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Synthesis of Well-Defined Reactive End- and Mid-Functional Polystyrene by Atom Transfer Radical Polymerization

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Synthesis of Well-defined Reactive End- and Mid-functional Polystyrene by Atom Transfer Radical Polymerization

M.Phil Thesis

A Dissertation

In Partial Fulfillment of the Requirements for the Degree of Master of Philosophy in Chemistry

SUBMITTED BY

Md. Samiul Islam Chowdhury

Examination Roll No: 12204

Registration No.: 1196

Session: 2012-2013

MOTIHAR GREEN
RAJSHAHI
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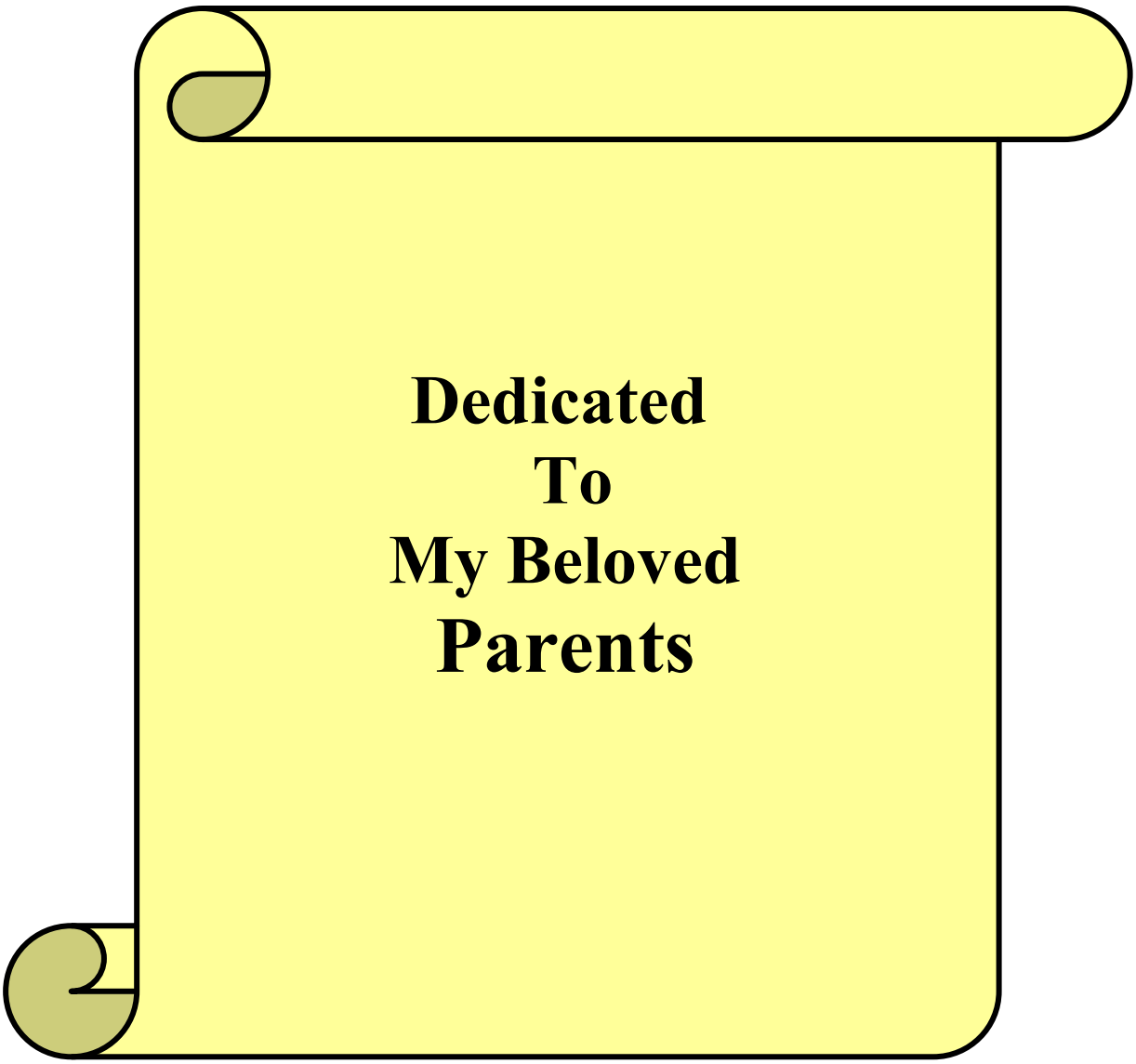
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF RAJSHAHI
RAJSHAHI-6205


Dedicated
To
My Beloved
Parents

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Md. Samiul Islam Chowdhury

ABSTRACT

Functional groups increase the utility of polymers and are fundamental to the development of many aspects of structure-property relationships. Reactive end- and mid-functionality play an important role in the properties of polymers and they allow the polymer to couple with other functionalities forming graft, blocks, cross-linking. Control over the synthesis of blocks and grafts the polymer architectures has become increasingly important in producing high value added materials for nanotechnology, biomaterials, blend modifiers and improving particular polymer properties by self-assembly. The end- and mid-functional polymers can be prepared by modifying end- and mid-group of polymers or most conveniently, by using functional initiators in living/controlled polymerization. Recently a method of living/controlled radical polymerization, atom transfer radical polymerization (ATRP) is versatile enough to synthesize end- and mid-functional polymers by using functional initiators.

Various α-haloesters have been successfully employed for Cu(I) mediated ATRP to synthesize functional polymers. Structural adjustment of the initiator provides a handle to fine-tune the rate of initiation in the ATRP system and functionality of end- and mid-group. Therefore, in this study, five new α-bromoester initiators bearing allyl, alkyne and dioxolane groups were synthesized and the polymerizations of styrene were carried out with Cu(I)-bypridine mediated ATRP by using those initiators for synthesis of polystyrene containing end- and mid-functionality.

This thesis includes seven chapters. The content of each chapter is as follows:

In chapter I, **general introduction** including **literature review** and **objective** of this research were discussed.

In chapter II, initiator N-allyl-2-bromopropinamide (**N-ABPN**) was synthesized and the structure of **N-ABPN** was characterized by ^{1}H and ^{13}C NMR analysis. The efficiency of **N-ABPN** as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at various reaction conditions. The molecular weight and molecular weight distribution of the polystyrene were determined by gel permeation chromatography (GPC). The structure of the polystyrene obtained with **N-ABPN** was characterized by NMR analysis.

In chapter III, synthesis and characterization of an initiator undecenyl-2-bromopropionate (**UBP**) was discussed. The efficiency of **UBP** as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at various reaction conditions. The molecular weight and molecular weight distribution of the polystyrene were determined by gel permeation chromatography (GPC). The structure of the polystyrene obtained with this catalyst system was determined by NMR analysis.

In chapter IV, synthesis and characterization of an initiator 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester **(BPE)** and 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl diester **(BPDE)** were discussed.

In chapter V, the efficiency of 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester **(BPE)** as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at different time duration. The molecular weight and molecular weight distribution of the polystyrene were determined by gel permeation chromatography (GPC). The structure of the polystyrene obtained with this catalyst system was determined by NMR analysis.

In chapter VI, the efficiency of 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl diester **(BPDE)** as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at different time duration. The molecular weight and molecular weight distribution of the polystyrene were determined by gel permeation chromatography (GPC). The structure of the polystyrene obtained with this catalyst system was determined by NMR analysis.

In chapter VII, initiator 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4-ylmethyl]ester (**BPDME**) was synthesized and characterized by spectral analysis. The polymerization of styrene was investigate by Cu(I)-bipyridine mediated ATRP using **BPDME** as initiator at various reaction conditions. The molecular weight and molecular weight distribution of the polystyrene were determined by gel permeation chromatography (GPC). The structure of the polystyrene obtained with **BPDME** was characterized by NMR analyses. Finally the end dioxolane group was converted to end-dihydroxyl group by Chemical reaction and the product was characterized by NMR analysis.

In chapter VIII, the results obtained in this study were summarized.

CONTENTS

CHAPTER I

Introduction

INTRODUCTION

1.1. General Introduction

Free-Radical polymerization is one of the most common and convenient ways of synthesizing polymers on an Industrial scale and has become an important process for the commercial production of high molecular weight polymer, with approximately 70% of vinyl polymers.[1,2] Various functional polymers are also being produced this way. Its versatility stems from several factors.[1,3]

(a) -tolerance to impurities, unprotected functionality in monomer and solvent and to trace amounts of oxygen and water,

(b) –the capability of polymerizing a wide range of monomers [e.g. styrene, vinyl acetate, methylacrylates, methylacrylamides, with a range of functional groups (e.g. COOH, OH, NR_2, $CONR_2$)

(c) –Its compatibility with a wide range of reaction conditions (it can be conducted under emulsion, suspension as well as a standard bulk and solution conditions.

(d) - The relative simplicity and low cost of implementation.

These factors give free-radical polymerization a competitive advantage over other techniques such as group transfer and ionic polymerization, which require ultra-pure reagents, anhydrous conditions and work with only a limited range of commercially interesting monomers. However, there are some associated disadvantages of free radical polymerization which include macromolecular architecture, copolymer compositions and the broad molecular weight distributions (MWDs) that can only be controlled to a limited extent by choosing the initiator concentration or through the use of transfer agents. Furthermore, the control of polymer architecture and the synthesis of block,

graft and end-functional polymers with chain length, composition and composition distribution remain difficult. This inability to precisely control the microstructure of the polymer chain restrict the control the macroscopic properties of the bulk polymers. These are now the most important problems.

These limitations have been mostly dissolved with the advent of living radical polymerization (LRP). There are currently three main techniques:

(a) Nitroxide Mediated polymerization (NMP),[4, 5]

(b) Atom Transfer Radical Polymerization (ATRP)[6] and

(c) Reversible Addition Fragmentation Chain Transfer (RAFT)[5,7].

These methods seek to combine the robustness and versatility of radical polymerization with the structural control of living polymerization. Out of these three main LRP techniques, ATRP is arguably the most versatile and convenient system because of many functional groups likes allyl, amino, epoxy, hydroxyl and vinyl groups present in the initiator.

Living radical polymerization techniques are readily applied to the synthesis of end-functional polymers. In an ideal living radical system all chain ends are retained and no new chains are formed and therefore are inherently pertinent to the introduction of end-functionality to radical polymers. Two main processes can be distinguished as α- and ω- end-fictionalization. These methodologies hold relevance to the design of the functional initiators (the alkoxyamines for NMP or the halo-compound for ATRP) and chain transfer agents (in the case of RAFT). They may be designed with a view to directly providing the polymer chains with the desired functionality or indirectly by transformation of dormant polymer chain ends post-polymerization. Chain functionality can thus be introduced into the polymer by adjusting the structure of the functional initiator or chain transfer agent.

There are many issues and synthetic implications to consider as each method has its own mechanistic limitations and complexities. Finding a system which provides an end-functional polymer with controlled molecular weights, polydispersities whilst minimizing any compromises in end-group purity and therefore eventual properties, for whatever application, can be a fundamental investigation in itself.

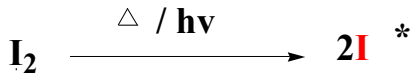
Recent developments in the production of segmented polymers using controlled or living polymerization techniques have resulted in the ability to make new materials by manipulation of new arrangements and building blocks of known monomers segments. The advent of controlled free radical polymerization has also allowed the production of materials that have only previously been possible via rigorous polymerization methods such as anionic polymerization.

Living radical polymerization techniques immediately lend themselves to the synthesis of block graft (segmented) and star copolymers by the production and exploitation of controlled end-functional polymers.

1.2. Literature Review

1.2.a. Radical Polymerization

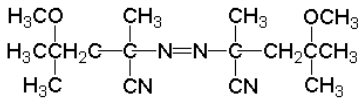
Free radical polymerization is a method of polymerization by which a polymer forms by the successive addition of free radical building blocks. Conventional free radical polymerization is a chain reaction which comprises three main processes; initiation, propagation and termination.[1] An additional process, chain transfer, also occurs under certain conditions. Initiation involves at least two-steps. The first is the formation of primary radicals (I*). This usually involves the decomposition of an initiator (I) by thermolysis or photolysis to produce radicals in pairs as shown in Scheme 1.1. However, primary radicals can also be formed by a redox reaction.



Scheme 1.1. Initiation by either thermolysis of photolysis.

The second step is the addition of the radicals (I*) to the vinyl monomer to initiate propagation by formation of I-M*, so that the polymer starts to grow. The primary radicals can also undergo termination by combination or disproportionation with each other or with other radicals leading to an overall loss in radicals and a reduction in initiator efficiency. When they react with propagating radicals the reaction is called primary radical termination. The primary radicals can also undergo fragmentation or rearrangement to produce secondary radicals which can react by similar pathways.

Some common initiators used in radical polymerization are the azo-initiators, for example, 2,2'-Azobis(4-methoxy-2.4-dimethyl valeronitrile) (1), water soluble initiators 2,2'-Azobis[2-(2-imidazolin-2-yl)propane] (2), 4,4′-azobis(4-cyanovaleric acid) (3) . Peroxide initiators are also quite commonly used, examples including, 1,1-Bis(*tert*-amylperoxy)cyclohexane (4**),** 2-Butanone peroxide (5) and Bis(1-methyl-1-phenylethyl) peroxide (6).



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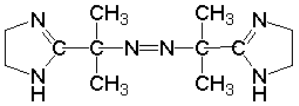

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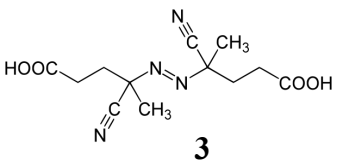

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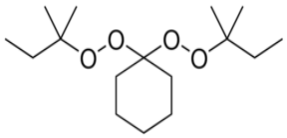

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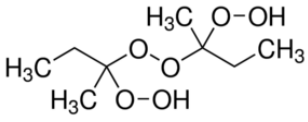

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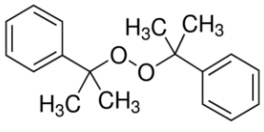

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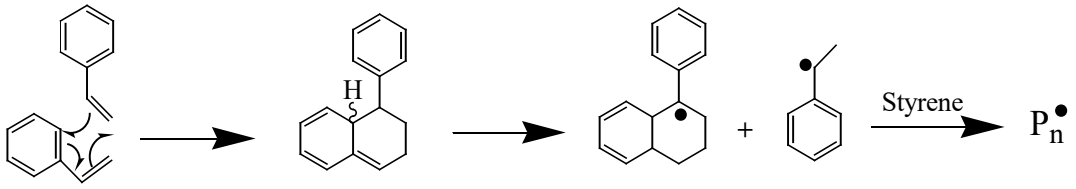
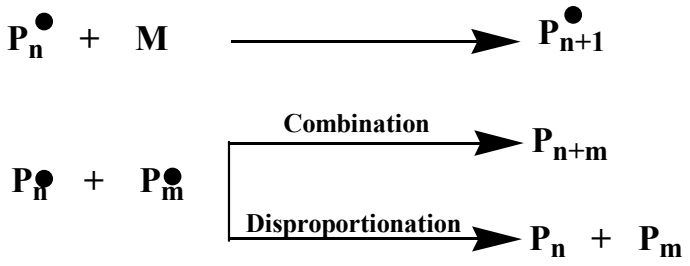
Some monomers, like styrene, also undergo thermally initiated polymerization by monomer derived radicals without the need of added initiator (scheme 1.2).



Scheme 1.2. Initiation of styrene by thermal Diels-Alder reaction, hydrogen donation and formation of the initiating radical (Mayo mechanism).

Propagation involved sequential addition monomer to the polymeric radical (P_n*) to produce a new polymeric radical (P_{n+1}*), one repeat unit longer (Scheme 1.3). The propagation process is repeated over and over to increase the chain length of the polymer. The majority of propagation events occur as "head-to-tail" addition, where the attacking radical adds to the least-substituted-end of the monomer double bond.



Scheme 1.3. Propagation and termination (radical-radical combination and disproportionation).

Termination is the process by which radicals are irreversibly destroyed, to leave an inactive or 'dead' polymer. This process can occur by either combination of two radicals to provide a polymer with the length equal to the sum of the two radicals or by disproportionation, to produce two polymer chains of the same length as the original radicals, (as shown in Scheme 1.3). Desproportionation, however, involves hydrogen atom transfer from one radical to the other, leaning an unsaturated end-group on one of the polymer

chains. This may react further if attacked by another radical. Overall the radical concentration is reduced thus terminating the chain reaction. For an ideal radical polymerization the molecular weight distribution (MWDs) or polydispersity (PD*) will be 2 for termination by disproportionation or chain transfer, or 1.5 for termination by combination.[1]

[*Polydispersity (PD) is the ratio of the weight average M_w to the number average molecular weights M_n:

$$PD = M_w / M_n$$

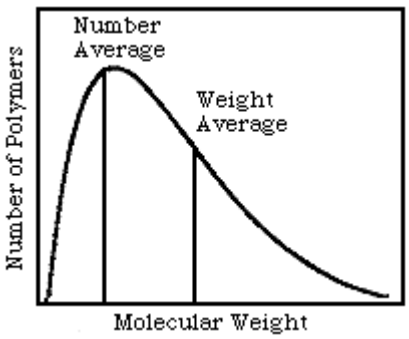
- The number average molecular weight or molar mass is simply the total weight of the sample divided by the number of molecules in the sample:

$$M_n = \overline{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}.$$

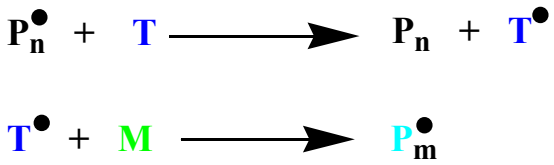
Where n_i is the number of chains of length i, w_i is the weight of chains of length i and M_i is the molecular weight of a chain of length i.

– The weight average molecular weight is the sum of the weights of chains of each molecular weight multiplied by their molecular weight divided by the total weight of the sample:

$$M_w = \overline{M}_w = \frac{\sum w_i M_i}{\sum w_i} = \frac{\sum n_i M_i^2}{\sum n_i M_i}.$$



Chain transfer, first recognized by Flory in 1937, terminates a propagating radical but does not terminate the chain reaction since there is no overall change in the radical concentration. A new radical is formed which can reinitiate propagation. As shown in Scheme 1.4 the propagating radical (P_n*) reacts with a transfer agent (T) to terminate one chain and leave a radical (T*) which can reinitiate a new monomer to produce another radical (P_m*). Transfer agents are usually used to control polymerization by lowering the molecular weight and the rate of polymerization and can also be used to control the nature of the end-group.



Scheme 1. 4. Chain transfer of radical from growing polymer chain to another molecule (e.g. solvent, monomer).

The steps of conventional radical polymerization, outlined above, occur concurrently and the time it takes for an individual polymer chain to be initiated, to propagate and then to terminate is of the order of seconds. However, the consumption of monomer can take from minutes to days. In order to consume the monomer to high conversion a continuous supply of radicals is required to maintain a relative constant radical concentration. This has the consequence of firstly forming high molecular weight material even during the initial stages of the reaction (and normally throughout the polymerization) with chains of different degrees of polymerization (DP*) being formed at the later stages due to changing reactant concentration and rate constants. The polydispersity (PD) of the final polymer will be spread over a range of DPs. Resulting a polymer with a broad polydispersity PD>1.5 (Figure 1.1).

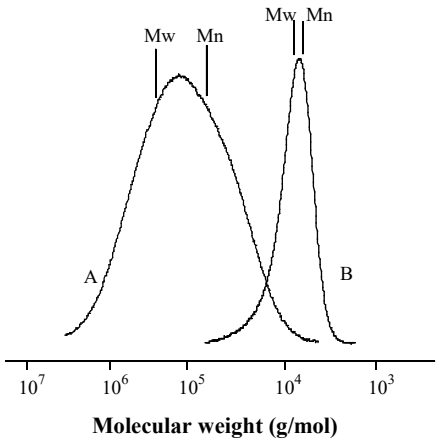


Figure 1.1. Molecular weight distributions for a conventional (broad, A) and living radical polymerization (narrow, B). Note: M_w is always greater than M_n.

1.2.b. Living Radical Polymerization (LRP)

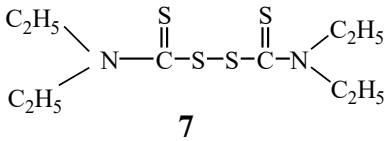
There was upsurge interest on living polymerization in the '80s when radical chemistry was applied to the established living polymerization techniques involving, anionic, coordination or group transfer mechanisms. Living radical polymerizations (LRP) do not meet the requirements of the term "living" as defined by Szwarc.[8] Since they involve radicals as intermediates they must involve a finite amount of termination. They were therefore considered less "alive" than that of the classical living polymerization techniques and were therefore referred to as pseudo-/ quasi-living,[1] controlled[9] rather than living[10] was surrounded by quotations or placed in italics.[7,8] The criteria for living polymerization can be stated as follows. Living polymerizations, if taken to full conversion of monomer, should continue to polymerize on further addition of monomer,[11] the number average molecular weight should be linearly dependant on conversion, the molecular weight should be controlled by stoichiometry, the number of polymer chains should remain constant during polymerization, the chain length distribution should be low (i.e. near monodisperse) (Figure 1.1), and chain end-functionality should be quantitatively retained. Living radical systems can meet all or most of these criteria.

Initial work by Otsu and Yoshida[12] utilized control agents they called "iniferters" that had the property of being initiators, transfer agents and chain terminators. One class of iniferters included certain diaryl-, dibenzoyl-, dixanthogen- and dithiuram- disulphides. The mechanism of polymerization is illustrated by considering dithiuram disulphide (**7**): Initiation of the polymerization is by hemolytic photodissociation of the S-S bond to form a pair of dithiocarbamyl radicals which can add to monomer (albeit slowly). Transfer from a propagating radical to the unreacted iniferter to give a dithiocarbamyl radical can also occur. Termination ends polymerization by the initiating radicals combining with a propagating polymer radical. The reaction is reversible only under photochemical conditions. Since the dithiocarbamyl end-groups are thermally stable but photochemically labile, only photo-initiated polymerizations could be described as living radical polymerizations.

The iniferter systems weren't perfect and they only displayed limited living characteristics with particular monomers, under certain reaction conditions, with side reactions occurring and polydispersities not narrowing significantly.

However, it uncovered interesting results and introduced the importance of reversible termination, giving insight into the requirements for living radical polymerization that would later form the basis of nitroxide mediated (NMP) and atom transfer polymerization (ATRP). The mechanistic step of transfer to the polymeric iniferter was not important because the transfer constants were low. Such transfer reactions are important with macromonomer and thiocarbonylthio based reversible addition-fragmentation chain transfer (RAFT) agents.

