Controlled Polymerization of Alkyl (Meth)acrylates

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Dedicated to parents and
husband

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December 2002

Declaration

The research work presented in this thesis entitled **"Controlled Polymerization of Alkyl (Meth)acrylates"** has been carried out under my supervision and is bonafide work of **Ms. Mahua Ganguly.** This work is original and has not been submitted for any other degree or diploma of this or any other University.

(Mahua Ganguly)
NCL, Pune
December, 2002

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Place: Pune

Date: 20-12-2002

(Dr. S. Sivaram)

(Research Guide)

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Controlled Polymerization of Alkyl (Meth)acrylates

Abstract

Controlled polymerization refers to a method of polymerization that affords a control over the molecular properties such as molecular weight, polydispersity, tacticity, and topology, all of which control the ultimate polymer properties. Living anionic polymerization has been a versatile technique for controlled synthesis of polymers with well-defined structures, e.g. block, graft, star, macromonomers and end-functionalized polymers. Anionic polymerization of alkylmethacrylates which is inherently complicated by side-reactions, proceeds in controlled manner only under carefully chosen conditions such as, low temperature, polar solvent, and bulky initiators. Moreover, the dynamics of ion-pair association equilibrium plays a major role in determining the degree of livingness of the system. The objective of the present study is to examine the anionic polymerization of methyl methacrylate (MMA) using suitable ligands as additives in conjunction with initiators, in order to achieve a living polymerization system, and investigate the effect of these additives on the kinetics of polymerization. Another objective is to synthesize terminal hydroxy-functional PMMA and utilize these macroinitiators for the preparation of well-defined block, star-branched polymers and macromonomers.

- The efficiency of various Li-salt additives that are strong Lewis acids has been studied in controlling DPHLi initiated anionic polymerization of MMA in THF and also in less polar toluene-THF (9:1 v/v) mixture solvent, at and below -40 °C. Presence of the $LiClO_4$, $LiBF_4$, and CF_3SO_3Li, added in 10:1 mole ratio with respect to the initiator, lead to formation of narrow molecular weight distribution polymers in less polar mixed solvent medium, in contrast to the broad and multimodal MWD in absence of the salts. Also, there was a good agreement between theoretical and observed molecular weights. However, none of the salts have any beneficial effect on the polymerization in less polar solvent at -40 °C, possibly due to side-reaction of the salts with the initiator/propagating anions at higher temperatures.

- The effect of $LiClO_4$ and LiCl additives on the kinetics of anionic polymerization of MMA was studied in less polar medium at -78 °C using DPHLi as initiator. Unlike polymerizations in absence of additives, polymerizations in presence of $LiClO_4$ (10x[DPHLi]) and LiCl (5x[DPHLi]) exhibit first-order kinetics free of termination and transfer reaction for various active center concentrations. Narrow unimodal molecular weight distribution characterize the polymers at all conversions. The order of the reaction with respect to the active centers is close to unity for both the salt systems, which suggests an effective complexation of the salts with the ion-pairs leading to disggregation to a single salt complexed active species in solution.

- Protected hydroxy-functional initiators were used to prepare well-defined hydroxy-PMMA in THF at -78 °C. ^1H NMR and MALDI-TOF analysis proved quantitative functionalization. These hydroxy-PMMA were further utilized to initiate ring-opening polymerization of ethylene oxide to form PMMA-*block*-PEO copolymers with narrow molecular weight distribution. The hydroxyl-end function were first converted to the corresponding oxyanion with potassium as counter-ion using trityl-K and then used for EO polymerization in THF at 27 °C. No untoward side-reaction leading to grafting could be detected.

- Hydroxy-functional star-branched PMMA have been prepared by linking the living chains of hydroxy-PMMA with bis-unsaturated monomer ethylene glycol dimethacrylate (EGDMA) in THF at -78 °C. The effect of arm length and ratio of EGDMA with respect to the initiator was studied. Increase in arm length leads to decrease in the number of arms of the star, possibly due to greater steric hindrance in relative to smaller arm length. Increase in EGDMA concentration also leads to increase in the number of arms, due to greater core size, and hence, more available space for accommodation of arms.

- Hydroxy-functional PMMA macromonomers with styryl and allyl end-groups were prepared using 4-vinylbenxylchloride (4-VBC) and allylmethacrylate AMA) to terminate the living chains of hydroxy-PMMA. Termination with AMA leads to

~100% functionalization whereas that with 4-VBC leads to only 50% functionalization even after 2 h of reaction. The reason for incomplete functionalization can be attributed to slow reaction of the $LiClO_4$-complexed hydroxy-PMMA chains with 4-VBC.

Abbreviations

ATRP	atom transfer radical polymerization
AMA	allyl methacrylate
n-BuLi	*n*-butyl lithium
t-BA	*tert*-butylacrylate
t-BMA	*tert*-butylmethacrylate
DCM	dichloromethane
DSC	differential scanning calorimetry
DPE	1,1'-diphenyl ethylene
DPHLi	1,1'-diphenylhexyl lithium
DME	dimethoxyethane
DVB	divinylbenzene
D_3	hexamethylcyclotrisiloxane
EGDMA	ethylene glycol dimethacrylate
EiBLi	ethyl-α-lithioisobutyrate
EO	ethylene oxide
GC	gas chromatography
GPC	gel permeation chromatography
GTP	group transfer polymerization
LAP	ligated anionic polymerization
LS	light scattering
LiOMe	lithium methoxide

$LiOBu^t$	lithium *tert*-butoxide
MALDI-TOF MS	matrix assisted laser desorption/ionization-time of flight mass spectrometry
MMA	methyl methacrylate
MWD	molecular weight distribution
PEO	poly(ethylene oxide)
PHP	potassium hydrogen phthalate
PMMA	poly(methyl methacrylate)
PS	polystyrene
PtBMA	poly(*tert*-butyl methacrylate)
RAFT	reversible addition fragmentation chain-transfer polymerization
SEC	size exclusion chromatography
SFRP	stable free radical polymerization
TBAF	tetrabutyl ammonium flouride
TBDMS	tert-butyldimethylsilyl chloride
TEA	triethyl aluminum
THF	tetrahydrofuran
TLC	thin layer chromatography
TMEDA	N,N,N’,N’-tetramethylethylenediamine
TPP	triphenylphosphine
TPM	triphenylmethane
4-VBC	4-vinyl benzyl chloride
VPO	vapor pressure osmometry

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Chapter 1: Living Anionic Polymerization of Alkyl Methacrylates

1.1. Introduction

A growing number of commodity and specialty applications of polymeric materials have triggered considerable research in the field of polymer science during the last few decades. The emphasis is on "control" in the synthesis, enabling "macromolecular engineering" for achieving the desired properties. Basically, this implies a control over the molecular parameters e.g. molecular weight, polydispersity, tacticity, and topology. Controlled polymerization techniques form the basis for such macromolecular engineering.[1-10] By far, living anionic polymerization has been the most versatile technique for the synthesis of polymers of controlled architecture and narrow molecular weight distribution.[7,9-14]

Recently controlled radical polymerizations have attracted significant attention due to some of its advantages over conventional anionic polymerization.[4,8,15-17] Stable free radical polymerization (SFRP), atom transfer radical polymerization (ATRP) and reversible addition fragmentation chain transfer polymerization (RAFT) are the most widely and successfully employed controlled radical polymerization techniques for preparing living polymers. In contrast to anionic polymerization, controlled radical polymerization is more tolerant towards protic and other impurities. They are also applicable to a broad range of monomers in solution, bulk, emulsion and suspension mode.

Despite this continuing effort for the development of newer controlled polymerization methods, anionic polymerization remains the most versatile and also the most established method for the synthesis of polymers of well-defined structures e.g. block, graft, star, macromonomers and end-functionalized polymers. These well defined polymers find numerous application in areas such as compatibilizers for polymer blends, emusifiers, adhesives, paints and varnishes, additives for lubricating oil, impact modifiers, textiles, optical fibres etc.

1.2. Anionic polymerization of methyl methacrylate (MMA)

Szwarc and co workers identified "living polymers" for the first time while polymerizing styrene with sodium naphthalenide as initiator.[9] The polymerization seemed to proceed with negligible termination and transfer reactions and the propagating chain-ends were still capable of adding to fresh molecules of monomer. Since then, the concept of living polymerization has received significant recognition from polymer chemists as the best method for macromolecular engineering of synthetic polymers. The earliest evidence of the feaibility of living anionic polymerization of MMA was provided by Rembaum and Szwarc in 1956.[18] They demostrated anionic polymerization of MMA in THF at -78 °C using sodium-naphthalenide and sodium-polystyryl as initiators. The polymerization seemed to be completed within seconds but the resulting polymer could not initiate further polymerization of MMA or styrene. This was explained as due to rapid self-termination of the PMMA chains caused by migration of the ester -CH_3 group to the carbanionic center.

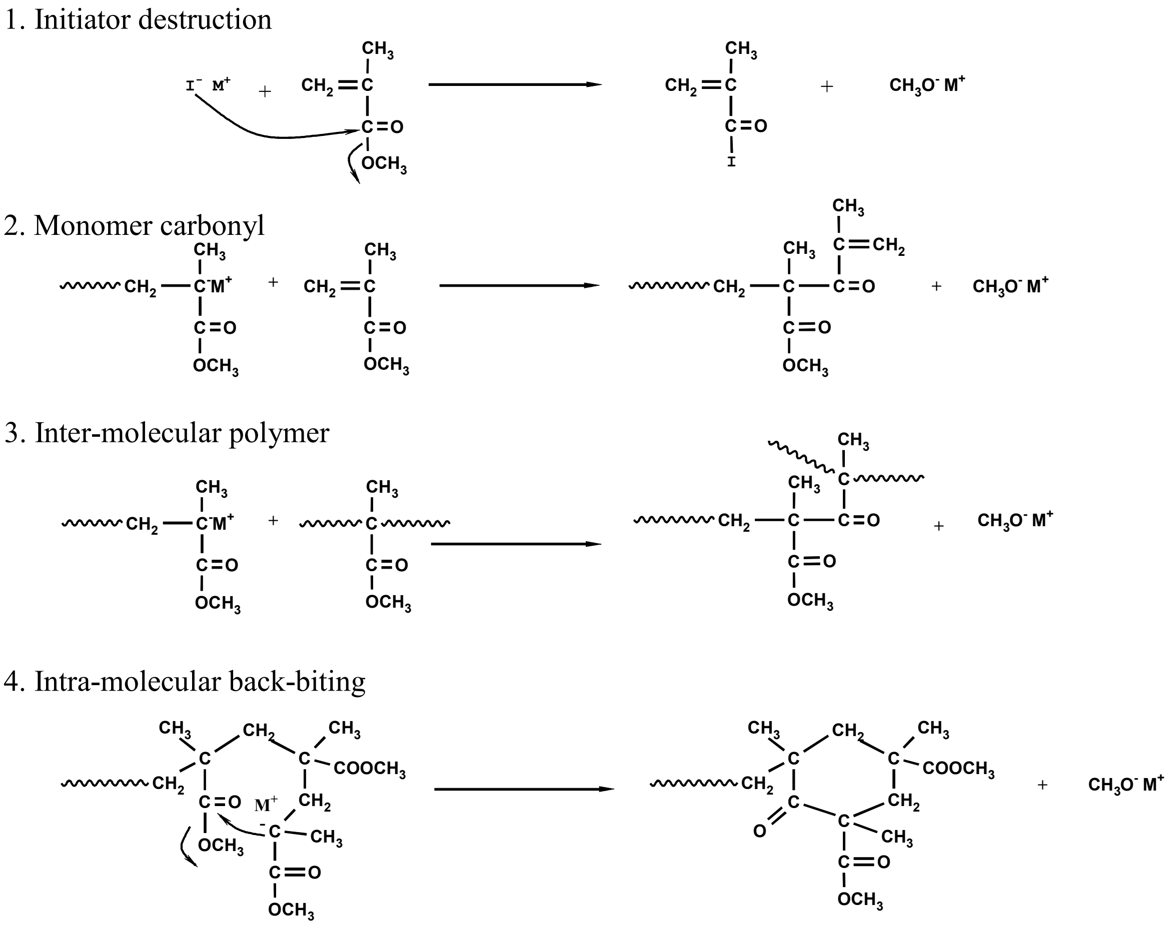
Shortly thereafter, Fox et al reported synthesis of stereospecific and crystalline PMMA by anionic polymerization of MMA in dimethoxyethane at -78 °C using fluorenyl lithium as initiator.[19] Following this work, Glusker et al demonstrated the partial living character of anionic polymerization of MMA when initiated by flourenyl lithium in toluene, within a temperature range of -50 to -78 °C.[20] The absence of termination was proved by formation of radioactive PMMA on quenching the polymerization with radioactive tritiated acetic acid. However, a very broad molecular weight distribution of the PMMA was obtained. Though the initiator disappeared fast, the active species did not propagate to produce any high molecular weight polymer. This was attributed to the formation of pseudo-terminated low molecular weight cyclized species that was reluctant to propagate any further.

Anionic polymerization of MMA using *n*-BuLi as an initiator in toluene was reported by Wiles and Bywater.[21] Upon polymerization at -30 °C, an appreciable amount of the monomer was consumed very rapidly. An examination of the reaction product revealed a broad molecular weigth distribution and the presence of a hexane soluble fraction of molecular weight of 500-800. It was found that almost 60 % of the initiator was lost and did not participate in initiation, which was attributed to reaction of *n*-BuLi with the ester group of MMA. With diphenylhexyllithum, virtually no methoxide was formed in the initial period when the low molecular weight polymer was produced.

1.2.1. Drawbacks:

1.2.1.1. Secondary reactions :

Anionic polymerization of methacrylates suffers from serious limitations due to side-reactions involving the ester group.[11] Solvation of the cation by the ester group of the monomer makes the latter more susceptible to nucleophilic attack by a base.



Scheme 1.1: Secondary reactions in methacrylate polymerization

Nucleophilic attack at the ester carbonyl by the initiator and propagating anion as well as intramolecular back-biting reaction by the propagating chain end at the antepenultimate ester group resulting in cyclic-ester formation are some of the significant termination and transfer pathways. Most of these side-reactions, as shown in scheme 1.1, were proposed by Schreiber[22] and Goodes.[23] Many research groups have reported occurrence of such side-reactions while studying anionic polymerization of MMA.[20-27] Based on IR results, it has been suggested that the major secondary reaction is intramolecular back-biting involving the attack of the propagating enolate anion to the antepenultimate ester group, resulting in a cyclic β-keto ester formation. Glusker also reported similar intramolecular cyclization of the active chains.[20a,b] An intercept in the first-order time-conversion plot was caused by rapid consumption of monomer in the initial period and formation of a peusdo-cyclised product, that slowly expelled methoxide ion forming the cyclic ester.

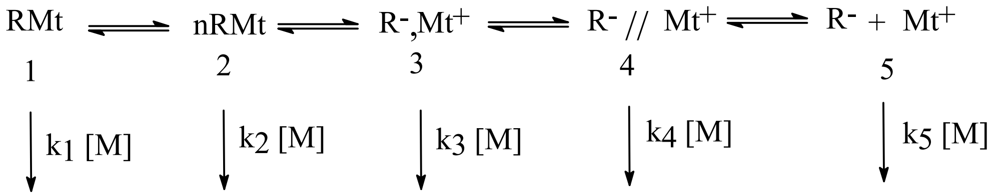
Anionic polymerization of MMA using *n*-BuLi as initiator was reported to be complicated by nucleophilic attack of the initiator at the ester group of the monomer or polymer backbone[21,24] resulting in the formation of significant amount of lithium-methoxide in the system. Kitayama et al polymerized deuterated MMA using undeuterated *n*-BuLi as initiator and they observed by NMR spectroscopy that the polymer chains had butylisopropenyl ketone unit.[25] This led them to conclude that the *n*-BuLi attacked the ester group of the polymer chain. However, such side-reactions were largely avoided using sterically hindered initiators e.g. diphenylhexyllithium (DPHLi).[27,30] MMA initiated by DPHLi as initiator led to broad unimodal distribution, unlike in the case of *n*-BuLi initiated polymerization that showed mulitmodal MWD.

However, in polar medium, coordination by the solvent molecules competes with intramolecular solvation and leads to the formation of solvent separated contact ion-pairs. This results in a considerable decrease in the termination and allows a more controlled polymerization with a simpler kinetic pathway.[31,32] PMMA with relatively low MWD was prepared by polymerizing meticulously purified MMA initiated by biphenylide salts of alkali metals in polar solvents like THF or DME at -78 °C.[31]

Termination reactions assume importance at higher temperatures as shown by broadening of molecular weight distributions, deviation from first-order kinetics and generation of alkali methoxide.[33,34] Hence, better control is achieved by employing a low reaction temperature.

1.2.1.2. Ion-pair aggregation:

In anionic polymerization, the propagating carbanions are unassociated ion-pairs **(2),** existing in equilibirum with aggregated ion-pairs **(1),** in hydrocarbon solvents.[35] In polar medium in addition to these two species, one has to consider the intervention of contact ion-pairs **(3)**, solvent separated ion-pairs **(4)** and free ions **(5)**, as shown in scheme 1.2, where M^+ represents a metallic counterion e.g. Li cation. The position of the equilibrium is guided by the structure of carbanion and cation, solvent polarity, and temperature.



Scheme 1.2: Equilibrium between different types of ion-pairs acting as propagating species

Each of these species can participate in propagation during anionic polymerization. However, each of these carbanionic species would be expected to react with the monomer with its own unique rate constant, the free ions reacting the fastest and the aggregates reacting very slow. Thus, the kinetics of propagation becomes complicated due to presence of such multiple active centers. The concentration of free ions in solvents such as ethers used in anionic polymerization is quite small as determined by conductance measurement.[36,37] Yet, these free ions are important as active species because of their exceptionally high reactivity towards monomers.[35] Addition of common ions effectively shifts the equilibrium towards ion-pairs, thus making the contribution of the free ions negligible.

Anionic polymerization of MMA in toluene is complicated by the presence of different kinds of aggregates taking part in the polymerization. However, in polar solvent such as THF, it is known through several kinetic investigations, that the propagating species are externally solvated contact ion-pairs existing in equilibrium with their aggregates and their dynamic equilibrium profoundly controls the molecular weight distribution of the resulting polymer.[11,24,38] Only faster rate of inter-conversion between the different co-existing ion-pairs can lead to a narrow molecular weight distribution.[34] In general, the degree of aggregation in non-polar solvents is more than in polar solvents and the rate of interconversion is also slow. Aggregation is less in case of the bulkier counter-ions as they are expected to offer greater steric hindrance.

Multinuclear NMR studies by Wang et al[39] and VPO studies by Lochmann[40] with α-methyl lithio-isobutyrate as a model for the propagating chain-end confirmed the existence of equilibrium between tetrameric and dimeric species in THF. Steric hindrance in polymeric system leads to existence of externally solvated contact ion-pairs in equilibrium with less reactive dimeric solvated ion-pairs. A slow dynamics between these propagating species leads to increase in polydispersity of the resulting polymer.

1.3. Criteria for living polymerization

Living polymerization is a chain polymerization that occurs in the absence of termination and transfer and the active centers retain the capability of adding to a fresh batch of monomer after the first batch of polymerization is over.[9,41] This enables one to prepare polymers with narrow molecular weight distribution and predictable molecular weight and a variety of architectures e.g. well-defined block-copolymers, chain-end functionalized polymers and star-branched polymers. The following criteria have been proposed and utilized as diagnostic characteristics for a living polymerization system.[2,3,42]

1) The rate of initiation should be higher or equal to the rate of propagation, so that all chains propagate for equal length of time.
2) The polymerization should be free of termination and transfer reactions. For MMA polymerization, this condition is fulfilled at low reaction temperature, polar solvent, bulky initiator, and in presence of special additives.
3) There should exist only one kind of active species, or else the rate of interconversion between the different species should be faster than the rate of monomer addition. This is true for MMA polymerization in presence of additives.
4) The rate constant of propagation should be independent of the degree of polymerization.

1.3.1. Kinetics of anionic polymerization:

Anionic polymerization of a monomer generally involves three major steps,

Initiation: $I^* + M \rightarrow P_1^*$

Propagation: $P_i^* + M \rightarrow P_{i+1}^*$

Termination: $P_i^* + X \rightarrow P_i$

Where, I* is the initiating molecule, P_i^* is the active chain end and P_i is a dead chain.
For a living anionic polymerization, the process should be free of termination and transfer and the rate of initiation is faster or at least equal to i.e rate of propagation i.e. $k_i \geq k_p$. This implies that the active center concentration will remain unchanged throughout the process, i.e. [P*] = constant. Also, the overall rate of polymerization is determined by the rate of propagation. Thus, the rate of polymerization is given by,

$$R = -d[M] / dt = k_p [M]. [P^*] \qquad (1.1)$$

Since, [P*] is a constant,

$R = -d[M] / dt = k_{app}.[M]$, i.e. the rate of polymerization follows a first-order kinetics with respect to the monomer.

Integrating the above equation,

$$\ln[M]_0 / [M]_t = k_{app}.\ t, \quad \text{where } k_{app} = -d\ln[M]/dt = k_{p.} [P^*] \qquad (1.2)$$

Thus, k_{app} is obtained from the slope of the first order plot of $\ln[M]_0 / [M]_t$ vs. t.

Now the number average degree of polymerization is related to the conversion in the following way-

$$\begin{aligned} \overline{P}_n &= \text{(number of monomers reacted) / (number of polymer chains)} \\ &= ([M]_0.\ x_p) / [P] \qquad (1.3) \end{aligned}$$

where [P] is the total concentration of polymer chains, active and dead which is same as the initial initiator concentration = $[I]_0$

$[M]_0$ is the initial monomer concentration and x_p is the fraction converted after a given time.

Now the initial active center concentration for a living process is given by

$[P^*]_0 = K.[P]$, where K is the number of active centers per polymer chain.

Thus, in case of a transfer-free reaction, a plot of $\overline{P}_n$ vs. x_p gives a straight line with slope $= [M]_0/[P]$. Termination will not change the total chain concentration, so a constancy in the slope of $\overline{P}_n$ vs. x_p plot implies absence of transfer reaction.

In case of some quenching of the active centers, the overall active center concentration in the system is decreased , and it is given by

$$[P^*] = f \, . \, [P^*]_0 \qquad (1.4)$$

where f is the initiator efficiency and can be determined from the ratio of the slope of experimental $\overline{P}_n$ vs. x_p plot to that of the theoretical plot.

Polymerization in presence of termination:

Polymerization that occurs in presence of unimolecular termination e.g. intramolecular back-biting, results in a decreases in the active center concentration and can be represented as,

$$d[P^*] / dt = k_t . [P^*] \qquad (1.5)$$

where k_t is the rate constant of termination

Integrating the above we get,

$$\ln[P^*] / [P^*]_0 = k_t . t$$

$$[P^*] = [P^*]_0 . e^{-kt \, . \, t} \qquad (1.6)$$

Substituting this value to [P*] in equation (1.1),

$$-d[M]/dt = k_p . [M] . [P^*]_0 . e^{-kt \, . \, t} \qquad (1.7)$$

Intergration of 1.7 leads to

$$\ln[M]_0/[M]_t = (k_{app}/k_t) (1 - e^{-kt \, . \, t}) \qquad (1.8)$$

Thus, using equation 1.8, the rate constants of polymerization and termination can be determined.

1.4. Strategies for achieving living anionic polymerization of MMA

1.4.1. Use of appropriate reaction conditions :

In case of anionic polymerization of MMA, a judicious choice of reaction conditions is of utmost necessity to suppress the undesirable secondary reactions to a considerable extent. Use of bulky initiator e.g. diphenylmethyl, diphenylhexyl, trityl salts of alkali metals, in polar solvents such as DME and THF, at low polymerization temperatures (< -65 °C), facilitates controlled synthesis of PMMA.[43-46] It was shown by Schulz and Mita that anionic polymerization of MMA in THF at <-65 °C in presence of Na^+ or Cs^+ as counterions proceeded without any significant termination.[32a, 47] The rate of propagation was first-order with respect to monomer and the number average degree of polymerization was a linear function of conversion

1.4.2. Purification of solvents and monomers:

The propagating enolate anions in MMA polymerization are extremely susceptible to protic impurities in the system. Such impurities are to be carefully eliminated in order to prevent quenching of active centers and ensure a perfectly living polymerization.[48] However, commercially available MMA contain considerable amount of alcoholic impurities. Similarly all other ingredients e.g. nitrogen, solvents and additives contain significant amount of moisture which have to be scrupulously removed before the polymerization is performed. McGrath suggested the use of trialkylaluminium for effective purification of alkylmethacrylates.[49] Trialkylaluminium reacts instantly with traces of moisture, alcohol and other protic components. The excess alkylaluminium forms a complex with the carbonyl group of the monomer, which gives a characteristic greenish-yellow color indicating the end-point of impurity titration. The pure monomer is then quickly distilled out under high vacuum. Aluminium alkyls when added in excess may initiate radical polymerization of MMA, and hence after addition of the aluminium alkyl to the monomer, it has to be degassed immediately and distilled fast, in order to prevent prolonged contact and polymerization.

1.4.3. Ligand modified polymerization of alkyl methacrylates :

Several strategies have been followed for accomplishing living anionic polymerization of alkyl methacrylates. To enhance the livingness and enable controlled polymerization, even at higher temperatures, some new methodologies have been adopted that modulates the reactivity of the anionic species by coordination with ligands.[6,7,50] The basic idea of such ligated anionic polymerization is to use suitable ligands that will interact coordinatively with the initiating or propagating ion-pairs and perform the following main functions:

1) perturb the classical slow equilibrium between different ion-pairs aggregates, resulting in new complexation equilibria with faster dynamics between the various ion-pair aggregates and hence leading effectively to a single active species,
2) modulate the electron density around the metal-enolate ion-pairs, thus affecting the stability and reactivity of the propagating anion. This also provides a steric barrier around the ion-pair that helps in minimizing the secondary reactions that lead to backbiting and chain termination.

Various ligands that have been used in conjunction with initiators to influence the equilibrium dynamics of ion-pair aggregates can be classified broadly as, a) σ-ligands e.g. crown ethers, cryptands[51-53], TMEDA[54,55;] b) μ-ligands e.g. alkali alkoxide[40,56-58] halides,[59-63] perchlorates,[64] aluminum alkyls,[65-72] silanolates,[73,74] c) μ-σ dual type, combining the advantages of the former two classes, e.g. amino alkoxides,[75,76] monodentate and polydentate dilithium alkoxyalkoxides.[77-83] Some of the important ligated initiators are discussed in the following paragraph.

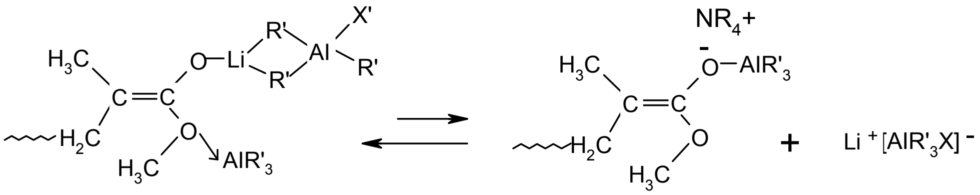
Alkali alkoxides have a stabilizing effect on the active centers in the polymerization of MMA, which results in higher limiting conversion and facilitates preparation of block copolymers.[58] Complexation of LiOBu^t with the ion-pairs decreases both the rate of polymerization and that of intramolecular cyclisation.[57] However, formation of highly stable mixed aggregate with the living dimer, which is in slow equilibrium with the non-aggregated ion-pairs, cause slight broadening of the MWD.

Teyssie and coworkers reported the effect of alkali halides, especially LiCl on the polymerization of alkali methacrylates in THF at -78 °C.[60,63] Preparation of well-defined PMMA with narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n \sim 1.08$) was made possible by addition of LiCl. The effect was attributed to the formation of a μ-complex by the propagating enolate ion-pairs with LiCl, forming mixed aggregates that shifts the classical ion-pair equilibria towards a single active species.[34] However LiCl cannot contribute much in enhancing livingness of the system in a low dielectric medium e.g. toluene/THF (9:1 v/v) mixed solvent. The effect of $LiClO_4$ in controlling the anionic polymerization of acrylates and methacrylates has been observed which functions in a way similar to LiCl and provides excellent control over these polymerization processes in both THF upto -20 °C as well as in toluene/ THF (9:1 v/v) mixture solvent of low polarity.[64a]

Chelating agents like crown ethers sterically hinder the propagating center thus reducing the extent of side-reactions. Intramolecular solvation of the cation favours the secondary reaction such as back-biting and hence external chelation reduces such termination reactions by decreasing intramolecular solvation. Living polymerization of MMA and *tert*-butylacrylate (*t*BA) was performed in presence of DB-18-CE-6 crown ether using diphenylmethylsodium in toluene at temperatures as high as 0 °C.[53] Also statistical copolymerization of MMA and *t*BA proceeded without any side-reactions in presence of DB-18-CE-6 at -78 °C.[52] Along the same line, cryptand K211-Li^+ pair has also been found to work efficiently in inducing an extremely low polydispersity of living PMMA in THF at -78 °C.[84]

Alkoxyalkoxide belong to family of ligands, which possess the properties of both alkali alkoxides and crown ethers, with the lithium alkoxide moiety functioning as the μ-type of coordination site and the polyether component as σ-type. Such μ/σ-dual type ligands are exceptionally effective in reacting with highly aggregated lithium ester enolate, thus inducing a fast-exchanging ligation equilibrium. This leads to an effectively single active species resulting in narrow molecular weight distribution of a variety of alkyl methacrylates and hydrocarbon monomers.[77-80] Anionic polymerization of MMA performed in the presence of polydentate dilithiumalkoxides in THF resulted in polymers of narrow MWD and high initiator efficiency at temperatures upto 0 °C.[83]

Aluminium alkyls form 'ate' complexes with *t*-BuLi and these serve as effective initiators for MMA polymerization in toluene at -78 °C.[65-67] These complexes provide highly syndiotactic polymer with narrow molecular weight distributions and high conversion in a period of 24 h. Controlled anionic polymerization of MMA at ambient temperatures in toluene was achieved using sterically hindered aluminium alkyls.[68] Later, the effect of tetraalkyl ammonium halide on living anionic polymerization of MMA was studied in presence of aluminium alkyls.[69-71] The living anionic polymerization of MMA initiated by ethyl α-lithioisobutyrate (EiBLi) in toluene at or below -20 °C was very fast compared to that in absence of the salt. Highly syndiotactic PMMA of molecular weight upto 250,000 and $\overline{M}_w/\overline{M}_n$ of 1.2 could be synthesized. Partial dissociation of enolate complexed by NR_4X/AlR'_3 (structure **1**, scheme 1.3) into more reactive ester enol aluminate (structure **2**), possibly leads to the observed effect. With this new initiating system, beside acrylate homopolymers, random and graft copolymers can be synthesized.



Scheme 1.3. Equilibrium between active species in anionic polymerization of MMA in presence of NR_4X/AlR'_3

Recently, Teyssie et. al. introduced a new class of μ-ligated initiator formed by association of BuLi and lithium silanolates. It has been found to be very effective in promoting living polymerization of MMA in toluene at 0 °C.[73,74] PMMA of molecular weight upto 100,000 can prepared with a very narrow MWD (~1.1). The stereoregularity of PMMA is extremely high, i.e. 95 % isotactic.

Aluminim porphyrins e.g. (tetraphenylporphinato)aluminium chloride, alkoxide, or carboxylate serve as excellent initiators for living polymerization of a wide variety of monomers, specialy epoxides. MMA polymerization were initiated by exposure to visible light yielding PMMA of narrow molecular weight distribution ($1.06 < \overline{M}_w / \overline{M}_n < 1.2$) and in quantitative yield.[85,86]

To summarize, implementation of these methodologies has enabled the synthesis of a huge range of new products namely monodisperse alkyl methacrylate homo and random copolymers, diblock copolymers between different methacrylates as also with styrene and dienes, triblock, star-diblock copolymers, macromonomers and telechelics.

1.4.3.1. Kinetics and mechanism of ligated anionic polymerization of MMA:

Kinetics of anionic polymerization of methacrylates, particularly MMA is complicated by presence of multiple active species (scheme 1.2), each of which can participate in propagation by reacting with monomer at a certain rate. The equilibrium that exists between different types of ion-pairs usually shifts towards the right in more polar solvent, i.e. towards more dissociated species, and towards left in non-polar medium, i.e. towards associated species, with different degrees of aggregation depending upon the dielectric of the medium. For alkyl lithium compounds, the degree of association also depends on the steric environment around the coordinating metal center as well as on temperature. Higher temperatures lead to greater association.

Kinetics in non-polar solvent:

Anionic polymerization of MMA in toluene initiated by alkyllithium compounds is characterized by broad and multimodal molecular weight distributions and termination reactions even at lower temperatures.[11,12,21,26-29] Initiation of MMA at -30 °C with *n*-BuLi resulted in 60 % loss of initiator due to attack on ester carbonyl leading to formation of methoxide.[21b, 27] During propagation also, methoxide may be released in two ways - due to cyclization of the active chain ends or interaction of polymer chains with the ester functionality of MMA. Kinetics showed a complex variable dependence of rate on monomer and initiator concentrations and no direct correlation between the observed molecular weight and the ratio of monomer to initiator. In addition, fractions of polymer having different molecular weights were found to have different tacticities. It was assumed that the LiOMe in the system associates with the propagating ion-pairs and these complexed species participate in propagation along with the uncomplexed but with a different rate and stereospecificity. Upon addition of methoxide externally, the rate of polymerization increased yielding polymers with higher isotacticity.

Using a bulkier initiator, e.g. adduct of alkyllithium with diphenylethylene which gives diphenylhexyllithium, the terminations could be minimized to a considerable extent.[27] Experiments revealed only 10 % loss of initiator due to reaction with ester group and the loss in even greater at 0 °C. Quite contrary to the expectation of a complex mechanism arising out of chain-end association in non-polar solvent, kinetic results of MMA polymerization in toluene using DPHLi as initiator at -78 °C revealed first-order plot for monomer conversion (upto 70% conversion) as a function of time. Expecting an equilibrium between predominantly aggregated ion-pairs and the unassociated species where only the latter reacts with the monomer, the rate of polymerization should have shown a fractional dependence on the active center concentration, i.e. an order of 1/n for a degree of association of 'n'. The first-order dependence was explained as due to the fomation of cross-associated species between the ion-pairs and the Li-methoxide formed in the system. This cross-associated species decreases the aggregation and is the predominant active species in solution that is capable of reacting with the monomer.

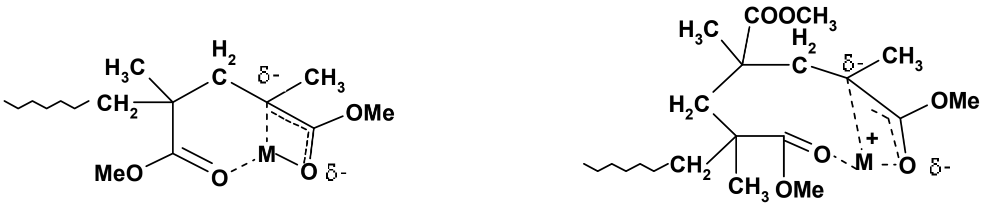
Unlike anionic polymerization of MMA in non-polar solvents which suffers from a lot of complexities, the polymerization of *tert*-butylmethacrylate (*t*BMA) in toluene with Li counterion was reported to be a well-controlled process following a first-order kinetics with respect to monomer as well as initiator. A linear plot of $\overline{P}_n$ vs. conversion indicated absence of transfer reaction and rather low molecular weight distributions of the polymers were obtained at higher conversions.

Kinetics in polar solvent:

Unlike the complexities associated with anionic polymerization of MMA in non-polar solvent, polymerization in a polar solvent proceeds with much simpler kinetics. Wenger reported that $PMMA^{-}Li^{+}$ remained living in THF at -78 °C for more than 40 h, which was proved by polymerization of a fresh batch of monomer, added to the living solution.[87] It was not until 1973 that kinetic experiments on MMA polymerization in THF were reported by Lohr et al[32a, 88] and Mita et al[47] using Na^{+} and Cs^{+} as counterions. They showed that the reaction proceeded in an ideal way at low temperatures (~-75 °C) yielding polymers with narrow molecular weight distribution. The initiation was fast compared to propagation, and the polymerization followed first-order kinetics with respect to the monomer concentration, implying absence of termination. The number average degree of polymerization was proportional to conversion, indicating a transfer-free polymerization. Consequently Lohr and Schulz obtained narrow molecular weight distributions.

Though conductance measurements revealed low dissociation constants of the ion-pairs, dependence of rate constants on the concentration of living ends clearly proved that both the anions and ion-pairs participated in the propagation. Both kinetic[24] and conductance studies[32a),88] established that at least two types of species, free ions and ion-pairs, were involved in anionic polymerization of MMA in THF with alkalimetal counter at temperatures < -75 deg. C. Subsequently, all studies were carried out in the presence of common-ion salts e.g. cesium triphenylcyanoborate, sodium tetraphenylborate, potassium tetraphenylborate and lithium tetraphenylborate, for cesium, sodium, potassium and lithium ions respectively. The half-lives for these polymerization were in the order of seconds and were almost 1000 times faster than the corresponding polymerization in toluene.[13]

Investigated was done into the kinetics of propagation within the temperature range of -100 °C to 20 °C using cumylcesium and benzyl-oligo-α-methyl styryl sodium as initiators in presence of common-ion salt.[89,90] Termination was significant at higher temperatures but linear first-order plots were obtained at lower temperatures implying termination free reactions. Linear $\overline{P}_n$ vs. x_p plots were obtained upto 20 °C indicating absence of chain transfer reactions. Molecular weight distributions were narrow, in the range of $1.01 \leq \overline{M}_w / \overline{M}_n \geq 1.1$. Linear Arrhenius plots were obtained, and were identical for both Cs^+ and Na^+ counter ions, indicating the presence of one kind of ion-pair, unlike kinetics of styrene polymerization which showed curved Arrhenius plot due to presence of temperature dependent equilibrium between contact and solvent separated ion-pairs. The observation in case of MMA polymerization was explained by assuming that the counter-ion was solvated intramolecularly by the penultimate or antepenultimate ester group of the polymer chain as shown in structures **1** and **2** in scheme 1.4 (where M: Na^+ or Cs^+)



1

2

Scheme 1.4: Intramolecularly solvated contact ion-pair

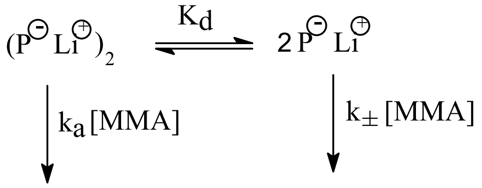
However, the hypothesis of intramolecular solvation could not explain the higher rate constants, which was almost identical for both the counter ions, obtained in DME having higher solvating power.[30] The existence of externally solvated contact ion-pairs was proposed where the true structure of the ion-pair was somewhere in between **3** and **4** (scheme 1.5), depending upon temperature, solvent and counter ion. Kinetic study of MMA polymerization in THF was later conducted using different counter-ions as well as Na^+ ion complexed by bicyclic cryptand 222 (Na^+, 222).[33,91] Linear Arrhenius plot implied presence of one type of active species. A distinct dependence of rate constants on the counter-ion size except for Cs^+, Na^+, K^+ was observed indicating that the active species were contact ion-pairs, so that larger inter-ionic distance for larger cations favored charge separation in the transition state, thus increasing the reaction rate. Based on these kinetic results, the structure proposed for the active centre was a contact ion-pair peripherally solvated by THF molecules (scheme 1.5, structure **3**). Deviation of Na and K from the straight line indicated that the interionic distance were larger than those expected from crystal radius due to peripheral solvation, that spread the charge over larger area. In case of Li, a strong p-π overlap led to a very tight bond between the anion and cation, thus decreasing the rate of polymerization.

3 **4**

Scheme 1.5: Externally solvated contact ion-pair

Existence of ion-pair aggregates:

Though the linear Arrhenius plot suggested the presence of one active species, the peripherally solvated ion-pair is not the only active species present in the system. Studies conducted at higher initiator concentration using metalloesters (alkali ester enolate) as initiators in THF[92] showed a strong dependence of rate constants on the active centre concentration. This effect was attributed to the existence of ion-pair associates of lower reactivity, in equilibrium with non-associated ones, as shown in scheme 1.6.



Scheme 1.6 : Propagation through ion-pair and its aggregate

A linear dependence of rate constant of polymerization on the inverse of square root of active chain end concentration was explained according with the mechanism shown in the above scheme and the kinetic equations 1.9 to 1.13.

$$k_p = \alpha . k_{\pm} + 1/2.(1-\alpha).k_a = 1/2\ k_a + (k_{\pm} - 1/2.ka) .\alpha \qquad (1.9)$$

where fraction of non-associated ion-pair, α is given by,

$$\alpha = \frac{[P^*_{\pm}]}{[P^*]} = \frac{(1 + 8\ K_d . [P^*])^{1/2} - 1}{4\ K_d . [P^*]} \qquad (1.10)$$

For $k_a . [(P^*_{\pm})_2] << k_{\pm} . [P_{\pm}^*]$

$$k_p = \alpha . k_{\pm} = k_{\pm} \cdot \frac{(1 + 8\ K_d . [P^*])^{1/2} - 1}{4\ K_d . [P^*]} \qquad (1.11)$$

$$\text{For} \quad K_d . [P^*] >> 1 \ , \quad k_p = \frac{k_{\pm}}{(2\ . K_d . [P^*])^{1/2}} \qquad (1.12)$$

$$\text{For} \quad Kd . [P^*] << 1 \ , \quad k_p = k_{\pm} - (2 . k_{\pm} . Kd . [P^*]) \qquad (1.13)$$

Kinetics studies of MMA polymerization in THF at -65 °C with Li^+ as counter-ion revealed a change of reaction order with respect to active centers from 0.75 to 0.5 for [P*] increasing from 10^{-4} to 2.10^{-3} mol/L, implying the presence of an approximately equal amount of associated and unassociated species.[34] The order of reactivity for MMA polymerization by ion-pairs is $Cs^+ \sim Na^+ \sim K^+ >> Li^+$, in both THF and glyme, over a wide range of temperature. This is consistent with the fact that contact ion-pairs are the predominant active species in solution[38] and not the solvent separated ones, which would have led to reverse order of reactivity.

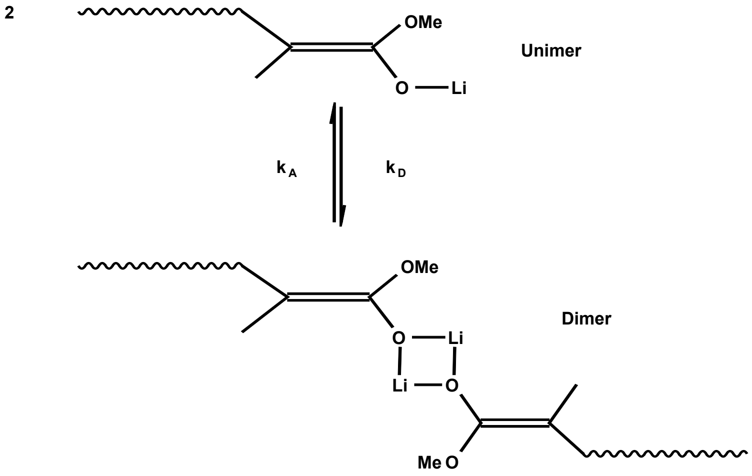
Viscosity measurements on living and terminated $PMMA^-Li^+$ chains in THF confirmed the existence of aggregated chain ends.[34] An increase in the fraction of aggregated chain was observed with increase in chain end concentration. ^{13}C and ^7Li measurements[39] in conjunction with vapour pressure osmometry measurements[40] with lithiated isobutyrates as models for active chain ends indicated an equlilibrium between dimers and tetramers at -78 °C, and as tetramers at room termperature. Steric strain exerted by polymers leads to a unimer to dimer equilibrium. The extent of aggregation is less in case of polymerization of *t*-BMA at -65 °C, possibly due to steric hindrance by the bulky ester group., and at ~-30 °C, the fraction of aggregates is negligible. However, for PtBA, tendency to aggregate is stronger due to lesser steric effect.

The tendency to aggregate slightly increases in the order

t-BMA < *t*BA < MMA

and the rate cosntants of polymerization strongly increases in the order,

*t*BMA < MMA << *t*BA



Scheme 1.7 : Unimer to dimer equlibrium of enolate anion

Association of the living chain ends has a tremendous influence on the molecular weight distribution of the resulting polymer.[34] In order to get a narrow polydispersity, the rate of interconversion between the non-aggregated and aggregated species has to be faster than the rate of monomer addition, so that the different active species become indistinguishable to the monomer. Assuming comparable rates of interconversion between ion-pairs in all the above monomer sytems, the rate of polymerization in THF at -65 °C being the slowest for *t*BMA, leads to the narrowest MWD (~1.1), that for MMA being ~1.3 and for *t*BA, the MWD is the broadest (~7.9).

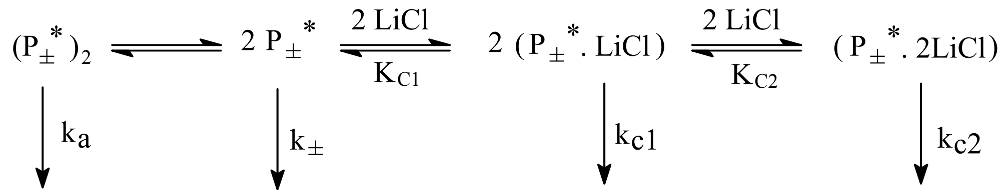
Effect of additives

Effect of alkali-alkoxides: Lochmann et al prepared α-lithio isobutyrate esters as models for the propagaing centre in MMA polymerization, and studied their interaction with alkali alkoxides.[40,56] In absence of the added alkoxide, the oligomers were found to undergo spontaneous self-cyclisation, which was higher in THF than in toluene. The rate of cyclisation dropped by addition of sodium *tert*-butoxide.[57]

Addition of lithium *tert*-butoxide markedly decreased both k_p and k_c, i.e. rate constant of propagation and cyclisation respectively of MMA polymerization in THF at 20 °C.[57,93] The effect on termination was ten times more pronounced, indicating a lower propensity towards cyclisation of the enolate-alkoxide adduct compared to free enolate. A slower equilibrium between free ion-pairs and adducts led to an increase in MWD of the resulting polymer.

Effect of aluminium alkyls: The kinetics of anionic polymerization of MMA was reported in toluene with alkyllithium initiators in presence of aluminium alkyls.[94] The polymerization was seen to be living but deviated from first-order kinetics and the polymers had broad molecular weight distribution (MWD > 1.5). On the basis of ^{13}C [95] and *ab initio* quantum chemical calculations[96] the structure of the active species was described as an ester enol-aluminate in equilibrium with its dimeric associate. The reason for such ill-controlled polymerization was the formation and precipitation of coordinative polymer network,[95] that could be suppressed by addition of Lewis bases, e.g. esters and crown ethers, resulting in well controlled polymerization with linear first-order time-conversion plot and narrow molecular weight distribution (MWD < 1.3) PMMA upto 0 °C.[69] In an alternative approach, the network formation was avoided by addition of tetraalkylammonium halides in conjunction with aluminium alkyls.[97] Using EiBLi in presence of these complexes as initiator for MMA polymerization in toluene at 0 °C, quantitative monomer conversion and narrow unimodal molecular weight distribution PMMA were obtained. Kinetic study[70] showed that the reaction followed a first-order kinetics upto -20 °C, with respect to $[P^*]_0$, $[MMA]_0$ and $[NR_4^+ [Al_2Et_6X]^-]$, but at low concentrations of complex, the first-order plots showed curvature. The molecular weight distribution of the polymers was bimodal during the initial period. This was explained by equilibrium between two types of active species (**1** and **2** in scheme 1.3) which slowly established during polymerization. Decreasing the temperature had a similar effect on the kinetics as decreasing the concentration of the complex.

