out work similar to Hatada *et al* except that the polymerizations were carried out at higher temperatures (between 0-10°C). Their work supported that of Hatada’s group in that they concluded that the nature of the living species was sensitive to the alkyl groups of both the aluminium and lithium

components. Contrary to Hatada's findings, however, they did have some success in producing narrow molecular weight distributions of polymers even when using butyllithium with triisobutylaluminium. It was noted that considerably narrower molecular weight distribution polymers were produced when the aluminium alkyl was premixed with the monomer before addition of the alkyllithium, as opposed to addition of the aluminium alkyl to the alkyllithium first in order to form the initiating complex. From this they concluded that the order of reagent addition is important since it determines the structure of the initiating species.

Muller *et al*^{77,78} carried out ¹³C NMR studies using ethyl α -lithioisobutyrate (EiBLi) as a model compound for the chain end of living PMMA, and methyl pivalate (MPiv) as a model for main chain PMMA, in toluene at -78°C . They proposed that the active centre of polymerization in the presence of lithium and aluminium alkyls was a bimetallic 'ate' complex ($\{\text{EiBLi-}\text{AlR}_3\}\text{Li}$), with an increased covalent character of the metal-oxygen bond as shown in scheme 1.14.

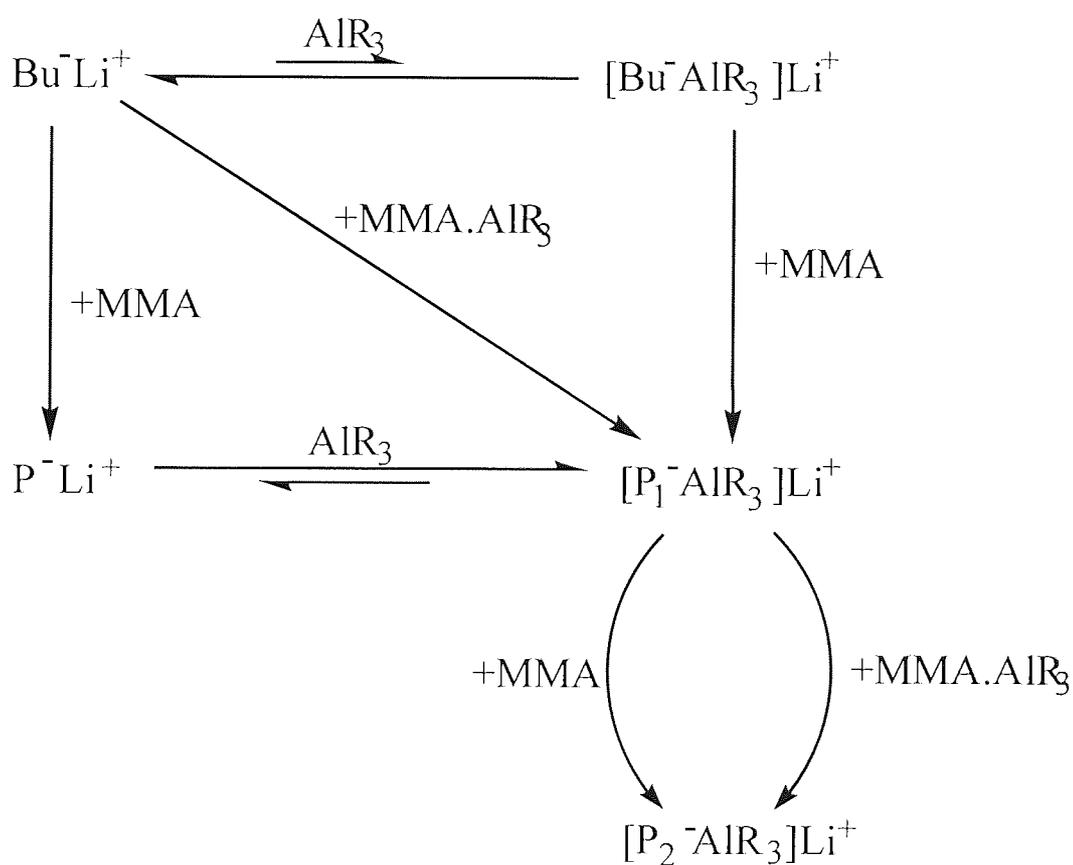
Scheme 1.14 Formation of Bimetallic 'Ate' Complex as Active Centre in the Presence of Aluminium Alkyls as Proposed By Muller *et al*



During the polymerization process, this can be formed from premixing the monomer with the aluminium alkyl followed by initiation using butyllithium, or, it can be

achieved by addition of the aluminium alkyl to the enolate formed, once butyllithium initiation has already taken place (see scheme 1.15). They proposed that excess aluminium alkyl co-ordinates to the ester carbonyl group of both the monomer and the polymer chains.

Scheme 1.15 Mechanism to Show Initiation and Propagation of Methyl Methacrylate in the Presence of Lithium and Aluminium Alkyls as Proposed by Muller *et al*



1.8 Block Copolymers

Block copolymers are defined as having a linear arrangement of blocks i.e. a block copolymer is a combination of two or more homopolymer chains joined end to end⁷. Star-block or radial block copolymers have branched structures, as do graft copolymers. Star-block and graft copolymers, although in many ways similar to block copolymers, have some interesting properties of their own.

Block copolymers are of particular interest because of the unusual behaviour they exhibit both in solution and in the solid state. These properties arise from the fact that the sequences of different chemical composition are usually incompatible and therefore have a tendency to aggregate in space. This leads to amphiphilic properties in solution and microdomain formation in the solid state.

Anionic polymerization is one of the preferred techniques for the preparation of well-defined block copolymers when such synthetic processes do not exhibit transfer and termination. These living polymerization systems allow the preparation of nearly pure block copolymers of desired molecular weight, composition and structure. There are other advantages of using anionic polymerization for the preparation of block copolymers; these apply mainly to the polymerization of dienes, non-polar vinylic monomers, cyclic ethers and cyclic sulphides:

- (i) Block copolymers can be obtained either by successive polymerization of the monomers or by polymerization of the second monomer with functionalized prepolymers of the first monomer.

- (ii) Multiblock copolymers of low polydispersity or of defined heterogeneity can be prepared by suitable coupling reactions or with bifunctional initiators.
- (iii) Functionalised block copolymers can be obtained with suitable initiators or with specific terminating reagents.

The high reactivity of the living end of polymers in anionic polymerization enables the preparation of functionalised polymers and therefore block copolymers by deactivating with appropriate compounds. The deactivation of living poly(styrene), poly(isoprene), poly(butadiene) and poly(ethylene oxide) with a great variety of reagents leading to such end groups as hydroxyl, vinyl, ether and ester has been extensively reviewed⁷⁹. Of special interest is the functionality of block copolymers with carboxyl or sulphonate groups because they lead to ionomer-type block copolymers.

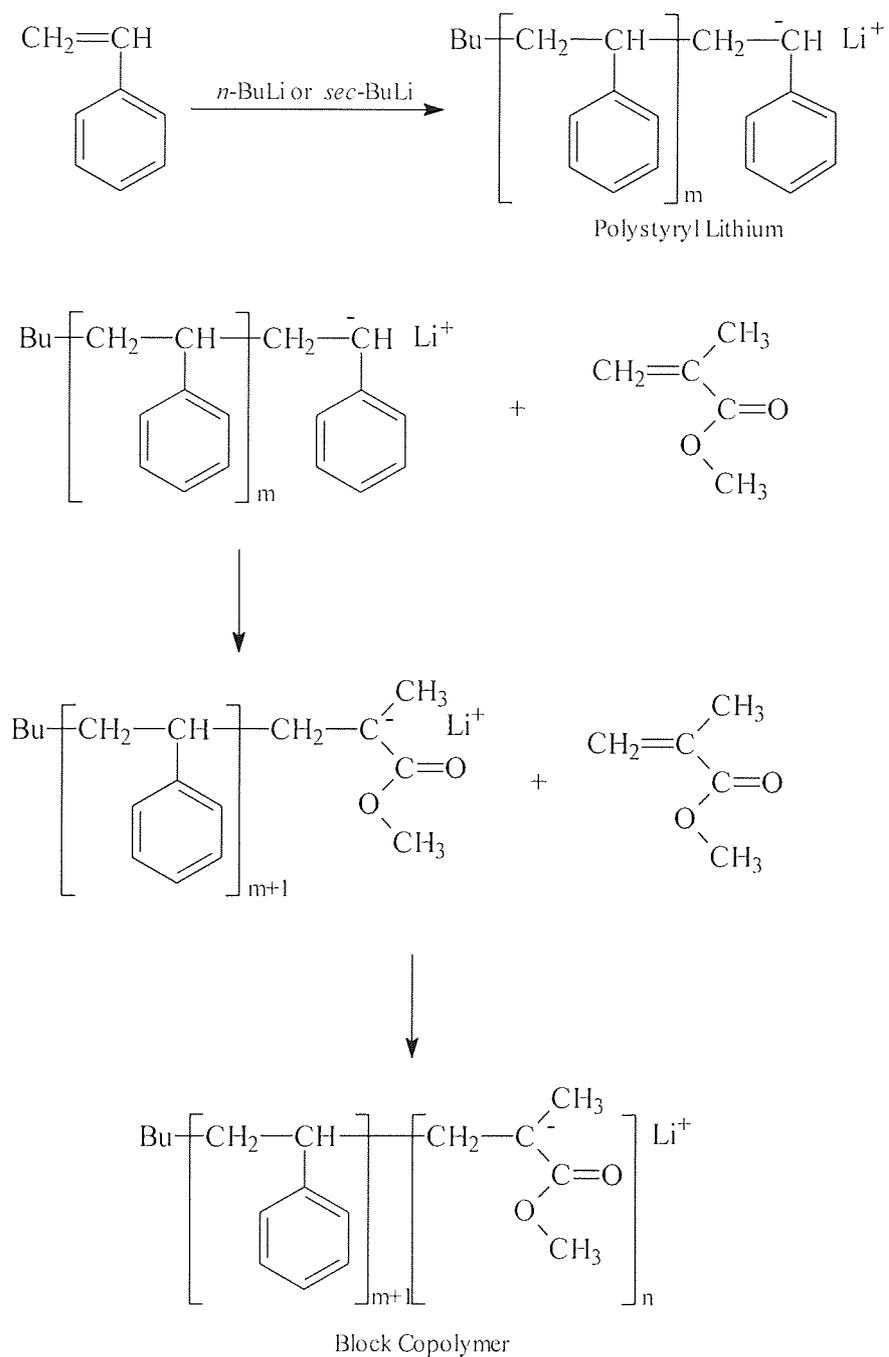
Methyl methacrylate can be used to prepare block copolymers. If methyl methacrylate is added to a living polystyrene system the methyl methacrylate will grow on the styrene end as shown in scheme 1.16. Styrene polymerization can be initiated using sodium naphthalide or butyllithium in THF. On addition of methyl methacrylate the mass gels when the polymerization is carried out at -78°C ⁴⁸. A problem encountered within this polymerization system is the high reactivity of polystyryl anions towards the carbonyl group of methyl methacrylate, leading to termination and transfer reactions. This side reaction can be avoided by addition of 1,1-diphenylethylene or α -methylstyrene to cap the polystyryl ends prior to the methyl methacrylate polymerization⁸⁰, which results in formation at the chain end of

diphenylmethyl anions or α -methyl styryl anions of lower nucleophilicity. These sites still initiate the polymerization of methacrylic esters, but they are unable to attack the ester carbonyls. The use of alkali metal alkoxides and also borate derivatives has been proposed to prevent attack on the carbonyl group by polystyryl anions or other anionic initiators^{54,55,80-83}.

Following the same concept, Teyssie *et al*⁶⁰ investigated the behaviour of alkali and alkaline earth metal halides in the anionic block copolymerization of methyl methacrylate. The conclusion drawn from this investigation was that LiCl was more effective in controlling the molecular weight distribution of the polymers than BaCl₂ or BaBr₂.

Copolymerization involving initiation of methyl methacrylate followed by addition of styrene to living poly(methyl methacrylate) is not a feasible reaction. The living ends of poly(methyl methacrylate) are not sufficiently active to initiate the polymerization of styrene, so that homo-polymerization of poly(methyl methacrylate) occurs and monomeric styrene is recovered.

Scheme 1.16 Mechanism of Block Copolymerization of MMA and Styrene



1.9 Other polymerization methods

In order to effect the controlled polymerization of acrylates and methacrylates, a number of methods have emerged including those already discussed. Some of are now briefly discussed.

1.9.1 Metal-free anionic polymerization

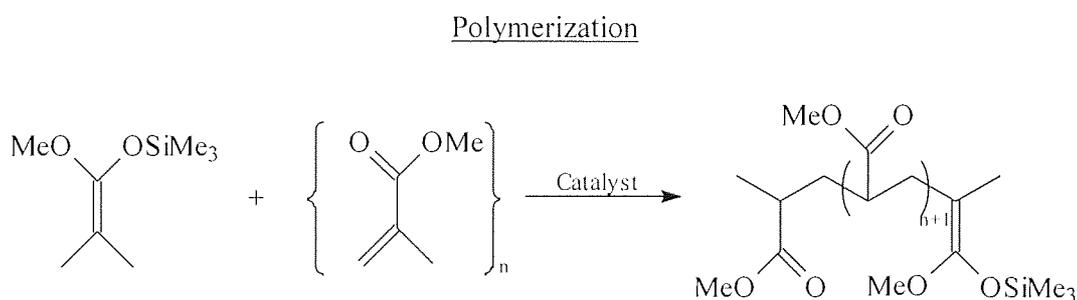
Since it has been established that the stability of the chain end in anionic polymerization can be changed by varying the counterion, the use of non-metallic initiators, e.g. $\text{EtC}(\text{CO}_2\text{Et})_2^-$, with non-metallic tetrabutylammonium as the gegenion has enabled acrylates and methacrylates to be polymerized at ambient temperatures⁸⁴. Polydispersities of around 1.3 were reported for the synthesis of poly(butyl acrylate). It has been suggested that the polymerization is effective even at high temperatures as termination reactions leading to the formation of tetrabutylammonium oxides are unfavourable both kinetically and thermodynamically. The mechanism of the polymerization is not well understood, but it is clear that it is not just a simple case of employing a large essentially free counterion, since the larger tetraoctylammonium ions have been found to be “not well suited for metalfree polymerizations”. It is to be noted that tetrabutylammonium salts are difficult to isolate, and hence it is hard to achieve the required purity needed for efficient anionic polymerization.

1.9.2 Group transfer polymerization (GTP)

GTP was first developed by Webster and Sogah at DuPont in the eighties⁸⁵. It offers equivalent polymerization control to classical anionic polymerization but has the advantage of operating at (and above) ambient temperatures, and is applicable to both acrylates and methacrylates.

GTP relies on a silicon-based initiator, most commonly the silyl ketene acetal, 1-methoxy-2-methyl-1-trimethylsiloxypropene (MTS). This initiator is unreactive to monomer except in the presence of a catalyst which may be either a nucleophile or Lewis acid. The process of polymerization is illustrated in Scheme 1.17.

Scheme 1.17 The Polymerization of Methyl Methacrylate by Group Transfer



The mechanism of GTP has been the subject of considerable debate, with three general mechanisms having been postulated. A good review article by Eastmond and Webster has been produced which considers these proposals in depth⁸⁶. Whatever the mechanism though, GTP has produced a synthetic tool which has proved useful to produce a wide variety of polymers including block copolymers, combs and stars.

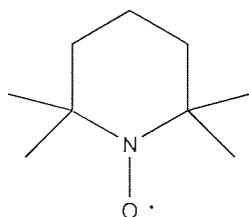
1.9.3 Immortal polymerization

This method, which utilises aluminium porphyrins as initiators, has been developed by Inoue. The initial work was carried out using a methyl-substituted aluminoporphyrin, which required irradiation from a xenon arc to initiate polymerization⁸⁷. The polymerization of MMA was found to be living and excellent control of molecular weight was achieved. Numerous variations on this initial system have been developed to cope with different monomers, to speed up the reaction (the system above achieves only 6.1% conversion after 2.5 hours), and to create initiators that do not require light.

Once again the mechanism of these polymerizations is not known although, since light is sometimes required for initiation, there may be bond homolysis followed by radical attack on a methacrylate, followed by co-ordination of this enol radical with the Al-porphyrin radical to yield the propagating centre.

1.9.4 Living free radical polymerization

While this process cannot be truly called a 'living' process, a great deal of success has been achieved in controlling the polymerization of MMA⁸⁸. The method operates by shielding the reactive chain end, preventing termination and transfer processes while allowing insertion of new monomer. The most successful work has used stable free radical nitroxides (such as TEMPO (see below)) to cap the growing macroradical chain end and producing polydispersities of 1.2 typically.



The radical enol chain end is stabilised by the nitrosyl radical. The nitrosyl radical enol bond is thermally labile, allowing propagation to occur. The term 'living' is misleading because termination can, and does, occur.

These systems are attractive because they allow polymerization at high temperatures (up to 160°C) and are much less sensitive to impurities than anionic polymerization, and therefore require less rigorous purification of reactants and solvents.

1.10 Molecular Weight Distribution and Polydispersity

Polymers with very narrow molecular weight distributions are obtained if all the chain ends are initiated simultaneously and if during the reaction, no further initiation or termination occurs. Under these conditions, the molecular weight distribution resulting was described by Flory⁸⁹:

$$\frac{\overline{M}_w}{\overline{M}_n} = 1 + \frac{1}{\bar{v}}$$

where, \overline{M}_w = weight average molecular weight,
 \overline{M}_n = number average molecular weight,
and \bar{v} = number average degree of polymerization

In the above case, where the polydispersity will tend towards zero, the polymer is said to be monodisperse and the conditions employed are said to be almost perfect. If, however, the initiating centres do not start growing at exactly the same time, the final polymer will be more disperse. Experimentally, non-uniformity of conditions for instance, poor agitation, too rapid monomer addition and irregular temperature control also cause broadening of molecular weight distributions.

Narrow molecular weight distributions are attributed to :

- (i) No termination or chain transfer.
- (ii) A rate of initiation, k_i , faster than the rate of propagation, k_p .
- (iii) Negligible extent of disproportionation during polymerization.
- (iv) Uniform polymerization conditions with respect to temperature and concentration of reactants.