Iniferters do, however, allow control over polymer end-functionality by the nature of the iniferter mechanism, hence dithiocarbamates like (**8**) and (**9**) have been used to prepare hydroxyl,[13] and amino[14] telechelic polymers (Figure 1.4), respectively. However, end-group purity is compromised by slow loss of the living chain ends due to the occurrence of various side reactions.[15,16]



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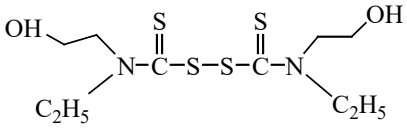

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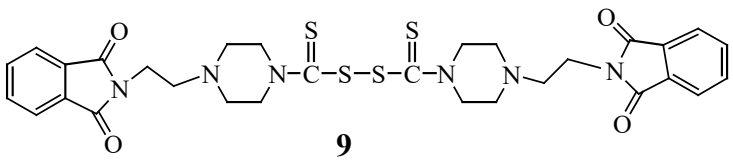

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A linear increase in molecular weight M_n with monomer conversion combined with a low PD (<1.5) as shown in Figure 1.2, with a first order kinetic plot is often considered a test for living systems. However these tests are not particularly definitive since first order kinetic plots are observed in conventional, non living radical polymerization under steady state conditions. Living radical polymerization systems always have <100% living ends since termination events always occur. Moreover, systems with 100% living chain ends may show a non-linear increase in molecular weight with conversion when initiation is slow compared to propagation.[17] A better test for the degree of livingness is the percentage of living functional end-groups.

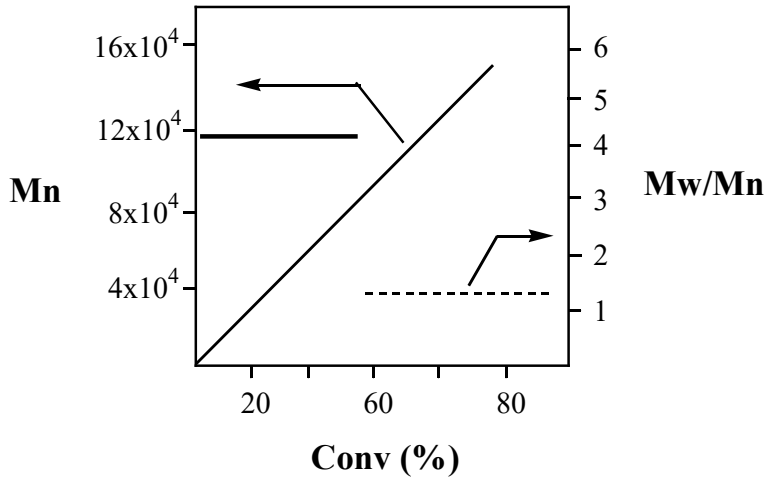


Figure 1.2. Evolution on molecular weight (M_n) and polydispersity (M_w/M_n) with monomer conversion.

Determining the amount of end-groups in low molecular weight polymers can easily be examined with NMR but this presents a challenge in accuracy when the DP exceeds 100. A way to circumvent this is to perform a chain extension test in conjunction with chromatographic analysis (e. g. GPC). The resulting polymer, acting as a macroinitiator, further polymerizes more monomer and if the living chain end purity is high, the final polymer correspondingly will have increased in molecular weight quantitatively.

1.2.c. End-functional Polymers

As discussed, LRP should provide predictable molecular weights with narrow molecular weight distributions and chain ends capped by functionalities. More importantly, the end-functionality should be quantitative with all chains carrying both an initiator derived α- end and terminated with an ω- end-group (Figure 1.3). Under specific conditions, functionality can also be placed in other key parts of the polymer chain (Figure 1.4). Functionalities should be selected to be compatible with LRP processes.

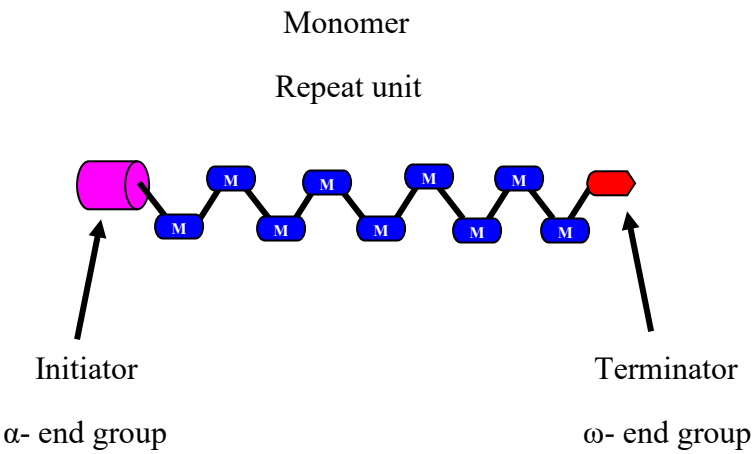


Figure 1.3. Structural features of an ideal living radically polymerized polymer, showing α- and ω- functionalities.

α-Functionalization:

The α-functionalization approach can be imparted using LRP by either the use of a functional initiator; the initiator fragment of the alkoxyamine nitroxide mediated polymerization (NMP) , the organic fragment of the organohalide initiator for atom transfer radical polymerization (ATRP) or by the radical leaving group from transfer agents (e.g. reversible-addition fragmentation chain transfer or RAFT). All chains should contain the functionality although other sources of initiation will reduce the level of functionality (e.g. thermal initiation of styrene or the use of an additional nonfunctional initiator).

ω-functionalization:

It is possible to introduce ω-fictionalization using NMP by placing the functionality in the nitroxide fragment of an alkoxyamine, in the Z group of the RAFT agent or by chemical transformation of the halo-end of a dormant ATRP polymer chain (this can also be applied to both the RAFT Z group and the nitroxide). Living radical polymerization allows the control over formation of block copolymers at the ω- chain end, thus functional monomers, short oligomers or blocks can be considered another method for ω-functionalisation.

The use of the functional initiator (**3**) has been applied to make polymers with mono functional end-groups such as mono amide-terminated polystyrene prepared under nitroxide mediated polymerization.[18] Using functional nitroxide (**10**) in conjunction with a functional initiator, a di-end-functional or telechelic polymer could be made.

It should be remembered that in attempting to prepare monofunctional polymers, any termination will give rise to a difunctional impurity. Equally, preparation of difunctional polymer will give some monofuntional impurity due to dispropotionation.

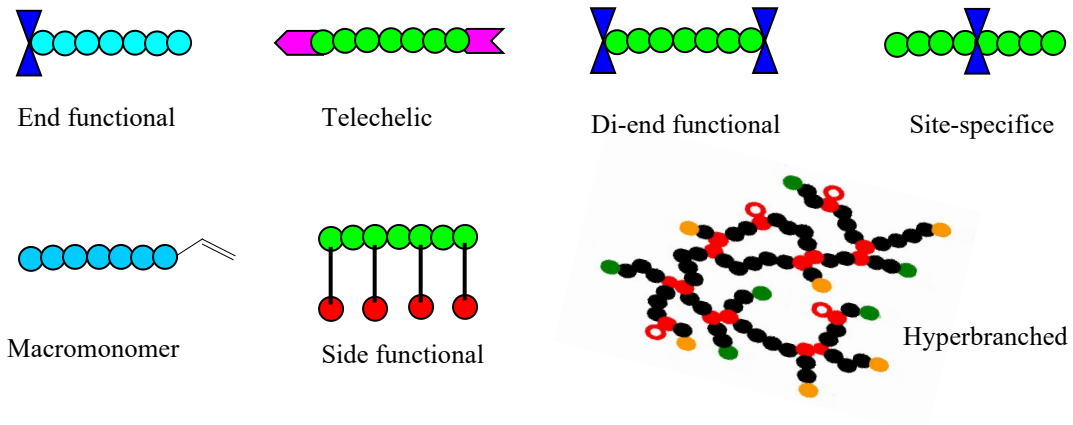


Figure 1.4. End-functional polymers synthesized by living radical polymerization.

End-functionality plays an important role in the polymer's ultimate property, for example it can affect the polymer's thermal stability,[19] and if reactive, it will allow the polymer to couple with other functionalities forming grafts or blocks, cross-linking. The ω-end, being living, can further chain extend, thereby allowing the formation of functional blocks (when functional monomers are used).[20,21] Control over the synthesis of blocks, grafts and the polymer architectures (Figure 1.5) has become increasingly important in producing high value added materials for nanotechnology, biomaterials, blend modifiers and improving or expressing particular polymer properties by self-assembly.[22,23]

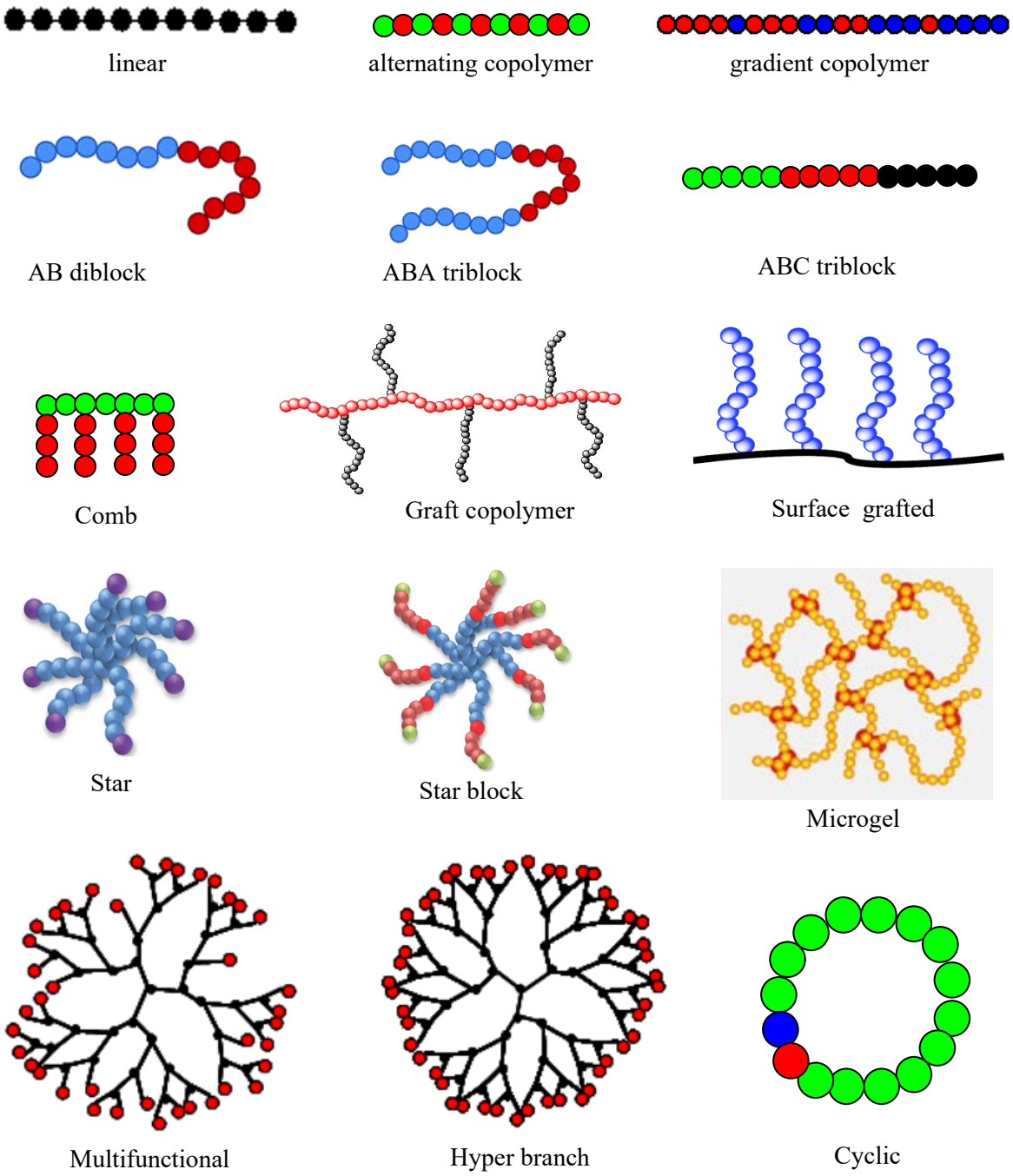
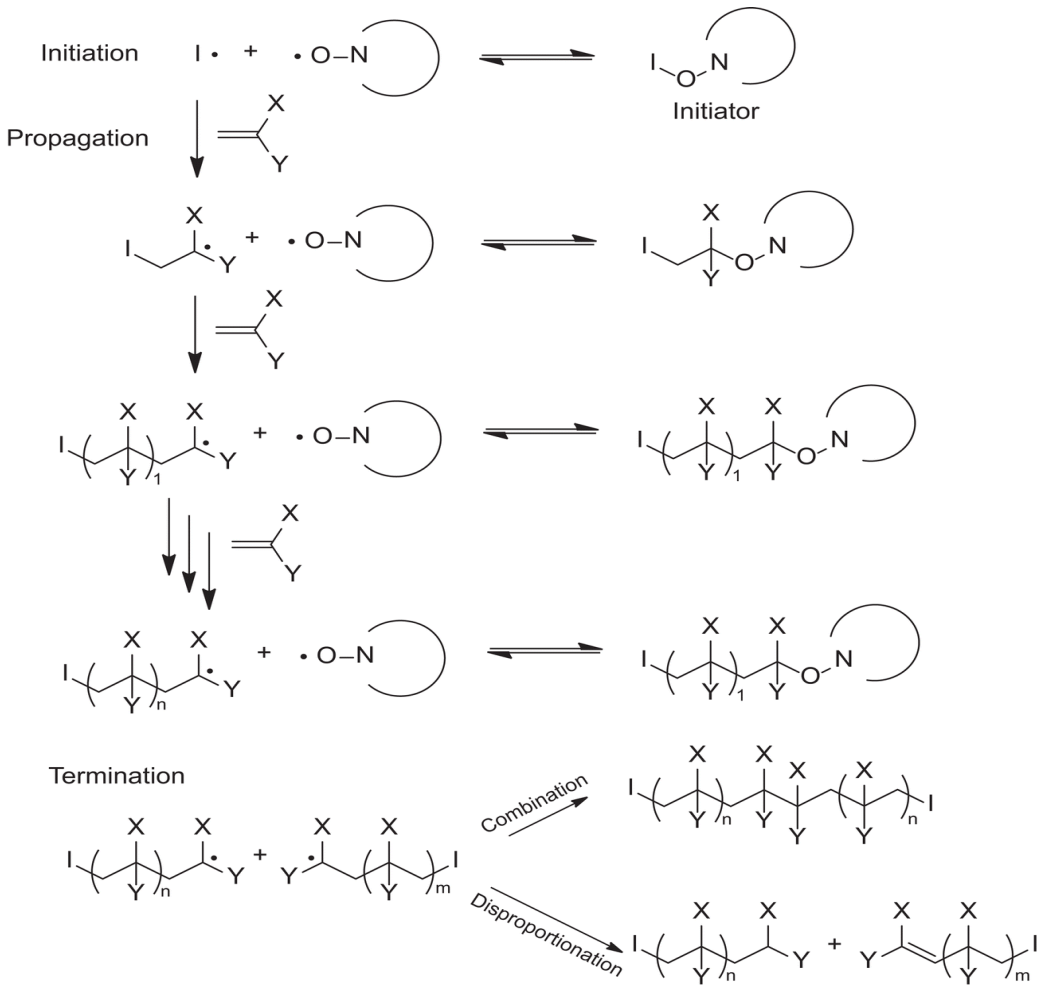


Figure 1.5. A variety of polymer architectures permitted by LRP.

Although these architectures can be made by other non radical polymerization techniques (i.e. ionic, group transfer polymerization), LRP's versatility and ability to utilize a larger range of vinyl monomers, allows a greater variety of polymer functionality, monomer compositions, well defined architectures and end-group functionalization.

1.2.d. Nitroxide-mediated Polymerization (NMP)

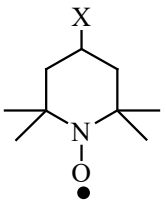
It wasn't until the mid '80s that living radical polymerization attained a further step towards better control. Nitroxide mediated polymerization (NMP) was born out of earlier nitroxide radical trapping work in studying the formation of initiator derived radicals but was also soon used as a reversible deactivator in radical polymerization. The initial work focused on synthesis of acrylic block copolymers and was not widely reported in the open literature. In 1990, Johnson *et. al.*[24] showed that it should be possible to use the method to make narrow polydispersity polymers. However, the method did not achieve popularity until 1993 when Georges *et. al.* demonstrated experimentally that it was possible to make low polydispersity polystyrene.[25]



Scheme 1.5. The general mechanism for nitroxide-mediated polymerization proposed in the CSIRO patent application.

NMP relies on "reversible termination" mechanism involving dissociation recombination of the C-O bond of the alkoxyamine group to control polymerization (Scheme 1.5). nitroxides provide a process for rapid and reversible deactivation of propagating radicals such that they spend the majority of their time a dormant state. The concentration of the reactive chain end is low and this reduces the significance of irreversible termination reactions such as combination and disproportionation.

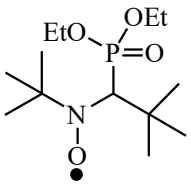
NMP was initially restricted to the control of polymerization of styrenic and acrylic monomers at high temperatures (>110- 140ºC). The development of imidazolidinones by Moad and coworkers[26] and later α-H nitroxides,[27] like **11**, by groups Benoit *et. al*.[28] and Hawker *et. al*.[4] permitted better control over the polymerization of a wider variety of monomers at lower temperatures, but effective control over methacrylates still remains difficult. [29-30]



10

a, X = H

b, X = OH



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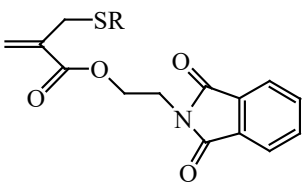
End-group control in NMP can be introduced by the alkoxyamine through a functionality either on the nitroxide fragment (ω-functional) or the initiator fragment (α-functional) or in the case of telechelic synthesis (α-, ω-), in both fragments. Functionality built into alkoxyamines can provide polymers with end-group incorporation levels of >95% for molecular weights up to 75k.[30] Interconversion of end-groups is also possible; however, it is likely that functionality levels will be lower due to the additional step(s) required. A review published by Hawker *et al*.[4] highlighted strategies for controlling polymeric structure and synthetic strategies for producing functionalized polymers employing nitroxides and alkoxyamines.

1.2.e. Reversible Addition-fragmentation Chain Transfer (RAFT)

Living radical polymerizations based on degenerative or reversible transfer are the most dynamic by nature since the number of radicals in these systems is determined by the addition of initiator, similar to conventional free-radical polymerization. The term "degenerative" refers to the fact that there is no effective change in the overall energy of the process, the radical being transferred from one chain to the other and the effective number of radicals remaining constant. Examples of reversible (degenerate) transfer exist in the work with alkyl iodides (e.g. 1-phenylethyl iodide) to mediate the polymerization.[30,31] More recently organotellurium mediated radical polymerization (TERP)[32] has been shown to be an example of degenerative transfer (a mixture of reversible transfer and dissociation-combination), able to polymerize (meth)acrylates and styrene with excellent control.

Allyl sulphides, although not showing true reversible characteristics, also work under an addition-fragmentation mechanism but are normally used to synthesise macromonomers or to introduce end-functionality, as has been done by Meijs *et. al*.[33] with a phthalimido functional allylic sulphide (**12**) and could equally be done with (**13**) to potentially synthesize amino end-functional polymers. Equally, allyl bromide has been used to produce α-bromo functionalized macromonomers from the α-bromo methacrylate, in emulsion systems.[34,35]



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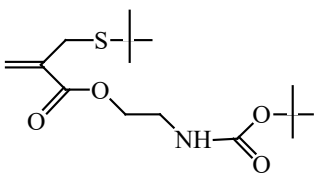

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It must be understood that the mechanism of RAFT is significantly different from that of NMP and ATRP, as it does not rely on reversible termination of

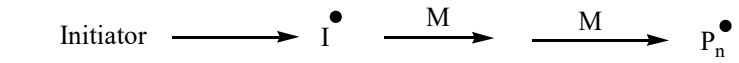
the propagating radical or the influence of deactivation-activation and the persistent radical effect, to determine the rate of polymerization. Nor does RAFT provide the initiating radicals as is provided by the alkoxyamines for NMP, or the organo-halo compound in ATRP. RAFT imparts its control through reversible chain transfer steps by which it sets up deactivation-activation equilibria. The reversible transfer mechanism can be broken up into two parts, see Scheme 1.6.

Firstly the reversible chain transfer or pre-equilibrium step, where the RAFT agent is transformed into a polymeric macro- RAFT agent. This occurs after initiation with the propagating radical (P_n*) adding to the thiocarbonylthio of (**14)** forming the intermediate (**15**) which fragments off the leaving/reinitiating group (R*) leaving the macro- RAFT (**16a**). Radical (R*) reinitiates monomer forming the new propagating radical (P_m*).

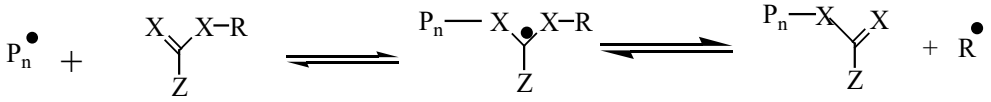
Secondly, when the initial RAFT agent is consumed, the chain equilibration mechanism becomes the dominant step, where (P_m*) adds to (**16a**) giving the intermediate (**17**) which can rapidly equilibrate between (**16a**) and (**16b**), setting up a fast equilibrium between propagating radicals (P_n* and P_m*). The dormant macro- RAFT agents thus provides equal opportunity for all propagating radicals to grow , thus narrowing the chain length dispersity and providing the greater majority of chains with a thiocarbonylthio α-R group.

Radicals are not formed or lost in the reversible transfer steps and thus a source of free radicals is required to initiate and maintain the polymerization. They also account for the formation of dead polymer, as is the case for the kinetics of conventional radical polymerization.

Initiation

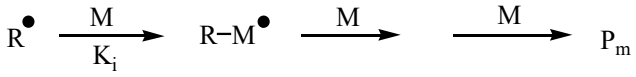


reversible chain transfer

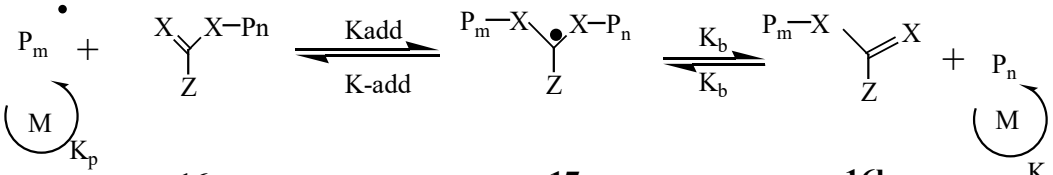


14 **15** **16a**

Reinitiation

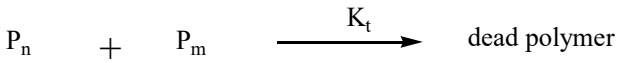


chain equilibration



16a **17** **16b**

Termination



X= CH_2, CH_2 macromonomer

X= S,S dithioester, trithiocarbonate , dithiocarbamate , xanthate

Scheme 1.6. General mechanism of RAFT polymerization.

