Controlled Macromolecular Architecture Using Living Polymerization Methods

A Thesis

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DOCTOR OF PHILOSOPHY
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by

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Dedicated to parents and teachers

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02-11-2001, PUNE *(V. Raghunadh)*

Declaration

I hereby declare that the thesis **"Controlled Macromolecular Architecture using Living Polymerization Methods"** has not been submitted to any other institute or university for any other degree and this work was carried out in National Chemical Laboratory, Pune.

(V. Raghunadh)

Pune,
November, 2001

Certificate

Certified that the work incorporated in the thesis **“ Controlled Macromolecular Architecture using Living Polymerization Methods”** submitted by **Mr. V. Raghunadh** was carried out by the candidate under my supervision, such material as has been obtained from other sources has been duly acknowledged.

Dr. S. Sivaram
(Supervisor)

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Abstract

This thesis deals with the controlled synthesis of poly(lauryl methacrylate) and its copolymers using living/controlled polymerization methods. A brief study of the usefulness of 2-tribromomethyl-2-oxazoline (TBO) as a trifunctional electrophilic terminating agent for living anionic chain ends has also been included.

Anionic Polymerization of lauryl methacrylate (LMA) with 1,1-diphenylhexyl lithium (DPHLi) in tetrahydrofuran (THF) at –40 °C results in multi-modal and broad molecular weight distribution (MWD) with poor initiator efficiency. In presence of additives the polymerization was better controlled. The method of purification of LMA is critical in obtaining well-defined polymers. Best results are obtained when the monomer was fractionated and then distilled over calcium hydride (CaH_2) prior to polymerization and also when it was treated with tri-ethyl aluminum and then passed through neutral alumina column.

The polymerization of LMA in presence of lithium-2-(2-methoxy) ethoxyethoxide (G2Li1) gave polymer with broad and unimodal MWD (1.40). However, use of a polydentate dilithium alkoxyalkoxide (G3Li2) gave very good control over polymerization resulting in polymers with narrow MWD (1.12). In this case it is necessary to maintain fast and uniform mixing in the batch polymerization and the monomer addition to the reaction mixture has to be faster than the half-life of the polymerization. Good results were also obtained when the polymerization was carried out in presence of both LiCl and $LiClO_4$. These additives resulted in polymers with narrow MWD ($\leq$ 1.10). From these results it is concluded that poly(lauryl methacrylate) (PLMA) with narrow MWD and required molecular weight can be prepared by anionic polymerization in THF at –40 °C in the presence of additives like LiCl, $LiClO_4$ and G3Li2.

Controlled polymerization of LMA has been achieved using atom transfer radical polymerization (ATRP), using different ligands [2,2'-dipyridine (DP), 4,4'-dimethyl-2,2'-dipyridine (DMDP), N,N',N',N",N"-pentamethyl diethylenetriamine (PDT) and N-(n-propyl)-2-pyridylmethanimine (PPMI)] in conjunction with CuBr. The obtained polymers were characterized by moderately narrow molecular weight distribution (< 1.3). Amongst the ligands used, PPMI gave the best results and the optimum concentration of ligand with respect to catalyst and initiator was 1:3 and the dilution required was 1:4 (v/v) monomer/solvent. The kinetic experiment shows a linear first order time-conversion plot. When PDT was used as ligand better results were obtained at low ligand concentration and the optimum value was found to be 1:1 with respect to catalyst and initiator. In this case the kinetics of ATRP of LMA clearly indicates the presence of both transfer and termination reactions.

The block copolymers of LMA and methyl methacrylate (MMA) were synthesized using both anionic polymerization and ATRP methods. Di-block copolymers of MMA and LMA were synthesized with good control over molecular weight and narrow MWD using DPHLi as initiator in THF at –40 °C in anionic polymerization. Initiation of LMA with lithium naphthalenide (LiNap) in THF at –40 °C resulted in PLMA with bi-modal distribution. Preparation of di-functional α-methyl styryl lithium with LiNap and α-methyl styrene *in situ* and using it as an initiator for LMA polymerization gave good control over polymerization over a wide range of molecular weight. The tri-block copolymers of LMA and MMA synthesized using this initiator had homopolymer contamination. This was attributed to the impurities entering the polymerization system during sample withdrawal and second monomer addition.

The di-block copolymers synthesized by ATRP using CuBr/PDT catalyst complex resulted in multi-modal distribution with apparently poor initiator efficiency. This result was attributed to the insolubility of the Cu(II) complex as the viscosity increases. Synthesis of di-block copolymers with CuBr/PPMI catalyst complex gave much better results. The reason could be better solubility of the catalyst complex. The multi-modal MWD of the block copolymer obtained from PLMA macro-initiator was attributed to the slow crossover reaction.

Model studies were carried out for checking the feasibility of star polymer synthesis using TBO and 4,4-dimethyl-2-tribromomethyl-2-oxazoline (DMTBO) as coupling agents. From these studies it was found that the oxazoline ring in both TBO and DMTBO is stable towards *n*-BuLi at low temperatures (≤ -40 °C). It was found that the coupling reactions of *n*-BuLi with tribromomethyl oxazolines are not quantitative presumably due to steric hindrance and possible side reactions, such as, metal-halogen exchange.

Glossary

AIBN	Azobis isobutyronitrile
ATRA	Atom transfer radical addition
ATRP	Atom transfer radical polymerization
n-BA	*n*-butyl acrylate
t-BA	*t*-butyl acrylate
BDMAS	Bis(dimethylamino) dimethylsilane
BPO	Benzoyl peroxide
n-BuLi	*n*-butyl lithium
CaH_2	Calcium hydride
CSA	Camphorsulfonic acid
CuBr	Copper(I) bromide
CuOAc	Copper acetate
dNbpy	4,4'-di(n-nonyl)-2,2'-bipyridine
DEPN	N-*t*-butyl-1-(P,P-diethoxyphosphono)-2,2-dimethylpropyl nitroxyl
DMDP	4,4'-dimethyl-2,2'-dipyridine
DME	1,2-dimethoxy ethane
DMF	N,N-dimethylformamide
DMSO	Dimethylsulfoxide
DMTBO	4,4-dimethyl-2-tribromomethyl-2-oxazoline
DNBP	4,4'-di-(5-nonyl)-2,2'-bipyridine
DP	2,2'-dipyridine
DPE	1,1-diphenyl ethylene
DPHLi	1,1-diphenylhexyl lithium
DPM	Diphenyl methane
DSC	Differential scanning calorimetry
DT	Degenerative transfer
EBI	Ethyl-2-bromoisobutyrate
FMPTS	2-fluoro-1-methylpyridinium *p*-toluene sulfonate
G2Li1	2-(2-methoxyethoxy)-ethoxy lithium
G3Li2	Bis lithiunm salt of triethylene glycol
GC	Gas chromatography

GPC	Gel permeation chromatography
GTP	Group transfer polymerization
HEA	2-Hydroxyethyl acrylate
HEMA	2-Hydroxyethyl methacrylate
HMPA	Hexamethylphosphoramide
IOMA	Isooctyl methacrylate
k_{app}	Apparent rate constant
LA	Lauryl acrylate
LAP	Ligated anionic polymerization
LMA	Lauryl methacrylate
LiCl	Lithium chloride
$LiClO_4$	Lithium perchlorate
LiNap	Lithium naphthalenide
MA	Methyl acrylate
Me_6TREN	Tris[2-(dimethylamino)ethyl]amine
MMA	Methyl methacrylate
MOX	2-methyl-2-oxazoline
α-MS	α-methyl styrene
MWD	Molecular weight distribution
NBS	N-bromo succinimide
NMP	Nitroxide mediated polymerization
P(*t*-BA)	Poly(*t*-butyl acrylate)
PDT	N,N',N',N",N"-pentamethyl diethylenetriamine
PHP	Potassium hydrogen phthalate
PLMA	Poly(lauryl methacrylate)
PMMA	Poly(methyl methacrylate)
PPMI	N-(*n*-propyl)-2-pyridylmethanimine
RAFT	Reversible addition fragmentation chain-transfer polymerization
SEC	Size exclusion chromatography
SFRP	Stable free radical polymerization
T_g	Glass transition temperature
TBAF	Tetrabutyl ammonium flouride
TBO	2-tribromomethyl-2-oxazoline

TEA	Triethyl aluminum
TEMPO	2,2,6,6-tetramethyl-1-piperidinyloxy
THF	Tetrahydrofuran
TIBAL	Tri isobutyl aluminum
TMEDA	N,N,N’,N’-tetramethylethylenediamine
TMOX	2,4,4-trimethyl-2-oxazoline
TPEs	Thermoplastic elastomers

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1. Introduction

Polymeric materials have become so pervasive in our modern life that it is difficult to imagine life without their use. Last century has witnessed the discovery of a variety of new polymeric materials and exploitation of their bulk physical properties for commodity plastics as well as high performance engineering materials. In recent years, the rapid growth of electronic and medical technologies has led to an understanding of the individual polymeric molecules and thus enables us to tailor them suitably to exhibit desirable properties. These properties are, in turn, governed by the molecular properties such as molecular weight, MWD (MWD) and topology. These parameters can be more precisely controlled in polymers prepared using living or controlled polymerization methods. Using these methods, it is possible to synthesize polymers with predicted molecular weight, narrow MWD and chain end functionality besides preparing polymers with a variety of architectures.

Living anionic polymerization is unique in its ability to produce polymers with controlled molecular weight and narrow MWD. It is possible to synthesis well-defined functional homo polymers and block, graft and star copolymers using anionic polymerization. Styrene-*b*-butadiene-*b*-styrene (SBS) thermoplastic elastomer is the best example of successful commercialization of living anionic polymerization. Several other methodologies were developed to attain control over polymerization and these include cationic, group transfer, metathesis and coordinated polymerizations. More recently a new methodology, atom transfer radical polymerization (ATRP), has been successfully developed for making polymers with good control. The advantages of ATRP over conventional living polymerization methods are: it is more tolerant towards protic and other impurities, it can be used for a wide range of monomers and can be used in bulk, solution, dispersion and emulsion modes.

1.1 Anionic polymerization

1.1.1. Introduction

Although the living nature of anionic polymerization was known earlier[1,2], it was Szwarc and co-workers[3,4] who first demonstrated the living polymerization of styrene and obtained polystyrene with narrow MWD. They found that under suitable conditions transfer and the termination reactions are absent and the active species remain active even after complete consumption of the monomer. Thus, the polymeric active species are capable of growing longer in chain length when provided with fresh monomer of the same type or a different monomer. Subsequently, several research groups started practicing this versatile method for preparing polymers with well-defined architectures[5-10].

The anionic polymerization involves three basic reactions, which can be classified as initiation, propagation and termination (Equations 1.1 to 1.3). Here I^*, M, P_n^*, P_n, E, and n are the initiator, monomer, polymer with chain-end active center and dead polymer chain, terminating agent and degree of polymerization with k_i, k_p, and k_t being rate constants for initiation, propagation and termination respectively.

$$I^* + M \xrightarrow{k_i} I^-M^* \qquad (1.1)$$

$$I^-M^* + n\,M \xrightarrow{k_p} P_n^* \qquad (1.2)$$

$$P_n^* + E \xrightarrow{k_t} P_n \qquad (1.3)$$

In an ideal anionic polymerization system, all the initiator molecules react with monomer before the propagation reactions commence, $k_\mathrm{i} \geq k_p$, which leads to uniform degree of polymerization in all the molecules. The polymerization proceeds without any termination or transfer reactions and after complete consumption of all the monomer the propagating chains remain active until they are terminated intentionally. When these conditions are met the concentration of the active center in the polymerization system remains constant through out the polymerization resulting in polymers with narrow molecular weight distribution (MWD).

In the living anionic polymerization the molecular weight is controlled by the stoichiometry of monomer and initiator. In the absence of side reactions, the theoretical molecular weight of the polymer initiated with mono-functional initiator can be calculated using equation 1.4.

$$M_n = \frac{\text{grams of monomer}}{\text{moles of initiator}} = \frac{[M]_0}{[I]_0} \times \text{Molecular weight of monomer} \qquad (1.4)$$

When a di-functional initiator is used the theoretical molecular weight is twice as calculated for the mono-functional initiator. In general, the average molecular weight of the polymer increases linearly with conversion in the absence of transfer reactions.

MWD for a living polymerization system with fast initiation was calculated by Flory as early as 1940 and follows a Poisson distribution[11,12]. The polydispersity index D, for such a system is given by:

$$D = \frac{P_w}{P_n} = 1 + \frac{P_n}{(P_n+1)^2} \cong 1 + \frac{1}{P_n} \qquad (1.5)$$

Here P_w and P_n are weight and number average degrees of polymerization. For higher values of P_n, D value reaches unity. In order to achieve a living polymerization following conditions have to be met:

1. The polymerization reaction should be free of termination and transfer reactions.
2. The rate of initiation must be higher or equal to the rate of propagation.
3. A single type of propagating species must exist; if different propagating species are present, then their inter conversion should be very fast.
4. The propagation rate should not depend on the degree of polymerization.
5. The number average molecular weight of the polymer should have a linear relation with conversion.

Thus, for performing living polymerization reactions, inert atmosphere or high vacuum technique is required in order to prevent adventitious termination reaction occurring from exposure to moisture, oxygen, carbon dioxide etc. Rigorous purification of the reagents is necessary in order to avoid side reactions arising from impurities present in them. Even with a small amount of impurities present in the monomer or solvent, the system results in polymers with broad MWD with low initiator efficiency13-18).

1.1.2. Monomers, solvents and initiators for anionic polymerization

1.1.2.1. Monomers

A wide variety of monomers undergo anionic polymerization by addition to carbon-carbon double bond (vinyl, diene type) and addition by ring opening (cyclic monomers). Vinyl monomers having an electron withdrawing substituents such as aromatic ring, double bond, carbonyl, ester, cyano, sulfoxide, sulfone and nitro groups are very susceptible to nucleophilic addition reaction with initiators. The range of monomers that undergo anionic polymerization without significant transfer and termination reactions are styrene, dienes, methacrylates, epoxides, episulfides, cyclic siloxanes and lactones5,8,19-22).

Monomers with polar substituents such as carbonyl, cyano and nitro groups often undergo side reactions with the initiator or with the propagating anions. In such a case the controlled polymerization is not possible due to side reactions. Acrylonitrile, cyano acrylates, propylene oxide, vinyl ketones, acrolein, vinyl sulfones, vinyl sulfoxides, vinyl silanes, halogenated vinyl monomers, ketenes, nitro alkenes and isocyanites are few examples of monomers which are problematic when subjected to anionic polymerization19,20,22,23).

The vinyl monomers having functional groups with relatively acidic protons such as amino, hydroxyl, carboxyl groups result in transfer and termination reactions in the anionic polymerization. However, these functional groups can be protected by converting them into suitable derivatives, which are stable towards anions before subjecting such a monomer into the anionic polymerization. The choice of the protecting group must be selected in such a way that it can be removed readily after polymerization24,25).

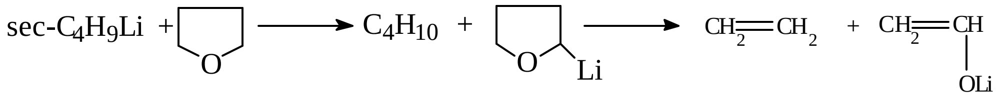
Another important aspect of the monomer reactivity in the anionic polymerization is the stability of the corresponding anions as deduced from the pK_a values of the conjugate acids of these anions. The monomers with a higher pK_a values result in anions that are less reactive and they require highly reactive organometallic initiators. The initiators with high reactivity lead to undesirable side reactions in some cases and those with less reactivity lead to a slow or an ineffective initiation. In general, the right choice of initiator for the anionic polymerization is supposed to have reactivity similar to that of the resulting propagating species8).

1.1.2.2. Solvents

Unlike in the case of radical polymerization, the nature of solvent affects the kinetics of the anionic polymerization to a greater extent. This is due the reason that in the anionic polymerization depending on the initiator, monomer and solvent the propagating species exist in the form of contact ion pairs, loose ion pairs, aggregated chains etc. These ion pairs are in equilibrium with one another and for obtaining narrow MWD the equilibrium constant should be high. This equilibrium dynamics depends on the nature of solvent *viz.* polarity, nucleophilicity etc. Generally free ions are more reactive than the ion pairs. Solvation of the ion pairs enhances the rate of reaction whereas for free ions, it retards the rate of reaction.

In anionic polymerization aliphatic, aromatic hydrocarbons and ethers are generally used as solvent as they do not react with the initiators and propagating species19,26,27). Initiation and propagation reactions were found to be faster in aromatic hydrocarbons when compared with the aliphatic hydrocarbons28,29). However they participate in metalation and chain transfer reactions under certain conditions. Benzene undergoes rapid metalation by butyllithium in the presence of N, N, N′, N′- tetramethyl ethylene diamine (TMEDA)14,30-33) . Toluene undergoes chain transfer reactions during styrene and diene polymerization34.35). These side reactions increase with increasing temperature. Ethers react with organometallic initiators, polystyryl and dienyl anions to terminate the chain growth14,30,36-39) (Scheme 1.1).

For example n-butyl lithium reacts with THF at 25 °C within 2 h38). Because of these reasons anionic polymerization in THF is usually performed at low temperatures. Thus, it is necessary to use saturated hydrocarbons as solvent for styrene and diene polymerizations. Highly polar solvents such as dimethylsulfoxide (DMSO), N,N-dimethylformamide (DMF) and hexamethylphosphoramide (HMPA) can be used for the polymerization of heterocyclic monomers whose propagating chain ends are less reactive (e.g.: epoxides)40).



Scheme 1.1: Butyl lithium decomposition by reaction with THF

1.1.2.3. Initiators

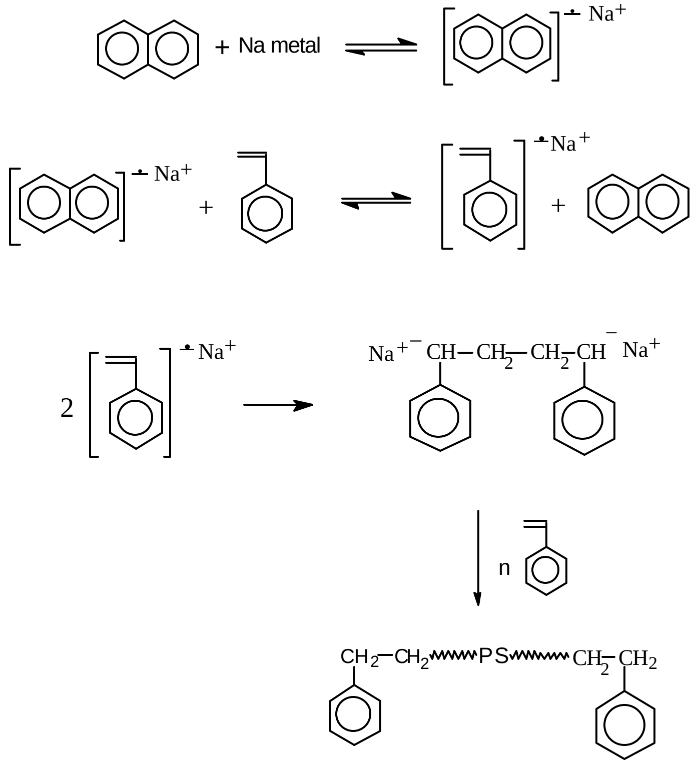
Organometallic reagents are generally used as initiators for the anionic polymerization. Alkali metals were first used as initiators for the anionic polymerization of dienes41). The mechanism42) (Scheme 1.2) follows an electron transfer from the metal surface to the absorbed monomer forming a monomer radical anion. The radical anion rapidly dimerizes resulting in dianions. This dianion acts as initiator to form oligomers, which finally desorb and grow in the solution. This is a heterogeneous process and the initiation reaction continues to generate new active centers. This leads to uncontrollable reactions with polymers having broad MWD, branching and gelation43).

$$\begin{aligned}
\mathrm{Mt} + \mathrm{M} &\longrightarrow \mathrm{Mt}^{+}, \mathrm{M}^{\dot{-}} \\
2\,\mathrm{Mt}^{+}, \mathrm{M}^{\dot{-}} &\longrightarrow \mathrm{Mt}^{+}, {}^{-}\mathrm{M{-}M}^{-}, \mathrm{Mt}^{+} \\
\mathrm{Mt}^{+}, {}^{-}\mathrm{M{-}M}^{-}, \mathrm{Mt}^{+} + n\,\mathrm{M} &\longrightarrow \mathrm{Mt}^{+}, {}^{-}\mathrm{M{-}[\,M\,]_{n}{-}M}^{-}, \mathrm{Mt}^{+}
\end{aligned}$$

Scheme 1.2: Mechanism for anionic polymerization initiated by alkali metals

But when monomers such as α-methyl styrene, 1,1-diphenyl ethylene react with alkali metals in polar solvents, (e.g.: THF), homogeneous difunctional anionic initiators could be formed44). Depending on the metal, temperature and concentration this reaction gives dimers or tetramers of α-methyl styrene45). After a careful filtration to remove residual metal particle, the solution containing dianion can be used for the initiation.

Radical anions generated by the reaction of higher aromatic hydrocarbons with alkali metals have been used in the anionic polymerization of styrene and dienes. Szwarc used sodium naphthalenide initiator for demonstrating the living nature of the anionic polymerization of styrene. These kinds of initiator form only in highly polar solvents such as THF. Addition of THF solution of sodium naphthalenide to benzene gave a finely divided suspension, which upon initiation of styrene gave polystyrene with narrow MWD46). The mechanism for this is shown in scheme 1.3.



Scheme 1.3: Anionic polymerization of styrene with sodium naphthalenide

Polymerization of dienes with these initiator systems results in polymers with high 1,2-linkages, which leads to inferior physical properties compared to that of polymers with 1,4-linkages. If the aromatic radical anions are too stable (e.g.: the radical anion of anthracene) then they will not initiate the polymerization.

The most important class of initiators used in anionic polymerization is alkyl lithium compounds. Alkyl lithium compounds exist as aggregated species in solid state, in solution and even in gas phase[14,47-49]. The degree of aggregation depends on the nature of substitution of alkyl group, type of solvent used and the reaction temperature. The reactivity of these alkyl lithium compounds is inversely proportional to their degree of aggregation. *n*-BuLi is more aggregated than *s*-BuLi, which is more aggregated than *t*-BuLi. Aggregation inversely affects the rate of initiation. Thus, when aggregation is more, the rate of initiation is reduced but the rate of propagation remains unaffected. In the case of polymerization of styrene and dienes in non-polar solvents with nBuLi as initiator this leads to incomplete initiation and broad MWD. Due to these reasons, *s*-BuLi is preferred for the polymerization of styrene and dienes in non-polar solvents Aromatic solvents tend to decrease the average degree of association and hence result in faster initiation rates than in aliphatic solvent[50-52]. Because of the hexameric aggregation of n-butyl lithium, the polymerization with this initiator is performed at 50°C to increase the rate of initiation relative to propagation[53]. Because of their reactivity towards ether solvents anionic polymerization using these initiators in THF should be carried out at low temperature. In aliphatic hydrocarbons these are quite stable and the decomposition rates are very low at room temperature.

The other initiators used in anionic polymerization reactions are cumyl potassium[54], flourenyl lithium[55-57] and ester enolates[58,59] besides various di-functional initiators based on the reaction of butyl lithium with di-vinyl substituted aromatic compounds[60-62].

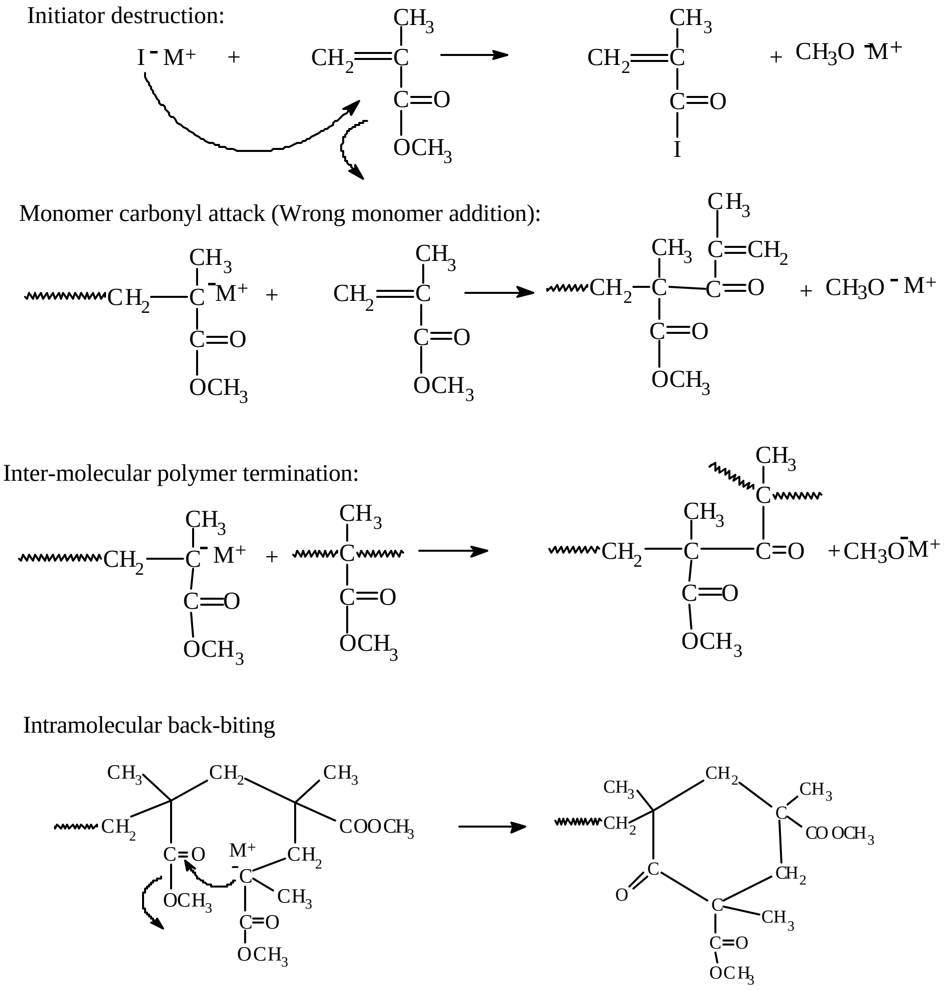
1.1.3. Living anionic polymerization of (meth)acrylates

1.1.3.1 Secondary reactions in anionic polymerization of (meth)acrylates

The anionic polymerization of MMA using classical alkyl lithium initiators proceeds with termination and transfer reactions in both polar and non-polar solvent even at low temperature (< -60 °C). The alkyllithium initiators used in anionic polymerization of styrene and diene type monomers are too reactive for alkyl methacrylates. This leads to the termination reactions involving initiator attack on the carbonyl group of monomer and polymer. (Scheme 1.4) and results in polymers with broad MWD and low conversion[63-68]. Further, it was found that the propagation rate constant is dependent on degree of polymerization[69] at the initial stages of MMA polymerization.