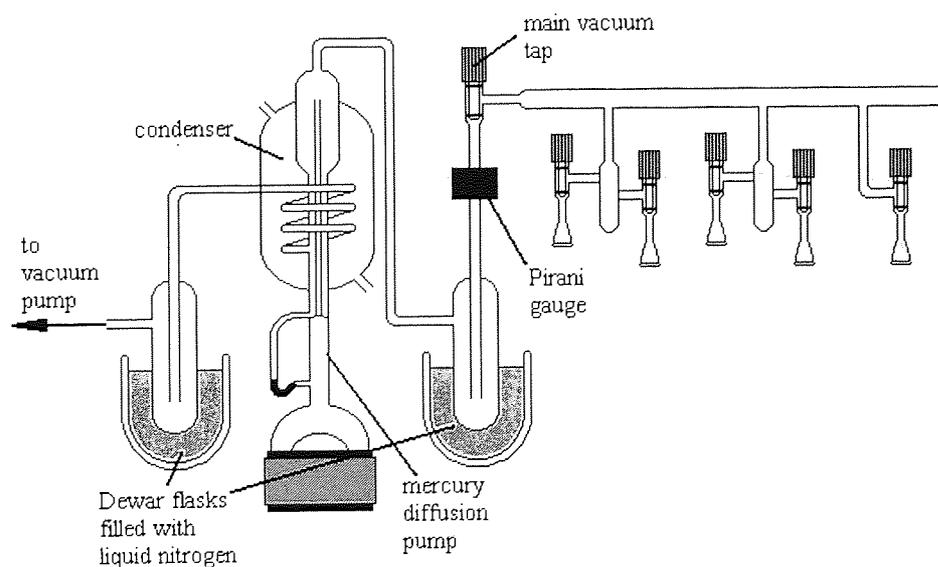
MATERIALS AND EXPERIMENTAL TECHNIQUES

2.1 Vacuum techniques

In order for a polymerization to be living, and to maintain its living character, it is normally necessary to exclude from the reaction all traces of impurities which may result in termination or transfer. Oxygen and water are capable of destroying the active centre in anionic polymerization, and the initiators and catalysts used in these systems are also sensitive to, and destroyed by, these impurities. For these reasons high vacuum, glove box and Schlenk techniques were employed both for the handling of solvents, initiators and catalysts, and for the polymerizations themselves.

2.1.1 The vacuum line

Figure 2.1 The Vacuum Line



The vacuum line (Fig. 2.1) was constructed of glass and consisted of two vacuum pumps, connected in series to a manifold, from which a number of taps and joints were suspended for the handling of materials. The two pumps were an Edwards rotary pump capable of reducing pressures to 10^{-3} mm Hg, and a mercury diffusion pump capable of further reducing the pressure to almost 10^{-5} mm Hg. The pressure inside the vacuum line was determined using a Pirani gauge. A liquid nitrogen trap was placed either side of the mercury diffusion pump, preventing mercury vapour from escaping into the atmosphere or into the manifold, and preventing vapours from the manifold being sucked into the pump during evacuation.

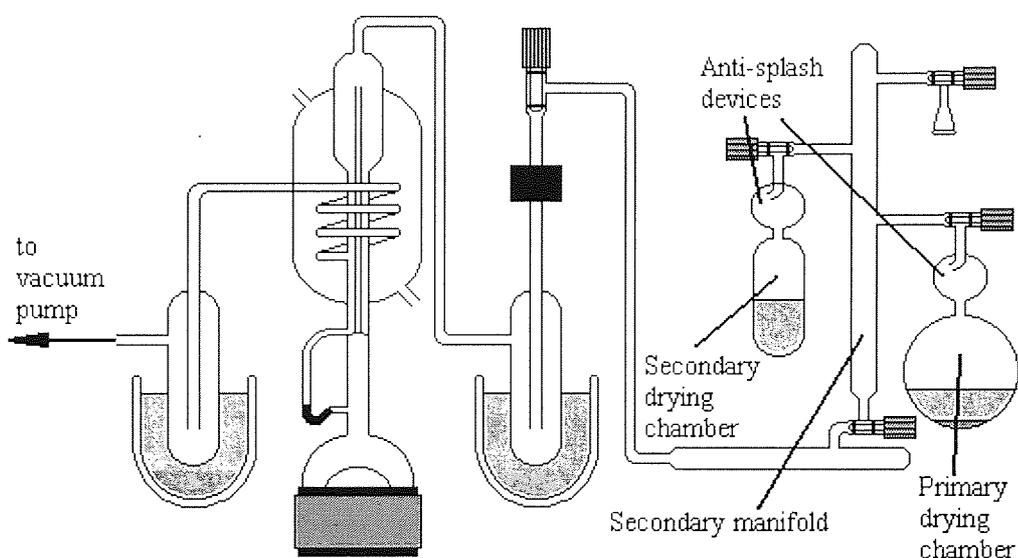
The manifold could be isolated from the pumps by means of a large PTFE tap for carrying out distillations and Schlenk transfers. The taps attached to the manifold were also PTFE and the joints were Quick-fit® to allow flasks to be connected. A PTFE tap attached to an argon inlet tube was also glass-blown onto the manifold, allowing it to be filled with argon for carrying out Schlenk techniques.

2.1.2 The solvent line

The solvent line (Fig. 2.2) was essentially similar to the vacuum line and was devised for the storing, drying and dispensing of solvents under high vacuum conditions. It differed from the vacuum line in that it had a secondary manifold from which emerged a primary and secondary drying chamber as well as a tap and joint for distilling dry solvent into a receiver vessel. The primary drying chamber consisted of a joint, so that a large round bottom flask, containing solvent and an initial drying agent, could be connected, and an anti-splash device so the solvent could be degassed by exposing it directly to the pump. From here the solvent could be distilled into the

secondary chamber. This was a fixed chamber that could contain either a further drying agent or an indicator of dryness, such as polystyryl lithium. The secondary chamber also had an anti-splash device for degassing. From here, the solvent could be dispensed by directly distilling into the required vessel.

Figure 2.1 The Solvent Line



2.1.3 Treatment of glassware

All vessels used in the handling of materials were rigorously cleaned by washing with toluene to remove all traces of polymer from previous reactions, before being soaked overnight in a solution of approximately 5% Decon 90 detergent in water. The vessels were then thoroughly rinsed with distilled water before being placed in a drying oven at 240°C for a period of at least 12 hours prior to use. On removal from the oven the vessels were quickly attached to the vacuum line and evacuated. The vacuum line and all vessels were also 'flamed out' using a Bunsen burner prior to use, to assist the removal of any final traces of moisture.

2.1.4 Freeze-thaw degassing of liquids

In order to distil a solvent under vacuum, it was necessary to remove all dissolved gases. This could be achieved by freeze-thaw degassing. The process involved firstly attaching the flask containing the solvent to the vacuum line and then immersing the flask in liquid nitrogen. Once the contents of the flask were frozen, the tap from the vessel to the vacuum line was opened and any gases above the surface of the frozen solvent were evacuated. Once the pressure in the vacuum line had reached a minimum (determined using the Pirani gauge) the tap was once again closed and the liquid nitrogen removed, allowing the solvent to thaw and release dissolved gases. Once the liquid had completely thawed, the vessel was re-immersed in liquid nitrogen and the process repeated until no increase of pressure was detected on opening the tap of the vessel when the solvent was frozen.

2.1.5 Degassing by direct evacuation

In certain circumstances, freeze-thaw degassing was problematic. Degassing large volumes of liquid can be very time consuming, and when some solvents, such as toluene, are frozen rapidly they can form glasses, which can shatter the vessel. In such cases the solvent was degassed by attaching the flask to the vacuum line and opening the appropriate taps so that the solvent was directly exposed to the pump without prior freezing. The dissolved gases in the solvent are then preferentially released, and only after the gases were given up would the solvent start to distil. That liquid was judged to be degassed when solvent could be seen being distilled into the protective traps of the vacuum line.

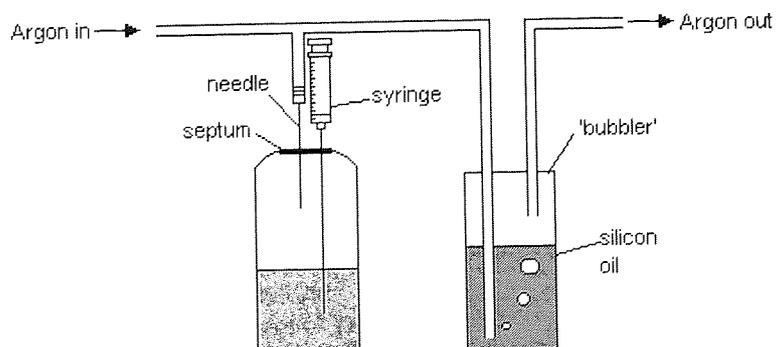
2.1.6 Trap-to-trap vacuum distillation

The following procedure was used for distilling from one vessel to another. Firstly, a receiver flask was placed on the vacuum line. This was then evacuated, if it was empty, otherwise its contents were frozen and it was then evacuated. The flask containing the solvent was then attached to the vacuum line and the contents were degassed. The receiver flask was then immersed in liquid nitrogen and the main tap of the manifold closed. The appropriate taps were then opened allowing the solvent to distil.

2.2 Schlenk techniques

In order to transfer air and moisture sensitive liquids and solutions, Schlenk techniques were sometimes advantageously employed. Such techniques employ the use of inert gases to enable transfer by syringe. The vacuum line was connected to an argon supply which facilitated the use of the line for such procedures. Argon was introduced into a vessel such as a reagent bottle via a needle attached to a bubbler system (Fig. 2.3) to create a slight positive pressure inside the vessel. The liquid inside could then be withdrawn using a syringe, without contaminating the solution inside.

Figure 2.3 Schlenk Transfer



It was also possible, by closing the main tap to the manifold of the vacuum line and allowing argon to fill the line, to create a slight positive pressure enabling a tap of a reaction vessel to be removed so that sensitive reagents could be introduced into a vessel without contamination.

2.3 The Glove Box

Another method of handling air- and moisture-sensitive compounds is by handling them inside a glove box. The glove box basically consists of an airtight box filled with an inert gas, with a window, a pair of gloves and an airtight port. The glove box used was manufactured by Halco Engineering. The atmosphere inside the glove box was argon at a slight positive pressure, and was continuously circulated through columns of a chemical adsorbant to remove unwanted compounds, particularly water and oxygen. It was also possible to operate the glove box at a negative pressure if particularly hazardous chemicals are used, in order to prevent any possible leakage to the operator. The adsorbant used was BASF R311 catalyst and 3Å molecular sieve and was capable of removing oxygen and water to below 2ppm and 10ppm respectively when operated at negative pressure, and 1ppm and 5ppm when used at positive pressure.

In order to introduce and remove components, a fully evacuable double door posting port was available. Items, such as vessels, reagent bottles, syringes, etc., were introduced to the glove-box by placing them into the port, sealing the port by closing the outer door, and then evacuating. Once all gases had been removed, the port was then filled with argon before re-evacuating. The cycle was typically repeated 5 times

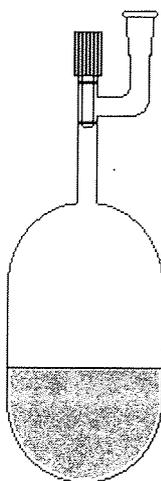
before the atmosphere in the port was judged to be similar in impurity level to that in the box. The inner door could then be opened and the items introduced into the main chamber of the glove box without contaminating the atmosphere inside.

2.4 Apparatus

The use of high vacuum techniques resulted in the need to design specialist glass vessels. The vessels, which were of varying sizes depending on their purpose, were constructed of glass and normally possessed a PTFE tap and a ground glass joint so that they could be affixed to the vacuum line (Fig. 2.4).

The vessels were designed in order to facilitate the distillation of solvents. The PTFE tap could also be removed allowing initiator solutions and catalyst to be syringed into and out of the vessel under a blanket of argon as described previously.

Figure 2.4 Solvent Vessel



2.5 Preparation and Purification of Materials

2.5.1 Monomers

2.5.1.1 Methyl Methacrylate (MMA)

Methyl methacrylate was obtained from the Aldrich Chemical Company. The monomer was of 99% purity and was inhibited with 65 ppm hydroquinone monomethyl ether. Sodium hydroxide pellets were added to the monomer in order to remove the inhibitor, before being removed by filtration after a period of at least 24 hours. The monomer was then vacuum distilled into a solvent flask containing calcium hydride in order to dry it. At least 24 hours was allowed for the drying to take place. The MMA was stored in the refrigerator at all times to prevent thermal initiation.

2.5.1.2 Styrene

Styrene was obtained from the Aldrich Chemical Company. The monomer was of 99% purity and was inhibited with 10-15 ppm 4-tertbutylcatechol. The monomer was prepared for use in the same way as MMA, i.e. using sodium hydroxide pellets to remove the inhibitor, and calcium hydride in order to dry it.

2.5.2 Solvents

2.5.2.1 Toluene

A.C.S. spectrophotometric grade toluene was obtained from the Aldrich Chemical Company. The solvent was of 99.5% purity. The toluene was prepared on the solvent line by firstly drying over calcium hydride in the primary chamber for at least 24 hours before being vacuum distilled into the secondary chamber containing low molecular weight polystyryl lithium. Since the living ends of polystyryl lithium are vivid red and are sensitive to impurities, this acted as an indicator that the toluene was dry.

The polystyryl lithium was made by introducing, under vacuum, a small amount of sec-butyl lithium (typically ~1ml of 1.4M solution in hexane) to the chamber. Dry toluene was then distilled in, followed by a small volume of styrene. The red colour developed within a few minutes and persisted throughout. Further addition of sec-butyl lithium and styrene were sometimes necessary to ensure the activity of the drying system.

2.5.2.2 Cyclohexane

A.C.S. spectrophotometric grade cyclohexane was obtained from the Aldrich Chemical Company. The solvent was of 99%+ purity. It was dried by storing over calcium hydride for at least 24 hours prior to use.

2.5.2.3 Dichloromethane (DCM)

Superpurity dichloromethane was supplied by Romil. The solvent was of 99.9% purity. It was dried over calcium hydride before being distilled under an atmosphere of argon into the desired vessel using a specially designed distillation apparatus. The first portion distilled was always discarded since DCM forms an azeotrope with water.

2.5.2.4 Tetrahydrofuran (THF)

HPLC grade sodium dried THF was obtained from Fisons. The solvent was of 99.9% purity. Additional sodium wire was added to the solvent to keep it dry. The THF was kept and dispensed in the glove box.

2.5.2.5 Methanol

Methanol was obtained from B.D.H. The solvent was of 99% purity. The methanol was used for precipitating polymer samples and was only degassed before use. This was to prevent oxidative coupling when used to terminate polymerization.

2.5.3 Initiators and Catalysts

2.5.3.1 sec-Butyl Lithium

sec-Butyl Lithium was obtained from the Aldrich Chemical Company as a 1.4M solution in hexane. The solution was supplied in a bottle with a 'sure seal' cap. This facilitated the use of Schlenk techniques to prevent contamination of the solution. The solution was stored under refrigeration to prevent decomposition.

2.5.3.2 tert-Butyl Lithium

tert-Butyl Lithium was obtained from the Aldrich Chemical Company as a 1.7M solution in pentane. The solution was stored and handled in the same manner as sec-Butyl Lithium.

2.5.3.3 Triisobutylaluminium

Triisobutylaluminium was obtained from the Aldrich Chemical Company at 93% purity. The liquid was supplied in a 'sure-pac' metal cylinder owing to its highly pyrophoric nature. A special attachment was screwed onto the vessel by means of which a blanket of argon could be passed over the top of the container prior to the tap of the vessel being opened allowing removal of the liquid by syringe.

2.5.4 Drying and Purification Agents

2.5.4.1 Calcium Hydride

Calcium Hydride of 95% purity was obtained from the Aldrich Chemical Company in powdered form and was used as supplied.

2.5.4.2 Sodium Metal

Sodium Metal was supplied in paraffin oil by B.D.H. The oil was removed using THF and the metal was squeezed through a die to produce a wire prior to use.

2.5.4.3 Sodium Hydroxide

A.C.S. grade sodium hydroxide of 97%+ purity was supplied in the form of pellets by the Aldrich Chemical Company and was used as supplied.

2.6 Analytical Techniques

2.6.1 Size Exclusion Chromatography (SEC)

2.6.1.1 Principles

Size exclusion chromatography (SEC), also known as gel permeation chromatography (GPC) is the most widely used analytical tool for determining molecular weight distributions of polymers. The technique operates by separating polymer chains according to their size. This separation takes place in a chromatographic column containing porous beads. These beads are most commonly made of highly cross-linked polystyrene. The pores are of roughly the same dimensions as the polymer molecule, once the beads are swollen with solvent.

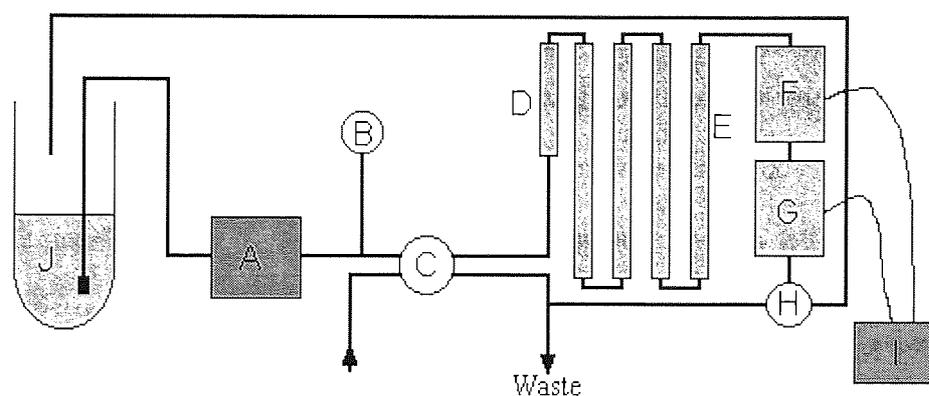
When a dilute solution of the polymer to be studied is passed through the column, it is only possible for a molecule to enter a pore if the molecule is of the same or smaller hydrodynamic volume as the pore. Hence, smaller molecules can enter more pores than larger ones resulting in them having a longer retention time in the column. A distribution of pore sizes is generally used, and so a separation occurs based on the hydrodynamic volume of the molecules.

2.6.1.2 Experimental

The SEC apparatus used is shown in Fig 2.6. The solvent used in the system was THF which was pumped round the system at a rate of 1 cm³ per minute by a Knauer HPLC pump (A). Polymer samples to be analysed were made up as a 2% solution in THF that also contained 0.25% toluene as a marker. The sample was introduced via a 100µl valve and loop injector system (C). The solution was then passed, via a guard

column to remove unwanted solids (D), through a series of 2 columns (E), a PLgel column with an exclusion limit of 10^3 \AA and a PLgel mixed B column.

Figure 2.5 Size Exclusion Chromatography Apparatus



A	HPLC pump	B	Pressure gauge	C	Valve and loop injector
D	Pre-column	E	PL-Gel columns	F	RI detector
G	UV detector	H	Solvent recycler	I	DCU
J	Solvent reservoir				

The polymer emerging from the columns was detected using a differential refractometer (F) and a UV/Visible spectrophotometric detector (G). The detectors were both manufactured by Polymer Laboratories and were linked to a data capture unit (I) that sent the data to a computer to be analysed by Polymer Laboratories software. The differential refractometer operated by continuously comparing the refractive index of the eluent with that of the pure solvent. The UV detector was used with polymers containing chromophoric groups, e.g. copolymers containing styrene.