It is a process that is simple to perform, is robust and has minimum sensitivity to impurities. It can be used with a large range of monomers, in a wide range of solvents and reaction conditions, providing control over molecular weight and at the same time giving very narrow polydispersities (<1.1) and can give end-functionality to the polymer.[36-38] The RAFT moiety,

which stays dormant, can also be further re-activated for chain extension and block synthesis and complex architectures.[20] This property may be used in end capping a polymer with a functional monomer or a short block of functional monomers.[21]

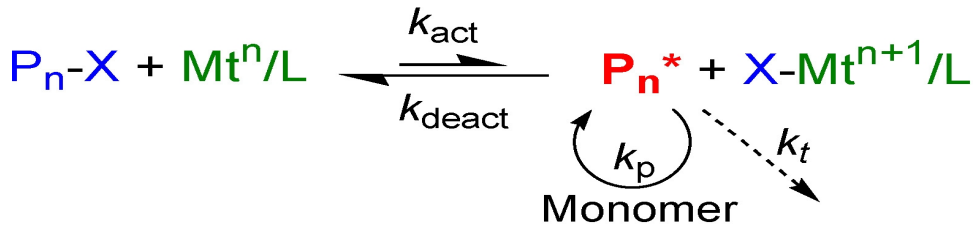
1.2.f. Atom Transfer Radical Polymerization (ATRP)

ATRP was generated from the initial work of atom transfer radical addition (ATRA), a radical technique for adding an organic halide to an alkene utilizing a metal complex catalyst, discovered in 1945 by Kharasch[39] and was later refined by Asscher[40] and Minisci.[41] Around 1995 separate research groups started to publish results on using ATRA for controlling polymerization; Wang and Matyjaszewski,[42] Kato and co workers[43], Percec and Barboiu.[44]

The ATRP process can be generally described as a radical polymerization with reversible termination by transfer to a ligand-metal complex. This usually involves the transfer of a halogen (typically bromine) from a dormant initiator or polymeric chain to a transition metal salt. A free radical is generated when the transition metal is oxidized by the halogen transferring, this free radical then adds of monomer. The catalyst is regenerated by the reduction of the oxidized transition metal complex, the polymer chain becomes dormant and the chain end is terminated with the halogen (Scheme 1.7). ATRP like NMP is also governed by the persistent radical effect.[45]

Polymerization of a range of (meth) acrylic, (meth) acrylonitrile and styrenic monomers has been popularized by ATRP being used in the synthesis of new polymer architectures. It is also versatile enough to synthesize end-functionalised polymers by using a functional initiator method or an end-capping method. ATRP does have some drawbacks, however; as it contains a transition metal catalyst and a halogen end-group the polymer prepared will be contaminated with some unremoved catalyst and the terminal halogen introduced in the polymer can be easily eliminated at elevated temperatures and

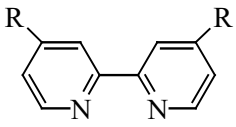
under basic conditions. Also, the polymerization of vinyl esters and halides is too slow and control over acrylic acids is problematic as it competes with the ligand forming a strong complex with the transition metal catalyst and thereby deactivating it.[6,9,46]



Scheme 1.7. General mechanism of ATRP polymerization, (Mt^n) transition metal coordinated ligands and halogen (X).

ATRP Ligands and Catalysts

Commonly used ligands are amino based *e.g.* bipyridine (bpy) R=H, 4,4′-(nonyl)-2,2′ bipyridine (dNbpy)R=C_9H_{19} (**18**) and Schiff base *N*-alkyl-2-pyridylmethanimine [*N*-(n-octyl)-2-pyridylmethanimine, (**19**) systems.



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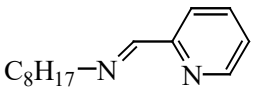

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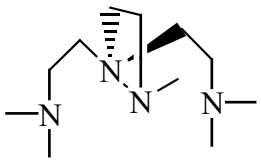
The transition metals halides used in ATRP (iron, nickel, palladium. Ruthenium) copper (I) is the more efficient catalyst and the most studied. The catalysts are complexes of metal and ligand and the ligands are playing the role of solubilizing the transition metal catalyst and modulating the redox potential of the M_t^n/ M_t^{n+1}X cycle. ATRP method is the use of large amounts of the CuX / ligand catalyst complex required.[6] The obtained polymers require tedious purification to remove the catalyst. Although various methods for catalyst

removal have been developed, the extra purification step is associated with longer time needed to obtain the final product, and generates chemical waste. [6]



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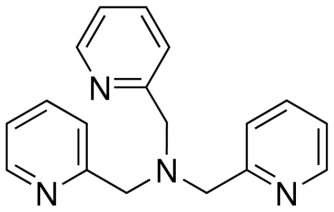

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The use of very active ligands tris[2-(dimethylamino)ethyl]amine (Me_6TREN (**20**),) and tris(2-pyridylmethyl)amine (TPMA) (**21**) alleviates this problem. These ligands can be used in new techniques called Activators Regenerated by Electron Transfer (ARGET)[6] and Initiators for Continuous Activator Regeneration (ICAR),[49] which decreases the amount of catalyst needed to only a few (often single-digit) ppm. The chemistry of metal catalyzed living radical polymerization has been reviewed by Kamigaito *et. al*.[46,47] and Matyjaszewski *et. al*.[6]

ATRP Initiators

The amount of the initiator in the ATRP determines the final molecular weight of the polymer at full monomer conversion. Multi-functional initiators may provide chain growth in several directions. Many different types of halogenated compounds are potential initiators. Some are discussed based on their structure as follows.

A. *Halogenated Alkanes*

Halogenated alkanes, such as $CHCl_3$ or CCl_4 are typically used in atom transfer radical addition and were among the first studied as ATRP initiators.[43,44] In the ruthenium-catalyzed ATRP of MMA,[48] molecular weights of the polymer increased linearly with the conversion; however, at high

monomer conversion, the molecular weight deviated from the theoretical values.[51] In contrast, di- or monochloromethanes were not able to polymerize MMA under similar conditions.[49]

CCl_4 has also been used in other catalytic systems, including the Cu-based one.[50] When $CuCl(bpy)_3$ was used as the catalyst for the ATRP of styrene at 130 °C, CCl_4 was found to act as a bifunctional initiator. Again deviation of the molecular weights from the theoretic values was observed, and this was tentatively explained by additionally generated chains resulting from the activation of the central dichloromethylated moiety which undergoes *ß*-scission. Control of the molecular weight is possible using $CHCl_3$ for the $CuCl(bpy)_3$ system, whereas di- and monochloromethanes lead to uncontrolled polymerizations.[50] In homogeneous systems, CCl_4 is sometimes less efficient due to a potential outer-sphere electron-transfer (OSET) reaction and the reduction of the radicals to anions. With CCl_4 and Ni{*o*.*o*-$(CH_2NMe_2)_2C_6H_3$}Br as the catalyst, the experimental molecular weight of PMMA increased with monomer conversion but showed deviation at high conversions,[51] similar to the ruthenium system.[48] Deviation of molecular weight was also observed for the $FeCl_2(PPh_3)_2$ catalytic system.[52]

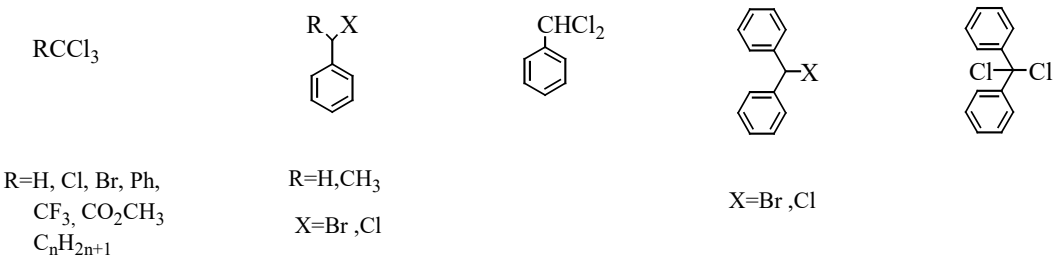
CCl_3Br successfully initiated the controlled polymerization of MMA catalyzed by $RuCl_2(PPh_3)_3$,[53] $NiBr_2(PPh_3)_2$,[54] $NiBr_2(pnBr_3)_2$,[55] or $Ni(PPh_3)_4$.[56] However, with the Ni(II)/$(PPh_3)_2$ system, other combinations of initiators and catalysts, such as $CCl_3Br/NiCl_2(PPh_3)_2$. $CCl_4/NiBr_2(PPh_3)_2$, or $CCl_4/NiCl_2(PPh_3)_2$, resulted in bimodal molecular weight distributions at high MMA conversions.[55]

B. ***Benzylic Halides***

Benzyl-substituted halides are useful initiators for the polymerization of styrene and its derivatives due to their structural resemblance. However, they fail in the polymerization of more reactive monomers in ATRP such as MMA.

For example, using $CuCl(NbPy)_2$ as the catalyst, inefficient initiation was observed when 1-phinylethyl chloride was employed as the initiator for the polymerization of MMA.[57] PMMA with much higher molecular weights than the theoretic values and high polydispersities (Mw/Mw= 1.5-1.8) were obtained. In contrast, a well-controlled polymerization was realized with benzhydryl chloride (Ph_2CHCl) as the initiator under similar conditions. In fact, the radical generation was so fast that slow addition of benzhydryl chloride was necessary to avoid a significant contribution of irreversible biradical termination early in the polymerization. Improvement of the initiation efficiency for the ATRP of MMA using primary and secondary benzylic halides is possible by employing the halogen exchange concept.[58]

Polyhalogenated benzylic halides have been used for the ATRP of MMA catalyzed by $RuCl_2(PPh_3)_3$/Al-(O^iPr)$_3$.[53] PMMA with very low polydispersities were obtained when Ph_2CCl_2 was used as the initiator. In contrast, $PhCCl_3$ led to a bimodal molecular weight distribution consisting of two narrowly distributed fractions, the higher of which was double the molecular weight of the other.[58] $PhCHCl_2$ has been also used in Cu-based ATRP of styrene and MMA, apparently providing two-directional growth of the polymeric chains.[59] Scheme 1.8 illustrates some examples of halogenated alkanes and benzylic halides used successfully in ATRP.

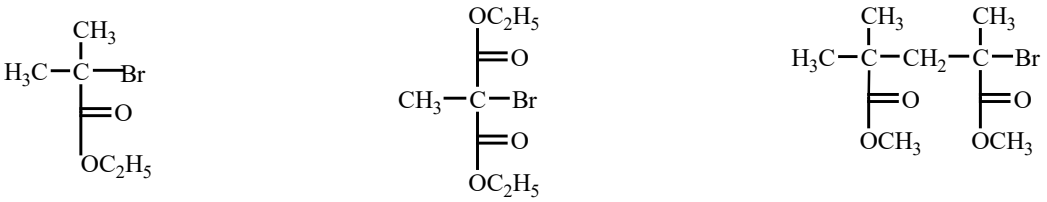


Scheme 1.8. Some Halogenated Alkanes and Benzylic Halides Used as ATRP Initiators.

C. *α –Haloesters*

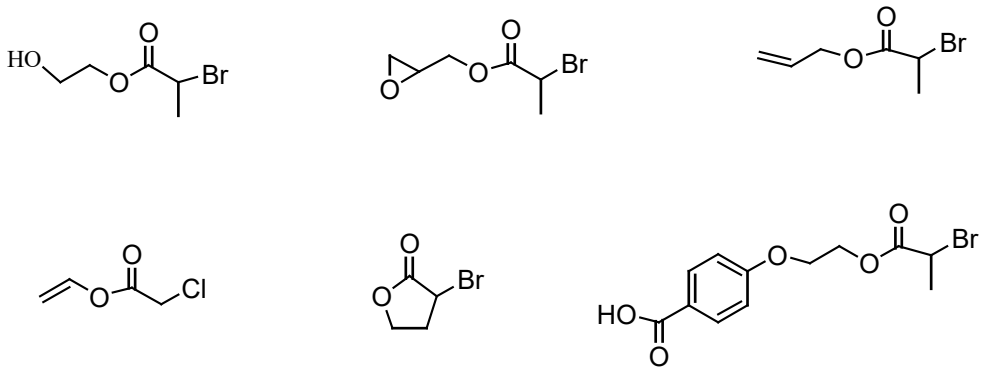
Various α-haloesters have been successfully employed to initiate well-controlled ATRP. In general, α-haloisobutyrates produce initiating radicals faster than the corresponding α-halopropionates due to better stabilization of the generated radicals after the halogen abstraction step. Thus, slow initiation will generally occur if α-halopropionates are used to initiate the polymerization of methacrylates. In contrast, α-bromopropionates are good initiations for the ATRP of acrylates due to their structural resemblance.

In their search for better initiators in ruthenium mediated ATRP, Sawamoto *et. al*. examined three α-bromoesters of different structures (Scheme 1.9).[45] The malonate with two geminal esters generates radicals faster than 2-bromoisobutyrate and leads to lower polydispersities. The dimeric model of the dormant chain end (dimethyl-2-bromo-2,4,4-trimethylglutatate) initiates a faster polymerization and provides PMMA with lower polydispersities than α-bromoisobutyrate.



Scheme 1.9. Various α-Bromoesters Used in Ruthenium-Mediated ATRP of MMA.

α-Haloesters with various functional groups attached can easily be prepared through a straightforward esterification reaction of the appropriate acid halides. Since ATRP can tolerate various functional groups, well-defined end-functional polymers have been conveniently prepared without the need for additional protecting reactions. A variety of functionalities, such as hydroxyl, epoxy, allyl, vinyl, γ-lactone, and carboxylic acid have been introduced onto the α-end of the polymer by use of a functional initiator (Scheme 1.10).[60- 62]



Scheme 1.10. Representative Functional Initiators Derived from α-Haloesters.

D. *α-Haloketones*

An α-bromoketone has been used to initiate the controlled polymerization of MMA catalyzed by Ni{*o*,*o*-(CH_2NMe_2)C_6H_3}Br[51] and Ni(PPh_3)$_4$.[56] Polyhalogenated α-haloketones (e.g., CCl_3COCH_3 and $CHCl_2COPh$) are among the best initiators for the ATRP of MMA catalyzed by ruthenium complexes.[48,63-64] Well-controlled polymers with low polydispersities (Mw/Mn < 1.20) have been obtained. The stronger electron-withdrawing power of the ketone's carbonyl induces further polarization of the carbon-chlorine bond, which is attributed to the faster initiation observed with the ketones than with the ester counterparts.

E. *α-Halonitriles*

α-Halonitriles are fast radical generators in ATRP, due to the presence of the strong electron-withdrawing cyano group. Moreover the radical formed after halogen abstraction is sufficiently reactive, which leads to fast initiation through rapid radical addition of the monomer. Of the initiators studied for the polymerization of acrylonitrile catalyzed by copper complexes, 2-bromopropionitrile resulted polymers with the lowest polydispersities.[65] 2-Bromopropionitrile is also the initiator of choice when a bromine initiator is desired in the iron-mediated ATRP of MMA.[66] However, α-halonitriles were

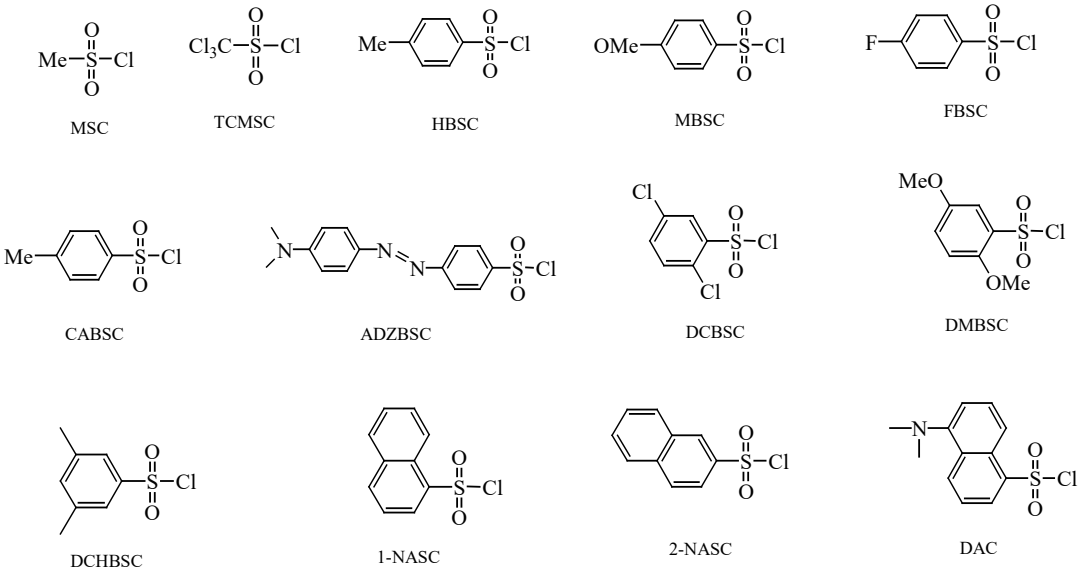
not used in ruthenium-catalyzed ATRP as the cyano group deactivates the catalyst by forming a strong complex with ruthenium.[48]

F. *Sulfonyl Halides*

As ATRP initiators, sulfonyl chlorides yield a much faster rate of initiation than monomer propagation.[67] The apparent rate constants of initiation are about four (for styrene and methacrylates) and three (for acrylates) orders of magnitude higher than those for propagation. As a result, well-control polymerizations of a large number of monomers have been obtained in copper-catalyzed ATRP.[68-69] End-functional polymers have been prepared using sulfonyl chlorides where functionalities were introduced onto the aromatic ring.[70] The phenyl group substituent has only a small effect on the rate constant of initiation because the sulfonyl radical and its phenyl group are not related through conjugation.

A unique feature of the sulfonyl halides as initiators is that although they are easily generated, they only dimerize slowly to form disulfones and slowly disproportionate. Thus, they can react with the monomers and initiate the polymerization efficiently.

When sulfonyl chlorides were used in the polymerization of MMA catalyzed by $RuCl_2(PPh_3)_3/Al(OPr)_3$. S-shaped conversion vs time profiles were obtained.[71] Moreover, experimental molecular weights were higher than the theoretical values, indicating low initiator efficiency. The polydispersities were around 1.2-1.5. The low initiator efficiency was explained by the formation of sulfonyl esters from sulfonyl chlorides and $Al(OPr)_3$ during the early stages of the polymerization . Examples of sulfonyl chlorides used as ATRP initiators are shown in Scheme 1.11.



Scheme 1.11. Examples of Sulfonyl Chlorides as ATRP Initiators.

General Comments on the Initiator Structure in ATRP

Two parameters are important for a successful ATRP initiating system. First, initiation should be fast in comparison with propagation. Second, the probability of side reactions should be minimized. Analogous to the "living" carbocationic systems, the main factors that determine the overall rate constants are the equilibrium constants rather than the absolute rate constants of addition.

Several Considerations for the Initiator Choice: [72-76]

(1) The stabilizing group order in the initiator is roughly CN > C(O)R > C(O)OR > Ph > Cl > Me. Multiple functional groups may increase the activity of the alkyl halide, e.g., carbon tetrachloride, benzhydryl derivatives, and malonates. Tertiary alkyl halides are better initiators than secondary ones, which are better than primary alkyl halides. Sulfonyl chlorides also provide faster initiation than propagation.

(2) 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.

(3) Successful initiation in ATRP can depend strongly on the choice of catalyst.

(4) The method or order of reagent addition can be crucial.

Range of available initiators for ATRP is much large than for other CRP methods. In fact, many NMP and RAFT reagents are prepared from ATRP initiators. Halogen end groups are an inherent part of the ATRP systems. They can be replaced by many synthetic methods to provide more useful functionalities and provide halogen-free products. Pseudohalogens such as (iso)thiocyanate and azide groups have also been used as exchangeable end groups in ATRP and are quite attractive, since they may be hydrolytically more stable and can provide direct pathways to end-functional activated halides which enable simultaneous growth of chains in several direction, leading to star, comb, and brush macromolecules.

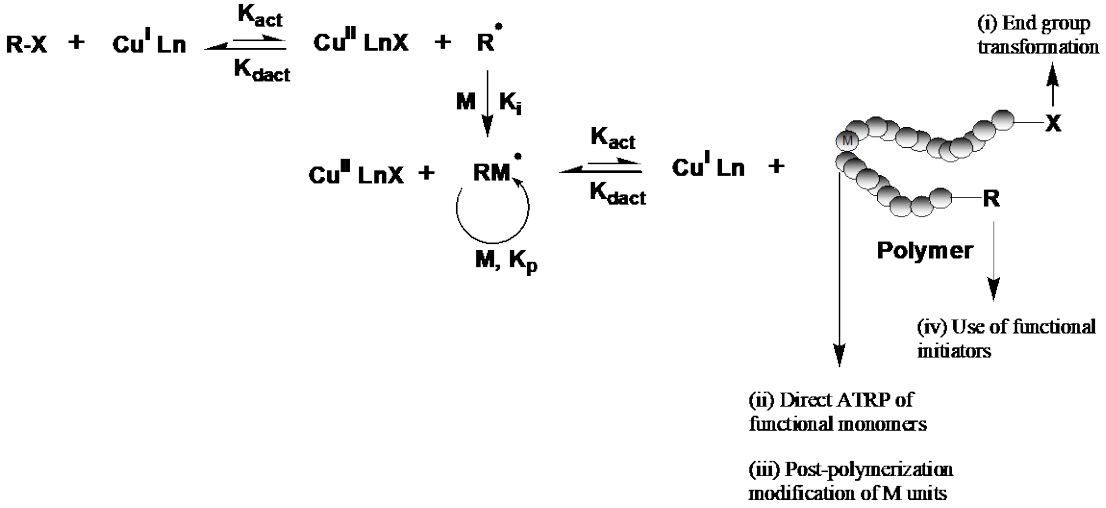
Functionalization by ATRP

Functional groups increase the utility of polymers and are fundamental to the development of many aspects of structure-property relationships. The functionality present on the monomer units determines the solubility of the polymer in a given solvent. One can control the hydrophilicity/phobicity, or polarity, the elasticity or modulus of a material by selecting appropriate monomers. End functionalized polymers are used for blend compatibilization during reactive processing, in all thermosetting compositions e.g.; epoxy-functional polymers, dioxolane-functional polymers and functional materials form the basis of the majority of products prepared for dispersant, coating, adhesive, and sealant, etc. applications.

Four synthetic strategies can be employed for the synthesis of well-defined polymers with site specific functional groups using ATRP.

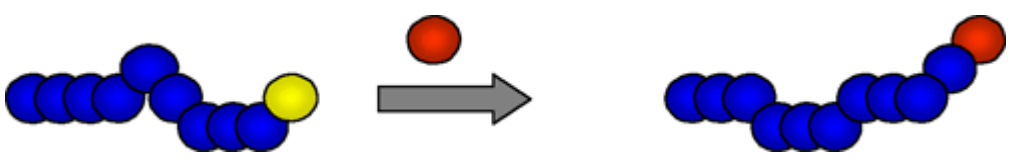
1. end-group transformation chemistry
2. direct polymerization of functional monomers
3. post-polymerization modification of monomer units
4. use of functional ATRP initiators

These approaches are summarized in the following scheme.



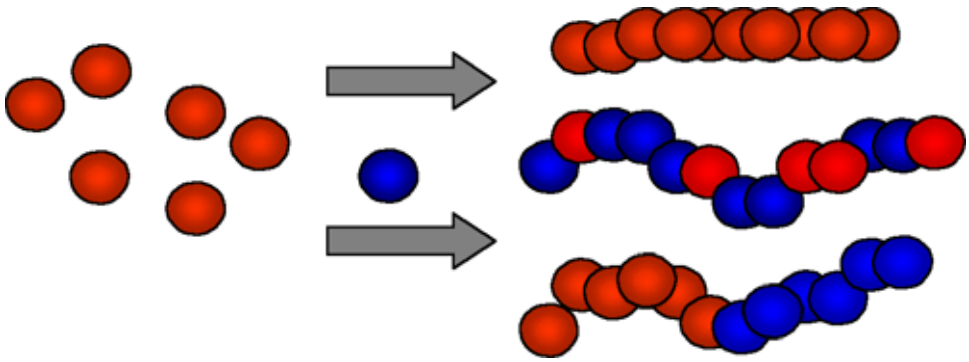
(i) End Group Transformation:

A number of nucleophilic substitution reactions have been employed to achieve this goal of post-polymerization functionalization making ATRP an attractive technique for the synthesis of well-defined end-functionalized polymers.