It is clearly established that intramolecular and intermolecular solvation of metal cation is one of the main reasons for the side reactions. The propagating centers in the anionic polymerization of methacrylates, exist as different aggregates and hence poses problems in controlling the anionic polymerization of alkyl methacrylates[70.71)]. The dynamics of equilibrium between aggregated and non-aggregated species strongly influence the MWD. The slow equilibrium dynamics leads to broad MWD[72-74)].

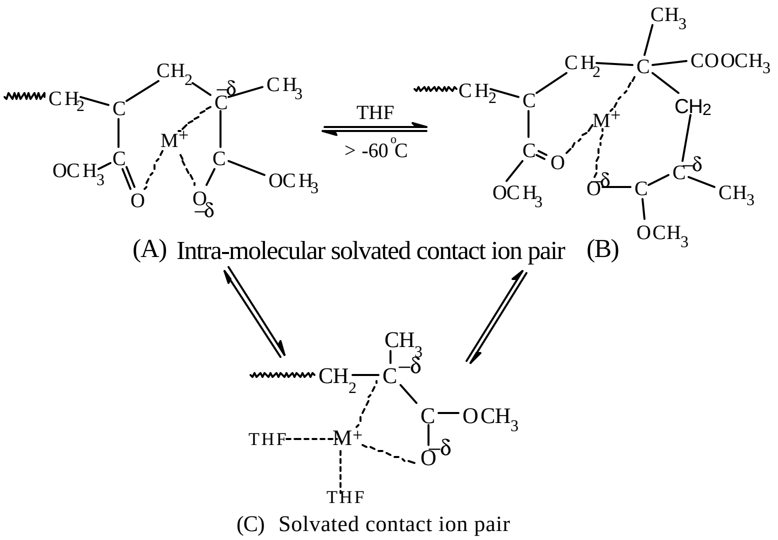
Solvent polarity has profound influence in the anionic polymerization of (meth)acrylates. Solvent polarity along with the cation size largely affects the reactivity of the propagating species besides dictating the mode of addition[75)]. Mono-disperse PMMA was prepared in THF using diphenyl sodium as initiator[70)]. Schulz[71-73)] and



Scheme 1.4: Secondary reactions in anionic polymerization of MMA

Mita[74)] have shown that the anionic polymerization of MMA in THF below – 65 °C using Na^+ or Cs^+ counterions proceeds with insignificant amount of termination. However, the control of the polymerization was lost at higher temperatures. When MMA polymerization was carried out in 1,2-dimethoxyethane (DME) with benzyl-oligo-α-methylstyryl sodium initiator, the obtained PMMA had narrower (< 1.01) MWD when compared to the polymer obtained in THF. This was explained by assuming that there exists an equilibrium between different types of contact ion pairs[75)] (Scheme 1.5).

Several research groups attempted to enhance the livingness in the anionic polymerization of (meth)acrylic monomers by using various strategies, which are briefly described below.

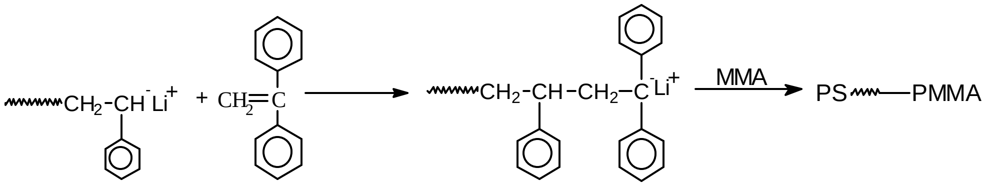


Scheme 1.5: Propagation via contact ion pairs in MMA polymerization

1.1.3.2 Strategies for enhanced livingness in (meth)acrylate polymerization

1.1.3.2.a Modifications in initiator systems

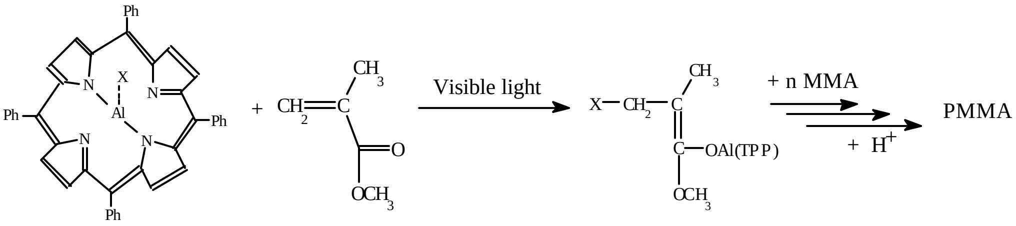
Rempp and coworkers[76)] reduced the reactivity of the propagating anion by end-capping the styryl anion with 1,1-diphenyl ethylene before initiating MMA polymerization in their successful attempt to make block copolymers with styrene and MMA(Scheme 1.7).



Scheme 1.6: Synthesis of PS-*b*-PMMA using DPE end-capped polystyryllithium

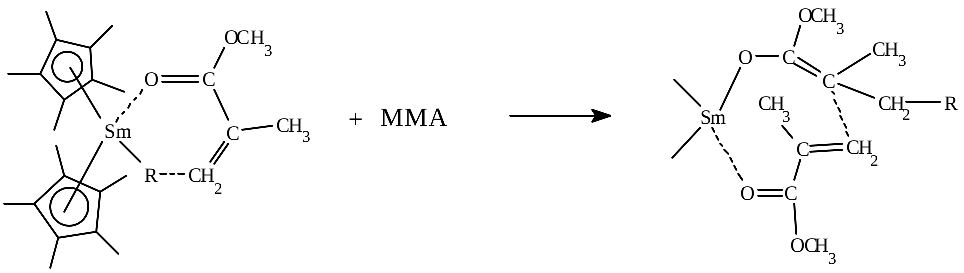
Bywater and coworkers[77)] used sterically hindered, less reactive 1,1-diphenylhexyllithium (DPHLi) as the initiator for the MMA polymerization in toluene. This reduces the extensive attack of initiator on the carbonyl group of the monomer and the obtained polymer exhibited a broad but uni-modal MWD unlike in the case of butyllithium initiated system where bi-modal MWD was observed. It was found that this initiator under favorable conditions could effectively initiate the polymerization of styrene and dienes[78)].

Inoue and co-workers[79-83)] used alkyl aluminum porphyrin compounds as initiators for the living polymerization of alkyl (meth)acrylates. The reaction proceeded only in the presence of visible irradiation with quantitative conversion and narrow MWD (Scheme 1.7).



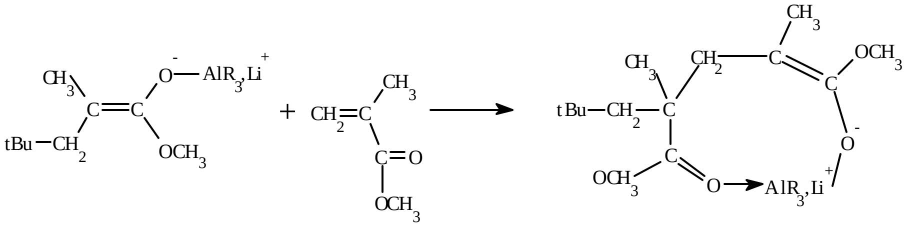
Scheme 1.7: Aluminum porphyrin initiated MMA polymerization

Organo lanthanide III complexes, when used as initiators for the polymerization of methacrylic monomers, gave polymers with high molecular weight and relatively narrow MWD (<1.3)[84-86)]. These initiators shows good catalytic activity in toluene in the temperature range of 40 and -78 °C and the polymerization was living even after one hour as demonstrated by the monomer resumption experiment. Yasuda and co-workers isolated and characterized the intermediate 1:2 adduct of $((C_5Me_5)_2\ SmH)_2$ with MMA. The proposed mechanism is shown in scheme 1.8.



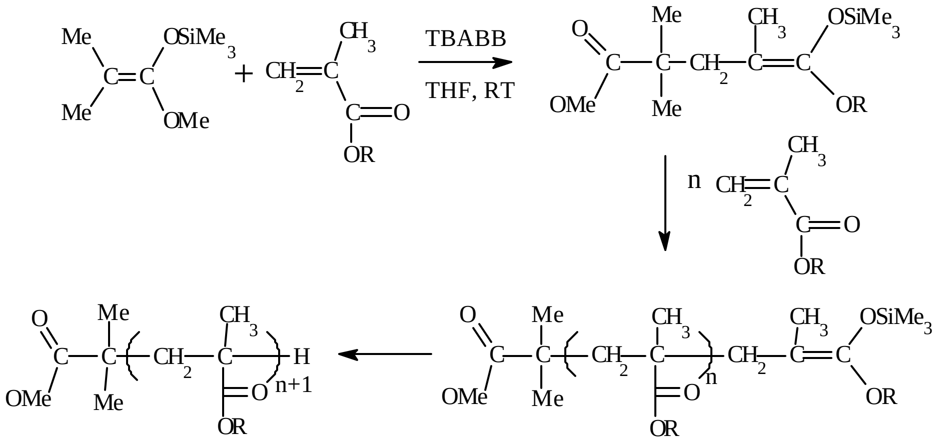
Scheme 1.8: Initiation of MMA with Lanthanide III complexes

Hatada and coworkers[87-89] reported the use of trialkyl aluminum- *t*-BuLi complex as initiator for the polymerization of MMA in toluene and produced highly syndiotactic PMMA with narrow MWD. For better control, the Al/Li ratio has to be higher than 3 and the complexation of the initiator and aluminum alkyl is essential prior to monomer addition. It was also shown that sterically hindered aluminum alkyls are required to achieve control at ambient temperature[90,91]. Müller and co-workers[92] identified the presence of enol-aluminate "ate" complex as the active center in MMA polymerization in the presence of trialkyl aluminum (Scheme 1.9). Their detailed kinetic studies have revealed that a sharp decrease in the reaction rate at certain monomer conversion as seen from the "kink" in the first-order time-conversion plots. The presence of "kink" was attributed to the formation of extended coordination of 'ate' complex, which leads to a network formation at higher conversion. Addition of lewis acids helped in reducing the network formation.



Scheme 1.9: Penultimate coordination of aluminum ate complex

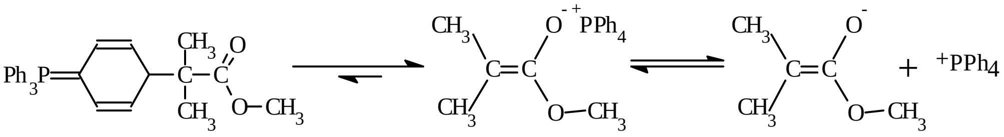
In a different strategy Webster and co-workers[10,93)], in DuPont, developed a new method called group transfer polymerization (GTP) for the living polymerization of methacrylic esters using silyl ketene acetal as initiator. In this process reactive chain ends are covalently bound to trialkyl silyl group and the polymerization proceeds by repeated monomer addition to the growing chain end carrying a catalyst coordinated silyl ketene acetal (Scheme 1.10). It was observed that the termination and transfer reactions are insignificant.



Scheme 1.10: Group transfer polymerization of methacrylic esters

One of the main driving forces for the side reactions in the anionic polymerization of (meth) acrylic esters is the coordination of metal cation with ester carbonyl group of the monomer and growing polymer chain. In order to circumvent this problem Reetz and co-workers[94,95)] and others[57,96-99)] used new initiators with metal free cations. They used tetrabutyl ammonium salts of malonates, thiolates, carbazols etc as initiators for the polymerization of *n*-BA and acrylic monomers. These systems were of great interest due to the fact that the polymerizations were carried out at ambient temperatures. However it has been demonstrated that the metal-free initiators result in incomplete initiation as a result of profound effect of ion pairing during initiation[100)]. Hence, anions of higher pKa values with smaller alkali cations are necessary in order to stabilize the resulting enolate anion through the increased formation of ion pairs and aggregates leading to a complete initiation.

Zagala and Hogen-esch[101)] reported a living polymerization of methacrylates using tetraphenylphosphonium counterion at ambient temperatures in THF resulting in polymers with predictable molecular weights with high initiator efficiency and narrow MWD. It was found that this polymerization involves a dynamic equilibrium between active species and dormant species with a phosphor ylide as dormant species[102,103] (Scheme 1.11).



Scheme 1.11: Dynamic equilibrium between ylide and phosphonium enolate

1.1.3.2.b Ligated anionic polymerization of (meth)acrylates

The effect of alkali metal alkoxides on the anionic polymerization of MMA was studied extensively[104-112]. It was shown that the addition of lithium-t-butoxide increases the stability of the active centers by forming a 1:1 adduct with the initiator[112]. This reduces the cyclization of oligomers in MMA polymerization thus increasing the higher limiting conversions and relatively narrow MWD[113]. Baskaran and co-workers[114] have used TMEDA as the chelating agent in the controlled anionic polymerization of MMA. The resulting polymers had predicted molecular weights and narrow MWD (1.2).

Teyssie and co-workers[115-118] first demonstrated the effect of alkali halide on the anionic polymerization of methacrylic monomers. They showed that the alkali halide forms a μ-type complex with the propagating ion pair, which perturbs the equilibrium dynamics of ion pairs resulting in the living nature in the polymerization of MMA and *t-BA*. It was also found that the use of LiCl as additive gives better results only in polar solvents, like THF at higher molar ratios of additive to initiator (≥10:1) and at low temperatures (-78 °C). Müller and his co-workers[119] studied the mechanism of this process and found that the rate of polymerization decreases with increasing concentration of LiCl. They also found that the formation of adduct actually reduces the aggregation and increases the rate of equilibrium between free and complex ion pairs than that of associated ion pairs. This results in apparently single distinguishable propagating species and hence lowers the MWD.

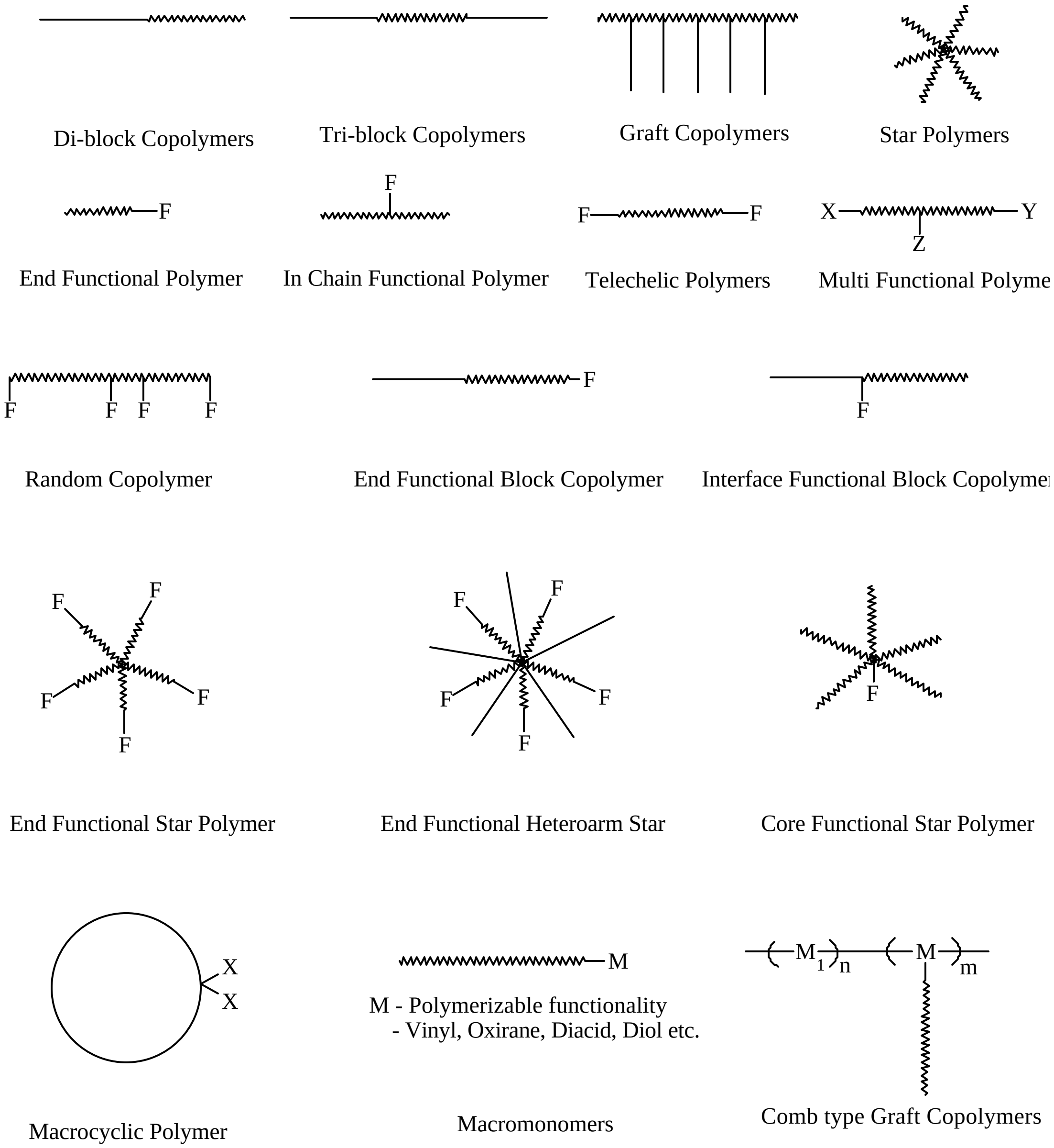
Teyssie and co-workers[120-122] successfully used DB-18-CE-6 crown ether to chelate the lithium cation in the anionic polymerization of MMA and *t*-BA in toluene with diphenylmethylsodium as initiator at 0 °C. Maruhashi and Takida employed alkali alkoxyalkoxides as additives in the anionic polymerization of methacrylic monomers123). Later, Teyssie and co-workers124-126) used lithium 2-(2-methoxy ethoxy ethoxide) as ligand. This gave very good control over the living polymerization of MMA and *t*-BA in THF and non-polar solvents at -78 °C.

Baskaran and Sivaram127) reported the anionic polymerization of MMA in the presence of $LiClO_4$. They showed that the anionic polymerization of MMA and *t-BA* in presence of $LiClO_4$ proceeds in a living manner at -78 °C in THF. The living nature of MMA polymerization was observed in toluene-THF mixed solvent (9:1 v/v) also and in THF, the polymerization being living even at higher temperature (-40 °C). From the kinetic studies, they obtained a fractional reaction order indicating the presence of associated ion pairs in equilibrium with non-associated species. The fractional reaction order indicates that the $LiClO_4$ does not perturb the aggregation effectively. However the propagation rate constant in presence of $LiClO_4$ was lower due to the formation of less reactive mixed aggregates.

More recently, Baskaran128) has reported the anionic polymerization of MMA in THF at higher temperature ranging between -40 and 30 °C using dilithium alkoxyalkoxides as additives in conjunction with 1,1-diphenylhexyllithium. Relatively narrow MWDs were obtained (1.1< MWD <1.3) and the living nature of the polymerization in this case was shown by monomer resumption experiment. It was assumed that additives of this type result in better co-ordination with enolate ion pairs forming mixed aggregates with faster equilibrium dynamics.

1.1.4 Architectural control using anionic polymerization

The major advantage of the living anionic polymerization lies in the fact that the process is free from termination and transfer reactions. This enables one to make polymers with predetermined chain length with narrow MWD. Utilizing this ability of living anionic polymerization it is possible to construct polymers with different architecture such as block copolymers, graft copolymers, functional polymers, telechelic polymers, star polymers etc. (Scheme 1.12) 40).



Scheme 1.12: Macromolecular architecture using anionic polymerization

1.1.4.1 Block copolymers

Block copolymers are considered to be a combination of two or more macromolecules joined covalently at its one or both ends. When these segments are incompatible the micro-phase separation takes place at the polymer interface forming domains and giving rise to useful properties in bulk and in solution[21,129-132)]. The block copolymers were used in various applications as compatibilizers, dispersing agents, thermoplastic elastomers etc. Anionic polymerization, due to its transfer and termination free nature, was proven to be the best method for preparing block copolymers with definite chain length of the blocks and narrow MWD[8,19,132,133)].

In general the block copolymers are made by sequential addition of monomers. In order to prepare pure block copolymers without homopolymer impurity it is essential to prevent any chain transfer and termination of the living carbanion chain ends. Besides this the crossover reaction from the living polymer chain end to the second monomer should be fast. This depends on the pK_a values of the conjugate acids of the monomers. Depending on this the monomer addition sequence has to be decided to achieve a successful block copolymerization[134)].

However, different approaches were used for making ABA type triblock copolymers[8,19,21,23,131-133,135)]. These include (a) the three-step sequential addition of monomers, (b) two-step sequential addition followed by coupling reaction and (c) the use of di-functional initiator with two-step sequential addition of monomers. The limitations of method (a) are the increased probability of introducing impurities and more importantly the differences in the crossover reactions in the final two steps. These limitations can be over come by using method (b). This reduces the extent of impurity introduction besides removing one crossover reaction from the process. However, in order to achieve pure block copolymer the coupling reaction has to be 100% efficient. Maintaining the stoichiometry of coupling agent with the living anion is quite difficult. This problem can be overcome by using method (c). The main drawback of this method is the difficulty associated with the preparation of di-functional initiators that are soluble in non-polar solvents for diene polymerization[6,42,136,137)].

1.1.4.2 Star polymers

Star polymers are branched polymers with several chains linked together at a single junction point[138-140)]. Well-defined star polymers with defined number of chains (arms), chain length, molecular weight and composition are very important to understand in general the effect of branching on the polymer structure. Different types of star polymers like homopolymers, heteroarm star polymers, star block copolymers etc. are known[141)]. Anionic polymerization provides the best method for preparing these polymers with high purity.

There are two ways to prepare star polymers based on the sequence of reactions. One is *arm-first* method and the other *core-first* method. In the *arm-first* method, linear polymer chains were prepared and these chain ends are coupled to form the star polymer[132,142)]. The coupling reactions include copolymerization/cross linking of living linear polymer chains with di-functional monomers like divinylbenzene and using multi-functional silyl halide type coupling agents. To determine the number of branches (degree of branching) it is essential to characterize the polymer in each step. In case of divinylbenzene type coupling agents, the degree of branching can be controlled by the ratio of anion to the difunctional monomer. But this often results in multi-modal and broad MWD with an average degree of branching. Star polymers with narrow MWD and uniform degree of branching can be obtained by using silyl halide type coupling agents by carefully maintaining the stoichiometry of coupling agents with the living anions.

In *core-first* method multi functional initiators are used to polymerize the monomer to yield star polymer[140)]. It is important that all the initiating sites initiate the polymerization simultaneously to get a narrow MWD. Star block copolymers can be prepared in a similar way by first making the block copolymers followed by coupling or by sequential addition of monomers to the multi-functional initiator. Hetero arm star polymers (mikto arm star polymers) are prepared by first making the star polymers using divinylbenzene type coupling agents and then using this as the multifunctional initiator to polymerize the second monomer[143)].

1.1.4.3 Functional polymers

Polymers with in-chain or end-chain functionality are used for chain extension, reaction blending, branching, cross linking with poly functional reagents, coupling with reactive groups of other oligomers or polymers, polymer supported organic synthesis, initiation and polymerization of other monomers[144-146)].

Living anionic polymerization provides one of the best methods for preparing functional polymers with known molecular weight, structural composition and narrow MWD and high functionality. The main approach involves the use of functional initiators[147)] or functional terminating agents[148)] in anionic polymerization to produce functional polymers. Important parameters for choosing these reagents are that, the protected functional group should not undergo undesired side reactions with the living anionic chain ends and the method of de-protection after the polymerization should be done at mild conditions. The major limitation of the functional initiator is their availability. The methodology involving termination of the living polymers with functional electrophiles is more suited in this regard. Substituted silyl halides$^{149,150)}$ and 1,1-diphenylethylenes$^{150,151)}$ are widely used for this purpose. It is very important to thoroughly characterize the prepared functional polymers in order to optimize these reactions for general utility.

1.1.4.4 Macromonomers

Macromonomers are defined as the macromolecular monomer or as the macromolecule with a polymerizable end group like vinyl, oxirane, diol etc. Though macromolecules with polymerizable groups are made earlier, it was Milkovich$^{153-156)}$ who presented the concept of macromonomer.

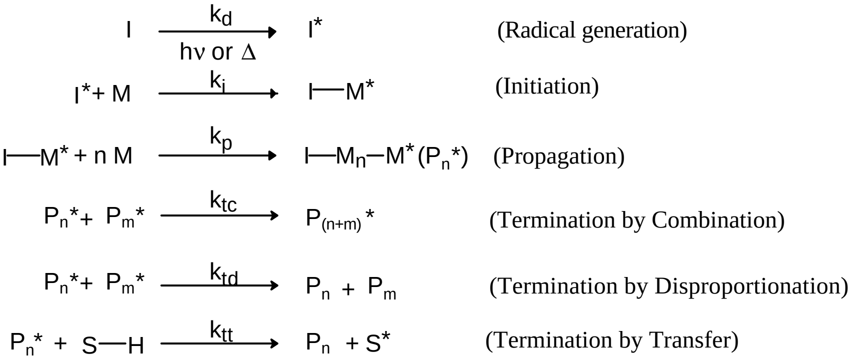
The preparation of macromonomers can be achieved by four methods$^{152)}$, namely, (1) initiation method – this involves the initiation of the living polymerization with a reagent processing a polymerizable group. (2) termination method – this involves the termination of living polymerization with an electrophile having a polymerizable group. (3) reaction of α-functional polymer with a compound having polymerizable group (2-step). (4) polyaddition using a bis-unsaturated monomer as one component. In all these methods care should be taken so that the reaction does not affect the polymerizable group. Several macromonomers with styrenic, methacrylic, vinylic, dicarboxylic, dihydroxylic diamino end groups with different backbone polymers have been prepared.

Macromonomers are used mainly for making well-defined graft and block copolymers. The conventional methods for making graft copolymer from a polymer backbone do not result in a defined structure. But by using the macromonomer technique it is possible to design graft copolymers with defined molecular weight, narrow MWD, number of grafted chains, combination of grafted and backbone polymer chains for desired purposes.