The differential refractometer was also connected to a solvent recycler (H) so that impurity-containing eluent could be sent to waste but uncontaminated eluent could be sent back to the solvent reservoir (J).

Calibration

In order for the calculation of molecular weights to be performed, the instrument had to be calibrated. This was achieved using samples of polystyrene of known molecular weight and of very low polydispersity. These were obtained from Polymer Laboratories. The samples were run through the apparatus and the software analysed the results to produce a graph of molecular weight against elution volume, i.e. the volume of eluent to pass through the system from the time of injection to the detection of the narrow standard. When unknown samples were run through, the software was then able to use the calibration information to calculate the M_n , M_w and polydispersity. Since the elution volume of a given molecule can vary according to factors such as temperature, a small amount of toluene was added with each sample for analysis. The computer was then able to compare the elution volume of this, compare it with the elution volume at the time of calibration, and adjust the calibration accordingly.

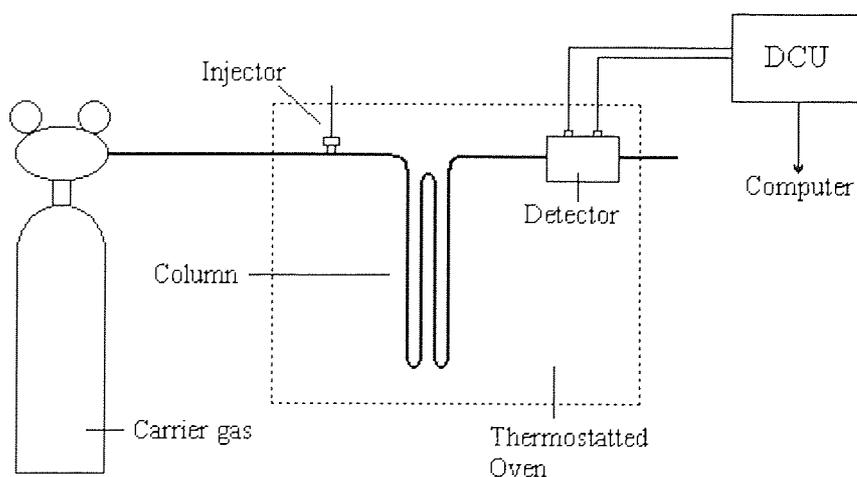
It should be noted that since the equipment was calibrated using polystyrene standards, the molecular weight information given for samples other than polystyrene are only polystyrene equivalents, not actual values.

2.6.2 Gas-liquid chromatography

2.6.2.1 Principles

Gas-Liquid Chromatography (GLC), otherwise known as Vapour Phase Chromatography, is used for the separation of mixtures of volatile compounds, which may differ in boiling point by as little as a fraction of a degree. The technique is in many ways similar to fractional distillation and generally consists of a 3-10m long coiled metal tube (diameter ~6mm) filled with ground firebrick (Fig 2.6). This tube acts as a support for the stationary phase which is generally a non-volatile liquid such as silicone oil or Carbowax. A sample is injected through a rubber septum into the column which is being swept with a current of inert gas. The sample first dissolves in the high-boiling phase, and then the more volatile components of the sample evaporate from the liquid and pass into the gas. By a process of repeated phase transition along the length of the column, separation of the various constituents is achieved. The separated components are then eluted from the column and pass over a detector. The time between injection and elution is known as the retention time.

Figure 2.6 Gas Chromatography Apparatus



2.6.2.2 Experimental

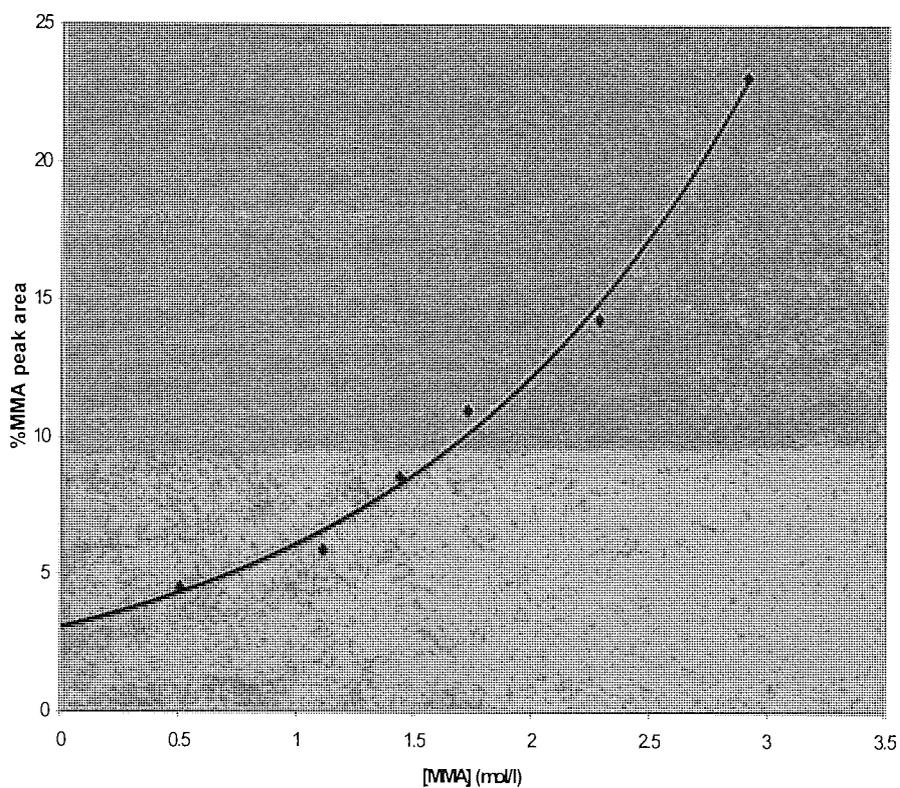
The chromatograph used for this work was a Pye Unicam GCD Chromatograph. In order to obtain a good separation between the peaks in the chromatograms obtained, a number of different combinations of columns and temperatures were tried. The best separation was obtained using a capillary column, rather than the more standard silicone grease column. Samples were introduced onto the column via the injection port, which consisted of an adapter over the inlet end of the column. The adapter contained a septum that was pierced using a microlitre syringe to introduce 1 μ l of the sample. The samples were then carried through the column by a stream of nitrogen. The best separation, for the mixtures of solvents used, was achieved with the detector at 130°C and the injector and the column both at 100°C.

As the components of the sample were eluted from the column, they were passed over a flame ionisation detector. The response from the detector was then sent to a computer that recorded the results and calculated the area under peaks to give a measure of the relative quantities of material present in the original sample.

GLC was used to determine the extent of conversion of samples gathered using a flow reactor by measuring the amount of MMA remaining relative to toluene. The areas under the MMA peaks were converted into concentrations by means of plotting a calibration curve (Fig 2.7). This was achieved by injecting samples of MMA of known concentrations made up as solutions in toluene that acted as standards. The peak areas of the MMA and toluene fractions at specific concentrations were measured and a calibration curve plotted. Comparison of the MMA and toluene peak

areas resulting from actual samples enabled the exact concentration of MMA, with respect to toluene, to be calculated. Hence, since initial concentrations were known, the extent of polymerization could be determined.

Figure 2.7 Graph for Calibration of GLC in Order to Calculate Concentration of MMA in Mixtures of MMA and Toluene



2.6.3 Nuclear Magnetic Resonance Spectroscopy

2.6.3.1 Principles

Nuclear magnetic resonance (NMR) spectroscopy is an extremely powerful tool for structure determination, in polymer science as in many other branches of chemistry. It makes use of the phenomenon of nuclear spin which results in some nuclei having angular momentum and hence an associated magnetic moment. Nuclei that show this property include ^1H , ^2H , ^{13}C , ^{15}N , ^{17}O , and ^{19}F . The angular moments are characterised by the spin quantum number, I . The nuclei listed above have values of I greater than 0 and therefore have magnetic moments and $2I+1$ spin states. The most commonly used nuclei are ^1H and ^{13}C which both have $I=1/2$ and therefore have two distinct energy states. Normally these states are degenerate but in a strong magnetic field the energy levels separate and transitions between them can be observed. The energy needed to induce these transitions is equal to the product of the magnetic moment and the magnetic field. In NMR spectroscopy these transitions are induced using electromagnetic radiation of the appropriate frequency.

What makes NMR spectroscopy useful is the fact the actual magnetic field experienced by the nucleus is not the same as that applied. This is because the electrons around the nucleus have a shielding effect so that the effective field strength is generally less than that applied. This situation can be represented as follows.

$$B_{\text{eff}} = B_0(1-\sigma)$$

Where σ is known as the screening constant. The size of σ depends on the chemical environment of the nucleus and so the effect is referred to a “chemical shift”. The result of this is that we can obtain a spectrum that consists of resonance lines each of

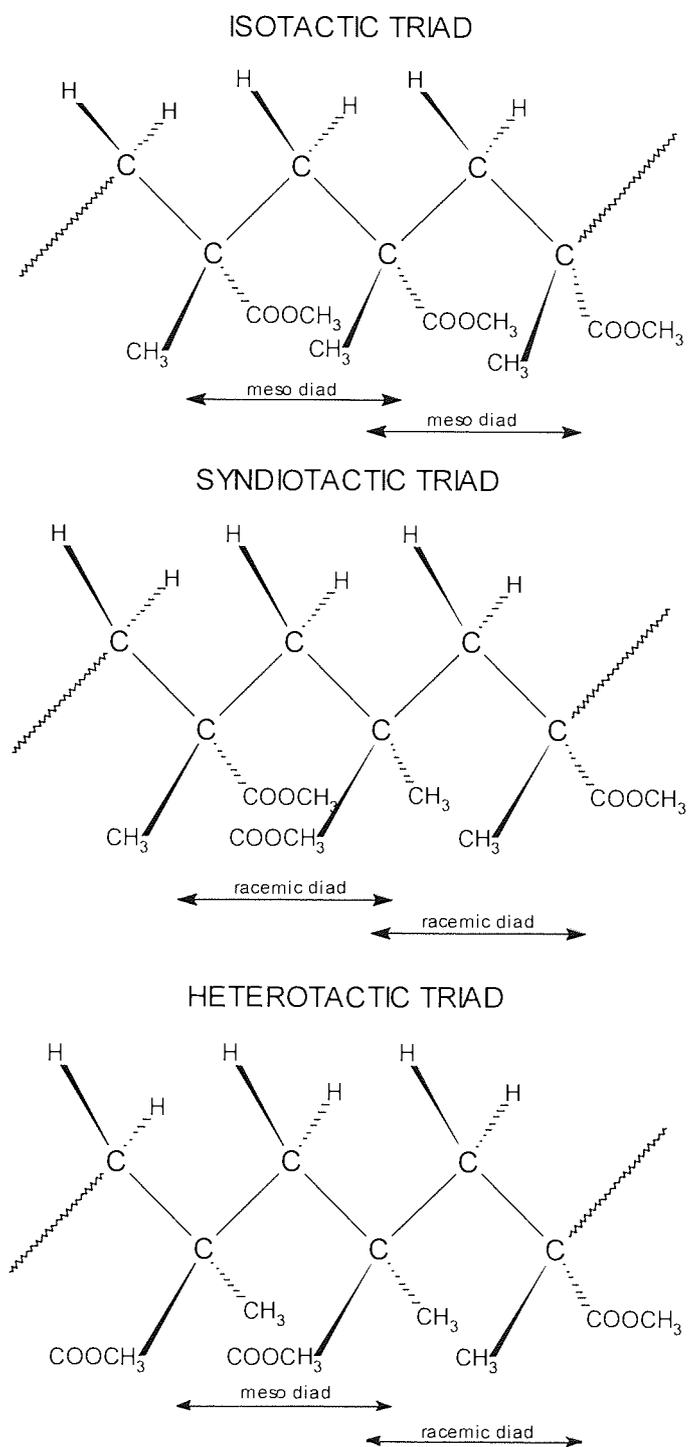
which corresponds to a particular chemical environment e.g. the different hydrogen atoms in a polymer. However, chemical shift is field dependent and so chemical shifts from different spectrometers cannot be compared. A non field dependent way of measuring chemical shift is by means of the δ scale which is measured in parts per million. The zero of the δ scale is a reference point provided by the single resonance of the equivalent protons (in the case of ^1H NMR) in a substance showing minimum chemical shift such as tetramethyl silane.

One complication that especially occurs in the case of proton NMR is the coupling of resonances of protons on adjacent carbon atoms. This happens because the apparent magnetic field observed by one nucleus is affected by the spin state of the other. The result of this is that the resonance line of this proton is split into two lines, or $n+1$ lines where there are n equivalent neighbouring protons. This phenomenon complicates the spectrum but also yields additional information about structure of the molecule being analysed.

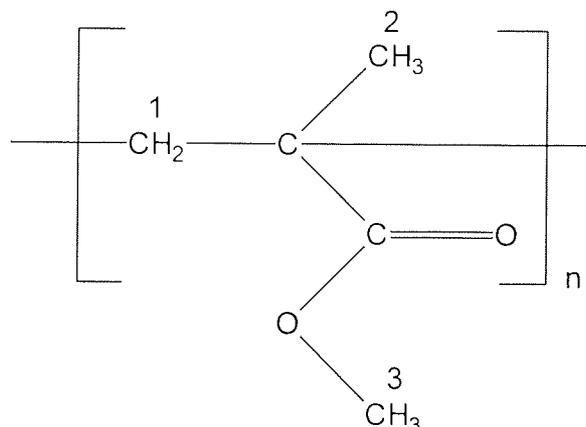
The application of NMR to polymer solutions has proved to be extremely useful not only for determining the general chemical structures of polymers, but also in the analysis of small changes in structure such as stereochemistry. In the case of PMMA, three different steric configurations of the polymer exist (Fig 2.8). These groups of three repeat units are known as triads. These triads can in turn be considered as a grouping of two diads. A diad is defined as comprising of two methine carbons and each diad can be described as either a meso (m), or racemic (r), diad. When all diads in a chain are of the meso type then the polymer is said to be isotactic. Similarly, a chain consisting entirely of racemic diads is said to be syndiotactic. A chain

consisting of a random or statistical distribution of diads is known as heterotactic (or atactic).

Figure 2.8 Three Steric Configurations of PMMA



PMMA contains protons in only three chemical environments.



Since there are no protons on neighbouring carbon atoms to any of these groups, there is no coupling induced splitting observed in the spectrum. However, three peaks can be seen associated with the α -CH₃ group. This is due to the three different steric configurations of PMMA; i.e. the protons adsorb radiation at slightly different frequencies depending on which type of triad of which the α -CH₃ group is at the centre. The area under each peak corresponds to the amount of triad present in the polymer chain. The fraction of each configuration, P_i (isotactic), P_s (syndiotactic), and P_h (heterotactic), as determined from the peak areas, can be related to σ , the probability of a diad in the chain being an isotactic diad.

By definition: -

$$P_i = \sigma^2 \quad (\text{mm})$$

$$P_s = (1-\sigma)^2 \quad (\text{rr})$$

$$P_h = 1 - P_i - P_s = 2(\sigma - \sigma^2) = 2\sigma(1-\sigma) \quad (\text{rm})(\text{mr})$$

The proportion of heterotactic units rises to a maximum at $\sigma = 0.5$ (random propagation). For a random polymer, the ratios $i : h : s = 1 : 2 : 1$.

2.6.3.2 Experimental

This work was carried out using an AC300 Bruker Fourier Transform spectrometer operating at 300 MHz. Solutions for analysis were made up in deuterated chloroform (CDCl_3). Both ^1H NMR and ^{13}C NMR spectra were obtained.

CHAPTER THREE

BULK POLYMERIZATIONS OF METHYL METHACRYLATE IN THE PRESENCE OF LITHIUM AND ALUMINIUM ALKYLs

3.1 Introduction

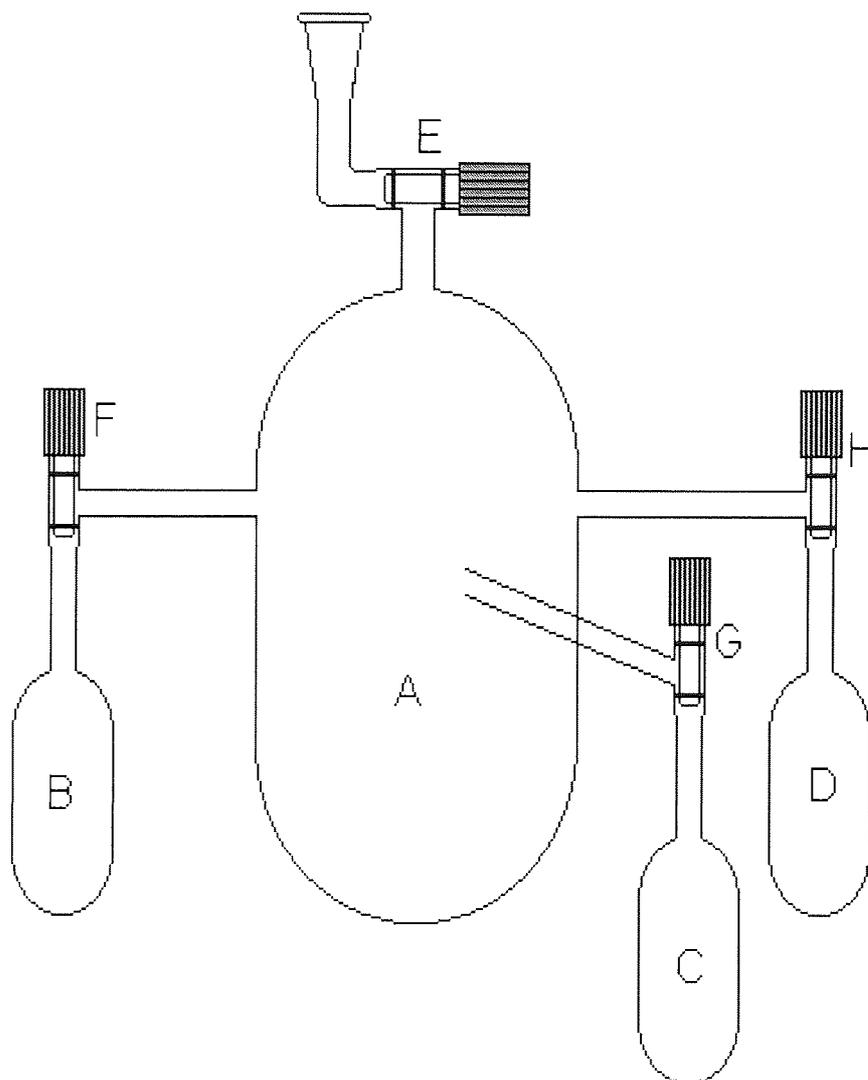
The use of aluminium alkyls to enhance the living character of methyl methacrylate polymerization is an area of study that has proved popular with researchers. However, despite this attention, little is known about the way these systems function.