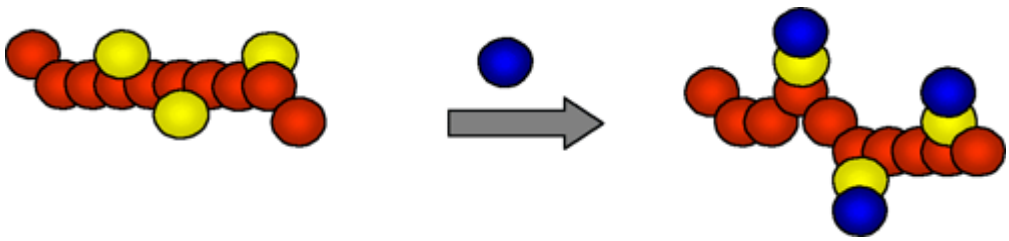
(ii) Direct ATRP of Functional Monomers:

One other obvious approach to functional materials is the direct polymerization, or copolymerization of a monomer containing the desired functionality.



ATRP is generally tolerant of various functional polar groups and this route has been successfully used in many instances to form homopolymers, random or gradient copolymers and block copolymers with controlled distribution of functional monomer units along the backbone.

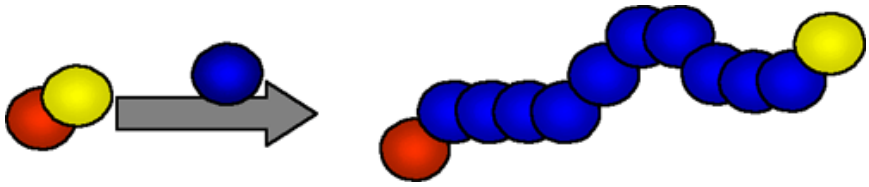
(iii) Post Polymerization Modification of M unit:



A number of nucleophilic substitution reactions have been employed to achieve this goal of post polymerization functionalization making ATRP an attractive technique for the synthesis of well-defined end-functionalized polymers.

(iv) Use of Functional Initiators:

The most obvious way to incorporate functionality is the use of functional initiators:



This approach can be used to prepare either homo- or hetero-telechelic polymers. Use of a mono-functional initiator with desired functionality leads to direct-functionalization of the polymer and no post-polymerization modification is required. In the vast majority of ATRP reactions the active or growing polymer chains are halogen-terminated, and can be further used as macroinitiators in chain-extension reactions or as precursors of end-functionalized polymers through end group transformations.

A wide range of functional initiators can use in ATRP so long as the initiator has a labile halogen and radical stabilizing groups. Various organohalides which are regularly exploited are the α-halo esters, amide, benzyl and sulphonyl halides, also simple compounds like α-halo nitriles, carbon tetrachloride and chloroform have been used.

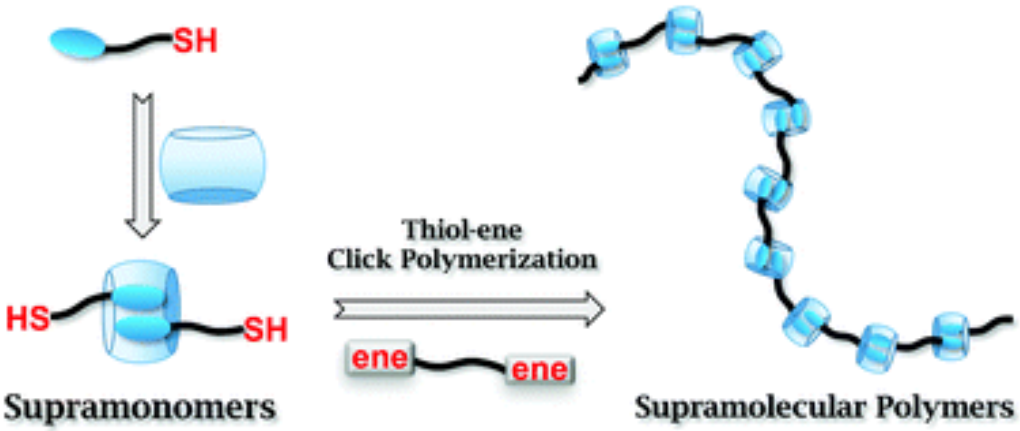
The strategies of end-functionalisation of ATRP polymers are thoroughly discussed in a review by Coessens *et. al.*[77]

Allyl group containing α-halo esters and amides are used as initiator to produce allyl end-functional polymers by ATRP. Allyl functionalized initiators are very important materials for conjugation of thiol group of any compounds, polymers and protein. Well defined block copolymers also obtain by chemical modification of alkenes.

This recent applications are the radical and based/nucleophile-initiated thiol-ene reaction in polymer and materials synthesis.[78]

Scheme 1.12. Thiol-ene click reaction.

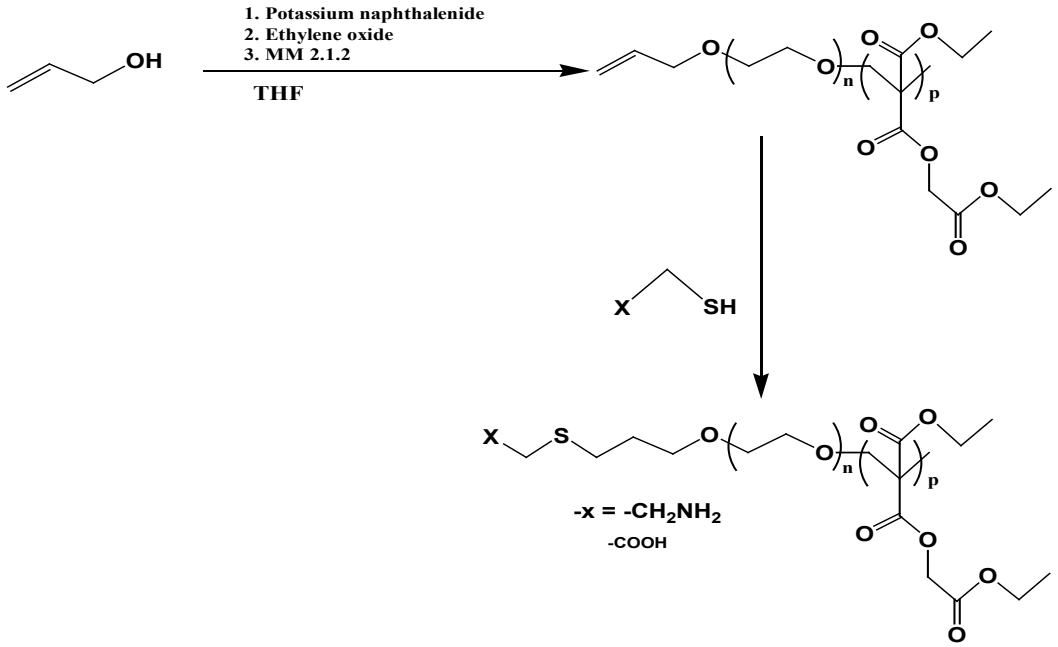
These Thiol-ene click reactions were used to generate block copolymers and telechelic polymers. The supramolecular polymers are obtained by thiol–ene click polymerization of the supramonomers with maleimide-terminated poly(ethylene glycol). [79]



Scheme 1.13. Synthesis of Supramolecular Polymer.

Allyl functionalized PEO-b-PMM block copolymers by sequential anionic polymerization initiated with allyl alcoholate for the preparation of allyl-terminated PEO. The reactivity of this unsaturated end group of the PEO block will be illustrated by further chemical modifications generating, with a same precursor block copolymer, carboxyl or amino functionalities, which are of interest for the coupling of various ligands like sugars, peptides, fluorescent markers, etc. Moreover, it will be demonstrated that these end-group modifications of the copolymers can be carried out under mild conditions,

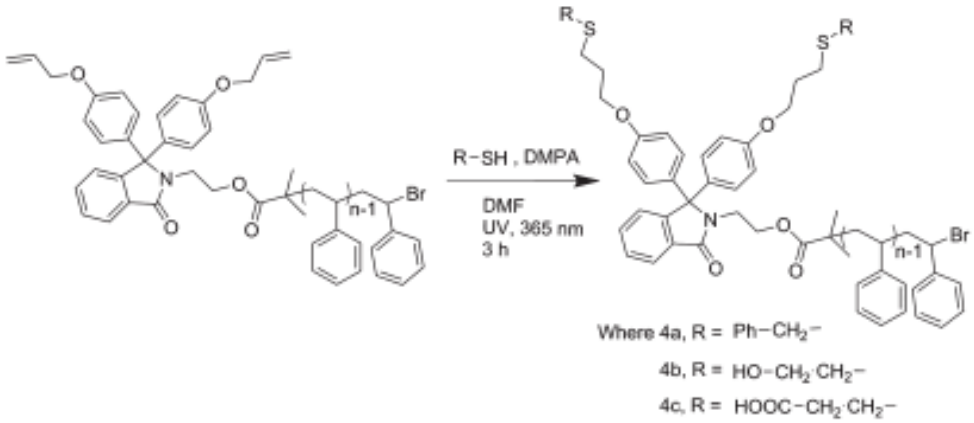
either in organic media such as in DMF, which is a common solvent of both PEO and PMM blocks, or in aqueous micellar dispersions, without any alteration of the polymer backbone.[80]



Scheme 1.14. Synthetic route to a-allyl functionalized PEO-b-PMM copolymers.

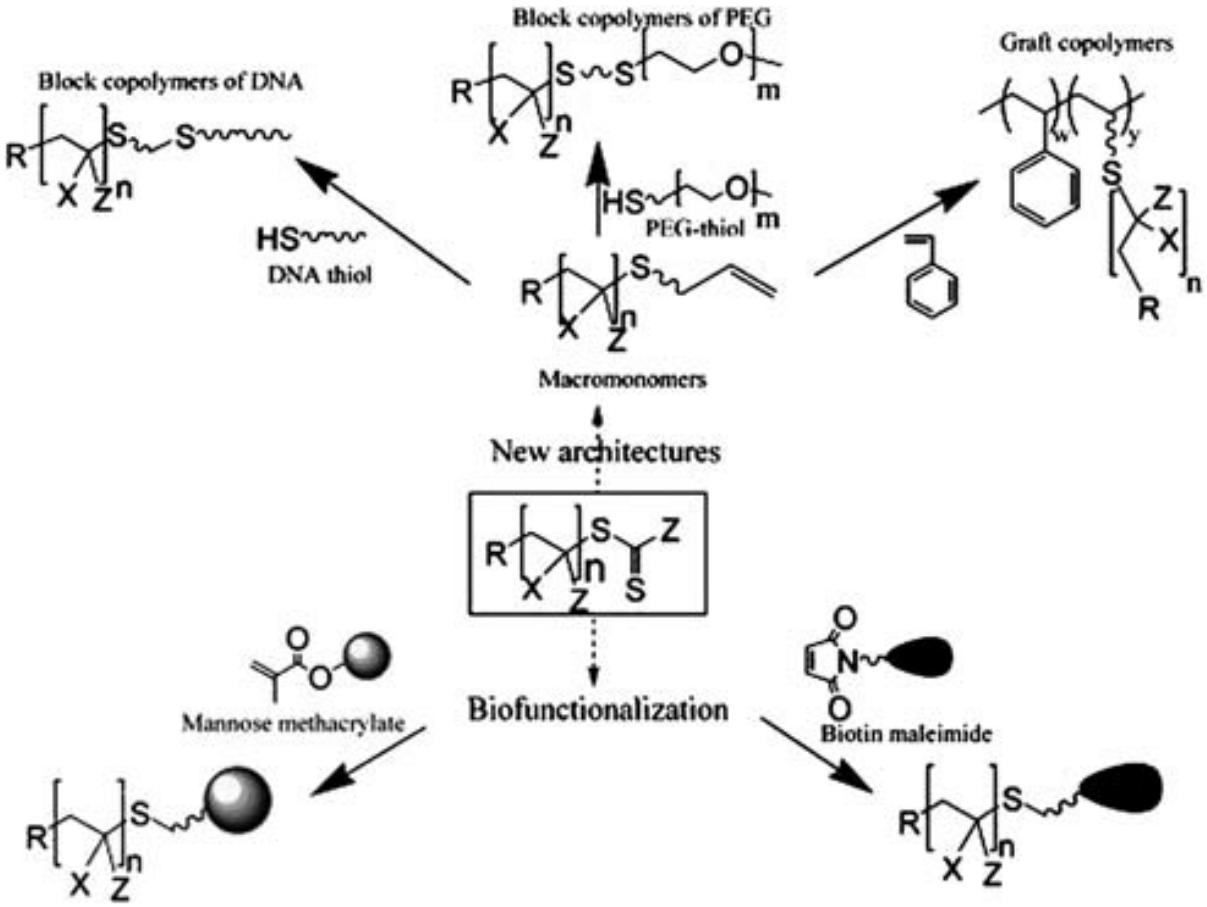
A new functional ATRP initiator containing allyl functional groups, namely 2-(1,1-bis(4-(allyloxy)phenyl)-3-oxoisoindolin-2-yl)ethyl 2-bromo-2 methylpropanoate, starting from phenolphthalein a commercially available and an inexpensive. An ATRP initiator containing allyl functional groups is of interest as allyl groups can subsequently be exploited in quantitative thiol-ene click reactions and several other useful organic transformations. α,α'-Bis-allyloxy functionalized polystyrene macromonomers with controlled molecular weight and narrow molecular weight distribution were synthesized employing ATRP. A metal-free photochemical thiol-ene click reaction of allyloxy end functional polystyrene with benzyl mercaptan as a model thiol reagent was performed to demonstrate the reactivity of the allyloxy groups. Furthermore,

the thiol-ene click reaction was extended to thiols containing reactive functional groups, namely 2-mercaptoethanol and 3-mercaptopropionic acid, to obtain α,α'-dihydroxyl and α,α'-dicarboxyl functionalized polystyrene macromonomers.[81]



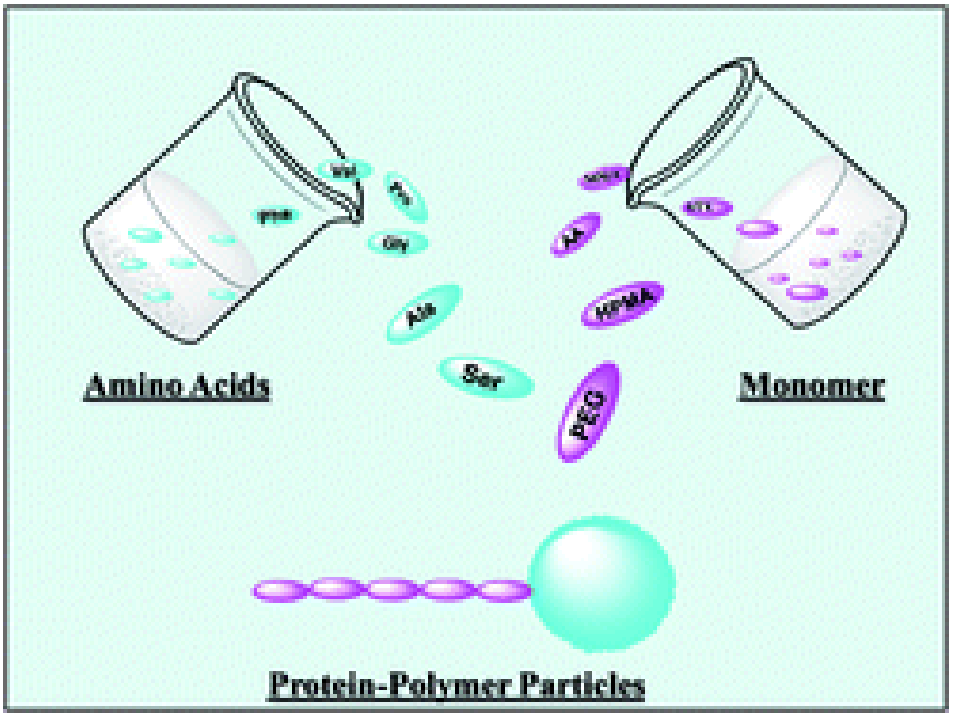
Scheme 1.15. photochemical thiol-ene click reaction of allyloxy end functional polystyrene

A comprehensive study of the modification of RAFT polymers via thiol–ene reactions has been recently reported, demonstrating the synthesis of novel architectures and biofunctionalisation of polymers. The first synthetic route involves simultaneous aminolysis and TEA mediated thiol–ene reaction with the diene species1,6-hexanediol diacrylate, yielding macromolecular monomers with defined structures and low polydispersities. This reaction has been proved successful for a variety of polymers; PMMA, PHPMA and PNIPAM and the resulting macromonomers have been used both in polymerizations with styrene yielding copolymers and in thiol–ene reactions with both PEG–thiol and DNA–thiol species.[82]



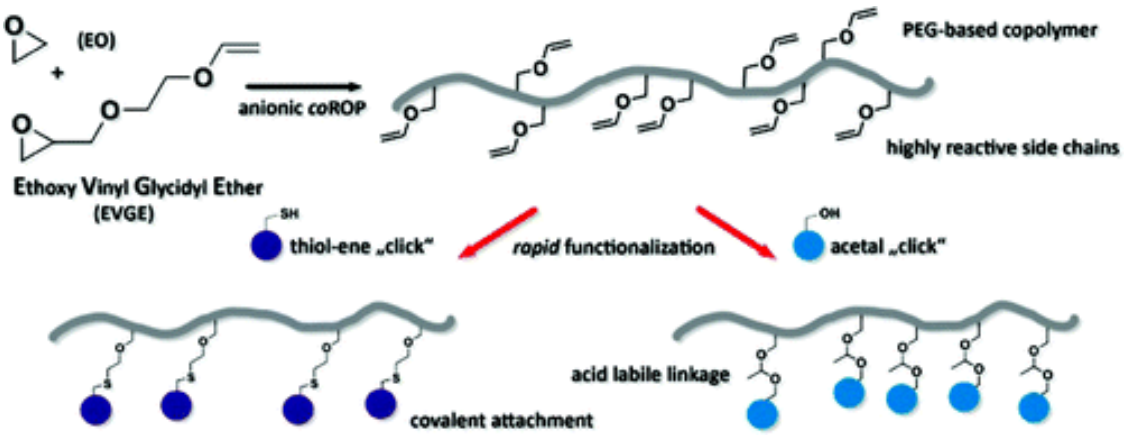
Scheme 1.16: A schematic overview of the synthesis of new architectures and biofunctionalisation of polymers by thiol–ene reactions.

Protein–polymer hybrid structures have many actual and potential uses in biomedicine, biotechnology and nanotechnology. The conjugation of synthetic polymers to proteins can impart beneficial properties such as tailored amphiphilicity and new self-assembly and phase-separation behavior to the resultant hybrids.[83]



Scheme 1.17: Conjugation of Protein–polymer hybrid.

Acetal formation, employing various model compounds. The strategies are very efficient, resulting in quantitative conversion. The rapid and complete acetal formation with alcohols results in an acid-labile bond and is thus highly interesting with respect to biomedical applications that require slow or controlled release of a drug.[84]

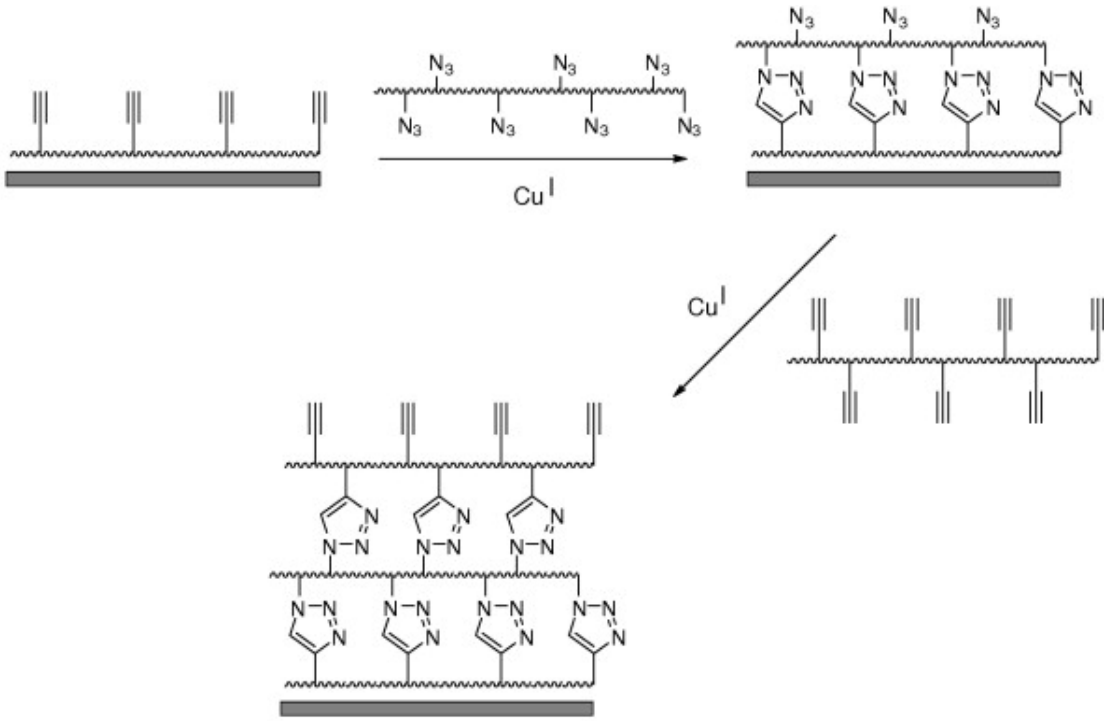


Scheme 1.18: Acetal formation with alcohols.