1.2 Atom transfer radical polymerization (ATRP)

1.2.1. Introduction

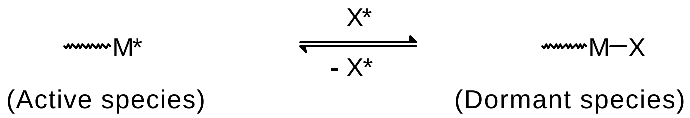
Radical polymerization involves radical generation, initiation, propagation, transfer and termination (Scheme 1.13). Here I, I^*, M, P^* and P are radical initiator, free radical, monomer, growing chain end and dead polymer respectively. k_d, k_i, k_p, k_{tc}, k_{td} and k_{tt} are rate constants for dissociation, initiation, propagation, termination by combination, disproportionation and transfer respectively. In order to achieve control over polymerization the initiation should be fast and the chain breaking reactions like transfer and termination has to be absent. But the radical active centers are highly reactive when compared to their ionic counter parts and hence it is quite difficult to avoid these undesired reactions.



Scheme 1.13 : General mechanism for free radical polymerization

The thrust towards achieving controlled radical polymerizations was provided by Fischer[157)] and later by Daikh and Finke[158)]. They discussed the concept of control and selectivity in addition reactions involving radical intermediates and predicted wide-ranging synthetic applications for the same. Several research groups attempted to apply this concept for achieving controlled radical polymerization. Various strategies were adapted to achieve controlled polymerization using radical initiated process. One approach was to reduce the active center concentration, which reduces the rate of termination to a greater extent when compared to rate of propagation. This is due to the fact that the rate of propagation is directly proportional to active center concentration where as the rate of termination is directly proportional to the square of active center concentration. Besides, due to the distinct diffusion rates of polymer radicals and monomer, termination reactions are reduced compared to propagation.

In a different approach, the propagating radicals are stabilized to minimize the undesired reactions. But stabilizing the propagating radical also decreases the rate of propagation to a great extent besides suppressing the termination reactions. Hence the best way to achieve control of the radical polymerization is to temporarily stabilize the active centers by converting them into persistent radicals or dormant species. To achieve control of the polymerization, the active centers should exist as dormant species, which should be in fast equilibrium with the active centers (Scheme 1.14).



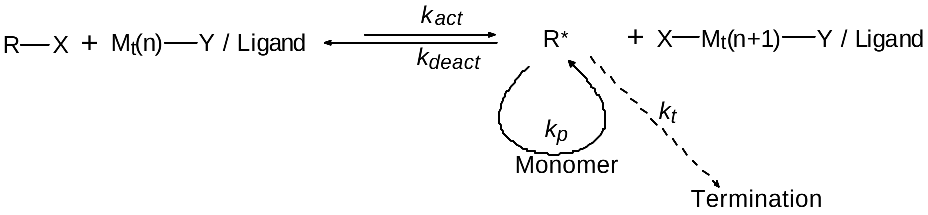
Scheme 1.14: Equilibrium between active and dormant specie

Extensive research has been devoted to achieve living/controlled radical polymerization in the last decade and the strategies adapted were described elaborately in several reviews[159-173)]. All these methods strive to establish a rapid equilibrium between the active and dormant species. These dormant species are alkoxy amines in stable free radical polymerization (SFRP) or more conveniently called as nitroxide mediated radical polymerization (NMP), thioesters in reversible addition fragmentation chain transfer polymerization (RAFT), alkyl halides in atom transfer radical polymerization (ATRP) or degenerative transfer polymerization (DT) and even organometallic species in transition metal mediated polymerization. Free radicals were generated by a spontaneous thermal process in NMP, reversible degenerative exchange process in DT and RAFT and by a catalyzed reaction in ATRP. Amongst these methods ATRP has been developing most rapidly and a brief introduction is given here to this method.

1.2.2. Atom transfer radical polymerization

Transition metal mediated atom transfer addition (ATRA) reactions are well known in the literature[174-177]. These reactions proceed by the transfer of an atom or molecule from the substrate to a transition metal complex generating radical intermediates. These radicals participate in further reaction by intra- or inter-molecular addition to unsaturated group. In ATRA the substrates are chosen in such a way that the addition product is much less stable than the initiating radical thus it irreversibly adds to the oxidized transition metal complex acting as a persistent radical to give the required product molecule. If the starting and product radicals are of similar reactivity it is possible to repeat the catalytic cycle for multiple additions of unsaturated monomers leading to a polymerization reaction.

Utilizing this transition metal mediated atom transfer addition mechanism Sawamoto[178] and Matyjaszewski[179] independently reported the controlled radical polymerization. This process was termed as atom transfer radical polymerization (ATRP) (Scheme 1.15). The polymerization is a multicomponent system composed of monomer, initiator, catalyst, ligand and solvent, which are discussed below.

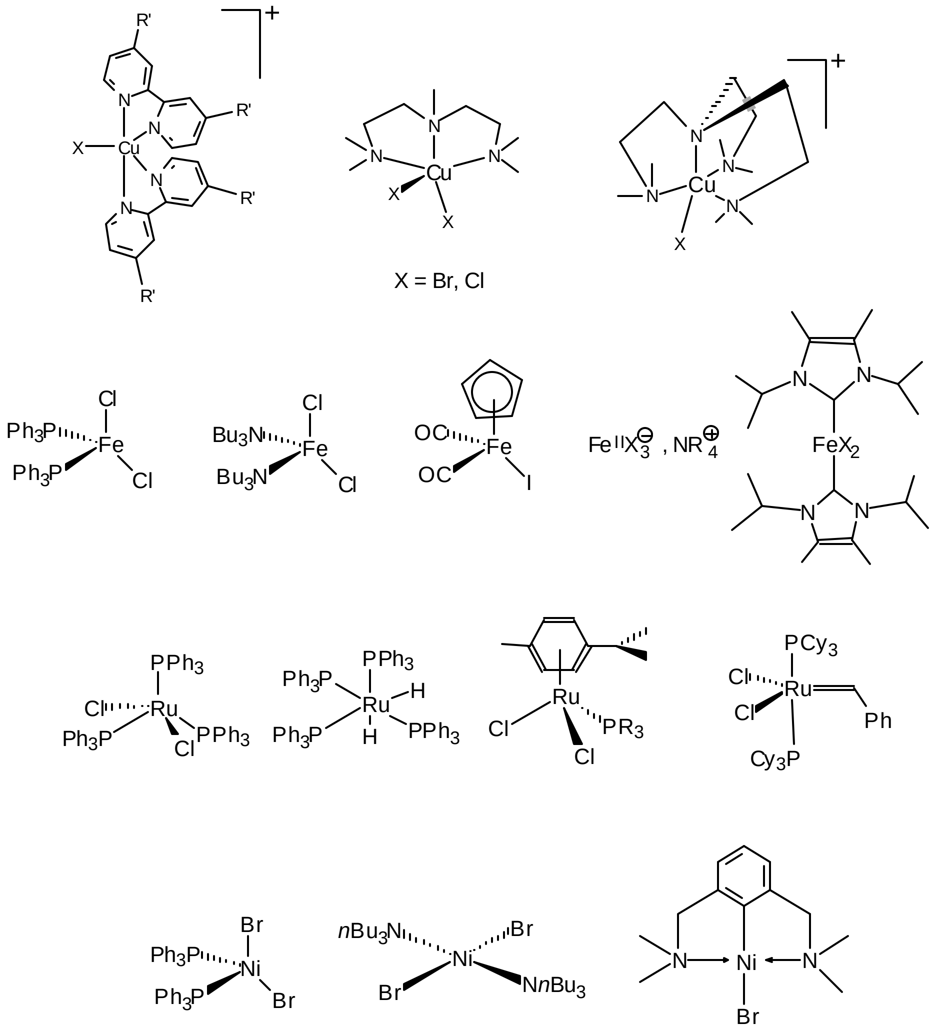


Scheme 1.15: Transition metal catalyzed ATRP

1.2.3. Components in ATRP

1.2.3.1. Catalysts

Catalyst is the most important component of ATRP for determining the position of equilibrium dynamics between active and dormant species. Mostly used catalysts in ATRP are transition metal catalysts based on copper[180-187], nickel[188,189], iron[190,191] and ruthenium[178,192] (scheme 1.16). The prerequisites for an efficient catalyst are 1) two readily available oxidation states separated by one electron, 2) reasonable affinity towards a halogen atom 3) relatively strong complexation with ligand and 4) an expandable coordination sphere to accommodate a (psuedo) halogen.



Scheme 1.16: Transition metal complexes used in ATRP

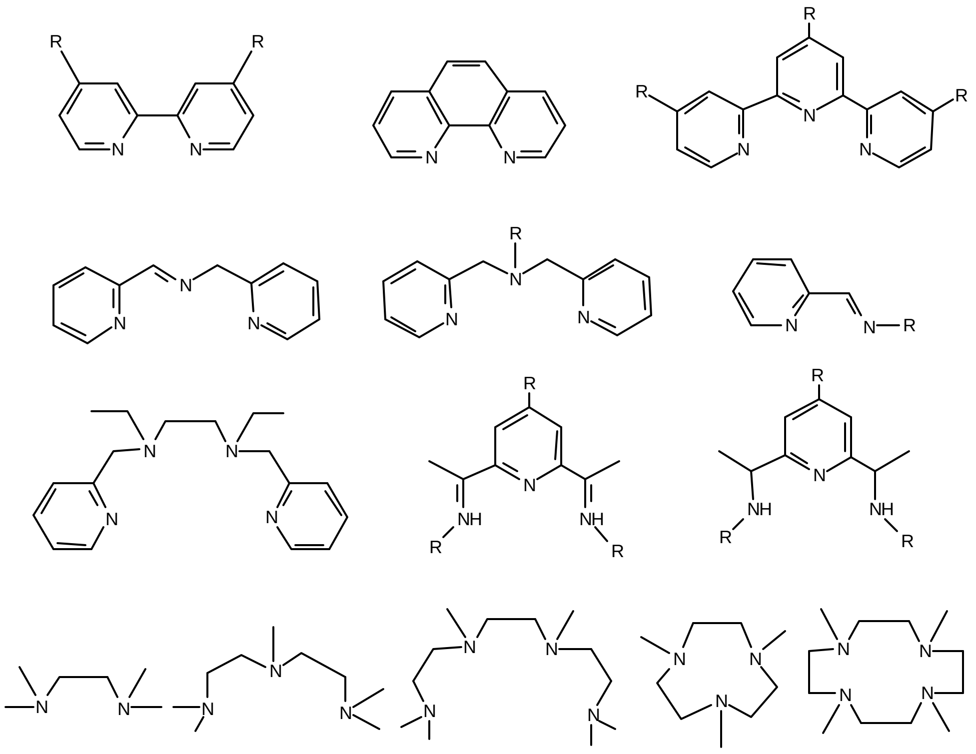
Copper mediated ATRP have been extensively studied with halides as counterions. Styrene, methyl acrylate (MA) and MMA were polymerized successfully with a linear increase in molecular weight (up to 100 000) and fairly narrow MWD (< 1.5) using cuprous halides complexed with bipyridyl ligands[193)]. Based on several experimental data it was proved that the polymerization using these catalyst systems proceed via radical pathway[194)]. Polymerization was tolerant to a variety of functional groups such as alcohols and amines and insensitive to additives such as water, methanol and acetonitrile [180)]. Reverse ATRP was achieved using Cu (II) complexes and azobis isobutyronitrile (AIBN)[193,195,196)]. Counterions other than halides, such as, carboxylates[197)], hexaflouro phosphate [198)], thiocyanate [199)], triflate[200)] and CuY (Y= O, S, Se, Te)[201)] have also been used in copper mediated ATRP The polymerization rate increased with copper acetate at the expence of control, but better control was achieved in this system by adding small amount of Cu(I) or Cu(II) halide, while maintaining the fast polymerization rate[198)].

The ideal catalyst for ATRP should be highly selective for atom transfer and should not participate in other side reactions such as redox process. The catalytic activity is different for different monomers and is strongly ligand dependent. Very active catalysts with equilibrium constants (K) > 10^{-8} are not suitable for methacrylates, whereas acrylamide requires higher catalytic activity[173)].

1.2.3.2. Ligands

Ligand plays a crucial role in ATRP by controlling the solubility of the complex in the reaction mixture and ensures stability of the complex in different monomers, solvents and temperatures. It adjusts the redox potential around the metal center, thus, affecting the reactivity and equilibrium dynamics of the atom transfer process[202)]. They can fine tune the selectivities and force the complex to participate in a one-electron transfer process needed for ATRP. The ligands can also facilitate the removal and recycling of the catalyst allowing the immobilization of the catalyst.

Various ligands based on nitrogen and phosphorous have been used in ATRP. Nitrogen based ligands (scheme 1.17) have been particularly successful in copper and iron mediated ATRP [191,202)] where as phosphorous, sulfur, oxygen based ligands have been less effective. The electronic and steric effects of the ligands are important[202)]. Catalytic activity is reduced when there is excessive steric hindrance around the metal center and also when the ligand used had strongly electron withdrawing substituents. It was also observed that the activity of N-based ligands in ATRP decreases with the number of coordinating sites i.e. $N_4 > N_3 > N_2 >> N_1$ and with the increasing number of linking C-atoms i.e. $C_2 > C_3 >> C_4$. Activity is usually higher for bridged and cyclic systems than for linear analogues. Another important consideration in choosing the ligand is the possible side reactions such as the reaction of amines (especially aliphatic) and phosphines with alkyl halides[203)]. These side reactions are reduced when tertiary amines are used as ligands and minimum when the ligands are complexed to CuBr[204)].



Scheme 1.17: Nitrogen based ligands used in ATRP

Phosphorous ligands have been used in ATRP in conjunction with most transition metals such as ruthenium[178,205)], rhodium[206,207)], rhenium[208)], nickel[189,209)], iron[190,191)] and palladium[210)]. Amongst the phosphorous based ligands (mostly PR_3 type), phosphines display a high catalytic activity and good control of the polymerization. Recently, cyclopentadienyl, indenyl and 4-isopropyl toluene type ligands were used in ruthenium based ATRP and these ligands result in more reactive catalysts than the ones obtained with phosphorous[205,211,212)]. Oxygen based ligands such as phenols and carboxylic acids have also been considered as ligands in ATRP[197,213)].

1.2.3.3. Monomers

Various monomers such as styrene, substituted styrenes, (meth)acrylates, (meth)acrylamides, dienes, acrylonitrile etc. have been successfully polymerized using ATRP. Each monomer has its own equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) for active and dormant species in ATRP even with the same catalyst and conditions. The product of k_p and K_{eq} determines the polymerization rate. Thus, the polymerization will occur very slowly if K_{eq} is too small. This could be the plausible reason why polymerization of less reactive monomers like olefins, halogenated alkenes and vinyl acetate are not yet successful173). Because of this reason, optimal conditions for ATRP such as the catalyst type, ligand, solvent, temperature and additives are to be chosen carefully for each monomer.

Styrene and its derivatives were polymerized using ATRP with copper180,214,215), ruthenium216), iron191), rhenium208) catalyst system to a molecular weight range of 1000 – 100 000. Amongst them, the polymerization using CuBr/dNbpy as the catalyst ligand complex and alkyl bromides as initiators at 110 °C has been extensively studied. When chloride was replaced in place of bromide, similar polymerization rates were obtained at 130 °C180). Good control was obtained even at 80-90 °C in a reasonable time when a more efficient CuBr/PDT217) or copper acetate (CuOAC)/CuBr/dNbpy197) catalyst systems were used. However, to maintain a sufficiently large propagation rate, to increase the solubility of the catalyst complex and to avoid vitrification at high conversions higher reaction temperatures (> 100 °C) are required for styrene. But better control is obtained at lower temperatures, presumably due to a lower contribution of the thermal self-initiation164, 218). The polymerization can be carried out in bulk or in solution, but as the stability of the halide end group depends on solvent219), non-polar solvents are preferred. A wide range of styrene derivatives were polymerized by ATRP in a controlled fashion and observed that the styrenes with electron withdrawing groups polymerize faster220).

ATRP of acrylates has been reported with copper179, 198,215), ruthenium205) and iron221) based catalyst systems. Amongst them copper systems appears to give best results and this could be due to the fast deactivation of the growing acrylic radicals with cupric halides173). Well define polymers in the molecular weight range up to 100 000 and MWD < 1.1 were prepared. Depending on the catalyst system used a wide range of temperatures can be used to achieve controlled polymerization within reasonable times. When tris[2-

(dimethylamino)ethyl]amine (Me_6TREN) was used in conjunction with CuBr as the catalyst system for methyl acrylate (MA) polymerization, poly(MA) was obtained in 1 h at ambient temperature with narrow MWD (1.10)222). A wide range of acrylates such as 2-hydroxyethyl acrylate (HEA)223,224), glycidyl acrylate225), *t*-butyl acrylate226), long chain alkyl acrylates227), and acrylates with fluorocarbon side chain 228,229) have been successfully polymerized using ATRP methods.

ATRP of MMA have been reported with copper230,231), ruthenium178,205), nickel188,209), iron190,191), palladium210), and rhodium207) catalyst complexes. The facile polymerizability and the large range of available catalysts for the ATRP of MMA is due to the relative ease of activation of the dormant species and the high values of K_{eq}173). The K_{eq} values are too high, when Me_6TREN was used as ligand, to obtain a controlled polymerization. Most polymerization were carried out at 70 – 90 °C. Solvent is necessary to solubilize the forming PMMA, and to keep the growing radical concentration low. Under comparable conditions MMA has a significantly higher K_{eq} than styrene and methyl acrylate, necessitating higher dilution and lower catalyst concentration173).

Initiation plays an important role in ATRP of MMA. Best initiators for MMA include sulfonyl chlorides231) and 2-halopropionitrile191) due to their sufficiently large apparent rates of initiation. Well-defined PMMA was obtained in the molecular weight range up to 180 000. Other methacrylic esters such as *n*-butyl methacrylate232-234), 2-(dimethylamino)ethyl methacrylate235), 2-hydroxyethyl methacrylate (HEMA)236 methacrylic acid in its alkyl protected form237), flourinated methacrylic esters228,229) and methacrylates with oligo(ethyleneoxide) substituent238) were successfully polymerized using ATRP. Other monomers polymerized by ATRP include acrylonitrile239), (meth)acrylamides240,241), 4-vinylpyridine242). Alternating copolymers of isobutene243) and maleimides167,243,244) were also attempted by ATRP methods.

1.2.3.4. Initiators

For a successful ATRP, initiating system is very important as it determines the molecular weight of the polymer. The initiating system must be capable of fast initiation, comparable to propagation, and cause minimal side reactions. A wide variety of compounds can be used as initiators in ATRP173) such as alkyl halides, benzylic halides, α-halo esters, α-halo ketones, α-halo nitriles, sulfonyl halides etc. The stabilizing group order in the initiator is roughly CN > C(O)R > C(O)OR > Ph > Cl > Me173). Multiple functional groups may increase the activity of the alkyl halide. Tertiary halides are better initiators than the secondary ones, which are better than the primary alkyl halides. Chlorides are least efficient initiators when compared with bromides and iodides. However, iodine based initiators are light sensitive and form complexes of unusual reactivity with metal centers and the R-I bond may be cleaved heterolytically thus complicating the ATRP with degenerative transfer245).

In general, same halogen is used in both the initiator and the catalyst, however, halogen exchange can be used some times to obtains better results246). In such a system (R-X/M_t-Y, X, Y = Br or Cl) the end group will be chlorine due to the stronger alkyl-chloride bond. Psuedo-halogens were also used ATRP199). It is necessary to have a structure reactivity correlation for a successful ATRP, and this should include both initiator and catalyst along with the effects of solvent and temperature.

1.2.3.5. Solvents, temperature and additives

ATRP can be carried out in bulk, solution, suspension or emulsion. Solvent is some times necessary to achieve good control over polymerization, especially when the growing polymer complex is not soluble in the monomer. Various solvents such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide, ethylene carbonate, alcohol, water, carbon dioxide and many others were used in ATRP for different monomers. Solvent for ATRP has to be chosen in such a way that the chain transfer to solvent, catalyst poisoning by the solvent180), solvent assisted side reactions219) should be minimum. The structure of the catalyst changes in different solvents247), and solubility of the catalyst is better in polar solvents248).

Temperature of the polymerization in ATRP affects the rate of polymerization proportionally. With increasing temperature both k_p and K_{eq} and k_p/k_t increases, thus, giving better control in the polymerization. However, chain transfer and other side reactions also increase at elevated temperatures218,219). Solubility of the catalyst improves with temperature, but catalyst decomposition can occur at higher temperatures189,249). The optimal temperature depends on monomer, catalyst, and the targeted molecular weight.

In some cases additives are necessary for a successful ATRP. Lewis acid additives such as aluminum alkoxides are needed for the controlled polymerization of MMA based on ruthenium based catalysts. Very slow or no polymerization is observed in the absence of these additives[178,250]. These additives presumably activate and stabilize the catalyst in higher oxidation state[250]. Adding polar solvents such as water can accelerate polymerization[238]. Addition of zero-valent copper in the copper based ATRP and iron powder in iron based ATRP accelarates the polymerization significantly without losing the control over molecular weight and MWD[251]. This helps in carrying out the polymerization even without removing the oxygen traces and inhibitor[252]. Various phenols and methyl hydroquinone were also used as additives in ATRP to enhance the rate of polymerization[253, 254].

1.2.4. Features of ATRP

ATRP is a versatile method for the controlled polymerization of (meth)acrylate/styrene monomers. Various features of ATRP have been reviewed thoroughly[162,170,255]. A wide range of monomers, like methacrylates, acrylates, acrylonitrile, styrene and its derivatives can be successfully polymerized with good control over molecular weight and MWD. Major advantages of ATRP over conventional living polymerization methods lies in the fact that it is somewhat more tolerant to the protic impurities and several functional groups. Like any typical free radical process it is inhibited by presence of oxygen. Use of zero-valent copper in ATRP improves the tolerance towards oxygen. Several research publications demonstrate the utility of ATRP for making block copolymers, graft copolymers, star polymers, hyperbranched polymers etc.

The transfer group in ATRP is a simple halogen molecule and, therefore, it is easy to synthesize polymers with well-defined architectures. The halogen end group can be converted to the required functionality by regular organic transformation reactions. Functional monomers can be polymerized utilizing the tolerance of the radicals towards these functionalities to get functional polymers[172]. Halogen containing initiators can be designed according to the requirement and easily prepared from the commercially available compounds. By manipulating the monomer feed composition and sequence a variety of polymer structures like random, tapered and block copolymers can be made. Recently, in a most promising development, ATRP has also been applied to water borne polymerization systems *i.e.* emulsion polymerization[233,256]. Though the attempts failed in achieving good control due to transfer and termination by the alkylsulfonate surfactants, good control was obtained when nonionic surfactants were used. This indicates that the ATRP can be used in bulk, solution, dispersion and emulsion polymerization methods within a wide temperature range (-20 to 130 °C).

In ATRP the catalyst has to be removed from the product after polymerization. This is one of the major disadvantages in this method. Other demerits include the unavoidable transfer and termination reactions. This results in homopolymer impurities in the block copolymer and star polymer synthesis. In the synthesis of star and hyperbranched polymer, the radical concentration is very high compared with the corresponding linear polymer synthesis. This results in higher degrees of termination and presence of coupled molecules in the product. To minimize this effect the polymerization in this case has to be limited to low conversions.

1.3. Scope and Objectives of present work

The prospect of synthesizing polymers of higher alkyl methacrylates, such as poly(laurylmethacrylate) (PLMA), with good control assumes importance because of their wide-ranging applications. Polymers and copolymers containing lauryl (meth)acrylate segments are used as adhesives[257,258], packaging materials in HPLC[259], oil additives such as pour-point depressant[260], viscosity index improver[260,261] etc. Another important characteristic of PLMA is its low glass transition temperature ($T_g \sim$ -65°C)[262]. Because of this reason, these monomers can be used in copolymerization with other acrylic monomers, with high T_g's to make completely acrylic-based thermoplastic elastomers. The controlled polymerization of higher alkyl methacrylates has received relatively less attention by researchers.

Objectives of the present work are:

1. To explore the feasibility of controlled polymerization of LMA using ligated anionic polymerization at temperatures higher than -40 °C. The anionic polymerization of LMA will be carried out in THF with 1,1-diphenylhexyllithium as initiator in presence of $LiClO_4$ as additive.
2. To explore the feasibility of controlled polymerization of LMA using atom transfer radical polymerization (ATRP). ATRP of LMA will be carried out in toluene at 95 °C

with ethyl-2-bromoisobutyrate as initiator and CuBr as catalyst in presence of different ligands. Kinetic experiments will be carried out for ATRP of LMA with different ligands.

3. To synthesize acrylic block copolymers containing LMA segments. Synthesis of di and tri-block copolymers of MMA and LMA will be attempted using anionic polymerization and ATRP. The block copolymers will be synthesized by sequential addition of monomers using mono and di-functional initiators.
4. To synthesize star polymers with a functional group at the core, using living anionic polymerization method. 2-tribromomethyl-2-oxazoline will be used as the coupling agent for the living polymer chain ends to produce core functional star polymer. Coupling reactions of TBO will be studied with model anions *viz.* *n*-BuLi, oligo styryl lithium etc.

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Chapter 2: General Experimental Procedure

Controlled polymerization methods require rigorous purification of all reagents, monomers and solvents. Besides this the reactions has to be performed under an inert atmosphere with no impurities like moisture, oxygen and other reactive gases. In order to achieve the best conditions for living/controlled polymerization under positive pressure, special care has to be taken for purification of nitrogen/argon gas. In this chapter, general purification methods, experimental setups and manipulations in the laboratory as well as characterization techniques used in this work are described.

2.1. Purification of gases, solvents and other reagents

2.1.1. Nitrogen or argon gas

The nitrogen or argon gas (INOX, IOC, Bombay), was used for the regular experimental purposes. Following methods were employed to remove impurities from the nitrogen gas.

The nitrogen gas was passed through activated A4 molecular sieves to remove moisture. Oxygen was removed by passing the gas through a copper catalyst at 200 °C. The set up for this purification contains five towers (1m × 3") (Fig. 2.1). The first and third towers contain A4 molecular sieves and the second and fourth contain copper catalyst with the fifth tower containing A5 molecular sieves. After passing the nitrogen gas through these towers it was passed through another column containing successive beds of anhydrous phosphorous pentoxide and calcium hydride. Finally the gas was passed through a trap of eight cylinders containing toluene solution of oligo-styryl lithium, which removes the last traces of reactive impurities besides acting as an indicator for the nitrogen purity. The purified nitrogen gas was then connected, using a rubber tube, to the manifold from which it was connected to the reactors.

