Controlled Synthesis of End-Functionalized Polymers and Block Copolymers

THESIS SUBMITTED TO THE
UNIVERSITY OF PUNE
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN
CHEMISTRY

By

DNYANESHWAR V. PALASKAR

RESEARCH GUIDE
DR. PRAKASH P. WADGAONKAR

POLYMER SCIENCE AND ENGINEERING DIVISION
NATIONAL CHEMICAL LABORATORY
PUNE-411 008, INDIA

(MARCH 2008)

To

My Son : Aditya and My Wife : Vaijyanti

for their patience and encouragement

Acknowledgements

My sincere appreciation goes to my advisor, Dr. Prakash P. Wadgaonkar for everything he has done for me. He is one of the most enthusiastic scientist I know and I cannot imagine I could have had a better teacher. I am very thankful to him for the help, numerous discussions and for keeping his doors always open for me. He was always ready to give me advice, support and was patient when I was slow and somewhat disorganized. I consider it a great honor to be part of his research group. I would also like to thank him for his diversified support, scientific guidance, and creative ideas during these years.

Dr. C. Bhaskar and Dr. P. G. Shukla are gratefully acknowledged for their help, guidance and scientific discussions during my work.

I thank Dr. C V. Avadhani, Dr. A.S. Jadhav, Dr. D. Baskaran, Mr. S. K. Menon, Mrs. D. A. Dhoble, Dr. S. D. Patil, Dr. N. N. Chavan, Dr. T. P. Mohandas, Dr. R. S. Khisti, Dr. R. A. Kulkarni, Dr. M. V. Badiger, Dr. R. P. Singh, Mr. A. S. Patil, Mr. K. G. Raut, Dr. B. B. Idage, Dr. B. D. Sarwade, Dr. (Mrs.) A. N. Bote and Dr. (Mrs.) S. B. Idage for their help on many occasions.

I am thankful to all my colleagues Ramanathan, Ganni, Mallikarjun, Neeta, Anjali, Mahesh, Ravi, Smitha, Bhoje, Malli, PK, Raghu, Govind, Kamendra, Rajkiran, Kedar, Sachin, Mukesh and Subramaniam for their cooperation during my stay at NCL.

Many of the former and current PPW group members Anjana, Sneha (Bapu), Sony, Arun, Vijay, Pandurang, Nilakshi, Arvind, Prakash, Mahadev, Anil, Vidya, Nagendra, Sandeep and Shivkumar made my life in the lab easier and more enjoyable. You guys are really fantastic. Thank you all !!!!

My friends during school days to college and to NCL namely Sanjay, Shailesh, Vikas, Sada, Kiran, Sharad, Nilesh, Dinesh, Gajanan, Abhimanyu, Shivdas, Rahul, Yogesh, Vijay, Santosh, Sandhya, Sudhir, Sidhendra, Abhimanyu and Sanjio are acknowledged for being a good friend and for sharing their knowledge of useful chemistry.

I am also thankful to my numerous Teachers during school and college studies for giving me a solid basis in science.

The rest of the PhD students at the department are acknowledged for creating an atmosphere that makes this department a good place to work.

my better half, my wife, Vaijyanti. I can't begin to thank her for being so understanding when I was stuck in the lab late or had to go in early morning. She allowed me to leave for my thesis work immediately after my marriage day without any hesitation. Her constant love and support without any complaint enabled me to complete my Ph.D. work successfully. I hope I can someday reciprocate that patience and perseverance to her. My son, "Aditya" gave me the happiest moments during the important days of tenure of Ph. D. His smile gave me a lot of energy and encouragement.

I would like to thank my family for their life-long invaluable love, support, faith and allowing me as I wanted. I especially owe to my parents and brothers for their support and bringing me to this stage, their consistent encouragement, and making me realize the value of hard work.

I must thank my in-laws, Mrs. and Mr. Vilasrao Shinde, Mrs. and Mr. Bachate (Aunty) for their help and support. Many thanks go to Mrs. and Mr. Chavan family, Panjab, Atish, Anup for their help during our stay in Pune. I am also thankful to Wagh family for the help and support during my stay in Pune.

I thank the members of central NMR facility, microanalysis, CMC, SMIS, glass blowing, stores and workshop for their help.

The administrative staff of PSE division and, stores and, purchase department are thanked for their help with paper work and everything else necessary for things to run smoothly.

Finally, I thank CSIR for the senior research fellowship and the Director, NCL for allowing me to carry out this work at this prestigious institute.

Dnyaneshwar

March, 2008

Certificate of the Guide

Certified that the work incorporated in the thesis entitled ñ**Controlled Synthesis of End-Functionalized Polymers and Block copolymers**ò submitted by Mr. Dnyaneshwar Vithoba Palaskar was carried out under my supervision. Such material as has been obtained from other sources has been duly acknowledged in this thesis.

March, 2008 **Prakash P. Wadgaonkar**

Pune **(Research Guide)**

Declaration by the Candidate

I declare that the thesis entitled ñ**Controlled Synthesis of End-Functionalized Polymers and Block Copolymers**ò is my own work conducted under the supervision of Dr. Prakash P. Wadgaonkar, at Polymer Science and Engineering Division, National Chemical Laboratory, Pune, India.

I further declare that to the best of my knowledge, this thesis does not contain any part of work, which has been submitted for the award of any degree either of this University or any other University without proper citation.

Prakash P. Wadgaonkar
(Research Guide)

Dnyaneshwar V. Palaskar
(Research Student)

CONTENTS

Chapter 3: Synthesis and Characterization of Functionalized Initiators for Atom Transfer Radical Polymerization

Chapter 4: Synthesis and Characterization of End-Functionalized Polymers by Atom Transfer Radical Polymerization

Chapter 7: Preparation of Polyurethane Microspheres Utilizing PEO-*b*-PLMA, PEO-*g*-PLMA, and Dihydroxyl-Terminated PLMA Macromonomers as Steric Stabilizers

Abstract

End-functionalized polymers and copolymers (block and graft) are of interest due to their potential applications in several areas. More specifically, end-functionalized polymers are useful as building blocks for synthesis of block, graft and star copolymers. These polymers also have potential applications in areas such as surface modification, coatings, adhesives, as well as compatibilization of polymer blends. Block and graft copolymers are promising materials because of their ambivalent properties and find many applications in areas such as thermoplastics, associative polymers containing hydrophilic and hydrophobic segments, etc. One of the most important applications of block copolymers at the industrial scale is their use as surfactants in pharmaceutical, oil, agriculture, paper and detergent industries.

For the synthesis of these polymers, living polymerization methods such as anionic, cationic, group transfer and controlled radical polymerization have been developed and demonstrated to provide a high degree of control. Amongst the controlled radical polymerization methods, Atom Transfer Radical Polymerization (ATRP) is a powerful technique to prepare polymers with predictable molecular weight and narrow molecular weight distribution. The increasing interest in ATRP technique is due to relatively mild reaction conditions compared to ionic polymerizations and a broad choice of monomers, initiators, catalysts, etc. Using ATRP technique, a variety of polymer architectures and compositions is accessible, e.g., block copolymers, graft copolymers, and hyperbranched polymers.[3-7] Functional groups can also be introduced easily at the chain ends either through functionalized ATRP initiators or halogen displacement through nucleophilic substituion.

The main objective of the present research was to synthesize atom transfer radical polymerization (ATRP) initiators containing functional groups and utilize them for the synthesis of end-functionalized polymers. Another objective of the work was to synthesize block and graft copolymers by ATRP and combination of ATRP and ring opening polymerization (ROP) of caprolactone.

Thus, efforts were made to design and synthesize ATRP initiators containing functional groups such as hydroxyl, carboxyl, lactone, carbonate and sulfonic acid and utilize

ow molecular weight end-functionalized polymers and macromonomers by polymerization of styrene, methyl methacrylate and lauryl methacrylate. ATRP initiators synthesized in the present work are listed below.

1 4-(Hydroxymethyl)benzyl-2-bromo-2-methylpropanoate **(HMBMP)**

2 4-(2-Bromo-2-methylpropanoyloxy) benzenesulfonic acid **(BMPBSA)**

3 4-[(4ô-Nitro) phenoxymethyl] benzyl bromide **(NPMBB)**

4 5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl-2-bromo-2-methylpropanoate) **(EDMBMP)**

5 2,2-Bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate **(BHMBMP)**

6 3,5-Bis(hydroxymethyl)phenyl-2-bromo-2-methylpropanoate **(BHMPBMP)**

7 5-(2-Bromo-2-methylpropanoyloxy)isophthalicacid **(BMPIPA)**

8 5-(2-Bromo-2-methylpropanamido)isophthalicacid **(BMPAIPA)**

9 4-[2-(7-Oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(OPCBMP)**

10 2-Oxo-1,3-dioxolan-4-yl-(methyl-2-bromo-2-methylpropanoate) **(ODMBMP)**

Of these, nine ATRP initiators have been synthesized for the first time. All the ATRP initiators and intermediates involved in the their synthesis were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Hydroxyl-terminated polystyrenes were synthesized by ATRP using 4 (hydroxymethyl)benzyl 2-bromo-2-methylpropanoate as initiator in the presence of CuBr/bipyridine as a catalyst. Hydroxyl-terminated polystyrenes were obtained with narrow MWD (M_w/M_n = 1.07 - 1.33) and initiator efficiency was in the range 0.65 to 0.88.

Dihydroxyl-terminated PLMAs were synthesized by ATRP using 5-ethyl-2,2-dimethyl 1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) as initiator catalyzed by CuBr/PMDETA. The polymers were obtained with narrow MWD (1.23-1.29) and initiator efficiency was in the range 0.80 to 1.05.

Bismethylol-terminated poly(methyl methacrylate) and poly(lauryl methacrylate) were synthesized using 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate as the initiator. The MWD of bismethylol-terminated PMMA was narrow (M_w/M_n - 1.18-1.24) and

nge 0.41 to 0.88. The MWD of bismethylol-terminated of PLMA was narrow (M_w/M_n - 1.12-1.19) and initiator efficiency was in the range 0.35 to 1.03.

Lactone-terminated polystyrene was synthesized by ATRP using 4-(2-(7-oxooxepan-3-yl) propan-2-yl) cyclohexyl 2-bromo-2-methyl propanoate as ATRP initiator with narrow MWD (M_w/M_n - 1.07 and 1.15) and initiator efficiency was in the range 0.80 and 0.84.

Cyclic carbonate-terminated PMMA was successfully synthesized by ATRP using 2-oxo-1,3-dioxolan-4-yl) methyl 2-bromo-2-methylpropanoate as initiator in the presence of CuCl/PMDETA as a catalyst. Cyclic carbonate-terminated PMMA were obtained with narrow MWD (M_w/M_n ï 1.16-1.24) and initiator efficiency was in the range 0.72 to 0.99. The reactivity of cyclic carbonate-terminated PMMA towards amine was evaluated by a model reaction using *n*-propyl amine and the results showed quantitative conversion to hydroxy urethane group.

Thus, ATRP initiators synthesized in the present work were found to be useful for synthesis of low molecular weight polystyrene and poly(alkyl methacrylate)s possessing functional end groups.

Well-defined diblock (PEO-*b*-PLMA) copolymers were synthesized using monofunctional PEO macroinitiators by ATRP using halide exchange technique. Diblock copolymers (PEO-*b*-PLMA) were synthesized with various M_n of PEO (350, 700, 2000 and 5000) and PLMA. PLMA-*b*-PEO-*b*-PLMA triblock copolymer was synthesized using difunctional PEO macroinitiator (M_n^{NMR} = 12650) using CuCl/PMDETA as catalyst.

PS-*b*-PCL was synthesized by ring opening polymerization of ε-caprolactone using hydroxyl-terminated polystyrene as macroinitiator in the presence of stannous octanoate as catalyst. Good agreement between the experimental (M_n^{NMR}) and theoretical molecular weight (M_n^{th}) were obtained and the MWD were in the range 1.26 to 1.44.

A novel mikto arm star cpolymer PMMA-b-$(PCL)_2$ was synthesized by ring opening polymerization of ε-caprolactone using dihydroxyl-terminated PMMA as macroinitiator in presence of stannous octanoate as catalyst. The formation of mikto arm star copolymer by successful ring opening polymerization was revealed from GPC and ^{1}H-NMR spectroscopy. However, control over molecular weight was poor and MWD obtained was relatively high (M_w/M_n = 1.39 to 1.49).

O copolymer was synthesized *via* grafting through approach by conventional free radical copolymerization of PEO macromonomer and lauryl methacrylate using AIBN as the initiator. Incorporation of PEO macromonomer in the resulting copolymer was low.

Polycaprolactone containing ATRP initiating sites was synthesized by ring opening copolymerization of ε-caprolactone and 4-[2-(7-Oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate using stannous octanoate as catalyst. PCL macroinitiator was successfully utilized for the synthesis of PCL-*g*-PMMA in presence of CuCl/CuBr complex with PMDETA as catalyst. The graft copolymers exhibited MWD in the range 1.36 to 1.71.

Two new polyurethane macroinitiators were synthesized by reaction of commercially available diol namely, ethylene glycol or poly(propylene glycol) (PPG) and a newly synthesized diol namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate with diisocyanates. PUM_2 macroinitiator was successfully demonstrated as ATRP macroinitiator in synthesis of PU-*g*-PLMA copolymer.

The efficacy of PEO-*b*-PLMA, PLMA-*g*-PEO and dihydroxyl-terminated PLMA as steric stabilizers in preparation of PU microsphere was examined in the dispersion polymerization of 2-ethyl-1,3-hexane diol and 2,4-toluene diisocyanate. Diblock copolymer (PEO-*b*-PLMA) with anchor moiety (PEO ï 350 and 700) did not produce PU microspheres. On the other hand, PEO-*b*-PLMA with anchor moiety (PEO ï 2000 and 5000) produced PU microspheres in sizes ranging from 1 to 20 micrometers. The balance between PEO and PLMA segments was crucial for the formation of PU microspheres.

Graft copolymers (PLMA-*g*-PEO) with anchor moiety (PEO - 1100) were successfully utilized to produce spherical and smaller PU microspheres at 10 wt % and 15 wt % (based on total weight of monomers) stabilizer concentration. Graft copolymers having anchor moiety (PEO - 2000 and 5000) were found to be effective steric stabilizers even at lower stabilizer concentration (1 wt %). Graft copolymer stabilizer with PEO of Mn ï 2000, produced PU microspheres with narrow particle size distribution ranging from 0.31 to 1.44 micrometers.

Dihydroxyl-terminated PLMA and bismethylol-terminated PLMA were employed as reactive steric stabilizers in dispersion polymerization and were found to be good reactive stabilizers for preparation of PU microspheres.

ctionalized ATRP initiators were designed and synthesized. These initiators were demonstrated to be useful in the synthesis of functionalized polystyrene and poly(alkyl methacrylate)s. Diblock, triblock and graft copolymers were synthesized utilizing ATRP or combination of ATRP and ROP. Dihydroxy-terminated PLMA, bismethylol-terminated PLMA, PEO-*b*-PLMA and PLMA-*g*-PEO were demonstrated as useful steric stabilizers in preparation of PU micrspheres.

List of Figures

List of Schemes

List of Tables

1.1 Introduction

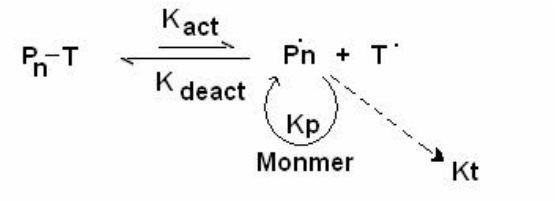
It is only in the last few decades of the past millennium that polymers have been recognized as materials that can truly form unique and intelligent materials, applicable to areas where metals and ceramics would not be usable. The reason behind this was the shift from research for new exotic monomers or combination of monomers and new fashionable initiators to research for gaining control over the microscopic structure of the polymer. Due to this, efforts have been put forward to develop living/controlled polymerization techniques by which control over chain-length distribution, monomer sequence distribution (for copolymers), tacticity, functionality distribution, architectures and the degree of branching for cross-linked materials can be gained. The development of functional polymers with predetermined, well-defined structures allows manufacturers to improve the properties of materials currently in the marketplace and create new markets for materials whose manufacture and processing conditions uniquely meet the targeted properties.

Until a little more than a decade ago, controlled/living radical polymerization (CRP) would have been an oxymoron.[1] Full control over all aspects of radical polymerization was deemed well-nigh impossible because radical termination reactions occur at diffusion-controlled rates. However, there are now several procedures for controlling radical polymerization, and companies are introducing products based on CRP into numerous high-value markets.[1-4]

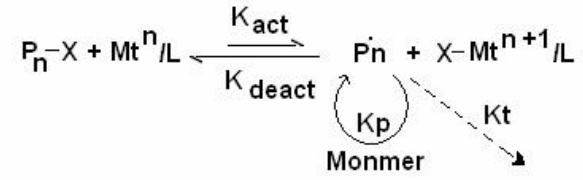
A number of CRP methods have been developed and the three most promising are: stable free radical polymerization (SFRP), most commonly known as nitroxide mediated polymerization (NMP)[5,6] **(Figure 1.1, Scheme 1)**; transition-metal-catalyzed atom transfer radical polymerization (ATRP)[7-10] **(Figure 1.1, Scheme 2)**; and reversible addition fragmentation chain transfer (RAFT) polymerization[11] **(Figure 1.1, Scheme 3)**. In order to extend the lifetime of the propagating chains, each of these methods relies on establishing a dynamic equilibrium between a low concentration of active propagating chains and a predominant amount of dormant chains that are unable to propagate or terminate. In the case of SFRP or ATRP, the equilibrium is pushed to the left-hand side (deactivated,

ormant species as a result of the persistent radical effect.[12] In all radical polymerizations, radical termination occurs at a rate, Rt, which is dependent on the concentration of radicals, [P*], where Rt = kt[P*].[1,13] Therefore, at the same polymerization rate (the same [P*]), essentially the same number of chains terminate regardless of being in conventional or CRP systems. However, in the conventional process all chains are terminated, whereas in CRP, as a result of the greater number of growing chains, the terminated chains constitute a small fraction of all the chains (~1-10%). The remaining chains are dormant species, capable of reactivation, functionalization, and chain extension to form block copolymers, etc. Thus, CRP behaves as a "living" system.[14,15] Additionally, relatively fast initiation, at least as fast as propagation, gives control over molecular weight (the degree of polymerization is defined by the ratio of concentrations of the consumed monomer to the introduced initiator, DPn = $\rho[M]/[I]_0$) and a narrow molecular weight distribution.

1. **SFRP or NMP**
   Thermal dissociation of dormant species (K_{act}) provides a low concentration of radicals



2. **ATRP**
   Transition metal activation (K_{act}) of a dormant species with a radically transferable atom



3. **Degenerative transfer or RAFT**
   Majority of chains are dormant species that participate in transfer reactions (K_{exch}) with a low concentration of active radicals

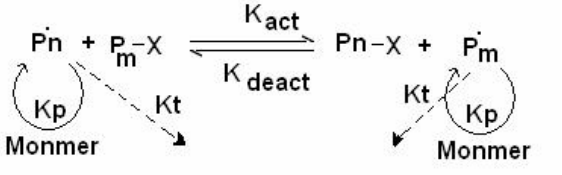


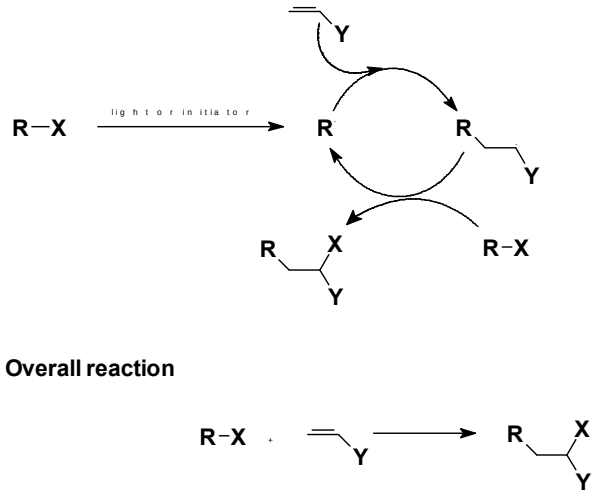
Figure 1.1: The three main CRP methods

synthesis of end-functionalized polymers, block and graft copolymers by atom transfer radical polymerization (ATRP) and combination of ATRP and ring opening polymerization (ROP), this review will deal with the brief survey of functionalized ATRP initiators and end-functionalized polymers synthesized *via* ATRP. Literature on synthesis of block copolymers specifically synthesized by ATRP or combination of ATRP and ROP is also presented.

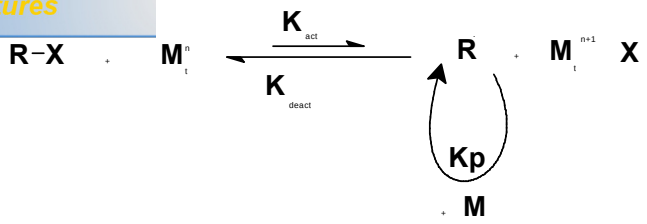
1.2 Atom Transfer Radical Polymerization

Matyjazewski et al[8] and Sawamoto et al[7] introduced ATRP in 1995 simultaneously. The principle is based on the Kharasch reaction, the Atom Transfer Radical Addition (ATRA), which is widely used by organic chemists for carbon-carbon bond formation **(Scheme 1.1).**[13]

The control in an ATRP system is induced by the presence of an organic halide initiator and a transition metal complex. The reversible exchange of the halogen atom between the growing polymer chain and the transition metal complex (in its higher oxidation state) ensures the control over the polymerization **(Scheme 1.2)**.



Scheme 1.1: Atom transfer radical addition chain reaction



Scheme 1.2: Mechanism of ATRP

ATRP has been demonstrated as a tool for synthesis of various polymers, which are useful in different fields. Apart from the academic interest in applications, ATRP has gained interest by commercial corporations to drive focused application research. Target applications, based on an analysis of patent applications, include the components of coatings, adhesives, nonionic surfactants, dispersants, polar thermoplastic elastomers, bulk performance materials, membranes, personal care products, detergents, double hydrophilic block copolymers for crystal engineering and drug delivery systems, gels and hydrogels, lubricants and additives, surface modifiers, hybrids with natural and inorganic polymers, various bio- and electronic materials, etc.

Ciba Specialty Chemicals, Degussa, PPG, and Kaneka have all been members of the ATRP and CRP Consortia at CMU[30] which provide access to CMU intellectual property. The companies discussed the status of their research on CRP based preparation of products at the 227th ACS National Meeting in 2004.[31,32] Ciba has focused on the preparation of amphiphilic graft copolymers by copolymerization of macromonomers with other monomers using both ATRP and NMP to give well-defined comb-copolymers.[33] Its first CRP based products are acrylic block copolymers, commercialized in 2004 through EFKA, which offer superior rheological performance and improved stabilization of pigment dispersions in coating applications.[34] This effort received the Ciba Specialty Chemicals R&D Award for 2004.

RohMax Oil Additives, a subsidiary of Degussa, discussed commercially feasible and economically acceptable conditions for ATRP preparation of additives based on long chain poly(alkyl methacrylates) that are suitable for use as components of lubricating oils. PPG indicated that materials prepared by ATRP offer many benefits over those prepared by other polymerization processes, including the ability to control the polymer molecular weight and achieve a narrow molecular weight distribution.[35] PPG also noted that another substantial benefit of ATRP is the ability to manipulate the composition, functionality, and

his permits the formation of complicated structures, such as block, gradient, comb, and star copolymers, which are being evaluated as components of various coating materials.

Kaneka announced that it currently has a large pilot unit producing commercial samples and is constructing a full-scale plant to produce reactive telechelic materials using ATRP. Products include a range of moisture-curable and addition-curable polyacrylates directed at sealant and adhesive markets. The main advantages over current products are high heat, oil, and ultraviolet resistance. One of the advantages that accrue from use of environmentally stable materials is their nonstaining characteristics. The benefits are seen in the lack of surface contamination on artificial marble attached to the exterior of buildings by sealants prepared using ATRP. The noncontamination properties of similar products also allow retention of the self-cleaning properties of TiO_2-treated glass currently being introduced by PPG for use in offices and residential buildings.[36] The heat and oil resistance of the materials prepared by ATRP also provide ideal materials for the formation of liquid-based gaskets for use in various engines.

1.2.1 Components in ATRP

a) Catalysts

The most important component of ATRP is the catalyst. It is the key to ATRP since it determines the position of the atom transfer equilibrium and the dynamics of the exchange between the dormant and active species.[3,4,37] There are several prerequisites for an efficient transition metal catalyst.

1. Metal center must have at least two readily accessible oxidation states by one electron
2. Metal center should have reasonable affinity towards halogen
3. Coordination sphere around the metal should be expandable on oxidation
4. Eventually, the position and dynamics of ATRP equilibrium should be appropriate for the particular system. To differentiate ATRP from the conventional redox-initiated polymerization and induce a controlled process, the oxidized transition metal should rapidly deactivate the propagating polymer chains to form the dormant species.

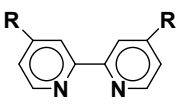
A variety of transition metal complexes with various ligands have been studied as ATRP catalysts. Transition metals such as copper[8,16], ruthenium[7,17,18] molybdenum[19], manganese, rhenium, iron[20-22], cobalt, nickel[23-25], rhodium[26] and palladium have been

t has to be complexed in order to be active and be able to control the polymerization. This is achieved using nitrogen-containing ligands, e.g. (substituted) 2,2ô-bipyridines[8,22] Schiff bases[27,28] multidentate tertiary amines[29], etc. Copper catalysts are superior in ATRP in terms of versatility and cost.

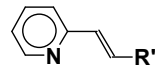
b) Ligands

The main role of the ligand in ATRP is to solubilize the transition metal salt in the organic media and to adjust the redox potential and halogenophilicity of the metal center forming a complex with an appropriate reactivity and dynamics for the atom transfer. [3,4,37] The ligands should complex strongly with the transition metal. It should also allow expansion of the coordination sphere and should allow selective atom transfer without promoting other reactions.

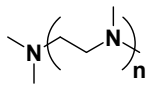
Nitrogen containing ligands are most extensively used and work well. **Figure 1.2** shows nitrogen-containing ligands **(L1 to 12)** used in copper-mediated ATRP.



R = H, 5-nonyl, n-heptyl, etc

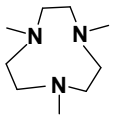


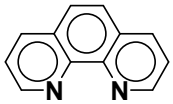
R = n-propyl, n-butyl

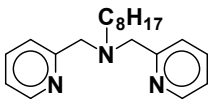


n =1,2,3

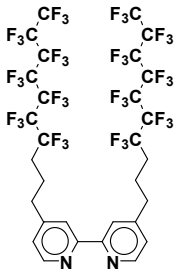
L1 **L2** **L3**

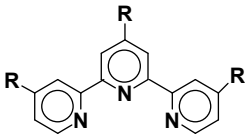


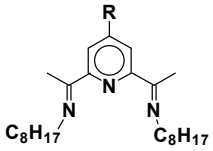




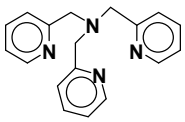
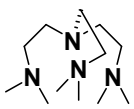
L4 **L5** **L6**







L7 **L8** **L9**

L10 **L11** **L12**

Figure 1.2: Selected nitrogen containing ligands used in ATRP

c) Monomers

A variety of monomers have been successfully polymerized using ATRP such as styrenes, acrylates, methacrylates, acrylamides, methacrylamides, acrylonitrile, vinyl acetate, etc.[2-4,37,38]

MMA is one of the most studied monomer by ATRP using catalytic systems based on copper, ruthenium, nickel, iron, palladium and rhodium. Other methacrylate esters that have been successfully polymerized include 2-(dimethylamino)ethyl methacrylate (DMAEMA), 2-hydroxy ethyl methacrylate (HEMA), glycidyl methacrylate, silyl protected HEMA, methacrylic acid in its alkyl protected form or as its sodium salt, methacrylates with a long oligo(ethylene oxide) substituent and fluorinated methacrylic esters.

d) Initiators

Initiator plays important role in ATRP. Initiator forms an initiating radical species *via* homolytic cleavage of C-halogen labile bond with the help of metal catalysts. Initiator is chosen such that it should initiate fast in comparison with propagation, quantitative initiation and the probability of side reaction should be minimum.[3,4,39a]

Most of the successful initiators employed in ATRP are organic halides with a potentially active carbon-halogen bond, which can easily generate a radical species through electronic and steric effects of their substituents. An organic halide, the structure of which is similar to that of the dormant chain end of the polymer, is preferentially used so that the activity of the carbon-halogen bond in the initiator is similar to that of the dormant polymer terminal. The general order of bond strength in the alkyl halides is R-Cl > R-Br > R-I. Thus, alkyl chlorides should be the least efficient initiators and alkyl iodides the most efficient. However, the use of alkyl iodides requires special precautions. They are light sensitive, can form metal iodide complexes with an unusual reactivity (e.g., CuI_2 is thermodynamically unstable and cannot be isolated), the R-I bond may possibly be

ere are potential complications of the ATRP process by degenerative transfer. The alkyl chlorides and bromides have been widely employed initiators in the ATRP. Haloalkanes, allyl halides, (haloalkyl) benzenes, haloketones, haloesters, haloamides, halonitriles, sulfonyl halides, etc. are utilized in ATRP.

i) Initiator efficiency

In general, the same halogen is used in the initiator and the metal salt (e.g., RBr/CuBr), however, the halogen exchange can sometimes be used to obtain better polymerization control.[39b] In a mixed halide initiating system, R-Br/Mt-Cl, the polymer chains are terminated by chlorine due to the stronger alkyl-chloride bond. Thus, the rate of initiation is increased relative to propagation e.g. ethyl 2-bromoisobutyrate/CuCl leads to a better controlled polymerization of MMA in comparison to using ethyl 2-bromoisobutyrate/CuBr.

In spite of choosing good initiating system based on the requirements, there are several reports where the initiator efficiencies were lower than 100 %. The initiator efficiency is especially important for the formation of block copolymers, functionalized polymers and telechelic polymers.[57]

The lowering of initiator efficiency for a particular initiating system is caused due to the factors like the functionality of initiator, concentration of initiator in reaction and temperature of the reaction. For example, Lu et al[57] showed that 5-chloromethyl-2-hydroxy-benzaldehyde **(Figure 1.3, a)** as initiator in ATRP of styrene in presence of CuCl/PMDETA as catalyst resulted with initiator efficiency in the range 0.08 to 1.02.

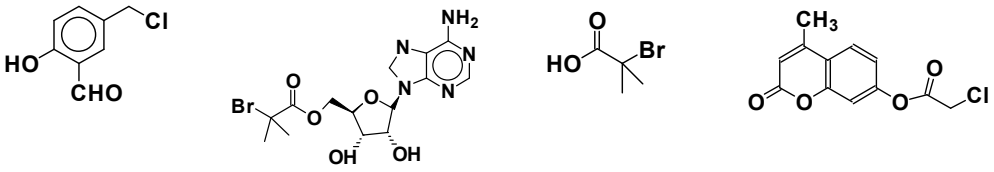
With decreasing mole ratio of monomer to initiator, efficiencies of the initiator reduced and the MWD of polystyrene expanded. The explanation provided was that at the lower mole ratio there are active species at the early stage of polymerization, and thus bimolecular termination becomes more significant. Due to the higher concentration of initiator, the inhibition of phenol group led to the wide polydispersity index and low efficiencies.[57]

Hadleton et al[96] reported that the initiator efficiency of unprotected uridine derived **(Figure 1.3, b)** initiator in ATRP of MMA using CuBr/ *N*-(*n*-pentyl)-2-pyridylmethanimine as catalyst was lower (0.46) as the M_n is increased.

Matyjazewski et al[60] observed the lower initiator efficiency in ATRP of styrene using alpha halocarboxylic acids **(Figure 1.3, c)** as initiator in presence of

which was attributed to intramolecular cyclization reaction forming gamma-butyrolactone.

Liu et al[67] studied the ATRP of styrene in presence of CuBr/bipyridine as catalyst using coumarin functonalized **(Figure 1.3, d)** initiator. The initiator efficiency was found to decrease with increasing monomer to initiator ratio and temperature.



a) **b)** **c)** **d)**

Figure 1.3: Structures of a) 5-chloromethyl-2-hydroxy-benzaldehyde b) unprotected uridine derived initiator c) alpha halocarboxylic acid and d) coumarin functonalized initiator

e) Solvents

ATRP can be carried out either in bulk, in solution, or in a heterogeneous system (emulsion, suspension, dispersion). Many solvents were utilized to carry out ATRP such as, toluene, benzene, anisole, diphenyl ether, ethyl acetate, acetone, N,N-dimethyl formamide, ethylene carbonate, alcohols, water, supercritical carbon dioxide, etc.[2,3,4]

Several factors affect solvent choice. Chain transfer to solvent should be minimal. In addition, potential interactions between solvent and the catalytic system should be considered. Catalyst poisoning by the solvent such as carboxylic acid and solvent assisted side reactions, such as elimination of HX from polystyryl halide, which is more pronounced in a polar solvent, should be minimized. The possibility that the structure of the catalyst may change in different solvents should also be considered.

f) Additives

Occasionally, polymerizations are slow in most cases due to low concentration of the radical species, as required by the general principle. Use of additive is unique solution for this problem. Some additives are needed for acceleration and/ or better control of the polymerizations. Additives most probably can effectively reduce the metal species in higher oxidation states or form more efficient catalysts *via* coordination.[2]

t metals such as Cu(0) and Fe(0) can effectively reduce $CuBr_2$ and $FeBr_3$ into active CuBr and $FeBr_2$, respectively, to dramatically increase the polymerization rate.[40] This allows the controlled radical polymerization even in the presence of oxygen or without purification of the monomer, where Cu(0) and Fe(0) can reduce the generated Cu(II) and Fe- (III) species into active Cu(I) and Fe(II), respectively.[41]

Phenols usually serve as radical inhibitors in conventional radical polymerization but can enhance the polymerizations of MMA.[42] Similar effects were observed for 4-methoxyphenol, phenol, and 2,6-di-*tert*-butylphenol.[42-44]

There are several examples in the literature where additives were utilized in ATRP to enhance the reaction rate or for better control over molecular weight and molecular weight distribution.

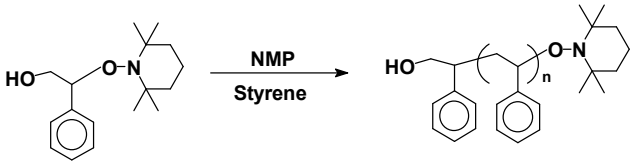
1.3 End-functionalized polymers

End-functionalized polymers are important class of polymers due to their potential applications as building blocks for block copolymers, surfactants, macromonomers.[39,45-48] A polymer can be considered to be telechelic if it contains end groups that react selectively to give a bond with another molecule.[47] Telechelic polymers are of great interest due to their ability to be used as cross-linkers, chain extenders, and precursors for block and graft copolymers. Moreover, star and dendritic polymers are obtained by coupling reactions of monofunctional and multifunctional telechelics with appropriate reagents.

1.3.1 Synthesis of end-functionalized polymers by CRP

1.3.1.1 End-functionalized polymers by NMP

NMP was reported as a successful method to obtain end-functional polymers. The utilization of functional alkoxyamine during polymerization generally gives functional polymers. For example, the use of TEMPO with a hydroxyl-functional initiator **(Scheme 1.3)** gives hydroxyl-terminated polymers.[49]



Scheme 1.3: Synthesis of hydroxyl-terminated polystyrene using NMP

lymers by RAFT polymerization

RAFT polymerization is an extremely versatile process and has been utilized in preparation of narrow MWD polymers or copolymers from most monomers amenable to radical polymerization already discussed above. There is compatibility with a wide range of functionality in monomers, solvents and initiators. Due to its compatibility with functional groups, it is also known for the synthesis of end-functionalized polymers *via* functional RAFT agent. In RAFT polymerization, an easy way to synthesize end-functionalized polymers is the polymerization in the presence of functionalized RAFT agents. **Figure 1.4** shows selected functionalized RAFT agents utilized in preparation of end-functional polymers through RAFT polymerization.[50-53]

There are certain reported difficulties with RAFT polymerization such as retardation and poor control which is frequently attributable to inappropriate choice of RAFT agent for the monomers and reaction conditions. RAFT agents that perform well under a given set of circumstances are not necessarily optimal for all circumstances.

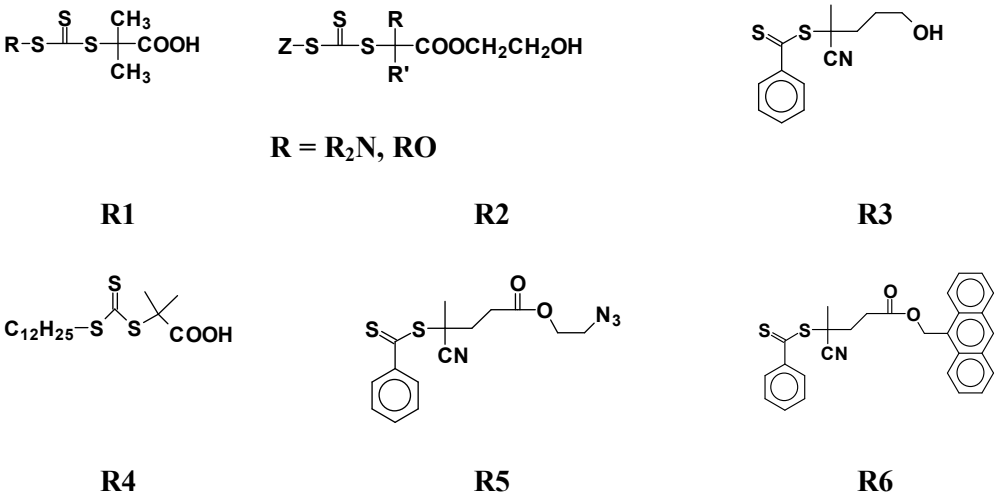


Figure 1.4: Selected functionalized RAFT agents[50-53]

1.3.1.3 End-functionalized polymers by ATRP

As in other living polymerizations, ATRP process can be effectively employed for the synthesis of end-functionalized polymers. Compared to NMP and RAFT polymerization, ATRP is known to be the most promising polymerization technique for synthesis of end-functionalized polymers on the basis of the present vast amount of literature. To this end, there are two general methods in ATRP, i.e., functional initiator

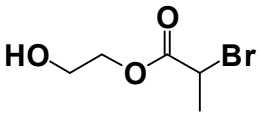
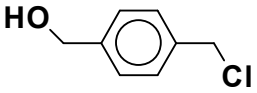
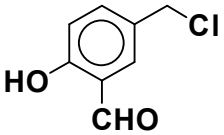
nt method. In the former, polymerization is initiated with a functionalized organic halide initiator coupled with a metal catalyst to form polymers with an R-end (head) functionality.[54] In the latter, end-functionalization is achieved through transformation of a stable carbon-halogen terminal bond. Examples of these approaches will be discussed below.

1.3.1.3.1 End-functionalized polymers *via* functional ATRP initiators

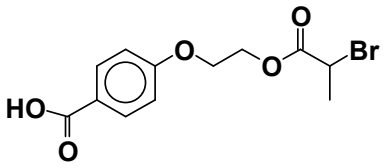
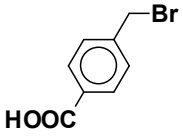
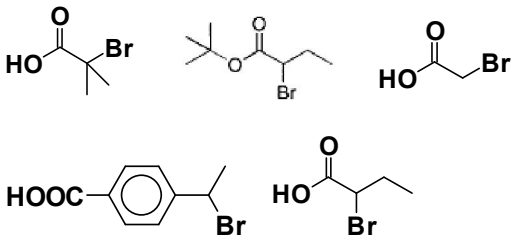
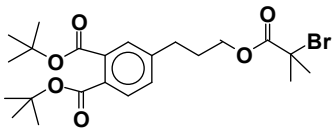
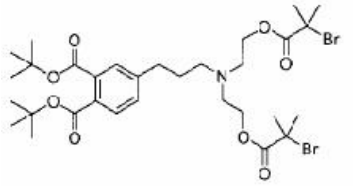
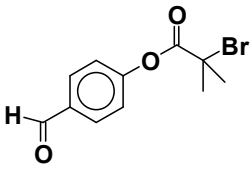
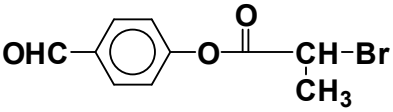
Taking advantage of the tolerance of ATRP for functional groups, a variety of functionalized initiators have been designed. A general way is to attach a functional group to a halogen compound such as haloester, (haloalkyl)benzene, haloalkane, or sulfonyl halide.[3,4] Most of the functional groups therein are insulated from the initiation moiety *via* a spacer to avoid possible side reactions.

Table 1.1 gives list of functionalized ATRP initiators employed for the synthesis of end-functionalized polymers.

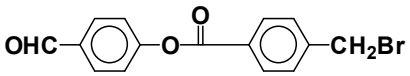
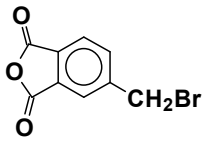
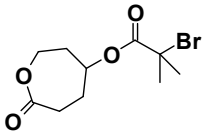
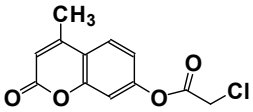
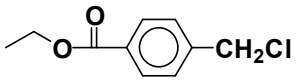
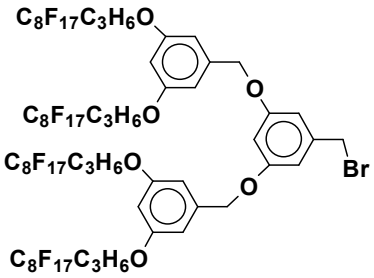
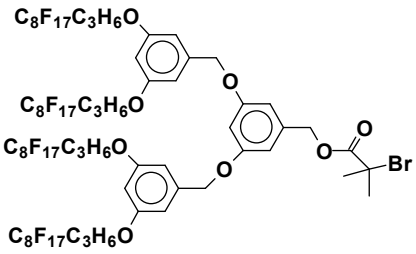
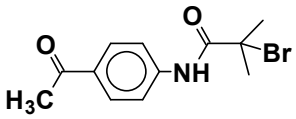
Table 1.1: Functionalized ATRP initiators

S. No.	Functionalized initiator	Monomers
1		MMA, styrene[55]
2		Stryene[56]
3		Styrene[57]

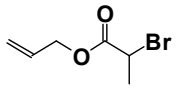
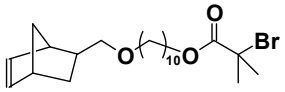
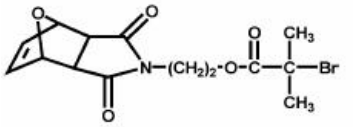
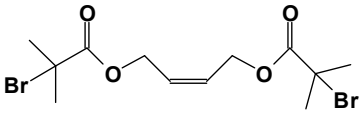
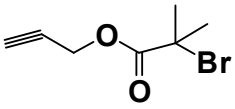
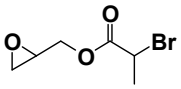
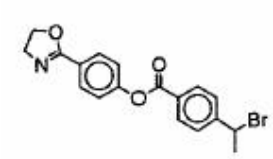
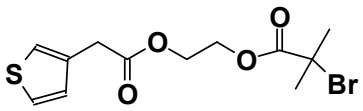
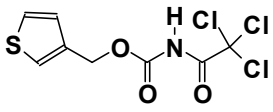
RP initiators……continued.

S. No.	Functionalized initiator	Monomers
4		Styrene[58]
5		Styrene[59]
6		Styrene[60]
7		MMA, styrene[61]
8		MMA, styrene[61]
9		MMA[62]
10		Styrene[63,64]

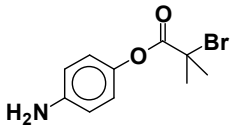
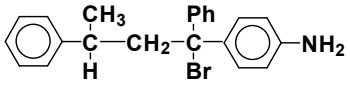
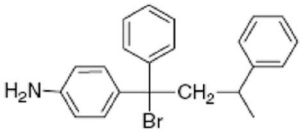
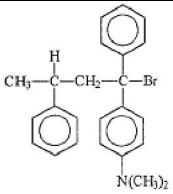
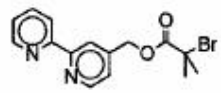
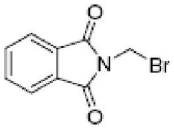
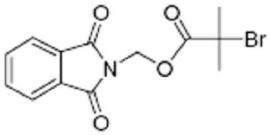
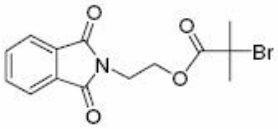
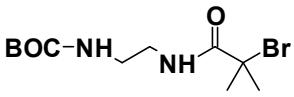
RP initiators……continued.

10		Styrene[63,64]
11		Styrene[65]
12		MMA[66]
13		Styrene[67]
14		Styrene[54]
15		Styrene, MMA[68]
16		Styrene, MMA[68]
17		MMA[69]

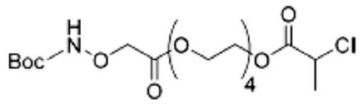
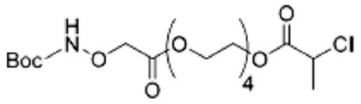
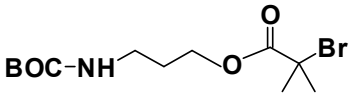
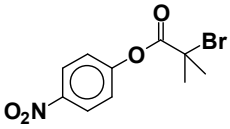
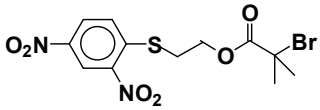
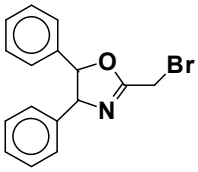
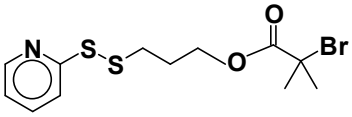
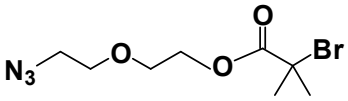
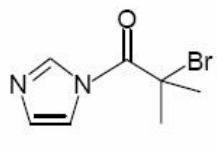
RP initiators……continued.

18		MMA, styrene[70]
19		Styrene, MMA, t-BMA[71]
		MMA[72]
20		t-BA[73]
21		2-(Dimethylamino) ethyl methacrylate (DMAEMA)[74]
22		MMA, stryene[75]
23		Stryene[76]
24		t-BA[77]
25		MMA[78]

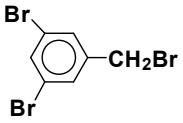
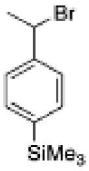
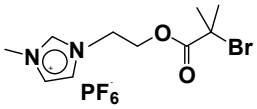
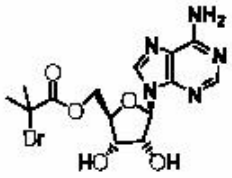
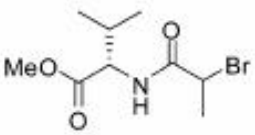
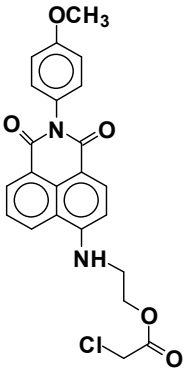
RP initiators……continued.

26		MMA[79]
27		Styrene[80]
28		Styrene[81]
29		Styrene[82]
30		Styrene[83]
31		Styrene[84]
32		Styrene[84]
33		Styrene[84]
34		MMA[85]

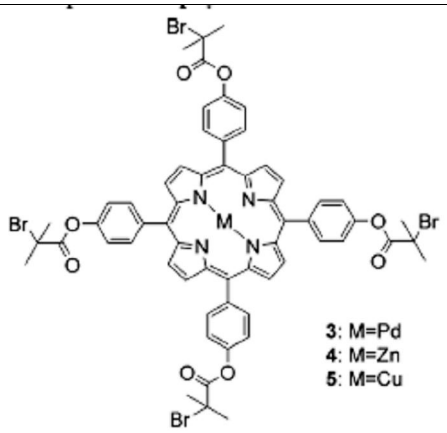
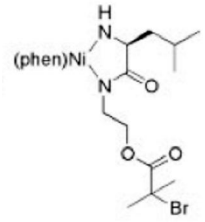
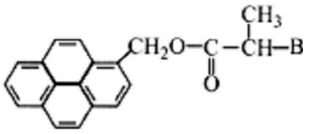
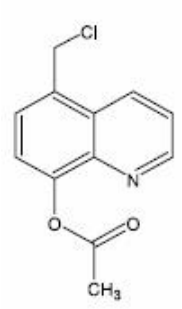
RP initiators……continued.

35		HEMA and PEGMA[86]
36		HEMA and PEGMA[86]
37		Styrene[87]
38		MMA[79]
39		MMA[88]
40		MMA[89]
41		HEMA[90]
42		2-(Dimethylamino) ethyl methacrylate (DMAEMA)[91]
43		n-BMA[92]

RP initiators……continued.

44		Styrene[93]
45		Stryene[94]
46		MMA[95]
47		MMA[96]
48		t-BA, styrene[97]
49		Styrene[98]

RP initiators……continued.

50		Styrene, MMA, MA, BMA, ODA[99]
51		MMA[100]
52		Styrene[101]
53		Styrene[102]

1.3.1.3.2 End-functionalized polymers *via* halide displacement

This is another important method for the synthesis of end-functionalized polymers by ATRP.[3] Polymers obtained by ATRP contain a halogen atom as end group, if termination and transfer reactions are essentially absent. The halogen atom can be replaced through a variety of reactions leading to end functional polymers. A common method of dehalogenation of organic compound is reaction of polymer synthesized by ATRP with

substitutions are often desirable for high-temperature applications where some evidence for halogen loss has been described.[105,106] By replacing tributyltin hydride with allyl tri-*n*-butylstannane, polymers with allyl end groups were produced.[104]

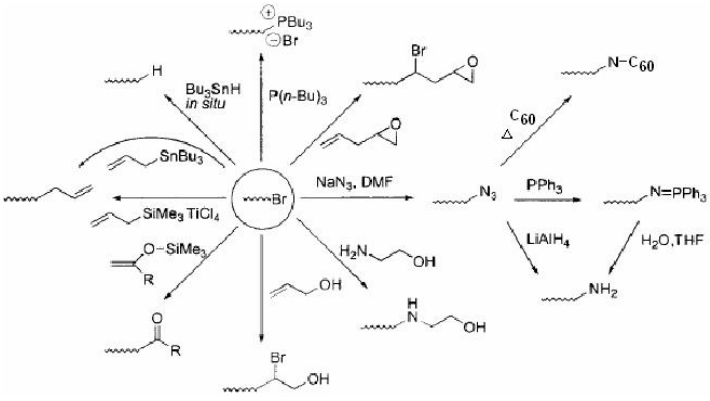
The terminal halogen can also be displaced by other methods such as nucleophilic substitution, cyclo-addition, free-radical chemistry, or electrophilic addition catalyzed by Lewis acids. **Scheme 1.4** illustrates the reactions used to replace halogen with azide leading to, in turn, amine groups.

The nucleophilic substitution reaction with trimethylsilyl azide yielded the azide terminal polymer. This was followed by a primary amino-functionalized chain end. This method of transformation was later expanded to include the transformation of halo-terminated acrylates to azide- and amine-terminal polymers.[108a] The nucleophilic displacement can be carried out also with NaN_3 in DMF solution also.

The azide-terminated polymers can undergo cycloaddition reaction with azide end group of polymer with C_{60} to result into C_{60}-terminated polymers.[108b]

Allyl and epoxide-terminated polymers are prepared using radical addition reactions. Addition of 1,2-epoxy-5-hexene at the end of reaction of ATRP, results into epoxy-terminated polymers and addition of allyl alcohol results into hydroxyl-terminated polymers.[107]

Hydroxyl-terminated polymer was resulted from nucleophilic substitution reaction between bromine-terminated polymer and amino ethanol.[108c,108d]



Scheme 1.4: End-functionalized polymers synthesized by displacement of terminal halogen atom using electrophilic substitution, nucleophilic substitution, cyclo addition and radical addition reactions [3]

Block copolymers represent a valuable class of polymeric materials with a wide range of applications. The properties of block copolymers can be tailored through combination of monomers that form the blocks, and the length of polymeric sequences.[109-112] Polymeric blocks are covalently bonded and in most cases are thermodynamically incompatible giving rise to microphase separation. The microphase separated structure formed depends on the copolymer architecture and composition.

In the solid and rubbery states they are used as thermoplastic elastomers with applications such as impact modification, compatibilization and pressure sensitive adhesives. In solution, their solution properties are exploited in foams, oil additives, solubilizers, thickners and dispersion agents.[109-112]

Linear block copolymers comprise of two or more polymer chains in sequence, whereas a starblock copolymers comprise more than two linear block copolymers attached at a common branch point. **Figure 1.5** shows selected architecture of block copolymers.

There are several specialized books appeared on synthesis, characterization, physical properties, thin film-morphology and nanoscience and technology applications of block copolymers. Goodman[113,114] edited books in 1980s and 1990s in two volumes, ñDevelopments in Block Copolymersò and Hamley[115] edited book entitled ñThe Physics of Block Copolymersò dealing with block copolymers. A review by Riess et al,[116] discusses about block copolymers, their properties and applications.[117]

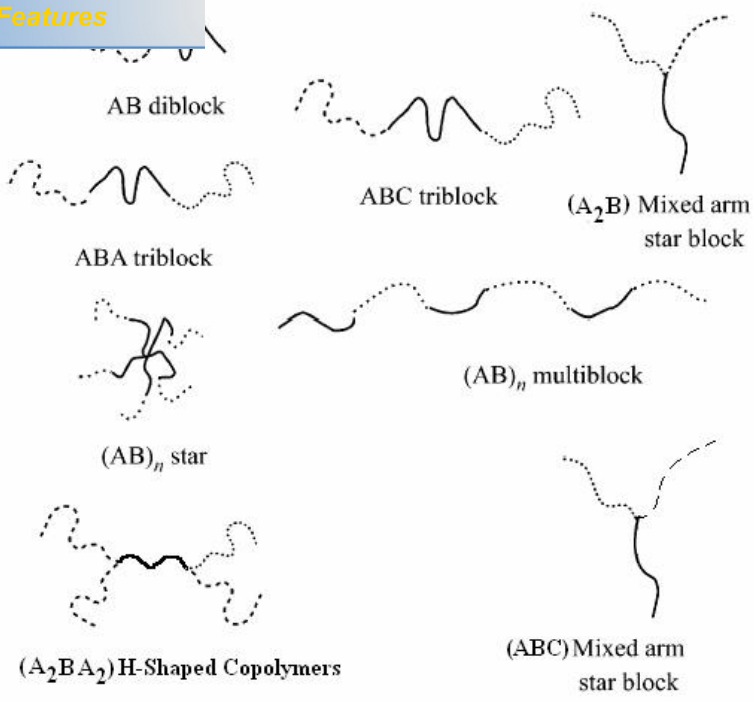


Figure 1.5: Selected architectures of block copolymers

1.4.1 Synthesis of block copolymers

The most widely used techniques for synthesis of block copolymers are anionic polymerization, cationic polymerization and controlled radical polymerization methods.[111,118a]

The older technique of anionic polymerization is still used widely in the industrial manufacture of block copolymers. Since its discovery by Szwarc[118b] in 1956 a large variety of block copolymers were prepared from styrene, dienes, methacrylates, oxiranes, thiiranes, lactones, cyclic siloxanes, etc.[116, 118c]

Cationic polymerization is also finding an extensive application in the preparation of block copolymers. Dreyfuss and Dreyfuss[118d] reported the first example of block copolymer based on styrene derivative and 3,3-bis-chloromethyl oxetane, after that a large variety of block copolymers were reported based on styrene derivative, isobutene, vinyl ethers, etc.[118e-118g]

A summary of block copolymer synthesis techniques has been provided by Hadjichristidis et al.[111] Undoubtedly, the main advance in block copolymer synthesis in the last two decades has been the development of techniques of living radical polymerization. The principle of controlled radical polymerization methods is already discussed in earlier

rization methods, ATRP has been used most extensively to synthesize block copolymers. The ATRP method, and its application to the synthesis of block copolymers, has been reviewed by several authors.[1-4,111,112,117] ATRP has been used to prepare AB diblock, ABA triblock[119] and most recently ABC triblock copolymers.[120] The technique has been used to create block copolymers based on polystyrene and various polyacrylates.[2,3,4,] However, it is possible to synthesize a macroinitiator by other polymerization (anionic, cationic, etc.), and use it in the ATRP of vinyl monomers.

1.4.1.1 Amphiphilic PEO-based block copolymers

Among the block copolymers synthesized by ATRP, PEO-based hydrophilic segment with other types of hydrophobic segments have attracted considerable interest due to the remarkable properties of PEO segment. The properties of PEO include solubility in water and various polar and non-polar organic solvents, the ability to complex metal cations and non-ionic nature.[121,122] These copolymers have attracted special attention in fundamental and applied research due to their unique solution and associative properties. On the basis of their amphiphilic nature, PEO-based block copolymers have found numerous applications as surfactants,[123,124] phase-transfer catalysts, solid polymer elctrolyte, etc. Their surfactive and self-associative characteristics lead to micellization in block selective solvent. Micellization is a well known property of these block copolymers. In block selective solvent, these polymers can reversibly assemble into micelles or aggregates. The covalent bond between the blocks prevents macrophase separation.[109-115, 125,126] However, in comparison with micellization of low-molar mass surfactants, these block copolymers have reduced mobility, slower diffusion rates, narrower solubility windows and much lower critical micelle concentration (CMC). The micellization of block copolymers can lead to more than 30 different morphologies, such as spheres, hexagons, rods, lamellaes, vesicles, etc.[127] The morphology is controlled by structural factors such as polarity of each block, relative length of block and overall molar mass of the copolymer.

a) Linear PEO-based block copolymers

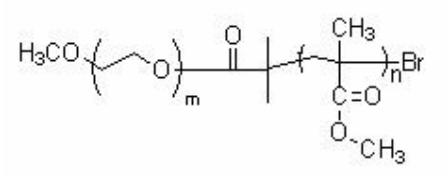
Block copolymers are considered to be a combination of two or more macromolecules joined covalently at its one or both ends in a linear arrangement e.g. a diblock copolymer AB composed of two different homopolymers linked end to end. An

to ABA or BAB triblocks and to $(AB)_n$ linear multiblocks, whereas ABC copolymers are obtained by the incorporation of a polymer segment having a third composition.[111]

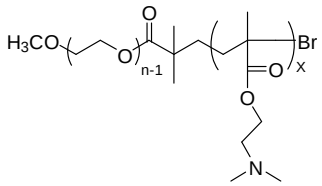
Generally, block copolymers can be synthesized in a traditional sequential fashion by the polymerization of one monomer, followed by a second monomer. This is also true for controlled radical polymerization, which permits the synthesis of a wide variety of block copolymers. Most of the block copolymers consist of methacrylate and / or acrylates and / or styrene and can be synthesized both *via* sequential controlled radical polymerizations or *via* controlled radical polymerization using macroinitiators.[128-133]

Kops et al[134] reported synthesis of PS-*b*-PEO-*b*-PS triblock copolymer by ATRP using PEO macroinitiator obtained by functionalizing HOï PEOï OH with 2-bromopropionyl or 2- chloropropionyl ester end group. The polymerization proceeded in a living manner to yield well-defined block copolymers, which are difficult to synthesize by the sequential anionic polymerization technique. The difficulties involved in synthesis block copolymer of PEO and alkyl methacrylate *via* anionic polymerizations are side reactions, low solubility of PEO in THF below 20^{o}C and at elevated temperatures transfer and termination reactions cannot be prevented.[135-137a] Thus, esterification of a hydroxyl group of preformed polymeric segments with halogenated acyl halide proved to be an excellent method for producing macroinitiators suitable for ATRP. With this approach, a number of block copolymers were synthesized from PEO macroinitiator. For example, Hocker and coworkers[137b] synthesized poly(ethylene oxide)-b-poly(hydroxyethyl methacrylate) (PEO-b-PHEMA) and PEO-b-PS block copolymers. **Figure 1.6** shows selected block copolymers containing PEO in combination with vinyl based monomers **(BC-1 to BC-31)**.

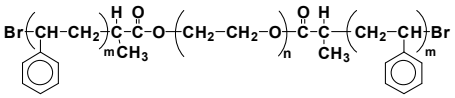
opolymers containing PEO in combination with vinyl based monomers



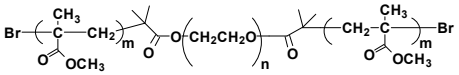
BC-1[138,139]



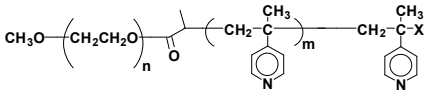
BC-2[140]



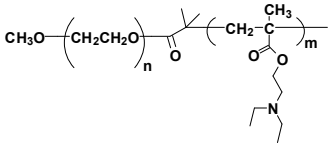
BC-3[141,142]



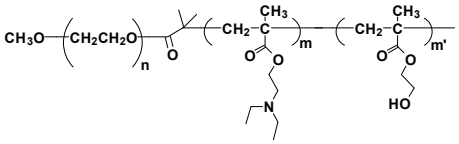
BC-4[143-145]



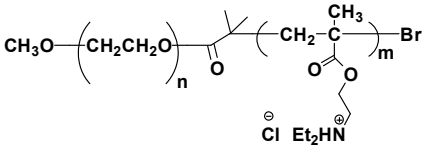
BC-5[146]



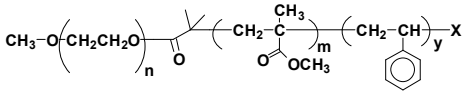
BC-6[147]



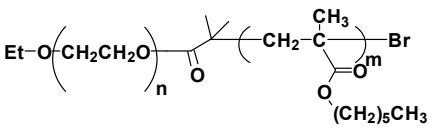
BC-7[148,149]



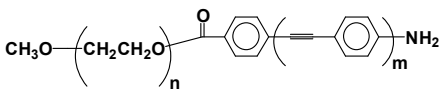
BC-8[147]



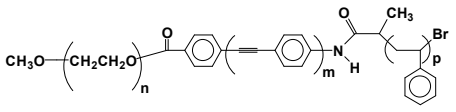
BC-9[150]



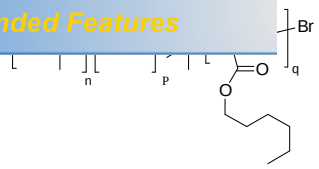
BC-10[151]



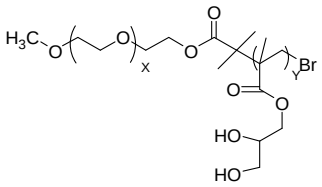
BC-11[152]



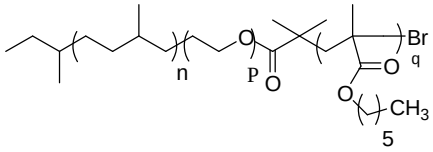
BC-12[152]



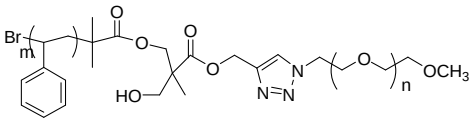
BC-13[153]



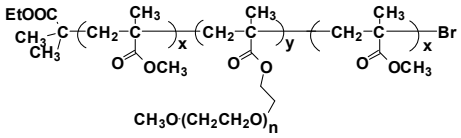
BC-14[154]



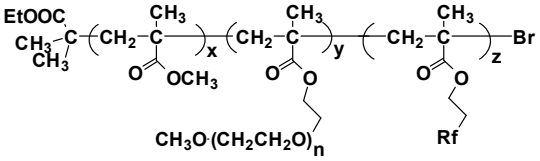
BC-15[155]



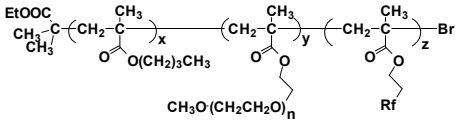
BC-16[156]



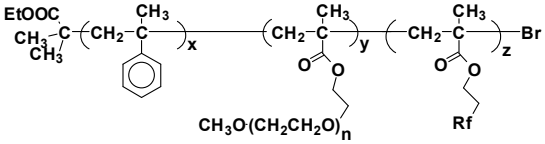
BC-17[120]



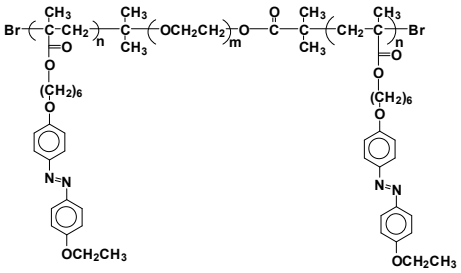
BC-18[120]



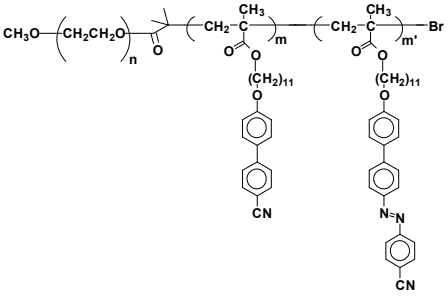
BC-19[120]



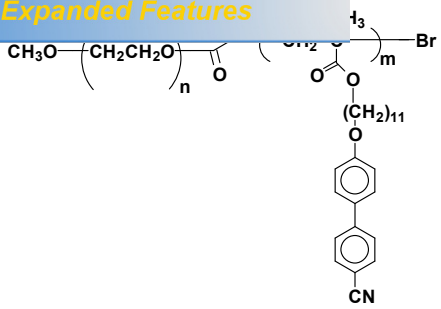
BC-20[120]



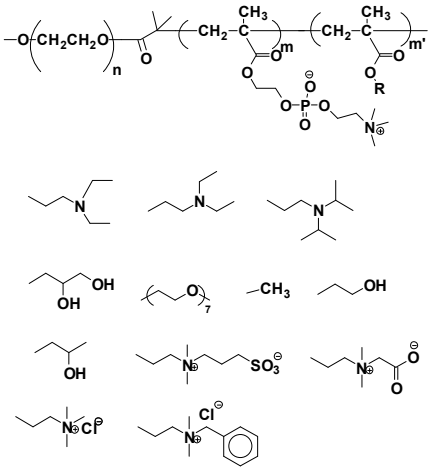
BC-21[157]



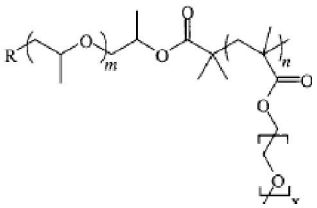
BC-22[144]



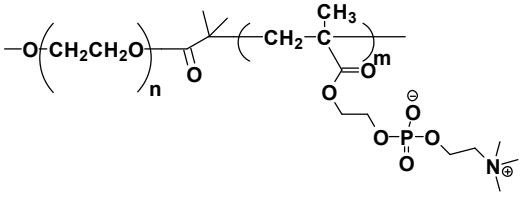
BC-23[144]



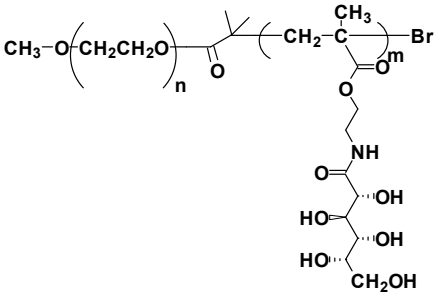
BC-24[161]



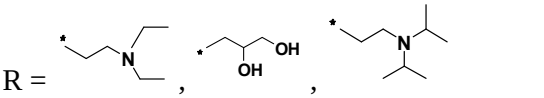
BC-25[162]



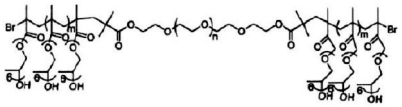
BC-26[161]



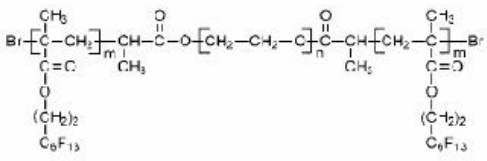
BC-27[163]



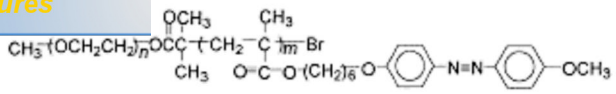
BC-28[163]



BC-29[164]



BC-30[165]



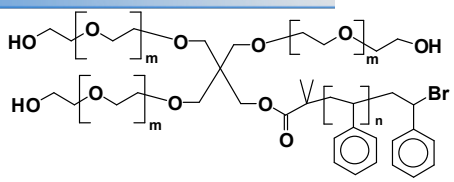
BC-31[166]

b) Non linear PEO-based copolymers

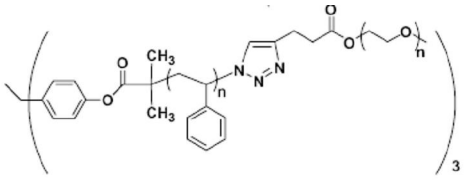
Distinct from linear block copolymers, such as AB diblock, ABA triblocks, etc., nonlinear block copolymer, such as star block copolymers, miktoarm star copolymers, etc. are formed by linking of a block copolymer chains by one of their ends to a multifunctional moiety.[111] Even more complex architectures have been reported, such as cyclic, heteroarm, ópalm treeôô, H-shaped, dumb-bell structures, etc.[127] Nonlinear block copolymers have attracted a great deal of attention due to their potential applications as thermoplastic elastomers, tough plastics, compatibilizing agents for polymer blends, polymer micelles, etc., Their segregation of incompatible blocks on molecular scale (5 ï 100 nm) can produce amazingly complex nanostructures. Compared to linear block copolymers, subtle variation in the composition or architecture of nonlinear block copolymers can lead to pronounced changes in morphology, as well as material properties, which is one of the driving forces for the synthesis of new nonlinear block copolymers. Also, the micellization behavior of such sophisticated structures has recently come under examination.[164]

In the literature these copolymers were synthesized by combining ATRP and other techniques like click chemistry in some of the examples. **Figure 1.7** shows selected structure of nonlinear block copolymers containing PEO as hydrophilic block with references **(BC-1 to BC-10)**.

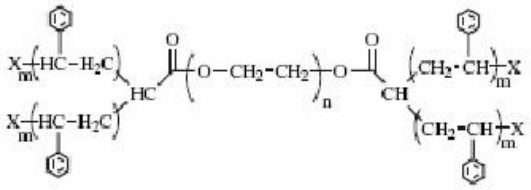
s of PEO based nonlinear block copolymers



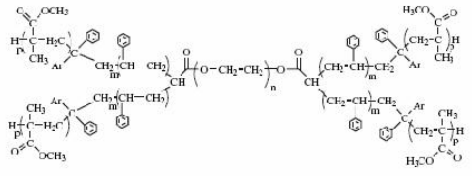
BC-1[165]



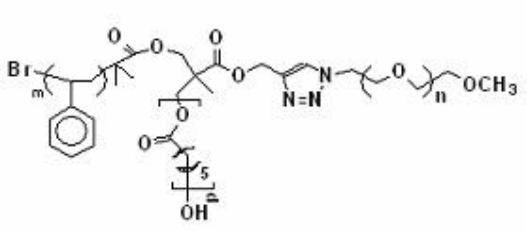
BC-2[166]



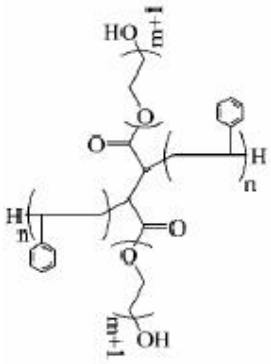
BC-3[167]



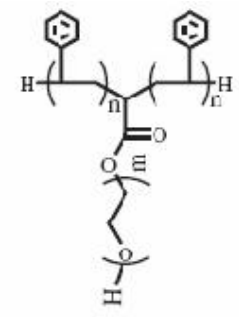
BC-4[167]



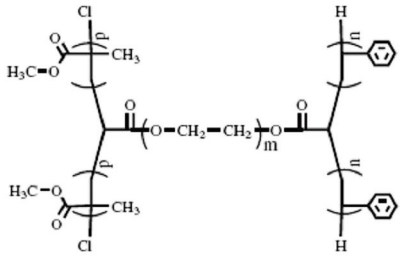
BC-5[156]



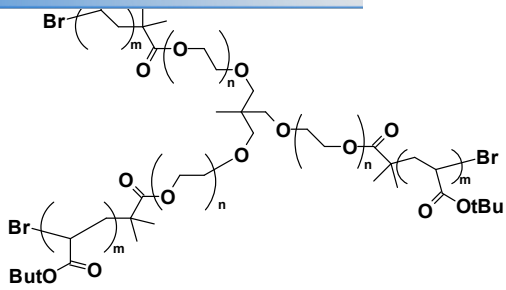
BC-6[156]



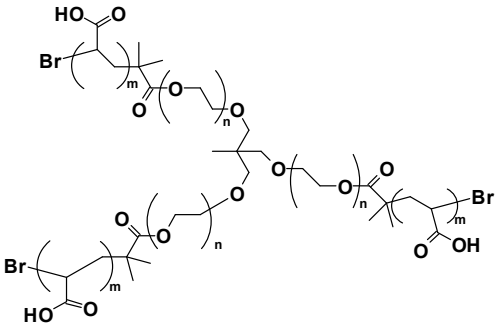
BC-7[168]



BC-8[168]



BC-9[169]



BC-10[169]

1.4.2 Synthesis of block copolymers based on PCL and other vinyl monomers

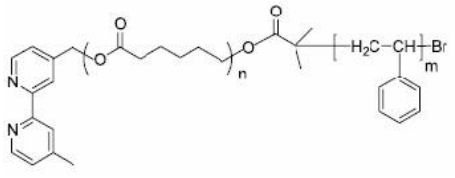
Since the number of monomers, and thus the resulting polymer structures are limited by any of the specific living polymerization techniques, appropriate combination of different polymerization mechanisms can lead to a variety of new and useful polymeric materials.[111-115] Therefore, combinations of controlled radical polymerizations with other polymerizations such as ROP applied to synthesize block copolymers have been developed [111] **(Figure 1.8 and 1.9)**. In most of the cases, polymers with active sites, such as carbon-halogen or nitroxide or dithioesters terminal groups, are synthesized by other living polymerizations and the product is further used to initiate the controlled radical polymerization.[170,171] The combination of controlled radical polymerizations with other living polymerizations can be realized by mechanism transformation. The transformation of an active chain end into another type of initiating site has been extensively used in the synthesis of block copolymers.[172] Recent advances in the synthesis of linear diblock, triblock and star copolymers *via* combination of controlled radical polymerizations with ROP are described herein.

1.4.2.1 PCL-based linear block copolymers

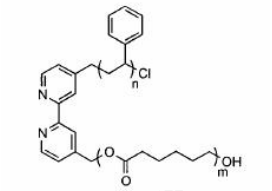
Synthesis of block copolymers using ROP of ε-CL with other living radical polymerizations has been described. Recently, the concept of using a single initiator (bifunctional, dual or double headed initiator) in order to perform two mechanically distinct polymerization, without the need of intermediate transformation or activation steps has been introduced.[111,173-175] The potential of this synthetic approach is to produce block copolymers consisting of monomers that are polymerized by different polymerization mechanisms in a simple and efficient way.

ROP, CRP techniques like NMP and RAFT are also utilized for synthesis of these copolymers. Click chemistry also serves its important role in synthesis of these types of copolymers. **Figure 1.8** shows selected structures of linear block copolymers consisting of PCL as one of the segment and other segment made from vinyl monomer **(BC-1 to BC-10)**.

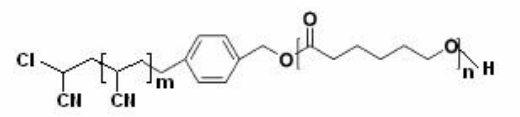
Figure 1.8: Selected structures of PCL based linear block copolymers



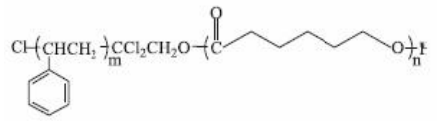
BC-1[176]



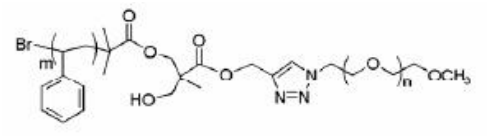
BC-2[177]



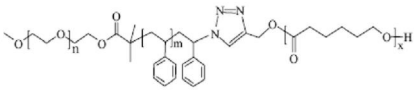
BC-3[178]



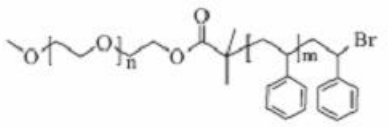
BC-4[179]



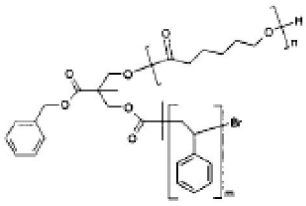
BC-5[156]



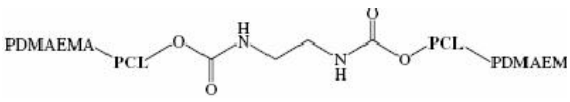
BC-7[180]



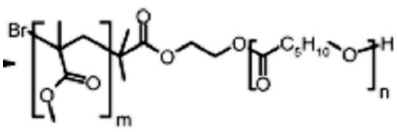
BC-7[180,176]



BC-8[183]



BC-9[181]



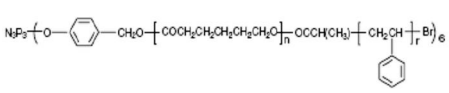
BC-10[182]

ymers along with vinyl monomers

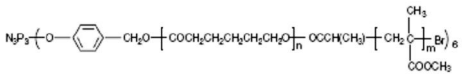
Star-block copolymers are actually star-shaped macromolecules where each arm is a block copolymer. The number of branches can be from a few to several tens. The topological difference of this kind of macromolecules with respect to linear block copolymers is focused on the existence of a central branching point, which, by itself, brings certain symmetry in the macromolecules and sometimes defines a certain amount of intramolecular ordering.[111,116]

Miktoarm star copolymer is another example of interesting nonlinear block copolymers. In the miktoarm star copolymer, arms of different chemical nature and/or composition are linked to the same branch point.[111,184-187] These types of copolymers are generally synthesized by anionic polymerization methods. Recently some examples are reported using controlled radical polymerizations combining with other living polymerization methods for the synthesis of mikto arm star copolymers.[156,188-190] The number of different kind of arms can be varied as well as the total number of arms, giving rise to a variety of miktoarm star like A_2B, A_3B, A_5B (or generally A_nB), A_nB_n, ABC or even ABCD. Several approaches have been reported for the synthesis of miktoarm star copolymers, with each one of them having specific advantages and disadvantages. Special reviews or book chapters have appeared on miktoarm copolymers.[185,111] **Figure 1.9** shows selected structures of PCL based star copolymers **(BC-1 to BC-12)** reported in the literature.