Previous work, carried out by this research group, has shown the effects of varying the nature of the initiator and the cocatalyst⁹⁰. This chapter describes work carried out on the bulk polymerization of methyl methacrylate initiated by tert-butyl lithium and using aluminium triisobutyl as the cocatalyst, and attempts to investigate the effect of varying other parameters in the reaction such as polymerization temperature, solvent polarity and order of addition of reactants.

3.2 Experimental

Bulk polymerizations were carried out in a specially designed vessel that allowed mixing of components under high vacuum conditions (Fig 3.1).

Figure 3.1 Reaction Vessel



In a typical polymerization the required amount of monomer (MMA) was distilled directly in bulb B of the vessel. The initiator and cocatalyst solutions were then transferred into bulbs C and D respectively, by removing taps G and H in turn, and transferring the required volumes of the solutions by syringe under Schlenk conditions. These were then degassed by the freeze-thaw technique. Finally, the solvent was then distilled into the main chamber, A, of the vessel. Whenever

mixtures of solvents were used, the solvent present in the smallest quantity was added first, either by distillation or by Schlenk transfer.

Prior to the commencement of the reaction, the vessel was removed from the vacuum line and allowed to equilibrate to the reaction temperature. For reactions carried out at room temperature or above, the vessel was immersed in a thermostatically controlled water bath for 20 minutes prior to the commencement of the polymerization. Lower temperatures were achieved using baths containing either water/ice mixtures or methanol/dry ice mixtures. The reaction was then started by opening the taps in the appropriate order, thus allowing the monomer, initiator and cocatalyst to flow into that main chamber as desired. Vigorous shaking between each addition ensured thorough mixing of components.

After allowing the appropriate reaction time, the reaction was terminated by opening the vessel to release the vacuum and pouring the contents into approximately 300ml of stirred degassed methanol. The polymer was then recovered by filtering the solid and leaving it to dry under vacuum at 40°C for 24 hours.

3.3 Studies of the effect of order of mixing of reactants

It has been observed by Haddleton *et al* that the order of addition of reagents was important in these systems⁷⁶, i.e. whether the initiator and cocatalyst are mixed prior to the addition of monomer (herein referred to as **pre-mixing**), or if the monomer and cocatalyst are mixed prior to the addition of initiator (referred to as **post-mixing**). His results show that polymers with narrow molecular weight distributions can be

produced by both methods and in both cases a linear relationship is seen between the number average molecular weight, M_n , at final conversion, and the monomer to initiator molar ratio. However, it was reported that, although neither initiation system delivered 100% initiator efficiency, i.e. 1 mole of initiator producing 1 mole of living polymer chains, the efficiency of post-mixing was seen to be considerably less than that of pre-mixing. The conclusion that was drawn from this work was that distinctly different initiating species are involved.

In order to investigate this phenomenon, the following experiments were carried out, firstly in order to observe the reported difference in initiator efficiency, and also to see if there is any observable effect on the yield of polymerization, the polydispersity of the polymer produced, or the stereoregularity of the polymer.

3.3.1 Pre-mixing

Polymerizations of MMA, using toluene as solvent, were carried out as described in section 3.2. The initiator and cocatalyst were admitted into the main chamber of the reaction vessel and allowed to mix before the addition of the monomer. The vessel was shaken vigorously after the addition of each reagent to ensure thorough mixing. Polymerization reactions were conducted at 25°C.

Each polymerization was allowed to proceed for approximately 2 hours. The reaction was then terminated and the polymer recovered as described in section 3.2.

The quantities of reagents used are shown in table 3.1 along with the calculated yield of each reaction.

Table 3.1 Concentrations of Reagents for Polymerization of MMA

Under Pre-mixing Conditions (PRE 1-3) and Percentage Yields of Those Reactions

Experiment Number	[MMA] (mol/l)	[tBuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	[MMA]/[tBuLi]	[Al(iBu) ₃]/[tBuLi]	Yield %
PRE 1	3.0	0.015	0.045	200	3	66
PRE 2	1.6	0.0078	0.024	200	3	34
PRE 3	2.8	0.0056	0.016	500	3	65

In each case, mixing of initiator and cocatalyst yielded no obvious colour change, however addition of monomer resulted in change to pale yellow. The reaction mixture became viscous very quickly and rapidly generated heat, as indicated by a significant temperature change. The yellow colour faded quickly.

The products were analysed by SEC and NMR spectroscopy.

3.3.1.1 SEC analysis

The analysis of products by size exclusion chromatography was carried out as described in section 2.7.1. A typical SEC chromatograph of a monodisperse polymer (POST 20) is shown in Appendix 1. The molecular weights and molecular weight distributions obtained from PRE 1-PRE 3 are shown in table 3.2, as well as the calculated initiator efficiencies. The initiator 'efficiencies' were calculated using the following formula.

$$\text{Efficiency} = \frac{\text{predicted molecular weight}}{\text{actual molecular weight}} \times 100$$

Table 3.2 Molecular Weight Distributions for the PMMA
Obtained From Polymerizations Under Pre-mixing
Conditions (PRE 1-3) and the Percentage Initiator Efficiencies

Experiment Number	$M_n / \text{g mol}^{-1}$	$M_w / \text{g mol}^{-1}$	Polydispersity	Initiator Efficiency (%)
PRE 1	123000	220000	1.80	17
PRE 2	50000	94000	1.87	40
PRE 3	58000	161000	2.75	84

3.3.1.2 NMR analysis

3.3.1.2.1 ^1H NMR

The polymer samples were analysed by NMR as described in section 2.6.3. Appendix 2 shows the ^1H NMR spectrum of PRE 1, which is typical of the spectra obtained for these samples of PMMA. The chemical shifts, δ , of the peaks corresponding to the spectrum of the polymer were assigned as shown in table 3.3.

The $\alpha\text{-CH}_3$ of PMMA is triad sensitive, and analysis of the relevant areas of the spectrum corresponding to the $\alpha\text{-CH}_3$ peaks can give a measure of the percentage isotactic, heterotactic and syndiotactic content of the polymer, and hence a value can be calculated for σ , the probability of a diad in the polymer chain being an isotactic diad.

Table 3.3 Assignment of Major Peaks in the ^1H NMR Spectrum of PMMA

Chemical Shift (ppm)	Assignment
0.76 - 0.81	syndiotactic (rr)
0.94 - 0.99	$\alpha\text{-CH}_3$ heterotactic (mr)
1.12 - 1.18	isotactic (mm)
1.78	-CH ₂ -
1.86	
1.99	
3.57	-O-CH ₃

The values of σ were calculated using the following formula, and are quoted in table 3.4, along with the iso-, hetero-, and syndiotactic contents which correspond to this.

$$P_s = (1 - \sigma)^2 = \frac{\text{Area under syndiotactic } -\text{CH}_3 \text{ peak}}{\text{Total area under } -\text{CH}_3 \text{ peaks}}$$

Table 3.4 Values of σ and Corresponding Tacticities of PRE 1-3

Sample name	σ	Ps	Ph	Pi
PRE 1	0.22	61	34	5
PRE 2	0.20	63	33	4
PRE 3	0.28	51	41	8

3.3.1.2.2 ^{13}C NMR

Appendix 3 shows the ^{13}C NMR spectrum of PRE 1, which is a spectrum typical of those of PMMA produced in these reactions. Table 3.5 assigns the chemical shifts, δ , of the peaks corresponding to the spectrum of the polymer.

The areas of peaks in ^{13}C NMR, unlike ^1H NMR, are not quantitative, and so the spectra obtained from samples can only give a qualitative verification of the presence of the various stereofoms to support the conclusions drawn from the proton spectra.

Table 3.5 Assignment of major peaks in the ^{13}C NMR spectrum of PMMA

Chemical Shift (ppm)	Assignment
16 – 22 (multiplet)	$\alpha\text{-}\underline{\text{C}}\text{H}_3$ syndiotactic (rr) heterotactic (mr) isotactic (mm)
44 – 46 (multiplet)	$\text{-}\underline{\text{C}}\text{H}_2\text{-}$ syndiotactic (rr) heterotactic (mr) isotactic (mm)
51.7	$\text{-O-}\underline{\text{C}}\text{H}_3$
54.36	quaternary carbon
176 – 179 (multiplet)	$\text{-}\underline{\text{C}}\text{=O}$ syndiotactic (rrr) heterotactic (rmmm) heterotactic (rrmm) heterotactic (rrrm) isotactic (mmm)

For the samples PRE 1 to PRE 3 the ^{13}C spectra give very good agreement with the ^1H results. The isotactic peaks due to -CH_3 and $\text{-CH}_2\text{-}$ are barely visible, especially for

PRE 1 and PRE 2. The multiplet due to -C=O is quite ill defined so a definite assignment to structures is not possible.

3.3.2 Post-mixing

Polymerizations of MMA, using toluene as solvent, were carried out as described in section 3.2. The monomer and cocatalyst were firstly allowed to mix with the solvent in the main chamber of the vessel. At this point, POST 1 and POST 2 showed no colour change, however, in the case of POST 3 and 4 the mixing resulted in the appearance of a pale yellow colour. The initiator was then allowed to enter the main chamber of the vessel, which was vigorously shaken to ensure quick and thorough mixing. The colour apparent in POST 3 and 4 faded rapidly on addition of initiator, and, in the case of POST 3 only, heat was generated. The reactions were conducted at 25°C .

The quantities of reagents used, and the calculated yields of reaction, are shown in table 3.6.

Table 3.6 Concentrations of Reagents for Polymerization of
MMA Under Post-mixing Conditions (POST 1-4) and
Percentage Yields of Those Reactions

Experiment Number	[MMA] (mol/l)	[t-BuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	[MMA]/[t-BuLi]	[Al(iBu) ₃]/[t-BuLi]	Yield %
POST 1	1.4	0.0097	0.030	150	3	1.6
POST 2	3.2	0.016	0.048	200	3	1.1
POST 3	2.6	0.013	0.039	200	3	69
POST 4	2.6	0.0052	0.015	500	3	9.8

Polymerization was allowed to proceed for approximately 2 hours. The reaction was then terminated and the polymer recovered as described in section 3.2.

Analysis of products was carried out by SEC and NMR spectroscopy.

3.3.2.1 SEC analysis

The analysis of products was carried out as described in section 2.7.1. The molecular weights and molecular weight distributions obtained from POST 1- POST 4 are shown in table 3.7, along with the calculated initiator efficiencies.

Table 3.7 Molecular weight distributions for the PMMA obtained from polymerizations under post-mixing conditions (POST 1-4) and the percentage initiator efficiencies.

Experiment Number	$M_n / \text{g mol}^{-1}$	$M_w / \text{g mol}^{-1}$	Polydispersity	Initiator Efficiency (%)
POST 1	77000	161000	2.10	19
POST 2	152000	278000	1.83	13
POST 3	73000	120000	1.64	28
POST 4	45000	91000	2.05	111

3.3.2.1.1 NMR analysis

3.3.2.1.1.1 ^1H NMR

The yields of reactions POST 1 and POST 2 were very small, so all polymer was used to carry out the SEC analysis. The calculated values of σ for the other two samples, along with the corresponding tacticity contents are shown in table 3.8.

Table 3.8 Values of σ and Corresponding Tacticities of POST 3-4

Sample name	σ	Ps	Ph	Pi
POST 3	0.21	63	33	4
POST 4	0.42	34	49	17

POST 3 shows quite a high level of syndiotacticity as expected, however POST 4 is predominately heterotactic. This, in addition to the high polydispersity and low yield, would indicate the reaction has not progressed in a living manner.

3.3.2.1.1.2 ^{13}C NMR

The results of the ^{13}C analysis confirm the findings of the proton studies. The spectrum of POST 3 shows large syndiotactic peaks from the $-\text{CH}_3$ and $-\text{CH}_2-$ and barely visible isotactic. POST 4, however shows large, clearly visible isotactic peaks.

3.3.3 Discussion

In general the polymerizations carried out by the post-mixing method seem to be less successful, giving lower yields and lower initiator efficiencies, with the exception of POST 4. However, it seems likely from the very high polydispersity, and the fact that the polymer produced is heterotactic, that this erroneous result is due to the polymerization progressing by a non-living mechanism, probably free-radical. This is most probably owing to the inadvertent ingress of some impurity at some stage in the experimental procedure.

Aside from the lower initiator efficiency of the post-mixing method, no other conclusions can be drawn such as trends in polydispersity or tacticity. It is clear, though, that these polymerizations suffer from a general lack of consistency which can be attributed to the sensitivity of the system combined with inadequate experimental technique, these experiments being the first carried out of this research.

3.4 Studies of the effect of temperature

In any polymerization, there are a number of different mechanistic steps which take place. Each of these has its own kinetic behaviour and hence the balance of these reactions changes with the reaction temperature. For example, if the rate of initiation is fast relative to that of propagation then this might be observed as a decrease in polydispersity. The rate of termination reactions, which generally have low activation energies, might also change in relation to propagation reactions, which are significantly dependent on temperature. It is possible that there might be a change in the association of species at the chain end which in turn might result in a change of tacticity of the polymer.

This section represents a series of experiments designed to show if any of these effects take place as reaction temperature changes, and to attempt to produce a more monodisperse, stereoregular polymer.

3.4.1 Experimental

Polymerizations of MMA, using toluene as solvent, were carried out as described in section 3.2. All polymerizations were carried out with pre-mixing of initiator and cocatalyst. The polymerizations at 0°C were carried out by placing the reaction vessel in a Dewar containing ice and water. Temperatures of -30°C were achieved in a similar manner except using a Dewar containing dry ice and acetone.

The quantities of reagents used and the reaction temperatures are shown in table 3.9.

Table 3.9 Concentrations of Reagents and Reaction Temperatures for the
Polymerization of MMA (PRE 4-8)

Experiment Number	[MMA] (mol/l)	[t-BuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	[MMA]/[t-BuLi]	[Al(iBu) ₃]/[t-BuLi]	Reaction Temp (°C)
PRE 4	3.7	0.0073	0.054	500	7.5	25
PRE 5	2.4	0.010	0.030	250	3	0
PRE 6	2.0	0.0025	0.016	800	6.5	0
PRE 7	2.5	0.016	0.040	150	2.5	-30
PRE 8	1.8	0.011	0.048	150	4.5	0

Polymerizations were allowed to proceed for approximately 2 hours. The reactions were then terminated and the polymer recovered as described in section 3.2.

3.4.2 Results

In all cases the mixing of initiator and cocatalyst resulted in no colour change and the addition of monomer resulted in a pale yellow colour being formed. The polymerization occurred rapidly and exothermically and the yellow colour faded over the course of a few seconds. The yields of polymerizations PRE 4-8 are given in table 3.10.

Table 3.10 Product Yields for Polymerization of MMA (PRE 4-8)

Experiment Number	Reaction Temp (°C)	% Yield
PRE 4	25	74
PRE 5	0	85
PRE 6	0	97
PRE 7	-30	70
PRE 8	0	78

Analysis of products was carried out by SEC and NMR spectroscopy.

3.4.2.1 SEC analysis

The analysis of products was carried out as described in section 2.7.1. The molecular weights and molecular weight distributions obtained from PRE 4- PRE 8 are shown in table 3.11, along with the calculated initiator efficiencies.

Table 3.11 Molecular Weight Distributions for the PMMA Obtained from Polymerizations PRE 4 – PRE 8 and the Percentage Initiator Efficiencies.

Experiment Number	$M_n / \text{g mol}^{-1}$	$M_w / \text{g mol}^{-1}$	Polydispersity	Initiator Efficiency (%)
PRE 4	38000	50000	1.32	133
PRE 5	42000	54000	1.30	56
PRE 6	49000	71000	1.46	166
PRE 7	48000	56000	1.16	31
PRE 8	93000	106000	1.14	18

3.4.2.2 NMR analysis

3.4.2.2.1 ¹H NMR

Proton NMR analysis was carried out on the five samples, and a value for σ was calculated from the relative integrals of the $-\text{CH}_3$ proton peaks. These values are shown in table 1.12, along with the corresponding percentage tacticities.

Table 3.12 Values of σ and Corresponding Tacticities of PRE 4-8

Sample name	σ	Ps	Ph	Pi
PRE 4	0.24	58	36	6
PRE 5	0.19	66	30	3
PRE 6	0.20	64	32	4
PRE 7	0.13	76	22	2
PRE 8	0.17	68	29	3

As can be observed, all of the polymers are predominately syndiotactic, and furthermore there seems to be a strong correlation between polymerization temperature and tacticity.

3.4.2.2.2 ¹³C NMR

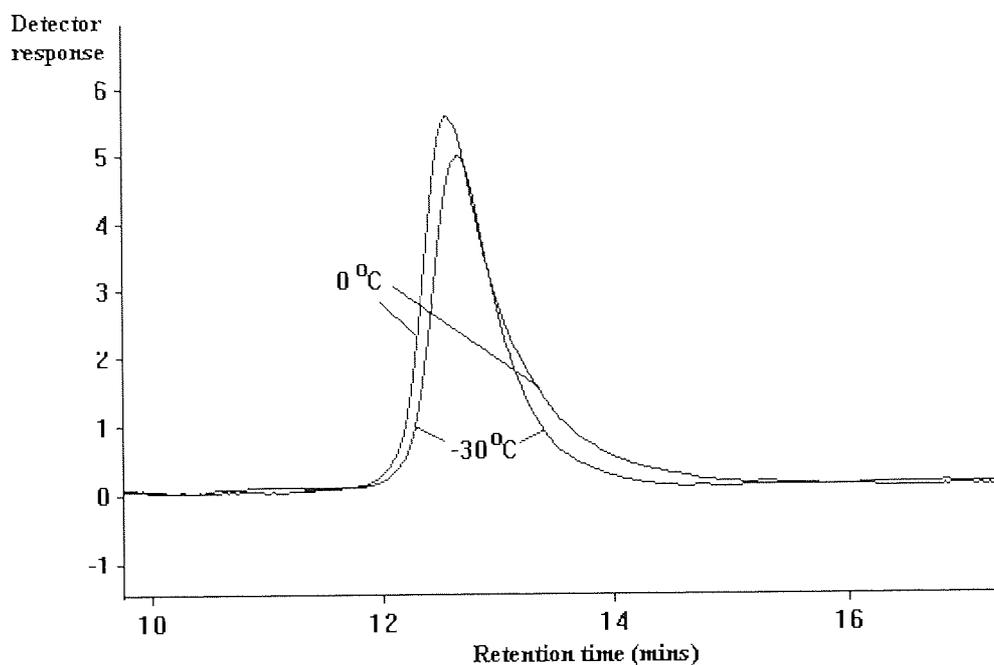
The results ¹³C NMR confirm the fact that the polymers produced are syndiotactic, but beyond that, information about the relative tacticities cannot be determined.