Effect of LiCl: The discovery of the effect of LiCl in controlling the anionic polymerization of acrylates and methacrylates[59,60] was a significant achievement in the field of polymer science. MMA polymerization in THF at -78 °C in the absence of LiCl yielded polymers with MWD of ~ 1.2 with an initiator efficiency of 0.66, whereas, in presence of one equivalent of LiCl the MWD decreased to 1.09 and initiator efficiency rose to 0.85. Increasing the number of equivalents of LiCl improved the situation even further. Other salts, such as $Li(Ph)_4B$, LiF, and LiBr did not have any influence in controlling MMA polymerization. In case of MMA polymerization in THF at -78 °C using α-methylstyryllithium as initiator, the MWD was < 1.1 at all conversions in presence of LiCl in equimolar quanity w.r.t. the initiator.[60] This lowering of polydispersity was explained by assuming that the equilibrium between the free ion-pairs and LiCl-complexed ion-pairs was faster than that between free and associated ion-pairs in absence of the salt. The rate of interconversion between different active species being faster than rate of polymerization, the monomer adds effectively to a single active species, thus leading to decrease in polydispersity. However, MMA polymerization in low polarity medium[60,98] was not much influenced by addition of LiCl, as evidenced from non-linear time-conversion plots and broad MWD at lower conversions. A study on the effect of LiCl on the kinetics of MMA polymerization in THF at -65 °C with lithiated methyisobutyrate as initiator[34] showed that rate constant of polymerization increased initially for $R=[LiCl]/[P^*] < 1$, and then decreased gradually to 50 % of the initial value for $R=10$. This was explained on the basis of formation of at least two new types of species of differing reactivity, by formation of 1:1 and 2:1 adduct of the living chain ends with the LiCl (scheme 1.8). Assuming that $k_a << k_\pm \approx k_{c1} >> k_{c2}$, the maxima can be explained as due to formation of the 1:1 adduct followed by less reactive 2:1 adduct at R>1.



Scheme 1.8 : Ion-pair equilibrium in presence of LiCl as ligand

No effect of LiCl on the rate of termination was observed. It was also found that LiCl did not have any significant effect on the stereochemistry of polymers formed, no matter what solvent was used. This indicates that the complexation of LiCl to the active species is not tight enough and hence does not provide sufficient steric hindrance to influence the stereoselectivity of the propagation. NMR and quantum mechanical studies of interaction of LiCl with methacrylate active centers using model compounds are in agreement with the kinetic studies.[120,121]

Influence of $LiClO_4$: Recently kinetics of MMA polymerization was studied in presence of $LiClO_4$ in 10:1 molar ratio with respect to diphenylhexylltihium as initiator, at –20 °C in THF.[64b] First-order kinetics free of termination and transfer was observed at different active center concentrations. Narrow and unimodal molecular weight distribution of polymers were observed at all conversions. A reaction order of 0.5 was obtained with respect to the active centers, which implied that the $LiClO_4$-complexed associated ion-pairs were in equilibrium with the non-associated ones. The same order was observed in the absence of any additive. This led to the conclusion that $LiClO_4$ did not bring about disaggregation of the active centers, but by complexing with the ion-pairs, established a faster equilibrium between the mixed complexes and their aggregates leading to a decrease in the MWD. Also, the rate of termination was unperturbed even in presence of excess $LiClO_4$.

The effect of $LiClO_4$ concentration on the kinetics was studied by performing the polymerizations at -20 °C in THF using different ratios of $LiClO_4$ to the initiator, i.e. $r = [LiClO_4]/[I]_0$ was varied from 0 to 10 for an initiator concentration of $[I]_0=4.8x10^{-3}$ m/L. Linear first-order plots were obtianed in all cases but the initiator efficiency first decreased from 80% to 60% for $r \leq 3$ and then increased to 100% for $r \geq 5$. This was attributed to the formation of unreactive mixed aggregates at lower values of r (≤ 3) which later breaks up into 1:2 and 1:1 mixed complexes with progressive increase in the concentration of $LiClO_4$. This also explained the steady decrease in the apparent rate constant of polymerization i.e. k_{app} with increase in ' r ' that finally reached half the initial value at r=10. It may be recalled that in the kinetic study performed in presence of LiCl at -65°C, Kunkel et al observed an initial increase and then a decrese in the rate of polymerization with increase in LiCl concentration.[34] The different observation in case of $LiClO_4$ system was possibly due to the use of higher temperature (-20 °C) for polymerization at which aggegation phenomenon is thermodynamically more favored. Hence addition of $LiClO_4$ to the enolate ion-pairs results in formation of predominantly mixed aggregates that may dissociate into 1:1 and 1:2 mixed complexes.

1.5. Polymer architectures via anionic polymerization

Living anionic polymerization proceeds in the absence of chain termination and transfer reaction and hence enables one to prepare polymers with well-defined structures and low compositional heterogeneity. Such controlled polymerization technique provides a versatile method for preparation of a variety of polymeric architectures, e.g. block, graft, star, functional polymers and macromonomers, with control over a wide range of composition and structural parameters including molecular weight, polydispersity, copolymer composition, stereochemistry, branching and chain-end functionality.

1.5.1. Block Copolymers

1.5.1.1. Introduction:

Block copolymers are one of the most important polymeric materials in technological applications and theoretical research, the synthesis of which was greatly stimulated by the development of living anionic polymerization techniques. They are linear sequences of blocks where each block contains monomer units that are chemically identical to those of the same block but different from those of the adjacent blocks either in chemical composition or stereochemistry. Thermodynamically incompatible blocks lead to micro-phase separation forming domains and this results in some useful properties in bulk and in solution.[101-104] Block copolymers are widely used as compatibilizers, dispersing agents and thermoplastic elastomers. They are synthesized by various methods such as condensation polymerization, anionic and cationic polymerization, Ziegler-Natta, group transfer polymerization (GTP) and living free radical methods.[105] Living anionic polymerization provides the best technique for preparing block copolymers with definite molecular weight of the blocks and narrow MWD.[101,105-107] Table 1.1 shows the common shorthand notations for representing block copolymers, where letter represents a block of the corresponding monomer.

1.5.1.2. Synthesis of block copolymer

Michael Szwarc, who had introduced the concept of living polymerization[9] in 1956, illustrated an important aspect of living polymerization, i.e. synthesis of block copolymers by sequential monomer addition. Stability of the carbanionic chain ends in living polymerization is responsible for successful synthesis of block copolymers.[109]

Table 1.1: Block copolymer notations

Polymer structure	Type of block	
	Notation	**Copolymer**
-AAAAAAAA-BBBBBBBB-	A-B	Diblock
-AAAAAAAA-BBBBBBBB-AAAAAAAA	A-B-A	Triblock
-AAAAAAAA-BBBBBBBB-CCCCCCCC-	A-B-C	Triblock
-AAAA-BBBB-(AAAA-BBBB)$_n$-AAAA-BBBB	(A-B)$_n$	Multiblock
(AAAAAAAA-BBBBBBBB)$_n$-X	(A-B)$_n$-X	Star

This becomes possible when impurities are absent in the solvents and monomers and in the absence of chain-terminating side reactions. The order of monomer addition is also an important factor that has to be taken into consideration before preparation of a block copolymer. In general, a carbanionic chain end formed from one monomer will initiate another monomer only when the corresponding carbanion of the second monomer is of higher or equal stability as the original carbanion.[108] The pKa values of the conjugate acids of the carbanion determine the relative stability of the carbanions. Monomers having higher pKa value of the conjugate acid are capable of initiating a monomer with an equal or lower pKa value of the conjugate acid. Thus, to prepare a styrene-methylmethacrylate block copolymer, styrene (of pKa=43) has to be polymerized first, followed by addition of MMA (pKa=30-31), to form the second block. The enolate from MMA cannot initiate polymerization of styrene. Due to similar reasons, enolate from MMA can initiate ring-opening polymerization of ethylene oxide but the reverse cannot take place.

However, for preparation of triblock copolymers, three methods are generally employed :

1) three-step sequential addition of monomers, 2) two-step sequential monomer addition followed by coupling, 3) difunctional initiation and two-step sequential addition.[101,105-110]

Using hydrocarbon monomers: Styrenes and dienes are the most important type of hydrocarbon monomers that undergo living alkyllithium-initiated polymerization in a controlled manner over a wide range of useful temperatures to form well defined block copolymers. Polymerization of dienes initiated by alkyl-lithium compound in hydrocarbon solvents lead to formation of elastomeric block segments with low glass

Table 1.2: Diblock and triblock copolymers by living anionic polymerization technique

A	B	C	Initiator	Solvent	Ref.
Methyl methacrylate (MMA)	*tert*-Butyl acrylate (*t*BA)		LiαMeSty	THF	63
*t*BA	MMA	*t*BA	$TPBLi_2$	THF	115
MMA	Ethylene oxide	MMA	Disodium salt of PEO	THF	117
Ethylene oxide	MMA		$Ph(Me)_2C^-K^+$	THF	118
Styrene	Ethylene oxide		*sec*-BuLi Cumyl potassium	C_6H_6/DMSO THF	119
Ethylene oxide	Styrene	Ethylene oxide	Potassium napthalene	THF	120
Styrene	TBA		LiαMeSty	THF	121
*t*BA	Styrene	*t*BA	BuLi/DPE Lithium naphthalene	THF	115 121
tert-Butyl methacrylate (*t*BMA)	Ethylene oxide		$Ph_2CH^-K^+$	THF	122
Ethylene oxide	TBMA		"	"	122
Ethylene oxide	TBMA	Ethylene oxide	"	"	122
*t*BMA	Ethylene oxide	*t*BMA	"	"	122
Styrene	Butadiene	MMA	BuLi	THF	123
Dimethyl -siloxane	2-Vinylpyridine		ethyl-3-lithio-propyl acetaldehyde acetal	THF	124
Styrene	2-VP	MMA	*sec*-BuLi	THF	125
2-(dimethyl amino) ethyl methacrylate	Propylene Oxide	DAEM	Potassium alcoholate of polypropylene oxide	THF	126
Styrene	Butadiene	Isoprene	sec-BuLi	Benzene, THF	127

transition temperatures, that are useful as elastomers and adhesives[105-109,111-113] and forms thermoplastic elastomers when block-copolymerised with styrene.

Using Polar monomers: Anionic polymerization of polar monomers suffers from several limitations arising out of inherent side-reactions involving the initiator, propagating chains and monomer. Either the polar functionality, e.g., an ester, nitro, carbonyl, etc or the acidic proton adjacent to this polar function is responsible for these undesirable side-reactions, thus resulting in poorly controlled polymerization. Polymerization of alkyl methacrylates is controlled by choosing a less reactive and hindered initiator and a low reaction temperature and polar solvent.[13,114] Block copolymers of styrene and alkyl methacrylate have been successfully prepared by end-capping styryl chain ends with 1,1'-diphenylethylene before addition of the methacrylate monomer.[115] Block copolymers of MMA and *t*BA have been prepared with good control over block length and molecular weight distribution by using LiCl as additive in THF at -78 °C.[63] Heterocyclic monomers such as oxiranes, thiiranes, cyclic siloxanes and lactones can undergo anionic polymerization to give block copolymers with controlled structures.[116] Table 1.2 shows some examples of the types of block copolymers that can be prepared by anionic polymerization of polar, vinyl and heterocyclic monomers.

1.5.2. Star-branched polymers

1.5.2.1. Introduction :

Branched polymers are high-molecular weight polymers having more than two chain ends. Each molecule consists of atoms or small multifunctional units called the branch point or junction points, from which the long chains or branches emanate. If a branched polymer has only one such junction point, to which several linear chains are linked together at one end of each chain, it is a star polymer.[128-130] Branching leads to a dramatic change in properties of a polymer compared to its linear analogue, since it affects the physical properties, crystallinity, solution and melt viscosities of the polymers.[128-132] However, in case of a polymer having random branching, it is quite difficult to understand and predict the relation between the structure and the properties exhibited by the polymer. Thus a clear understanding of the effect of branching on the polymer properties is possible only when the structure of the polymer is well-defined with respect to the number of branches, branch length, distribution of the branches and distance between two branch points.[133]

Beyond regular star polymers, various other kinds of star-shaped macromolecules[134] have attracted interest and have lead to specific applications:

1) Heterostar copolymers, in which the cores carry equal numbers of branches of two kinds, differing by chemical nature as well as average length.

2) Star-block copolymers, in which each branch is constituted of two homopolymeric blocks of different chemical nature, usually exhibiting different properties.
3) Functional star polymers in which well-defined functionalities are located at the outer end of each branch;

The following portion of the chapter will discuss the methodologies developed to prepare regular star-branched polymers, where all arms exhibit low degrees of compositional heterogeneity with respect to molecular weight and distribution.

1.5.2.2. Synthesis of star polymers:

Living polymerization, which proceeds in the absence of termination and transfer, is the ideal method for the synthesis of regular star-branched polymers and copolymers having well-defined structures with predictable molecular weights and narrow molecular weight distributions. Most star polymers have been synthesized anionically, although recent attempts by cationic polymerization,[135,136] by group transfer polymerization[137,138] (GTP) and by controlled radical polymerization[139] methods have been successful.

Several routes can be followed to synthesize star polymers[140-142] by anionic polymerization method: either living polymeric chains are made first and used to generate the core; or the core is made first and it subsequently serves as a plurifunctional initiator to grow the arms from the core; or a three-step method combining the advantages of both procedures.

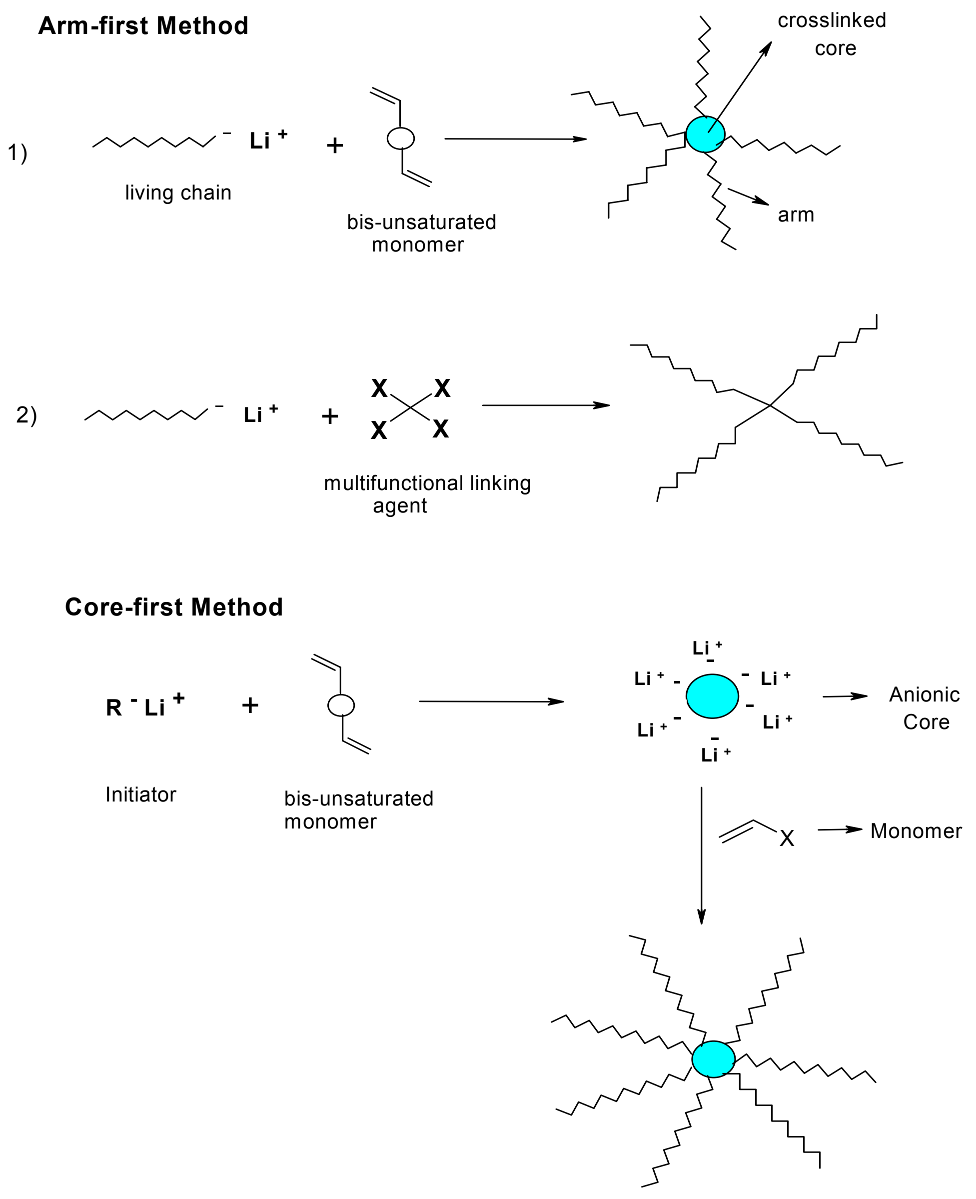
1) Arm-first methods:

In this method, living polymer chains of known length and low polydispersity serves as a precursor. The active sites located at polymeric chain ends can be used in two different ways,

1) they can be reacted with a compound carrying a number of appropriate reactive functional groups, whereupon the living chains get chemically linked to the functional reagent,
2) they can be used to initiate polymerization of a small amount of an appropriate bis-unsaturated monomer, thus leading to the formation of small crosslinked cores.

Using functional linking agents:

When living anionic polymer chains are deactivated stoichiometrically by a plurifunctional reagent (an electrophilic compound), chemical links are formed between



Scheme 1.9: Methods of synthesis of star-branched polymers

the precursor chains and that reagent.[101,143-146] The former becomes the branches and the latter the core. The number of arms per star molecule is determined by the functionality of the electrophilic compound used provided the yield of the coupling reaction is close to quantitative. Since fluctuations in length of the branches are averaged, molar mass distribution in such star polymer samples is expected to be narrow. Some examples of such electrophilic linking agents are, phosphorous trichloride (3), silicon tetrachloride (4), hexachlorodisilane (6), 1,2,4,5-*tetra*(chloromethyl)benzene (4) and tin tetrachloride (4), where the figures in bracket refer to the corresponding theoretical functionalities. The most important of these linking agents are the chlorosilanes and chloromethyl and bromomethyl[145-147] benzene derivatives. Silicon halides are one the best reagents that react quantitatively with carbanions derived from styrene, dienes, and other living polymers to yield well-defined star polymers.[145,146,148] A vast majority of studies till today have been limited to styrene and diene monomers and relatively little work has been reported on methacrylates possibly due to the inherent problems associated with methacrylate polymerization that necessitates a low reaction temperature. At this low temperature, linking reaction with chlorosilane is not efficient because of the bulky nature of the methacrylate anion. Moreover, side-reactions may take place forming an unstable silyl ketene acetal due to linking of the silane with the O atom of the carbonyl instead of the required carbanionic center.

Using bis-unsaturated monomer:

Living anionic polymer chains can serve as an initiator for polymerization of a small amount of a bis-unsaturated monomer, such as divinylbenzene (DVB) or ethylene glycol dimethacrylate (EGDMA). Small microgel nodules are formed, each connected with the precursor chains that initiated the crosslinking process, thus forming a star-shaped polymer. The branches exert a shielding effect on the crosslinked cores so as to prevent linking between individual star molecules. The average length of the branches is given by the molar mass of the precursor chains. The average functionality of the crosslinked cores can be determined from the ratio of the molar mass of the stars to that of the precursor polymer (account being taken, if necessary, of the weight fraction of the cores). The average number of branches per star molecule is influenced mostly by the overall concentration of the reaction medium and the proportion of bis-unsaturated monomer introduced (expressed as the mole ratio of that monomer to the active sites, i. e. [DVB]/[I]). This method has been successfully employed for preparing narrow molecular weight distribution stars with poly(styryl) and poly(dienyl) lithium living chains, using DVB as the difunctional monomer.[140,145,146] PMMA and P*t*BA stars have been prepared by coupling with EGDMA as crosslinker, and the effects of arm molecular weight and the mole ratio of EGDMA to initiator were studied in details.[149,150] The concentration of the reaction medium, the average length of the arms, and the molar ratio of the bis-unsaturated monomer to the active centres, were found to determine the number of arms formed per star molecule.

Anionic arm-first methods also can be applied for the synthesis of star-block copolymer.[151] When a living diblock copolymer prepared from sequential copolymerization of two appropriate monomers are used as living precursor chains to initiate a divinylic compound, it leads to the formation of a star-block copolymer. Star-block copolymers of narrow polydispersity have been prepared by Teyssie et al by coupling of living PMMA-b-P*t*BA chains with EGDMA.[152] Alternately, if functional polymeric precursor chains prepared using functional initiators are used to form such star polymers, and subsequently the functionalities on the star are utilized to initiate polymerization of some appropriate monomer, star-block copolymers can result.

2) Core-first methods:

Multifunctional organometallic initiators have been utilised to synthesize star polymers ever since Burchard and coworkers prepared stable suspensions of plurifunctional lithium-organic "cores," arising from controlled anionic polymerization of divinylbenzene using butyllithium in benzene.[153,154] This living core was then successfully applied to initiate polymerization of vinylic and acrylic monomers yielding star molecules of extremely high molar mass. However, such initiators are usually insoluble, even in polar solvents such as THF, because of the tendency of metalorganic functions to associates. Synthesis of poly(*tert*-butyl acrylate) and poly(ethylene oxide) star have been reported in THF.[155,156] Recently, a novel hydrocarbon soluble trifunctional initiator prepared by reacting *sec*-BuLi with 1,3,5-tris(1-phenylethynyl)benzene has been proposed by Quirk et. al. for polymerizing styrene in THF.[157]

For the core-first method, a wider range of monomers can be used compared to arm-first processes e.g. styrene, dienes, vinylpyridines, alkyl methacrylates, oxirane, and various other anionically polymerizable monomers. However, the polydispersity of star polymers obtained is always high, possible due to the large fluctuations in size of the initiating cores.

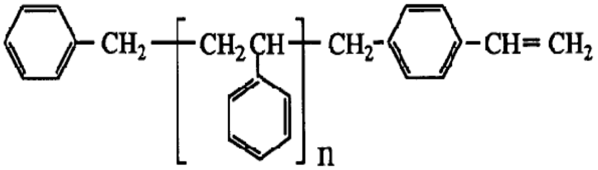
Once the growth of the arms is over, their outer end carrying a living anionic site can be subsequently reacted with appropriate electrophilic compounds for functionalization, e.g., reaction with ethylene oxide yield alcohol function, carbon dioxide to form carboxylic function. Alternately, these carbanionic sites can be used to initiate polymerization of another monomer to yield star-block copolymers e.g. amphiphilic star-block copolymers have been prepared where each branch is constituted of an inner hydrophobic block (e.g., polystyrene) and an outer hydrophilic block (e.g., poly(ethylene oxide). [158]

A combination of arm-first and core-first methods, called "in-out" method utilizes the advantages of both the methods.[155,159] It is meant to allow a better control of polydispersity of the samples and to provide possibilities of functionalization at the outer end of the branches. P*t*BA star polymers having 10 to 15 branches have been prepared from a small macroinitiator prepared from living polystyrene and divinylbenzene.

1.5.3. Macromonomers

1.5.3.1. Introduction:

Macromonomer, an abbreviation of macromolecular monomer, is a concept of developed by Milkovich, and is defined as a reactive oligomer or polymer in which a polymerizable functional group is connected to the chain end.[160-168] This polymerizable entity can either be an unsaturation e.g. a vinyl group, or an heterocyclic ring such as oxirane (epoxide). Polystyrene macromonomer having a vinylbenzyl end group; i.e., styrene end group, is an example of the simplest form.



However, a condensation-type macromonomer has two reactive functionalities e.g. hydroxy, amino, carboxyl or isocyanate, at one chain-end that participates in step-growth polymerization with other difunctional monomers.[164,169,170] Macromonomers can be further copolymerized with other vinyl and heterocyclic monomers by a variety of mechanisms to form branched polymers of well-defined structure[171,172] e.g. the homopolymerization of macromonomers yields comb-like polymers and their copolymerization with a comonomer results in graft copolymers. This aspect of macromonomers differentiates them form telechelics, which are α-ω-difunctionalized oligomers[164,166] Telechelics undergo chain extension reactions yielding linear macromolecules and are used to make block copolymers and they do not yield branched structures.

By using macromonomers, one can utilize the unique properties of oligomers that are different from those of small monomers and polymers such as non-volatility, high solubility, and so on. Macromonomers in the oligomer region are used directly as a reactive reagent in the reaction injection molding and as a reactive compatibilizer in polymer blends and alloys.[164-173] However, in most cases, they are used as the precursor or the building block for multibranched polymers, graft copolymers, and network polymers.[174-176] Polymacromonomers are considered to be interesting model branched polymers for the study of the effect of branching architecture on both molecular and bulk properties.[177-179]

1.5.3.2. Synthesis of macromonomers :

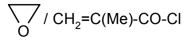
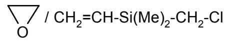
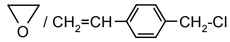
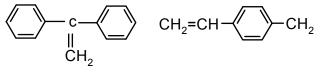
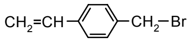
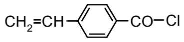
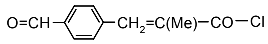
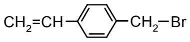
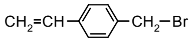
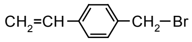
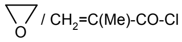
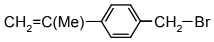
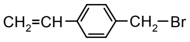
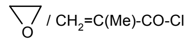
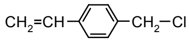
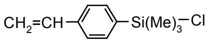
Among the methods that have been developed to produce a wealth of macromolecular monomers with low fluctuation in size and high functionality, "living" anionic polymerization, due to absence of spontaneous transfer and termination, is the best suited one. It enables accurate control of the macromonomer length as well as functionalization of the chain end. In the case of macromonomers designed for chain polymerizations, the polymerizable group e.g. vinyl group, may be introduced by one of the two following methods.

1) Using an unsaturated end-capping agent whose role is to introduce the unsaturation through deactivation of the growing "living" sites. This unsaturated deactivator is an electrophile when the chain termini are anionic species and a nucleophile in the case of cationic growing polymers.
2) Using an initiator endowed with a polymerizable moeity, which will stay free of any interference during polymerization of the monomer.

These two synthetic pathways have been successfully applied to monomers polymerizing either anionically, cationically, or via group-transfer process. Though some sporadic attempts of end-capping polymer chains with unsaturations were made as early as 1960, the domain of macromonomers was truly developed by Milkovich.[162,180]. He synthesised macromonomers involved end-capped living polystyrene carbanions with ethylene oxide and acryloyl chloride to derive PS macromonomers of unambiguous functionality. Since this pioneering work, almost all types of anionically polymerizable monomers have been subjected to macromonomer synthesis.[164,165,168]

Termination method: Deactivation of living anionic sites by an unsaturated electrophile (Table 1.3) has to been done such as to avoid reactions between the unsaturation introduced and the "living" sites to be deactivated. The commonly employed electrophiles are alkyl halides, benzyl halides, chlorosilanes, and acyl chlorides containing styryl, methacryloyl, or alkyl unsaturations. In case of highly reactive anionic species, it is necessary to reduce the basicity of the "living" anions by end-capping with diphenylethylene, ethylene oxide, or benzaldehyde so as to transform growing carbanions into less nucleophilic anions prior to functionalization. Apart from styrene and various methacrylates, vinylpyridines and *t*BA are the other vinylic monomers from which macromonomers have been prepared via electrophilic deactivation (Table 1.3). Among the cyclic monomers that polymerize anionically by ring-opening, oxirane, hexamethylcyclotrisiloxane, and ε-caprolactone have been employed for macromonomer synthesis. Termination of oligomeric organolithium compounds by unsaturated alkyl halides suffers from several side-reactions such as metal-halogen exchange, coupling reactions to form dimeric species by the anionic chains, and elimination of hydrogen when present vicinal to halogen. Deactivation of polystyryl lithium by *p*-vinylbenzylchloride in benzene yielded only 50 % of the macromer, but in a predominantly THF solution, quantitative yield of macromonomer was obtained.[181,182] Similar reactions with PMMA anions showed that the termination with *p*-vinylbenzyl iodide and bromide took place yielding the corresponding macromer, but the chloride failed to react.[183] However, trityl-lithium initiated PMMA reacted with chloride to give 0.86-0.92 degree of functionality at -78 °C after 2 h.[184] Using LiCl as ligand, controled polymerization of *t*BA and the synthesis of the corresponding macromonomer using vinylbenzylbromide have been reported.[63]

Table 1.3: Macromonomers by deactivating living anionic species

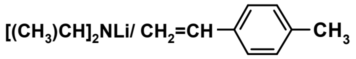
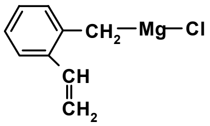
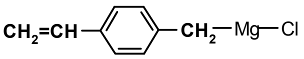
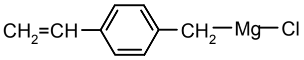
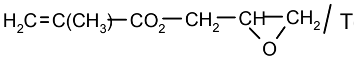
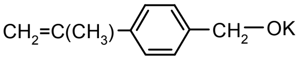
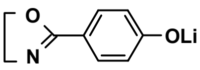
Monomer	Electrophile
Styrene	   
Methyl methacrylate	  
n-Butyl methacrylate	
t-Butyl methacrylate	
Trimethyl ethylsilyl methacrylate	
2-Vinylpyridine, 4-Vinylpyridine	 
t-Butyl acrylate	
Ethylene oxide	 
Hexamethylcyco trisiloxane (D3)	$CH_2=C(Me)—CO_2—(CH_2)_3—Si(Me)_3Cl$  $CH_2=C(Me)—CO-Cl$

Controlled synthesis of 1,1-diphenylethylene-functionalized macromonomers e.g. PS macromers by the reaction of polystyryllithium (no.-av. mol. wt. 14,000) with 3 equiv of 1,3,5-tris(1-phenylethenyl)benzene have been studied by Quirk et al.[185]

Initiator method: In some cases, macromonomers have been obtained by using unsaturated anionic initiator (Table 1.4). Macromonomer with styrenic polymerizable group was synthesized by anionic polymn. of ethylene oxide initiated by potassium vinyl benzyl alcoholate. The *p*-vinylbenzyl-terminated polyoxyethylene macromonomer (PEO-VB) was then copolymd. with styrene in water/alc. continuous phase.[186] Lithium diallylamide capped with dimethylacrylamide and *t*BMA were used for preparing alkylmethacrylate macromonomers.[187] A relatively small number of macromonomers have been prepared by this method possibly due to the difficult finding suitable compounds containing both a polymerizable group as well as a function that is capable of initiating an anionic process. Monomers exhibiting a high electron affinity such as oxirane, lactones, siloxane, and lactam rings are well suited for the approach involving an unsaturated initiator

Macromonomers of poly(ethylene oxide), of various polyesters and of polysiloxanes and polyamides have been prepared following this pathway. Only a few vinylic monomers, essentially polar ones, have been transformed into macromonomers by the unsaturated initiator method, due to the restriction that the active anionic chains should not attack the unsaturation in the initiator. Compounds containing styrenic unsaturations have been used to polymerize methacrylates and vinylpyridine (Table 1.4).

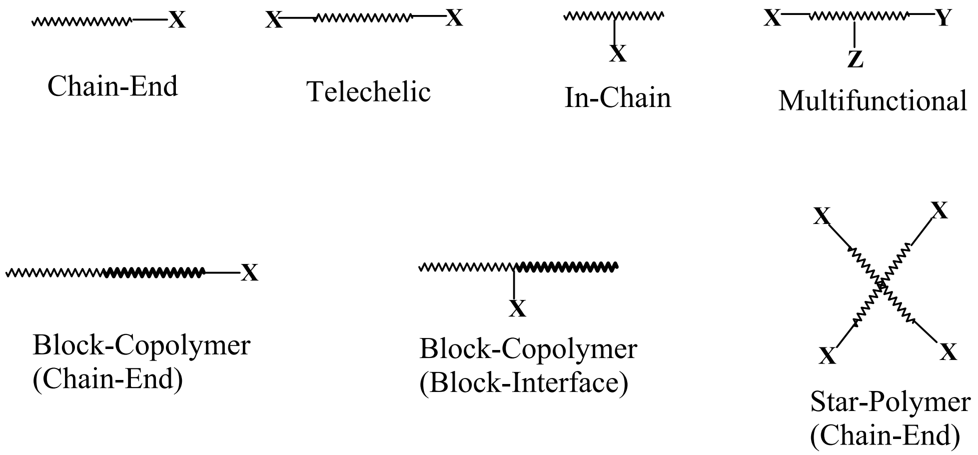
Table 1.4: Macromonomer using an unsaturated anionic initiator

Monomer	Unsaturated Initiator
Styrene	
Methyl methacrylate	
	
4-Vinylpyridine	
Methylacrylate	2-Methyl-2-oxazoline/Bu_4NOH
Acrylonitrile	 $H_2C{=}C(CH_3){-}CO_2{-}CH_2{-}CH{-}CH_2$ (epoxide, O) / Tertiary amine
Oxirane	
	
Propriolactone	$CH_2{=}C(CH_3){-}CO_2K$/ DB18C6
ε−Caprolactone	$CH_2{=}C(CH_3){-}CO_2{-}CH_2O{-}$A1(B)2
Hexamethylcyclotrisiloxane	BuLi/alkenyl silanol

1.5.4. Functional Polymers

1.5.4.1. Introduction :

Functional polymers are reactive prepolymers bearing functional groups either in the main chain or at the chain ends.[188-191] The chain end functional group may be simple reactive functionalities e.g. -OH, -COOH, -NCO, -SH, $-NH_2$, etc., or groups such as vinyl and methacryloyl that allows homopolymerization. The latter class of functional polymers are termed as macromonomers. Reactive oligomers are of great interest, due to many applications. Their low molecular weights and hence low melt viscosities enable them to be processed without solvent. They are less toxic and have lower vapor pressure then their corresponding monomers. These functional groups can participate in chain extension, branching, or cross-linking reactions with polyfunctional reagents, coupling and linking with reactive groups on other oligomers or polymer chains and initiation of polymerization of other monomers. Exploiting the unique potential of functionalized polymers, a variety of precisely designed macromolecular architectures (scheme 1.10) including networks, block, and graft copolymers can be successfully prepared. The method of living anionic polymerization is particularly suitable for synthesis of well-defined functional polymers since these polymerizations proceed with negligible chain termination or chain transfer reactions.[12,35]



Scheme 1.10 : Molecular architecture with functionalized polymers

The main drawback of this method is that, some of these functional groups such as hydroxy, amino, mercapto, and carbonyl, are generally not compatible with anionic species at the chain ends of living polymers. To overcome this obstacle, Nakahama and

Hirao have introduced the concept of protective group into anionic living polymerization.[192-194] The strategy involves protecting the functional groups in living anionic polymerization, followed by subsequent deprotection to regenerate the original functional group from the resulting polymer. The choice of an appropriate protecting group for a functional group, which is stable during living anionic polymerization and is quantitatively removable after the polymerization to produce the desirable end-functional polymer[195] is of paramount importance.

1.5.4.2. Synthesis :

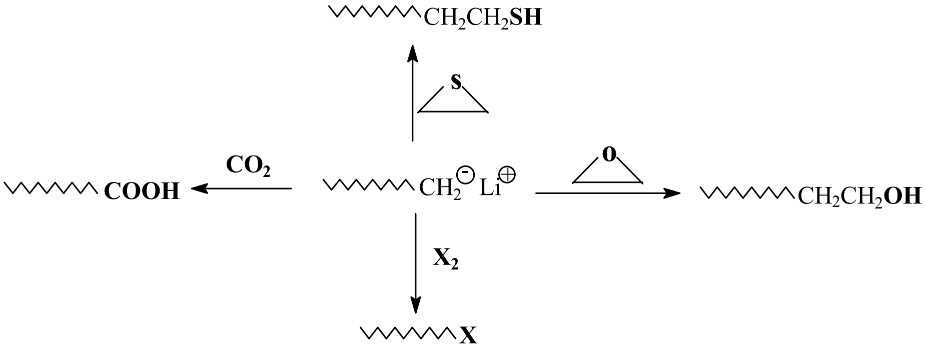
Two approaches for the preparation of end-functionalized polymers by living anionic processes[196] are available, namely, (1) use of electrophilic terminating agents and (2) use of functional initiators.

1) End-functionalization with electrophilic reagents:

The most general method for preparing chain-end functionalized polymers is by utilizing post-polymerization reactions of the anionic living polymer with a variety of electrophiliic reagents[107-109,188,197] according to the reaction depicted in eqn. 1.14.

$$PLi + X\text{-}Y = P\text{-}X + LiY \qquad (1.14)$$

For e.g., termination with CO_2 or oxirane yields polymers with -COOH or $-CH_2OH$ end groups, as shown in scheme 1.11.



Scheme 1.11: Functionalization of living anionic polymer by eletrophilic termination

Some common functionalization reactions are being discussed in the following section.

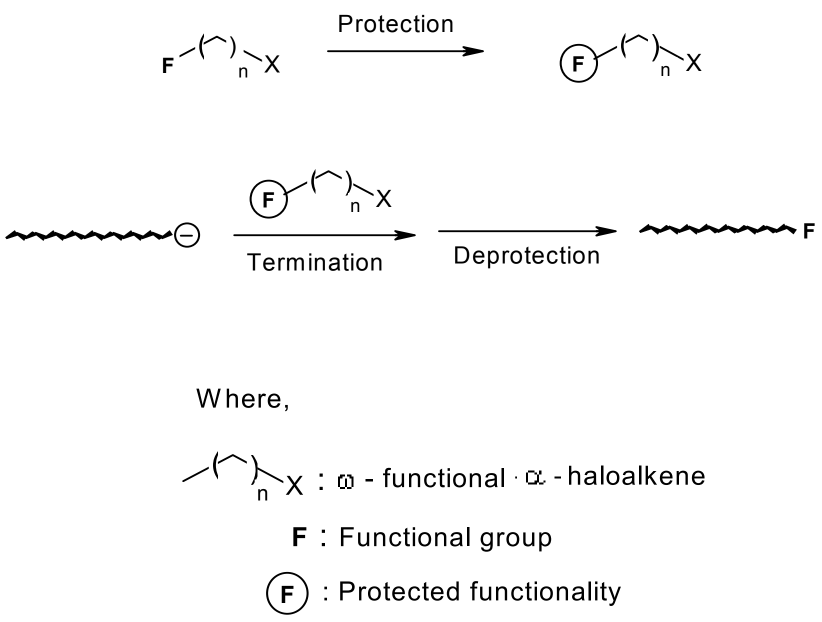
Carboxylation: It has been reported that >90 % yields of carboxylated polymers can be obtained simply by pouring hydrocarbon/THF (99.5/0.05 v/v) solution of the living polymer anion onto solid carbon dioxide.[198] Conversion to the corresponding Grignard reagent prior to gaseous CO_2 termination has also been reported to produce >90 % yield of carboxylated polymer. Such carboxylation reaction is ideal since it is possible to analyse the reaction products in various ways, e.g., SEC, end-group titration, osmometry, ^{13}C NMR, FTIR, and TLC. The pure functionalized polymer can be separated from unfunctionalized chains by column chromatography using toluene as eluent. This methodology has also been applied to the preparation of -COOH terminated PMMA.[199]

Hydroxylation: Preparation of hydroxyl-terminated polymers by reacting polymeric organolithium compounds with ethylene oxide is a very simple and efficient functionalization reaction. Direct reaction of polymeric organolithium compound with ethylene oxide produces the corresponding hydroxyethylated polymer in quantitative yield without any significant formation of oligomeric ethylene oxide block.[200] Telechelic dihydroxy polymers can be prepared from the corresponding α,ω-dithium polymeric chains by reaction with ethylene oxide.[201]

Sulfonation: The simplest way of sulfonation of polymeric organolithium compounds is the direct reaction of the living chains with sultones. However, a poor yield of functionalized polymer was obtained till the concept of end-capping the polymeric chains with 1,1-diphenylethylene was introduced. This strategy helped in increasing the steric congestion around the carbanion and decreased the basicity, thus allowing a significantly higher degree of functionalization.[202]

Amination: Amination of polymeric living chains with primary amines is complicated by the presence of acidic hydrogen, due to which it needs to be protected. Nakahama et al reported high yields (96-100%) of primary amine functionalized polymers by reacting polystyryllithium with 1.5-2 equivalents of the protected imine, *N*-(benzylidene)-trimethylsilyl amine in benzene at R.T.[203] Primary amine-functionalized polystyrene have been prepared by the reaction of polystyryllithium with the product of reaction of methoxyamine and methyllithium at low temperatures.[204]

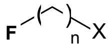
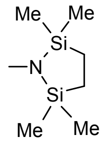
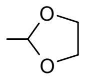
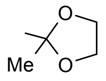
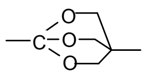
Recently a more simple but general method of end-functionalization of anionic chain ends have been proposed, using ω-functional-α-halo alkanes as chain terminating agents (scheme 1.12) where the functionality is suitably protected to avoid reaction with



Scheme 1.12: Functionalization by chain termination with ω-functional-α-halo alkanes

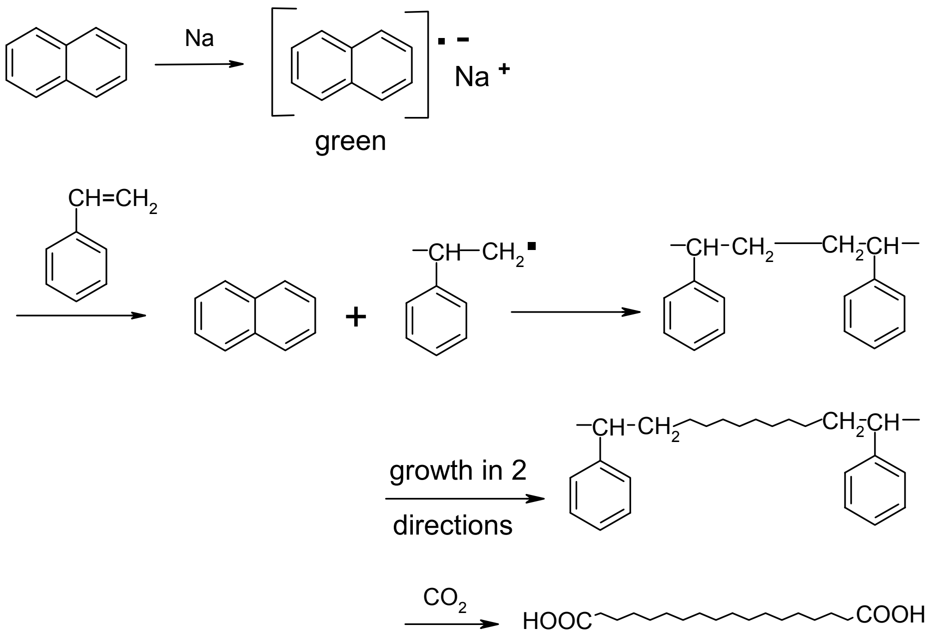
the living polymeric chain during the reaction.[196] A list of such terminators are shown the Table 1.5.

Table 1.5: Functional groups and protected functionalities used as terminators

	(X = Cl, Br, I; n = 2, 3, 4)	
Functional Group	Protected Functionality	
-OH	$-O-SiMe_3$	$-O-SiMe_2Bu^t$
$-NH_2$	$-N(SiMe_3)_2$	
-SH	$-S-SiMe_2Bu^t$	
-CHO	$-CH(OEt)_2$	
$-COCH_3$	$-C(Me)(OMe)_2$	
-COOH	$-C(OMe)_3$	
-C≡CH	$-C\equiv C-SiMe_3$	

Using these functional terminators, nearly quantitative functionalization have been obtained for styrene and isoprene polymerization with the end-functionalized polymers having controlled molecular weight and narrow molecular weight distribution. Also, this method can be extended to synthesize end-functionalized polymers with carboxy, thiol, aldehyde, ketone and ethynyl groups, with almost quantitative functionalization in all cases.

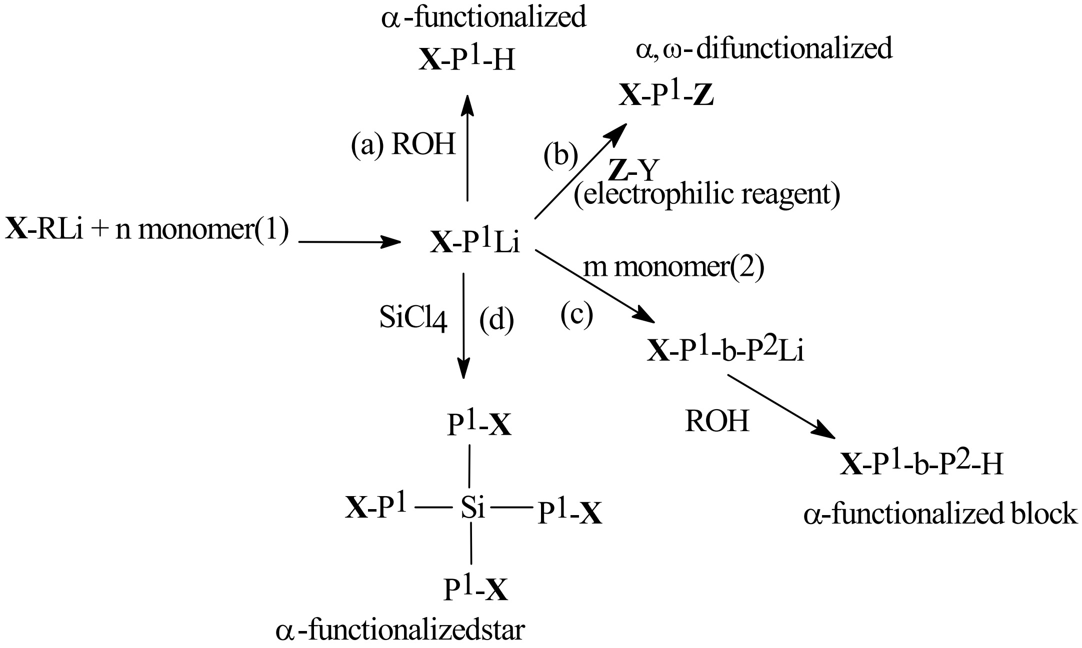
Telechelics : Initiation with bifunctional anionic initiators followed by electrophlilic termination at the end of polymerization yields telechelics (scheme 1.13).



Scheme 1.13: Telechelic polymer using difunctional initiator

2) End-functionalization using functional initiators:

Post-polymerization reactions with electrophiles suffer from several drawbacks, for example, many of these functionalization reactions are not quantitative and produce polymeric side-products in addition to unfunctionalized polymer chains. The alternative approach for the preparation of functionalized polymers involves the use of functionalized alkyllithium initiators, as shown in scheme 1.14, which is a much simpler and, in some respect, superior method of functionalization. Since the functional group is attached to the initiator, it is quantitatively introduced at the polymer chain end as shown in path (a) in scheme 1.14. However, as mentioned earlier, most of the functional groups of interest e.g. hydroxy, carboxy, amino, are reactive to simple or polymeric organolithium reagents. Hence, they need to be protected by suitable protecting groups. The choice of protecting groups should be such that it is not only stable to anionic chain ends but is also easily removable after the polymerization to generate the required functionality.[113,192,195]



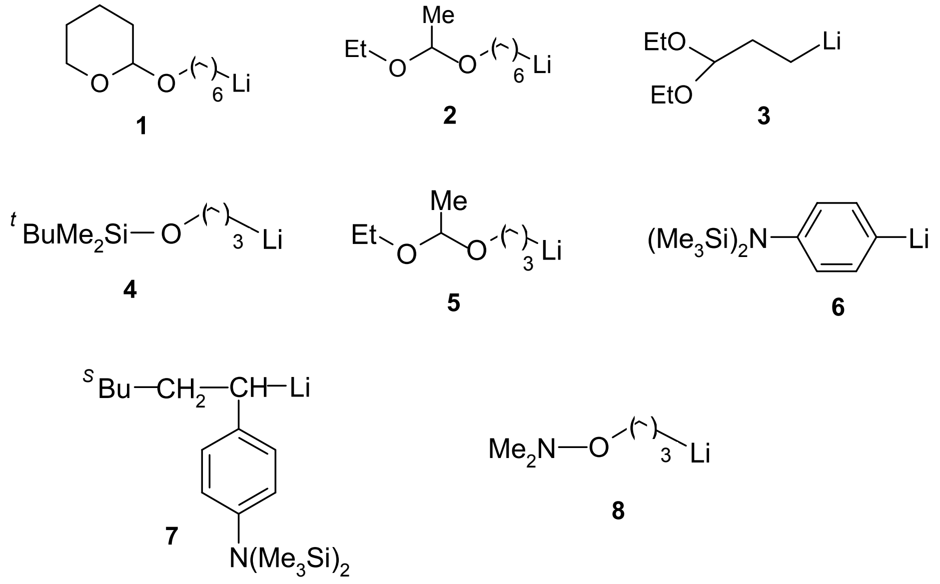
Scheme 1.14: Polymer synthesis with functionalized initiators

Advantages:

There are several advantages of using functionalized alkyl lithium initiators for preparing chain-end functional polymers.[205] In case of living anionic polymerization with functional initiator, each initiator molecule will produce one macromolecule with a functional group attached to the initiator residue at the initiating (α) chain end and with an active carbanionic propagating species at the terminal (ω) chain end, irrespective of the molecular weight. Unlike functionalization by eletrophilic termination, it is not necessary to be concerned about efficient and rapid mixing of reagents with the viscous polymer solutions or the stability of chain-ends at higher temperatures that is often employed. Also, the problem of quenching of active centers by protic impurities introduced from the added electrophile leading to unfunctionalized chains, does not exist in this case, and hence leads to quantitative functionalization. Another advantage of using functionalized initiator is that it is possible to prepare telechelic [(b) in scheme 1.14] by eletrophilic termination of the functionalized active chain ends, or, by coupling of two functionalized polymer chains using a difunctional coupling agent. Moreover, functional block [(c) in scheme 1.14] as well as star-branched polymers with functional groups at initiating ends of each branch [(d) in scheme 1.14] can be prepared. A major limitation of using functional initiators is that they are not readily available and often exhibit limited solubility in hydrocarbon solvents.[191]

Synthesis:

Hydroxylation : The synthesis and use of protected functional initiators was used by Schulz and co workers[191,206] for the first time in 1974. They synthesized two organolithium initiators with acetal protected hydroxy groups, 2-(6-lithio-*n*-hexoxy)tetrahydropyran and (6-lithiohexyl)acetaldehyde acetal (**1** and **2** in scheme 1.15), and used them in anionic polymerization of 1,3-butadiene in diethyl ether to yield



Scheme 1.15 : Protected functional initiators for synthesis of functional polymers

polymers with well-controlled molecular weight, molecular weight distribution (~1.05) and after deprotection yielded the hydroxy function of 0.87 to 1.02 per chain. Other protected hydroxy-functionalized initiators reported are (3-lithiopropyl)acetaldehyde acetal[207], 3-(*tert*-butyldimethylsilyloxy)-1-propyllithium[208] (**3** and **4** in scheme 1.15) and 6-(*tert* -butyldimethylsilyloxy)-hexyllithium, the later two being commercialied by FMC, Lithium Division. Initiator **3** was used to prepare hydroxy-functionalized PMMA and the resulting hydroxyl function was further utilized to initiate D_3 to give well-defined PMMA-*b*-PDMS block copolymers.[209] Hydroxy-functionalized linear and star PMMA were prepared using **4** as initiator after end-capping with diphenylethylene.[208] 3-lithiopropionaldehyde diethyl acetal (**5** in scheme 1.15) was used effectively to afford polystyrene with formyl end group after deprotection.[210]

Amination: Primary amine terminated polymers have been prepared with organolithium initiators containing protected amine functionality. *p*-lithio-*N,N*-bis(trimethylsilyl)aniline (**6** in scheme 1.15) was used to polymerize both butadiene and isoprene.[211] Using a mixed solvent of hexane and ether for soluibilzing the initiator, narrow molecular weight distribution polymers were prepared with functionality 0.6-1.0. Coupling of living polyisoprene chains with dichlorodimethylsilane led to formation of α,ω-diaminopolyisoprenes with relatively broad molecular weight distributions.