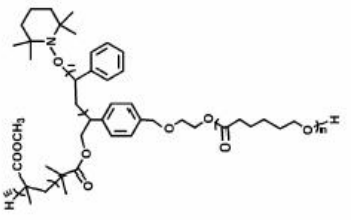
Figure 1.9: Selected structures of PCL based star copolymers



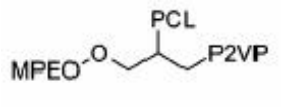
BC-1[191]



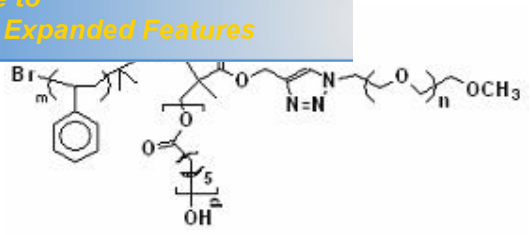
BC-2[191]



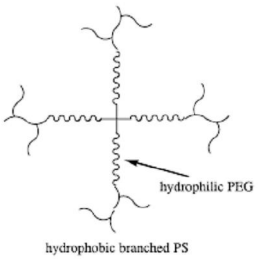
BC-3[192]



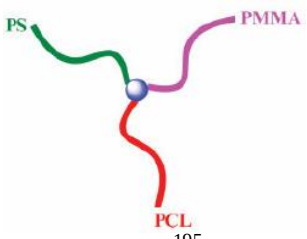
BC-4[193]



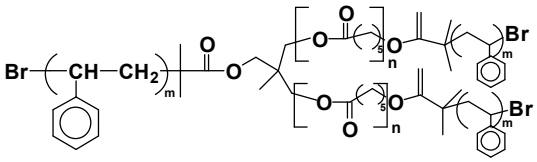
BC-5[159]



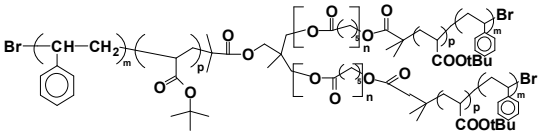
BC-6[197]



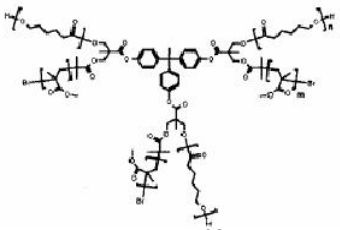
BC-7[195]



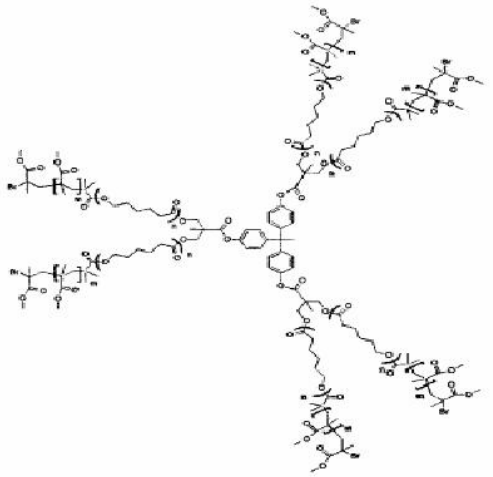
BC-8[184]



BC-9[184]



BC-11[196]



BC-12[197]

A graft copolymer can be defined as a chemically linked set of homopolymers, for example backbone of a parent polymer A is attached to (or grafted) with segments of B. A representative structure of a graft copolymer is shown in **Figure 1.10**.[198] Graft copolymers represent valuable polymeric materials, since a variety of molecular parameters can be varied like backbone and branch polymer type, degree of polymerization of backbone and branches, graft density and distribution of the grafts.[199,200]

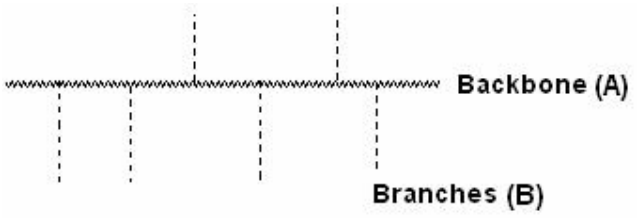


Figure 1.10: Architecture of graft copolymer

Grafted chains generally possess molecular weights less than that of the main chain. With the help of these parameters, various materials such as thermoplastic elastomers and amphiphilic copolymers can be obtained. Using appropriate backbone and branches of graft copolymer one can assume applications as hydrogels, stabilizers, surfactants, surface-modifying agents, dispersants, emulsifiers and compatibilizers in polymers blends.[201-204] Compatibilization represents a major area of application for graft copolymers because the grafted chains can be used to solubilize a polymer blend system containing two immiscible polymers.[205,206] Additionally, graft copolymers offer unique solution, mechanical and morphological properties that make them ideal for utilization as viscosity modifiers and thermoplastic elastomers. The unique molecular architecture of graft copolymers leads to peculiar morphological properties. The chain lengths of the grafted arms and backbone block dictate the morphology that arises in the polymer. The changes in composition of graft copolymer alter the resulting polymer morphology. A variety of morphologies is possible ranging from lamellar to cylindrical to spherical.[207]

Typical synthesis of the grafts occurs by polymerization initiated at some reactive point along the backbone or by copolymerization of a macromonomer with other comonomer. Polymerization from the polymer backbone is possible *via* anionic, cationic, and radical techniques, but all require some functional unit capable of further reaction.[208]

lymers by combination of ATRP and other techniques

General methods for synthesis of graft copolymer are, 1) grafting onto 2) grafting through, and 3) grafting from.[209,111,116]

1.5.1.1 Grafting onto approach

Grafting onto approach requires the presence of complimentary functionalities on the branches and the backbone **(Figure 1.11)**. A coupling reaction is carried out between the branches and backbone with desired proportion and under the appropriate experimental conditions to obtain desired graft copolymer. Before grafting onto approach, using controlled polymerization, molecular weight, molecular weight distribution and the chemical composition of the backbone and branches can be controlled. Additionally, both backbone and branches can be isolated before coupling reaction and characterized separately. [209,111,116]

Figure 1.11: Graft copolymer by grafting onto approach

1.5.1.2 Grafting through approach

Grafting through approach utilizes macromonomers and their homo- or co polymerization with another monomer to produce graft copolymer **(Figure 1.12)**.[45] Here, the obtained graft copolymer consists of branch of the copolymer and the backbone is formed in-situ. The number of branches per backbone depends on ratio of the molar concentration of macromonomer and comonomer and their reactivity ratio.[209,111,116]

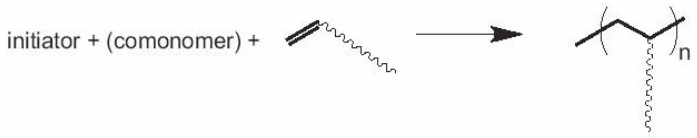


Figure 1.12: Graft copolymer by grafting through approach

1.5.1.3 Grafting from approach

In the grafting from approach, backbones containing reactive sites that are capable of initiating a polymerization are synthesized and further polymerization of another monomer gives graft copolymer. **Figure 1.13** illustrates synthesis of graft copolymers by grafting from approach. The number of branches can be controlled by the concentration of active sites generated along the backbone, assuming that each one of them participates in

[111,116] The new advances in the living (controlled) radical polymerization techniques led to the preparation of several well-defined graft copolymers.

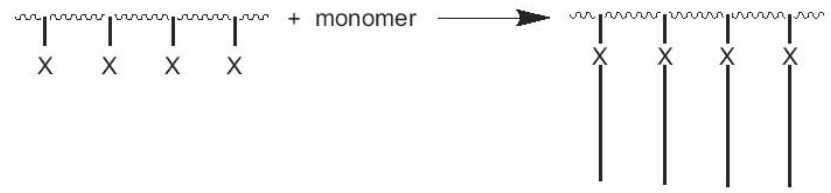


Figure 1.13: Graft copolymers by grafting from approach

Each method suffers from its own particular disadvantages, but steric hindrance of the reactive center is common to all the graft copolymer routes, affecting the grafting efficiency.

Matyjaszewski et al[210] demonstrated that the grafting of styrene and MMA using polyisobutylene (PIB) backbone is better controlled by applying the halogen exchange technique, as shown schematically in **Figure 1.14**.

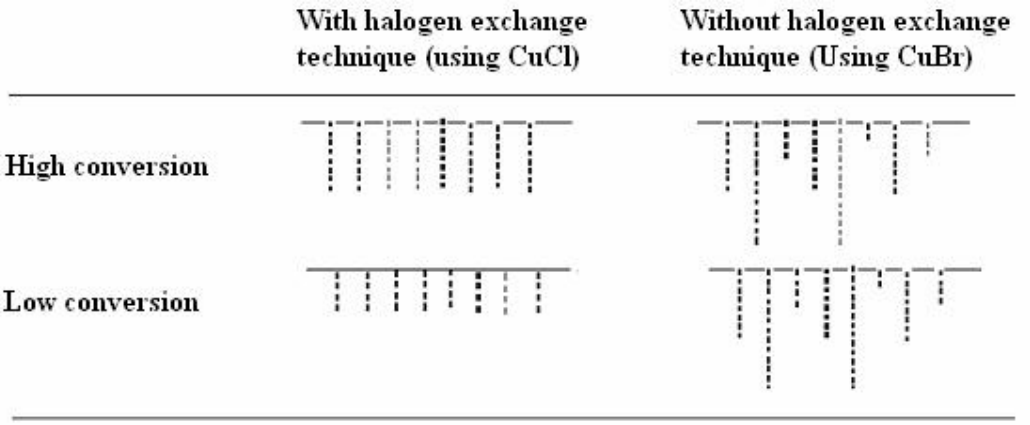


Figure 1.14: Graft copolymers synthesized from functionalized PIB

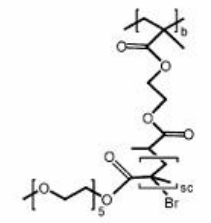
By using CRP methods graft copolymers can be synthesized by one of three approaches: ñgrafting fromò, ñgrafting throughò, and ñgrafting ontoò. The first two approaches have been extensively studied for synthesis of various kinds of graft (co)polymers with different chemical compositions.

In ñGrafting fromò approach a backbone macroinitiator is used and further CRP resulted in the preparation of well-defined graft copolymers. The controlled synthesis of graft copolymers was described for styrene,[211] MMA,[212] butyl acrylate, glycidyl methacrylate,[213] etc.

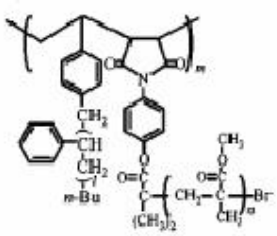
approach was adapted for synthesis of numerous graft copolymers by homopolymerization of macromonomers or copolymerization of a macromonomer (MM) with a low molecular weight comonomer (e.g., polystyrene-MM/ *N*-vinylpyrrolidinone,[209] PMMA macromonomer with nBA,[209] etc). Macromonomers with hydrophilic poly(ethylene oxide) (PEO) segments have been used to prepare biocompatible materials, which find applications in aqueous-based systems.[214-216]

In the present thesis, synthesis of graft copolymers was carried out using combination of ATRP and other polymerization techniques. Hence, only the graft copolymers obtained from ATRP and other polymerization techniques are cited **(Figure 1.15, GP-1 to GP-39)**.

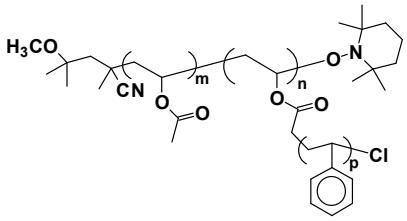
Figure 1.15: Selected structures of graft copolymers obtained through combination of ATRP and other polymerization techniques



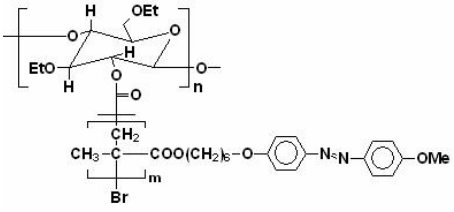
GP-1[217]



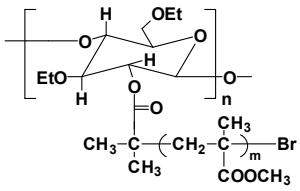
GP-2[218]



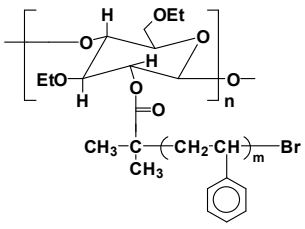
GP-3[219]



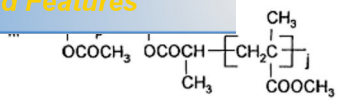
GP-4[220]

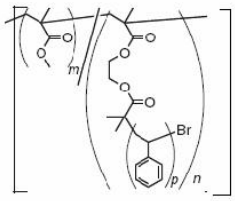


GP-5[221]

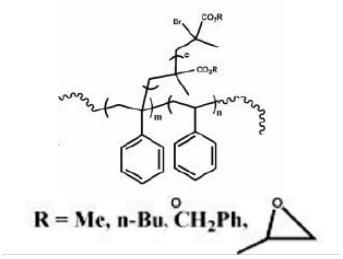


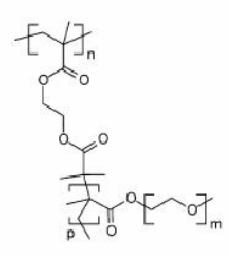
GP-6[221]



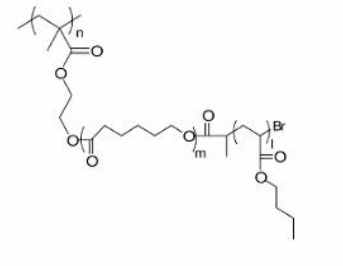


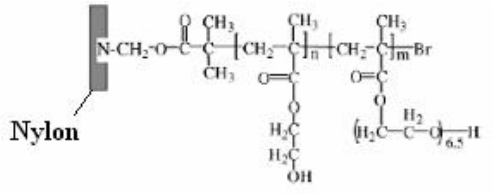
GP-7[222] **GP-8**[223]



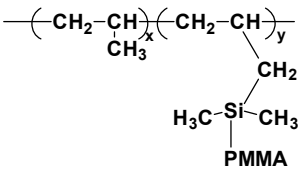


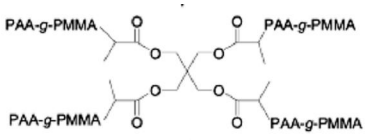
GP-9[213] **GP-10**[224]



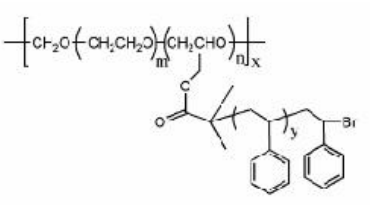


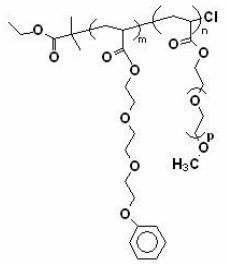
GP-11[225] **GP-12**[226]



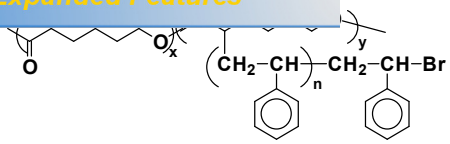


GP-13[227] **GP-14**[228]

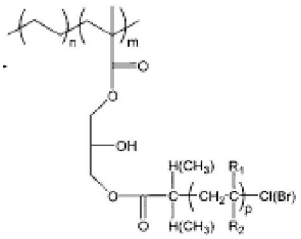




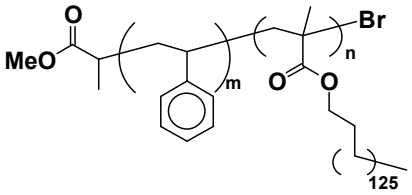
GP-15[229] **GP-16**[230]



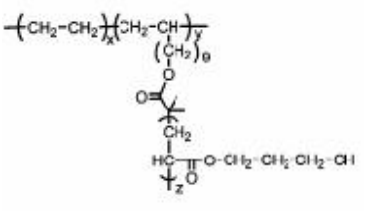
GP-17[231]



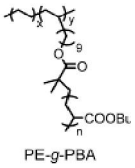
GP-18[232]



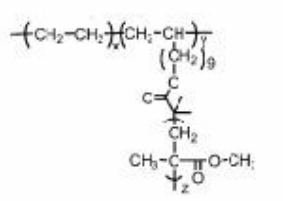
GP-19[233]



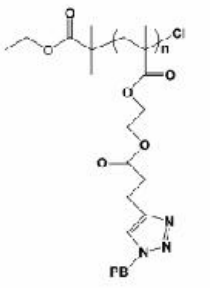
GP-20[234]



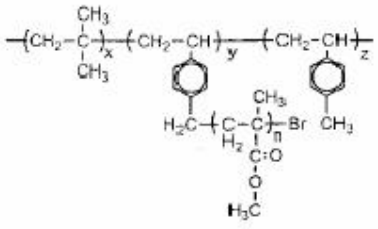
GP-21[235]



GP-22[234]

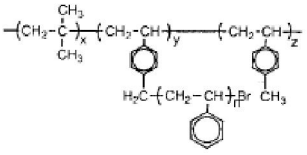


GP-23[235]



GP-24[236]

Polyimide-g-poly(pentaflurostyrene)

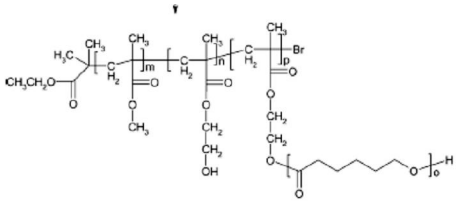


GP-25[237]

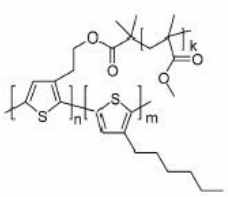
GP-26[236]

styrene)-b-PHEMA **Polyimide-g-PHEMA**

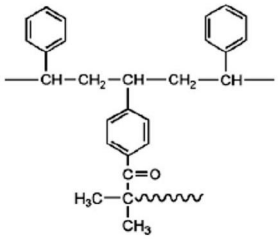
GP-27[237]



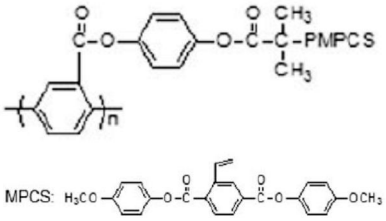
GP-28[237]



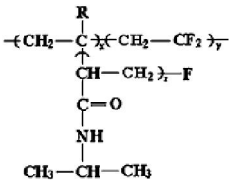
GP-29[238]



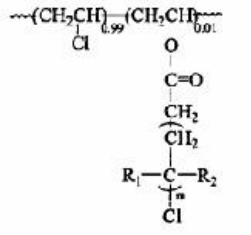
GP-30[206]



GP-31[239]



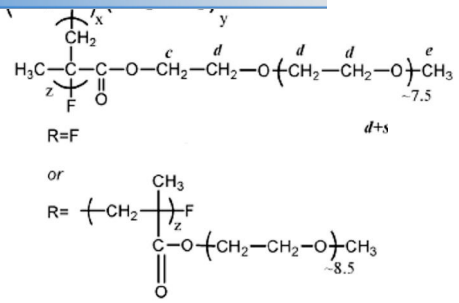
GP-32[240]



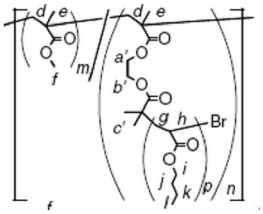
(A) R_1= Ph, R_2=H
(B) R_1= CO_2Me, R_2=H
(C) R_1= CO_2Me, R_2=CH_3
(D) R_1= CO_2Bu, R_2=H

GP-33[241]

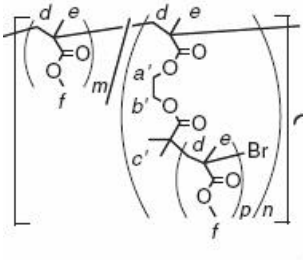
GP-34[242]



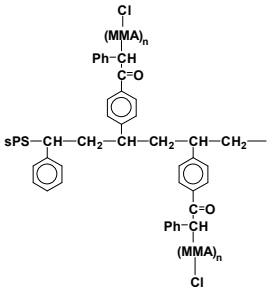
GP-35[243]



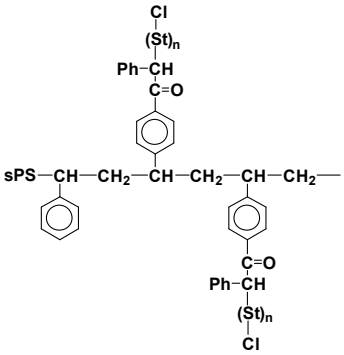
GP-36[244]



GP-37[244]



GP-38[245]



GP-39[245]

Since its discovery in 1994, great progress has been made in various aspects of ATRP. The main advantages of ATRP include versatility toward a variety of monomers, feasibility in a wide range of reaction conditions and relatively easy access to the materials. This permits many researchers to use the system for precision synthesis of various polymers with controlled architectures.

The coming years will undoubtedly be devoted to not only further developments in fundamental research but also to industrial applications of ATRP.

1. K. Matyjaszewski and J. Spanswick, *Materialstoday*, 26, March, **2005**
2. K. Matyjaszewski and T. P. Davis, Editor, ñ*Handbook of Radical Polymerization*ò, Wiley-Interscience Inc., **2002**
3. K. Matyjaszewski and J. Xia, *Chem. Rev*., 101, 2921, **2001**.
4. M. Kamigaito and M. Sawamoto, *Chem. Rev*., 101, 3689, **2001**
5. a) M. K. Georges, *Macromolecules,* 26, 2987, **1993** b) C. J. Hawker, *Chem. Rev*., 101(12), 3661, **2001**
6. V. Sciannamea, R. Jerome and C. Detrembleur, *Chem. Rev.*, ASAP, **2008**
7. M. Kato, M. Kamigaito, M. Sawamoto and T. Higashimura, *Macromolecules*, 28, 1721, **1995**
8. J. S. Wang and K. Matyjaszewski, *J. Am. Chem. Soc*., 117, 5614, **1995**
9. N. V. Tsarevsky and K. Matyjaszewski, *J. Polym. Sci. Part A: Polym. Chem*., 44, 5098, **2006**
10. T. E. Patten and K. Matyjaszewski, *Adv. Mater*.,10, 901, **1998**
11. J. Chiefari, *Macromolecules*, 31, 5559,**1998**
12. H. Fischer, *Chem. Rev*., 101, 3581, **2001**
13. M. S. Kharasch, B. M. Kuderna and W. Urry, *J. Org. Chem*., 13, 895, **1948**
14. D. Greszta, *Macromolecules*, 27, 638, **1994**
15. A. Goto and T. Fukuda, *Prog. Polym. Sci*., 29, 329, **2004**
16. K. Matyjaszewski, T. E. Patten and J. Xia, *J. Am. Chem. Soc*., 119, 674, **1997**
17. F. Simal, A. Demonceau and A. F. Noels, *Tet. Lett*., 40, 5689, **1999**
18. F. Simal, A. Demonceau and A. F. Noels, *Angew. Chem. Int. Ed*., 38, 538, **1999**
19. J. A. M. Brandts, G. P. van de van, E. E. Faassen, J. Boersma and G. Van Koten, *J. Organomet. Chem*., 584, 246, **1999**
20. M. Teodorescu and K. Matyjaszewski, *Macromolecules*, 32, 4826, **1999**
21. T. Ando, M. Kamigaito and M. Sawamoto, *Macromolecules*, 30, 4507, **1997**
22. K. Matyjaszewski, M. Wei, J. Xia and N. E. McDermott, *Macromolecules*, 30, 8161, **1997**
23. C. Granel, P. Dubois, R. Jerome and P. Teyssie, *Macromolecules*, 29, 8576, **1996**
24. H. Uegaki, Y. Kotani, M. Kamigaito and M. Sawamoto, *Macromolecules*, 30, 2249, **1997**

M. Kamigaito and M. Sawamoto, *Macromolecules*, 31, 6756, **1998**

26. V. Percec, B. Barboiu, A. Neumann, J. C. Ronda and M. Zhao, *Macromolecules*, 29, 3665, **1996**
27. D. M. Haddleton, C. B. Jasieczek, M. J. Hannon and A. J. Shooter, *Macromolecules*, 30, 2190, **1997**
28. D. M. Haddleton, D. J. Duncalf, D. Kukulj, M. C. Crossman, S. G. Jackson, S. A. F. Bon, A. J. Clark and A. J. Shooter, *Eur. J. Inorg. Chem.,* 1799, **1998**
29. J. Xia, S. G. Gaynor and K. Matyjaszewski, *Macromolecules*, 31, 5958, **1998**
30. www.chem.cmu.edu/groups/maty/
31. A. Muehlebach, *Polym. Mater. Sci. Eng*. 90, 180, **2004**
32. S. Coca and B. E. Woodworth, *Polym. Mater. Sci. Eng*. 90, 182, **2004**
33. A. Muehlebach and F. Rime, *J. Polym. Sci. Part A: Polym. Chem*. 41, 3425, **2003**
34. C. Auschra, *Eur. Coatings J*. 26, 34, **2004**
35. S. Coca, and B. E. Woodworth, *Polym. Mater. Sci. Eng*. 90, 182, **2004**
36. C. B. Greenberg, PPG Industries, Inc., USA, *US 6,413,581*, **2002**
37. W. A. Braunecker and K. Matyjaszewski, *J. Mol. Cat. A: Chemical,* 254, 155, **2006**
38. M. Kamigaito, T. Ando and M. Sawamoto, *The Chemical Record*, 4, 159, **2004**
39. a) V. Coessens, T. Pintauer and K. Matyjaszewski, *Prog. Polym. Sci*. 26, 337, **2001** b) D. A. Shipp, J. L. Wang and K. Matyjaszewski, *Macromolecules*, 31, 8005, **1998** c) J. D Tong, G. Moineau, P. Leclere, J. L. Bredas, R. Lazzaroni and R. Jerome, *Macromolecules*, 33, 470, **2000** d) P. Leclere, G. Moineau, M. Minet, P. Dubois, R. Jerome, J. L. Bredas and R. Lazzaroni, *Langmuir,* 15, 3915, **1999** e) G. Moineau, M. Minet, P. Teyssie and R. Jerome. *Macromol. Chem. Phys.*, 201, 1108, **2000**
40. K. Matyjaszewski, S. Coca, S. G. Gaynor, M. Wei and B. E. Woodworth, *Macromolecules*, 30, 7348, **1997**
41. K. Matyjaszewski, S. Coca, S. G. Gaynor, M. Wei and B. E. Woodworth, *Macromolecules*, 31, 5967, **1998**
42. D. M. Haddleton, A. J. Clark, M. C. Crossman, D. J. Duncalf, A. M. Heming, S. R. Morsley and A. J. Shooter, *Chem. Commun.*, 1173, **1997**

Kukulj, D. J. Duncalf, A. M. Heming and A. Shooter, *Macromolecules*, 31, 5201, **1998**

44. D. M. Haddleton, A. J. Shooter, A. M. Heming, M. C. Crossman, D. J. Duncalf and S. R. Morsley, ñ*Controlled Radical Polymerization*,ò K. Matyjaszewski, Ed., ACS Symposium Series 685, American Chemical Society, Washington, DC, Chapter 17, 284, **1998**
45. P. F. Rempp and E. Franta, *Adv. Polym. Sci*., 58, 1, **1984**
46. C. Cheng, E. Khoshdel and K. L. Wooley, *Macromolecules*, 38, 9455, **2005**
47. E. J. Goethals, ñ*Telechelic Polymers: Synthesis and Applications*,ò CRC Press, Boca Raton, Florida, **1989**
48. J. C. Brosse, D. Derouet, F. Epaillard, J. C. Soutif, G. Legeay and K. Dusek, *Adv. Polym. Sci*., 81, 167, **1986**
49. J. L. Pradel, B. Boutevin and B. Ameduri, *J. Polym. Sci. Part A: Polym. Chem*., 38, 3293, **2000**
50. J. T. Lai and R. Shea, *J. Polym. Sci. Part A: Polym. Chem*., 44, 4298, **2006**
51. L. Zhang and Y. Chen, *Polymer*, 47, 5259, **2006**
52. V. Lima, X. Jiang, J. Brokken-Zijp, P. J. Schoenmakers, B. Klumperman and R. V. D. Linde, *J. Polym. Sci. Part A: Polym. Chem*., 43, 959, **2005**
53. G. Moad, J. Chiefari, Y. K. Chong, J. Krstina, R. T. A. Mayadunne, A. Postma, E. Rizzardo and S. H. Thang, *Polym. Int.*, 49, 993, **2000**
54. J. Lu, Q. Xu, X. Yuan, X. Xia, J. Zhai, and L. Wang, *J. Appl. Polym. Sci*., 104, 75, **2007**
55. D. M Haddleton, C. Waterson, P. J. Derrick, C. B. Jasieczek and A. J. Shooter, *Chem. Commun.*, 683, **1997**
56. S. H. Yim, J. Huh, C. H. Ahn and T. G. Park, *Macromolecules*, 40, 205, **2007**
57. Z. Yang, J. Lu, S. Yao, and L. Wang *J. Macromol. Sci. Part A, Pure and Appl. Chem.* A41(10), 1105, **2004**
58. X. Zhang and K. Matyjaszewski, *Macromolecules,* 32, 7349, **1999**
59. G. J. Summers, B. M. P. Beebeejaun and C. A. Summers, *Polym. Int.* 49, 722, **2000**
60. X. Zhang and K. Matyjaszewski, *Macromolecules*, 32, 7349, **1999**
61. B. Moon, T. R. Hoye, and C. W. Macosko, *Macromolecules*, 34, 7941, **2001**
62. D. M. Haddleton and C. Waterson, *Macromolecules*, 32, 8732, **1999**

d Y. Yagci, *Macromol. Chem. Phys*., 204, 1771, **2003**

64. A. E. Muftuoglu, I. Cianga, S. Yurteri and Y. Yagci, *J. Appl. Polym. Sci*., 93, 387, **2004**
65. H. Malz, H. Komber, D. Voigt, I. Hopfe and J. Pionteck, *Macromol. Chem. Phys.* 200, 642, **1999**
66. D. Mecerreyes, B. Atthoff, K. A. Boduch, M. Trollsa°s, and J. L. Hedrick, *Macromolecules,* 32, 5175, **1999**
67. C. Liu, R. Bao, J. Qiu, F. HU, Y. Xu, C. Zhao and Y. Zhou, *Polym. Bull*., 57, 139, **2006**
68. A. P. Narrainen, L. R. Hutchings, I. Ansari, R. L. Thompson and N. Clarke, *Macromolecules*, 40, 1969, **2007**
69. C. L. Lin, P. H. Tung and F. C. Chang, *Polymer*, 46, 9304, **2005**
70. Y. Nakagawa and K. Matyjaszewski, *Polym. J.*, 30, 138, **1998**
71. C. Cheng, E. Khoshde and K. L. Wooley, *Macromolecules*, 38(23), **2005**
72. B. Gacal, H. Durmaz, M. A. Tasdelen, G. Hizal, U. Tunca, Y. Yagci and A. L. Demirel, *Macromolecules,* 39, 5330, **2006**
73. J. A. Johnson, D. R. Lewis, D. D. Dḗaz, M. G. Finn, J. T. Koberstein and N. J. Turro, *J. Am. Chem. Soc*., 128, 6564, **2006**
74. W. Agut, D. Taton and S. Lecommandoux, *Macromolecules*, 40, 5653, **2007**
75. K. Matyjaszewski, V. Coessens, Y. Nakagawa, J. Xia, J. Qiu, S. Gaynor, S. Coca and C. Jasieczek, *ACS Symp. Ser*, 704,16, **1998**
76. H. Malz, H. Komber, D. Voigt, I. Hopfe and J. Pionteck, *Macromol. Chem. Phys*., 200, 642, **1999**
77. A. Cuendias, R. Backov, E. Cloutet and H. Cramail, *J. Mater. Chem*., 15, 4196, **2005**
78. S. Alkan, L. Toppare, Y. Hepuzer and Y. Yagci, *J. Polym. Sci. : Part A: Polym. Chem.*, 37, 4218, **1999**
79. D. M. Haddleton and C. Waterson, *Macromolecules*, 32, 8732, **1999**
80. G. J. Summers, M. P. Ndawuni and C. A. Summers, *Polym. Int.,* 52, 158, **2003**
81. A. Postma, T. P. Davis, G. Moad and M. S. O. Shea, *React. Funct. Polym.*, 66, 137, **2006**
82. G. J. Summers, M. P. Ndawuni and C. A. Summers, *J. Polym. Sci. Part A: Polym. Chem.*, 39, 2058, **2001**

raser, *J. Polym. Sci. Part A: Polym. Chem*. 40, 4250, **2002**

84. A. Postma, T. P. Davis, G. Moad, M. S. O. Shea, *React. Funct. Polym.*, 66, 137, **2006**
85. V. B. Sadhu, J. Pionteck, D. Voigt, H. Komber, D. Fischer and B. Voit, *Macromol. Chem. Phys*., 205, 2356, **2004**
86. K. L. Heredia, Z. P. Tolstyka and H. D. Maynard, *Macromolecules*, 40, 4772, **2007**
87. G. Toquer, S. Monge, K. Antonova, C. Blanc, M. Nobili and J. Robin, *Macromol. Chem. Phys*., 208, 94, **2007**
88. G. Carrot, J. Hilborn, J. L. Hedrick and M. Trollsås, *Macromolecules*, 32, 5171, **1999**
89. L. Zhang, Q. Xu, J. Lu, X. Xia and L. Wang, *Eur. Polym. J*. 43, 2718, **2007**
90. D. Bontempo, K. L. Heredia, B. A. Fish and H. D. Maynard, *J. Am. Chem. Soc*., 126, 15372, **2004**
91. W. Agut, D. Taton and S. Lecommandoux, *Macromolecules*, 40, 5653, **2007**
92. A. Zhu, Z. Wang, M. Xie and Y. Zhang, *e-Polymers*, 009, **2007**
93. S. Tarkuc, E. Sahin, L. Toppare, D. Colak, I. Cianga and Y. Yagci, *Polymer*, 47, 2001, **2006**
94. Y. Qin, C. Cui and F. Ja1kle, *Macromolecules*, 40, 1413, **2007**
95. S. Gong, H. Ma and X. Wan, *Polym. Int.* 55, 1420, **2006**
96. A. Marsh, A. Khan, D. M. Haddleton and M. J. Hannon, *Macromolecules*, 32, 8725, **1999**
97. S. Venkataraman and K. L. Wooley, *Macromolecules*, 39, 9661, **2006**
98. J. Zhengneng, L. Jianmei, X. Qingfeng, W. Lihua and X. Xuewei, *e-Polymers*, 006, **2007**
99. L. R. H. High, S. J. Holder and H. V. Penfold, *Macromolecules*, *40,* 7157, **2007**
100. S. Steig, F. Cornelius, A. Heise, R. J. I. Knoop, G. J. M. Habraken, C. E. Koning and H. Menzel, *Macromol. Symp*., 248, 199, **2007**
101. M. Erdogan, Y. Hepuzer, I. Cianga, Y. Yagcē and O. Pekcan, *J. Phys. Chem. A*, 107, 8363, **2003**
102. C. M. Liu, J. Qiu, R. Bao, Y. Xu, X. Cheng and F. Hu, *Polymer*, 47, 2962, **2006**
103. D. P. Curran, *Synthesis,* 417, **1988**
104. V. Coessens and K. Matyjaszewski, *Macromol. Rapid Commun,* 20, 66, **1999**
105. A. M. Kasko, A. M. Heintz and C. Pugh, *Macromolecules,* 31,256, **1998**

Novak, *Macromolecules*, 31, 2391, **1998**

107. V. Coessens, J. Pyun, P. J. Miller, S. G. Gaynor and K. Matyjaszewski, *Macromol. Rapid. Commun.*, 21, 103, **2000**

108. a) V. Coessens, Y. Nakagawa and K. Matyjaszewski, *Polym. Bull.*, 40, 135, **1998** b) L.Li, C. Wang, Z. Long and S. Fu, *J. Polym. Sci. Part A: Polym. Chem*., 38, 4519, **2000** c) V. Coessens and K. Matyjaszewski, *Macromol. Rapid Commun.*, 20, 127, **1999** d) R. Francis, B. Lepoittevin, D. Taton and Yves Gnanou, *Macromolecules,* 35, 9001, **2002**

109. L H. Sperling, ñ*Polymeric Multicomponent Materials*,ò Wiley Interscience Publications, New York, NY, **1997**

110. A. Noshay and J. E. McGrath, ñ*Block Copolymers: Overview and Critical Survey*,ò Academic Press, Inc. New York, NY, **1997**

111. a) N. Hadjichristidis, S. Pispas and G. Floudas, ñ*Block Copolymers: Synthetic Strategies, Physical Properties and Applications*,ò John Wiley and Sons, New Jersey, **2003** b) A. Ruzette and L. Leibler, *Nature Materials*, 4, 19, Jan **2005** c) M. Pitsikalis, S. Pispas, J. W. Mays and N. Hadjichristidis, *Adv. Polym. Sci*., 135, **1998** d) J. F. Lutz, *Polym Int*, 55, 979, **2006** e) V. Butun, S. Liu, J. V. M. Weaver, X. Bories-Azeau, Y. Cai and S. P. Armes, *React. Funct. Polym*., 66, 157, **2006**

112. I. W. Hamley, ñ*Developments in Block Copolymer Science and Technology*,ò John Wiley and Sons, England, **2004**

113. I. Goodman, ñ*Developments in Block Copolymers –1*,ò Applied Science, London, **1982**

114. I. Goodman, ñ*Developments in Block Copolymers –2*,ò Elsevier Applied Science, London, **1985**

115. I. W. Hamley, ñ*The Physics of Diblock Copolymers*,ò Oxford, New York, **1998**

116. G. Riess, G. Hurtrez, and P. Bahadur, ñ*Encyclopedia of Polymer Science and Engineering*,ò edited by H. F. Mark and J. I. Kroschwitz, Wiley, New York, Vol. 2, 324, **1985**

117. G. Riess and C. Labbe, *Macromol. Rapid Commun*., 25, 401, **2004**

118. a) H. L. Hsieh and R. P. Quirk, ñ*Anionic Polymerization: Principles and Practical Applications*,ò Marcel Dekker, Inc., New York, **1996** b) M. Szwarc, *J. Am. Chem. Soc*., 78, 2656, **1956** c) R. P. Quirk, D. J. Kinning and L. J. Fetters, ñ*Block Copolymers: Comprehensive Polymer Science 7"*, Oxford: Pergamon Press; 1,

uss and P. A. Dreyfuss, *Polymer*, 6, 93, **1965** e) T. Higashimura, M. Mitsuhashi and M. Sawamoto, *Macromolecules*, 12, 178, **1979** f) B. Charleux and R. Faust, *Adv Polym Sci,* 142, 1, **1999**

119. S. M. Timol and D. Jhurry, *Eur. Polym. J*., 43, 3042, **2007**
120. R. Shunmugam, C. E. Smith and G. N. Tew, *J. Polym. Sci. Part A: Polym. Chem*., 45, 2601, **2007**
121. H. Q. Xie and D. Xie, *Prog. Polym. Sci*., 24, 275, **1999**
122. M. Teodorescu, M. Dimonie, C. Draghici and G. Vasilievici, *Polym. Int*., 53, 1987, **2004**
123. J. H. Truelsen, J. Kops, W. Batsberg and S. P. Armes, *Macromol. Chem. Phys*., 203, 2124, **2002**
124. G. Riess and C. Labbe, *Macromol. Rapid. Commun*., 25, 401, **2004**
125. C. J. Brinker and Y. Lu, *Adv. Mater*. 11, 579, **1999**
126. J. R. Hernandez and S. Lecommandoux, *Prog. Polym. Sci*, 30, 691, **2005**
127. G. Riess, *Prog. Polym. Sci*., 28, 1107, **2003**
128. Y. Kotani, M. Kato and M Sawamoto, *Macromolecules*, 29, 6979, **1996**
129. S. Zhu and D. Yan, *J. Polym. Sci. Part A: Polym. Chem*. 38, 4308, **2000**
130. D. A. Shipp and J. L. Wang, *Macromolecules*, 31, 8005, **1998**
131. Y. Liu, L.X. Wang and C.Y. Pan, *Macromolecules*, 32, 8301, 1999
132. B. Liu and C. P. Hu, *Eur. Polym. J*., 37, 2025, **2001**
133. Z. Zhang, S. K. Ying and Z. Shi, *Polymer*, 40, 5439, **1999**
134. K. Jankova, X. Chen, J. Kops and W. Batsberg, *Macromolecules,* 31, 538, **1998**
135. H. Reuter, I. V. Berlinova, S.Ho¨ring and J. Ulbricht, *Eur. Polym. J*., 27, 673, **1991**
136. T. Suzuki, Y. Murakami and Y. Takegami, *Polym. J*. (Tokyo), 12, 183, **1980**
137. a) A. H. E. Mu¨ller, ó*Recent Advances in Anionic Polymerization*ô, Elsevier, New York, 205, **1987** b) B. Reining, H. Keul and H. Hocker, *Polymer*, 43, 3139, **2002**
138. K. Ishizu, M. Makino and S. Uchida, *Macromol. Rapid Commun*., 28, 882, **2007**
139. X. Sun, H. Zhang, L. Zhang, X. Wang and Q. F. Zhou, *Polym. J*., 37, 102, **2005**
140. N. Karanikolopoulos, M. Pitsikalis and N. Hadjichristidis, *Langmuir*, 23, 4214, **2007**
141. D. M. Xu, K. D. Zhang and J. F. Wu, *J. Appl. Polym. Sci*., 101, 727, **2006**
142. K. Jankova, X. Chen, J. Kops and W. Batsberg, *Macromolecules,* 31, 538, **1998**

B. L. Fgren and J. S. La, *J. Polym. Sci. Part A: Polym. Chem*. 43, 5049, **2005**

144. H. Yu, A. Shishido, T. Ikeda and T. Iyoda1, *Macromol. Rapid Commun*., 26, 1594, **2005**
145. R. Krishnan, ñ*Kinetics, Synthesis and Characterization of Homo and Block Copolymers by Atom Transfer Radical Polymerization*,ò Ph.D. Thesis, University of Madras, **2004**
146. K. R.M. Vidts and F. E. D. Prez, *Eur. Polym. J*. 42, 43, **2006**
147. D. J. Adams, M. F. Butler and A. C. Weaver, *Langmuir,* 22, 4534, **2006**
148. Y. Cai and S.P. Armes, *Macromolecules*, 38, 271, **2005**
149. Y. Cai and S.P. Armes, *Macromolecules,* 37, 7116, **2004**
150. X. Suna, H. Zhanga, X. Huanga, X. Wanga and Q. F. Zhou, *Polymer*, 46, 5251, **2005**
151. S. Mahajan, S. Renker, P. F. W. Simon, J. S. Gutmann, A. Jain, S. M. Gruner, L. J. Fetters, G. W. Coates and U. Wiesner, *Macromol. Chem. Phys*., 204, 1074, **2003**
152. K. Xu, Y. Wang, R. Bai, W. Lu and C. Pan, *Polymer*, 46, 7572, **2005**
153. R. B. Grubbs, *Macromol. Chem. Phys*., 206, 625, **2005**
154. C. Giacomelli, V. Schmidt and R. Borsali, *Macromolecules*, 40, 2148, **2007**
155. S. Mahajan, B. K. Cho, J. Allgaier, L. J. Fetters, G. W. Coates and U. Wiesner, *Macromol. Rapid. Commun*., 25, 1889, **2004**
156. G. Deng, D. Ma and Z. Xu, *Eur. Polym. J*., 43, 1179, **2007**
157. X. Tang, L. Gao, X. Fan and Q. Zhou, *J. Polym. Sci. Part A: Polym. Chem*., 45, 2225, **2007**
158. Y. Ma, Y. Tang, N. C. Billingham and S. P. Armes, *Macromolecules*, 36, 3475, **2003**
159. K. L. Robinson, M. V. de Paz-Ba´nëez, X. S. Wang, and S. P. Armes, *Macromolecules*, 34, 5799, **2001**
160. R. N. and S. P. Armes, *Biomacromolecules*, 4, 1746, **2003**
161. J. H. Truelsen, J. Kops, W. Batsberg and S. P. Armes, *Macromol. Chem. Phys*., 203, 2124, **2002**
162. H. Hussain, H. Budde, S. Ho¨ring, K. Busse and J. Kressler, *Macromol. Chem. Phys*., 203, 2103, **2002**
163. X. He, H. Zhang and X. Wang, *Polym. J*., 34, 523, **2002**

. Talmon, M. A. Hillmyer and T. P. Lodge, *Science*, 306, 98, **2004**

165. O. Glaied, C. Delaite and P. Dumas, *J. Polym. Sci. Part A: Polym Chem*., 45, 4179, **2007**
166. H. Gao, K. Min and K. Matyjaszewski, *Macromol. Chem. Phys*., 208, 1370, **2007**
167. X. Yu, G. Zhang, T. Shi, Y. Han and L. An, *Polymer*, 48, 2489, **2007**
168. X. Yu, T. Shi, G. Zhang and L. An, *Polymer*, 47, 1538, **2006**
169. S. Hou, E. L. Chaikof, D. Taton and Y. Gnanou, *Macromolecules,* 36, 3874, **2003**
170. A. A. Farah, N. Hall, S. Morin and W. J. Pietro, *Polymer*, 47, 4282, **2006**
171. T. He, D. Li, X. Sheng and B. Zhao *Macromolecules,* 37, 3128, **2004**
172. M. J. Stewart, ñ*New Methods of Polymer Synthesis*,ò J. R. Ebdon, Blackie, London, 107, **1991**
173. C. J. Hawker, J. L. Hedrick, E.E. Malmstrom, M. Trollsas, D. Mecerreyes, G. Moineau, Ph. Dubois and R. Jerome, *Macromolecules,* 31, 213, **1998**
174. B. As, A. R.A. Palmans, A. Heise and E. W. Meijer, *Polym. Prepr.*, 44, 615, **2003**
175. U. Meyer, A. R.A. Palmans, T. Loontjens and A. Heise, *Macromolecules*, 35, 2873, **2002**
176. A. A. Farah, N. Hall, S. Morin and W. J. Pietro, *Polymer*, 47, 4282, **2006**
177. A. P. Smith and C. L. Fraser, *Macromolecules*, 35, 594, **2002**
178. R. M. Ho, T. C. Wang, C. C. Lin and T. L. Yu, *Macromolecules*, 40, 2814, **2007**
179. K. Sha, D. Li, S. Wang, L. Qin and J. Wang, *Polym. Bull*., 55, 349, **2005**
180. X. He, L. Liang, M. Xie, Y. Zhang, S. Lin and D. Yan, *Macromol. Chem. Phys*., 208, 1797, **2007**
181. S. M. Timol and D. Jhurry, *Eur. Polym. J*., 43, 3042, **2007**
182. J. Zhou, S. Villarroya, W. Wang, M. F. Wyatt, C. J. Duxbury, K. J. Thurecht and S. M. Howdle, *Macromolecules*, 39, 5352, **2006**
183. U. Meyer, A. R. A. Palmans, T. Loontjens and A. Heise, *Macromolecules*, 35, 2873, **2002**
184. G. Deng, L. Zhang, C. Liu, L. He and Y. Chen, *Eur. Polym. J*., 41, 1177, **2005**
185. N. Hadjichristidis, *J. Polym. Sci. Part A: Polym. Chem.*, 37, 857, **1999**
186. K. Ishizu and S. Uchida, *Prog. Polym. Sci.*, 24, 1439, **1999**
187. N. Hadjichristidis, M. Pitsikalis, S. Pispas and H. Iatrou, *Chem Rev*, 101, 3747, **2001**

and B. Zhao, *Macromolecules*, 37, 3128, **2004**

189. K. Van Butsele, F. Stoffelbach, R. Je´roÊme, and C. Je´roÊme, *Macromolecules*, 39, 5652, **2006**
190. O. Glaied, C. Delaite and P. Dumas, *J. Polym. Sci. Part A: Polym. Chem*., 44, 1796, **2006**
191. W. Yuan, X. Huang and X. Tang, *Polym. Bull*. 55, 225, **2005**
192. T. He, D. Li, X. Sheng and B. Zhao, *Macromolecules*, 37, 3128, **2004**
193. K. V. Butsele, F. Stoffelbach, R. Je´roÊme, and C. Je´roÊme, *Macromolecules*, 39, 5652, **2006**
194. S. G. An, G. H. Li and C. G. Cho, *Polymer*, 47, 4154, **2006**
195. O. Altintas, B. Yankul, G. Hizal and U. Tunca, *J. Polym. Sci. Part A: Polym. Chem*., 45, 3588, **2007**
196. A. Heise, Mikael Trollsa°s, T. Magbitang and J. L. Hedrick, C. W. Frank and R. D. Miller, *Macromolecules*, 34, 2798, **2001**
197. J. L. Hedrick, M. Trollsås, C. J. Hawker, B. Atthoff, H. Claesson, A. Heise, and R. D. Miller, *Macromolecules*, 31, 8691, **1998**
198. H. G. Borner and K. Matyjaszewski, *Macromol. Symp*., 177, 1, **2002**
199. A. Bhattacharya and B. N. Misra, *Prog. Polym. Sci.*, 29, 767, **2004**
200. K.A. Davis and K. Matyjaszewski, *Adv. Polym. Sci*., 159, 107, **2002**
201. P. F. Rempp and P. J. Lutz, ñ*Comprehensive Polymer Science*,ò Editors - G. Allen, J. C. Evington, Pergamon Press, Oxfors, Vol- 6, 403, **1989**
202. S. G. Roos, A. H. E. Muller, M. Kaufmann, W. Siol and C. Auschra, *ACS Symp. Ser*. 696, 209, **1998**
203. H. G. Borner and K. Matyjaszewski, *Macromol. Symp*. 177, 1, **2002**
204. M. Pitsikalis, S. Pispas, J. W. Mays, N. Hadjichristidis, *Adv. Polym. Sci*., 135, 1, **1998**
205. Y. Inoue, T. Matsugi, N. Kashiwa and K. Matyjaszewski, *Macromolecules*, 37, 3651, **2004**
206. K. H. Kim and W. H. Jo, *Macromolecules*, 40, 3708, **2007**
207. S. P. Gido, C. Lee, D. J. Pochan, S. Pispas, J. W. Mays and N. Hadjichristidis, *Macromolecules*, 29, 7022, **1996**
208. G. Odian, ñ*Principles of Polymerization*,ò 3rd editon. New York, John Wiley and Sons, Inc., **1991**

atyjaszewski, *Macromol. Symp*. 177, 1, **2002**

210. S. C. Hong, T. Pakula and K. Matyjaszewski, *Macromol. Chem. Phys*., 202, 3392, **2001**
211. D. Shen, H. Yu and Y. Huang, *J. Polym. Sci. Part A: Polym. Chem*., 43, 4099, **2005**
212. F. G. Garcia, M. R. Pinto and B. G. Soares, *Eur. Polym. J*., 38, 759, **2002**
213. A. V. Vivek and R. Dhamodharan, *J. Polym. Sci. Part A: Polym. Chem*., 45, 3818, **2007**
214. D. M. Haddleton, S. Perrier and S. A. F. Bon, *Macromolecules*, 33, 8246, **2000**
215. X. S. Wang, F. L. G. Malet, S. P. Armes, D. M. Haddleton and S. Perrier, *Macromolecules*, 34, 162, **2001**
216. S. Perrier, S. P. Armes, X. S. Wang, F. L. G. Malet and D. M. Haddleton, *J. Polym. Sci., Part A: Polym. Chem.*, 39, 1696, **2001**
217. D. Neugebauer, Y. Zhang, T. Pakula, S. S. Sheiko and K. Matyjaszewski, *Macromolecules*, 36, 6746, **2003**
218. K. Ishizu and H. Yamada, *Macromolecules*, 40, 3056, **2007**
219. H. Kaneyoshi and K. Matyjaszewski, *J. Polym. Sci. Part A: Polym. Chem*. 45, 447, **2007**
220. X. Tang, L. Gao, X. Fan and Q. Zhou, *J. Polym. Sci. Part A: Polym. Chem*., 45, 1653, **2007**
221. D. Shen, H. Yu and Y. Huang, *J. Polym. Sci. Part A: Polym. Chem*., 43, 4099, **2005**
222. F. G. Garcia, M. R. Pinto and B. G. Soares, *Eur. Polym. J*., 38, 759, **2002**
223. Y. Miura, K. Satoh, M. Kamigaito and Y. Okamoto, *Polym. J*., 38(9), 930, **2006**
224. L. He, J. Huang, Y. Chen, X. Xu and L. Liu, *Macromolecules*, 38, 3845, **2005**
225. H. Lee, W. Jakubowski, K. Matyjaszewski, S. Yu and S. S. Sheiko, *Macromolecules*, 39, 4983, **2006**
226. F. J. Xu, J. P. Zhao, E. T. Kang, K. G. Neoh and J. Li, *Langmuir*, 23, 8585, **2007**
227. H. Li, H. Zhao, X. Zhang, Y. Lu and Y. Hu, *Eur. Polym. J*., 43, 109, **2007**
228. D. Peng, X. Zhang and X. Huang, *Macromolecules*, 39, 4945, **2006**
229. P. Li, Z. Li and J. Huang, *Polymer*, 48, 1557, **2007**
230. D. Neugebauer, Y. Zhang and T. Pakula, *J. Polym. Sci. Part A: Polym. Chem*., 44, 1347, **2006**

Fua, W. Yanga, Q. Huanga and Y. Zhang, *Polymer*, 46, 10601, **2005**

232. K. Matyjaszewski, M. Teodorescu, P. J. Miller and M. L. Peterson, *J. Polym. Sci. Part A: Polym. Chem*., 38, 2440, **2000**
233. H. Kaneyoshi and K. Matyjaszewski, *J. Appl. Polym. Sci*., 105, 3, **2007**
234. Y. Inoue, T. Matsugi, N. Kashiwa and K. Matyjaszewski, *Macromolecules*, 37, 3651, **2004**
235. H. Gao and K. Matyjaszewski, *J. Am. Chem. Soc.,*129, 6633, **2007**
236. S. C. Hong, T. Pakula and K. Matyjaszewski, *Macromol. Chem. Phys*., 202, 3392, **2001**
237. F. J. Xu, J. P. Zhao, E. T. Kang, and K. G. Neoh, *Ind. Eng. Chem. Res.*, 46, 4866, **2007**
238. S. Villarroya, J. Zhou, K. J. Thurecht and S. M. Howdle, *Macromolecules*, 39, 9080, **2006**
239. Y. Gao, H. Li and X. Wang, *Eur. Polym. J*., 43, 1258, **007**
240. L. Sun, X. Fan, X. Chen, X. Liu and Q. Zhou, *J. Polym. Sci. Part A: Polym. Chem*., 45, 2543, **2007**
241. W. Wang and L. Chen, *J. Appl. Polym. Sci*., 104, 1482, **2007**
242. H. Paik, S. G. Gaynor and K. Matyjaszewski, *Macromol. Rapid Commun*., 19, 47, **1998**
243. J. F. Hester, P. Banerjee, Y.Y. Won, A. Akthakul, M. H. Acar, and A. M. Mayes, *Macromolecules*, 35, 7652, **2002**
244. Y. Miura, K. Satoh, M. Kamigaito and Y. Okamoto, *Polym. J*., 38, 930, **2006**
245. M. Abbasian, S. Rahmani, R. Mohammadi and A. A. Entezami, *J. Appl. Polym. Sci*., 104, 611, **2007**

Controlled synthesis of polymers with well-defined end groups and various architectures continues to be a synthetic challenge in polymer chemistry. End-functionalized polymers are of interest due to their utility as building blocks for synthesis of block copolymers, graft copolymers, star-branched and networked structures. [1-4] These polymers have potential applications in areas such as surface modification, coatings, adhesives, as well as compatibilization of polymer blends.[5,6]

Copolymers such as block and graft are very promising materials for widespread applications due to their self-assembly properties,[7] either in the solid state or in a selective solvent of one block,[8] which provides a great variety of morphologies in the nanometer size range.[9-13] The multifaceted role played by these materials make them useful as compatibilizers, viscosity modifiers, dispersants to stabilize colloidal suspensions, nanocarriers for the encapsulation[14-15] and controlled release of drugs and templates for mineralization and supports for catalysis.[16-18] These polymers also find many applications in areas such as thermoplastics,[19,20] associative polymers containing a hydrophilic and a hydrophobic segments, etc.[10-12] One of the most important applications of block copolymers at the industrial scale is their use as surfactants in pharmaceutical, oil, agriculture, paper and detergent industries.[21]

A wide range of controlled polymerization techniques are available for synthesis end-functionalized polymers.[10,21-24] During the past decade, ATRP has been developed as one of the most successful controlled polymerization techniques to polymerize styrene or substituted styrenes, (meth)acrylates and a variety of other monomers, yielding polymers with predetermined molecular weight and narrow molecular weight distribution.[22-27] There are several advantages of ATRP over other controlled polymerization methods such reversible-addition fragmentation termination (RAFT),[28] nitroxide mediated (NMP),[29,30] anionic,[31-33] cationic[34] and group transfer polymerization (GTP).[35] One of the most important advantages of ATRP is tolerance of functionality on monomer leading to polymers with functionalities along the chains. By using functionalized initiators, polymers with functionalities such as carboxyl,[36-38] hydroxyl,[39] nitro,[40] phenol,[41] epoxide,[42] etc., at one chain end and halide at the other chain end have been synthesized. The halide end group of polymers obtained *via* ATRP can be transformed to other

philic substitution reactions or electrophilic addition reactions.[26]

The overall goal of the present research was to design and synthesize functionalized ATRP initiators, end-functionalized polymers and copolymers (block and graft copolymers).

The following specific work was undertaken for the present thesis.

1. To design and synthesize new ATRP initiators containing various functional groups such as hydroxyl, carboxyl, lactone, cyclic carbonate, nitro and sulphonic acid.
2. To utilize functionalized ATRP initiators for the synthesis of end-functionalized polymers viz., hydroxyl-terminated polystyrene, dihydroxyl-terminated poly(lauryl methacrylate) (PLMA), bismethylol-terminated poly(methyl methacrylate) (PMMA), bismethylol-terminated poly(lauryl methacrylate) (PLMA), lactone-terminated polystyrene and cyclic carbonate-terminated PMMA.
3. Utilization of synthesized end-functionalized polymers for the synthesis of poly(styrene-*block*-poly(ε-caprolactone)) (PS-*b*-PCL) and poly(methyl methacrylate)-*block*-[poly(ε-caprolactone)]$_2$ [PMMA-*b*-(PCL)$_2$] AB$_2$ type mikto arm star copolymer starting from hydroxyl-terminated polystyrene and bismethylol-terminated PMMA, respectively *via* ring opening polymerizations of ε-caprolactone.
4. Synthesis and characterization of poly(ethylene oxide)-*block*-poly(lauryl methacrylate) (PEO-*b*-PLMA) utilizing macroinitiators derived from commercially available monomethoxy poly(ethylene glycol)s of varying molecular weight (M_n- 350, 700, 2000 and 5000).
5. Synthesis and characterization of poly(lauryl methacrylate)-*block*-poly(ethylene oxide)-*block*-poly(lauryl methacrylate) (PLMA-*b*-PEO-*b*-PLMA) copolymer utilizing difunctional macroinitiator derived from poly(ethylene glycol).
6. Synthesis and characterization of graft copolymers namely, poly(lauryl methacrylate)-*graft*-poly(ethylene oxide) (PLMA-*g*-PEO), poly(ε-caprolactone)-*graft*-poly(methyl methacrylate) (PCL-*g*-PMMA) and

poly(lauryl methacrylate) (PU-*g*-PLMA) using a combination of polymerization techniques.

7. Utilization of PEO-*b*-PLMA, PLMA-*g*-PEO, dihydroxyl-terminated PLMA and bismethylol-terminated PLMA as steric stabilizers in preparation of polyurethane microspheres.

1. Y. Zhang, S. Guo, C. Lu, L. Liu, Z. Li, and J. Gu, *J. Polym. Sci. Part A: Polym. Chem*., 45, 605, **2007**
2. H. Wang, X. Chen and C. Y. Pan, *Eur. Polym. J*., 43, 1905, **2007**
3. A. O. Patil, D. N. Schulz and M. Novak, ñ*Functional Polymers: Modern Synthetic Methods and Novel Structures*ò, ACS Symposium Series 704; American Chemical Society: Washington, DC, **1998**
4. R. P. Quirk, J. J. Ma, G. Lizarraga, Q. Ge, H. Hasegawa, Y. J. Kim, S. H. Jang and Y. Lee, *Macromol. Symp*. 37, 161, **2000**
5. P. F. Rempp and E. Franta, *Adv. Polym. Sci*., 58, 1, **1984**
6. C. Cheng, E. Khoshdel and K. L. Wooley, *Macromolecules*, 38, 9455, **2005**
7. D. Wang, Z. Peng, X. Liu, Z. Tong, C. Wang and B. Ren, *Eur. Polym. J.,* 43, 2799, **2007**
8. V. Butun, S. Liu, J. V. M. Weaver, X. Bories-Azeau, Y. Cai and S. P. Armes, *React. Funct. Polym.*, 66, 157, **2006**
9. Hamley, I. W. ñ*The Physics of Block Copolymers*,ò Oxford Science, Publication: Oxford, U.K., **1998**
10. N. Hadjichristidis, S. Pispas and G. A. Floudas, ñ*Block Copolymers: Synthetic Strategies, Physical Properties, and Applications*;ò Wiley- Interscience, John Wiley & Sons, Inc. Publication: New York, **2003**
11. X. Tang, Y. Hu and C. Pan, *Polymer*, 48, 6354, **2007**
12. D. J. Siegwart, W.Wu, M. Mandalaywala, M. Tamir, T. Sarbu, M. S. Silverstein, T. Kowalewski, J. O. Hollinger and K. Matyjaszewski, *Polymer*, 48, 7279, **2007**
13. G. Riess, *Prog. Polym. Sci*, 28, 1107, **2003**
14. N. Karanikolopoulos, M. Pitsikalis and N. Hadjichristidis, *Langmuir*, 23, 4214, **2007**
15. C. Giacomelli, V. Schmidt and R. Borsali, *Macromolecules,* 40, 2148, **2007**
16. T. P. Lodge, *Macromol. Chem. Phys.*, 204, 265, **2003**
17. H. A. Klok and S. Lecommandoux, *Adv. Mater*, 13, 1217, **2001**
18. M. Lazzari and G. Liu, Lecommandoux, ñ*Block Copolymers in Nanoscience*,ò Wiley-VCH Verlag GmbH & Co., KgaA, Weinheim, Germany, **2006**
19. D. P. Chatterjee and B. M. Mandal, *Macromol. Symp*., 240, 224, **2006**

I. Kamigaito, Y. Okamoto, T. Kaneko, H. Jinnai and S. Kobukata, *Macromolecules*, 40, 465, **2007**

21. I. W. Hamley, *"Developments in Block Copolymer Science and Technology,"* New York: Wiley, **2004**
22. K. Matyjaszewski and J. Spanswick, *Mater. Today*, 26, March, **2005**
23. K. Matyjaszewski, and J. Xia, *Chem. Rev*., 101, 2921, **2001**
24. M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev.*, 101, 3689, **2001**
25. W. A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci*., 32, 93, **2007**
26. V. Coessens, T. Pintauer and K. Matyjaszewski, *Prog. Polym. Sci*., 337, 26, **2001**
27. K. Matyjaszewski, *Chem. Eur. J*., 5, 3095, **1999**
28. C. L. Moad, *Macromolecules*, 29, 7717, **1996**
29. M. K. Georges, *Macromolecules*, 26 2987, **1993**
30. C. J. Hawaker, *Chem. Rev*. 101, 3661, **2001**
31. H. L. Hsieh and R. P. Quirk, ñ*Anionic Polymerization: Principles and Practical Applications*,ò New York, Marcel Dekker Inc. **1996**
32. D. Baskaran, *Prog. Polym. Sci*., 28, 521, **2003**
33. G. Mahua, ñ*Controlled Polymerizations of Alkyl (meth)acrylates*ò, Ph.D. thesis, University of Pune, Pune, India, **2002**
34. M. Sawamoto, ñ*Cationic Polymerization*,ò Ed- K. Matyjaszewski, Marcel Dekker: New York, 412, **1996**
35. O. W. Webster and D. Y. Sogah, ñ*Recent Advances in Mechanistic and Synthetic Aspects of Polymerization"*, 3, **1987**
36. X. Zhang and K. Matyjaszewski, *Macromolecules,* 32, 7349, **1999**
37. H. Malz, H. Komber, D. Voigt, I. Hopfe and J. Pionteck, *Macromol. Chem. Phys*. 200**,** 642, **1999**
38. G. J. Summers, B. M. Parveen, and C. A. Summers, *Polym Int.* 49, 1722, **2000**
39. D. M. Haddleton, C. Waterson, P. J. Derrick, C. B. Jasieczek and A. J. Shooter *Chem. Commun.*, 683, **1997**
40. D. M. Haddleton and C. Waterson, *Macromolecules*, 32, 8732, **1999**
41. S. Yurteri, I. Cianga and Y. Yagci, *Macromol. Chem. Phys*., 204, 1771, **2003**
42. K. Matyjaszewski, V. Coessens, Y. Nakagawa, J. Xia, J. Qiu, S. Gaynor, S. Coca and C. Jasieczek, *ACS Symp. Ser.*, *704*,16, **1998**

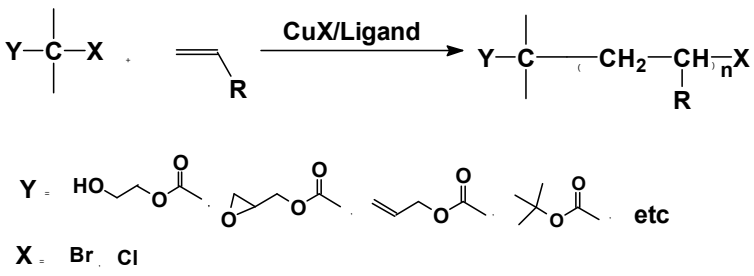
. M. Haddleton and M. J. Hannon, *Macromolecules*, 32, 8725, **1999**

3.1 Introduction

Atom transfer radical polymerization (ATRP) has emerged as one of the most powerful synthetic techniques in polymer science. Similar to well established living polymerization methods such anionic, cationic, etc, ATRP allows synthesis of (co)polymers with predetermined molecular weight, narrow molecular weight distribution and desired composition.[1,2] Moreover, with the help of functional ATRP initiators it is possible to obtain polymers with well-defined end groups.[3]

The initiator is a very important component in ATRP due to its key role in controlling the molecular weight as well as rate of initiation. The amount of initiator determines molecular weight of the polymer and its efficiency determines the number of chains initiated. In the initiation step, the transition metal complex abstracts halogen from the organic halide (RX), creating a radical R· that adds to double bond of the monomer and the sequence continues.[4] Structural adjustment of the alkyl part R and the leaving group X in order to make the R-X bond more labile than the propagating polymer-X bond provides a handle to fine-tune the rate of initiation in ATRP system. Also, incorporation of the alkyl group R at one chain end and halogen at the other chain end provides a route to synthesize end-functional polymers using initiators containing functional groups **(Scheme 1)**.

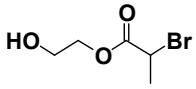
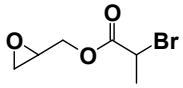
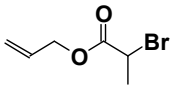
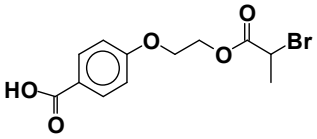
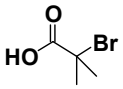
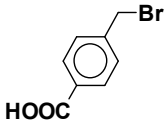
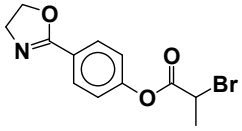
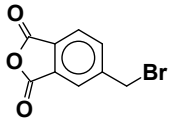
A variety of initiators such as haloesters, haloalkyl benzenes, haloalkanes, sulphonyl halides, etc. have been used successfully for ATRP.[1,2] Benzyl substituted halides are useful initiators for polymerization of styrene and styrene derivatives due to their structural resemblance, while, haloesters are useful for acrylates, methacrylates as well as for styrenes. [1,2]



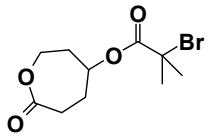
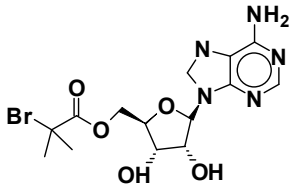
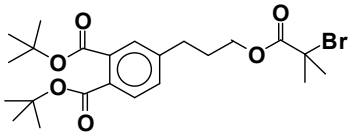
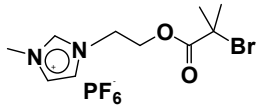
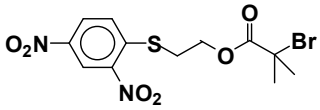
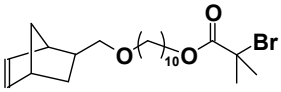
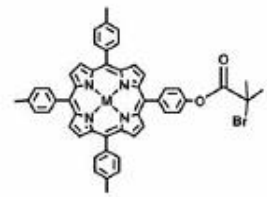
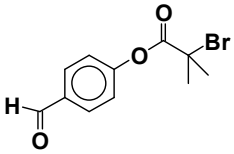
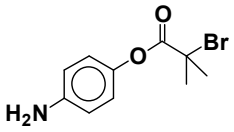
Scheme 3.1: Approach to synthesize end-functionalized polymers by ATRP

...e tolerance of ATRP for functional groups, a variety of functionalized initiators containing hydroxyl[5], adenosine[6], carboxyl[7], amine[8], allyl[9], thiophene[10], oxazoline[11], pyrene[12], bipyridine[13,14,] aldehyde[8] N,N-dimethylaniline[15] norbornenyl[16], epoxy[17], anhydride[11], lactone[18], etc., have been synthesized and used for preparation of end functionalized polymers. Selected functionalized ATRP initiators employed for synthesis of end-functionalized polymers are presented in **Table 3.1.**

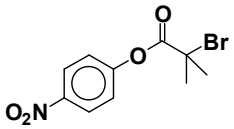
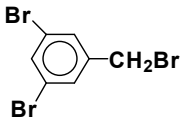
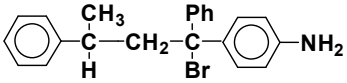
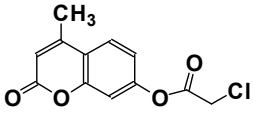
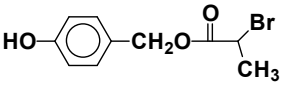
Table 3.1: Selected functionalized ATRP initiators

Sr. No.	Functionalized initiator	Monomers polymerized
1		MMA, styrene[5]
2		MMA, stryene[17]
3		MMA, styrene[9]
4		Styrene[7]
5		Styrene[7]
6		Styrene[9]
7		Stryene[8]
8		Styrene[19]

RP initiators……..continued

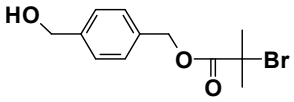
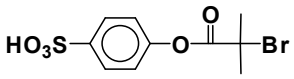
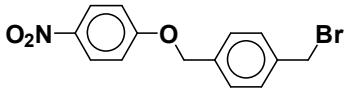
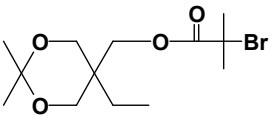
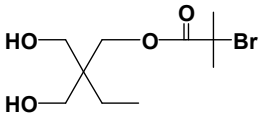
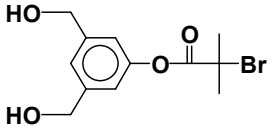
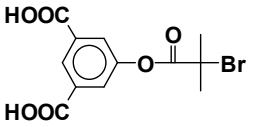
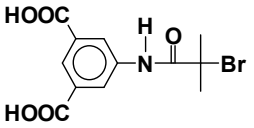
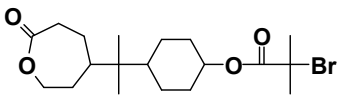
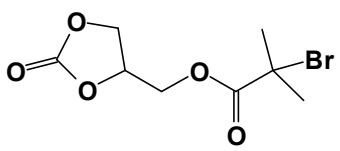
10		MMA[18]
11		MMA[6]
12		MMA, styrene[20]
13		MMA[21]
14		t-BA, mPEGMA[22]
15		Styrene, MMA, t-BMA[16]
16		Styrene[23]
17		MMA[8]
18		MMA[8]

RP initiators……..continued

19		MMA[8]
20		Styrene[24]
21		Styrene[8,25]
22		Styrene[26]
23		Styrene[27]

with synthesis and characterization of following ten functionalized ATRP initiators **(Table 3.2)**.

Table 3.2: Functionalized ATRP initiators synthesized

1	4-(Hydroxymethyl)benzyl-2-bromo-2-methylpropanoate **(HMBMP)**	
2	4-(2-Bromo-2-methylpropanoloxy) benzenesulfonic acid **(BMPBSA))**	
3	4-[(4ô-Nitro) phenoxymethyl] benzyl bromide **(NPMBB)**	
4	5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl-2-bromo-2-methylpropanoate) **(EDMBMP)**	
5	2,2-Bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate **(BHMBMP)**	
6	3,5-Bis(hydroxymethyl)phenyl-2-bromo-2-methylpropanoate **(BHMPBMP)**	
7	5-(2-Bromo-2-methylpropanoyloxy) isophthalicacid **(BMPIPA)**	
8	5-(2-Bromo-2-methylpropanamido) isophthalicacid **(BMPAIPA)**	
9	4-[2-(7-Oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(OPCBMP)**	
10	2-Oxo-1,3-dioxolan-4-yl-(methyl-2-bromo-2-methylpropanoate) **(ODMBMP)**	

3.2.1 Materials

1,4-Bis(bromomethyl) benzene, sodium 4-hydroxybenzenesulfonate, 1,4-benzene dimethanol, 5-hydroxy isophthalic acid, 5-amino isophthalic acid, trimethylol propane (TMP), 2,2-dimethoxy propane, 2,2-bis-(4-hydroxycyclohexyl) propane (HBPA), N,N-dimethylamino pyridine (DMAP 99%), benzyl triethyl ammonium chloride (BTEAC 99%), 2-bromoisobutyryl bromide (98%) and lithium aluminum hydride (LAH) were purchased from Aldrich and were used as received. Triethyl amine (TEA), dichloromethane (DCM), 18-crown-6, 4-nitrobenzoyl chloride, *p*-toluene sulfonic acid (PTSA), *p*-chloronitrobenzene, tetrahydrofuran (THF), ammonia, ethanol, anhydrous sodium sulphate, potassium hydroxide, sodium hydrogen carbonate, sodium hydroxide, methanol and chloroform, all received from S.D. Fine-Chem. Ltd., India were used as received.

Pyridinium chlorochromate (PCC) was prepared according to the reported procedure.[28]

3.2.2 Purifications

Tetrahydrofuran was stirred over calcium hydride for 12 h, filtered and distilled. Further it was refluxed over sodium-benzophenone complex for 2-3 days, then distilled and used. Dichloromethane was stirred over calcium hydride and distilled before use. Triethyl amine was stirred over calcium hydride, distilled and stored over potassium hydroxide.

3.2.3 Measurements

Melting points were determined by open capillary method and are uncorrected.

FTIR spectra were recorded on a Perkin-Elmer *Spectrum GX* spectrophotometer in nujol or in chloroform.

NMR spectra were recorded on a Bruker 200 MHz spectrometer at resonance frequencies of 200 MHz for ^{1}H-NMR and 50 MHz for ^{13}C-NMR measurements using $CDCl_3$ or DMSO-d_6 as a solvent.

3.3 Synthesis

3.3.1 Synthesis of 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate (HMBMP)

bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were taken 1,4-benzene dimethanol (2.0 g, 0.014 mol), triethyl amine (1.6 ml, 0.012 mol) and dry tetrahydrofuran (40 mL). The mixture was cooled to 5^{o}C in an ice water bath and 2-bromoisobutyryl bromide (2.75 g, 0.012 mol) was added dropwise. The reaction mixture was allowed to stir for 1h at 5^{o}C and then for 5 h at room temperature. The reaction mixture was filtered and tetrahydrofuran was removed under vacuum. The crude product was chromatographed using silica gel with hexane/ethyl acetate (75:25, v/v) as eluent and further purified by distillation under vacuum to obtain a colorless liquid.

BP- 123^{o}C/0.014 mm Hg

Yield: 1.50 g. (37%)

3.3.2 Synthesis of 4-(2-bromo-2-methylpropanoyloxy) benzenesulfonic acid (BMPBSA)

Into a 100 ml round bottom flask equipped with a magnetic stirring bar and an addition funnel, were placed sodium 4-hydroxybenzenesulfonate (10.0 g, 0.05 mol), sodium hydroxide (2.0 g, 0.05 mol), benzyltriethylammonium chloride (10 mg) and water (20 mL). The reaction mixture was cooled to 10^{o}C. The solution of 2-bromoisobutyryl bromide (7.5 mL, 0.06 mol) in dichloromethane (10 mL) was added over a period of 1h to the reaction mixture. The reaction mixture was stirred for 3 h after which the mixture was neutralized with dilute hydrochloric acid and solid obtained was recrystallized from water.

Yield: 7.52 g. (51 %)

3.3.3 Synthesis of 4-[(4'-nitro) phenoxymethyl] benzyl bromide (NPMBB)

Into a 250 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser were charged 1,4-bis (bromomethyl) benzene (3.50 g, 0.013 mol), p-nitrophenol (1.82 g, 0.013 mol), potassium carbonate (4.96 g, 0.035 mol), 18-crown-6 (0.15 g , 0.0005 mol) and dry acetone (100 mL). The reaction mixture was refluxed for 24 h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature, filtered and solvent was evaporated under reduced pressure. The product was purified by column chromatography using hexane/ethyl acetate (97:3, v/v %) as eluent to obtain 4-[(4ô-nitro) phenoxymethyl] benzyl bromide as a solid.

Yield: 1.60 g (27%)

3.3.4 Synthesis of 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl (methyl 2-bromo-2-methylpropanoate)

3.3.4.1 Synthesis of 5-ethyl 5-hydroxy methyl-2,2-dimethyl-1,3-dioxane

Into a 250 mL round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were added trimethylol propane (20 g, 0.149 mol), 2,2-dimethoxy propane (23.2 g, 0.22 mol), p-toluene sulfonic acid (1.40 g, 0.0074 mol) and acetone (100 mL). The reaction mixture was stirred for 5 h at room temperature. The acid catalyst was then neutralized by adding 2 ml of ammonia/ethanol (50:50, v/v) solution. The solvent was evaporated off and the residue was dissolved in chloroform (500 ml) and washed with water (2 x 100 mL). The organic phase was dried over anhydrous sodium sulphate, filtered and solvent was evaporated off to obtain a colourless liquid, which was purified by vacuum distillation to yield 5-ethyl 5-hydroxy methyl-2,2-dimethyl-1,3-dioxane.

B.P.: 78^{o}C/0.014 mm Hg

Yield ï 23.0 g. (89 %)

3.3.4.2 Synthesis of 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) (EDMBMP)

Into a 250 ml round bottom flask equipped with a magnetic stirring bar and an addition funnel were charged 5-ethyl 5-hydroxy methyl-2,2-dimethyl-1,3-dioxane (5.0 g, 0.0287 mol), triethyl amine (4.34 g, 0.043 mol) and chloroform (50 mL). The reaction mixture was cooled to 0^{o}C in an ice bath and 2-bromoisobutyryl bromide (9.85 g, 0.043 mol) was added dropwise under nitrogen atmosphere. The reaction mixture was stirred overnight at room temperature. The solid that separated out from the reaction mixture was removed by filtration and organic layer was washed with 5 % aqueous sodium hydroxide (2 x 20 mL) followed by water (2 x 20 ml). The organic phase was dried over anhydrous sodium sulphate, filtered and solvent was removed to obtain product as a brown viscous liquid. Further, EDMBMP was purified by passing through a neutral alumina column using dichloromethane as eluent.

Yield - 8.30 g. (90 %)

(hydroxymethyl)butyl 2-bromo-2-methyl propanoate (BHMBMP)

Into a 100 ml round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) (2.0 g. 3.53 x 10^{-3} mol) and a mixture of tetrahydrofuran/ dilute hydrochloric acid (10 mL, 80:20, v/v). The reaction mixture was stirred overnight at room temperature after which the solvent was removed and the residue was dissolved in dichloromethane (70 mL). The dichloromethane solution was washed with brine (2 x 20 mL), water (2 x 20 mL), dried over anhydrous sodium sulphate, filtered and solvent was removed to afford a product. Further, BHMBMP was purified by passing through a neutral alumina column using dichloromethane as eluent

Yield-1.56 g. (90 %)

3.3.6 Synthesis of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (BHMPBMP)

3.3.6.1 Preparation of 5-hydroxy dimethyl isophthalate

Into a 250 ml one neck round bottom flask equipped with a magnetic stirring bar and a reflux condenser were placed 5-hydroxy isophthalic acid (25 g, 0.13 mol), methanol (125 ml) and sulfuric acid (1 mL). The reaction mixture was refluxed for 8 h and excess methanol was removed on a rotary evaporator. The resulting product was dissolved in chloroform (125 ml) and washed with water (2 x 70 ml). The organic layer was dried over anhydrous sodium sulphate, filtered and solvent was removed to obtain the crude product, which was recrystallized from methanol to afford pure dimethyl-5-hydroxyisophthalate.

Yield- 26.0 g. (91%)

M. P. 161 ^{o}C (Lit. M. P.: 160 ^{o}C)[29]

3.3.6.2 Preparation of 3,5-bis(hydroxymethyl) phenol (BHMP)

Into a flame dried three-necked 500 mL round bottom flask equipped with a magnetic stirring bar, an addition funnel, a reflux condenser and a nitrogen inlet were charged lithium aluminum hydride (5.7 g, 0.15 mol) and dry tetrahydrofuran (120 mL). Dimethyl 5-hydroxy isophthalate (10.0 g, 0.047 mol) in 120 ml of dry tetrahydrofuran was added dropwise over a period of 1h at room temperature. The reaction mixture was refluxed for 12 h and then cooled to room temperature. Aqueous sulphuric acid (10 %)

with vigorous stirring at room temperature to the reaction mixture until no more hydrogen was evolved. The reaction mixture was filtered and solvent was evaporated off to obtain a crude product, which was purified by column chromatography using dichloromethane/methanol (95:5%, v/v) as eluent to obtain pure 3,5-bis(hydroxymethyl) phenol.