3.4.3 Discussion

A number of observations can be made on consideration of the results presented above. Firstly, there appears to be a trend towards lower polydispersity as the reaction temperature decreases. This trend is not as clear as it might be since reactions at 0°C appear to yield quite a range of polydispersities. The ‘poor’ result from PRE 6 may be put down to the lower concentration of initiator used, as this results in the reaction being more susceptible to the level of impurity present. It is also noteworthy that the polydispersity of PRE 8 (conducted at 0°C) is as low as that of PRE 7 (conducted at –30°C). If one were to analyse the shape of the SEC traces (Fig 3.2) then it can be seen that the shape of the peak is actually narrower in the case of PRE 7 but the peak also has a low molecular weight tail which is responsible for the polydispersities of the two polymers being roughly equal.

An analysis of the dependence of molecular weight distribution on temperature shows that the polydispersity narrows with decreasing temperature. It can then be deduced that either the rate of initiation increases relative to the rate of propagation, or that the rate of termination falls with respect to initiation and propagation. It is likely that both of these are true to some degree, however, if the latter situation was predominant then low molecular weight tailing would be apparent at higher temperatures. This appears not to be the case as PRE 4 displays virtually no tailing, and so the former situation is most likely the case.

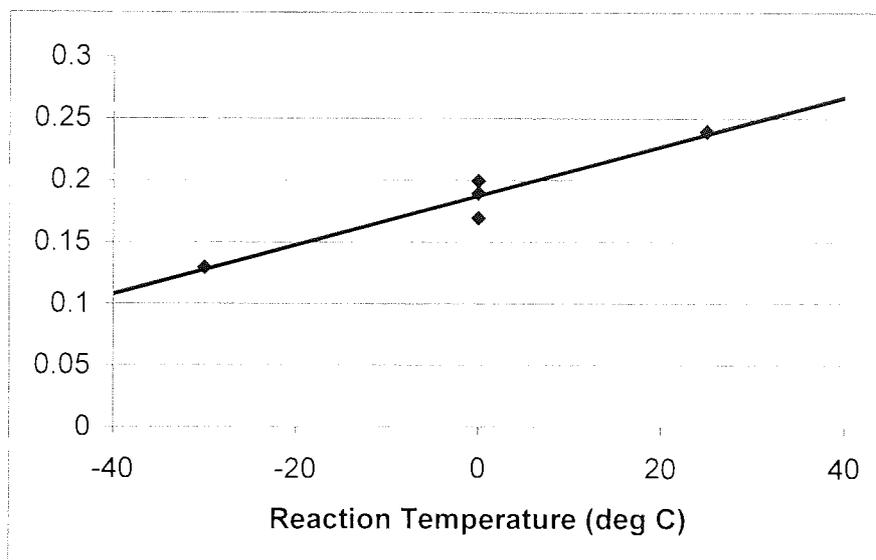
Fig 3.2 Overlay of the SEC Traces of Polymer Produced from PRE 7 and PRE 8



The presence of the low molecular weight tail in the case of PRE 7 may be due to a thermodynamic effect, where the rate of polymerization falls more than the rate of termination, but may also be due to a small amount of a terminating impurity being present in the system.

The other observable effect is a very clear link between polymerization temperature and tacticity. This can be seen quite clearly in table 3.3. This effect can be attributed to closer associations as the chain end. The precise nature of these associations is unknown although it is likely that coordination of aluminium alkyl to the penultimate ester carbonyl group will have some effect.

Figure 3.3 Plot of σ Against Reaction Temperature



3.5 Studies of the effect of varying solvent polarity

As described in the introduction of this thesis, the progression of an anionic polymerization can vary greatly depending on the propagating species, which is, in turn, influenced by the polarity of the solvent used. A polar solvent will result in the propagating species favouring of free ion pairs. A non-polar solvent will cause the propagating species to tend towards covalent bonds and close contact ion pairs. The series of experiments described in this section were conducted in order to investigate the effect of making small changes in the polarity of the solvent in terms of factors such as initiator efficiency and polydispersity, and also looking for changes in the tacticity of the produced polymers to see if a closer association between the propagating ion pairs results in a more stereoregular structure.

3.5.1 Polymerizations using toluene/cyclohexane mixtures as solvents

Polymerizations of MMA, were carried out using mixtures of toluene and cyclohexane(CHex) in varying proportions as the solvent in order to investigate the effect of lowering the polarity slightly. The reactants were combined by pre-mixing monomer and cocatalyst. Low temperature reactions were attained by placing the reaction vessel in a dewar containing ice and water (0°C). Reactions at room temperature and above were carried out by immersing the reaction vessel in an electrically regulated water bath.

In all cases, on mixing the monomer and cocatalyst, the characteristic pale yellow colour appeared. On addition of initiator, however, there was what appeared to be an immediate precipitation that would not dissolve on shaking. This was originally thought to be insolubility of the initiator in the less polar medium, although it was also

a possibility that the phenomenon was not precipitation but a process of coacervation, that is a process of phase separation brought about by the higher solubility of the initiator in toluene than in cyclohexane. In an attempt to disturb this phase separation, the reaction was also carried out at both lower and higher temperature, but the behaviour persisted. Despite this the yellow colour faded as expected, and polymer was produced.

The yields of the reactions, the quantities of reagents used and the reaction temperatures are shown in table 3.13.

Table 3.13 Concentrations of Reagents for Polymerization of

MMA Using Mixtures of Toluene and Cyclohexane as Solvent (POST 5-8)

Expt Number	[MMA] (mol/l)	[t-BuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	% (v/v) Chex	[MMA]/ [t-BuLi]	[Al(iBu) ₃] /[t-BuLi]	Reaction Temp (°C)	% Yield
POST 5	0.74	0.015	0.047	47	50	3.1	25	77
POST 6	0.81	0.016	0.056	22	50	3.4	25	71
POST 7	0.73	0.019	0.050	17	39	2.7	0	70
POST 8	0.66	0.014	0.044	25	46	3.1	40	63

Polymerization was allowed to proceed for approximately 1 hour before terminating by addition of degassed methanol and recovery of the polymer

Analysis of products was carried out by SEC and NMR spectroscopy. The results are discussed in chapter 3.5.4.

3.5.1.1 SEC analysis

The analysis of products was carried out as described in section 2.7.1. The molecular weights and molecular weight distributions obtained from POST 5- POST 8 are shown in table 3.14, along with the calculated initiator efficiencies.

Table 3.14 Molecular Weight Distributions for the PMMA Obtained From Polymerizations

POST 5 – POST 8 and the Percentage Initiator Efficiencies.

Experiment Number	Reaction Temp (°C)	$M_n / \text{g mol}^{-1}$	$M_w / \text{g mol}^{-1}$	Polydispersity	Initiator Efficiency (%)
POST 5	25	21000	27000	1.26	24
POST 6	25	19000	24000	1.28	26
POST 7	0	15000	19000	1.21	26
POST 8	40	21000	41000	1.96	22

3.5.1.2 NMR analysis

Based on the proton NMR of these samples, calculations of σ and the tacticity of the polymers could be made. This information is shown in table 3.15.

Table 3.15 Values of σ and Corresponding Tacticities of POST 5-8

Sample name	Temp (°C)	σ	Ps	Ph	Pi
POST 5	25	0.107	80	19	1
POST 6	25	0.149	72	25	2
POST 7	0	0.172	69	28	3
POST 8	40	0.216	61	34	5

The polymers show high syndiotacticity, which is born out by the ^{13}C NMR results which display spectra which are typical of syndiotactic PMMA (see Appendix 3).

3.5.2 Polymerizations using toluene/tetrahydrofuran mixtures as solvents

This series of experiments was carried out using mixtures of toluene and tetrahydrofuran (THF) in order to investigate the effect of slightly increasing the solvent polarity. The reactions were all carried out at 25°C, which was achieved by placing the vessel in a regulated waterbath, and with pre-mixing of monomer and aluminium triisobutyl.

The quantities of reagents and the yields of the reactions are shown in table 3.16.

Table 3.16 Concentrations of Reagents for Polymerization of MMA
Using Mixtures of Toluene and Tetrahydrofuran as Solvent (POST 9-14)

Experiment Number	[MMA] (mol/l)	[t-BuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	% THF (v/v)	[MMA]/[t-BuLi]	[Al(iBu) ₃]/[t-BuLi]	Yield (%)
POST 9	0.80	0.012	0.054	7.3	66	4.4	0
POST 10	0.78	0.035	0.043	6.4	23	1.2	0
POST 11	0.94	0.019	0.059	5.0	51	3.2	9
POST 12	0.48	0.012	0.032	11.4	41	2.7	0
POST 13	0.64	0.017	0.037	10.7	39	2.2	15
POST 14	0.41	0.0086	0.028	7.4	48	3.3	0

Polymerization was allowed to proceed for approximately 1 hour before the reaction was terminated and the polymer recovered.

As is apparent from the reaction yields, this series of reactions proved to be problematic. Experiment POST 9 was conducted using dried distilled THF transferred straight from the bottle in the glove box. When the monomer and cocatalyst were mixed, the expected pale yellow appeared very briefly but then immediately disappeared. This was perceived as being due to the THF not being sufficiently dry, and the moisture destroying the aluminium trialkyl. However, in subsequent experiments, using THF stored over sodium wire and vacuum distilled directly into the reaction vessel, the same behaviour was observed.

Analysis of the two polymers was carried out by SEC and NMR spectroscopy. The discussion of these results appears in section 3.5.4.

3.5.2.1 SEC analysis

The analysis of products was carried out as described in section 2.7.1. The molecular weights and molecular weight distributions obtained from POST 11 and POST 13 are shown in table 3.17, along with the calculated initiator efficiencies.

Table 3.17 Molecular Weight Distributions for the
PMMA Obtained From Polymerizations

POST 11 and POST 13 and the Percentage Initiator Efficiencies.

Experiment Number	$M_n / \text{g mol}^{-1}$	$M_w / \text{g mol}^{-1}$	Polydispersity	Initiator Efficiency (%)
POST 11	9000	12000	1.38	56
POST 13	3500	12000	3.34	111

3.5.2.2 NMR analysis

Based on the proton NMR of these samples, calculations of σ and the tacticity of the polymers could be made. This information is shown in table 3.18.

Table 3.18 Values of σ and Corresponding Tacticities of POST 11 and 13

Sample name	σ	Ps	Ph	Pi
POST 11	0.285	51	41	8
POST 13	0.389	37	48	15

POST 11 appears to be only slightly syndiotactic, and POST 13 is heterotactic, findings which are born out by the ^{13}C results.

3.5.3 Polymerizations using toluene/dichloromethane mixtures as solvents

As the previous series of experiments was unsuccessful in terms of reaction yields, further polymerizations were carried out using a different polar co-solvent. Mixtures of toluene and dichloromethane (DCM) were used as the solvent in reactions where reactants were combined with pre-mixing of monomer and cocatalyst, and which were carried out at 25°C.

The quantities of reagents used and the reaction temperatures are shown in table 3.19.

Table 3.19 Concentrations of Reagents for Polymerization of MMA

Using Mixtures of Toluene and Dichloromethane as Solvent (POST 16-20)

Experiment Number	[MMA] (mol/l)	[t-BuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	% DCM (v/v)	[MMA]/[t-BuLi]	[Al(iBu) ₃]/[t-BuLi]	Yield (%)
POST 16	0.51	0.0071	0.0371	5.9	72	5.2	45
POST 17	1.21	0.0109	0.0728	26	111	6.7	29
POST 18	0.99	0.0176	0.0553	7.5	56	3.1	96
POST 19	0.79	0.0055	0.0680	28	145	12.5	38
POST 20	1.30	0.0239	0.0765	7.9	54	3.2	82

Each reaction was allowed to progress for one hour before being terminated by addition of degassed methanol. In each case, mixing of monomer and cocatalyst resulted in a pale yellow colour being formed, although the colour was more notably strong in POST 18 and POST 20. On addition of initiator, reactions proceeded exothermically, and with an increase in viscosity.

Analysis of products was carried out by SEC and NMR spectroscopy.

3.5.3.1.1 SEC analysis

The analysis of products was carried out as described in section 2.7.1. The molecular weights and molecular weight distributions obtained from POST 16- POST 20 are shown in table 3.20, along with the calculated initiator efficiencies.

Table 3.20 Molecular Weight Distributions for the
PMMA Obtained from Polymerizations

POST 16 – POST 20 and the Percentage Initiator Efficiencies.

Experiment Number	$M_n / \text{g mol}^{-1}$	$M_w / \text{g mol}^{-1}$	Polydispersity	Initiator Efficiency (%)
POST 16	60000	291000	4.81	12
POST 17	31000	77000	2.52	36
POST 18	24000	30000	1.25	23
POST 19	54000	120000	2.21	27
POST 20	18000	22000	1.19	30

3.5.3.1.2 NMR analysis

Based on the proton NMR of these samples, calculations of σ and the tacticity of the polymers could be made. This information is shown in table 3.21.

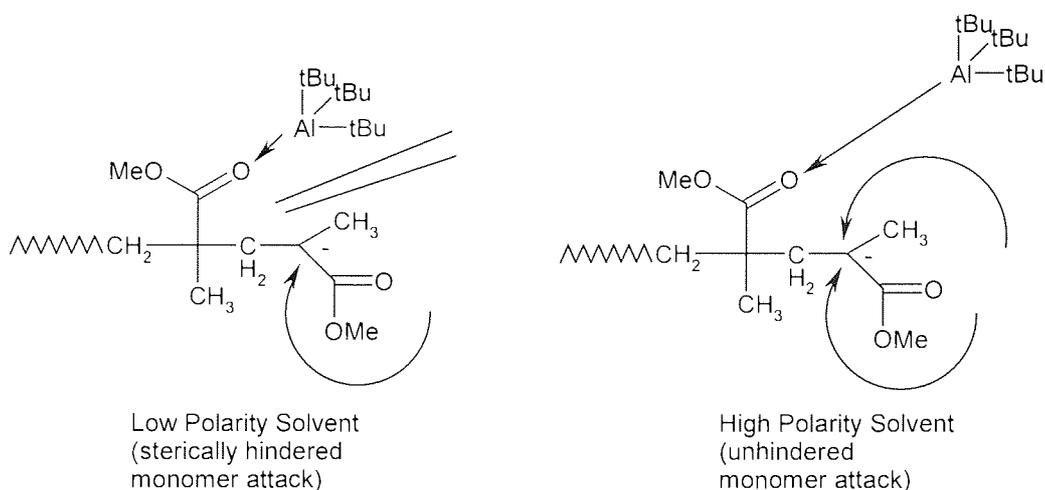
Table 3.21 Values of σ and Corresponding Tacticities of POST 16-20

Sample name	σ	Ps	Ph	Pi
POST 16	0.386	38	47	15
POST 17	0.153	72	26	2
POST 18	0.183	67	30	3
POST 19	0.163	70	27	3
POST 20	0.188	66	30	4

Aside from POST 16 the polymers produced all display quite high polydispersities. This is confirmed by the ^{13}C NMR studies.

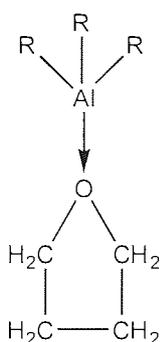
3.5.4 Discussion

Reactions, carried out in mixtures of cyclohexane and toluene, were designed to show the effect of lowering slightly the polarity of the solvent. As toluene itself is relatively non-polar, quite a large amount of cyclohexane was added to the solvent mixtures so that any effect could be clearly observed. The most obvious effect of this was the precipitation/coacervation effect described. This is most likely as a result of the initiator being insoluble in less polar solutions. As a result of this, as one would expect, the initiator efficiencies of the polymerizations are very low. However, despite this, the reactions produce quite high yield, low polydispersities, and high syndiotacticity. The polydispersities of the polymers, aside from POST 8 conducted at elevated temperature, are comparable to those of polymerizations in toluene only. This is most likely due to a closer association between chain-end and counterion, which suppresses termination reactions such as backbiting. The polymers are also significantly more syndiotactic than those produced in reactions involving only toluene as solvent, again with the exception of POST 8. This points to the fact that closer interaction between ion pairs and also associations such as $\text{Al}(\text{iBu})_3$ to ester carbonyl groups, either on the monomer, or close to the living end, mean that the mode of addition of monomer is more restricted leading to greater stereoregularity. This is shown schematically below.



Reactions in THF/toluene mixtures were particularly disappointing, since most yielded no polymer at all, and those that did produced polymer with high polydispersity and very low syndiotacticity. It can be assumed that this polymer was not produced by the same mechanism as those in neat toluene. There are two possible reasons for this. The first is lack of purity of the solvent. Since THF is hydrophilic it has a tendency to hold onto water. The generally accepted way of drying THF for use in anionic polymerization is to use sodium benzophenone. However, previous work carried out by this research group has shown that when THF is distilled from this drying agent traces of the drying agent may be carried over. However, sodium wire alone is a very good drying agent and should be dry enough. If moisture in the solvent was responsible for the failure of the reactions, then those polymers produced are most likely to have been produced by a free-radical mechanism. The second possibility is that there is some reaction, or association, between aluminium alkyl and THF. The oxygen atom of THF is highly electronegative and so there would undoubtedly be some tendency for aluminium alkyls to coordinate at the oxygen atom (scheme 3.1).

Scheme 3.1 Possible Association of Aluminium Alkyl to Tetrahydrofuran



If this were the case then very little aluminium alkyl would be available to take part in the polymerization and would be effectively removed from the system. Any polymerization would then progress in a similar way to unmediated polymerization. This would produce polymer of high polydispersity, as is observed, but also isotactic polymer rather than heterotactic, indicating that this proposed mechanism might not be entirely responsible for the observed behaviour. It is also conceivable that a more destructive reaction occurs between aluminium alkyl and THF. This might result in products that might kill any living chains, and might also initiate free-radical polymerization.

An interesting phenomenon can be seen when polymerizations are carried out in mixtures of toluene and dichloromethane (DCM). In general it would seem that the more successful reactions, in terms of yield and polydispersity, are those using lower concentrations of DCM. This seems reasonable since a more polar solvent leads to a more open system in terms of ion pairs and other associations, thus making termination reactions such as backbiting more likely.

The exception to this is POST 16, the polydispersity and tacticity of which seem typical of a polymerisation that has taken place by a free-radical mechanism. If this is the case then it is most likely as a result of ingress of some impurity at some stage in the reaction.