Dickstein and Lillya synthesized a useful protected primary amine initiator by reaction of *sec*-butyllithium with *p*-bis(trimethylsilyl)-aminostyrene (**7** in scheme 1.15) under careful control of stoichiometry of the reagents, and was used to prepare primary amine functionalized poly(dimethylsiloxane) and polystyrene.[212]

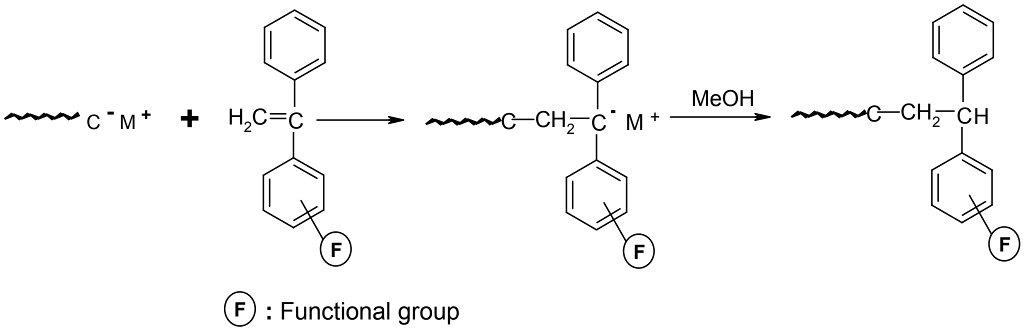
Telechelics using both functional initiators and terminators :

Asymmetric di-end-functionalized polymers are synthesized by a combination of functional initiation and electrophilic terminations techniques. A series of α-acetal-ω-styryl polystyrenes were prepared by anionic polymerization of styrene with initiator **5,** followed by treatment with 4-chloromethylstyrene as a functional terminator.[213] Also, α-acetal-ω-amino polystyrene was prepared following a similar strategy.[210] Gnanou et al synthesized α-hydroxy-ω-styryl end-functionalized polystyrene, and used the alkoxide derived from the hydroxy group to polymerize ethylene oxide, to prepare monodisperse polystyrene latex particles.[207]

1.5.4.3. End-functionalized polymers by using functional 1,1-diphenylethylene derivatives

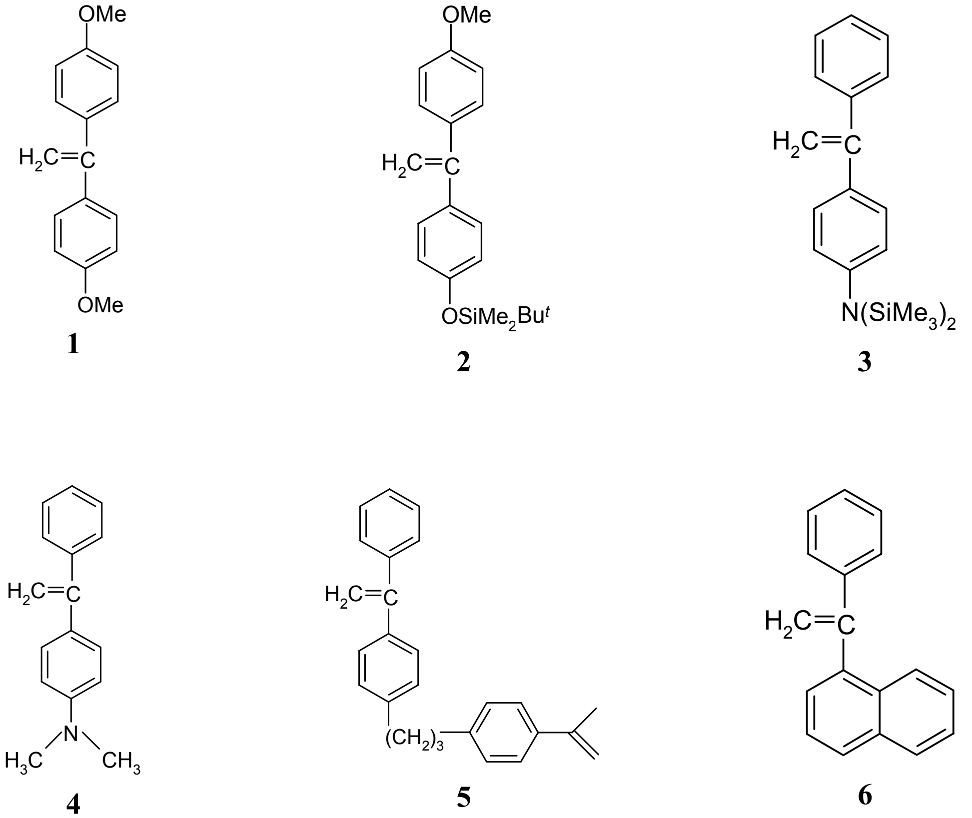
1,1-Diphenylethylene (DPE) and its derivatives react readily with anionic initiators e.g. organolithium compounds in monoaddition manner to yield 1:1 adducts quantitatively. No further addition of DPE occurs under usual conditions due to steric hindrance, and hence they are incapable of hompolymerization.[214,215] This simple addition reaction of organolithium to 1,1-DPE provide an excellent methodology for functionalization of living chain ends because, a) the rate and efficiency of functionalization can be monitored by UV-visible spectroscopy, 2) copolymerization of substituted DPE with other monomers can result in polymers with multiple functional groups along the chain, 3) a variety of substituted 1,1-diphenylethylenes bearing different functionalities on the aromatic ring can be prepared readily.[12,35,216-218] The simple or polymeric organolithium compounds, by monoaddition of DPE, are transformed into a more stable 1,1-diphenylalkyl type carbanion capable of initiating anionic polymerization of additional monomers like vinyl and heterocyclic monomers, especially alkyl acrylates and methacrylates. This method can be used to synthesize polymers with functional groups at the initiating ends (α) terminating end (ω), or within the polymer chain, which can be further utilized to prepare well-defined block, regular and heteroarm star-branched, and graft copolymers. The importance of these DPE derivatives in preparing functionalized polymers have been extensively reviewed by Quirk et al[219-221] and Hirao et al.[196,222-224]

End-functionalized polymers at terminating chain-ends: This method involves reaction of living anionic polymers with diphenylethylene substituted with various functional groups on the aromatic ring (scheme 1.16).



Scheme 1.16 : End-functionalization of polymers by termination with DPE-derivarives

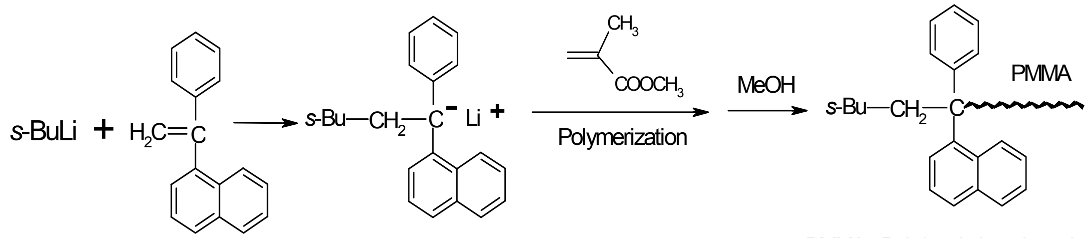
These groups are usually converted to their stable protected forms to avoid undesirable side-reactions with the polymeric carbanion. Hocker et al[169] and Quirk et al[225] successfully applied this method in synthesizing phenol end-functionalized polystyrenes. To the living polystyryl solution was added either 1,1-bis(4-methoxyphenyl)ethylene or 1-(4-*tert*-butyldimethylsilyloxyphenyl)-1-phenyl-ethylene (**1** and **2** in scheme 1.17), yielding polystyrene with two phenol or one phenol group respectively after deprotection of the respective methoxy and *tert*-butyldimethylsilyl groups. The introduction of two phenol groups at polymer chain end was used as a method for making condensation macromonomers. Essentially quantitative functionalization was obtained as evidenced by end- group titration, elemental analysis, ^{1}H NMR, ^{13}C NMR and TLC.



Scheme 1.17: Diphenylethylene derivatives for functionalization of polymers

In an analogous fashion 1-[4-[*N,N*-bis(trimethylsilyl)amino]phenyl]-1-phenylethylene and 1-(dimethylaminophenyl)-1-phenylethylene (**3** and **4** in scheme 1.17) was used to prepare amine-terminated polymers.[226,227] The substitued diphenylethylene was readily prepared from the corresponding benzophenone derivative via the Wittig reaction. The living amine-functionalized diphenylalkyl carbanion was further reacted with butadiene to form a styrene-*block*-butadiene with amine functionality at the junction.[227] This strategy has been used in preparing polymers labeled with fluorescent group, e.g. pyrene and naphthalene fluorescent groups.[228,229] Substituted DPE has also been used to prepare carboxy end-functionalized polymers using oxazoline a protecting group.[230]

End-functionalized polymers at initiating chain-ends: The above method of reacting substituted DPE with polymeric anions suffers from the limitation that less nucleophilic living anionic polymers of alkyl methacrylates, acrylates and ethylene oxide do not react with them. In order to circumvent this problem, the concept of using the monoaddition product of substituted diphenylethylene and a low molecular weight organolithium compound, as initiating anion was introduced. The anion generated from **6** (scheme 1.17) and butyl-lithium was employed as anionic initiator for MMA to prepare fairly monodisperse PMMA end-functionalized with a fluorescent naphthalene group[231,232] as shown in scheme 1.18. Similarly, adduct anions prepared by reacting *sec*-BuLi with **4** and **6** (scheme 1.18) were used to initiate MMA to produce well-defined *tert*-amine-functionalized PMMA[227] and α-methylstyryl-functionalized PMMA[233] respectively, with quantitative functionalization.



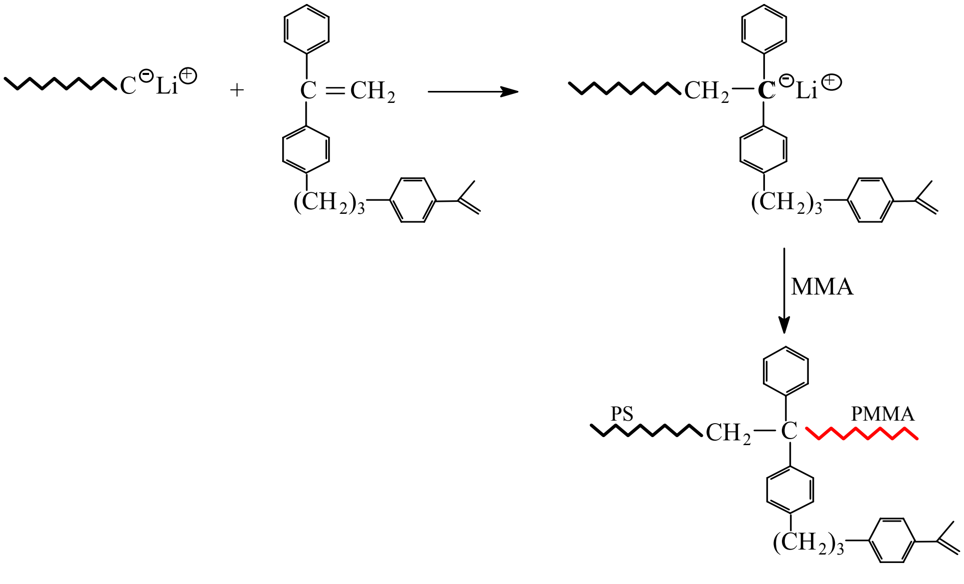
PMMA : Poly(methyl methacrylate)

Scheme 1.18: Synthesis of naphthalene end-functionalized PMMA using functional initiator

The adduct anion of *sec*-BuLi and **4,** which is a more stable and less nuclephilic anion, efficiently polymerised styrene and 1,3-butadiene yielding *tert*-amine functionalized polymers at the initiating end. Further reaction of the functional living polystyryl chains with **4** yielded α,ω-bis(*tert*-amine)-functionalized polystyrene.[227] Also asymmetric α,ω-difunctionalized polymer may be prepared by employing two different DPE derivatives for the initiating and terminating processes.

In-chain functionalized polymers: The methodology of using DPE derivatives for end-functionalization of polymers can be use to prepare in-chain functional polymers. In this case, a DPE derivative is first reacted with living polymeric anion so as to form a stabler and bulkier diphenylalkyl anion, which is then used to initiate a fresh batch of monomer, either same or different from the original one to give in-chain functional homopolymer or block copolymer. A *tert*-amine-functionalized polystyrene-*block*-PMMA was obtained with controlled MWD and quantitative functionalization.[227] Well-defined PS-*block*-PMMAs functionalized with α-methylstyryl (scheme 1.19) and 1,3-butadiene groups between blocks were made by similar methods.[233]

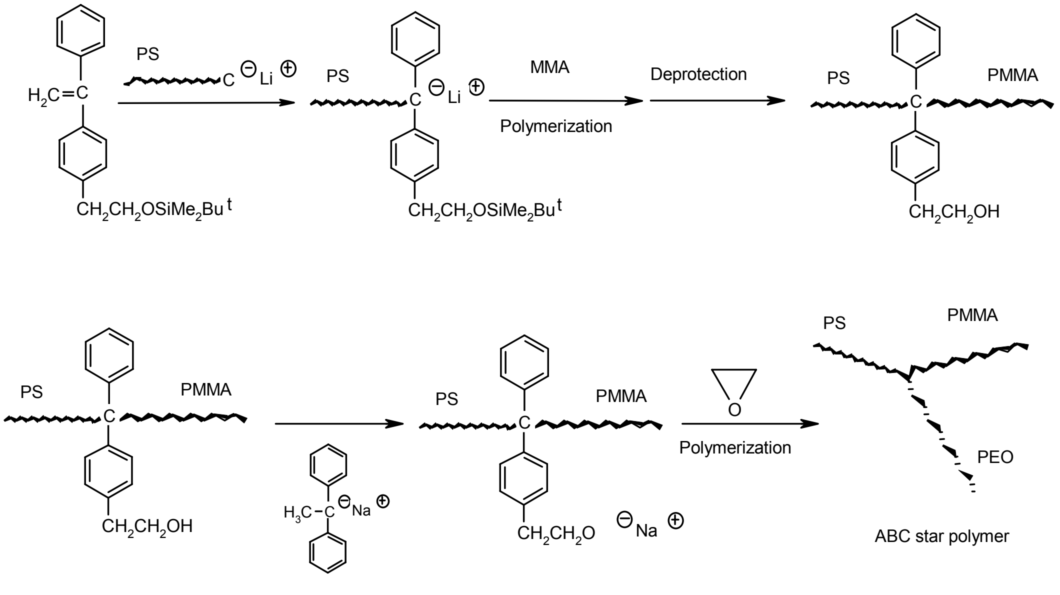
Synthesis of star-branched polymers: Well-defined star-branched polymers with controlled number of arms and arm length are important for model studies of polymers and elucidating their stucture-property relationships. Heteroarm star polymers are the ones where the arms differ either in arm length or composition and these exhibit interesting physical and rheological properties in solution, bulk and melt states. One of the most important synthetic utilities of DPE-functionalized polymers is the synthesis of heteroarm



Scheme 1.19: Synthesis of PS-b-PMMA with in-chain α-methylstyryl function

star-copolymers by linking of living anionic polymers to DPE-functionalized macromonomers, followed by living anionic polymerization of additional monomers.

Fujimoto et al synthesized ABC type heteroarm star polymers starting from substituted DPE-functionalized poly(dimethylsiloxane) macromonomer which was then linked with poly(styryllithium) living chains to generate the corresponding diphenylalkyl anions that was used to initiate polymerization of *t*BMA.[234] Similar procedure was applied for synthesizing ABC star copolymer of polystyrene, polybutadiene, and PMMA or poly(2-vinylpyridine).[235,236] Lambert et al synthesized different ABC star polymers by following a similar strategy[237,238] At first, living polystyryl chains were linked to 1-[4-(2-*tert*-butyldimethylsilyloxy)ethyl]phenyl-1-phenylethylene, as shown in scheme 1.20. The corresponding diphenylalkyl anion thus formed was used to initiate MMA polymerization to form PS-*block*-PMMA with protected hydroxyl function at the junction. The -OH group obtained by deprotection was then treated with diphenylmethyl sodium and the resulting sodium alcoholate was used to initiate ethylene oxide or ε-caprolactone polymerization, to create the third arm. Utilizing similar concepts, a variety of four-arm and six-arm stars have been prepared.



Scheme 1.20 : Synthesis of ABC star-branched polymer using functionalized DPE

Thus, the methods of using DPE derivatives are becoming a more general and versatile procedure for the synthesis of functional polymers of different architectures.

These methods are potentially applicable to a wide range of functional groups as well as to most of the monomers that polymerize anionically.

Besides these, there are reports of numerous other synthetic methods developed for preparing newer and more complex architectural functional polymers, homopolymers, block, star, and graft copolymers. These have been reviewed by Hirao et al and by Hajichristidis and coworkers recently.[14,222]

1.6. Scope and objectives :

The possibility of controlling the anionic polymerization of methacrylates in low polarity medium and at higher temperatures continues to pose a challenge, due to the inherent termination and transfer reactions that gain prominence at higher temperatures and non-polar solvent.[14] "Ligated Anionic Polymerization" is the strategy that has been often chosen for accomplishing a perfectly living polymerization of methacrylates.[6,7,50] Only few ligands till now are known to be effective in controlling the polymerization in such non-polar medium e.g. alkoxy-alkoxides, aluminium alkyls and silanolates. Alkali salts, e.g. LiCl and $LiClO_4$ which happen to strong Lewis acids, have been found to be very efficient in promoting living polymerization of MMA in THF. However, toluene is a poor solvent for these salts. Additionally, due to the complication arising out of ion-pairs aggregation during methacrylate polymerization in non-polar medium, it is necessary to add a very small amount of polar solvent like THF to a predominantly toluene medium. LiCl has been reported to be less effective in controlling the polymerization in toluene-THF (9:1 v/v) mixture, but $LiClO_4$ has been quite efficient in this regard. Though detailed study of the kinetics of MMA polymerization in presence of $LiClO_4$ has been done by Baskaran et al,[64b] there has been no report on the effect of these salts on the kinetics in toluene-THF mixture solvent.

Examples of the synthesis of "well-defined" functional polymers of methacrylate monomers are rare in literature. Functional initiators have been used to synthesize polymers with an appropriate end-function in a quantitative manner and the functionality has been exploited further in chain extension to give block, graft, star copolymers and so on.[14,220,222] However, most of the study has been limited to non-polar monomer e.g. styrene, isoprene, butadiene, because of the relative ease of achieving controlled polymerization of these monomers even at ambient temperatures. Very few studies are available on the synthesis of end-functionalised polymers with polar monomers e.g. methacrylates, due the difficulty in controlling these polymerization, especially at higher temperatures which is often needed for the reaction, thus restricting the prospects of extensive research.

Polymethylmethacrylate-*b*-polyethylene oxide block copolymers are an interesting class of amphiphilic copolymers that contain a hydrophobic amorphous segment and a hydrophilic semi-crystalline segment. They may find applications as surface-active agents, emulsifiers, stabilizers for dispersions, high impact plastics, compatibilizers, solubilizers and membrane precursors. However, previous attempts at synthesizing well-defined PMMA-*b*-PEO copolymers have not met with much success. Synthesis of these block copolymers by addition of ethylene oxide to living PMMA chains or by initiating MMA by PEO oxyanionis have been reported by several research groups.[117,118,122,239,240] In none of these reports unequivocal evidence for synthesis of well-defined PMMA-*b*-PEO block copolymers are available. Several side-reactions can compliate such reactions e.g. the attack of the oxyanion of the PEO living chains onto the ester group of MMA or PMMA, leading to grafting, and a broad multimodal distribution of the resulting diblock.

1.6.1. Objectives of the present work:

1) To study the efficiency of various Li-salt additives in controlling the anionic polymerization of MMA in a low polarity mixed solvent, at and below -40 °C. Results of polymerization in absence of any salt will be compared with those in presence of $LiClO_4$, $LiBF_4$, CF_3SO_3Li salts, in both pure THF and THF-toluene (9:1 v/v) using diphenylhexyllithium as initiator.

2) To investigate the effect of $LiClO_4$ and LiCl additives on the kinetic behavior of anionic polymerization of MMA in less polar medium. The degree of livingness at all monomer conversions will be studied both in presence and absence of the salts. The effect of these salts on ion-pair aggregation, and hence on the order of the reaction with respect to the active centers will be analysed.

3) To synthesize protected-hydroxy end functionalized initiators for the preparation of hydroxy functional polymethylmethacrylates. The initiators are basically adducts of a diphenylethylene component and an alkyllithium component, either of which bears a protected -OH function. Well-defined hydroxy functionalised PMMA will be prepared. Using these functional polymers as initiators, PMMA-*b*-PEO copolymers will be prepared.

4) To prepare hydroxy-functional star-branched PMMA using functional initiator to initiate MMA and further cross-linking of living chains by ethylene glycol dimethacrylate (EGDMA). The effect of arm length and ratio of EGDMA : initiator on the no. of arms will be studied. Also the -OH function on the star will be utilized to initiate ethylene oxide polymerization to prepare star-block copolymer.

5) Hydroxy-functionalised PMMA macromonomers containing styrenic and allyl end-groups will be prepared by terminating living chains with allyl methacrylate and *p*-chloromethylstyrene.

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Chapter 2: General Experimental Procedure

Living anionic polymerization necessitates scrupulous purification of the all the ingredients involved in a polymerization reaction.[1] The monomers, solvents and other reagents have to be purified and dried in multiple steps to eliminate even traces of impurities, especially, the protic ones. The reactions are conducted under inert atmosphere of nitrogen or argon gas, which have to be made free of moisture, oxygen and other reactive gases. This chapter describes the general purification methods, experimental procedures as well as the characterization techniques used in this work.

2.1. Materials and purification

2.1.1. Nitrogen or argon gas :

Nitrogen or argon (INOX, Bombay) contains traces of moisture, oxygen and hydrogen. To make the nitrogen free of these impurities, it was passed through three columns containing activated 4A molecular sieves and two columns containing active Cu deposited on keiselguhr kept at ~200 ^{0}C. The activated molecular sieves absorb moisture and the Cu absorbs the oxygen present in the gas forming CuO. Activation of molecular sieves and Cu columns were done from time to time. Cu columns were activated by passing H_2 gas at 180 ^{0}C for 7-8 h and the water formed by reaction of H_2 and CuO was removed under vacuum. The copper catalyst turns blackish brown in color after activation as against a pale green color of the deactivated one. Molecular sieves were activated by heating at ~200 ^{0}C under vacuum for 6 h and cooled under N_2.

Nitrogen gas, thus purified by passing through the above-mentioned columns, was then passed through a dark red solution of living oligomers of styryllithium in toluene. The moisture in N_2 quenches the living oligomers and thus the gas is made dry. This purified nitrogen was finally passed through another column containing successive beds of anhydrous phosphorous pentoxide, calcium hydride and activated molecular sieves. From here the nitrogen was fed to the manifold (Fig. 2.1) though rubber tubings for further use.

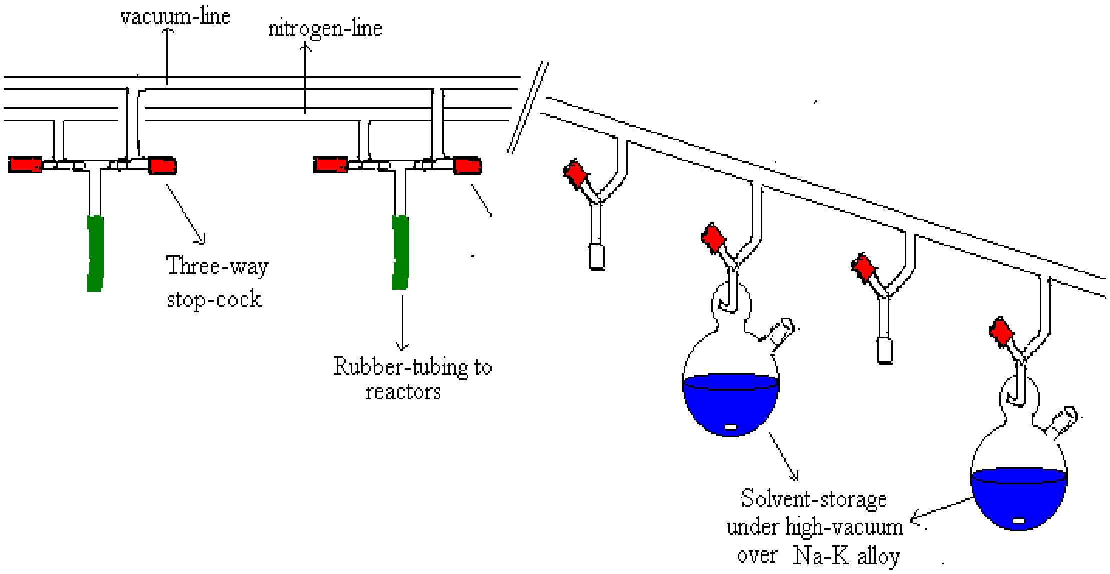

Fig. 2.1: Manifold for performaing reactions under inert atmoshphere

2.1.2. Solvent:

The solvents THF, toluene, cyclohexane (S. D. Fine Chem., Bombay or E.Merck, Bombay) were first refluxed over calcium hydride and then fractionally distilled and stored over activated molecular sieves. This fractionated solvent was further refluxed over K-metal or Na-benzophenone complex in a Dean-Stark apparatus for 2-3 days and then distilled. The distilled solvent was then stored (after proper degassing) in graduated solvent storage flasks over Na-K alloy, under high vacuum (Fig. 2.1). Required amount of solvent was distilled out from here into ampoules (Fig. 2.2) using liquid N_2, just prior to polymerization reaction.

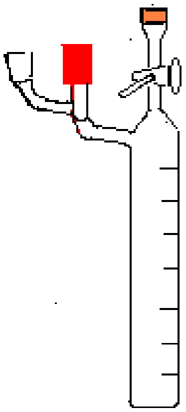

Fig. 2.2: Ampoule for solvent distillation

2.1.3. Monomer:

Methyl methacrylate (MMA, Schuchardt, Germany) was first stirred over CaH_2 for almost 6-8 h, degassed and distilled under vacuum and stored under N_2 pressure at 0-4 °C. Before polymerization this pre-purified monomer was taken in the bulb of a monomer distillation unit (Fig. 2.3) and titrated by triethylaluminium (TEA, Schering, Germany) till a persistent greenish yellow color was observed.[2] This color is due to the formation of a complex of TEA with MMA and indicates the end-point of impurity titration of the monomer. The monomer was degassed and then pure MMA was distilled under vacuum into the graduated ampoule portion of monomer distillation unit. This freshly distilled MMA was then added to the reaction flask using a cannula that has been flamed under nitrogen flow and subsequently cooled under nitrogen just prior to use.

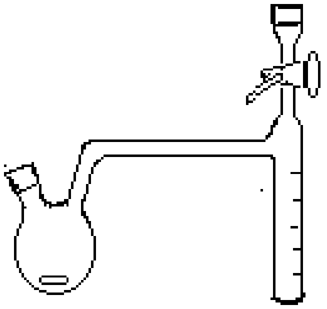

Fig. 2.3: Apparatus for monomer-distillation

In case of kinetic study of anionic polymerization of MMA, the monomer was fractionally distilled over CaH_2 under reduced pressure and stored under vacuum over CaH_2. GC analysis was done to ensure that the fractionated MMA was almost completely free of methanol. The required quantity was freshly distilled over CaH_2 along with *n*-octane, in a monomer distillation unit just prior to polymerization.

2.1.4. Additives

The Lewis acid salts used as additives for MMA polymerization were purified by vacuum drying. $LiClO_4$ and $LiBF_4$ (Aldrich, USA) were taken in required amounts in r.b. flasks, and heated to ~80 °C with continuous stirring under dynamic high vacuum. Li-triflouromethanesulfonate (Li-triflate) was prepared in the laboratory by addition of n-BuLi to a solution of trifluoromethanesulfonic acid (triflic acid) in dry THF at -40 °C.

2.2. Preparation of initiators

2.2.1. Preparation of *n*-BuLi:

n-Butyl lithium was prepared by the reaction of *n*-butyl chloride (*n*-BuCl, Aldrich, USA) with lithium metal in cyclohexane. The metallic lithium was washed several times with hexane to remove the oil and then cut into small pieces and added to a 3-necked r.b. flask (1L) along with a small piece of sodium, under flush of argon gas (Fig. 2.4). To the middle neck was connected a water condensor fitted with an oil-bubbler at the top. Through the third neck, the required volume of cyclohexane was poured into the flask, and then connected a dropping funnel containing the *n*-BuCl. The system was continuously flushed with argon, and cooled to 0°C with ice while adding the *n*-BuCl dropwise to the metal. After the addition was completed within few hours time, the reaction mixture was heated to ~60 °C for another 4-5 hours and then cooled under argon. The Li metal was allowed to settle down and the *n*-BuLi, seen as a pale yellow solution in cyclohexane, was decanted off from the top and transferred to ampoules with cannula under argon pressure.

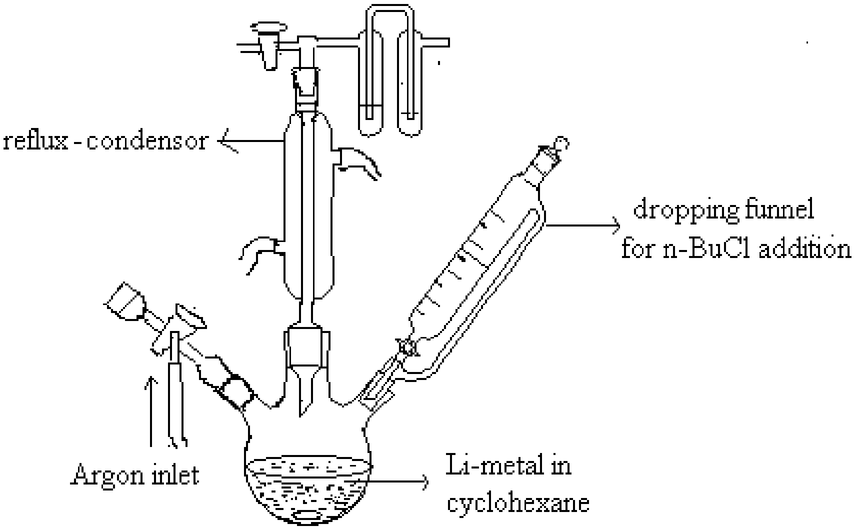

Fig. 2.4: Apparatus for *n*-BuLi preparation

2.2.2. Preparation of diphenylhexyllithium:

Diphenylhexyllithium (DPHLi) was prepared by reacting diphenylethylene (DPE, Aldrich, USA) with *n*-BuLi in THF as solvent. Prior to this, DPE was taken in the r.b. portion of a monomer distillation unit and then added *n*-BuLi dropwise till a persistent wine-red color develops. The impurities are quenched by *n*-BuLi and the end-point is indicated by the formation of wine-red color of DPHLi formed by reaction of *n*-BuLi with DPE. The rest of the DPE was then degassed and distilled under high-vacuum into the graduated ampoule part of the distillation unit. The required quantity of DPE was dissolved in freshly distilled THF and the temperature was brought down to -40 ^{0}C by dry-ice-acetonitrile bath. This was followed by dropwise addition of *n*-BuLi, first to titrate the solvent impurities and then the required amount for formation of DPHLi. The solution turned to a deep red color indicating the formation of DPHLi. The solution was stirred for 4-5 hours and the temperature allowed to rise gradually to room temperature. The initiator thus prepared was stored under N_2 pressure in a refrigerator.

2.3. Standardization of initiators

The initiators were standardized using Gilman`s double titration method.[3] Here, a known quantity of DPHLi (say 2 mL) was added to excess (say 0.4 mL) of dry 1,4-dibromobutane (Aldrich, USA, distilled over CaH_2) dissolved in freshly distilled THF (2 mL), maintained at 0 ^{0}C. The mixture was stirred for almost 30 mins to ensure that all the DPHLi was converted into LiBr. At the same time, the same quantity of DPHLi (2 mL) was taken in dry THF (2 mL) in another r. b. flask without adding 1,4-DBB. This is called the blank. Finally, water (1-2 mL) and methanol (3-4 mL) were added to both the systems to quench them completely to form LiOH. This LiOH was then titrated against standard potassium hydrogen phthalate (PHP) solution from the burette, using phenolphthalein as indicator.

The difference in the burette reading between the blank and the previous titration after reaction with I,4-DBB gave the quantity of PHP equivalent to the actual amount of active DPHLi present in 2 mL of the initiator. Thus, the initiator strength is given by,

$$S = [(V-V_{bl}) \text{ x } S_{PHP}] / V_i$$

where V= volume of PHP required to titrate the LiOH after reaction of initiator with 1,4-DBB, i.e. volume of initiator quenched due to impurities.

V_{bl} = volume of PHP required to titrate the LiOH formed by quenching the total initiator, active and end, i.e. the blank value.

Vi= volume of initiator taken,

S_{PHP} = Molarity of potassium hydrogen phthalate solution.

2.4. General procedures for anionic polymerization of MMA

2.4.1. Procedure for batch polymerization:

Anionic polymerization of MMA was done in a bench-top single-neck glass reactor fitted to three-way stop-cock and equipped with magnetic stirring bar (Fig. 2.5). The detailed experimental procedure for a typical polymerization reaction is given below.

A clean and perfectly dry 250 mL single-necked round-bottomed flask fitted with a 3-way stop-cock with septum adapter was thoroughly conditioned under vacuum and then filled with N_2. This step was repeated twice, and finally the reactor was filled with pure nitrogen.

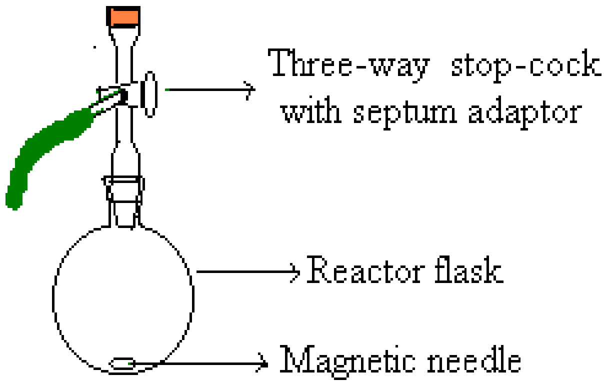

Fig. 2.5: Bench-top reactor for MMA polymerization

The required quantity of solvent, i.e. THF was distilled out into solvent ampoules under high vacuum and transferred into the flask under N_2 pressure with the help of a flame-dried cannula. This was followed by addition of required amount of a solution of the additive ($LiClO_4$, $LiBF_4$) in THF, to the reactor flask by a syringe. In case of Li-triflate, the compound was synthesized in THF and this solution was directly added to the flask by a syringe. The temperature of the flask was the brought down to -40 °C or -78 °C using dry ice-acetonitrile bath or dry ice-acetone bath respectively. Then the initiator, i.e. DPHLi solution, either in pure THF or in toluene-THF (9:1 v/v) depending on the reaction medium, was added dropwise to the reactor containing solvent and additive, by a syringe till a persistent red color of the initiator was observed. Subsequently the desired amount of DPHLi was added to the system as initiator for anionic polymerization of MMA. In the mean time, MMA previously distilled over CaH_2 was distilled once again over Et_3Al in a monomer distillation unit. This freshly distilled monomer was then transferred within 5-6 seconds using a flamed cannula into the initiator solution under N_2 pressure, keeping a sufficiently high stirring rate for homogenous mixing.

For THF as solvent, the reaction was quenched after 10-15 min with distilled methanol and in case of mixed solvents the reaction is continued upto 2-2.5 h before being quenched.

The polymer solution was concentrated and then the polymer, i.e. PMMA was precipitated *n*-hexane by dropwise addition of the polymer solution into the non-solvent under continuous stirring. The polymer was then filtered out and then dried in air or in vacuum-oven to determine the conversion gravimetrically.

2.4.2. Procedure for kinetic study:

The kinetics of anionic polymerization of MMA in a medium of low polarity i.e. toluene-THF (9:1 v/v) mixture was studied using bench-top single-neck glass reactor (Fig. 2.5) connected to a 3-way stop-cock with septum-adaptor and provided with a magnetic stirring bar.

The required amount of toluene and THF (usually 90 mL and 10 mL respectively) were distilled out in separate solvent ampoules from the solvent storage flask. The solvents were transferred to the reactor flask under N_2-pressure using a flame-dried cannula in the usual way. A solution of the additive (say, $LiClO_4$) in THF was made and the required quantity transferred to the reactor with syringe. MMA, which was fractionally distilled over CaH_2 previously and stored over CaH_2, was freshly distilled over CaH_2 after few hours of stirring. *n*-Octane (S.D. Fine Chem., Bombay), which was used as the internal standard for GC analysis, was previously distilled over CaH_2 and stored over molecular sieves. Before adding to the polymerization system, it was co-distilled along with MMA over CaH_2. The temperature of the flask was brought down to -78 °C by dry-ice-acetone mixture. Subsequently, the solvent containing additive was titrated in the usual way, by the initiator i.e. DPHLi solution [prepared in toluene-THF (9:1 v/v)]. This was followed by addition of the required amount of DPHLi as initiator. Then the freshly distilled mixture of monomer and n-octane was added to the reactor (maintained at -78 °C under a high pressure of N_2) by a syringe. A small amount of this monomer-octane mixture was preserved for GC analysis of the zero-time concentration of MMA. The reaction was usually continued for 2 h and pick-outs were taken at different time intervals by the help of syringe. The pick-outs were quenched by distilled methanol and then analyzed by GC to determine the monomer conversion.

The following equation was used to determine the monomer conversion at each time with respect to that at zero time, as shown below:

$$x_p = 1 - \left[(M_t/I_t) / (M_o/I_o) \right]$$

Where x_p is the conversion at time t,
M_t and M_o are the molar concentration of MMA at time t and 0 respectively,
I_t and I_o are the molar concentration of *n*-octane at time t and 0 respectively.

From each pick-out the polymer was recovered by driving off the solvent, re-dissolving the polymer in benzene, filtering and then freeze-drying. The polymer was analyzed by GPC for determining the number average molecular weight and the molecular weight distribution.

2.5. Characterization of polymers

All polymers were characterized by Size Exclusion Chromatography (Thermoseparation Products) equipped with one UV and one RI detector, for determining the molecular weight and molecular weight distribution. Measurements were made relative to a calibration plot using PMMA standards (Polymer Standard Services or Polymer Laboratories). THF (Merck) was used as eluent at a flow rate of

1mL/min. The columns used were two 60 cm PSS SDV-gel columns: 1 × 100Å and 1 × linear ($10^2 – 10^5$ Å) at room temperature.

For kinetic experiments, the monomer conversions at different time intervals were determined by Gas Chromatography (Perkin Elmer, Autosystem XL) using N_2 as carrier gas (7 psi) and FID as detector. The column used was BP-1 (SGE, Australia) which was non-polar, with a length of 25 m and an inner diameter of 0.1 μ. The temperature conditions used were, oven temp. = 50 °C, injector temp. = 200°C and detector temp. = 250 °C. The monomer conversion was measured with respect to an internal standard, which in our case was *n*-octane.

The stereochemistry of PMMA was determined by ^{1}H NMR spectroscopic analysis using (200 MH_Z, Bruker) spectrophotometer. During the synthesis of hydroxy-functional initiators, the products at different steps were confirmed by ^{1}H NMR of the column-purified compound, using the same instrument. ^{1}H NMR (500 Hz, Bruker) was used to quantify the protected hydroxy end-function of the functional PMMA prepared using the functionalized initiators. It was also used to determine the end-functionality of hydroxy-functional PMMA macromonomers containing allyl or styryl end-function.
^{13}C NMR (200 MHz, Bruker) and ^{1}H NMR (200 MHz and 500 MHz, Bruker) were also used to confirm the structure of PMMA-*b*-PEO and also to determine the copolymer composition.

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Chapter 3: Controlled Anionic Polymerization of Methyl Methacrylate in Presence of Various Lithium Salts in Toluene-THF Mixed Solvent

3.1. Introduction

The modern era of anionic polymerization started with Szwarc`s work[1] in mid 1950s and culminated in the discovery, recognition and significant development of living polymerization. A tremendous amount of research activity has been devoted to living anionic polymerization of alkyl methacrylates in the last few decades. Unlike commercial free radical methods, anionic polymerization allows precise control of molecular characteristics, e.g. molecular weight, molecular weight distribution, stereochemistry, and also enables preparation of polymers with special architectures, with well-controlled structure and dimensions.[2,3] Despite a tremendous progress in the field of controlled radical polymerization in recent years,[4] living anionic polymerization continues to be the most versatile method that has been ever employed for precise macromolecular engineering of polymers required for specific applications.

However, anionic polymerization of methyl methacrylate (MMA) suffers from severe secondary reactions due to the presence of the ester group, e.g. attack of the initiating or propagating species on the ester carbonyl, and intramolecular backbiting reactions forming β-keto cyclic ester. These undesirable reactions result in polymers with broad molecular weight distribution and low conversion.[5-10,13,14] Several mechanistic and kinetic studies have helped in optimizing the reaction conditions wherein a controlled anionic polymerization of methacrylates is achieved. Use of polar solvents such as THF,[11,12] bulky initiators e.g. 1,1`-diphenylhexyllithium (DPHLi)[15,16] and low reaction temperatures[17,18] (-78 °C) are employed to suppress the secondary reactions significantly.

The presence of a dynamic equilibrium between propagating enolate ion-pairs with aggregated ones in MMA polymerization was demonstrated by Kunkel et al[18] and was later confirmed by multinuclear NMR studies with models of the propagating chain-end.[19] The externally solvated contact ion-pairs of $PMMA^-Li^+$ are believed to be in equilibrium with dimeric solvated ion-pairs such that the position of equilibrium and the rate of interconversion between the different co-existing ion-pairs strongly affect the distribution of the resulting polymer, a higher rate of inter-conversion leading to narrower MWD.

Use of ligands and salts as additives is becoming an increasingly efficient tool for controlling the living polymerization of alkyl methacrylates. A multitude of additives has been used to affect the kinetics and mechanism of propagation and termination leading to considerable enhancement of the living character even in non-polar solvents and at fairly high temperatures. These ligands coordinate effectively with the initiating/propagating ion-pairs and are known to function in the following ways -

1) Change the stability and, hence, the reactivity of the ion-pairs by changing the electronic environment around it.
2) Replaces a slow dynamics between the different ion-pairs and/or aggregates by a faster equilibrium leading to an effectively single active species.
3) Coordination to the active site providing sufficient steric hindrance and, thus, minimizing undesired side -reactions

A variety of ligands found until now that significantly influence the kinetics of propagation and termination are classified as:

a) common-ion salts e.g. $NaBPh_4$;

b) σ-type ligands e.g. TMEDA[20], crown ethers and cryptands[21], that form complex with the counter-ions and increase the inter-ionic distance in the ion-pair

c) μ-type ligands e.g. alkali alkoxides[22], alkali halides[23], lithium perchlorate[24], alkyl silanolates[25] and aluminum alkyls[26], which coordinate with the ion-pair as such and lead to reasonably good control on the polymerization process,

d)μ-σ dual type, e.g amino alkoxides[27], monoalkoxyalkoxides[28] and dilithium alkoxy alkoxides[29], that combine the advantages of both the former types of ligands.

Teyssie and coworkers[23a] studied the effect of various lithium salts, e.g. LiF, LiCl, LiBr, and $Li(C_6H_5)_4B$ on the anionic polymerization of MMA. In comparison to the other additives, addition of LiCl led to much better control on the polymerization at -78 °C in THF yielding well-defined polymers with predictable molecular weight and narrow molecular weight distribution ($M_w/M_n \leq 1.05$). Due to a strong Lewis acid character of LiCl, it coordinates very effectively with the propagating enolate ion-pairs forming μ-complexes that are in faster equilibrium with free ion-pairs in comparison to the slower equilibrium between free and associated ion-pairs existing in absence of the salt. This leads effectively to a single active species and, hence, a narrow molecular weight distribution of the resulting polymer. Besides perturbing the ion-pair equilibrium, formation of LiCl-adduct with ion-pairs decreases the extent of aggregation, as corroborated by viscometric measurements. However LiCl requires a polar solvent and low reaction temperature to yield PMMA with narrow MWD and high initiator efficiency. In mixed solvent of toluene-THF (9:1 v/v), the effect of LiCl in controlling the polymerization was not significant.

Later, the effect of $LiClO_4$ in controlling the anionic polymerization of *tert*-butylacrylate and MMA was studied by Baskaran et al.[24] $LiClO_4$, being a strong Lewis acid, functions in a way similar to LiCl and provides excellent control over these polymerization processes not only in polar solvent like THF, but also in less polar mixed solvent of toluene and THF (9:1 v/v) and at higher temperatures. The control on polymerization was influenced significantly by the ratio of $LiClO_4$ to the active centers. In toluene-THF mixed solvent medium of low polarity, the maximum control was achieved on increasing the ratio to 5.0 and extremely narrow MWD polymers were obtained, with high initiator efficiency. Further increase in ratio did not have any significant effect in decreasing the MWD. However, $LiClO_4$ did not have much influence on the rate of termination and the extent of aggregation of the ion-pairs.