Yield = 6.10 g (82 %)

M. P.: 72-73°C, (Lit. M. P.: 71-73 °C)[30]

3.3.6.3 Synthesis of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (BHMPBMP)

Into a 250 mL round bottom flask equipped with a magnetic stirring bar and an addition funnel were placed 3,5-bis(hydroxymethyl) phenol (3.1 g, 0.02 mol), triethyl amine (3.88 mL, 0.028 mol) and dry tetrahydrofuran (135 mL). The reaction mixture was cooled to 10°C and 2-bromoisobutyryl bromide (2.41 mL, 0.02 mol) was added dropwise. The reaction mixture was stirred at 10°C for 1 h and then at room temperature for 12 h. The reaction mixture was filtered and solvent was evaporated off to obtain a viscous liquid, which was purified by column chromatography using hexane/ethyl acetate (75:25 %, v/v) as eluent to obtain pure 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate as a white solid.

Yield- 1.66 g (28 %)

M. P.: 96-97°C.

3.3.7 Synthesis of 5-(2-bromo-2-methylpropanoyloxy)isophthalic acid (BMPIPA)

Into a 100 ml round bottom flask equipped with a magnetic stirring bar and an addition funnel were placed 5-hydroxy isophthalic acid (3.0 g, 0.016 mol), 0.2 M sodium hydroxide (10 mL) and benzyltriethylammonium chloride (10 mg). The reaction mixture was cooled to 10°C. A solution of 2-bromoisobutyryl bromide (3.0 mL, 0.025 mol) dissolved in dichloromethane (10 mL) was added over a period of 30 minutes to the reaction mixture and stirred for 1 h. The reaction mixture was neutralized with dilute hydrochloric acid and the solvent was distilled off to obtain a crude solid product, which was purified by recrystallization from water/methanol mixture to obtain 5-(2-bromo-2-methylpropanoyloxy)isophthalic acid.

Yield: 3.90 g (72 %)

3.3.8 Synthesis of 5-(2-bromo-2-methylpropanamido)isophthalic acid (BMPAIPA)

Into a 100 ml round bottom flask equipped with a magnetic stirring bar and an addition funnel were placed 5-amino isophthalic acid (3.0 g, 0.016 mol), sodium carbonate (5.4 g, 0.05 mol) and water (30 mL) and the reaction mixture was cooled to 10^{o}C. A solution of 2-bromoisobutyryl bromide (5.0 mL, 0.025 mol) in dichloromethane (15 mL) was added over a period of 30 minutes to the reaction mixture and stirred for 1 h. The reaction mixture was neutralized with dilute hydrochloric acid and solvent was removed to obtain a solid, which was purified by recrystallization from water/methanol mixture to afford pure 5-(2-bromo-2-methylpropanamido)isophthalic acid.

Yield: 3.17 g (60 %)

M.P.: 297-298^{o}C.

3.3.9 Synthesis of 4-[2-(7-oxooxepan-3-yl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate (OPCBMP)

3.3.9.1 Synthesis of 4-[2-(4-hydroxycyclohexyl)propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate

Into a 250 ml two necked-round bottom flask equipped with a magnetic stirring bar and an addition funnel were placed 2,2-bis-(4-hydroxycyclohexyl) propane (10.0 g, 0.04 mol), triethyl amine (3.78 g, 0.037 mol) and dry tetrahydrofuran (100 mL). The reaction mixture was cooled to 10^{o}C and 2-bromoisobutyryl bromide (8.56 g, 0.037 mol) was added dropwise over a period of 1h. The reaction mixture was stirred for 1h at 10^{o}C and then for 12 h at room temperature. The reaction mixture was filtered and tetrahydrofuran was removed to obtain crude product. The crude product was dissolved in dichloromethane (300 mL), washed with dilute hydrochloric acid (3 x 70 mL) and water (3 x 70 mL). The organic layer was dried over anhydrous sodium sulphate, filtered and dichloromethane was removed to obtain a solid product, which was chromatographed using hexane/ethyl acetate (95:5 %, v/v) as eluent to obtain 4-[2-(4-hydroxycyclohexyl)propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate as a white solid.

Yield: 6.48 g. (40 %)

3.3.9.2 Synthesis of 4-[2-(4-oxocyclohexyl)propan-2-yl]cyclohexyl 2-bromo-2-methylpropanoate

Into a 100 ml round bottom flask equipped with a magnetic stirring bar and an addition funnel were charged finely ground mixture of pyridinium chlorochromate (2.80 g, 0.013 mol), silica gel (3.0 g, 100-200 mesh) and dichloromethane (50 mL). The suspension was stirred and 4-[2-(4-hydroxycyclohexyl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate (3.38 g, 0.008 mol) in 50 mL dichloromethane was added dropwise at room temperature. The reaction mixture was stirred for 4 h and then filtered through a short silica gel column. The solution obtained was washed with saturated brine (2 × 50 mL) and water (2× 50 mL). The organic layer was dried over anhydrous sodium sulfate, filtered and solvent was evaporated off to obtain a crude product, which was recrystallized from hexane/toluene mixture (75:25 %, v/v) to afford pure 4-[2-(4-oxocyclohexyl)propan-2-yl]cyclohexyl 2-bromo-2-methylpropanoate as a white solid.

Yield: 3.0 g (90 %)

M.P.: 90-91^{o}C

3.3.9.3 Synthesis of 4-[2-(7-oxooxepan-3-yl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate (OPCBMP)

Into a 250 mL round bottom flask equipped with a magnetic stirring bar and an addition funnel were placed *m*-chloroperbenzoic acid (3.30 g, 0.02 mol) and chloroform (30 mL). To the reaction mixture, 4-[2-(4-oxocyclohexyl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate (3.30 g, 0.008 mol) in chloroform (50 mL) was added dropwise. The reaction mixture was stirred for 24 h and then filtered through celite column. The organic layer was washed with saturated sodium bicarbonate (3 x 20 mL), brine (20 mL) and water (3 x 20 mL). The organic layer was dried over sodium sulfate, filtered and solvent was removed. The crude product thus obtained was purified by column chromatography using hexane/ethyl acetate (90:10, v/v %) as eluent to afford pure 4-[2-(7-oxooxepan-3-yl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate as white solid**.**

Yield: 2.38 g (70 %)

M.P.: 109-110^{o}C

,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) (ODMBMP)

Into a 250 mL round bottom flask equipped with a magnetic stirring bar and an addition funnel were charged 4-(hydroxymethyl)-1,3- dioxolan-2-one (4.0 g, 0.033 mol), triethyl amine (4.89 g, 0.05 mol) and chloroform (50 mL). The reaction mixture was cooled to 0^{o}C and 2-bromoisobutyryl bromide (11.64 g, 0.05 mol) was added dropwise over a period of 1h. The reaction mixture was stirred overnight at room temperature and then filtered. The organic layer was washed with sodium bicarbonate solution (3 x 20 mL) followed by water (2 x 20 mL), dried over anhydrous sodium sulfate, filtered and the solvent was removed to obtain a crude product. The product thus obtained was purified by recrystallization from hexane/toluene mixture (75:25 %, v/v) to afford pure 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate).

Yield ï 7.0 g (77 %)

M.P.: 44-45^{o}C

3.4 Results and Discussion

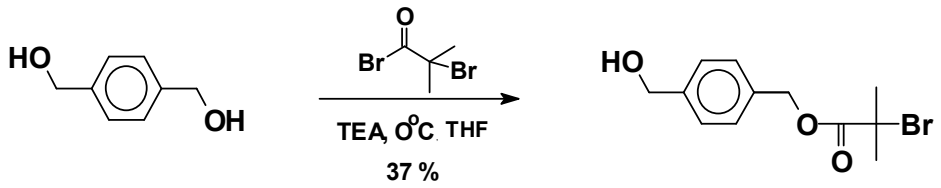
3.4.1 Synthesis and characterization of 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate (HMBMP)

Hydroxyl-terminated polymers are valuable intermediates for the preparation of polyurethanes and polyesters and hence of high importance in polymer science.[31,32] Hydroxyl functionality facilitates ring opening polymerization of lactones[33] and lactides. Acrylic end groups can be introduced by modification of hydroxyl groups to obtain macromonomers.

The preparation of 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate was undertaken with a view to synthesize hydroxyl-terminated polymers by ATRP. **Scheme 3.2** depicts route for synthesis of 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate. Subsequent to completion of synthesis of HMBMP in our laboratory, Heise et al[34] reported synthesis of HMBMP and its utility in the synthesis of PMMA-*b*-PCL.

The reaction of 1,4-benzene dimethanol and 2-bromoisobutyryl bromide in the presence of triethyl amine was carried out in tetrahydrofuran at room temperature. The target product, monoester was separated by column chromatography using hexane/ethyl

system, which was further purified by distillation under reduced pressure.



Scheme 3.2: Synthesis of 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate

The characterization of HMBMP was carried out by FTIR, ^{1}H and ^{13}C-NMR spectroscopy.

FTIR spectrum of HMBMP is depicted in **Figure 3.1.** The absorption bands observed at 3370 cm^{-1} and 1734 cm^{-1} correspond to hydroxyl group and ester carbonyl group, respectively.

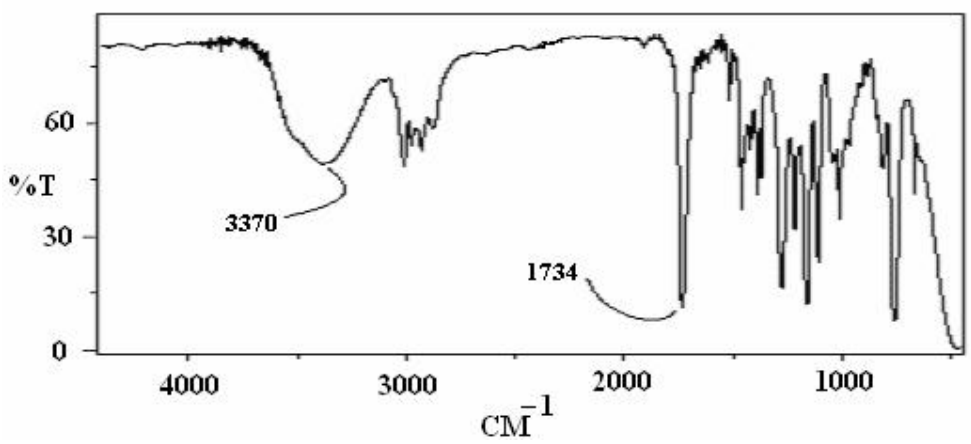


Figure 3.1: IR spectrum of 4-(hydroxymethyl) benzyl 2-bromo-2-methylpropanoate

^{1}H-NMR spectrum of HMBMP along with assignments is presented in **Figure 3.2.** The singlets at 7.34 and 5.18 δ ppm arise due to the four aromatic protons (Hb) and benzylic protons (Hc) attached to ester group, respectively. The benzylic protons (Ha) attached to hydroxyl group appeared as a singlet at 4.65 δ ppm and the protons (Hd) from the two methyl groups appeared as a singlet at 1.93 δ ppm.

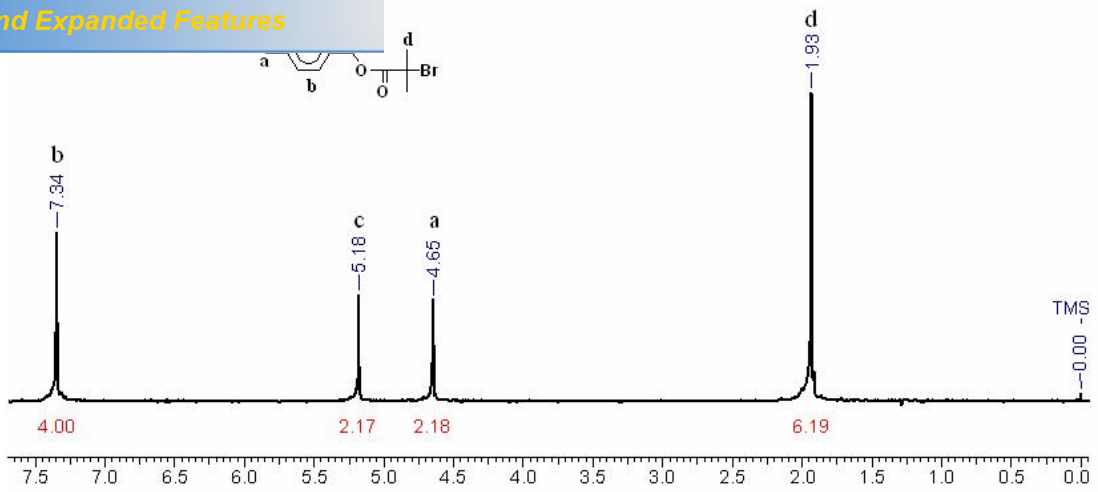


Figure 3.2: ^{1}H-NMR spectrum of 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate in $CDCl_3$

^{13}C-NMR spectrum of HMBMP along with assignments is presented in **Figure 3.3**. The peak corresponding to ester carbonyl carbon (C7) appeared at 171.37 δ ppm. The peak for quaternary aromatic carbon C5 was observed at 140.97 δ ppm. The peak at 134.44 δ ppm was attributed to C2 quaternary aromatic carbon and peaks observed at 127.91 and 126.96 δ ppm correspond to aromatic carbons C4 and C3, respectively. The peaks observed at 67.20 and 64.43 δ ppm are due to carbon C6 (**C**H_2 group attached to ester) and C1 (**C**H_2 attached to hydroxyl group), respectively. The peaks at 55.58 and 30.58 δ ppm correspond to quaternary carbon (C8) and methyl carbon (C9), respectively.

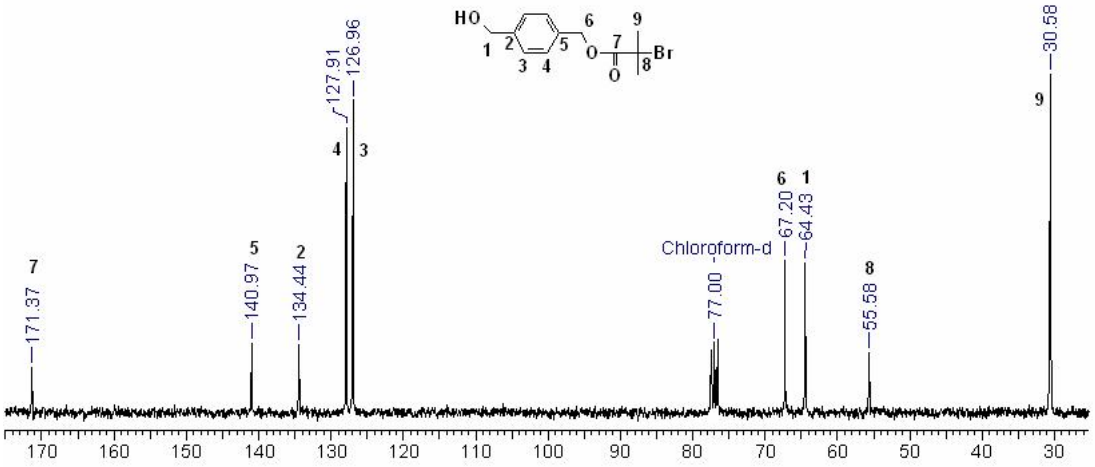
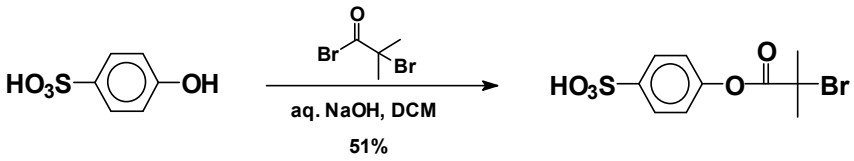


Figure 3.3: ^{13}C-NMR spectrum of 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate in $CDCl_3$

racterization of 4-(2-bromo-2-methylpropanoyloxy) benzenesulfonic acid (BMPBSA)

Polymers containing sulfonic acid group are important as they find potential application as water-soluble polymers,[35] polymeric membranes,[36] ion exchange resins[36] and proton ion conductors.

The synthesis of 4-(2-bromo-2-methylpropaoyloxy) benzenesulfonic acid was carried out by reaction of sodium 4-hydroxybenzenesulfonate with 2-bromoisobutyryl bromide in the presence of aqueous sodium hydroxide as a base and catalytic amount of phase transfer catalyst, viz., benzyltriethylammonium chloride (**Scheme 3.3**).[37] The product obtained was neutralized with dilute hydrochloric acid and recrystallized from water.



Scheme 3.3: Synthesis of 4-(2-bromo-2-methylpropanoyloxy) benzenesulfonic acid

The structure of 4-(2-bromo-2-methylpropaoyloxy) benzenesulfonic acid was confirmed by FTIR, ^{1}H and ^{13}C-NMR spectroscopy.

FTIR spectrum of BMPBSA is shown in **Figure 3.4**. IR spectrum of BMPBSA exhibited a band at 1752 cm^{-1} which corresponds to phenolic ester group.[38] The bands at 1210 cm^{-1} and 1069 cm^{-1} are attributed to S=O symmetric and asymmetric stretching vibrations, respectively.

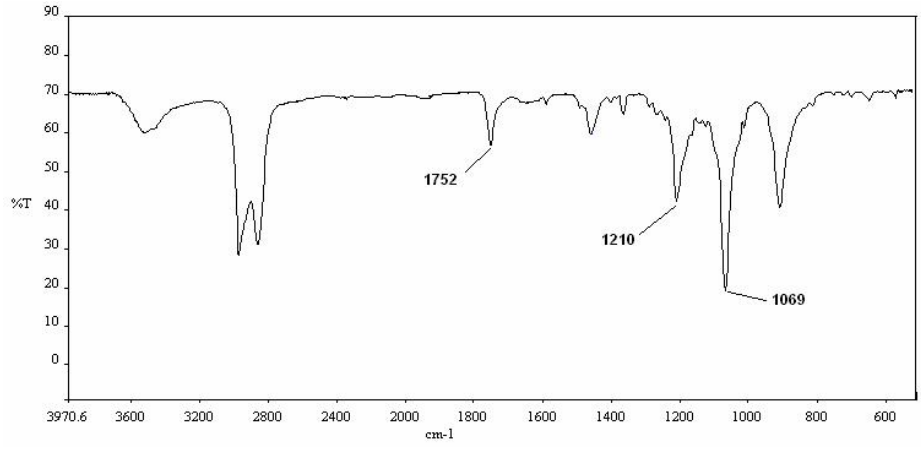


Figure 3.4: IR spectrum of 4-(2-bromo-2-methylpropanoyloxy) benzenesulfonic acid

NMR spectrum of BMPBSA along with assignments. The doublets at 7.70 and 7.13 δ ppm correspond to aromatic protons *ortho* and *meta* to sulfonic acid group, respectively, whereas the singlet at 2.04 δ ppm correspond to methyl protons (Hd).

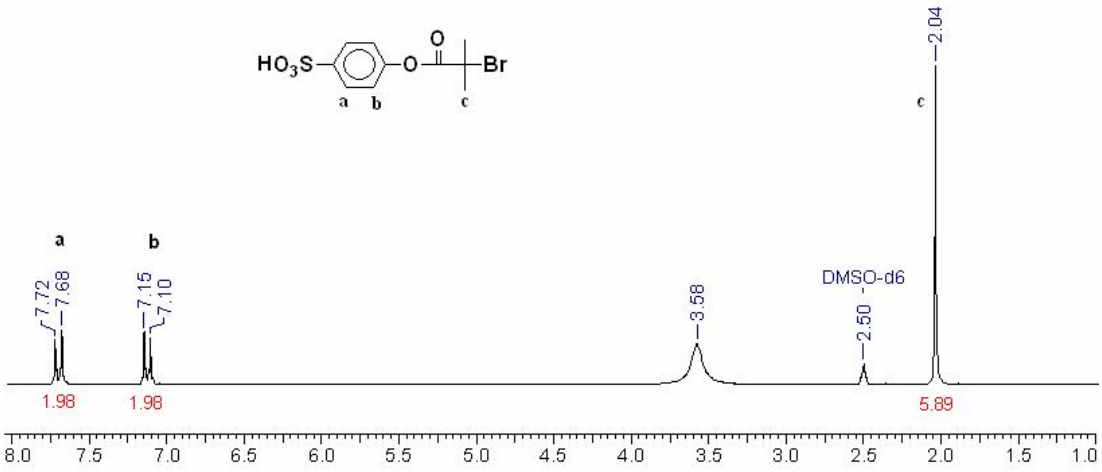


Figure 3.5: ^{1}H-NMR spectrum of 4-(2-bromo-2-methylpropanoyloxy) benzenesulfonic acid in DMSO-d_6

In ^{13}C-NMR spectrum of BMPBSA **(Figure 3.6),** the peak corresponding to ester carbonyl carbon (C3) appeared at 170.0 δ ppm. The peaks at 150.75 and 146.16 δ ppm were assigned to quaternary carbon (C7) to which sulfonic acid group is attached and carbon (C4) to which ester group is attached, respectively. The peaks of aromatic carbons *ortho* (C6) and *meta* (C5) to sulphonic acid group were observed at 127.48 and 120.86 δ ppm, respectively. The peak for quaternary carbon (C2) to which bromine is attached appeared at 57.30 δ ppm, whereas the peak for methyl carbons (C1) appeared at 30.34 δ ppm.

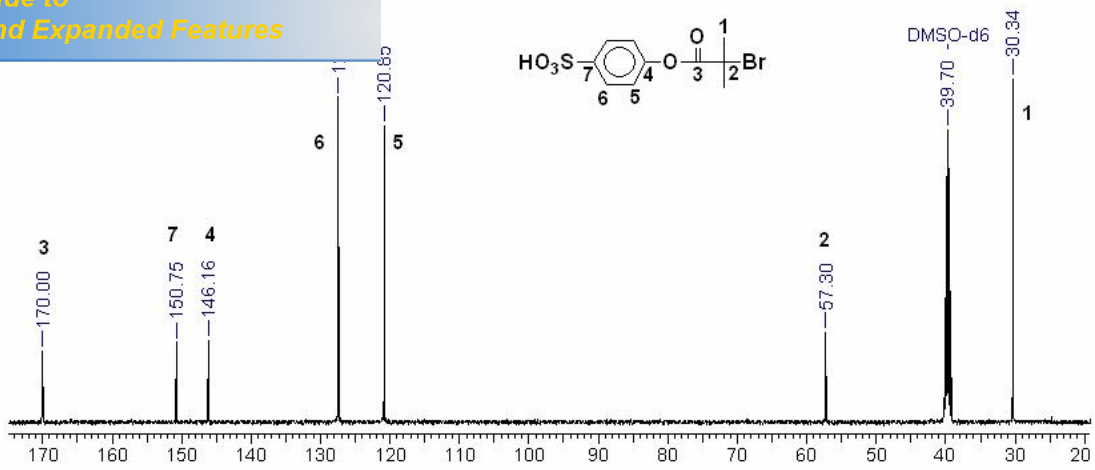
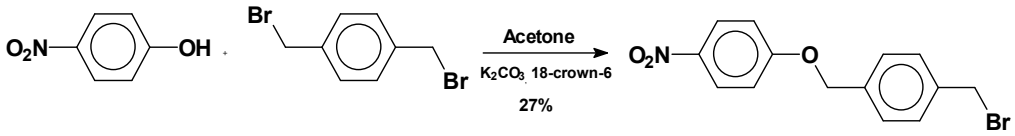


Figure 3.6: ^{13}C-NMR spectrum of 4-(2-bromo-2-methylpropanoyloxy) benzenesulfonic acid in DMSO-d_6

3.4.3 Synthesis and characterization of 4-[(4'-nitro)phenoxymethyl] benzyl bromide (NPMBB)

Nitro functionalized ATRP initiators are important as they are precursors of amino-terminated polymers which finds application as reactive compatibilizers. Nitro group can be converted into amino group v*ia* simple reduction step using various regents such as H_2 Pd/C[39,40], hydrazine hydrate Pd/C[41], $SnCl_4$[8], etc.

NPMBB was synthesized by nucleophilic displacement of bromo atom in 1,4-bis (bromomethyl) benzene with 4-nitrophenol in the presence of potassium carbonate and 18-crown-6 **(Scheme 3.4)**.[42] The reaction was carried out in dry acetone at reflux temperature for 24 h. The product was purified by column chromatography.



Scheme 3.4: Synthesis of 4-[(4'-nitro)phenoxymethyl] benzyl bromide

The structure of 4-[(4ô-nitro)phenoxymethyl] benzyl bromide was confirmed by FTIR, ^{1}H and ^{13}C-NMR spectroscopy.

IR spectrum of NPMBB exhibited bands at 1520 and 1345 cm^{-1} which correspond to asymmetric and symmetric stretching vibration of nitro group, respectively **(Figure**

236 cm^{-1} corresponds to ether group (C-O-C) stretching vibration.

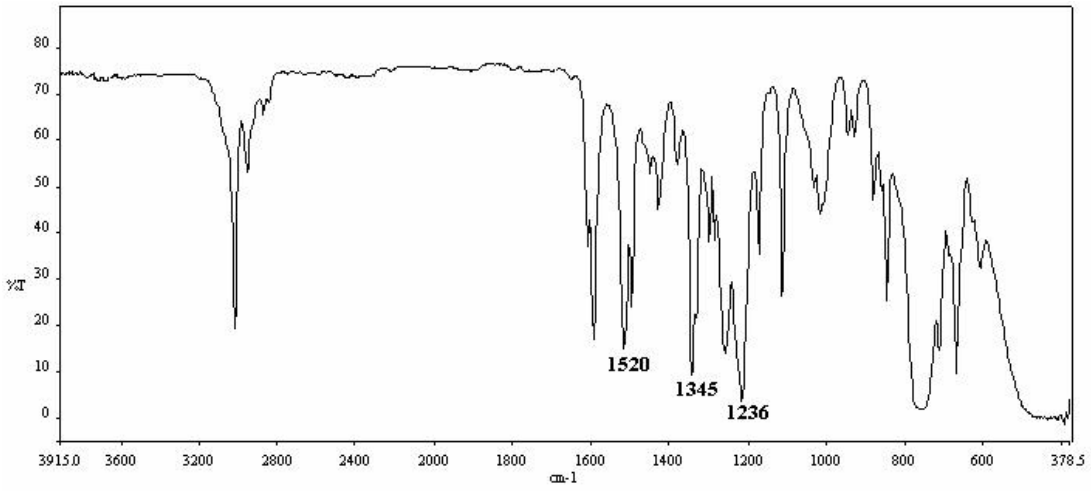


Figure 3.7: IR spectrum of 4-[(4'-nitro)phenoxymethyl] benzyl bromide

Figure 3.8 shows ^{1}H-NMR spectrum of NPMBB along with assignments. The doublets at 8.21 δ ppm (Ha) and 7.03 δ ppm (Hb) are due to aromatic protons *ortho* and *meta* to nitro group, respectively. The peak at 7.43 δ ppm arises due to four aromatic protons (Hd and He). The methylene protons (Hc) appeared as a singlet at 5.16 δ ppm, whereas methylene protons (Hf) to which bromine is attached appeared as a singlet at 4.51 δ ppm.

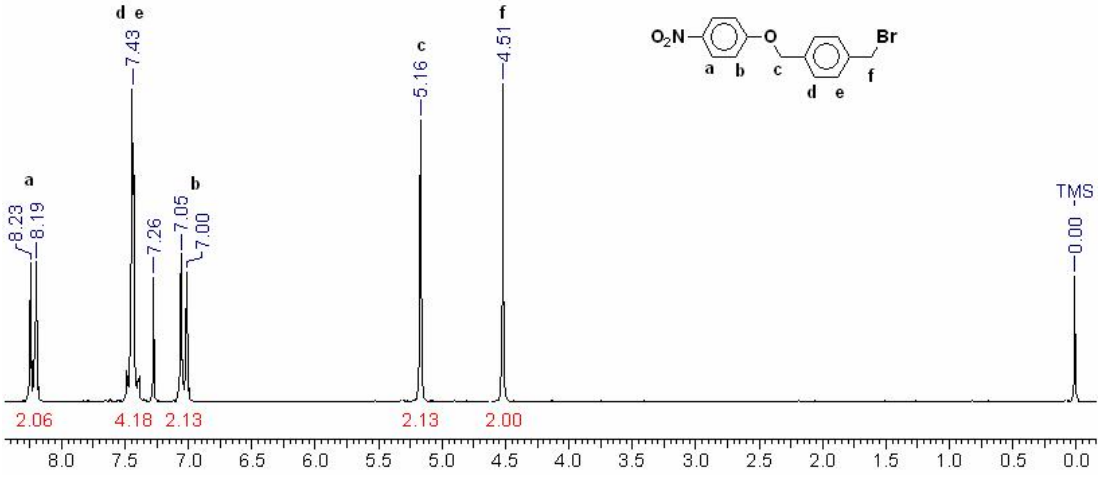


Figure 3.8: ^{1}H-NMR spectrum of 4-[(4'-nitro)phenoxymethyl] benzyl bromide in $CDCl_3$

NPMBB along with assignments is presented in **Figure 3.9.** The peak at 163.42 δ ppm was ascribed to carbon (C4) to which oxygen is attached. The peak observed at 141.59 δ ppm corresponds to quaternary aromatic carbon (C1) to which nitro group is attached, whereas the peaks observed at 129.39 and 114.74 δ ppm correspond to carbon (C2) *ortho* to nitro group and (C3) *meta* to nitro group, respectively. The quaternary carbon (C9) to which bromomethyl group is attached appeared at 135.67δ ppm and carbon (C6) *para* to bromomethyl group appeared at 138.0 δ ppm. The peaks observed at 70.07 δ ppm and 32.36 δ ppm correspond to carbon (C5) and bromomethyl carbon (C10), respectively.

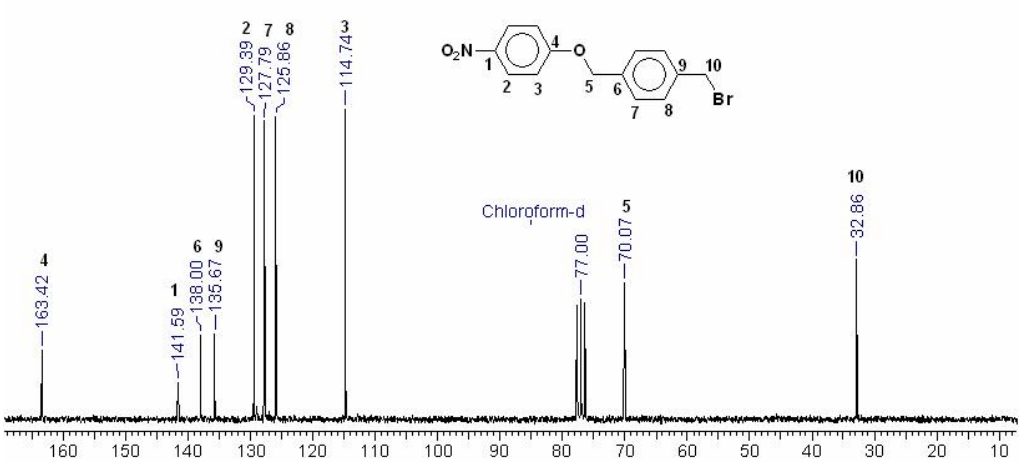
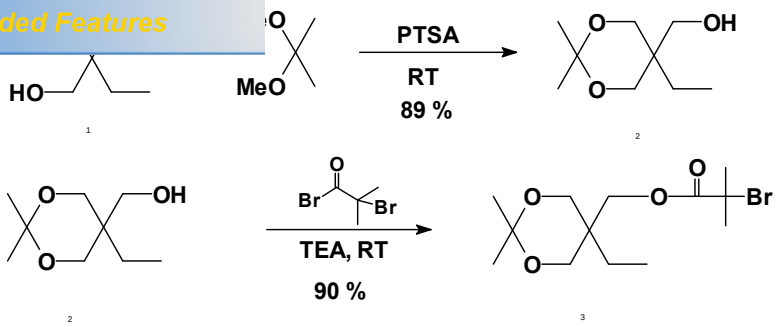


Figure 3.9: ^{13}C-NMR spectrum of 4-[(4'-nitro)phenoxymethyl] benzyl bromide in $CDCl_3$

3.4.4 Synthesis and characterization 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2- methylpropionate) (EDMBMP)

Dihydroxyl and dicarboxylic acid functionalized condensation macromonomers have shown to be important in preparation of graft copolymers (having condensation polymer backbone), branched polymers.[43] and reactive stabilizers in preparation of polyurethane particles.[44-46]

ATRP initiator containing protected dihydroxyl groups namely, 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropionate) was synthesized in two steps. **Scheme 3.5** depicts the route for synthesis of EDMBMP.



Scheme 3. 5: Synthesis of 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate)

Cyclic ketal and acetal groups are formed after protection of bis-hydroxyl groups utilizing ketones or aldehydes.[47,48] The quantitative deprotection of the cyclic ketal group after polymerization to regenerate the hydroxyl group can be carried out using dilute hydrochloric acid.

In the first step, protection of trimethylol propane **(1)** using 2,2-dimethoxy propane in presence of *p*-toluene sulphonic acid as catalyst was carried out.[49]

The protection of trimethylol propane yielded a cyclic ketal intermediate **(2)** viz., 3-ethyl 5-hydroxy methyl-2,2-dimethyl-1,3-dioxane containing one free hydroxyl group, which was purified by vacuum distillation to afford a colorless liquid.

The structural characterization of the cyclic ketal intermediate, 5-ethyl 5-hydroxy methyl-2,2-dimethyl-1,3-dioxane was carried out by FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of 5-ethyl 5-hydroxy methyl-2,2-dimethyl-1,3-dioxane (**Figure 3.10)** showed bands at 3450 cm^{-1} and 1210 cm^{-1} for hydroxyl and ether group (C-O-C) stretching vibrations, respectively.

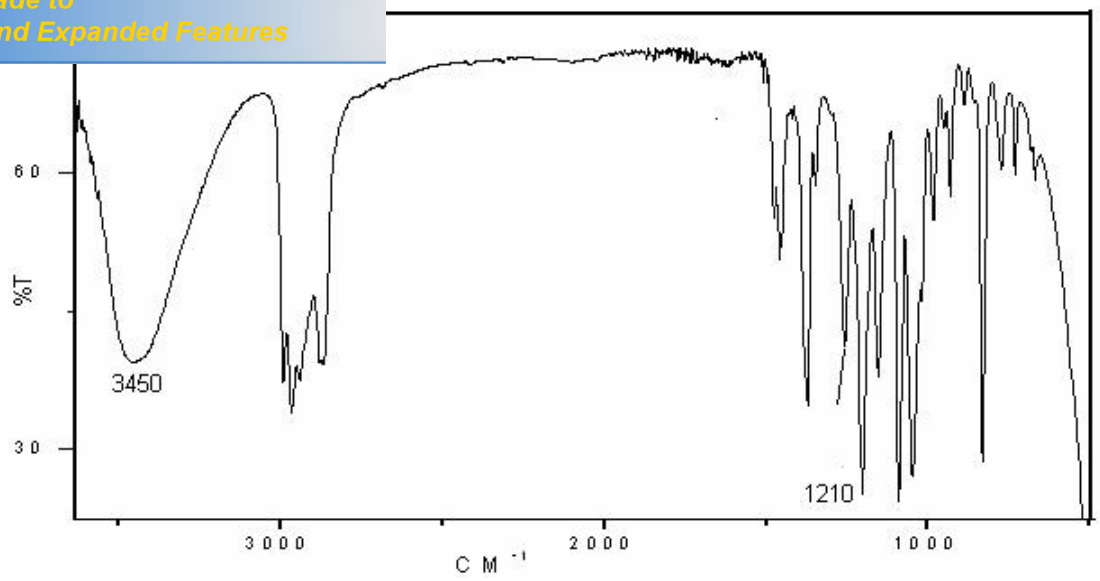


Figure 3.10: IR spectrum of 5-ethyl 5-hydroxy methyl-2, 2-dimethyl-1,3-dioxane

Figure 3.11 shows ^{1}H-NMR spectrum of 5-ethyl 5-hydroxy methyl-2, 2-dimethyl-1,3-dioxane along with assignments. The methylene protons (Hc) adjacent to hydroxyl group exhibited a peak at 3.75 δ ppm and a singlet for methylene protons (Hd) adjacent to ether linkage appeared at 3.67 δ ppm. The two methyl group protons (He) appeared at 1.42 δ ppm as a doublet and methylene protons (Hb) appeared as a triplet at 1.29 δ ppm. The methyl protons (Ha) appeared as a triplet at 0.85 δ ppm.

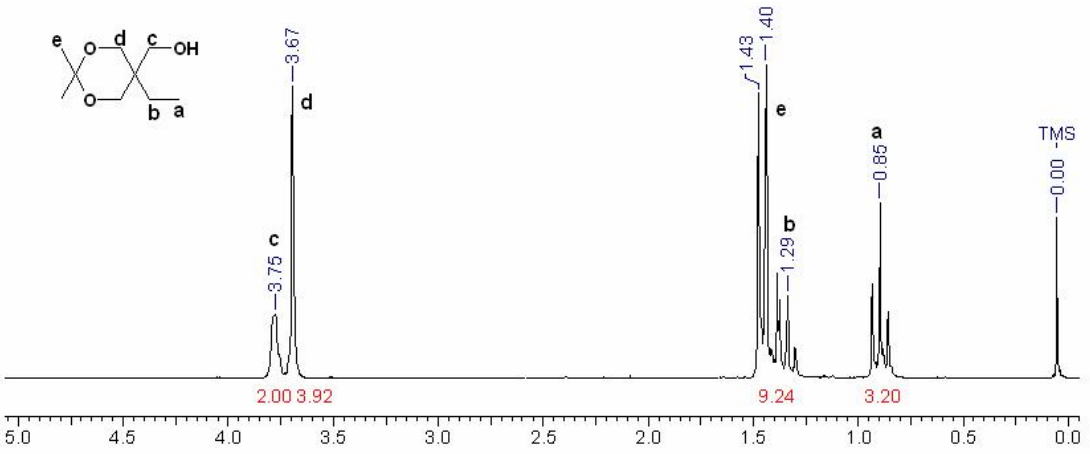


Figure 3.11: ^{1}H-NMR spectrum of 5-ethyl 5-hydroxy methyl-2, 2-dimethyl-1,3-dioxane in $CDCl_3$

5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) was obtained by the reaction of 5-ethyl 5-hydroxy methyl-2, 2-dimethyl-1,3-dioxane with slight excess of 2-bromoisobutyryl bromide in the presence of triethyl amine.

The product obtained, EDMBMP was characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of EDMBMP exhibited a band for ester carbonyl at 1732 cm^{-1}, while ether stretching vibration band was observed at 1210 cm^{-1} **(Figure 3.12)**.

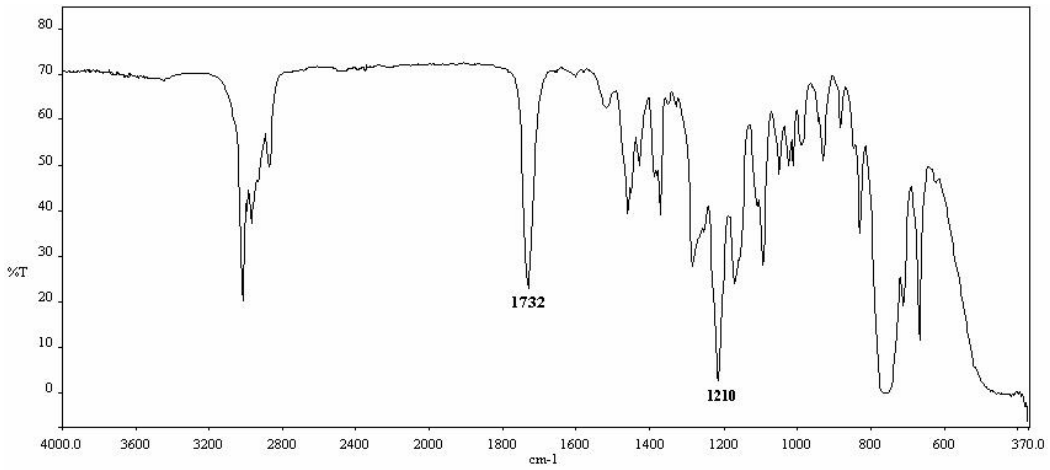


Figure 3.12 IR spectrum of 5-ethyl 2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate)

^{1}H-NMR spectrum of EDMBMP along with assignments is shown in **Figure 3.13**. The singlet at 4.30 δ ppm was attributed to methylene protons (Hc), the downfield shift was observed due to electron withdrawing ester group. The peaks at 3.69 and 1.94 δ ppm correspond to methylene protons attached to ester group and methyl protons (Hf). The multiplets in region 1.50 to 1.25 δ ppm was observed due to methylene protons (Hb) and methyl protons (He) whereas the methyl protons (Ha) appeared as a triplet at 0.86 δ ppm.

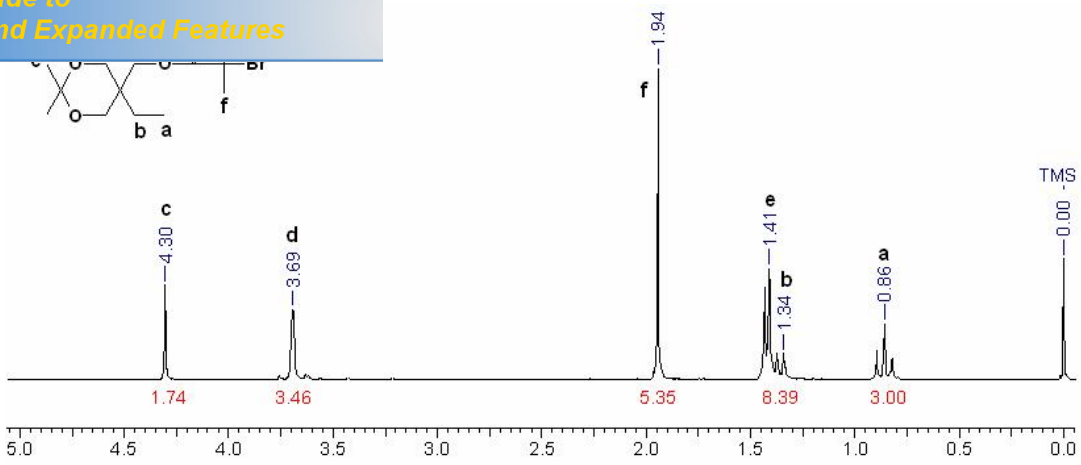


Figure 3.13 ^{1}H-NMR spectrum of 5-ethyl 2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2- methylpropanoate) in $CDCl_3$

^{13}C-NMR spectrum of EDMBMP along with assignments is presented in **Figure 3.14**. The presence of ester carbonyl carbon (C8) was confirmed by the appearance of a peak at 171.36 δ ppm. The signals for quaternary carbons C1, C9 and C4 appeared at 98.22, 55.69 and 36.26 δ ppm, respectively. The peaks at 65.38 and 64.91 δ ppm correspond to methylene carbon (C5) attached to ester group and two methylene carbons (C3), respectively. The signals for two methyl group carbons (C10) and methyl carbon (C7) appeared at 30.69 and 6.92 δ ppm, respectively. The peaks at 26.75 and 20.49 δ ppm correspond to two methyl carbons C2 and C2ô, respectively.

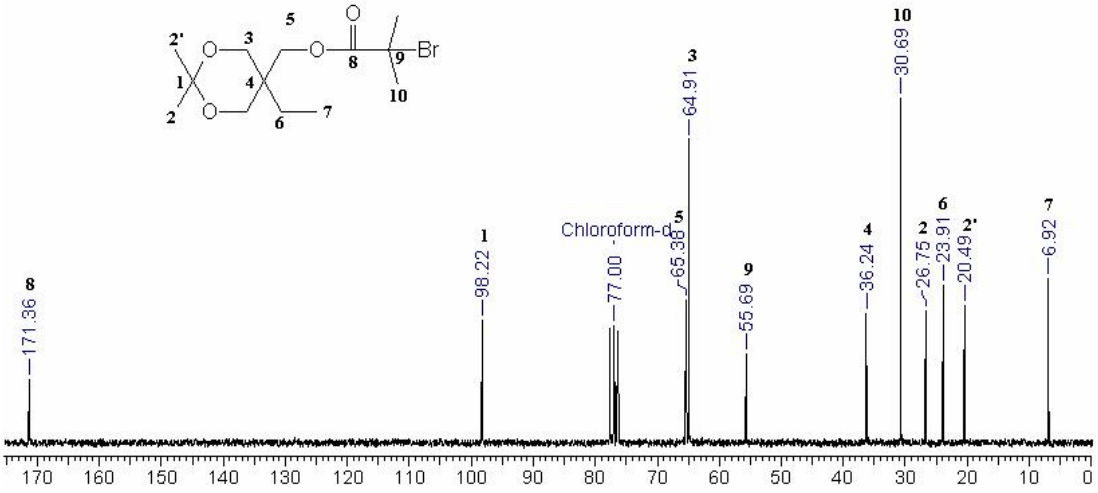
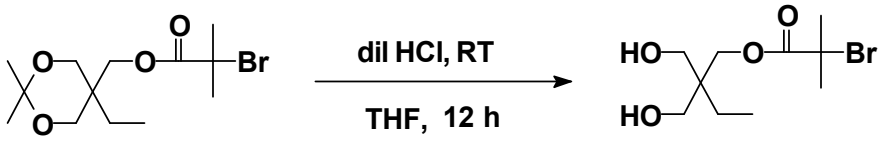


Figure 3.14 ^{13}C-NMR spectrum of 5-ethyl 2,2-dimethyl 1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) in $CDCl_3$

cterization of 2,2-bis(hydroxymethyl)butyl 2-bromo-2 methyl propanoate (BHMBMP)

The synthesis of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate was carried out as shown in **Scheme 3.6.** The ketal deprotection of 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) was carried out using catalytic amount of dilute hydrochloric acid in tetrahydrofuran as solvent.



Scheme 3.6: Synthesis of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate

The characterization of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate was carried out using FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate is shown in **Figure 3.15**. The broad band at 3393 cm^{-1} arises due to hydroxyl stretching vibration and ester carbonyl band appeared at 1733 cm^{-1}.

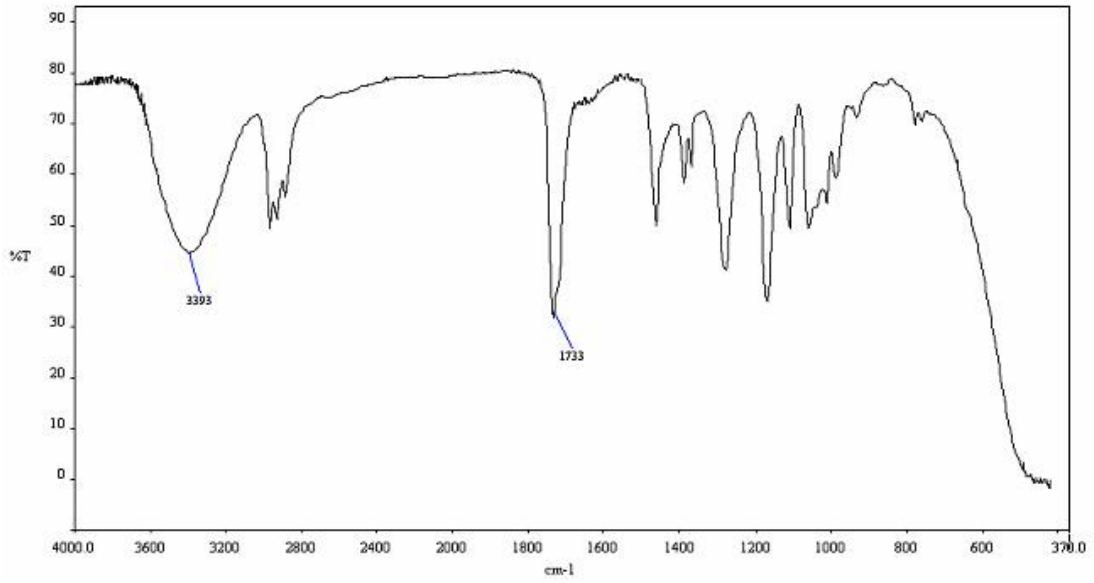


Figure 3.15: FTIR spectrum of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate

2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate along with assignments is shown in **Figure 3.16**. The peaks at 4.24 and 3.61 δ ppm correspond to methylene protons (Hd) and (Ha) attached to ester group and hydroxyl group, respectively. The singlet at 1.93 δ ppm was attributed to six methyl protons (He), while other methyl protons (Hc) appeared as a triplet at 0.88 δ ppm. The peak at 1.32 δ ppm corresponds to methylene protons (Hb).

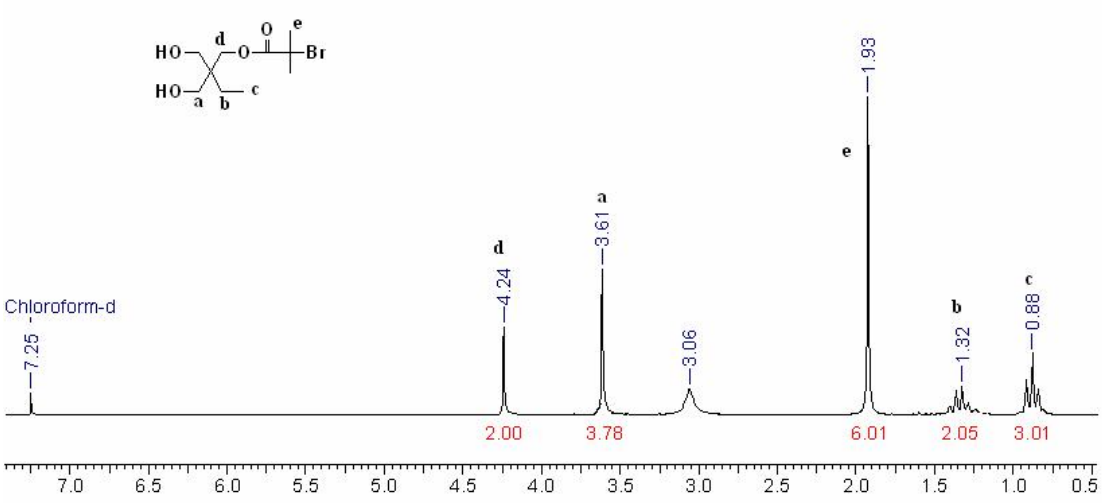


Figure 3.16: ^{1}H-NMR spectrum of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate

^{13}C-NMR spectrum of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate along with assignments is shown in **Figure 3.17**. The peak at 172.14 δ ppm corresponds to the ester carbonyl carbon (C6). The peak for methylene carbon (C5) to which ester group is attached appeared at 65.43 δ ppm and peak at 64.66 δ ppm corresspond to methylene carbon (C1) to which hydroxyl group is attached. The tertiary carbons C7 and C2 appeared at 55.72 and 42.98 δ ppm, respectively. The peaks at 30.56 and 7.26 δ ppm correspond to the methyl carbons C8 and C4, respectively. The methylene carbon C3 appeared at 22.21 δ ppm.

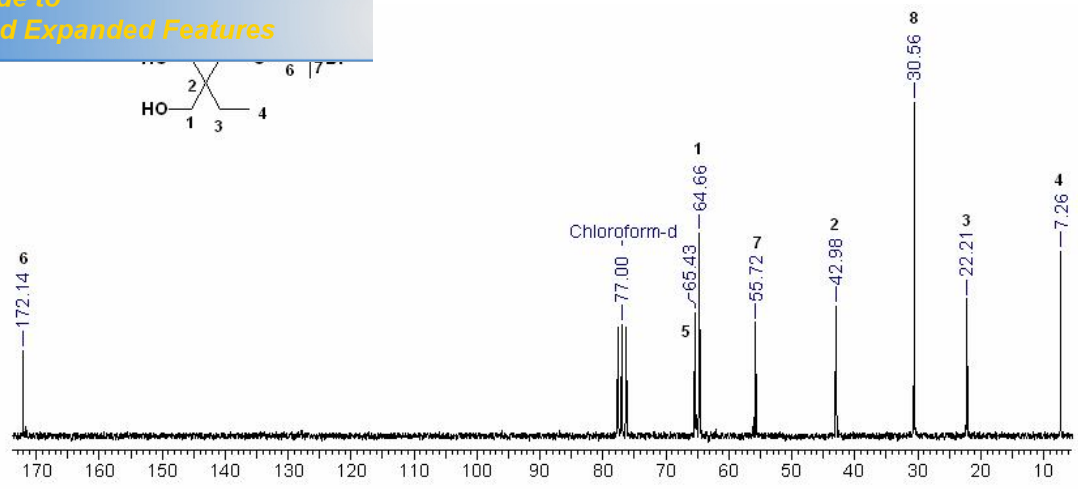
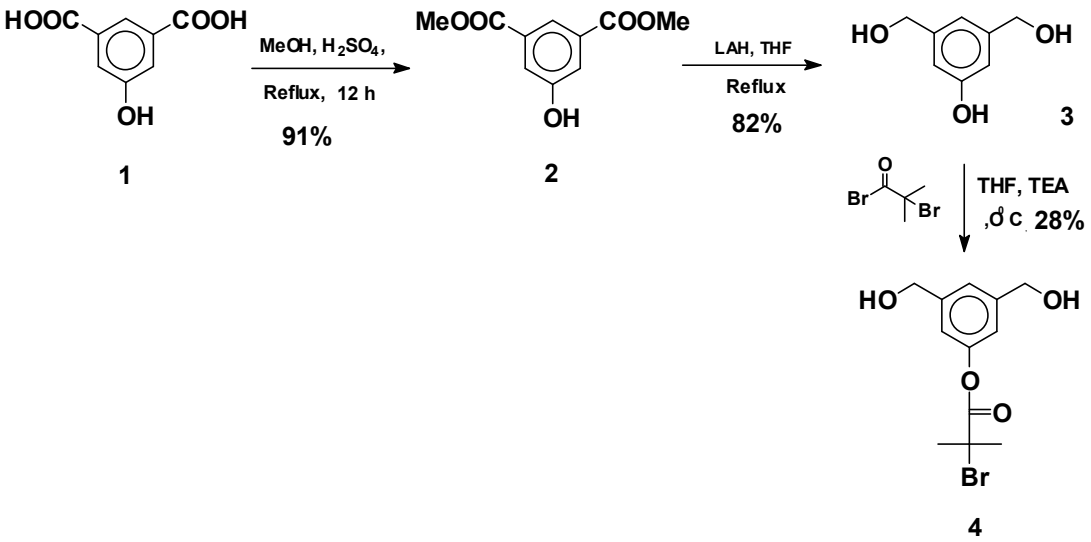


Figure 3.17: ^{13}C-NMR spectrum of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate

3.4.6 Synthesis and characterization 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (BHMPBMP)

Synthesis of bismethylol functionalized ATRP initiator namely, 3,5-bis(hydroxymethyl)phenyl 2-bromo-2 methylpropanoate was carried out using commercially available 5-hydroxy isophthalic acid as the starting material **(Scheme 3.7)**.



Scheme 3.7: Synthesis of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2 methylpropanoate

roxy isophthalic acid **(1)** was converted into dimethyl-5-hydroxyisophthalate **(2)** by esterification with methanol in the presence of sulphuric acid as catalyst.[29]

The product obtained dimethyl-5-hydroxyisophthalate **(2)**, was characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Methyl ester formation was confirmed by IR spectroscopy, where the spectrum showed band at 1760 cm^{-1} characteristic of ester carbonyl group and the phenolic hydroxyl group appeared at 3350 cm^{-1}.

^{1}H-NMR spectrum of dimethyl-5-hydroxyisophthalate **(2)** along with assignments is shown in **Figure 3.18.** The singlet at 8.03 ŭ ppm was assigned to aromatic proton (Hc) flanked by two electron withdrawing ester groups and the singlet at 7.59 ŭ ppm correspond to protons *ortho* to hydroxyl group. The singlet at 3.80 ŭ ppm is due to the six methyl protons of the methyl ester group.

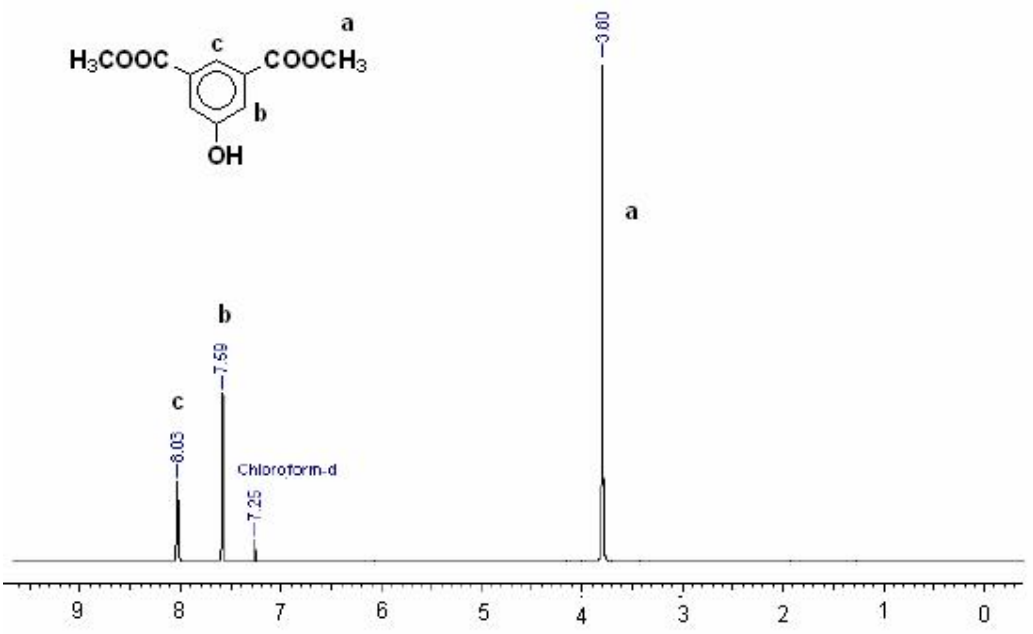


Figure 3.18: ^{1}H-NMR spectrum of dimethyl-5-hydroxyisophthalate (2) in $CDCl_3$

In the second step, reduction of dimethyl-5-hydroxyisophthalate **(2)** using lithium aluminium hydride (LAH) was carried out in dry tetrahydrofuran to obtain 3,5-bis(hydroxymethyl) phenol **(3)** following the protocol by Inouye et al.[30] The other reagents generally used for the reduction of methyl ester to hydroxy methyl group are sodium bis(2-methoxyethoxy) aluminum hydride[51] and borane-dimethyl sulfide complex activated

[2,53] The efficiency of lithium aluminium hydride in the reduction of methyl ester made it the reagent of choice.

The product obtained 3,5-bis(hydroxymethyl) phenol **(3)**, was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

In FTIR spectrum, absence of band at 1760 cm^{-1} corresponding to ester group and the presence of a broad band at 3400 cm^{-1} corresponding to both hydroxy methyl group and phenolic hydroxyl group confirmed the reduction of methyl ester group.

^{1}H-NMR spectrum of 3,5-bis(hydroxymethyl) phenol **(3)** along with assignments is shown in **Figure 3.19.** The peak at 6.66 ŭ ppm corresponds to aromatic proton (Hb) flanked by two hydroxy methyl groups and the peak at 6.59 ŭ ppm corresponds to two aromatic protons (Hc) *ortho* to the phenolic hydroxyl group. The singlet at 4.38 ŭ ppm was attributed to the four methylene protons (Ha).

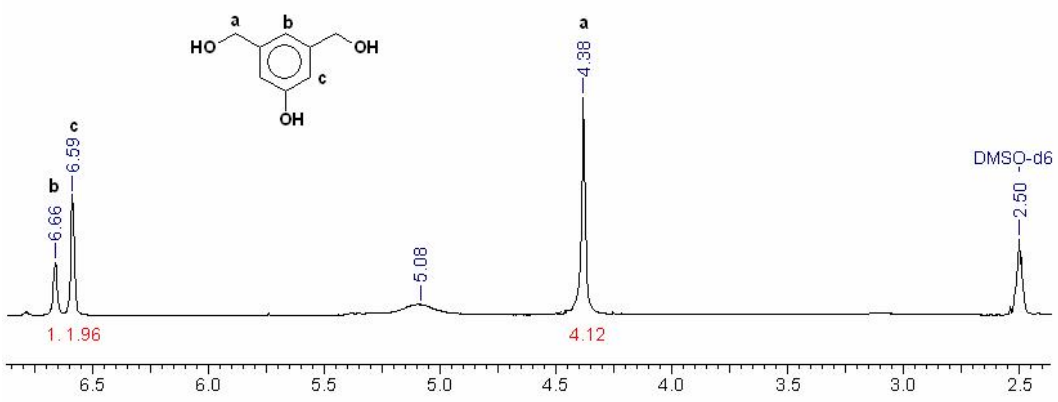


Figure 3.19: ^{1}H-NMR spectrum of 3,5-bis(hydroxymethyl) phenol (3) in DMSO-d_6

Figure 3.20 shows ^{13}C-NMR spectrum of BHMP along with assignments. The peak at 157.44 ŭ ppm was ascribed to quaternary carbon (C5) to which phenolic hydroxyl group is attached. The peak of aromatic carbon C3 appeared at 115.57 ŭ ppm and the peak for two aromatic carbons (C4) that are *ortho* to phenolic hydroxyl group was observed at 112.06 ŭ ppm. The peaks at 63.35 and 143.95 ŭ ppm were assigned to two bis-hydroxy methyl carbons (C1) and quaternary carbon (C2) to which hydroxy methyl group is attached, respectively.

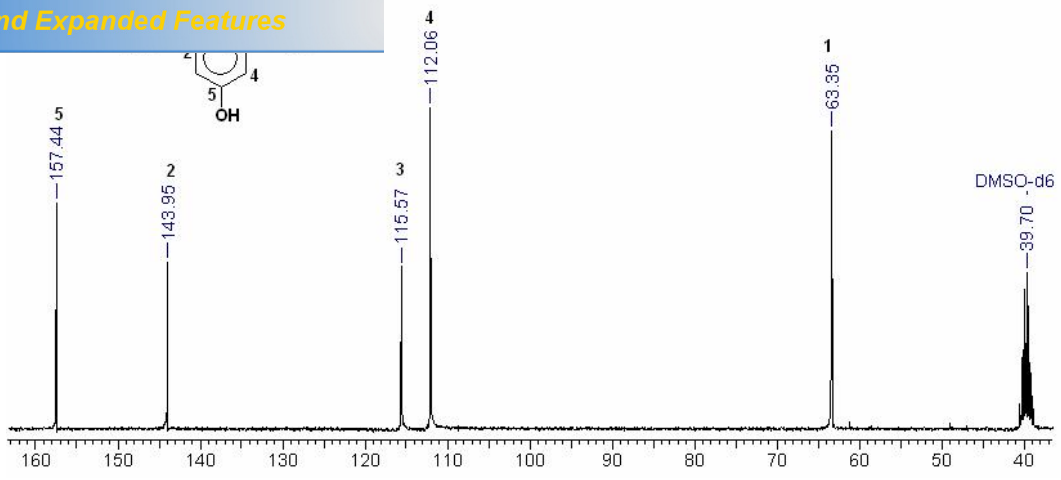


Figure 3.20: ^{13}C-NMR spectrum of 3,5-bis(hydroxymethyl) phenol (3) in DMSO-d_6

In the third step, equivalent quantities of BHMP **(3)** and 2-bromoisobutyryl bromide were reacted in the presence of triethyl amine as an acid chloride acceptor to afford 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate **(4)**. The yield of the desired product i.e. phenolic ester was low due to the formation of multiple products as BHMP contains two aliphatic hydroxyl and one phenolic hydroxyl groups. The target compound viz., 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate **(4)** was separated from the product mixture by column chromatography.

The structure of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate **(4)** was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of BHMPBMP **(4)** is shown in **Figure 3.21**. The spectrum exhibited hydroxyl absorption band at 3402 cm^{-1} and band for phenolic ester was observed at 1750 cm^{-1}

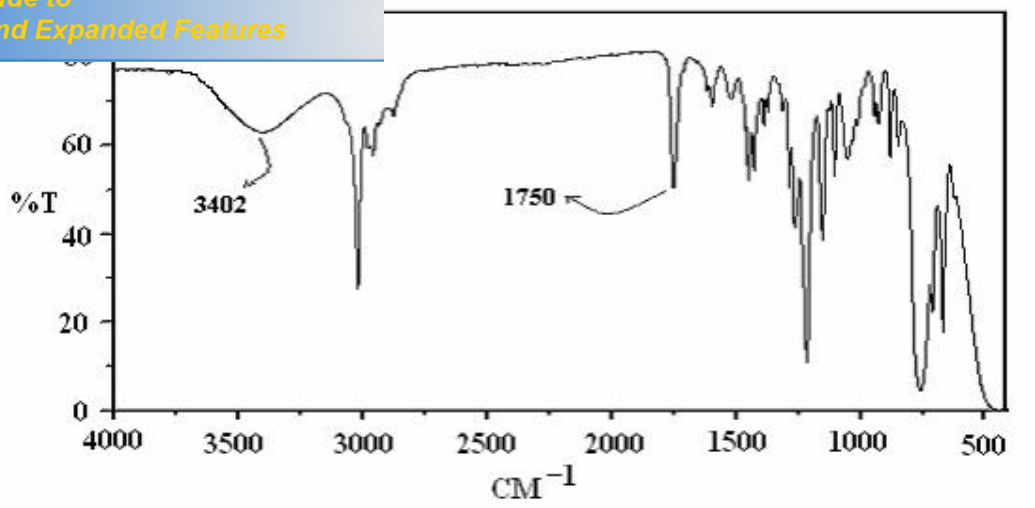


Figure 3.21: IR spectrum of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (4)

Figure 3.22 shows ^{1}H-NMR spectrum of BHMPBMP along with the assignments. The singlet at 7.14 ŭ ppm was assigned to aromatic proton (Hb) flanked by hydroxymethyl groups and the singlet at 6.95 ŭ ppm was ascribed to two aromatic protons (Hc) *ortho* to phenolic ester group. The singlet at 4.55 ŭ ppm was attributed to methylene protons (Ha) to which hydroxyl group is attached and the singlet at 1.96 ŭ ppm was assigned to six protons (Hd) of two methyl groups.

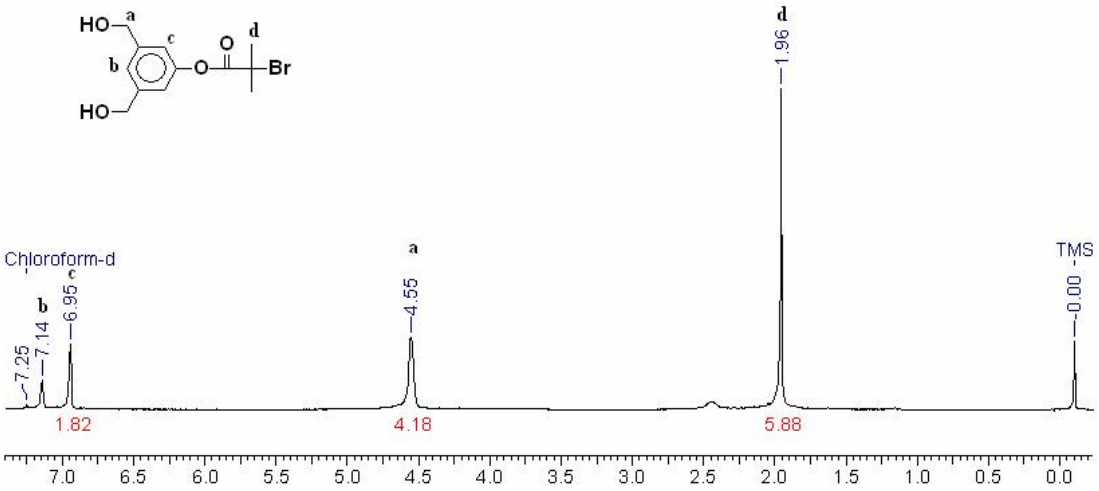


Figure 3.22: ^{1}H-NMR spectrum of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (4) in $CDCl_3$

C-NMR spectrum of BHMPBMP along with assignments. The phenolic ester carbonyl carbon (C6) appeared at 169.34 ŭ ppm. The quaternary aromatic carbon (C5) to which the ester group is attached and C2 to which hydroxy methyl group is attached appeared at 149.96 and 143.16 ŭ ppm, respectively. The peaks at 121.55 and 116.81 ŭ ppm correspond to tertiary aromatic carbons C3 and C4, respectively. The peak at 62.59 ŭ ppm corressponds to two hydroxy methyl group carbons (C1). The signals due to quaternary carbon (C7) and two methyl group carbons (C8) appeared at 54.95 and 29.73 ŭ ppm, respectively.

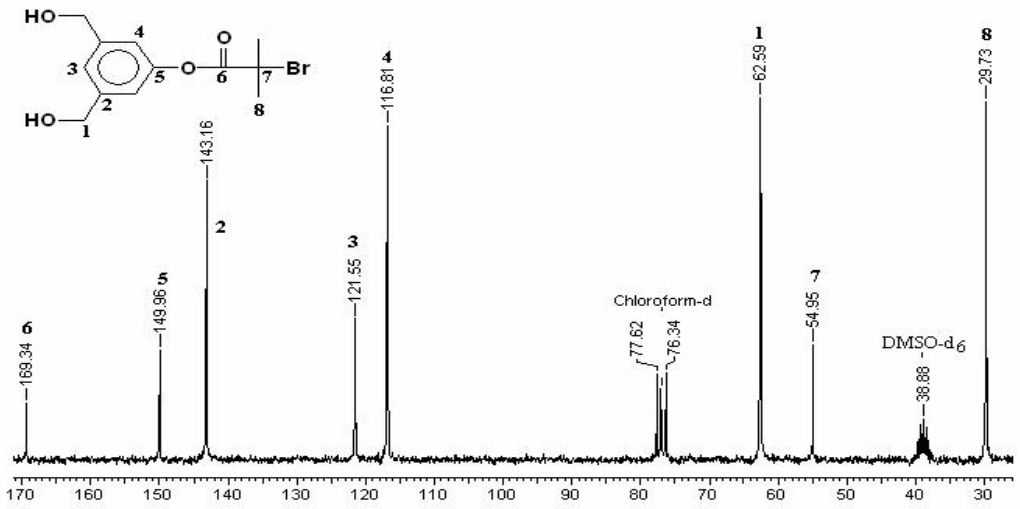


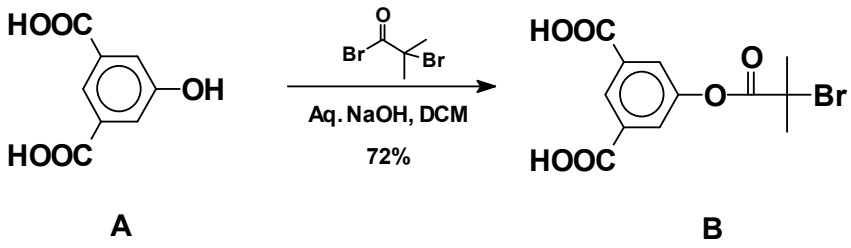
Figure 3.23: ^{13}C-NMR spectrum of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (4) in a mixture of $CDCl_3$ and DMSO-d_6

3.4.7 Synthesis and characterization of 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid (BMPIPA)

Dicarboxylic acids have been utilized for the synthesis of high performance condensation polymers like polyesters, polyamides, etc.[54,55] Carboxylic acid functionality can be easily converted to other functional groups such as aldehyde, amino, isocyanate, etc by simple organic transformations.[56,57] Therefore, dicarboxylic acids are important in polymer chemistry.

Scheme 3.8 depicts synthesis of dicarboxylic acid containing ATRP functionality namely, 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid. 5-Hydroxy isophthalic acid **(A)** was reacted with of 2-bromoisobutyryl bromide in the presence of aqueous sodium

phase transfer catalyst following the Schotten-Baumann procedure.[27]



Scheme 3.8: Synthesis of 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid (B)

5-(2-Bromo-2-methylpropanoyloxy) isophthalic acid **(B)** was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Figure 3.24 shows FTIR spectrum of 5-hydroxy isophthalic acid (A) and BMPIPA (B) for ease of comparison. The spectrum B shows absorption bands at 1763 cm^{-1} and 1725 cm^{-1} corresponding to phenolic ester carbonyl and acid carbonyl stretching, respectively confirming the formation of desired product.

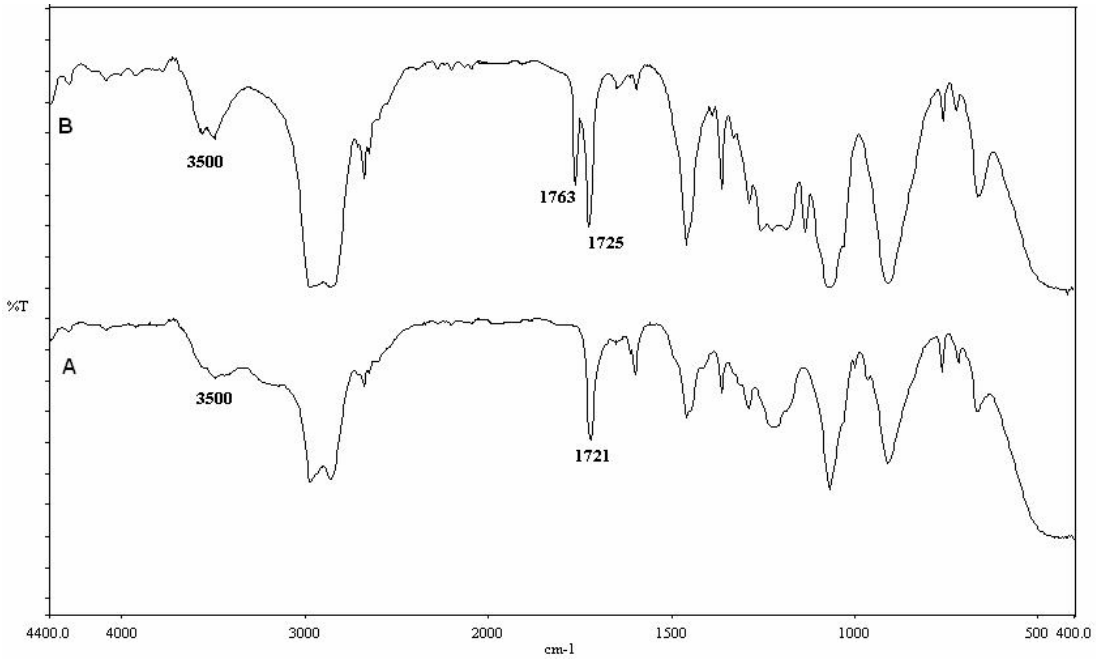


Figure 3.24: IR spectra of 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid (B) and 5-hydroxy isophthalic acid (A)

^{1}H-NMR spectrum along with assignments of BMPIPA is shown in **Figure 3.25**. The singlet at 8.62 δ ppm was assigned to aromatic proton (Hb) flanked by two carboxylic

7.98 δ ppm is due to two aromatic protons (Ha) *ortho* to ester group. The singlet for six protons of two methyl groups appeared at 2.08 δ ppm.

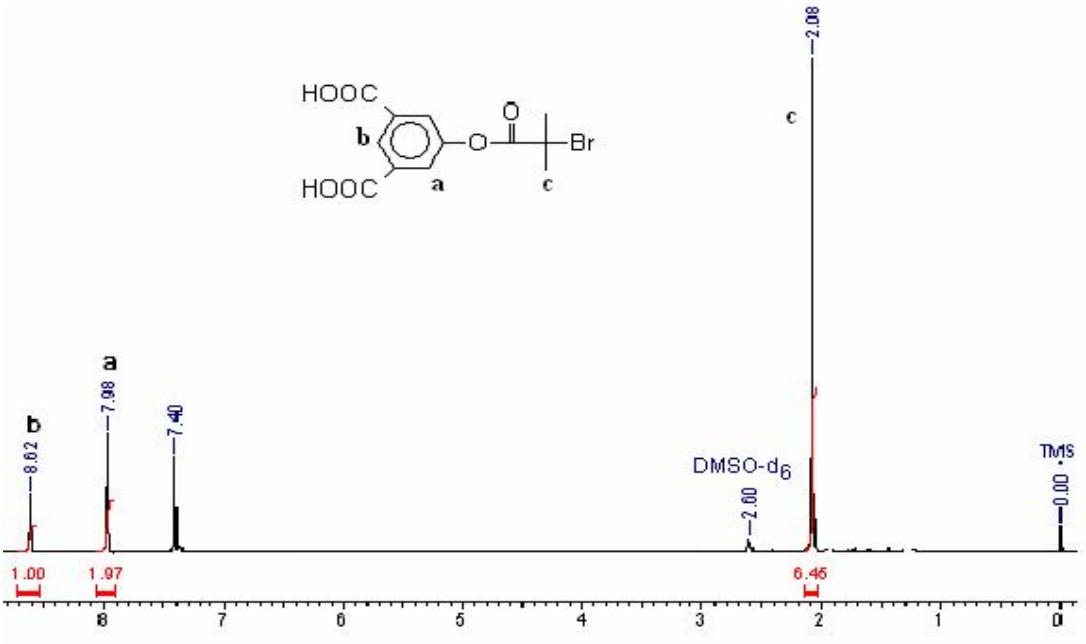


Figure 3.25: ^{1}H NMR spectrum of 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid in mixture of DMSO-d_6 and $CDCl_3$

Figure 3.26 shows ^{13}C-NMR spectrum of BMPIPA along with assignments. The peaks at 169.79 δ ppm and 165.96 δ ppm arise due to ester carbonyl carbon (C6) and two carboxylic acid carbons (C1), respectively. The quaternary aromatic carbon (C5) appeared at 150.75 δ ppm and two aromatic quaternary carbons (C2) appeared at 133.26 δ ppm. The tertiary carbon (C7) to which bromine is attached appeared at 57.14 δ ppm and methyl carbon (C8) appeared at 30.15 δ ppm.

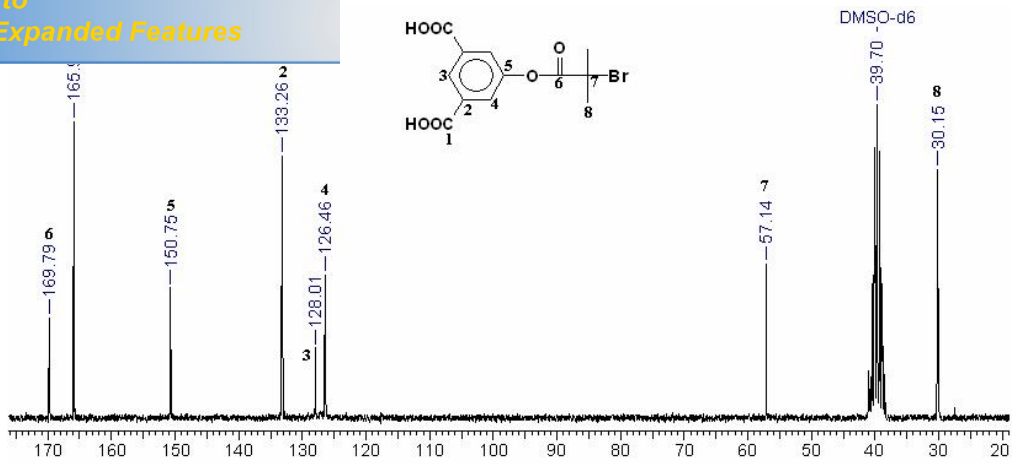
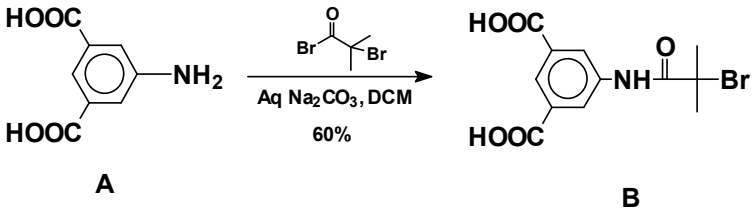


Figure 3.26: ^{13}C-NMR spectrum of 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid in DMSO-d_6

3.4.8 Synthesis and characterization of 5-(2-bromo-2-methylpropanamido) isophthalic acid (BMPAIPA)

Scheme 3.9 depicts synthesis of 5-(2-bromo-2-methylpropanamido) isophthalic acid by condensation reaction between 5-amino isophthalic acid and 2-bromoisobutyryl bromide in the presence of sodium carbonate. The product was purified by recrystallization from a mixture of water and methanol.



Scheme 3.9: Synthesis of 5-(2-bromo-2-methylpropanamido) isophthalic acid

The structure of 5-(2-bromo-2-methylpropanamido) isophthalic acid was confirmed by FTIR, ^{1}H and ^{13}C-NMR spectroscopy.

Figure 3.27 shows FTIR spectra of BMPAIPA (B) and 5-amino isophthalic acid (A). The spectrum of BMPAIPA exhibited a band for amide carbonyl at 1696 cm^{-1} and an acid carbonyl stretching vibration at 1720 cm^{-1}.