Alkynes group containing α-halo esters are used as a initiator to produce alkynes end-functional polymers by ATRP. Alkynes functionalized polymers are very much important materials to the polymer researcher, because of these polymers contain a clickable alkyne group. Alkyne functionalized polymers are precursors to obtain well defined block copolymers by ligated with well defined azide bearing polymers via azide- alkyne click chemistry.[85]

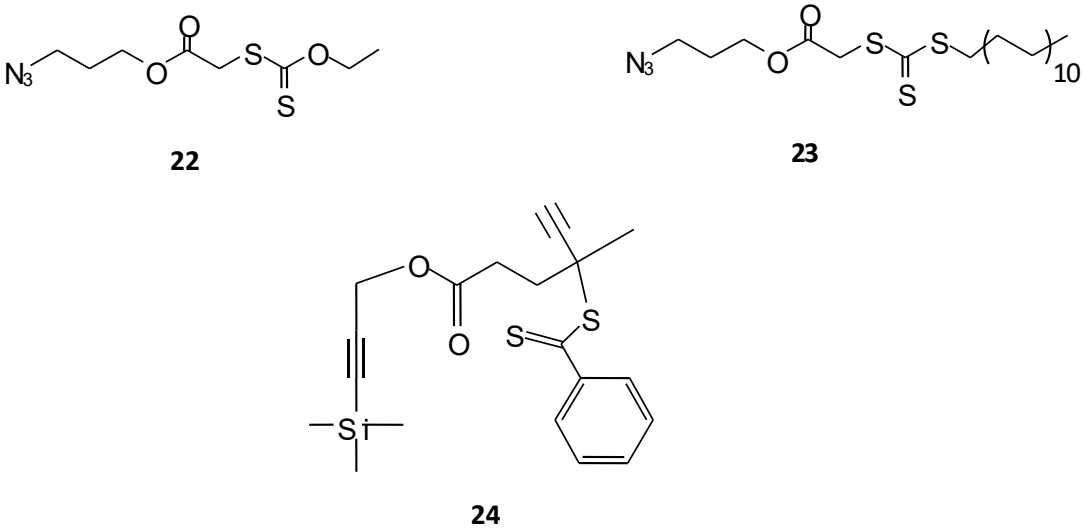
A large number of research articles have been reported to produce polymers by using azide-alkyne click reaction.[86] For example, CuAAC has been used to couple end-functional polymers to modularly synthesize block copolymers. Block copolymers of PCL and ATRP derived polystyrene and PEO to give A-B diblock or A-B-C triblock copolymers[87]

The combination of RAFT and click chemistry has been reported in a number of publications. For example, Alkyne and azide functional monomers, based on acrylic acid, were polymerized via RAFT mediated polymerization by Caruso and coworkers.[88] and the polymers obtained were used to produce an ultra thin polymer multilayer by applying click chemistry to these polymers (Scheme 1.19).



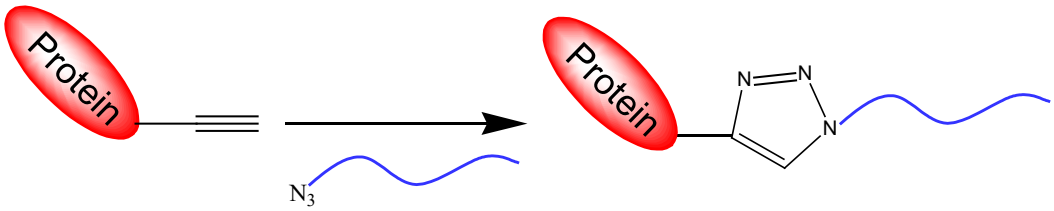
Scheme 1.19. Schematic overview for the synthesis of ultra thin polymer multilayers.

A TMS protected alkyne RAFT agent (24) and azide functional RAFT agents (22 and 23) have been reported (Scheme 1.20).[89,90] The azide and alkyne functionality are introduced in the R group of the RAFT agent.



Scheme 1.20: Structures of azide (22 and 23) and TMS protected alkyne (24) functional RAFT agents.

These and similar RAFT agents were used to generate block copolymers and telechelic polymers,[89,90] block copolymers, polymers with fluorescent end/groups,[91] bio/conjugates (Scheme 1.21),[92,93] folate (targeting ligand) functionalized thermoresponsive block copolymers[94] and branched poly(N/isopropyl acrylamide) (PNIPAM).[95-97]

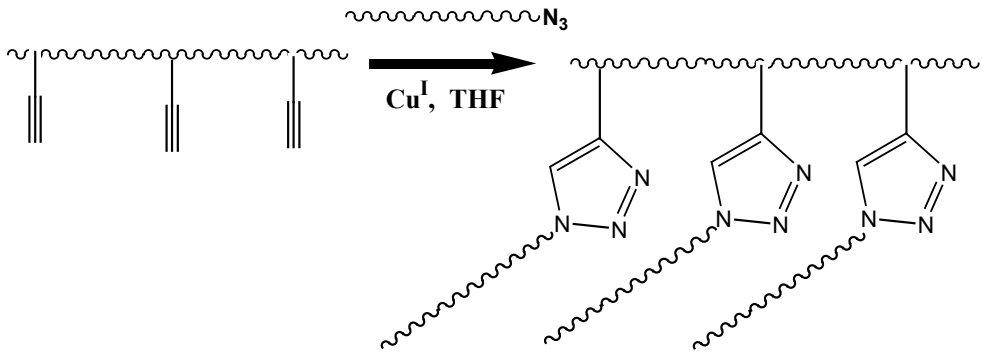


Scheme 1.21 Protein conjugates synthesized by Sumerlin et al.

Block copolymers of polyisobutylene and NIPAM were obtained when a alkyne functional trithiocarbonate was clicked on an azide functional polyisobutylene.[98]

The synthesis of cyclic PSTY via RAFT and click chemistry has been reported.[99] The azide group was introduced via the R group of the RAFT agent and the alkyne was introduced via the removal of the Z group. The Z group was removed using the addition of radicals formed from azobis(4-cyano valeric acid) esterified with propargyl alcohol under a procedure first reported by Perrier et al.[100]

Graft copolymers of vinyl acetate have been reported using a TMS protected propargyl methacrylate monomer.[101] In this case a backbone was grown via RAFT using alkyne functional monomers. These alkyne functions were used for click chemistry with polymers bearing an azide end/group (obtained from an azide functional RAFT agent) (Scheme 1.22).



Scheme 1.22. Schematic overview of the synthesis of brushes via click chemistry.

Thiol-ene click chemistry and was used for the synthesis of three armed stars of *n*-butyl acrylate. The thiol end-functional poly(*n*-butyl acrylate) was obtained via RAFT-mediated polymerization and subsequent aminolysis. The thiol end-functional polymers were reacted *in situ* via phosphine-catalyzed thiol-ene click chemistry. End-group modification of p(NIPAM) was also achieved via thiol-ene and thiol-yne click chemistry.[102]

Recently, a type of click chemistry based on nucleophilic substitution involving RAFT-moieties was reported. The “thio-bromo” click reaction was reported by

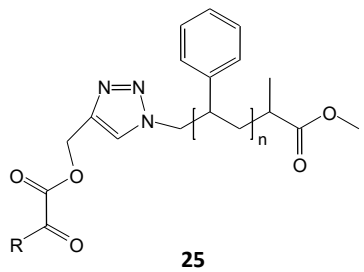
Davis, Lowe and co-workers.[103] After model reactions on low molar mass RAFT agents, they show that α-bromo esters can conveniently be used to create a thioether-functionalized polymer.

ATRP and click chemistry have been used together extensively. This combination is very popular because ATRP and click chemistry can both be carried out with the same copper catalyst and the halogen terminus of polymer chains obtained via ATRP can easily be converted into the corresponding azide derivative. The first report on the combination of click chemistry and ATRP was in 2004 by Matyjaszewski et al.[104]

End/group functionalization via click chemistry of polymers (suitable for click chemistry) has been reported. Functional groups like carboxylic acids, alkenes, and alcohols have been introduced.[105]

Polymer end-group functionalization allows for the synthesis of macromonomers via ATRP.[106] End-group modification has been proven to influence the thermoresponsive properties of polyNIPAM.[107]

Telechelic polymers are polymers where both α and ω chain-ends have a functional group. Taking the end-group modification one step further, telechelic polymers suitable for click chemistry have been reported (Figure 1.6).[108,109]



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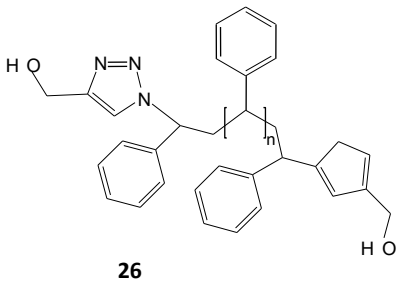

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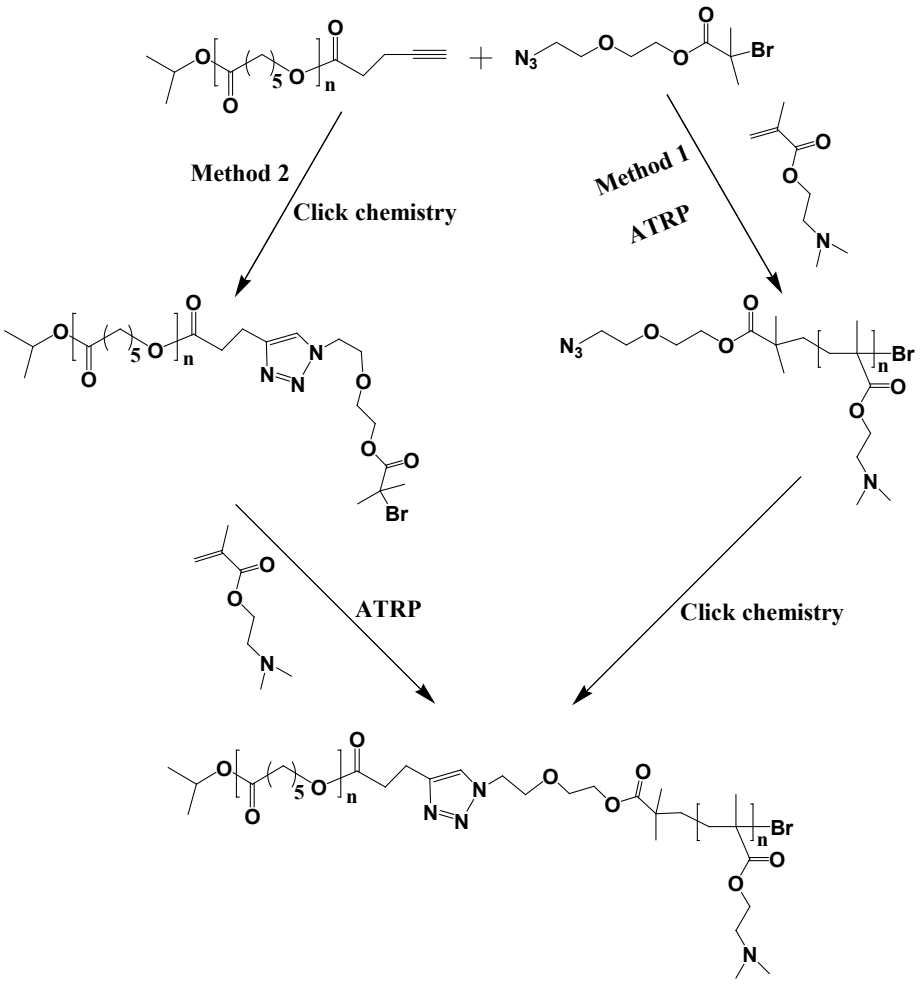
Figure 1.6. Structure of macromonomer (25) and telechelic polymer (26) synthesized via ATRP and click chemistry.

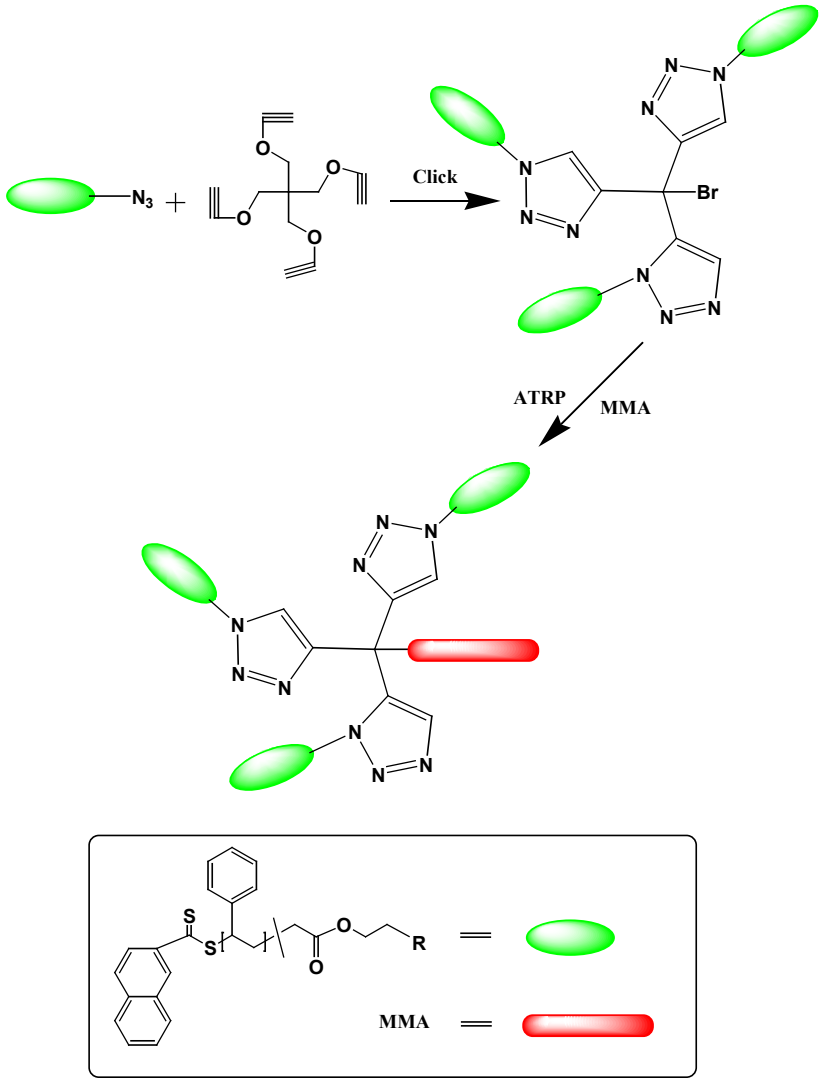
Block copolymers have been prepared from the obtained telechelic polymers. First α-acetylene-ω-azido-terminated PSTY was chain extended via step-growth click polymerization.[110] When telechelic polymers were used multiblocks of polystyrene and PEG were obtained.[111] Ring opening polymerization (ROP) was also used in combination with ATRP. Poly(ε-caprolactone) was clicked on a poly(N,N-dimethylamino-2-ethyl methacrylate) (p-(DMAEMA)) block.[112] The same block copolymer was later reported in a one-pot synthesis (Scheme 1.24).[113] Block copolymers of acrylic acid and 1-ethoxyethyl acrylate have also been synthesized using this method.[114] ABA polymers of PEO and p(STY) were reported.[115]

ABC triblock copolymers were reported.[87] PSTY, poly(tert-butyl acrylate) and PMMA containing azide and tri-isopropylsilyl protected end groups have been synthesized and clicked to each other sequentially. First the azide-functional PSTY was clicked onto the alkyne functional poly(tert-butyl acrylate).The remaining protected alkyne (on the PS) was deprotected and the diblock was clicked onto the azide-functional PMMA.[116] ROP was used for the synthesis of ABC-triblock copolymers in combination with ATRP and click chemistry. A macro ATRP initiator of poly(ethylene oxide) (PEO) was prepared via esterification of PEO with 2-bromo-2-methylpropionyl bromide and a PS block was synthesized via ATRP using this initiator. Then the bromine end-group was replaced by with an azide. Poly(ε-caprolactone) was synthesized via ROP using propargyl alcohol as the initiator. The poly(ε-caprolactone) was clicked on the azide-functional PEO-block-PSTY.



Scheme 1.24. The synthesis of block copolymers of p/(DMAEMA) and p/(ε-carpolactone) via ATRP and click chemistry.

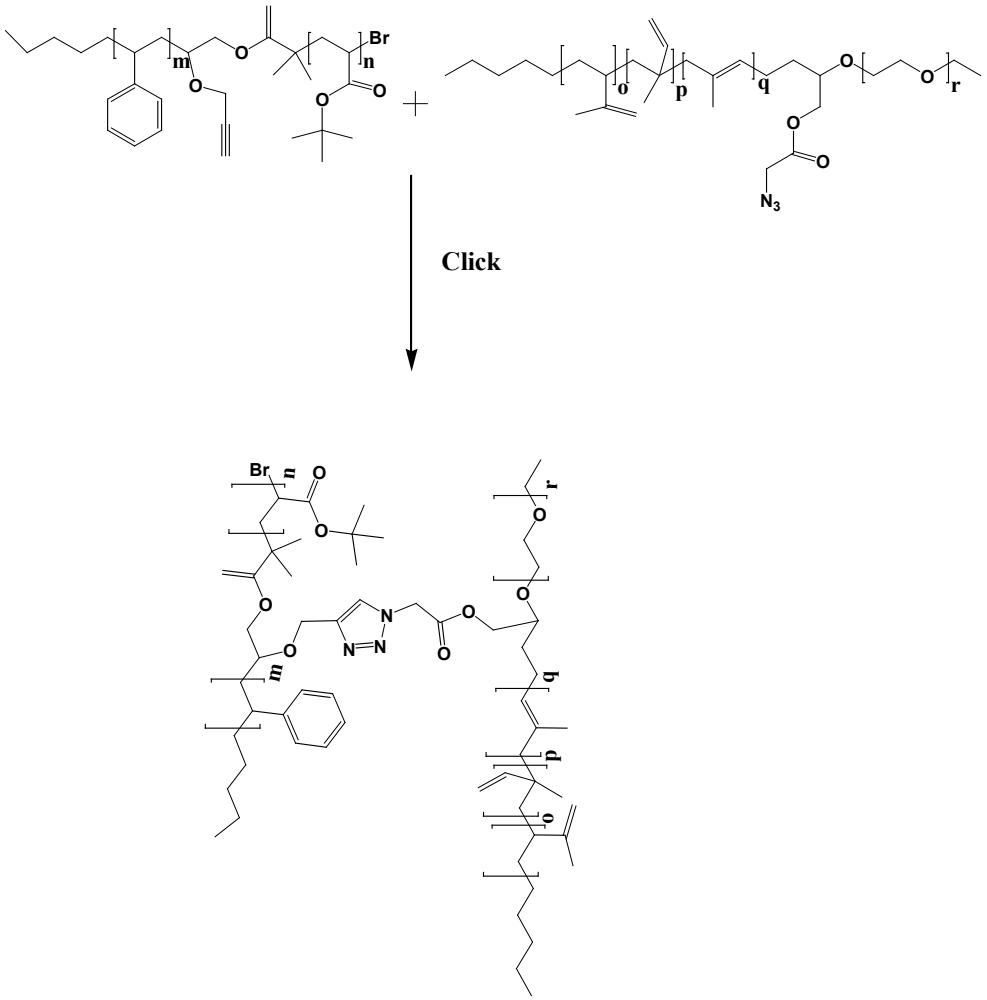
Star shaped polymers have been prepared in a number of ways.[117-125] Cores like pentaerythritol, esterified with pentynoic acid. Polymer chains synthesized via ATRP were azide functionalized and clicked on the core.[126] To obtain hetero arms a combination of RAFT and ATRP was used. Azide functional chains obtained via RAFT polymerization were clicked on a trialkyne functional alkyl bromide. After clicking the azide functional polymers on the core, this three armed star was used as an ATRP initiator (Scheme 1.25).[127]



Scheme 1.25. Schematic overview of the preparation of four armed star.

Star block copolymers have been prepared using a three armed star ATRP initiator to polymerize styrene. Subsequently, the bromides were substituted with azides and an alkyne functional PEO was clicked on the three armed star.[128] ABCD four armed star polymers were achieved via a combination of anionic polymerization, ATRP, ROP and click chemistry. PS and polyisoprene were polymerized using butyl lithium. The active lithium chain ends were functionalized. Polystyrene was functionalized with propargyl and 2-bromoisobutyryl groups. Subsequently ATRP of butyl acrylate was carried out yielding a PS-block-polybutylacrylate with a propargyl group at the junction.

The polyisoprene was functionalized with a hydroxyl group and a protected hydroxyl group. The hydroxyl group was used for the ROP of ethylene oxide yielding a polyisoprene-block-PEO, with a protected hydroxyl group at the junction point. This protected hydroxyl group was de-protected and modified into an azide via a bromoacetyl group. The two block copolymers were clicked together to form an ABCD star polymer (Scheme 1.26).[129] Star shaped polymers with as much as twenty-one arms have been reported from the combination of ATRP and click chemistry.[130]

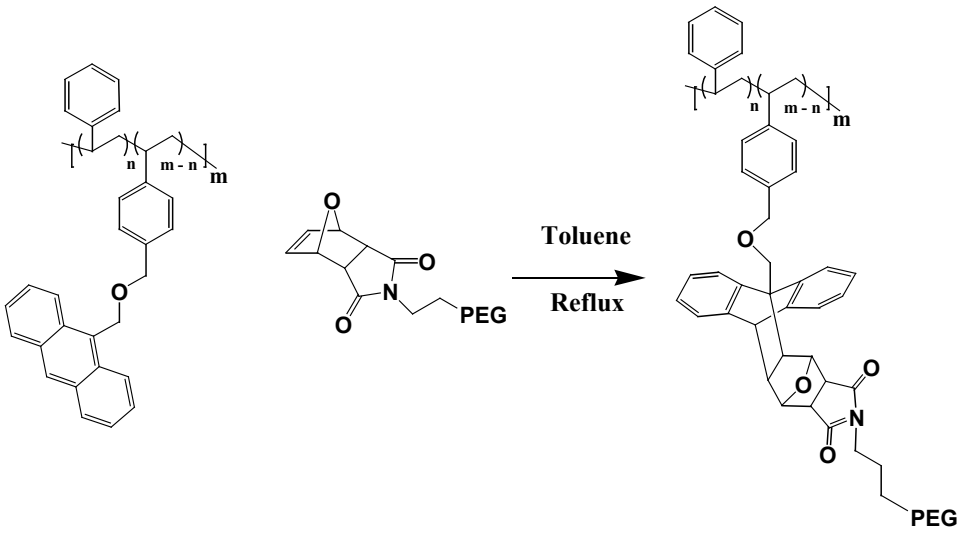


Scheme 1.26 Synthesis of ABCD four armed star copolymers.

Poly(2-hydroxyethyl methacrylate) synthesized via ATRP was reacted with pentynoic acid to yield an alkyne grafted polymer. On these alkyne groups,

polymers with azide functionality were clicked so that densely grafted polymers were obtained (Scheme 1.19).[131]

A combination of NMP, click chemistry and ATRP was used to produce well-defined multifunctional graft copolymers of poly(pentafluorostyrene).[132] Diels Alder click chemistry between maleimide and anthracene was used to prepare PSTY-graft-PEO.[133] 3-Acetyl-N-(2-hydroxyethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxamide functional PEG was used for an in situ retro Diels Alder and Diels Alder reaction with anthracene functionalized polymers (Scheme 1.27).



Scheme 1.27. Grafted copolymers synthesized via anthracene and maleimide Diels Alder click chemistry.