Lithium halides have a strong propensity to complexes with alkyl lithium compounds producing so-called "mixed aggregates" that have different reactivity in comparison to the uncomplexed species.[31] Such inorganic salts are known to interact strongly with a growing ion-pair, and, by perturbing the ion-pair association equilibrium, affect the course of anionic polymerization of alkyl methacrylates.[32] The effect of a salt is specifically related to the steric and electronic effect exerted during its complexation with the propagating enolate ion-pairs.[33] It is known that Li-salts with soft anions have Lewis acid character and, consequently, they coordinate with nucleophilic centers and greatly influence the course of a reaction. Therefore, our aim was to use those Li-salts that exhibit Lewis acidity, and which are capable of complexing with the propagating anion in methacrylate polymerization. Through complexation, they are expected to change the electronic environment around the anionic centre and perturb the ion-pair association equilibrium in a more favorable way, so as to decrease the polydispersity of the resulting polymer. Moreover, these Li-salts, due to softness of the anions, have more covalent nature and are highly soluble in relatively low polarity solvents. Hence, they are expected to coordinatively interact with the propagating enolate ion-pairs even in low polarity solvent such as toluene-THF (9:1 v/v) mixture, and affect a controlled polymerization. LiCl has more ionic character and, hence, has limited solubility in low polarity solvents. This factor may be responsible for its inability to promote a controlled polymerization of methacrylates in less polar medium, as reported earlier.[23a] Also, coordination of the salt with the propagating anion modulates the steric environment around the ionic center. This, as well as the strength of coordination of the added Li-salt with the growing ion-pair, influence the mechanism of monomer insertion and hence, the stereochemistry of the polymer chains. In the present study, we have chosen Li-salts with Lewis acidic properties that are highly soluble in toluene-THF (9:1 v/v) mixed solvent. They are expected to complex with the ion-pairs with different efficiencies, and influence the ion-pair aggregation and mechanism of monomer insertions to different extents. The influence of $LiClO_4$, $LiBF_4$ as well as Li-trifluoromethanesulfonate on the mechanism of anionic polymerization of MMA was studied in details.

3.2. Experimental

3.2.1. Materials and purification:

The source and purification of nitrogen, solvents like THF, toluene and the monomer, i.e. MMA were the same as described in chapter 2. $LiBF_4$ and $LiClO_4$ were procured from Aldrich, USA and were dried by heating to ~80 °C under high vacuum for 12 h. Li-triflouromethanesulfonate (Li-triflate) was prepared by dropwise addition of *n*-BuLi to a solution of trifluoromethanesulfonic acid (triflic acid, Aldrich) in dry THF at -40 °C under inert atmosphere. A small amount of DPE (Aldrich) was added so as to form red-colored DPHLi as an indicator at the end-point of the reaction.

3.2.2. Polymerization:

The polymerization was carried out in flamed glass apparatus under inert atmosphere as has been described earlier in chapter 2. All the batch polymerizations conducted in pure THF were continued for 10-15 mins. before termination with distilled methanol and those conducted in toluene-THF (9:1v/v) were continued usually for 2-2.5 h before termination. The polymers in mixed solvent were concentrated, then diluted with THF, and finally precipitated in *n*-hexane in the usual way, to facilitate the drying process.

3.2.3. Analysis:

The conversion was calculated from the gravimetric yield of the polymer. Characterization of PMMA was carried out by using Waters GPC 150C equipped with 100Å, 500Å, 10^3Å, 10^5Å, and one linear μ-Ultrastyragel columns and THF as eluent at a flow rate of 1mL min^{-1} at 30 °C. One RI and one UV detector were connected to the instrument.

3.3. Results and discussion

3.3.1. Polymerization of MMA in the absence of any additive:

Anionic polymerization of MMA in THF using DPHLi as initiator at -40 °C and -78 °C in the absence of any additive proceeds rapidly to 100% conversion but with poor agreement between targeted and observed molecular weight, as seen from the results in Table 3.1.

Table 3.1: Anionic polymerization of MMA polymerization in THF using DPHLi as initiator in presence and absence of $LiClO_4$.

Run no.	$[M]_o$ m/L	$[I]_o \times 10^3$ m/L	$[LiClO_4]/[I]_o$	Temp. (°C)	Conv.$^{a)}$ %	$\bar{M}_{n,calc.}$	$\bar{M}_{n,sec.}$	MWD	f
9	0.25	1.65	0	-40	100	16300	24200	1.54	0.67
7	0.10	1.65	0	-40	80	5000	7900	1.23	0.64
8	0.25	1.65	10	-40	95	15500	18100	1.16	0.86
6	0.37	1.65	10	-40	88	21100	22700	1.14	0.93
3	0.31	1.29	0	-78	100	25400	40400	1.18	0.63
2	0.26	1.28	10	-78	100	28800	30000	1.07	0.96

a) Rxn. time was 10-15 mins.

The poor initiator efficiency, i.e. the ratio between calculated and observed number average molecular weight, may be due to loss of initiator by side-reactions with the ester group of the monomer, at the beginning of the reaction. The molecular weight distribution (MWD) of PMMA prepared at -78 °C are fairly narrow ($\overline{M}_w/\overline{M}_n \leq 1.18$), whereas PMMA prepared at higher temperatures, i.e. -40 °C, have a broad MWD ($\overline{M}_w/\overline{M}_n \leq 1.54$), as well as poor initiator efficiency, indicating absence of any control on the polymerization.

However, MMA polymerization at -78 °C in less polar toluene/THF (9:1 v/v) mixed solvent in the absence of any additive, results in an ill-controlled polymerization.[24] The resulting polymers exhibit broad multimodal molecular weight distributions ($\overline{M}_w/\overline{M}_n \approx 2.8$) with no correlation between targeted and observed molecular weight. In the absence of any additive, a slow dynamic equilibrium exists between different ion-pairs and their aggregates. These aggregated and unaggregated ion-pairs are capable of adding on to monomers at different rates, thus, leading to a broad and multimodal distribution of the resulting PMMA.

Thus solvent polarity plays a significant role in solvation of the countercation in anionic polymerization of MMA. This largely affects the ion-pair association equilibrium. The nature and reactivity of the propagating species is also influenced by polarity of the solvent.[11] Polymerizations are much simpler and more controlled in pure THF but are complicated due to aggregation in low polarity medium.[10]

3.3.2. Effect of $LiClO_4$ on anionic polymerization of MMA:

3.3.2.1. Polymerization in THF:

In contrast to polymerizations that proceed without much control in the absence of any Lewis acid additive, MMA polymerization in THF in the presence of $LiClO_4$, added in 10:1 molar ratio with respect to DPHLi as initiator, is a sufficiently controlled process both at -40 °C and -78 °C. The results in Table 3.1 shows that the presence of $LiClO_4$ provides a perfect control on the polymerization at -78 °C, resulting in PMMA with narrow molecular weight distribution, i.e. $\overline{M}_w/\overline{M}_n = 1.07$, in contrast to 1.18 in the absence of the salt. Also, the conversion was almost quantitative. Unlike the polymerization in the absence of additive, there is good agreement between theoretical molecular weight calculated on basis of gravimetric conversion, and observed molecular weights, i.e. initiator efficiency '*f*' is close to unity. Even for polymerizations at -40 °C, presence of $LiClO_4$ in ten moles excess over DPHLi, significantly narrows the molecular weight distribution and improves the initiator efficiency. However, the efficiency of the salt in promoting a living anionic polymerization of MMA is greater at lower temperatures, e.g. -78 °C, as evident from the lower polydispersity of the PMMA compared to that at -40 °C.

3.3.2.2. Polymerization in toluene-THF (9:1 v/v):

The effect of $LiClO_4$ on MMA polymerization in a mixed solvent of toluene-THF (9:1 v/v), at -78 °C and -40 °C, is evident from the results given in Table 3.2. For MMA polymerizations at -40 °C in the presence of $LiClO_4$, the molecular weight distributions of the resulting polymers are found to be significantly broad, with tailing on the low molecular weight side and occasional hump on high molecular weight side (Fig. 3.1). The initiator efficiencies are also low as well as inconsistent. Also, increasing additive concentration to 20 times over the initiator (Table 3.1, run. no. 18) does not have any improved effect. Thus, it seems that $LiClO_4$ has no beneficial effect on anionic polymerization of MMA at -40 °C in a less polar medium of toluene-THF (9:1 v/v) mixture. Possibly the initiator and the propagating species undergoes some side-reactions with $LiClO_4$ at -40 °C, leading to a quenching of the initiator and active centers, resulting in a poor control over molecular weight and MWD. In contrast to the polymerization at -40 °C, $LiClO_4$ has a dramatic effect in controlling the anionic polymerization of MMA at -78 °C, in less polar mixed solvent, as evident from the results in Table 3.2. The conversions, determined gravimetrically, were usually 90-100 % within a polymerization time of 2-2.5 h. GPC analysis of the resulting PMMA show very narrow molecular weight distribution, usually, less than 1.08 (Fig. 3.2). Also, there is a good agreement between theoretical molecular weight that is calculated on the basis of conversion and the observed molecular weight.

Table 3.2 : Anionic polymerization of MMA in toluene-THF (9:1 v/v) using DPHLi as initiator in presence of $LiClO_4$ (in 10:1 mole ratio w.r.t. DPHLi).

Run no.	$[M]_o$ m/L	$[I]_o \times 10^3$ m/L	tol:THF	Temp. (°C)	Conv.[a] %	$\overline{M}_{n,calc.}$	$\overline{M}_{n,sec}$	MWD	*f*
10	0.25	0.85	9:1	-40	44	13400	20300	1.48	0.66
14	0.19	0.75	8.7:1.3	-40	85.7	22200	21600	1.63	1.03
15	0.21	0.75	8.7:1.3	-40	91	27000	23100	1.46	1.16
16	022	0.76	8.9:1.1	"	55	16400	25000	1.47	0.66
19	0.21	1.01	9:1	"	78	18200	17000	1.39	1.07
34	0.26	1.09	8.5:1.5	"	70	18000	22000	1.39	0.82
35	0.26	1.09	8.5:1.5	"	80	20600	27200	1.47	0.76
18[b)]	0.33	1.59	9.4:0.6	"	66	15400	13000	1.46	1.19
25	0.28	1.52	9:1	-78	90	12900	13000	1.07	0.99
28	1.51	0.28	9:1	"	82	15300	14000	1.08	1.09
29	1.51	0.31	9:1	"	80	16800	14200	1.08	1.18
30	1.09	0.21	9:1	"	88	9000	9100	1.07	0.99
31	1.09	0.24	9:1	"	94	16500	17900	1.10	0.92
32	6.93	0.12	8.7:1.3	"	~100	1900	2200	1.08	0.83

a) Rxn. time was 2-2.5 h

b) *b)* $LiClO_4$ added in 20:1 mole ratio w.r.t. DPHLi

Also, the percentages of syndiotactic, isotactic and atactic placements as determined by ^1H NMR (200 MHz, Bruker) spectroscopy of the PMMA prepared in the absence of any additive are 55 %, 27 % and 18 % respectively, as shown in Fig. 3.3. In the presence of $LiClO_4$, the stereochemistry is significantly changed, with the extent of syndiotactic placements increased to 64 %, and the atactic decreased to 9% (Fig. 3.4).

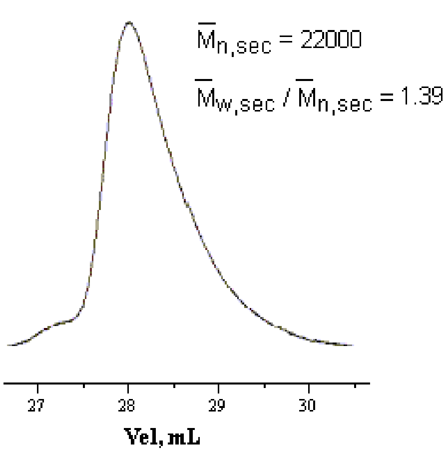

Fig. 3.1: Typical GPC elugram of PMMA prepared in toluene-THF (9:1 v/v) at –40 °C in presence of $LiClO_4$. Shows hump on high molecular wt. side and tailing on low mol. wt. side (run no. 34, Table 3.2).

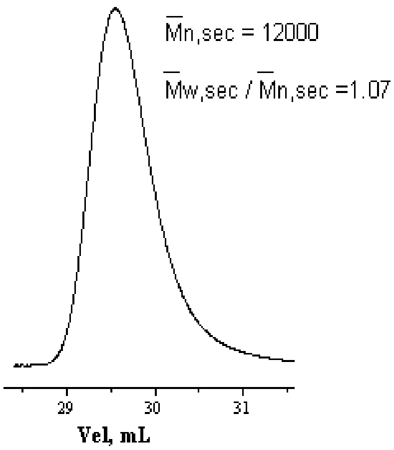

Fig. 3.2: Typical GPC elugram of PMMA prepared in toluene-THF (9:1 v/v) at –78 °C in presence of $LiClO_4$. Shows narrow molecular weight distribution (run no. 25, Table 3.2)

This implies that presence of 10 moles excess of the salt over the active center concentration leads to an effective coordination of the salt with the propagating species and makes it possible to control the placement of the incoming monomer during polymerization.

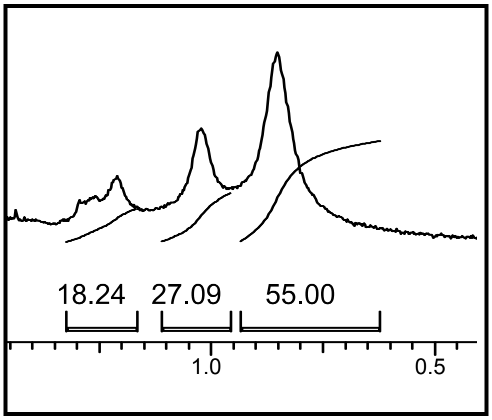

Fig. 3.3: ^{1}H NMR (200 MIHz, $CDCl_3$) of PMMA prepared in absence of additive in toluene-THF (9:1 v/v). Peaks between 0.5 to 1.3 ppm corresponding to -$C(CH_3)$ group show 55% syndiotactic, 27 % isotactic and 18 % atactic placements.

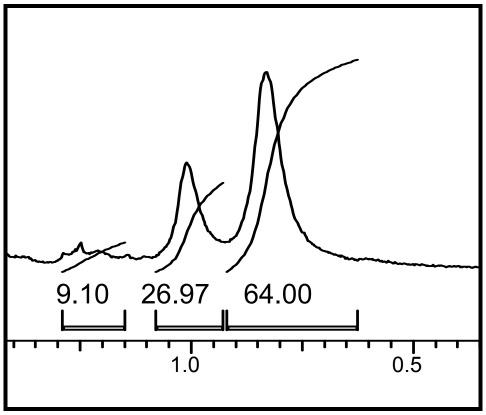

Fig. 3.4: ^{1}H NMR (200 MHz, $CDCl_3$) of PMMA prepared in toluene -THF (9:1 v/v) in presence of $LiClO_4$ at - 78 °C. The syndiotactic, isotactic and atactic percentages are 64%, 27%, and 9% respectively.

Also, the rate of interconversion of the associated and unassociated species determines the time of availability of the unassociated species to the monomer, which is higher for a faster rate of interconversion. Since monomer addition to the unassociated species takes place through an energetically more favorable syndiotactic insertion, so a faster equilibrium leads to higher syndiotacticity of the resulting PMMA.

Thus, $LiClO_4$ added in excess over the initiator concentration is effective in promoting a well-controlled anionic polymerization of MMA even in less polar mixed solvent of toluene-THF (9:1 v/v). Under similar conditions LiCl, when added in equimolar quantity with respect to the initiator, was reported to have little effect in controlling the polymerization of MMA, and the resulting polymers showed broad multimodal MWD upto 50 % conversion.[23a] Later, it was reported that LiCl when added in 5:1 with respect to the initiator in toluene-THF mixture, resulted in polymers with MWD of 1.17.[30] LiCl that has a poor solubility in toluene-THF (9:1 v/v) mixed solvent, and may lead to a homogeneous solution only on addition of DPHLi, i.e. the LiCl-DPHLi complex is more soluble in the medium. In contrast to LiCl, $LiClO_4$ has a much higher solubility in the mixed solvent and the solution is homogeneous even when $LiClO_4$ is added in 10 molar excess over the initiator. Possibly, $LiClO_4$ being a strong Lewis acid, coordinates with the active centers more effectively and perturbs the ion-pair association equilibrium in a more favorable way. Formation of ion-pair-$LiClO_4$ mixed aggregates in faster equilibrium with the non-associated ones results in propagation through an effectively single active species and, hence, leads to narrow MWD. Our investigations clearly demonstrate the remarkable ability of $LiClO_4$ in promoting a perfectly controlled polymerization even in toluene-THF (9:1 v/v) mixture.

3.3.3. Effect of Li-triflate on anionic polymerization of MMA:

3.3.3.1. Polymerization in THF:

Li-triflate being a strong Lewis acid was also expected to function in the same way as $LiClO_4$ in promoting a controlled anionic polymerization of MMA at lower temperatures. The results of polymerization in THF at -78 °C and -40 °C, as determined by GPC analysis are shown in Table 3.3. In contrast to the polymers prepared at -78 °C in absence of any additive, that show a relatively broad MWD, the PMMA prepared in presence of the triflate salt in ten moles excess over DPHLi exhibit a much better control on the molecular weight and molecular weight distribution. The conversions are quantitative and the polymers show relatively narrow MWD, i.e. $\overline{M}_w/\overline{M}_n \leq 1.10$. Also, the conversions are very high within 10-15 mins reaction time, and there is a fairly good agreement between theoretical and observed molecular weight, as evident from the 'f' values close to 1.0. The ability of the salt in enhancing the livingness of the

Table 3.3: Anionic polymerization of MMA in THF using DPHLi as initiator in presence of Li-triflate (in 10:1 molar ratio w.r.t. DPHLi)

Run no.	$[M]_o$ m/L	$[I]_o\times10^3$ m/L	Temp. (°C)	Conv.[a)] %	$\overline{M}_{n,calc.}$	$\overline{M}_{n,sec.}$	MWD	f
3	0.28	0.80	-40	96	35500	42700	1.17	0.83
20	0.34	0.94	-40	87	31000	31100	1.16	0.99
13	0.37	0.90	"	88	35200	38800	1.15	0.90
12	0.27	0.90	-78	90	27700	23500	1.09	1.16
18	0.27	0.94	-78	83	23800	20900	1.10	1.13
19	0.34	0.94	"	87	31000	27400	1.10	1.13

a) Rxn. time was 10-15 mins.

polymerization is evident even at -40 °C. Fairly narrow MWD and high initiator efficiencies characterize the PMMA prepared in presence of the salt at-40 °C.

Thus Li-triflate, just like $LiClO_4$, effectively coordinates with the enolate ion-pairs in a polar medium, and establishes a faster equilibrium between different salt-complexed ion-pairs and aggregates, leading to a narrow distribution of the resulting PMMA. Upon comparing the GPC data for the polymerization in the presence of $LiClO_4$ with those of Li-triflate, it is observed that the MWD of the polymers prepared under similar conditions using $LiClO_4$ have lower polydispersity ($\bar{M}_w/\ \bar{M}_n \leq 1.08$) than those in presence of the triflate salt. In Li-triflate, the anion is relatively softer compared to that of $LiClO_4$. It is known that a harder base binds more strongly with a hard acid and since Li^+ is a hard acid in this case, complexation of $LiClO_4$ with the Li-enolate ion-pair is comparatively stronger. A less effective complexation of Li-triflate with the propagating enolate ion-pair in comparison to $LiClO_4$ causes lesser perturbation of the ion-pair equilibrium and less control on the polymerization.

3.3.3.2. Polymerization in toluene-THF (9:1 v/v) mixed solvent:

We had earlier discussed about anionic polymerization of MMA that proceeds without any control over molecular weight and MWD in absence of any salt-additive in a mixed solvent toluene-THF (9:1 v/v) of lower polarity. Addition of Li-triflate in 10:1 ratio with respect to DPHLi brings about a significant improvement in the situation. The results of the polymerization are given in Table 3.4. Unlike the broad and multimodal MWD of the PMMA prepared in absence to the additive, those prepared in presence of the salt at -78 °C, exhibit sufficiently narrow unimodal MWD (Fig. 3.6) with good correlation between theoretical and observed molecular weights. The gravimetric conversions are usually 40-50 % after a polymerization time of 3.5-4 h. Possibly, complexation of Li-triflate with the enolate ion-pairs creates a sterically hindered environment around the propagating center, thus decreasing the reactivity of the ion-pairs relative to that in presence of $LiClO_4$. The theoretical molecular weights were calculated based on the gravimetric conversion. Although the beneficial effect of Li-triflate in controlling anionic polymerization of MMA is observed at lower temperatures, i.e. -78 °C, the results of polymerization conducted at higher temperatures, i.e. -40 °C in presence of excess Li-triflate, are not encouraging.

Table 3.4: Anionic polymerization of MMA in toluene-THF (9:1 v/v) mixture using DPHLi as initiator in presence of Li-triflate (in 10:1 molar ratio w.r.t DPHLi)

Run no.	$[M]_o$ m/L	$[I]\times10^3$ m/L	Temp.	Time of rxn.(h)	Conv.$^{a)}$ %	$\overline{M}_{n,\ calc.}$	$\overline{M}_{n,\ sec}$	MWD	*f*
4	0.22	0.94	-40	3.5	53	12400	26200	1.75	0.47
16	0.26	0.90	-40	3.5	51	18760	35300	1.59	0.53
17	0.32	0.90	-78	3.5	43	18690	27000	1.08	0.70
21	0.35	0.89	-78	4.0	52	20600	20000	1.11	1.03
22	0.21	0.89	-78	4.0	44	10460	11200	1.11	0.93

a) Rxn. time was 3.5-4 h

Much alike $LiClO_4$ system, Li-triflate fails to impart much control over the polymerization at temperatures at -40 °C in a less polar medium. This may be due to some inherent side-reactions involving the initiating/propagating species with the salt that gain prominence at higher temperatures, resulting in a loss of active centers.

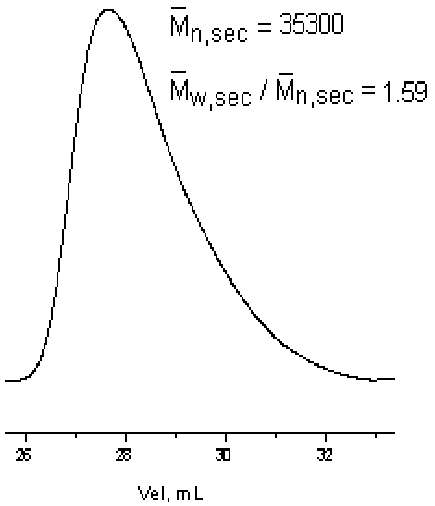

Fig. 3.5: Typical GPC elugram of PMMA prepared in presence of Li-riflate in toluene-THF (9:1 v/v) at -40 °C (run no. 16, Table 3.4)

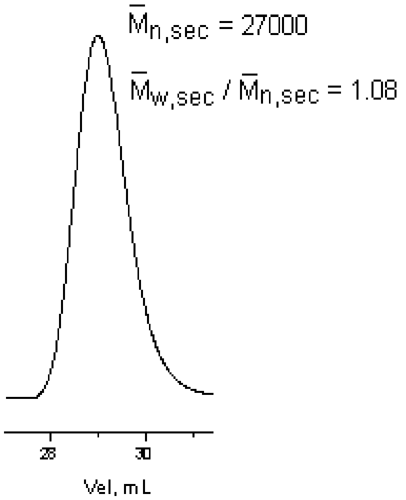

Fig. 3.6: Typical GPC elugram of PMMA prepared in presence of Li-riflate in toluene-THF (9:1 v/v) at -78 °C (run no. 17, Table 3.4)

The runs 4 and 16 in Table 3.4, show the poor control over MMA polymerization in toluene-THF (9:1 v/v) mixture even in the presence of the salt in 10:1 molar ratio with respect to the initiator. Broad MWD ((Fig. 3.5) and poor agreement between theoretical and observed molecular weight characterize the polymers prepared at -40 °C.

The difference in the MWD of PMMA prepared at -78 °C in mixed solvent system in presence of $LiClO_4$ and Li-triflate suggests a difference in the coordination pattern of the two salts. This is also reflected to some extent in the microstructure of the polymers prepared in presence of the two salts, as determined by ^1H NMR analysis. The percentage of syndiotactic, isotactic and atactic placements of PMMA prepared in mixed solvent system at -78°C in presence of Li-triflate (Fig. 3.7) is 58, 34, 8 respectively, as against 64, 27 and 9% respectively for $LiClO_4$ system. So it seems that a stronger complexation of $LiClO_4$ with the ion-pairs result in a faster equilibrium dynamics in comparison to Li-triflate, thus leading to slightly higher syndiotacticity, since a faster equilibrium favors a syndiotactic placement of the incoming monomer (section 3.3.2.2). A relatively weaker coordination of Li-triflate with the ion-pairs results in a small increase in isotacticity with a corresponding decrease in the syndiotacticity from that observed in the presence of $LiClO_4$.

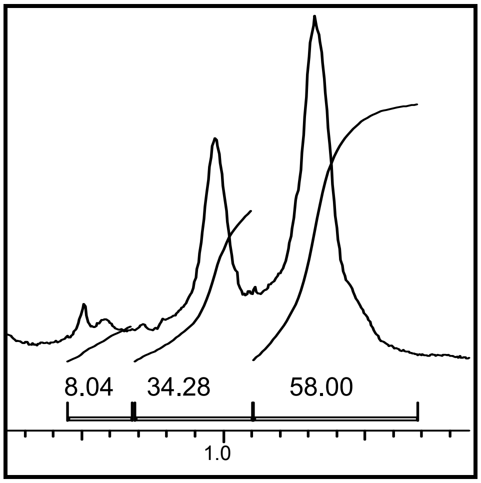

Fig. 3.7: ^1H NMR (200 MHz, $CDCl_3$) of PMMA prepared in presence of Li-triflate in toluene-THF (9:1 v/v) at -78 °C show 58 % syndiotactic, 34 % isotactic and 8 % atactic placements.

3.3.4. Effect of $LiBF_4$ on anionic polymerization of MMA

The usefulness of yet another strong Lewis acid i.e. $LiBF_4$ in controlling the anionic polymerization of MMA was studied both in THF as well as toluene/THF (9:1v/v) mixture solvent at -78 °C and at -40 °C using DPHLi as initiator. The results of GPC analysis of the resulting PMMA are shown in Table 3.5.

Table 3.5: Anionic polymerization of MMA in THF and toluene-THF (9:1 v/v) using DPHLi as initiator in presence and absence of $LiBF_4$.

Run no.	$[M]_o$ m/L	$[I]_o$ $\times 10^3$ m/L	Tol:THF (v/v)	$[LiBF_4]/[I]_o$	Temp. (°C)	Conv.[a)] %	$\overline{M}_{n,calc.}$	$\overline{M}_{n,sec}$	MWD	f
9	0.27	1.5	0:1	10	-40	88	15900	22200	1.16	0.71
13	0.26	0.69	0:1	10	-78	80	30700	28500	1.09	1.07
1	0.28	1.7	8.9:1.1	0	-40	90	14800	25300	2.62	0.58
2	0.28	1.7	8.9:1.1	1.12	-40	92	15200	24700	1.54	0.61
3	0.28	1.7	9:1	2.25	-40	90	14800	23400	1.61	0.63
4	0.28	1.7	8.9:1.1	5.65	-40	92	15200	28700	1.74	0.53
12	0.32	0.69	9:1	10	-40	37	17000	23600	1.70	0.68
11	0.26	0.69	9:1	10	-78	30	11500	10300	1.09	1.11

a) Rxn. time was 10 min. for polymn. in THF and 2 h for polymn. in toluene-THF (9:1 v/v)

For MMA polymerizations in THF at -78 °C, addition of $LiBF_4$ in 10:1 mole ratio with respect to DPHLi, helps in narrowing down the molecular weight distribution (MWD~1.09) from that observed in absence of the salt. Conversions, determined gravimetrically, are greater than 80 % within a polymerization time of 10 min. The theoretical molecular weights calculated on the basis of conversion are in close agreement with the observed value, i.e. the initiator efficiency is close to 1.0. Though this beneficial effect of $LiBF_4$ on MMA polymerization is still present at -40 °C, it is clear from the results in Table 3.5, that the MWD of the PMMA prepared at -40 °C is broader and the initiator efficiency lower than those prepared at -78 °C. Possibly the $LiBF_4$-ion-pair complexation at higher temperatures was not quite effective as that at -78 °C. In this respect, $LiBF_4$ acts exactly in the same way as other salts, which are capable of imparting greater control at -78 °C in comparison to -40 °C.

$LiBF_4$ is as effective as $LiClO_4$ and Li-triflate in enhancing the livingness of MMA polymerization in a less polar medium of toluene/THF (9:1 v/v) mixture when the polymerization is performed at -78 °C. However, the polymerization seems to be slow as the conversions reaches 30 % after 2h. The theoretical molecular weight calculated on basis of conversion is in agreement with the observed molecular weight. The polymers also exhibit sufficiently low polydispersity (M_w/ $\overline{M}_n$ = 1.09) as seen in Fig. 3.9 (for run no. 11, Table 3.5). This implies that $LiBF_4$, being a strong Lewis acid, is capable of coordinating with the propagating enolate-ion-pairs and perturbing the ion-pair association equilibrium in a manner similar to LiCl or $LiClO_4$. The classical slow equilibrium between different ion-pair aggregates in absence of any Lewis acid additive is affected by $LiBF_4$ addition, resulting in formation of mixed aggregates in rapid equilibrium with the unassociated ion-pairs. This leads to a significant improvement in the polydispersity and initiator efficiency of the resulting PMMA. The microstructure of the PMMA prepared in the mixed solvent medium in presence of 10 moles excess of $LiBF_4$ (Fig. 3.10) revealed 61 % syndiotacticity, 31 % isotacticity and 8 % atacticity. A slightly higher percentage of

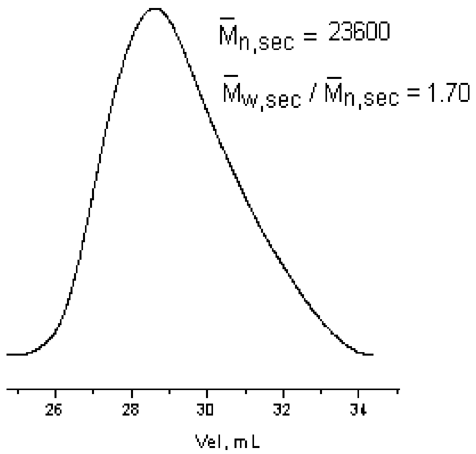

Fig. 3.8: Typical GPC elugram of PMMA prepared in presence of $LiBF_4$ in toluene-THF (9:1 v/v) at -40 °C (run no. 12, Table 3.5).

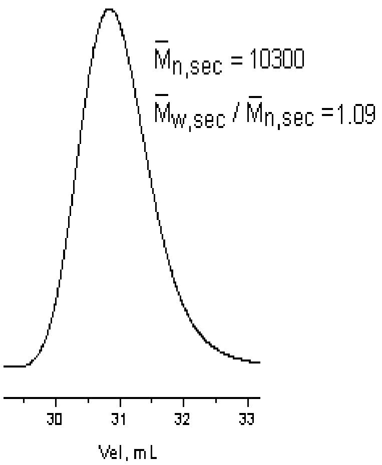

Fig. 3.9: Typical GPC elugram of PMMA prepared in presence of $LiBF_4$ in toluene-THF (9:1 v/v) at -78 °C (run no. 11, Table 3.5).

isotacticity and lower percentage of syndiotacticity in comparison to the $LiClO_4$ system possibly arises out of different coordinating abilities of $LiBF_4$ and $LiClO_4$ with the enolate ion-pairs, and different equilibrium dynamics. However, the difference is too small to reflect the strength of complexation of $LiBF_4$ with the ion-pairs relative to $LiClO_4$ and Li-triflate.

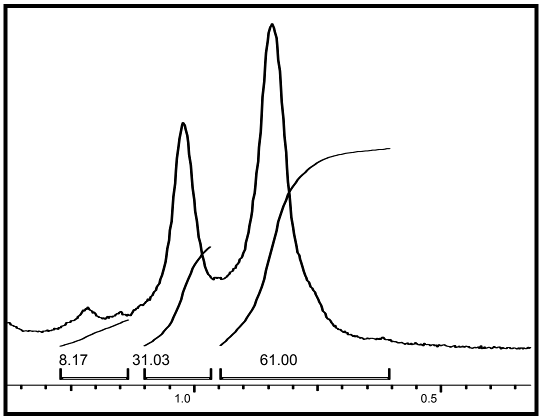

Fig. 3.10: ^{1}H NMR (200 MHz, $CDCl_3$) of PMMA prepared in presence of $LiBF_4$ in toluene-THF (9:1 v/v) at -78 °C show 61% syndiotactic, 31 % isotactic and 8 % atactic placements.

Much like the $LiClO_4$ and Li-triflate systems, polymerizations conducted in toluene-THF mixture solvent at -40 °C in presence of $LiBF_4$ proceeds without much control (Fig. 3.8). The resulting polymers showed increasing polydispersity and decreasing initiator efficiency with increase in the ratio from 0 to 10. This partially substantiates our assumption that the initiating and/or propagating species undergoes undesirable side-reactions with the salt at higher temperatures. With increase in the concentration of the salt with respect to the initiator or active species, the extent of side-reactions increases, resulting in broader MWD and lower 'f' values. Thus, like other Li-salts that have been studied, $LiBF_4$ also does not contribute much to enhancing the livingness of anionic polymerization of MMA at temperatures higher than -78 °C in low polarity medium.

3.4. Conclusion

Anionic polymerization of MMA in THF and toluene-THF (9:1 v/v) mixed solvent using DPHLi as initiator, proceeds with enhanced control over the polydispersity and molecular weight of the resulting PMMA, in the presence of various common-ion salts e.g. $LiClO_4$, $LiBF_4$, and Li-triflate. These Li salts possess Lewis acid character and thus coordinate with the propagating Li-enolate ion-pairs, forming mixed complexes in a way similar to LiCl. Moreover, these salts have significant covalent character due to presence of large polarizable anions, resulting in a higher solubility in a less polar mixed solvent of toluene-THF (9:1 v/v). Thus, they are capable of promoting a controlled polymerization of MMA even in a non-polar medium, where an ionic salt like LiCl is reported to be ineffective. The salt-ion pair complexation perturbs the dynamic equilibrium that exists between Li-enolate ion-pairs and their aggregates. Such complexation also changes the steric environment around the propagating center. The extent of aggregation being higher in non-polar medium, control over the polymerization becomes a major challenge in such case. Multiple active species in slow equilibrium lead to an ill-defined product that exhibits broad multinomial MWD and poor correlation between targeted and achieved molecular weight. The above Li-salts have a high propensity to complex with the ion-pairs, and in the process they establish a new and relatively rapid equilibrium where the newly formed "mixed aggregates" are of comparable stability as the unassociated ion-pairs. The monomer sees an effectively single active species and hence leads to a narrow MWD of the resulting PMMA.

However, in toluene-THF (9:1 v/v) mixture, the use of salts result in a truly controlled polymerization only at -78 °C. For polymerizations at -40 °C in mixed solvent medium, the presence of these salts fail to impart any control over the MWD and the molecular weight of the obtained PMMAs. The progressive broadening of MWD and decreasing 'f ' with increasing ratio of $LiBF_4$ to DPHLi in toluene/THF mixture at -40 °C suggests that the salts possibly undergo side-reactions with the initiator or the propagating species at higher temperatures in a low dielectric medium. The nature of the side-reactions have not been identified.

The microstructures of the PMMA prepared in toluene-THF (9:1 v/v) mixed solvent in presence of the three salts at -78 °C was determined by ^1H NMR spectroscopy. The microsturcture in presence of $LiBF_4$, Li-triflate and $LiClO_4$ were found to differ from each other, but not significantly. The differences are too small to conclude anything regarding the strength of salt-ion pair complexation. The differences in microstructure imply different coordinating abilities of the salts with the ion-pairs. Among the three salts, presence of $LiClO_4$ results in the highest syndiotacticity of the resulting polymer. This suggests a stronger coordinating ability of $LiClO_4$ that leads to a faster equilibrium between the complexed aggregates and unaggragated species. This results in a greater availability of the unassociated active species where the monomer insertion takes place in a more energetically favorable syndiotactic manner.

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Chapter 4: Kinetics of Anionic Polymerization of Methyl Methacrylate in Toluene-Tetrahydrofuran Mixed Solvent in Presence of $LiClO_4$ and LiCl

4.1. Introduction

Our understanding of the mechanisms of controlled anionic polymerization of alkyl(meth)acrylates has made substantial progress over the last decade.[1-3,13] Anionic polymerization of methyl methacrylate proceeds in a controlled manner only under judiciously chosen reaction condition because the initiating and propagating species undergo secondary reactions with the ester group.[4-7] This is especially true in non-polar solvent, such as, toluene, wherein broad and multimodal molecular weight distribution are observed. Experimental evidence suggest the existence of a large quantity of oligomeric side-products and complex kinetics.[8-11, 35]

Moreover, anionic polymerization of methyl methacrylate (MMA) in toluene is complicated by the presence of different kinds of aggregates taking part in the polymerization. In polar solvents, such as THF, several kinetic investigations have revealed that the propagating species are externally solvated contact ion-pairs existing in equilibrium with their aggregates[12,13] and the dynamic equilibrium between ion-pairs and their aggregates profoundly controls the molecular weight distribution of the resulting polymer.[14] Only faster rate of inter-conversion between the different co-existing ion-pairs can lead to a narrow molecular weight distribution.[15] VPO and multinuclear NMR studies with models of the propagating chain-end confirmed the existence of tetramer to dimer equilibrium in THF. However, steric hindrance in polymeric system results in the externally solvated contact ion-pairs to be in equilibrium with less reactive dimeric solvated ion-pairs. Recent kinetic studies have revealed a fractional reaction order with respect to active centers thus giving a clear evidence of coexistence of ion-pairs and their aggregates even in polar medium like THF.[37] However, in non-polar solvent, extensive aggregation of propagating enolate ion-pairs leads to the formation of multiple active species exhibiting a slow equilibrium dynamics.[8-11] Thus, the polymerization of MMA in toluene or in a mixture of toluene-THF (9:1 v/v) often results in gel formation and the polymer exhibits multi-modal distribution due to the presence of various kinds of active aggregates.

In (meth)acrylate polymerization, 'Ligated Anionic Polymerization' or LAP, has become an efficient tool for perturbing the equilibrium dynamics of the ion-pair aggregates in a direction that favors synthesis of polymers with narrow molecular weight distribution.[18] Additives that have been used in alkyl (meth)acrylate polymerization are alkali metal salts of alkoxide,[19] halides,[20] perchlorates,[21] alkyl silanolates,[22] aluminum alkyls,[23-25] TMEDA,[28,29] amino alkoxides,[30] and polydentate dilithium alkoxides.[32] These additives coordinate with propagating enolate ion-pairs forming mixed aggregates of similar reactivity, thus replacing the slow dynamics between the aggregated and non-aggregated ion-pairs by a relatively faster one.

Kunkel et al[15] studied the kinetics of anionic polymerization of MMA in THF in presence of LiCl. They observed an increase in the rate of polymerization when the ratio (R) of LiCl to active center concentration [P*], i.e. R was less than 1.0, and reached the maximum at R=1 corresponding to the formation of reactive 1:1 adduct of the salt with the growing ion-pair. However, further increase in R decreased the polymerization rate due to the formation of a less reactive 1:2 adduct at higher concentration of LiCl. Viscometric measurements revealed that complexation with LiCl led to de-aggregation of Li-enolate in THF. A faster exchange rate between free and complexed ion-pairs compared to that between free and associated ion pairs led to narrow molecular weight distribution. These findings were later confirmed by ^{13}C and ^{7}Li NMR studies by Wang et al.[33]

In presence of t-BuOLi, coordination of the additive with the PMMA ion-pairs reduced the rate of termination ten times of that of propagation. However, in case of *tert*-butyl acrylate, stable adducts between the active centers and the alkoxide were formed, that interconverted slowly on the time-scale of monomer addition. This led to increase in polydispersity of the resultant polymers.[34]

Recently kinetics of MMA polymerization was studied in presence of $LiClO_4$ in THF at –20 °C.[37] The reaction was seen to follow first-order kinetics free of termination and transfer. Narrow and unimodal molecular weight distribution of polymers at all monomer conversions characterized the polymerization process. A reaction order of 0.5 was obtained that was consistent with the fact that $LiClO_4$-complexed propagating enolate ion-pairs were in equilibrium with their dimeric associates.

Although many additives provide excellent control over MMA polymerization in THF, only few additives e.g. aluminium alkyls and alkyl silanolates, are effective in non-polar solvent. Kinetic study of MMA polymerization in less polar mixed solvent of toluene-THF (9:1 v/v) showed a non-linear plot of conversion vs. time which was only slightly improved on addition of equimolar amount of LiCl.[20b] The distribution remained broad and multimodal upto 50 % conversion even in presence of LiCl. However, Baskaran and Sivaram reported the beneficial effect of $LiClO_4$ in controlling MMA polymerization in low polarity mixed solvent of toluene-THF (9:1 v/v) at -78 °C in a way similar to that in pure THF.[21] In this chapter, we have examined the kinetics of he polymerization of MMA in presence of $LiClO_4$ as well as LiCl in toluene-THF (9:1v/v) at -78 °C, with a view to gain a better understanding of the role of salts in controlling the polymerization.

4.2. Experimental section

4.2.1. Materials and purification:

MMA (Schuchardt, Germany) was fractionally distilled over CaH_2 under reduced pressure, and stored over CaH_2 under nitrogen. GC analysis was done to confirm the purity of MMA. The amount of methanol was found to be less than few nanograms.

n-Octane (S. D. Fine Chem., Bombay) was stirred over CaH_2, degassed and distilled under high vacuum and stored over molecular sieves under nitrogen. Just prior to polymerization, it was stirred along with the required amount of n-octane over CaH_2 for ~3 h, in a monomer distillation apparatus, degassed and then and distilled under vacuum in the usual manner. Solvents like THF, toluene and cyclohexane (S.D. Fine Chem.) were purified in the usual manner (refer chapter 2). Preparation and standardization of *n*-butyl lithium and 1,1-diphenylhexyllithium (DPHLi) are the same as described in chapter 2, except that DPHLi for kinetic study was prepared in toluene-THF (9:1 v/v mixture) instead of pure THF. Lithium perchlorate ($LiClO_4$, Aldrich) and lithium chloride (LiCl, Aldrich) was dried under vacuum at ~80 °C for 24 h.

4.2.2. Polymerization procedure:

All experiments were carried out in flame-dried single-necked glass reactors as usually followed for batch polymerization of MMA (refer chapter 2). In this case, a mixture of MMA and *n*-octane (30% v/v), freshly distilled over CaH_2 was added by syringe to the reactor. Use of cannula for transferring MMA was avoided as it would be necessary to release some pressure from inside the reactor during the transfer, and that would hamper syringing out of pick-outs which requires high nitrogen pressure. A part of the MMA-octane mixture was preserved in refrigerator for determining the zero-time monomer concentration. Pick-outs were taken from time to time using syringe cooled under N_2 and the living solution was quenched by distilled methanol. The polymer samples of the aliquotes were recovered by removing the solvent under vacuum, then re-dissolving in benzene, filtering and then freeze-drying to yield a fluffy powder.

4.2.3. Analysis

Monomer conversion was determined by GC (Perkin Elmer) using *n*-octane as internal standard. The column used was BP-1 (non-polar), and the oven, injector, and detector temperatures were maintained at 50 °C, 200 °C, and 250 °C respectively. The conversion at the different reaction times were determined using the following equation,

$x_p = 1 - [(M_t/I_t)/(M_0/I_0)]$

where x_p is the conversion at a given time t,

M_t/It is the mole ratio of monomer to internal standard (n-octane) at time = t, which is same as their peak area ratio,

M_0/I_0 is the mole ratio of monomer to internal standard at zero time determined in the same way.

The molecular weight and molecular weight distribution of the polymers were determined by GPC analysis.

4.3. Results and discussion

4.3.1. Effect of $LiClO_4$ on the kinetics of anionic polymerization of MMA in toluene-THF (9:1 v/v) mixture:

Polymerization of MMA in toluene-THF (9:1 v/v) mixture using DPHLi as initiator, was carried out at -78 °C in the absence of additive and in the presence of $LiClO_4$ (10:1 with respect to DPHLi). The results are given in Table 4.1 and 4.2. The reaction in the absence of additive was found to proceed much faster and the first-order time-conversion plot shows a downward curvature at higher conversion (Fig. 4.1). This indicates the presence of termination competing with propagation that decreases the apparent rate constant during polymerization.

The first-order rate equation for a termination free reaction polymerization is given by eqn. 4.1.

$$\ln \frac{[M]_0}{[M]_t} = k_{app} .t \qquad \text{................ Eqn. 4.1}$$

where $k_{app} = k_p.[P^*]$, k_p being the rate constant of propagation,

$[P^*] = f. [I]_0$ is the active center concentration,

$[I]_0$ is the initial initiator concentration,

f is the initiator efficiency determined from the ratio of calculated and experimental number-average degree of polymerization.

Thus the slope of the first-order curve gives the value of apparent rate constant k_{app}.

However, the polymerization in absence of additive is associated with unimolecular termination and the rate equation is given by[35] eqn. 4.2.

$$\ln \frac{[M]_0}{[M]_t} = \frac{k_{app}}{k_t} (1- e^{-k_t.t}) \qquad \text{...............Eqn. 4.2}$$

where k_t = rate constant of termination, determined from non-linear curve fitting procedure using eq. 4.2.

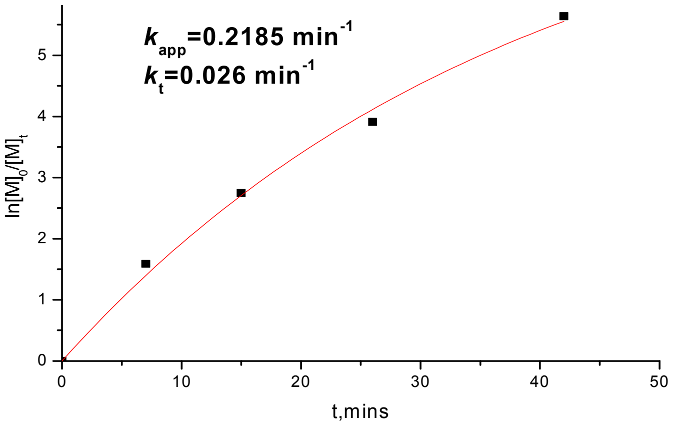

Fig. 4.1: First-order time-conversion plot of MMA polymerization in toluene-THF (9:1 v/v) in the absence of additive at –78 °C; $[I]_0$=1.5x10^{-3} mol/L; $[M]_0$=0.28 mol/L

The reaction mixture in absence of additive becomes too viscous at higher conversions, though no physical gel formation was observed. Broad and multimodal MWD at all conversions (Fig. 4.2) indicate the presence of multiple active species.

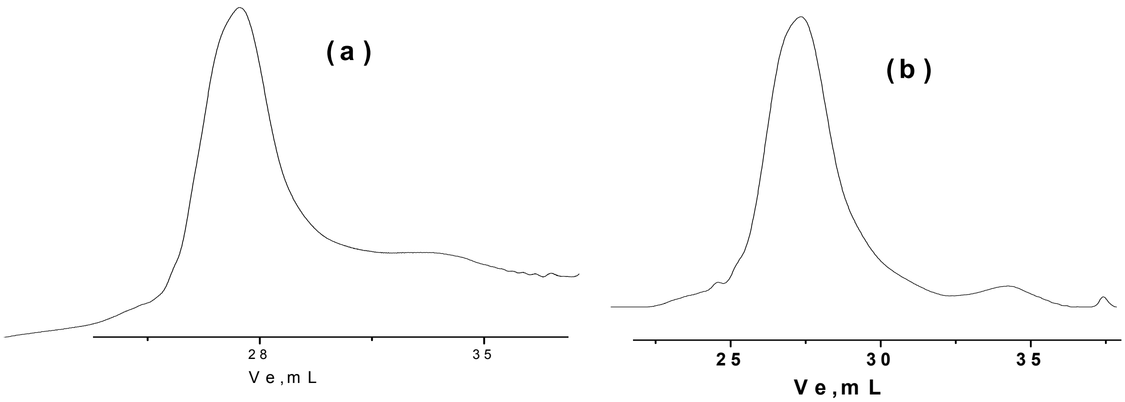

Fig. 4.2: SEC curves of PMMA prepared at –78□C in toluene-THF (9:1 v/v). (a) t=7 mins, xp=79.5%, $M_{n,sec}$=9373, MWD=6.9, (b) t=42 mins, xp=99.6%, $M_{n,sec}$=14345, MWD= 5.4

The situation was significantly improved upon addition of $LiClO_4$ in 10:1 ratio with respect to the initiator concentration. First-order time conversion plots at different active center concentrations in the presence of $LiClO_4$ are linear as seen in Fig. 4.3. This indicates absence of termination during the polymerization. The rate constants of polymerization at different active center concentrations, shown in Table 4.2, were obtained from the slope of the respective first-order plots, in accordance to eqn. 4.1.