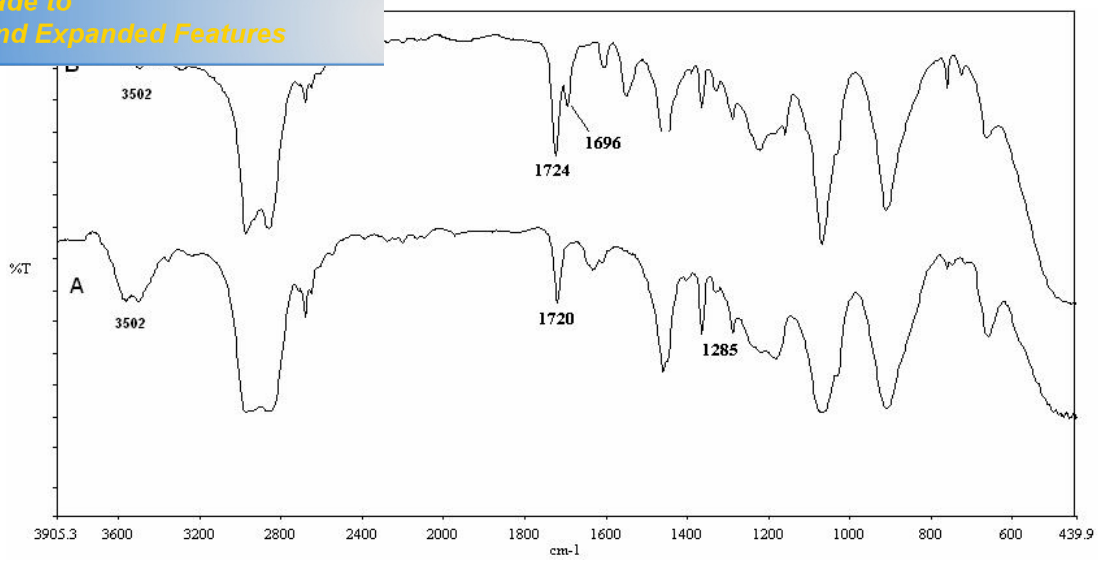


Figure 3.27: IR spectra of 5-(2-bromo-2-methylpropanamido) isophthalic acid (B) and 5-amino isophthalic acid (A)

Figure 3.28 shows ^{1}H-NMR spectrum along with the assignments of BMPAIPA. The singlet at 9.55 δ ppm was designated to the amide proton (Hc). The two aromatic protons (Hb) *ortho* to the amide group and one proton (Ha) flanked by carboxylic acid groups appeared as singlets at 8.53 and 8.44 δ ppm, respectively. The singlet at 2.06 δ ppm correspond to six protons (Hd) of two methyl groups.

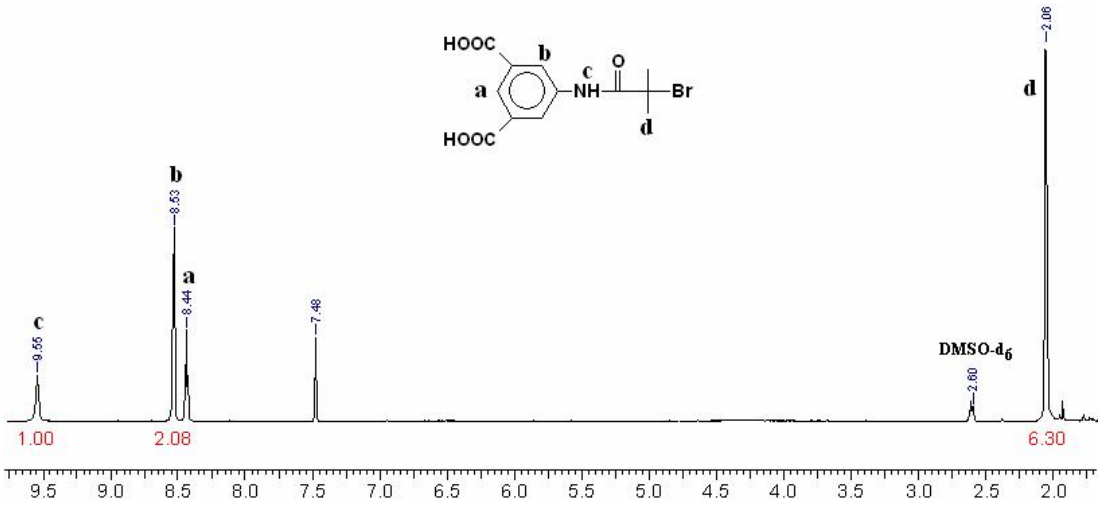


Figure 3.28: ^{1}H-NMR spectrum of 5-(2-bromo-2-methylpropanamido) isophthalic acid in a mixture of DMSO-d_6 and $CDCl_3$

^{13}C-NMR spectrum along with assignments of BMPAIPA is shown in **Figure 3.29**. The amide carbonyl carbon (C6) appeared at 170.17 δ ppm while acid carbonyl carbon

m. The quaternary carbon (C5) to which amide group is attached appeared at 139.64 δ ppm and the quaternary aromatic carbon (C2) to which carboxylic acid group is attached appeared at 131.91 δ ppm. The signals for carbon C3 and C4 appeared at 125.56 and 125.25 δ ppm, respectively. The quaternary carbon (C7) to which bromine is attached appeared at 60.56 δ ppm. The peak at 30.83 δ ppm correspond to two methyl group carbons (C8).

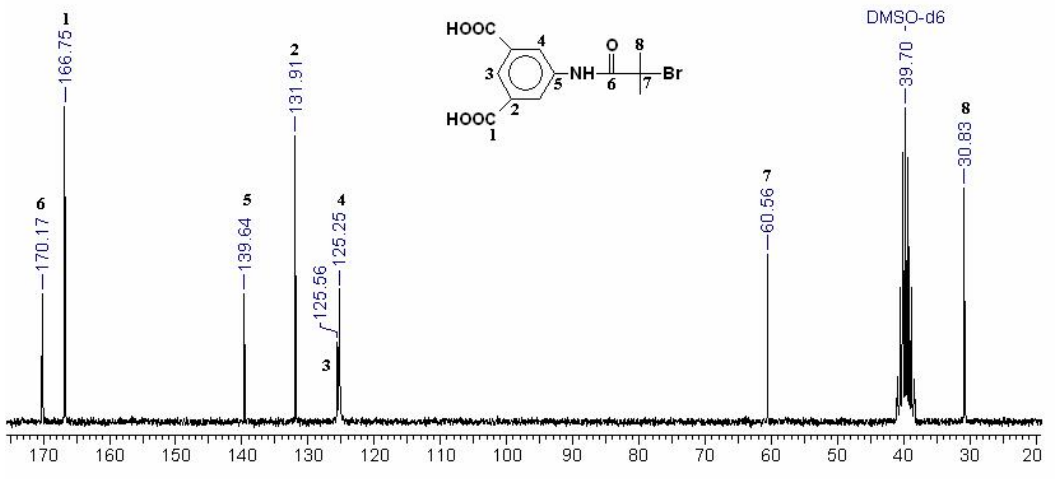
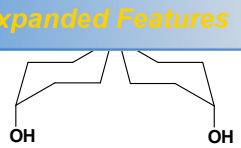


Figure 3.29: ^{13}C-NMR spectrum of 5-(2-bromo-2-methylpropanamido) isophthalic acid in DMSO-d_6

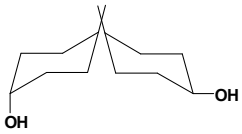
3.4.9 Synthesis and characterization of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (OPCBMP)

Lactone, a reactive functional group, can undergo ring opening in the presence of nucleophiles such as alcohol, amine, etc.[58] Lactone containing compounds are important as monomers in the preparation of polymers for biomedical applications and can be used as coupling reagents.[59]

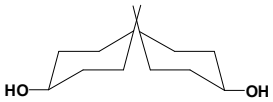
Lactone containing ATRP initiator namely, 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (OPCBMP) was synthesized starting from hydrogenated bis-phenol A (HBPA). HBPA is commonly used in industries for the preparation of aliphatic polyesters, polycarbonates and epoxies. It is prepared by catalytic hydrogenation of bisphenol-A (BPA) which typically provides HBPA as a mixture of three isomers: cis, cis **(Figure 3.30, I)**; cis, trans **(Figure 3.30, II)**; and trans, trans **(Figure 3.30, III)**.[58,61]



I: cis, cis
(axial, axial)



II: cis, trans
(axial, equatorial)

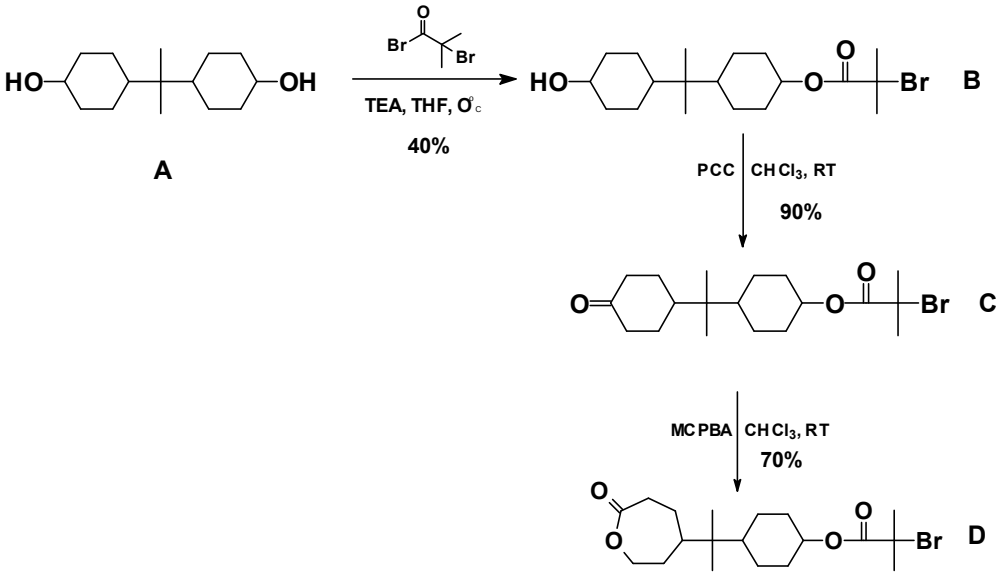


III: trans, trans
(equatorial, equatorial)

Figure 3.30: Isomers of HBPA (A) obtained from hydrogenation of BPA

Scheme 3.10 depicts route for the synthesis of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(D)**.[18,61]

In the first step, HBPA **(A)** and 2-bromoisobutyryl bromide were reacted in the presence of triethyl amine as an acid acceptor to yield the intermediate, 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(B)** which was purified by column chromatography.



Scheme 3.10: Synthesis of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (D)

The structure of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Figure 3.31A shows IR spectrum of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(B)**. The band at 3453 cm^{-1} corresponds to

e band observed at 1724 cm^{-1} corresponds to ester carbonyl stretching vibration.

Figure 3.36 shows ^{1}H-NMR spectra of HBPA, 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(B)**, intermediate ketone 4-[2-(4-oxocyclohexyl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(C)** and 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(D)**. The two isomeric forms of HBPA can be distinguished from ^{1}H-NMR spectrum **(Figure 3.36 A)** as axial and equatorial protons were observed at 3.52 δ ppm (Haδ) and 4.04 δ ppm (Ha), respectively. Similarly, the axial and equatorial protons were present in intermediate **B**, as seen from ^{1}H-NMR spectrum **(Figure 3.36 B)**. The new peak at 4.68 δ ppm corresponds to the proton attached to ester group (Hi) and the singlet at 1.91 δ ppm is due to six protons of the two-methyl groups.

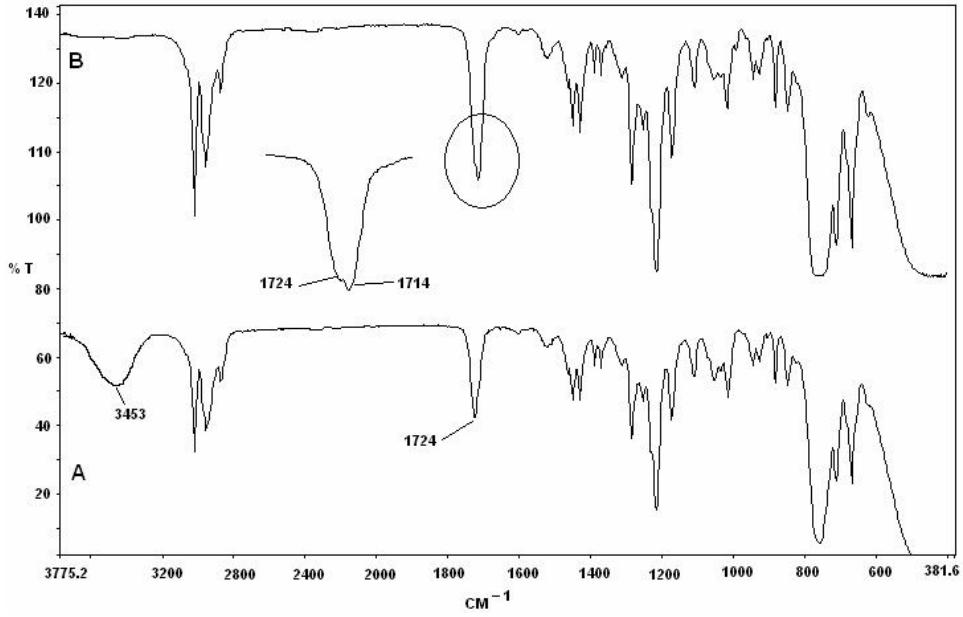


Figure 3.31: IR spectra of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (B) and 4-[2-(4-oxocyclohexyl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (C)

^{13}C-NMR spectrum along with assignments of intermediate **B** is shown in **Figure 3.32**. The spectrum indicates the presence of cis/trans isomers, where signals for the carbons C1 and C1ô appeared at 71.12 and 65.83 δ ppm, respectively. The peak at 171.08

yl carbon (C11), while secondary carbons (C1) and (C10) appeared at 71.12 and 75.35 δ ppm, respectively.

No efforts were made to separate the isomers of intermediate **B** as it was beyond the scope of work.

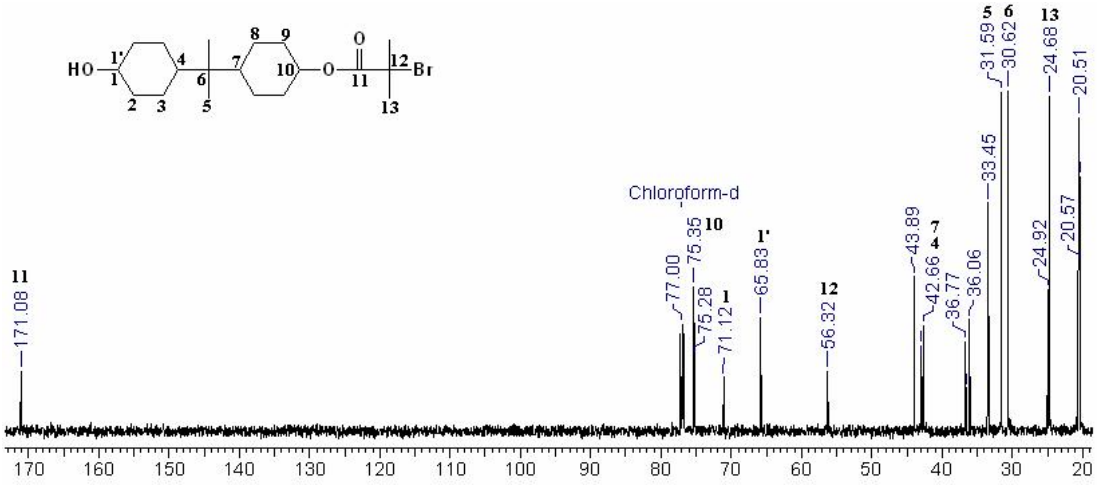


Figure 3.32: ^{13}C-NMR spectrum of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (B) in $CDCl_3$

In the second step, oxidation of intermediate alcohol **B** was carried out using pyridinium chlorochromate (PCC) as oxidizing agent to give intermediate ketone **C**. In the literature a variety of reagents have been reported for the oxidation of alcohols of which the most common are chromic acid ($H_2Cr_2O_7$) and pyridinium chlorochromate (PCC).[28]

The characterization of intermediate **C** was carried out by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

IR spectrum confirms the formation of ketone, which shows carbonyl (C=O) stretch at 1714 cm^{-1} as an intense absorption band. The band at 1724 cm^{-1} confirms presence of ester group **(Figure 3.31B and 3.35)**.

^{1}H-NMR spectrum of the intermediate **C** shows absence of the both axial and equatorial protons (4.05 δ and 3.53 δ pm), which were attached to the secondary carbon to which hydroxyl group is attached **(Figure 3.36C and B)**. The other peaks corresponding to protons are similar to intermediate **B**.

Further, the formation of intermediate ketone **C** was confirmed by ^{13}C-NMR spectroscopy, where carbonyl carbon appeared at 212.16 δ ppm **(Figure 3.33)**.

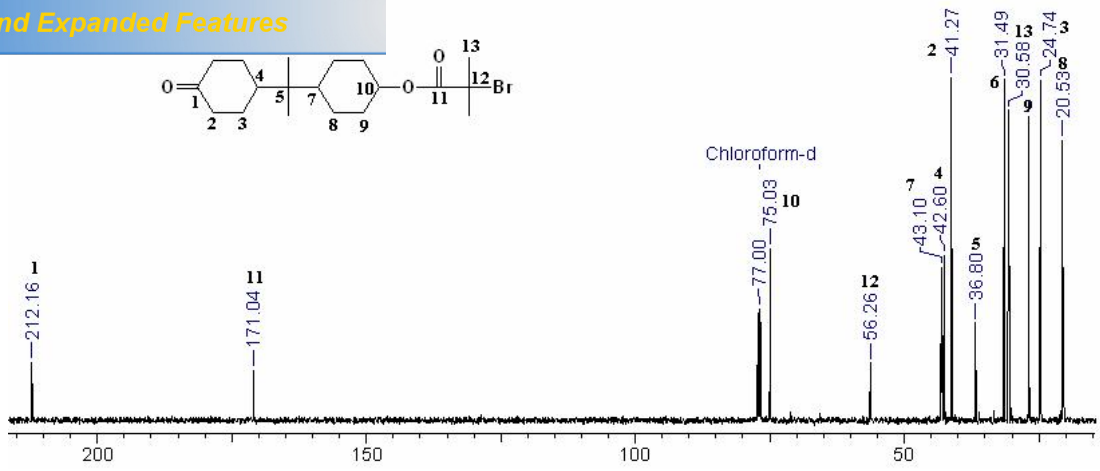


Figure 3.33: ^{13}C-NMR spectrum of 4-[2-(4-oxocyclohexyl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (C) in $CDCl_3$

In the third step the lactone functionalized ATRP initiator, namely 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(D)** was obtained by Bayer-Villiger oxidation of intermediate **C** using m-chloroperbenzoic acid as a reagent.

The structure of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(D)** was confirmed by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Figure 3.34 and **Figure 3.35** shows IR spectrum of **D** and partial IR spectra (overlayed) of the intermediates, respectively. The disappearance of the band of ketone (1714 cm^{-1}) and appearance of a strong carbonyl absorption signal due to both lactone as well as linear ester carbonyl at 1726 cm^{-1} confirmed the conversion of ketone to lactone.

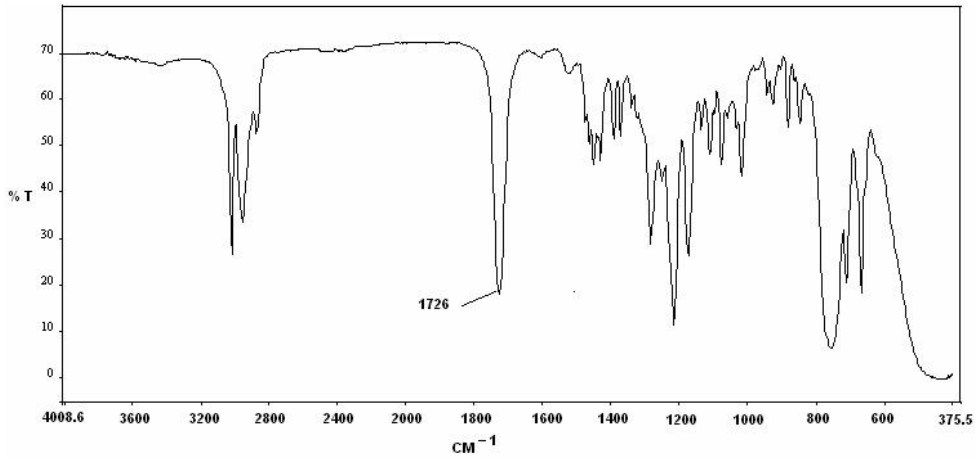


Figure 3.34: IR spectrum of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (D)

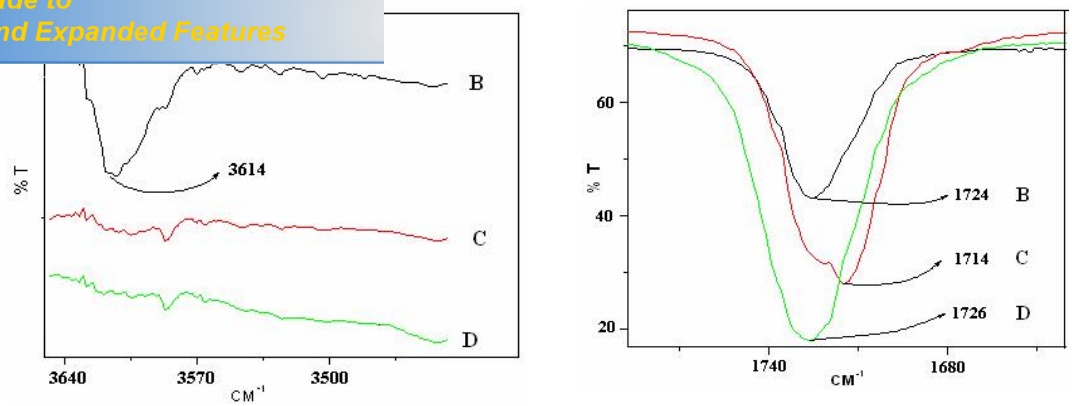


Figure 3.35: Selected region of IR spectra of 4[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (B), 4-[2-(4-oxocyclohexyl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (C) and 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (D)

^{1}H-NMR spectrum of lactone-functionalized initiator, **D** along with assignments is shown in **Figure 3.36D.** The new peaks appeared at 4.34 δ ppm and 4.16 δ ppm due to two protons (Hbô) of methylene group from the lactone ring. Another new peaks appeared at 2.56-2.72 δ ppm (Hdô), which corresponds to the two protons of methylene group from lactone ring. The peaks due to the dimethyl protons (Hj) and (He) appeared at 1.91 and 0.78 δ ppm, respectively.

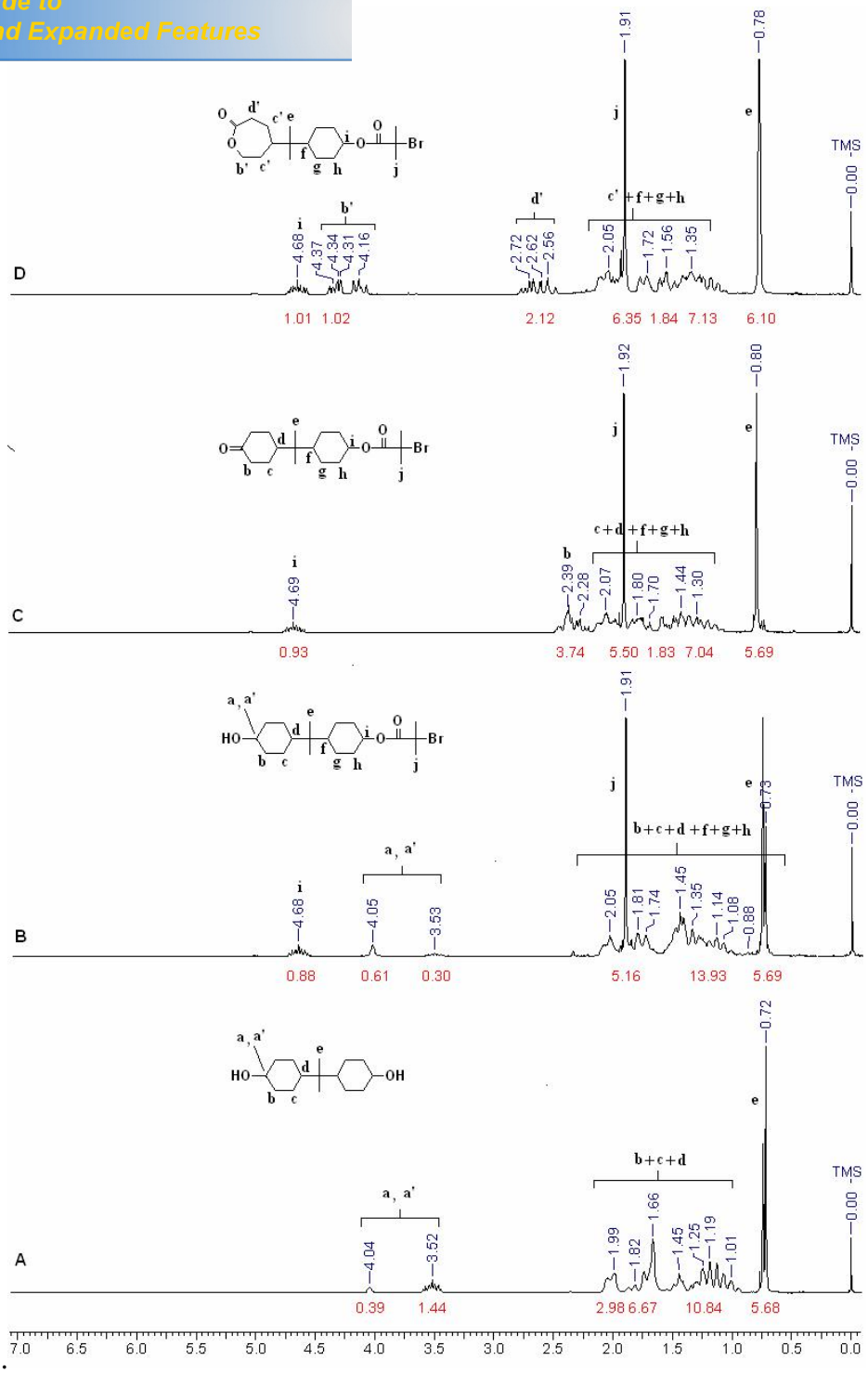


Figure 3.36: ^{1}H-NMR spectra of HBPA (A), 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (B), 4-[2-(4-oxocyclohexyl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (C) and 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (D) in $CDCl_3$

C-NMR spectrum of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (**D)** along with the assignments. The spectrum showed peaks at 176.14 δ ppm for the lactone carbonyl carbon (C6) and at 170.99 δ ppm for ester carbonyl carbon (C13). Quaternary carbons C7 and C14 (to which bromine is attached) exhibited peaks at 37.25 and 56.22 δ ppm, respectively. The carbons of lactone ring C5, C4, C3, C2 and C1 appeared at 23.07, 29.71, 46.47, 33.37 and 68.53 δ ppm, respectively, whereas the carbons in cyclohexane ring C9, C10, C11 and C12 appeared at 42.57, 31.37, 24.61 and 74.87 δ ppm, respectively. The peaks at 20.47 and 30.54 δ ppm were attributed to methyl group carbons (C8) and (C15), respectively.

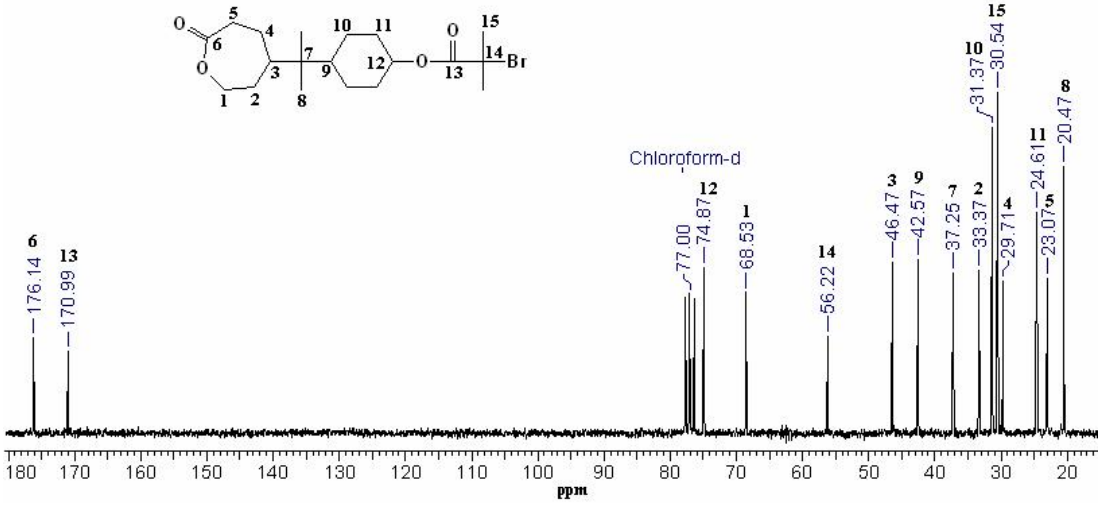


Figure 3.37: ^{13}C-NMR spectrum of 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (D) in $CDCl_3$

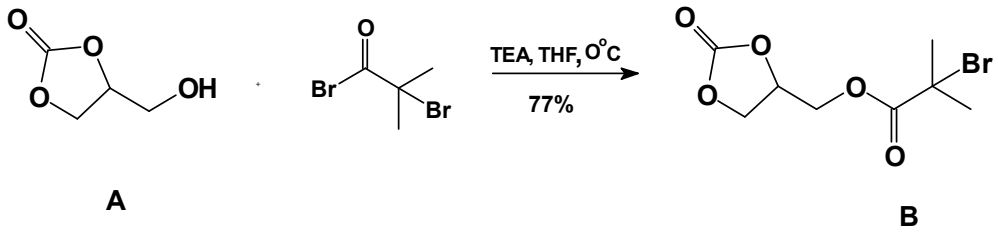
3.4.10 Synthesis and characterization of 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate)

Cyclic carbonate functionality has attracted considerable interest both academically and industrially due to its polar nature and high reactivity towards aliphatic and aromatic amines, alcohols, thiols and carboxylic acids.[62-65] Cyclic carbonate groups are known to react with amino groups in proteins under mild conditions, resulting in stable urethane structures.[66] Using the advantage of reaction of carbonate and amino group, cellulose derivatives containing cyclic carbonate groups and copolymers of vinylene

ported as matrices for immobilization of enzymes, antigens, etc. [66-69]

Cyclic carbonate functionalized ATRP initiator namely, 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) **(B)** was synthesized from glycerol carbonate **(A)** as the starting material. Glycerol carbonate is a commercially available chemical and there are many routes for its synthesis starting from glycerol.[70]

Scheme 3.11 shows route for synthesis of ODMBMP **(B)**. The reaction of glycerol carbonate and 2-bromoisobutyryl bromide in the presence of triethyl amine as hydrogen bromide acceptor afforded the product which was purified by recrystallization.



Scheme 3.11: Synthesis of 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate)

2-Oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) was characterized using FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Figure 3.38 shows FTIR spectra of ODMBMP **(B)** and glycerol carbonate **(A)**. The hydroxyl stretching absorption band of glycerol carbonate at 3405 cm^{-1} disappeared in the IR spectrum of ODMBMP, while a new band appeared at 1744 cm^{-1} corresponding to ester carbonyl group. The broad band at 1820 cm^{-1} indicates the presence of carbonate group in ODMBMP.

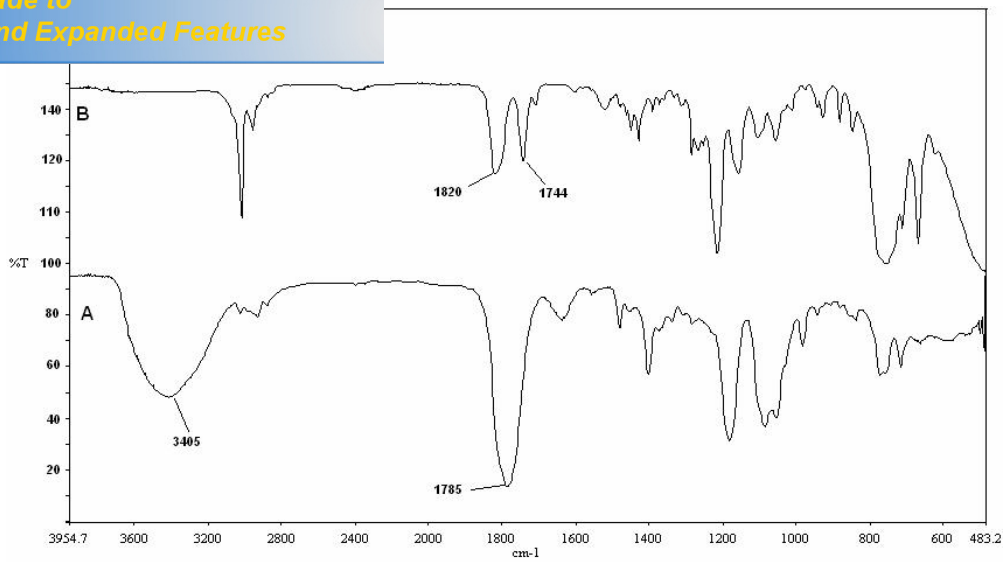


Figure 3.38: IR spectrum of 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) (B) and glycerol carbonate (A)

^{1}H-NMR spectrum of ODMBMP along with assignments is shown in **Figure 3.39**. The methine proton (Hb) of cyclic carbonate ring exhibited a multiplet centered at 5.0 δ ppm. The four protons of two methylene group; one attached to ester group (Hc) and other in the cyclic carbonate ring (Ha) appeared as multiplets in the region 4.30 to 4.65 δ ppm. The six protons (Hd) of two-methyl groups appeared as a singlet at 1.95 δ ppm,

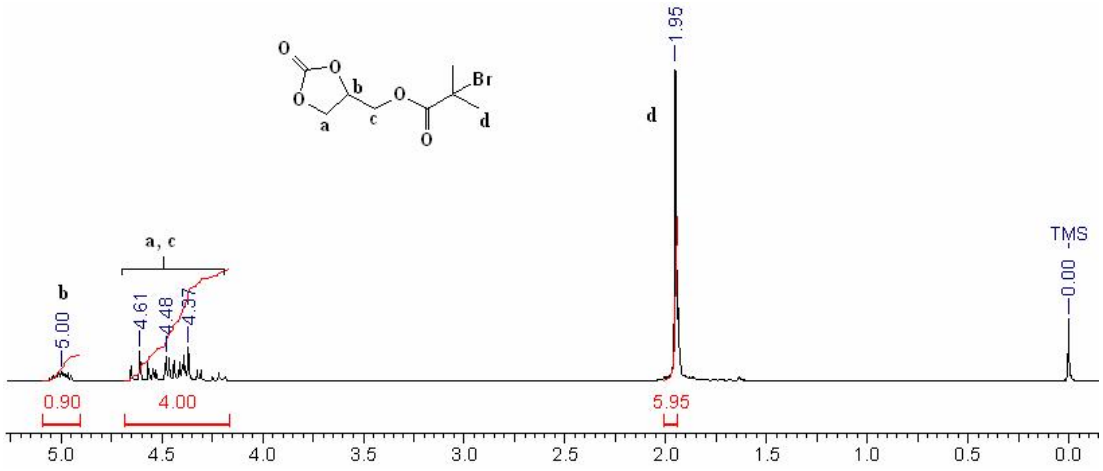


Figure 3.39: ^{1}H-NMR spectrum of 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) in $CDCl_3$

^{13}C-NMR spectrum of ODMBMP along with assignments is shown in **Figure 3.40**. The peak due to ester carbon (C5) appeared at 171.04 δ ppm, while the peak due to carbonate carbon (C1) appeared at 154.34 δ ppm. The peaks of methylene carbons (C4)

65.82 δ ppm, respectively. The peaks at 54.87 and 30.37 δ ppm correspond to tertiary carbon (C6) and methyl carbon (C7), respectively.

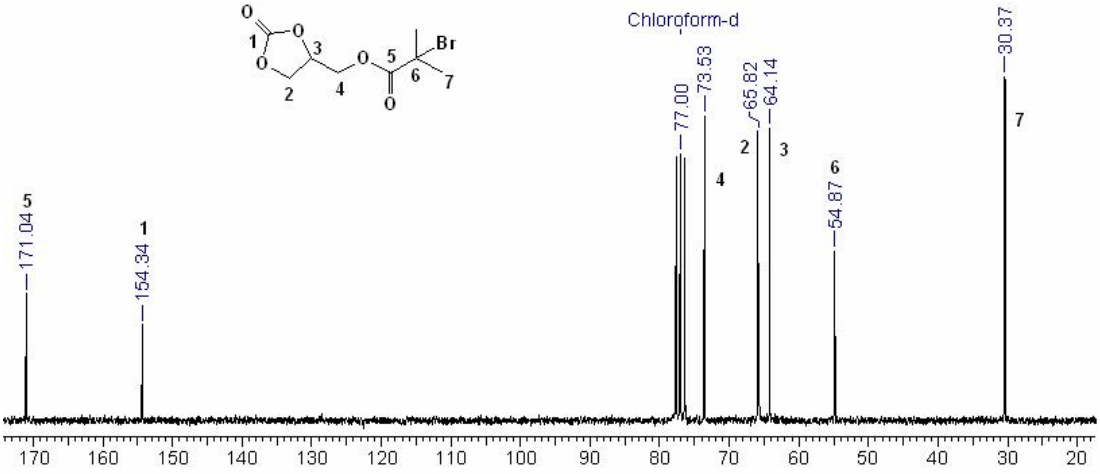


Figure 3.40: ^{13}C-NMR spectrum of 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) (B) in $CDCl_3$

1. A hydroxyl-functionalized ATRP initiator namely, 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate was prepared by reaction of 1,4-benzene dimethanol with 2-bromoisobutyryl bromide.
2. A new sulfonic acid functionalized ATRP initiator namely, 4-(2-bromo-2-methylpropanoyloxy) benzenesulfonic acid was synthesized by reaction of 4-hydroxy benzene sulfonic acid with 2-bromoisobutyryl bromide.
3. A new nitro-functionalized ATRP initiator namely, 4-[(4ô-nitro) phenoxymethyl] benzyl bromide was synthesized by reaction of 4-nitrophenol and 1,4-bis(bromomethyl) benzene.
4. A new protected dihydroxyl-functionalized ATRP initiator namely, 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) was synthesized starting from trimethylol propane.
5. A new dihydroxyl functionalized ATRP initiator namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate was synthesized by deprotection of 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl-2-bromo-2-methylpropanoate) in the presence of dilute hydrochloric acid.
6. A novel bismethylol functionalized ATRP initiator namely, 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate was successfully synthesized starting from commercially available 5-hydroxy isophthalic acid.
7. Two new dicarboxylic acids containing ATRP functionality viz., 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid and 5-(2-bromo-2-methylpropanamido) isophthalic acid were synthesized starting from 5-hydroxy isophthalic acid and 5-amino isophthalic acid, respectively.
8. A new lactone functionalized ATRP initiator namely, 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate was synthesized starting from hydrogenated bisphenol-A.
9. A new cyclic carbonate functionalized ATRP initiator namely, 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) was synthesized by reaction of commercially available glycerol carbonate with 2-bromoisobutyryl bromide.

1. K. Matyjaszewski and J. Xia, *Chem. Rev*., 101, 2921, **2001**
2. M. Kamigaito, T. Ando, and M. Sawamoto, *Chem. Rev*., 101, 3689, **2001**
3. V. Coessens, T. Pintauer and K. Matyjaszewski, *Prog. Polym. Sci*., 26, 337, **2001**
4. K. Matyjaszewski, *Macromolecules*, 31, 4710, **1998**
5. D. M. Haddleton, C. Waterson, P. J. Derrick, C. B. Jasieczek and A. J. Shooter, *Chem. Commun*., 683, **1997**
6. A. Marsh, A. Khan, D. M. Haddleton and M. J. Hannon, *Macromolecules*, 32, 8725, **1999**
7. X. Zhang and K. Matyjaszewski, *Macromolecules,* 32, 7349, **1999**
8. D. M. Haddleton and C. Waterson, *Macromolecule*s, 32, 8732, **1999**
9. Y. Nakagawa and K. Matyjaszewski, *Polym. J*., 30, 138, **1998**
10. A. Cuendias, R. Backov, E. Cloutet and H. Cramail, *J. Mater. Ch*em., 15, 4196, **2005**
11. H. Malz, H. Komber, D. Voigt, I. Hopfe, and J. Pionteck, *Macromol. Chem. Phys*. **200,** 642, **1999**
12. M. Erdogan, Y. Hepuzer, I. Cianga, Y. Yagcē and O. Pekcan, *J. Phys. Chem. A*, 107, 8363, **2003**
13. S. Qin, D. Qin, W. T. Ford, D. E. Resasco and J. E. Herrera, *J. Am. Chem. Soc*., 126, 170, **2004**
14. A. P. Smith and C. L. Fraser, *J. Polym. Sci., Part A: Polym. Chem*., 40, 4250, **2002**
15. G. J. Summers, M. P. Ndawuni and C. A. Summers, *J. Polym. Sci. Part A: Polym. Chem.*, 39, 2058, **2001**
16. C. Cheng, E. Khoshdel and K. L. Wooley, *Macromolecules*, 38, 9455, **2005**
17. K. Matyjaszewski, V. Coessens, Y. Nakagawa, J. Xia, J. Qiu, S. Gaynor, S. Coca and C. Jasieczek, *ACS Symp. Ser*. 704,16, **1998**
18. D. Mecerreyes, B. Atthoff, K. A. Boduch, M. Trollsas and J. L. Hedrick, *Macromolecules*, 32, 5175, **1999**
19. H. Malz, H. Komber, D. Voigt, I. Hopfe, and J. Pionteck, *Macromol. Chem. Phys*. 200, 642, **1999**
20. B. Moon, T. R. Hoye, and W. Christopher, *Macromolecules*, 34, 7941, **2001**
21. S. Gong, H. Ma and X. Wan, *Polym. Int.,* 55, 1420, **2006**

. L. Hedrick and M. Trollsås, *Macromolecules*, 32, 5171, **1999**

23. F. de Loos, Irene C. Reynhout, J. L. Jeroen, M. Cornelissen, A. E. Rowan and R. J. M. Nolte, *Chem. Commun*., 60, **2005**
24. D. D. Colak, I. Cianga, A. E. Muftuoglu and Y. Yagci, *J. Polym. Sci. Part A: Polym. Chem.*, 44, 727, **2006**
25. G. J. Summers, M. P. Ndawuni and C. A. Summers, *Polym Int*, 52, 158, **2003**
26. C. Liu, R. Bao, J. Qiu, F. Hu, Y. Xu, C. Zhao and Y. Zhou, *Polym. Bulle.* 57, 139, **2006**
27. S. Yurteri, I. Cianga and Y. Yagci, *Macromol. Chem. Phys*., 204, 1771, **2003**
28. E. J. Corey and J. W. Suggs, *Tet. Lett*., 31, 2647, **1975**
29. A. Sarkar, ñ*Synthesis and Characterization of Polyamides, Polyimides and Polyesters Containing Flexibilizing Groups*,ò Ph.D. Thesis, University of Pune, India, **2005**
30. M. Inouye, K. Fujimoto, M. Furusyo and H. Nakazumi, *J. Am. Chem. Soc*., 121, 1452, **1999**
31. J. C. Brosse, D. Derouet, F. Epaillard, J. C. Soutif, G. Legeay and K. Dusek, *Adv. Polym. Sci*., 81, 167, **1986**
32. R. D. Athey, *Prog. Org. Coat*., 7, 289, **1979**
33. C. J. Hawker, J. L. Hedrick, E.E. Malmstrom, M. Trollsas, D. Mecerreyes, G. Moineau, Ph. Dubois and R. Jerome, *Macromolecules,* 31, 213, **1998**
34. M. Geus, J. Peeters, M. Wolffs, T. Hermans, A. R. A. Palmans, C. E. Koning and A. Heise, *Macromolecules*, 38, 4220, **2005**
35. A. C. Perricone, D. P. Enright and J. M. Lucas, *SPE Drilling Engineering* 1, 5, 358, **1986**
36. S. L. Chena, L. Krishnana, S. Srinivasana, J. Benzigerb and A. B. Bocarslya, *J. Memb. Sci*., 243, 327, **2004**
37. I. Villegas-Coss, F.A. Ruiz-Trivino and S. Hernandez-Loez, *J. Polym. Sci. Polym. Phys*., 44, 256, **2006**
38. E. Bucio, J. C. I. Lara-Estevez, F. A. Ruiz-Trivino and A. Acosta-Huerta, *Polym. Bull*., 56, 163, **2006**
39. E. J. Goethals, ñ*Telechelic Polymers: Synthesis and Applications*,ò CRC Press, Boca Raton, Florida, **1989**

aga, J. J. Iruin, O. Miquel, D. Mecerreyes and J. Jouanneau, *React. Func. Polym.*, 66, 1073, **2006**

41. C. P. Yang, S. H. Hsiao and K. L. Wu, *Polymer*, 44, 7067, **2003**
42. V. Percec, M. Grigoras, R. S. Clough and J. Fanjul, *J. Polym. Sci., Part A: Polym. Chem*., 33, 331, **1995**
43. V. Deimede and K. Kallitsis, *Chem. Eur. J*., 8, 467, **2002**
44. L.S. Ramanathan, P.G. Shukla and S. Sivaram, *Pure Appl. Chem*, 70, 1295, **1998**
45. L. S. Ramanathan, ñ*Studies on Particle Forming Polycondensation and Ring Opening Polmerization Processes*ò, Ph.D. Thesis, University of Pune, India, **2000**
46. B. Radhakrishnan, ñ*Elaboration En Milieu Disperse De Materiaux Polyurethane A Structure Coeur – Ecorce",* Ph. D. Thesis, Universite´ Bordeaux 1, France, **2003**
47. E. C. L. Gautier, N. J. Lewis, A. MeKillop and R. J. K. Taylor, *Tet. Lett.*, 35, 8759, **1994**
48. A. E. Graham, D. McKerrecher, H. Davies and R. J. K. Taylor, *Tet. Lett.*, 37, 7445, **1996**
49. B. Radhakrishnan, P. Chambon, E. Cloutet and H. Cramail, *Colloid Polym. Sci*. 281, 516, **2003**
50. H. Zhanga, X. Jiang and R. Linde, *Polymer*, 5, 1455, **2004**
51. B. Praad, A. K. Saund, J. M. Bora and N. K. Mathur, *Ind. J. Chem*., 12, 290, **1974**
52. G. A. Smith and R. E. Gawley, *Org. Synth*., 63,136, **1985**
53. J. R. Gage and D. A. Evans, *Org. Syn.*, 77**, 1989**
54. E. Ferrero, J. F. Espeso, J. G. de la Campa, J. D. de Abajo and A. E. Lozano, *J. Polym. Sci. Part A: Polym. Chem.*, 40, 3711, **2002**
55. Y. Chen, R. Wombacher, J. H. Wendorff and A. Greiner, *Polymer*, 44, 5513, **2003**
56. B. Perly, A. Douy and B. Galot, *Makromol. Chem.*, 177, 2569, **1976**
57. D. C. Allport and W. H. Janes, ñ*Block Copolymers*;ò Applied Science Publishers, London, 20, **1973**
58. A. Terada, *Bull. Chem, Soc. Japan*, 39, 2194, **1966**
59. N. G. Kulkarni, ñ*Studies in Polyester Forming Reactions*,ò Ph.D. Thesis, University of Pune, **2005**
60. R. C. Gaughan and J. F. Schabron, *J. Liq. Chrom*, 7, 13, **1984**
61. J. L. Hedrick, B. Atthoff, K. A. Boduch, C. J. Hawker, D. Mecerreyes, R. D. Miller and M. Trollsas, *Polym. Mater. Sci. and Eng*. 104, 80, **1999**

aram, *Chem Rev.*, 96, 951, **1996**

63. T. Nishikubo, A. Kameyama and M. Sasano, *J. Polym., Sci., Part A: Polym. Chem.* 32, 301, **1994**
64. N. Kihara and T. Endo, *J. Polym., Sci., Part A: Polym. Chem*, 31, 2765, **1993**
65. D. C. Webster and A. L. Crain, *Prog. Org. coat.*, 40, 275, **2000**
66. S. A. Barker, S. H. Doss, C. J. Gray, J. F. Kennedy, M. Stacey and T. H. Yeo, *Carbohydr. Res.,* 20, 1, **1971**
67. S. Dumitriu, V. Bulacovschi, L. Baston, and Cr. Simionescu, *Acta Polym.,* 35, 536**, 1984**
68. N. W. H. Cheethan and G. N. Richards, *Carbohydr. Res.,* 30, 99, **1973**
69. Mauz and K. Sauber, *Ann. N. Y. Acad. Sci.,* 434, 251, **1984**
70. M. Aresta, A. Dibenedetto, F. Nocito and C. Pastore, *J. Mol. Cat. A: Chem*., 257, 149, **2006**

4.1 Introduction

End-functionalized polymers are useful as building blocks for synthesis of block, graft and star copolymers.[1-3] These polymers also have potential applications in several areas like surface modification, catalysis, coatings, adhesives, as well as compatibilization of polymer blends.[4]

Living polymerization methods like anionic,[5,6] cationic,[7] group transfer[8] and controlled radical polymerization[9,10] (CRP) techniques are being used for synthesis of end-functionalized polymers either by using functional initiators or by an approach involving functionalization of living chain ends. Synthesis of end-functionalized polymers by termination reaction of a living polymer requires careful optimization of the reaction conditions to ensure quantitative functionalization. The use of functional initiators ensures that each polymer chain contains functional group at one chain end.

Of late, ATRP technique has been widely studied and has been demonstrated to be a promising method for the synthesis of functionalized polymers.[9-14] ATRP is generally tolerant of various functional groups and this route has been successfully used in synthesis of polymers from functional monomers and for the synthesis of end-functionalized polymers.[14]

This chapter deals with synthesis of polystyrene, polymethyl methacrylate, and polylauryl methacrylate terminated with functional groups such as hydroxyl, bismethylol, lactone and carbonate using corresponding functionalized ATRP initiators. The synthesis of low molecular weight (M_n^{th} - 1500 to 10000) end-functionalized polymers was targeted in the present study. End-functionalized polymers were characterized by FTIR and NMR spectroscopy. The molecular weight and molecular weight distribution of end-functionalized polymers was determined by gel permeation chromoatography (GPC).

4.2.1 Materials

ATRP initiators, viz., 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate (HMBMP), 5-ethyl-2,2-dimethyl 1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) (EDMBMP), 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (HMPBMP), 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (OPCBMP) and 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) (ODMBMP) were synthesized as described in **Chapter 3**. Lauryl methacrylate (LMA 98%), methyl methacrylate (MMA 98%), styrene (98%), copper bromide (CuBr 99.9%), copper chloride (CuCl 98%), 2,2ô-bipyridine (By 99%), N,Nô,Nôô,Nò-penta methyl diethylene triamine (PMDETA 99%), calcium hydride and 4-nitro benzoyl chloride (99%) were purchased from Aldrich. Tetrahydrofuron, potassium hydroxide, acetic acid, sodium hydrogen carbonate, sodium hydroxide, methanol, ethanol and chloroform were purchased from S.D. Fine-Chem. Ltd., India and were used as received.

4.2.2 Purifications of reagents and solvents

Tetrahydrofuron, methanol, ethanol and chloroform were purified according to the reported procedures.[15]

Purification of copper bromide or copper chloride: Into a 100 mL round bottom flask equipped with a nitrogen inlet and a magnetic stirring bar were taken CuBr/CuCl (2.0 g) and glacial acetic acid (60 mL). The mixture was stirred for 12 h, filtered, washed repeatedly with ethanol and dried at room temperature under vacuum for 24 h.[16]

Anisole and toluene were stirred over CaH_2 for 12 h and fractionally distilled. The fractionated solvent was further refluxed over sodium-benzophenone complex for 2-3 days, then distilled and used.

Triethyl amine was stirred over calcium hydride, distilled and stored over potassium hydroxide until use.

4.2.3 Characterization

4.2.3.1 FTIR spectroscopy

FTIR spectra of end-functionalized polymers were recorded on a Perkin-Elmer *Spectrum GX* spectrophotometer.

NMR spectra were recorded on a Bruker 200 or 500 MHz spectrometer at resonance frequencies of 200 or 500 MHz for ^{1}H-NMR and 50 or 125 MHz for ^{13}C-NMR measurements using $CDCl_3$ as a solvent. M_n^{NMR} of end-functionalized polymers were calculated by comparing integrals of repeating unit protons and end group protons wherever possible.

4.2.3.3 Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution of polymers were determined using GPC (Thermo separation products) equipped with spectra series UV 100 and spectra system RI 150 detectors. Two 60 cm PSS SDV-gel columns (10^2 ï 10^5 A^o and 1 x 100 A^o) were used at 25^{o}C. The sample concentration was 2 to 3 mg /mL and the injection volume was 50 µL. HPLC grade tetrahydrofuran was used as eluent at room temperature with a flow rate of 1 mL / min. Polystyrene was used as the calibration standard.

4.3 Synthesis

4.3.1 Synthesis of hydroxyl-terminated polystyrene using 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate as the initiator

Into a 50 ml two necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adaptor were charged copper bromide (0.31g, 0.002 mol), 2,2ô bipyridine (0.70 g, 4.4 x 10^{-3} mol) and deoxygenated styrene (4.54 g, 0.04 mol). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. 4-(Hydroxymethyl)benzyl 2-bromo-2-methylpropanoate (0.62 g, 0.002 mol) was added under a stream of nitrogen and the flask was sealed with a stopper. The reaction mixture was heated in an oil bath maintained at a temperature at 110^{0}C for 1.5 h. The polymerization was quenched by cooling reaction mixture in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and solution was passed through neutral alumina column to remove copper. The solution was concentrated and poured into excess methanol to precipitate out the polymer. The polymer was dried under high vacuum for 24 h and weighed.

Yield- 3.60 g. (80%)

xyl-terminated PLMA using 5-ethyl-2,2-dimethyl 1,3-dioxan-5-yl(methyl 2-bromo-2-methylpropanoate) as the initiator

4.3.2.1 Synthesis of protected dihydroxyl-terminated PLMA using 5-ethyl-2,2-dimethyl 1,3-dioxan-5-yl(methyl 2-bromo-2-methylpropanoate) as the initiator

Into a 50 ml two necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adaptor were charged copper bromide (0.06 g, 4.19 x 10^{-4} mol), N,Nô,Nôô,Nò-pentamethyldiethylenetriamine (0.07 g, 4.19 x 10^{-4} mol), deoxygenated lauryl methacrylate (4.54 g, 0.017 mol) and anisole (5 mL). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. 5-Ethyl-2,2-dimethyl 1,3-dioxan-5-yl(methyl 2-bromo-2-methylpropanoate) (0.14 g, 4.19 x 10^{-4} mol) was added under a stream of nitrogen and the flask was sealed with a stopper. The reaction mixture was heated in an oil bath maintained at 60^0C for 12 h. The polymerization was quenched by cooling the reaction mixture in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and solution was passed through neutral alumina column to remove copper. The solution was concentrated and poured into excess methanol to precipitate out the polymer. The polymer was dried under high vacuum for 24 h and weighed.

Yield- 4.0 g (90 %)

4.3.2.2 Deprotection of ketal protected PLMA to dihydroxyl-terminated PLMA

Into a 250 ml round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged ketal protected PLMA (3.0 g Mn^{NMR}-3640 / PDI-1.23) and a mixture of THF/ 7 % hydrochloric acid (37 mL, 80/20, v/v). The reaction mixture was stirred overnight at room temperature. The formed product was recovered by precipitation into excess methanol, separated, washed repeatedly with methanol and dried at room temperature.

Yield-2.60 g. (86 %)

4.3.3 Synthesis of bismethylol-terminated poly(alkyl methacrylate)s using 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate as the initiator

A representative procedure for synthesis of bismethylol-terminated PLMA is described below.

d round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adaptor were charged copper bromide (0.047g, 3.34 x 10^{-4} mol), N,Nô,Nôô,Nò-pentamethyldiethylenetriamine (0.057 g, 3.34 x 10^{-4} mol), deoxygenated lauryl methacrylate (2.80 g, 0.011 mol) and anisole (3.0 mL). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. 3,5-Bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate (0.10 g, 3.34 x 10^{-4} mol) was added under a stream of nitrogen and the flask was sealed with a stopper. The reaction mixture was heated in an oil bath at 60^0C for 12 h. The polymerization was quenched by cooling reaction flask in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and solution was passed through neutral alumina column to remove copper. The solution was concentrated and poured into excess methanol to precipitate out the polymer. The polymer was dried under high vacuum for 24 h and weighed.

Yield- 2.52 g. (90 %)

4.3.4 Synthesis of lactone-terminated polystyrene using 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate as the initiator

Into a 50 ml two necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adaptor were charged copper bromide (0.06 g, 3.84 x 10^{-4} mol), 2,2ô-bipyridine (0.18 g, 1.15 x 10^{-3} mol) and deoxygenated styrene (1.98 g, 0.019 mol). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. 4-(2-(7-Oxooxepan-3-yl) propan-2-yl) cyclohexyl 2-bromo-2-methyl propanoate (0.15 g, 3.84 x 10^{-4} mol) was added under a stream of nitrogen and the flask was sealed with a stopper. The reaction mixture was heated in an oil bath at 90^0C for 17 h. The polymerization was quenched by cooling reaction mixture in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and the solution was passed through neutral alumina column to remove copper. The solution was concentrated and poured into excess methanol to precipitate out the polymer. The polymer was dried under high vacuum for 24 h and weighed.

Yield- 1.70 g (80 %)

rbonate-terminated PMMA using 2-oxo-1,3-dioxolan-4-yl(methyl 2-bromo-2-methylpropanoate) as the initiator

Into a 50 ml two necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adaptor were charged copper chloride (0.09 g, 9 x 10^{-4} mol), N,Nø,Nø,Nøø,Nø-pentamethyldiethylenetriamine (0.15 g, 9 x 10^{-4} mol) and deoxygenated methyl methacrylate (4.50 g, 0.045 mol). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. 2-Oxo-1,3-dioxolan-4-yl(methyl 2-bromo-2-methylpropanoate) (0.24 g, 9 x 10^{-4} mol) was added under a stream of nitrogen and flask was sealed with a stopper. The reaction mixture was kept in an oil bath at 60^0C for 1 h. The polymerization was quenched by cooling reaction mixture in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and solution was passed through neutral alumina column to remove copper. The solution was concentrated and poured into excess hexane to precipitate out the polymer. The polymer was dried under high vacuum for 24 h and weighed.

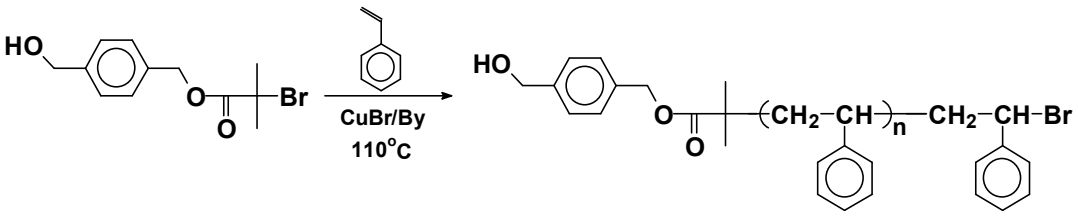
Yield- 2.34 g. (52 %)

4.4 Results and Discussion

4.4.1 Synthesis and characterization of hydroxyl-terminated polystyrene

4.4.1.1 Synthesis of hydroxyl-terminated polystyrene

ATRP of styrene in bulk was performed using HMBMP as the initiator, CuBr as the catalyst and 2,2ø-bipyridine as the complexing ligand **(Scheme 4.1).**[17-22]



Scheme 4.1: Synthesis of hydroxyl-terminated polystyrene

The reaction conditions and results of synthesis of hydroxyl-terminated polystyrene are presented in **Table 4.1**. The conversions were determined gravimetrically. As expected, polymers with increasing molecular weights were obtained upon increase in ratio of molar concentration of monomer to initiator. The molecular weight determined by

ith the theoretical values except for Run 4. The theoretical molecular weight was calculated according to the following equation:

$$\bar{M}n_{th} = \frac{[Mo]}{[Io]} \times 104 \times (conversion)/_{100} + \bar{M}n,initiator$$

where M_o and I_o are the initial molar concentrations of the monomer and initiator, respectively.

The MWD of the hydroxyl-terminated polystyrenes were narrow (M_w/M_n = 1.13 - 1.33) which is characteristic of a living/controlled radical polymerization. A typical GPC trace of hydroxyl-terminated polystyrene is shown in **Figure 4.1**.

Table 4.1 Reaction conditions and results of synthesis of hydroxyl-terminated polystyrene

Run	[M]:[I]:[Cu]:[By][a]	Time (h)	Conv.[b] (%)	$^cM_n^{th}$	GPC[d]		I^e_{eff}
					M_n	M_w/M_n	
1	[20]:[1]:[1]:[3]	1.5	80	1700	1980	1.33	0.85
2	[25]:[1]:[1]:[3]	3.5	93	2550	3000	1.13	0.85
3	[67]:[1]:[1]:[3]	6	78	5240	5900	1.24	0.88
4	[77]:[1]:[1]:[3]	5	76	6300	9670	1.19	0.65

a = [M]:[I]:[Cu]:[By] = Styrene/HMBIB/CuBr/2,2ô-bipyridine, b = gravimetry, c = $[St]_o/[I]_o$ x 104 x conv./100 + 187, d = PS calibration, e = M_n^{th}/M_n^{GPC}

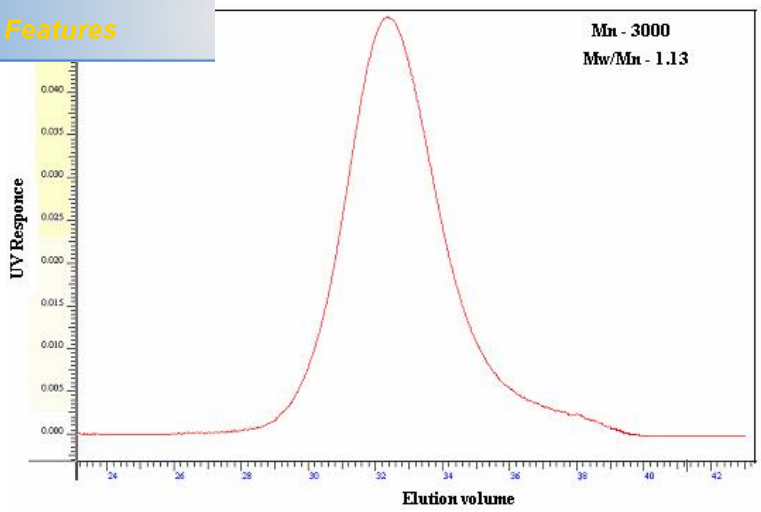


Figure 4.1: GPC trace of hydroxyl-terminated polystyrene (Run 2, Table 4.1)

4.4.1.2 Characterization of hydroxyl-terminated polystyrene

The structure of hydroxyl-terminated polystyrene was characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of hydroxyl-terminated polystyrene exhibited bands at 3427 cm^{-1} and 1714 cm^{-1} which correspond to hydroxyl and ester carbonyl stretching absorptions, respectively (**Figure 4.2**). The band observed at 1601 cm^{-1} is characteristic of C=C stretching vibration of aromatic ring.

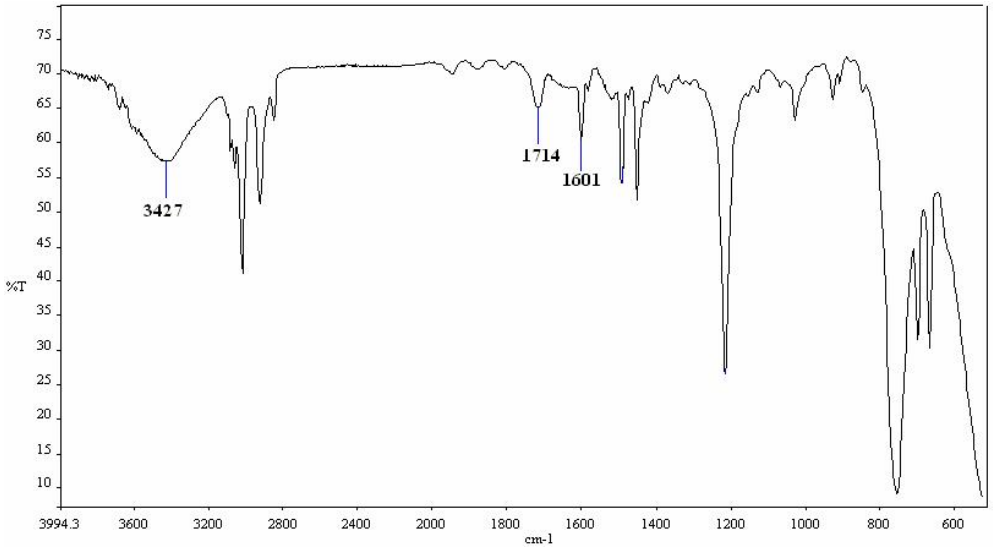


Figure 4.2: IR spectrum of hydroxyl-terminated polystyrene

^{1}H-NMR spectrum of hydroxyl-terminated polystyrene along with assignments is shown in **Figure 4.3.** The peaks in region 6.25 to 7.25 ŭ ppm correspond to aromatic

d aromatic protons (Hb) of initiator fragment. The peaks in the range 4.33 to 4.57 ŭ ppm appeared due to the methylene protons (Ha) to which hydroxyl group is attached (C**H**$_2$OH), methine proton (C**H**-Br, Hg) to which bromine is attached and methylene protons (Hc) attached to ester group. The peaks in the region 1.45 to 2.39 ŭ ppm were due to methylene and methine (He) protons of the polystyrene backbone.

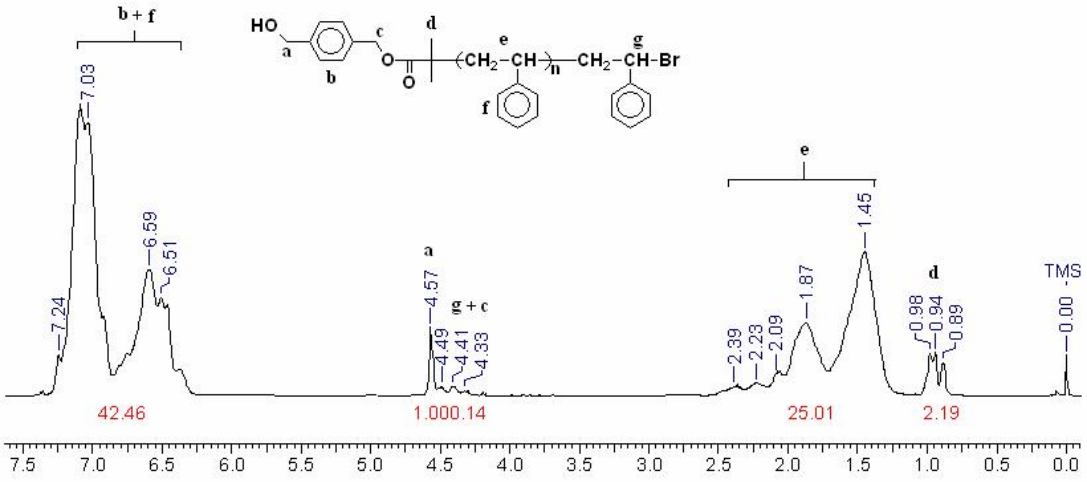


Figure 4.3: ^{1}H-NMR spectrum of hydroxyl-terminated polystyrene in $CDCl_3$

^{13}C-NMR spectrum of hydroxyl-terminated polystyrene along with assignments is shown in **Figure 4.4**. In addition to peaks characteristic of polystyrene chain,[23] the peak of ester carbonyl carbon (C7) was observed at 176.99 ŭ ppm. The signal for benzylic carbons C6 and C1 were observed at 65.23 and 64.82 ŭ ppm, respectively. The benzylic carbon (C11) to which bromine is attached appeared at 52.40 ŭ ppm.

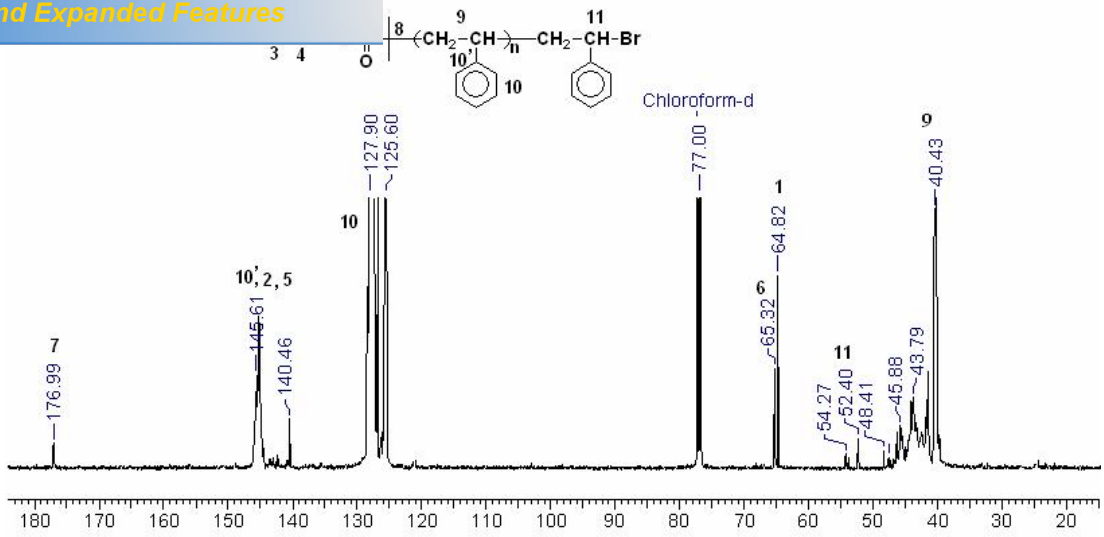
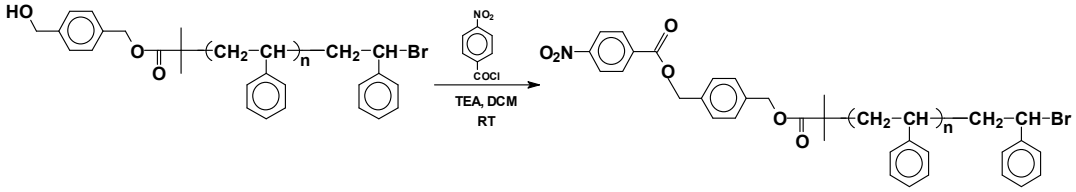


Figure 4.4: ^{13}C-NMR spectrum of hydroxyl-terminated polystyrene in $CDCl_3$

Further, the presence of hydroxyl end group in polystyrene was confirmed by derivatization using 4-nitrobenzoyl chloride. The reaction of hydroxyl-terminated polystyrene with 4-nitrobenzoyl chloride was carried out in the presence of triethyl amine **(Scheme 4.2).** The formed product was purified by repeated precipitation in methanol and the structure was confirmed by ^{1}H-NMR spectroscopy.



Scheme 4.2: Reaction of hydroxyl-terminated polystyrene with 4-nitro benzoyl chloride

Figure 4.5 shows ^{1}H-NMR spectrum of the product of reaction between hydroxyl-terminated polystyrene and 4-nitrobenzoyl chloride. The peaks observed in region 8.20 to 8.40 ŭ ppm correspond to aromatic protons (Ha + Haô) *ortho* and *meta* to nitro group. The peak at 5.40 ŭ ppm corresponds to methylene protons (Hb) attached to ester group. The peaks in the region 4.30 to 4.70 ŭ ppm correspond to the benzylic protons Hd and Hg.

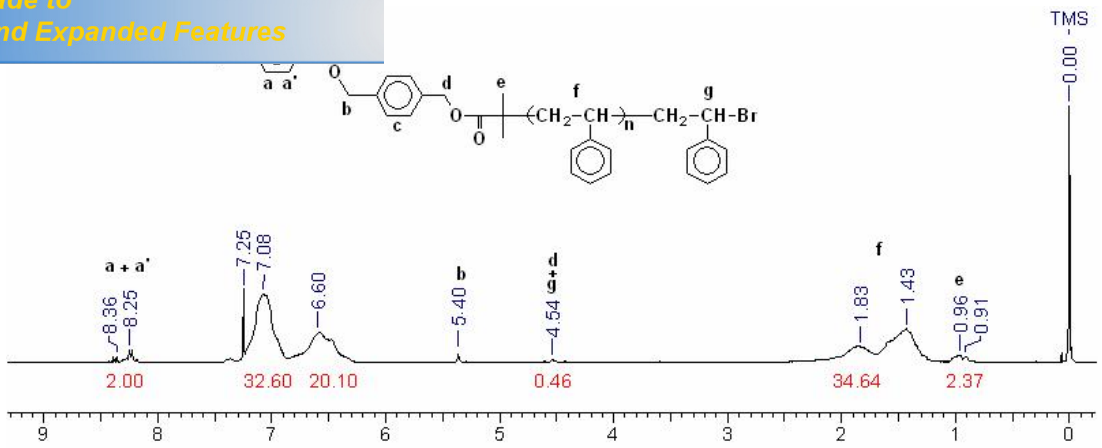


Figure 4.5: ^{1}H-NMR spectrum of the product of reaction between hydroxyl-terminated polystyrene and 4-nitrobenzoyl chloride in $CDCl_3$

4.4.2 Synthesis and characterization of dihydroxyl-terminated PLMA using 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl(methyl 2-bromo-2-methylpropanoate) as the initiator

4.4.2.1 Synthesis of protected dihydroxyl-terminated PLMA

Cramail et al[24] have demonstrated ATRP of butyl acrylate using 5-ethyl 5-(2-methyl 2-bromopropionate) methyl-2,2-dimethyl-1,3-dioxane **(Figure 4.6)** as the initiator in presence of CuBr complex with PMDETA as catalyst. The obtained poly(butyl acrylate)s exhibited narrow MWD (M_w/M_n ï 1.10 to 1.40).

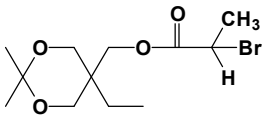
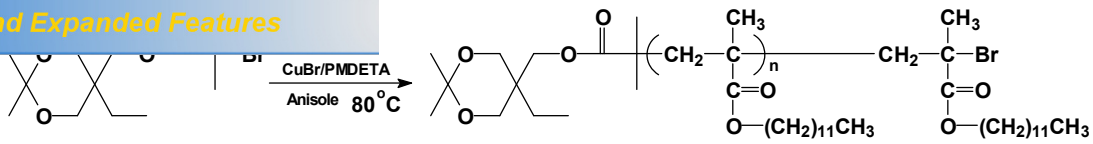


Figure 4.6: Structure of 5-ethyl 5-(2-methyl 2-bromopropionate) methyl-2,2-dimethyl-1,3-dioxane

Similarly, in the present work 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl(methyl 2-bromo-2-methylpropanoate) as initiator was designed for alkyl methacrylate polymerization. The solution ATRP of LMA using EDMBMP as an initiator was carried out in the presence of CuBr/PMDETA as catalyst complex **(Scheme 4.3)**.



Scheme 4.3: Synthesis of protected dihydroxyl-terminated PLMA

The polymerization conditions and results are presented in **Table 4.2**. The polymerization reactions were carried out at 60°C in anisole as the solvent for 12 h. Anisole has been shown to be a good solvent for ATRP of various monomers due to its relatively high polarity compared to toluene and it allows formation of a homogeneous solution with CuBr/PMDETA catalyst.[25]

The conversions were determined gravimetrically and were in the range 90 to 94 %. The experimental molecular weight (Mn^{NMR}) agreed reasonably well with theoretical molecular weight (Mn^{th}) showing good initiator efficiency.

Table 4.2: Reaction conditions and results of synthesis of protected dihydroxyl-terminated PLMA

Run	[a][M]:[I] [Cu]:[L]	[b]Conv. (%)	[c]M_n^{th}	M_n^{NMR}	[d]GPC		[e]I^{eff}
					M_n	M_w/M_n	
1	[12]:[1] [1]:[1]	90	3040	3810	7070	1.23	0.80
2	[28]:[1] [1]:[1]	94	6990	6600	9430	1.27	1.05
3	[40]:[1] [1]:[1]	90	9440	11170	11790	1.29	0.84

Reaction temperature - 60°C, reaction time - 12 h, Solvent ï anisole (50%, w/v w.r.t. monomer), a - [M]:[I] [Cu]:[L] = $[LMA]:[I]_o:[CuBr]_o:[PMDETA]_o$, b - gravimetry, c - $[LMA]_o/[I]_o$ x 254 x conv./100 + 325, d - PS calibration, I^{eff} - M_n^{th}/M_n^{NMR}

As expected, polymers with increasing molecular weights were obtained upon increasing the ratio of initial concentration of monomer to initiator. The molecular weight distributions of PLMA were relatively narrow (M_w/M_n - 1.23 to 1.29). **Figure 4.7** shows GPC trace of protected dihydroxyl-terminated PLMA (Run- 3, **Table 4.2**). Xu et al[25] obtained similar results for LMA polymerization using ethyl-2-bromoisobutyrate as initiator in presence of CuCl/PMDETA as the catalytic system in anisole.

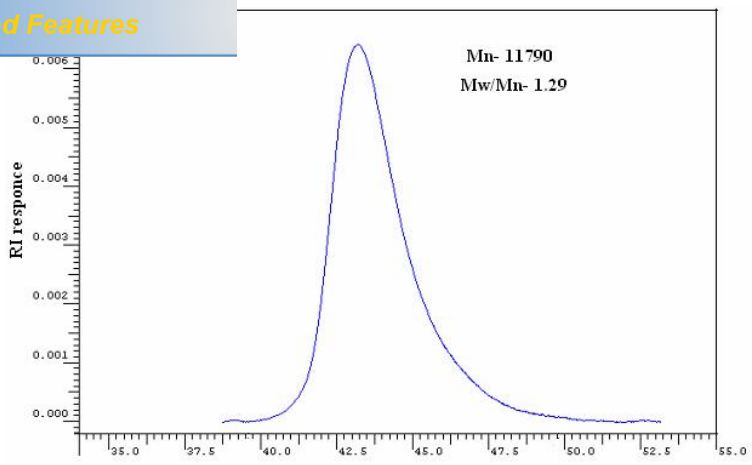


Figure 4.7: GPC trace of protected dihydroxyl-terminated PLMA (Run- 3, Table 4.2)

4.4.2.2 Structural characterization of protected dihydroxyl-terminated PLMA

The structure of protected dihydroxyl-terminated PLMA was confirmed by ^{1}H-NMR spectroscopy.

Figure 4.8 shows ^{1}H-NMR spectrum of protected dihydroxyl-terminated PLMA along with assignments. The peak at 3.57 ŭ ppm (Hb) was attributed to methylene protons (-OC**H**$_2$) attached to ether group of the initiator fragment.[24,26] The peaks observed at 3.86 and 0.82 ŭ ppm correspond to methylene protons (Hf) (COOC**H**$_2$) attached to ester group and terminal methyl group protons (Hh) of alkyl chain, respectively. The peak at 1.20 ŭ ppm is due to the alkyl chain protons (Hg).