The molecular sieves and the copper catalyst were activated from time to time. The molecular sieves were reactivated by heating the column (~ 200 °C) under reduced pressure for 10-12 hours. For reactivating the copper catalyst, hydrogen gas was passed through the towers at 200 °C for 7-8 hours and then the water formed was removed by applying vacuum. The activated copper catalyst is dark brown in color while the catalyst before activation is pale green in color. This acts as the visual indicator for determining the appropriate time for reactivation.

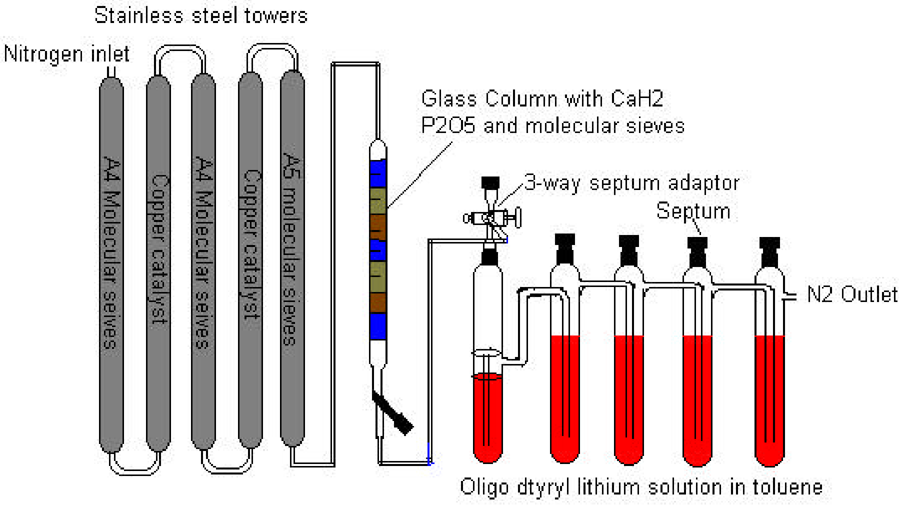

Fig. 2.1: Set-up for nitrogen gas purification

2.1.2. Solvents

All the solvents used in the present work (THF, toluene and cyclohexane, S.D.Fine Chemicals, Bombay or E-Merck, Bombay) were first subjected to fractional distillation using a 1.5 m column. The fractionated solvents were then distilled over calcium hydride after refluxing over night using a Dean-Stark type distillation unit. This was followed by distillation over sodium-benzophenone complex before storing in graduated bulbs over sodium-potassium alloy under high vacuum. These graduated bulbs were directly connected to the manifold set-up with provision for applying vacuum and/or nitrogen (Fig. 2.2). The required amount of solvent was condensed into an ampoule from these bulbs under vacuum using liquid nitrogen bath. N,N-Dimethyl formamide (S. D. Fine Chemicals, Bombay) was stirred over CaH_2 for four hours and distilled under reduced pressure prior to reaction. The solvents used for precipitation of polymers (methanol, hexane and acetone, S. D. Fine Chemicals, Bombay or E-Merck, Bombay) were used after simple distillation. All the solvents were transferred into the reactor using stainless steel capillary through a rubber septum under a positive pressure of nitrogen.

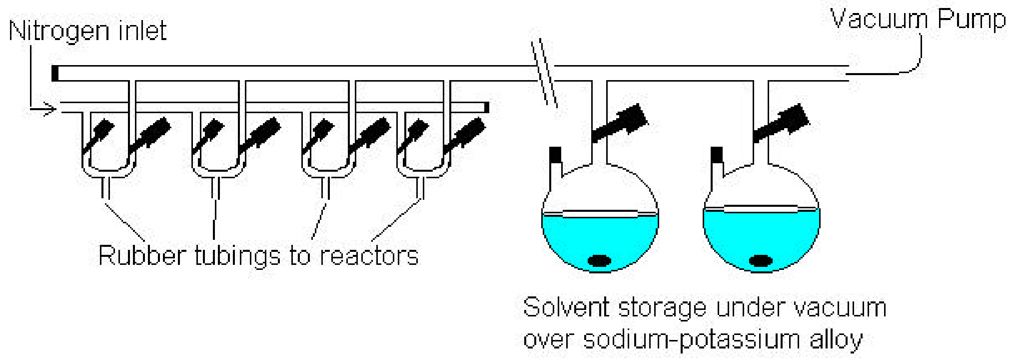

Fig. 2.2: The manifold set-up for polymerization reactions in inert atmosphere

2.1.3. Monomers

All the monomers were purchased from Aldrich, USA. The monomers were stirred over CaH_2 for 5 h, fractionally distilled and finally distilled under reduced pressure. The distilled monomer was stored at 5 °C under positive pressure of nitrogen. The required amount of pre-distilled monomer was again subjected to further purification in inert atmosphere prior to the polymerization by freeze-thaw method using the apparatus shown in fig 2.3.

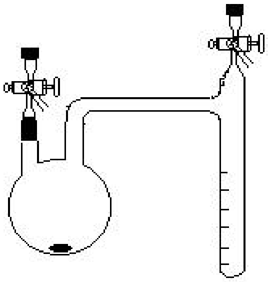

Fig. 2.3: Apparatus for monomer distillation

MMA was purified by distillation, over tri-ethyl aluminum (TEA), using freeze-thaw technique. MMA was taken into the distillation unit and a 1.0 M solution of TEA in toluene was added drop-wise until persistent greenish yellow color appears. This color represents the formation of a complex of TEA with MMA and acts as an indicator for monomer purity¹⁾. The pure monomer was then condensed into the side arm of the monomer purification assembly using liquid nitrogen and transferred into the reactor by capillary or syringe. LMA was stirred over TEA for few minutes and this greenish yellow color solution was passed through a column of activated neutral alumina (2” × 1”). This process removes the excess TEA and the TEA-LMA complex to give the pure monomer for direct use into the polymerization reaction. Styrene (supplied by Thermax industries, Pune) was purified by distillation over a toluene solution of fluorenyl lithium.

2.2. Synthesis of Initiators

2.2.1. *n*-Butyl lithium

n-Butyl lithium was prepared by the reaction of *n*-butyl chloride with lithium metal in cyclohexane. The reaction set-up is shown in figure 2.4. The reaction and addition of all reagents were carried out under argon (INOX, Bombay) atmosphere. Required amount of lithium metal was taken into the reaction bulb containing dry cyclohexane in the form of small pieces and a small piece of sodium metal was added to it for fast initiation of the reaction.

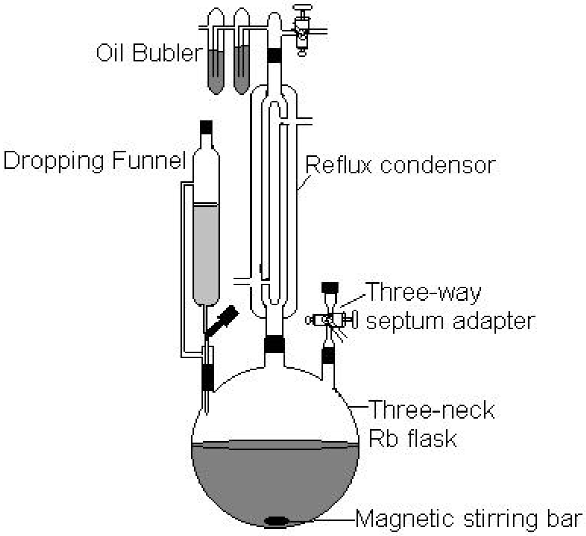

Fig. 2.4: Apparatus for making *n*-BuLi

Initially *n*-butyl chloride was added continuously while stirring at room temperature until a slight exotherm was observed. At this point the temperature was brought down to 0 °C using an ice-bath and the rate of addition was reduced to drop-wise addition. After the complete addition of the required amount of n-butyl chloride, ice-bath was replaced by an oil-bath and the temperature was increased to 65 °C (± 5 °C) and stirred overnight. The reaction mixture was cooled to room temperature and the precipitated lithium chloride and the excess metal were allowed to settle down. The supernent clear solution was transferred into storage ampoules using capillary and stored under positive nitrogen pressure at 5 °C.

2.2.2. 1,1-Diphenylhexyllithium

1,1-Diphenylhexyllithium (DPHLi) was prepared from the reaction of 1,1-diphenyl ethylene (DPE, Aldrich, USA) with *n*-BuLi (prepared in the laboratory) in THF. In order to purify DPE, *n*-BuLi was added drop-wise under stirring to neat DPE until persistent dark red color appears. This color is characteristic of the DPHLi anion which is formed after all the impurities in DPE were consumed by *n*-BuLi. The excess DPE was distilled off over this anion using freeze-thaw technique. The reaction set-up for preparing DPHLi contains single neck round bottomed flask equipped with a magnetic stirring bar and three-way septum adapter. Freshly condensed dry THF was transferred into the reaction bulb followed by the required amount of freshly distilled DPE. Temperature of the solution was brought down to -40 °C and n-BuLi was added drop-wise with vigorous stirring until the red color characteristic of DPHLi anion appears. After waiting some time, to ensure the color does not disappear, calculated amount of n-BuLi was added slowly. After stirring approximately for an hour the temperature of the initiator solution was brought to room temperature and stirred for further two hours and stored under positive nitrogen pressure at 5 °C.

2.2.3. Lithium Naphthalenide

Lithium naphthalenide was used as the di-functional initiator for the preparation of tri-block copolymers. This initiator was prepared by the reaction of lithium metal with naphthalene in THF. In a single neck round bottomed flask freshly sublimed naphthalene was dissolved in THF. In another flask containing magnetic stirring bar required amounts of lithium metal and THF were transferred. Naphthalene solution was transferred slowly into the flask containing metal using capillary with continuous stirring at room temperature. Dark green color characteristic of lithium naphthalenide radical anion was observed immediately. After complete addition the solution was stirred for two hours and the solution was filtered through a column containing sintered glass bed (G0). The solution was transferred into an ampoule and stored under nitrogen positive pressure at 5 °C.

2.2.4. Determination of initiator concentration

Concentration of the initiator solutions, *n*-BuLi, DPHLi, LiNap, were determined using Gillman2) double titration method. In this method two sets of titration were carried out. In the first set a definite amount of initiator solution (2 mL) was reacted with small excess of 1,4-dibromo butane (Aldrich, USA, distilled over CaH_2) in dry THF to convert the lithium in the form of R-Li to LiBr. After 15 minutes water (1 mL) and methanol (5 mL) were added to this mixture, which converts the other lithium species like alkoxides to LiOH. This solution was then titrated against the standard solution of potassium hydrogenphthalate (PHP) (titer value A mL). In another set the same quantity of initiator solution was treated with water to convert all lithium species into LiOH and then titrated against PHP Titer value B mL). The difference (B – A) gives the LiOH concentration corresponding to the active initiator R-Li present in the solution and the actual initiator concentration can be calculated accurately.

2.3. General Polymerization Procedure for alkyl methacrylates

2.3.1. Anionic polymerization

2.3.1.1. Homopolymerization of alkyl methacrylates

Anionic polymerization of alkyl methacrylates (MMA, LMA) was carried out on a bench top single neck reactor equipped with a three-way septum adapter and a magnetic stirring bar (Fig. 2.5). The reaction bulb was assembled and flame dried under vacuum before filling the bulb with nitrogen gas. Into this freshly distilled dry THF (100 mL) was transferred using a stainless steel capillary. Into this, calculated amount of additive as a solution of THF was added using syringe. Temperature of the solution was brought down to – 40 °C. DPHLi was added drop-wise until persistent, faint, red color of DPHLi appeared in the solution. This gives the end-point for the titration of traces of impurities, usually 0.2 to 0.6 mL of 0.1 M initiator solution is consumed for this purpose. Calculated amount of initiator (0.2 – 2 mL) was then transferred into the solution by syringe and required amount of freshly distilled monomer (3 – 5 mL) was added either neat or as solution of THF. The contents were stirred for 15 minutes and 1 mL of methanol was added to quench the polymerization.

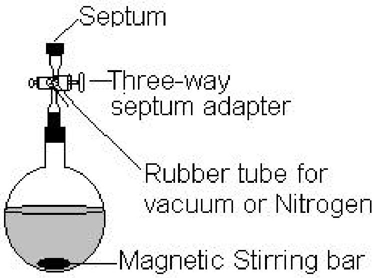

Fig. 2.5: Bench-top reactor for anionic polymerization

The polymer solution was concentrated and poured drop-wise with stirring into n-hexane (E-Merck, Bombay, for precipitating PMMA) or 20% aqueous methanol (for precipitating PLMA). The polymer was filtered and dried under vacuum for 5 - 8 hours at 20 °C. In the case of PLMA the polymer was dissolved in benzene (S. D. Fine Chemicals, Bombay), filtered to remove lithium salts and then freeze dried.

2.3.1.2. Synthesis of block copolymers of MMA and LMA

Block copolymers were synthesized by sequential monomer addition. In this process after complete polymerization of the first monomer a small fraction of the solution was withdrawn for analysis using syringe and the second monomer was added. In these manipulations, involving monomer additions and sample withdrawal, it is possible that some impurities may enter. This results in homopolymer contamination in the final block copolymer, as the living chain ends of the first block are quenched partially by the impurities. To overcome this problem a special apparatus (Fig. 2.6) was used for the preparation of block copolymers. The monomers were directly distilled into ampoules and then connected to the apparatus. The apparatus was flame dried under vacuum and after filling the apparatus with nitrogen, required amounts of solvent and additive were transferred. Temperature of the solution was reduced to –40 °C and required amount of initiator was added after titrating the solution for impurities. The first monomer was added by opening the stopcock of the ampoule and the solution was stirred for 15 minutes. The apparatus was tilted towards the constructed side arm so that a small portion of the solution flows into it. The stopcock of the second ampoule was opened to add the second monomer and the solution was stirred for another 15 minutes. 1 mL of methanol was added to terminate the reaction. The block copolymers of LMA and MMA were precipitated into methanol (E-Merck, Bombay).

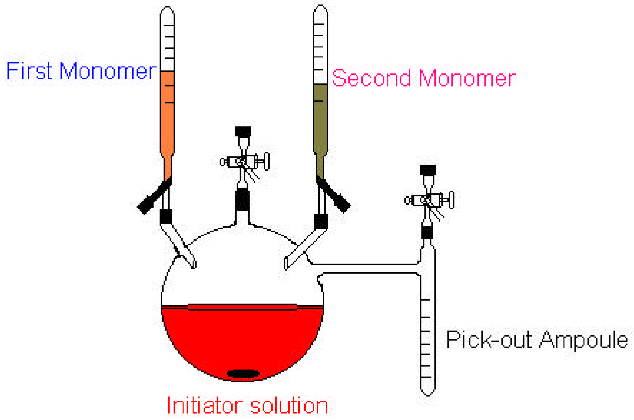

Fig. 2.6: Apparatus for block copolymer preparation

2.3.2. Atom transfer radical polymerization (ATRP)

2.3.2.1. Homopolymerization of alkyl methacrylates

ATRP of alkyl methacrylates (MMA, LMA) was carried out on a bench top reactor similar to the one shown in fig. 2.5. ATRP was carried out with copper bromide (CuBr, Aldrich, USA) as catalyst, in presence of different ligands in toluene at 95 °C with ethyl-2-bromoisobutyrate (EBI, Aldrich, USA) as initiator. EBI was distilled over CaH_2 prior to the reaction and CuBr was used as received. The preparation and purification of ligands is described in the appropriate Chapters.

In a typical polymerization reaction the calculated quantities of CuBr, monomer, solvent and ligand were transferred into the reaction flask in that order. The solution was cooled with a liquid nitrogen bath and, when the contents are half frozen, vacuum was applied (0.007 mbar). After keeping the flask under vacuum for approximately 10 minutes, cooling bath was removed and the temperature was allowed to come to room temperature. The flask was filled with nitrogen gas again. This cycle was repeated two more times to ensure complete removal of oxygen and other reactive gases. The temperature of the reaction flask was increased to 95 °C and calculated amount of EBI was added with stirring. The reaction was quenched after 6 hours by cooling it in liquid nitrogen bath and THF was added to the contents. The solution was passed through a column of neutral alumina (1" × 4") to remove the catalyst complex. Polymers (PMMA) were recovered by precipitating the concentrated solution into non-solvent. In the case of PLMA, Polymer was recovered by removing the solvent under reduced pressure. This crude PLMA was further purified by freeze drying from benzene. All the polymers were dried under vacuum for 5-8 hours at 20 °C, before analysis.

2.3.2.2. Synthesis of block copolymers of MMA and LMA

Block copolymers were prepared by sequential monomer addition. The apparatus used was simple bench-top reactor (Fig. 2.5). Either LMA or MMA were polymerized as described in the earlier paragraph and after stirring for six hours, a small portion of this solution was withdrawn using a syringe. The syringe was used while it was still hot. After this the second monomer was added into the reaction flask with stirring of the contents. The reaction was continued for another six hours before quenching. The polymer, after removing the catalyst was precipitated into methanol, filtered and dried under vacuum.

2.3.2.3. Kinetics of ATRP of alkyl methacrylates

The kinetics of ATRP of alkyl methacrylates was studied using gas chromatography (GC) by estimating the unreacted monomers. Diphenylmethane (DPM), was used as the internal standard. The ratio of the monomer to internal standard, prior to polymerization, was determined by using GC. Small fractions of the reaction mixture were taken out, using syringe, at several intervals of time. At each interval the ratio of monomer to internal standard was determined to calculate the conversion from the following equation:

$$X_p = 1 - \left[\left\{ \frac{M_t}{I_t} \right\} \Big/ \left\{ \frac{M_0}{I_0} \right\} \right]$$

Here, X_p is the conversion of monomer at a given time, t. M_t and M_0 are peak area of monomer at time t and 0 respectively. I_t and I_0 are the peak area of initiator at time t and 0 respectively.

A semi-logarithmic plot of time *Vs* conversion gives the kinetic details of the polymerization. Linearity of the graph indicates the absence of termination reaction and non-linear curve indicating the presence of side reactions. The reaction rate can be determined using the following equation:

$$ln\left[\frac{M_0}{M_t}\right] = \frac{k_{app}}{k_t} \bullet \left(1 - e^{-k_t \cdot t}\right)$$

Here k_{app} is the apparent rate constant, defined as $k_p.[P^*]$, k_p and k_t are the rate constants for propagation and termination respectively and $[P^*] = f\ .\ [I_0]$ is the active center concentration. The presence of the termination and transfer reactions can be confirmed from the linearity of the plots of molecular weight and molecular weight distribution against conversion.

2.4. Characterization techniques

Molecular weight and molecular weight distribution of the alkyl methacrylate polymers were determined from SEC (*Thermoquest*) equipped with UV and RI detectors. PMMA standards (*Polymer Laboratories*) were used for calibration. THF was used as eluent at 1mL/min. flow rate and two 60 cm PSS SDV-gel columns: 1 × 100Å and 1 × linear (10^2 – 10^5 Å) at room temperature. ^{1}H NMR (*Bruker-200 MHz*) was used for determining the copolymer composition. This was calculated using the integration values, per proton, of $–OCH_3$ protons of MMA (3.6 δ) and $–OCH_2$ protons of LMA (3.9 δ). The conversion of monomers in kinetic experiments was determined by using gas chromatography (*PERKIN-ELMER AUTO-SYSTEM XL*) by calculating the disappearance of monomer with respect to an internal standard. BP 1 capillary column (SGE, Australia) (25m long with 0.1µ inner diameter) was used with oven temperature- 220 °C, injector temperature- 300 °C, detector (FID) temperature- 325 °C and nitrogen (at 7psi) as carrier gas. Calorimetric measurements were performed with a Mettler-Toledo star system 821^e in the range of – 100 °C to +200 °C at heating/cooling rate of 10 °C/min in a continuous nitrogen flow (100mL/min).

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Chapter 3: Anionic Polymerization of Lauryl Methacrylate

3.1. Introduction

Anionic polymerization of alkyl (meth)acrylates is the method of choice for the synthesis of well-defined acrylic polymers(1,2). However, living anionic polymerization of alkyl methacrylates is possible only under selected conditions(3). This is due to the side reactions of ester groups with anions(4-6) and the tendency of ester enolate ion-pairs to achieve stabilization through aggregation. These problems cause difficulties in controlling alkyl (meth)acrylate polymerization(7,8). Recently several new strategies have been shown to give improved control on the polymerization of methacrylic esters. These strategies include the use of silyl ketene acetal containing initiators(9), metal-free anions(10-13), phosphrous-ylide mediated metal-free anions(14), transition metal containing initiators(15), aluminum coordinated initiating systems(16-20) and ligand-modified classical anions(21-33).

Despite this the anionic polymerization of higher alkyl (meth)acrylates such as lauryl methacrylate has received relatively less attention. This can be attributed to the low solubility of these monomers at low temperatures and high levels of alcoholic impurities present in the commercial monomer. Controlled anionic polymerization of alkyl (meth)acrylates can be accomplished only at low temperature (≤ -60 °C) in polar solvents like tetrahydrofuran (THF). But at these temperatures higher alkyl methacrylates tend to precipitate from the solution, even in THF. This results in a heterogeneous reaction medium unsuitable for anionic polymerization. Besides, for obtaining these monomers with adequate purity, the higher alcohol impurities in commercial monomer are to be removed completely. This is quite difficult considering the fact that the boiling points of the monomer in question and the corresponding alcohol are quite close to each other. This renders the controlled polymerization of higher alkyl methacrylates, by anionic polymerization, difficult.

Sannigrahi(34) reported the controlled polymerization of LMA by GTP method. The polymers were obtained with good control over molecular weight and reasonably narrow MWD (≥ 1.18). But this method resulted in polymers with broad MWD when targeted for higher molecular weights (> 30,000). Jerome and co-workers(35) used ligated anionic polymerization for the preparation of poly(isooctylacrylate) and its copolymers. This process involves two steps namely the synthesis of poly(*t*-butylacrylate) and its copolymers followed by transalcoholysis with the required alcohol. Recently Mishra and co-workers[36)] have described the anionic polymerization of long-chain alkyl methacrylates in THF in presence of LiCl additive at – 30 °C. The polymerization resulted in good control over molecular weight and narrow MWD ($\leq$ 1.2) but the control was lost if the addition of monomer was slow. In this chapter we describe our results on anionic polymerization of LMA.

3.2. Experimental Methods

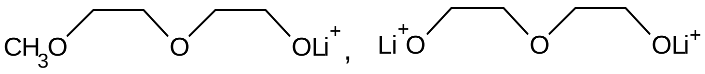
3.2.1. Materials

Sodium metal, potassium metal, triethyleneglycol, 2-methoxy (2-ethoxyethanol), and all solvents – tetrahydrofuran (THF), toluene, methanol, benzene were procured from S. D. Fine Chemicals, Bombay. Lithium chloride (LiCl), lithium perchlorate ($LiClO_4$), 1,1-diphenyl ethylene (DPE), bis(dimethylamino) dimethylsilane (BDMAS), tetrabutyl ammonium flouride (TBAF) (1.0 M solution in THF), calcium hydride (CaH_2), methyl methacrylate (MMA), and lauryl methacrylate (LMA) were procured from Aldrich, USA. Triisobutyl aluminum (TIBAL) and triethyl aluminum (TEA) were procured from Schering AG, Germany. *n*-BuLi and DPHLi were prepared in the laboratory as described in chapter 2.

3.2.2. Purification

Different methods were used for LMA purification. a) LMA was taken into the monomer distillation unit and a 1.0M solution of TEA in toluene was added drop-wise until pale yellow color was observed[37)]. The solution was then distilled under dynamic vacuum. b) Pre-distilled LMA was treated with BDMAS in presence of small amount of TBAF for 1 h at 30 °C and distilled under vacuum using freeze thaw cycle. c) LMA was treated with excess triethyl aluminum (TEA) and this yellow color solution was filtered through a column containing neutral alumina bed (10 cm × 1 cm) under nitrogen atmosphere and the resulted clear monomer was used as such for the polymerization. d) LMA was first fractionated while distilling under vacuum over CaH_2 and the fraction collected at 104 °C at 0.007m.bar pressure was stored under nitrogen blanket at 4 °C. Prior to polymerization it was again distilled over CaH_2.

Lithium salts of triethyleneglycol (G_3Li_2) (fig. 3.1a) and 2-(2-methoxyethoxy) ethanol (G_2Li_1) (fig. 3.1b) were prepared by reacting the corresponding alcohol with *n*-BuLi in THF at –40 °C in the presence of a small amount of DPE, which acts as an indicator. The additives used in the anionic polymerization are shown in fig. 3.1



(G_2Li_1)
(a)

(G_3Li_2)
(b)

Fig. 3.1: Additives used in anionic polymerization of LMA

3.2.3. Polymerization

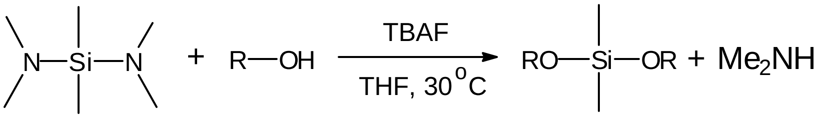
The reaction set-up for anionic polymerization of LMA is shown in fig. 2.5 (Chapter 2). In a polymerization reaction (run 4 in table 3.1), 100 mL of THF was transferred into a 250-mL single neck round bottomed polymerization flask and 0.17 g of $LiClO_4$ was added as solution of THF. Temperature of the solution was brought down to –40 °C using solid CO_2-acetonitrile. DPHLi solution (0.08 M) was added drop-wise until a persistent color characteristic of the initiator was observed. This required ~1.6 mL of the 0.08 M initiator solution to completely quench all the impurities. Subsequently, 2 mL of this DPHLi solution was added. Neat LMA (3 mL) was added to this solution using a stainless steel capillary under N_2 pressure while maintaining a steady stirring. The monomer addition took approximately 5 seconds. The reaction was terminated after 15 min by adding 1 mL of degassed methanol. The solvent was evaporated and the polymer was dissolved in 20 mL of benzene. The benzene solution was filtered and freeze-dried to recover the poly(lauryl methacrylate) (PLMA).