Neo-glycopolymers were synthesized via a trimethylsilyl protected alkyne functional monomer which was polymerized via ATRP. The alkyne functionalities were de/protected and sugars containing azide groups were clicked on the backbone (Figure 1.7).[134] In a similar fashion phenylpropagyl ether was clicked on azide functional backbones.[135]

Cyclic polymers have been reported via alkyne functional ATRP initiators where the alkyne functionality was either trimethylsilyl protected or unprotected. After polymerization, the bromide terminus was substituted with an azide (and if necessary, the alkyne was deprotected). A click reaction in highly dilute solution yielded cyclic PSTY and cyclic poly(methyl acrylate)-block-PSTY.[136,137] A similar approach was followed to synthesize cyclic polyNIPAM,[138] p(STY-block-PEO)[139] and grafted PEG.[140]

Eight-shaped copolymers were obtained when a difunctional ATRP initiator with two hydroxyl groups was used for ROP and ATRP and subsequent click cyclization (Figure 1.7).[141]

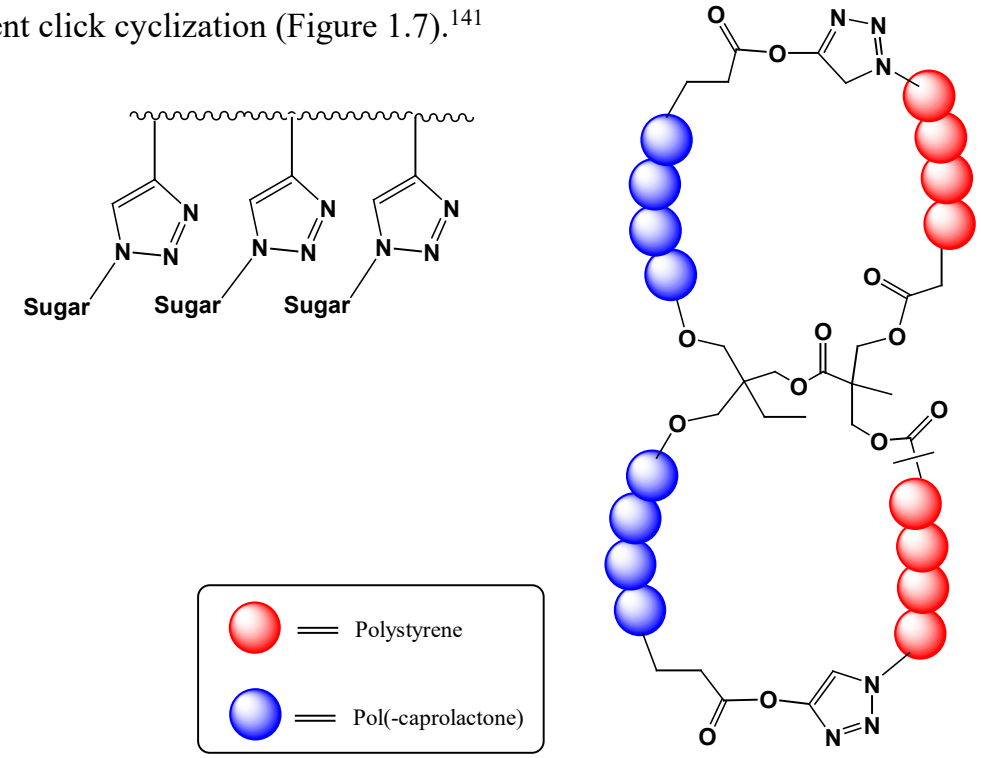


Figure 1.7. Neo-glycopolymer (left) and eight shaped block copolymer (right) synthesized via ATRP and click chemistry.

H-shaped polymers have been synthesized combining NMP, ATRP and click chemistry.[142] The synthesis started with the difunctional initiator (ATRP and NMP) that carries an alkyne functionality as reported by Tunca and coworkers.[143]

The field of pharmaceutical and biomedical applications in polymer science is a growing field of interest. The combination of ATRP and click chemistry has been reported in the field of gene delivery. PDMAEMA is a well known cationic polymer that condenses DNA. In principle, a high molecular weight polymer is needed. However, the higher molecular weight PDMAEMA is very cytotoxic. To overcome this problem, low molecular weight PDMAEMA was synthesized via ATRP and subsequently azide functionalized. The azide functional groups were clicked on a backbone via a degradable linker to obtain a degradable high molecular weight PDMAEMA with reduced toxicity (Figure 1.8).[144]

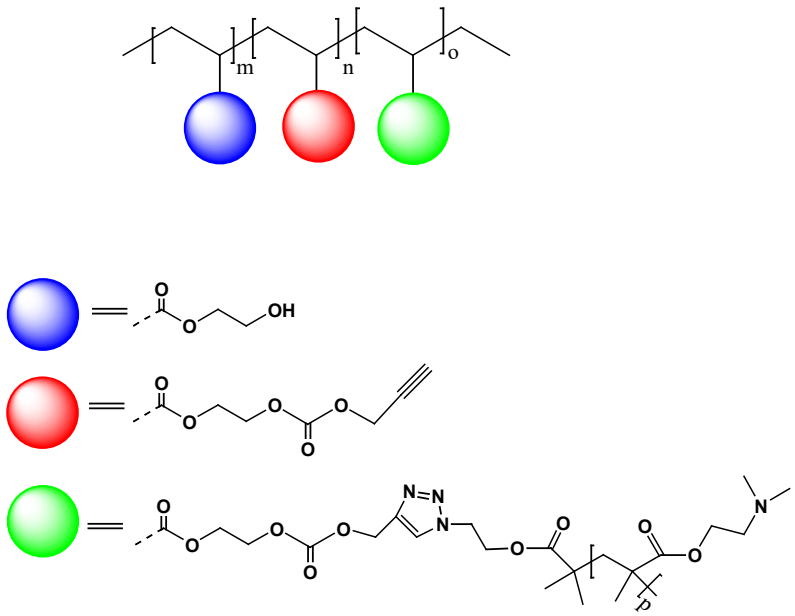


Figure 1.8 Grafted copolymer containing a hydrolysable link for non/viral gene theraphy.

Bioconjugation is another field where the combination of ATRP and click chemistry has been reported. The easy access to azide end-functional polymer makes ATRP a good candidate for polymer-peptide conjugation. Solid phase synthesis of peptides on poly(oligo(ethylene glycol) acrylate) has been reported. Click chemistry between an azide-functional polymer and an alkyne-functional FMOC-amino acid was used to obtain the starting point of the solid phase synthesis.[145] A biotin conjugate using the same polymer was reported.[146]

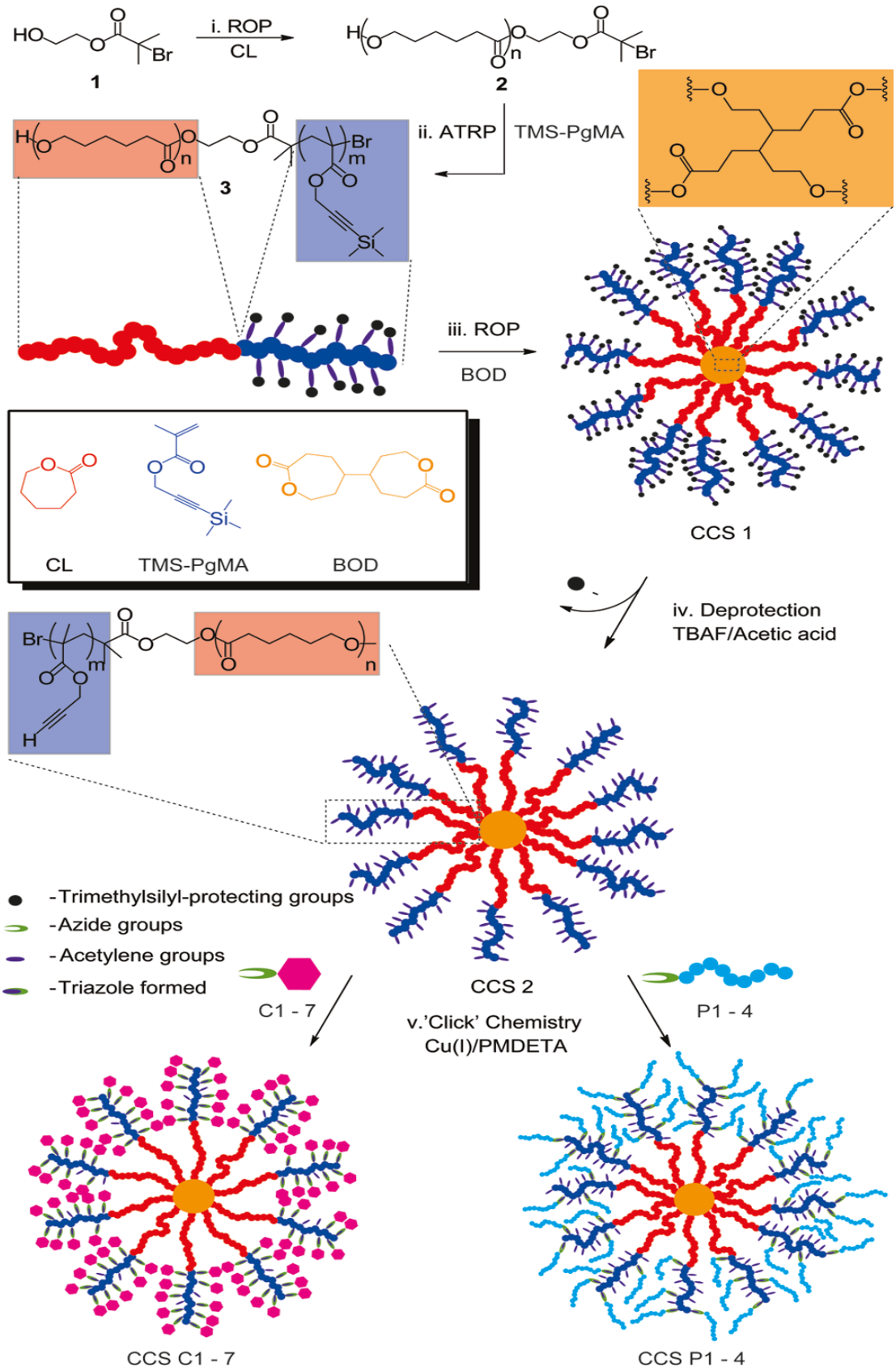
Another approach consists of attaching the ATRP initiator to the biomolecule and polymerizing from the biomolecule. This technique was reported by Wang et al.[147] In the same publication an alkyne functionality was introduced on a nanoparticle. To this alkyne, an azide functional fluorescent marker was clicked. Velonia et al.[148] reported the polymerization of an alkyne functional monomer onto a protein. After the polymerization, a hydrophobic azide was clicked to the molecule so that a giant amphiphilic conjugate was formed. Complex bioconjugates were obtained via ATRP and click chemistry, up to four different functionalities were attached to a polymer.[149]

Conjugates with other molecules have also been reported. Single-walled carbon nanotubes were functionalized with alkynes. Styrene that was polymerized via ATRP was azide functionalized and clicked onto the carbon nanotube.[150] Fullerenes were modified in a similar fashion.[151]

Shell cross-linked micelles were also produced using ATRP and click chemistry. When block copolymers were used that respond to different stimuli like pH and temperature the drug release or conformation of these micelles could be influenced.[152-155] Similar to the work of Brittain et al.[156] silica nanoparticles were modified with ATRP. After the polymerization the bromide end-group was reacted with sodium azide and different alkynes were clicked on the polymer chains.[161] Electrospinning was used to obtain nanofibers. These fibers were modified to have azide functionalities on the surface. After the spinning alkyne end-functional poly(NIPAM) was clicked on the surface and thermo-responsive nanofibers were obtained.[157]

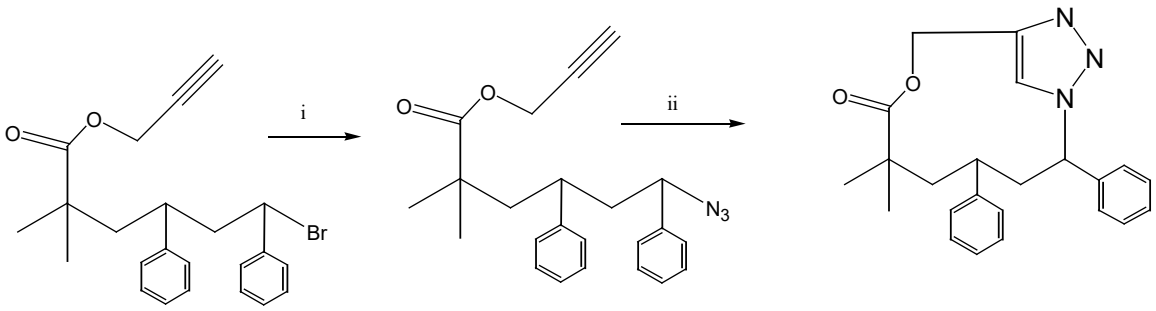
Poly(HIPE) was obtained and modified using ATRP. The obtained polymers were used in a click chemistry reaction with a fluorescent dye yielding fluorescent poly(HIPE).[158]

Because of this wide scope, the combination of ATRP and click chemistry has become an important topic. Jing M. Ren, James T. Wiltshire, Anton Blencowe, and Greg G. Qiao synthesized a star polymer library with a diverse range of highly functionalized macromolecular architectures.[159] The alkyne CCS(core cross-linked star) polymer scaffold was initially prepared via an improved arm-first approach, through ring-opening polymerization (ROP) of 4,40-bioxepanyl-7,70-dione (BOD) with a poly(caprolactone-b-propargylmethacrylate) macroinitiator and stannous triflate ($Sn(OTf)_2$) catalyst. Highly functionalized fluorescent, saccharide and amphiphilic CCS polymers were synthesized by grafting the alkyne CCS polymer with the corresponding azido substituted compounds via copper catalyzed 1,3-dipolar azide_alkyne cycloaddition (CuAAC), 'click' chemistry. (Scheme 1.28)



Scheme 1.28. Synthetic routes for the preparation of highly corona-functionalized CCS Polymers via sequential ROP, ATRP, and CuAAC Chemistry.

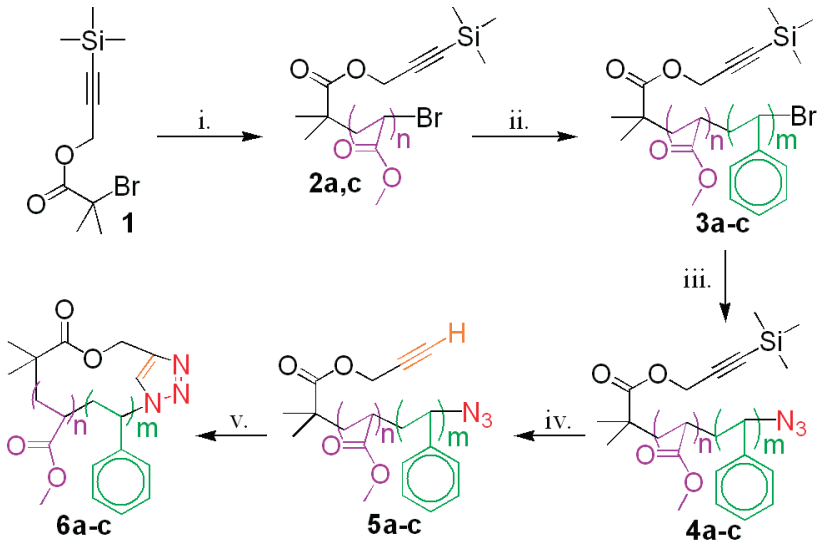
Boyd A. Laurent and Scott M. Grayson synthesized well-defined macrocyclic polymers from alkyne end-functional polystyrene via "Click" cyclization.[160] The linear poly(styrene) (*l*-PS) precursors were prepared using the standard ATRP techniques developed by Matyjaszewski and co-workers. Propargyl 2-bromoisobutyrate was used as initiator with Cu(I)Br and N,N,N',N'',N'' pentamethyldiethylenetriamine (PMDETA) as catalyst. The bromine-terminated product (*l*-PS-Br) was purified by extraction from water into CH_2Cl_2 and precipitation into methanol. Azidation of the end group was carried out in DMF with sodium azide. (Scheme 1.29)



(i) NaN_3 in DMF, 25 ^{0}C; (ii) CuBr/Bipy, in degassed DMF

Scheme 1.29. The Terminal Azidation (i) and "Click" Cyclization (ii) of Polystyrene Prepared via ATRP.

Cyclic block copolymers also prepared from the alkyne end-functional polymers. Dawanne M. Eugene and Scott M. Grayson reported an efficient preparation of cyclic poly(methylacrylate)-*block*-poly(styrene) by combination of Atom Transfer Radical Polymerization and Click cyclization.[161] (Scheme 1.30)



(i) methyl acrylate, Cu(I)Br, N,N,N',N',N''-pentamethyldiethylene triamine (PMDETA), in bulk 50°C; (ii) styrene, Cu(I)Br, PMDETA, anisole, 90°C; (iii) NaN_3, dimethylformamide; (iv) $(C_4H_9)_4NF$, tetrahydrofuran; (v) Cu(I)Br, PMDETA, dimethylformamide, N_2 120°C

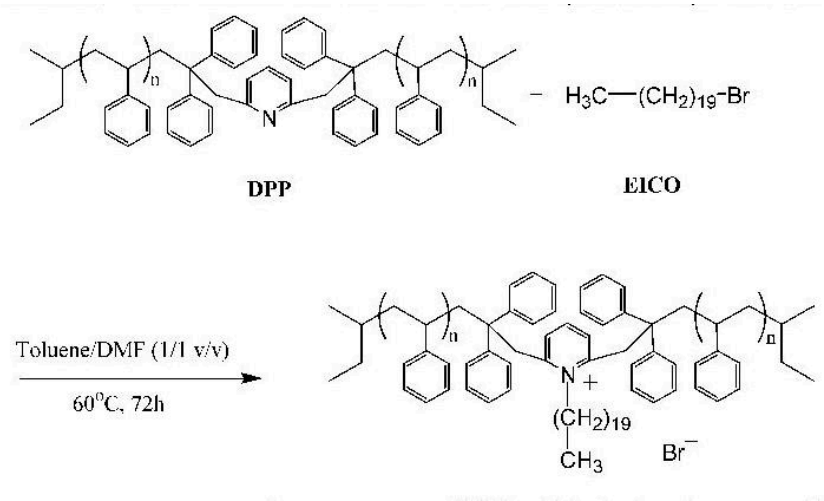
Scheme 1.30. Polymerization and Cyclization of Poly(methylacrylate (MA))-*b*-poly(styrene (S)).

Reactions between functional groups distributed randomly on one polymer and end-functional groups on the other polymer. A number of model studies have focused on end coupling in polymer melts but coupling with the mid-functional is still difficult and challenging because of the kinetic excluded-volume effect and steric hindrance due to the polymer chain. Very limited research has been published for mid-functional modification.

The effect of functional group location along a chain on the coupling rate between two complementary functional polymers under various reaction conditions: solution, homogeneous melt, static flat interface, and heterogeneous blend in the mixer. We used phthalic anhydride end and mid-functional PMMA (PMMA-eAn and PMMAmAn) fluorescently labeled with 7-nitrobenz-2-oxa-1,3-diazole (NBD) and anthracene, respectively. Investigated that the competitive couplings with amine terminal PMMA (PMMA-NH_2) and polystyrene (PS-NH_2) for homogeneous and heterogeneous reactions in the

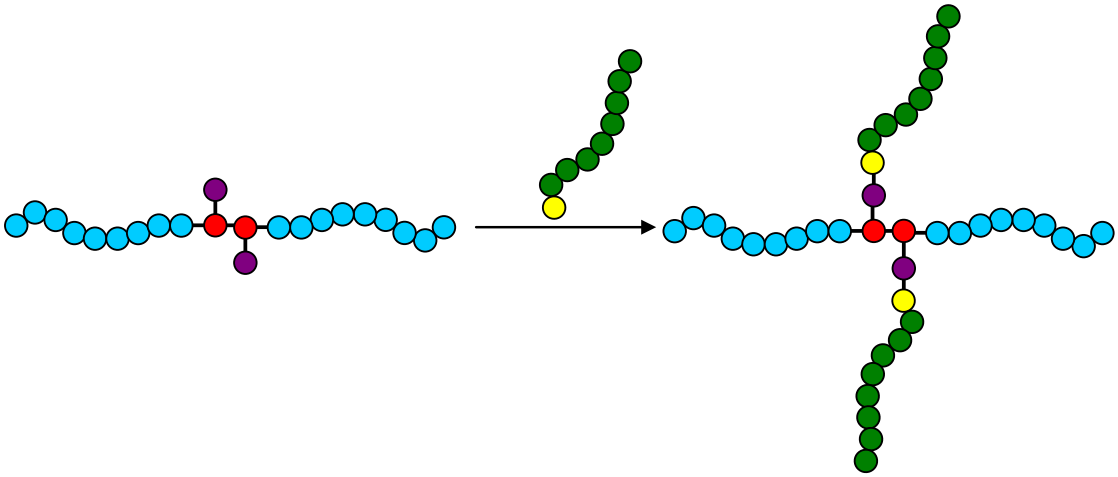
melt, respectively. By comparing reactions in homogeneous melts and in heterogeneous blends, explore the effect of the interface on reaction rate. The effect of flow on interfacial reaction by comparing results from static flat interfaces to heterogeneous blends prepared in a mixer.[162]

The reactive mixtures of polystyrene having a pyridyl group at the chain center with 1-bromoeicosane or 1-bromooctadecane as model compounds of end-functional oligomers.[163]



Scheme 1.31. Mid coupling of polystyrene and end functional oligomer.

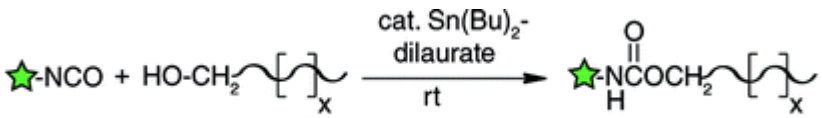
The photoinduced radical coupling (RC) of structurally well-controlled polymers prepared by Organotellurium-mediated living radical polymerization (TERP) in the presence of dienes or styrenes. Two molecules of dienes or styrenes were selectively inserted into the middle of the polymer chain by tuning the RC conditions. Furthermore, diverse functional groups were successfully introduced by employing functionalized dienes and styrenes. Therefore, the current method allowed a modular synthesis of mid-chain functionalized polymers with well-controlled structures in terms of their MW, MWD, functionality, and position from the starting polymers and coupling agents. The facile synthesis of a 4-miktoarm star polymer starting from a midchain-functionalized polymer have been shown in Scheme **1.32**.[164]



Scheme 1.32. Synthesis of midchain-functionalized 4-miktoarm star polymer.