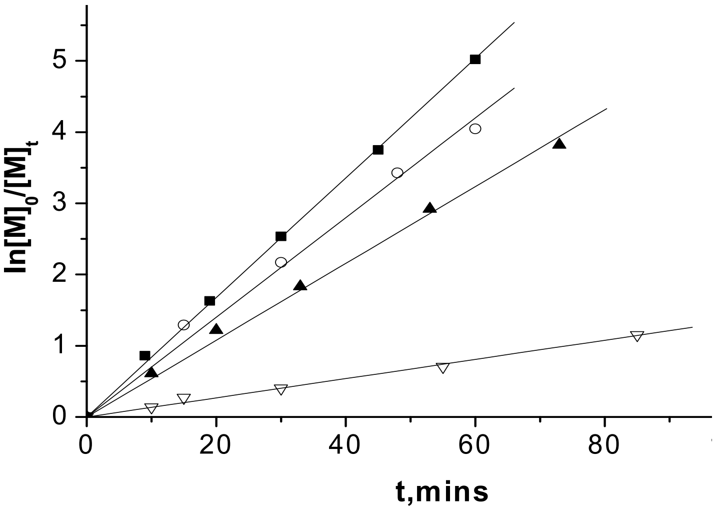

Fig. 4.3: First-order time-conversion plot of MMA polymerization in the presence of $LiClO_4$ (10:1 w.r.t. DPHLi) in toluene-THF (9:1v/v) at -78 °C at different active centre concentrations; [P*](mol/L) = (!) 6.21x10^{-3}; (o) 5.15x10^{-3}; (7) 4.43x10^{-3}; (∇) 1.35x10^{-3}

Table 4.1: Kinetic results of MMA polymerization in the absence and presence of $LiClO_4$ at – 78 °C in toluene-THF (9:1 v/v) using DPHLi as initiator

Run[a)]	$[DPHLi]_0$ x 10^3 mol/L	$[LiClO_4]/[DPHLi]_0$	$t_{max,}$[b)] min	$x_{p,max}$[c)]	$\bar{P}_{n,th}$[d)] at x_{pmax}	$\bar{P}_{n,sec}$[e)] at x_{pmax}	$\bar{M}_w/\bar{M}_n$ at x_{pmax}	f[g)]
1	1.5	0	42	0.99	133	141	5.38	0.94
2	1.5	10	85	0.68	122.00	129.50	1.05	0.89
3	6.3	10	73	0.97	43.30	64.00	1.08	0.70
4	5.8	10	60	0.98	48.60	59.90	1.09	0.88
5	6.9	10	60	0.99	43.40	49.00	1.07	0.90
6[f)]	1.7	10	90	0.76	120	176	1.44	0.71

a) All the polymerizations were performed at $[M]_0 = 0.28$ mol/L,
b) Longest reaction time
c) Conversion obtained at t_{max}
d) $P_{n,th}=([M]_0/[I]_0)*x_{pmax}$
e) $P_{n,sec}=(M_{n,sec}-M_{ini})/M_{monomer}$
f) Reaction done at –40 °C.
g) Initiator efficiency from ratio of slope of $P_{n,th}$ vs. x_p and $P_{n,sec}$ vs. x_p curves

$P_{n,sec}$ vs. x_p plots at different active center concentrations are linear as evident from Fig. 4.4. This implies that the polymerizations are free of transfer reactions at all concentrations of the active center.

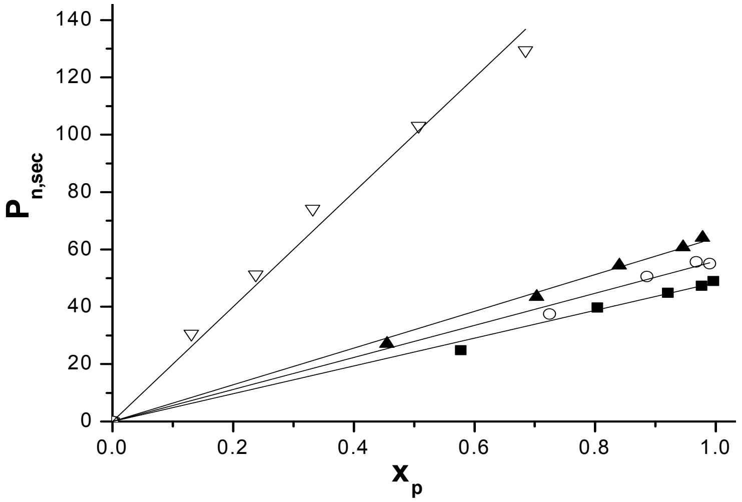

Fig. 4.4: $P_{n,sec}$ vs. x_p plot for MMA polymerization in the presence of $LiClO_4$ (10:1 w.r.t. DPHLi) in toluene-THF (9:1v/v) at -78 °C at different active centre concentrations; [P*](mol/L) = (!) 6.21x10^{-3}; (o) 5.15x10^{-3}; (7) 4.43x10^{-3}; (∇) 1.35x10^{-3}.

The initiator efficiency, i.e. the ratio of theoretical and observed molecular weight, *f,* is obtained from the ratio of slope of $P_{n,theo}$ vs. x_p (not shown) and that of $P_{n,sec}$ vs. x_p plots. They usually vary from 0.7 to 0.9 and are lower than those of batch polymerizations due to possible quenching of living ends while taking of pick-outs by syringe from the reactor.

The MWD of PMMAs obtained in presence of $LiClO_4$ in toluene-THF mixture solvent are narrow at different conversions as shown in Fig. 4.5. Absence of oligomers at higher conversion indicates the termination and transfer free nature of polymerization in the presence of $LiClO_4$ in toluene-THF (9:1 v/v) mixed solvent at –78 °C.

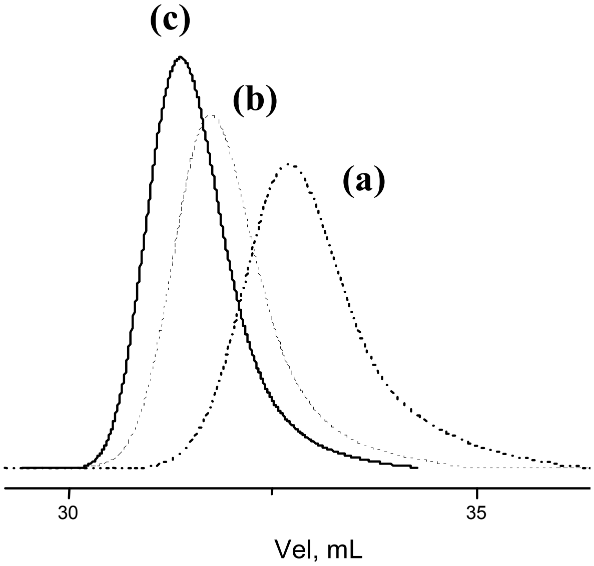

Fig. 4.5: GPC elugrams at different conversions for MMA polymerization in the presence of $LiClO_4$ in toluene-THF (9:1v/v) at -78 °C (run no. 5 Table $[I]_0$=6.9x10^{-3} mol/L). (a) t=9 mins, $M_{n,\ sec}$=2700, MWD=1.12; (b) t=19 mins, $M_{n,\ sec}$=4200, MWD=1.09; (c)t=60 mins, $M_{n,\ sec}$=5150, MWD=1.07

The MWD of the polymers becomes narrower with increased conversion of MMA, and reaches a value of MWD ≤ 1.09 (Fig. 4.6) for the final polymer. This indicates the existence of an equilibrium between $LiClO_4$ coordinated non-aggregated ion-pairs with aggregated ones during the course of polymerization.[23, 35]

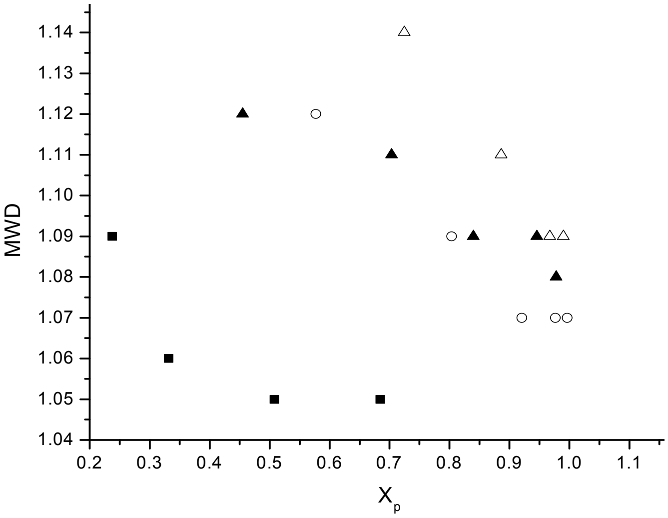

Fig. 4.6: Dependence of $\bar{M}_w/\bar{M}_n$ on x_p for MMA polymerization at - 78 °C in toluene-THF (9:1 v/v) in presence of $LiClO_4$, $[I]_0$/(mol/L) = (!) $1.5x10^{-3}$; (7) $6.3x10^{-3}$; (Δ) $5.8x10^{-3}$; (o) $6.9x10^{-3}$

However, a kinetic experiment performed at –40 °C shows a non-linear first-order plot , as shown in Fig. 4.7, indicating presence of termination reactions (run no 6, Table 4.1). The rate of reaction seems to be very fast and all the active centers are almost quenched before 70 % conversion. The molecular weight distributions are broad at lower conversions and reaches a final value of MWD~1.4 for the highest conversion.

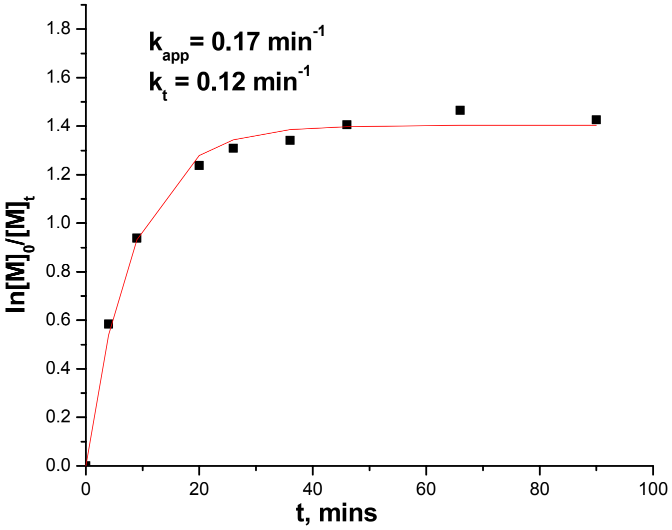

Fig. 4.7: First-order time-conversion plot for MMA polymerization in toluene-THF (9:1 v/v) at -40 °C in presence of $LiClO_4$, $[I]_0=1.7x10^{-3}$ m/L, $[M]_0=0.28$ m/L.

This is consistent with the results of batch polymerization of MMA in mixed solvent medium at -40 °C that we had described in the previous chapter. We had found that $LiClO_4$, as also the other Lewis acid salts studied, are not capable of imparting much control over MMA polymerization at -40 °C, with the polydispersity of the final polymer remaining broad even in presence of excess salt.

PMMA-$LiClO_4$ complexation phenomenon:

An unusual observation was made during the process of recovering the polymer samples from the kinetic experiments performed in toluene-THF (9:1v/v) mixture at –78 °C in presence of $LiClO_4$. While attempting to dissolve the polymer sample in benzene before freeze-drying, the material was found to be partly soluble in benzene unlike PMMA which is highly soluble in benzene. A significant portion of it was found to remain as an insoluble residue. The material balance indicated that entire quantity of insoluble material could not be accounted for by just $LiClO_4$. Such an observation is unprecedented in literature. Polymerization in absence of $LiClO_4$, or polymerization in pure THF does not produce any benzene insoluble residue. Both the benzene-soluble and insoluble portions were analyzed by GPC and ^1H NMR, but no major difference in polydispersity or structure were observed.

It is conceivable that PMMA and $LiClO_4$ form a type of strong association by extended coordination between the polymer chains via a number of $LiClO_4$ molecules. Such a behaviour is not observed upon separate mixing of a PMMA sample and $LiClO_4$ in a mixed solvent. This suggests that the association occurs only during polymerization in the low polar mixture solvent. Further studies are necessary to delineate the precise nature of association.

4.3.1.1. Effect of $LiClO_4$ on reaction-order:

The rate constant of propagation are obtained from the slopes of the respective first-order plots at different active center concentrations (Table 4.2). They are further used to determine the reaction order with respect to the active centers, according to the eqn. 4.3,

$k_{app} = k_p.[P^*]^n$ where n= reaction order w.r.t. [P*]

$\log k_{app} = \log k_p + n\log [P^*]$ ……….Eqn. 4.3

Thus a plot of log k_{app} vs. log [P*], yields 'n' i.e. reaction order from the slope.

Table 4.2: Rate constants as function of [P*] for MMA polymerization at -78 °C in toluene-THF (9:1 v/v) in presence of $LiClO_4$.

Run[a)]	$[P^*]\times10^{3}$ [b)] mol/L	$[LiClO_4]/[I]_0$	k_{app} s^{-1} x 10^4	$k_p = k_{app} / [P^*]$ L mol^{-1} s^{-1} x 10^2	k_t , s^{-1} x 10^4
1	1.41	0	36.41	25.8	4.33
2	1.34	10	2.23	10	-
3	4.43	10	8.98	12.16	-
4	5.15	10	11.65	13.57	-
5	6.21	10	13.98	13.51	-
6[c)]	1.21	10	28.3	91.73	20.0

a) All the polymerizations were performed at $[M]_0 = 0.28$ mol/L,
b) $[P]^* = [I]_0 x f$
c) Reaction done at -40 °C

Fig. 4.8 shows a bilogarithmic plot of k_{app} vs. [P*], the slope of which gives the reaction order with respect to the active center concentration. The plot is seen to be linear with a slope of 1.2 that implying a reaction order of almost unity. This indicates that the rate of polymerization primarily depends on one particular type of active species.

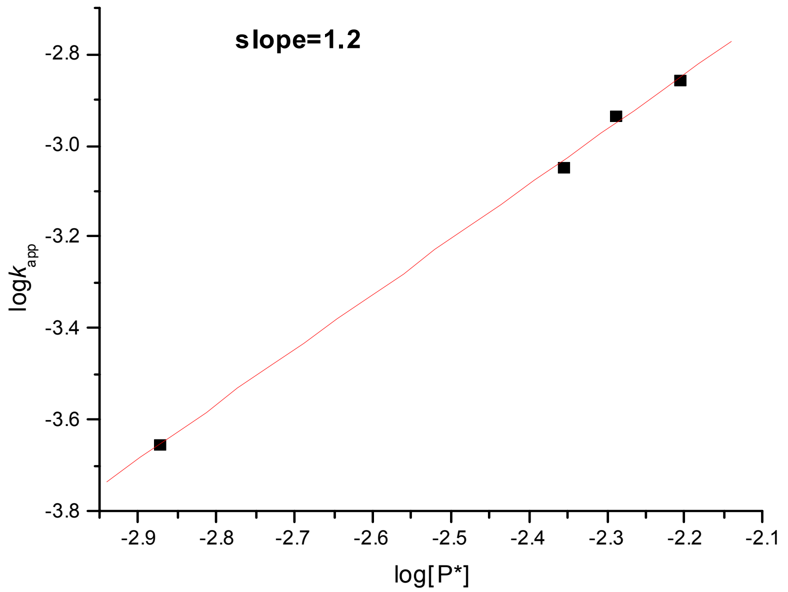

Fig. 4.8: Reaction order w.r.t. active centre concentration for MMA polymerization in toluene-THF (9:1 v/v) at -78 °C in presence of $LiClO_4$

Bywater had reported a first-order kinetics with respect to the active center concentration in anionic polymerization of MMA in toluene in the presence of $LiOCH_3$.[8-10] Similar reports were made by Muller et al for MMA polymerization in toluene in the presence of trialkylaluminium.[36] However for MMA polymerization in the presence of $LiClO_4$ in THF at –20 °C, Baskaran et al obtained a fractional reaction order (n=0.5) with respect to the active centers, indicating the presence of a dynamic equilibrium between propagating ion pairs and aggregates.[37] In the present case, for MMA polymerization in toluene-THF (9:1v/v) at -78 °C, an order of unity was observed, which at the outset appears rather unusual. This can be explained by assuming that an effective coordination of $LiClO_4$ with the propagating ion-pairs in a less polar medium leads to dissociation of the enolate ion-pairs with the formation of a unique salt coordinated species. Narrow MWD of the polymers obtained suggests that the $LiClO_4$ coordinated active species are in rapid equilibrium with the associated species. Therefore, we assume that the $LiClO_4$ coordinated aggregated ion-pairs have a very high dissociation rate constant which results in a first-order dependence with respect to [P*]. This difference in reaction order in the case of polymerization in pure THF and in toluene-THF (9:1v/v) mixture also reveals that the coordination of these salts with propagating enolate ion-pairs is controlled by the dielectric constant of the medium. It was shown by Wang et al[31] that there is no significant difference of the ^{13}C NMR chemical shifts of α-methyl lithio-isobutyrate, a model ester enolate of active centers of MMA polymerization, in pure THF and in toluene-THF (9:1 v/v) mixture solvent. However, there seems to exist differences in the syndiotacticity of the PMMA (as calculated from ^{1}H NMR spectras, Fig. 4.9 and 4.10) synthesized in these solvents and half-lives of the polymerization, both in the absence and in the presence of additive (Table 4.3). The half-lives of the MMA polymerization in the presence of $LiClO_4$ in toluene-THF (9:1 v/v) is increased by ~ 100 times compared to that in pure THF. The results suggest that the presence of a small amount of THF (10 % by volume) would not completely change the nature of propagating ion-pairs to one similar to that in pure THF.

Table 4.3: Comparison of half-lives of the MMA polymerization and stereochemistry of polymer obtained in different solvent system at -78 °C using $[I]_0 = 1.4\text{x}10^{-3}$ mol/L

Solvent/additive-system	Additive/$[I]_0$	Half-life	Syndiotacticity %	Reference
THF/Li	-	52.9 sec	75	36
THF/Li-$LiClO_4$	10	35.7 sec	80	36
PhCH3-THF (9:1 v/v)/Li	-	3.15 min	55	This work
PhCH3-THF (9:1 v/v)/Li-$LiClO_4$	10	51.7 min	64	This work
PhCH3-THF (9:1 v/v)/Li-LiCl$^{a)}$	5	-	72	33(c)

a) $[I]_0$=2.5x10^{-3} mol/L

In bulk THF, the solvent molecules compete with $LiClO_4$ for coordination with the active centers and possibly due to this reason, efficient coordination of the salt with the ion-pairs is prevented. So there was found to be no change in the aggregation of the ion-pairs in presence of $LiClO_4$. But in toluene-THF (9:1 v/v) mixed solvent system, it appears that presence of only 10 % THF is quite small to compete with the salt for coordination with ion-pairs, thus enabling a strong $LiClO_4$-ion-pairs complexation resulting in the formation of unique salt coordinated species.

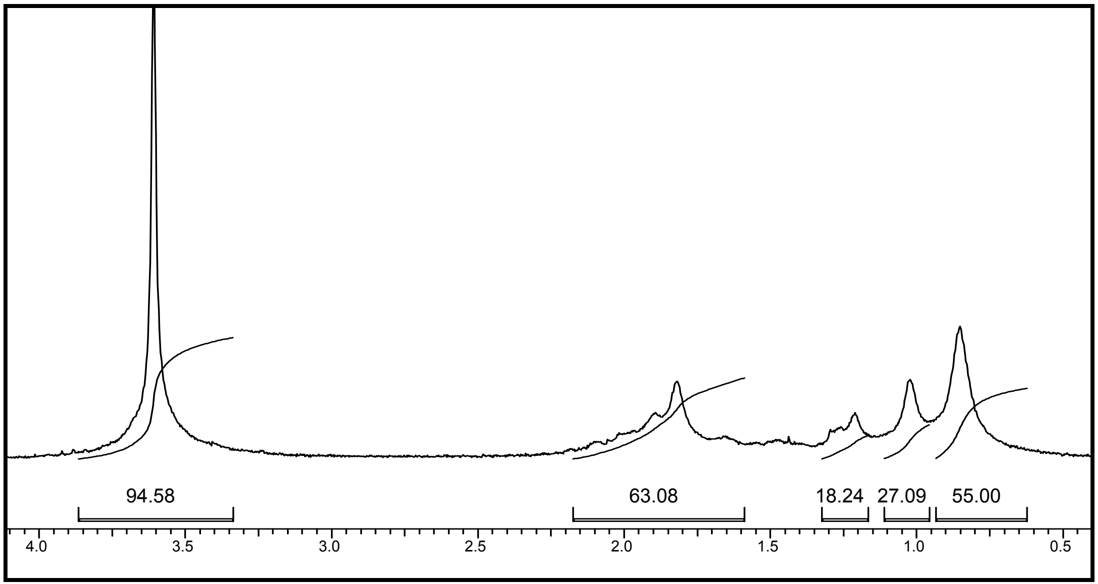

Fig. 4.9: ^{1}H NMR (200 MHz, $CDCl_3$) spectra of PMMA prepared in toluene -THF (9:1 v/v) at - 78 °C in the absence of any additive. The resonance absorption between 0.5 to 1.3 ppm are due to the -$C(CH_3)$ protons. The percentages of syndiotactic, isotactic and atactic placements are 55%, 27%, and 18% respectively.

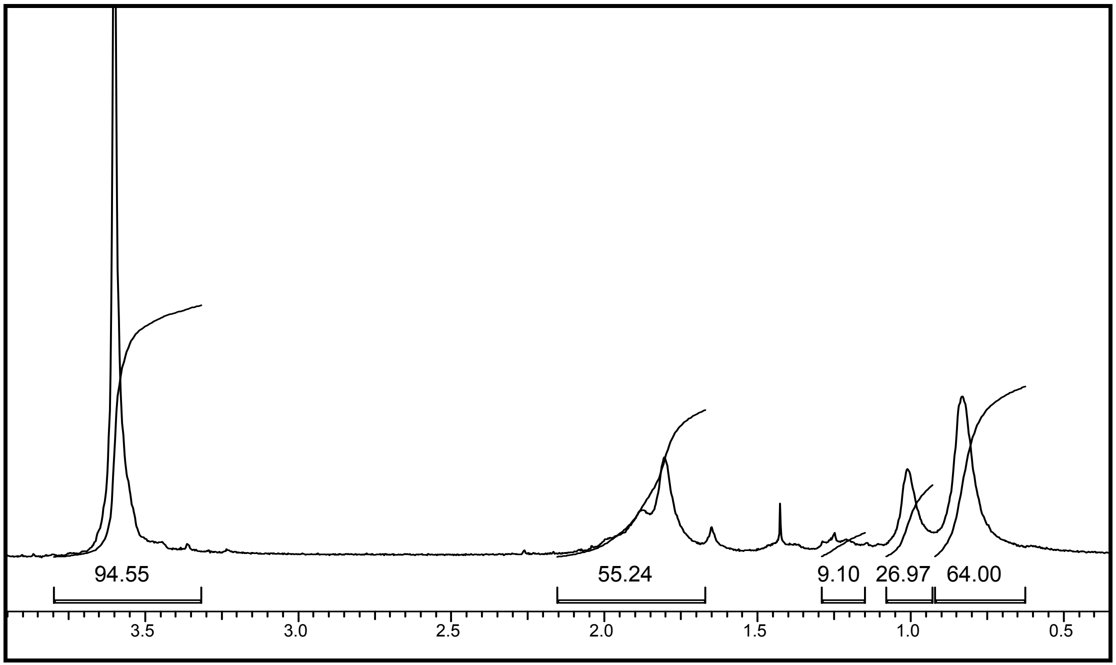

Fig. 4.10: ^{1}H NMR (200 MHz, $CDCl_3$) spectra of PMMA prepared in toluene -THF (9:1 v/v) at - 78 °C in presence of $LiClO_4$. The resonance absorption due to the -$C(CH_3)$ protons appearing between 0.5 to 1.3 ppm are split due to syndiotactic, isotactic and atactic placements, the percentages being 64%, 27%, and 9% respectively.

4.3.2. Effect of LiCl on kinetics of MMA polymerization in toluene-THF (9:1 v/v) :

It has been reported earlier by Teyssie et al that anionic polymerization of MMA in toluene-THF (9:1 v/v) at -78 °C is not quite controlled even in the presence of LiCl added in equimolar quantity with respect to the initiator.[20b] The molecular weight distributions were broad and multimodal till 50 % conversion, indicating that the LiCl complexed non-associated ion-pairs and the aggregated species propagate at different rates during polymerization. The presence of termination was also evident from the non-linear first-order plot. However, the beneficial effect of excess LiCl (5:1 with respect to DPHLi) on MMA polymerization in toluene-THF (9:1 v/v) was later observed by the same group[33(c)]. They reported an unimodal MWD of ~1.17 of the final polymer but there was no report on a detailed kinetic study of the polymerization.

The kinetics of MMA polymerization in the presence of excess LiCl ($[LiCl]_0/[DPHLi]_0=5$) shows linear first-order time-conversion plots over a range of active center concentrations, as shown in Fig. 4.10. In the presence of equimolar quantity of LiCl and DPHLi also, the observed first-order time-conversion plot is linear as shown in dotted line in Fig. 4.10, implying absence of termination. reactions.

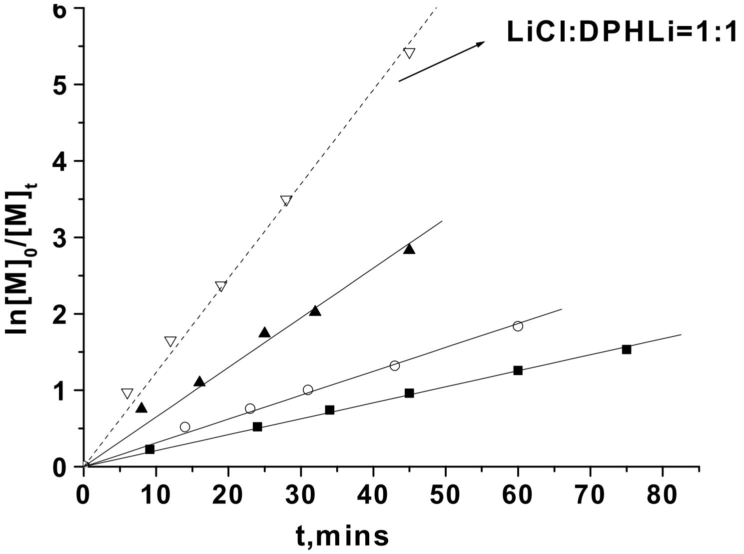

Fig. 4.11: First-order time conversion for MMA polymerization in presence of LiCl (5:1 wrt DPHLi) at -78 °C in toluene-THF (9:1v/v) at different active centre concentrations; (!) $[P^*]=1.5\times10^{-3}$ mol/L, (o) $[P^*]=2.8\times10^{-3}$ mol/L, (7) $[P^*]=4.8\times10^{-3}$ mol/L; (---∇---) reaction at with 1:1 LiCl :DPHLi, $[P^*]=5.1\times10^{-3}$

This is in contrast to the earlier observation of non-linear first-order plot under similar conditions by Teyssie et al.[20b] The rate of polymerization in the presence of equimolar amount of LiCl is much faster (Fig. 4.11) compared to the reactions carried out at $[LiCl]_0/[DPHLi]_0 = 5$. Possibly, addition of excess LiCl leads to formation of a complex of different stoichiometry with the propagating ion-pairs which is of lower reactivity compared to a 1:1 complex.

The plot of $P_{n,sec}$ vs. x_p plots at different active center concentrations are found to be linear, as shown in Fig. 4.12. This indicates the absence of transfer reaction during the polymerization. Fig. 4.13 shows that the molecular weight distribution of the polymers are fairly narrow and unimodal at all conversions.

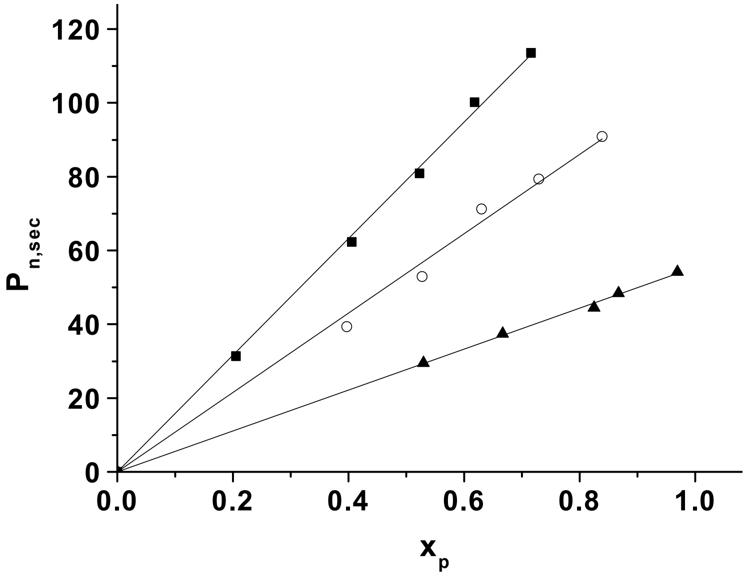

Fig. 4.12: $P_{n,sec}$ vs. x_p plot for MMA polymerization in presence of LiCl (5:1 w.r.t. DPHLi) in toluene-THF (9:1v/v) at -78 °C at different active centre concentrations; (!) $[P^*]=1.5\times10^{-3}$ mol/L; (o) $[P^*]=2.8\times10^{-3}$ mol/L, (▲) $[P^*]=4.8\times10^{-}$ mol/L

It is known that an insufficient amount of LiCl ($[LiCl]_0/[DPHLi]_0<1$) would lead to polymers with broad MWD due to a slow interconversion between the different aggregated active centers. In fact, at $[LiCl]_0/[DPHLi]_0=1$, the polymers exhibit broad but unimodal ($M_w/\ \bar{M}_n \sim 1.53$) molecular weight distribution. It should be mentioned that the solubility of LiCl is quite low in toluene-THF (9:1 v/v) mixture solvent. Addition of excess LiCl invariably results in some quantity of the salt to remain insoluble in the system. However, excess LiCl helps in increasing the amount of soluble LiCl dissolved in the presence of DPHLi. This factor appears to be responsible for the well-controlled polymerization. Thus, both $LiClO_4$ and LiCl are equally effective in controlling the anionic polymerization of MMA in low polarity mixture solvent at low temperatures. A comparison of rate constants in Table 4.2 and Table 4.4 for similar [P*] values shows that the polymerization MMA is faster in presence of LiCl than in presence of $LiClO_4$. This may be attributed to the fact that active centres complexed with LiCl are sterically less hindered than those complexed with $LiClO_4$.

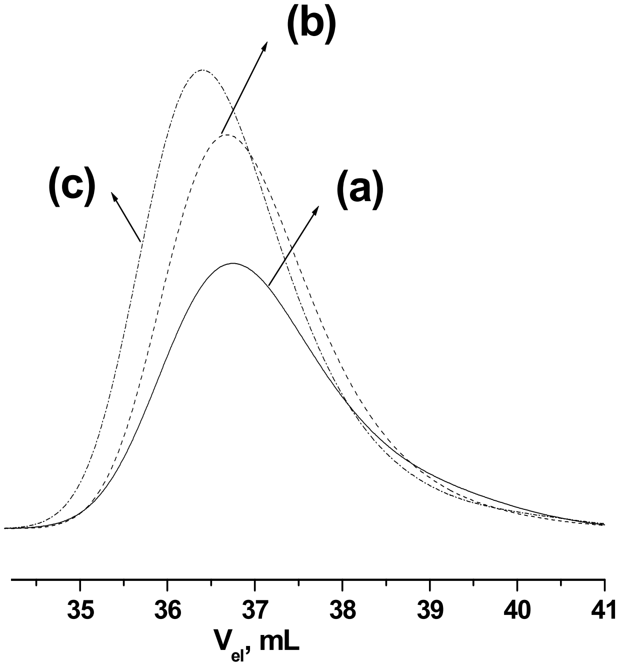

Fig. 4.13: GPC elugrams at different conversion for MMA polymerization (run no. 5, Table 4.4) at -78 °C in toluene-THF (9:1 v/v) using LiCl in 5:1 ratio over DPHLi (a) t=10 mins, x_p=36.2 %, $M_{n,sec}$=3193, MWD = 1.25; (b) t=25 mins, x_p = 64.9 %, $M_{n,sec}$=5761, MWD=1.22; (c) t=100 mins, x_p=95.9 %, $M_{n,sec}$=8923, MWD=1.17

4.3.2.1. Effect of LiCl on reaction-order:

The rate constants of polymerization in toluene-THF (9:1 v/v) mixture, in the presence of LiCl, as obtained from the slopes of first-order plots at different active centre concentrations are shown in Table 4.4.

Table 4.4: Rate constants as function of [P*] for MMA polymerization at -78 °C in toluene-THF (9:1 v/v) in presence of LiCl using DPHLi as initiator.

Run[a)]	$[P^*]\times10^3$ m/L	$[LiCl]_0/[I]_0$	Time (mins)	$x_{p,max}$	$P_{n,sec}$	MWD	k_{app} s^{-1} x 10^4	$k_p = k_{app}/[P^*]$ $Lmol^{-1}s^{-1}$
1[b)]	5.1	1	60	99.9	61	1.53	20.8	0.41
2	1.5	5	60	71.6	113	1.20	3.3	0.22
3	2.0	5	75	79.3	136	1.18	3.4	0.17
4	2.8	5	60	83.9	91	1.19	5.1	0.18
5	2.9	5	75	92.0	77	1.17	6.7	0.22
6	4.8	5	61	96.9	54	1.20	10.8	0.22

a)All the polymerizations were performed at $[M]_0 = 0.28$ mol/L
b)Reaction performed using 1:1 LiCl : DPHLi

As in $LiClO_4$ system, a bilogarithmic plot of k_{app} vs. [P*] as shown in Fig. 4.14 is linear with a slope close to unity, i.e. the order of the reaction with respect to the active centers is unity.

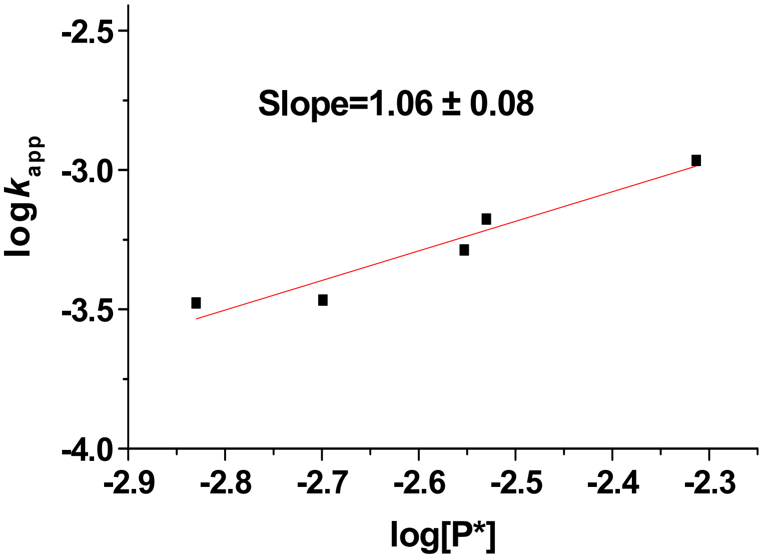

Fig. 4.14: Reaction-order plot for MMA polymerization in toluene-THF (9:1 v/v) at -78 °C using LiCl as additive in 5:1 ratio over DPHLi

It is once again evident that the dielectric of the medium plays a major role in determining the extent of coordination of the enolate ion-pairs with Lewis acids. Probably, like $LiClO_4$, strong complexation of LiCl with the propagating enolate ion-pairs leads to complete disaggregation of the ion-pairs, into a single salt-complexed species, in a predominantly non-polar solvent. The unique coordination of $LiClO_4$ and LiCl with enolate ion-pair is also evident from the microstructures of the polymers obtained as given in Table 4.3. Wang et al[33c] reported an increase in syndiotacticity upto 15 % of the PMMA synthesized in the presence of $[LiCl]/[DPHLi]_0 = 5$, which is quite in agreement with our results (Fig.4.15) that show almost 19 % increase over that observed in absence of any salt (Fig. 4.9)

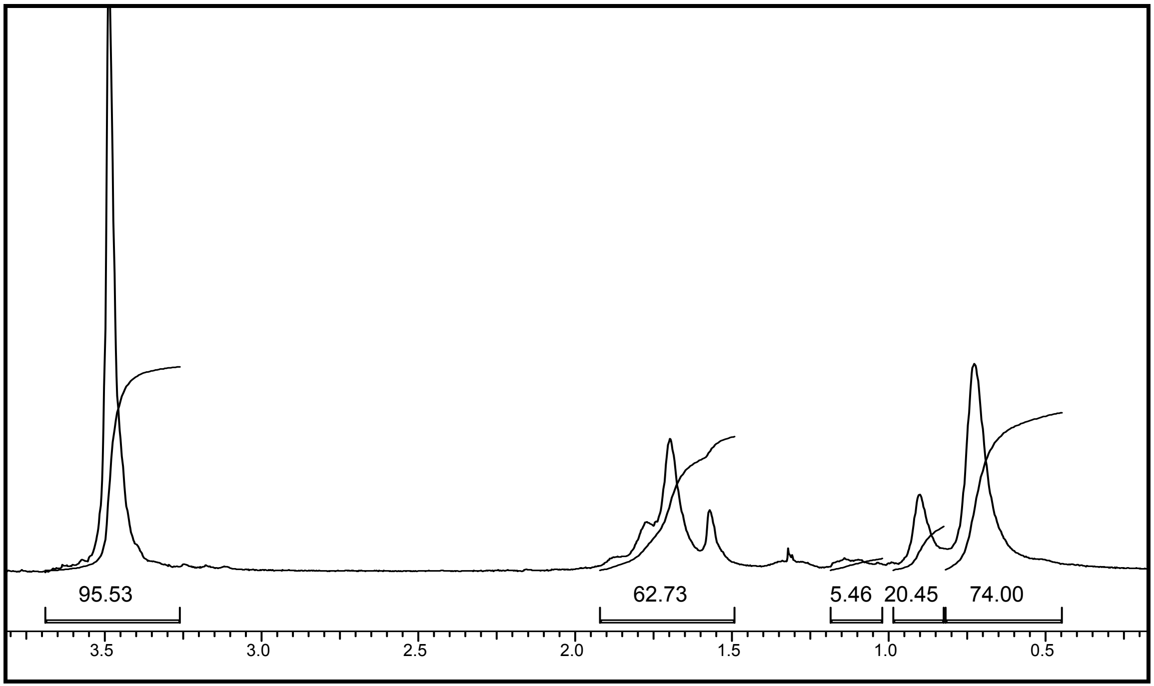

Fig. 4.15: ^{1}H NMR spectra of PMMA prepared in toluene -THF (9:1 v/v) at - 78 °C in the presence of LiCl (5:1 w.r.t. DPHLi). The resonance absorption between 0.5 to 1.3 ppm are due to -C(CH_3) protons. The percentages of syndiotactic, isotactic and atactic placements are 74%, 20.45%, and 5.46% respectively.

Similar results have been obtained in presence of $LiClO_4$ also. Unlike in pure THF, the changes in the stereochemistry of PMMA in toluene-THF (9:1 v/v) mixture solvent are significant in the presence of the salt (Table 4.3). This supports the formation of unique complex between the LiCl or $LiClO_4$ and the active centers in low polar medium, which in turn controls the placement of the incoming monomer. Also the different coordinating ability of $LiClO_4$ and LiCl with the ion-pairs results in establishment of different aggregation equilibrium with a characteristic equilibrium constant. Possibly, a faster dynamics in case of LiCl gives a greater chance of monomer insertion onto the unassociated ion-pair that occurs in a more favored syndiotactic fashion, resulting in a higher syndiotacticity of the PMMA compared to that in presence of $LiClO_4$. The reaction order of unity with respect to the active species in the presence of LiCl and $LiClO_4$ also confirms the formation of unique salt-coordinated active species in toluene-THF (9:1 v/v) solvent.

4.4. Conclusion

Anionic polymerization of MMA in toluene-THF (9:1 v/v) mixture solvent using DPHLi as initiator shows little control in absence of any salt additive with non-linear first-order plot and broad and multimodal MWD at all conversions. Addition of common ion Lewis-acid salts i.e. $LiClO_4$ and LiCl, in 10:1 and 5:1 molar ratio over the initiator respectively, remarkably improves the system resulting a termination-free and transfer-free polymerization as evident from linear first-order and P_n vs. xp plots for diferent initiator concentrations. From the slope of the bilogarithmic plot of rate constant of polymerization, k_{app} vs. the active centre concentration, [P*], the order of the reaction w.r.t. the active centres is found to be almost unity for both $LiClO_4$ and LiCl systems, indicating the formation of a unique salt-coordinated active species responsible for the propagation. In comparison to the fractional reaction order reported for MMA polymerization in THF in presence of $LiClO_4$, this order of unity in toluene-THF (9:1 v/v) mixed solvent implies stronger and more efficient coordination of the salts with the ion-pairs in absence of competitive coordination by THF molecules that formed only 10 % of the system. The strong salt-ion pair coordination in mixed solvent system is also reflected in the microstructure of the PMMA. The syndiotacity of PMMA increased significantly in the presence of the LiCl and $LiClO_4$.

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Chapter 5: Controlled Synthesis of Hydroxy-functionalized Poly(methyl methacrylate) Using Protected Functional Initiators: Synthesis of PMMA-PEO Block Copolymers

5.1. Introduction

Recent years have witnessed enormous progress in the development of new synthetic strategies for the preparation of well-defined polymers with reactive functional groups.[1-6,13] These functional polymers expand the range of properties and applications over their non-functional counterparts. Living anionic polymerization, particularly alkyllithium-initiated polymerization, due to the absence of termination and transfer reactions is the most versatile method for synthesizing well-defined functional polymers with predictable molecular weight, narrow molecular weight distribution and quantitative functionalization.[7-11] One of the most important uses of these functional polymers is that, they can be further exploited to prepare a variety of chain architectures e.g. block, graft, star-branched, networks, etc, which have a wide range of applications.[12]

Preparation of end-functional polymers can be accomplished mainly in two ways,[2,13] 1) stable carbanionic chain-ends generated by anionic initiators can be converted into a diverse array of functional group by reaction with a variety of electrophiles, 2) using protected functionalized alkyllithium initiator to initiate anionic polymerization of the required monomer and subsequent deprotection after the polymerization. The success of the former method is often determined by the nature of electrophile and the reactivity of the propagating anions. Chain-end functionalization by termination method, if the reaction condition and electrophile are not appropriately chosen, leads to incomplete functionalization. Certain electrophiles such as chlorosilanes and activated alkyhalides give quantitative functionalization without any side reaction, used with hydrocarbon monomers such as styrene and diene.[10,26,27] However, reaction of living anions of poly(methyl methacrylate) with electrophiles is complicated due to the poor stability of propagating lithium enolate chain-ends at functionalization reaction condition and the possibility of both C- and O- addition.[14] Therefore, the method of functional initiation is often the preferred method for introducing functionalities at the chain-end in a simple and quantitative manner. However, most of the study on functional polymer synthesis using termination method has been limited to non-polar monomers, because of the high stability of the propagating anions of the non-polar monomers even at ambient temperatures. Fewer studies have focussed on the synthesis of end-functionalized polymers with methacrylates, since it is difficult to control these polymerizations, especially at higher temperatures where inherent termination and transfer reactions gain prominence. Moreover, lower reactivity of the lithium enolate anions and the necessity to perform the reaction at lower temperature restricts the prospects of functionalization by termination.

Synthesis of hydroxy end-functionalized polymers utilizing hydroxyl-protected alkyllithium has been extensively studied for non-polar monomers in hydrocarbon solvents.[10,12] The protection of the hydroxy group, as any other function that is reactive towards organolithium reagents, becomes necessary with a suitable group that is stable toward the anionic chain end, and also easily removable after polymerization.[15] For e.g., *tert*-butyldimethylsilylchloride has been used to protect the hydroxy groups in alkyllithium initiators very effectively, and used for functionalization of polystyrene, polyisoprene and polybutadiene.[10,11] Anionic polymerization of methylmethacrylate (MMA) proceeds in a predictable manner only under careful selection of solvent, temperature and initiator.

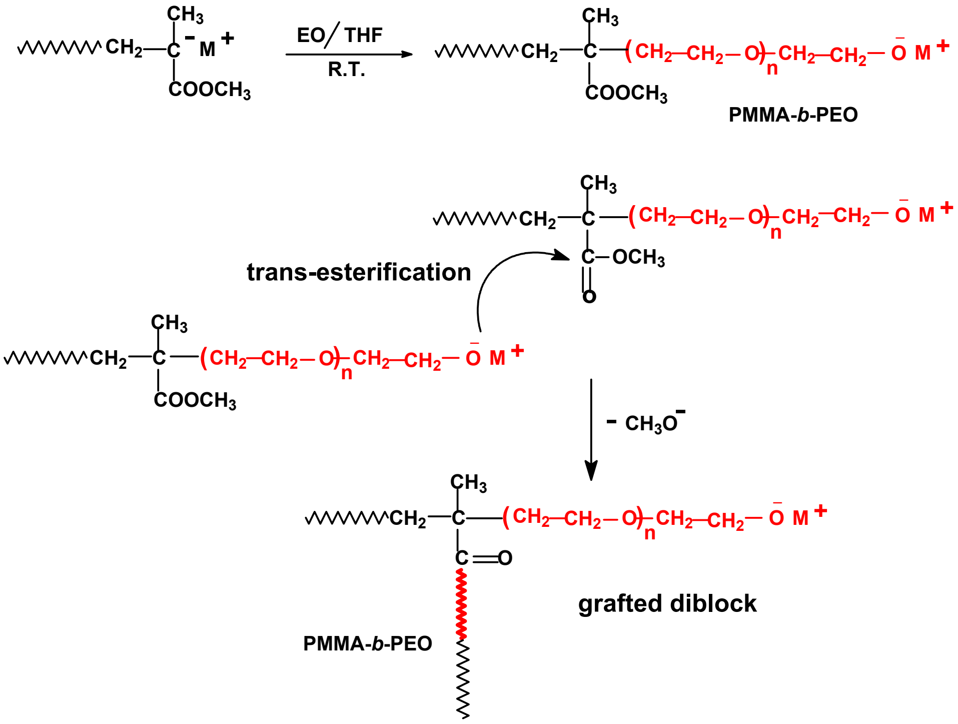
Synthesis of hydroxy-end functionalized PMMA was reported using various protected functional initiator.[16-19] Anderson et al used an acetal-protected hydroxy-functional initiator for quantitative synthesis of hydroxy-PMMA.[16] Ethyl 3-lithiopropyl-acetaldehyde acetal was added to diphenylethylene in THF at 0 °C to give the corresponding diphenylmethyl anion that was used to initiate MMA at -78 °C in THF with 100% efficiency. After acid hydrolysis, hydroxy end-functionalized PMMA were obtained with degree of polymerization from 1-500 and MWD <1.2. Using 1,4-bis(bromomethyl)benzene as a coupling agent, α,ω-dihydroxy-PMMA was also synthesized with 90 % yield. However, no detailed data on the results of polymerization and the functionalization were given in any of the above publications.

Ohata et al prepared a telechelic poly(methyl methacrylate) having α-OH and ω-COOH groups by anionic polymerization with the initiator made by the reaction between 4-[2-(*tert*-butyldimethylsiloxy)-ethyl]-α-methylstyrene and *n*-butyllithium, followed by termination with carbon dioxide and hydrolysis of the *tert*-butyldimethylsiloxy group.[17]

Mason et al prepared hydroxy end-functionalized PMMA using functionalized initiator, ethyl-5,5'-diphenylpentyl lithium acetaldehyde acetal, and used the terminal -OH group to initiate hexamethylcyclotrisiloxane polymerization to get monodisperse block copolymers. Using similar strategy they prepared triblock and star-block copolymers of PMMA and PDMS.[18,19]

Protected hydroxy-functional initiator was used to prepare functionalized linear and star-branched PMMA using ethyleneglycol dimethacrylate as cross-linking agent by Quirk et al.[10] An adduct of 3-(*tert*-butyl dimethylsilyloxy)-1-propyllithium and DPE was used to initiate MMA polymerization to yield functionalized PMMA with narrow molecular weight distribution (M_w/M_n=1.09) and quantitative functionalization. Using a 3:1 ratio of EGDMA to initiator, star-branched PMMA with an average of 10 arms carrying -OH groups at their ends was prepared. However, only one polymerization result was reported for the preparation of both linear and star polymer. No detailed report on the characterization of the functionalized polymer was, however, provided.