It is interesting that the polymers produced with less polar solvent (POST 18 and POST 20), in addition to having lower polydispersities, also show lower stereoregularity than those carried out in more polar solvent mixtures (POST 17 and POST 19). The effect is only small, and possibly a result of experimental error. It is quite difficult to rationalize these findings, especially in the light of the results from experiments carried out in toluene/cyclohexane mixtures. However, maybe it is not so surprising, given that MMA polymerization in THF, a very polar solvent, yields highly syndiotactic polymer. This is a kinetic phenomenon, and the results yielded by the mixed system might be seen as a tendency toward this sort of system.

3.6 Studies of the effect of adding a second batch of monomer

Since living polymerizations do not, by definition, have an intrinsic termination step, once a reaction is finished, i.e. all the available monomer has been consumed, the active chain end should remain active indefinitely. In practice this is not strictly possible, since some feasible slow side reactions are unavoidable. However, the living ends should remain active for a considerable period of time.

This phenomenon is often used to test that a polymer is living; a second batch of monomer added to a system once the first batch has been entirely consumed, should also be consumed and results in polymer with a unimodal molecular weight

distribution and a narrow polydispersity. This section details such a test of the system.

3.6.1 Experimental

In order to facilitate the second addition of monomer whilst using the same reaction vessel, a slightly different procedure from that described in section 3.2 was adopted. MMA was distilled into bulb B (see figure 3.1), and the initiator and cocatalyst solutions were transferred into bulbs C and D, respectively. A second portion of monomer was then distilled into the main chamber, A. The solvent was then distilled into the main chamber to mix with the monomer.

Prior to the commencement of the reaction, the vessel was removed from the vacuum line and placed in a dewar containing a mixture of methanol and solid carbon dioxide (cardice), which was maintained at -30°C . The vessel was left for 20 minutes to equilibrate. The reaction was then started by first allowing the cocatalyst to enter the main chamber of the vessel and mix with the monomer (i.e. post-mixing), before introducing the initiator. Vigorous shaking between each addition ensured thorough mixing.

Since previous polymerizations have demonstrated rapid increases in viscosity on initiation, propagation must be fast, and so two hours was judged to be sufficient time to ensure that all available monomer had been consumed. At this point a small portion of the reaction solution was tipped into one of the now empty side arms of the vessel and the tap closed for later analysis. The monomer in bulb B was then added to the reaction mixture and the polymerization allowed to continue for a further 2

hours. The polymer was recovered from both the main chamber, and bulb B as described in section 3.2.

The quantities of reagents used are shown in table 3.22. It should be noted that the exact concentrations at the second stage of the reaction are not known since the volume of the portion of the reaction mixture removed is unknown. However, since the portion was small (approximately 2-3ml cf. generally about 40ml reaction mixture) an approximation of concentrations can be made.

Table 3.22 Concentrations of Reagents for Polymerization of MMA with Addition of a Second Batch of Monomer (MON 1-3)

Experiment Number	[MMA] (mol/l)	[t-BuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	[MMA]/ [t-BuLi]	[Al(iBu) ₃]/ [t-BuLi]
MON 1.1	1.4	0.032	0.078	42	2.4
MON 1.2	2.9	0.026	0.063	111	2.4
MON 2.1	1.7	0.035	0.104	50	3.0
MON 2.2	3.0	0.029	0.086	105	3.0
MON 3.1	0.84	0.020	0.048	42	2.3
MON 3.2	1.5	0.019	0.044	79	2.3

3.6.2 Results

As in previous post-mixing reactions, mixing of monomer and cocatalyst resulted in a pale yellow colour. Addition of initiator to this resulted in the yellow colour fading quickly. Further to that, when the second batch of monomer was added, the yellow colour returned before fading once more. The polymerization was rapid and exothermic, resulting in a large change in viscosity.

As the volume of the portion of reaction mixture removed after the first stage of the procedure was unknown, it is impossible to give a true yield for each stage of the reaction. However, the weight of polymer recovered at each step is given in table 3.23, as well as a total percentage yield calculated from total weight of monomer added to the system and the total weight of polymer recovered from the reaction.

Table 3.23 Weights of Polymer Recovered and Total Product Yields for
Polymerization of MMA in Second Monomer Addition Reactions (MON1-MON3)

Experiment Number	Weight of polymer (g)	Total % Yield
MON 1.1	0.71	20
MON 1.2	1.70	
MON 2.1	0.79	62
MON 2.2	7.43	
MON 3.1	0.62	81
MON 3.2	3.20	

Analysis of products was carried out by SEC.

3.6.2.1 SEC analysis

The analysis of products was carried out as described in section 2.7.1. The molecular weights and molecular weight distributions obtained from MON 1 – MON 3 are shown in table 3.24, along with the calculated initiator efficiencies. It should be noted that, since the exact number of propagating centres present in the second stage of the reaction is unknown, the quoted initiator efficiencies are only approximate.

Table 3.24 Molecular Weight Distributions for the PMMA Obtained from Polymerizations MON 1 – MON 3 and the Percentage Initiator Efficiencies.

Experiment Number	M_n / gmol^{-1}	M_w / gmol^{-1}	Polydispersity	Initiator Efficiency (%)
MON 1.1	22000	35000	1.61	19
MON 1.2	26000	61000	2.37	43
MON 2.1	115000	185000	1.61	4
MON 2.2	190000	301000	1.58	6
MON 3.1	14000	18000	1.27	30
MON 3.2	20000	26000	1.29	40

3.6.3 Discussion

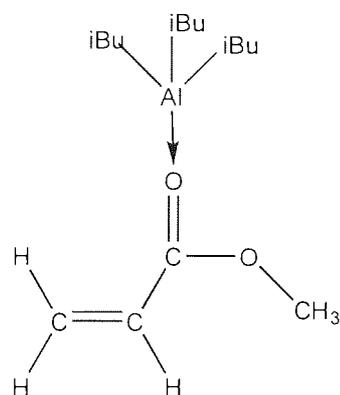
In all three reactions there is an increase in molecular weight to be observed when a second batch of initiator is added to the reaction. However, in the reaction MON 1, there is also a significant increase in the polydispersity of the sample. The SEC trace for MON 1.2 shows a high molecular weight shoulder. This would seem to indicate that many of the living chain ends have been terminated before the addition of the

second monomer batch. MON 2 and MON 3, on the other hand do demonstrate an increase in molecular weight, and also show no increase in polydispersity. MON 2 shows very low initiator efficiency, and higher polydispersity, than MON 3, which is most likely owing to some impurity in the system. The results of MON 2 and MON 3 do show that the living end remains 'living' after all monomer has been consumed.

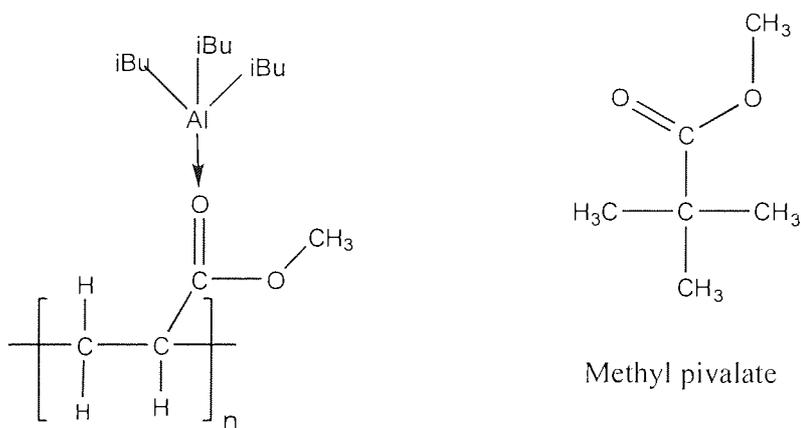
The colour changes that take place in this series of reactions are also notable. Mixing of the initiator and cocatalyst yielded no colour change, but then addition of monomer yielded a pale yellow colour which faded as the reaction progressed. Once the second batch of monomer was added, the yellow colour returned briefly before once again fading.

Since the reaction yields polymer with a unimodal, and indeed narrow, molecular weight distribution, even after the second monomer addition, it can be concluded that the fading of the pale yellow colour is not a result of the 'living' chain ends being killed. It is also notable that in the case of reactions of the post-mixing type, mixing of monomer and cocatalyst also produces the characteristic yellow colour. In this case the colour only fades once the initiator is added.

From these observations it can be seen that there is an interaction between triisobutyl aluminium and *tert*-butyl lithium which is responsible for the colouration. This is believed to be complexation of the aluminium alkyl to the carbonyl group of the monomer. This is in agreement with ^{13}C NMR analyses carried out by Muller⁷⁸.



If aluminium alkyl associates to the carbonyl group of the monomer, then it follows that there is also likely to be association with the carbonyl group of the polymer. This is also in agreement with the ^{13}C work of Muller using methyl pivalate as a model for the polymer chain.



If this is the case, then it is logical to say that the complex of aluminium alkyl to polymer is colourless. The colour difference between the two types of associated species is due to the conjugation to the double bond. During the course of the polymerization, there must be a dynamic equilibrium between non-associated species and the associated ones which, if understood could help in the understanding of the mechanism of polymerization.

CHAPTER FOUR

KINETIC STUDIES OF THE POLYMERIZATION OF METHYL METHACRYLATE IN THE PRESENCE OF LITHIUM AND ALUMINIUM ALKYL

4.1 Introduction

This chapter describes work carried out to elucidate the kinetics of polymerization of methyl methacrylate in toluene, initiated by alkyl lithiums, and using aluminium *triisobutyl* to enhance the living character. It is hoped that the kinetics will give some insight into the actual mechanism of polymerization.

4.2 Sampling Reactions

4.2.1 Experimental

In order to facilitate a sampling reaction, a new method for using the polymerization vessel (Fig. 3.1) needed to be devised. Owing to the extreme sensitivity of this system to atmospheric impurities, conventional methods of conducting sampling reactions, involving the removal of samples by syringe via a rubber septum, were deemed unsuitable.

The reactants were introduced to the vessel in the manner described in section 3.2 which was then placed in a dewar containing acetone and dry ice to reduce the temperature to -30°C . The reaction was then started by opening the taps in the appropriate order, with pre-mixing of initiator and cocatalyst. The reacting mixture was then, very quickly,

divided roughly equally between the three side arms and the main chamber of the vessel and replaced in the cold dewar. After a specified time, the samples, four in total, could then be taken by introducing to each chamber in turn, starting with the main chamber, a small volume (~0.5 ml) of degassed methanol to destroy the propagating end without precipitating the polymer. Once the final portion of reaction mixture had been quenched the 'samples' could then be removed individually and the polymer recovered as described in section 3.2. In general the first samples were taken as quickly as possible, and the final sample left for a time considered sufficient to allow the polymerization to go to completion.

The quantities of reagents used, along the reaction times of the samples, are shown in table 4.1.

4.2.2 Results

In all cases, mixing of initiator and cocatalyst produced no change in colour, as expected. However, on addition of monomer, only SAMP 2 and SAMP 3 resulted in the characteristic pale yellow colour and subsequent increase in viscosity and production of heat. Yields of polymerization cannot be quoted since the size of each sample is unknown. It should be noted that SAMP 1 yielded virtually no polymer at all.

Analysis of products was carried out by SEC.

Table 4.1 Reaction times and concentrations of reagents for polymerization of MMA (SAMP 1-3)

Experiment Number	[MMA] (mol/l)	[t-BuLi] (mol/l)	[Al(iBu) ₃] (mol/l)	[MMA]/[t-BuLi]	[Al(iBu) ₃]/[t-BuLi]	Time (mins)
SAMP 1.1	1.47	0.0073	0.0355	201	4.9	2
SAMP 1.2	1.47	0.0073	0.0355	201	4.9	5
SAMP 1.3	1.47	0.0073	0.0355	201	4.9	10
SAMP 1.4	1.47	0.0073	0.0355	201	4.9	210
SAMP 2.1	1.90	0.0396	0.1014	48	2.6	2
SAMP 2.2	1.90	0.0396	0.1014	48	2.6	3
SAMP 2.3	1.90	0.0396	0.1014	48	2.6	5
SAMP 2.4	1.90	0.0396	0.1014	48	2.6	120
SAMP 3.1	0.68	0.0235	0.0856	29	3.6	2
SAMP 3.2	0.68	0.0235	0.0856	29	3.6	4
SAMP 3.3	0.68	0.0235	0.0856	29	3.6	6
SAMP 3.4	0.68	0.0235	0.0856	29	3.6	120

4.2.2.1 SEC analysis

The analysis of products was carried out as described in section 2.7.1. The molecular weights and molecular weight distributions obtained from SAMP 1 – SAMP 3 are shown in table 4.2. Theoretical initiator efficiencies are also quoted for the final sample of each reaction, which are based on the actual molecular weight of polymer produced and the calculated molecular weight if the reaction goes to completion at 100% yield.

4.2.3 Discussion

From the low yields and broad polydispersity of SAMP 1, it would appear that there was some problem with either the purity of one or more of the reactants, or a defect in

the sealing of the system, e.g. a leaking tap. SAMP 2 and SAMP 3, on the other hand, show extremely low polydispersities, and therefore a very controlled polymerization. From an examination of the average molecular weights of SAMP 2 and SAMP 3 it would appear that the reaction had already gone to, or very nearly gone to, completion by the time the first sample was taken. Since the first sample was taken as soon as possible after the start of the reaction, it was clear that if the kinetics of this system were to be studied then traditional sampling reactions would not be suitable. Another technique would have to be used, especially if the early stages of the polymerization were to be analysed.

Table 4.2 Molecular Weight Distributions for the PMMA
Obtained from Sampling Polymerizations (SAMP 1-3) and the
Percentage Initiator Efficiencies

Experiment Number	$\overline{M}_n/\text{gmol}^{-1}$	$\overline{M}_w/\text{gmol}^{-1}$	Polydispersity	Initiator Efficiency (%)
SAMP 1.1	4000	9000	2.27	-
SAMP 1.2	16000	36000	2.29	-
SAMP 1.3	14000	22000	1.63	-
SAMP 1.4	14000	25000	1.84	144
SAMP 2.1	10000	11000	1.09	-
SAMP 2.2	10000	11000	1.12	-
SAMP 2.3	10000	11000	1.10	-
SAMP 2.4	10000	11000	1.10	48
SAMP 3.1	8000	9000	1.07	-
SAMP 3.2	13000	14000	1.09	-
SAMP 3.3	12000	13000	1.11	-
SAMP 3.4	13000	14000	1.10	22

4.3 Quench Flow Reactions

In order to measure the kinetics of polymerization it was necessary to develop a polymerization technique that would enable fast reactions to be studied. The solution to this was to construct a quench flow reactor.

The general principle of the quench flow reactor is to pump the reactants, in the appropriate concentrations, to a mixing head where very rapid mixing takes place. The polymerizing mixture is then pumped down a tube of known dimensions and is quenched as it emerges at the far end. The turbulent mixing ensures that laminar flow does not occur along the reaction tube, and so all emerging polymerizing mixture has reacted for the same length of time. The analysis of this polymer provides a 'snap-shot' of the reaction up to that time. A full picture can therefore be built up by altering the reaction time before quenching by either altering the dimensions of the reaction tube, or, more easily, altering the rate of pumping.

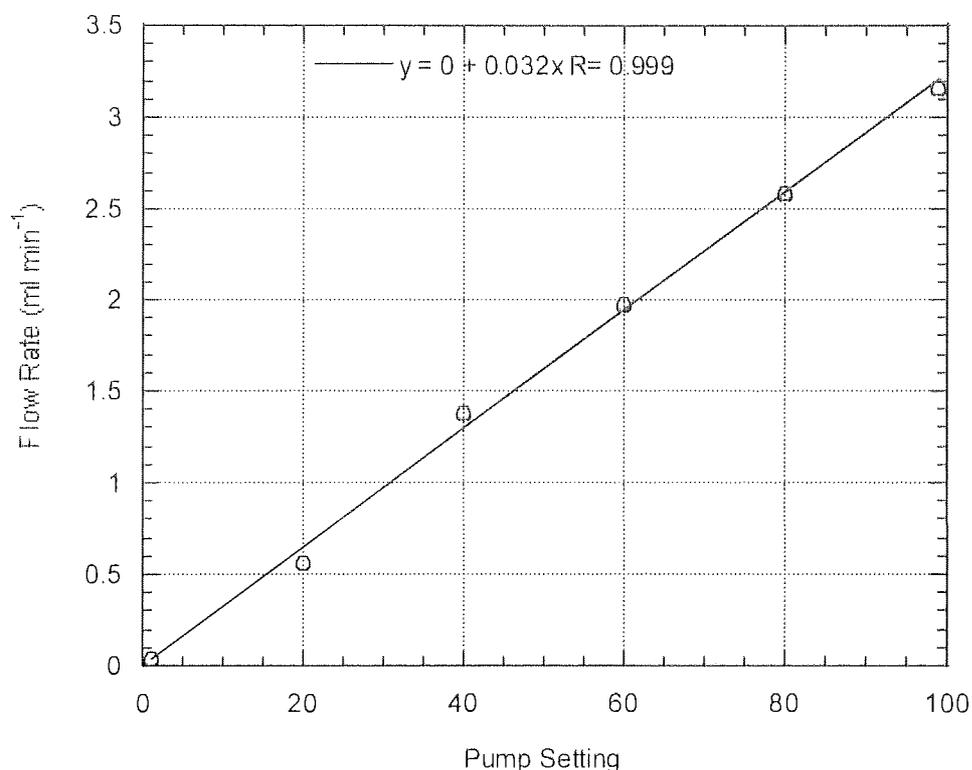
The experimental apparatus used for these experiments underwent a great deal of modification over the course of the period of study. For this reason the experimental detail is split into three sections detailing three different versions of the apparatus.

4.3.1 Pump Calibration

In order to calculate reaction times by this method it is vital to know both the exact dimensions of the reaction tube, and the speed at which the reactant is being pumped through it. In order for the flow rates to be known, the pump had to be calibrated for the tubing used. This was achieved by pumping water through the peristaltic pump tubing

to be used at varying speeds and measuring the amount pumped in set periods of time. The results were shown as a calibration plot (Fig 4.1) of flow rate against pump setting.