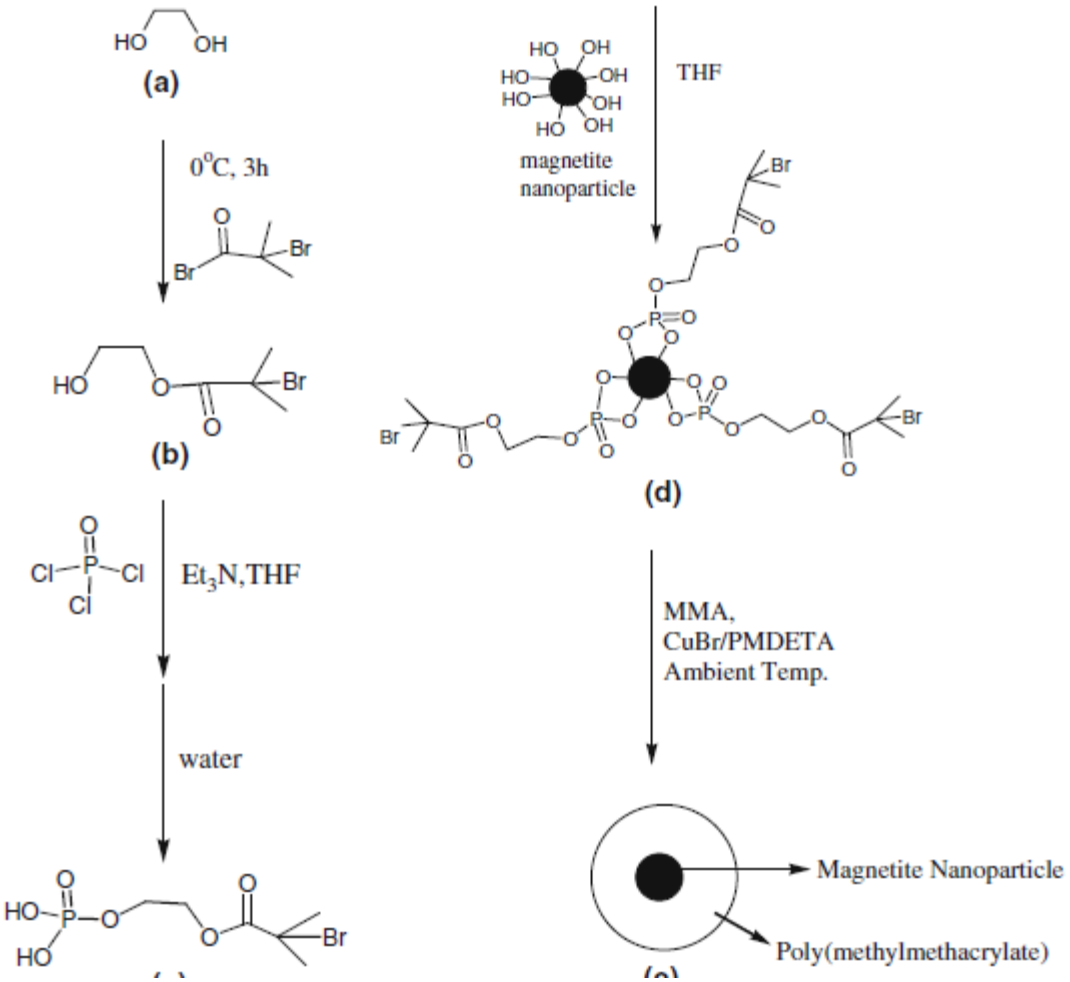
Design and synthesis of new ATRP initiators bearing a di-*tert*-butyl phthalate (DTBP) group and the use of these initiators to obtain *end*- and *mid*-DTBP functionalized poly(methyl methacrylate) (PMMA) and polystyrene (PS). Understanding reactivity differences between *end*- vs *mid*-functional polymers in reactive blending is important, since it could shed light on fundamental aspects of the effect of polymer architecture on polymer coupling reactions. Very clean generation of the phthalic anhydride group was achieved by subsequent thermal pyrolysis. Generation of the anhydride group was quantitative, and reactive blending experiments with these polymers showed that phthalic anhydride reacts faster than aliphatic succinic anhydride in polymer-polymer coupling reactions.[165]

The post polymerization functionalization of hydroxyl-group terminated polymers with a wide range of functional isocyanate derivatives such a azobenzene, viologen and anthracene has been investigated.



Scheme 1.33. Postpolymerization functionalization of hydroxyl-group terminated polymers.

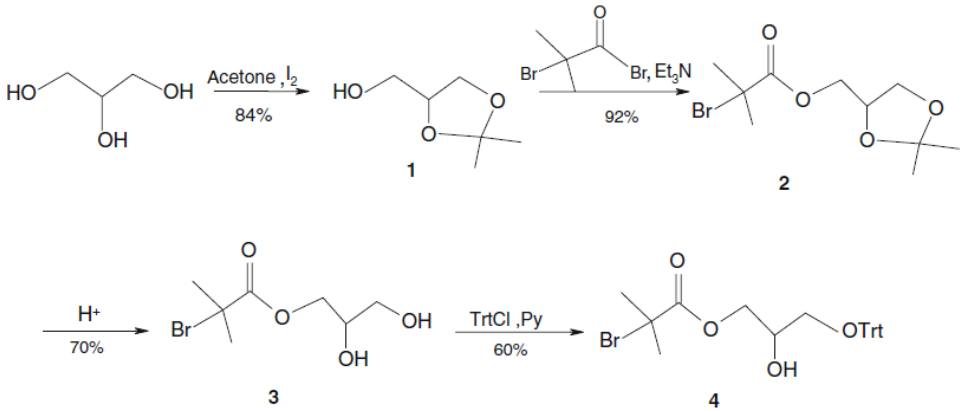
Poly(methyl methacrylate) in the brush form is grown from the surface of magnetite nanoparticles by ambient temperature atom transfer radical polymerization (ATATRP) using a phosphonic acid based initiator. The surface initiator was prepared by the reaction of ethylene glycol with 2-bromoisobutyrl bromide, followed by the reaction with phosphorus oxychloride and hydrolysis. This initiator is anchored to magnetite nanoparticles via physisorption.[166]



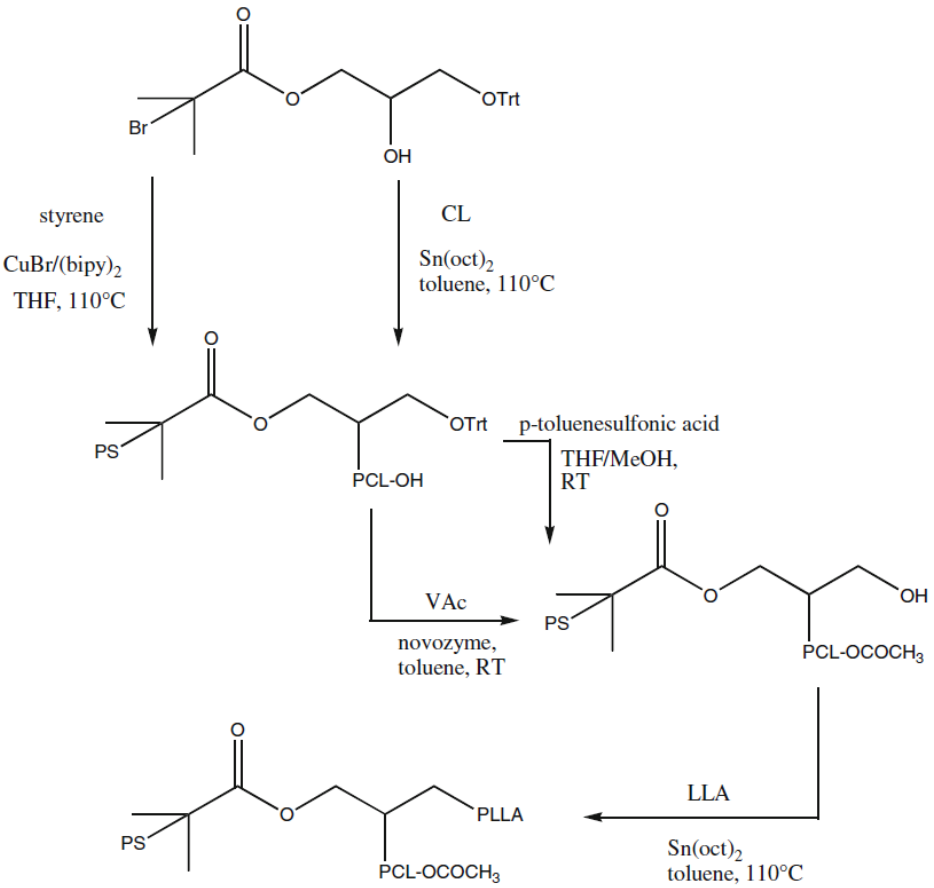
Scheme 1.34. ATRP initiator and anchoring on magnetite nanoparticle.

Dioxolane group containing α-halo ester used as initiator to produce dioxolane end-functional polymers by ATRP. Dioxolane group is very interesting because deprotection gives free dihydroxy groups that can be used for synthesis of dendrimer cores and nano-particle coated initiators. These initiators can produce tri-arm block copolymers and Miktoarm star block copolymers.

Well-defined ABC star block copolymer was synthesized using of a new heterotrifunctional initiator. That way, well-defined PCL-arm–PS-arm–PLLA star block copolymers have been synthesized from a heterotrifunctional initiator bearing two hydroxyl groups able to initiate ROP of CL and LLA (using $Sn(Oct)_2$ as coinitiator) and a bromide function able to initiate ATRP of styrene.[167]

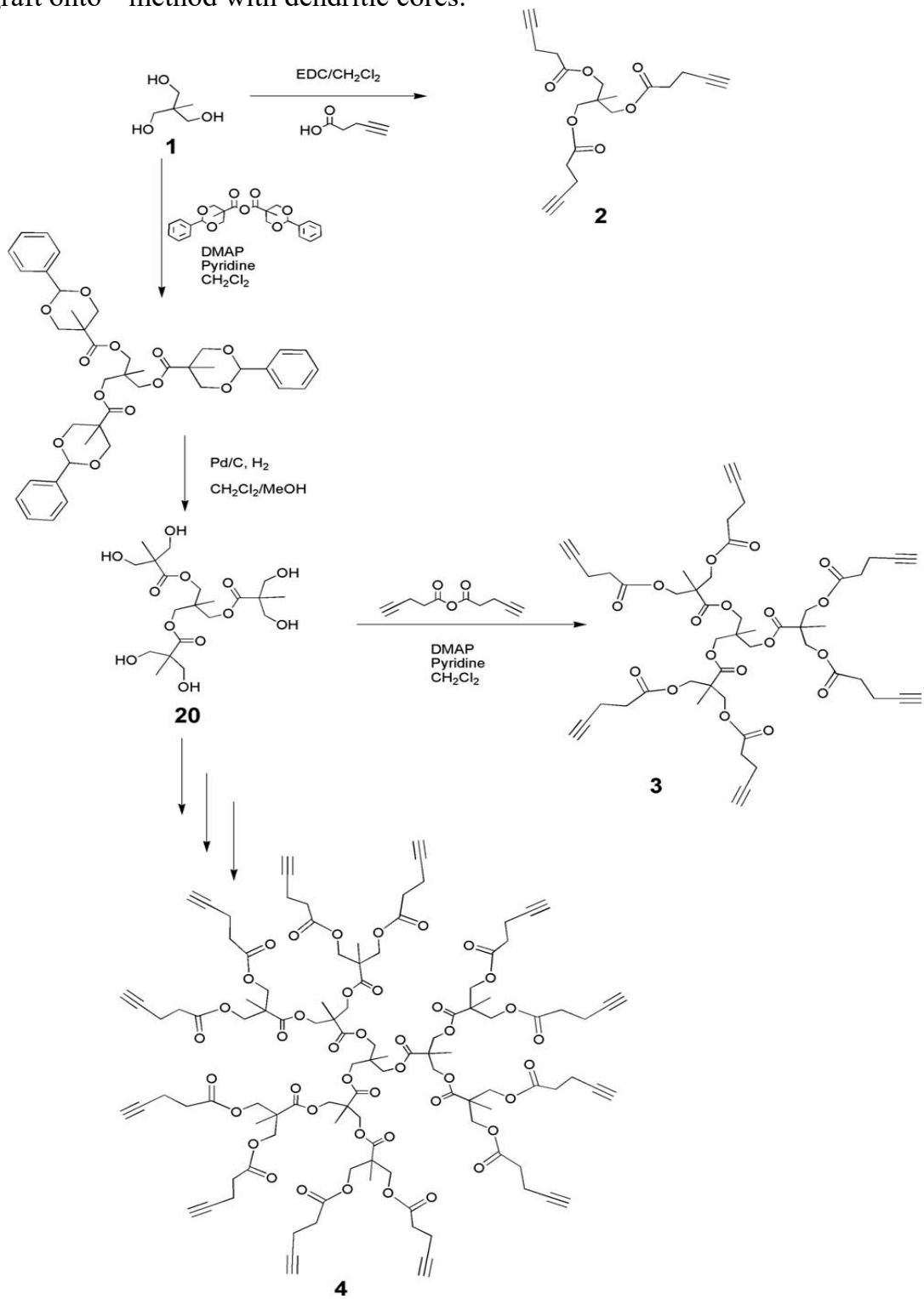


Scheme 1.35. Synthesis of the heterotrifunctional initiator.

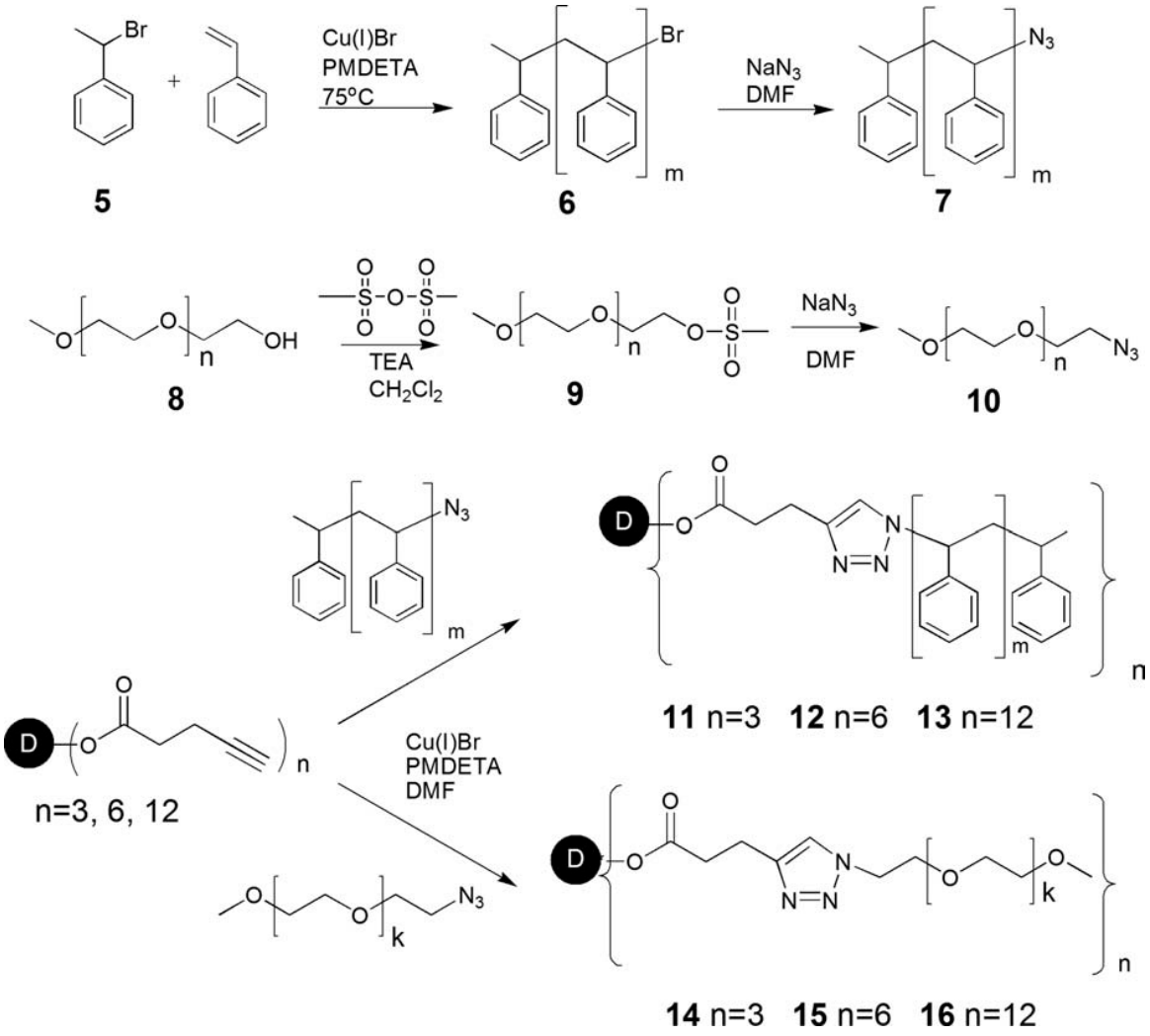


Scheme 1.36. Synthetic strategy for the synthesis of ABC miktoarm star block copolymers from the heterotrifunctional initiator, coupling ROP and ATRP.

The copper (I)-catalyzed azide-alkyne cycloaddition ‘‘click’’ reaction was successfully applied to prepare well-defined 3, 6, and 12-arms polystyrene and polyethylene glycol stars. In the case of star polymers, this has been demonstrated with both hydrophobic and hydrophilic arms attached via the ‘‘graft onto’’ method with dendritic cores.[168]



Scheme 1.37 Synthesis of alkynylated dendrimer cores.



Scheme 1.38 Synthesis of 3, 6, and 12-arm star PS and PEG.

Objectives of this research:

End- and mid-functionality plays an important role in the polymer's property and it allows the polymer to couple with other functionalities forming graft, blocks, star and cross-linking. Control over the synthesis of blocks and grafts the polymer architectures has become increasingly important in producing high value added materials for nanotechnology, biomaterials, blend modifiers and improving particular polymer properties by self-assembly. The end- and mid-functional polymers can be prepared by modifying end- and mid-group of polymers or most conveniently, by using functional initiators in living/controlled polymerization. In mid-1990, a new effective and attractive method of living/controlled radical polymerization, atom-transfer radical polymerization (ATRP) was developed. Atom Transfer Radical Polymerization (ATRP) is particularly suitable for the preparation of well-defined polymers with side and chain-end functional groups by using functional initiators.

Recent advances in "living" or controlled polymerization techniques have enabled facile synthesis of numerous functional polymers with controlled compositions and variable functionalities. When these techniques are combined with highly efficient linking reactions such as thiol-ene, azide−alkyne cycloaddition click reaction and ring opening reaction, star and branched polymers with extended compositions were successfully obtained. Star polymers have been extensively investigated due to their variable chain length and arm number, rich chemical variability, versatile properties, and potential applications in many fields. Thiol-ene click reaction, azide−alkyne click reaction and dioxolane ring opening reaction are used as a precursor to obtain well defined block copolymer and star polymers. Thus vinyl, alkyne and dihydroxyl functional polystyrene has enormous impotency to synthesis various polymers with complex architectures.

Therefore, in this study, five α-bromoester initiators bearing allyl, alkyne and dioxolane group were synthesized and polymerizations of styrene

with Cu(I)-bypridine mediated ATRP were carried out by using those initiators for synthesis of end- allyl, alkyne and dihydroxyl functional and mid- alkyne functional polystyrene.

The purpose of this thesis is as follows:

1. A initiator allyl-2-bromopropinamide (**N-ABPN**) was synthesized and the structure of **N-ABPN** was characterized by ^{1}H and ^{13}C NMR analysis. The efficiency of **N-ABPN** as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at various reaction conditions. The structure of the polystyrene obtained with **N-ABPN** was characterized by NMR analysis.
2. To synthesis and characterization of an initiator undecenyl-2-bromopropionate (**UBP**) was discussed. The efficiency of UBP as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at various reaction conditions. The structure and thermal properties of the polystyrene obtained with this catalyst system was determined by NMR analysis and DSC.
3. Synthesis and characterization of initiator 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester **(BPE)** and 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl diester **(BPDE)** were discussed.
4. The efficiency of **BPE** as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at different time duration. The structure of the polystyrene obtained with this catalyst system was determined by NMR analysis.
5. The efficiency of **BPDE** as initiator on Cu(I)-bipyridine mediated ATRP of styrene were studied at different time duration. The structure of the polystyrene obtained with this catalyst system was determined by NMR analysis
6. A initiator 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4- ylmethyl] ester (**BPDME**) was synthesized and characterized by spectral analyses. The polymerization of styrene was investigate by Cu(I)-bipyridine

mediated ATRP using **BPDME** as initiator at various reaction conditions. The structure of the polystyrene obtained with **BPDME** was characterized by NMR analysis. Finally the dioxolane end group was converted to dihydroxyl end-group by Chemical modification and characterized by NMR analysis.

CHAPTER

II

Synthesis of N-allyl-2-bromopropionamide and Its Application as Initiator on the ATRP of Styrene

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Synthesis of N-allyl-2-bromopropinamide and Its Application as Initiator on the ATRP of Styrene

2.1. Introduction

The development of Living Radical Polymerization (LRP) techniques constitutes one of the key developments in the field of synthetic polymer chemistry, allowing for the synthesis of a variety of polymers with narrow molecular weight distributions and with precise control over the compositions and structures.[43,169] Synthesis of well defined reactive end-functional polymers has great importance for their use as macromonomer, macroinitiator, precursor for block copolymers etc. Recently a living radical polymerization method "Atom Transfer Radical Polymerization" (ATRP) has emerged as a versatile technique that has been applied broadly because of the robustness of the chemistry and the commercial availability of many initiators, catalysts and ligands.[170,171] As with other LRP techniques, control of the α-chain terminus is accessed from the initiator design, which for ATRP most often involves an alkyl halide with an activating substituent on the α-carbon that undergoes homolytic cleavage in the presence of catalyst to initiate polymerization. Since ester groups are good activating groups, α-haloester-based compounds are commonly used as ATRP initiators, whereby the ester unit can also carry functionality.[6] The functionality incorporated into the polymer via an ester linkage is prone to hydrolysis; however, this lability has been overcome by their replacement with amide linkages through the use of α- halo amide-based initiators.[66,172] The presence of amides are often considered to present unique challenges for ATRP in the production of polymers with narrow molecular weight distribution and having molecular weights in agreement with theoretical values. A recent report from Haddleton's laboratory thoroughly examined the conditions under which amide containing ATRP initiators gave well-controlled

polymerization of various methacrylates and styrene.[66] Prior work in Sawamoto's laboratory demonstrated the preparation of poly (methyl methacrylate) with narrow Polydispersity Index (PDI) using N,N-dimethyl-2-bromopropanamide as the initiator.[172] Matyjaszewski's laboratory has studied the polymerization of methacrylamides using a model α-haloamide-based initiators, obtaining well defined block copolymers. Recently, scientists Xia et al.,[173] have employed various chloro-propionamides as initiators to polymerize N-isopropylacrylamide with narrow molecular weight distribution to study the influence of the end group composition resulting from the initiators on the thermal properties. Well-defined end-functional polymers are useful as building blocks for design and synthesis of various complex macromolecular architectures such as block,[174] graft,[175] star [176] copolymers etc. which find applications in biomedica,[177] tissue engineering,[178] composite materials[179] and surface sciences.[180] Although various end-functional polymers are reported so far, the synthesis of amide group containing reactive end-functional polymers still have an interest due to it's protein coupling ability to polymer and biomedical applications.[93] Therefore, in this study amide group containing end-allyl functional N-allyl-2-bromopropinamide (N-ABPN) was synthesized and the ATRP of styrene was investigated using N-ABPN as initiator to obtain end-allyl functional polystyrene (PSt). The initiator efficiency and polymer properties also studied.

2.2. Experimental Section

2.2a. Materials: Styrene was purchased from Sigma and it was purified by passing through an alumina column to remove stabilizer and then stirred with CaH_2 for 8 hrs and filtered. Finally it was stored at 0 ºC under nitrogen prior to use. CuBr was purified by recrystalization in methanol and wash with ether. Bipyridine from fluka, 2-bromopropinyl bromide and allyl amine were purchased from Aldrich and used without further purification. Triethylamine was distilled over CaH_2. All solvents were purified by distillation followed by refluxed with sodium and benzophenone.

2.2b. Polymerization Procedure: Polymerization was carried out in a 25 mL schelnk reactor equipped with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuBr, bipyridine and a tiny magnetic capsule. Three cycles of vacuum-evacuation of reactor and fill-up with nitrogen gas were performed, and the reactor was then sealed with rubber septum. A required amount of degassed styrene and initiator **N-ABPN** were added with a syringe. The rector was placed in an oil bath to keep desired temperature by tuning thermostat and the reaction mixture was stirred for certain time using magnetic stirrer. At certain interval, the polymerization was stopped by addition of methanol followed by cooling the reactor into ice-water and the polymer was precipitated in methanol by stirring for overnight. The polymers obtained were filtered, adequately washed with methanol and dried under vacuum at 60 ºC for 6 hrs.