Earlier, several research groups[21-25] attempted to synthesize amphiphilic diblock copolymers by using various strategies. It is known that block copolymerization of ethylene oxide can not be performed using sequential monomer addition in the presence of lithium counter ions due to the strong aggregation of lithium methoxide chain ends, which renders it unreactive towards ethylene oxide monomer. However, ethylene oxide polymerization can be preformed using anions with bulky counterions such as potassium, sodium, and non-metal counterion (P4-base) in polar solvent at temperatures (≥ 25 °C). However, at higher temperatures, unwanted side-reactions involving the ester group of the PMMA segment become significant, leading to ill-defined block copolymers. In fact, a few earlier reports on such block copolymerization have suggested trans-esterification at the ester group leading to grafting on the block-copolymer chain. Seow et. al. reported initiation of EO by living PMMA chains. They observed that the living diblock chains attacked the ester group of PMMA leading to grafted diblock copolymers[21], as shown in scheme 5.1. It was reported by Suzuki et al that the disodium salt of poly(ethylene glycol) was capable of initiating MMA polymerization to yield diblocks, although, according to the well understood monomer reactivity scale, PEO anions are not reactive enough to



Scheme 5.1: Trans-esterification reaction during synthesis of PEO-*block*-PMMA

initiate alkyl methacrylate polymerization.[22] This was explained by enhanced reactivity of the PEO dianion due to chelation of the counter-ion by the polyether backbone. However, trans-esterification could not be avoided resulting in broad multimodal distribution of the resulting copolymer. Also the ^1H NMR spectra of the diblock showed that the ratio of intensities of peaks corresponding to $-OCH_3$ and the tertiary $-CH_3$ group of PMMA block was less than 1.0. This implied that some of the methoxy groups were eliminated by the living diblock chains attacking at the ester carbonyl. Later Garg et al reported synthesis of PEO-PMMA block copolymers by initiating MMA using living PEO chains.[23] They did not observe any trans-esterification reaction, although no sufficient characterization data was given in support of their veiw.

However, well-defined di and triblocks of poly(*tert*-butylmethacrylate) and PEO have been successfully prepared.[24,25] This is because the PtBMA anions are much stable and the polymerization proceeds without side-reactions even at ambient temperatures.

In this chapter we report our efforts to synthesize different hydroxy-functional anionic initiators and their utilization in preparing well-defined hydroxy end-functional

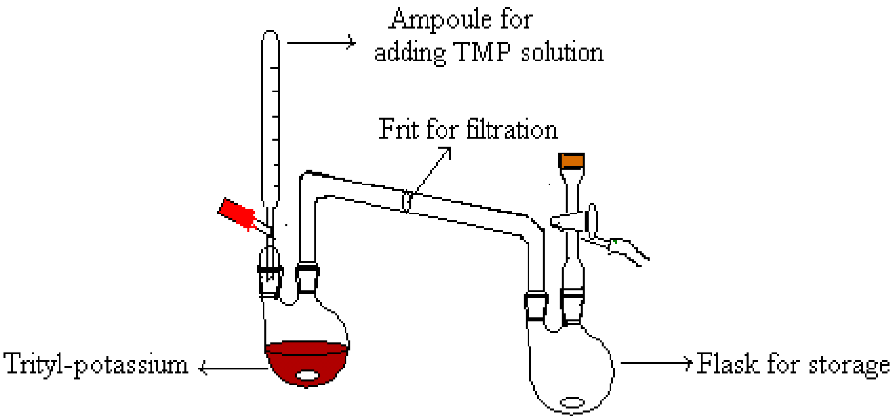
PMMA by living anionic polymerization method. Also, the feasibility of using the hydroxy-functional PMMA as macroinitiators for controlled synthesis of PMMA-PEO block copolymers has been investigated.

5.2. Experimental

5.2.1. Materials and purification:

4-hydroxybenzophenone (Aldrich, USA) was recrystallised from aqueous ethanol and imidazole (Aldrich) recrystallised from dichloromethane(DCM)-pet ether (S.D. Fine Chemicals, India) mixture. *tert*-Butyldimethylsilylchloride (TBDMSCl) and triphenylphosphine (Ph_3P), procured from Aldrich, were used as such from the bottle. 6-chlorohexanol (Aldrich) was first washed with saturated $NaHCO_3$ solution, and then with water till the aqueous layer was neutral. It was then dried over Na_2SO_4, and the purified compound was stored in refrigerator. Methyl iodide (Merck, Germany) was purified by fractional distillation just prior to use. Dichloromethane (DCM) and THF (S.D. Fine Chemicals, India) used in organic synthesis were dried over CaH_2 (Aldrich) and stored over molecular sieves. Benzene, ethyl acetate, pet-ether were purified by simple fractional distillation. Diphenylethylene (DPE), MMA, $LiClO_4$, all purchased from Aldrich, and THF were purified in the usual way (refer chapter 2). Ethylene oxide (EO, Pest Control Ltd., India) from the cylinder was first passed through a tower containing activated molecular sieves and CaH_2 before condensing into an ampoule. Before reaction, the required amount was transferred by cannula into monomer distillation apparatus maintained at 0°C, stirred over CaH_2 for 3 hours and distilled under vacuum. Subsequently, it was transferred to another monomer distillation assembly, and added *n*-BuLi (prepared in laboratory, refer chapter 2) at 0 °C till a white solid appeared, and then it was degassed and distilled under vacuum just before polymerization.

Triphenylmethyl potassium was prepared by reaction between triphenylmethane (TPM, E.Merck) and metallic potassium (Aldrich) in THF, using the apparatus shown in scheme 5.2. TPM was crystallized from methanol and dried under vacuum. It (~500 mg) was then taken in a flame-dried ampoule under nitrogen flush, and then applied vacuum and distilled THF (~25 mL) directly into the same ampoule. The ampoule was then fitted to one of the flasks shown in scheme 5.2, containing K-metal (1.0 g) along with a small piece of Na, and provided with magnetic stirring bar.

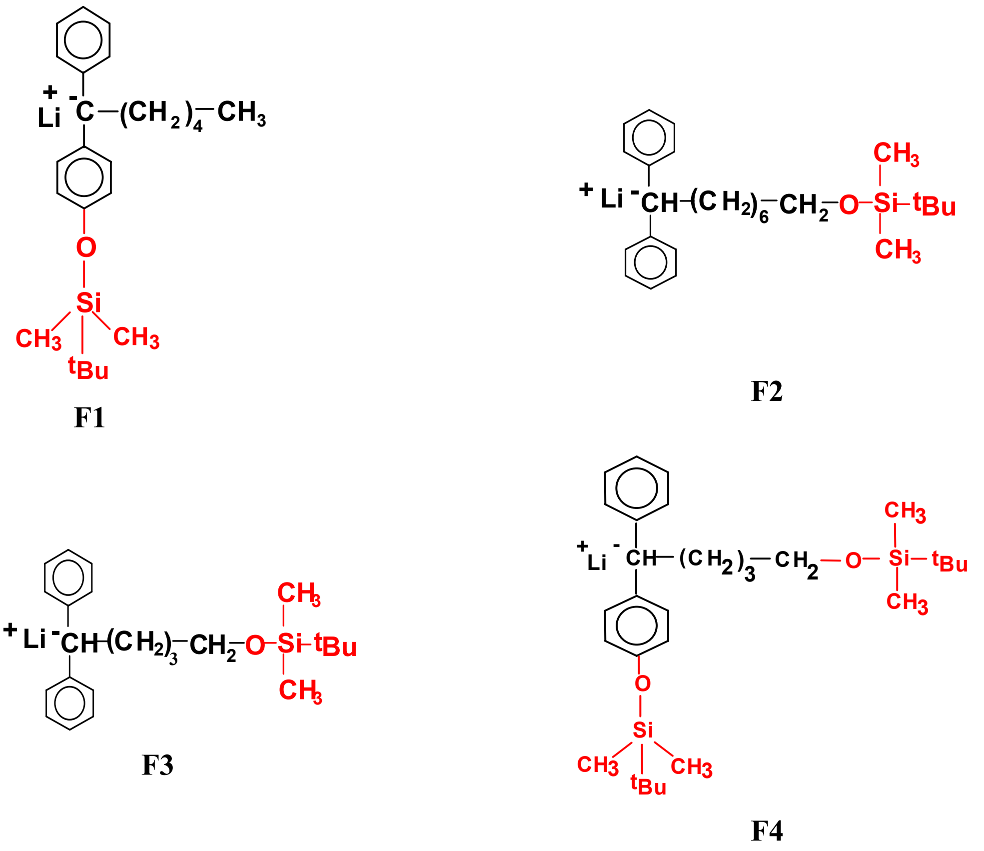


Scheme 5.2: Preparation of trityl-potassium

The metal was then melted by flaming under vacuum to form a shining liquid. After cooling the flask, the stop-cock of the ampoule was opened and the solution of TPM in THF was added fast into the metal that was stirred fast in order to break the metal into fine particles. A red color appeared after 2-3 mins, that indicated the formation of triphenylmethyl potassium (trityl-K). The red color intensified with time, and the reaction was allowed to proceed for another 3-4 h. The initiator solution was then degassed and then the solution was transferred into the other flask for storage, via the connecting glass-bridge while the transfer of the metal and other solids was prevented by the frit connected the middle of the bridge. The storage flask with initiator was then disconnected from the system under N_2-flush, followed by degassing of the trityl-K once again.

5.2.2. Procedure for synthesis of hydroxy-functional initiators:

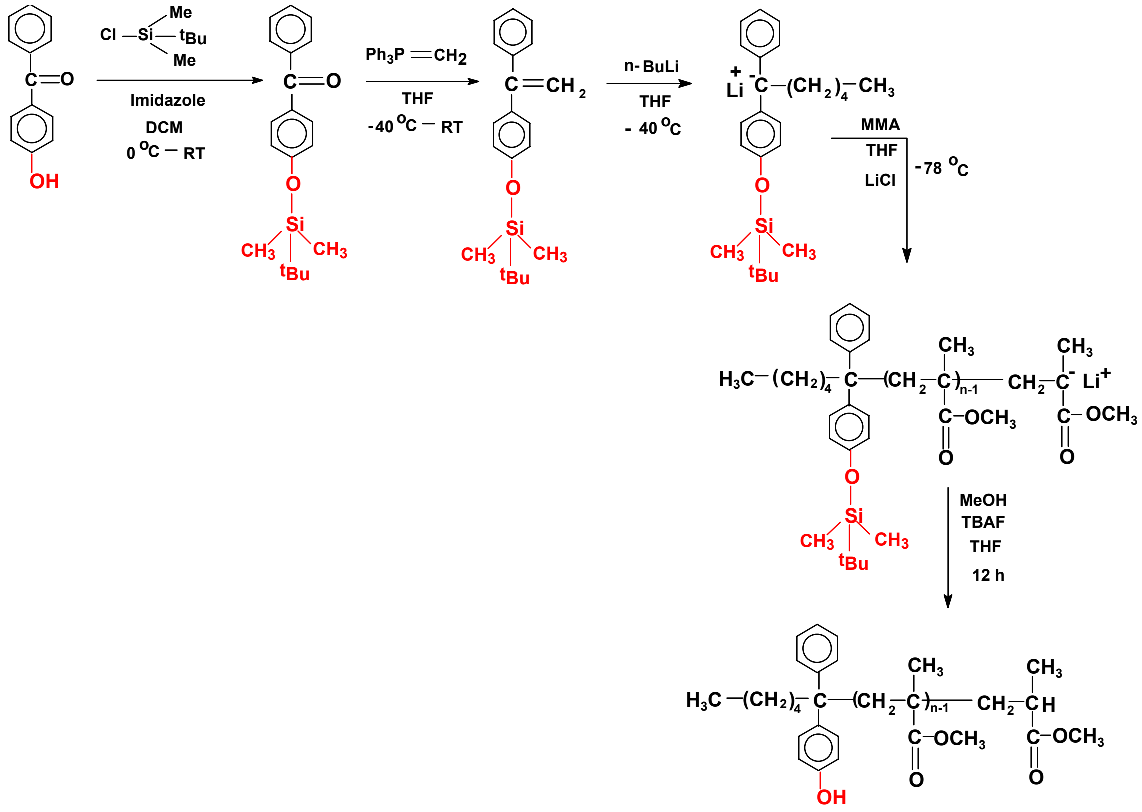
The protected hydroxy-functional initiators used for anionic polymerization of MMA, were prepared by reaction between a diphenylethylene component and an alkyllithium component, either or both of which contained a protected hydroxy group. Four different functional initiators, namely, **F1**, **F2** and **F3** and **F4** that were prepared are shown in scheme 5.3.



Scheme 5.3: Different functional initiators used for preparing hydroxy end-functionalized PMMA

The functional initiators were prepared as follows:

1) Addition of *n*-BuLi to 1-[*p*-(*t*-butyldimethylsilyloxy)]phenyl-1`-phenylethylene to form initiator **F1** (scheme 5.4).
2) Addition of 6-(*t*-butyldimethylsilyloxy)hexyllithium to DPE to give initiator **F2** (scheme 5.5).
3) Addition of 3-(*tert*-butyldimethylsilyloxy)propyllithium (FMC, Lithium Division, USA) to DPE to give initiator **F3** (similar to scheme 5.5**,** only propyl group has to be considered in place of hexyl group)
4) Addition of 3-(*tert*-butyldimethylsilyloxy)propyllithium to 1-[*p*-(*tert*-butyldimethylsilyloxy)]phenyl-1`-phenylethylene (scheme 5.6) to give initiator **F4** containing two hydroxy groups.



Scheme 5. 4: Synthesis of protected hydroxy-functional initiator F1 and hydroxy-PMMA using F1

The methods of synthesis of the initiators are described in details in the following section.

5.2.2.1. Preparation of functional initiator F1:

Synthesis of 1-[p-(tert-butyldimethylsilyloxy)] phenyl-1`-phenylethylene: As shown in scheme 5.4, the first step in the synthesis of the above compound involves protection of the hydroxy function of 4-hydroxybenzophenone by *tert*- butyldimethylsilyl group by using TBDMSCl in presence of imidazole as base, in DCM. 4-hydroxybenzophenone (2.0 g), TBDMSCl (2.32 g) and imidazole (2.1 g) were taken in 1:1.5:3 molar ratio in DCM (20 mL), and stirred under N_2 atmosphere overnight. Progress of the reaction was monitored by TLC, which showed complete conversion into the products within 12 h. The excess TBDMSCl was removed under vacuum, and the product, 4-*tert*-butyldimethylsilyloxybenzophenone was purified by column chromatography using pet-ether containing 5-10 % ethyl acetate for elution of the pure compound. Yield was between 80-90%. ^{1}H NMR (200 MHz, Bruker) spectra of the product (Fig. 5.1) shows characteristic resonance absorption of the *tert*-butyldmethylsilyl group at δ 0.0 (6 H of Si-

CH_3 groups) and δ 0.75 for the (9 H for $-C(CH_3)_3$ group). Rest of the spectra is in agreement with the structure of the required compound.

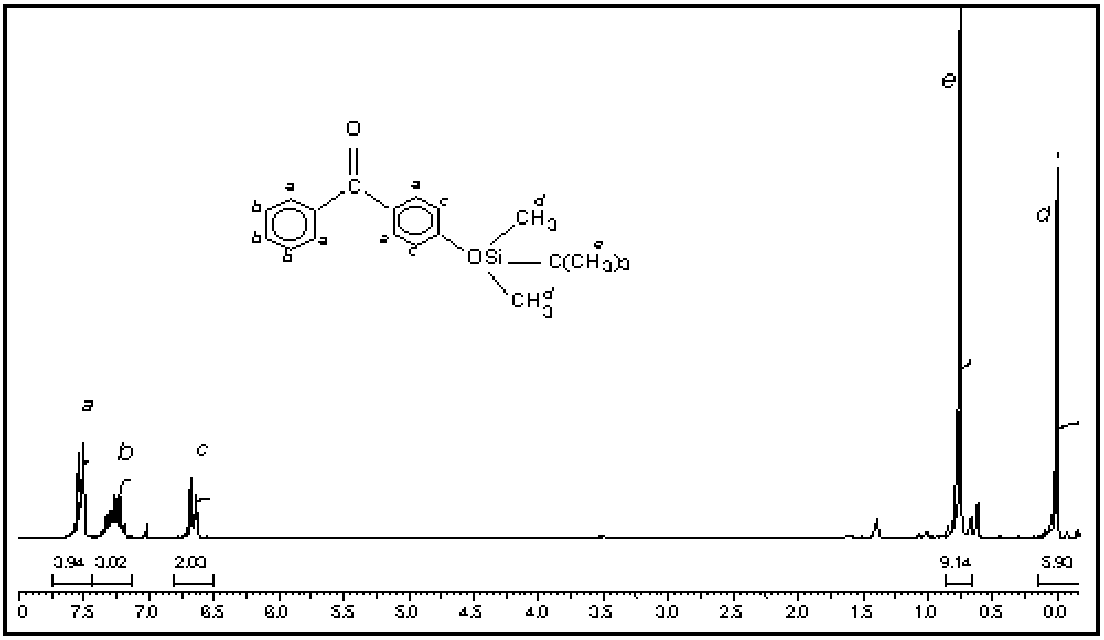


Fig. 5.1: ^{1}H NMR spectra (200 MHz, acetone-d$_6$) of 4-(*tert*-butyldimethylsilyloxy) benzophenone

In the next step, the protected hydroxy-benzophenone was converted into the corresponding diphenylethylene compound by Wittig reaction. Ph_3P (12 g) was dissolved in benzene (20 mL) and then CH_3I (3 mL) was added dropwise at 0 °C, and the reaction mixture was stirred under N_2 overnight. CH_3I and Ph_3P were added in 1.2:1 molar ratio. The resultant white solid i.e. the Wittig salt, $Ph_3P^+CH_3I^-$, was then filtered and washed thoroughly with benzene to remove phosphine oxide formed during reaction. It was then dried in vacuum, and required amount (say, 10 g) transferred to a r.b. flask and added dry THF (60 mL) via cannula under N_2 pressure. Subsequently, almost equimolar amount of *n*-BuLi (13 mL of 1.7 [M]) was added dropwise to the Wittig salt in THF at -40 °C to form the corresponding ylide, $Ph_3P=CH_2$ that showed a characteristic deep orange color. It was stirred under N_2 for 30-45 mins and then the supernatant orange solution was transferred by cannula to another flask containing the protected hydroxy-benzophenone (2.4 g) dissolved in THF (10 mL), such that the ylide was in 3:1 molar ratio over the benzophenone. Reaction was allowed to proceed for another 2 h. Column chromatography was done using pet-ether for elution of the pure Wittig product, with a yield of 60-70%. ^{1}H

NMR (200 MHz, Bruker) spectra of the product (Fig. 5.2) shows characteristic resonance absorption of the =CH_2 group, seen as a doublet between δ 5.1 to δ 5.3.

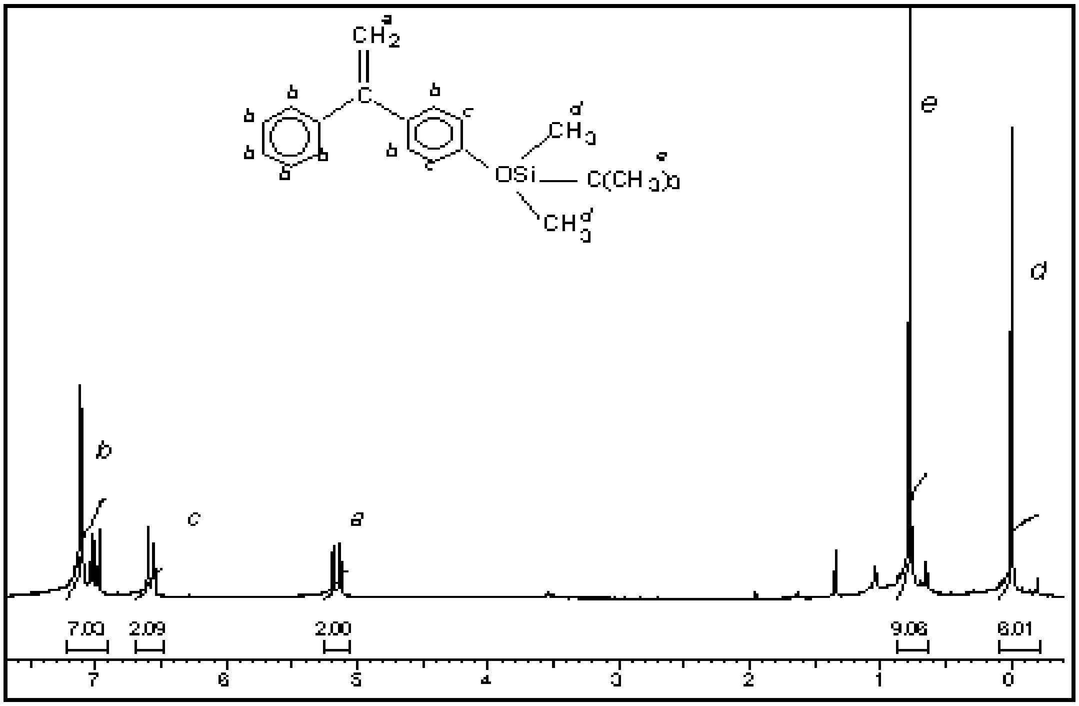


Fig. 5.2: ^{1}H NMR spectra (200 MHz, acetone-d$_6$) of Wittig product, 1-(*tert*-butyldimethylsilyloxy)phenyl-1'-phenyl ethylene

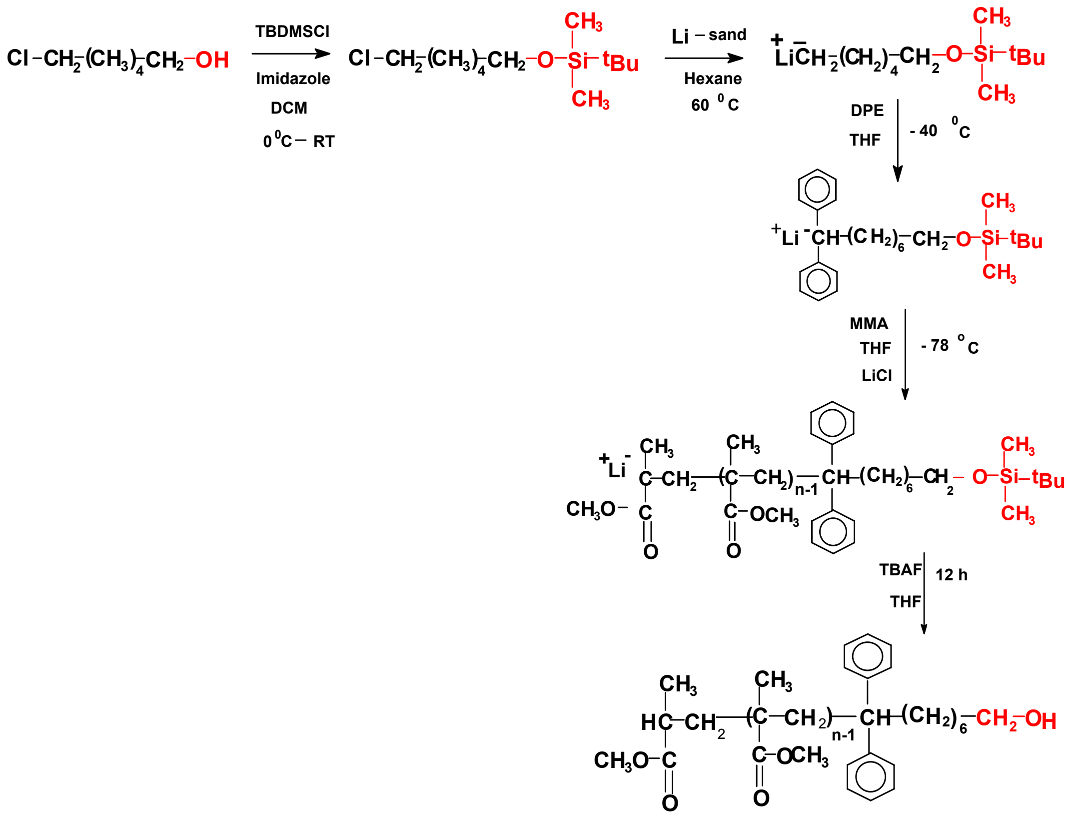
Preparation of F1 :

The required amount of 1-[*p*-(*tert*-butyldimethylsilyloxy)]phenyl-1`-phenylethylene (say 1.0 g), as prepared before, was dried under vacuum by azeotropic distillation with toluene. Then it was dissolved in freshly distilled dry THF (30 mL) and the temperature of the flask was brought down to -40 °C with dry ice-acetonitrile bath. Then *n*-BuLi (1mL of 2.25 [M] BuLi) was added dropwise to the system when a deep reddish orange color of the corresponding initiator, 1-[*p*-(*tert*-butyldimethylsilyloxy)]phenyl-1'-phenylhexyl`lithium was observed. The amount of *n*-BuLi added was such that the mole ratio of the diphenylethylene component to *n*-BuLi was 1.2:1.

The initiator was standardized by the Gilman`s double titration method.

5.2.2.2. Preparation of functional initiator F2:

Preparation of 6-(tert-butyldimethylsilyloxy)hexyllithium: In the first step, the hydroxy group of 6-chlorohexanol (4 g) was protected by reacting with TBDMSCl (5 g) in presence of imidazole (5 g) in DCM (25 mL) as shown in scheme 5.5.



Scheme 5.5: Synthesis of protected hydroxy-functional initiator F2 and hydroxy-PMMA using F2

The molar ratio of 6-chlorohexanol : TBDMSCl : imidazole was 1:1.2:3. The reaction was allowed to stir overnight under N_2 and was found to be complete within 10 h. The elution of the pure product, i.e. protected chlorohexanol was done by pet-ether containing 0-5% ethyl acetate. Fig. 5.3 shows the ^1H NMR spectra of the pure silyl-protected chlorohexanol. Yield was almost 90 %. ^1H NMR shows characteristic absorption at δ 0.0 (6 H of Si-CH_3 groups) and 0.75 for the (9 H for -$C(CH_3)_3$ group). Rest of the spectra is in good agreement with the structure of the required compound. In the next step, the protected chlorohexanol was lithiated, using Li-sand in cyclohexane. Li-metal, in almost 10:1 molar ratio with respect to the chloro-compound, was taken in paraffin oil in a 2-necked r.b. flask. The flask was flamed while stirring the metal pieces at a very high speed with a

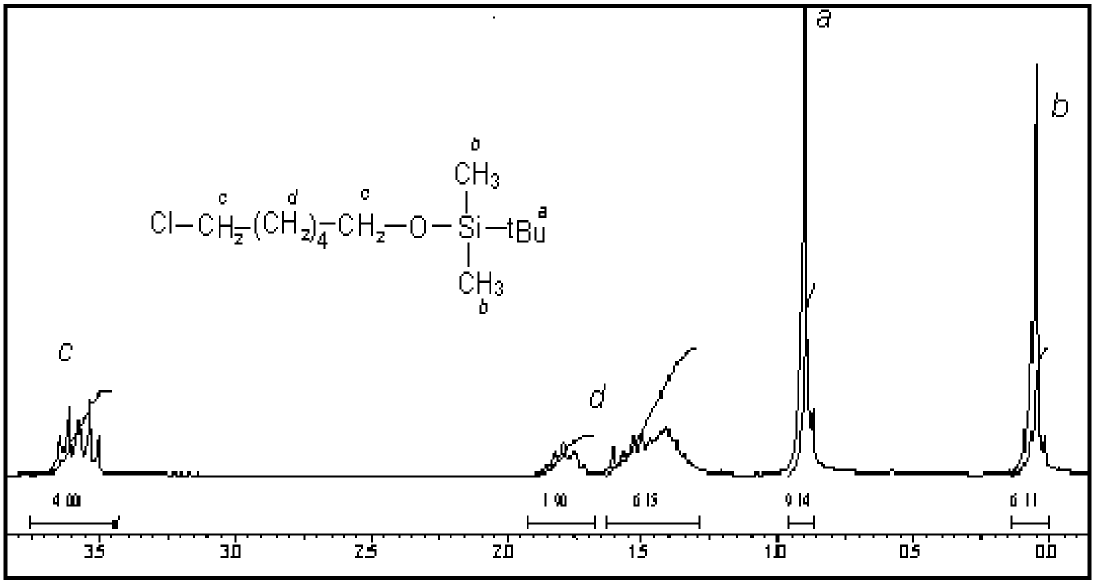


Fig. 5.3: ^{1}H NMR spectra (200 MHz, $CDCl_3$) of 6-chloro-(*tert*-butyldimethylsilyloxy) hexane

magnetic stirrer. By this process, Li-sand was formed in paraffin oil. The sand was then washed several times with dry hexane to remove the oil completely, and then added the required amount of dry and distilled cyclohexane. This was followed by dropwise addition of the protected chlorohexanol from a dropping funnel connected to one neck of the r.b. flask, while connecting the other neck to a water-condenser. After the addition was over, the mixture was allowed to heat at 60-65°C for ~4 h and then allowed to settle. The supernatant yellow solution of protected hydroxy-hexyllithium was carefully transferred by cannula into storage ampoules. It was then titrated using the Gilman`s double titration method and was found to have a strength of 0.23 [M].

Preparation of F2:

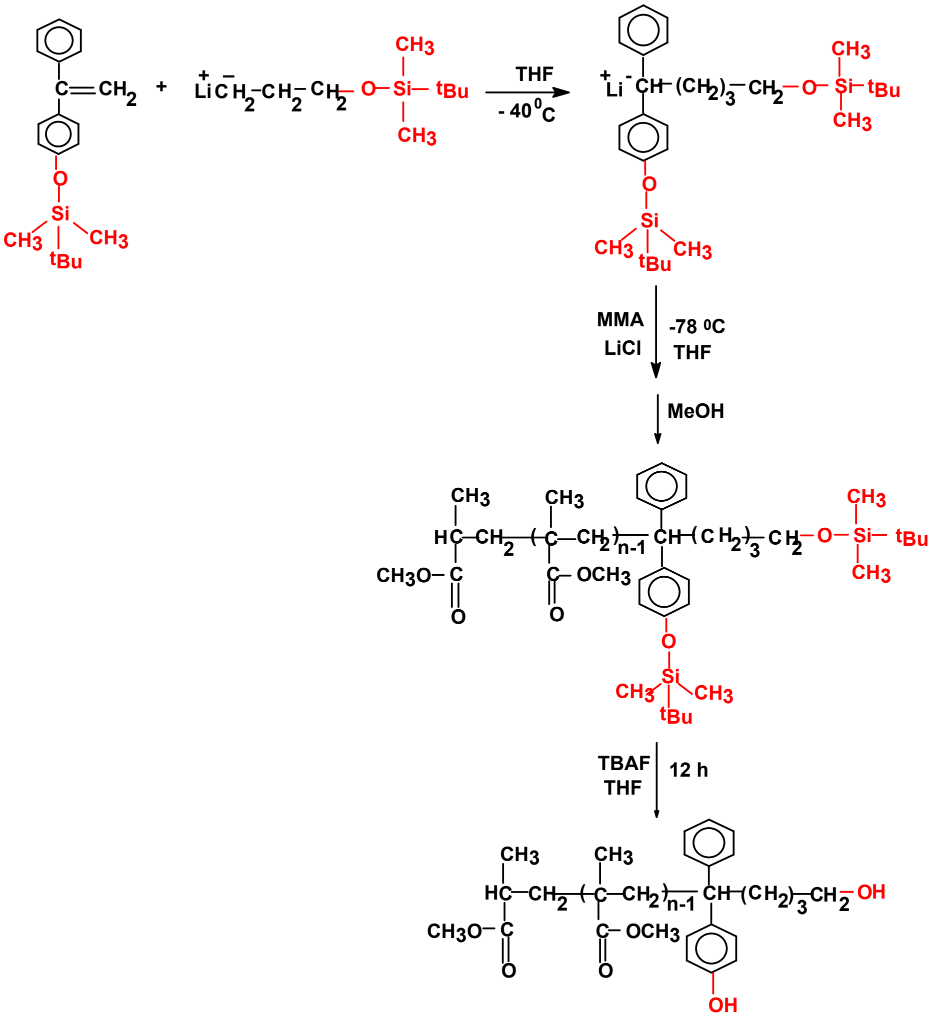
The protected hydroxy hexyllithium was used to prepare the functional initiator Fi-2 by reacting with DPE. The required amount of DPE (3 mL) was transferred by a syringe into a r.b. flask, and dissolved in freshly distilled THF (20 mL). Then the temperature was lowered to -40 °C using dry ice-acetonitrile bath, followed by dropwise addition of the protected hydroxy hexyllithium (10 mL), such that the mole ratio of DPE to the hexyllithium was 1.2:1. The development of an orangish red color indicated the formation of the functional anionic initiator F2. This was then standardized using the Gilman`s double titration method.

5.2.2.3. Preparation of functional initiator F3:

The preparation of the third functional initiator, **F3**, involved reaction between 3-(*tert*-butyldimethylsilyloxy) propyl lithium (commercial, from FMC) with diphenylethylene. The procedure is same as that followed for preparation of **F2**. Appearance of a deep red color of characteristic of diphenylalkylanion indicated the formation of **F3**. The initiator thus prepared was standardized by the Gilman's double titration method.

5.2.2.4. Preparation of functional initiator F4:

Scheme 5.6 shows the preparation of the dihydroxy-functional initiator **F4** by reacting 3-(*tert*-butyldimethylsilyloxy) propyl lithium with 1-[*p*-(*tert*-butyldimethylsilyloxy)]phenyl-1`-phenylethylene.



Scheme 5.6: Preparation of protected α, α'-dihydroxy-functional initiator (F4) and α, α'-dihydroxy-PMMA using F4

The appearance of reddish-orange color of the product indicated the formation of the difunctional initiator. It was standardised in the usual manner.

5.2.3. Polymerization with protected hydroxy-functional initiators:

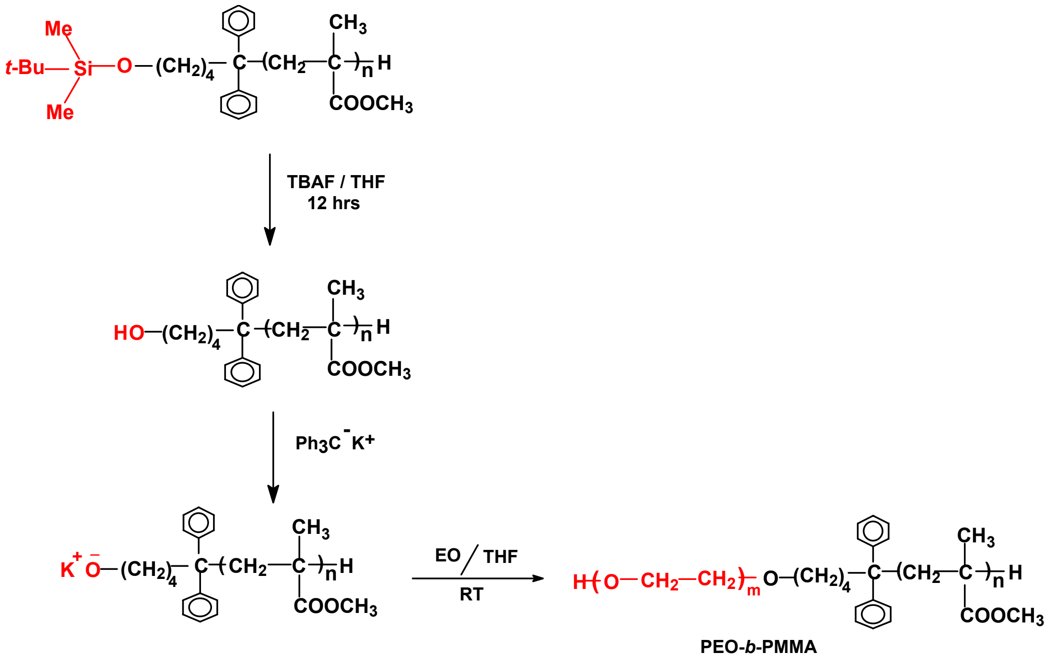
Polymerization with functional initiators were done in the usual way as for simple MMA polymerization using DPHLi as initiator in flamed glass reactors under N_2 atmosphere (refer chapter 2). All reactions were carried out in THF at -78 °C in presence of $LiClO_4$ (10x$[DPHLi]_0$) as additive. The reactions were continued for 10-15 mins, and the yields were determined gravimetrically.

5.2.4. Deprotection of the hydroxy group :

In order to generate the free hydroxy group from its protected analogue, the *tert*-butyldimethylsilyl-protected hydroxy end-functionalized PMMA was treated with 3-4 moles excess of TBAF (1[M] in THF) in dry THF, and stirred for ~12 h under N_2 atmosphere. The THF was then driven off, and the resulting polymer was dissolved in ethyl acetate and washed several times with water saturated with NaCl and NH_4Cl, to remove the water-soluble inorganic impurities. It was then re-precipitated in *n*-hexane several times to get a pure hydroxy-PMMA.

5.2.5. Synthesis of PMMA-*block*-PEO :

The hydroxy-PMMA synthesized using the functional initiators **F1**, **F2** and **F3,** were used as macroinitiators for anionic ring-opening polymerization of ethylene oxide, resulting in the formation of PMMA-*block*-PEO copolymers (scheme 5.7). The hydroxy-PMMA sample was dissolved in benzene, filtered and freeze-dried. Before using for block copolymerization, it was dried by azeotropic distillation 3-4 times by toluene, and then kept in high vacuum for ~48 hours at 60 °C. A known amount (say, 0.750 g) of the perfectly dry and purified polymer was taken in a 250 mL r.b. flask, and dissolved in freshly distilled THF (30 mL). To this polymer solution was added tritylpotassium (Ph_3C^- K^+) to convert the -OH end-groups into the corresponding oxyanion (scheme 5.7). The addition was continued until the red color of the initiator persisted for sufficiently long time or the rate of disappearance of the red color decreased. Ethylene oxide (2 mL) was distilled once over CaH_2 and subsequently over *n*-BuLi, and then added to the system at 25 °C. The reaction was continued for 36 h, and finally quenched with distilled methanol.



Scheme 5.7. : Synthesis of PMMA-*b*-PEO using hydroxy-PMMA as macroinitiators

The PMMA-PEO block copolymer, thus formed, was precipitated in large excess of cold *n*-hexane.

5.2.6. Characterization:

The $\overline{M}_n$, $\overline{M}_w$ and MWD of the polymers were determined by Gel Permeation Chromatography (Thermoseparation Products), equipped with two detectors, UV and RI, and two 60 cm PSS SDV-gel columns: 1 × 100Å and 1 × linear ($10^2 - 10^5$ Å) at room temperature. THF was used as eluent at a flow rate of 1mL/min.

^{1}H NMR (500 MHz, Bruker) was used to determine the end-functionalization of PMMA chains by comparing the peak intensities, per proton, corresponding to phenyl, $-OCH_3$, and $-Si-CH_3$ groups. The hydroxy end-functional PMMA were also analyzed by MALDI-TOF MS i.e. Matrix-Assisted Laser Desorption/ Ionization Mass Spectrometry [Voyager Elite DE system (PerSeptive Biosystems, Framingham, MA), or Kratos, PCKompact SEQ]. Dithranol was used as matrix, CF_3COOK was used as source of K^+ ion, and THF as solvent. Determination of copolymer composition of the PMMA-*block*-PEO copolymers was done by ^{1}H NMR (500 MHz, Bruker).

5.3. Results and discussion

5.3.1. Anionic Polymerization of MMA using protected hydroxy-functional initiators:

Anionic polymerization of MMA was done using the four hydroxy-functional initiators, **F1**, **F2**, **F3** and **F4** (scheme 5.3), in THF at -78 °C in presence of $LiClO_4$ as additive added in 10:1 molar ratio with respect to the initiator. The results of polymerization are discussed in details in the following section.

5.3.1.1. Hydroxy-functional PMMA from initiator F1 :

Anionic polymerization of MMA in THF at -78°C using the functional initiator **F1** (scheme 5.4), is a perfectly controlled system. The results obtained from GPC analysis (Table 5.1) show that the polymers exhibit relatively narrow molecular weight distribution. Also, there is a good agreement between theoretical and observed molecular weight i.e. the initiator efficiency 'f ' is close to unity, except for the sample F1-PMOH-4, for which the initiator efficiency is seen to be low. The initiator **F1** contains a protected hydroxy group on the phenyl ring, and by initiating MMA polymerization, the initiator moiety with the functionality gets introduced at the chain-end, thus yielding PMMA with a silyl-protected hydroxy end group. The presence of this protected-hydroxy group was detected by ^1H NMR (500 MHz) analysis of the polymer samples.

Table 5.1: Anionic polymerization of MMA using hydroxy-functional initiator **F1** at -78 °C in THF

Sample	$[I]_0 x10^{-3}$ m/L	$[M]_0$ m/L	Conv.$^{a)}$ %	$M_{n,sec}$	$M_{n,calc}$	MWD	f
F1-PMOH-4	9.47	0.12	~100	2000	1300	1.06	0.65
F1-PMOH-5	3.67	0.12	~100	3200	3300	1.07	0.97
F1-PMOH-1	4.12	0.18	100	5500	4400	1.10	0.80
F1-PMOH-2	2.70	0.18	90	10800	9800	1.06	0.91
F1-PMOH-7	3.21	0.23	"	10800	10000	1.08	0.92
F1-PMOH-6	2.88	0.41	"	14100	14400	1.09	1.02
F1-PMOH-8	0.97	0.45	"	52000	46400	1.06	0.89

a) Rxn. time was 10-15 mins.

Fig. 5.4 shows the ^1H NMR spectra of sample F1-PMOH-7. The peak intensities at δ 0.0 (6 H of -Si(CH_3)$_2$ group), δ 3.65 (310 H of -OCH_3 groups of PMMA of $M_{n,sec}$=10800) and δ 6.7-7.6 (9 H for 2 phenyl groups) are in agreement with quantitative functionalization of PMMA chains.

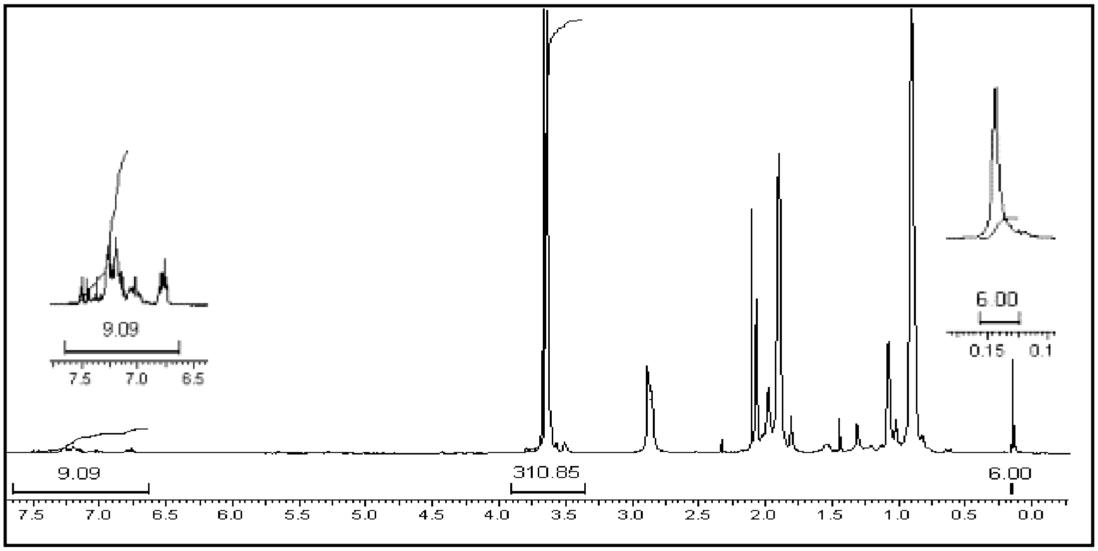


Fig. 5.4: ^{1}H NMR spectra (500 MHz, acetone-d_6) of silyl-protected hydroxy-PMMA (sample F1-PMOH-7, Table 5.1) using initiator F1

On treatment with TBAF solution, the silyl-protected hydroxy end-function underwent deprotection leading to formation of a free hydroxy group at the chain-end. The F^- ion being a strong nucleophile attacks the -O-Si bond resulting in formation of -$O^-NH_4^+$ and $^tBu(Me)_2Si^+F^-$. Subsequent aqueous work-up yields PMMA with free -OH group. This end-functionality was determined by MALDI-TOF mass spectrometric analysis. Fig. 5.5 shows a typical spectrum, corresponding to sample F1-PMOH-7. The expected end-group molecular weight is calculated by summing the mass of the initiator fragment (**F1** after desilylation, scheme 5.3) and that of the last monomer unit and including mass of K^+, i.e. the theoretical end-group mass = 253+101+39 = 393. From the molecular weight of each polymer chain as obtained from the mass-spectrum of sample F1-PMOH-7 (Fig. 5.6), the end-group mass is calculated to be ~ 396. For example, if we choose the signals corresponding to m/z=10595.0 and 14093.1, then the end-group mass are found to be 395 and 393.2 respectively, which is in agreement with the theoretical value. This is true for all the molecular weights observed in the spectra. Also, only a single type of polymers is present, as is evident from a zoomed portion of the spectra. This proves that the sample consists of only hydroxy end-functionalized PMMA chains with no unfunctionalized chain.

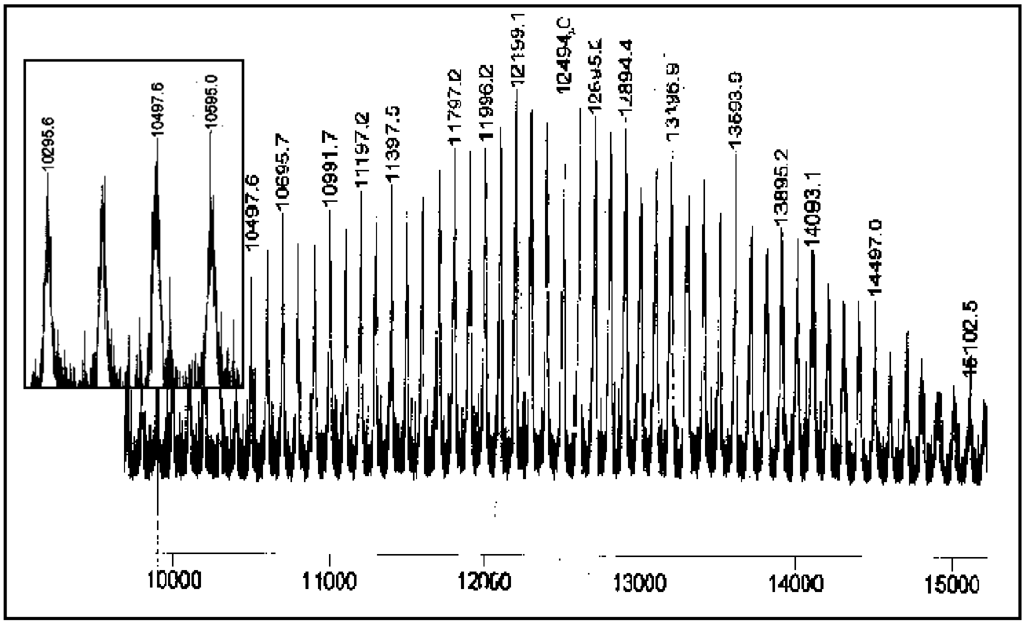


Fig. 5.5: MALDI-TOF mass spectrum of hydroxy-PMMA (sample F1-PMOH-7, Table 5.1) prepared using functional initiator F1

5.3.1.2. Hydroxy-PMMA from functional initiator F2:

Controlled anionic polymerization of MMA in THF at -78 °C using hydroxy-functional initiator **F2** (scheme 5.5) resulted in hydroxy end-functionalized PMMA with narrow molecular weight distributions (Table 5.2). However, the initiator efficiencies are much lower than unity. We have no reasonable explanation for the observed poor agreement between predicted and observed molecular weight. Possibly, the initiator loses its activity rapidly relatively fast upon storage even at low temperatures.

Table 5.2: Anionic polymerization of MMA using hydroxy-functional initiator **F2** at -78 °C in THF

Sample	$[I]_0$ x10^{-3} m/L	$[M]_0$	Conv. $^{a)}$ %	$M_{n,sec}$	$M_{n,calc}$	MWD	*f*
F2-PMOH-3	12.5	0.12	100	1800	1000	1.06	0.55
F2-PMOH-4	7.46	0.17	100	3200	2400	1.07	0.75
F2-PMOH-5	5.50	0.21	"	5000	3800	1.08	0.77
F2-PMOH-6	4.31	0.27	"	7200	6400	1.09	0.88

a) Rxn. time was 10-15 mins.