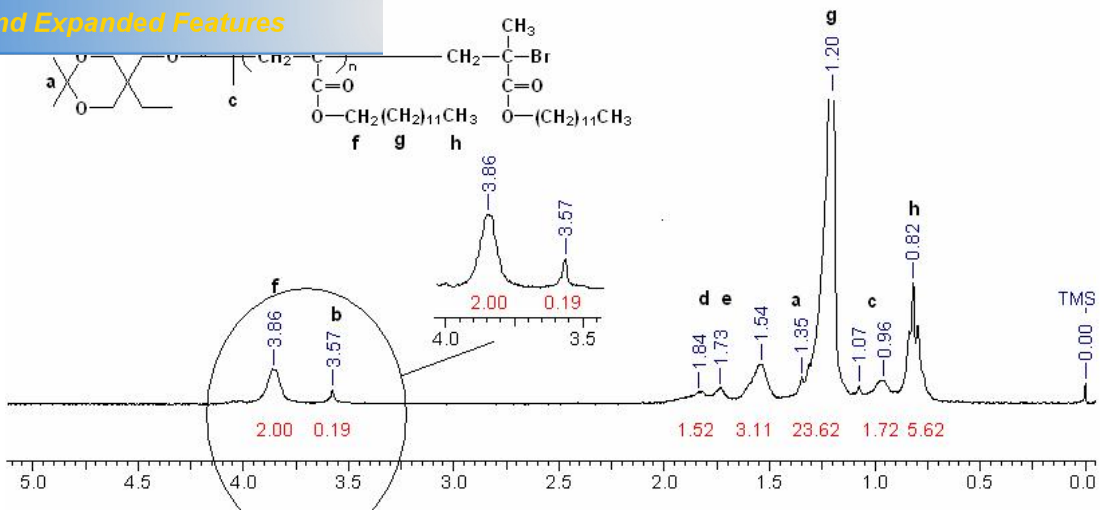
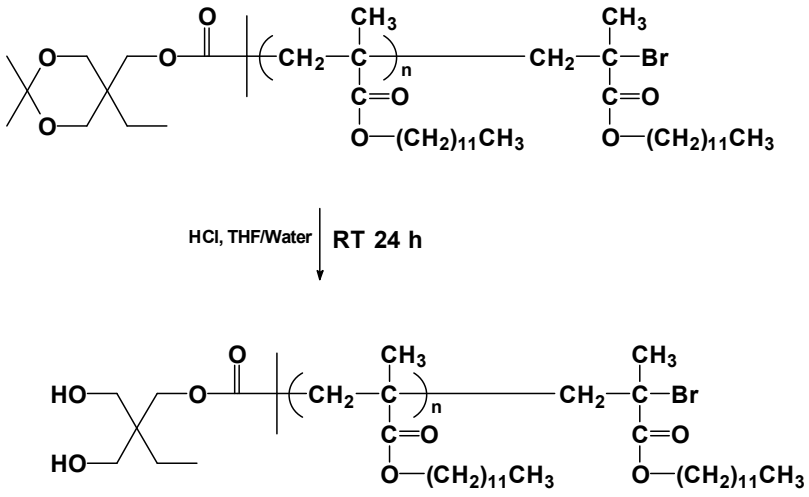


Figure 4.8: ^{1}H-NMR spectrum of protected dihydroxyl-terminated PLMA in $CDCl_3$

4.4.2.3 Synthesis of dihydroxyl-terminated PLMA (Deprotection of ketal group)

Scheme 4.4 shows synthesis of dihydroxyl-terminated PLMA. The deprotection of ketal group of PLMA was carried out using dilute hydrochloric acid in THF/water mixture at room temperature. The product was purified by dissolving in dichloromethane and precipitating into excess methanol. [24,26]



Scheme 4.4: Synthesis of dihydroxyl-terminated PLMA

rization of dihydroxyl-terminated PLMA (after deprotection of ketal group)

The structure of dihydroxyl-terminated PLMA was confirmed by FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of dihydroxyl-terminated PLMA is given in **Figure 4.9**. A broad band observed at 3411 cm^{-1} corresponds to hydroxyl group, which confirmed the deprotection of ketal group by dilute hydrochloric acid, while the band observed at 1719 cm^{-1} is due to ester carbonyl group of the PLMA segment and initiator fragment.

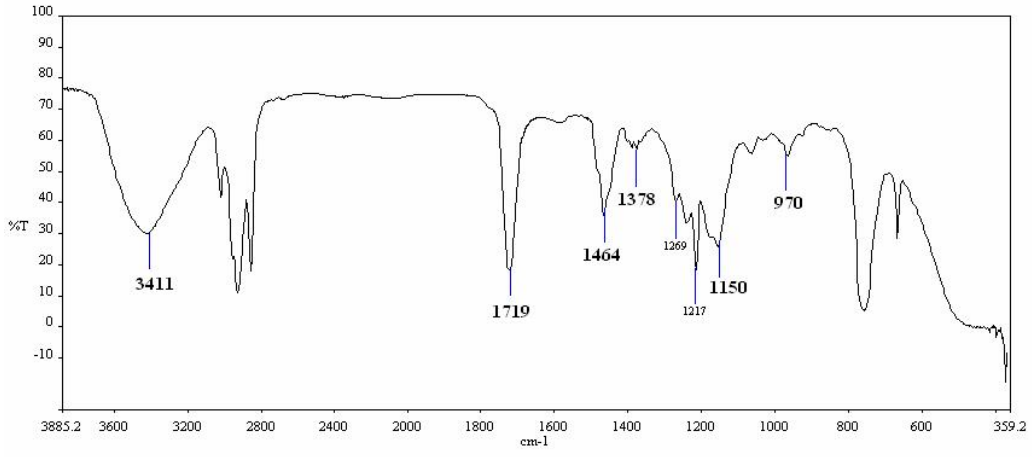


Figure 4.9: FTIR spectrum of dihydroxyl-terminated PLMA (after deprotection of ketal group)

Figure 4.10 shows ^{1}H-NMR spectrum of dihydroxyl-terminated PLMA along with assignments. The peaks observed at 3.63 and 3.91 ŭ ppm correspond to methylene protons (Ha) attached to hydroxyl group (C**H**$_2$OH) and methylene protons (He) attached to ester group (COO-C**H**$_2$), respectively. The peak at 1.27 ŭ ppm and triplet at 0.89 ppm appeared due to methylene protons (Hf) (-(C**H**$_2$)$_{10}$-) and methyl protons (Hg) (-C**H**$_3$) of the alkyl chains of PLMA, respectively.

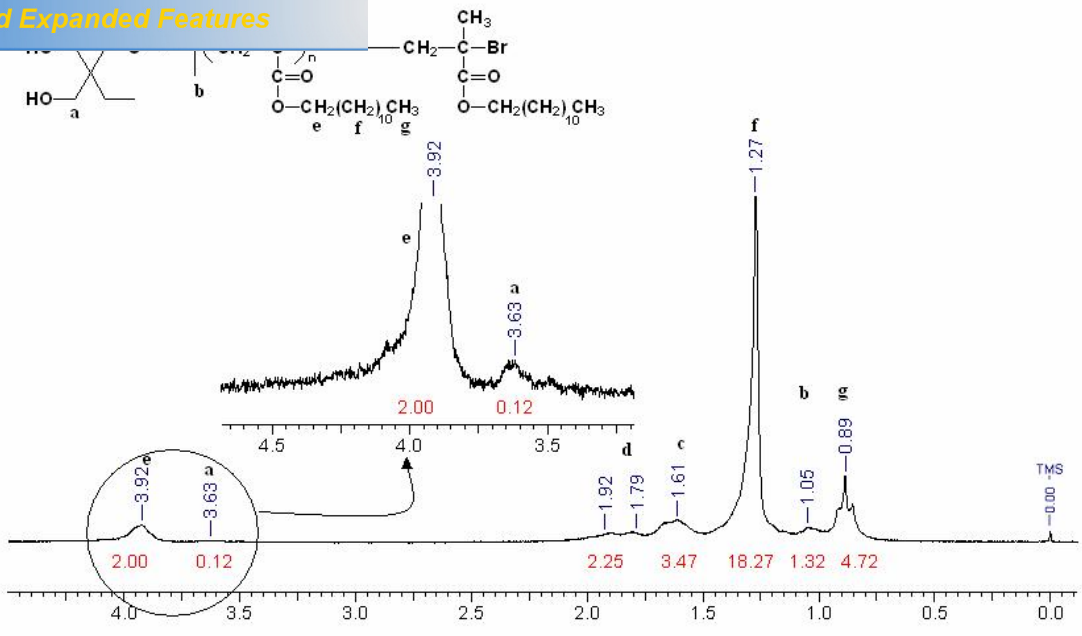


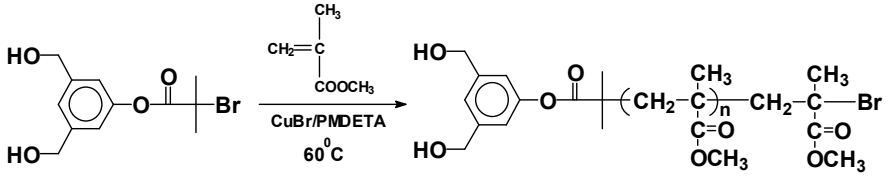
Figure 4.10: ^{1}H-NMR spectrum of dihydroxyl-terminated PLMA in $CDCl_3$

4.4.3 Synthesis and characterization of bismethylol-terminated PMMA and PLMA using 3,5-bis(hydroxymethyl) phenyl 2-bromo-2-methylpropanoate (HMPBMP)

4.4.3.1 Synthesis and characterization of bismethylol-terminated PMMA

4.4.3.1.1 Synthesis of bismethylol-terminated PMMA

The bulk ATRP of MMA was carried out at 60^{o}C using 3,5-bis(hydroxymethyl) phenyl 2-bromo-2-methylpropanoate as the initiator, CuBr as the catalyst and PMDETA as the complexing ligand. **Scheme 4.5** depicts synthesis of bismethylol-terminated PMMA.



Scheme 4.5: Synthesis of bismethylol-terminated PMMA

The polymerization conditions and results are presented in **Table 4.3.** The conversions were determined gravimetrically. As expected, polymers with increasing

ed upon increasing the initial concentration of monomer to the initiator.

Table 4.3: Reaction conditions and results of synthesis of bismethylol-terminated PMMA

Run	[a][M]:[I]: [CuBr]: [PMDETA]	Time (h)	[b]Conv (%)	[c]M_n^{th}	M_n^{NMR}	[d]GPC		[e]I_{eff}
						M_n	M_w/M_n	
1	[32]:[1]:[1]:[1]	3	78	2570	3320	3620	1.24	0.77
2	[60]:[1]:[1]:[1]	3	58	3790	4300	5190	1.18	0.88
3	[100]:[1]:[1]:[1]	5	80	8240	20000	13620	1.14	0.41

Reaction temperature = 60°C, a ï [M] - MMA, b - gravimetry, c = $[MMA]_o/[I]_o$ x 100 x conv./100 + 303, d = PS calibration, e = M_n^{th}/M_n^{NMR}

In case of Run 1 and 2, the experimental molecular weight (Mn^{NMR}) agreed reasonably well with theoretical molecular weight (Mn^{th}) indicating good initiator efficiency. Muller et al[27] also showed good initiator efficiency using 2-hydroxy ethyl 2-bromo isobutyrate as the hydroxyl-functionalized ATRP initiator in MMA polymerization in presence of CuBr/PMDETA as the catalyst.

However, the experimental molecular weight (Mn^{NMR}) was higher than theoretical molecular weight (Mn^{Th}) in Run 3 indicating lower initiator efficiency (0.41), which may be attributed to the some side reactions (radical coupling) during polymerization.[28-30]

A typical GPC trace of bis-methylol-terminated PMMA is shown in **Figure 4.11**. The obtained molecular weight distributions of the polymers were narrow, which indicates a living/controlled polymerization using HMPBMP as the initiator.

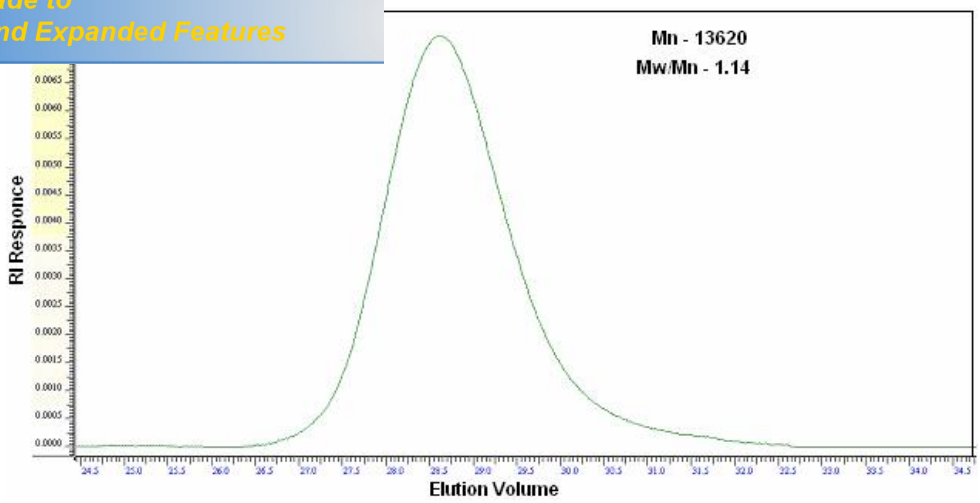


Figure 4.11: GPC trace of bismethylol-terminated PMMA, (Run 3, Table 4.3)

4.4.3.1.2 Structural characterization of bismethylol-terminated PMMA

The structural characterization of bismethylol-terminated PMMA was carried out using FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of bismethylol-terminated PMMA is shown in **Figure 4.12**. FTIR spectrum exhibited a broad band of hydroxyl group absorption at 3340 cm^{-1} from initiator fragment. The band observed at 1730 cm^{-1} corresponds to ester carbonyl of PMMA and ester carbonyl of initiator fragment.

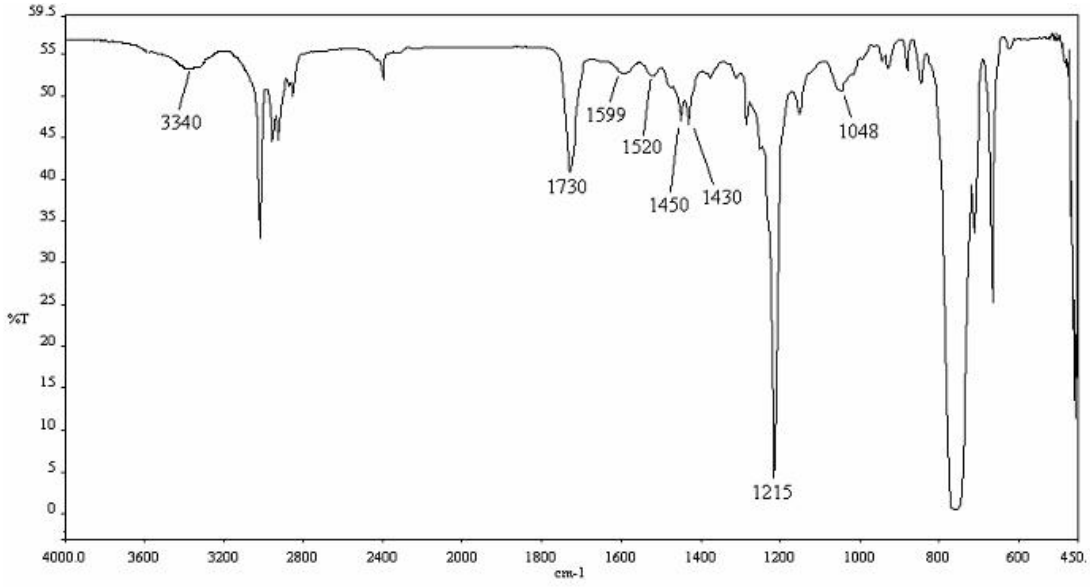


Figure 4.12: FTIR spectrum of bismethylol-terminated PMMA

bismethylol-terminated PMMA along with assignments is shown in **Figure 4.13**. The aromatic proton (Hb) from the initiator fragment appeared as a singlet at 7.36 ŭ ppm, while the two aromatic protons (Hc) *ortho* to the ester group appeared as a singlet at 7.02 ŭ ppm. The singlet at 4.73 ŭ ppm was attributed to methylene protons (Ha) to which hydroxyl group is attached, while the singlet at 3.60 ŭ ppm correspond to methyl protons (Hf) (COOC**H**$_3$) of the PMMA chain. The peaks in the range 0.50 to 2.0 ŭ ppm (Hd, He) correspond to protons of PMMA backbone.

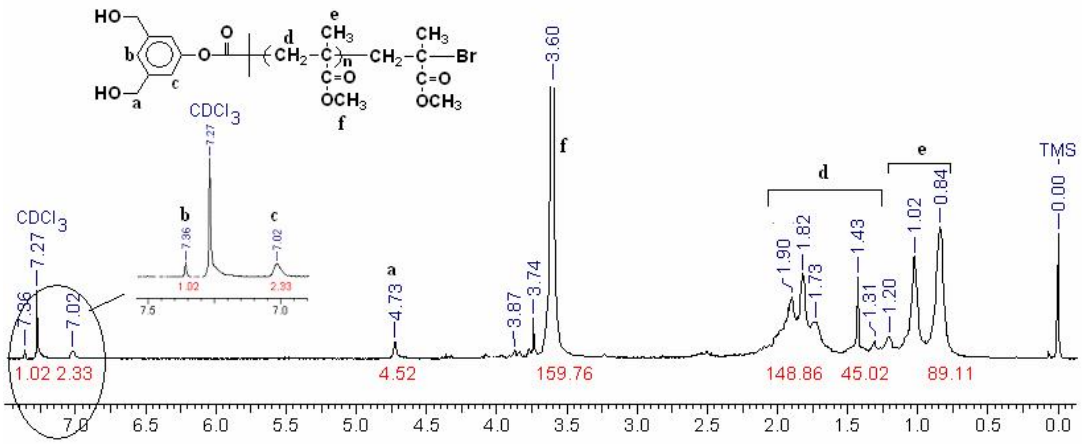
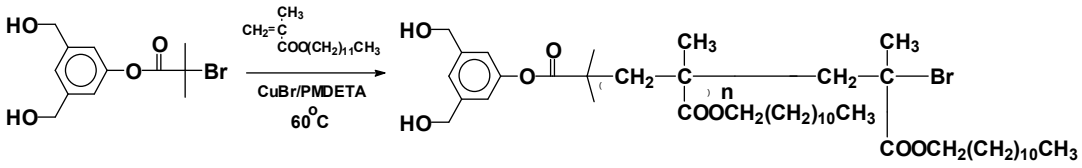


Figure 4.13: ^{1}H-NMR spectrum of bismethylol-terminated PMMA in $CDCl_3$

4.4.3.2 Synthesis and characterization of bismethylol-terminated PLMA

4.4.3.2.1 Synthesis of bismethylol-terminated PLMA

Scheme 4.6 depicts the synthesis of bismethylol-terminated PLMA. ATRP of lauryl methacrylate using BHMPBMP as an initiator was carried out using copper bromide complex with PMDTA as the catalyst system. The polymerizations were carried out in toluene and anisole as solvents at 60^{o}C.



Scheme 4.6: Synthesis of bismethylol-terminated PLMA

erization conditions and results of synthesis of bismethylol-terminated PLMA. The conversions were determined gravimetrically. The polymers with increasing molecular weights were obtained upon increasing initial monomer to initiator ratio.

Table 4.4: Polymerization conditions and results of synthesis of bismethylol-terminated PLMA

Run	[a][M]:[I]: [CuBr]: [PMDETA]	[b]Conv. (%)	[c]M_n^{th}	M_n^{NMR}	[d]GPC		[e]I^{eff}
					M_n	M_w/M_n	
1	[20]:[1]:[1]:[1] [f]	78	4200	4060	5160	1.19	1.03
2	[33]:[1]:[1]:[1] [g]	90	7540	14220	14060	1.16	0.53
3	[40]:[1]:[1]:[1] [g]	92	9940	27940	20670	1.12	0.35

Reaction temperature - 60°C, Reaction time- 12 h a ï [M] - LMA, b - gravimetry, c - $[LMA]_o/[I]_o$ x 254 x conv./100 + 303, d - PS calibration, e - $M_n^{th}/M_n^{NMR,}$, f - Toluene as solvent (50 %, w/v w.r.t. monomer), g - anisole as solvent (50 %, w/v w.r.t. monomer)

When toluene was utilized as a solvent (Run 1, **Table 4.4**), there was obtained good agreement between theoretical molecular weight (M_n^{th}) and experimental molecular weight (M_n^{NMR}), which indicates good initiator efficiency. The MWD was narrow (M_w/M_n -1.19) indicating living/controlled polymerization of LMA using BHMPBMP as an initiator.

In case of ATRP in anisole as the solvent, (Run 2 and 3, **Table 4.4**) the PLMAs with narrow MWD were obtained. However, the theoretical molecular weight (M_n^{th}) was higher than experimental molecular weight (M_n^{NMR}) indicating lower initiator efficiency. The observed lower initiator efficiency may be due to high percentage of initiator deactivation at the beginning of the polymerization by bimolecular termination combined with high activity of the catalyst in anisole as a solvent.[31] **Figure 4.14** shows GPC trace of bismethylol-terminated PLMA.

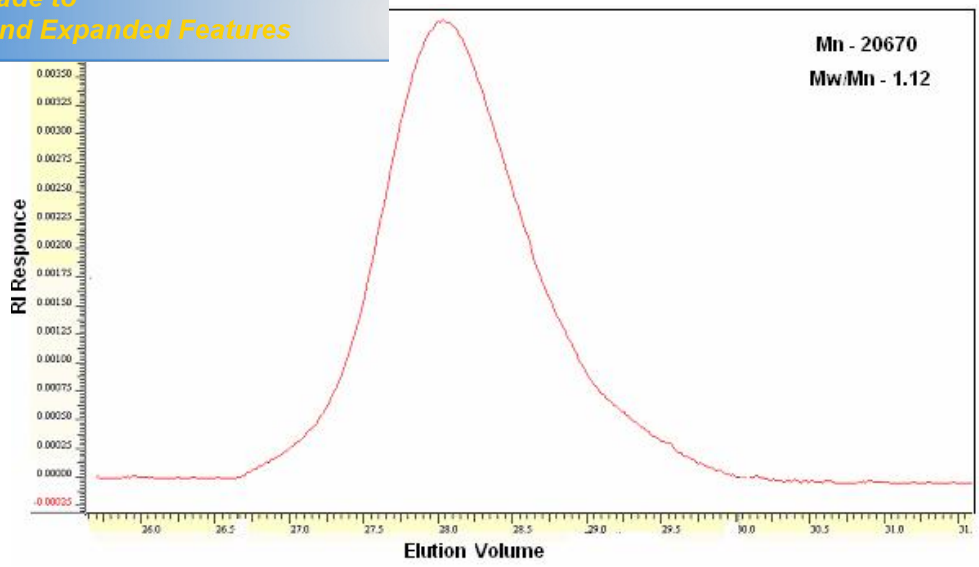


Figure 4.14: GPC trace of bismethylol-terminated PLMA (Run 3, Table 4.4)

4.4.3.2.2 Structural characterization of bismethylol-terminated PLMA

FTIR, and ^{1}H-NMR spectroscopy was used for the characterization of bis-methylol terminated PLMA.

Figure 4.15 shows FTIR spectrum of bismethylol-terminated PLMA. A broad absorption band observed at 3422 cm^{-1} corresponds to hydroxyl stretching of initiator fragment of PLMA. The band at 1722 cm^{-1} was ascribed to ester carbonyl group of PLMA segment and initiator fragment.

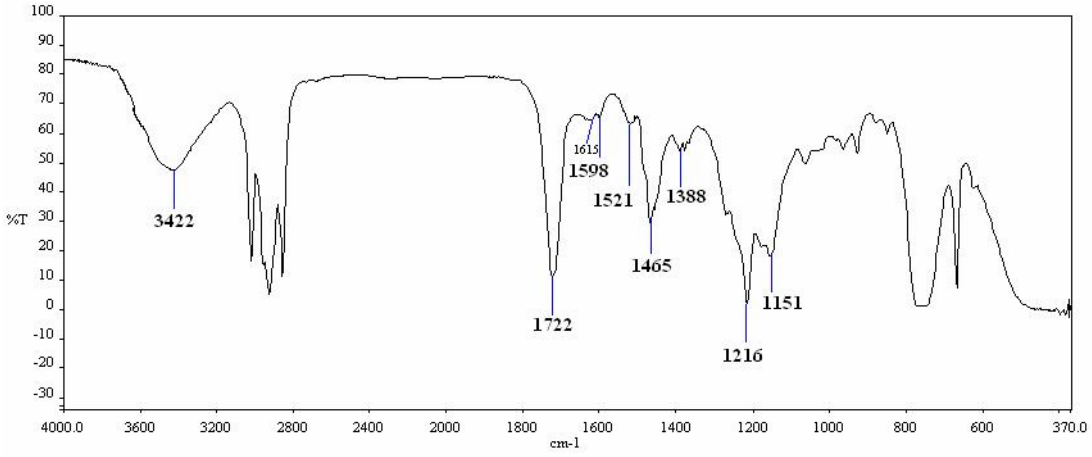


Figure 4.15: IR spectrum of bismethylol-terminated PLMA

bismethylol-terminated PLMA along with assignment is shown in **Figure 4.16**. The aromatic proton (Hb) and two protons (Hc) *ortho* to ester group from initiator fragment appeared at 7.23 and 7.02 ŭ ppm, respectively. The singlet for the benzylic protons (Ha) originating from initiator fragment appeared at 4.71 ŭ ppm. The singlet at 3.93 ŭ ppm corresponds to methylene protons (Hg) attached to ester group of PLMA chain. The peak at 1.27 ŭ ppm and the triplet at 0.89 ŭ ppm (Hg) were due to methylene protons (Hh) (-(C**H**$_2$)$_{10}$-) and methyl protons (Hi) (-C**H**$_3$) of the of PLMA segment, respectively.

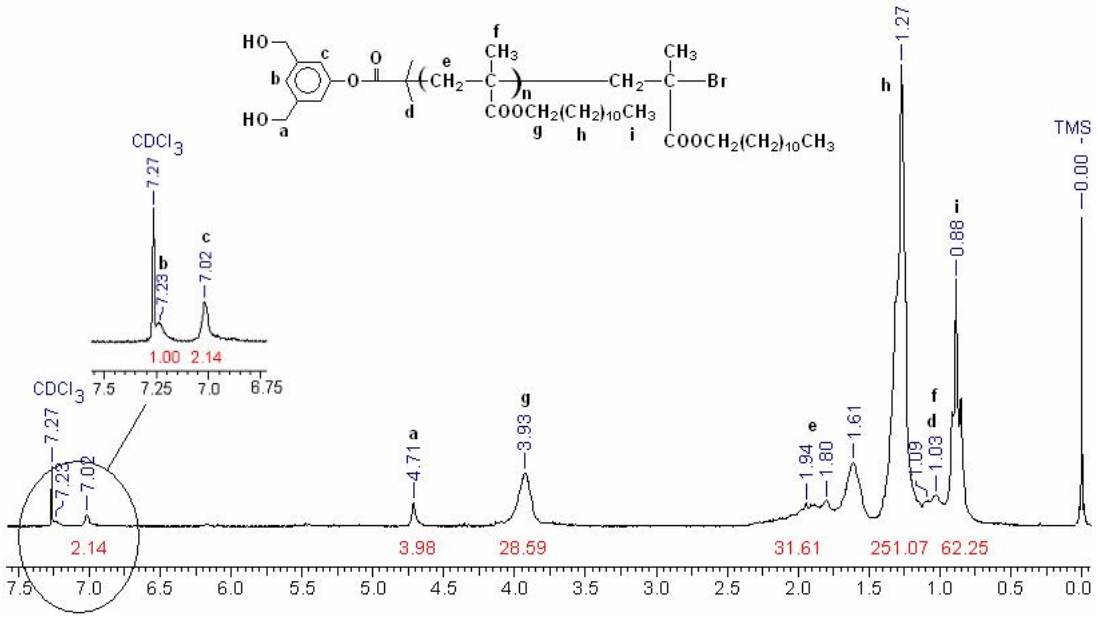
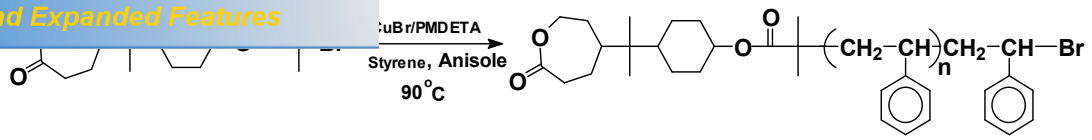


Figure 4.16: ^{1}H-NMR spectrum of bismethylol-terminated PLMA in $CDCl_3$

4.4.4 Synthesis and characterization of lactone-terminated polystyrene using 4-[2-(7-oxooxepan-3-yl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate as the initiator

4.4.4.1 Synthesis of lactone-terminated polystyrene

ATRP of styrene was carried out using OPCBMP as initiator in the presence of CuBr complex with two different ligands *viz*., 2,2ô-bipyridine and PMDETA **(Scheme 4.7).** The polymerization reactions were carried out in bulk and in anisole as solvent. The bulk polymerization was carried out in presence of CuBr as catalyst and 2,2ô-bipyridine as ligand at 90^{o}C, while solution polymerization in anisole was carried out using CuBr as catalyst and PMDETA as ligand at 90^{o}C.



Scheme 4.7: Synthesis of lactone-terminated polystyrene

Table 4.5 shows reaction conditions and results of synthesis of lactone-terminated polystyrene. The conversions were calculated gravimetrically. The obtained experimental molecular weight determined by ^{1}H-NMR spectroscopy (Mn^{NMR}) and theoretical molecular weight (Mn^{th}) were in good agreement, which indicates good initiator efficiency. Similar results were obtained by Hedrick et al for ATRP of MMA using lactone-functionalized initiator.[32,33]

The molecular weight distributions were narrow indicating living/controlled polymerization of styrene using OPCBMP as the initiator. It was also noted that use of anisole as solvent and CuBr/PMDETA as a catalyst gave polymer with narrower MWD than bulk polymerization, which was expected due to homogeneity of the reaction medium. **Figure 4.17** shows GPC trace of lactone-terminated polystyrene.

Table 4.5: Reaction conditions and results of synthesis of lactone-terminated polystyrene

Run	[M]:[I]:[Cu]:[L]	[c]Conv (%)	[d]M_n^{th}	M_n^{NMR}	[e]GPC		[f]I^{eff}
					M_n	M_w/M_n	
1[a]	[50[:[1]:[1]:[3]	80	4160	3500	4410	1.15	0.84
2[b]	[50]:[1]:[1]:[1]	41	2130	2400	2640	1.07	0.80

a - [M]:[I]:[Cu]:[L] = [St]:[I]:[CuBr]:[By] bulk 15 h, b - [St]:[I]:[CuBr]:[PMDETA] anisole (50%, w/v w.r.t. monomer) 8 h, c - gravimetry, d = $[St]/[I]_o$ x 104 x conv./100 + 403, e - PS calibration, f - M_n^{th}/M_n^{NMR}, Reaction temperature - 90^{o}C

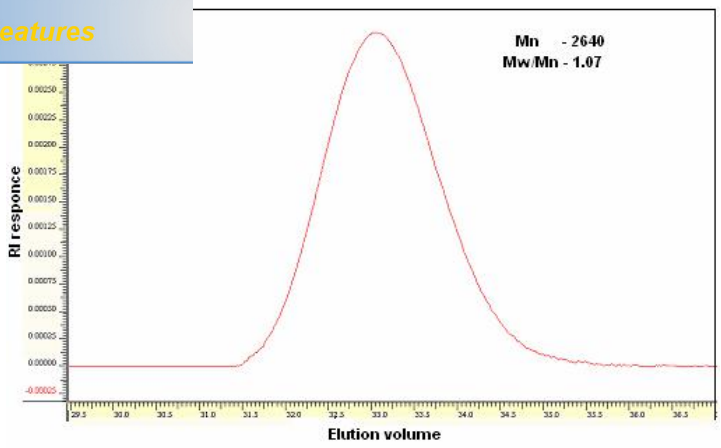


Figure 4.17: GPC trace of lactone-terminated polystyrene (Table 4.6, Run 2)

4.4.4.2 Structural characterization of lactone-terminated polystyrene

Lactone-terminated polystyrene was characterized by IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of lactone-terminated polystyrene is presented in **Figure 4.18**. The band of ester and lactone group from initiator fragment was observed at 1724 cm^{-1}.

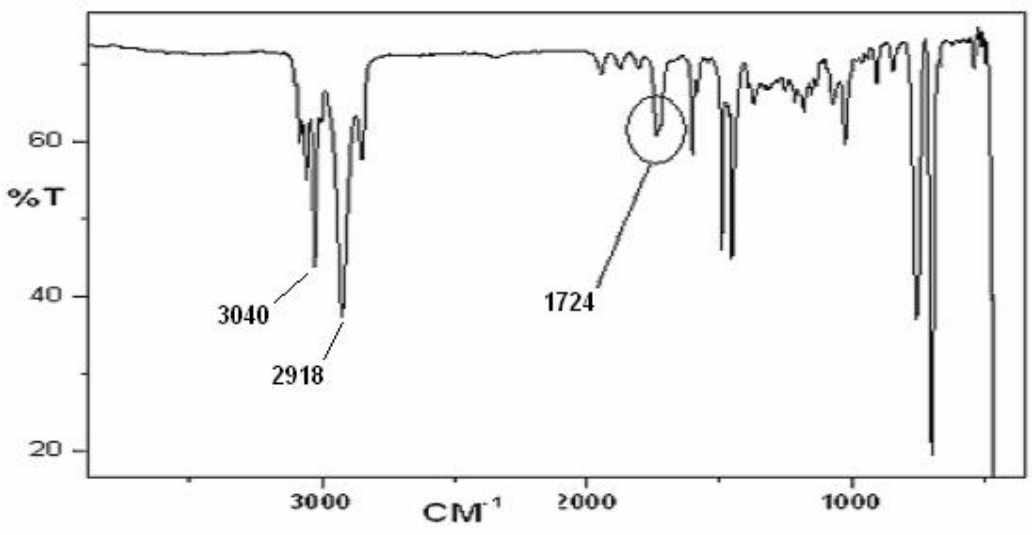


Figure 4.18: IR spectrum of lactone-terminated polystyrene

^{1}H-NMR spectrum of lactone-terminated polystyrene along with assignments is presented in **Figure 4.19**. In addition to peaks characteristic of polystyrene chain,[34] the characteristic peaks of the protons of initiator fragment Ha (C**H**$_2$-COO-) at the end of polystyrene chain could be pointed out at 2.69 and 2.55 ŭ ppm, while peaks at centered

d to Hb (-COO-C**H**$_2$-) protons. Two-geminal methyl group protons (Hd) from initiator fragment appeared at 0.75 ŭ ppm.

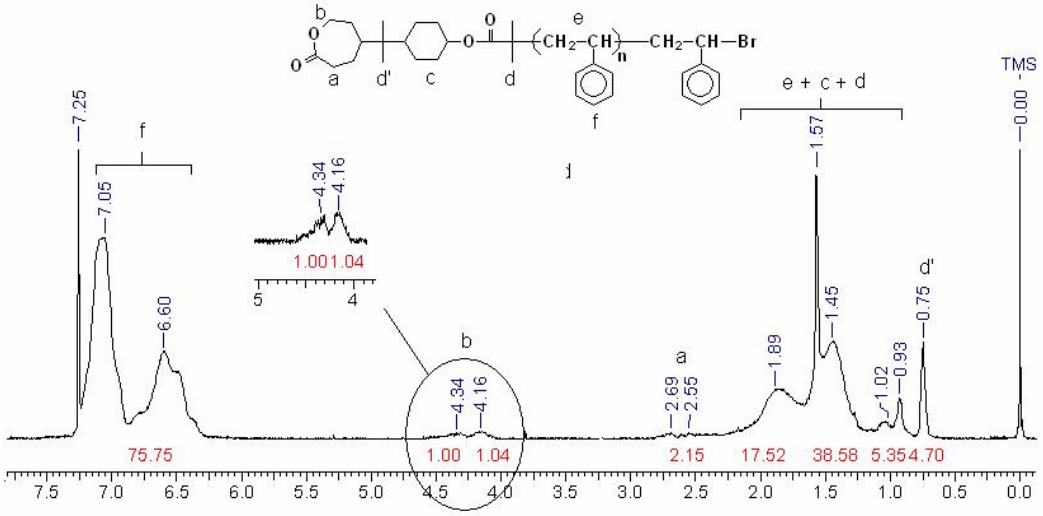


Figure 4.19: ^{1}H-NMR spectrum of lactone-terminated polystyrene in $CDCl_3$

Figure 4.20 shows ^{13}C-NMR spectrum of lactone-terminated polystyrene along with assignments. In addition to peaks characteristic of polystyrene chain, [23] the signal at 176.04 ŭ ppm is assigned to lactone and ester carbonyl carbon (C1) of initiator fragment and the signal at 46.59 ŭ ppm is assigned to secondary carbon (C7) of initiator fragment to which ester group is attached. The peaks at 33.50, 64.06, 46.59, 20.55 and 37.30 ŭ ppm were assigned to carbon number C2, C3, C4, C5 and C6, respectively of the initiator fragment.

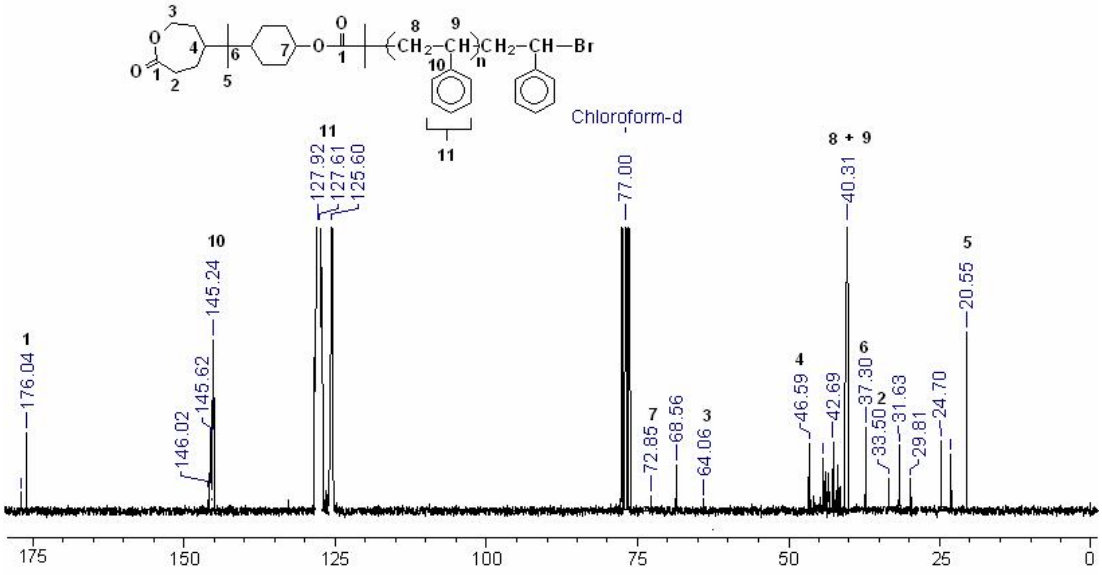


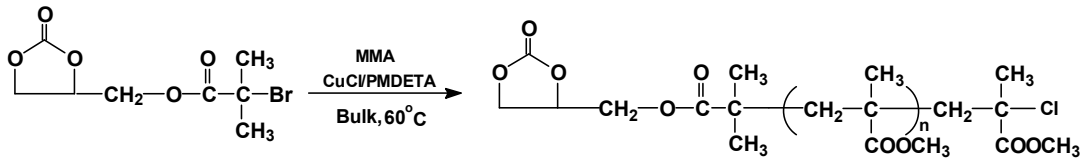
Figure 4.20: ^{13}C-NMR spectrum of lactone-terminated polystyrene in $CDCl_3$

erization of cyclic carbonate-terminated PMMA

4.4.5.1 Synthesis of cyclic carbonate-terminated PMMA

Cyclic carbonate is a polar and highly reactive functional group and reacts with aliphatic and aromatic amines, alcohols, thiols and carboxylic acids which is advantageous for the synthesis of new polymeric materials. [35-41]

Cyclic carbonate-terminated PMMA was obtained by ATRP of MMA using 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) as the initiator in the presence of copper chloride complex with PMDETA as catalyst system. **Scheme 4.8** shows route for synthesis of carbonate-terminated PMMA. The ñhalide exchange techniqueò was used for controlled ATRP of MMA.



Scheme 4.8: Synthesis of cyclic carbonate-terminated PMMA

Table 4.6 summarizes the reaction conditions and results for synthesis of cyclic carbonate-terminated PMMA. The conversions were determined by gravimetric analysis. Polymerization reactions were carried out in bulk as well as in solvent (anisole and acetone).

The bulk polymerization reactions were carried out at 60°C. The experimental molecular weights obtained by ^{1}H-NMR spectroscopy (M_n^{NMR}) were in reasonably good agreement with theoretical molecular weight (M_n^{th}), indicating good initiator efficiency. The molecular weight distributions were narrow indicating living/controlled polymerization.

In case of acetone (50 %) as the solvent, ATRP of MMA using CuCl/PMDETA as the catalyst was carried out at 60°C for 4 h (**Table 4.6**, Run 3). The polymer obtained showed reasonably good agreement between theoretical molecular weight (M_n^{th}) and experimental molecular weight (M_n^{NMR}).

In case of ATRP in anisole (50 %) as the solvent, polymerization reactions were conducted using CuCl/PMDETA as catalyst at 40°C. There was observed good agreement between theoretical molecular weight (M_n^{th}) and experimental molecular weight (M_n^{NMR})

ncy **(Table 4.6,** Run 4). **Figure 4.21** shows a representative GPC trace of cyclic carbonate-terminated PMMA (**Table 4.6**, run 1).

Table 4.6: Reaction conditions and results of synthesis of cyclic carbonate-terminated PMMA

Run	[a][M]:[I]:[Cu]:[L]	Time (h)	[b]Conv. (%)	[c]M_n^{th}	M_n^{NMR}	[d]GPC		$^eI^{eff}$
						M_n	M_w/M_n	
1 [f]	[50]:[1]:[1]:[1]	0.5	42	2400	3330	3570	1.17	0.72
2 [f]	[50]:[1]:[1]:[1]	1	52	2950	3500	7560	1.24	0.84
3 [g]	[74]:[1]:[1]:[1]	4	63	4810	6260	12040	1.16	0.77
4 [h]	[40]:[1]:[1]:[1]	3	36	1730	1740	1750	1.20	0.99

a- [M]:[I]:[Cu]:[L] = $[MMA]_o$:$[I]_o$:[CuCl]:[PMDETA], b - gravimetry, c - $[MMA]/[I]_o$ x 100 x conv./100 + 267, d - PS calibration, e - I^{eff} - M_n^{th}/M_n^{NMR}, f ï (60 ^oC, bulk), g ï (60 ^oC, acetone, 50 % w/v w.r.t. monomer), h ï (40 ^oC, anisole, 50 % w/v w.r.t. monomer)

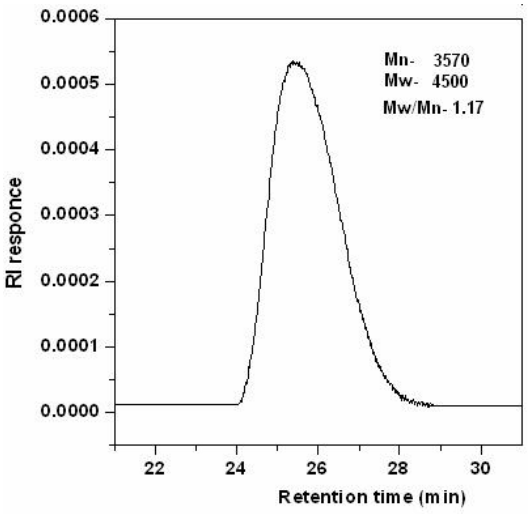


Figure 4.21: GPC trace of cyclic carbonate-terminated PMMA (Table 4.7, Run 1)

4.4.5.2 Characterization of cyclic carbonate-terminated PMMA

Cyclic carbonate-terminated PMMA was characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of cyclic carbonate-terminated PMMA showed an absorption band at 1817 cm^{-1} corresponding to carbonate group stretching arising from the initiator

cm^{-1} corresponds to both ester carbonyl group of PMMA polymer chain as well as that of initiator fragment **(Figure 4.22)**.

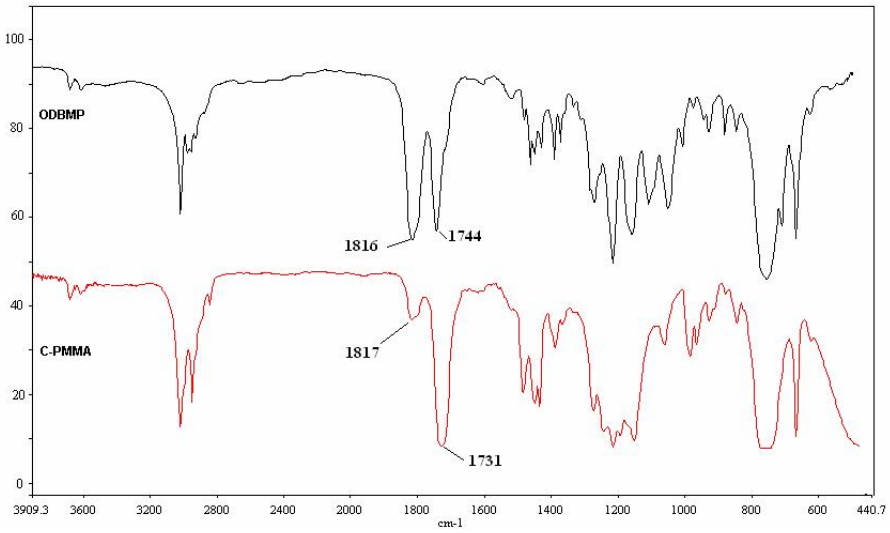


Figure 4.22: IR spectra of ATRP initiator ODBMP and cyclic carbonate-terminated PMMA

^{1}H-NMR spectrum of cyclic carbonate-terminated PMMA along with assignments in shown in **Figure 4.23(2)**. The broad signal at 4.96 δ ppm and multiplets in the range 4.25-4.75 δ ppm correspond to methine proton (Ha) and methylene protons (Hb and Hc) of the initiator fragment, respectively. The peak at 3.60 δ ppm was assigned to methyl ester protons (Hg) (-COOC**H**$_3$) of the PMMA segment. The peaks in the region 0.83 to 1.27 δ ppm were assigned to methylene (He) and methyl protons (Hf) of PMMA chain.

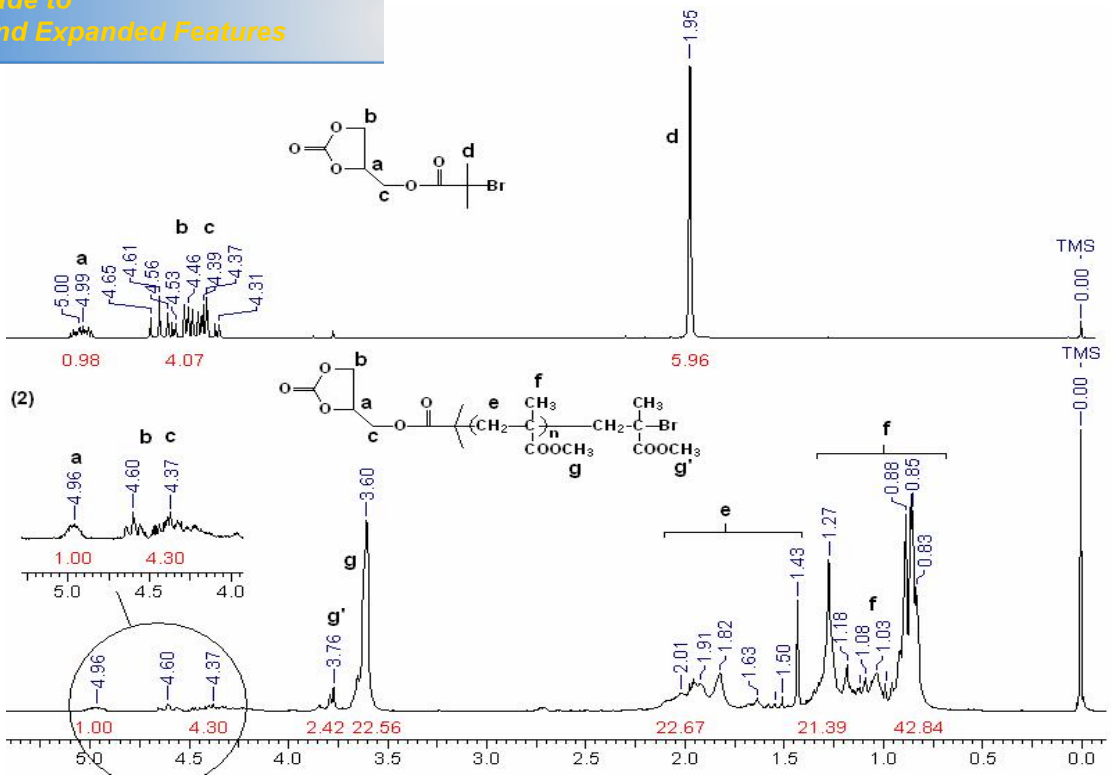


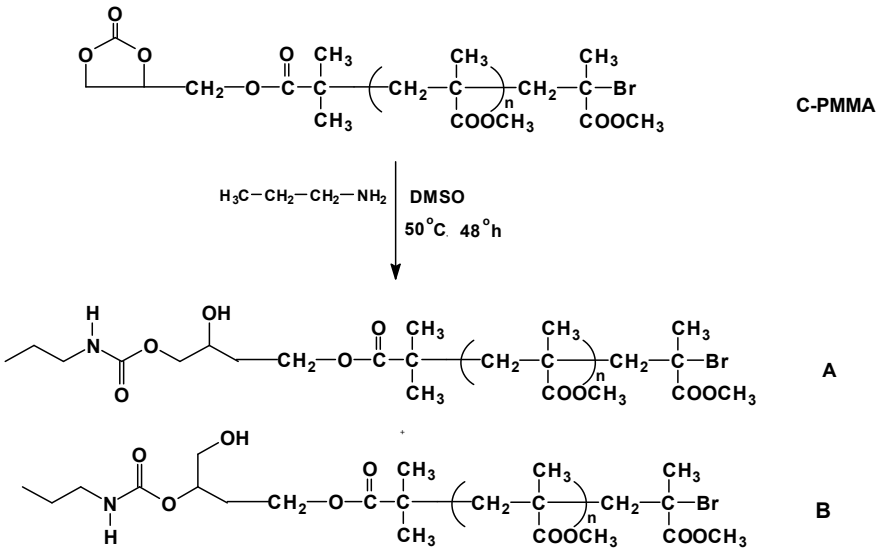
Figure 4.23: ^{1}H-NMR spectra of ODBMP (1) and cyclic carbonate-terminated PMMA (2) in $CDCL_3$

^{13}C-NMR spectroscopy also proved the presence of cyclic carbonate end group in PMMA. In addition to peaks characteristic of PMMA chain,[42,43] the peak of carbonate carbon was observed at 154.41 δ ppm and the peak corresponding to methine carbon from the initiator fragment appeared at 64.14 δ ppm.

4.4.5.3 Reaction between cyclic carbonate-terminated PMMA and *n*-propyl amine

As the reaction of cyclic carbonate with amino group finds various applications such as crosslinking reaction in coatings [35-38] and for enzyme immobilization[39] it was of interest to examine the reactivity of cyclic carbonate-terminated PMMA with a model amine namely, *n*-propyl amine. The reaction between cyclic carbonate-terminated PMMA and n-propyl amine was performed in dimethyl sulfoxide as a solvent at 50^{o}C for 48 h **(Scheme 4.9)**. It is known from earlier reports that reaction of cyclic carbonate with amine, gives hydroxyl-urethane *via* ring opening by nucleophilic attack of amine group onto the carbonyl group of cyclic carbonate.[40] Endo et al reported that addition reaction of cyclic carbonate with benzyl amine gave two isomers of hydroxy urethane.[41] The same

reaction of cyclic carbonate-terminated PMMA with *n*-propyl amine (Isomers A and B, **Scheme 4.9).**



Scheme 4.9: Reaction of cyclic carbonate-terminated PMMA with n-propyl amine

The ring opening reaction of cyclic carbonate-terminated PMMA with *n*-propyl amine to form urethane group was confirmed by IR and ^{1}H-NMR spectroscopy **(Figure 4.24 and 4.25).**

Figure 4.24 shows FTIR spectrum of product of reaction between cyclic carbonate-terminated PMMA and n-propyl amine. The spectrum shows absorption band at 3432 cm^{-1} due to hydroxyl and N-H stretching, the band at 1731 cm^{-1} was attributed to carbonyl group stretching from both urethane group as well as PMMA ester groups. The band due to NH deformation from urethane group appeared at 1524 cm^{-1}.

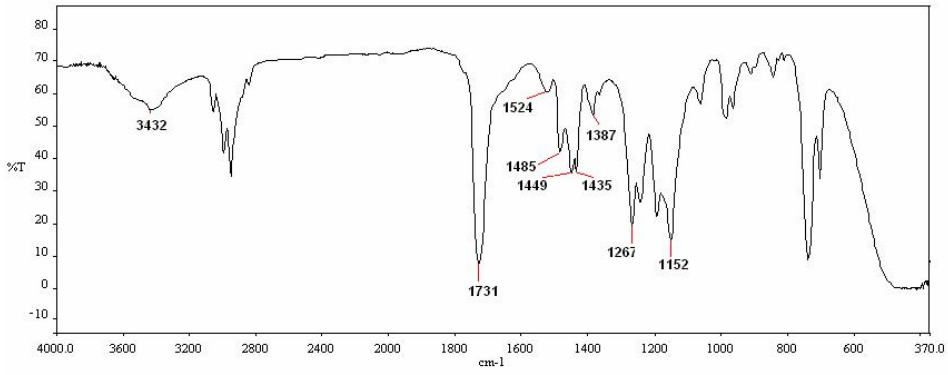


Figure 4.24: IR spectrum of product obtained by reaction of cyclic carbonate-terminated PMMA with n-propyl amine (A/B)

H-NMR spectrum of product obtained from reaction of cyclic carbonate-terminated PMMA with n-propyl amine alongwith assignments. Owing to the complexity of NMR spectrum, the regioselectivity of the product of reaction between cyclic carbonate-terminated PMMA and n-propyl amine could not be determined.

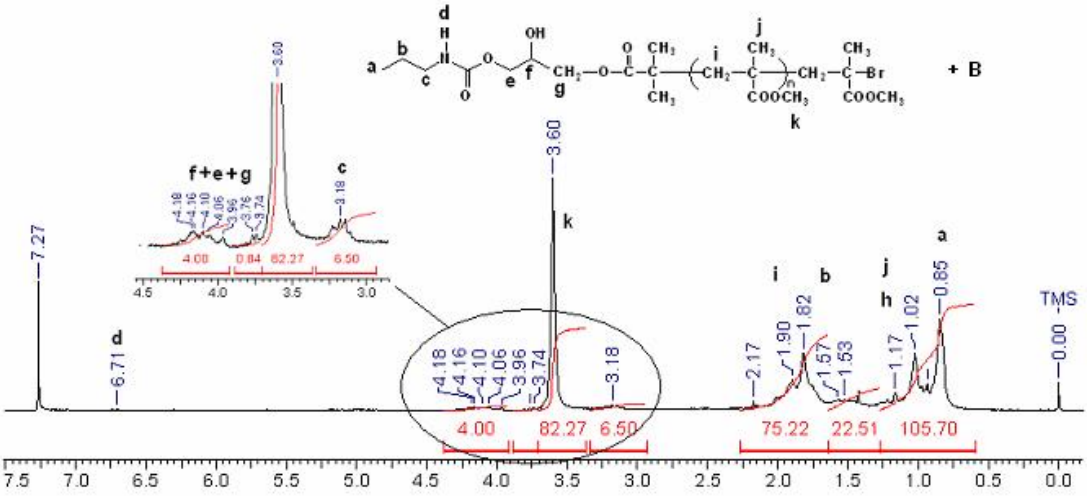


Figure 4.25: ^{1}H-NMR spectrum of product (A/B) obtained from reaction of cyclic carbonate-terminated PMMA with n-propyl amine in $CDCl_3$

1. Hydroxyl-terminated polystyrenes were successfully synthesized by ATRP of styrene using 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate as the initiator. The molecular weight of hydroxyl-terminated polystyrene was in the range 1980 to 9670 with narrow MWD (M_w/M_n -1.13 -1.33) and initiator efficiency was in the range 0.65 to 0.88.
2. Dihydroxyl-terminated poly(lauryl methacrylate)s were successfully synthesized by ATRP of LMA using 5-ethyl-2,2-dimethyl 1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) as the initiator. The molecular weight of dihydroxyl-terminated poly(lauryl methacrylate) was in the range 3810 to 11170 with narrow MWD (M_w/M_n - 1.23 - 1.29) and the initiator efficiency was in the range 0.80 to 1.05.
3. Bismethylol-terminated poly(methyl methacrylate) and poly(lauryl methacrylate) were synthesized using 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate as the initiator. The molecular weight of bismethylol-terminated poly(methyl methacrylate) was in the range 3320 to 20000 with narrow MWD (M_w/M_n - 1.18 -1.24) and the initiator efficiency was in the range 0.41 to 0.88. The molecular weight of bismethylol-terminated poly(lauryl methacrylate) was in the range 4060 to 27940 with narrow MWD (M_w/M_n - 1.12-1.19) and the initiator efficiency was in the range 0.35 to 1.03.
4. Lactone-terminated polystyrenes were synthesized by ATRP of styrene using 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate as the ATRP initiator. The molecular weight of lactone-terminated polystyrenes were 3500 and 2130 with narrow MWD (M_w/M_n - 1.07 and 1.15) and the initiator efficiency was 0.80 and 0.84.
5. Cyclic carbonate-terminated PMMAs were successfully synthesized by ATRP of MMA using 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) as the initiator. The molecular weight of cyclic carbonate-terminated PMMA was in the range 3330 to 6260 with narrow MWD (M_w/M_n - 1.16-1.24) and the initiator efficiency was in the range 0.72 to 0.99. The reactivity of cyclic carbonate group in cyclic carbonate-terminated PMMA with n-propyl amine was demonstrated.

ismethylol, lactone and carbonate-functionalized ATRP initiators were successfully utilized for the synthesis of polystyrene, PMMA and PLMA possessing corresponding functional groups.

1. Y. Zhang, S. Guo, C. Lu, L. Liu, Z. Li, and J. Gu, *J. Polym. Sci. Part A: Polym. Chem*., 45, 605, **2007**
2. H. Wang, X. Chen, C. Y. Pan, *Eur. Polym. J.,* 43, 1905, **2007**
3. A. O. Patil, D. N. Schulz and M. Novak, ñ*Functional Polymers: Modern Synthetic Methods and Novel Structures*;ò ACS Symposium Series 704; American Chemical Society: Washington, DC, **1998**
4. A. Akelah, *J. Mater Sci*., 21, 2977, **1986**
5. D. B. Brestensky, T. R. Hoye and C. W. Macosko, *J. Polym. Sci. Polym. Chem.* 33, 1957, **1995**
6. H. L. Hsieh, R. P. Quirk, ñ*Anionic Polymerization: Principles and Practical Applications*,ò New York, Marcel Dekker Inc. **1996**.
7. M. Sawamoto, ñ*Cationic Polymerization*,ò Ed- K. Matyjaszewski, Marcel Dekker: New York, 412, **1996**
8. O. W. Webster and D. Y. Sogah, ñ*Recent Aadvances in Mechanistic and Synthetic Aspects of Polymerization"*, 3, **1987**
9. K. Matyjaszewski, and J. Xia, *Chem. Rev*., 101, 2921, **2001**
10. M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev*., 101, 3689, **2001**
11. A. Postma, T. P. Davis, G. Moad, M. S. O_Shea, *React. Funct. Polym.*, 66, 137, **2006**
12. A. P. Narrainen, L. R. Hutchings, I. Ansari, R. L. Thompson and N. Clarke, *Macromolecules*, *40,* 1969, **2007**
13. W. Agut, D. Taton and S. Lecommandoux, *Macromolecules*, 40, 5653, **2007**
14. V. Coessens, T. Pintauer and K. Matyjaszewski, *Prog. Polym. Sci*., 337, 26, **2001**
15. D. D. Perrin and W. L. F. Armarego, ñ*Purification of Laboratory Chemicals",* Pergamon Press, New York, **1989**
16. R. N. Keller and H. D. Wycoff, *Inorg. Synth*, 2, 1, **1946**.
17. T. Sarbu, K.Y. Lin, J. Spanswick, R. R. Gil, D. J. Siegwart, and K. Matyjaszewski, *Macromolecules*, 37, 9694, **2004,**
18. F. Schon, M. Hartenstein and A. H. E. Muller, *Macromolecules*, 34, 5395, **2001**
19. D. M. Haddleton, C. Waterson, P. J. Derrick, C.B. Jasieczek and A. J. Shooter, *Chem, Commun*. 683, **1997**
20. Y. Y. Durmaz, I. Cianga and Y. Yagci, *e-Polymers*, 050, **2006**

M. Wolffs, T. Hermans, A. R. A. Palmans, C. E. Koning and A. Heise, *Macromolecules*, 38, 4220, **2005**

22. S. Yurteri, I. Cianga and Y. Yagci, *Macromol, Chem, Phys*. 204, 1771, **2003**
23. Y. Haba, Y. S. Balazs, O. Carmiel, I. Katz, M. Narkis and A. Schmidt, *Polym. Adv. Technol*., 18, 756, **2007**
24. B. Radhakrishnan, P. Chambon, E. Cloutet and H. Cramail, *Colloid Polym. Sci*. 281, 516, **2003**
25. W. Xu, X. Zhu, Z. Cheng and J. Chen, *J. Appl. Polym. Sci*. 1117, 90, **2003**
26. M. Schappacher, J. Bernard and A. Deffieux, *Macromol. Chem. Phys*. 204, (5/6), 762, **2003**
27. F. Schon, M. Hartenstain and A. H. E. Muller, *Macromolecules*, 34, 5394, **2001**
28. A. Marsh, A. Khan, D. M. Haddleton and M. J. Hannon, *Macromolecules,* 32, 8725, **1999**
29. V. Karavia, V. Deimede and J. K. Kallitsis, *J. Macromol. Sci. Part A: Pure and Appl. Chem A*, 41(2), 115, **2004**
30. J. M. Lu, Q. F. Xu, X. Yuan, X. Xia, J. Zhai and L. Wang, *J. Appl. Polym. Sci*., 104, 75, **2007**
31. J. Gromada, J. Spanswick, K. Matyjaszewski, *Macromol. Chem. Phys*. 205, 551, **2004**
32. J. L. Hedrick, B. Atthoff, K.A. Boduch, C.J. Hawker, D. Mecerreyes, R.D. Miller and M. Trollsas, *Polym. Mater. Sci. and Eng*. 104, 80, **1999**,
33. D. Mecerreyes, B. Atthoff, K.A. Boduch, M. Trollsas and J. L. Hedrick, *Macromolecules*, 32, 5175, **1999**
34. Z. Jiaming, L. Rui, H. Jianying, C. Jiayan, L. Xurong, L. Yutai, Z. Yousi, *J. Polym. Sci. Part A: Polym. Chem*., 45, 4082, **2007**
35. A. G. Shaikh, S. Sivaram, *Chem Rev*., 96, 951, **1996**
36. T. Nishikubo, A. Kameyama, M. Sasano, *J. Polym., Sci., Part A: Polym. Chem.* 32, 301, **1994**
37. N. Kihara, T. Endo, *J. Polym., Sci., Part A: Polym. Chem*, 31, 2765, **1993**
38. D. C. Webster, A. L. Crain, *Prog. Org. Coat.*, 40, 275, **2000**
39. D. C. Webster, *Prog. Org. Coat*, 47, 77, **2003**
40. N. Kihara, T. Endo, *Makromol, Chem*, 193, 1481, **1992**

eyama, M. Sasano, *J. Polym., Sci., Part A: Polym. Chem*., 32, 301, **1994**

42. F. A. Bovey and G. V. D. Tiers, *J. Polym. Sci*., XLIV, 173, **1960**
43. A.S. Brar, G. Singh and R. Shankar, *J. Molecular. Struct*., 703, 69, **2004**

5.1 Introduction

Block copolymers are attractive class of polymeric materials which consist of different polymeric segments covalently linked together to yield a material with hybrid properties.[1-3] Block copolymers find various applications as surfactants, thermoplastic elastomers, structure directing agents, etc. As shown in **Figure 5.1**, nearly unlimited number of molecular architectures can be engineered using two, three or more different monomers.

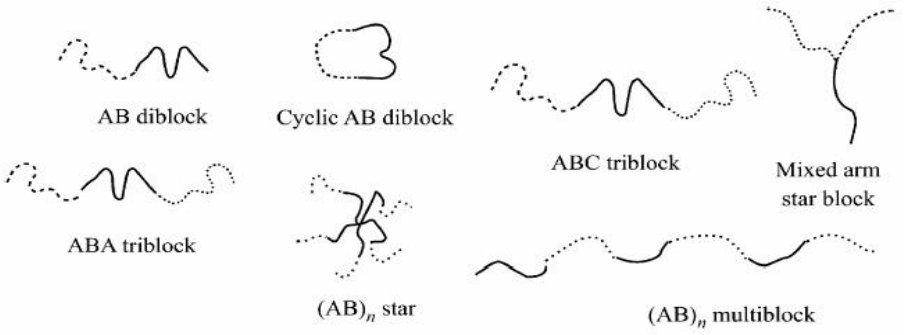


Figure 5.1: Selected block copolymer architectures

Block copolymers can be divided into two categories from the point of view of topology; linear and nonlinear. A linear AB diblock copolymer consists of a chain of monomers of type A attached at the end to a chain of type B monomers. Similarly, the chains of monomers A, B and C or more monomer types are joined together to form ABC triblock copolymer or multiblock copolymers. When three or more different polymer chains are connected at one point a nonlinear block copolymer namely, miktoarm star copolymer is formed.[3]

The most important properties of block copolymers are microphase separation (which is possible due to the covalent linkage between incompatible polymer segments) and micellization in selective solvent.[1, 2]

Among the block copolymers, amphiphilic block copolymers which consist of hydrophilic polymer segment and hydrophobic polymer segment in the same molecule are

ymers have attracted special attention in fundamental and applied research due to their unique chain architectures and physical properties. In particular, block copolymers composed of a hydrophilic poly(ethylene oxide) (PEO) segment have been extensively studied and have a wide variety of potential applications as polysoaps, polymeric surfactants, solution modifiers, emulsifiers, wetting agents, foam stabilizers and drug carriers.[3,4] Micellization of block copolymers can lead to different morphologies, such as spheres, hexagons, rods, lamellae, vesicles[2-4], etc. The morphology is controlled by structural factors such as polarity of each block, relative length of block and overall molar mass of the copolymer.[4,5]

Recently, the combination of various living polymerization techniques such as ATRP and ring opening polymerization (ROP) to synthesize novel diblock and star shaped block copolymers has attracted much interest since these combinatorial methods not only enrich the types of polymerizable monomers but also enable variable compositions, properties and architectures into one polymeric structure.[6,7] Combining ATRP and ROP of ε-caprolactone, complex architectures like mikto arm star copolymer is possible. Interest in poly(Ů-caprolactone) (PCL) is mainly due to its miscibility with different commercial polymers such as SAN, ABS, PVC, nitrocellulose, etc. Furthermore, PCL possesses properties such as permeability, biodegradability and ability to disperse pigments which makes it potentially useful as a biomaterial. [8,9]

This chapter deals with synthesis of block copolymers using ATRP as well as a combination of ATRP and ROP. The copolymers synthesized are listed below.

1) Poly(ethylene oxide)-*block*-poly(lauryl methacrylate) (PEO-*b*-PLMA) copolymers were synthesized by ATRP of lauryl methacrylate using PEO macroinitiators of varying number-average molecular weights.
2) Poly(styrene)-*block*-poly(ε-caprolactone) (PS-*b*-PCL) copolymers were synthesized by ROP of Ů-caprolactone using hydroxyl-terminated polystyrene as the macroinitiator. Hydroxyl-terminated polystyrenes were in turn prepared by ATRP using 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate as the initiator.
3) Poly(lauryl methacrylate)-*block*-poly(ethylene oxide)-*block*-poly(lauryl methacrylate) (PLMA-*b*-PEO-*b*-PLMA) copolymers were synthesized by ATRP in two steps. In the first step, difunctional Br-PEO-Br macroinitiator was prepared

ilable polyethylene glycol of M_n ï 20,000 by reaction with 2-bromoisobutyryl bromide. In the second step, ATRP of lauryl methacrylate using Br-PEO-Br macroinitiator was carried out to obtain PLMA-*b*-PEO-*b*-PLMA copolyner.

4) Poly(methyl methacrylate)-*block*-[poly(ε-caprolactone)]$_2$ [PMMA-*b*-(PCL)$_2$] mikto arm star copolymers were synthesized by ROP of Ůcaprolactone using bismethylol-terminated polymethyl methacrylate as macroinitiator (M_n^{NMR} ï 4300) which in turn was synthesized by ATRP.

5)

5.2 Experimental

5.2.1 Materials

Poly(ethylene glycol) mono methyl ether (mPEO, M_n-350, 700, 2000, 5000), poly(ethylene glycol) (PEO, M_n- 20000), stannous 2-ethylhexanoate (Sn(Oct)$_2$, 99%), ε-caprolactone (CL, 99%) lauryl methacrylate (LMA, 98%), copper bromide (CuBr, 99.9%), copper chloride (CuCl, 98%), 2,2ô-bipyridine (By, 99%), N,N-dimethyl amino pyridine (DMAP, 99%), N,N,Nô,Nô,Nò-penta methyl diethylene triamine (PMDETA, 99%) and 2-bromoisobutyryl bromide (98%) were purchased from Aldrich. Triethyl amine (TEA), toluene, dichloromethane (DCM), and tetrahydrofuron (THF) were purchased from S. D. Fine Chem., India and were dried and distilled according to the reported procedures.[10] Potassium hydroxide, sodium hydrogen carbonate, sodium hydroxide, methanol and chloroform, all received from S.D. Fine-Chem. Ltd. India were used as received.

5.2.2 Purification of reagents

Poly(ethylene glycol) mono methyl ether and poly(ethylene glycol) were dried by azeotropic distillation with toluene.

Purification of CuBr/CuCl : Into a 100 mL round bottom flask equipped with a nitrogen inlet and a magnetic stirring bar, CuBr/CuCl (2.0 g) and glacial acetic acid (60 mL) were added. The mixture was stirred for 12 h, filtered, washed with ethanol several times and dried at room temperature under vacuum for 24 h.[11]

ε-Caprolactone was dried over calcium hydride, distilled and stored under nitrogen.

calcium hydride, distilled under reduced pressure and was stored under nitrogen.

5.2.3 Measurements

FTIR spectra of polymers were recorded on a Perkin-Elmer *Spectrum GX* spectrophotometer in chloroform.

NMR spectra were recorded on a Bruker 200 or 400 MHz spectrometer at resonance frequencies of 200 or 400 MHz for ^{1}H-NMR and 50 or 100 MHz for ^{13}C-NMR measurements using $CDCl_3$ as a solvent.

Molecular weight and molecular weight distribution of the polymers were determined using GPC (Thermo separation products) equipped with spectra series UV 100 and spectra system RI 150 detectors. Two 60 cm PSS SDV-gel columns (10^2 ï 10^5 A^o and 1 x 100 A^o) were used at 25^{o}C. The sample concentration was 2 to 3 mg /mL and the injection volume was 50 µL. HPLC grade tetrahydrofuran was used as eluent at room temperature with a flow rate of 1 mL / min. Polystyrene was used as the calibration standard.

5.3 Synthesis

5.3.1 Synthesis of PEO-*b*-PLMA diblock copolymer

5.3.1.1 Preparation of poly(ethylene glycol) mono methyl ether macroinitiator (mPEOBr)

Into a 250 ml three-necked round bottom flask equipped with an addition funnel, a nitrogen inlet and a magnetic stirring bar were charged N,N-dimethylamino pyridine (0.45 g, 3 x 10^{-4} mol), triethyl amine (0.64 g, 6 x 10^{-3} mol) and dichloromethane (10 mL). The reaction mixture was cooled to 0^{o}C. 2-Bromoisobutyryl bromide (1.44 g, 6 x 10^{-3} mol) in dichloromethane (10 mL) was added over a period of 10 minutes into the reaction mixture which was followed by dropwise addition of poly(ethylene glycol) monomethyl ether (15.0 g, 3.0 x 10^{-3} mol) in dichloromethane (100 mL) over a period of 1.5 h under nitrogen atmosphere. Subsequently, the reaction mixture was allowed to attain room temperature. The reaction mixture was stirred overnight at room temperature and filtered, washed with saturated sodium bicarbonate solution (3 x 100 mL) and water (3 x 100 mL). The solution was dried over anhydrous sodium sulphate, filtered and dichloromethane was removed under vacuum to obtain mPEOBr macroinitiator which was purified by dissolution in

precipitation into excess hexane. The purification procedure was repeated three times and mPEOBr macroinitiator was dried under high vacuum for 24 h and weighed.

Yield- 13.50 g. (87 %)

5.3.1.2 Synthesis of PEO-*b*-PLMA diblock copolymer by ATRP

Into a 50 ml two necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adaptor were charged PEO macroinitiator (1.38 g, 5.6 x 10^{-4} mol, M_n^{NMR} = 2450, M_w/M_n = 1.09), lauryl methacrylate (4.54 g, 0.017 mol), N,N,N',N'',N'''-pentamethyldiethylenetriamine (0.10 g, 5.6 x 10^{-4} mol) and toluene (5 mL). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. Copper bromide (0.08 g, 5.6 x 10^{-4} mol) was added under a stream of nitrogen and flask was sealed with a stopper. The reaction mixture was degassed and then heated at 80^{o}C under nitrogen for 3 h and subsequently quenched by cooling in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and the solution was passed through neutral alumina column to remove catalyst. The solution was concentrated and precipitated in excess methanol. Further, polymer was purified by dissolution in dichloromethane (10 mL) and precipitation into excess methanol. The purification procedure was repeated three times and polymer was dried under high vacuum for 24 h and weighed.

Yield- 4.72 g. (80 %)

5.3.2 Synthesis of PS-*b*-PCL diblock copolymer by ROP

Into a 50 ml two necked round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged stannous 2-ethylhexanoate (0.010 g, 2.46 x 10^{-5} mol) ε-caprolactone (5.0 g, 0.043 mol) and hydroxyl-terminated polystyrene (PS-OH, 0.30 g, 5.0 x 10^{-5} mol, M_n^{NMR}- 5900). The reaction was carried out under nitrogen atmosphere at 140^{o}C for 12 h. The flask was cooled to room temperature, diluted with dichloromethane (20 mL) and precipitated into excess cyclohexane to obtain a white polymer. Further, polymer was purified by dissolution in dichloromethane (10 mL) and precipitation into excess cyclohexane. The purification procedure was repeated three times and polymer was dried under vacuum at room temperature for 24 h.

Yield- 4.77 g. (94 %)

PEO-*b*-PLMA triblock copolymer by ATRP

5.3.3.1 Preparation of difunctional poly(ethylene glycol) macroinitiator (Br-PEO-Br)

Into a 250 ml round bottom flask equipped with an addition funnel and a magnetic stirring bar were charged N,N-dimethylamino pyridine (0.22 g, 1.8 x 10^{-3} mol), triethyl amine (0.22 g 2.5 x 10^{-3} mol) and dichloromethane (10 mL). The reaction mixture was cooled to 0^{o}C. 2-Bromoisobutyryl bromide (0.51 g, 2.5 x 10^{-3} mol) in dichloromethane (10 mL) was added over a period of 10 minutes to the reaction mixture, followed by dropwise addition of poly(ethylene glycol) (15 g, 7.5 x 10^{-4} mol) in dichloromethane (100 mL) over a period of 1.5 h under inert atmosphere. Subsequently, the reaction mixture was allowed to attain room temperature. The reaction mixture was stirred overnight at room temperature and filtered, washed with saturated sodium bicarbonate solution (3 x 100 mL) and water (3 x 100 mL). The solution was dried over anhydrous sodium sulphate, filtered and dichloromethane was removed under vacuum to obtain Br-PEO-Br macroinitiator. Further, macroinitiator was purified by dissolution in dichloromethane (10 mL) and precipitation into excess hexane. The purification procedure was repeated three times and macroinitiator was dried under vacuum at room temperature for 24 h.

Yield- 14.0 g. (93 %)

5.3.3.2 Synthesis of PLMA-*b*-PEO-*b*-PLMA triblock copolymer

Into a 50 ml two necked round bottom flask equipped with a stirring bar and a nitrogen inlet were charged Br-PEO-Br macroinitiator (1.05 g, 8.3 x 10^{-5} mol) and dimethyl formamide (3 mL). The macroinitiator was dissolved by heating the reaction mixture at 50^{o}C. Lauryl methacrylate (4.54 g, 0.017 mol), copper chloride (0.023 g, 1.61 x 10^{-4} mol) and N,N,N̊,N̊,Ǹ-penta methyl diethylene triamine (0.028 g, 1.61 x 10^{-4} mol) were added to the reaction mixture under nitrogen atmosphere and the reaction mixture was degassed by three freeze-pump-thaw cycles. The reaction mixture was heated at 60^{o}C under nitrogen for 2.5 h. Reaction was quenched by cooling the reaction mixture in liquid nitrogen bath. The reaction mixture was dissolved in tetrahydrofuran (30 mL) and filtered through neutral alumina column. The solution was concentrated and polymer was precipitated into excess methanol. The precipitated product was dried under vacuum at room temperature for 24 h.

Yield- 5.13 g. (92 %)

-(PCL)$_2$ mikto arm star copolymers by ROP

Into a 50 mL two necked round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged bismethylol-terminated PMMA (Mn^{NMR}- 4300, M_w/M_n - 1.19) (0.20 g, 4.65 x10^{-5} mol), stannous 2-ethylhexanoate (0.015 g, 3.70 x 10 ï5) and ε-caprolactone (0.50 g, 4.38 x 10^{-3} mol). The reaction was carried out under nitrogen atmosphere at 140^{o}C for 8 h. The reaction mixture was cooled to room temperature, diluted with dichloromethane (10 mL) and precipitated into excess hexane to obtain a white polymer. Further, polymer was purified by dissolution in dichloromethane (10 mL) and precipitation into excess cyclohexane. The purification procedure was repeated three times and polymer was dried under vacuum at room temperature for 24 h.

Yield- 0.58 g. (85 %)

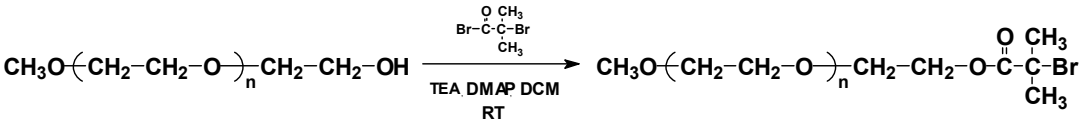
5.4 Results ad Discussion

5.4.1 Synthesis and characterization of PEO-*b*-PLMA diblock copolymers

5.4.1.1 Preparation and characterization of mPEOBr macroinitiator

Kops et al[12] functionalized poly(ethylene glycol)s by transforming hydroxyl groups into 2-bromo propionate or 2-chloropropionate groups to obtain mono or difunctional PEG macroinitiators. They found PEO macroinitiators to be efficient initiators for ATRP of styrene and obtained PEO-*b*-PS and PS-*b*-PEO-*b*-PS copolymers with predetermined molecular weight with narrow MWD. Krishnan et al[17,18] utilized difunctional PEO macroinitiators and synthesized PMMA-*b*-PEO-*b*-PMMA utilizing halide exhange technique. Later, Hocker et al utilized PEO macroinitiators for synthesis of methacrylic block copolymers such as poly(ethylene oxide)-*b*-poly(hydroxy ethyl methacrylate).[19,20]

mPEOBr macroinitiators were synthesized by reacting poly(ethylene glycol) mono methyl ether of different molecular weight with 2-bromoisobutyryl bromide in the presence of triethyl amine and N,N-dimethyl amino pyridine in dry dichloromethane **(Scheme 5.1)**



Scheme 5.1: Synthesis of mPEOBr macrointiators

cterization data of mPEOBr macroinitiators. The M_n^{NMR} of mPEOBr macroinitiators were calculated for each macroinitiator by comparing the integral ratio of peak b to peak a **(Figure 5.3)**.

Table 5.1: Characterization of mPEOBr macroinitiators

Macroinitiator code	[a]M_n	M_n^{NMR}	[b]GPC		
	mPEO-OH	mPEOBr	M_n	M_w	M_w/M_n
$mPEOBr_{10}$	350	470	-[c]	-	-
$mPEOBr_{18}$	700	790	990	1060	1.07
$mPEOBr_{55}$	2000	2450	3350	3700	1.09
$mPEOBr_{139}$	5000	6120	11900	13000	1.09

a- data provided by supplier (Aldrich), b - PS calibration, c- not determined

mPEOBr macroinitiators were characterized by FTIR, ^1H and ^{13}C-NMR spectroscopy.