Figure 4.1 Typical Pump Calibration Plot
Showing Flow Rate against Pump Setting

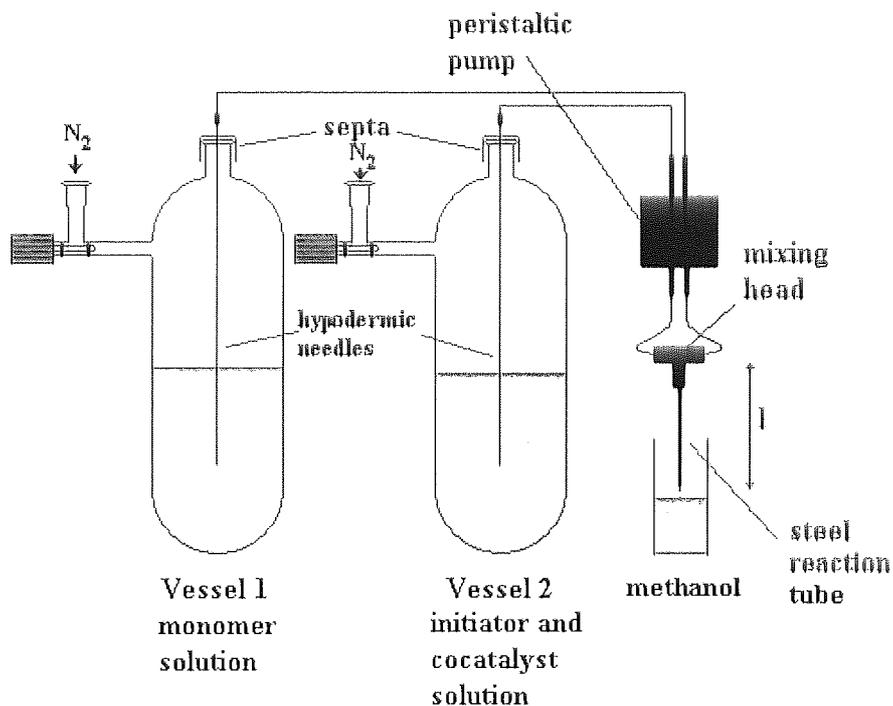


4.3.2 Experimental (Version 1)

The original design for the reactor (Version 1; Figure 4.2) consisted of two solvent vessels; one of which contained a monomer solution, the other a solution of initiator and cocatalyst. After fitting each vessel with a septum, the solutions are made up in such a way that when mixed in equal proportions the concentrations of reactions were as desired. The vessels were attached to the vacuum line, and were then filled with argon.

In order to pump the reactants to the mixing head, a peristaltic pump was utilised, capable of pumping through up to four different tubes simultaneously.

Figure 4.2. Version 1 of the Quench Flow Apparatus



The mixing head and the reaction tube were both made of stainless steel. The reacting mixture then emerged into methanol. The reactor was allowed to run for a period of approximately ten minutes before samples were taken, to ensure that the tubing was dry.

4.3.3 Results (Version 1)

Two reactions were undertaken using the apparatus described in the previous section. Both reactions were carried out using a 32cm reaction tube of 1mm internal diameter. Details of these reactions are as follows.

FR1

Reaction solutions were made up so that, after mixing, the concentrations were MMA, 1.27mol/l; Al(*i*Bu)₃, 0.0053 mol/l; *t*BuLi, 0.0159M mol/l.

The reaction was carried out and the following samples were taken (Table 4.3). The reaction times were calculated by taking the pump setting and converting this to a flow rate for each reaction tube. Once the speed at which reactants are entering the reaction tube is known, this can be combined with the dimensions of the tube, which are also known, to give a residence time.

The main purpose of this initial experiment was to test that the apparatus would produce polymer, and so on this occasion the time over which the samples were taken was not recorded.

Table 4.3 Samples Taken During Quench Flow Reaction FR1 Showing Reaction Time and the Weight of Polymer Produced

Sample Name	Pump Setting	Reaction Time (seconds)	Weight of Polymer (mg)
FR 1.1	10	23	2.1
FR 1.2	5	46	2.1
FR 1.3	2	113	1.8

After collecting the samples, the precipitate was filtered off and dried. The filtrate was analysed by GLC. In this way the responses from MMA and toluene, the initial proportions of which are known, could be compared and an extent of reaction could be calculated using the calibration described in section 2.6.2. The analysis, however, showed that no MMA was present in the sample, as can be seen in Appendix 5. Appendix 4 shows the gas chromatograph of a mixture of methanol, toluene and MMA for comparison purposes.

SEC analysis of the very small amounts of precipitate produced showed no real polymer present, maybe a small amount but very broad.

FR2

Owing to the very low amounts of polymer produced in the previous reaction, the concentration of reactants for this polymerization was increased. Solutions were made up so that, after mixing, the concentrations were MMA, 2.54 mol/l; Al(iBu)₃, 0.0243mol/l; tBuLi, 0.0149mol/l. The reaction was carried out and the following samples were taken (Table 4.4).

Table 4.4 Samples Taken During Quench Flow Reaction FR2 Showing Reaction Time, the Weight of Polymer Produced, and Calculated Yield Based on 100% Conversion

Sample Name	Pump Setting	Reaction Time (seconds)	Weight of Polymer (mg)	Yield(%)
FR 2.1	20	12	2.5	0.2
FR 2.2	10	23	52.4	4.3
FR 2.3	5	46	23.1	8.1

Once again the precipitate was filtered off and dried, and the filtrate analysed by GLC. However, the GLC traces showed no MMA peak. This is probably due to a combination of the concentration of MMA being very low compared with that of methanol, MMA being lost through evaporation during the filtration process, and possibly through MMA not consumed in the reactor polymerizing in a slow uncontrolled fashion before GLC analysis could be carried out.

SEC analysis was carried out on the samples, the results of which are shown in table 4.5. The polydispersities of the resultant polymers, although quite high, are less than one would expect for a completely uncontrolled reaction, indicating that the reaction is occurring in at least a partially living fashion, but the molecular weights produced seem to decrease with increasing reaction time. It is likely that this is either as a result of impurities in the system such as oxygen entering through leaks where types of tubing meet (i.e. nylon and peristaltic pump tubing) or through the system not been sufficiently dry.

Table 4.5 Information Gained Through SEC Analysis of Samples

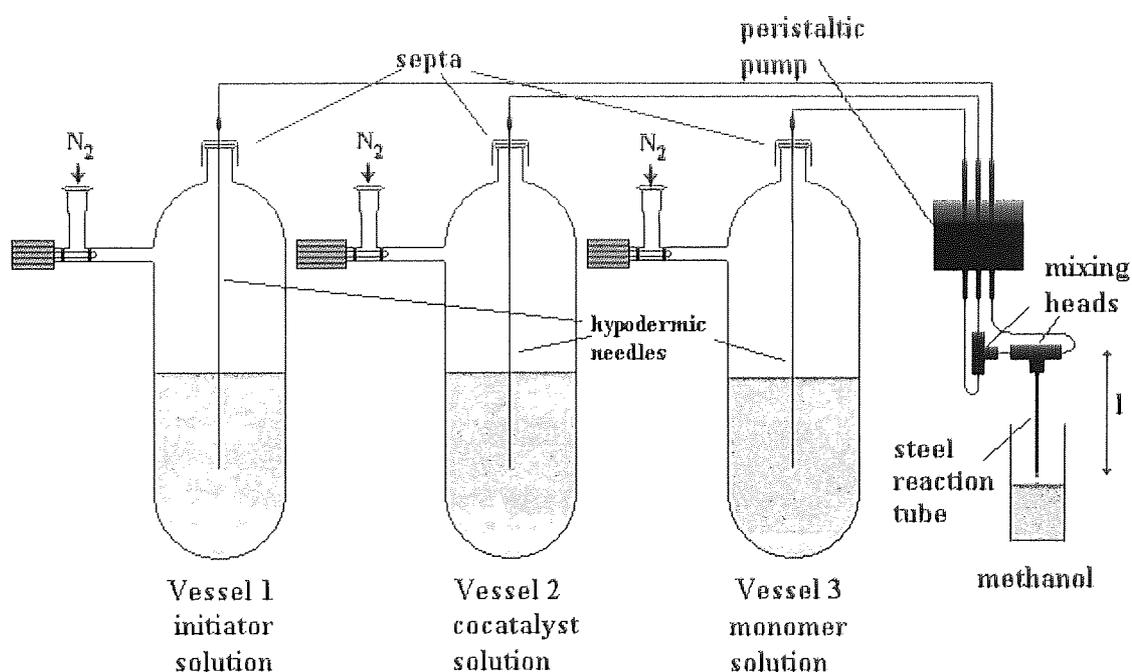
Obtained From the Quench Flow Reaction FR2

Sample Name	\bar{M}_n	Polydispersity
FR 2.1	68,000	1.62
FR 2.2	28,000	1.59
FR 2.3	21,000	1.71

4.3.4 Experimental (Version 2)

In order to overcome the problems experienced in the previous series of experiments the quench flow reactor was altered so that the reactants were pumped from 3 vessels, each containing a solution of monomer, initiator or cocatalyst. The advantage of this system was firstly that it was possible to alter the order of addition of reactants, and secondly, so it was possible to run only the $\text{Al}(\text{iBu})_3$ solution through the apparatus for a while to dry the mixing heads and reaction tube. A schematic of the revised apparatus is shown in figure 4.3.

Figure 4.3 Version 2 of the Quench Flow Apparatus



It was also decided that polystyryl lithium (PStLi) should be used as the initiator. The reason for this is that the distinctive red colour resulting from the living ends in solution gives a clear indication that the solution is still active at the time of the reaction. The PStLi was made by firstly making up a solution of *sec*BuLi (except for FR3 in which

tBuLi was used) in toluene by the normal combination of Schlenk and vacuum techniques. A few millilitres of styrene were then distilled into the vessel to produce the desired living polymer chains. The concentration of PStLi shown in the details of the experiments is equivalent to the concentration of living ends, assuming 100% initiation.

Aside from this, the method of reaction is identical to that using version 1 of the apparatus.

4.3.5 Results (Version 2)

A 32cm reaction tube of 1mm internal diameter was used for all the following reactions. Details of these reactions are given below.

FR3

Reaction solutions were prepared so that, after mixing, the concentrations were MMA, 0.134mol/l; Al(iBu)₃, 0.0211 mol/l; PStLi, 0.0767 mol/l.

Table 4.6 Samples taken during quench flow reaction FR3 showing reaction time, the weight of polymer produced, and calculated yield based on 100% conversion

Sample Name	Pump Setting	Reaction Time (seconds)	Weight of Polymer (grams)	Yield(%)
FR 3.1	99	Initiator solution only		
FR 3.2 – 3.7	No product owing to PstLi tube blockage			
FR 3.8	20	8	0.0018	7
FR 3.9	15	10	0.0047	3
FR 3.10	10	16	0.0220	32
FR 3.11	5	31	0.0075	22

Details of the samples that were taken during the reaction are shown in table 4.6. The first sample taken was PstLi solution only so that the starting point of the reaction could be seen.

As can be seen in the table, the experiment was hindered by problems of tube blockages. The results of the SEC analysis are shown in table 4.7.

Table 4.7 Information Gained Through SEC Analysis of Samples
Obtained From the Quench Flow Reaction FR3

Sample Name	\overline{Mn}	Polydispersity
FR 3.1	5300	1.3
FR 3.8	6600	1.3
FR 3.9	5400	1.2
FR 3.10	6800	1.3
FR 3.11	6800	1.3

As can be seen, polydispersities are once again quite low, and although it is true that this may largely be due to the amount of PMMA compared with that of polystyrene being small, i.e. the polydispersity of the polystyryl lithium is dominant, there would never the less be some observable broadening if the MMA polymerization were not living. There can be no doubt, however, that there seems to be no correlation between reaction time and molecular weight.

FR4

Reaction solutions were made up so that, after mixing, the concentrations were MMA, 0.900 mol/l; Al(iBu)₃, 0.0223; PStLi, 0.0697M. Details of the samples that were taken during the reaction are shown in table 4.8 shown below. The first sample taken was PStLi solution only.

Table 4.8 Samples Taken During Quench Flow Reaction FR4 Showing Reaction Time, the Weight of Polymer Produced, and Calculated Yield Based on 100% Conversion

Sample Name	Pump Setting	Reaction Time (seconds)	Weight of Polymer (grams)	Yield(%)
FR 4.1	99	Initiator solution only		
FE 4.2	60	3	0.032	3.5
FE 4.3	40	4	0.0299	5
FE 4.4	No product owing to blockage			
FE 4.5	20	8	0.0353	15
FE 4.6	10	16	0.0268	8.5
FE 4.7	5	31	0.0220	9.5
FE 4.8	3	52	0.0137	9
FR 4.9	40	4	0.0494	8
FR 4.10	2	78	0.0049	5

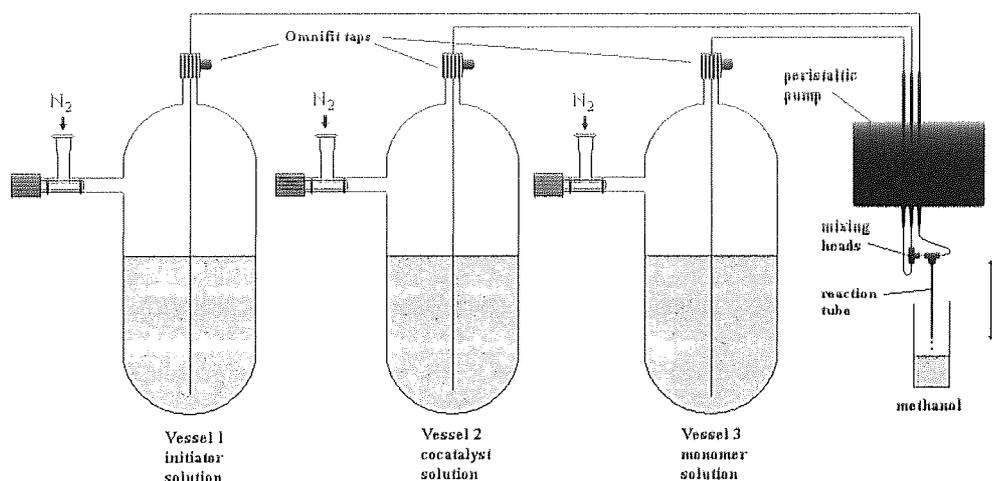
Once again there seems to be no correlation between reaction time and reaction yield. Also the precipitate that forms seems to be largely insoluble even at elevated

temperature. This seems to indicate that the precipitate is generally just cocatalyst residue, and so SEC analysis was not carried out.

4.3.6 Experimental (Version 3)

It is clear from the previous experiments that, although some quite low molecular weight polymer has been produced using the second version of the flow reactor, the main problem seems to be a lack of consistency, even within experiments.

Figure 4.4 Version 3 of the Quench Flow Apparatus



In order to counteract this, the experimental apparatus was altered once again. The main change, see figure 4.4, is the addition of Omnifit taps to the solution vessels. These are PTFE connectors which screw onto a glass thread which is glass blown onto the vessel. The connectors contain an arrangement of PTFE cones, which will grip the end of a piece of tubing from above and another from below, and have a tap so that solution flow can be turned off. The advantage of this was two-fold. Firstly, it eliminated the messy way that the syringe needles, used to puncture the septa in

versions 1 and 2, were connected to the nylon tubing. This had been achieved by pushing together small lengths of different sized tubing, and was very prone to leaking. Secondly, it gave the ability to stop and restart the reaction easily. This was seen as a particular advantage, since tube blockages of both peristaltic pump and reaction tubing were very common and resulted in numerous experiments having to be abandoned.

The other major change to the system was that a nylon reaction tube was used, instead of the stainless steel one previously. This was so that a new piece of tubing could be used for each reaction, ensuring that there was no contamination from that source. It also saved on the labour of cleaning out the reaction tube after each reaction or blockage.

4.3.7 Results (Version 3)

Reactions were carried out using a reaction tube 10cm long and of 1mm internal diameter. A number of experiments were undertaken using both pre-mixing and post-mixing methodologies. However, the Omnifit joints used did not generally prevent leaks as was hoped, and many had to be abandoned, or yielded very poor results, i.e. only small amounts of insoluble material were produced. The best of these series of experiments is shown here as FR 5.

FR 5

Reaction solutions were made up so that, after mixing, the concentrations were MMA, 2.16 mol/l; Al(iBu)₃, 0.0337; tBuLi, 0.0697M. Details of the samples that were taken during the reaction are shown in table 4.9 shown below. The reaction was carried out with pre-mixing of initiator and cocatalyst.

Table 4.9 Samples Taken During Quench Flow Reaction FR5 Showing Reaction Time, the Weight of Polymer Produced, and Calculated Yield Based on 100% Conversion

Sample	Pump Setting	Reaction Time (seconds)	Weight of Polymer (grams)	Yield(%)
FR 5.1	50	1.0	0.45	10
FR 5.2	30	1.6	0.19	7
FR 5.3	70	0.7	0.08	-

Sample 5.3 was interrupted by a tube blockage and so the time over which the sample was collected was not known. Hence the yield for that sample could not be calculated. The samples were mostly insoluble although enough soluble polymer was present to run SEC. The results of the analysis are shown in table 4.10.

Table 4.10 Information Gained Through SEC Analysis of Samples Obtained From The Quench Flow Reaction FR5

Sample Name	\overline{Mn}	Polydispersity
FR 5.1	21500	1.78 (bimodal)
FR 5.2	14800	1.96 (bimodal)
FR 5.3	17700	1.80 (bimodal)

All three chromatographs appear as a broad peak with a high molecular weight shoulder. This would tend to indicate that there is more than one polymerization mechanism occurring. However, since previous bulk reactions have not demonstrated this, it is probably due to ingress of some contaminant in the system, or oxidative coupling as the polymer is quenched.

4.3.8 Discussion

A number of conclusions can be drawn from these experiments, despite the fact that no practical kinetic data were obtained.

The initial sampling reactions have shown that the reaction is very fast, and the fact that some polymer of narrow polydispersity has been produced in the flow reactor would seem to indicate that the timescale on which the experiment was run was not unreasonable.

However, the very low yields were not concurrent with a polymerization running to completion. Since previous experiments (Chapter 3) have shown the system to be good, the fault must lie with the experimental procedure. Three main problems can be identified in this regard. Firstly, the fact that the reaction did not run cleanly can be put down to leaks in the system and the apparatus not being completely clean. The latter is clearly borne out by some of the experiments where the yield was seen to increase markedly in the latter stages. The second problem is that of blockages which were responsible for the majority of failed reactions. This was in part due to the use of the peristaltic pump to drive the reaction, since it does not have the power to overcome blockages. The third problem was one of turnaround time of reactions, i.e. the time it takes to clean out the relevant pieces of tubing and dry them in preparation for the next experiment. In theory this should be a simple job of pumping solvent through the system, but as the system being was prone to blockages this was rarely the case.

In order to overcome these problems, a number of steps could be taken. Firstly, the whole system would benefit from the use of all-metal tubing and joints, i.e. HPLC type

equipment. This would ensure that there were absolutely no leaks in the system, and would allow very rigorous cleaning and drying by use of extreme heat. Secondly, the peristaltic pump would need to be replaced, partly for the reasons stated in the paragraph, and because the joint between the peristaltic pump tubing and other tubing will always be a source of possible ingress of impurity to the system. Additionally it is not possible to clean and dry the tubing as rigorously as with glass and metal parts. A good replacement would be an array of motor-driven syringes, since this would ensure all metal joints, and the solutions would always be at positive pressure so any leaks in the system would not result in impurities being pulled in.