The PMMA prepared by using the above functional initiator contains a silyl-protected hydroxy-function at the chain-end that bears the initiator moiety. ^{1}H NMR analysis of the protected hydroxy-PMMA (sample F2-PMOH-3, Table 5.2) was done to determine the end-functionality, as shown in Fig. 5.6 The resonance absorption at δ 0.0 (6 H of -$Si(CH_3)_2$ group), δ 3.63 (47 H of -OCH_3 groups of PMMA of $M_{n,sec}$= 1800) and δ 7.1-7.5 (10 H for 2 phenyl groups) are in agreement with quantitative functionalization of PMMA chains.

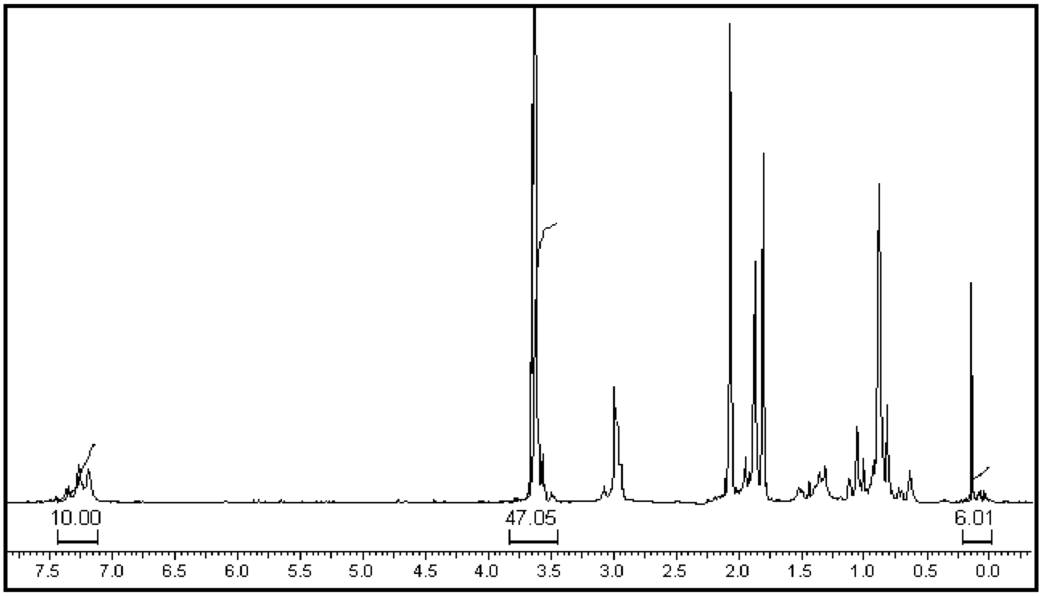


Fig. 5.6: ^{1}H NMR spectra (500 MHz, acetone-d_6) of silyl-protected hydroxy-PMMA (sample F2-PMOH-3, Table 5.2) using Fi-2 as initiator

Desilylation of the samples was done by TBAF treatment in the usual manner. Subsequent MALDI-TOF analysis of the hydroxy-PMMA sample F2-PMOH-4 revealed that only partial desilylation had occurred (Fig. 5.7) which may be due to improper drying of THF used as solvent while desilylation. As expected, two types of polymers are seen in the spectrum, the molecular weights being clearly seen in the zoomed portion of the spectrum. It was established by calculation of end-group mass, that the major peak is due to silyl-protected hydroxy-PMMA, whereas the smaller peak is due to the deprotected analogue bearing a free hydroxy-end group. The theoretical mass of the end groups in the silyl-protected hydroxy-PMMA chains = sum of mass of initiator **F2** (scheme 5.3) with that of terminal MMA unit, and mass of K^+ ion, i.e. = 395+101+39 = 535. The end-group mass for the deprotected chain = 421 (subtracting mass of the *tert*-butyldimethylsilyl group).

The higher intensity peaks give a consistent end-group mass of 539, close to the value calculated for the protected-hydroxy PMMA chains. The second generation peaks of low intensity, e.g. the signals corresponding to m/z values of 2919.84 and 3019.09 as shown in the zoomed region of the spectrum, give an end-group mass = 419, in close agreement with theoretical value for the hydroxy-PMMA chains.

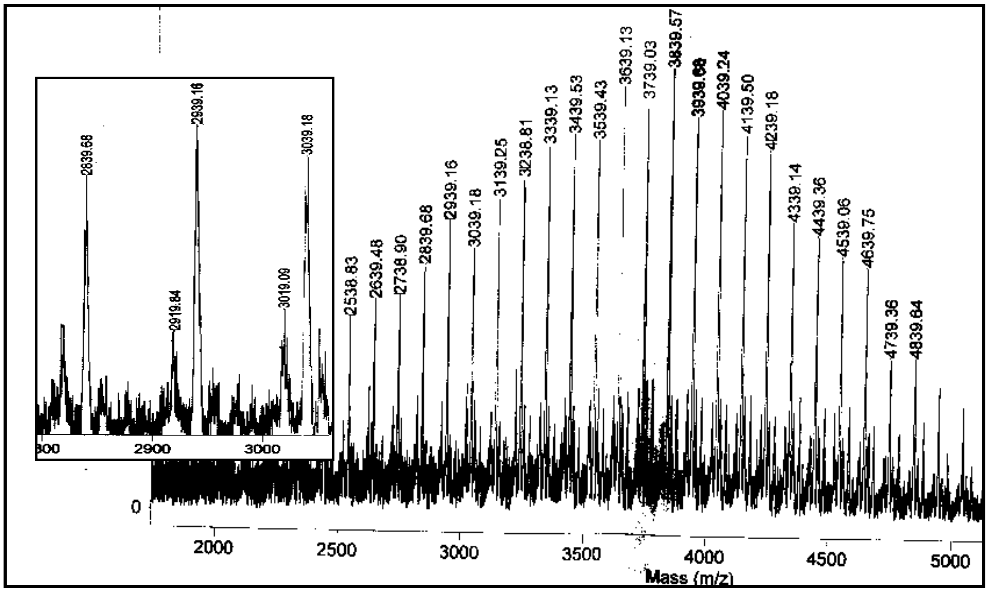


Fig. 5.7: MALDI-TOF mass spectrum of hydroxy-PMMA (sample F2-PMOH-4, Table 5.2) using functional initiator F2

5.3.1.3. Hydroxy-PMMA using functional initiator F3:

The adduct of 3-*tert*-butyldimethylsilyloxy propyllithium with DPE, i.e. functional initiator **F3**, was used to initiate living anionic polymerization of MMA in THF at -78 °C to yield PMMA having a silyl-protected hydroxy-function at the chain-end containing the initiator moiety. The polymers have been characterized by GPC and ^{1}H NMR (500 MHz). The results of GPC analysis, given in Table 5.3, are in agreement with a perfectly living polymerization yielding polymers with narrow molecular weight distribution. Also, there is a good agreement between predicted and observed molecular weight, as evident from the initiator efficiency values close to unity. The conversions are usually quantitative.

Table 5.3: Anionic polymerization of MMA using **F3** at -78 °C in THF

Sample	$[I]_0$ x10^{-3} m/L	$[M]_0$	Conv.$^{a)}$ %	$M_{n,sec}$	$M_{n,calc}$	MWD	*f*
F3-PMOH-K	4.45	0.09	100	2300	2000	1.09	0.87
F3-PMOH-H	3.22	0.27	100	8500	8300	1.09	0.98
F3-PMOH-D	2.79	0.33	100	11500	11700	1.07	1.02
F3-PMOH-E	3.70	0.40	100	11660	10900	1.08	0.94
F3-PMOH-F	1.89	0.25	100	14000	13300	1.08	0.95
F3-PMOH-J	1.84	0.37	100	21700	20300	1.07	0.93
F3-PMOH-I	1.80	0.42	100	22100	23400	1.09	1.06

a) Rxn. time was 10-15 mins.

The functional initiator introduces the functionality at the initiator-end of each PMMA chain. The degree of functionalization was confirmed by ^{1}H NMR (500 MHz) analysis of the polymers. The ^{1}H NMR spectra for sample F3-PMOH-D containing a silyl-protected –OH end-group is shown in Fig. 5.8. The resonance absorptions at δ 0.0 (6 H of -$Si(CH_3)_2$ group), δ 3.65 (342 H of -OCH_3 groups of PMMA of $M_{n,sec}$= 11500) and δ7.1-7.4 (10 H for 2 phenyl groups) suggest that the PMMA chains are quantitatively functionalized.

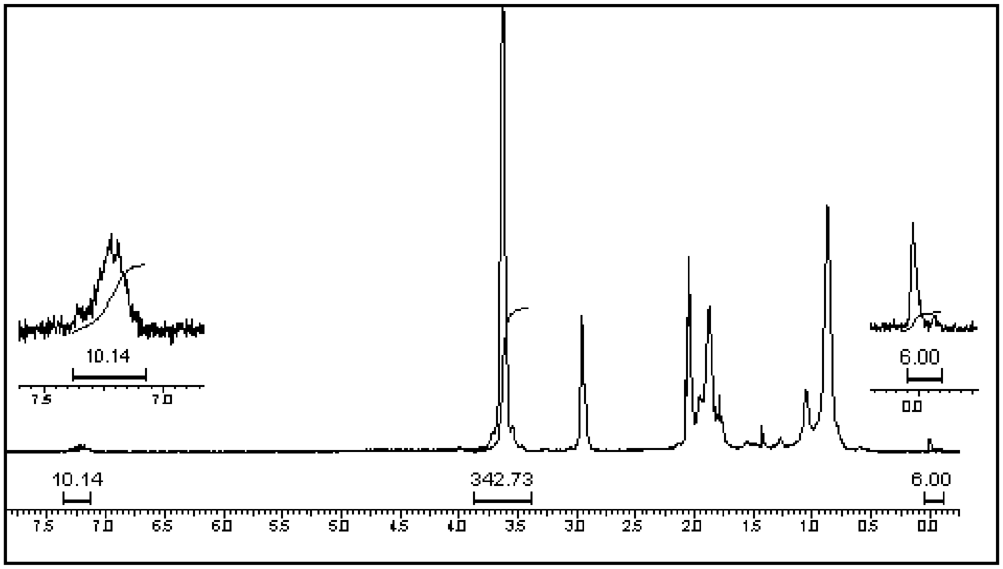


Fig. 5.8: ^{1}H NMR (500 MHz, acetone-d_6) spectra of silyl-protected hydroxy-PMMA (sample F3-PMOH-D, Table 5.3), prepared using functional initiator F3

MALDI-TOF mass spectrometric analysis of the silyl-protected hydroxy-PMMA sample F3-PMOH-K confirmed the presence of the protected-hydroxy group at the terminus of each polymer chain, as shown in Fig. 5.9.

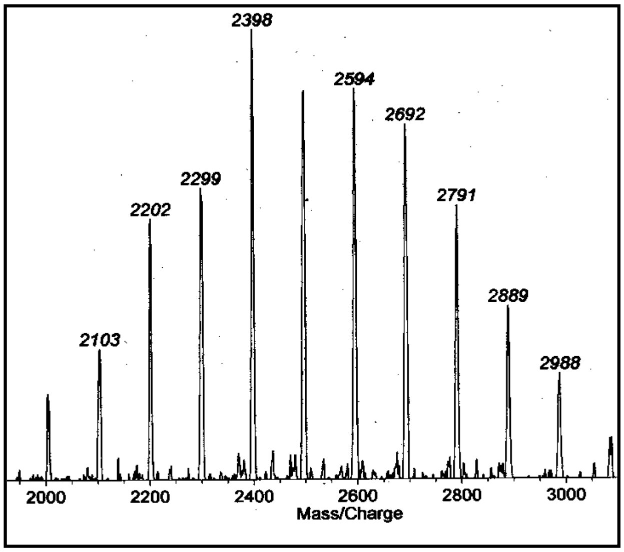


Fig. 5.9: MALDI-TOF spectra of silyl-protected hydroxy-PMMA (sample F3-PMOH-K, Table 5.3) prepared using functional initiator F3

The theoretical end-group mass for F3-PMOH-K is calculated as sum of the initiator fragment (**F3**, scheme 5.3) with that of a monomer unit at the other chain end, and mass of K^+, i.e. 354+101+39= 493. The observed end-group mass can be calculated from the mass spectrum of F3-PMOH-K (Fig. 5.9), by randomly choosing any signal corresponding to a particular value of molecular weight. For the peaks corresponding to, say, m/z = 2597 and 2791, the end-group mass = 494 and 491 respectively i.e., both of which are close to the theoretical value. Also, the spectrum shows a single type of polymer, which prove that the sample is a pure hydroxy end-functionalized PMMA without any unfunctionalized chains.

5.3.1.4. Hydroxy-PMMA using functional initiator F4:

The functional initiator **F4** was made by forming an adduct between 1) a silyl-protected hydroxy-propyl lithium and 2) silyl-protected hydroxy-DPE component, and thus it is expected to contain two protected hydroxy groups. Hence, anionic polymerization of MMA in THF in presence of **F4** (scheme 5.6) led to formation of PMMA with two protected-hydroxy functionalities at the chain end that contains the initiator moiety. Only one polymerization was done using **F4**, and the resulting hydroxy-PMMA is seen to have narrow MWD with fairly high initiator efficiency (Table 5.4).

Table 5.4: Anionic polymerization of MMA using **F4** at -78 °C in THF

Run no.	$[I]_0$ x10^{-3} m/L	$[M]_0$	Conv. %	$M_{n,sec}$	$M_{n,calc}$	MWD	*f*
F4-PMOH-1	3.46	0.37	~100	9600	10800	1.09	0.88

The presence of two silyl-protected functionalities were confirmed by ^{1}H NMR (500 MHz) analysis of sample F4-PMOH-1, as shown in Fig. 5.10. The resonance absorptions at δ 0.0 (12 H of two -$Si(CH_3)_2$ groups), δ 3.65 (192 H of -OCH_3 groups of PMMA of $M_{n,sec}$= 9600) and δ 6.7-7.5 (9 H of 2 phenyl groups) suggest that the PMMA chains are quantitatively functionalized.

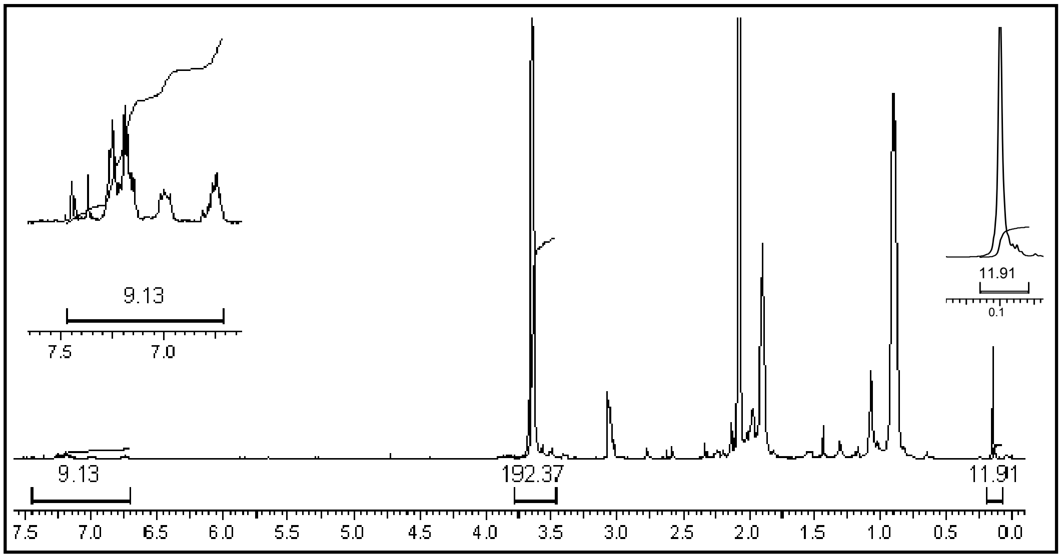


Fig. 5.10: ^{1}H NMR (500 MHz, acetone-d_6) of silyl-protected α,α'-dihydroxy functionalized PMMA (sample F4-PMOH-1, Table 5.4) prepared using F4

5.3.2. PMMA-PEO block copolymers using hydroxy-PMMA as macro-initiator

The hydroxy-functional PMMA prepared using the functional initiators **F1, F2** and **F3** were utilized to initiate the ring-opening polymerization of ethylene oxide (EO) to enable the synthesis of PMMA-*b*-PEO copolymers, as shown in scheme 5.7. The hydroxy end-function was converted into the corresponding oxyanion with potassium as counter-ion by reacting with triphenylmethylpotassium. This oxyanion is reactive enough to initiate ethylene oxide polymerization. The corresponding Li salt leads to ring opening of just one unit of EO without promoting further polymerization. This unreactivity of the chain-ends is presumed to result from a high degree of aggregation of Li-alkoxides and the strength of the association, even in polar solvents.

The PMMA-*b*-PEO block copolymers synthesized from the hydroxy-PMMA prepolymers, were analyzed by GPC, ^{1}H and ^{13}C NMR in order to establish the formation of the required block copolymer. The results are given in Table 5.5. The hydroxy-PMMA samples from all the three functional-initiator systems initiated EO polymerization at room temperature, leading to formation of PMMA-*b*-PEO copolymers. However the rate of EO polymerization seems to be very slow. The conversions, determined from the gravimetric yield of the block copolymers, were found to be only 50-60 % after a reaction time of almost 36 h.

All the PMMA-*b*-PEO copolymers as prepared, showed a characteristic tailing in the low molecular weight region when analysed by GPC. These copolymers were then purified by mixing with hot water and keeping overnight. The water-insoluble portion was then recovered, dried and analyzed by GPC and NMR. The GPC elugrams of some of the block copolymers before and after washing are shown in Fig. 5.11. As evident from the elugrams, the tailing totally disappears after giving the water-wash.

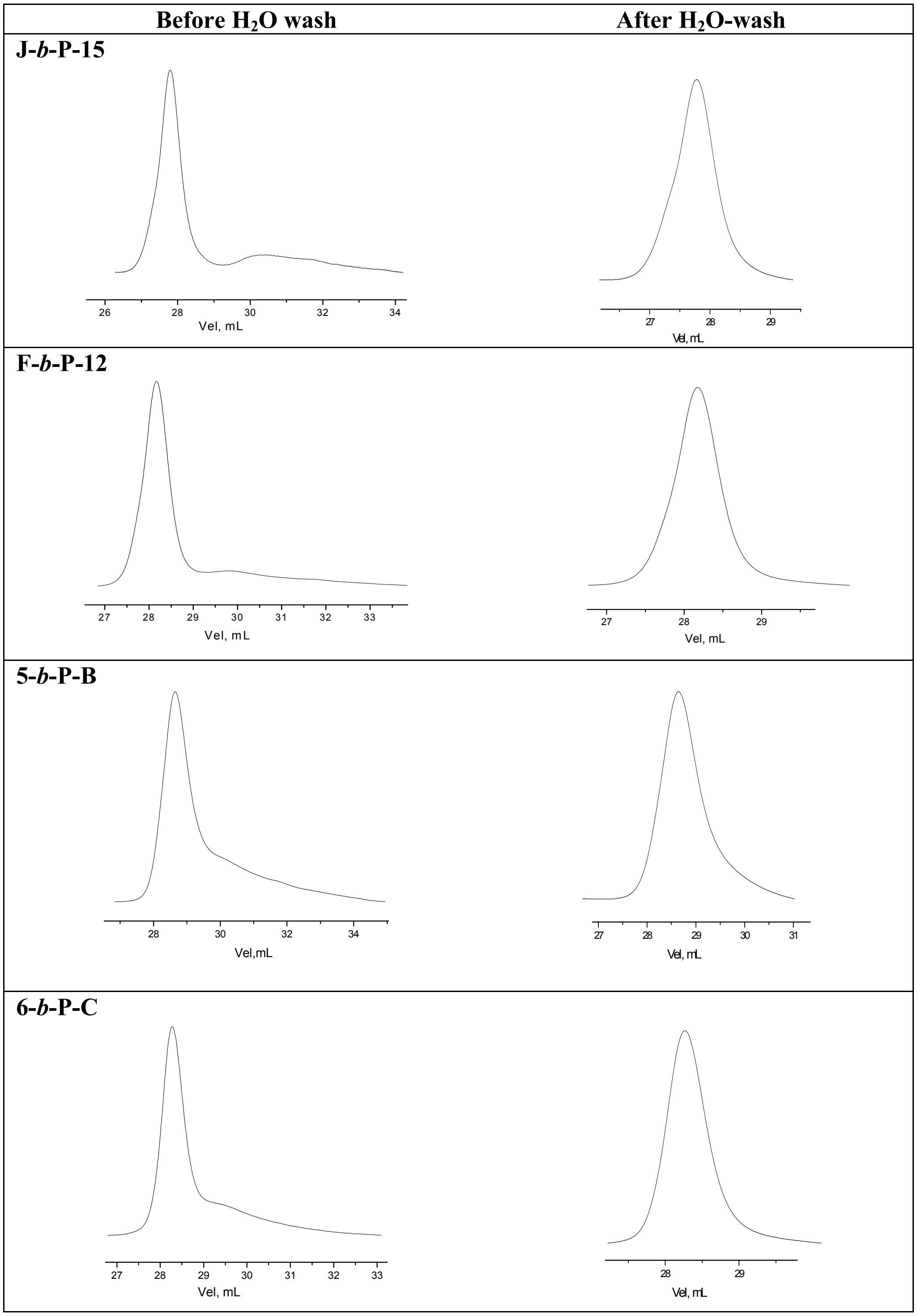


Fig. 5.11: GPC elugram of PMMA-*b*-PEO copolymer samples show tailing in low molecular weight region before washing with warm water. Pure diblock copolymer after washing shows narrow unimodal MWD

The GPC elugrams show a shift in the peak maxima elution volume (V_p) of the product from that of the precursor hydroxy-PMMA, as shown in Fig. 5.12 for the hydroxy-PMMA sample PMOH-D (Table 5.5) and the corresponding PMMA-*b*-PEO copolymer sample D-*b*-P-11 (Table 5.5). This suggests an increase in molecular weight of the product, and hence proves the formation of the PMMA-PEO block copolymer.

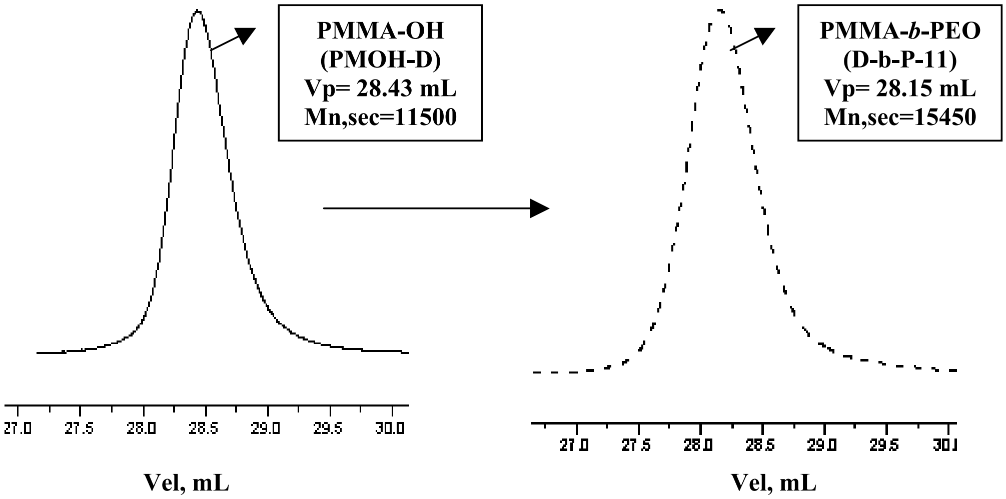


Fig. 5.12: GPC elugram of hydroxy-PMMA (sample PMOH-D, Table 5.5) and that of the corresponding PMMA-*b*-PEO (sample D-b-P-15, Table 5.5). Shift in Vp suggests increase in molecular weight.

Table 5.5 shows the molecular weights of the individual blocks as determined from GPC and ^{1}H NMR analysis of the purified copolymer. The $\overline{M}_{n,\ sec}$ of the PEO block was calculated by the difference of $\overline{M}_{n,\ sec}$ of block copolymer over the $\overline{M}_{n,\ sec}$ of the precursor hydroxy-PMMA. However, THF being not a good solvent for PEO, the SEC data for the PEO block is expected to be different from the actual value. So, the molecular weight of the PEO block was also calculated from the ^{1}H NMR spectra of the respective diblock copolymer. The block-copolymer samples, H-b-P-15, 4-b-P-A and 6-b-P-D (Table 5.5) totally dissolved in water and hence could not be purified. Copolymerization with EO increased the overall hydrophilicity of the block copolymer to the extent that it became completely water-soluble in spite of the presence of a significantly long hydrophobic PMMA segment. For these three samples, the GPC and ^{1}H NMR data of the pure block copolymers were not available. The ^{1}H and ^{13}C NMR analysis of the pure block copolymers clearly prove the formation of the block copolymers. Fig. 5.13 (a) shows the ^{1}H NMR (200 MHz, $CDCl_3$) spectra of the hydroxy-PMMA sample PMOH-J, where the characteristic absorption of the $-OCH_3$ group of PMMA block is seen at δ 3.58.

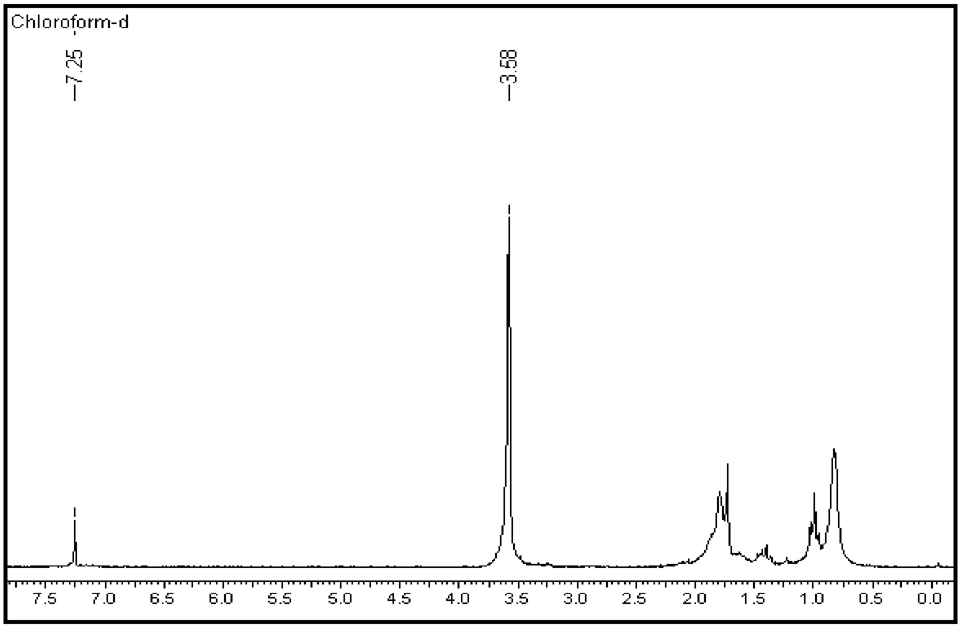
Table 5.5: Synthesis of PMMA-*b*-PEO copolymers using hydroxy-PMMA as macroinitiator

Fnl. Initiator	PMMA-OH				Feed concn. of EO (moles/L)	PMMA-*b*-PEO				PEO block	
	Sample no.	$\overline{M}_n$ (SEC)	MWD (SEC)	Feed concn. x10^3 (moles/L)		Sample no.	Conv.$^{a)}$	$\overline{M}_n$ (SEC)	MWD (SEC)	$\overline{M}_n$ $^{b)}$ (SEC)	mol. wt. (^{1}H NMR)
F3	PMOH-D	11500	1.07	2.30	0.9	D-b-P-8	0.51	15400	1.20	3900	7500
		"	"	2.08	0.9	D-b-P-11	0.53	15900	1.20	4400	11000
	PMOH-F	14000	1.08	2.50	1.0	F-b-P-12	0.49	16400	1.21	2400	6300
		"	"	2.60	1.0	F-b-P-13	0.56	17300	1.15	3300	8800
	PMOH-H	8500	1.09	2.80	1.1	H-b-P-14*	0.60	-	-	-	-
	PMOH-J	21700	1.07	2.80	1.3	J-b-P-15	0.62	27100	1.25	5400	10600
F2	PMOH-4	3200	1.07	3.00	1.2	4-b-P-A	0.50	-	-	-	-
	PMOH-5	5000	1.08	3.31	1.0	5-b-P-B	0.50	8000	1.27	3000	5000
	PMOH-6	7200	1.09	2.80	1.0	6-b-P-C	0.58	13700	1.18	6500	10000
		"	1.09	2.25	1.0	6-b-P-D*	0.61	-	-	-	-
F1	PMOH-6	14100	1.09	1.00	1.8	6-b-P-1	0.55	40700	1.27	26600	51200

a) Conversion was determined from gravimetric yield of a block copolymer.

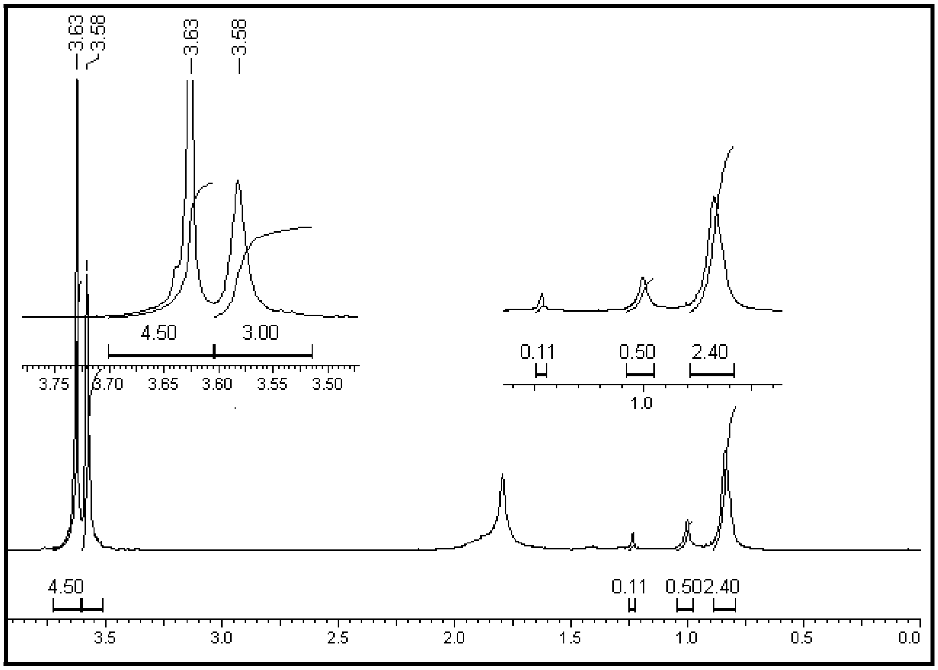
b) $\overline{M}_n$(SEC) of PEO block = { $\overline{M}_n$(SEC) of PMMA-*b*-PEO } - { $\overline{M}_n$(SEC) of PMMA-OH }

(*) Denotes block copolymers that dissolved completely in water, so GPC and ^{1}H NMR analysis of the pure diblock could not be done.



(a)

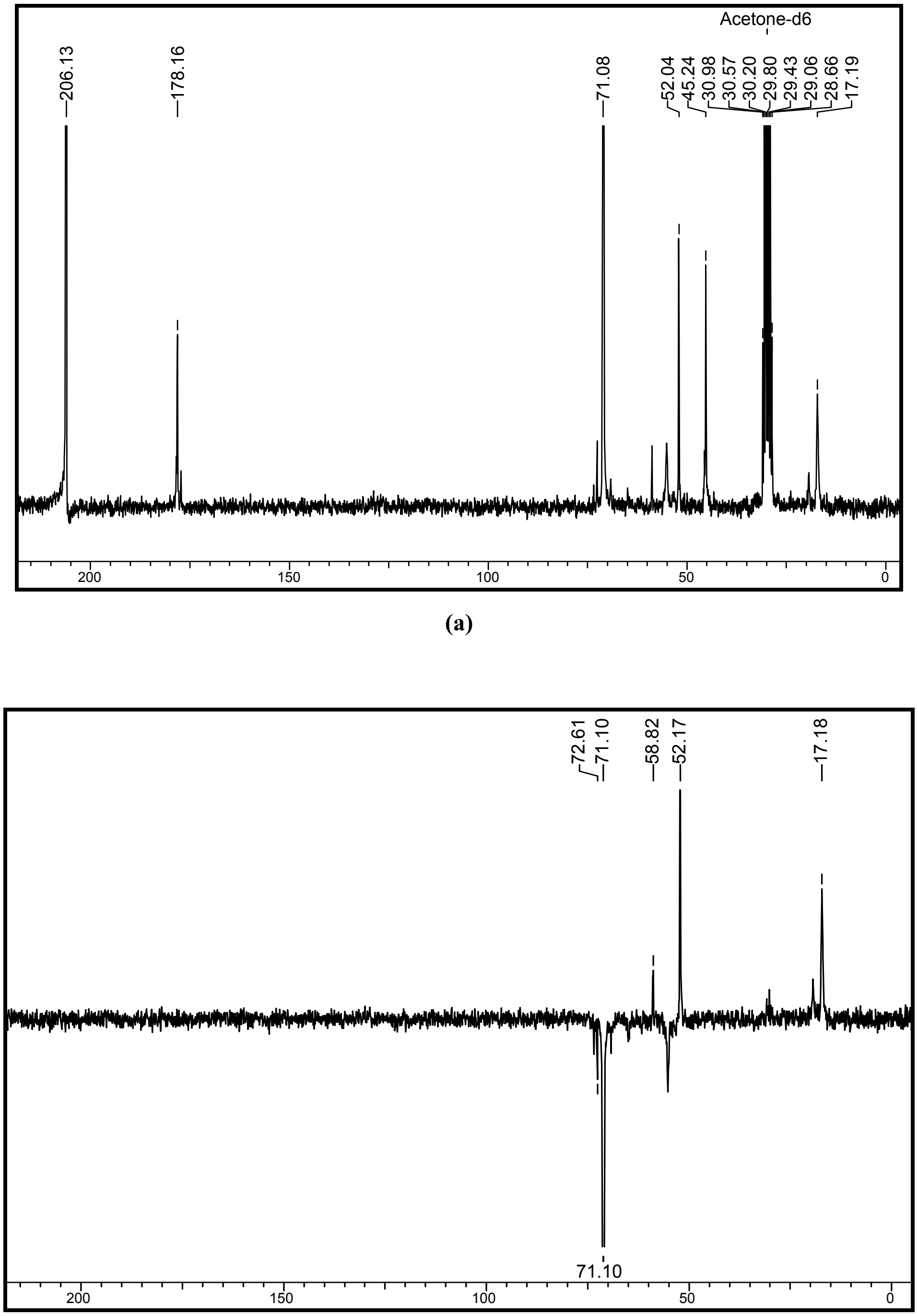
Whereas, in the ^{1}H NMR spectra [5.13(b)] of the corresponding PMMA-PEO block copolymer sample, J-*b*-P-15 (Table 5.5), an additional significant absorption at δ 3.62 is seen which is a characteristic of the -OCH$_2$ group of the PEO block.



(b)

Fig. 5.13: (a) ^{1}H NMR spectra (200MHz,CDCl$_3$) of hydroxy-PMMA (sample PMOH-J, Table 5.5); (b) ^{1}H NMR spectra (500MHz, CDCl3) of the corresponding PMMA-*b*-PEO copolymer (sample J-b-P-15, Table 5.5)

Fig. 5.14 (a) shows the ^{13}C NMR spectra of the PMMA-*b*-PEO copolymer sample, J-b-P-15. A predominant peak at δ 71.08 is inverted in the DEPT [Fig. 5.14(b)], thus suggesting the presence of a significantly long PEO block, where the carbon of the -OCH$_2$ groups shows the characteristic absorption at δ 71.08.



(a)

(b)

Fig. 5.14: (a) ^{13}C NMR and (b) DEPT (200 MHz, acetone-d$_6$) of PMMA-*b*-PEO copolymer (sample J-b-P-15, Table 5.5)

From the knowledge of $\overline{M}_n$ (SEC) of the PMMA block, and the ratio of peak intensities for the -OCH_3 (δ 3.58) and OCH_2 (δ 3.63) group of PMMA and PEO blocks respectively, the molecular weight of the PEO block was calculated. The molecular weight of the PEO block of the pure diblock copolymers, calculated on the basis of the ^1H NMR data (Table 5.5) are found to be almost 2 to 2.5 times higher than those calculated from GPC data.

The results of GPC analysis of PMMA-*b*-PEO copolymer imply that the block copolymerization reaction is sufficiently controlled. Previous reports on PMMA-PEO block copolymerization suggested some trans-esterification reaction by the living diblock that led to grafting onto the PMMA backbone (scheme 5.1), and resulted in broad bimodal molecular weight distribution of the PMMA-*b*-PEO copolymer. Contrary to these earlier results, the present block copolymers show fairly narrow and unimodal molecular weight distribution. So we conclude that no significant trans-esterification and grafting reaction has occurred.

Also, from the ^1H NMR spectra of the pure diblock copolymer (Fig. 5.11), the ratio of peak intensities of the -OCH_3 group (appearing at δ 3.58) to that of -CH_3 group (attached to the quaternary C atom on PMMA backbone, appearing at δ 0.5-1.2) was almost 1:1. In case of significant trans-esterification, this ratio is expected to be less than one, implying loss of -OCH_3 groups by the reaction of living alkoxide chain-end.[22] The fact that there was a tailing in the GPC elugrams that disappeared on giving a hot water-wash, suggested that the block copolymer was contaminated by small amount of polyethylene oxide homopolymer (present in 2-4 % of the total polymer weight). The ^1H NMR spectra (200 MHz, $CDCl_3$) of the water soluble portion is shown in Fig. 5.15, clearly prove that the water-soluble portion is an ethylene oxide homopolymer. The single siginificant peak at δ 3.62 corresponds to the -OCH_2 protons of the polymer. Absence of any phenyl absorption near δ 7.0 suggests that the PEO hompolymer is not due to EO initiation by excess trityl-K added to the system during titration of the -OH group. This was possibly caused by attack of living chains on the ester group of PMMA block. However, the extent of such a side-reaction was too low to be detected either by GPC or by NMR analysis of the block-copolymer.

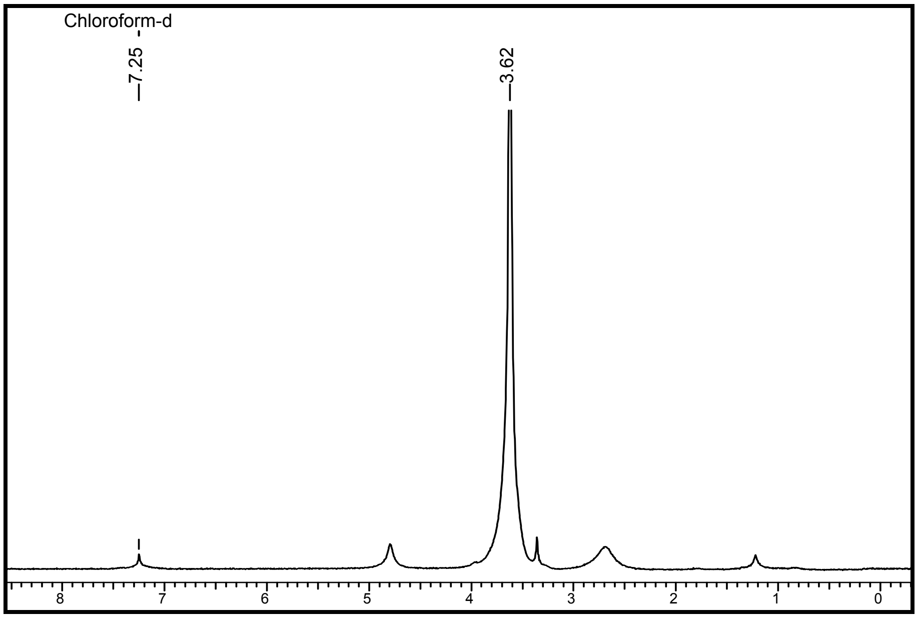


Fig. 5.15: ^{1}H NMR (200 MHz, $CDCl_3$) spectra of water-soluble portion recovered from PMMA-*b*-PEO after washing with hot water

Also it was possible for us to purify the block copolymer by a simple method of washing with warm water, and to recover a relatively pure PMMA-*b*-PEO copolymer with a sufficiently low polydispersity. This is in contrast to the earlier work by Seow et al[21] and Suzuki et al[22] where it was reported that significant trans-esterification of the ester group by the living chain end occurred resulting in block copolymers with broad multimodal distribution.

5.4. Conclusion

Well-defined hydroxy end-functionalized PMMA were successfully prepared using functional initiation approach. In contrast to functionalization by electrophilic termination, use of functional initiators are simple and clean, leading to quantitative end-functionalization. Further, these hydroxy terminated PMMA were successfully utilized for ring-opening polymerization of ethylene oxide yielding PMMA-PEO block copolymers. Earlier, attempts to synthesize of such diblocks using different experimental strategies failed due to some potential problems involving side-reactions of living alkoxide chains with ester group of PMMA. Broad, multimodal MWD of the block-copolymers was obtained. In contrast, use of well-defined hydroxyl end-functionalized PMMA as macroinitiators led to controlled polymerization of ethylene oxide. No untoward side-reactions were observed and products were purified by an easy procedure to give pure

PMMA-PEO block-copolymers. Block-copolymers with narrow unimodal molecular weight distribution were prepared. These well-defined copolymers are expected to find a number of applications as amphiphilic polymers and surface-active agents, for emulsion and dispersion polymerization.

5.5. References

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Chapter 6: Synthesis of Hydroxy-Functional Star-branched PMMA and Macromonomers

6.1: Introduction

One of the major applications of living anionic polymerization is the synthesis of functionalized polymers with well-defined structures and low compositional heterogeneity.[1,2] End-functionalized polymers, both telechelics and macromonomers are industrially important prepolymers for preparing block, graft, star-branched copolymers and network structures. In contrast to free-radical polymerization methods, anionic polymerization can be made free of termination and transfer processes under carefully selected conditions. Synthesis of functional polymers is usually accomplished either by termination of the active anionic chain end using suitable electrophiles, or by using functionalized initiator for initiating the polymerization (see chapter 5). In case of functional initiation, the active chain end of the functionalized polymer can be further utilized by post-polymerization reactions to make star-branched polymers or macromonomers.

Star-branched copolymers :

Star-shaped polymers, i.e. polymers with several linear polymer chains connected to a central atom or group of atoms, exhibit the simplest form of branching. Using controlled polymerization methods, it is possible to synthesize star-branched polymers with narrow MWD and predictable structure and arm length that are well-suited for investigations into structure-property relationship of branched polymers. The three generally applied methodologies of preparing star-branched polymers are- 1) using multifunctional organometallic compounds to initiate polymerization of several branches, 2) linking living anionic polymers to a an electrophilic multifunctional coupling agent, 3) using bis-unsaturated compounds e.g. divinyl benzene to link the living chains.[3,4]

Compared to the vast majority of the work reported on synthesis of well defined stars using non-polar polymers, e.g. polystyrene and dienes,[5] relatively little work has been conducted with methacrylate stars. This is partly because anionic polymerization of

MMA needs to be done at lower temperatures. Under these conditions many of the linking reactions do not occur efficiently. Also, the bulky nature of the methacrylate chain ends prevents synthesis using multifunctional electrophilic linking agents. Moreover, PMMA does not react with divinyl-benzene.

Star-branched copolymers of methyl and ethyl methacrylates were synthesized by Simms et al by group transfer polymerization of MMA and linking the living arms using ethylene glycol dimethacrylate (EGDMA).[6] GTP enabled reaction to be performed at 25 °C resulting in a star polymer with large number of arms. However, the polydispersity was high, with viscosity and molecular weight increasing upon storage. Later, Mays et al prepared PMMA stars by anionically polymerizing MMA and linking the living chains with EGDMA[7]. The effect of arm length and EGDMA concentration on the degree of branching was studied.The star polymers were characterized by SEC, light scattering and viscometry. Combining the concept of functionalization of PMMA chains using functionalized initiator, and EGDMA for coupling the living polymers, Quirk et al prepared PMMA stars with hydroxy group at the end of each chain[8]. They prepared PMMA star polymer with 10 arms, characterized by SEC. Only one polymerization was reported, and no detailed characterization of the star was given.

Macromonomers:

The advent of macromonomers,[9] i.e. reactive prepolymers with polymerizable end-group has provided a facile means to the synthesis of well-defined graft copolymers. made a breakthrough in the synthesis of well-defined graft copolymers. Unlike macromonomers based on hydrocarbon monomers that have been investigated extensively, few reports on macromonomers based on methacrylic esters are available. This is, presumably, a reflection of the inherent problems associated with methacrylate polymerization, e.g. the side-reactions involving the ester group, under classical conditions of initiation and propagation. The low temperature required for controlled polymerization limits the range of chemical reactions that can be used for functionalization.

Andrews et al synthesized PMMA macromonomers with allylic and styrenic end-function by polymerizing MMA using DPHLi as initiator at -78 °C followed by deactivating the living chains by allyl bromide, and vinylbenzyl iodide or bromide respectively[10]. Vinylbenzyl chloride failed to react with the living PMMA anion. Teyssie et al prepared well-defined t-butyl acrylate macromonomers with methacryloyl or styrenic end-function, by polymerizing t-BuA using LiCl-modified initiator and terminating the living ends with eletrophiles bearing styrenic or methacryloyl unsaturation[11]. ^{1}H NMR spectroscopy and SEC analysis of the macromonomers confirmed efficient functionalization. Alkyl methacrylate macromonomers have been prepared by Lutz et al by deactivation of the chain-end carbanionic sites with p-vinyl- or p-isopropenylbenzyl bromide[12]. Synthesis of PMMA macromonomers by termination of living chains by benzaldehyde or 4-vinylbenzoyl chloride have also been reported.[13] Highly syndiotactic PMMA of low polydispersity (1.11-1.17) have been prepared with Ph_3Cli in THF or THF-PhMe, and coupled with p-(chloromethyl)styrene at -78° yielding PMMA macromonomers with one vinylbenzyl group per polymer chain[14]. Hatada et al polymerized MMA with o-vinylbenzylmagnesium chloride[15] in toluene and in THF at -78° producing PMMA macromonomers with one vinylbenzyl group at the α-end of the chain.

In this chapter we have investigated the possibility of using the hydroxy-functional PMMA as a precursor for star-branched polymers by cross-linking with EGDMA. The effect of increase in arm-length and concentration of EGDMA on the number of arms have been investigated. We have also explored the feasibility of preparing hydroxy-functional PMMA macromonomers by deactivating the living chains with allyl methacrylate and with 4-vinylbenzyl chloride, so as to form α-hydroxy-ω-allyl and α-hydroxy-ω-styryl PMMA macromonomers

6.2. Experimental

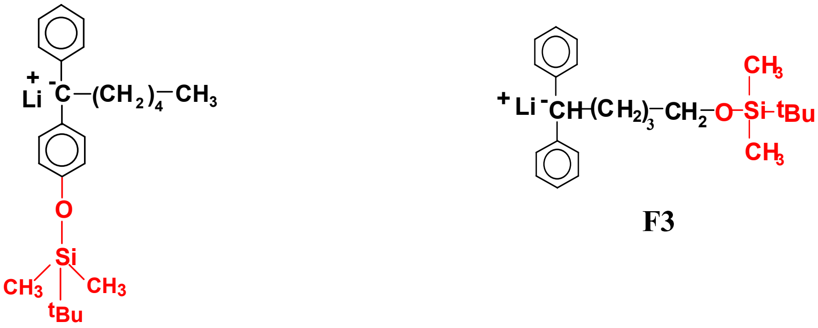
6.2.1. Materials and purification:

Ethyleneglycol dimethacrylate (EGDMA, Aldrich, USA) was fractionally distilled over CaH_2 under reduced pressure. The middle fraction was collected and stored over activated molecular sieves. Before adding to the polymerization system, it was stirred over CaH_2 for ~ 2 h, and then degassed and distilled under dynamic vacuum. 4-vinyl benzyl chloride (4-VBC) and allylmethacrylate (AMA) were procured from Aldrich, USA. They were purified in the same way as EGDMA. The protected-hydoxy functional initiators were prepared in the laboratory as described in chapter 5.