3.3. Results and Discussion

3.3.1. Anionic polymerization of LMA with different purification methods

Methacrylate monomers are, generally, purified by first distillation over calcium hydride and then a second distillation prior to polymerization over a slight excess of trialkyl aluminum37). This procedure removes traces of alcohol impurities in all acrylic monomers. This procedure, when applied to LMA, using tri-isobutyl aluminum (TIBAL), resulted in broad MWD (run 1, table 3.1). The reason for this could be the high boiling point of LMA (104 °C at 0.007 mbar) on account of which it is necessary to apply heat for distillation even under vacuum. Under these conditions a small amount of TIBAL co-distills along with the monomer. The monomer thus purified polymerizes immediately before adding to the polymerization reactor, due to the presence of traces of trialkylaluminum. To overcome this problem, different methods of purification of LMA were attempted.

1. Predistilled LMA was treated with BDMAS in the presence of a small amount of TBAF (1.0 M solution in THF) for 1 h at 30 °C and distilled under vacuum using freeze thaw cycle[34,38)] (scheme 3.1). This method was used to purify MMA in GTP where the products of the reaction, dialkoxydimethyl silane and dimethyl amine, does not interfere with the polymerization.



Scheme 3.1: Reaction of alcohol with BDMAS

2. LMA was treated with excess triethyl aluminum (TEA) and the yellow colored solution was filtered through a column containing neutral alumina beads (10 cm × 1 cm) under nitrogen atmosphere. The pure monomer (colorless) was used for polymerization.
3. LMA was first fractionated (LMA pure fraction was collected at 104 °C at 0.007 mbar) after stirring over CaH_2 for 10 hours and stored under nitrogen blanket. Prior to polymerization it was again purified by flash distillation over CaH_2.

LMA purified using methods described as above was used for anionic polymerization using DPHLi as initiator in THF in the presence of $LiClO_4$ at -40 °C and the results are given in table 3.1. The polydispersity index of the obtained PLMA was used to determine the efficiency of various purification procedures. It is observed that best results are obtained when LMA was purified by distillation over CaH_2 (run 4, table 3.1).

Thus, in all further polymerization reactions fractionated LMA was used after second distillation over CaH_2 prior to polymerization.

Table 3.1: Anionic polymerization of LMA using DPHLi (I) as initiator in the presence of $LiClO_4$ (A): $[A]_0 / [I]_0 = 10$: in THF at $-40\ ^0C$.

Run. No.	Method of Purification	$[I]_0 \times 10^3$ m/L	$[M]_0$ m/L	Yield %	$M_{n, cal} \times 10^{-3}$	$M_{n,SEC} \times 10^{-3}$	MWD	f^c
1	Distilled over TIBAL	1.428	0.097	> 85	17.3	47.0	1.26	0.36
2	Distilled over BDMAS and TBAF	0.737	0.062	>95	21.7	19.6	1.19	1.10
3	Filtered through alumina column after TEA treatment	1.445	0.109	100	20.3	28.0	1.16	0.73
4	Distilled the fractionated LMA over CaH_2	1.600	0.120	100	19.2	19.3	1.07	0.99

[a] $M_{n,\ cal.} = \{[M]_0\ /\ [I]_0\} \times$ Mol. Wt. of monomer [b] Number average molecular weights were determined using PMMA calibration [c] f = Initiator efficiency = $M_{n,\ cal.}\ /\ M_{n,\ SEC}$

3.3.2. Anionic polymerization of LMA in presence of different additives

Anionic polymerization of LMA in THF with DPHLi as initiator at –40 °C in the absence of any additive results in broad and multi-modal MWD (run 1, table 3.2). The number average molecular weight of PLMA in the absence of additive is very high and the polymer is contaminated with oligomers as seen from the SEC elugram (fig. 3.1) indicating the presence of termination reaction. Hence, the polymerization was studied in presence of different additives such as lithium chloride, lithium perchlorate and the lithium salts of 2-(2-methoxyethoxy) ethanol (G_2Li_1) and triethylene glycol (G_3Li_2) and the results are given in table 3.2. In all the reactions the ratio of additive to initiator was kept constant ($[A]_0 / [I]_0 = 10$).

The polymerization of LMA in the presence of G_2Li_1 gave broad MWD (1.40) (run 2). Jerome and coworkers[31)] reported that G_2Li_1 gives excellent control over the polymerization of both acrylates and methacrylates at temperatures < -20 °C in THF as well as toluene. Müller and coworkers[32)] showed that the rate of MMA polymerization in the presence of G_2Li_1 is extremely high even in toluene ($k_p > 10^4$ $l.mol^{-1}$ sec^{-1} and half life

< 1 s). Under these conditions, to achieve controlled polymerization, mixing of the monomer and the initiator has to be faster than the half-life of the polymerization. Thus, it is necessary to carry out the reaction at low temperature ($\leq$ -78 °C). In the present study, in a batch reactor and at –40 °C, presumably, these conditions are not met resulting in broad MWD.

Table 3.2: Anionic polymerization of LMA using DPHLi as initiator in the presence of different additives ($[A]_0 / [I]_0 = 10$) at -40 °C in THF

Run. No.	Additive $[A]_0$	$[I]_0 \times 10^{-3}$ m/L	$[M]_0$ m/L	Yield %	$M_{n\,cal} \times 10^{-3}$	$M_{n,SEC}^{a} \times 10^{-3}$	M_n / M_w	¦^{c}
1	-	1.43	0.114	>95	20.3	57.3	2.61^{d}	0.35
2	G_2Li_1	1.82	0.067	>95	9.30	7.67	1.40	1.21
3	G_3Li_2	2.00	0.074	100	9.30	7.20	1.12	1.29
4	LiCl	1.82	0.033	>95	4.65	4.24	1.11	1.09
5	$LiClO_4$	2.04	0.073	100	18.2	18.6	1.07	0.98
6	$LiClO_4$	1.70	0.130	100	19.2	19.3	1.07	0.99
7	$LiClO_4$	0.13	0.850	100	38.3	34.6	1.06	1.10
8	$LiClO_4$	0.60	0.094	>95	61.2	70.3	1.15	0.87
9	$LiClO_4$	0.13	0.340	>97	95.8	111.6	1.18	0.85

[a] $M_{n,\,cal.} = \{[M]_0 / [I]_0\} \times$ Mol. Wt. of monomer [b] Number average molecular weights were determined using PMMA calibration [c] ¦ = Initiator efficiency = $M_{n,\,cal.} / M_{n,\,SEC}$ [d] Multi-modal distribution

When G_3Li_2 was used as additive for the anionic polymerization of LMA (run 3), it was possible to obtain better control over molecular weight and narrow MWD (1.12). Baskaran[33)] reported the polymerization of MMA in the presence of G_3Li_2 in THF using DPHLi as initiator. It was demonstrated that the polymerization of MMA in presence of G_3Li_2, resulted in polymers with good control over molecular weight and MWD, at temperatures as high as –20 °C. It was postulated that the presence of a higher numbers of oxygen and lithium atoms leads to a better coordination with enolate ion pairs forming mixed aggregates which have faster equilibrium dynamics. Even in this case it is important to have fast and uniform mixing of monomer into the reaction mixture without spilling the contents on to the reactor surface. When the rate of mixing is not uniform or slow the polymerization in presence of G_3Li_2 resulted in broad MWD.

While our work was in progress, Mishra and coworkers reported[35)] the anionic polymerization of LMA in presence of LiCl at –30 °C. They found that the slow and drop-wise addition of monomer (10 mL/min) leads to broad MWD (≥ 3.4). Polymers with narrow MWD (≤ 1.2) were obtained, when monomer addition was fast (10-20 mL/s). Besides, they reported that the polymerization is not living for a long time though the polymerization resulted in narrow MWD. They attributed this to the fast polymerization rate and the high heats of polymerization, which causes the side reactions to increase

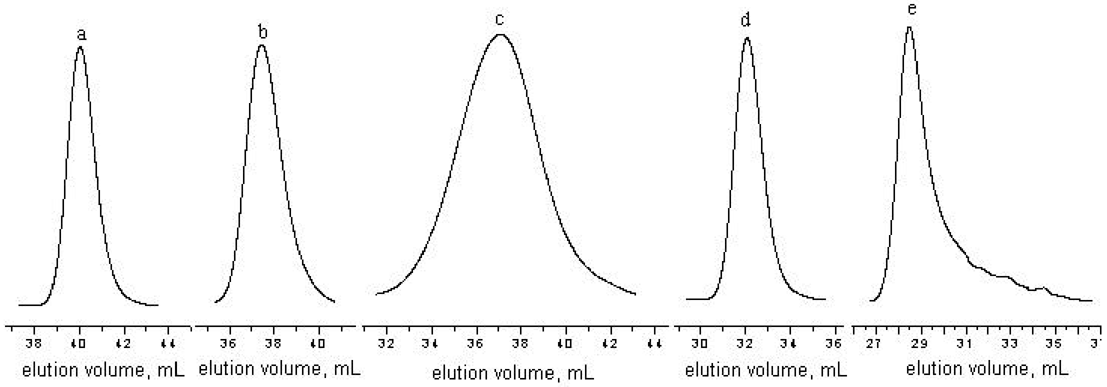


Fig. 3.2: GPC traces of PLMA prepared by anionic polymerization in THF at -40 °C in the presence of - a) LiCl, b) G_3Li_2, c) G_2Li_1, d) $LiClO_4$ and e) in the absence of additive

It is pertinent to mention that the purification method used by Mishra and coworkers was to pass the monomer through a column of activated basic alumina. The commercial monomer normally contains lauryl alcohol as an impurity, which is difficult to completely remove by this method. Since the rate of these impurities quenching the growing polymer chain is slow compared to the rate of polymerization, the reaction yields narrow MWD polymers (≤ 1.18), when addition rates are fast. But when rate of addition is slow, chain termination becomes more prominent. Additionally, mixing becomes difficult. This explains, to an extent, the failure of monomer resumption experiment carried out by Mishra and coworkers. Besides, it is reported39) that upon increasing the temperature from -78 °C to -40 °C, control over molecular weight and MWD was lost in the polymerization of MMA in THF in the presence of LiCl.

In the present work, it was found that the rate of monomer addition does not play a major role in controlling the polymerization. In our study, the monomer was added using a stainless steel capillary under a positive pressure of nitrogen at an approximate rate of 35 mL/min (which is near the slow rate of addition in the work of Mishra and coworkers).

The anionic polymerization of LMA in presence of $LiClO_4$ at –40 °C produces PLMA with excellent control of molecular weight and narrow MWD (≤1.10) (Runs 5 and 6). All further reactions were, thus, carried out in the presence of $LiClO_4$. A very good control was obtained over a wide range of molecular weights with narrow MWD (≤ 1.18). As the initiator concentration was reduced (or monomer concentration was increased) to prepare high molecular weight polymers, relative reduction in initiator efficiency and slight broadening of MWD were observed. This could be due to the traces of slow reacting impurities still present in the monomer or entering in to the system during monomer addition. Mishra and coworkers used higher monomer concentration (0.34 mol/L) in their reactions and the MWD values obtained were also in the range of 1.18. The living nature of the chain ends was confirmed by preparing block copolymers by sequential addition of LMA and MMA with no homopolymer contamination. These results will be discussed in chapter 5.

3.4. Conclusions

Anionic Polymerization of LMA with DPHLi in THF at –40 °C results in multi-modal and broad MWD with poor initiator efficiency. In presence of additives the polymerization was better controlled. The method of purification of LMA is critical in obtaining well-defined polymers. Best results are obtained when the monomer was fractionated and then distilled over CaH_2 prior to polymerization and also when it was treated with tri-ethyl aluminum and then passed through neutral alumina column.

The polymerization of LMA in presence of lithium-2-(2-methoxyethoxy) ethoxide (G_2Li_1) gave polymer with broad and unimodal MWD (1.40). However, use of a polydentate dilithium alkoxyalkoxide (G_3Li_2) gave very good control over polymerization resulting in polymers with narrow MWD (1.12). In this case it is necessary to maintain fast and uniform mixing in the batch polymerization and the monomer addition to the reaction mixture has to be faster than the half-life of the polymerization. Good results were also obtained when the polymerization was carried out in presence of both LiCl and $LiClO_4$. These additives resulted in polymers with narrow MWD (≤ 1.10). From these results it is concluded that PLMA with narrow MWD and desired molecular weight can be prepared by anionic polymerization in THF at –40 °C in the presence of additives like LiCl, $LiClO_4$ and G_3Li_2.

3.5. References

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Chapter 4: Atom Transfer Radical Polymerization of Lauryl Methacrylate

4.1. Introduction

Living anionic polymerization is so far the best method for preparing polymers with well-defined structures. The merits and demerits of anionic polymerization and the advantages of controlled radical polymerization over anionic polymerization were discussed in detail in chapter 1. The advantages of radical polymerization include the possibility of performing the reactions in solution, emulsion, suspension as well as bulk. Besides this can be used for a wide range of monomers and monomers with functional groups. The quest for controlled/living radical polymerization, conceptualized by Otsu and coworkers1) and Fischer2), reached its zenith in the early nineties. New techniques like stable free radical polymerization (SFRP)3-5), atom transfer radical polymerization (ATRP)6,7) and reversible addition fragmentation chain transfer polymerization (RAFT)8-11) entered the armory of the synthetic polymer chemists. Amongst these ATRP has been extensively studied for various monomers with different transition metal catalysts and ligands12,13).

In-spite of these developments, the controlled polymerization of higher alkyl methacrylates, such as lauryl methacrylate, has received relatively less attention as compared to lower alkyl methacrylates. Haddleton and coworkers14) reported the ATRP of higher alkyl methacryltes. They polymerized *n*-butyl, *n*-hexyl and *n*-octyl methacrylates in xylene solution with CuBr as catalyst, N-(n-butyl)-2-pyridylmethanimine as ligand and ethyl-2-bromoisobutyrate as initiator. The obtained polymers were characterized with relatively narrow MWD (≤ 1.27).

More recently Beers and Matyjaszewski15) reported the polymerization of lauryl acrylate (LA) using ATRP. The polymerization was carried out in toluene with CuBr as catalyst, 4,4'-di(5-nonyl)-2,2'-bipyridine as ligand and methyl-2-bromopropionate as initiator. ATRP conditions that were suitable for *n*-butyl and *t*-butyl acrylate were found to be unsuitable for LMA. Using 4,4'-di(5-nonyl)-2,2'-bipyridine as ligand enabled homogeneous polymerization in toluene with no precipitation of polymer. However, even under these conditions, polydispersities were ~1.4 at 90% conversion. This was attributed to the competition between conventional and controlled radical polymerizations and the consequent reduction in the generation of Cu(II) deactivator. Addition of Cu(II)Br_2 (4 mol % excess to CuBr) to the reaction, circumvented the problem and the polydispersity narrowed to 1.25. This work clearly illustrates the need to choose suitable conditions for ATRP based on the nature of propagating radical. We, therefore, choose to explore the ATRP of LMA with a view to define optimum conditions for controlled polymerization.

4.2. Experimental Methods

4.2.1. Materials

LMA, calcium hydride (CaH_2), Copper bromide (CuBr), 2,2'-dipyridine (DP), 4,4'-dimethyl-2,2'-dipyridine (DMDP), pyridine-2-carboxaldehyde, ethyl-2-bromoisobutyrate (EBI) and N,N',N',N",N"-pentamethyl diethylenetriamine (PDT) were procured from Aldrich, USA. Sodium and potassium metals sodium sulfate, activated alumina (neutral) and all solvents like toluene, THF, methanol, ethanol, diethyl ether were procured from S. D. Fine Chemicals, Bombay, India.

4.2.2. Purification

LMA was purified by fractional distillation, after stirring over CaH_2 for 12 hours at room temperature. CuBr was purified as reported earlier16), by stirring in glacial acetic acid under nitrogen followed by filtration. It was then washed with absolute ethanol and dried under vacuum. DP and DMDP were used as received. EBI and PDT were distilled by freeze-thaw cycles under vacuum after stirring over CaH_2 for about 4 hours. Fractionated toluene was refluxed over potassium metal and stored over Na-K alloy in a vacuum line and prior to polymerization required amount was condensed into an ampoule under reduced pressure and transferred under nitrogen atmosphere into the polymerization reactor.

4.2.3. Synthesis and purification of N- (n-propyl)-2-pyridylmethanimine (PPMI)14):

Pyridine-2-carboxaldehyde, 14.5 mL (0.152 mol), was taken into the reaction flask containing 20 mL diethyl ether. 15 mL of n-propyl amine (0.183 mol) was added drop-wise, while stirring, to this solution at 0 °C. After complete addition, 3 g of anhydrous sodium sulfate was added and the slurry was stirred at 25 °C for 2 hours. The solution was filtered after 2 hours, solvent was removed and the product was purified by distillation under reduced pressure (31-35 °C at ~0.1 mmHg). Isolated Yield: 85%. ^{1}H NMR ($CDCl_3$) (Fig. 4.1): δ 0.85 (t, 3H), 1.62 (m, 2H), 3.53 (t, 2H), 7.18 (m, 1H), 7.61 (m, 1H), 7.86 (m, 1H), 8.27 (s, 1H), 8.54 (m, 1H). Analytical analysis: Calculated for $C_9H_{12}N_2$: C - 72.97; H – 8.10; N – 18.92. Found: C – 72.31; H – 8.60; N – 19.33.

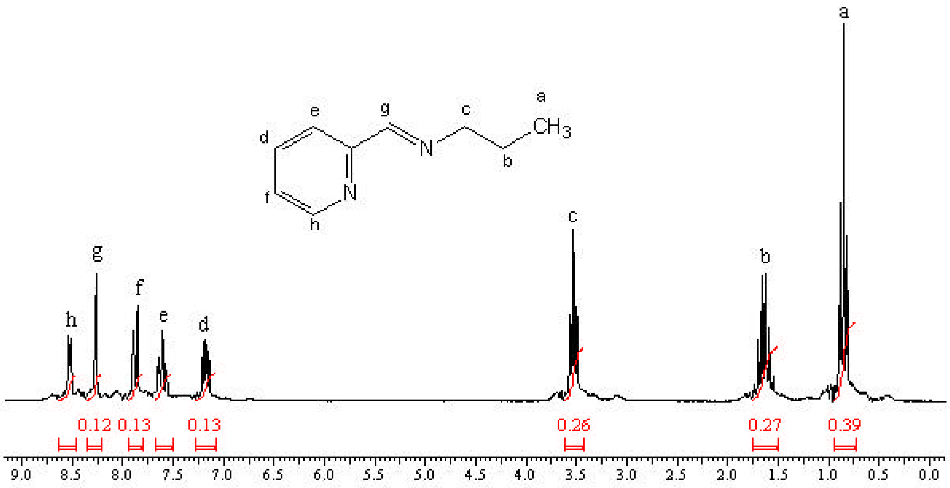


Fig. 4.1: ^{1}H NMR spectrum of PPMI in $CDCl_3$

4.2.4. Polymerization

The reaction set-up for the ATRP of LMA is similar to the one shown in fig. 2.5 (Chapter 2). In a typical polymerization reaction (run 1 in table 4.1), 0.109 g, (0.76 mmol) of CuBr, 0.324 g (2.97 mmol) of DP, 5 mL (17.05 mmol) of LMA and 20 mL of toluene were added in that sequence. The reaction setup was cooled using a liquid nitrogen bath and when the contents were half frozen, vacuum was applied (0.007mbar). After keeping the solidified reaction mixture under dynamic vacuum for 10 to 15 minutes, the liquid nitrogen bath was removed and the contents were thawed and filled again with nitrogen gas. This procedure is repeated two more times to remove the traces of oxygen. The contents were found to be heterogeneous at lower temperature. Temperature of the reaction mixture was then increased to 95 °C using an oil bath. It was observed that the solution became homogeneous at this temperature. While maintaining the temperature at 95 °C, 0.1 mL (0.68 mmol) of EBI was added with continuous stirring.

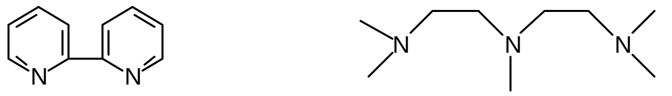
The polymerization was quenched, after stirring for 5 hours, by freezing the reaction mixture in liquid nitrogen bath. The mixture was diluted with THF and passed through activated alumina column to remove the catalyst. Polymers were precipitated into water-methanol (20/80 v/v) mixture. The polymer was dissolved in diethylether and stirred over anhydrous sodium sulfate. The solution was filtered, solvent removed and the polymer dried under dynamic vacuum for 8 hours. Yield was determined by gravimetry.

4.2.5. Kinetics of ATRP of LMA

The reaction setup is similar to the one used for batch reactions. In a kinetic experiment, 0.1g (0.70 mmol) of CuBr was taken in the reaction flask. To this, 5 mL (17.05 mmol) of LMA, 2 mL (11.96 mmol) of diphenyl methane (as an internal standard for GC), 0.2 mL (1.35 mmol) of PPMI and 20 mL of toluene were added in that sequence. A small portion of this solution was withdrawn using a syringe for GC analysis to determine M_0. The solution was deoxygenated by 3 cycles of vacuum and nitrogen. Temperature of the solution was increased to 95°C. Upon attaining the required temperature, 0.1 mL (0.68 mmol) of EBI was added with continuous stirring. After one hour a small portion (~ 2 mL) was withdrawn from the reaction mixture using a syringe and added into precooled THF. This solution was passed through neutral alumina column (1” × 10”) to remove the catalyst complex. The monomer conversion was determined using GC by calculating the disappearance of monomer with respect to internal standard (The details of GC analysis were given in chapter 2) and M_n was determined using GPC. In a similar way samples were withdrawn in 1-hour intervals and the conversion and molecular weight of each sample were determined using GC and GPC.

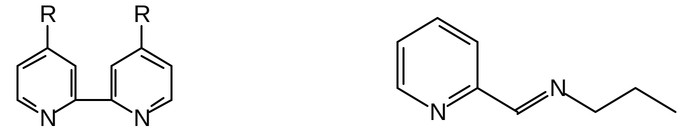
4.3. Results and Discussion

Atom transfer radical polymerization of LMA was studied in toluene at 95 °C using EBI as initiator and CuBr as catalyst in conjunction with different ligands (fig 4.2). Kinetic experiments of ATRP of LMA were carried out using PDT and PPMI ligands.



2,2'-bipyridine (DP)

N,N',N',N",N"-Pentamethyldiethylenetriamine (PDT)



4,4'-dimethyl-2,2'-bipyridine (DMDP)

N-(n-propyl)-2pyridylmethanmine (PPMI)

Fig. 4.2: Ligands used in ATRP of LMA

4.3.1. ATRP of LMA in presence of DP and DMDP ligands

The polymerization systems with the catalyst complexes of CuBr formed with DP and DMDP ligands were heterogeneous. It is known that the control in polymerization can be obtained only when the equilibrium between the activation and deactivation steps is maintained so that the rate of deactivation is higher than the rate of propagation[17]. But when the reaction mixture is heterogeneous, the intermolecular catalyst complexation becomes slow thus disturbing the activation and deactivation equilibrium. As a result the rate of reversible deactivation decreases compared to the rate of rate of propagation. This increases the amount of irreversible termination and results in polymers with broad MWD and poor initiator efficiency. MMA polymerization in ethyl acetate with EBI initiator in presence of these catalyst ligand complexes gave polymers with broad MWD[18]. A similar result is observed here using these ligand complexes for the polymerization of LMA in toluene, where the polarity of the system is less than that of the above system. The polymers (PLMA) obtained in the presence of these ligands exhibited broad MWD (≤ 1.33), (fig. 4.3) and apparently low initiator efficiency (based on PMMA standards).

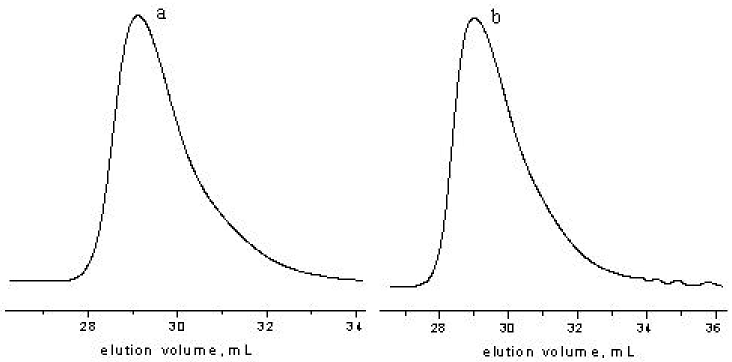


Fig. 4.3: GPC traces of PLMA prepared by ATRP in presence of DP - (a) and DMDP - (b)

Table 4.1: ATRP of LMA with CuBr catalyst, EBI initiator and toluene solvent at 95°C

Run. No.	Ligand	$[M]_0$ moles/L	$[C]_0:[I]_0:[L]_0$	Yield a) %	M_n(cal) b) $\times 10^{-3}$	M_n(SEC) $\times 10^{-3}$	M_w / M_n	¦ d)
1	DP	0.68	1:1:3	43	2.8	11.9	1.31	0.23
2	DMDP	0.68	1:1:3	44	2.8	13.6	1.33	0.20
3	PDT	1.14	1:1:3	93	6.0	15.6	1.45 f)	0.38
4	PDT	1.14	1:1:1	65	4.2	7.8	1.29	0.54
5	PDT	1.14	1:1:0.5	33	2.1	9.0	1.20	0.23

a) Yield was determined gravimetrically b) All the reactions were carried out for 5 hours. c) $M_{n,\ cal.} = [\{[M]_0 / [I]_0\} \times$ Mol. Wt. of monomer $\times$ yield/100] d) ¦ = Initiator efficiency = $M_{n,cal.} / M_{n,SEC}$ e) PMMA standards were used for calibration f) bi-modal molecular weight distribution.

4.3.2. ATRP of LMA in the presence of PDT

Matyjaszewski and coworkers[19,20] have reported the use of PDT/CuBr complex in ATRP for several acrylates. The system was homogeneous and the polymerization resulted in polymers with narrow MWD and good initiator efficiency. When this catalyst/ligand system was used for the polymerization of LMA, it was observed that the polymerization mixture was homogeneous even at room temperature. However, after commencing the polymerization at 95 °C, it was noticed that the Cu (II) species slowly precipitated out during the polymerization (run 3, table 4.1). This results in decreasing the rate of reversible deactivation and increasing the irreversible termination. The PLMA obtained had broad and multi-modal MWD (fig. 4.4). This result, coupled with the higher yield of polymer, indicates that the rate of propagation is very high compared to the rate of equilibrium between active and dormant species.