A further improvement to the set-up would be to have a further mixing head at the end of the reaction tube in which the polymerization mixture would be mixed with a quenching agent such as wet THF. This would negate any possible end-effects as the polymer emerges from the reaction tube. It would also mean that the entire apparatus could be submerged in a high- or low-temperature bath to study the effects of temperature on kinetics. If the experiment was to be taken to significantly shorter reaction times, then the efficiency of the mixing head will need to be considered, and a specially designed mixing head would have to be used. However, for the reaction times studied the speed of mixing was judged sufficiently fast

To conclude, the series of experiments has shown that the system is extremely sensitive to impurity and requires an experimental set-up that is even more rigorous than that used in this work. The technique is in essence good since other authors have used similar systems successfully, however the cost of the equipment and the time needed to perfect the work were not available for this project.

CHAPTER FIVE

CONCLUSIONS AND SUGGESTIONS FOR FURTHER WORK

The initial aim of this body of work was to increase the pool of knowledge about the system used, i.e. the aluminium alkyl mediated anionic polymerization of methyl methacrylate initiated by alkyl lithiums, and during the course of the investigation a number of trends were noted which have not been reported elsewhere in the literature.

A series of experiments was carried out to demonstrate that the polymerization of methyl methacrylate was indeed 'living'. These consisted of carrying out a polymerization which was allowed to go to completion. After a significant period of time, a second batch of monomer was added to the reaction and the polymerization was once again left to go to completion. If no transfer or termination reactions are taking place then the molecular weight of the polymer should increase between the completion of the first stage of the reaction and the completion of the second, and the polydispersity should remain the same (or very slightly decrease). This behavior was conclusively observed in these experiments, indicating that the polymerization is truly 'living' process.

The work that was carried out to investigate the effect of changing various different reaction parameters was particularly interesting. The effect of varying the order of addition of reactants was studied in order to confirm the findings of Haddleton *et al* who reported that when monomer and cocatalyst, i.e. aluminium alkyl, were mixed prior to

addition of initiator, then the observed initiator efficiency was considerably lower than when cocatalyst and initiator were pre-mixed. This effect was seen, as well as lower reaction yields in the former case, but was not as marked as reported. The results of this section of work show a large degree of experimental scatter, though, and more reactions would be needed to conclusively state these findings. There appeared to be no correlation between order of addition of reactants and either polydispersity or tacticity of the polymer produced.

The reactions carried out to assess the effect of temperature on the system demonstrated that polydispersity and tacticity are both influenced by the reaction temperature. The polymers produced showed a clear increase in syndiotacticity with decreasing temperature which was attributed to closer associations at the chain end due to the lower kinetic energy of the system. The changes in polydispersity were not as conclusive. However, the polymerization did seem to produce less polydisperse polymer at lower temperature. This was most likely due to the speed of propagation decreasing with respect to that of initiation. In order to confirm these observations it would be desirable to carry out reactions to fill in the gaps between the temperatures studied, and extend the series to lower temperature in order to see if the low molecular weight tail seen at -30°C is a genuine low temperature phenomenon, or due to impurities in that reaction.

The effect of varying solvent polarity proved particularly interesting. When mixtures of toluene and cyclohexane were used in order to lower slightly the effective polarity of the solvent, there were found to be problem due to low solubility of the initiator. Despite this, the polymers that were produced seemed to show decreasing polydispersity with decreasing solvent polarity, and a strong tendency to higher syndiotacticity. This can be

viewed as suppression of intramolecular termination reactions and restriction of the mode of attack of monomer resulting in higher stereoregularity, resulting from both closer association between the active center and the counter-ion, and closer association between aluminium alkyl and ester carbonyl groups. Reactions conducted in mixtures of toluene and tetrahydrofuran, designed to investigate the effect of slightly increasing solvent polarity, failed to produce polymer, most probably due to some association or reaction between aluminium alkyl and THF. Mixtures of toluene and dichloromethane, however, did yield polymer when used as solvent. The polymer produced demonstrated higher polydispersity and lower yield with increasing solvent polarity. This can be explained in similar terms to the trends observed for the reactions in toluene/cyclohexane mixtures, i.e. lower solvent polarity leading to looser associations which increase the likelihood of unwanted side-reactions occurring. It was surprising to note that the syndiotacticity of produced polymer increased with increasing solvent polarity. The reason for this trend is unclear, but could be due to some other association such as inter- or intra-chain interactions. This could be addressed by any further investigation.

It was desired that this body of work should include a kinetic study of the system in the hope that this could help to form more of a mechanistic understanding of the processes taking place. To this end, a series of sampling reactions were undertaken which showed only that the polymerization was too fast to be studied by this technique. A great deal of effort was then put into the design of a quench flow reactor capable of studying very fast reaction times. However, this failed to produce any useful kinetic data owing to difficulties in ensuring the system was free of leaks and of sufficient purity. Some polymer of narrow polydispersity was produced which indicated that the reaction is possible in such a reactor. An extensive list of the changes which could be made in order

to get the technique to work are given in the conclusion to the chapter, however such modifications were beyond both the time available and the budget of this project.

In conclusion, the system of aluminium alkyl mediated polymerization of methyl methacrylate initiated by alkyl lithium has been shown to be capable of producing poly(methyl methacrylate) in a living fashion, with low polydispersity and high stereoregularity. The system is obviously a complicated one, and its extremely fast reaction rates make it difficult to study. The interesting chemistry involved certainly makes the system worthy of further study; however the extreme sensitivity of the system to impurities makes it undesirable industrially and it is likely that less rigorous techniques such as 'living' free-radical polymerization will continue to grow in popularity.

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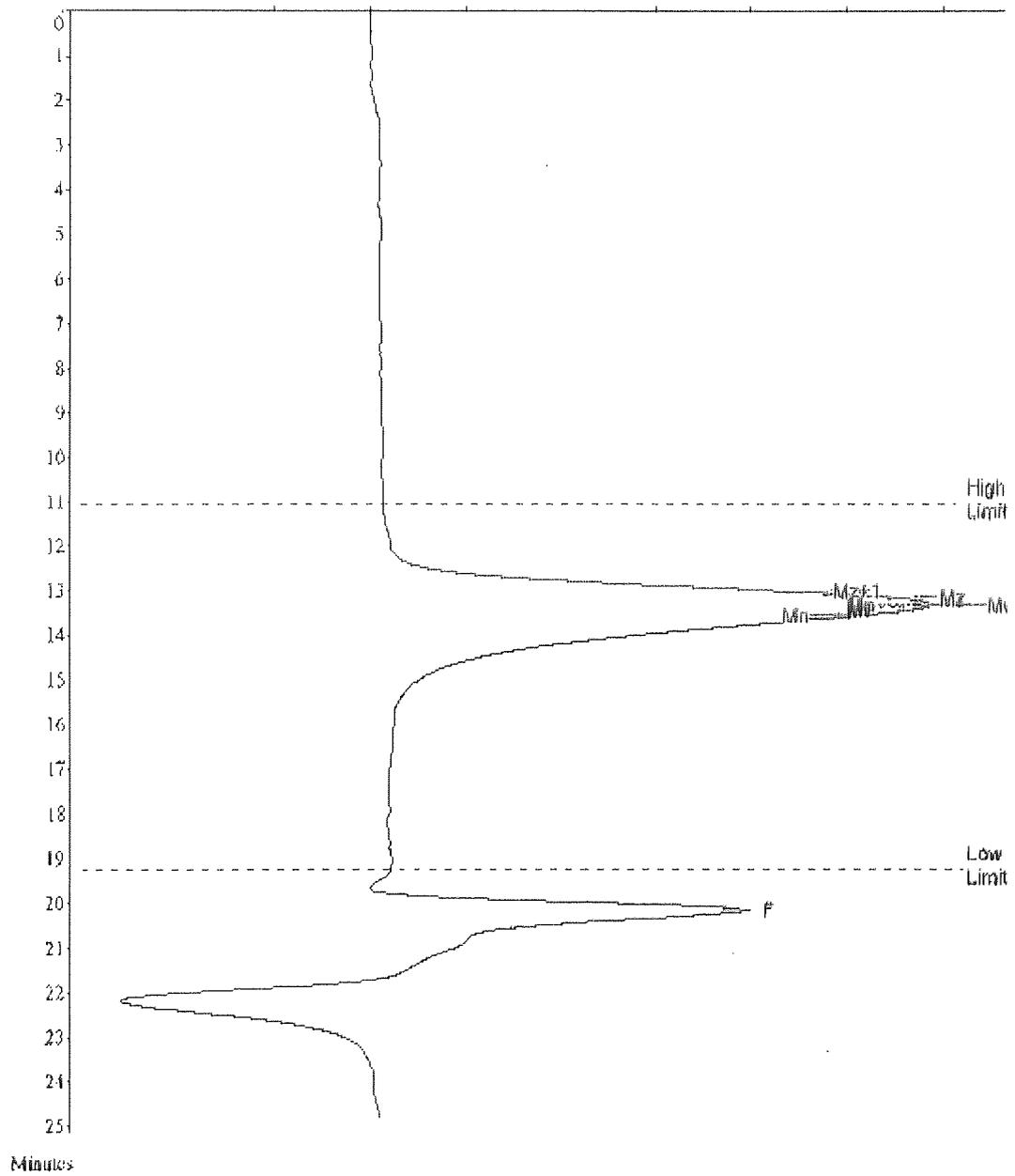
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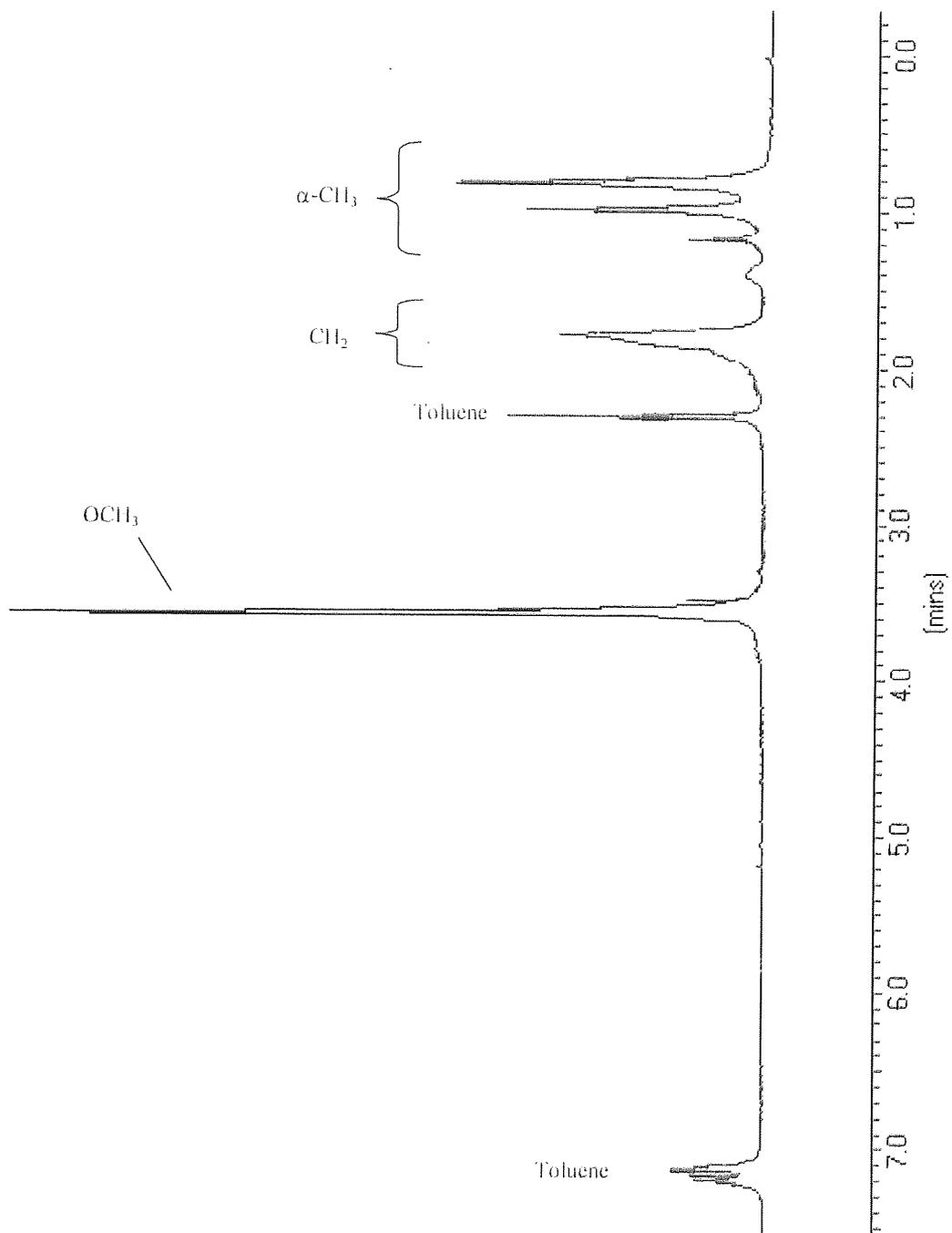
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APPENDICES

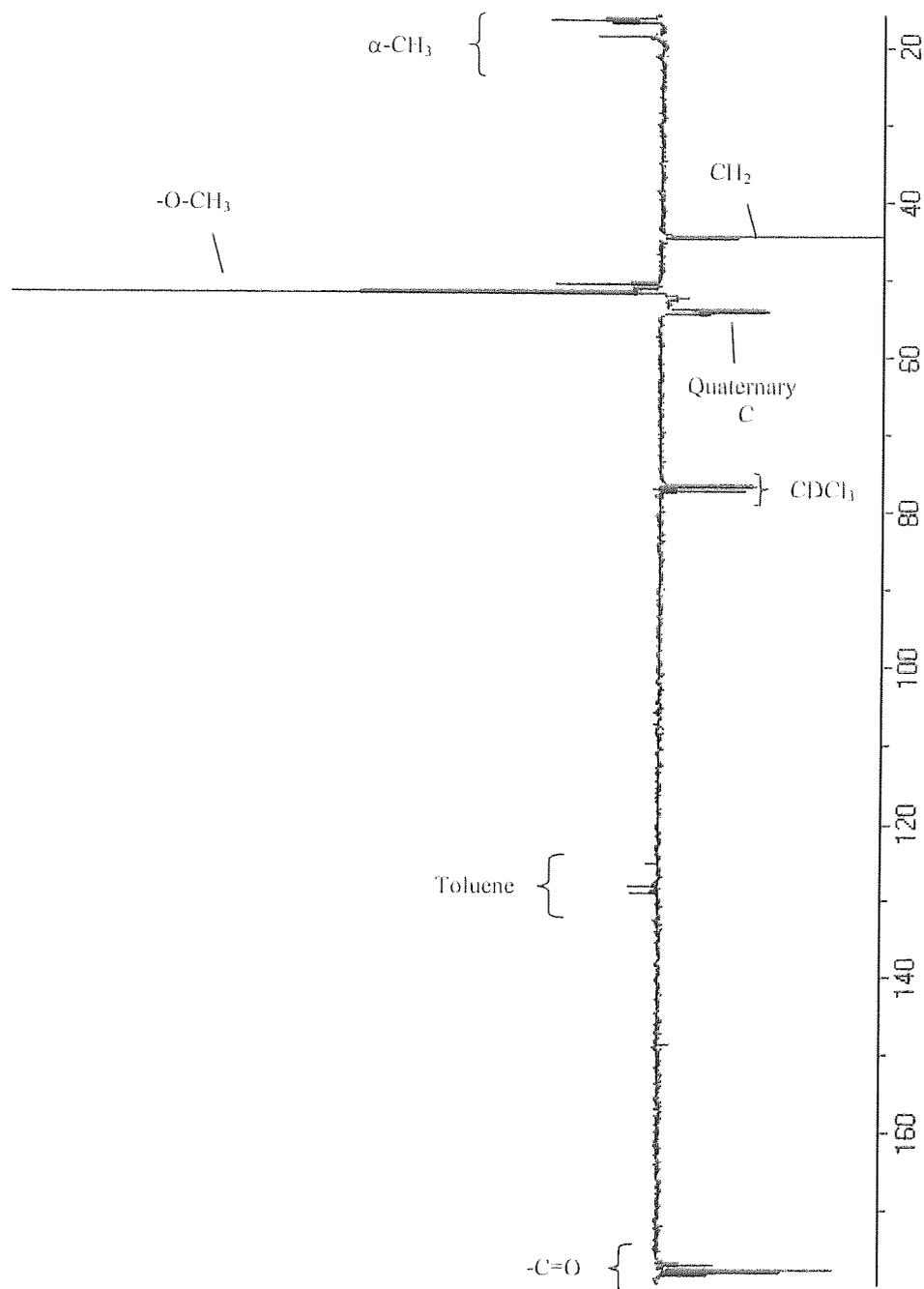
Appendix 1 Typical SEC Chromatogram of PMMA Produced by Living Anionic Polymerization (POST 20)



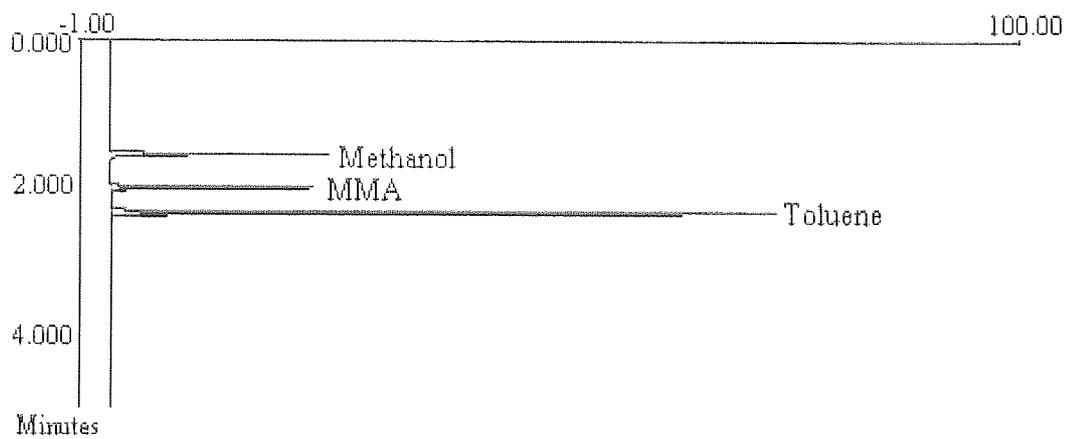
Appendix 2 Typical ^1H NMR Spectrum of Syndiotactic PMMA (PRE 1)



Appendix 3 Typical ^{13}C NMR Spectrum of Syndiotactic PMMA (PRE I)



Appendix 4 Gas Chromatogram of a Mixture of Methanol, MMA and Toluene to Demonstrate the Clarity of Separation



Appendix 5 Gas Chromatogram of the Filtrate from FR 2.2 After
Precipitation and Removal of Polymer