Figure 5.2 shows a representative FTIR spectrum of mPEO macroinitiator. The appearance of ester carbonyl peak at 1736 cm^{-1} confirmed the formation mPEO macroinitiator.[12]

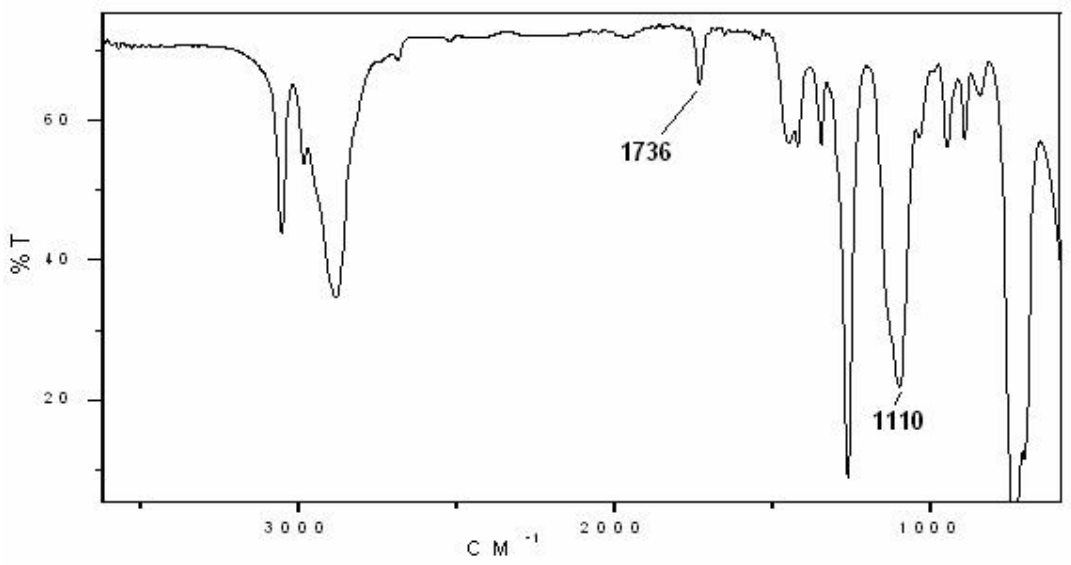


Figure 5.2: FTIR spectrum of mPEOBr macroinitiator

NMR spectrum of mPEOBr macroinitiator along with assignments is shown in **Figure 5.3**. The peaks at 1.94 δ ppm was assigned to six protons (Hd) of two methyl groups (-OCO-C(C**H**$_3$)$_3$ and the triplet at 4.33 δ ppm (Hc) is due to methylene protons (C**H**$_2$) alpha to ester group.[12] The singlets for poly(oxyethylene) (C**H**$_2$C**H**$_2$O) protons and methoxy group protons (OC**H**$_3$) were observed at 3.64 (Hb) and 3.38 δ ppm (Ha), respectively.

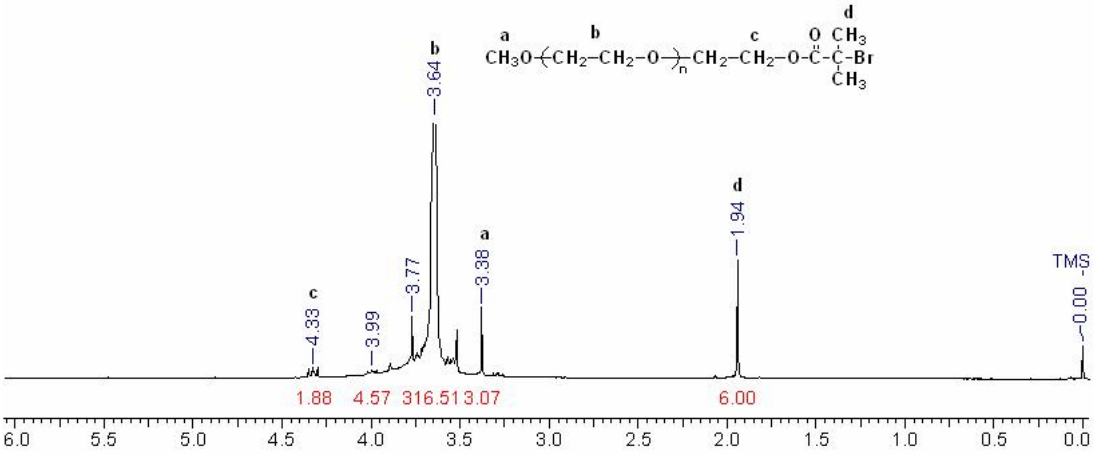


Figure 5.3: ^{1}H-NMR spectrum of mPEOBr macroinitiator

^{13}C-NMR spectrum of mPEOBr macroinitiator along with assignments is shown in **Figure 5.4**. The peak at 170.77 δ ppm correspond to the ester carbonyl carbon (C5) while methylene carbon (C4) attached to ester group appeared at 71.23 δ ppm. The peaks at 68.29 δ ppm and 55.09 δ ppm were ascribed to methoxy carbon (C1) and quarternary carbon (C6) attached to bromine, respectively.

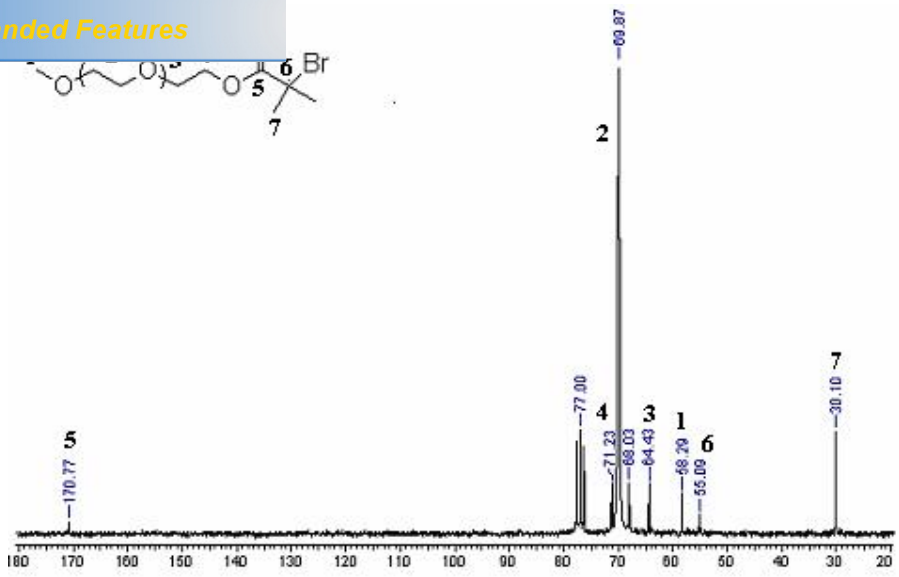
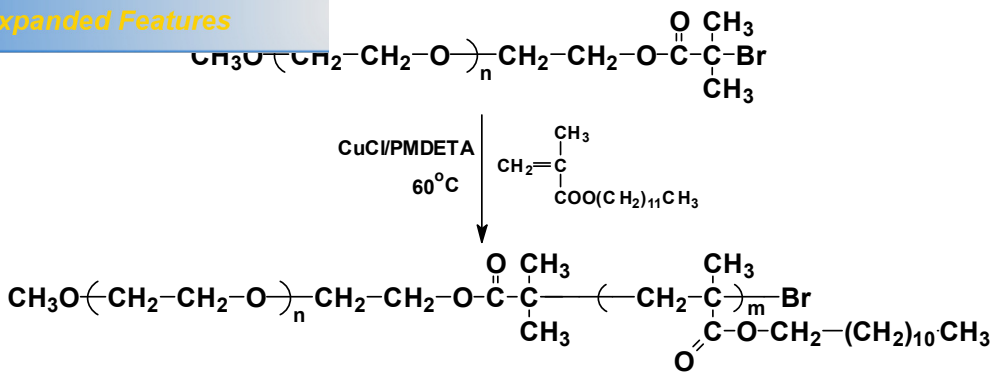


Figure 5.4: ^{13}C-NMR spectrum of mPEOBr macroinitiator

5.4.1.2 Synthesis and characterization of PEO-*b*-PLMA diblock copolymer

Synthesis of PEO containing block copolymers with alkyl methacrylates *via* sequential anionic polymerization is difficult owing to side reaction between living PEO and the alkyl ester group of poly(alkyl methacrylate) causing the formation of inhomogeneous copolymers. The other obstacle encountered in the synthesis of block copolymers through addition of alkyl methacrylate to living PEO is the low solubility of PEO in THF (soluble above 20^{o}C) whereas classical anionic polymerization of methacrylates proceeds well only below ï 75^{o}C. Elevated temperatures lead to transfer and termination reactions in methacrylate polymerization.[21,22,23]

ATRP of lauryl methacrylate was initiated by mPEOBr macroinitiator to obtain PEO-*b*-PLMA diblock copolymer **(Scheme 5.2).** Polymerizations were carried out in the presence of CuBr or CuCl as catalysts with 2,2ô-bipyridine or PMDETA as complexing ligands. The polymerization reactions were performed with various monomer to macroinitiator concentration ratios to obtain copolymers with different molecular weights. The polymerization reactions were carried out in bulk as well as in toluene as a solvent.



Scheme 5.2: Synthesis of PEO-*b*-PLMA diblock copolymer

Table 5.2 shows reaction conditions and results of synthesis of PEO_{55}-*b*-PLMA diblock copolymers. The diblock copolymers were purified by repeated precipitation in methanol/water mixture (75:25, v/v) at room temperature. The purified copolymers were dried *in vacuo* at room temperature.

Table 5.2: Reaction conditions and results of synthesis of PEO_{55}-*b*-PLMA in bulk and in toluene

Run	[M]:[I]: [CuBr]:[L]	Time (h)	[a]Conv. (%) (LMA)	[b]M_n^{th}	M_n^{NMR}	[c]GPC		
						M_n	M_w	M_w/M_n
1	30:1:1:3 [d]	5	93	9630	11350	12,000	14,500	1.18
2	30:1:1:1 [e]	3	73	8010	10150	10000	12,900	1.25
3	54:1:1:1 [e]	3	78	12300	12450	13300	17,000	1.28
4	55:1:1:1 [e]	12	90	14040	21850	19500	25100	1.28

[M] = LMA, [I] = ($mPEO_{55}Br$ macroinitiator, M_n^{NMR} ï 2450), [L]= bipyridine/PMDETA, a ï NMR spectroscopy, b- $[LMA]_o/[I]_o$ x 254 x conversion/100 + $M_n(mPEO_{55}Br)$, c ï PS calibration, d - Bulk ATRP at 130°C and [L]= 2,2ô-Bipyridine, e - Solution ATRP in toluene at 80°C and [L]= PMDETA

In the synthesis of PEO-*b*-PLMA, the conversion of lauryl methacrylate was determined from ^{1}H-NMR spectroscopy by recording NMR spectrum of the reaction mixture **(Figure 5.5).** The peak at 4.49 δ ppm corresponds to the methylene protons (Hc)

CO macrointiator. A triplet at 4.13 δ ppm correspond to methylene protons (Hl) attached to ester group of lauryl methacrylate and a broad peak at 3.92 δ ppm correspond to methylene protons (Hh) attached to ester group of PLMA segment from block copolymer. The peak at 3.63 δ ppm corresponds to methylene protons (Hb) of PEO macroinitiator and PEO segment from block copolymer.

Using ^{1}H-NMR spectroscopy the composition and number average molecular weight (M_n^{NMR}) of the PEO-b-PLMA diblock copolymers were determined, which are given in **Tables 5.2 to 5.5**. M_n^{NMR} of PLMA segment was determined by comparing the integral ratio of the signals originating from PLMA segment at 3.93 δ ppm due to protons of CH_2 group (Hh) with that of PEO segment (of known M_n) (CH_2CH_2O) protons (Hb) appearing at 3.65 δ ppm.

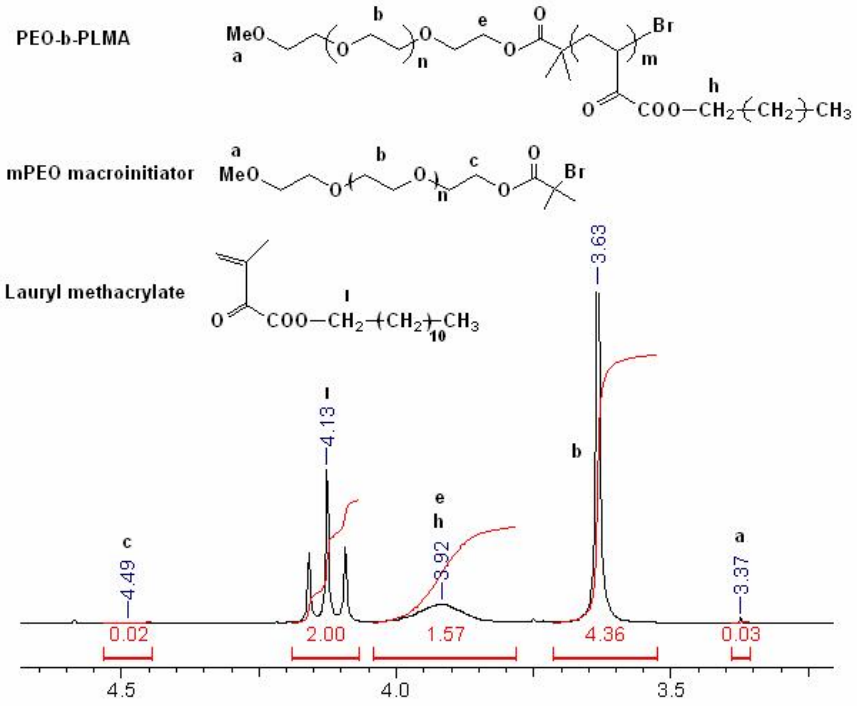


Figure 5.5: Partial ^{1}H-NMR spectrum of reaction mixture during synthesis of PEO-*b*-PLMA

Initially, $mPEO_{55}Br$ macroinitiator in the presence of CuBr/2,2ô-bipyridine as catalyst at 130°C was used for bulk ATRP of LMA. The polymerizations in toluene were carried out using CuBr/PMDETA at 60°C.

Figure 5.6 shows GPC traces of $mPEO_{55}Br$ macroinitiator as well as PEO_{55}-*b*-PLMA diblock copolymers. GPC curve shifts from higher elution volume to lower elution

ease in molecular weight from mPEO macroinitiator to diblock copolymer. As seen from data in **Table 5.2** the molecular weight distributions were narrow (1.18 to 1.28) indicating a living/controlled polymerization. Except for Run 4, the obtained molecular weights (Mn^{NMR}) agreed reasonably well with theoretical values (Mn^{th}). The theoretical molecular weight values (Mn^{th}) were calculated according to the following equation.

$$\mathbf{M_n^{th} = [LMA]_o/[I]_o \times 254 \times conversion/100 + M_n(mPEOBr)}$$

where $[LMA]_o$ and $[I_o]$ are the initial molar concentrations of the lauryl methacrylate and PEO macroinitiator, respectively.

The polymerizations using $mPEO_{10}Br$ macroinitiator were carried out in bulk at 60°C using CuCl/PMDETA and CuBr/PMDETA as catalysts. ñHalide exchangeò technique was utilized to improve the control over molecular weight as reported by Matyjaszewski et al,[26] as the mixed halide system R-Br/CuCl would give faster initiation, slower propagation and therefore better control over molecular weight and MWD.

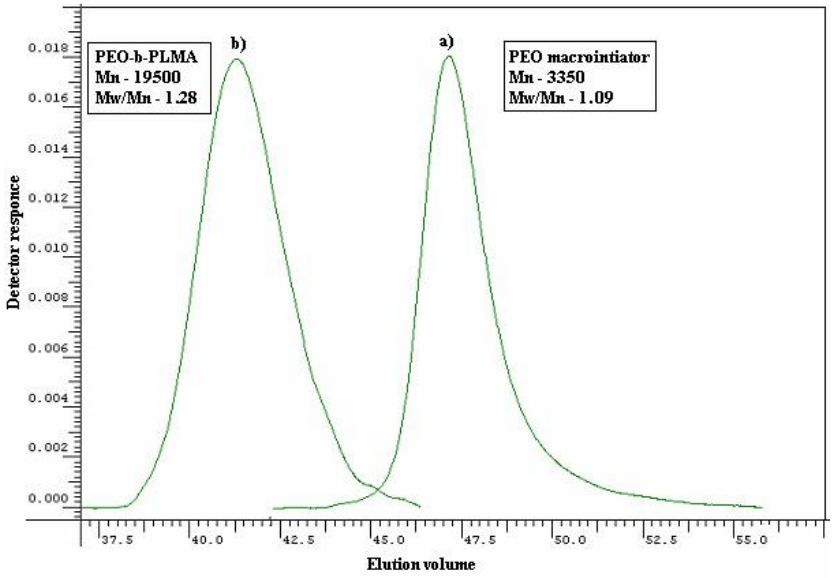


Figure 5.6: GPC traces of a PEO macroinitiator and PEO-b-PLMA copolymer (Run 4, Table 5.2)

The reaction conditions and results of synthesis of PEO_{10}-*b*-PLMA diblock copolymer are presented in **Table 5.3**.

s and results of synthesis of PEO_{10}-*b*-PLMA in bulk

Run	[M]:[I]:[CuX]:[L]	Time (h)	[b]Conv. (%) (LMA)	[c]M_n^{th}	M_n^{nmr}	[d]GPC		
						M_n	M_w	M_w/M_n
1	[a]100:1:1:1	1.5	75	19350	23660	25570	30420	1.19
2	[e]160:1:2:2	2	94	31900	36940	42970	50700	1.18
3	[a]160:1:2:2	3	88	36370	44710	45180	53760	1.19

Reaction temperature - 60°C, [M] = LMA, [I] = $mPEO_{10}Br$ macroinitiator, M_n^{nmr}- 470), [L] = PMDETA, a - [CuX] = CuCl, b - NMR spectroscopy, c - $[LMA]_o/[I]_o$ x 254 x conversion/100 + $M_n(mPEO_{10}Br)$, d - PS calibration, e - CuBr

Experimental molecular weights determined by ^{1}H-NMR spectroscopy (M_n^{NMR}) were slightly higher than the theoretical molecular weights as was observed for PEO_{55}-*b*-PLMA using $mPEO_{55}Br$ macroinitiator. PEO_{10}-*b*-PLMA diblock copolymers showed narrow MWD in range 1.18 to 1.19. Zhang et al[24] observed similar results where PEOBr macroinitiator was used in conjunction with CuCl/2,2ô-bipyridine as mixed halide catalyst for the ATRP of MMA, which resulted in PEO-*b*-PMMA with narrow MWD (1.05 to 1.10).

The polymerizations using $mPEO_{18}Br$ macroinitiator were carried out in bulk at 60°C using CuCl/PMDETA and CuBr/PMDETA as catalysts. **Table 5.4** shows reaction conditions and results of synthesis of PEO_{18}-*b*-PLMA copolymers. PEO_{18}-*b*-PLMA diblock copolymers obtained using halide exchange technique were found to have slightly higher molecular weight (M_n^{NMR}) than theoretical molecular weight with MWD in the range 1.17 to 1.36.

s and results of synthesis of PEO_{18}-*b*-PLMA in bulk

Run	[M]:[I]: [CuX]:[L]	Time (h)	[b] Conv. (%) (LMA)	[c] M_n^{th}	M_n^{nmr}	[d] GPC		
						M_n	M_w	M_w/M_n
1	[a] 75:1:1:1	1	32	6930	8460	21490	29220	1.36
2	[e]120:1:1:1	1.5	77	24370	34650	38100	44960	1.18
3	[a]120:1:1:1	1.5	68	26510	36120	63720	74550	1.17
4	[a] 150:1:2:2	2	91	35540	39490	68040	87770	1.29

Reaction temperature - 60°C, [M] = LMA, [I] = ($mPEO_{18}Br$ macroinitiator, M_n^{nmr}- 790), [L] = PMDETA, a - [CuX] = CuCl, b -NMR spectroscopy, c - $[LMA]_o/[I]_o$ x 254 x conversion/100 + $M_n(mPEO_{18}Br$, d - PS calibration, e - [CuX] = CuBr

For the synthesis of PEO_{139}-*b*-PLMA diblock copolymer, $mPEO_{139}Br$ macroinitiator was used. ATRP of LMA was carried out in bulk at 60°C in presence of CuCl/PMDETA and CuBr/PMDETA as catalysts.

Table 5.5 shows reaction conditions and results of synthesis of PEO_{139}-*b*-PLMA diblock copolymers. The obtained molecular weights of the diblock copolymers agreed reasonably well with theoretical molecular weights and MWD was narrow (M_w/M_n -1.14 and 1.22).

Table 5.5: Reaction conditions and results of synthesis of PEO_{139}-*b*-PLMA in bulk

Run	[M]:[I]: [CuX]:[L]	Time (h)	[a]Conv (%) (LMA)	[b]M_n^{th}	M_n^{nmr}	[c]GPC		
						M_n	M_w	M_w/M_n
1	[d]150:1:1:1	1	75	37760	39000	39650	45480	1.14
2	[e]150:1:1:1	1	41	22920	26870	19880	24430	1.22

Reaction temperature - 60°C, [M] = LMA, [I] = ($mPEO_{139}Br$ macroinitiator, M_n^{nmr}-6120), [L] = PMDETA, a ï ^{1}H-NMR spectroscopy, b - $[LMA]_o/[I]_o$ x 254 x conversion/100 + $M_n(mPEO_{139}Br)$, c - PS calibration, d - [CuX] = CuBr, e - [CuX] = CuCl

ation of PEO-*b*-PLMA diblock copolymers

PEO-*b*-PLMA diblock copolymers were characterized by FTIR and ^{1}H-NMR spectroscopy.

A representative IR spectrum of PEO-*b*-PLMA diblock copolymer is shown in **Figure 5.7**. The bands at 1728 cm^{-1} and 1112 cm^{-1} correspond to ester carbonyl group of PLMA segment and ether group of PEO segment, respectively.

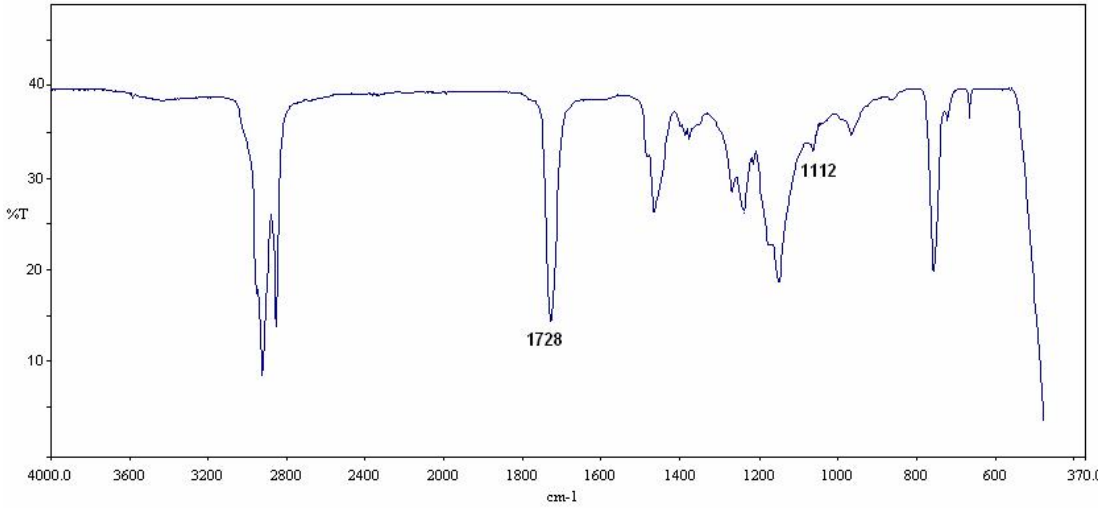


Figure 5.7: IR spectrum of PEO-*b*-PLMA copolymer

^{1}H-NMR spectrum of PEO-*b*-PLMA diblock copolymer along with assignments is shown in **Figure 5.8**. The signals from PEO segment i.e. singlets for oxyethylene protons (CH_2CH_2O) (Hb) and methoxy protons (OCH_3) (Ha) were observed at 3.65 ŭ ppm and 3.38 ŭ ppm, respectively. PLMA segment showed characteristic signals for methyl protons (CH_3) (Hk) at 0.89 ŭ ppm and methylene protons attached to ester group ($COOCH_2$) (Hh) at 3.92 ŭ ppm. The signal for methylene group protons (Hj) of PLMA segment was observed at 1.27 ŭ ppm.

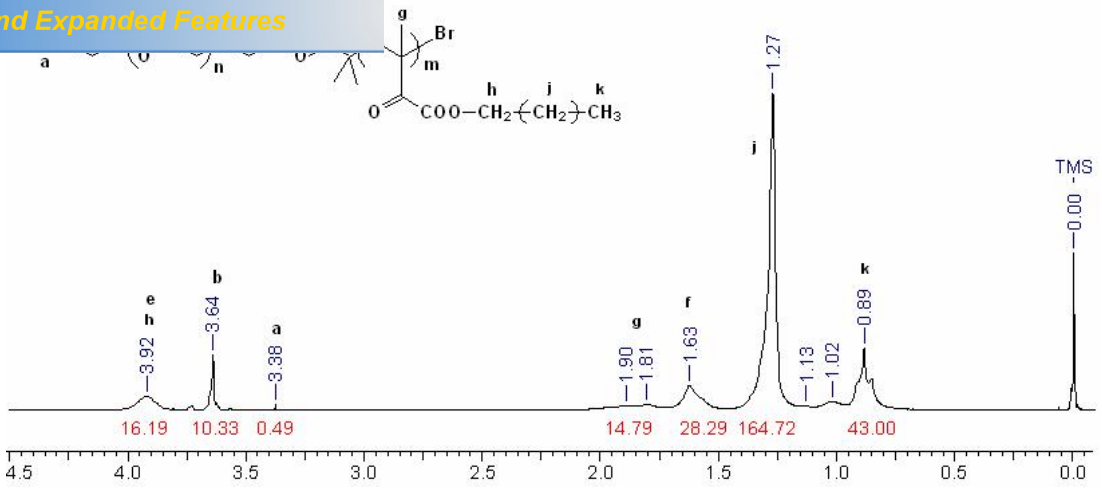


Figure 5.8: ^{1}H-NMR spectrum of PEO-*b*-PLMA copolymer in $CDCl_3$

5.4.2 Synthesis and characterization of PS-*b*-PCL diblock copolymer

5.4.2.1 Synthesis of PS-*b*-PCL diblock copolymers

PS-*b*-PCL copolymer was synthesized using the concept of dual living polymerization techniques namely, ATRP and ROP. Using this concept, Jerome et al used hydroxy β-functionalized alkoxyamine as dual functionalized molecule for living free radical copolymerization of styrene and ROP of ε-CL in two steps for synthesis of PS-*b*-PCL.[27] Enzymatic polymerization and ATRP were also applied as dual polymerization techniques using dual functionalized initiator for synthesis of diblock copolymers.[28, 29]The advantage of this route lies in possibility of synthesis of a block copolymer with monomers that are polymerized by different polymerization mechanisms in a simple and efficient way.

4-(Hydroxymethyl)benzyl 2-bromo-2-methylpropanoate (**Figure 5.9**, reported in **Chapter 3**) provided access to hydroxyl-functionalized polystyrene by ATRP which was utilized for ROP of ε-caprolactone (CL) sequentially.

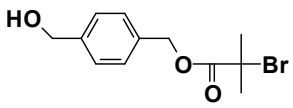
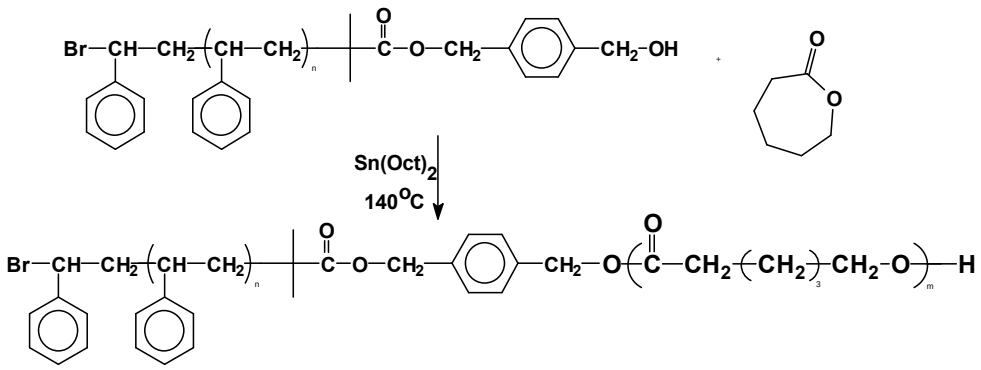


Figure 5.9: Structrue of 4-(hydroxymethyl)benzyl 2-bromo-2 methylpropanoate

Scheme 5.3 shows synthesis of PS-*b*-PCL diblock copolymers. Hydroxyl-terminated polystyrene with three different molecular weights (synthesized in **Chapter 4**)

for ROP of ε-CL in the presence of stannous octanoate at 140°C.



Scheme 5.3: Synthesis of PS-*b*-PCL diblock copolymer

Table 5.6 shows reaction conditions and results of synthesis of PS-b-PCL copolymers. The conversions were determined gravimetrically. The molecular weight of block copolymer could be controlled by varying molar ratio of ε-CL to polystyrene macroinitiator.

Table 5.6: Reaction conditions and results of synthesis of PS-*b*-PCL copolymer

Run	[a]PS-OH		$[\varepsilon CL]_o$:$[PS]_o$	[b]Conv. (%)	[c]Mn^{th}	Mn^{NMR}	[a]GPC *total*	
	M_n	M_w/M_n					M_n	M_w/M_n
1	5900	1.24	826	89[d]	89700	92690	11660	1.44
2	3000	1.13	206	92 [e]	28620	27070	8890	1.26
3	3000	1.13	157	41 [f]	15380	14320	4470	1.27
4	6200	1.14	25	83 [e]	8990	8240	9550	1.26

Catalyst: stannous octanoate - 0.085 mol %, a- PS calibration, b- gravimetry, c- $[\varepsilon\text{-CL}]_o/[\text{PS-OH}]_o$ x 114 x conversion/100 + M_n (PS-OH), Reaction temperature - 140°C, Reaction time d = 15 h, e = 12 h, f = 9 h.

GPC analysis showed an increase in molecular weight after macro-initiation of ε-caprolactone **(Figure 5.10)**. The molecular weights of PS-*b*-PCL copolymer determined

^{NMR}) agreed well with theoretical molecular weight **(Table 5.6)**. The obtained PS-*b*-PCL copolymers showed MWD in range 1.26 to 1.44.[27]

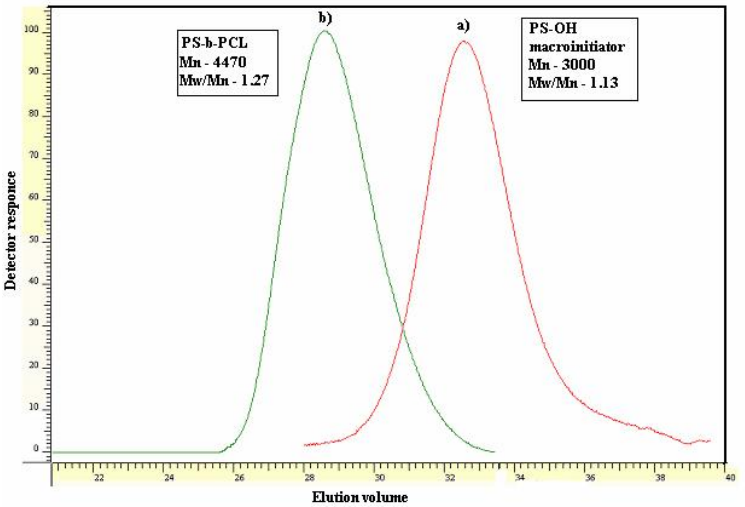


Figure 5.10: GPC traces of a) PS-OH macroinitiator and b) PS-*b*-PCL copolymer (run-3, Table 5.6)

5.4.2.2 Structural characterization of PS-*b*-PCL copolymers

The structural characterization of PS-*b*-PCL copolymer was carried out by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Figure 5.11 shows representative FTIR spectrum of PS-*b*-PCL diblock copolymer. The band at 1728 cm^{-1} corresponds to ester carbonyl group of PCL segment. Polystyrene block exhibits band at 1602 cm^{-1} due to aromatic C=C stretching and the weak band at 3441 cm^{-1} corresponds to the hydroxyl end group.

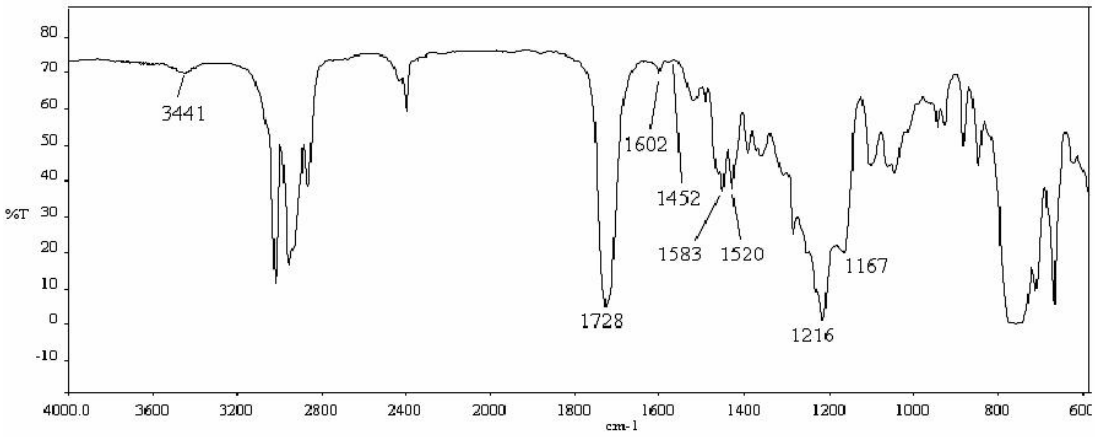


Figure 5.11: IR spectrum of PS-*b*-PCL copolymer

PS-*b*-PCL diblock copolymer along with assignments is shown in **Figure 5.12**. The characteristic peaks for both polystyrene and poly(ε-caprolactone) blocks are present in the spectrum. The peak in the region 7.10 to 6.50 ŭ ppm arises due to the aromatic protons (Ha) of PS block, while the triplet at 4.06 ŭ ppm arises due to methylene protons (Hf) of PCL block.

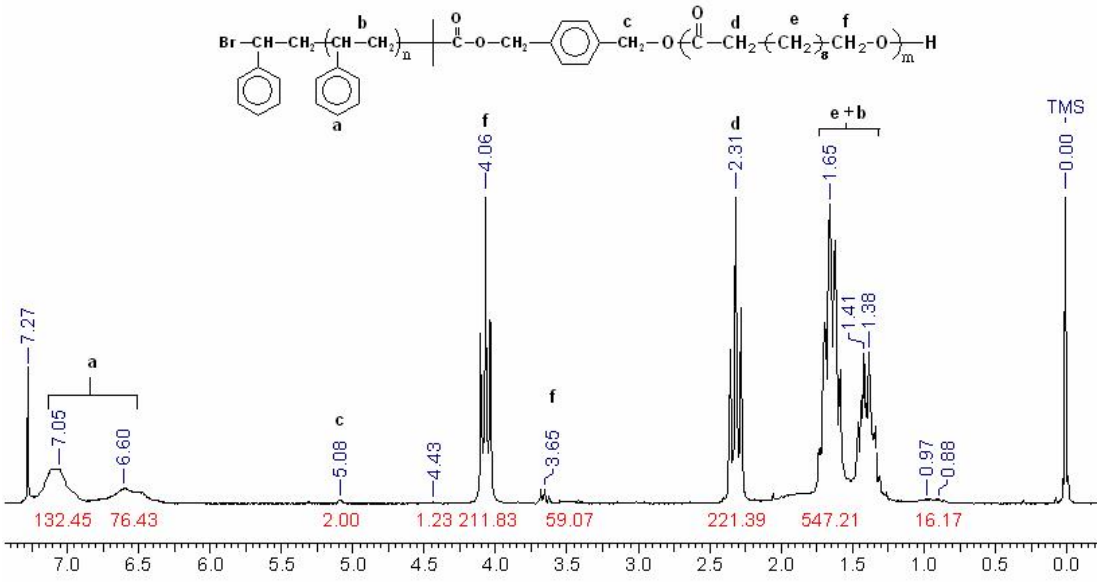


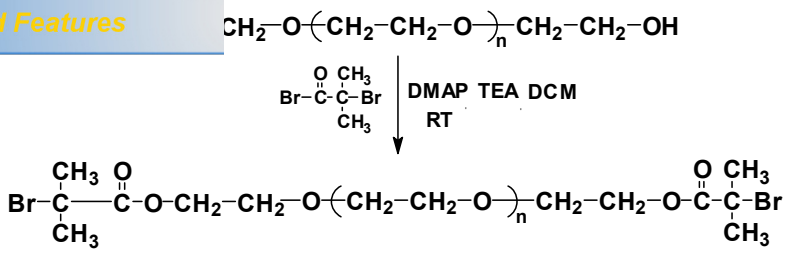
Figure 5.12: ^{1}H-NMR spectrum of PS-*b*-PCL diblock copolymer

The peak corresponding to benzylic protons (Hc) shifted from 4.60 to 5.08 ŭ ppm confirming the macroinitiation of ε-CL by PS-OH.[31] M_n^{NMR} was calculated from integration ratios of aromatic protons of polystyrene block (known M_n) and methylene protons (Hd) of PCL block, while the contribution due to aromatic protons from initiator fragment was neglected.

5.4.3 Synthesis and characterization of PLMA-*b*-PEO-*b*-PLMA copolymer

5.4.3.1 Synthesis and characterization of difunctional Br-PEO-Br macroinitiator

Difunctional Br-PEO-Br macroinitiator was synthesized according the procedure reported by Kops et al.[12] Reaction of poly(ethylene glycol) with excess of 2-bromoisobutyryl bromide was carried out in the presence of N,N-dimethylamino pyridine and triethyl amine as hydrogen bromide acceptors **(Scheme 5.4)**.



Scheme 5.4: Synthesis of Br-PEO-Br macroinitiator

The characterization of Br-PEO-Br macroinitiator was carried out by FTIR and ^{1}H-NMR spectroscopy.

Table 5.7 shows characterization data of Br-PEO-Br macroinitiator. The M_n^{NMR} of macroinitiator was calculated by comparing the integral ratio of peak c to peak a **(Figure 5.14)**.

Table 5.7: Characterization of Br-PEO-Br macroinitiator

Macroinitiator	M_n^{NMR}	^{b}GPC		
		M_n	M_w	M_w/M_n
Br-PEO-Br	12650	24590	25570	1.04

a - polystyrene calibration

Figure 5.13 shows FTIR spectrum of Br-PEO-Br macroinitiator. The band at 1733 cm^{-1} corresponds to ester carbonyl group of difunctional macroinitiator. The band at 1110 cm^{-1} corresponds to the ether group (C-O-C).

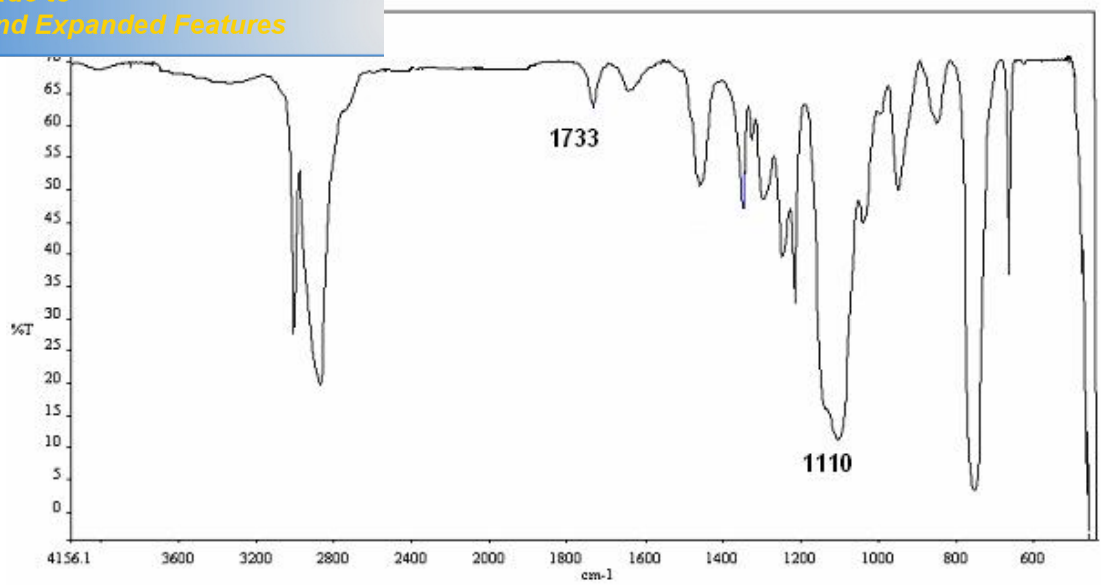


Figure 5.13: FTIR spectrum of Br-PEO-Br macroinitiator

^{1}H-NMR spectrum of Br-PEO-Br macroinitiator along with assignments is shown in **Figure 5.14**. The peak at 1.94 ŭ ppm (Ha) was attributed to twelve protons from four methyl groups (-OCO-C(C**H**$_3$)$_2$ and the multiplet at 4.33 ŭ ppm was assigned to methylene protons (Hb) attached to ester group. The peak at 3.65 ŭ ppm corresponded to oxyethylene protons (Hc) of Br-PEO-Br macroinitiator. From the intensity ratio of peak c to a, M_n^{NMR} was calculated.

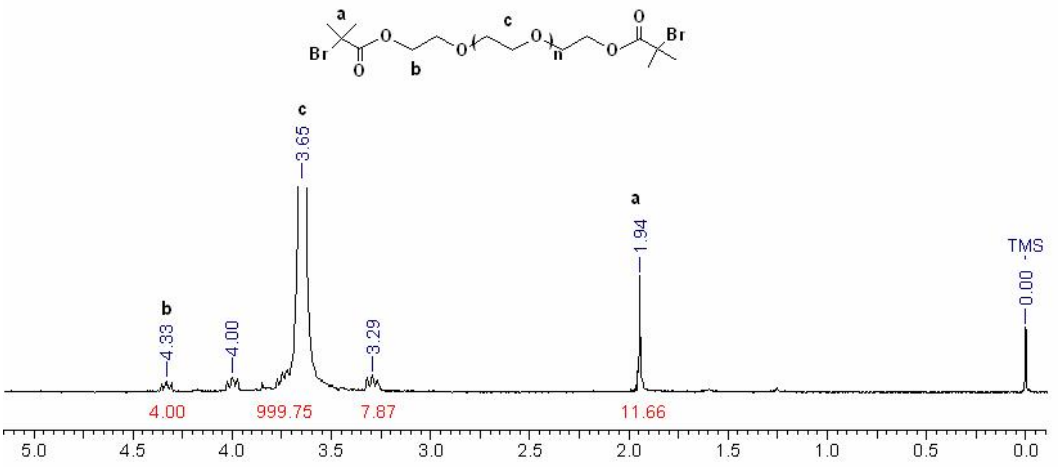


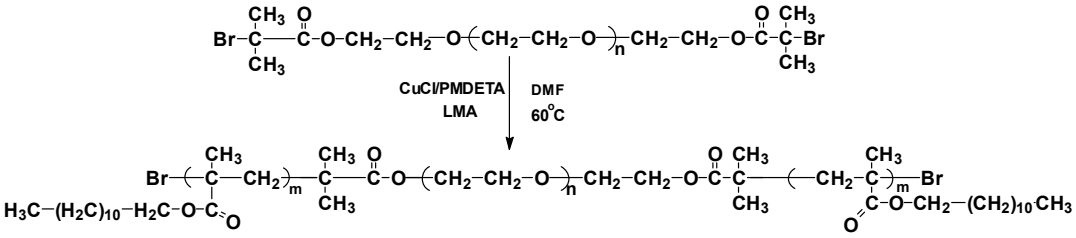
Figure 5.14: ^{1}H-NMR spectrum of Br-PEO-Br macroinitiator

5.4.3.2 Synthesis of PLMA-*b*-PEO-*b*-PLMA copolymer

Synthesis of symmetric linear ABA triblock copolymers by living radical polymerization could be achieved either by the use of difunctional macroinitiator or by

ethod. Kops et al[12] reported synthesis of amphiphilic PS-*b*-PEO-*b*-PS by ATRP using PEO macroinitiator. Busse et al[32] utilized difunctional macroinitiator for synthesis of triblock copolymer, poly(perfluorohexylethyl methacrylate)-b-PEO-b-Poly(perfluorohexylethyl methacrylate) in the presence of CuBr/PMDETA. Using this approach, various triblock copolymers with PEO as the middle block and (meth)acrylate or styrene as outer blocks have been synthesized which are otherwise difficult to synthesize by classical anionic polymerization method.[12,33-35]

PLMA-*b*-PEO-*b*-PLMA triblock copolymer was synthesized **(Scheme 5.5)** by ATRP of LMA with Br-PEO-Br macroinitiator at 60°C in presence of CuCl /PMDETA as catalyst (halide exchange technique) in DMF as solvent.[36]



Scheme 5.5: Synthesis of PLMA-*b*-PEO-*b*-PLMA copolymer

Table 5.8 gives reaction conditions and results of synthesis of PLMA-*b*-PEO-*b*-PLMA copolymer. The triblock copolymer was purified by dissolving in dichloromethane and precipitation into excess methanol at room temperature. The purified copolymer was dried *in vacuo* at room temperature and the conversion was determined gravimetrically.

GPC trace of triblock copolymer is shown in **Figure 5.15**. PLMA-*b*-PEO-*b*-PLMA copolymer was obtained with narrow MWD (M_w/M_n ï 1.26).

Table 5.8: Reaction conditions and results of synthesis of PLMA-*b*-PEO-*b*-PLMA copolymer

Run	[a][LMA]:[I] :[CuCl]:[PMDETA]	Time (h)	[b]Conv. (%)	[c]M_n^{th}	M_n^{NMR}	[d]GPC	
						M_n	M_w/M_n
1	[205]:[1]:[2]:[2]	2.5	90	59510	60640	40400	1.26

a - [I] = (Br-PEO-Br macroinitiator, M_n^{NMR}- 12650, M_w/M_n ï 1.04),b - gravimetry, c - $[LMA]_o/[I]_o$ x 254 x conversion/100 + M_n (Br-PEO-Br), d - PS calibration

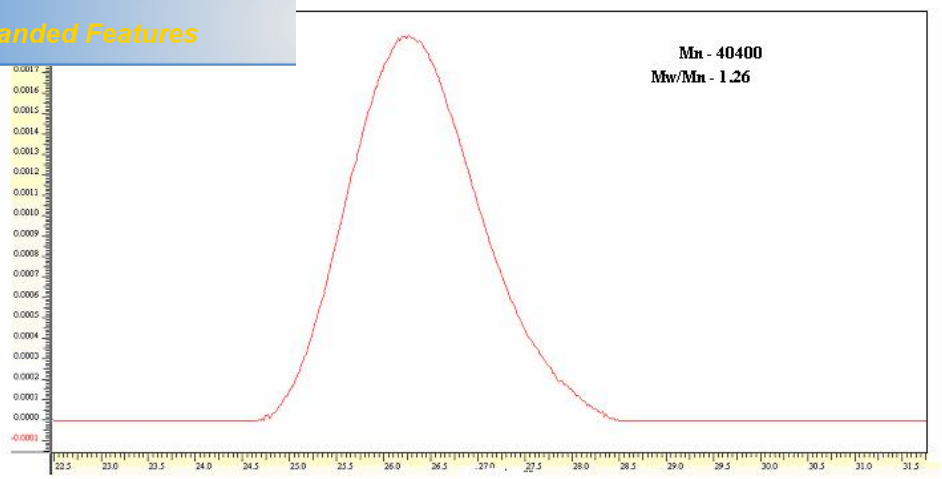


Figure 5.15: GPC trace of PLMA-*b*-PEO-*b*-PLMA copolymer (Run 1, Table 5.8)

5.4.3.3 Structural characterization of PLMA-*b*-PEO-*b*-PLMA triblock copolymer

The structure of PLMA-*b*-PEO-*b*-PLMA copolymer was confirmed by FTIR and ^{1}H-NMR spectroscopy.

Figure 5.16 shows FTIR spectrum of PLMA-*b*-PEO-*b*-PLMA copolymer. The band at 1720 cm^{-1} arises due to stretching vibration of ester carbonyl group of PLMA segments and the band corresponding to ether group of the PEO block appeared at 1115 cm^{-1}.

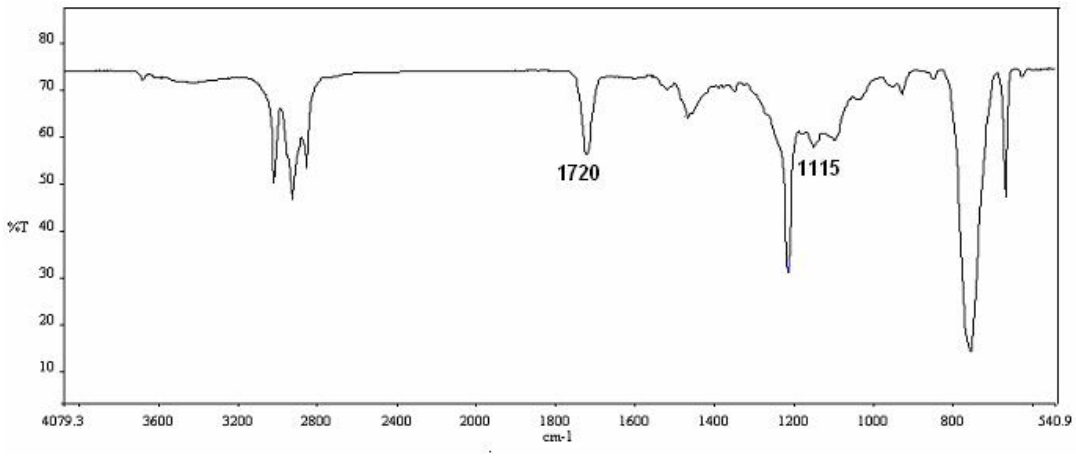


Figure 5.16: FTIR spectrum of PLMA-*b*-PEO-*b*-PLMA copolymer

^{1}H-NMR spectrum of PLMA-*b*-PEO-*b*-PLMA copolymer along with assignments is shown in **Figure 5.17**. The singlet observed at 3.65 ŭ ppm corresponds to oxyethylene protons (Hf) of PEO segment. The signal for protons from PLMA segment appeared at

esponding to methyl protons (Ha), methylene protons (Hb) and methylene protons (Hc) attached to ester group (COO-C**H**$_2$-), respectively.

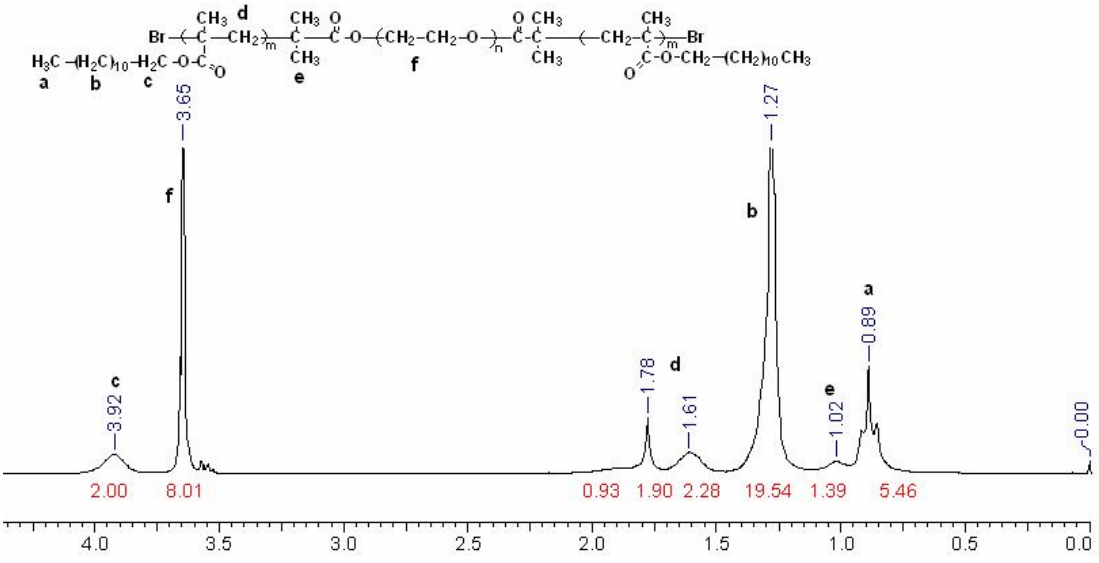


Figure 5.17: ^{1}H-NMR spectrum of PLMA-*b*-PEO-*b*-PLMA copolymer in $CDCl_3$

5.4.4 Synthesis of AB_2 mikto arm star copolymers by ROP

The special topology of mikto arm star copolymers and chemical incompatibility of the arms leads to special behavior which is unobtainable from their linear counterparts.[37] They have the potential to create new nanostructures through phase separation or supramolecular assembly in bulk and in solution, exhibiting possible applications such as multifunctional sensors, multiselective catalysts for sequential or simultaneous chemical reactions, multicomponent drug carriers, etc[38-42]

Mikto functional initiators are used to grow chains from a central core resulting in macromolecules with well-defined structures in terms of both the number and length of the arms. For example, Deng et al[43] used modified dimethylolpropanoic acid as a mikto functional initiator for the synthesis of ABC type mikto star copolymer. The use of 2-hydroxyethyl 3-[(2-bromopropanoyl)oxy]-2-{[(2-bromopropanoyl)oxy]methyl}-2-methyl-propanoate as mikto functional initiator for synthesis of AB_2 mikto star copolymer was reported by Erdogan et al.[44]

5.4.4.1 Synthesis of PMMA-*b*-$(PCL)_2$ mikto arm star copolymers

A novel mikto functional initiator was used for synthesis of AB_2 mikto arm star copolymer **(Figure 5.18)**.

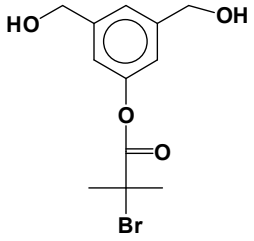
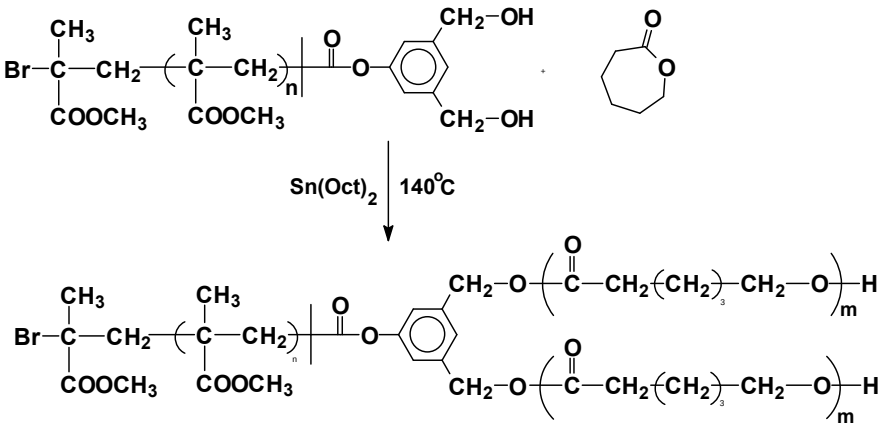


Figure 5.18: Structure of 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate

AB_2 type PMMA-*b*-$(PCL)_2$ mikto arm star copolymer was synthesized sequentially. In the first step, bismethylol-teminated PMMA was synthesized by ATRP using 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate as the initiator. **(Chapter 4)**.

In the second step, ROP of CL using a bismethylol-teminated PMMA as macroinitiator was carried out in the presence of stannous octanoate as catalyst in bulk at 140°C **(Scheme 5.6)**.



Scheme 5.6: Synthesis of mikto arm star copolymer PMMA-*b*-$(PCL)_2$

Table 5.9 shows reaction conditions and results of synthesis of PMMA-*b*-$(PCL)_2$ copolymer. The conversions of ε-CL were determined by gravimetry. The number-average molecular weights determined by ^{1}H-NMR spectroscopy (Mn^{NMR}) agreed reasonably well with theoretical molecular weights. Although the polymerizations were successful, the control in MWD was compromised as evidenced by broad distribution (M_w/M_n = 1.39 to 1.42). GPC traces of PMMA macroinitiator and PMMA-*b*-$(PCL)_2$ copolymer are shown in **Figure 5.19.**

ns and results of synthesis of PMMA-*b*-(PCL)$_2$ mikto arm star copolymers

Run	[M]/[Mac]	Time (h)	[a]Conv (%)	[b]M_n^{th}	M_n^{nmr}	[c]GPC *total*		
						M_n	M_w	M_w/M_n
1	3010	12	89	309220	345430	18950	26900	1.42
2	1508	5	90	158590	132970	19440	27430	1.41
3	94	8	76	12760	16360	12800	17280	1.39

Catalyst: stannous octanoate - 0.085 mol %, [M] = ε-caprolactone, [Mac] = (bismethylol-terminated PMMA, M_n^{nmr} ï 4300, M_w/M_n- 1.18), a ï gravimetry, b- M_n^{th} = $[M]_o/[I]_o$ x 114 x conversion/100 + M_n^{nmr} of PMMA, c- PS calibration

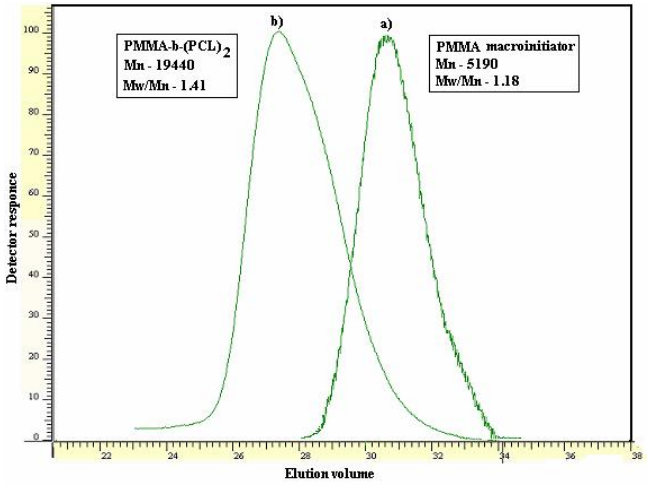


Figure 5.19: GPC traces of a) PMMA macroinitiator and b) PMMA-*b*-(PCL)$_2$ mikto arm star copolymer (run-2, Table 5.9)

5.4.4.2 Structural characterization of PMMA-*b*-(PCL)$_2$ mikto arm star copolymers

The structure of PMMA-*b*-(PCL)$_2$ mikto arm star copolymer was confirmed by FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of mikto arm star copolymer is shown in **Figure 5.20**. Ester carbonyl group stretching band from PCL as well as PMMA appeared together at 1728 cm^{-1}. The band observed at 3433 cm^{-1} was attributed to the hydroxyl group at the chain end PCL block.

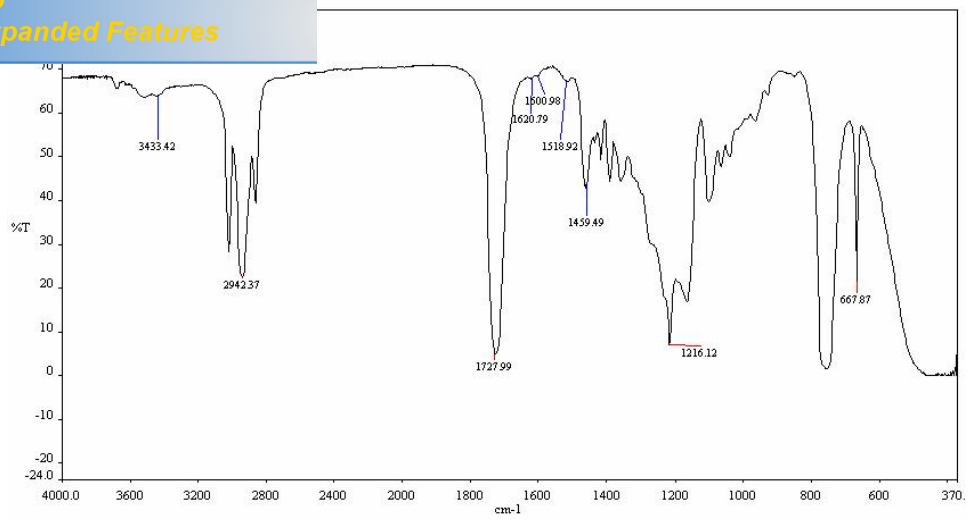


Figure 5.20: FTIR spectrum of PMMA-*b*-(PCL)$_2$ mikto star copolymer

Figure 5.21 shows ^{1}H-NMR spectrum of mikto arm star copolymer PMMA-*b*-(PCL)$_2$ along with assignments. The signals from aromatic protons (Hc) and (Hd) of core appeared at 7.0 and 7.20 ŭ ppm, respectively. PMMA segment showed a characteristic signal for the methoxy (CO-OC**H$_3$**) group protons (Ha) at 3.60 ŭ ppm. The two peaks for methyl protons (Hb) of PMMA backbone appeared at 1.02 and 0.84 ŭ ppm. The triplet at 2.31 ŭ ppm was ascribed to methylene protons (Hf) attached to ester group (OCOC**H$_2$**) and and the triplet at 4.06 ŭ ppm was due to methylene protons (Hh) (-C**H$_2$**OCO-) from PCL segments. The peak at 3.65 ŭ ppm (Hhô) corresponds to methylene protons (C**H$_2$**OH) attached to hydroxyl end group of PCL block. The peak at 4.60 ŭ ppm of dihydroxyl-terminated PMMA (Ph-C**H$_2$**OH, in the shaded region in **Figure 5.21**) shifted downfield to 5.10 ŭ ppm (He) after ROP of lactone (Ph-C**H$_2$**O-CO-).

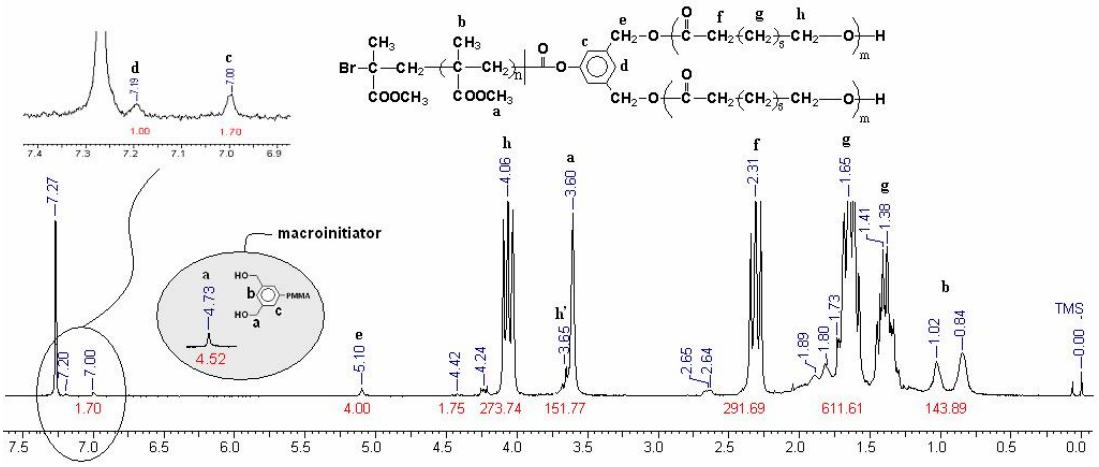


Figure 5.21: ^{1}H-NMR spectrum of PMMA-*b*-(PCL)$_2$ mikto arm star block copolymer

Thus, it was demonstrated that bismethylol-terminated PMMA could be successfully used as macroinitiator for ROP of ε-CL in the presence of stannous octanoate as catalyst for synthesis of PMMA-*b*-$(PCL)_2$ mikto arm star copolymers.

1) PEO-*b*-PLMA diblock copolymers were synthesized by ATRP using PEO macroinitiators of different chain length. The chain length of PLMA block was also varied. The experimental molecular weights (M_n^{NMR}) were slightly higher than theoretical molecular weights. The MWD of PEO-*b*-PLMA diblock copolymer was in range 1.17 to 1.36.
2) PS-*b*-PCL diblock copolymers were synthesized by stannous octanoate catalyzed ROP of ε-CL using hydroxyl-terminated polystyrene as macroinitiator. The experimental molecular weights (M_n^{NMR}) agreed well with theoretical molecular weights and MWD of PS-*b*-PCL was in the range 1.26 to 1.44.
3) PLMA-*b*-PEO-*b*-PLMA tiblock copolymer was synthesized by ATRP of LMA using difunctional Br-PEO-Br macroinitiator in the presence of CuCl/PMDETA as catalyst. Difunctional Br-PEO-Br macroinitiator was derived from commercially available polyethylene glycol of M_n ï 20000. The experimental molecular weight of PLMA-*b*-PEO-*b*-PLMA (M_n^{NMR}) agreed well with theoretical molecular weight and MWD was narrow (M_w/M_n -1.26).
4) A new mikto arm star PMMA-*b*-$(PCL)_2$ copolymer was synthesized using bismethylol-terminated PMMA as macroinitiator for ROP of ε-CL in the presence of stannous octanoate as catalyst. The experimental molecular weights (M_n^{NMR}) agreed well with theoretical molecular weights and MWD was in the range 1.39 to 1.42.

1. N. Hadjichristidis, S. Pispas and G. Floudas, ñ*Block Copolymers: Synthetic Strategies, Physical Properties and Applications*,ò John Wiley and Sons, New Jersey, **2003**
2. I. W. Hamley, ñ*The Physics of Diblock Copolymers,"* Oxford, New York, **1998**
3. I. W. Hamley, ñ*Developments in Block Copolymer Science and Technology*,ò John Wiley and Sons, England, **2004**
4. G. Riess, *Prog. Polym. Sci*. 28, 1107, **2003**
5. C. J. Brinker and Y. Lu, *Adv. Mater*. 11, 579, **1999**
6. C. J. Hawker, J. L. Hedrick, E.E. Malmstrom, M. Trollsas, D. Mecerreyes, G. Moineau, Ph. Dubois and R. Jerome, *Macromolecules*, 31, 213, **1998**
7. M. Shi, H. Zhang, J.Chen, X.Wan and Q. Zhou, *Polym. Bull.*, 52, 401, **2004**
8. J. Heuschen, R. Jerome and Ph. Teyssie, *Macromolecules*, 14, 242, **1981**
9. J. V. Koleske and R. D. Lundberg, *J. Polym. Sci. Part A: Polym. Chem.*, 7, 795, **1969**
10. D. D. Perrin and W. L. F. Armarego, ñ*Purification of Laboratory Chemicals"*, Pergamon Press, NewYork, **1989**
11. R. N. Keller and H. D. Wycoff, *Inorg. Synth*, 2, 1, **1946**
12. K. Jankova, X. Chen, J. Kops and W. Batsberg, *Macromolecules*, 31, 538, **1998**
13. I. Piirma, ñ*Polymeric Sufactants, Sufactant Science Series"*, M. Dekker, New York, **1992**
14. Laschewsky, *Adv. Polym. Sci.*, 1, **1995**
15. R.S. Velichkova and D.C. Chrstova, *Prog. Polym. Sci*., 20, 819, **1995**
16. K. J. Janakova, J. H. Truelsen, X. Chen, J. Kops, and W. Batsberg, *Polym. Bull.,* 42, 153, **1999**
17. R. Krishnan, K. S. V. Srinivasan, *Eur. Polym. J.*, 39, 205**, 2003**
18. R. Krishnan, ñ*Kinetics, Synthesis and Characterization of Homo and Block Copolymers by Atom Transfer Radical Polymerization*,ò Ph.D. Thesis, University of Madras, **2004**
19. B. Reining and H. Keul, H. Hocker, *Polymer*, 40, 3555, **1999**
20. B. Reining and H. Keul, H. Hocker, *Polymer*, 43, 3139, **2002**
21. T. Suzuki, Y. Murakami and Y. Takegami, *Polym. J.* (Tokyo), 12, 183, **1980**

ent Advances in Anionic Polymerizationò, Elsevier, New York, p.205, **1987**

23. H. L. Hsieh and R. P. Quirk, ñ*Anionic Polymerization: Principles and Practical Applications*,ò Marcel Dekker, Inc., New York, **1996**
24. X. Sun, H. Zhang, L. Zhang, X. Wang and Q. Zhou, *Polym. J*., 37, 102, **2005**
25. S. Mahajan, S. Renkar, P. F. W. Simon, J. S. Gutmann, A. Jain, S. M. Gruner, L. J. Fetters, G. W. Coates and U. Wiesner, *Macromol. Chem. Phys*., 204, 1047, **2003**
26. K. Matyjaszewski, J. Wang, T. Grimaud, and D. A. Shipp, *Macromolecules*, 31(5), 1527, **1998**
27. C. J. Hawker, J. L. Hedrick, E.E. Malmstrom, M. Trollsas, D. Mecerreyes, G. Moineau, Ph. Dubois and R. Jerome, *Macromolecules,* 31, 213, **1998**
28. B. As, A. R.A. Palmans, A. Heise and E. W. Meijer, *Polym. Prepr.*, 44, 615, **2003**
29. U. Meyer, A. R.A. Palmans, T. Loontjens and A. Heise, *Macromolecules*, 35, 2873, **2002**
30. C. J. Hawker, J. L.Hedrick, E.E. Malmstrom, M. Trollsas, D. Mecerreyes, G. Moineau, Ph. Dubois and R. Jerome, *Macromolecules*, 31, 213, 1998
31. M. Shi, H. Zhang, J. Chen, X.Wan and Q. Zhou, *Polym. Bull.*, 52, 401, **2004**
32. H. Hussain. K. Busse and J. Kressler, *Macromol, Chem. Phys*. 204, 936**, 2003**
33. R. Krishnan and K.S.V. Srinivasan, *J. Appl. Polym. Sci*. 97, 989, **2005**
34. M. Bednarek, T. Biedron and P. Kubisa, *Macromol. Rapid. Commun*.20, 59,**1999**
35. B. Reining, H. Keul, and H. Hocker, *Polymer*, 43, 3139, **2002**
36. G. Street, D. Illsley and S. J. Holder, *J. Polym. Sci. Part A, Polym.Chem.* 43, 1129, **2005**
37. N. Hadjichristidis, H. Iatrou, M. Pitsikalis and S. Pispas, A. Avgeropoulos, *Prog. Polym. Sci*., 30, 725, **2005**
38. Z. Li, E. Kesselman, Y. Talmon, M. A. Hillmyer and T. P. Lodge, *Science*, 306, 98, **2004**
39. N. Hadjichristidis, *J. Polym. Sci. Part A: Polym. Chem.*, 37, 857, **1999**
40. K. Ishizu and S. Uchida, *Prog Polym Sci*, 24, 1439, **1999**
41. N. Hadjichristidis, M. Pitsikalis, S. Pispas and H. Iatrou, *Chem Rev*, 101, 3747, **2001**
42. Li. Z. Kesselman, E. Talmon, Y. M. A. Hillmyer and T. P. Lodge, *Science*, 306, 98, **2004**

Z. Xu, *Eur. Polym. J.*, 43, 1179, **2007**

44. T. Erdogan, Z. Ozyurek, G. Hizal and U. Tunca, *J. Polym. Sci: Part A, Polym. Chem.* 42, 2313, **2004**

Characterization of Graft Copolymers by Combination of Atom Transfer Radical Polymerization and Ring Opening Polymerization

6.1 Introduction

Graft copolymers consist of a main polymer chain (backbone) having one or more side polymer chains attached to it through covalent bonds (branches) **(Figure 6.1)**.[1] Graft copolymers represent valuable polymeric materials since molecular parameters such as backbone and branch polymer type, degree of polymerization of backbone and branches, graft density and distribution of the grafts can be varied producing thermoplastic elastomers and amphiphilic copolymers.[2] By selecting appropriate polymers for backbone and branches they find applications as hydrogels[2], stabilizers, surfactants,[3] surface-modifying agents, dispersants, emulsifiers and compatibilizers in polymers blends.[4]

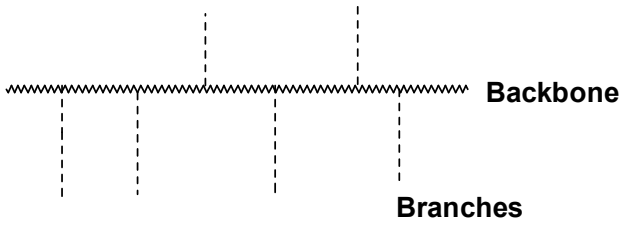


Figure 6.1: Architecture of graft copolymer

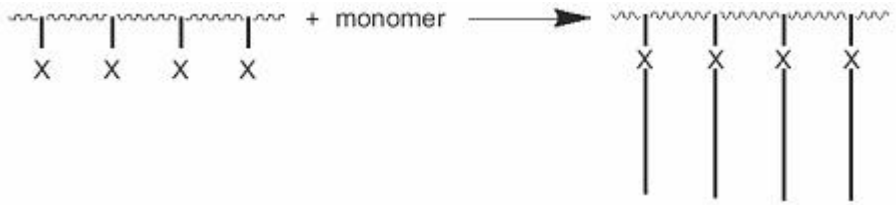
Interest in branched arrangements of hydrophilic and hydrophobic components arose with the discovery that the latter structures exhibit a quite different behavior from that observed for linear homologues: for instance, linear amphiphilic polymers tend to aggregate *via* intermolecular interaction and are known to form micelles of lesser stability than monomolecular micelles that could be obtained with certain branched homologues.[5,6] It is also well established that branched systems give better surface activity for applications such as the stabilization of dispersions because of their peculiar topology. [5,6]

General methods for synthesis of graft copolymer are, 1) ñgrafting ontoò 2) ñgrafting throughò, and 3) ñgrafting fromò. Grafting onto approach requires the presence of complimentary functionalities on the graft unit and the backbone. ñGrafting throughò approach utilizes macromonomers and their homo or copolymerization with another monomer

In the ñgrafting fromò technique, backbones containing reactive sites that are capable of initiating polymerization are synthesized and further polymerization of another monomer gives graft copolymer. Each method suffers from its own particular disadvantages, the major one being steric hindrance of the reactive center affecting the grafting efficiency. **Figure 6.2** illustrates the three approaches for synthesis of graft copolymers.

Grafting onto

Grafting from



Grafting through

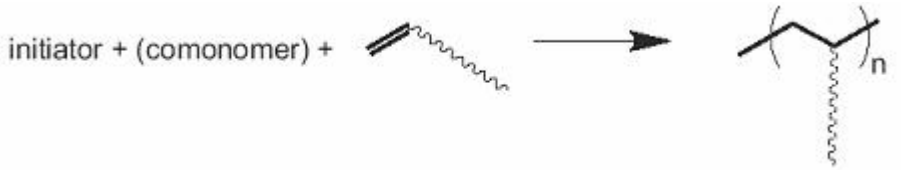


Figure 6.2: Synthetic approaches for graft copolymers

Recently dual living controlled polymerization processes have been established with ATRP, ring opening polymerization (ROP), nitroxide mediated polymerization (NMP) and reversible addition fragmentation chain transfer termination (RAFT) polymerization to obtain well-defined graft and block copolymers.[7,8-10a] Graft copolymers, prepared with a combination of radical polymerization and ROP, have already been used as surfactants for the synthesis of microspheres with controlled diameters and size distributions using dispersion polymerization.[10b] Careful control of the stabilizer properties has been shown to greatly affect steric stabilizing properties, and the optimum balance must be achieved for effective

ic copolymers are preferred because they are less sensitive to the ionic interactions and hence give more stable systems in the presence of salts.

The present chapter deals with synthesis and characterization of following three graft copolymers

1. Poly(lauryl methcrylate)-*graft*-poly(ethylene oxide) (PLMA-*g*-PEO) was synthesized *via* ñgrafting throughò approach using conventional free radical polymerization of PEO macromonomer with lauryl methacrylate.
2. Poly(ε-caprolactone)-*graft*-poly(methyl methacrylate) (PCL-*g*-PMMA) was synthesized *via* ñgrafting fromò approach. First PCL macroinitiator was synthesized using ROP of ε-CL and 4-[2-(7-Oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate and later ATRP of methyl methacrylate was carried out using PCL macroinitiator to obtain PCL-*g*-PMMA copolymer.
3. Poly(urethane)-*graft*-poly(lauryl methacrylate) (PU-*g*-PLMA) was synthesized *via* ñgrafting fromò approach. First PU macroinitiator was synthesized from commercially available diols viz., ethylene glycol, poly(prolylene glycol) and a newly synthesized diol namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate with 2,4-diisocyanate or isophorone diisocyanate and later ATRP of lauryl methacrylate was carried out to obtained PU-*g*-PLMA copolymer.

6.2 Experimental

6.2.1 Materials

Poly(ethylene glycol) mono methyl ether (PEO, M_n- 2000), poly(ethylene glycol) mono methyl ether methacrylate (PEOMA, M_n-1100), lauryl methacrylate (LMA), 2,4-toluene diisocyanate (TDI), isophorone diisocyanate (IPDI), copper bromide (CuBr), copper chloride (CuCl), azobisisobutyronitrile (AIBN), 2,2ô-bipyridine (By), N,N-dimethylamino pyridine (DMAP), N,N,Nô,Nô,Nò-penta methyldiethylenetriamine (PMDETA), 2-bromoisobutyryl bromide, ε-caprolactone (ε-CL) and stannous octanoate were purchased from Aldrich. Triethyl amine, toluene, methanol, dichloromethane, chloroform, tetrahydrofuran, potassium hydroxide, sodium hydrogen carbonate and sodium hydroxide were purchased from S. D. Fine Chem., India.

l ATRP initiator namely, 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate (OPCBMP) was synthesized as described in **Chapter 3**. Methacryloyl chloride was prepared according to the reported procedure.[12a]

6.2.2 Purification of reagents

ε-Caprolactone, methyl methacrylate and lauryl methacrylate were stirred over calcium hydride, vacuum distilled and stored under nitrogen.

Poly(ethylene glycol) mono methyl ether was dried by azeotropic distillation with toluene and dried under vacuum overnight.

Triethyl amine, cyclohexane, toluene, dichloromethane and tetrahydrofuron were dried and distilled according to reported procedure.[12b] 2,4-Toluene diisocyanate and isophorone diisocyanate were used as received.

Purification of CuBr/CuCl: Into a 100 mL round bottom flask equipped with a nitrogen inlet and a magnetic stirring bar were charged CuBr/CuCl (2.0 g) and glacial acetic acid (60 mL). The mixture was stirred for 12 h, filtered, washed with ethanol several times and dried at room temperature under vacuum for 24 h.[13]

6.2.3 Characterization

FTIR spectra of polymers were recorded on a Perkin-Elmer *Spectrum GX* spectrophotometer in chloroform.

NMR spectra were recorded on a Bruker 200 or 400 MHz spectrometer at resonance frequencies of 200 or 400 MHz for ^{1}H-NMR and 50 or 100 MHz for ^{13}C-NMR measurements using $CDCl_3$ as a solvent.

Molecular weight and molecular weight distribution of the polymers were determined using GPC (Thermo separation products) equipped with spectra series UV 100 and spectra system RI 150 detectors. Two 60 cm PSS SDV-gel columns (10^2 ï 10^5 A^o and 1 x 100 A^o) were used at 25^{o}C. The sample concentration was 2 to 3 mg /mL and the injection volume was 50 µL. HPLC grade tetrahydrofuran was used as eluent at room temperature with a flow rate of 1 mL / min. Polystyrene was used as the calibration standard.

6.3.1 Synthesis of PLMA-*g*-PEO copolymer

6.3.1.1 Preparation of mPEO methacrylate macromonomer (mPEOMA)

Into a 250 ml two-necked round bottom flask equipped with an addition funnel, a nitrogen inlet and a magnetic stirring bar were charged N, N-dimethylamino pyridine (0.22 g, 1.85 x 10^{-3} mol), triethyl amine (1.50 g, 0.015 mol), poly(ethylene gycol) methyl ether (Mn-5000, 10.0 g, 5 x 10^{-3} mol) and toluene (100 mL). The reaction mixture was cooled to 10^{o}C. Methacryloyl chloride (1.56 g, 0.015 mol) in dry toluene (25 mL) was added over a period of 30 minutes to the reaction mixture. Subsequently, the reaction mixture was allowed to attain room temperature and stirred overnight. Solvent was removed and the crude product obtained was dissolved in dichloromethane, washed with sodium bicarbonate solution (3 x 70 mL), brine (2 x 70 mL), water (2 x 70 mL), dried over anhydrous sodium sulphate and filtered. Dichloromethane was evaporated off to obtain mPEOMA macromonomer which was purified by repeated precipitation by dissolving in dichloromethane (10 mL) and pouring into excess hexane.