Few experiments were, then, carried out at low concentration of ligand with respect to CuBr. It was observed that the solubility of the catalyst complex was low at lower concentration of ligand. However, homogeneous mixture was observed at 95 °C before adding the initiator. But after adding the initiator, slow precipitation of Cu (II) species was observed as the reaction progressed. The resulting polymer had improved initiator efficiency and relatively narrow MWD (run 4, table 4.1, fig. 4.4). These results along with the reduced yield shows that the rate of polymerization decreased profoundly. Further decreasing the ligand ratio resulted in insufficient complexation leading to partial dissolution and thus a heterogeneous system. The obtained polymer had narrow MWD, poor initiator efficiency and poor yield (run 5, table 4.1, fig. 4.4). These results indicate that it is necessary to have at least an equimolar amount of ligand with respect to CuBr or initiator for a successful polymerization.

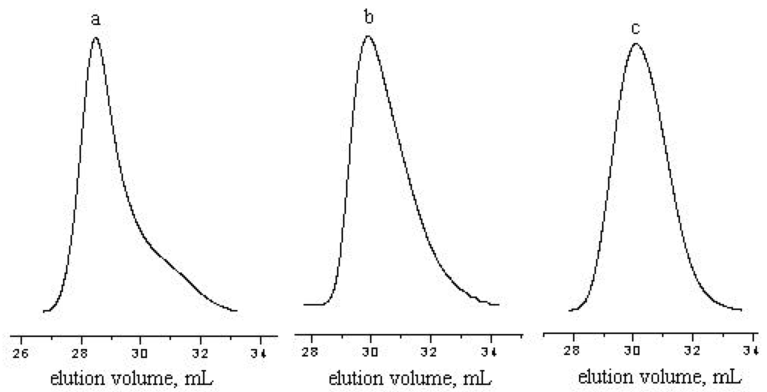


Fig. 4.4: GPC traces of PLMA prepared by ATRP in presence of CuBr/PDT complex $[EBI]_0 : [CuBr]_0 : [PDT]_0 = 1:1:3$ - (a), 1:1:1 - (b) and 1:1:0.5 - (c)

4.3.3. Kinetic studies of ATRP of LMA in presence of PDT

Kinetic study of ATRP of LMA was carried out in the presence of PDT ligand and the results are given in table 4.2. The first order time-conversion plot (fig. 4.5 a) is not linear indicating the presence of termination reactions and using the non-linear curve fit the rate constants, k_{app} and k_t, were found to be 0.01266 min^{-1} and 0.00511 min^{-1} respectively. A plot of $M_{n,(SEC)}$ *vs* conversion (fig. 4.5 b) showed an upward curvature at higher conversion indicating the presence of transfer reactions. It is important to note that the molecular weight was determined using PMMA calibration. Due to the higher hydrodynamic volume of PLMA compared to PMMA, the obtained values for molecular weights are overestimated and, hence, are only treated as apparent molecular weight. Similarly the initiator efficiency values were based on these apparent molecular weights and hence they are only used for relative comparison.

Table 4.2: Kinetics of LMA polymerization by ATRP in the presence of CuBr/PDT complex at 95 °C in toluene

Run. No.	Time min.	Conversion[a] %	$M_{n,\,cal}$[b] $\times 10^{-3}$	$M_{n,\,SEC}$ $\times 10^{-3}$	MWD
1	60	50	3.2	5.2	1.15
2	120	68	4.4	5.9	1.17
3	180	76	4.9	6.0	1.18
4	240	82	5.3	6.2	1.18
5	300	86	5.5	6.3	1.18

a)Conversion determined by GC using diphenyl methane as internal standard b)$M_{n,\,cal.}$ = $[\{[M]_0\ /\ [I]_0\} \times$ Mol. Wt. of monomer $\times$ conversion/100] e)PMMA standards were used for calibration.

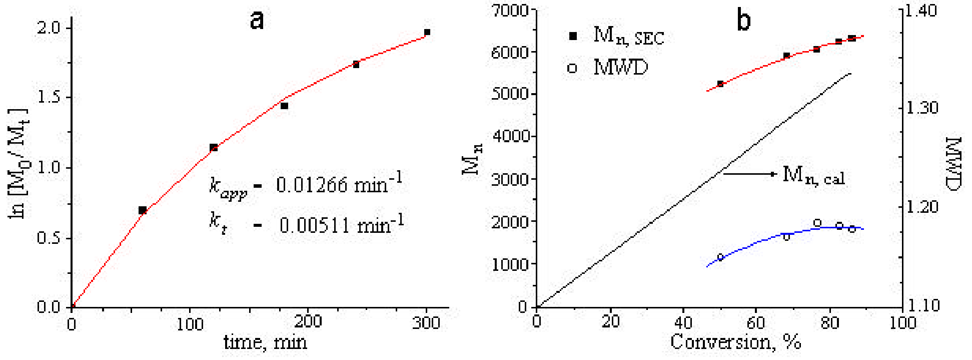


Fig. 4.5: Kinetics of ATRP of LMA at 95 °C; $[CuBr]_0 = [PDT]_0 = [EBI]_0 = 0.67$ mmol, $[DPM]_0 = 8.9$ mmol, $[LMA]_0 = 17.05$ mmol, toluene - 10 mL. - a) First order time-conversion plot - b) Plot of molecular weight and MWD against conversion

The GPC elugram (fig. 4.6) shows the presence of oligomers and the area of these oligomer peaks did not increase with conversion with respect to the polymer peak. This indicates that several growing chains are terminated at the initial stages of the polymerization. The decrease in the active center concentration resulted in high molecular weight polymer at the beginning of the polymerization. Although the MWD of the polymer was narrow through out the polymerization, a slight increase in MWD was noticed with conversion supporting the presence of transfer reaction.

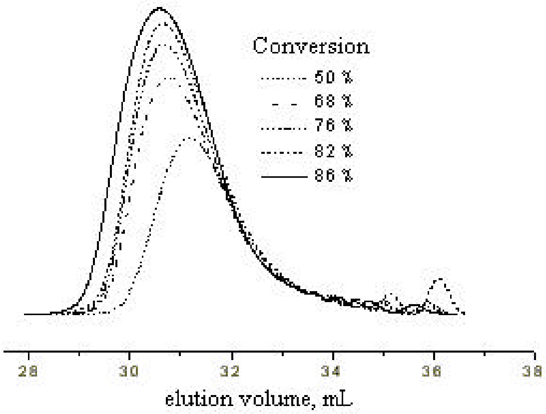


Fig. 4.6: GPC traces of PLMA prepared by ATRP at different conversions. $[LMA]_0 = 17.05$ mmol, toluene - 10 mL, $[CuBr]_0 = [PDT]_0 = [EBI]_0 = 0.67$ mmol

4.3.4. ATRP of LMA in presence of PPMI

Haddleton and coworkers[14)] have reported the use of substituted pyridinemethanimines as ligands in the Cu catalyzed ATRP of MMA. The obtained polymers had relatively narrow MWD (≤ 1.28) with good initiator efficiency. We have examined the efficiency of CuBr/PPMI catalyst system in the ATRP of LMA with EBI initiator and the results are given in table 4.3.

It was observed that this complex results in a heterogeneous mixture at room temperature. But the reaction mixture became homogeneous at the reaction temperature (95 °C). No precipitate was observed with conversion at that temperature, throughout the reaction. The polymers obtained had narrow MWD (≤ 1.24) and reasonably good initiator efficiency (table 4.3). It is also observed that with increasing dilution, yield is reduced suggesting that the rate of propagation is reduced and the obtained polymers showed much narrower MWD (runs 2-5, table 4.3, fig. 4.7). Changing the ligand concentration with respect to the initiator from 1:3 to 1:1 (run 6, table 4.3) resulted in improved yield with marginal change in MWD.

Table 4.3: ATRP of LMA with CuBr/PPMI catalyst system, EBI initiator in toluene at 95°C

Run. No.	$[M]_0$ moles/L	$[C]_0$:$[I]_0$:$[L]_0$	Yield^a %	M_n(cal)^b $\times 10^{-3}$	M_n(SEC) $\times 10^{-3}$	MWD	¦^{d}
1	0.68	1:1:3	70	4.5	10.8	1.19	0.41
2	1.14	1:1:3	69	4.4	9.4	1.29	0.47
3	0.68	1:1:3	65	4.2	8.3	1.24	0.51
4	0.49	1:1:3	58	3.7	8.2	1.18	0.45
5	0.26	1:1:3	22	1.4	3.7	1.16	0.38
6	1.14	1:1:1	82	5.3	9.7	1.24	0.55

$^{a)}$Yield was determined by gravimetry $^{b)}$ PMMA standards were used for calibration $^{c)}$$M_{n,\ cal.} = [\{[M]_0 / [I]_0\} \times$ Mol. Wt. of monomer $\times$ yield/100$]$ $^{d)}$¦ = Initiator efficiency = $M_{n,\ cal.} / M_{n,\ SEC}$.

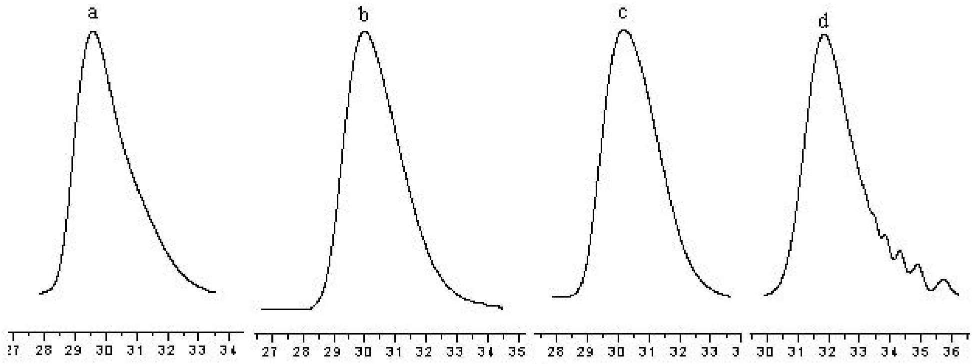


Fig. 4.7: GPC traces of PLMA prepared by ATRP at 95 °C in toluene. $[CuBr]_0 = [EBI]_0 = 0.67$ mmol, $[PPMI]_0 = 2.0$ mmol, $[LMA]_0 = 1.14$ mmol- (a), 0.68 mmol- (b), 0.49 mmol- (c) and 0.26 mmol- (d)

4.3.5. Kinetics of ATRP of LMA in presence of PPMI

Kinetics of ATRP of LMA was carried out using EBI as initiator in the presence of CuBr/PPMI catalyst complex and the results are given in table 4.4. The polymerization in toluene proceeds in a controlled manner as seen by the linear first-order rate plot passing through origin (fig. 4.8 a) and from this plot the apparent rate constant, k_{app}, was found to be 0.00888 min^{-1}. The molecular weight increases linearly with conversion.

Molecular weight distribution remains narrow (≤ 1.21) through out the reaction. But the presence of transfer reactions in the later stages of polymerization is seen from the upward curvature of the M_n *vs* conversion and the increasing MWD with conversion (fig 4.8 b). The GPC traces of these polymers were shown in fig. 4.9.

Table 4.4: Kinetics of LMA polymerization by ATRP in the presence of CuBr/PPMI complex with EBI as initiator in toluene at 95 °C

Run. No.	Time, min.	Conversion %	$M_{n,\,cal} \times 10^{-3}$	$M_{n,\,SEC} \times 10^{-3}$	MWD
1	60	36	2.4	5.2	1.25
2	120	66	4.2	6.1	1.24
3	180	78	5.0	6.5	1.26
4	240	87	5.6	6.4	1.27
5	300	93	6.0	6.4	1.28
6	360	96	6.2	6.8	1.27

[a] Conversion determined by GC using diphenyl methane as internal standard [b] $M_{n,\ cal.} = [\{[M]_0\ /\ [I]_0\} \times$ Mol. Wt. of monomer $\times$ conversion/100] [e] PMMA standards were used for calibration.

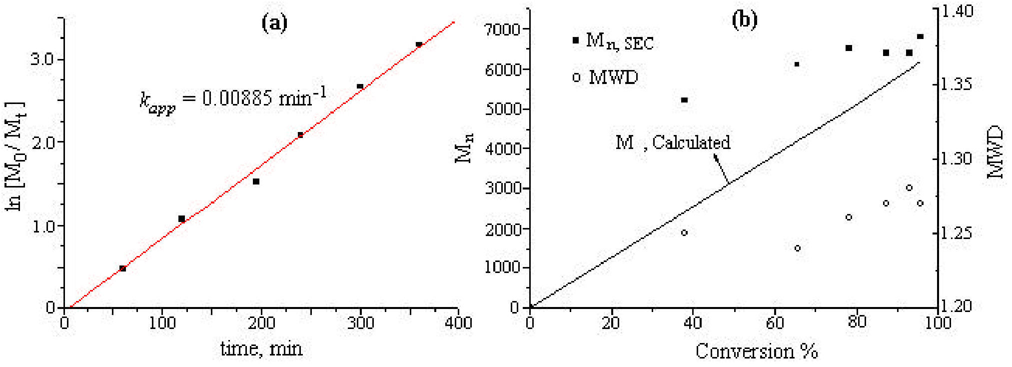


Fig. 4.8: Kinetics of ATRP of LMA at 95 °C. $[LMA]_0$= 17.05 mmol, $[DPM]_0$= 8.9 mmol, toluene - 20 mL, $[CuBr]_0$= $[EBI]_0$= 0.67 mmol, $[PPMI]_0$= 1.36 mmol.(a) First order time-conversion plot (b) Plot of M_n and MWD against conversion

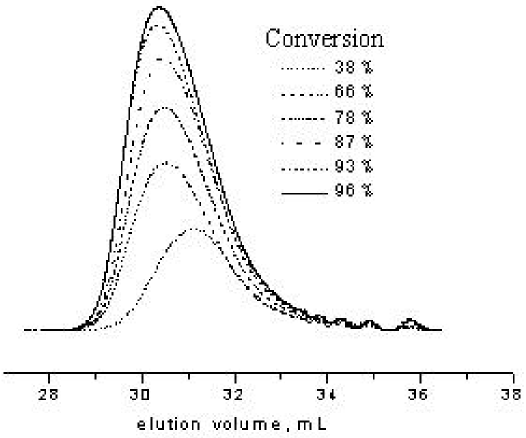


Fig. 4.9: GPC traces of PLMA prepared by ATRP at different conversions. $[LMA]_0 = 17.05$ mmol, toluene= 20mL, $[CuBr]_0 = [EBI]_0 = 0.67$ mmol, $[PPMI]_0 = 1.36$ mmol

4.3.6. Kinetics of ATRP of MMA in presence of PPMI

For purpose of comparison kinetics of ATRP of MMA was carried out under identical conditions. Haddleton and coworkers$^{14)}$ have reported the polymerization of MMA in xylene at 90 °C. They reported an induction period of 20 minutes in this reaction and attributed it to the presence of residual oxygen. We performed the reaction at 95 °C in toluene. The polymerization of MMA proceeds in a controlled manner as evidenced by the first order time conversion plot (fig. 4.10). An induction period of 7.5 minutes was

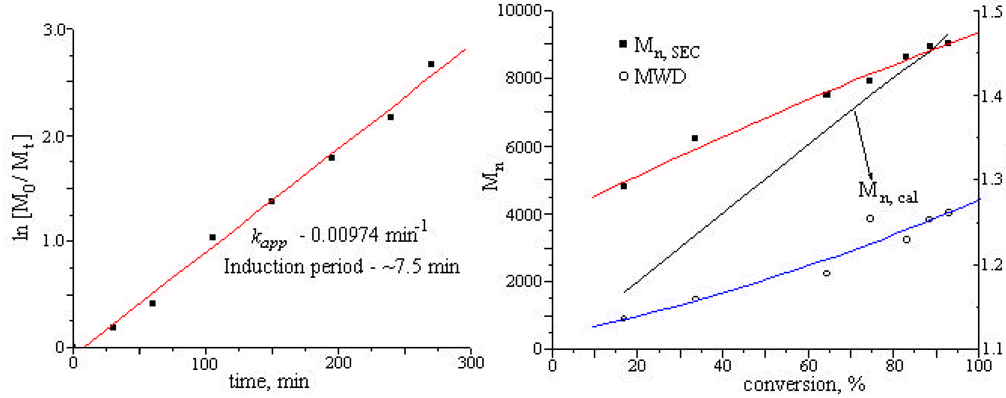


Fig. 4.10: Kinetics of ATRP of MMA in toluene at 95°C $[CuBr]_0:[EBI]_0:[PPMI]_0:[MMA]_0:[Toluene] = 1:1:2:100:200$ a) First order time conversion plot - b) Plot of M_n and MWD *Vs* conversion

observed and the rate constant for the polymerization was calculated as 0.00974 min^{-1}. The reported14) value of rate constant in toluene is 0.00731min^{-1}.

These differences in induction period and rate constants could be due to the increased reaction temperature or differing amounts of residual oxygen between experiments. The polymers had higher molecular weights than the calculated values and the difference was prominent at the beginning of the polymerization. This is in agreement with the results obtained by Haddleton and coworkers. The MWD of the obtained polymers were narrow but slight broadening was observed with conversion indicating the presence of transfer reactions. This is in contrast to the reported data wherein the MWD narrows down with conversion. These results indicate that the reaction temperature has an important role in determining the kinetics polymerization. Even a slight increase in the reaction temperature affects the rate of polymerization and increases the unwanted side reactions.

4.4. Conclusions

Controlled polymerization of LMA has been achieved using ATRP. The obtained polymers were characterized by moderately narrow molecular weight distribution (< 1.3). Among the ligands used, PPMI gave the best results and the optimum concentration of ligand with respect to catalyst and initiator was 1:3 and the dilution required was 1:4 (v/v) monomer/solvent. The kinetic experiment shows a linear first order time-conversion plot. The rate of polymerization of LMA was marginally lower than that of MMA. When PDT was used as ligand better results were obtained at low ligand concentration and the optimum value was found to be 1:1 with respect to catalyst and initiator. In this case the kinetics of ATRP of LMA clearly indicates the presence of both transfer and termination reactions.

4.5. References

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Chapter 5: Synthesis of acrylic block copolymers containing lauryl methacrylate segments

5.1. Introduction

Block copolymers are a combination of two or more macromolecules joined covalently either at one or both ends. When these segments are incompatible micro-phase separation takes place at the polymer interface forming domains and giving rise to useful properties in bulk and in solution. Block copolymers have widespread applications as compatibilizers, dispersing agents, and thermoplastic elastomers (TPEs) etc.[1-5]. Anionic polymerization, due to its transfer and termination free nature, has proven to be the best method for preparing block copolymers with controllable chain length of the blocks and narrow MWD[5-8]. In general block copolymers are made by sequential addition of monomers. In order to prepare pure block copolymers without homopolymer impurity it is essential to prevent any chain transfer and termination of the living carbanion chain ends. Besides this the crossover reaction from the living polymer chain end to the second monomer should be fast. This depends on the pK_a values of the conjugate acids of the monomers. The monomer addition sequence is determined by this factor[9].

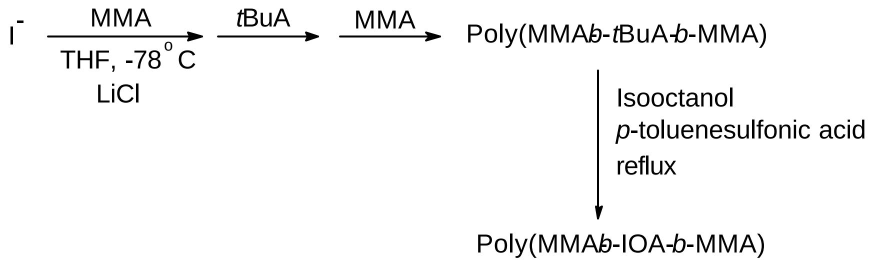
Anionic polymerization techniques have been used for the preparation of styrene-*b*-butadiene-*b*-styrene (SBS) tri-block copolymers. They find applications mainly as TPEs. These copolymers are characterized with poor oxidation resistance, which is due to the center diene block, poor solvent resistance and low service temperature (60-70 °C). This has led to the search for improved materials useful as TPEs. With the successful development of ligated anionic polymerization of (meth)acrylate monomers it is possible to make fully acrylic block copolymers. This can be achieved merely by changing the alkyl substituent of the ester group. Thus, tri-block copolymers containing inner poly(laurylmethacrylate) (PLMA) soft segments (Tg = ~ -65 °C)[10] and outer poly(methyl methacrylate) (PMMA) hard segments (T_g = ~ 110 °C) can be prepared. Such polymers could show improved properties as new class of TPEs. The vast difference between the T_g values of these blocks coupled with the immiscibility of PMMA and PLMA could lead to new solid-state morphologies.

Sogah and coworkers[11] have reported the synthesis of PMMA, PLMA di-block copolymers by sequential addition of monomers using group transfer polymerization. The obtained polymers had molecular weight in the range of 6500 with narrow MWD ($\leq$ 1.14). Later, Sannigrahi and co workers[12)] reported the preparation of di-block copolymers of MMA and LMA in the molecular weight range of 40,000 with narrow MWD ($\leq$ 1.15) using GTP. Although the method provides controlled polymerization of alkyl (meth)acrylates at ambient temperature, molecular weight control is lost when higher molecular weights ($M_n > 50,000$) are targeted.

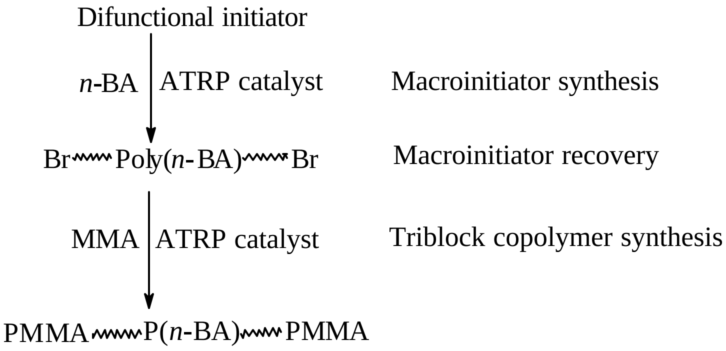
Anderson and co workers[13)] attempted the synthesis of block copolymer of MMA and LMA by anionic polymerization. The polymers were prepared in THF using 1,1-diphenylhexyllithium (DPHLi) at –78 °C by sequential addition of monomers. The obtained polymers had shown broad MWD (1.32 for PMMA, 1.72 for intermediate PMMA-*b*-PLMA and 3.56 for the final PMMA-*b*-PLMA-*b*-PMMA). The broadening of MWD was attributed mainly to the low solubility of LMA at –78 °C in THF and other kinetic aspects. Two T_gs at –5 and 105 °C were reported for the intermediate di-block copolymer ($(PMMA)_{200}$-*b*-$(PLMA)_{67}$). Three T_gs at –44, 0 and 104 °C were reported for another intermediate di-block copolymer ($(PMMA)_{200}$-*b*-$(PLMA)_{134}$) and the final triblock copolymer ($(PMMA)_{200}$-*b*-$(PLMA)_{200}$-*b*-$(PMMA)_{200}$). But, the conditions of thermal characterization were not given. Nakagawa and co-workers[14)] reported controlled synthesis of di-block and triblock copolymers of LMA and MMA with *t*-BuLi/TEA in toluene at –78 °C. The rate of reactions in this case is slow and requires long reaction times for 100% conversion. The obtained copolymers had narrow MWD ($\leq$ 1.22, $M_n \leq$ 23,000). These copolymers had high syndiotacticity and formed stereo complexes with isotactic and syndiotactic PMMA.

Jerome and co-workers[15)] have reported a two-step synthesis of fully acrylic block copolymers using ligated anionic polymerization (scheme 5.1). In this method fully acrylic tri-block copolymers with center poly(*t*-butyl acrylate) (poly(*t*-BA)) blocks were prepared by ligated anionic polymerization followed by selective transalcoholysis of poly(*t*-BA) blocks with the desired alcohol to yield the required poly(*n*-alkyl acrylate) blocks. Using this method they reported the synthesis of triblock copolymers of MMA and isooctyl acrylate (IOA), (poly(MMA-*b*-IOA-*b*-MMA)), in the molecular weight range of 100,000 – 300,000 (PMMA content 6.5 – 22 mole%) with narrow MWD ($<$ 1.2). These polymers show a T_g at –45 °C and were independent of PMMA content in the polymer.

But the T_g corresponding to PMMA blocks were not clearly seen in these polymers and this was attributed to low PMMA content.



Scheme 5.1: Synthesis of copolymers of MMA and alkyl acrylates by ligated anionic polymerization



Scheme 5.2: Syntheis of fully acrylic triblock copolymers by ATR

More recently Jerome and co-workers[16)] have reported the synthesis of fully acrylic block copolymers using ATRP. They prepared di-functional poly(*n*-butyl acrylate) macro initiator and it was used to initiate the polymerization of MMA (scheme 5.2). The block copolymers were prepared in presence of different catalyst complexes and better results were obtained with copper chloride/4,4'-(dinonyl)-2,2'-bipyridine (CuCl/dNBiPy) complex in the presence of excess deactivator ($CuCl_2$). The block copolymers were prepared in the molecular weight range of 60,000 with narrow MWD ($\leq$ 1.15). We have explored the synthesis of block copolymers of MMA and LMA using both living anionic as well as controlled radical polymerization techniques. The results of this study are reported in this chapter.

5.2. Experimental Procedure

5.2.1. Materials

Lithium, sodium and potassium metals, sodium sulfate, activated alumina (neutral), naphthalene and all solvents – tetrahydrofuran (THF), toluene, methanol, ethanol, diethyl ether and benzene were procured from S. D. Fine Chemicals, Bombay. Lithium perchlorate ($LiClO_4$), 1,1-diphenylethylene (DPE), calcium hydride (CaH_2), methyl methacrylate (MMA), lauryl methacrylate (LMA), α-methyl styrene, copper bromide (CuBr), pyridine-2-carboxaldehyde N,N',N',N'',N''-pentamethyl diethylenetriamine (PDT) and ethyl-2-bromoisobutyrate (EBI) were procured from Aldrich, USA. Triethyl aluminum (TEA) was procured from Schering AG, Germany. *n*-BuLi, DPHLi and lithium naphthalenide were prepared in the laboratory as described in chapter 2.

5.2.2. Purification

THF and toluene were fractionated and purified as described in chapter 2. All solvents were used after simple distillation. Metals were used as received. $LiClO_4$ was dried under dynamic high vacuum at 100 °C for 24 hours and used as a solution in THF. TEA was diluted with toluene (1.0M) and used. Purification of MMA and determination of initiator concentration has been described in chapter 2. Purification of LMA, CuBr, PDT and EBI has been described in chapter 4. Naphthalene was purified by sublimation before use. α-methyl styrene was distilled by freeze thaw technique after stirring over CaH_2 for 6 hours.