6.2.2. Polymerization procedure:

6.2.2.1. Procedure for synthesis of hydroxy-functional star-branched polymer :

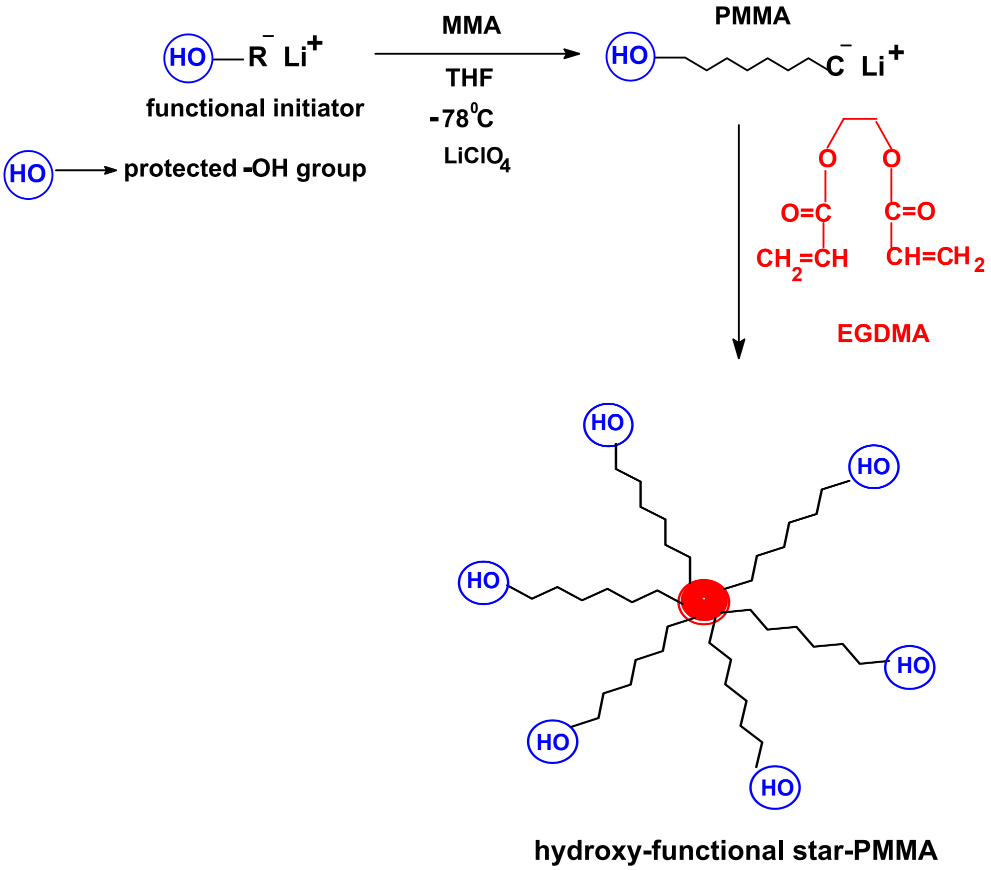
Anionic polymerization of MMA was performed in THF at -78 °C using silyl-protected hydroxy-functional initiators, **F1** and **F3** (scheme 6.1, see chapter 2 for details).



F1 **F3**

Scheme 6.1: Hydroxy-functional initiators for synthesis of precursor hydroxy-PMMA used for preparing PMMA-stars and macromonomers

To the living solution of silyl-protected hydroxy-PMMA, freshly distilled EGDMA diluted with THF (1:3 volume ratio of EGDMA to THF) was added dropwise, under constant stirring of the solution. The molar concentration of EGDMA was maintained at 3:1 or 6:1 ratio with respect to the initiator. For a typical polymerization, 3.5 g of MMA (0.33 mol/L), 3 mL of 0.1[M] functional initiator ($3x10^{-3}$ mol/L) were taken in 100 mL THF. This was followed by addition of 0.16 mL of EGDMA ($9x10^{-3}$ mol/L) dissolved in 0.5 mL THF to the living solution (when a 3:1 ratio over the initiator was maintained). After addition of EGDMA, the reaction was continued at -78 °C for another 30 mins. and then quenched by methanol. The resulting silyl-protected hydroxy-functional star-branched PMMAs were precipitated in *n*-hexane. Scheme 6.2 illustrates the steps in preparing the star polymers. The polymers were desilylated using TBAF (1[M] solution in THF) in dry THF to liberate the free hydroxy group. TBAF was added in 4-5 moles excess over the polymer to ensure complete desilylation.

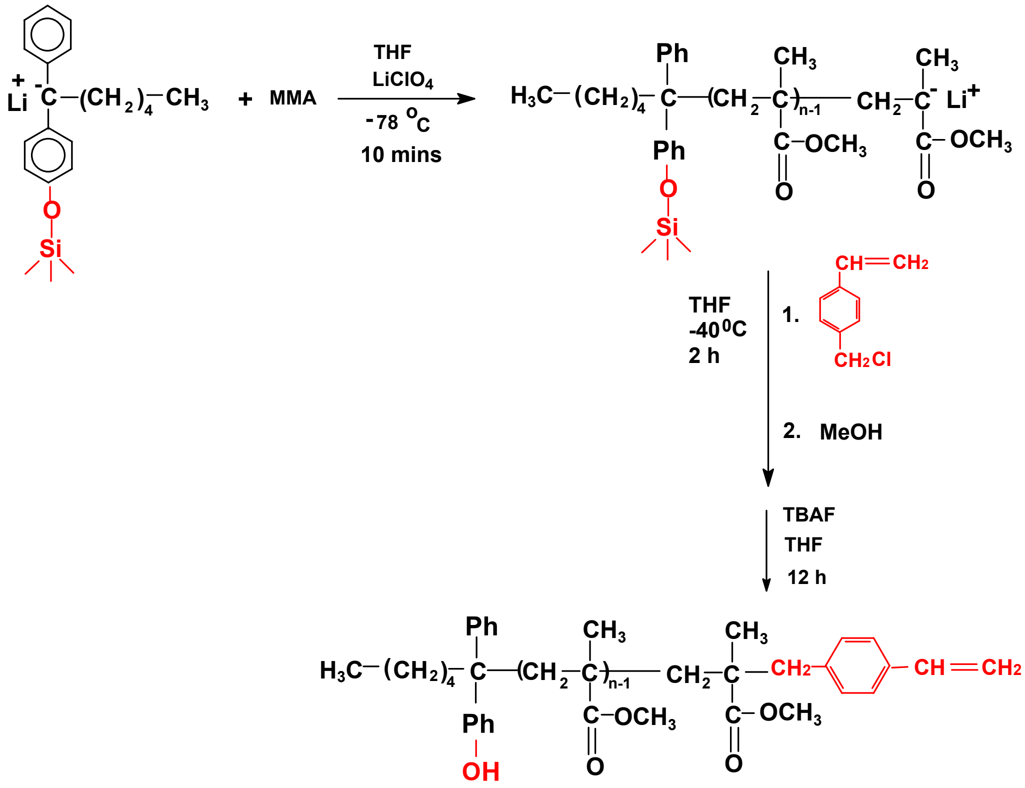


Scheme 6.2: Preparation of hydroxy-PMMA and the corresponding star-branched polymer

Fractionation of the star polymers was necessary to remove contamination by a small amount of linear polymer corresponding to the arms, in order to give pure star-branched PMMA. To a 1.0 % (by weight) solution of the star in toluene was added methanol dropwise till turbidity appeared. The solution was warmed to dissolve the precipitate. Methanol was further added methanol till turbidity appeared again. The process was repeated 3-4 times. Finally the solution was poured in a separating flask and allowed to stand for ~24 h, so that the pure star-polymer settled down. This purified polymer was dissolved in THF and reprecipitated in hexane, and dried in air.

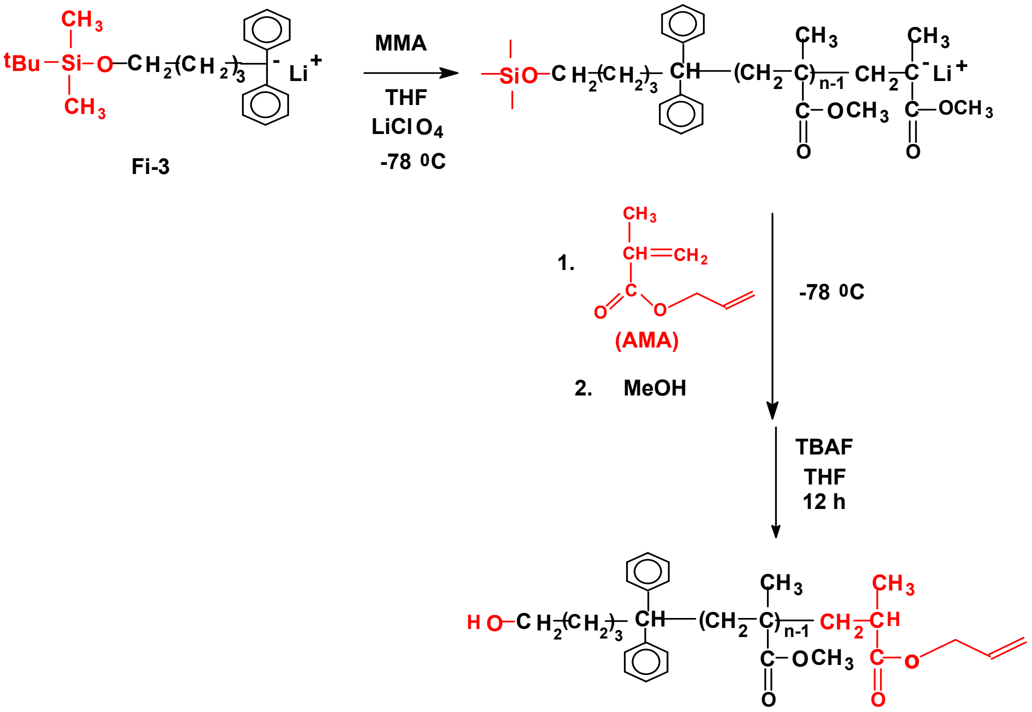
6.2.2.2. Preparation of hydroxy-functional PMMA macromonomer:

The preparation of the silyl-protected hydroxy-functional PMMA macromonomers is shown in scheme 6.3 and scheme 6.4. The functional initiators **F1** and **F3** were used to initiate MMA polymerization in THF at -78 °C in presence of $LiClO_4$ ($10x[I]_0$).



Scheme 6.3: Synthesis of αhydroxy-ω-styryl PMMA macromonomer using functional initiation and eletrophilic termination using F1

The polymerizations were done in bench-top glass reactors, under inert atmosphere, as described for a batch polymerization of MMA in chapter 2. Syringes and cannulas were used for transferring all reagents under N_2 pressure. For a typical polymerization, 3 mL of MMA was polymerized using 9 mL of 0.1 [N] functional initiator in 75 mL THF, and the reaction continued for 10 min. Then to the living solution of silyl-protected hydroxy-PMMA was added freshly distilled 4-VBC (~0.16 mL diluted with 1 mL THF) or AMA (0.12 mL diluted with 1 mL THF). The synthetic schemes are shown in scheme 6.3 and 6.4. The THF used for dilution of 4-VBC and AMA was previously titrated with the initiator for quenching all the protic impurities. Solutions of 4-VBC and AMA in THF were added dropwise to the living PMMA solution which was being stirred continuously and maintained at -78 °C. The concentration of 4-VBC was maintained in slightly excess over the initiator concentration. In case of termination by AMA, the concentration was maintained exactly equimolar with respect to the initial initiator concentration. Reactions were continued for additional 2 h in case of 4-VBC and 30 mins. in case of AMA. The product was quenched with methanol. The polymers were precipitated in *n*-hexane and then dried in air.



Scheme 6.4: Synthesis of α-hydroxy-ω-allyl PMMA macromonomer using functional initiation by F3 followed by eletrophilic termination

6.2.3. Analysis:

All polymers were characterized by Gel Permeation Chromatography (Thermoseparation Products), equipped with two detectors, UV and RI, and two 60 cm PSS SDV-gel columns: 1 × 100Å and 1 × linear ($10^2 - 10^5$ Å) at room temperature. THF was used as eluent at a flow rate of 1mL/min.

The functionality of the linear protected-hydroxy PMMA was determined by ^{1}H NMR (Bruker, 500 MHz). The presence of styryl and allyl end-functions of the hydroxy-functionalized PMMA macromonomers was determined by ^{1}H NMR (Bruker, 500 MHz). The star-branched PMMA were characterized by light scattering using Malvern Photon Correlation Spectrophotometer, Model 4700, at a wavelength of 488 nm using THF as solvent. The weight average molecular weights were obtained using a Debye plot (Fig. 6.1). The dn/dc value of PMMA in THF was 0.088 as obtained from literature. Titration of the hydroxy group (ASTM Standard E222-73, 1979) was done to determine the average number of arms of the star. A known amount (say 1.0 gm) of thoroughly dried PMMA star polymer was taken in 250 mL r.b. flask and 10 mL of pyridine/acetic anhydride (10:1 v/v) mixture was added. The contents were refluxed for about 6 h and cooled. 10 mL of distilled water was then added and again refluxed for about 30 minutes. The flask was then cooled using ice water mixture and titrated against 0.5 N NaOH solution (alcoholic). Similarly a blank run was carried out without sample. From the difference in the two readings, the number of moles of hydroxy group present per mole of the star polymer was calculated.

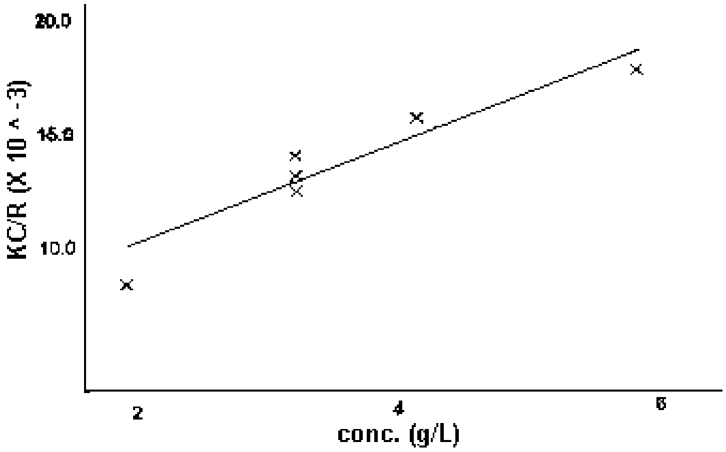


Fig. 6.1: Typical Debye-plot for PMMA in THF (sample F3-S1, Table 6.1)

6.3. Results and discussion

6.3.1. Synthesis of star-branched hydroxy-PMMA

The living chains of silyl-protected hydroxy-PMMA chains were cross-linked with the bis-unsaturated monomer, EGDMA, to give PMMA star polymers with hydroxy group at the end of each arm of the star. The presence of a protected hydroxy-function at the precursor PMMA chain-end was determined by ^{1}H NMR (Bruker, 200 MHz) spectroscopy of an aliquot taken before adding the EGDMA solution. For example, Fig 6.2 shows the spectra for the linear hydroxy-PMMA ($M_{w,sec}$=11700) corresponding to PMMA star sample, F3-S3 (Table 6.1) prepared using initiator **F3**.

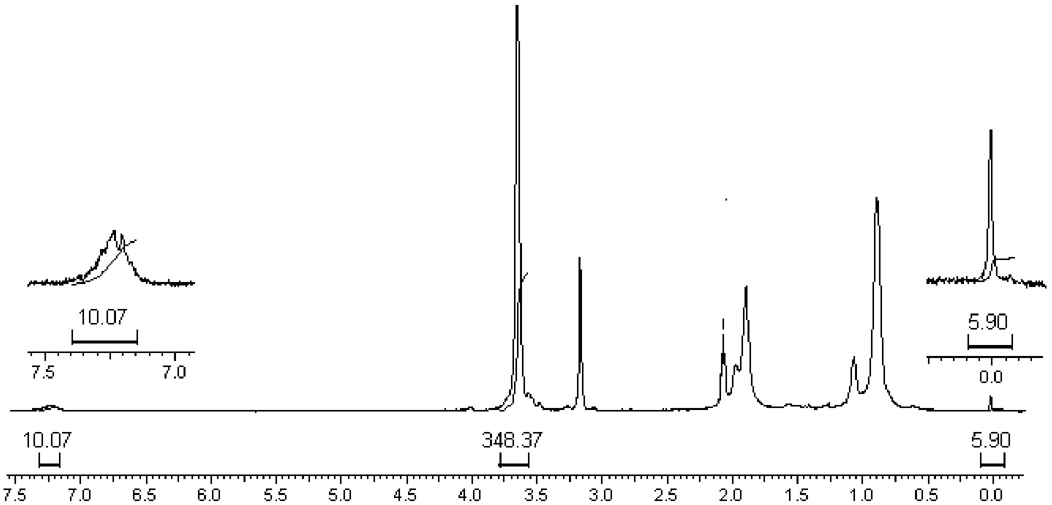
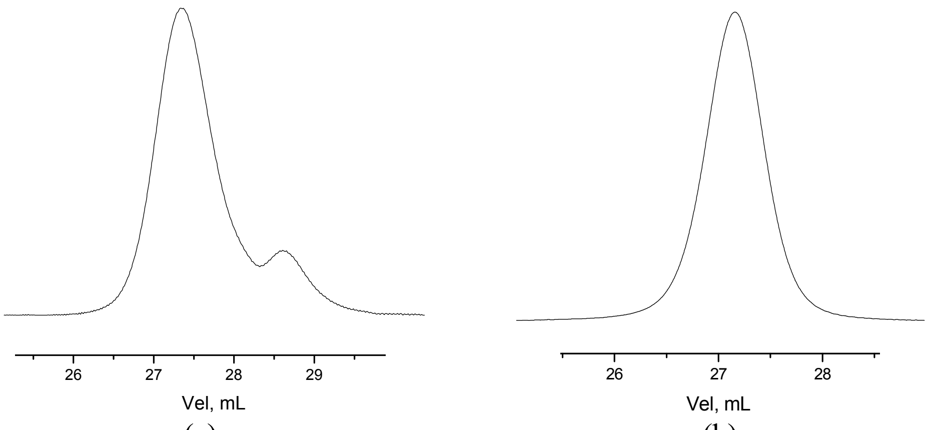


Fig. 6.2: ^{1}H NMR spectra (200 MHz, acetone-d_6) for linear silyl-protected hydroxy-PMMA prepared using F3. Subsequent linking by EGDMA produces hydroxy-functionalized star-PMMA (sample F3-S3, Table 6.1)

The resonance absorption at δ 7.1-7.4 corresponds to 10 phenyl protons from the initiator moiety, and that at δ 0.0 is due to the 6 protons of two Si-Me a group of the hydroxy-protecting group. The absorption at δ 3.58 is due to the -OMe protons of the methacrylate chain. Thus the spectra is consistent with quantitatively functionalized hydroxy-PMMA.

Functional initiator **F3** was used for the first five samples in Table 6.1 and the arm molecular weights were varied from 7000 to 20000. The molar ratio of EGDMA to the initiator was usually maintained at 3:1, though one reaction was performed using 6:1 ratio also (sample F3-S5, Table 6.1). Initiator **F1** was used to prepare the precursor hydroxy-PMMA for the star polymers F1-S1 and F1-S3 (Table 6.1), using 3:1 and 6:1 molar ratio of EGDMA to initiator respectively. The GPC analysis of the all the unfractionated stars showed contamination by small amount of residual arm material, as seen in the elugrams in Fig. 6.3 (a), 6.4 (a) and 6.5 (a) for the star-PMMA samples F3-S2, F3-S3 and F3-S4.

The presence of such unreacted linear PMMA along with the corresponding star-branched polymer was reported during synthesis of PMMA star-branched polymers using EGDMA as cross-linking agent.[7] The authors attributed this phenomenon to steric effect rather than chain-deactivation due to introduction of impurities during or before addition of cross-linker. In fact, with increase in the number of arms, the central cross-linked core becomes sterically more congested and resists further incorporation of arms.

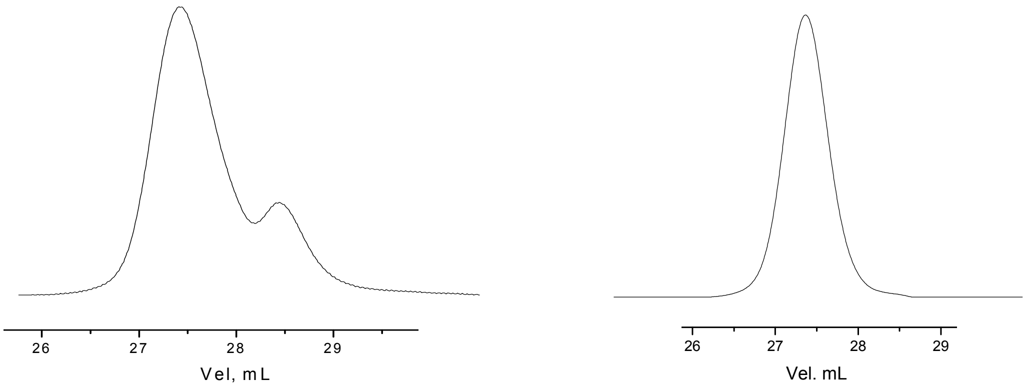


(a) (b)

Fig 6.3 : GPC elugrams of PMMA star (sample F3-S2, Table 6.1); (a) unfractionated PMMA star with residual arm material where $M_{w,sec}$ (arm) = 9100; (b) pure star after fractionation

Hence, some unreacted chains are always left behind along with the required star-branched polymer. In view of the break-seal technique that was applied by the authors, reason for the presence of residual unreacted arm could have been steric hindrance only. However, in our case, where all manipulations were done under nitrogen atmosphere, factors other than steric may be responsible for linear PMMA contamination.

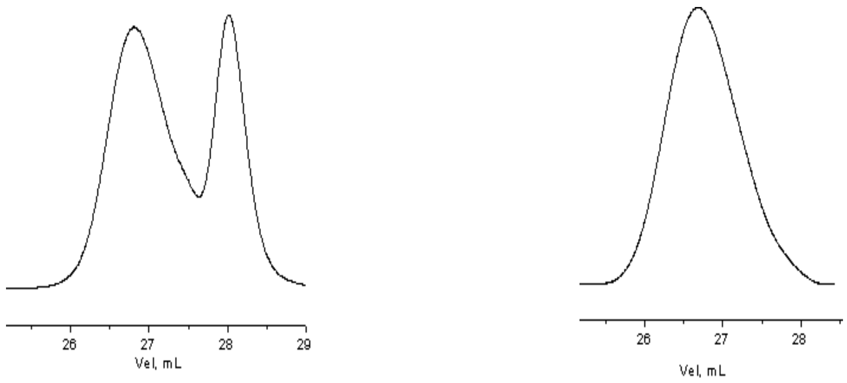
The protected hydroxy end-functions were deprotected by TBAF treatment in order to form the stars with free hydroxy groups at the periphery. This was then followed by fractionation of the star polymers to separate the pure star from the residual arms. The GPC elugram of the pure hydroxy-PMMA star polymers F3-S2, F3-S3 and F3-S4 are shown in Fig. 6.3 (b), 6.4 (b) and 6.5 (b) respectively.



(a) (b)

Fig 6.4 : GPC elugrams of PMMA star (sample F3-S3, Table 6.1); (a) unfractionated PMMA star with residual arm material where $M_{w,sec}$ (arm) = 11700; (b) pure star after fractionation

The elugrams show that the purification of the stars polymers by removal of the arm contamination using solvent/non-solvent fractionation was successful, since no peak corresponding to the linear PMMA was observed in the elugrams of the fractionated stars. In fact, the presence of hydroxy end-groups obtained after desilylation greatly aids in the separation of the star from the linear polymer. Fractionation of the protected hydroxy functional star PMMA was not found to be much effective in completely separating the stars from the residual arms. The solubility of the hydroxy-PMMA stars in the mixed solvent of methanol and toluene is a function of molecular weight. The linear hydroxy-PMMA is sufficiently soluble in the predominantly alcoholic medium, but the star polymer surrounded by hydroxy groups at the periphery is insoluble. Hence the separation becomes convenient.



(a) (b)

Fig 6.5 : GPC elugrams of PMMA star (sample F3-S4, Table 6.1); (a) unfractionated PMMA star with residual arm material where $M_{w,sec}$ (arm) = 21000; (b) pure star after fractionation

Table 6.1 shows the molecular weights, polydispersities and degree of branching of the pure hydroxy-PMMA star-branched polymers as analyzed by GPC, light scattering and end-group titration methods. The molecular weight and MWD of the arms of each star-branched PMMA sample were determined by GPC analysis of the fraction remaining after separating the pure star polymer, or by analyzing the pick-out taken from the PMMA living solution prior to EGDMA addition (samples F3-S2 and F3-S5). Syringing out of aliquots prior to EGDMA addition were usually avoided in order to prevent quenching of the active centers due to additional manipulation.

Table 6.1: Molecular weights, polydispersities and degree of branching of hydroxy-PMMA stars and arm precursors

Sample	EGDMA / initiator	Arm results			Star results				No. of arms
		$\bar{M}_n$ (SEC)	$\bar{M}_w$ (SEC)	$\bar{M}_w/\bar{M}_n$	$\bar{M}_w$ (SEC) x 10^{-3}	$\bar{M}_w/\bar{M}_n$ (SEC)	$\bar{M}_w$ (LS) x10^{-3}	$\bar{f}_w$ [a)]	(by -OH titrn.)
F3-S1	3:1	7000	7600	1.09	55.0	1.11	74.6	9.8	9.3
F3-S2	3:1	8500	9100	1.07	54.5	1.12	70.0	7.7	7.4
F3-S3	3:1	11000	11700	1.07	60.0	1.09	75.4	6.4	6.0
F3-S4	3:1	19700	21000	1.07	97.8	1.15	120.0	5.7	-
F3-S5	6:1	8600	9400	1.08	75.0	1.10	90.0	9.5	9.0
F1-S1	3:1	5100	5500	1.08	35.0	1.10	39.0	7.1	-
F1-S2	6:1	5000	5500	1.09	48.0	1.12	-	-	9.4

a) $f_w = \bar{M}_{w,LS}$ (star) / $\bar{M}_{w,sec}$ (arm)

The molecular weight distribution of the arms is seen to be quite narrow, usually 1.09 ≤ M_w/ M_n ≤1.07. The $\bar{M}_w$ of the stars that were determined from light scattering measurements are higher than the ones obtained from GPC analysis. This is expected since in GPC the separation of polymers occurs on the basis of hydrodynamic volume, which is less for a star polymer than a linear polymer of same molecular weight. The MWD of the star polymers are quite narrow ($\bar{M}_w/ \bar{M}_n$ ~1.1-1.2). This is in contrast to a polydispersity greater than 2.0 of PMMA stars reported earlier.[7] The weight average number of arms, f_w is calculated by dividing the $\bar{M}_w$ of the star as measured by light scattering, with that of the $\bar{M}_{w,\ sec}$ of the respective arm. Titration of the -OH groups present at the terminus of each arm of the fractionated hydroxy-PMMA star was done, and the degree of branching calculated therefrom is found to be close to those calculated on the basis of light scattering data.

6.3.1.1. Effect of am length:

The results of the first four runs in Table 6.1 show that, for a given ratio of EGDMA to initiator, the number of arms increases with decrease in the arm molecular weight. Compared to smaller arms, the larger arms shield the core to a greater extent, i.e. they exert greater steric hindrance to incoming chains and thereby allow lesser number of arms to get linked to the core. Due to the same reason, a greater amount of the residual or unreacted arms in the star polymer are seen in case of higher arm length [Fig. 6.5 (b)]. This effect of arm molecular weight on the degree of branching was observed by Mays et al while synthesizing PMMA stars.[7] They observed an increase in the number of arms from 18.7 to 6.7 for a decrease in arm molecular weight from 10,000 to 40,000. However, the number of arms of the PMMA stars observed by them is significantly greater than those observed by us for hydroxy-PMMA stars, for a similar arm length and ratio of EGDMA to initiator. In fact, our results agree well with those of Quirk et al[8] who have reported results of only one polymerization using hydroxy-PMMA of $M_{n,sec}$= 8000 and obtained almost 10.7 arms for the corresponding star using EGDMA as cross-linker. Possibly the bulky protected-hydroxy functionality in the present case plays a role in resisting arm incorporation to the core, unlike the case where unfunctionalized PMMA chains are linked.

6.3.1.2. Effect of EGDMA to initiator ratio:

The molar ratio of EGDMA to the initiator at a given arm length is also seen to have some effect on the degree of branching. As evident from Table 6.1, an increase in this ratio for a given arm molecular weight leads to a small but finite increase in the number of arms of the hydroxy PMMA-star polymer. For example, for star samples F3-S2 and F3-S5, the number of arms increases from 7 to 9 on increasing the ratio from 3:1 to 6:1, for an arm molecular weight of about 9000-9500. A similar observation is made with the samples F1-S1 and F1-S2 prepared using initiator **F1** and adding EGDMA at 3:1 and 6:1 mole ratio respectively with respect to the initiator. This is due to the fact that increase in the amount of the bis-unsaturated monomer with respect to the chain-end concentration leads to greater size of the core and, hence, provides more space for accommodating a greater number of arms.

6.3.2. Synthesis of hydroxy-PMMA macromonomers:

The hydroxy-functional PMMA macromonomers were prepared by anionic polymerization of MMA using protected hydroxy-functional initiators **F1** and **F3** in THF at -40 °C or -78 °C in presence of $LiClO_4$ (added in 10:1 molar ratio with respect to the initiator). Initiation by hydroxy-functional initiator **F1** followed by termination of the living chains by 4-VBC leads to formation of α-hydroxy-ω-styryl PMMA (sample F1-

PMVB-1 in Table 6.2). Using **F3** as initiator and subsequent termination of living chains by AMA gives α-hydroxy-ω-allyl PMMA (F3-PMAM-1 in Table 6.2). The results of GPC analysis are shown in Table 6.2. The polymerizations are seen to be sufficiently well-controlled as the resulting polymers show quite narrow molecular weight distribution and a good agreement between observed and targetted molecular weight, i.e. the initiator efficiency is close to 1.0.

Table 6.2: Characterization of α-hydroxy-ω-allyl and α-hydroxy-ω- styryl PMMA macromonomers

Sample	$[I]_0$ x10^{-3} m/L	$[M]_0$ x10 m/L	Temp. °C	Time of rxn. (mins)	Yield %	$M_{n,theo}$	$M_{n,sec}$	MWD	polymerizable functionality %
F3-PMAM-1	3.0	1.75	-78 °C	30	100	5800	6000	1.09	~100
F1-PMVB-1	6.8	2.54	-40 °C	120	"	3730	4100	1.07	50

6.3.2.1. Termination with 4-vinylbenzyl chloride:

Termination of PMMA living chains by 4-vinylbenzyl chloride was done at -40 °C and the reaction was continued for almost 2 h. However, only 50 % of the chains were coupled as evident from ^{1}H NMR (500 MHz, Bruker) of the sample F1-PMVB-1 before deprotection of the hydroxy-function, shown in Fig. 6.6. The characteristic absorption at δ 5.1-5.8 (two doublets) correspond to the two terminal vinyl protons [marked (a) in Fig 6.6] of the styryl end-function. The peak at δ 0.0 correspond to the 6 protons [marked (d) in Fig. 6.6) of the $Si(Me)_2$ group attached to the initiator-end of PMMA chain. The peak intensity per proton of the vinyl group is exactly half of that of the $Si\text{-}(Me)_2$ group, which makes it clear that only half of the hydroxy-PMMA chains have reacted with 4-vinylbenzylchloride. This explains the intensity of ~2.5 at δ 6.8 that corresponds to one proton of the -CH= group (marked b) and the two phenyl protons ortho to the -OSi group (marked c) in Fig. 6.6. The remaining 7 phenyl protons of the initiator moiety and the 4 phenyl protons of the styryl end-function appears together near δ 7.0-7.4.

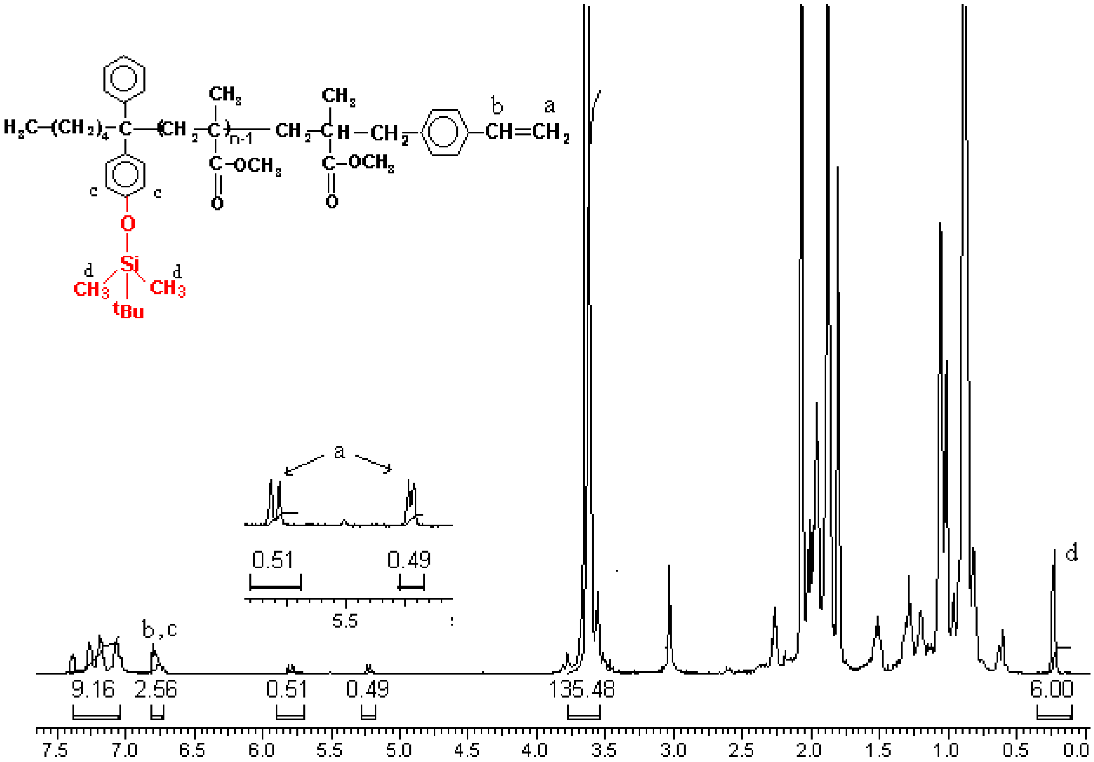


Fig. 6.6: ^{1}**H NMR (500 MHz, acetone-d**$_6$**) of silyl-protected hydroxy-PMMA macromonomer with styryl end-function (sample F1-PMVB-1, Table 6.2)**

The most probable reason for such partial functionalization is a slow reaction between the enolate ion-pair with 4-VBC at a temperature of -40 °C. Earlier, Andrews et al[10] had reported that living PMMA chains did not react with 4-vinylbenzyl chloride. However, reaction with the corresponding bromide or iodide gave >90% yield of the macromonomer. Later, Ishizu et al had prepared PMMA macromonomers from $Ph_3C^-Li^+$ initiated polymerization of MMA at -78 °C after termination with 4-VBC, and obtained almost 92% functionalization.[14] However, they observed a relatively broad MWD, i.e. $\overline{M}_w/\ \overline{M}_n$ ~ 1.1. They explained the failure of this reaction by the previous group as due to insufficient purification of 4-VBC. However, unlike the polymerization reported by these authors, our polymerization was conducted in presence of $LiClO_4$ as additive added in 10 mole excess of the initiator. This enabled us to prepare polymers with narrow molecular weight distribution (MWD ~ 1.07). $LiClO_4$ being a strong Lewis acid complexes effectively with the enolate ion-pairs and establishes a relatively faster equilibrium between the different mixed complexes in solution, thus narrowing down the MWD. Also, it is probable that the complexation of $LiClO_4$ with the ion-pairs creates a sterically hindered atmosphere around the propagating anionic center. This may effectively reduce the reactivity of the anion with the added 4-VBC. This could lead to a retardation of the reaction resulting in functionalization of only 50 % after 2 h. A longer reaction time may be necessary for greater yield of the macromonomer. Deprotection of the hydroxy group by TBAF in THF gives PMMA with a phenolic hydroxy group at one end and a polymerizable styrene function at the other end.

6.3.2.2. Termination with allyl methacrylate:

Anionic polymerization of MMA in THF at -78 °C using functional initiator **F3** was followed by termination of the living chains with allyl methacrylate to yield allyl terminated hydroxy-PMMA. The reaction led to almost 100 % functionalization with the allyl group remaining intact, as evident from the ^{1}H NMR spectra (Fig. 6.7) of sample F3-PMAM-1 (Table 6.2) prepared using **F3** as functional initiator.

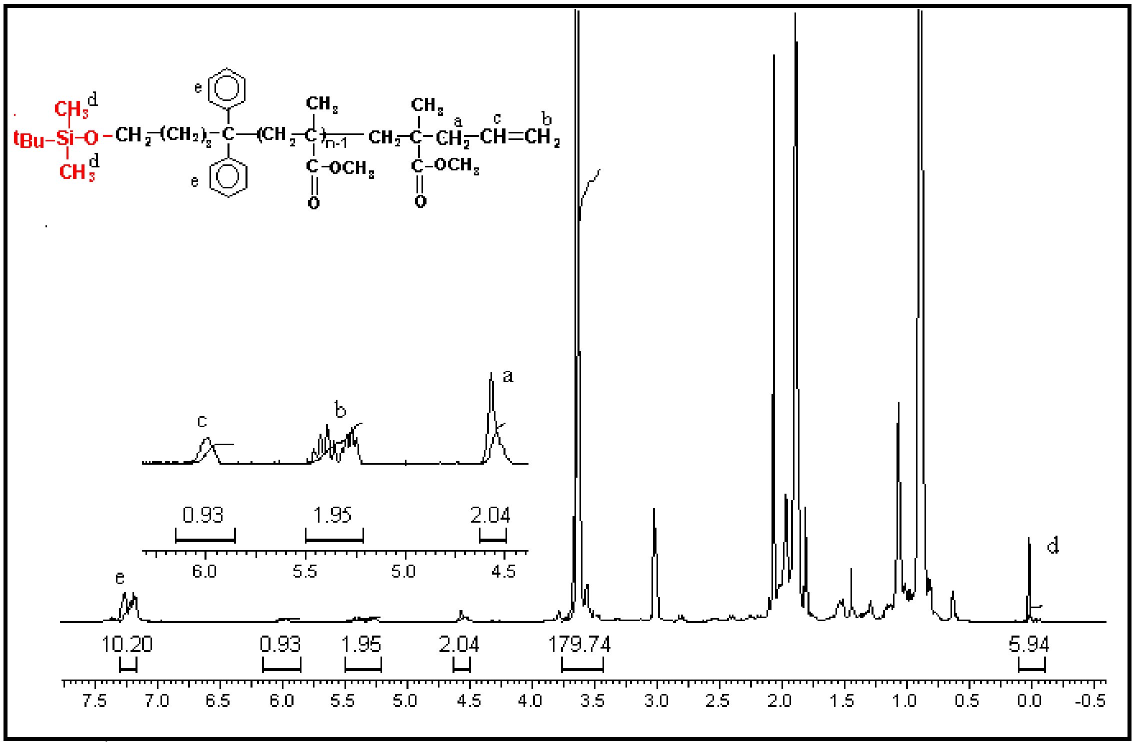


Fig. 6.7: ^{1}H NMR (500 MHz, acetone-d_6) of silyl-protected hydroxy-PMMA macromonomer with allyl end-function using functional initiation by F3 followed by electrophilic termination by AMA (sample F3-PMAM-1, Table 6.2)

The characteristic absorption at δ 4.55, δ 5.2-5.5 (two doublets) and δ 6.0 correspond to the allylic protons marked (a), (b), and (c) respectively in structure shown Fig. 6.7. The absorption at δ 0.0 correspond to the 6 protons of -Si(Me)$_2$ groups and at δ 7.1-7.4 is due to the 10 phenyl protons of the initiator moiety attached to the other end of the PMMA chain. The intensity per proton of the phenyl and Si-Me group is almost equal to the peak intensity per proton of the allylic group. This proves the presence of one allyl group per chain of hydroxy-PMMA, i.e. a quantitative functionalization. Desilylation by TBAF in THF leads to liberation of the free hydroxy group yielding α-hydroxy-ω-allyl PMMA macromonomer.

6.4. Conclusion

We have been successfully prepared well-defined PMMA star-branched polymer with hydroxy groups at the outer end of each arm using protected hydroxy-functional initiators for anionic polymerization of MMA followed by cross-linking of the living PMMA anions by bis-unsaturated monomer, EGDMA. The number of arms could be varied by changing either the arm molecular weight or the molar ratio of EGDM to initiator. Smaller arms exert less steric hindrance to incoming arms, thus leading to an increase in the number of arms per core, leaving a relatively smaller amount of unreacted linear chains. Again an increase in the cross-linker concentration with respect to the active centers, leads to a larger core size and hence provides space for accommodating higher number of arms. However, due to inherent drawbacks of our system where reactions are performed under nitrogen atmosphere and all additions done with the help of syringes and cannulas, it is difficult to maintain the livingness of the system during and after addition of the cross-linker. Thus the number of arms obtained are restricted and do not show any significant increase on increasing the concentration of the cross-linking agent even to twice the original amount. It has been shown in the previous chapter that hydroxy-PMMA can be utilized as macroinitiator for ethylene-oxide polymerization yielding well-defined PMMA-PEO block copolymers. The same concept can be used to prepare PMMA-PEO star-block copolymers by initiating ring opening polymerization of EO using the hydroxy groups at the star-periphery.

Controlled anionic polymerization of MMA with hydroxy-functional initiator followed by termination of living chains by 4-vinylbenzyl chloride and allyl methacrylate yielded hydroxy-PMMA macromonomers with styryl and allyl end-functions. The enolate ion-pairs react with 4-VBC, but the functionalization seems to be slow as only 50 % of the chains were functionalized after 2 h. In contrast, the end-functionalization with allyl methacrylate seems to occur smoothly within a short time leading to quantitative functionalization.

6.5. References

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Chapter 7: Summary and Conclusions

7.1. Summary and conclusions

Anionic polymerization of methylmethacrylate in low polarity medium is complicated due to ion-pair aggregation phenomenon and the consequent presence of multiple active species. Moreover, polymerization at higher temperatures is still more difficult to control since a number of secondary reactions involving the ester group become significant resulting in incomplete monomer conversion, and a poor correlation between observed and targeted molecular weight. So anionic polymerization of MMA in less polar medium at higher temperatures continues to be a challenge to polymer chemists. Complexation of living chains of poly(alkylmethacrylate) with LiCl has been a well-known strategy for perturbing the ion-pair aggregation equilibrium leading to perfectly controlled polymerization in THF at lower temperatures. Following a similar strategy, we have studied the effect of Li-salts that are Lewis acids on the association of ion-pairs. We were able to achieve a controlled polymerization even in less polar medium of toluene-THF (9:1 v/v) at -78 °C using $LiClO_4$, $LiBF_4$ and Li-trifluoromethane sulfonate as salt-additives. Coordinative interaction of these salts with the ion-pairs perturb the ion-pair association equilibrium such that the newly formed salt-complexed "mixed aggregates" are at a faster equilibrium with the unassociated ion-pairs in contrast to the slow classical ion-pair equilibrium in the absence of any salt. Thus, monomer addition to an effectively single active species leads to a narrow molecular weight distribution. The salts coordinate with the ion-pairs with different efficiencies depending upon their Lewis acidity and thus influence the mechanism of monomer insertion mechanism in different ways which is reflected in the microstructures of the resulting PMMA.

The presence of $LiClO_4$ and LiCl in 10:1 and 5:1 ratio with respect to the initiator concentration had a significant effect on the kinetics of the polymerization in the less polar mixed solvent medium. Unlike polymerization in the absence of any salt-additive, MMA polymerization in the presence of $LiClO_4$ or LiCl proceeded without termination and transfer at all active center concentrations producing polymers with narrow and unimodal MWD at all conversions. A reaction-order of unity with respect to the active centers was observed in presence of both the salts. This suggests the formation of a single salt-complexed active species in these systems. Possibly, the complexation of the salts with the ion-pairs was more effective in the absence of significant competition by THF molecules to solvate the ion-pairs in a predominantly non-polar medium (9:1v/v of toluene-THF).

Synthesis of well-defined hydroxy-functional PMMA using functional anionic initiators have not been reported till date. This could be due to inherent problems associated with methacrylate polymerization. In contrast, well-defined hydroxyl-terminated vinyl and diene polymers have been prepared using functional anionic initiators. We have been successful in synthesizing well-defined hydroxy-functional anionic initiators and using them for the preparation of hydroxy-PMMA in a controlled fashion. In contrast to functionalization through electrophilic termination, such functional initiation procedures are much simpler and yield almost quantitatively functionalized PMMA. These hydroxy-PMMA were further used as macroinitiators to initiate ring opening polymerization of ethylene oxide (EO) at 27 °C to yield well-defined PMMA-*block*-PEO with low polydispersity. Synthesis of PMMA-*b*-PEO have hitherto been reported to be complicated by side-reactions involving the ester group of the PMMA backbone, leading to the formation of grafted diblock with broad and multimodal MWD. However, the diblocks prepared using the present procedure were purer and exhibited relatively narrow and unimodal distribution. A very small amount (3-4 % by weight) of homo-PEO contamination in the block copolymer was observed, suggesting some reactions of the living chain-ends with the ester group of the PMMA backbone generating methoxy anion which presumably initiated EO homopolymerization. However the extent of such side-reactions appears to be very small and could not be detected by either GPC or ^{1}H NMR. The diblock copolymers could be purified easily by easy removal of the homopolymer of PEO.

The living arms of silyl-protected hydroxy-PMMA were linked by using EGDMA as cross-linker in order to form PMMA-star polymers with protected-hydroxy groups at the periphery. In general, the number of arms of a star is found to be a function of arm length and ratio of EGDMA to initiator. Smaller arm length allows greater number of arms to be linked to the core, and greater mole ratios of EGDMA leads to larger size of the core and hence space for accommodating more number of arms. The increase in degree of branching with increase in EGDMA concentration is less than expected, probably due to the inherent drawbacks of the system where polymerization is performed under nitrogen atmosphere. Proper dilution of the cross-linker and the speed of agitation, influence significantly the degree of branching. However manipulation under nitrogen pressure introduces impurities into the system and lead to quenching of the active chains. Thus, neither dilution of EGDMA, nor increased rate of agitation actually helped in increasing the number of arms of the star to any reasonable extent.

The termination of hydroxy-PMMA living chains by 4-vinylbenzyl chloride (4-VBC) and allyl methacrylate (AMA) led to formation of hydroxy-functional PMMA macromonomers bearing styryl and allyl end-functions with narrow molecular weight distribution and high initiator efficiency. The end-functionalization using AMA was quantitative. However, with 4-VBC the reaction appears to be quite slow and led to only 50 % styryl end-functionalized chains. In contrast to quantitative functionalization of trityl-Li initiated PMMA living chains reported earlier, our observation of partial functionalization may be due to lower reactivity of the protected hydroxy-PMMA chains, complexed by $LiClO_4$.

7.2. Future prospects of research

The present research on controlled anionic polymerization of methylmethacrylate has opened up many new prospects of research with methacrylates. The following section deals with the future scope for further study.

- A kinetic study of anionic polymerization of MMA in toluene-THF (9:1 v/v) mixture solvent in presence of $LiClO_4$ and LiCl may be conducted at higher temperatures, i. e. at -40 °C, and the reaction order with respect to the active centers may be determined. This study will give a better insight into the role of the salts on ion-pair aggregation phenomenon in low polarity medium.
- Living chains of hydroxy-end functional PMMA can be coupled with suitable difunctional linking agent, in order to form α, ω-dihydroxy PMMA. Initiation of ethylene oxide polymerization by both the end-hydroxy groups can lead to the formation of well-defined PEO-PMMA-PEO triblock copolymers.
- The terminal hydroxy groups of α, α'-dihydroxy PMMA can be used to initiate ring-opening polymerization of EO to form AB_2 type of tri-arm star polymer.
- The hydroxy-groups at the each chain terminus of a hydroxy-PMMA star-branched polymer can also be exploited to initiate EO polymerization resulting in formation of

star-block copolymers, i.e. star polymer with each arm being a PMMA-PEO block copolymer.

- The hydroxy-functional PMMA macromonomers with styryl end-function can be copolymerized with styrene by free radical polymerization, in order to form graft copolymers with styrenic back-bone and hydroxy-PMMA branches.