Yield: 9.0 g, (90 %)

6.3.1.2 Synthesis of PLMA-*g*-PEO copolymer by conventional free radical polymerization

Into a 50 ml two-necked round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged mPEOMA macromonomer (2.0 g, 9.60 x 10^{-4} mol), lauryl methacrylate (8.0 g, 0.031 mol), azobisisobutyronitrile (0.05 g, 3 x 10^{-4} mol) and toluene (100 mL). The reaction mixture was carefully degassed by bubbling nitrogen into the reaction mixture and heated at 70^{o}C under nitrogen atmosphere for 24 h. The reaction mixture was concentrated and precipitated into excess methanol. The obtained polymer was separated and purified by repeated precipitation by dissolving in dichloromethane (10 mL) and pouring into excess methanol. The polymer was dried under high vacuum for 24 h and weighed.

Yield: 8.50 g. (85 %)

MA copolymer by combination of ROP and ATRP

6.3.2.1 Synthesis of PCL macroinitiator (PCLM) by ROP

Into a 25 mL two-necked round bottom flask equipped with a magnetic stirring bar and a nitrogen inlet were charged stannous octanoate (0.015 g, 3.70 x 10^{-5} mol), ε-caprolactone (5.0 g, 0.043 mol) and 4-(2-(7-oxooxepan-3-yl) propan-2-yl) cyclohexyl 2-bromo-2-methyl propanoate (0.36 g, 8.90 x 10^{-4} mol). The reaction was carried out under nitrogen atmosphere at 140^{o}C for 8 h. The reaction mixture was cooled to room temperature, diluted with dichloromethane (30 mL) and precipitated into excess hexane. The polymer was dried under vacuum at room temperature for 24 h.

Yield- 4.66 g. (87 %)

6.3.2.2 Synthesis of PCL-*g*-PMMA copolymer

Into a 50 ml two-necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adapter were charged PCL macroinitiator (0.52 g, 9 x 10^{-5}, Mn^{GPC}- 5760), methyl methacrylate (1.80 g, 0.018 mol) and N,N,N',N',N''-pentamethyldiethylenetriamine (0.043 g, 2.52 x 10^{-4} mol). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. Copper chloride (0.025 g, 2.52 x 10^{-4} mol) was added under a stream of nitrogen and the flask was sealed with a stopper. The reaction mixture was degassed and then heated at 60^{o}C under nitrogen for 7 h and subsequently quenched by cooling the mixture in liquid nitrogen bath. The reaction mixture was diluted with tetrahydrofuran (50 mL) and solution was passed through neutral alumina column to remove copper. The solution was concentrated and poured into excess hexane to precipitate out the polymer. The polymer was dried under high vacuum for 24 h and weighed.

Yield- 1.0 g. (43 %)

6.3.3 Synthesis of PU-*g*-PLMA copolymer

6.3.3.1 Synthesis of PU macroinitiator based on ethylene glycol, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate and isophorone diisocyanate (PUM_1)

Into a 50 mL two-necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a reflux condenser were charged dibutyl tin dilaurate (0.07 g, 1.11 x 10^{-4}

.77 x 10^{-3} mol), 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate (0.5 g, 1.76 x 10^{-3} mol), isophorone diisocyanate (0.77g, 3.46 x 10^{-3} mol) and dry acetone (20 mL). The reaction was carried out under nitrogen atmosphere at 60^{o}C for 7 h. The crude product was purified by dissolution in acetone (10 mL) and precipitation into excess water/methanol mixture (50:50, v/v). The purification procedure was carried out three times. The polymer was separated and dried under vacuum at room temperature for 24 h.

Yield: 1.10 g. (80 %)

6.3.3.2 Synthesis of PU macroinitiator based on poly(propylene glycol), 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate and 2,4-toluene diisocyanate (PUM_2)

Into a 50 mL two-necked round bottom flask equipped with a magnetic stir bar, a nitrogen inlet and a reflux condenser were charged poly(propylene glycol) (6.0 g, 3 x 10^{-3} mol), 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate (1.06 g, 3.75 x 10^{-4} mol) and 2,4-toluene diisocyanate (1.12 g, 3.24 x10^{-3} mol). The reaction was carried out under nitrogen atmosphere at 60^{o}C for 60 h. The reaction mixture was diluted with acetone and methanol was added to quench the isocyanate. The crude product was dissolved in acetone (10 mL) and precipitated into excess methanol/water mixture (50:50, v/v). The polymer was separated and dried under vacuum at room temperature for 24 h.

Yield: 7.52 g. (92 %)

6.3.3.3 Synthesis of PU-*g*-PLMA copolymer

Into a 50 ml two-necked round bottom flask equipped with a magnetic stirring bar, a nitrogen inlet and a vacuum adaptor were charged PUM_2 macroinitiator (0.25 g), N,N,N',N',N''-pentamethyldiethylenetriamine (0.043 g, 2.5 x 10^{-4} mol), lauryl methacrylate (2.7 g, 0.01 mol) and acetone (3 mL). The reaction mixture was carefully degassed *via* three freeze-pump-thaw cycles to remove dissolved oxygen. Copper chloride (0.024, 2.5 x 10^{-4} mol) was added under a stream of nitrogen and flask was sealed with a stopper. The reaction mixture was again degassed and then heated at 60^{o}C under nitrogen for 4 h. Subsequently, the reaction mixture was quenched by cooling in liquid nitrogen bath. The mixture was diluted with tetrahydrofuran (30 mL) and solution was passed through neutral alumina column to remove catalyst. The solution was concentrated and precipitated into excess methanol. The

olved in dicholoromethane (10 mL) and precipitated into excess methanol. The polymer was dried under high vacuum for 24 h and weighed.

Yield: 1.40 g. (51 %)

6.4 Results and Discussion

6.4.1 Synthesis and characterization of PLMA-*g*-PEO copolymer

PLMA-*g*-PEO copolymer was designed to ensure an efficient stabilization process of polyurethane microspheres prepared by dispersion polymerization in organic media. PEO segment was chosen as an anchor moiety of the surfactant, while PLMA segment was chosen as stabilizing moiety due to its organophilicity.

6.4.1.1 Preparation and characterization of PEOMA macromonomer

Poly(ethylene glycol) methacrylate macromonomer (PEOMA) was prepared by reacting dried poly(ethylene glycol) mono methyl ether with methacryloyl chloride in the presence of triethyl amine as hydrogen chloride acceptor and N,N-dimethylamino pyridine.[14] The complete functionalization of hydroxyl end group of poly(ethylene glycol) mono methyl ether was achieved by taking an excess of methacryloyl chloride. The purification of poly(ethylene glycol) macromonomer was carried out by dissolving in dichloromethane and precipitating into excess hexane.

The characterization of PEOMA macromonomer was carried out by FTIR, ^{1}H and ^{13}C-NMR spectroscopy. **Table 6.1** shows characterization data of PEOMA macromonomer analyzed by ^{1}H-NMR spectroscopy and GPC.

Table 6.1: Characterization of PEOMA macromonomers

Macromonomer	[a]M_n PEO	[b]M_n PEOMA	[b]Degree of functionalization (%)	[c]M_w/M_n
$PEO_{24}MA$*	1100	1125	98	1.06
$PEO_{68}MA$*	2000	3060	99	1.07

* - $PEO_{24}MA$ and $PEO_{68}MA$ values obtained from ^{1}H-NMR spectroscopy, a- values commercially obtained, b = ^{1}H-NMR spectroscopy, c = GPC with PS calibration

spectrum of PEOMA macromonomer. The band at 1715 cm^{-1} appeared due the presence of ester carbonyl and double bond appeared at 1641 cm^{-1}.

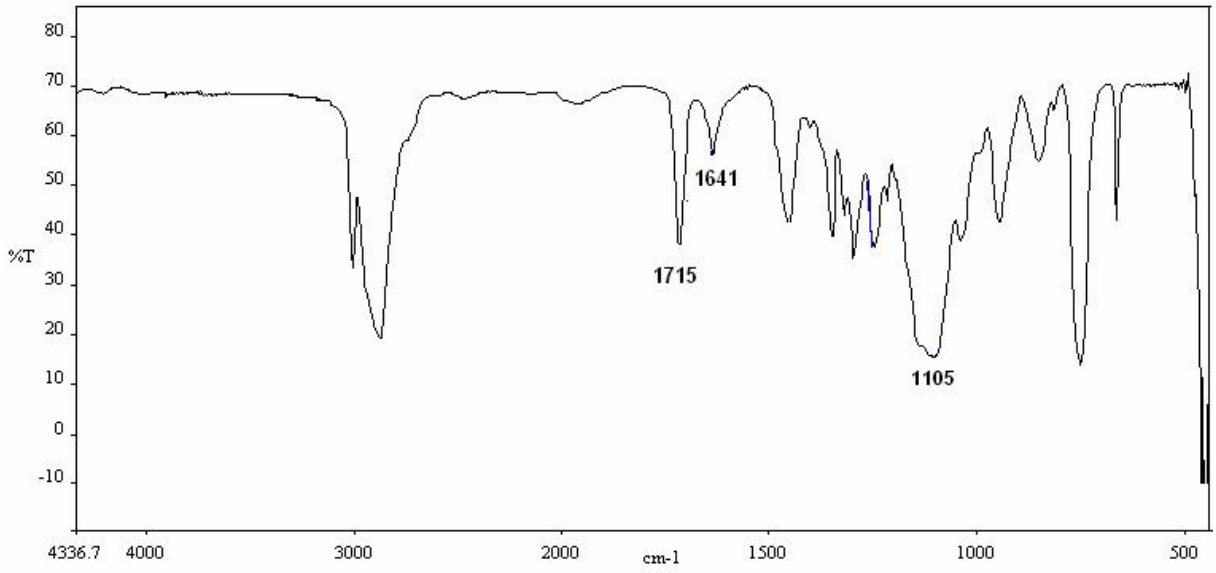


Figure 6.3: IR spectrum of PEOMA macromonomer

^{1}H-NMR spectrum of PEOMA macromonomer along with assignments is shown in **Figure 6.4**. The peaks at 3.65 and 3.38 δ ppm were assigned to oxyethylene protons (He) and methoxy (OC**H**$_3$) protons (Hf) of PEO. The peaks at 5.58 (Ha) and 6.14 δ ppm (Hb) correspond to the vinyl protons, while methyl protons (Hc) appeared at 1.95 δ ppm. The degree of functionalization of PEOMA macromonomers was calculated from ^{1}H-NMR spectroscopy by comparing the integration of methyl protons (Hc) from end group with methylene protons (He) of repeating unit of PEO and the values were found to be almost quantitative **(Table 6.1)**.

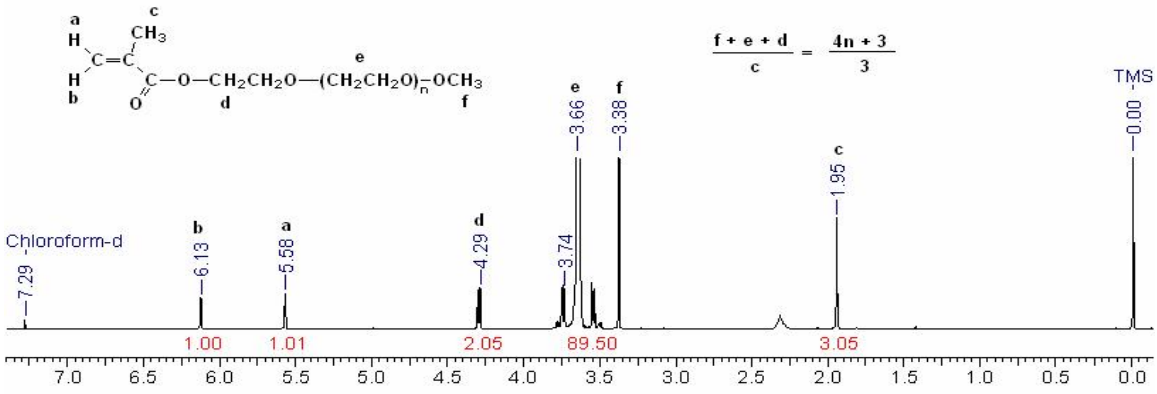
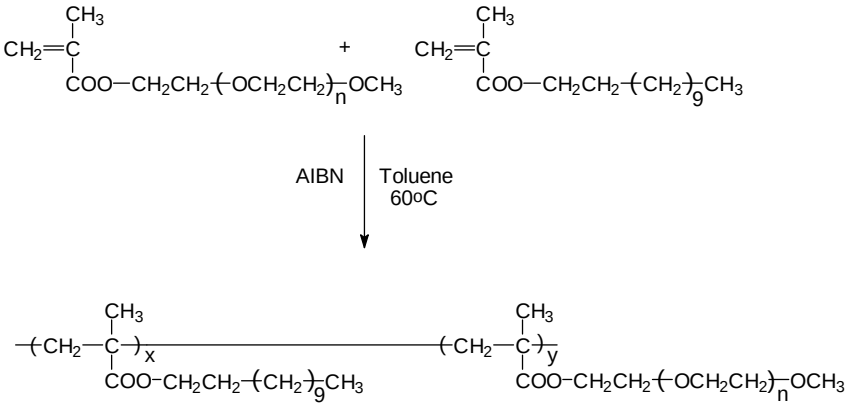


Figure 6.4: ^{1}H-NMR spectrum of PEOMA macromonomer in $CDCl_3$

g-PEO copolymer *via* conventional free radical polymerization

PLMA-*g*-PEO copolymers were synthesized by free radical solution copolymerization using the ñgrafting throughò approach. **Scheme 6.1** shows route for synthesis of PLMA-*g*-PEO copolymer *via* free radical polymerization. PEOMA macomonomer and lauryl methacrylate (LMA) were copolymerized using AIBN as initiator in toluene.[15]



Scheme 6.1: Synthesis of PLMA-*g*-PEO copolymer *via* conventional free radical polymerization

Table 6.2 presents reaction conditions and characterization data of PLMA-*g*-PEO copolymers. The broad MWD for graft copolymers GP1 and GP2 was ascribed to higher number of chain transfer reactions in conventional free radical polymerization used for the synthesis.[16,17]

and results of synthesis of PLMA-*g*-PEO copolymers by conventional free radical polymerization

Copolymer	[a]M_n PEOMA	PEO (mol %)		[b]GPC		
		Feed	[a]Experimental	M_n	M_w	M_w/M_n
GP1a	1125	5.42	1.55	68,300	2,32,000	2.90
GP1b	1125	5.42	2.20	94910	3,50,000	3.68
GP2a	3060	2.95	1.64	34170	96,560	2.82
GP2b	3060	2.95	1.50	45670	120350	2.63

AIBN - 0.05 g, 3 x 10^{-4} mol, toluene (50 %, w/v), reaction temp - 70^{o}C, reaction time - 24 h, a ï determined by ^{1}H-NMR spectroscopy, c ï PS calibration

Using $PEO_{24}MA$ macromonomer, graft copolymers (GP1a and GP1b) were obtained along with trace amount of gel indicating homopolymerization of PEOMA macromonomer with the degree of polymerization exceeding limit of gel formation.[18] In case of graft copolymerization using $PEO_{68}MA$ macromonomer no gel formation was observed.

In PLMA-g-PEO copolymer, PEO segment is hydrophilic and PLMA segment is hydrophobic. The purification of this type of graft copolymer is very difficult because there is very small difference in solubility between homopolymer of LMA and graft copolymer, in most of the solvents.[19] The graft copolymer rich in PLMA segment can be precipitated in methanol, as it is non-solvent of PLMA. The methanol soluble fraction may contain unreacted mPEO macromonomer, mPEOMA homopolymer and the methanol soluble graft copolymer.

6.4.1.3 Structural characterization of PLMA-*g*-PEO copolymer

The characterization of PLMA-*g*-PEO copolymer was carried out by FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of PLMA-*g*-PEO copolymer is shown in **Figure 6.5**. The bands at 1723 cm^{-1} and 1125 cm^{-1} correspond to ester carbonyl group of PLMA segment and ether bond of the PEO segment, respectively.

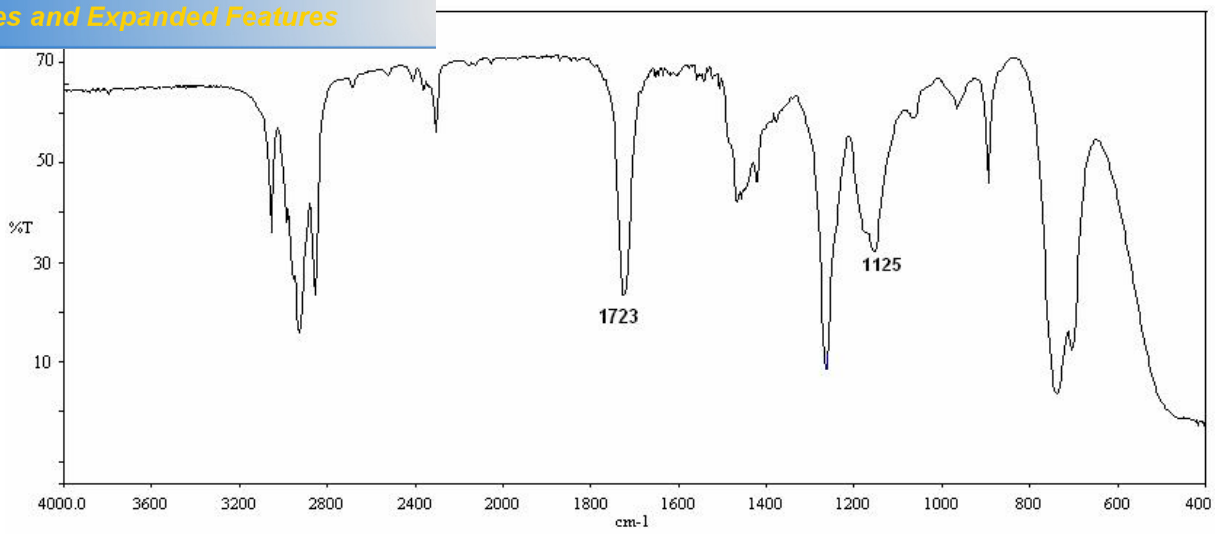


Figure 6.5: IR spectrum of PLMA-*g*-PEO copolymer

^{1}H-NMR spectrum of PLMA-*g*-PEO along with assignments is shown in **Figure 6.6**. The peaks at 0.89 and 1.27 δ ppm were assigned to methyl protons (He) and methylene protons (Hd) of PLMA segment. The peak at 3.92 δ ppm was ascribed to methylene protons (Hc) adjacent to ester group of PLMA segment. The oxyethylene protons (Hf) (OC**H**$_2$C**H**$_2$) of PEO appeared at 3.65 δ ppm and the singlet at 3.38 δ ppm was attributed to methoxy protons (Hg) from PEO segment. The molar ratio of PLMA/PEOMA in graft copolymer was calculated from relative integration of the peaks at 0.89 (He) and 3.38 δ ppm (Hg).

The PEO content of the copolymers were calculated from ^{1}H-NMR spectra and the values are given in **Table 6.2.** The values of experimentally determined PEO content were lower than feed which could be attributed to homopolymerization of PEOMA methacrylate macromonomer and / or presence of unreacted macromonomer.

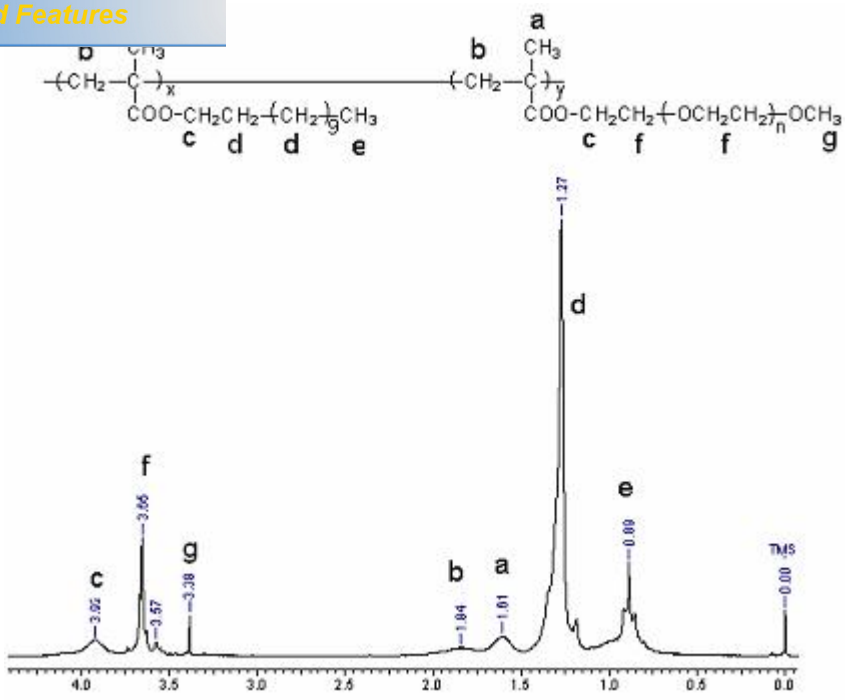


Figure 6.6: ^{1}H-NMR spectrum of PLMA-*g*-PEO graft copolymer in $CDCl_3$

6.4.2 Synthesis and characterization of PCL-*g*-PMMA by combination of ROP and ATRP

Copolymers containing PCL segments are interesting because they are miscible with a variety of polymers such as PVC, ABS, SAN and PC.[20] Another interesting characteristic of PCL is the ability of the ester linkage to undergo exchange reactions with other polyesters and polycarbonates.[21-23] PCL combined with other polymeric segments can be utilized as a compatibilizer in polymeric blends.

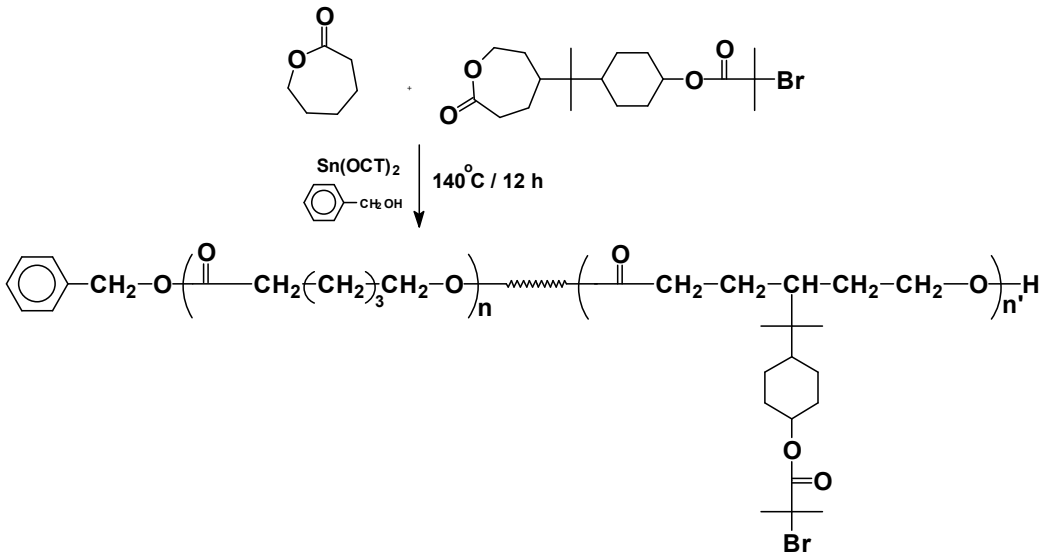
PCL-*g*-PMMA copolymer was synthesized by ñgrafting fromò approach in two steps.[7,8] In the first step, PCL macroinitiator was synthesized by ring opening copolymerization of ε-caprolactone and 4-(2-(7-oxooxepan-3-yl) propan-2-yl) cyclohexyl 2-bromo-2-methyl propanoate. In the second step, ATRP of MMA was carried out using PCL macroinitiator.

6.4.2.1 Synthesis of PCL macroinitiator *via* ROP

In ROP of lactones and lactides, tin complexes are generally used as catalyst. Amongst the tin complexes, tin(II) 2-ethyl hexanoate [Sn(Oct)2] is the most widely used catalyst due to

ciency, versatility, ease of solubility in common organic solvents and cyclic ester monomers.[25]

Scheme 6.2 depicts route for synthesis of PCL-*g*-PMMA by ñgrafting fromò approach. PCL macrointiator was obtained by ring opening copolymerization of ε-caprolactone and a new lactone containing ATRP initiator namely, 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate using benzyl alcohol as initiator in the presence of stannous octanoate as catalyst. ROP were carried out in bulk at 140°C for 12 h.



Scheme 6.2: Synthesis of PCL macroinitiator by ROP

It has already been demonstrated that 2-bromo isobutyric ester of lactone-functionalized ATRP initiator does not interfere with ROP reaction under the given conditions.[26-28] **Table 6.3** present reaction conditions and results of synthesis of PCL macroinitiators. The conversions were determined by gravimetry. The composition of PCL macroinitiator was determined by ^{1}H-NMR spectroscopy and found to be in reasonably good agreement with feed ratio. Molecular weight distribution of two PCL macroinitiators utilized in the present study was 1.15 and 1.47.

ns and results of synthesis of PCL macroinitiators synthesized by ROP

MI	[c]Yield. (%)	Composition (Mol %)				[e]GPC		
		Feed		[d]Measured				
		CL	OPCBMP	CL	OPCBMP	M_n	M_w	M_w/M_n
[a]PCLM-1	74	99	1	99.2	0.80	5760	6660	1.15
[b]PCLM-2	87	95	5	95.7	4.30	4240	6240	1.47

Catalyst conc. (Stannous octanoate) ï 1.28 x 10^{-4} mol, Initiator conc. (Benzyl alcohol) - 1.8 x 10^{-3} mol, reaction temperature 140^{o}C, Reaction time -12 h, a- [CL] ï 0.026 mol, b - [CL] ï 0.017 mol, c - gravimetry, d - ^{1}H-NMR spectroscopy, e - PS calibration,

6.4.2.2 Structural characterization of PCL macroinitiator

PCL macroinitiators were characterized by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

Figure 6.7 shows FTIR spectrum of PCL macroinitiator. The bands at 1723 cm^{-1} and 3440 cm^{-1} correspond to ester carbonyl and hydroxyl end group.

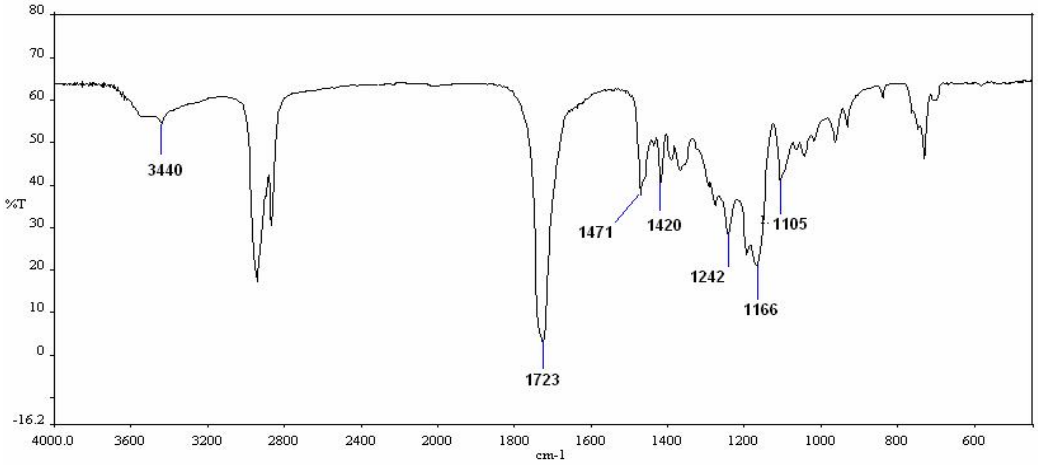


Figure 6.7: FTIR spectrum of PCL macroinitiator

^{1}H-NMR spectrum along with assignments of PCL macroinitiator is shown in **Figure 6.8**. The peaks at 7.35 and 5.12 δ ppm correspond to five aromatic protons (Ha) and two

from initiator fragment (benzyl alcohol), respectively.[29] The triplets observed at 4.06 ppm (Hd) and 2.31 δ ppm (Hc) corresspond to methylene protons from PCL segment. The peak appearing at 3.65 δ ppm (He) was attributed to methylene protons to which hydroxyl end group is attached. The peak due to methyl protons (Hg) appeared at 1.91 δ ppm and the peak at 0.78 δ ppm correspond to geminal dimethyl protons (Hf) of comonomer segment (OPCBMP). The peaks in the region 1.25 to 1.75 δ ppm were ascribed to methylene protons (cô) of PCL, methylene protons (cô) and protons from cyclohexane ring of comonomer segment (OPCBMP).

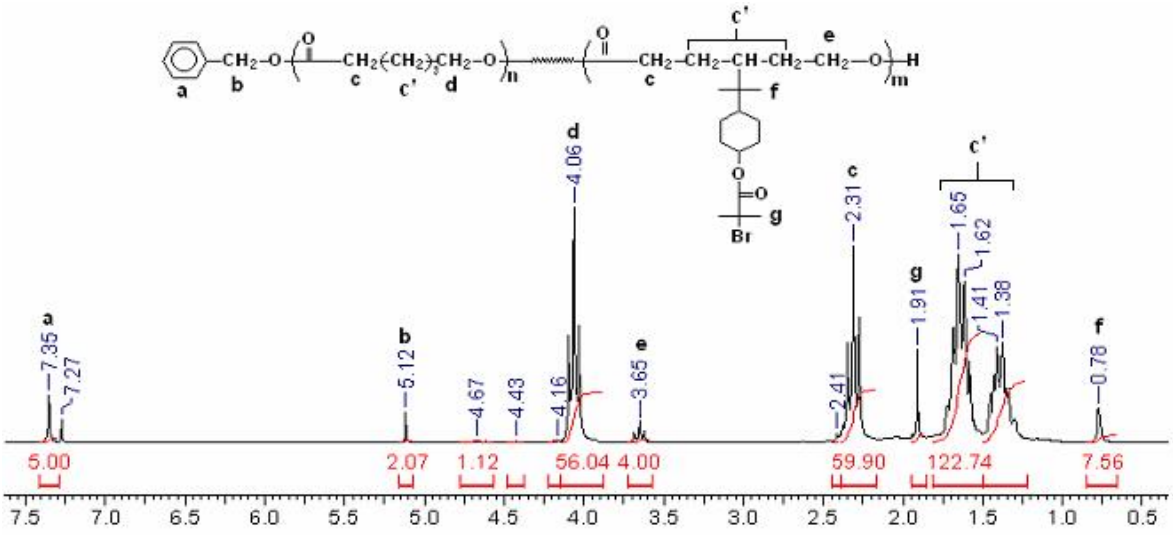


Figure 6.8: ^{1}H-NMR spectrum of PCLM-2 macroinitiator in $CDCl_3$

Figure 6.9 shows ^{13}C-NMR spectrum along with assignments of PCL macroinitiator. Aromatic carbons from initiator fragment (benzyl alcohol) C1, C2, C3 and C4 appeared at 128.34, 127.96 and 135.81 δ ppm, respectively. The peaks at 173.36 and 170.89 δ ppm were due to the ester carbonyl carbons (C6, C10) of PCL and comonomer segment carbons (C19) (OPCBMP), respectively. The peaks at 65.93 and 74.91 δ ppm confirmed the presence of benzylic carbon (C5) and secondary carbon (C18), respectively. The tertiary carbons (C16) attached to geminal dimethyl group and the quarternary carbon (C21) attached to bromine appeared at 38.02 and 56.14 δ ppm, respectively.

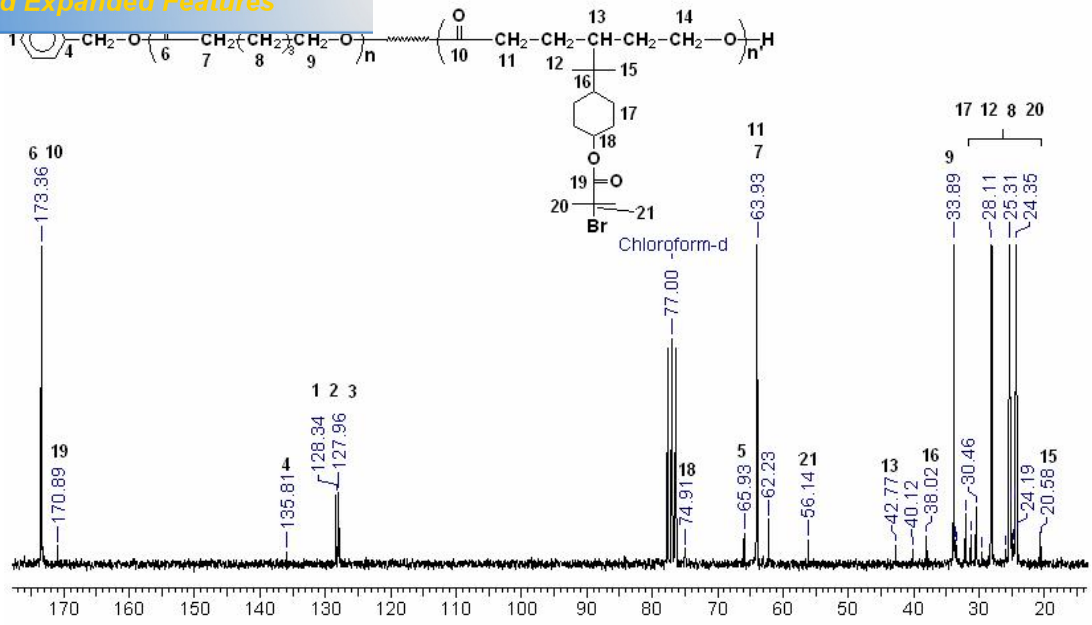
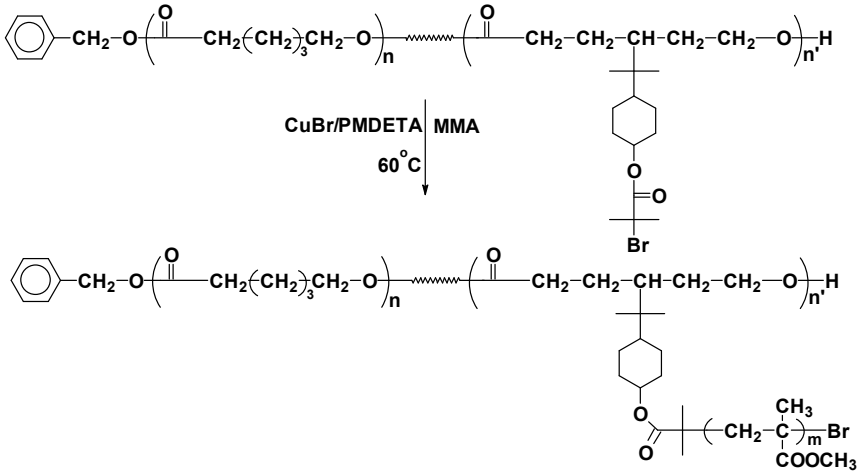


Figure 6.9: ^{13}C-NMR spectrum of PCLM-2 macroinitiator in $CDCl_3$

6.4.2.3 Synthesis and characterization of PCL-*g*-PMMA copolymer by ATRP

The reaction pathway for synthesis of PCL-*g*-PMMA is shown in **Scheme 6.3**. The ñgrafting fromò approach was utilized for synthesis of PCL-*g*-PMMA using PCLM as macrointiator.



Scheme 6.3: Synthesis of PCL-*g*-PMMA *via* "grafting from" approach

ATRP of MMA was carried out at 60°C in the presence of CuBr or CuCl as catalyst and PMDETA as ligand for 3 h.[29-34] **Table 6.4** shows reaction conditions and results for

ne monomer conversion was determined gravimetrically. **Figure 6.10** shows GPC traces of PCL macroinitiator (PCLM-2) and PCL-*g*-PMMA copolymer **(Run 3, Table 6.4)**.

Use of CuCl/PMDETA as catalyst (halide exchange technique) showed improvement in MWD (M_w/M_n ï 1.36) of PCL-g-PMMA copolymers compared with ATRP using CuBr/PMDETA as catalyst where graft copolymer exhibited relatively broader MWD (M_w/M_n ï 1.71).

When CuCl was used as a catalyst with bromine initiating group in PCL, the halogen exchange reaction occurred, leading to chlorine as initiating groups.[35] The shift of the atom transfer equilibrium to PCL-Cl originates in the differences in bond energies between the C-Cl and C-Br. The stronger C-Cl bond in the PCL leads to the lower concentration of the free radical propagating chains during ATRP than that with PCL-Br/CuBr initiated polymerization, resulting in lower polymerization rates.

Matyjaszewski et al had demonstrated that using CuCl complexed with simple linear amine ligands in conjunction with bromo-terminated macroinitiators leads to graft copolymers of narrow MWD with uniform graft chains.[36] Similar observation was made in the present work when halogen exchange technique was utilized for synthesis of PCL-*g*-PMMA copolymer, which gave a MWD of 1.36 **(Table 6.4)**. This is due to the fact that replacement of bromine atom by chlorine atom suppresses undesirable secondary reactions by decreasing the radical concentration, while the initiation remains fast compared to propagation.

s and results of synthesis of PCL-*g*-PMMA copolymer using PCLM macroinitiators

Run	[MMA]:[PCLM]:[CuX]:[PMDETA]	[a]Conversion. (%)	Composition by ^{1}H-NMR spectroscopy (mol %)		[b]GPC	
			PCL (feed)*	PMMA (feed)*	M_n	M_w/M_n
1	[c][775]:[1]:[1]:[1]	28	4.0 (5.5)	96 (94.5)	88640	1.71
2	[d][356]:[1]:[1]:[1]	17	14.0 (13.50)	86 (86.50)	44500	1.52
3	[e][200]:[1]:[1]:[1]	27	19.0 (22.40)	81.0 (77.60)	70800	1.36

catalyst conc. - 1 x 10^{-4} mol, reaction temperature - 60^{o}C, ( )* - values in parentheses represent feed values, a - gravimetry, b - PS calibration, c ï {[PCLM] = PCLM-2, [CuX] = CuBr}, d ï {[PCLM] = PCLM-1, [CuX] = CuBr}, e ï {[PCLM] = PCLM-1, [CuX] = CuCl}

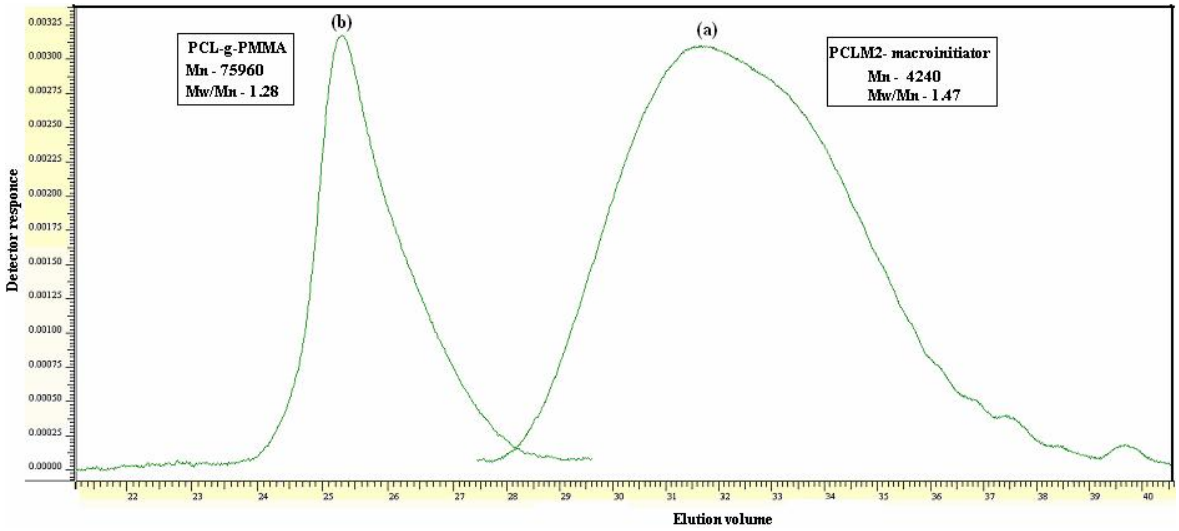


Figure 6.10: GPC traces of a) PCLM-2 macroinitiator and b) PCL-*g*-PMMA copolymer (Run 3, Table 6.5)

6.4.2.4 Structural characterization of PCL-*g*-PMMA copolymer

The structure of PCL-*g*-PMMA copolymer was confirmed by FTIR, ^{1}H and ^{13}C-NMR spectroscopy.

spectrum of PCL-g-PMMA copolymer. The peak at 1729 cm^{-1} corresponds to the ester carbonyl group of PCL and PMMA. The broad band at 3540 cm^{-1} was attributed to hydroxyl end group of PCL backbone.

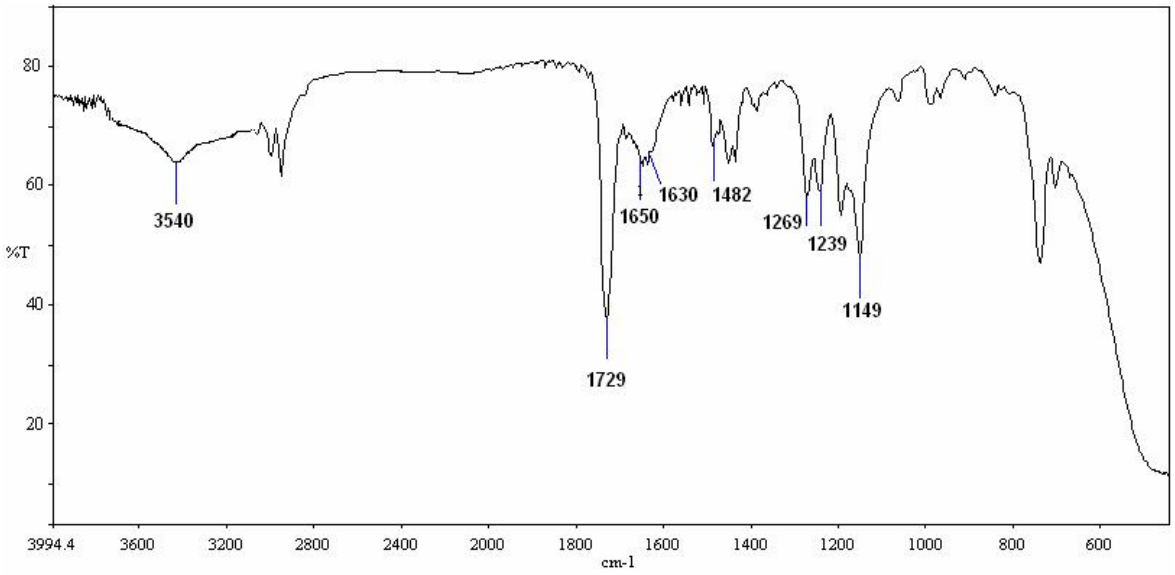


Figure 6.11: IR spectrum of PCL-*g*-PMMA copolymer

Figure 6.12 shows ^{1}H-NMR spectrum along with assignments of PCL-*g*-PMMA. The peaks at 7.35 and 5.11 δ ppm arise from five aromatic protons (Ha) of initiator fragment and benzylic methylene protons (Hb), respectively. The peaks from methylene protons (He) (-C**H**$_2$OCO-) and (Hc) (-COO-C**H**$_2$-) of PCL backbone appeared at 4.06 and 2.31 δ ppm, respectively. The peaks from PMMA branches appeared at 3.60 and at 1.02 and 0.84 δ ppm which correspond to OC**H**$_3$ protons (Hh) and methyl protons (Hg), respectively.

The composition of PCL-*g*-PMMA copolymers were determined from ^{1}H-NMR spectra by comparing the integral ratios of the peak at 4.06 δ ppm of PCL segment and the peak at 3.60 δ ppm of PMMA segment **(Table 6.4)**. The composition was found to be in reasonably good agreement with feed values.

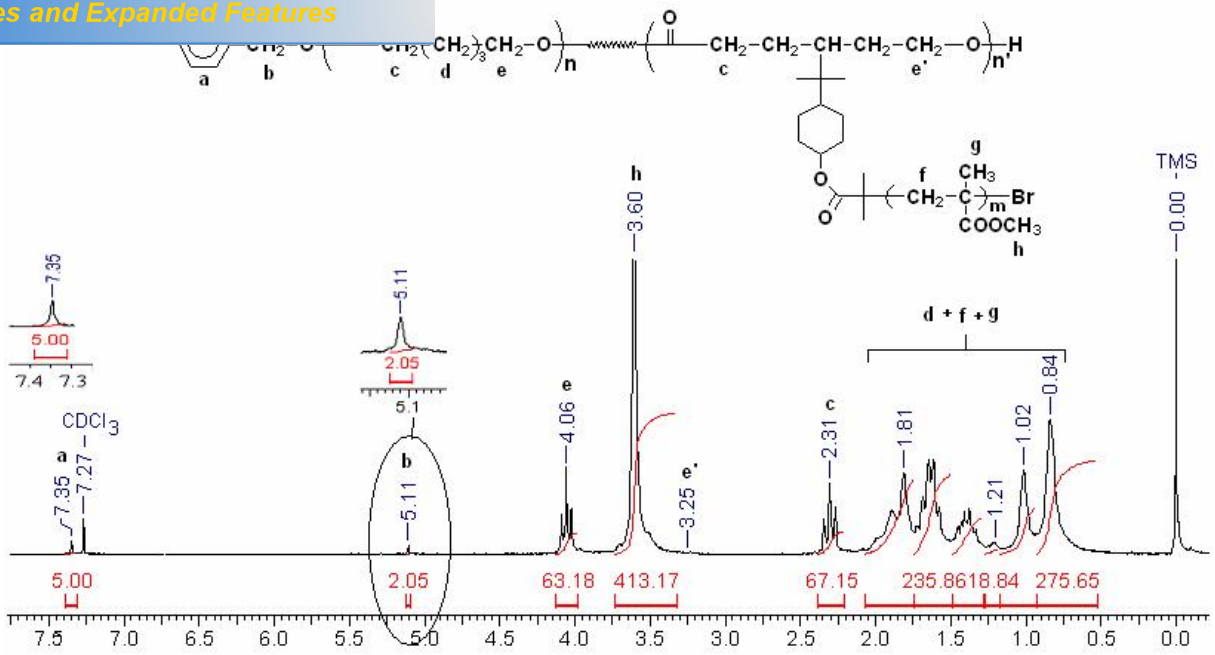


Figure 6.12: ^{1}H-NMR spectrum of PCL-*g*-PMMA copolymer in $CDCl_3$

6.4.3 Synthesis and characterization of PU-*g*-PLMA copolymer

Polyurethanes find wide applications in industries like automotive, footwear, cosmetics, biomedical, etc. due to the ease of synthesis and versatile properties.[37-39] The properties such as tensile strength and elongation at break are tailorable by adjustment of the chain length of the polyol segment, the crosslinking agent and the curative used. Branching of the main polyol chain introduces free volume in the cured network preventing close packing of the chains when temperature is lowered.[40] This helps in improving the low temperature flexibility and related mechanical performance. One method of introducing pendant chain in the main backbone is by grafting. Introduction of uniform size graft chains can be conveniently achieved by the well-known ñgrafting fromò approach. Papon et al[41] synthesized and studied adhesive properties of comb-like PU-*g*-PBA and demonstrated that these types of architecture have a special influence on the adhesive property.

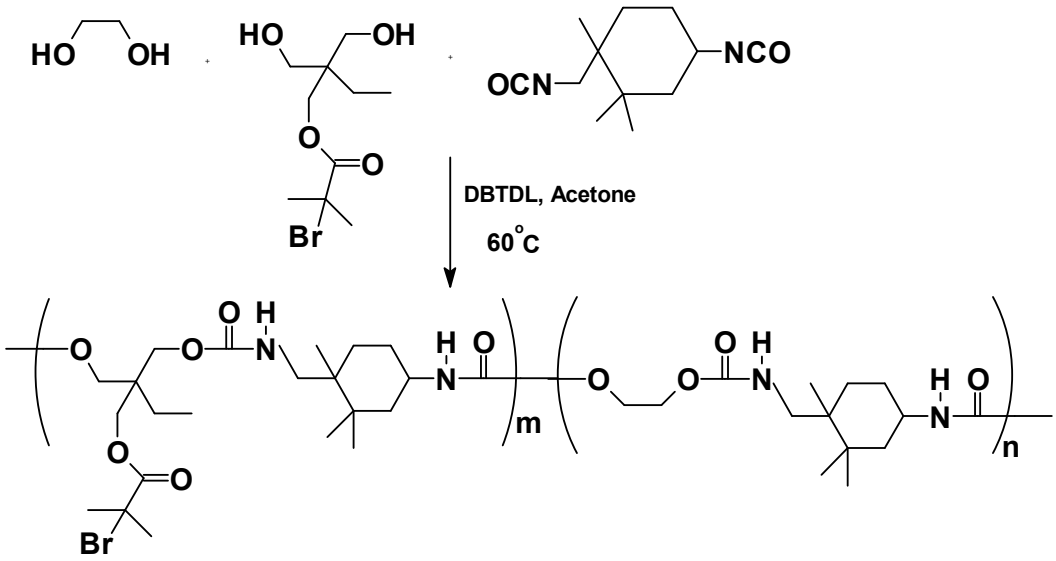
The synthesis of PU-*g*-PLMA copolymer was carried out in two steps. The first step involved the synthesis of PU macroinitiator containing pendent ATRP initiator sites while in the second step ATRP of lauryl methacrylate was carried out using PU macroinitiator to obtain PU-*g*-PLMA copolymer.

zation of PU macroinitiators

PU macroinitiators based on two commercially available diols namely, ethylene glycol, polypropylene glycol and a newly synthesized diol namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate were synthesized using isophorone diisocyanate / 2,4-toluene diisocyanate.

6.4.3.1.1 PU macroinitiator based on ethylene glycol, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate and isophorone diisocyanate (PUM_1)

Scheme 6.4 shows route for synthesis of PUM_1 macroinitiator. PUM_1 was synthesized by copolymerization of ethylene glycol and 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate with isophorone diisocyanate in presence of dibutyl tin dilaurate as catalyst.[37-40] The polymerization was carried out in acetone at 60°C for 7 h. A viscous polymer was obtained, which was purified by dissolving in acetone and precipitated into excess methanol/water mixture (75:25, v/v) repeatedly.



Scheme 6.4: Synthesis of PUM_1 macroinitiator

Table 6.5 shows reaction conditions and results for synthesis of PUM_1 macroinitiator. The composition of the copolymer was calculated by ^{1}H-NMR spectroscopy and 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate content was found to be 33 mol %.

and results of synthesis of PUM_1 macroinitiator

MI	[a]Yield (%)	Feed (mol %)		^{1}H-NMR (mol %)		[b]GPC		
		EG	BHMBMP	EG	BHMBMP	M_n	M_w	M_w/M_n
PUM_1	80	50	50	67	33	1030	1460	1.42

catalyst conc. (0.1 wt %) - [DBTDL], reaction temp - 60°C, reaction time - 7 h, a - gravimetry, b ï PS calibration

The structural characterization of PUM_1 was carried out using FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of PUM_1 is shown in **Figure 6.13**. The band observed at 1732 cm^{-1} is due to urethane carbonyl and ester carbonyl from 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate fragment, while the band at 3409 cm^{-1} corresponds to N-H group stretching vibration.

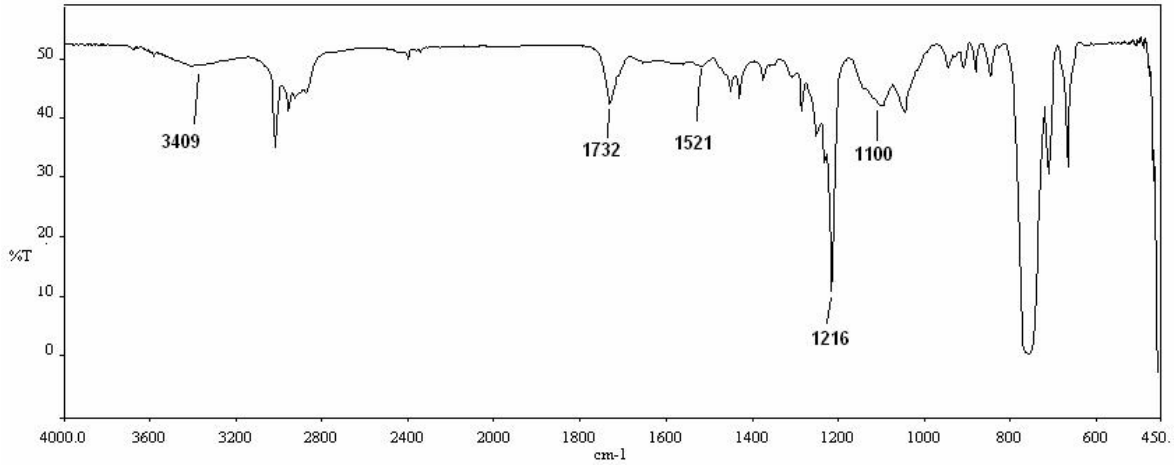


Figure 6.13: IR spectrum of PUM_1 macroinitiator

^{1}H-NMR spectrum of PUM_1 along with assignments is shown in **Figure 6.14**. The peaks for ethylene glycol unit appeared in the range 4.02 to 4.28 δ ppm. The presence of 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate unit in PU macroinitiators was confirmed from the peak at 1.94 δ ppm corresponding to dimethyl protons (Ha). The protons (Hg, Hf) from isophorone unit appeared in the range from 0.93 to 1.75 δ ppm. Three protons

s of methylene group from 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propionate appeared in the range 0.80 to 1.07 δ ppm.

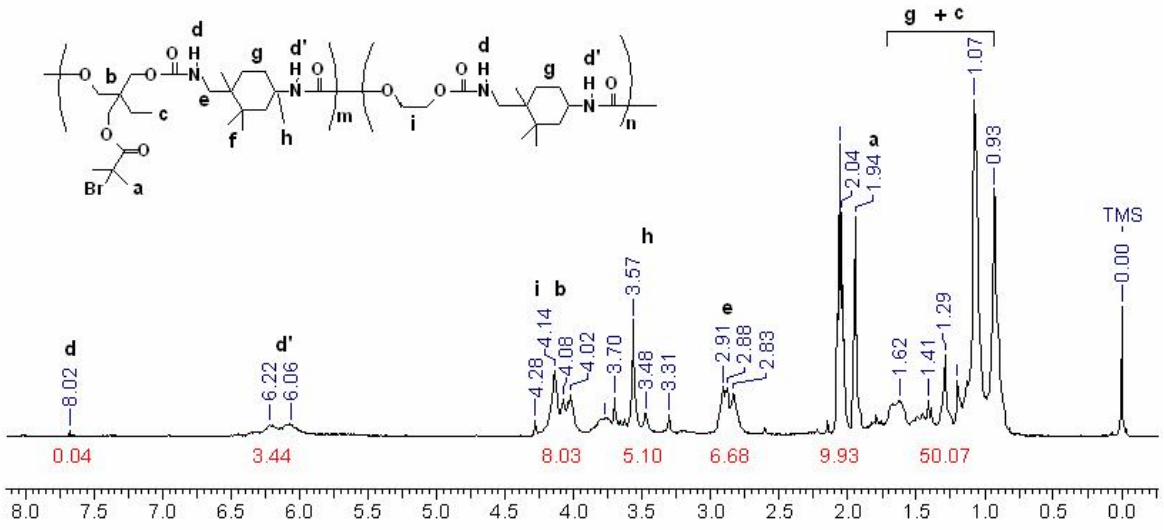
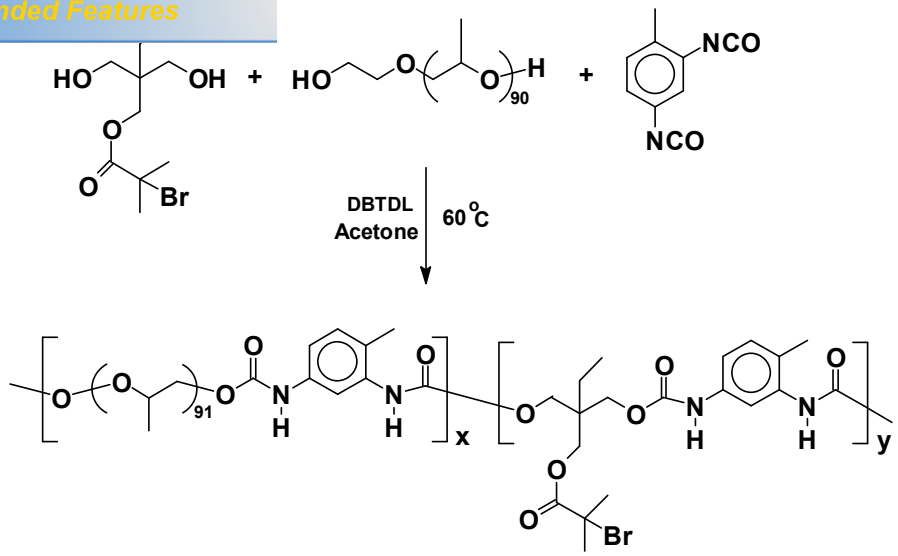


Figure 6.14: ^{1}H-NMR spectrum of PUM_1 macroinitiator in acetone-d_6

6.4.3.1.2 PU macroinitiator based on poly(propylene glycol), 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate and 2,4-toluene diisocyanate (PUM_2)

Scheme 6.5 depicts synthesis of PU macroinitiator based on poly(propylene glycol). PUM_2 was synthesized by copolymerization of poly(propylene glycol) and 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate with 2,4-toluene diisocyanate at 60^{o}C.[37-40] The polymer was purified by dissolving in acetone and precipitated into excess methanol/water mixture (50:50, v/v).



Scheme 6.5: Synthesis of PUM_2 macroinitiator

Table 6.6 shows reaction conditions and results of synthesis of PUM_2 macroinitiator. The composition of copolymer was calculated by ^{1}H-NMR spectroscopy. 2,2-Bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate content was found to be 2.30 mol % in PUM_2 macroinitiator.

Table 6.6: Reaction conditions and results of synthesis of PUM_2 macroinitiator

MI	[a]Yield (%)	Feed (mol %)		^{1}H-NMR (mol %)		[b]GPC		
		PPG	BHMBMP	PPG	BHMBMP	M_n	M_w	M_w/M_n
PUM_2	92	90	10	97.70	2.30	7630	13300	1.75

catalyst conc. [DBTDL] - (0.1 wt %), reaction temp - 60^{o}C, reaction time - 60 h, a-gravimetry, b - PS calibration

The structural characterization of PUM_3 macroinitiator was carried out by FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

FTIR spectrum of PUM_2 macroinitiator is presented in **Figure 6.15**. The band at 1719 cm^{-1} corresponds carbonyl group from urethane and bromoester of BHMBMP segment in the PUM_3 macroinitiator. The band observed at 1598 cm^{-1} was assigned to stretching

The band corresponding to NH stretching of urethane group appeared at 3439 cm^{-1}. The band appearing at 1105 cm^{-1} was ascribed to ether group of PPG segments.

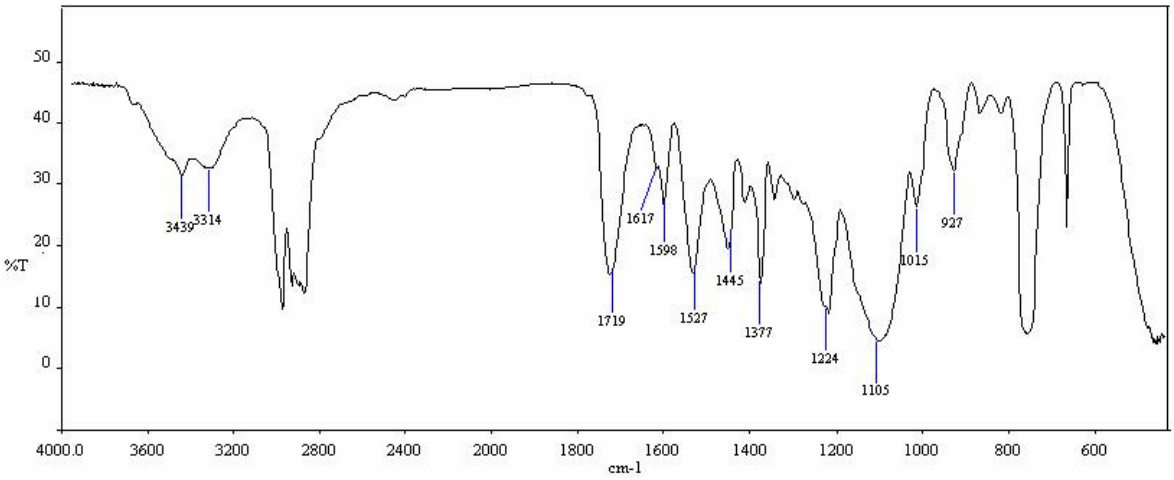


Figure 6.15: IR spectrum of PUM_2 macroinitiator

Figure 6.16 shows ^{1}H-NMR spectrum of the PUM_2 macroinitiator along with the assignments. The peaks for aromatic protons appeared at 7.78, 7.06 and 6.53 δ ppm protons (Hd), (He) and (Hf), respectively and the peak for methyl protons (Hg) on aromatic ring appeared at 2.19 δ ppm. The peaks for poly(propylene glycol) segement appeared at 1.14 (Ha) and in the range 3.25 to 3.75 δ ppm (Hb and Hc). The peaks at 4.20 (Hh), 3.92 (Hh'), 1.94 (Hi) and 0.79 δ ppm (Hj) were attributed to BHMBMP segment.

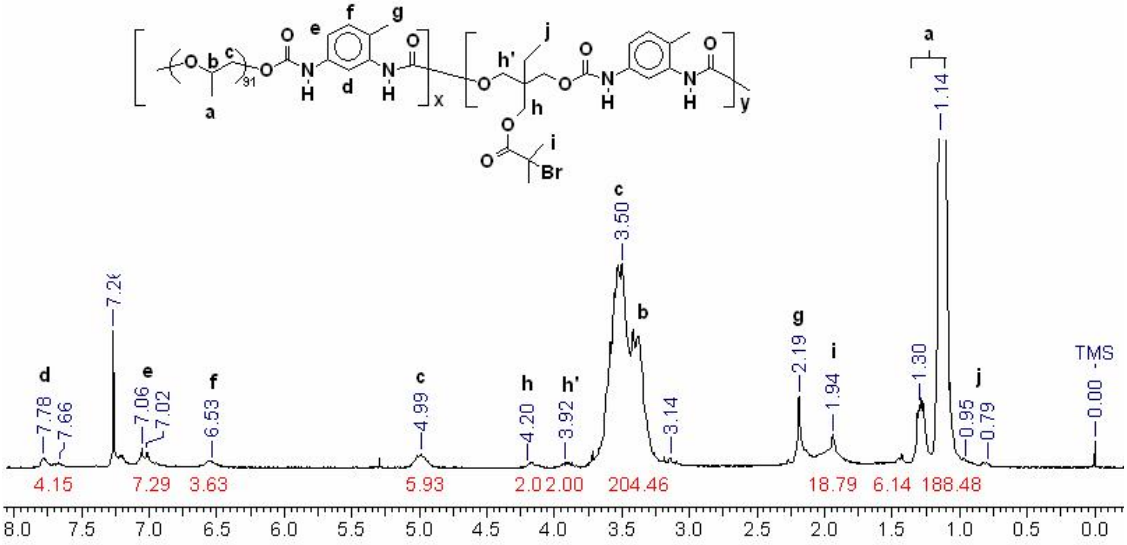


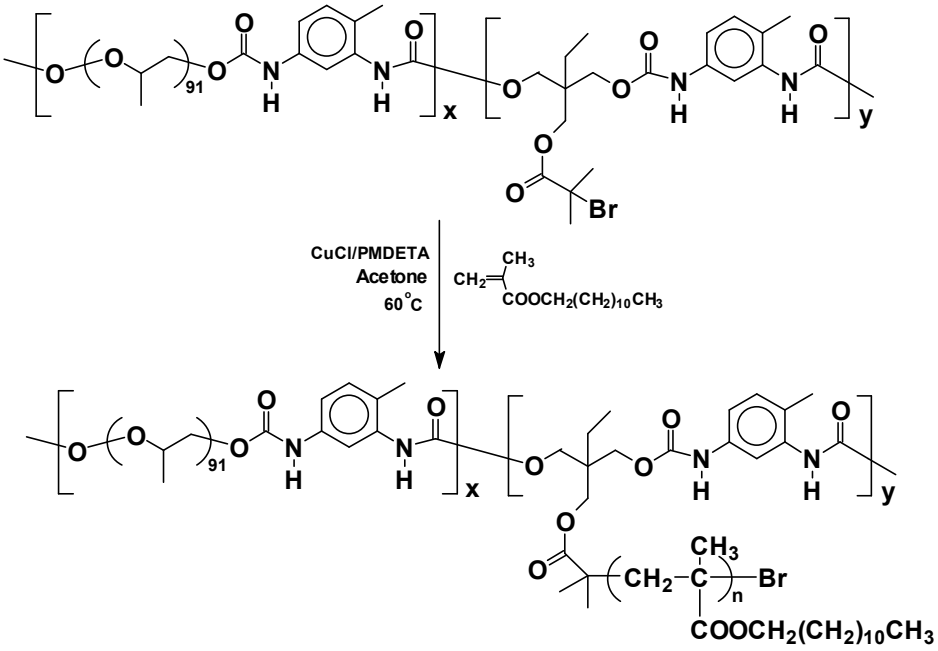
Figure 6.16: ^{1}H-NMR spectrum of PUM_2 macroinitiator

zation of PU-*g*-PLMA copolymer

6.4.3.2.1 Synthesis and characterization of PU-*g*-PLMA copolymer using PUM_2 macroinitiator

The grafting from approach was utilized for ATRP of LMA using PU macroinitiator to provide a PU-g-PLMA graft copolymer with a PU backbone and PLMA as side chains. **Scheme 6.6** shows the synthesis of PU-g-PLMA copolymer.

PU-*g*-PLMA copolymer was obtained by ATRP of LMA using PUM_2 as macroinitiator in presence of CuCl/PMDETA as catalyst in acetone (50%, w/v) as the solvent at 60°C for 4 h. **Table 6.7** shows reaction conditions and results for synthesis of PU-*g*-PLMA. The graft copolymer was purified by dissolving in dichloromethane and precipitated into excess of methanol repeatedly. GPC analysis of the purified PU-*g*-PLMA copolymer showed increase of molecular weight from 7630 to 24090 **(Figure 6.17,** Run 1, **Table 6.7)**.



Scheme 6.6: Synthesis of PU-*g*-PLMA copolymer using PUM_2 macroinitiator

and results of synthesis of PU-*g*-PLMA copolymer using PUM_2 macroinitiator

Run	Feed (wt %)		[d]Conv. (%)	[e]Composition (mol %)		[f]GPC		
	[a]PUM_2	LMA		PPG	PLMA	M_n	M_w	M_w/M_n
1	8.50	91.50	53	5	95	24090	35850	1.48

a ï PUM_2 = M_n- 7630 , M_w/M_n ï 1.75, b - [LMA]:[PUM_2]:[CuCl]:[PMDETA] = [324]:[1]:[1]:[1], Catalyst conc. = 2.5 x 10^{-4} mol, d - gravimetry, e - ^{1}H-NMR spectroscopy, f - PS calibration, acetone (50 %), reaction temperature - 60^{o}C, reaction time - 4 h,

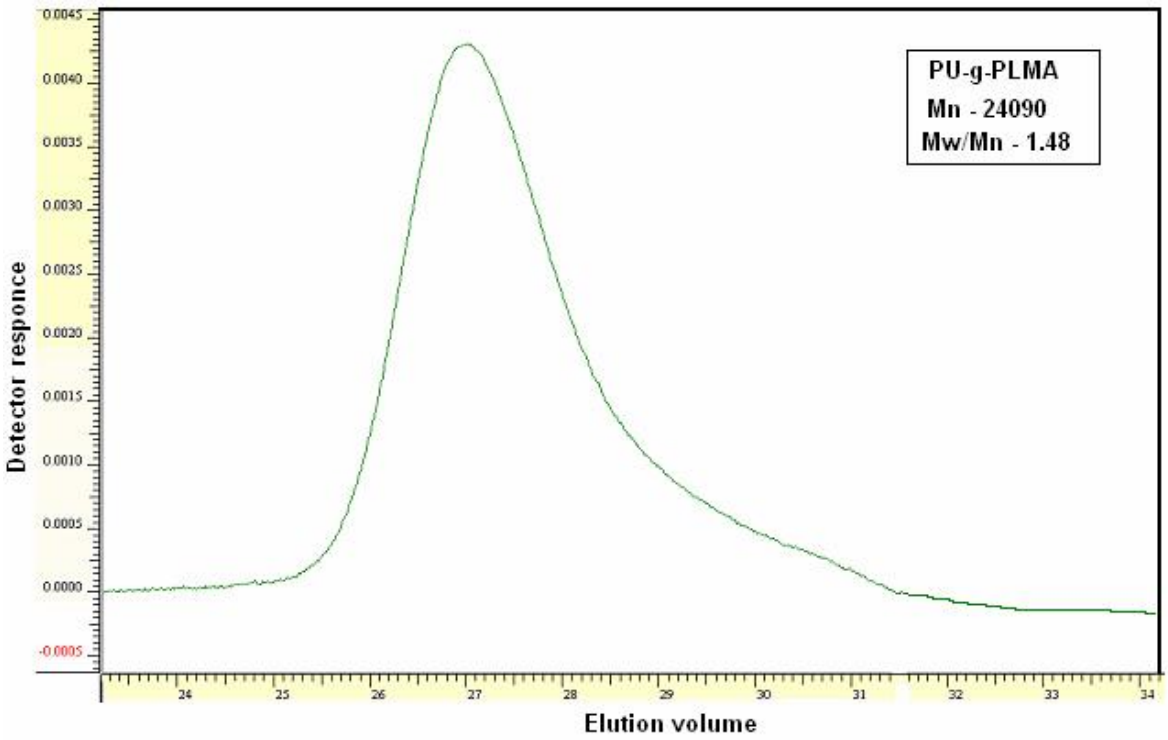


Figure 6.17: GPC trace of PU-g-PLMA copolymer (Run 1, Table 6.12)

The characterization of PU-g-PLMA copolymer was carried out by FTIR and ^{1}H-NMR spectroscopy.

FTIR spectrum of PU-*g*-PLMA copolymer using PUM_2 is shown in **Figure 6.18**. The band for carbonyl group from ester as well as urethane appeared at 1719 cm $^{-1}$. The bands at

pond to aromatic ring and NH stretching, respectively. The strong band appearing at 1214 cm^{-1} corresponds to ether group of PPG segment.

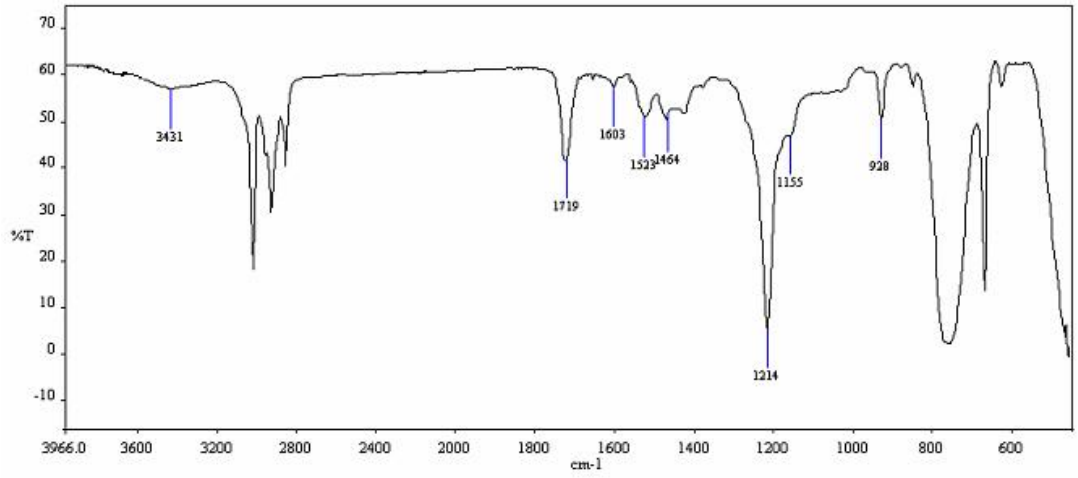


Figure 6.18: IR spectrum of PU-*g*-PLMA copolymer using PUM_2 macroinitiator

^{1}H-NMR spectrum of PU-*g*-PLMA copolymer using PUM_2 as a macroinitiator along with assignments is shown in **Figure 6.19**. The peak for methylene protons (Hc) and methine proton (Hb) appeared at 3.53 ŭ ppm. The peak appearing at 3.91 ŭ ppm corresponds to methylene protons (Hl) attached to ester group of PLMA branches. The peak at 2.17 ŭ ppm was ascribed to methyl protons (Hg) attached to the aromatic ring of PU backbone. The peaks appearing in the range 0.50 to 2.0 ŭ ppm were assigned to protons Hj, Hk, Hm, Hn and Ha.

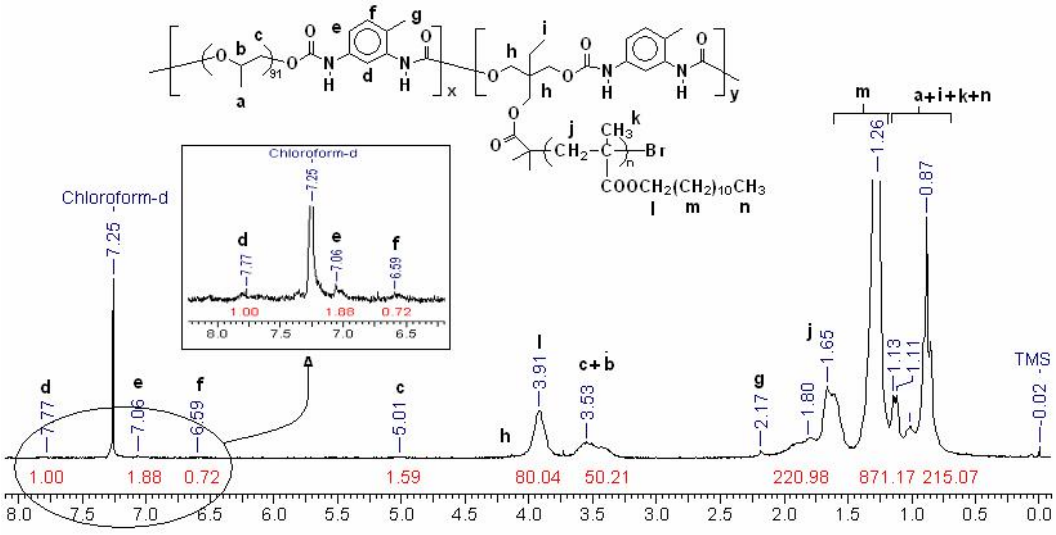


Figure 6.19: ^{1}H-NMR spectrum of PU-*g*-PLMA copolymer using PUM_2 macroinitiator in $CDCl_3$

studies indicated that PU macroinitiators containing ATRP functionality could be successfully utilized for the synthesis of PU-g-PLMA. However, additional studies such as determination of molecular weight, MWD and graft density of branches are required to fully validate the potential of this synthetic approach.

1 PLMA-*g*-PEO copolymer was synthesized *via* ñgrafting throughò approach using conventional free radical copolymerization of PEO macromonomer with lauryl methacrylate.

2 A new PCL macroinitiator containing pendent ATRP initiator functionality was synthesized by ROP of ε-caprolactone and 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate using stannous octanoate as catalyst. PCL containing ATRP initiating sites was successfully utilized as the macroinitiator for ATRP of MMA to obtain PCL-*g*-PMMA copolymer.

3 Two new polyurethane macroinitiators were synthesized from commercially available diols viz., ethylene glycol and PPG and a newly synthesized diol namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate by reaction with diisocyanate. The utility of PUM_2 macroinitiator in synthesis of PU-*g*-PLMA copolymer was demonstrated.

1. N. Hadjichristidis, S. Pispas and G. Floudas, ñ*Block Copolymers: Synthetic Strategies, Physical Properties and Applications*,ò John Wiley and Sons, New Jersey, **2003**
2. K.A. Davis and K. Matyjaszewski, *Adv. Polym. Sci*., 159, 107, **2002**
3. S. Sosnowski, M. Gadzinowski and S. Slomkowski, *Macromolecules*, 29, 4556, **1996**
4. C. L. Zhang, L. F. Feng, X. P. Gu, S. Hoppe and G. H Hu, *Polymer*, 48, 5940, **2007**
5. I. Piirma, ñ*Polymeric Surfactants*,ò Vol. 42, Marcel Dekker, Inc., New York, **1992**
6. A. Guyot and K. Tauer, *Adv. Polym. Sci.*, 111, 43, **1994**
7. D. Mecerreyes, M. Trollsas and J. L. Hedrick, *Macromolecules,* 32*,* 8753, **1999**
8. G. Wang, Y. Shia, Z. Fu, W. Yang, Q. Huang and Y. Zhang, *Polymer,* 46, 10601, **2005**
9. A. A. Farah, N. Hall, S. Morin and W. J. Pietro, *Polymer*, 47, 4282, **2006**
10. a) C. J. Hawker, J. L. Hedrick, E. E. Malmstrom, M. Trollsas, D. Mecerreyes, G. Moineau, Ph. Dubois and R. Jerome, *Macromolecules*, 31, 213, **1998** b) W. Jakubowski, J. Lutz, S. Slomkowski and K. Matyjaszewski, *J. Polym. Sci. Part A: Polym. Chem*., 43, 1498, **2005**
11. C. Lepilleur and E. J. Beckman, *Macromolecules*, 30, 745, **1997**
12. a) G. H. Stempel, R. P. Cross and R. P. Mareiolla, *J. Am. Chem. Soc.*, 72, 2299, **1950** b) D. D. Perrin and W. L. F. Armarego, ñ*Purification of Laboratory Chemicals"*, Pergamon Press, NewYork, **1989**
13. R. N. Keller and H. D. Wycoff, *Inorg. Synth*, 2, 1, **1946**
14. K. Jankova, X. Chen, J. Kops and W. Batsberg, *Macromolecules*, 31, 538, **1998**
15. X. Zushun, Y. Changfeng, C. Shiyuan and F. Linxian, *Polym. Bull.* 44, 215, **2000**
16. K. Matyjaszewski and J. Xia, *Chem. Rev*., 101, 2921, **2001**
17. M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev*., 101, 3689, **2001**
18. P. Gramain and Y. Frere, *Polym Commun*. 27, 16, **1986**
19. Yamashita, Huthig and W. Verlag, *"Chemistry and Industry of Macromonomers*ò, Basel, **1993**
20. O. Olabisi, L. E. Robeson and M. T. Shaw, ñ*Polymer Polymer Miscibility,"* New York: Academic, **1979**

a, A. Duchesne, M. Stamm, S. Fakirov and H. Keul, *Macromol. Chem. Phys.,* 199 2153, **1998**

22. H. Kricheldorf and I. Kreiser, *J. Macromol. Sci. Chem.*, A, 24, 1345, **1987**
23. M. Jonza and R. S. Porter, *Macromolecules*, 19, 1946, **1986**
24. M. Moller, R. Kanje and J. L.Hedrick, *J. Polym. Sci. Part A: Chem*., 38, 2067, **2000**
25. H. Schenck, M. Ryner, A. C. Albertsson and M. Svensson, *Macromolecules,* 35, 1556, **2002**
26. T. Erdogan, Z. Ozyurek, G. Hizal and U. Tunca, *J. Polym. Sci., Part A: Polym. Chem*. 42, 2313, **2004**
27. W. Jakubowski and K. Matyjaszewski, *Macromol. Symp*. 240, 213, **2006**
28. A. Heise, M. Trollsas, T. Magbitang, J. L. Hedrick, C.W. Frank and R. D. Miller *Macromolecules*, 34, 2798, **2001**
29. D. Mecerreyes, B. Atthoff, K.A. Boduch, M. Trollsas and J. L. Hedrick, *Macromolecules*, 32, 5175, **1999**
30. P. Lecomte, R. Riva, S. Schmeits, J. Reiger, K. V. Butsele, C. Jerome and R. Jerome, *Macromol. Symp*. 240, 157, **2006**
31. Tian, P. Dubois, C. Grandfils and R. Jerome, *Macromolecules*, 30, 406, **1997**
32. D. Tian, P. Dubois and R. Jerome, *Macromolecules*, 30, 2575, **1997**
33. P. Lecomte, R. Riva, S. Schmeits, J. Rieger, K. V. Butsele, C. Jerome and R. Jerome, *Macromol. Symp*., 240, 157, **2006**
34. B. Parrish, R. Breitenkamp and T. Emrick, *J. Am. Chem. Soc*., 127, 7404, **2005**
35. K. Matyjaszewski, D. A. Shipp, J. L. Wang, T. Grimaud and T. E. Patten, *Macromolecules,* 31, 6836, **1998**
36. S. C. Hong, T. Pakula and K. Matyjaszewski, *Macromol. Chem. Phys*., 202, 3392, **2001**
37. C. S. Schollenberger, ñ*Handbook of Adhesives: Polyurethane and Isocyanate-based Adhesives*,ò I. Skeits, Ed.,Van Nostrand Reinhold, New York **1990**, Chapter 20
38. G. Woods, ñ*The ICI Polyurethanes Book*,ò Wiley, New York, **1990**
39. M. Dollhausen, ñ*Polyurethane Handbook: Polyurethane Adhesives*,ò Ed. G. Oertel, Hanger, Munich, **1985**, Chapter 11

and D. J. Francis, *Eur. Polym. J*. 33(I), 89, **1997**

41. A. Baron, E. Cloutet, H. Cramail and E. Papon, *Macromol. Chem. Phys*. 204, 1616, **2003**

Polyurethane Microspheres Utilizing PEO-*b*-PLMA, PLMA-*g*-PEO and Dihydroxyl-Terminated PLMA Macromonomers as Steric Stabilizers

7.1 Introduction

Polymer microspherges show great potential in several applications in both chemical and life sciences.[1,2] Efforts to prepare polymer microspheres with uniform size have been continuing for a long time due to their applications in paint industry and so on.[3]

Polymer microspheres are prepared by either *in situ* polymerization of respective monomer(s) or physicochemical or mechanical processes using preformed polymer. Microspheres prepared by polymerization processes from vinyl monomers are well known. However, polycondensation processes for preparation of microspheres in non-aqueous medium are far less developed.[3] Generally, steric stabilizers which play an important role in stabilizing the particles formed during polymerization include homopolymers, amphiphilic block or graft polymers and polymerizable stabilizers.[4,5]

Polyurethane (PU) microspheres have applications in the field of coatings, paints, powder molding and in controlled release systems. Preparation of polyurethane microspheres in non-aqueous medium was described from our laboratory for the first time using polybutadiene-*b*-polyethylene oxide as a steric stabilizer.[6,7] It was demonstrated that the process developed can be employed for the preparation of polyurethane microcapsules containing highly reactive water soluble active agent.[8,9] Further, it was shown that the polymerizable stabilizer synthesized by conventional radical polymerization, namely poly(lauryl methacrylate) having two hydroxyl groups (PLMA macrodiol) can be effectively used for the preparation of polyurethane microspheres.[10,11] Recently, Cramail et al[12-15] reported the usefulness of ω-(hydroxy)$_n$ (n = 1 or 2) polymers such as poly(n-butyl acrylate), polystyrene, polybutadiene, polydimethyl siloxane as good steric stabilizes in preparation of PU particles.