5.2.3. Synthesis of block copolymers by anionic polymerization

Block copolymers of MMA and LMA were synthesized using anionic polymerization. The reaction was carried out in a bench top single neck reactor equipped with a three-way septum adapter and a magnetic stirring bar (fig. 2.5, chapter 2). The reaction bulb was assembled and flame dried under vacuum before filling the bulb with nitrogen gas. In a polymerization reaction (run 1, table 5.1) 100 mL of THF was transferred using a stainless steel capillary. Into this, $LiClO_4$ (1.89 mmol) as a solution of THF was added using syringe. Temperature of the solution was brought down to – 40 °C. DPHLi was added drop-wise until persistent, faint, red color of DPHLi appeared in the solution. This gives the end-point for the titration of traces of impurities and usually 0.2 to

0.6 mL of 0.1 M initiator solution is consumed for this purpose. DPHLi (1.887 × 10^{-3} mol/L) was then transferred into the solution by syringe and MMA (0.262 mol) was added. The contents were stirred for 15 minutes and a small portion was withdrawn for analysis. LMA (0.096 mol) was added to the living PMMA solution and stirred for another 15 minutes. 1 mL of methanol was added to quench the polymerization. The polymer solution was concentrated and the polymer was precipitated into methanol. The polymer was filtered and dried under vacuum for 5 - 8 hours at 20 °C. Tri-block copolymers were prepared in a similar way using difunctional oligomeric α-methyl styryllithium as initiator.

5.2.4. Synthesis of block copolymers using ATRP

Synthesis of block copolymers using ATRP was carried out by sequential addition of monomers. The polymerization was carried out in toluene at 95 °C with EBI as initiator in presence of both CuBr/PDT and CuBr/PPMI catalyst complexes. In a reaction, (run 1, table 5.4) CuBr ((0.67 mmol), LMA (0.55 mol/L), toluene (10 mL) and PDT (0.34 mmol) were transferred into the reaction flask (fig 2.5, chapter 2) in that sequence. The contents were de-oxygenated by three cycles of vacuum and nitrogen. After increasing the reaction temperature to 95 °C EBI (0.67 mmol) was added and the contents were stirred for 6 hours. After 6 hours, a small portion was withdrawn from the reaction mixture and MMA (1.86 mol/L) was added to the rest and stirred for another 6 hours. The reaction flask was cooled in a liquid nitrogen bath to quench the polymerization. The reaction mixture was diluted with THF and passed through activated alumina (neutral) to remove the catalyst complex. The solution was concentrated and the polymer was precipitated into methanol, filtered, and dried under vacuum for 5-6 hours at 40 °C.

5.2.5. Characterization

Molecular weight and molecular weight distribution of the alkyl methacrylate polymers were determined from SEC (*Thermoquest*) equipped with UV and RI detectors. PMMA standards (*Polymer Laboratories*) were used for calibration. THF was used as eluent at 1mL/min. flow rate and two 60 cm PSS SDV-gel columns: 1 × 100Å and 1 × linear (10^2 – 10^5 Å) at room temperature. ^{1}H NMR (*Bruker-200 MHz*) was used for determining the copolymer composition. This was calculated using the integration ratios corresponding to $-OCH_3$ protons of MMA (3.6 δ) and $-OCH_2$ protons of LMA (3.9 δ). Calorimetric measurements were performed with a Mettler-Toledo star system 821^e in the range of – 100 °C to +200 °C at heating/cooling rate of 10 °C/min in a continuous nitrogen flow (100mL/min).

5.3. Results and Discussion

5.3.1. Synthesis of MMA, LMA di-block copolymers using anionic polymerization

Di-block copolymers of LMA and MMA were synthesized using anionic polymerization in THF with DPHLi as initiator in the presence of $LiClO_4$ at – 40 °C and the results are shown in table 5.1. These reactions were carried out by sequential addition of monomers. First MMA was polymerized and after 15 minutes a small portion was withdrawn for analysis. To the residual reaction mixture LMA was added and the reaction was quenched after stirring for another 15 minutes. The obtained block copolymers exhibited good control over molecular weight and gave narrow MWD polymer with no homopolymer contamination (fig 5.1).

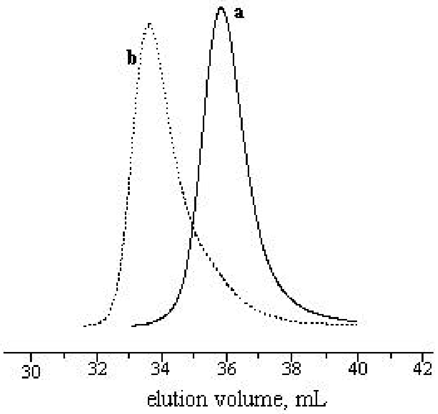


Fig. 5.1: GPC traces of polymers in run 2, table 5.1
PMMA - (a) and PMMA-b-PLMA - (b)

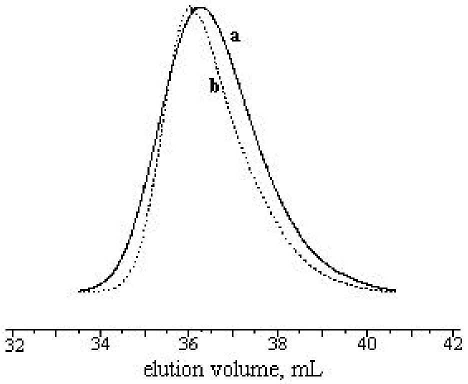


Fig. 5.2: GPC traces of polymers in run 4, table 5.1
PLMA - (a) and PLMA-*b*-PMMA - (b)

Very good results were obtained even for the reverse sequence of monomer addition i.e. polymerizing LMA first followed by MMA addition (fig 5.2). This clearly shows that the LMA polymerization is living under the present polymerization conditions. The monomer content in the block copolymers was calculated from ^1H NMR from the integration ratios corresponding to $-OCH_2$ protons of LMA (3.9 δ) and $-OCH_3$ protons of

MMA (3.6 δ) (fig 5.3). The calculated monomer composition was in agreement (with ± 5% error) with the feed ratio (table 5.1) in each case.

Table 5.1: Synthesis of LMA, MMA block copolymers in THF at -40 °C in the presence of $LiClO_4$ ($[A]_0 / [I]_0 = 10$)

Run. No.	$[I]_0 \times 10^3$ mol/L	[MMA] mol/L $[M]_0$	[LMA] mol/L $[L]_0$	Homopolymer			Block copolymer			
				$M_{n,\,cal}$ $\times 10^{-3}$	$M_{n,\,SEC}$ $\times 10^{-3}$	MWD	$M_{n,\,cal}$ $\times 10^{-3}$	$M_{n,\,SEC}$ $\times 10^{-3}$	MWD	$[M]_0$:$[L]_0$ ^{1}H NMR
1	1.887	0.202	0.174	10.8	15.2	1.160	34.3	41.5	1.30	47:53
2	2.807	0.306	0.128	10.9	13.0	1.150	21.8	27.4	1.19	65:35
3	1.887	0.262	0.154	13.9	13.7	1.130	34.6	32.9	1.20	58:42
4^d	2.400	0.093	0.068	7.30	7.20	1.109	11.2	11.1	1.16	58:42

$^{a)}M_{n,\ cal.} = \{[M]_0 / [I]_0\} \times$ Mol. Wt. of monomer $^{b)}$Number average molecular weights were determined using PMMA calibration $^{c)}$¦ = Initiator efficiency = $M_{n,\ cal.} / M_{n,\ SEC}$ $^{d)}$LMA was polymerized first.

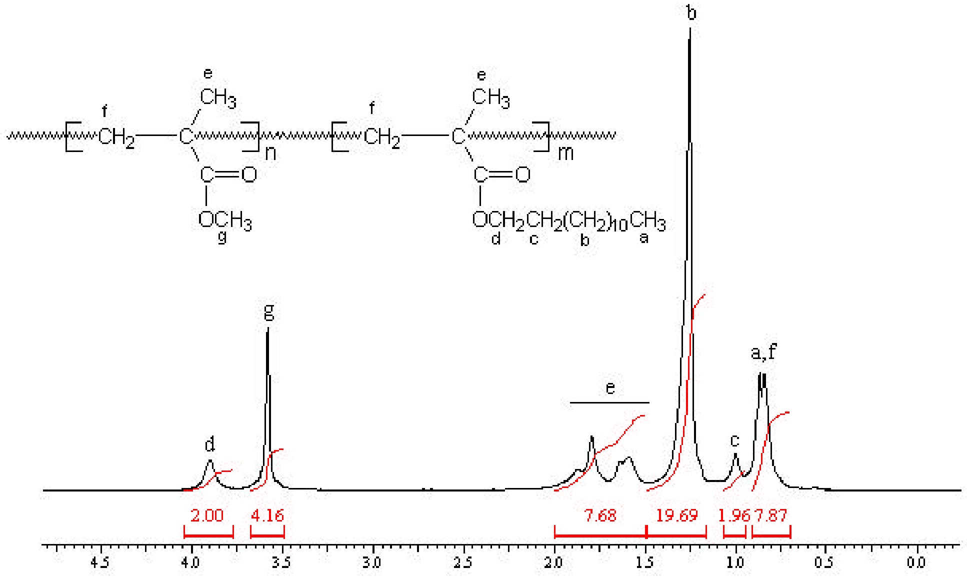


Fig. 5.3: ^{1}H NMR spectrum of PLMA-b-PMMA, run 4, table 5.1

The DSC thermograms (fig. 5.4, fig. 5.5) of these polymers show two distinct T_g values at –49 °C, corresponding to PLMA, and 115 °C corresponding to PMMA. These different values of T_g suggest the phase separation in the block copolymers. These values are similar to those reported by Anderson and coworkers[13)]

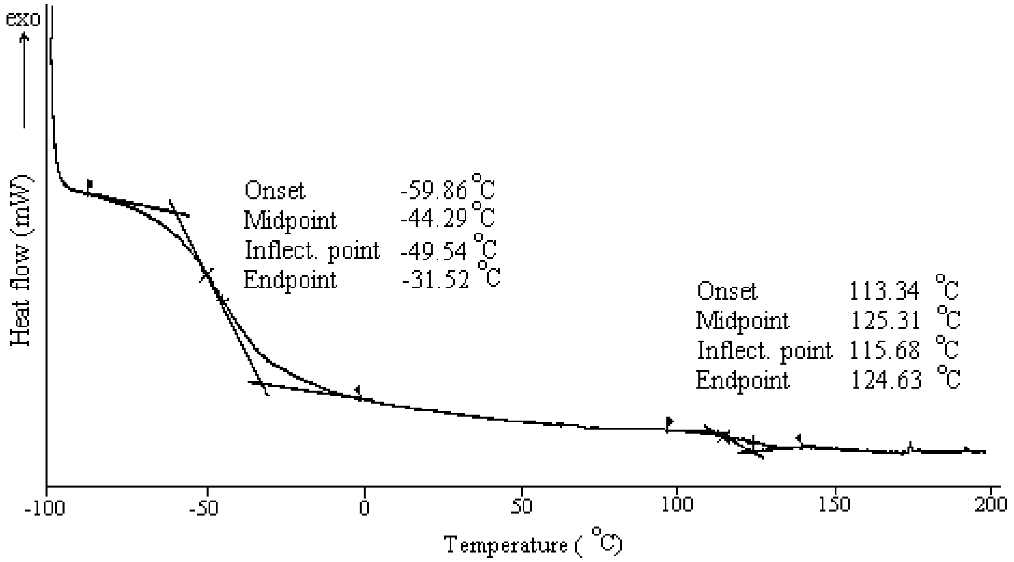


Fig. 5.4: DSC thermogram of PMMA-*b*-PLMA, run1, table 5.1

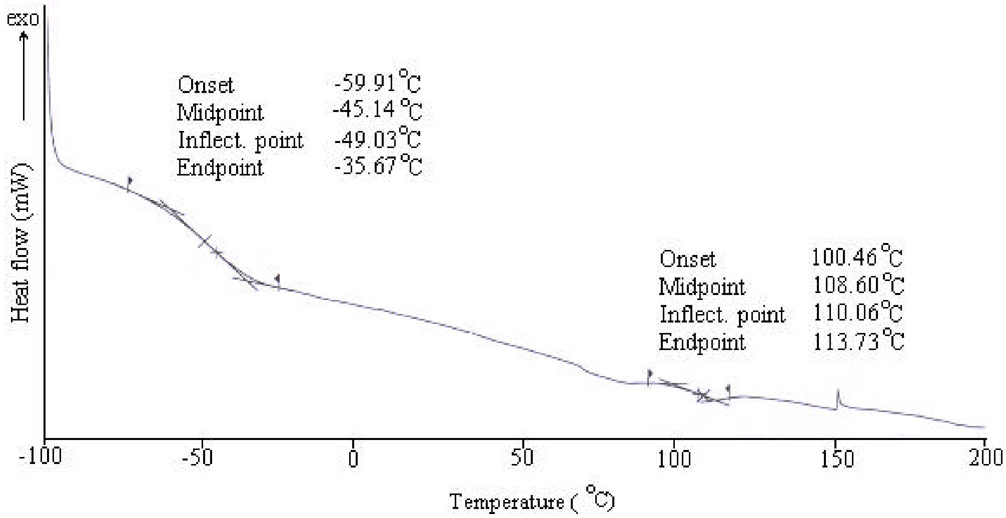
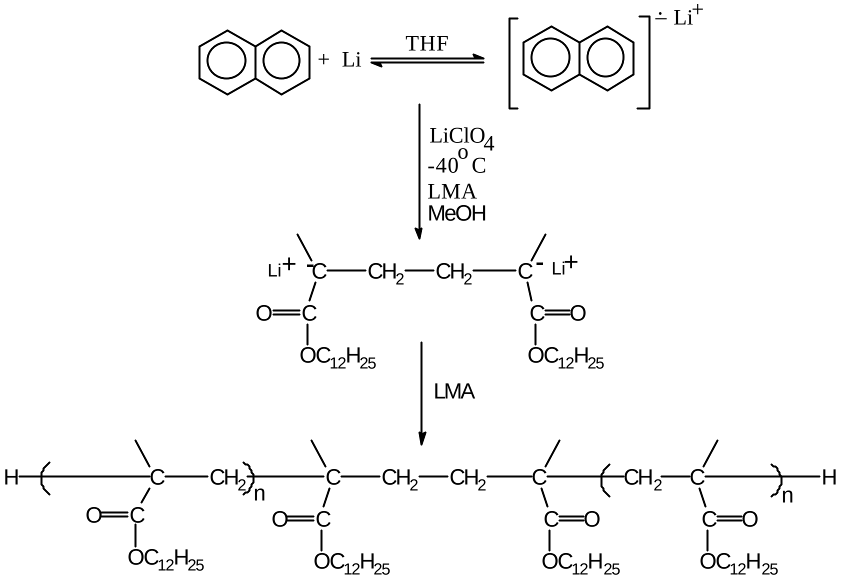


Fig. 5.5: DSC thermogram of PLMA-*b*-PMMA, run 4, table 5.1

5.3.2. Anionic polymerization of LMA using lithium naphthalenide initiator

Anionic polymerization of LMA was carried out using LiNap, a di-functional initiator, as a first step towards the synthesis of tri-block copolymers of LMA and MMA (scheme 5.3). The polymerization was carried out in THF at –40 °C in presence of $LiClO_4$. The results are shown in table 5.2. When LiNap was used as initiator the resulting polymers had bi-modal distribution with a hump at low molecular weight side of the SEC chromatogram (runs 1 and 2 in table 5.2) (fig 5.6). The molecular weight of the low molecular weight hump was approximately equal to the single site initiation. In order to achieve better control over initiation, di-functional α-methyl styryl lithium was prepared in-situ by adding LiNap to the reaction medium containing 10 mole excess of α-methyl styrene at –40 °C and stirred for 5 minutes before adding the monomer (runs 3-5 in table 5.2). The anionic polymerization of LMA using this initiator gave very good control over molecular weight and the resulting polymers had narrow MWD. The SEC chromatogram of these polymers does not show the low molecular weight hump (fig. 5.6).



Scheme 5.3: Anionic polymerization of LMA using lithium naphthalenide initiator

Table 5.2: Homo polymerization of LMA using LiNap as initiator in the presence of $LiClO_4$ ($[A]_0 / [I]_0$ =10) at -40 °C in THF

S. No.	Initiator	$[I]0 \times 10^3$ m/L	[M] m/L	Yield %	$M_{n,cal}$ $\times 10^{-3}$	$M_{n,SEC}{}^a$ $\times 10^{-3}$	M_n / M_w	¦ ^{c}
1	LiNap	2.880	0.068	100	12.0	14.6	1.24^d	0.82
2	LiNap	2.880	0.102	92	18.1	30.2	1.08^d	0.60
3	LiNap + α-MS	2.860	0.096	96	17.0	29.4	1.12	0.59
4	-do-	1.430	0.102	100	36.5	54.5	1.14	0.67
5	-do-	0.858	0.102	>94	60.7	101.0	1.24	0.60

[a] $M_{n,\ cal.} = \{[M]_0 / [I]_0\} \times$ Mol. Wt. of monomer [b] Number average molecular weights were determined using PMMA calibration [c] ¦ = Initiator efficiency = $M_{n,\ cal.} / M_{n,\ SEC}$ [d] Bi-modal distribution

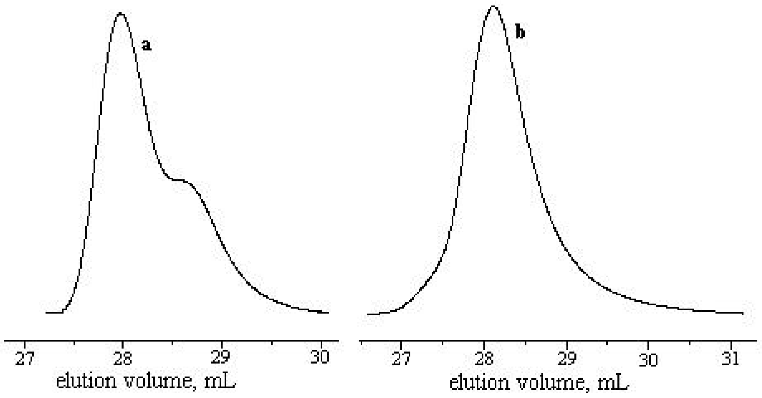


Fig. 5.6: GPC traces of PLMA by anionic polymerization in THF at -40 °C initiated by LiNap - (a) and LiNap + α-MS - (b)

5.3.3. Synthesis of LMA, MMA tri-block copolymers using anionic polymerization

Synthesis of tri-block copolymers of LMA and MMA was attempted using this initiator in THF at –40 °C in presence of $LiClO_4$. The results are shown in table 5.3. The block copolymer obtained had bi-modal distribution (runs 1-2, table 5.3). The polymerization reactor used for these reactions was a single neck round bottomed flask (fig 2.5, chapter 2) and the polymerizations were performed under a positive pressure of nitrogen. All additions and withdrawals were carried out using syringe or cannula. It is conceivable that during this manipulation some impurities may enter the system, terminating a few homopolymer chains. This could be the reason for homopolymer contamination.

To avoid this problem, an alternative reaction vessel (fig 2.6, chapter 2) was designed for block copolymer preparation. This reactor contains a side arm into which a small portion of the reaction solution can be withdrawn just by tilting the reactor. The monomers were directly distilled into graduated ampoules and these ampoules were connected to the reactor before conditioning. After adding the required initiator, the monomers were added by opening the stopcock of the ampoule. This reactor reduces the manipulation difficulties and prevents fresh impurities from entering the polymerization system. Though the resulting polymer still had bi-modal MWD (runs 4-6, table 5.3), the amount of homopolymer contamination reduced considerably. This confirms the fact that some impurities were entering the system during the manipulations. But the presence of low molecular weight hump indicates that the termination of active chain ends is still present in the system (fig. 5.7). This could be due to the time taken from distillation to addition of the monomers (especially second monomer). During this time the second monomer (neat) may start polymerizing. Providing a cooling jacket to the ampoules can prevent this problem. Further refinements in the experimental techniques are necessary to obtain well defined triblock copolymers of MMA and LMA without homopolymer contamination.

Table 5.3: Synthesis of LMA, MMA tri-block copolymers in THF at -40 °C in the presence of $LiClO_4$ ($[A]_0$ / $[I]_0$ = 10)

Run. No.	$[I]\times10^3$ mol/L	[LMA] mol/L $[M]_0$	[MMA] mol/L $[L]_0$	Homopolymer			Block copolymer			
				$M_{n,cal}$ $\times10^{-3}$	$M_{n,SEC}$ $\times10^{-3}$	MWD	$M_{n,cal}$ $\times10^{-3}$	$M_{n,SEC}$ $\times10^{-3}$	MWD	$[M]_0$:$[L]_0$ ^{1}H NMR
1	2.487	0.074	0.244	15.2	18.0	1.155	34.9	44.6	1.561	-
2	2.487	0.059	0.236	12.2	18.9	1.134	31.2	40.7	1.558	-
3	2.043	0.073	0.228	18.2	28.9	1.149	44.4	49.4	1.270	75:25
4	2.043	0.048	0.267	12.2	16.9	1.116	31.9	53.2	1.258	83:17
5	2.600	0.093	0.255	18.2	30.8	1.140	37.9	55.3	1.263	73:27
6	2.600	0.062	0.212	12.2	27.7	1.112	31.9	40.5	1.289	77:23

[a] $M_{n,\ cal.}$ = {$[M]_0$ / $[I]_0$}× Mol. Wt. of monomer [b] Number average molecular weights were determined using PMMA calibration [c] ¦ = Initiator efficiency = $M_{n,\ cal.}$ / $M_{n,\ SEC}$ [d] All the polymers had bi-modal distribution

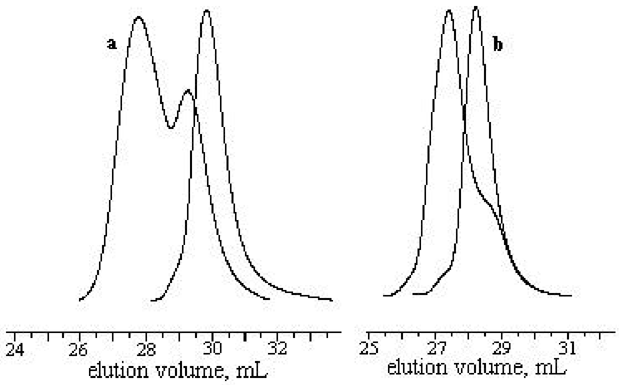


Fig. 5.7: GPC traces of PLMA and PMMA-b-PLMA-b-PMMA prepared by anionic polymerization in single neck reactor - (a) and designed reactor - (b)

5.3.4. Synthesis of LMA, MMA di-block copolymers using ATRP:

Synthesis of block copolymers by ATRP is a two-step process[16)] involving the synthesis and isolation of macro-initiator followed by block copolymer synthesis using this macro-initiator. We attempted a single pot synthesis of LMA, MMA diblock copolymers by sequential addition of monomers in ATRP. PPMI and PDT ligands were used for this purpose. First LMA or MMA macro-initiators were prepared by ATRP (described in section 5.2.3) and after six hours a small fraction was withdrawn for analysis and second monomer was added. After continuing the reaction for another six hours the polymers were quenched by cooling in liquid nitrogen bath and polymers were isolated. The results are shown in table 5.4.

Table 5.4: Synthesis of LMA, MMA di-block copolymers by ATRP using CuBr catalyst, EBI initiator, in toluene at 95 °C.

Run. No.	[MMA] mol/L	[LMA] mol/L	Homopolymer			Block copolymer			
	$[M]_0$	$[L]_0$	$M_{n,\,cal}$ $\times 10^{-3}$	$M_{n,\,SEC}$ $\times 10^{-3}$	MWD	$M_{n,\,cal}$ $\times 10^{-3}$	$M_{n,\,SEC}$ $\times 10^{-3}$	MWD	$[M]_0$:$[L]_0$ ^{1}H NMR
1^c	1.86	0.55	5.1	9.1	1.25	14.9	42.1	1.14	76:24
2	1.86	0.55	5.1	12.5	1.46	14.2	40.3	1.37	76:24
3^c	1.86	0.55	5.1	8.5	1.22	14.9	16.7	1.28	70:30
4	1.86	0.55	5.0	7.7	1.16	14.2	16.9	1.13	80:20

[a)] $M_{n,\,cal.} = \{[M]_0 / [I]_0\} \times$ Mol. Wt. of monomer, and calculated for yield [b)]Number average molecular weights were determined using PMMA calibration [c)]LMA was polymerized first. [d)] Ligand used was PDT in runs 1 & 2 and PPMI in runs 3 & 4. [e)] $[c]_0:[I]_0:[L]_0$ = 1:1:0.5 for PDT and 1:1:2 for PPMI

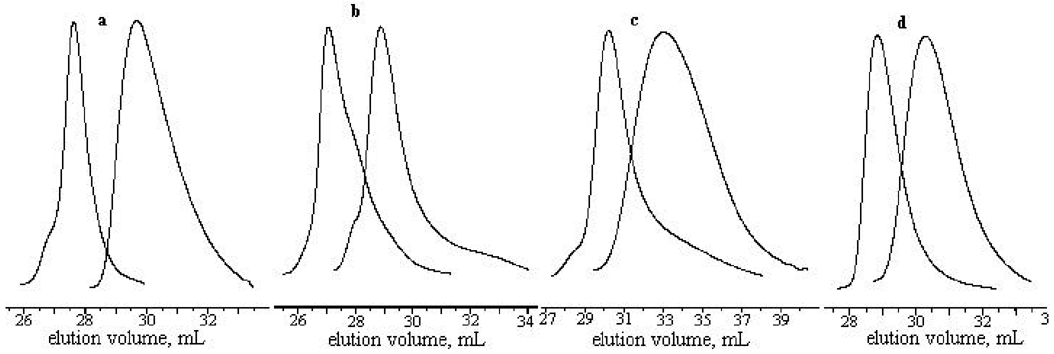


Fig. 5.8: GPC traces of block copolymers of LMA and MMA prepared by ATRP in a one pot synthesis. (a) Run 1 - (b) Run 2 - (c) Run 3 and (d) Run 4 in table 5.4

The macro initiators prepared with PDT ligand gave reasonably good control over molecular weight and relatively narrow MWD. Viscosity of the reaction mixture increased considerably after second monomer addition. The block copolymers had low molecular weight tailing (fig 5.8) and poor initiator efficiency, presumably, due to the increased viscosity of the reaction medium. This may reduce the rate of reversible deactivation. Besides, it was observed that the concentration of insoluble Cu(II) complex increased with viscosity. This further reduces the reversible deactivation and thus losing control over polymerization. The increment in viscosity in the polymerization of MMA initiated by PLMA macro-initiator was less than that observed in the polymerization of LMA initiated by PMMA macro-initiator. The obtained block copolymer had multi-modal, but narrow MWD.

The macro initiators prepared using PPMI ligand gave better initiator efficiency with narrow MWD. Even in these reactions viscosity increased after second monomer addition. The block copolymers formed had narrow MWD with good initiator efficiency. In the case of block copolymer preparation with PLMA macro initiator the obtained block copolymer showed low molecular weight tailing and a slight high molecular weight hump. This indicates a slow crossover reaction from LMA to MMA. In the case of LMA initiation with PMMA macro initiator the obtained block copolymer had very narrow MWD coupled with very good initiator efficiency. The better results in the case of this ligand system can be attributed to the better solubility of the catalyst/ligand complex.

5.4. Conclusions

The block copolymers of LMA and MMA were synthesized using both anionic polymerization and ATRP methods. Di-block copolymers of MMA and LMA were synthesized with good control over molecular weight and narrow MWD using DPHLi as initiator in THF at –40 °C in anionic polymerization. Initiation of LMA with lithium naphthalene in THF at –40 °C resulted in PLMA with bi-modal distribution. Preparation of di-functional α-methyl styryl lithium with LiNap and α-methyl styrene *in situ* and using it as an initiator for LMA polymerization gave good control over polymerization over a wide range of molecular weight. The tri-block copolymers of LMA and MMA synthesized using this initiator had homopolymer contamination. This was attributed to the impurities entering the polymerization system during sample withdrawal and second monomer addition.

The di-block copolymers synthesized by ATRP using CuBr/PDT catalyst complex resulted in multi-modal distribution with poor initiator efficiency. This result was attributed to the insolubility of the Cu(II) complex as the viscosity increases. Synthesis of di-block copolymers with CuBr/PPMI catalyst complex gave much better results. The reason could be better solubility of the catalyst complex. The multi-modal MWD of the block copolymer obtained from PLMA macro-initiator was attributed to the slow crossover reaction.

5.5. References

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Chapter 6: Synthesis of well-defined star polymers using multi-functional coupling agents

6.1. Introduction

Star polymers are branched polymers with several chains linked together at a single junction point[1-3]. These polymers represent the simplest form of branching and, thus, are well suited for studying structure-property relationships of branched polymers[4]. For this purpose it is essential to have star polymers with defined number of chains (arms), chain length, molecular weight and composition. Synthesis of star polymers was first reported by Flory and Schaefgen[5] in 1948 and since then enormous developments have taken place in the synthesis of different types of star polymers like homopolymers, heteroarm star polymers, star block copolymers etc.[6].

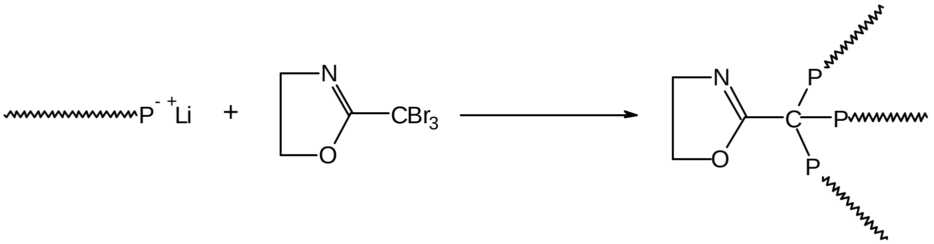
There are two strategies applied for preparing star polymers. In the first strategy, known as core-first method, polymerization of a monomer is started from a multi functional initiator to grow the star polymer from the core[2]. This strategy provides a clean approach for the synthesis of well-defined star polymers. However, this method requires the synthesis of appropriate multi functional initiators, which is not always easy. Besides, it is important that all the initiating sites initiate the polymerization simultaneously and with identical rates. The other approach is known as arm-first method and involves coupling of the prepolymerized living linear polymer chains with a suitable coupling agent[7,8]. This method has been more extensively used for the synthesis of star polymers[9-11]. This approach has an advantage of sampling the linear polymer before coupling which facilitates the rigorous characterization of the product. Anionic polymerization methods remain the best technique for preparing star polymers with high purity[12].

More recent developments in the star polymer synthesis by anionic polymerization involve the usage of 1,1-diphenyl ethylene (DPE) based compounds in both core-first and arm-first strategies. Quirk and co-workers have used this methodology for the synthesis of wide variety of star polymers like homopolymers, miktoarm star polymers and star block copolymers[13,14]. The major advantage of this method is the possibility of synthesizing ω-functionalized star polymers by terminating the reaction with suitable electrophilic reagents. Major shortcoming of this method is that the maximum number of arms that can be achieved is limited due to the number of DPE functionalities that can be incorporated into a single molecule. Besides, it is difficult to characterize individual side chain, as sampling is not possible here. Rate constants for the initiation for different sites will be different and leads to broad MWD.

Synthesis of star polymers by coupling the living linear polymer chains with difunctional monomers, especially divinylbenzene, has been extensively studied15-18). This method is experimentally straightforward for the synthesis of regular star polymers, miktoarm star polymers and partially ω-functionalized star polymers. Though, by varying the ratio of anion and difunctional monomer, degree of branching can be controlled, this often results in multi-modal and broad MWD with an average degree of branching and in some cases, inter-connected stars are also obtained15). Star polymer with narrow MWD and uniform degree of branching can be obtained by using silyl halide type coupling agents by carefully maintaining the stoichiometry of coupling agents with the living anions. Star block copolymers can be prepared in a similar way by first making the block copolymers followed by coupling or by sequential addition of monomers to the multifunctional initiator. Heteroarm star polymers (miktoarm star polymers) are prepared by first making the star polymers using divinylbenzene type coupling agents and then using this as the multifunctional initiator to polymerize the second monomer.

Functional polymers, especially, polymers having functional groups with different polarity and reactivity from the back bone, have unique properties and applications, leading to enhanced reactivity, phase separation or association, ability to form self-assemblies and supramolecular structures19,20). Most functional polymers are based on simple linear backbone such as telechelic polymers, block or graft copolymers etc. There is an increasing interest towards functional polymers with special topologies like star polymers, hyperbranched polymers and dendrimers21-24). However, these polymers are difficult to prepare due to the competition between the propagation and the reaction of the active center with the functional group resulting in chain termination or transfer. In order to avoid this problem, protecting groups were used in the initiators or termination agents to mask the functional group.

The oxazoline ring system was used extensively as a protecting group for the carboxylic acid functionality and possesses considerable utility in organic synthesis due to its inertness towards various reagents 25). Appropriate manipulation of the oxazoline ring leads to the aldehydes, ketones, lactones, amino acids, thiiranes, olefins and homologated carboxylic acids[25]. 2-Substituted oxazolines are important monomers in polymer chemistry to prepare poly(ethyleneimines)[26]. Bera and Sivaram[27] reported the use of 2-tribromomethyl-2-oxazoline (TBO) as a tri-functional initiator in the cationic ring opening polymerization of 2-methyl-2-oxazoline (MOX) to produce a three-arm star polymer. This indicates a strong electrophilic nature of C-Br bonds in TBO. It was, therefore, of interest to explore whether TBO could function as a tri-functional linking agent in living anionic polymerization (scheme 6.1).



Scheme 6.1: Synthesis of star polymers with TBO coupling agent

This could lead to the preparation of well-defined three arm star polymers with a polymerizable group at the core. This star polymer can be used in the preparation of well-defined graft copolymers by copolymerization with 2-methyl-2-oxazoline (MOX). Besides the oxazoline ring can be hydrolyzed to generate carboxylic acid functionality at the core. It was, therefore, proposed to study the reaction of TBO with a model nucleophile, *n*-BuLi, to explore the feasibility of TBO as coupling agent for the living anionic chain ends.

6.2. Experimental methods

6.2.1. Materials

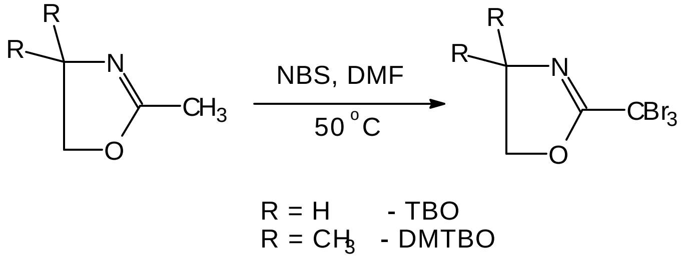
2-Methyl-2-oxazoline (MOX), 2,4,4-trimethyl-2-oxazoline (TMOX) and CaH_2, were procured from Aldrich, USA. Benzoyl peroxide (BPO), N,N-dimethyl formamide (DMF), and other solvents like hexane, THF, and toluene were procured from S. D. Fine Chemical Ltd., Bombay, India. N-bromosuccinimide (NBS) was procured from Loba Chemie Industries, Bombay, India.

6.2.2. Purification

MOX and TMOX were purified by freeze-thaw distillation after stirring over CaH_2 for 6 hours at 25 °C. BP was re-precipitated from chloroform into methanol, filtered, dried under vacuum at 0 °C for 4 hours and stored in dark at 5 °C. NBS was re-crystallized from hot water and dried overnight under dynamic vacuum. THF was purified and dried as described in chapter 2. DMF was distilled under reduced pressure after stirring over CaH_2 for 4 hours. All solvents were used after simple distillation. Preparation of *n*-BuLi and determining the concentration are described in chapter 2.

6.2.3. Synthesis of coupling agents[28)]

TBO was synthesized by exhaustive bromination of MOX (11.7 mmol) with NBS (35 mmol) in DMF (30 mL) in presence of catalytic amount of BPO (0.1 g) at 30 °C (scheme 6.2). After 2 hours, the reaction mixture was poured in excess cold water. Precipitated product was re-crystallized from n-hexane. Yield was 3.0 g (82%). m.p. 104.5 °C (literature m.p. 105-106 °C)[28)]. ^1H NMR (in $CDCl_3$) (fig. 6.1): 4.1δ (t, N-CH_2) and 4.6 δ (t, O-CH_2). Elemental analysis: Calcd. %: C- 14.93, H- 1.25, N- 4.35 and Br- 74.5; found: C- 15.10, H- 1.50, N- 4.32 and Br- 74.51.



Scheme 6.2: Synthesis of TBO and DMTBO

In a similar way 4,4-dimethyl-2-tribromomethyl-2-oxazoline (DMTBO) was synthesized from TMOX with 80% yield. m.p. 88 °C. ^1H NMR (in $CDCl_3$) (fig. 6.2): 4.35 δ (s, O-CH_2) and 1.4 δ (s, -$C(CH_3)_2$). Elemental analysis: Calcd. %: C- 20.57, H- 2.28, and Br- 68.5; Found: C- 20.65, H- 2.31, N- 4.31 and Br- 68

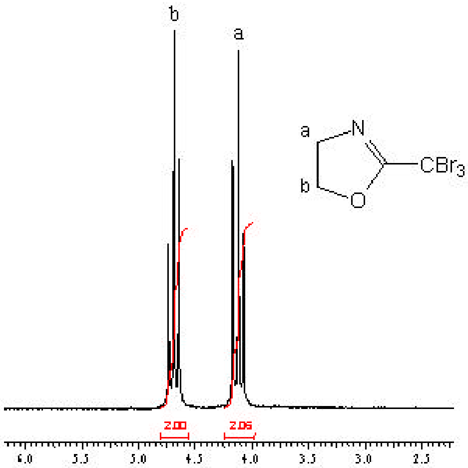


Fig. 6.1: ^{1}H NMR of TBO in CDCl$_3$

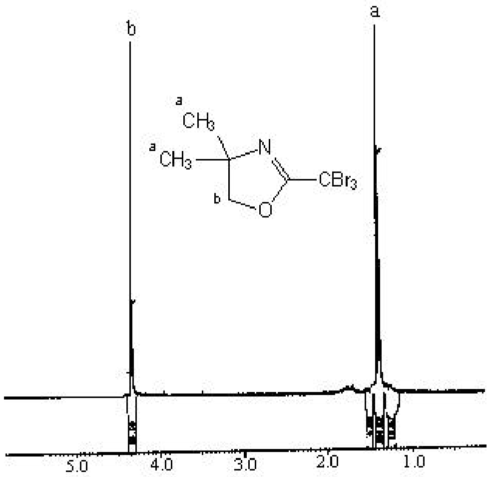


Fig. 6.2: ^{1}H NMR spectrum of DMTBO in CDCl$_3$

6.2.4. Model reactions

TBO (36 mmol) was taken into a reaction flask and 50 mL of dry THF was transferred into it. The solution was pale yellow in color. Temperature of the reaction was reduced to -78 °C and n-BuLi (0.145 mol/L) was added drop-wise. The color changes to dark brown color. After 0.5 - 1h, water was added to quench the reaction. THF was removed under reduced pressure and the product was extracted into chloroform, washed with water several times. The organic layer was separated, dried over sodium sulphate, solvent was removed and the product analyzed by ^{1}H NMR.

6.3. Results and Discussion

6.3.1. Stability of oxazoline ring in the presence of anions

Model reactions of TBO and DMTBO with *n*-BuLi were, initially, carried out in cyclohexane at room temperature. TBO or DMTBO was dissolved in cyclohexane and nBuLi was added drop-wise. The reaction was terminated after 30 min. by adding water. After aqueous work-up, the resultant product was analyzed by using ^{1}H NMR. The NMR spectra showed several unidentifiable signals, which indicates the reaction is not clean and several undesired reactions are taking place. It was assumed that at room temperature the oxazoline ring might react with nucleophiles. To confirm this, excess DPHLi anion was added to 2-methyl-2-oxazoline in THF at 30 °C. The red color of DPHLi anion disappeared slowly within 30 minutes (in case of 2,4,4-trimethyl-2-oxazoline within 90 min.). After the red color disappearance methyl iodide was added. The resulting product mixture was analyzed by using ^{1}H NMR, and it exhibited the presence of very small quantity of 2-ethyl-2-oxazoline along with several other signals. From these results it was inferred that the 2-methyl-2-oxazoline was undergoing metalation followed by undesired side reactions in the presence of anions at 30 °C.

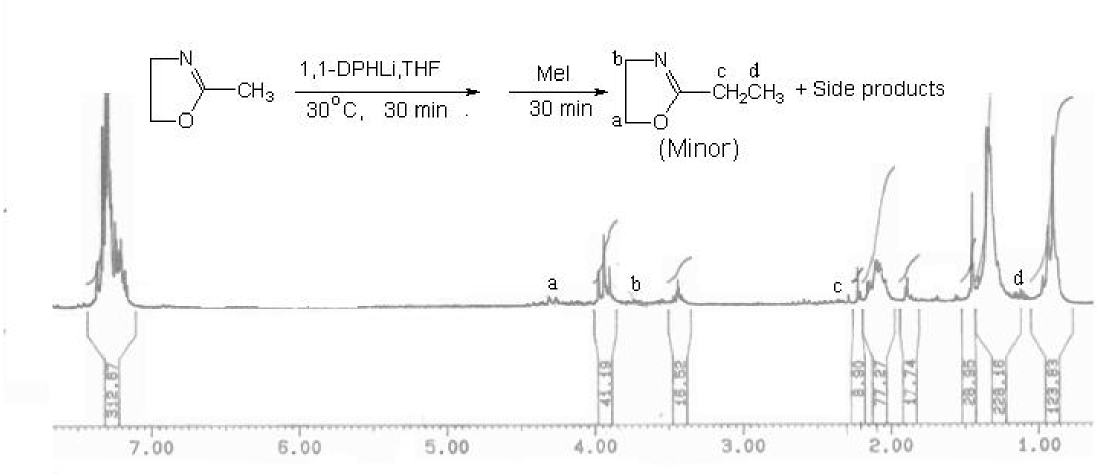
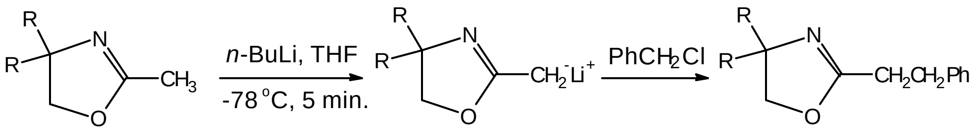


Fig. 6.3: ^{1}H NMR spectrum of (MOX + DPHLi + MeI) reaction product in $CDCl_3$

Meyers and coworkers25,29) showed that 2,4,4 tri-substituted oxazoline ring is stable towards nucleophiles at – 78 °C. They prepared various homologated aromatic and aliphatic carboxylic acids29), by metalating the oxazoline ring exclusively at 2-substituted methyl group followed by reacting with the required alkyl or aryl halide. Their attempts to alkylate all the hydrogen of 2-methyl group were not successful. This was explained by the inability of removing the tertiary proton, at low temperatures, by the base. When the tertiary alkylation was attempted at 20 °C, it was found that the anion is not stable and rearranges rapidly into corresponding ketenimines. But in all their studies, simple MOX was not studied.

Sogah and coworkers have reported30) the facile alkylation of MOX to prepare some novel 2-substituted-2-oxazolines. They reported that lithiation of MOX with lithium diisopropylamide (LDA) at –78 °C and consequent alkylation. But prolonged use of LDA and use of *n*-BuLi or *t*-BuLi for lithiation results in some unidentified side product, which is not reported in a similar reaction with 2,4,4-trimethyl-2-oxazoline (TMOX).

In order to check the stability of oxazoline ring in presence of nucleophiles, such as *n*-BuLi, different oxazoline compounds were lithiated with *n*-BuLi in THF at -78 °C and benzyl chloride was added (scheme 6.3). Both substituted and un-substituted oxazolines gave targeted molecules in almost 100 % yield, as was confirmed by ^{1}H NMR (fig 6.3). This is in agreement with the results obtained by Sogah and coworkers[30)], where they found that the reaction of lithio methyl oxazoline with benzyl bromide gives side products due to a possible electrophilic ring opening, where as the same reaction with benzyl chloride gives alkylated product in almost 98% yield. This in turn proves that the oxazoline ring is stable towards nucleophiles such as *n*-BuLi, at low temperatures, even in highly polar solvents like THF.



Scheme 6.3: Reaction to check the oxazoline ring stability

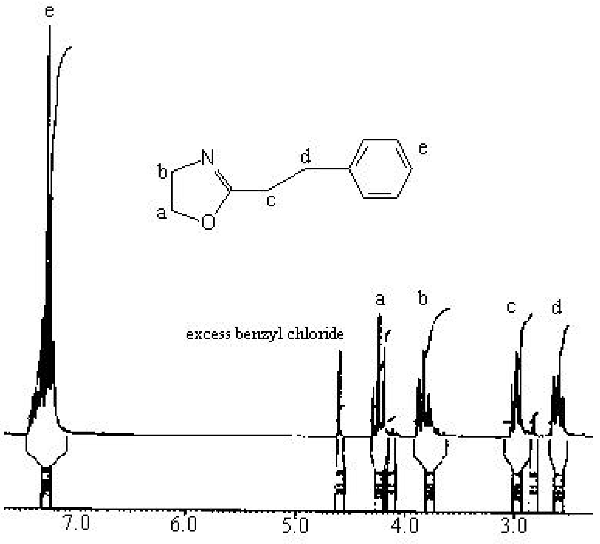


Fig. 6.4: ^{1}H NMR spectrum of 2-(2-phenylethyl)-2-oxazoline in $CDCl_3$

6.3.2. Model reactions of TBO and DMTBO with *n*-BuLi in THF at low temperatures

The model studies of TBO/DMTBO with nBuLi in THF at low temperatures were carried out. THF solution of TBO/DMTBO was added, drop-wise to nBuLi (10 mol% excess) in THF solvent at -78 °C or at -40°C. After 30 min. 1 mL of water was added to terminate the reaction. The ^{1}H NMR spectra of the product (fig. 6.4) showed the oxazoline ring -CH2 signals as mixture of triplets, between the known chemical shift values of tribromo compound (4.2 and 4.5δ) and methyl oxazoline (3.8 and 4.2δ). The integration values of oxazoline $-CH_2-$ signals (3.8-4.3δ) and that of n-butyl $-CH_3$ signals (0.9 δ) do not match even for a mono-adduct. From these integration ratios it was approximately calculated that 90% of the product was mono-adduct. The rest can be attributed to the presence of small quantities of di- and tri-adducts (<10%) or the presence of side reaction products. The reaction time was increased in the next set of reactions to 1h and very little improvement was observed. The results are tabulated below.

Table 6.1: Model studies of TBO with *n*-BuLi in THF at low temperatures

Run. No.	[oxa] m/L	[nBuLi] m/L	Temp. °C	Time h	Results (From NMR)
1	0.036	0.145	-78	0.5	> 90 % mono adduct < 10 % di- and tri-adducts.
2	0.032	0.115	-78	1	> 80 % mono adduct < 20 % di- and tri-adducts.
3	0.032	0.115	-40	0.5	> 80 % mono adduct < 20 % di- and tri-adducts.
4*	0.029	0.089	-40	1	Mixture of mono-, di- and tri-adducts.

*DMTBO was used

From these results it is difficult to establish conclusively whether tribromomethyl oxazolines can be used as coupling agents for the synthesis of tri-arm core-functional star polymers. From the literature it is known that the reactions between linear alkyl lithium compounds and alkyl halides involves certain extent of metal-halogen exchange even at low temperatures leading to a mixture of products. The reaction of TBO with either oligomers of butadienyl lithium (product of 1,4-addition) or allyl lithium needs to be examined to rule out the possibility of steric effects as the inhibiting factor.

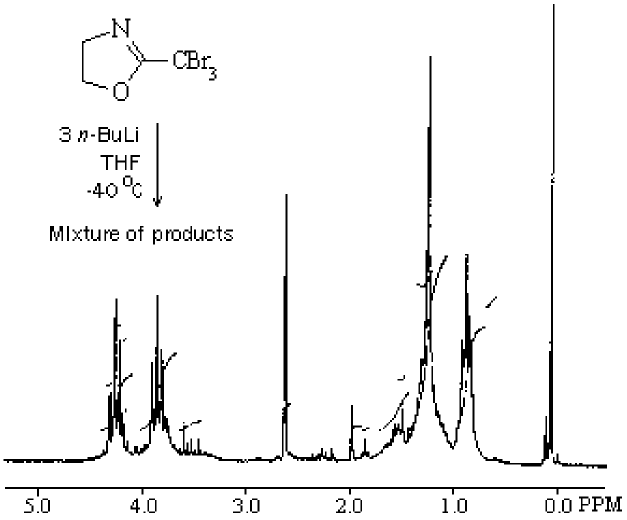


Fig. 6.5: ^{1}H NMR spectrum of (TBO+*n*-BuLi) reaction product in $CDCl_3$

6.4. Conclusions

The oxazoline ring was found to be stable towards nucleophiles like *n*-BuLi at low temperatures. Coupling of *n*-BuLi with tribromomethyl oxazolines is not quantitative, presumably, due to steric hindrance and possible side reactions like metal-halogen exchange.

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Chapter 7: Summary and conclusions

7.1. Summary and conclusions

The difficulties involved in performing anionic polymerization of higher alkyl (meth)acrylates such as lauryl methacrylate are low solubility at low temperatures and high levels of alcoholic impurities present in the commercial monomer. These could be the reasons for the relatively less attention paid to this monomer in the literature. In the present study, anionic polymerization of LMA with DPHLi and di-functional α-methyl styryl lithium initiators in THF at –40 °C was carried out in presence of additives ($LiClO_4$, LiCl and G_3Li_2). The PLMA polymers were formed with reasonably good molecular weight control and narrow MWD ($\leq$ 1.16). Purification of the monomer is very important and the best results can be obtained by carefully fractionating the monomer and further distillation over CaH_2. The di-block copolymers of LMA and MMA were synthesized without homopolymer contamination. However, tri-block copolymers could not be prepared without homopolymer contamination. This was attributed to inadequacy with respect to experimentation. The results can be improved by modifying the polymerization reactor so that syringe and cannula modes of addition can be kept to a minimum. The monomers have to be maintained at polymerization temperatures (-40 °C) after their purification up to their addition time.

Copper mediated ATRP of LMA in toluene with different ligands (DP, DMDP, PDT and PPMI) at 95 °C produce polymers with moderately narrow molecular weight distribution (< 1.3). For PPMI ligand optimum concentration of ligand with respect to catalyst and initiator was 1:3 and the dilution required was 1:4 (v/v) monomer/solvent, whereas for PDT it was found to be 1:1 and 1:2 respectively. Transfer and termination reactions were observed in PDT/CuBr based ATRP presumably due to the high reaction rates and poor solubility of the Cu(II) species. Synthesis of di-block copolymers by ATRP resulted in multi-modal distribution with apparently poor initiator efficiency. When CuBr/PPMI complex was used and LMA was added to PMMA macroinitiator, better results were obtained with narrow MWD and without homopolymer contamination, apparently due to the better solubility of the Cu(II) complex facilitating better equilibrium dynamics. However, isolating the homopolymer and using it as macroinitiator for the other monomer may improve the results.

Synthesis of tri-arm star polymers with oxazoline ring at the core paves way for the synthesis of well-defined graft copolymers (comb polymer) and functional polymers. To study the feasibility of preparing such polymer, model studies were carried out for TBO and DMTBO as coupling agents with *n*-BuLi. It was found that the coupling is not quantitative presumably due to steric hindrance and possible side reactions, such as, metal-halogen exchange. De-localized, sterically less hindered anions may be used for this study to avoid these problems.

7.2. Scope for further research

These results obtained in the present study provide an excellent scope for further studies such as:

- Synthesis of tri-block copolymers of LMA with MMA other methacrylic monomers without homopolymer contamination, in different compositions of monomers and a wide molecular weight range, and comparing the properties of these polymers with SBS thermoplastic elastomers.
- Studies toward finding much better catalytic conditions for the polymerization of LMA by ATRP and synthesis of di- and tri-block copolymers of LMA with other methacrylic monomers.
- Synthesis of oxazoline-functional star polymers after checking the feasibility by carrying out model studies for TBO, DMTBO with allyllithium and butadienyl lithium.