This chapter deals with the preparation of polyurethane microspheres by dispersion polymerization of 2,4-toluene diisocyanate and 2-ethyl 1,3-hexane diol using newly

bilizers viz., PEO-*b*-PLMA, PLMA-*g*-PEO and dihydroxyl-terminated PLMAs. For both PEO-*b*-PLMA diblock copolymer and PLMA-*g*-PEO graft copolymer, the effect of stabilizer concentration and molar mass of PEO as an anchor moiety were studied. The effect of concentration and molar mass of reactive steric stabilizer having PLMA as a stabilizing moiety on PU particle size was examined.

7.2 Experimental

7.2.1 Materials and purifications

2-Ethyl 1,3-hexane diol (99%, EHG), dibutyl tin dilaurate (DBTDL) and 2,4-toluene diisocyanate (99%, TDI) were purchased from Sigma-Aldrich, Inc., USA and were used as received.

Paraffin oil and n-hexane were purchased from s.d fine-Chem. India Ltd. n-Hexane was stirred over calcium hydride for 12 h and distilled.

Polymeric stabilizers namely, PEO-*b*-PLMA and hydroxyl-terminated PLMA of different molecular weights were synthesized by ATRP as described in **Chapters 4** and **5**. PLMA-*g*-PEO was synthesized by conventional free radical polymerization as described in **Chapter 6**.

7.2.2 Characterization

FTIR spectra of samples were recorded on a Perkin-Elmer *Spectrum GX* spectrophotometer.

NMR spectra were recorded on a Bruker 200 MHz spectrometer at resonance frequencies of 200 MHz for ^{1}H-NMR measurements using acetone-d_6 or chloroform-d as solvent.

Scanning electron microscopy images were obtained using Leica (stereoscan 440) scanning electron microscope (Cambridge, UK) at an accelerating voltage 20Kv.

7.2.3 Particle size analysis

PU particles were dispersed in paraffin oil and particle size was measured using an optical microscope.

n range was measured using Malvern Photon Spectrometer, model 4700 with a vertically polarized 25 mW He-Ne laser as light source.

7.3 Preparation of polyurethane microspheres

7.3.1 Preparation of polyurethane microspheres using PEO-*b*-PLMA or PLMA-*g*-PEO copolymers as steric stabilizers

A representative protocol followed in the preparation of PU microspheres is given below.

Into a three necked round bottom flask equipped with an addition funnel, a nitrogen inlet and an overhead stirrer were placed polymeric stabilizer, PLMA-*g*-PEO (0.24 g, 5 wt % ($w_{stabilizer}/w_{monomers}$)), dibutyl tin dilaurate (0.003 g, 4.7 x 10^{-6} mol), 2-ethyl 1,3-hexane diol (2.0 g, 0.02 mol) and paraffin oil (25 g). The reaction mixture was heated to 65^{o}C at a constant stirring speed of 1000 rpm under an atmosphere of nitrogen. 2,4-Toluene diisocyanate (2.86 g, 0.024 mol) was added dropwise through an addition funnel over a period of 30 min. The reaction was stopped after 4 h and the obtained polyurethane particles were washed repeatedly with n-hexane, centrifuged and dried under vacuum at room temperature for 12 h.

7.3.2 Preparation of polyurethane microspheres using dihydroxyl-terminated poly(lauryl methacrylate) or bismethylol-terminated poly(lauryl methacrylate) as reactive stabilizers

A representative protocol followed in the preparation of PU microspheres is given below.

Into a three necked round bottom flask equipped with an addition funnel, a nitrogen inlet and an overhead stirrer were placed dihydroxyl-terminated PLMA (0.43 g, 10 wt % ($w_{stabilizer}/w_{monomers}$)), Mn^{NMR} = 3640, M_w/M_n = 1.23), dibutyl tin dilaurate (0.003 g, 4.7 x 10^{-6} mol) and paraffin oil (25 g). Toluene-2,4-diisocynate (2 equivalent w.r.t. dihydroxyl-terminated PLMA) was added and the reaction mixture was stirred at 65^{o}C for 5 h. 2-Ethyl 1,3-hexane diol (2. g, 0.02 mol) was then added in one lot and the reaction mixture was stirred at 500 rpm for 30 min. Toluene-2, 4-diisocynate (2.86 g, 0.024 mol) was added dropwise

period of 30 min. The reaction was stopped after 5 h and the obtained polyurethane particles were washed repeatedly with hexane, centrifuged and dried under vacuum at room temperature for 12 h.

7.4 Results and Discussion

7.4.1 Prepration of polyurethane microspheres using block and graft copolymers

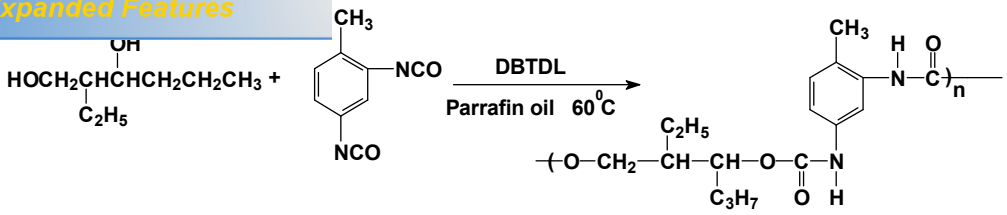
The most utilized surfactants in preparation of polymeric particles reported in the literature are block copolymer, graft copolymer and reactive polymers. These surfactants were designed according to the principle given by Barrett[3], which states that surfactant having anchor moiety should have poor solubility in the dispersion medium, while the stabilizing moiety should have good solubility in the dispersion medium.

The published literature suggests that commercially available surfactants such as AOT ($RO_2CCH_2CH(SO_3Na)$-CO_2R; R= 2-ethylhexyl), Emerest 2622 (PEG 200 dilaurate), pluronics L 70 poly(ethylene oxide-b-propylene oxide) and di-n-hexadecyl phosphate failed to produce polyurethane particles. It was concluded that poor solubility and less number of anchoring moieties were responsible for the results. These surfactants were unable to provide adequate steric barrier to prevent agglomeration during polymerization.[11] Therefore, it was essential to use well-defined steric stabilizers to prepare polyurethane microspheres.

Later, Sivaram et al[11] designed and synthesized well defined poly(isoprene-*b*-ethylene oxide) copolymers and used them successfully as steric stabilizer in the preparation of PU microspheres. Cramail et al[20] utilized PS-*b*-PEO as steric stabilizer and elegantly demonstrated that the appropriate balance of PS and PEO blocks was essential to get PU microspheres.

In the present study, amphiphilic block and graft copolymers were designed and synthesized for preparation of PU mcrospheres.

A model reaction for preparation of polyurethane microspheres was carried out by reacting 2-ethyl, 1,3-hexane diol and 2,4-toluene diisocynate in the presence of DBTDL as a catalyst **(Scheme 7.1)**.



Scheme 7.1: Preparation of PU microspheres

Paraffin oil was utilized as a dispersion medium for synthesis of polyurethane microspheres as earlier studies showed it to be a good dispersion medium for preparation of PU microsphere.[11] The choice of dispersion medium is based on the following parameters, reported in the book review by Barrett.[3]

i) Dispersion medium should be non-solvent for polymer microspheres

ii) All the reaction components such as monomers, catalyst and stabilizer should be soluble in dispersion medium.

7.4.1.1 Preparation of PU microspheres by dispersion polymerization using PEO-*b*-PLMA copolymer as steric stabilizer

Dispersion polymerization is a type of precipitation polymerization where once the oligomeric chains reach a critical chain length they precipitate to form nuclei, either by self or aggregative mechanism. These nuclei are unstable and aggregate with each other leading to coagulation. This may be prevented by employing appropriate stabilizer in the dispersion medium. These stabilizers adsorb on the surfaces of nuclei, prevent their coagulation thereby forming stable (mature) particles. It has demonstrated that increase in stabilizer concentration leads to smaller particles.[3]

There exists an equilibrium between the adsorbed stabilizer, free stabilizer molecules and the stabilizer micelles when the stabilizer concentration in the dispersion medium exceeds that of critical micelle concentration (cmc).[3] The dissociation rate of micelles into free stabilizer molecules will dictate the equilibrium. Adsorption of stabilizer on polymer surface will be favored if the equilibrium shifts to free stabilizer. Thus, to achieve a better stabilization micelle formation should be avoided. Equilibrium of polymeric stabilizers in non-aqueous media will be less dynamic because of its high molecular weight and

rate of desorption or release from the aggregates can be expected. Adsorption efficiency of free stabilizer on polymer surface will depend on size of the anchoring group and its specific interaction within the dispersed polymer.

PEO-*b*-PLMA **(Figure 7.1)** diblock copolymer was used as a steric stabilizer in preparation of polyurethane microspheres.

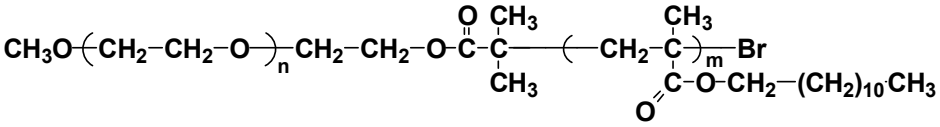


Figure 7.1: Structure of PEO-*b*-PLMA diblock copolymer stabilizer

In block copolymer, PLMA acts as the stabilizing moiety, which is soluble in the dispersion medium (paraffin oil), while PEO acts as the anchoring moiety due to its poor solubility in the dispersion medium. **Table 7.1** shows characteristics of PEO-*b*-PLMA copolymers.

Table 7.1: Characteristics of PEO-*b*-PLMA diblock copolymer stabilizers

Stabilizer	$^{a}M_n$ PEO	$^{a}M_n$ PLMA	$^{b}M_w/M_n$
S1	350	23660	1.19
S2	700	34650	1.18
S3	2000	21850	1.28
S4	5000	26870	1.22

a = NMR, b = GPC with PS calibration

The results of preparation of polyurethane microspheres using PEO-*b*-PLMA as a steric stabilizer are compiled in **Table 7.2**. It is known that in dispersion polymerization

rious parameters such as monomer addition time, stirring speed, monomer to solvent ratio and surfactant concentration.

Table 7.2: Results of preparation of polyurethane microspheres using PEO-*b*-PLMA as a steric stabilizer

Stabilizer	[a]Stabilizer conc. (wt %)	M_n PEO block	[b]Particle size range (μ)	Observations
S1	3	350	-	Coagulation
	5	350	-	Coagulation
	10	350	-	Coagulation
S2	3	700	-	Coagulation
	5	700	-	Coagulation
	10	700	-	Coagulation
S3	0.5	2000	4 to 20	Spherical particles
	1	2000	2 to 16	Spherical particles
	3	2000	2 to 12	Spherical particles
	5	2000	2 to 10	Spherical particles
S4	1	5000	1 to 20	Spherical particles
	3	5000	1 to 18	Spherical particles
	5	5000	1 to 10	Spherical particles

a = based on monomer weight., b = measured by optical microscope, TDI addition time = 10 min, monomer to solvent ratio = 1:5 (w/w), stirring speed = 300 rpm

During evaluation of diblock copolymers as a steric stabilizer, initially, the parameters like TDI adiition time (10 min), stirring speed (300 rpm) and monomer to solvent ratio (1:5, v/v) were kept constant while varying the stabilizer concentration.

ed out without stabilizer **(S0)**, which obviously resulted in coagulation of PU due to absence of steric stabilizer.

PEO-*b*-PLMA **(S1)** diblock copolymer stabilizer having PEO (M_n- 350) and PLMA (M_n- 25570) was inefficient to stabilize polyurethane microspheres at 3 wt %, 5 wt % and 10 wt % stabilizer concentration resulting in coagulation of PU **(Table 7.2)**.

PEO-*b*-PLMA **(S2)** copolymer when used as the steric stabilizer having anchor moiety PEO (Mn- 700) and stabilizing moiety PLMA (Mn- 26850) at 3 wt %, 5 wt % and 10 wt % concentration, did not produce polyurethane particles due to its inefficient participation in stabilization process. Similar results were also obtained by Cramail et al,[20] when PS_{120}-*b*-PEO_{245} was utilized as a steric stabilizer in preparation of PU particles.

It was concluded that the formation of stable micelles of block copolymer in reaction medium, results in the poor PU particle stabilization. This may be attributed to the low dissociation rate of diblock copolymer micelles to free polymer in organic solvents and the unavailability of free stabilizers results in coagulation of PU.[3,21]

PEO-*b*-PLMA **(S3)** copolymer when used as the stabilizer with anchor moiety, PEO (M_n- 2000) and stabilizing moiety PLMA (M_n- 21300), it produced polyurethane microspheres with spherical sizes at 0.5 wt %, 1 wt %, and 5 wt % stabilizer concentrations **(Table 7.2)**. The formation of PU particles was successful when PEO-*b*-PLMA **(S4)** copolymer stabilizer with anchor moiety, PEO (Mn- 5000) and stabilizing moiety PLMA (Mn- 20760) was utilized at 0.5 wt %, 1 wt % and 3 wt % stabilizer concentrations. The formation of spherical PU particles using these stabilizers may be due to their low concentrations in dispersion medium (conc. < CMC) or due to fast dissociation rate of micelles to single molecules.

From the above study, it was concluded that PEO-*b*-PLMA diblock copolymers could act as steric stabilizers depending on the hydrophile (anchor, PEO) lipophile (stabilizing moiety, PLMA) balance (**Table 7.2**).

7.4.1.2 Structural characterization of PU microspheres

The structural characterization of the PU microsphere was carried out by FTIR and ^{1}H-NMR spectroscopy.

ntative FTIR spectrum of PU microspheres synthesized using PEO-*b*-PLMA as steric stabilizer. The N-H vibration band appeared at 3303 cm^{-1} and urethane carbonyl vibration band was observed at 1702 cm^{-1}.

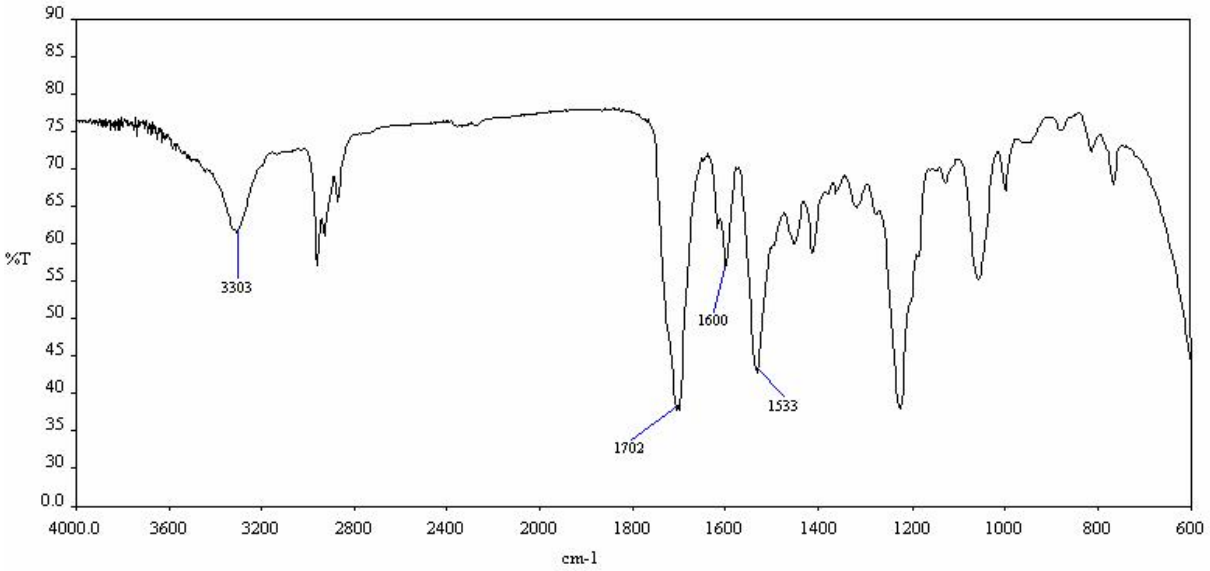


Figure 7.2: A representative IR spectrum of PU microspheres

^{1}H-NMR spectrum along with assignments for PU microspheres synthesized using PEO-*b*-PLMA as steric stabilizer is shown in **Figure 7.3**. The signal for aromatic proton (Ha) flanked by urethane groups appeared at 7.89 ŭ ppm, the other two aromatic protons (Hb,Hc) appeared at 7.30 and 7.11 ŭ ppm, respectively. The singlet at 2.89 ŭ ppm correspond to methyl protons (Hd) present on aromatic ring. The methylene protons (Hf) and methine protons (Hi) appeared as a multiplet centered at 4.17 ŭ ppm. The remaining methylene (Hj,Hk,Hg) and methyl protons (Hh and Hl) appeared in the range 0.80 to 2.20 ŭ ppm.

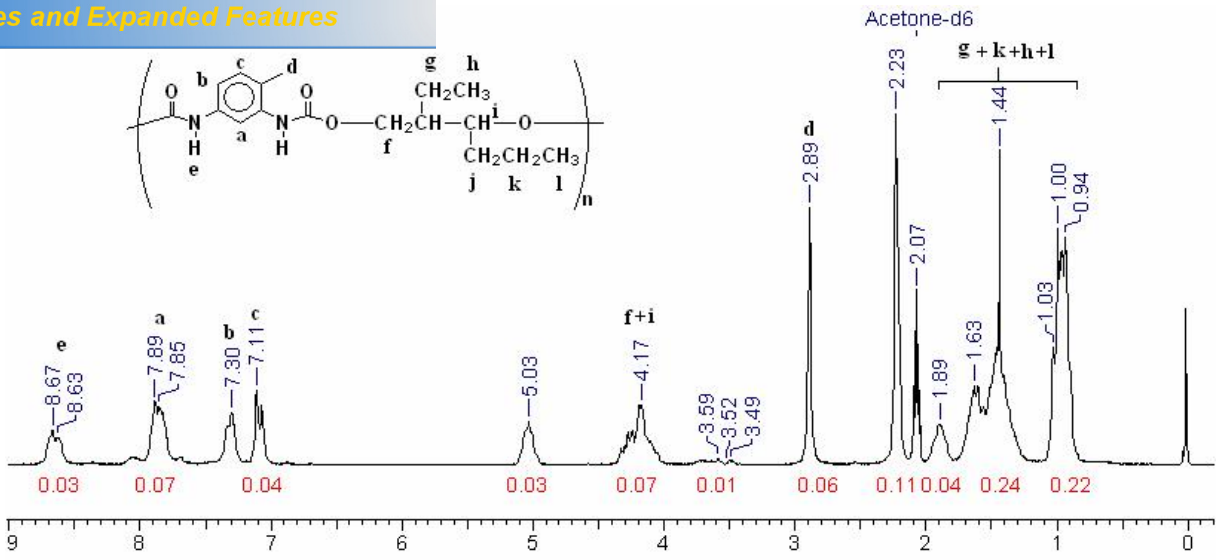


Figure 7.3: A representative ^{1}H-NMR spectrum of PU microspheres in acetone-d_6

7.4.1.3 Preparation of PU microspheres by dispersion polymerization using PLMA-*g*-PEO copolymer as steric stabilizer

Graft copolymers are known to be good steric stabilizers due to the availability of more number of anchoring moieties as compared to diblock copolymers. PLMA-*g*-PEO copolymer prepared by ñgrafting throughò approach by conventional free radical polymerization was evaluated as steric stabilizer in preparation of polyurethane microspheres.

. **Figure 7.4** shows structure of PLMA-*g*-PEO copolymer stabilizer. **Table 7.3** shows characteristics of PLMA-*g*-PEO copolymer stabilizer.

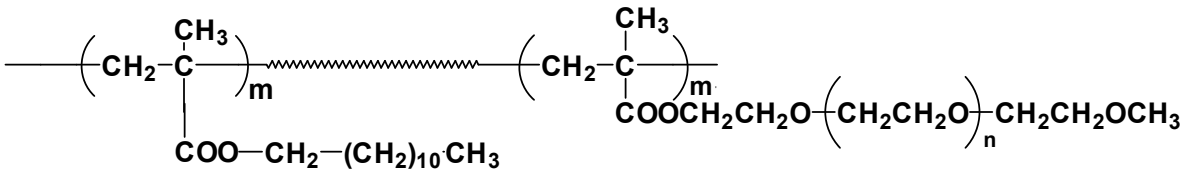


Figure 7.4: Structure of PLMA-*g*-PEO copolymer stabilizer

MA-*g*-PEO copolymer stabilizers

Stabilizer	[a]M_n PLMA-*g*-PEO	M_n PEO	[a]M_w/M_n
S5	68300	1100	2.90
S6	34170	2000	2.82

a = GPC with PS calibration

The dispersion polymerization of 2-ethyl 1,3-hexane diol and 2,4-toluene diisocyanate was carried out in the presence of PLMA-*g*-PEO copolymers as steric stabilizers. In this study, two graft copolymer stabilizers were utilized, **S5** and **S6** having M_n - 1100 and 2000 as anchor (PEO) moieties, respectively. Evaluation of graft copolymers as steric stabilizer in preparation of PU microspheres was studied by keeping stirring rate constant (1000 rpm), monomer to dispersion medium ratio (1:7, w/w) and TDI addition time (30 min).

Table 7.4 shows the particle size data obtained from optical microscope of PU microspheres prepared using graft copolymer stabilizer **S5** having anchor moiety (PEO, M_n ï 1100) and total M_n- 68300.

Table 7.4 Effect of stabilizer S5 (PEO = 1100) concentration on PU particle size

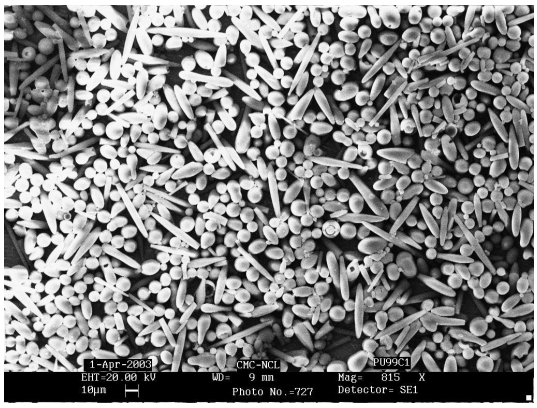
Run	[a]Conc of stabilizer (wt %)	[b]Particle size range (μm)	[b]Observations
1	1	-	Most of particles were needle and egg shaped
2	3	-	Spherical with few needles and irregular shaped particles
3	5	2 to 20	Spherical with some needles and egg shaped particles
4	10	1 to 10	Spherical particles
5	15	1 to 8	Spherical particles

a ï based on monomer weight, b = particle size was analyzed by optical microscope, stirring speed = 1000 rpm, Monomer to solvent ratio = 1:7 (w/w), TDI addtition time = 30 min

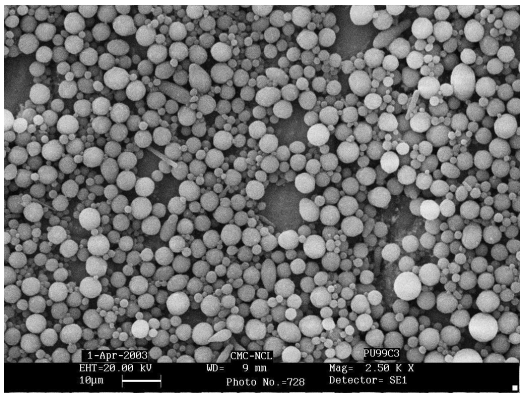
entration of **S5**, the obtained PU particles were irregular, egg and needle shaped. This irregularity in the shape of PU particles was due to the insufficient stabilizer concentration.

As the stabilizer concentration was increased the particle size decreased. The minimum stabilizer concentration (for **S5**) needed to get stable spherical particles was found to be 10 wt % where only spherical particles were obtained **(Table 7.4).**

It was concluded that stabilizer concentrations of 1, 3 and 5 wt % was not enough for the stabilization of particles in nucleation stage, which resulted in irregular shapes **(Figure 7.5)**. However, at higher concentrations of S_5 (10 and 15 wt %) (Run 4 and 5, **Table 7.4)**) resulted in spherical PU micropsheres with smaller size (1-10 μm).



PEO = 1100, Conc.= 1 wt %



PEO = 1100, Conc.= 3 wt %

Figure 7.5: SEM micrographs of PU microspheres synthesized using stabilizer S5

On the other hand, when graft copolymer **(S6)** with anchor moiety (PEO of M_n- 2000) was used as a steric stabilizer, it was found to be an efficient steric stabilizer. Spherical polyurethane particles with narrow particle size distribution were obtained even at low concentration (1 wt %). **Table 7.5** shows results of the effect of stabilizer **(S6)** concentration on PU particles.

(PEO = 2000) concentration on PU particle size

Run	[a]Conc. of stabilizer (wt %)	[b]Average particle size (μm)	[b]Observation
6	1	1.45	Monomodal
7	3	0.54	Monomodal
8	15	0.31	monomodal

a = based on monomer weight, b = particle size was analyzed by light scattering particle size analyzer, stirring speed = 1000 rpm, monomer to solvent ratio = 1:7 (w/w), TDI addtition time = 30 min

As reported in the literature,[11] increase in stabilizer concentration decreases particle size (**Table 7.5**). **Figure 7.6** shows a graphical presentation of the effect of stabilizer concentration (**S6**, PEO of M_n-2000) on size of PU microspheres.

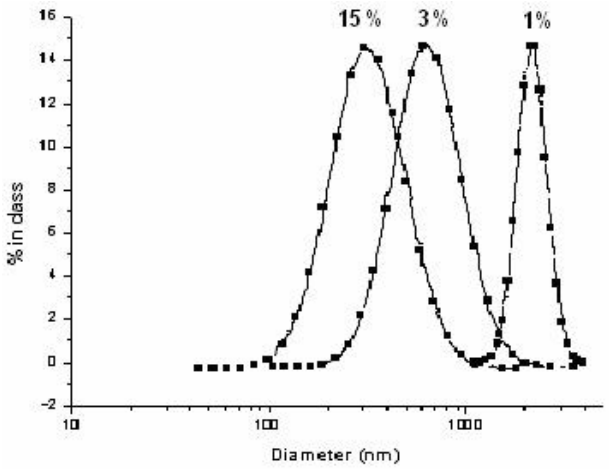
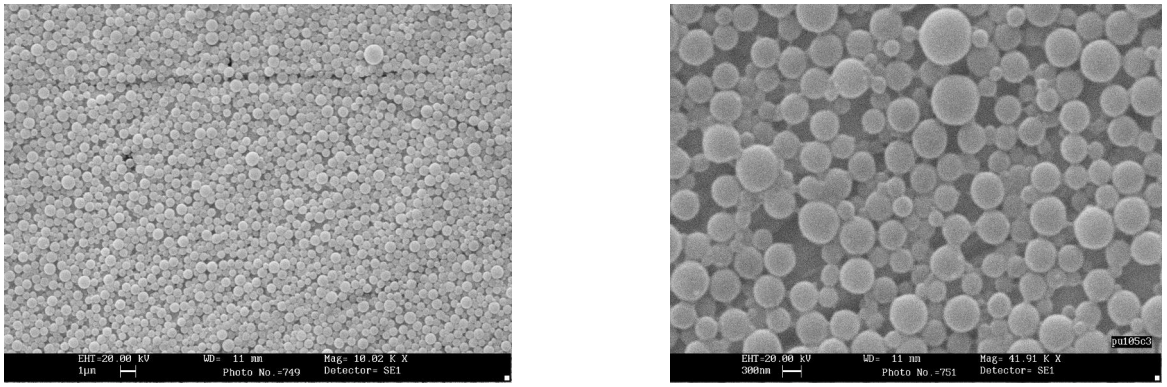


Figure 7.6: Effect of stabilizer concentration S6 (PEO = 2000) on particle size of polyurethane microspheres

micrographs of PU microspheres synthesized using PLMA-*g*-PEO **(S6)** as steric stabilizer. SEM micrograph reveals that the particles are nearly monodisperse.



a) Lower magnification **b) Higher magnification**

Figure 7.7: SEM micrographs of PU microspheres synthesized using stabilizer S6 at 3 wt % concentration

7.4.2 Synthesis of polyurethane microspheres using dihydroxyl-terminated poly(lauryl methacrylate) as reactive stabilizer

The major disadvantage of steric stabilizers such as block and graft copolymers which stabilize the PU particles by physical adsorption is that high shear stress may lead to their desorption from the surfaces leading to destabilization. To overcome this drawback reactive type steric stabilizers were developed. Reactive stabilizers covalently link to polyurethane particles by forming block or graft copolymers leading to increased stability.[15]

In this study, dihydroxyl-terminated PLMA **(Figure 7.8)** and bismethylol-terminated PLMA **(Figure 7.9)** were utilized as reactive steric stabilizers in preparation of PU microspheres.

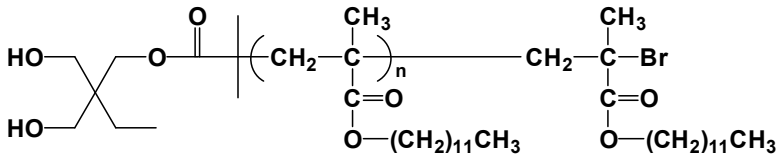


Figure 7.8: Structure of dihydroxyl-terminated PLMA (S7 to S10)

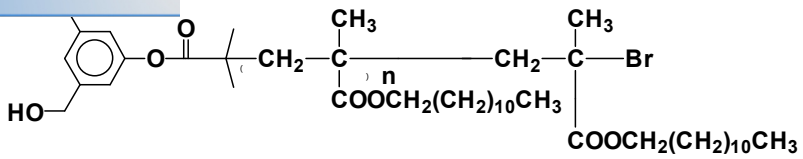


Figure 7.9: Structure of bismethylol-terminated PLMA (S11)

Table 7.6 shows characteristics of dihydroxyl-terminated and bismethylol-terminated PLMA.

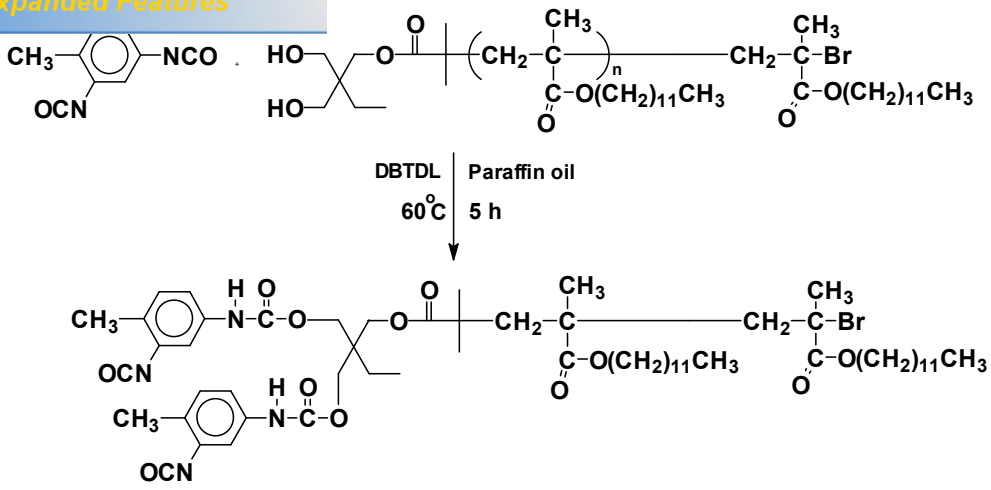
Table 7.6: Characteristics of dihydroxyl-terminated PLMA

Stabilizer	$^{a}M_n$ PLMA	$^{b}M_w/M_n$
S7	3640	1.23
S8	5080	1.41
S9	6040	1.27
S10	8070	1.29
S11	14700	1.19

a = ^{1}H-NMR, b = GPC with PS calibration

Dispersion polymerization of 2-ethyl-1,3-hexane diol and 2,4-toluene diisocyanate using dihydroxyl-terminated PLMA as steric stabilizer in presence of dibutyl tin dilaurate as the catalyst was carried out in paraffin oil as a dispersion medium.

Sivaram et al[10,11] and Cramail et al[12-14,20] have independently reported that the reactivity of hydroxyl-terminated PLMA, PS and PBA is less, hence dihydroxyl-terminated PLMA has to be first converted to isocyanate-terminated PLMA *in situ* using a slight excess (with respect to OH functionality) of TDI in presence of DBTDL as a catalyst to form the reactive stabilizer.[11,20] **Scheme 7.2** depicts synthesis of isocyanate-terminated PLMA.



Scheme 7.2: Synthesis of isocyanate-terminated PLMA

Once the isocyanate-terminated PLMA was formed, further dispersion polymerization was carried out by adding 2-ethyl-1,3-hexane diol in one lot and allowed to react for 30 min. 2,4-Toluene diisocyanate was then added dropwise over a period of 30 min and after 4 h the formed polyurethane microspheres were separated and washed with n-hexane. Polyurethane microspheres were characterized by optical microscopy.

7.4.2.1 Effect of stabilizer PLMA-(OH)$_2$ concentration

Dihydroxyl-terminated PLMA (**S9**, M_n-6000) was utilized as a reactive stabilizer to study of the effect of stabilizer concentration on PU microspheres. The polymerizations were carried out in paraffin oil as dispersion medium at 65^{o}C. In this study, stirring rate (500 rpm), monomer to paraffin oil ratio (1:5, w/w) and TDI addition rate (30 min) were kept constant **(Table 7.7)**. Stabilizer concentration was varied from 2 wt % to 15 wt % with respect to monomers.

From the results in **Table 7.7,** it was observed that an increase in stabilizer concentration leads to a decrease in average particle diameter, and these results are in good agreement with the results reported in literature.[22]

Table 7.7: Effect of stabilizer (S9) concentration on size of PU microspheres

Run	[a]Stabilizer conc. (wt %)	[b]Particle size range (μm)	[b]Observations
1	2	-	Coagulation
2	5	10 to 50	Spherical particles
3	10	5 to 35	Spherical particles
4	15	5 to 30	Spherical particles

a = based on monomer weight, b = particle size was analyzed by optical microscope, stirring speed = 500 rpm, monomer to solvent ratio = 1:5 (w/w), TDI addition time = 30 min

7.4.2.2 Effect of PLMA molar mass

To study the effect of chain length of dihydroxyl-terminated PLMA on polyurethane microspheres, dihydroxyl-terminated PLMA of different molecular weight were utilized **(Table 7.6)**. Isocyanate-terminated PLMA was synthesized *in situ* and dispersion polymerization was carried out. From the results presented in **Table 7.8** it could be concluded that the size of polyurethane microspheres is dependent on the molar mass of PLMA

n of PLMA on size of PU microspheres

Run	M_n PLMA	[a] Particle size range (μm)	[a] Observations
1	3640	10 to 50	Spherical particles
2	5080	5 to 50	Spherical particles
3	6040	5 to 45	Spherical particles
4	8070	3 to 30	Spherical particles

a = particle size was analyzed by optical microscope, stabilizer concentration 10 wt %, stirring speed = 500 rpm, monomer to solvent ratio = 1:5 (w/w), TDI addition time = 30 min

It was found that at constant stabilizer concentration of 10 wt %, the particle size of the polyurethane microspheres decreased with increase in molar mass of PLMA. Similar observations has been made previously by Sivaram et al[23] using dihydroxyl-terminated poly(lauryl methacrylate) as reactive steric stabilizer in preparation of polyurethane particles.

7.4.3 Synthesis of polyurethane microspheres using bis-methylol-terminated PLMA as reactive stabilizer (S11)

Bismethylol-terminated PLMA (**S11**, M_n^{NMR}-14700) was utilized as a reactive stabilizer in preparation of PU microspheres. Isocyanate-terminated PLMA was synthesized in same manner as described in Section 7.4.2.2. The polymerization was carried out in paraffin oil as dispersion medium at 65^oC. In this study, stabilizer concentration was 5 wt % and TDI was added over a period 30 minutes. Monomer to paraffin oil ratio was (1:5, w/w), while stirring rate was 500 rpm **(Table 7.9)**. The particle size of obtained PU microspheres at 5 wt % stabilizer concentration was in the range 4 to 18 μm **(Table 7.9)**. The optical micrograph of PU microspheres is depicted in **Figure 7.10**, which showed spheres with narrow particle size distribution.

J microspheres using bismethylol-terminated PLMA as reactive steric stabilizer (S11)

Run	[a]Stabilizer conc (wt %)	[b]Particle size range (μm)	[b]Observations
1	5	4 to 18	Spherical particles

a- based on monomer weight, b = particle size was analyzed by optical microscope, stirring speed = 500 rpm, monomer to solvent ratio = 1:5 (w/w), TDI addition time = 30 min

.

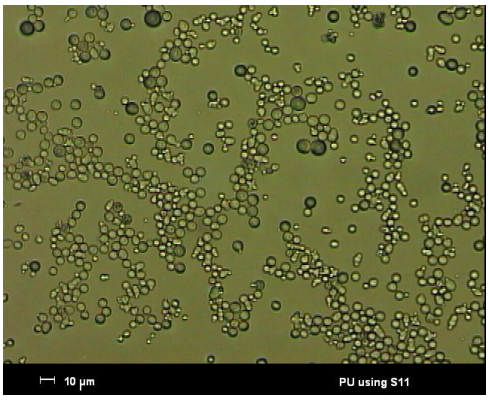


Figure 7.10: Optical micrograph of PU microspheres synthesized using stabilizer S11 at 5 wt % concentration

Thus, utility of PEO-*b*-PLMA, PLMA-*g*-PEO, dihydroxyl-terminated PLMA and bismethylol-terminated PLMA as steric stabilizers in the preparation of polyurethane microspheres was demonstrated.

1. The utility of PEO-*b*-PLMA, PLMA-*g*-PEO, diydroxyl-terminated PLMA and bismethyol-terminated PLMA as steric stabilizers was studied in the preparation of polyurethane microspheres by dispersion polymerization of 2-ethyl 1,3-hexane diol and 2,4-toluene diisocyanate in paraffin oil as a dispersion medium.
2. PEO-*b*-PLMA diblock copolymer (PEO of M_n-350 and 700) was found to be ineffective as steric stabilizer due the coagulation of PU during polymerization.
3. PEO-*b*-PLMA diblock copolymer (PEO of M_n-2000 and 5000) was found to be effective stabilizer resulting in the formation of polyurethane microspheres.
4. Graft copolymer (PLMA-*g*-PEO) with anchor moiety (PEO of M_n- 1100) produced spherical polyurethane microspheres at 10 wt % and 15 wt % stabilizer concentration, while, graft copolymer having anchor moiety (PEO - 2000) was found to be effective even at lower stabilizer concentration (1 wt %) and it afforded polyurethane microspheres with a narrow particle size distribution.
5. Dihydroxyl-terminated PLMA and bismethylol-terminated PLMA were shown to be efficient reactive stabilizers in preparation of polyurethane microspheres. The effect molar mass of dihydroxyl-terminated PLMA on polyurethane microspheres was studied; the increase of molar mass of PLMA chain resulted in decrease in the polyurethane particle size at constant stabilizer concentration.

1. R. Arshady, ñ*Microspheres, Microcapsules and Liposomes,"* Vol.1 & 2, Citus Book, London UK, **1999 2**
2. C. Dinnella, M. Laus, G. Lanzarini and M. Doria, ñ*Polymers for Advanced Technologies"*, 7, 548, **1996.**
3. K. E. J. Barrett, ñ*Dispersion Polymerisation in Organic Media"* Wiley International Sci Publication London, **1975**
4. P. Bahadur and G. Riess, ñ*Tensides-Surfactants-Detergents",* 28, 173, **1991**
5. A. Guyot and K. Tauer, *Adv. Polym. Sci,.* 111, 43, **1994**
6. P.G. Shukla and S. Sivaram, *U.S Patent*, 5814675, **1998**
7. P.G. Shukla and S. Sivaram, *U.S Patent*.5814675, **1998**
8. P.G. Shukla, N. Rajagopalan and S. Sivaram, *U.S Patent*, 5962003, **1999**
9. P.G. Shukla and S. Sivaram, *J. Microencap*, 16, 517, **1999**
10. L.S. Ramanathan, P.G. Shukla and S. Sivaram, *Pure Appl. Chem, 70,* 1295, **1998**
11. L. S. Ramanathan, ñ*Studies on Particle Forming Polycondensation and Ring Opening Polmerization Processes",* Ph. D. Thesis, University of Pune, Pune, India, **2000**
12. B. Radhakrishnan, G. Balredi, E. Cloutet and H. Cramail, *Macromol. Symp*. 229, 56, **2005**
13. B. Radhakrishnan, P. Chambon, E. Cloutet and H. Cramail, *Colloid. Polym. Sci*., 281, 516, **2003**
14. E. Cloutet, B. Radhakrishnan and H. Cramail, *Polym. Int*., 51, 978, **2002**
15. P. Chambon, A. Chemtob, E. Cloutet, H. Cramail, S. Gibanel, Y. Gnanou, V. Heroguez, D. Quemener and B. Radhakrishnan, *Polym. Int.*, 55, 1146, **2006**
16. J. Liu, C. H. Chew, L. M. Gan, W. K. Teo and L. H. Gan, *Langmuir*, 13, 4988, **1997**
17. F. Bai, X. Yang, Y. Zhao and W. Huang, *Polym. Int*. 54, 168, **2005**
18. F. Bai, X. Yang and W. Huang, *Macromolecules*, 37, 9746, **2004**
19. J. Huang, S. Wan, M. Guo and H. Yan, *J. Mater. Chem*., 16, 4535, **2006**
20. B. Radhakrishnan, ñ*Elaboration En Milieu Disperse De Materiaux Polyurethane A Structure Coeur – Ecorce",* Ph. D. Thesis, Universite´ Bordeaux 1, France, **2003**

M. A. Winnik, M. D. Croucher and G. Riess, *Eur, Polym. J.* 30, 121, **1994**

22. P. Chambon, E. Cloutet, H. Cramail, T. Tassaing and M. Besnard, *Polymer*, 46, 1057**, 2005**

23. L.S. Ramanathan, P. G. Shukla and S. Sivaram, *Pure & Appl. Chem*., 70, 1295, **1998**

Chapter 8. Summary and Conclusions

The synthesis of chain-end-functionalized polymers is of great importance due to the fact that they have various practical and potential applications such adhesives, sealants, reactive compatibilizers, etc. One of the important applications of end-functionalized polymers is their demonstrated utility as building blocks for synthesis of block, graft and star copolymers.

The main objective of the research work was to design and synthesize functionalized ATRP initiators and utilize these initiators for synthesis of functionally-terminated polymers and macromonomers. The second objective was to synthesize block and graft copolymers using ATRP or combination ATRP and ROP techniques. The third objective was to study the utility of dihydroxyl-terminated macromonomers, PEO-*b*-PLMA and PLMA-*g*-PEO copolymers as steric stabilizers in preparation PU microspheres.

A hydroxyl functionalized ATRP initiator namely, 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate was prepared by reaction of commercially available 1,4-benzene dimethanol with 2-bromoisobutytryl bromide.

Protected dihydroxyl functionalized initiator namely, 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl-2-bromo-2-methylpropanoate) was synthesized starting from trimethylol propane.

A new dihydroxyl functionalized ATRP initiator namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate was obtained by deprotection of 5-ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl-2-bromo-2-methylpropanoate) in presence of dilute hydrochloric acid.

A novel bismethylol functionalized ATRP initiator namely, 3,5-bis(hydroxymethyl)phenyl 2-bromo-2-methylpropanoate was successfully synthesized starting from commercially available 5-hydroxy isophthalic acid.

A new nitro functionalized ATRP initiator namely, 4-[(4ô-nitro)phenoxymethyl] benzyl bromide was synthesized by reaction of 4-nitrophenol with 1,4-bis(bromomethyl) benzene.

containing dicarboxylic acid functionality viz., 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid and 5-(2-bromo-2-methylpropanamido) isophthalic acid were synthesized by reaction of 2-bromoisobutyryl bromide with 5-hydroxyisophthalic acid and 5-aminoisophthalic acid, respectively.

A new lactone functionalized ATRP initiator namely, 4-[2-(7-oxooxepan-3-yl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate was synthesized starting from hydrogenated bisphenol A (HBPA).

A new cyclic carbonate functionalized ATRP initiator namely, 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) was synthesized by reaction of commercially available glycerol carbonate with 2-bromoisobutyryl bromide.

A new sulfonic acid functionalized ATRP initiator namely, 4-(2-bromo-2-methylpropanoloxy) benzenesulfonic acid was synthesized by reaction of commercially available 4-hydroxy sulphonic acid with 2-bromoisobutyryl bromide.

Thus, a total of ten functionalized ATRP initiators were designed and synthesized starting from commercially available chemicals. ATRP initiators and the intermediates involved in their synthesis were characterized by spectroscopic techniques such as FTIR, ^{1}H-NMR and ^{13}C-NMR spectroscopy.

These functionalized ATRP initiators were utilized in the synthesis of low molecular weight end-functionalized polymers and macromonomers.

Hydroxyl-terminated polystyrene was synthesized by ATRP using 4-(hydroxymethyl)benzyl 2-bromo-2-methylpropanoate as initiator in presence of CuBr/2,2ô-bipyridine as a catalyst. Low molecular weight (M_n^{GPC} ï 1980 to 9670) hydroxyl-terminated polystyrenes were obtained with narrow MWD (M_w/M_n = 1.07 - 1.33) and initiator efficiency was in the range 0.65 to 0.88.

Dihydroxyl-terminated PLMAs were successfully synthesized by ATRP using 5-ethyl-2,2-dimethyl 1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) as initiator in presence of CuBr/PMDETA as the catalyst. The low molecular weight dihydroxyl-terminated PLMAs (M_n^{NMR} ï 3810 to 11170) were obtained with narrow MWD (M_w/M_n = 1.23-1.29) and initiator efficiency was in the range 0.80 to 1.05.

henyl 2-bromo-2-methylpropanoate was demonstrated as a useful initiator for synthesis of novel bismethylol-terminated poly(methyl methacrylate) and poly(lauryl methacrylate). The molecular weight of bismethylol-terminated poly(methyl methacrylate) was in the range 3320 to 20000 (M_n^{NMR}) and the MWD was narrow (M_w/M_n - 1.18-1.24). The M_n^{NMR} of bismethylol-terminated of PLMAs were in the range 4060 to 27940 with narrow MWD (M_w/M_n - 1.12-1.19).

Low molecular weight (M_n^{NMR} ï 2400 and 3500) lactone-terminated polystyrenes with narrow MWD (M_w/M_n - 1.07 and 1.15) were synthesized by ATRP using 4-[2-(7-oxooxepan-3-yl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate as ATRP initiator and initiator efficiencies were 0.80 and 0.84, respectively.

Cyclic carbonate-terminated PMMAs were successfully synthesized by ATRP using 2-oxo-1,3-dioxolan-4-yl-(methyl 2-bromo-2-methylpropanoate) as initiator in presence of CuCl/PMDETA as a catalyst. The molecular weight of cyclic carbonate-terminated PMMAs were in the range 1740 to 6260 (M_n^{NMR}) with narrow MWD (M_w/M_n ï 1.16-1.24) and initiator efficiency was in the range 0.72 to 0.99. The reactivity of cyclic carbonate-terminated PMMA towards amine was evaluated by a model reaction using n-propyl amine and the results showed quantitative conversion to hydroxy urethane group.

Thus, new functionalized ATRP initiators were successfully demonstrated in the synthesis of end-functionalized polymers such as polystyrene, PMMA and PLMA.

Well-defined diblock (PEO-*b*-PLMA) copolymers were synthesized using monofunctional PEO macroinitiators of varying number average molecular weight (M_n^{NMR} - 470, 790, 2450 and 6120) for polymerization of lauryl methacrylate by ATRP using copper /PMDETA as catalyst. GPC and ^{1}H-NMR analysis confirmed the formation of block copolymers. Molecular weight of the block copolymer, determined by ^{1}H-NMR spectroscopy, was slightly higher than theoretical molecular weight. The molecular weight distribution was in the range 1.18 to 1.36.

PLMA-*b*-PEO-*b*-PLMA triblock copolymer was synthesized using difunctional PEO macroinitiator using CuCl/PMDETA as catalyst. The difunctional Br-PEO-Br macroinitiator was derived from commercially available poly(ethylene glycol) of M_n ï 20,000. The

(M_n^{NMR}) of PLMA-*b*-PEO-*b*-PLMA agreed well with theoretical molecular weight and MWD was narrow (M_w/M_n – 1.26).

PS-*b*-PCL was synthesized by ring opening polymerization of ε-caprolactone using hydroxyl-terminated polystyrene as macroinitiator in the presence of stannous octanoate as catalyst. Good agreement between the experimental (M_n^{NMR}) and theoretical molecular weight (M_n^{th}) was observed and the MWD was in the range 1.26 to 1.44.

A novel AB_2 mikto arm star cpolymer PMMA-b-$(PCL)_2$ was synthesized by ring opening polymerization of ε-caprolactone using bismethylol-terminated PMMA as macroinitiator in presence of stannous octanoate as catalyst. The formation of mikto arm star copolymer was confirmed from GPC and ^{1}H-NMR spectroscopy. However, control over molecular weight was poor and the molecular weight distributions obtained were relatively broad (MWD = 1.39 to 1.49).

Amphiphilic PLMA-*g*-PEO copolymer was synthesized *via* ñgrafting throughò approach by conventional free radical copolymerization of PEO methacrylate macromonomer and lauryl methacrylate using AIBN as an initiator. Incorporation of PEO macromonomer in the resulting copolymer was low.

Polycaprolactone containing ATRP initiating sites was synthesized by ring opening copolymerization of ε-caprolactone and 4-[2-(7-oxooxepan-3-yl) propan-2-yl]cyclohexyl 2-bromo-2-methyl propanoate using stannous octanoate as catalyst. PCL macroinitiator containing pendent ATRP initiator functionality was successfully utilized for the synthesis of PCL-*g*-PMMA in presence of CuCl/PMDETA as catalyst. The graft copolymers exhibited MWD in the range 1.36 to 1.71.

Two new polyurethane macroinitiators were synthesized from commercially available doils viz., ethylene glycol, poly(prolylene glycol) and a newly synthesized diol namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate by reaction with diisocyanate. PUM_2 macroinitiator was demonstrated as useful ATRP macroinitiator for the synthesis of PU-*g*-PLMA copolymer.

The efficacy of PEO-*b*-PLMA, PLMA-*g*-PEO and hydroxyl-terminated PLMA as steric stabilizers in preparation of PU microspheres by dispersion polymerization of 2-ethyl-1,3-hexane diol and 2,4-toluene diisocyanate was examined. PU microspheres were

(PEO-*b*-PLMA) with anchor moiety (PEO ï 350 and 700) did not produce PU microspheres, on the other hand, PEO-*b*-PLMA with anchor moiety (PEO ï 2000 and 5000) did produce PU microspheres in sizes ranging from 1 to 20 micrometers. The balance between the PEO and PLMA segments was crucial for the formation of PU microspheres.

Graft copolymers (PLMA-*g*-PEO) with anchor moiety (PEO - 1100) were successfully utilized to produce spherical and smaller PU microspheres at 10% and 15% stabilizer concentration, while, graft copolymer having anchor moiety (PEO - 2000 and 5000) were found to be an effective steric stabilizer even at lower stabilizer concentration (1 wt %). Graft copolymer stabilizer with PEO of Mn ï 2000, produced PU microspheres with narrow particle size distribution ranging from 0.31 to 1.45 micrometers.

Dihydroxyl-terminated PLMAs and bismethylol-terminated PLMA were employed as reactive steric stabilizers in dispersion polymerization. Hydroxyl group of PLMA macrodiol being less reactive as compared to 2-ethyl-1,3-hexane diol necessitated the conversion of hydroxyl group to isocyanate. Dihydroxyl-terminated PLMA and bismethylol-terminated PLMA were shown to be efficient reactive stabilizers in preparation of polyurethane microspheres. The effect of molar mass of dihydroxyl-terminated PLMA on polyurethane microspheres was studied; the increase in molar mass of PLMA chain resulted in decrease in the polyurethane particle size at constant stabilizer concentration.

The present work on design and synthesis of new functionalized ATRP initiators, end-fuctionalized polymers and copolymers (block and graft) has opened up many new prospects for the future work.

- The present work on synthesis of new ATRP initiators has expanded the range of functionalized ATRP initiators available for the synthesis of end-functionalized polymers and macromonomers.
- ATRP initiators containing dicarboxylic acid functionality viz., 5-(2-bromo-2-methylpropanoyloxy) isophthalic acid and 5-(2-bromo-2-methylpropanamido) isophthalic acid are potentially useful for synthesis of a host of high performance polymers such as (co)polyamides, and (co)polyesters by polycondensation with commercially available aromatic diamines and diphenols, respectively. Polyamides and polyesters containing pendant ATRP initiator functionality could be further utilized for initiation of controlled radical polymerization of styrene or alkyl methacrylates to obtain corresponding graft copolymers
- Dihydroxyl-terminated polymers synthesized using 5-ethyl-2,2-dimethyl 1,3-dioxan-5-yl-(methyl 2-bromo-2-methylpropanoate) as initiator could be modified into ATRP macroinitiator by reaction with 2-bromoisobutyryl bromide and resulting macroinitiator could subsequently be utilized for the synthesis of AB_2 type mikto arm star copolymers.
- Mikto arm star AB_2 type copolymer [PMMA-b-$(PCL)_2$] is potentially useful as a compatibilizer for blend of PMMA and polycarbonate.
- A newly synthesized copolymer of ε-caprolactone and 4-[2-(7-oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate could be utilized in synthesis of graft copolymers with different polymeric branches such as polystyrene, PBA, PLMA, etc. These graft copolymers are potentially useful as compatibilizers for polymeric blends as well as in the modification of properties of polycaprolactone.

nopsis of the Thesis Entitled

"Controlled Synthesis of End-Functionalized Polymers and Block Copolymers"

Introduction

One of the main goals in modern synthetic polymer chemistry is to synthesize polymers with predetermined molecular weight, narrow molecular weight distribution and well-defined architecture. For this purpose, living polymerization methods which include anionic, cationic, group transfer and controlled radical polymerization have been developed and demonstrated to provide high degree of control for the synthesis of polymers.[1-7]

End-functionalized polymers and copolymers, in particular, block and graft copolymers are some of the most important materials due to their potential applications in several areas.[8] More specifically, end-functionalized polymers are useful as building blocks for synthesis of block, graft and star copolymers. These polymers also have potential applications in areas such as surface modification, coatings, adhesives, as well as compatibilization of polymer blends.[8, 9] Block and graft copolymers are very promising materials because of their ambivalent properties.[10] They find many applications in areas such as thermoplastics, associative polymers containing a hydrophilic and a hydrophobic segments, etc.[11] One of the most important applications of block copolymers at the industrial scale is their use as surfactants in pharmaceutical, oil, agriculture, paper and detergent industries.[12]

Amongst the controlled radical polymerization methods, Atom Transfer Radical Polymerization (ATRP) is a powerful technique to prepare polymers with predictable molecular weight and low polydispersity. The increasing interest in ATRP technique is due to relatively mild reaction conditions and a broad choice of monomers, initiators, catalysts, etc.[3-7] With this controlled radical polymerization method, a variety of polymer architectures and compositions is accessible, e.g., block copolymers, graft copolymers, and hyperbranched polymers.[3-7] Functional groups can also be introduced easily at the chain ends either through functionalized ATRP initiators or halogen replacement through nucleophilic substituion.[13]

The aim of the present work was to design and synthesize functionalized ATRP initiators, end-functionalized polymers and copolymers (block and graft) *via* combination of suitable polymerization techniques.

taining various functional groups such as hydroxyl, carboxyl, lactone, carbonate, nitro and sulphonic acid were designed and synthesized. These functionalized ATRP initiators were utilized for synthesis of end-functionalized polymers. The synthesized end-functionalized polymers were used in chain extension reactions to obtain block copolymers using appropriate polymerization techniques.

By keeping the above objectives in mind, the following specific work was selected for the present thesis.

1. Synthesis and characterization of ATRP initiators containing functional groups viz., hydroxyl, carboxyl, lactone, cyclic carbonate, nitro and sulphonic acid.
2. Synthesis and characterization of poly(lauryl methacrylate) (PLMA) and poly(styrene) (PS) containing hydroxyl groups at one end of the chain.
3. Synthesis and characterization of hydroxyl-terminated poly(methyl methacrylate) (PMMA) and PLMA macromonomers.
4. Synthesis and characterization of lactone and carbonate-terminated PMMA.
5. Synthesis and characterization of poly(ethylene oxide)-*block*-poly(lauryl methacrylate) (PEO-*b*-PLMA), poly(lauryl methacrylate)-*block*-poly(ethylene oxide)-*block*-poly(lauryl methacrylate) (PLMA-*b*-PEO-*b*-PLMA), poly(styrene)-*block*-poly(ε-caprolactone) (PS-*b*-PCL) and poly(methyl methacrylate)-*block*-[poly(ε-caprolactone)]$_2$ [PMMA-*b*-(PCL)$_2$].
6. Synthesis and characterization of poly(lauryl methacrylate)-*graft*-poly(ethylene oxide) (PLMA-*g*-PEO), poly(ε-caprolactone)-*graft*-poly(methyl methacrylate) (PCL-*g*-PMMA) and polyurethane-*graft*-poly(lauryl methacrylate) (PU-*g*-PLMA) using a combination of different polymerization techniques.
7. Synthesis and characterization of polyurethane microspheres utilizing PLMA-*g*-PEO, PEO-*b*-PLMA and hydroxyl-terminated PLMA as steric stabilizers.

ıto following eight chapters.

Chapter 1: Introduction and Literature Survey: Controlled Synthesis of End-Functionalized Polymers and Copolymers (Block and Graft)

A comprehensive review of literature on living radical polymerization methods, viz., ATRP, Reversible Addition Fragmentation chain Transfer Polymerization (RAFT) and Nitroxide Mediated Polymerization (NMP) is presented. Furthermore, a brief introduction to the synthesis of end-functionalized polymers and block copolymers by ATRP, RAFT and NMP is provided. An introduction to synthesis of block copolymers *via* combination of ATRP and ROP is also presented.

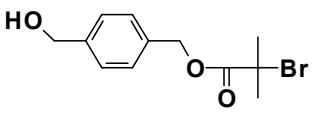
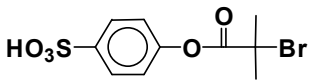
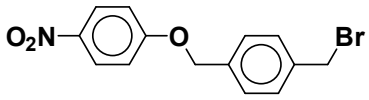
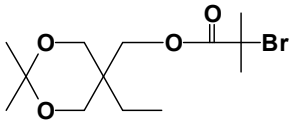
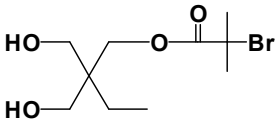
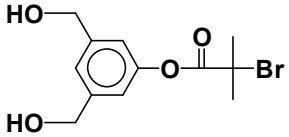
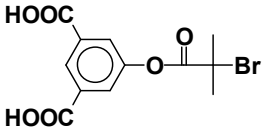
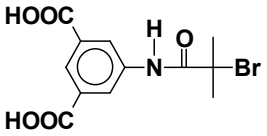
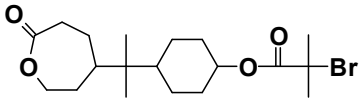
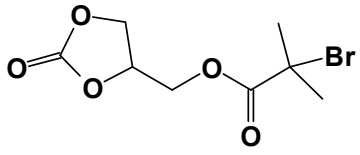
Chapter 2: Scope and Objectives

This chapter discusses scope and objectives of the thesis.

Chapter 3: Synthesis and Characterization of Functionalized Atom Transfer Radical Polymerization Initiators

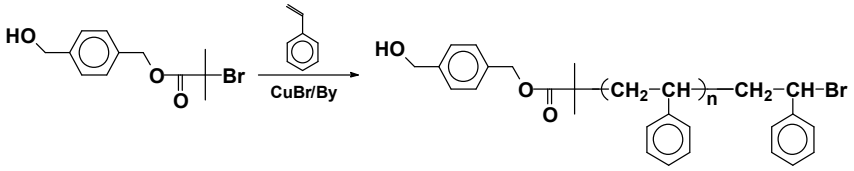
This chapter describes synthesis of functionalized ATRP initiators **(Table 1)**. Nine new ATRP initiators were synthesized.

Initiators Synthesized

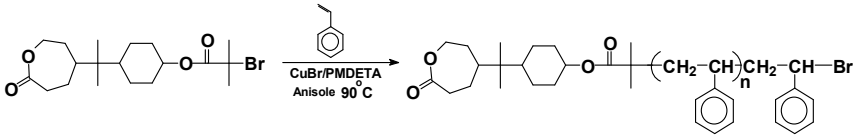
1	4-(Hydroxymethyl)benzyl-2-bromo-2-methylpropanoate **(HMBMP)**	
2	4-(2-Bromo-2-methylpropanoloxy) benzenesulfonic acid **(BMPBSA))**	
3	4-[(4ô-Nitro) phenoxymethyl] benzyl bromide **(NPMBB)**	
4	5-Ethyl-2,2-dimethyl-1,3-dioxan-5-yl-(methyl-2-bromo-2-methylpropanoate) **(EDMBMP)**	
5	2,2-Bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate **(BHMBMP)**	
6	3,5-Bis(hydroxymethyl)phenyl-2-bromo-2-methylpropanoate **(BHMPBMP)**	
7	5-(2-Bromo-2-methylpropanoyloxy) isophthalicacid **(BMPIPA)**	
8	5-(2-Bromo-2-methylpropanamido) isophthalicacid **(BMPAIPA)**	
9	4-[2-(7-Oxooxepan-3-yl) propan-2-yl] cyclohexyl 2-bromo-2-methyl propanoate **(OPCBMP)**	
10	2-Oxo-1,3-dioxolan-4-yl-(methyl-2-bromo-2-methylpropanoate) **(ODMBMP)**	

Chapter 4: Synthesis and Characterization of End-functionalized Polymers by Atom Transfer Radical Polymerization

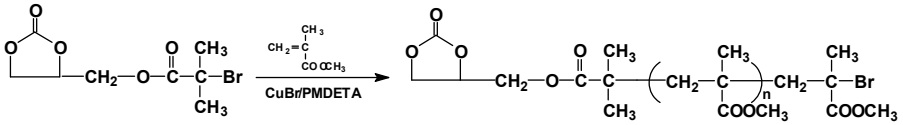
This chapter discusses synthesis of end-functionalized polymers, viz., PMMA, PLMA and PS using the synthesized ATRP initiators **(Scheme 1 to 4)**. End-functionalized polymers were characterized by fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and size exclusion chromatography (SEC).



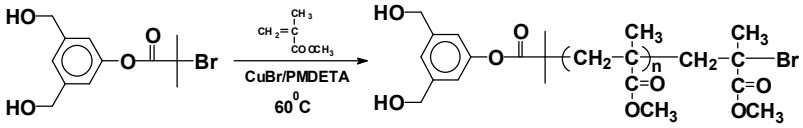
Scheme 1: Synthesis of hydroxyl-terminated polystyrene



Scheme 2: Synthesis of lactone-terminated polystyrene



Scheme 3: Synthesis of carbonate-terminated polymethyl methacrylate

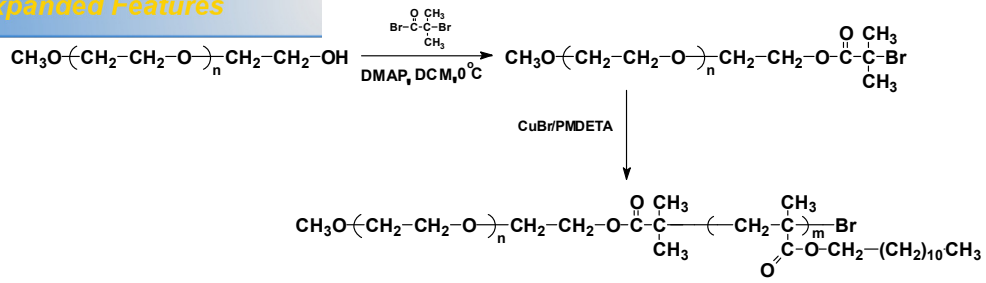


Scheme 4: Synthesis of hydroxyl-terminated PMMA macromonmer

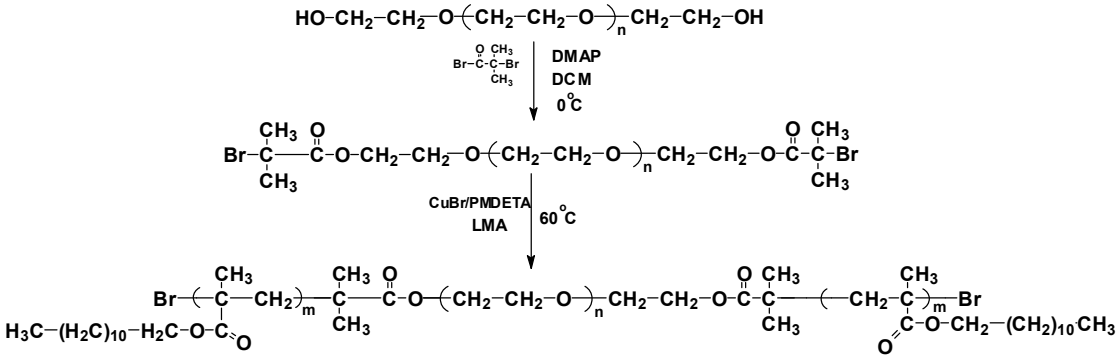
Chapter 5: Synthesis and Characterization of Block Copolymers by Combination of Atom Transfer Radical Polymerization and Ring Opening Polymerization

This chapter describes:

A) Synthesis of PEO-*b*-PLMA and PLMA-*b*-PEO-*b*-PLMA by ATRP using poly(ethylene oxide) (PEO) macroinitiators of different molecular weights **(Scheme 5 and 6)**.

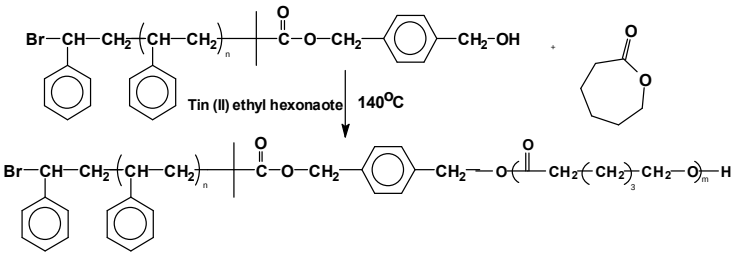


Scheme 5: Synthesis of PEO-*b*-PLMA diblock copolymer



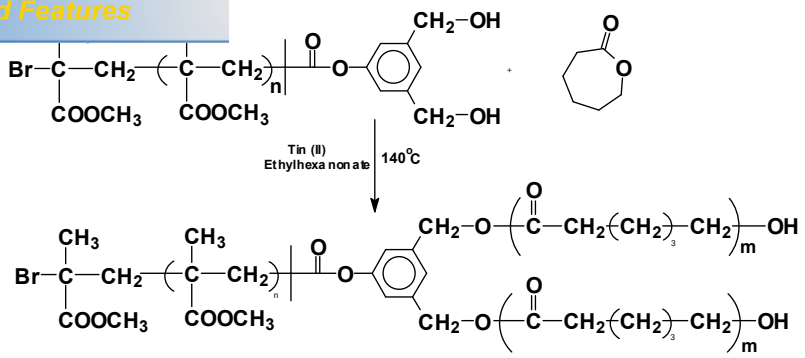
Scheme 6: Synthesis of PLMA-*b*-PEO-*b*-PLMA triblock copolymer

B) PS-*b*-PCL is a diblock copolymer potentially useful as a compatibilizer for SAN/ABS/PVC/PC/PS/PCL blends.[14] It was synthesized by ROP of ε-caprolactone using hydroxyl-terminated PS which in turn was synthesized by ATRP **(Scheme 7)**.



Scheme 7: Synthesis of PS-*b*-PCL diblock copolymer

C) Miktoarm star copolymers are a special class of nonlinear block copolymers where arms of the different polymer segment are linked to the same branch point.[11] Miktoarm star copolymer [PMMA-*b*-$(PCL)_2$] was synthesized using bismethylol-terminated PMMA as a macroinitiator for ROP of Ü-caprolactone in presence of stannous octanoate as a catalyst **(Scheme 8)** .

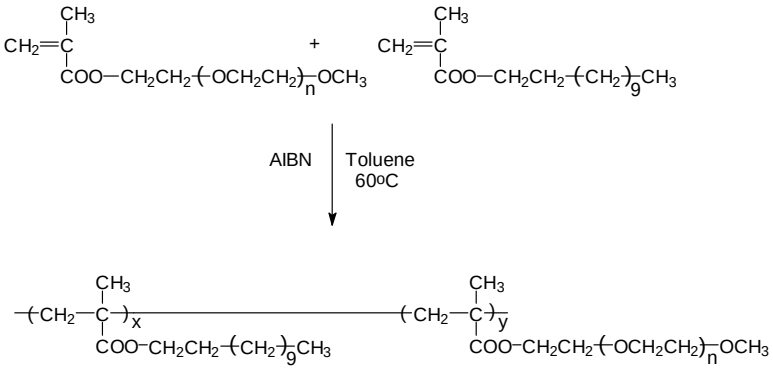


Scheme 8: Synthesis of PMMA-*b*-(PCL)$_2$ star copolymer

Chapter 6: Synthesis and Characterization of Graft Copolymers by Combination of Atom Transfer Radical Polymerization and Ring Opening Polymerization

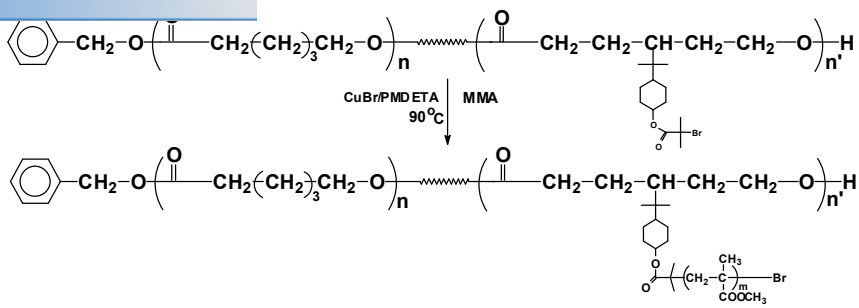
This chapter describes:

A) Synthesis of PLMA-*g*-PEO *via* macromonomer approach, in which PEO methacrylate macromonomer was copolymerized with lauryl methacrylate by conventional free radical polymerization using azobisisbutyronitrile as a radical initiator **(Scheme 9)**.



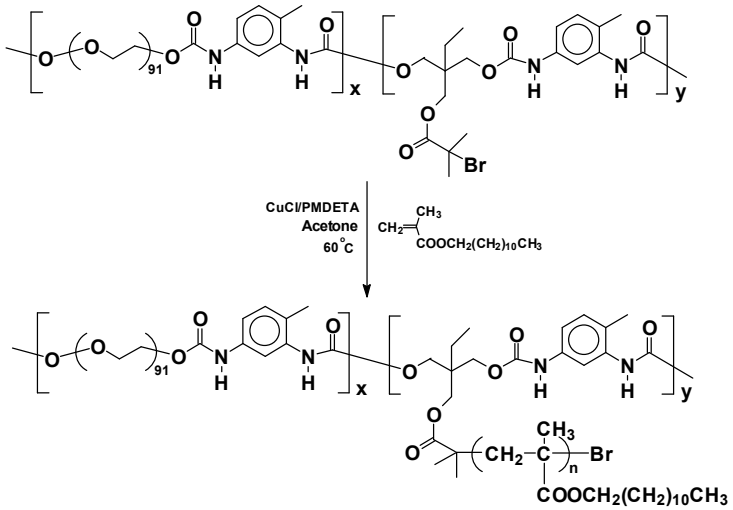
Scheme 9: Synthesis of PLMA-*g*-PEO *via* "grafting through" approach

B) PCL and its copolymers possess excellent biocompatibility and permeability and hence find application as biomaterials.[15] To modify the properties of PCL, introduction of functional groups and grafting of other polymers onto PCL is utilized.[16-18] Lactone containing ATRP initiator was copolymerized with ε-caprolactone to achieve PCL macroinitiator for ATRP. Using PCL macroinitiator, PCL-*g*-PMMA was synthesized by ATRP **(Scheme 10)**.



Scheme 10: Synthesis of PCL-*g*-PMMA *via* "grafting from" approach

C) Polyurethane-*graft*-poly(alkyl (meth)acrylate) (PU-*g*-PAM) was synthesized in two steps. In the first step, PU macroinitiators were synthesized from commercially available doils viz., ethylene glycol, poly(prolylene glycol) and a newly synthesized diol namely, 2,2-bis(hydroxymethyl)butyl 2-bromo-2-methyl propanoate with isophorone diisocyanate or toluene diisocyanate. In the second step, ATRP of alkyl methacrylate using PU macroinitiator was carried out to obtain PU-*g*-PAM **(Scheme 11)**.



Scheme 11: Synthesis of PU-*g*-PLMA *via* "grafting from" approach

Chapter 7: Preparation of Polyurethane Microspheres Utilizing PEO-*g*-PLMA, PEO-*b*-PLMA and Hydroxyl-Terminated PLMA as Steric Stabilizers

This chapter describes applications of PLMA-*g*-PEO, PEO-*b*-PLMA, and hydroxyl-terminated PLMA as a steric stabilizer in the preparation of polyurethane microspheres.

Chapter 8: Summary and Conclusions

This chapter summarizes the results, salient conclusions and future prospects of the work reported in the thesis.

References:

1. J. I. Kroschwitz, *Encyclopedia of Polymer Science and Engineering,* Wiley-Interscience, New York, USA, pp. 380, **1989**
2. D. Baskaran, *Prog. Polym. Sci*., 28, 521, **2003**
3. O. W. Webster, *Adv. Polym. Sci.* 167, 1, **2004**
4. N. V. Tsarevsky and K. Matyjaszewski, *J. Polym. Sci. Part A Polym. Chem. Ed*., 44, 5098, **2006**
5. K. Matyjaszewski, and J. Xia, *Chem. Rev*., 101, 2921, **2001**
6. M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev*., 101, 3689, **2001**
7. W. A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci*. 32, 93, **2007**
8. P. F. Rempp and E. Franta, *Adv. Polym. Sci*., 58, 1, **1984**
9. C. Cheng, E. Khoshdel, K. L. Wooley, *Macromolecules*, 38, 9455, **2005**
10. G. Riess, *Prog. Polym. Sci*. 28, 1107, **2003**
11. N. Hadjichristidis, S. Pispas and G. Floudas, *Block Copolymers: Synthetic Strategies, Physical Properties and Applications*, John Wiley and Sons, New Jersey, **2003**
12. I. W. Hamley, editor, *Developments in Block Copolymer. Science and Technology,* New York: Wiley; **2004**
13. V. Coessens, T. Pintauer and K. Matyjaszewski, *Prog. Polym. Sci*. 26, 337, **2001**
14. I. D. McKay, *J. App. Polym. Sci.*, 42, 281, **1991**
15. R. Chandra and R. Rustgi, *Prog. Polym. Sci.*, 23, 1273, **1998**
16. M. Okada, *Prog. Polym. Sci*, 27, 87, **2002**
17. S. Lenoir, R. Riva, X. Lou, C. Detrembleur, R. Jerome and P. Lecomte, *Macromolecules*, 37, 4055, **2004**
18. D. Mecerreyes, B. Atthoff, M. Trollsas and J. L. Hedrick, *Macromolecules*, 32, 5175, **1999**

(Dnyaneshwar V. Palaskar)
Student

(Prakash. P. Wadgaonkar)
Research Guide

List of publications

1 Preparation of polyurethane microspheres using polymerizable stabilizer
Lalgudi S. Ramanathan, Parshuram G. Shukla, **Dnyaneshwar V. Palaskar**, and Swaminathan Sivaram
27th International Symposium on "Controlled Release of Bioactive Materials" Paris, France 2000 page no. 5010

2 Preparation and characterization of microcapsules of water-soluble pesticide monocrotophos using polyurethane as carrier material
Parshuram G. Shukla, B. Kalidhass, Anjali Shah and **Dnyaneshwa r V. Palaskar**
J. Microencapsul. 19, 293, 2002

4 Direct assembly of gold nanoparticle "shells" on polyurethane microsphere "cores" and their application as enzyme immobilization templates
Sumant Phadtare, A. Kumar, V.P. Vinod, C. Dash, **Dnyaneshwar V. Palaskar**, Mala Rao, Parshuram G. Shukla, Swaminathan Sivaram and Murali Sastry.
Chem. Mater, 15, 1944, 2003

5 Enhancing the reusability of endoglucanase-gold nanoparticle bioconjugates by tethering to polyurethane microspheres
Sumant Phadtare, S. Vyas, **Dnyaneshwar V. Palaskar**, Anil Lachke, Parshuram G. Shukla, Swaminathan Sivaram and Murali Sastry
Biotechnol. Prog. 20, 1840, 2004

6 Synthesis of amphiphilic block and graft copolymers of poly(ethylene oxide) and poly(lauryl methacrylate) and their utilization as steric stabilizer in preparing polyurethane microspheres in non-aqueous medium

ar, Lalgudi S. Ramanathan, Parshuram G. Shukla and Prakash P. Wadgaonkar
Manuscript under preparation

7 A New Atom Transfer Radical Polymerization Initiator for Synthesis of Cyclic Carbonate-Terminated Poly(methyl methacrylate)
Dnyaneshwar V. Palaskar and Prakash P. Wadgaonkar
Manuscript under preparation

8 Synthesis of lactone-terminated polymers by ATRP and PCL-*g*-PMMA graft copolymers *via* grafting from approach
Dnyaneshwar V. Palaskar and Prakash P. Wadgaonkar
Manuscript under preparation

9 Synthesis and characterization of PU-*g*-PLMA *via* grafting from approach
Dnyaneshwar V. Palaskar and Prakash P. Wadgaonkar
Manuscript under preparation

Posters and Presentations

1 Preparation of amphiphilic graft copolymers PLMA-g-PEO and their use as a steric stabilizer for the preparation of polyurethane microspheres in non-aqueous medium
Dnyaneshwar V. Palaskar, Parshuram G. Shukla and Prakash P. Wadgaonkar
Macro-2002 (Seventh National Conference of the Society for Polymer Science, India) International Seminar on " Frontiers of Polymer Science and Engineering" December 9-11, 2002, IIT, Kharagpur

2 Amphiphilic block copolymers synthesized by ATRP: Two-dimensional self-assembly at air-water interface

ar, Rahul D. Shingte, Jennifer L. Logan, Shenda M. Baker and Prakash P. Wadgaonkar

IUPAC symposium on "Ionic Polymerization 2005" The Leela, Goa, 23-28 October 2005