2.2c. Analytical Methods: Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by gel permeation chromatography (Toyo soda HLC-802; Column, GMH6 × 2 + G4000H8) and eluent, $CHCl_3$ as solvent and calibrated by polystyrene standards. ^1H and ^{13}C NMR spectra of organic products and polymers were recorded at room temperature on a JEOL GX 400 spectrometer pulse Fourier transforms mode with choloroform-*d* as solvent. The peak of chloroform-*d* (7.2 ppm for ^1H and 77 ppm for ^{13}C) was used as internal reference.

2.2d. Synthesis of Initiator N-ABPN: 2.26 mL (30 mmol) of allyl amine (**1**) and 6.0 mL (43 mmol) of triethylamine dissolved in 40 mL of THF. The solution was cooled in an ice-water bath. To this solution, 3.2 mL (30 mmol) of 2-bromopropinyl bromide (**2**) in 20 mL of THF was added drop-wise. The mixture was stirred for 2 hrs at room temperature (**1** reacted with **2** to yield **N-ABPN** and HBr; HBr was absorbed by triethylamine). Triethylamine hydrogen bromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolved in diethyl ether and washed with 50 mL of water three times. The aqueous part were combined and shaken with 50 mL of fresh diethyl ether. The total ether solution was then dried over anhydrous sodium sulphate for over night. After filtering off the drying agent, ether was distilled out under vacuum. A yellowish liquid was obtained. A further distillation under high vacuum gave a light yellow color liquid; yield 1.8 mL, (69%). The structure of the product was characterized by NMR analysis.

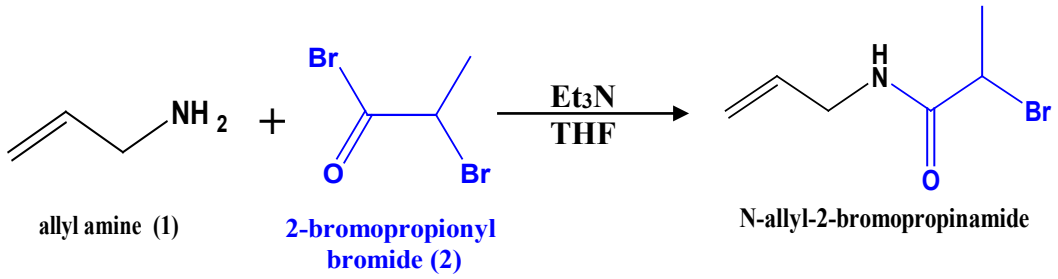
^{1}H NMR ($CDCl_3$): 6.9 ppm (s, 1H, -*N**H***); 5.8 ppm (m, 1H, CH_2=*C**H***-); 5.1 ppm (dd, 2H, *C**H**$_2$*=CH-); 4.4 ppm (q,1H, -*C**H***Br-CH_3); 3.8 ppm (d, 2H, CH-*C**H**$_2$*-NH-); 1.7 ppm (d, 3H, -CH-*C**H**$_3$*).

^{13}C NMR ($CDCl_3$): 169 ppm (-***C***=O); 133 ppm (CH_2=***C****H*-); 116 ppm (***C****H*$_2$=CH-); 44 ppm (-***C****H*Br-CH_3); 42 ppm (=CH-***C****H*$_2$-NH-); 22.6 ppm (-CHBr-***C****H*$_3$).

2.3 Result and Discussion

2.3a. Characterization of Initiator N-ABPN

The initiator **N-ABPN** was synthesized from the reaction between allyl amine and 2-bromopropionyl bromide in the presence of triethylamine according to the procedure described in experimental section.



Scheme 2.1. Synthesis of N-ABPN.

The product **N-ABPN** was characterized by ^{1}H NMR and ^{13}C NMR analysis. In the ^{1}H NMR spectrum of the **N-ABPN** (Figure 2.1), several signals were appeared clearly assigned as follows: singlet at 6.9 ppm was appeared for assumable to –N**H**– proton. A mutiplate at 5.8 ppm and a double doublet at 5.1 ppm assignable to -C**H**=CH_2 and -CH=C**H**$_2$ protons, respectively, were labeled as 'b' and 'a' which indicates the presence of vinyl group. The splitting (double doublet) of the vinyl (CH_2=) protons indicates the presence of *cis-trans* isomers of **N-ABPN**. A doublet appeared at 3.8 ppm was assigned to =CH-C**H**$_2$-NH- proton. Two signals appeared at 4.4 ppm and 1.7 ppm assignable to (-C**H**Br-) and (-C**H**$_3$) protons, respectively, were labeled as e and f in Figure 2.1.

In the ^{13}C NMR spectrum of the **N-ABPN**, the vinilene and vinyl carbons were appeared at 133.2 and 116 ppm respectively; the (-C=O) carbon of ester group was appeared at 169.46 ppm, and the rest three signals appeared at up-field were clearly assigned to the saturated carbons of **N-ABPN** (Figure 2.2). The signals appeared were clearly assigned to the all carbons of **N-ABPN**, which indicate the purity of **N-ABPN**.

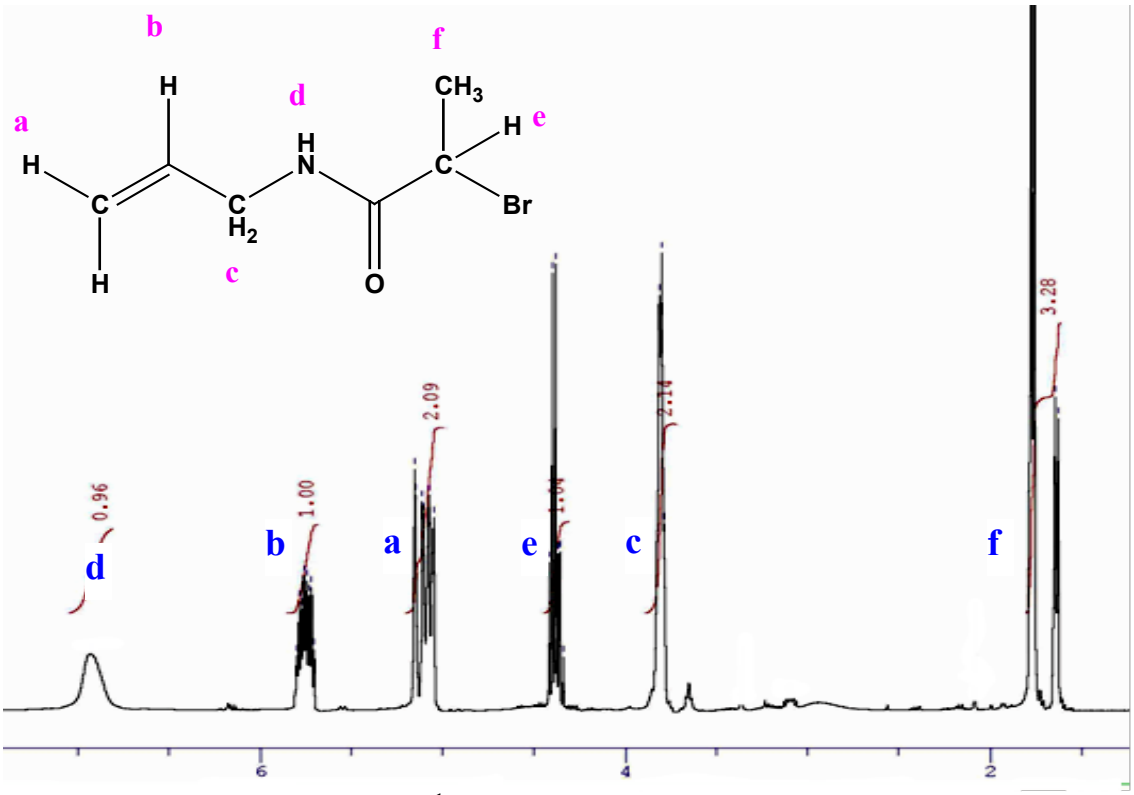


Figure 2.1. ^{1}H NMR spectrum of **N-ABPN.**

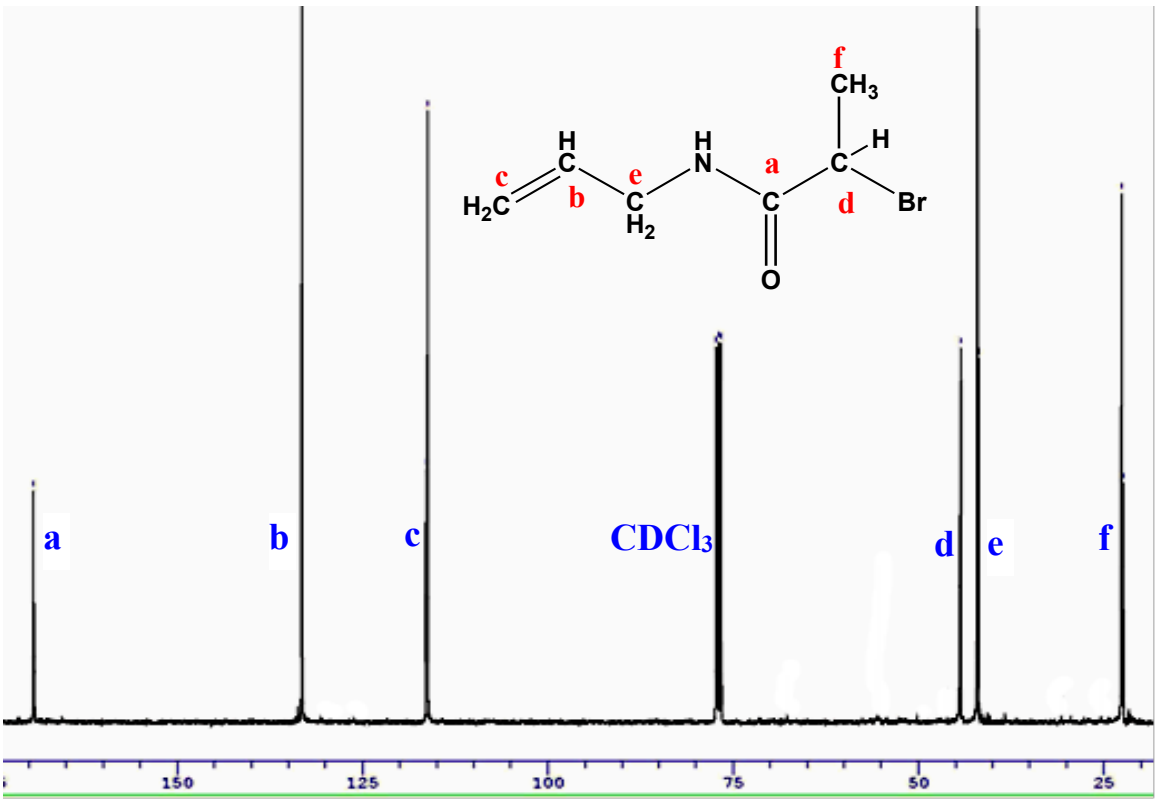


Figure 2.2. ^{13}C NMR spectrum of **N-ABPN.**

2.3b. Polymerization of Styrene by ATRP using N-ABPN as Initiator

The polymerization of styrene was carried out by **N-ABPN**/CuBr/BiPy at various temperatures under nitrogen atmosphere. The results are listed in table 2.1. At 75 ^{0}C, a trace amount of polymer was obtained whereas the yield was increased with increasing polymerization temperature.

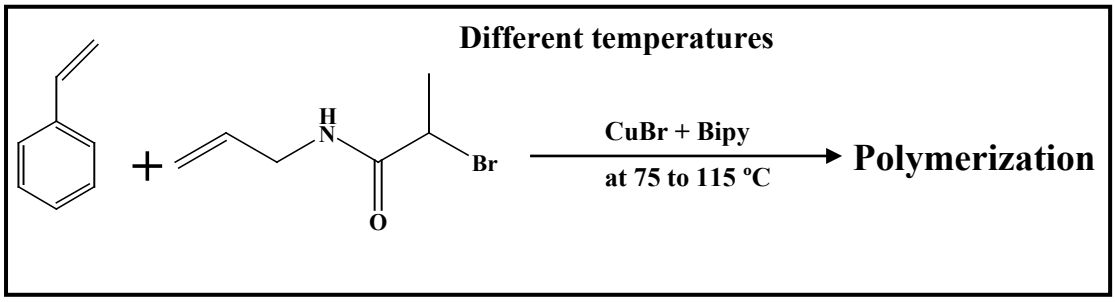


Table 2.1: Effect of the Temperature on Polymerization of Styrene with CuBr/BiPy/ N-ABPN.

Entry	St/N-ABPN	Temperature (º C)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
1	500	75	trace	-	-	-
2	500	100	0.23	10.57	14.45	1.36
3	500	115	1.43	28.49	33.82	1.20

Polymerization conditions [CuBr = 0.054 mmol, Bipy = 0.108 mmol, Styrene = 3.1 mL (27mmol), time = 8 h]

The polymer obtained with narrow M_w/M_n at higher temperature. These results suggest that initiator works well at high temperature because C-Br bond of amide functional initiators need more energy. The GPC curves are displayed in figure 2.3. The molecular weight of polymer was increased almost tree times when temperature was increased only 15 ^{0}C (entry 2 and 3).

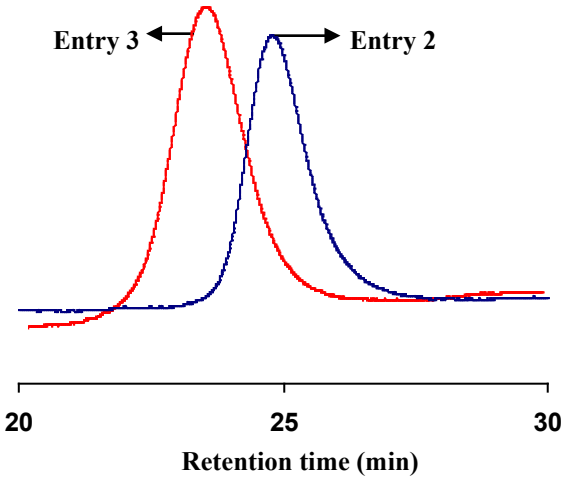
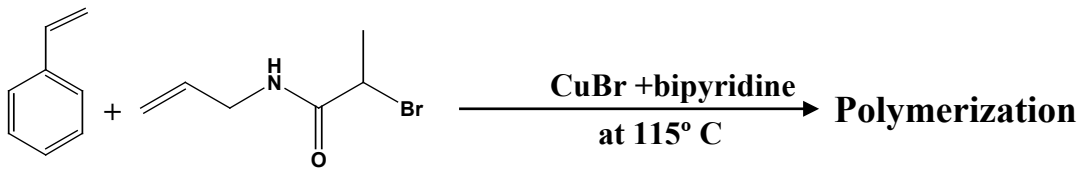


Figure 2.3: GPC curves of polystyrene obtained by N-ABPN.

Styrene was polymerized by ATRP at 115 ºC initiated using three different ratio of **N-ABPN** and styrene (St/ **N-ABPN** = 250, 500 and 1000) in conjunction with Cupper(I)bromide-bipyridine catalyst under nitrogen atmosphere. The results of the polymerization are summarized in Table 2.2. The ratio of styrene and **N-ABPN** (St/**N-ABPN**) significantly affects the results of polymerization. The yield of polymers was increased with the increasing of ratio of styrene and **N-ABPN**.

Different Ratio of Monomer and Initiator



The molecular weight and molecular weight distribution of the polymers obtained were measured with gel permeation chromatography (GPC). The polymers obtained with high molecular weight (M_n). The M_n value of the polymers was increased with the increasing St/N-ABPN ratio. The molecular weight distribution of polymer was narrow (M_w/M_n ~1.18). The GPC curves of the polymers obtained from the feed ration St/ N-ABPN = 1000, St/ N-ABPN = 500 and St/ N-ABPN = 250 are displayed in Figure 2.4.

Table 2.2. Effect of the Ratio of Styrene/ N-ABPN on Polymerization of Styrene.

Entry	St/N-ABPN	Temperature (°C)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
4	250	115	0.99	11.74	14.17	1.18
5	500	115	1.43	28.49	33.82	1.20
6	1000	115	1.81	41.90	55.41	1.32

Polymerization conditions [CuBr = 0.054 mmol, Bipy = 0.108 mmol, Styrene = 3.1 mL (27mmol), time = 8 hrs]

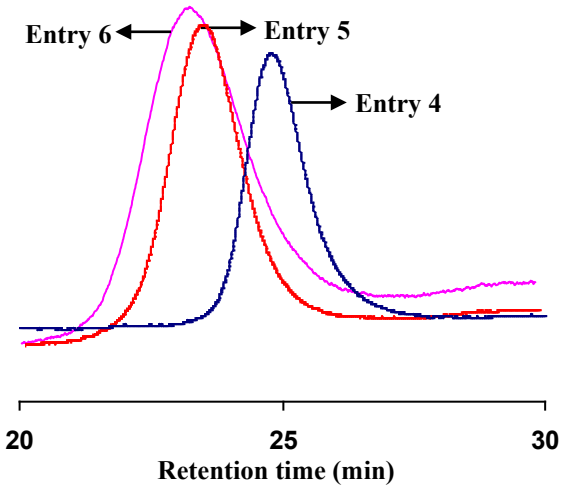


Figure 2.4: GPC curves of PSt by N-ABPN.

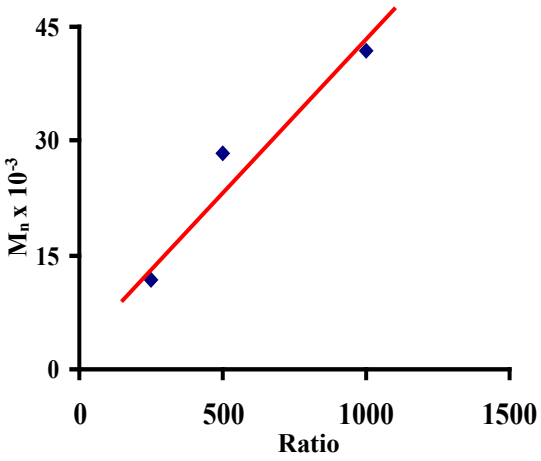


Figure 2.5: Plot of M_n against ratio of PSt by N-ABPN.

The GPC curve of the polymer was obtained from higher monomer concentration (St/N-ABPN = 1000) shifted to the higher molecular weight region than that of the polymer obtained from lower monomer concentration (St/N-ABPN = 500). The M_n value (42 x 10^3) of the polymer obtained from the higher feed ration (St/N-ABPN = 1000) was more than the M_n value (28.5 x 10^3) of the polymer obtained from the lower feed ration (St/ N-ABPN = 500). These results suggest that the higher propagation rate occurred at higher monomer concentration. The linear relationship of molecular weight of the polymers with ratio (Figure 2.5) also supports the above results.

To produce polymer with narrow polydispersity is one of the main criteria for a living polymerization system. The initiator N-ABPN combined with CuBr/bipyridene catalyst system gave the polymers with narrow polydispersity (M_w/M_n = 1.18 at 115 ºC (entry 4). This result therefore promotes us to make sure the living nature of N-ABPN /CuBr/bipyridene catalyst system at 115 ºC. The dependence of polymer yield and M_n on polymerization time was investigated by batch method to check the living nature of this catalyst system. The molecular weight and molecular weight distribution of the polymers obtained by different polymerization time were measured by GPC and the results are summarized in Tab 2.3.

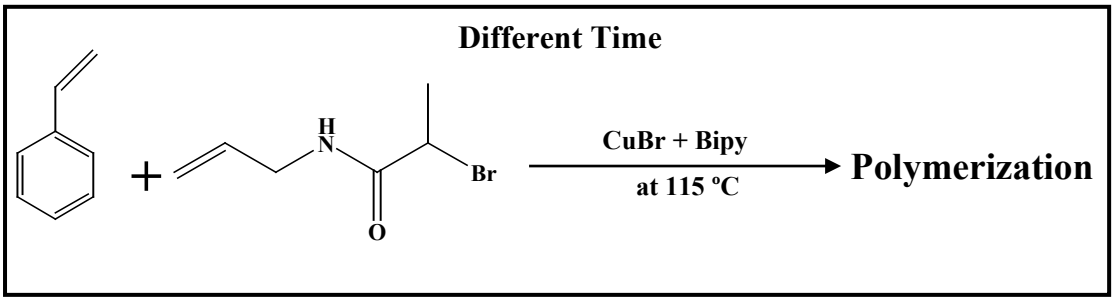


Table 2.3: Effect of Time on Polymerization of Styrene with CuBr/Bipyridine/ N-ABPN.

Entry	Initiators	Time (h)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
7	**ABPN**	6	0.73	14.88	18.91	1.27
8	"	8	1.43	28.49	33.82	1.20
9	"	9	2.07	41.38	49.94	1.20

Polymerization conditions; CuBr = 0.054 mmol, Bipy = 0.108, mmol, Styrene = 3.1 mL, temperature = 115 ºC.

The GPC curves of polymers obtained from different period of time (6, 8 and 9 hours) were compared in Figure 2.6. The GPC curves were shifted to the higher molecular weight region with increasing polymerization time with keeping narrow M_w/M_n. The plot of time vs M_n showed linear relationship with a slop at

initial period in Figure 2.7. These results suggest that the living polymerization of styrene proceeded at 115 ºC N-ABPN/CuBr/BiPy catalyst system with slow initiation.

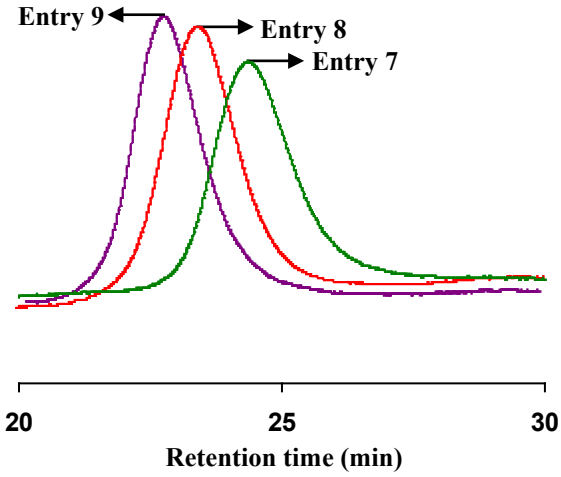


Figure 2.6: GPC curves of PSt by N-ABPN.

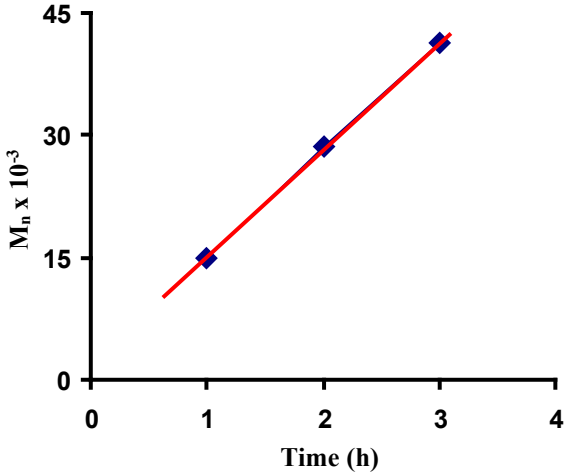


Figure 2.7: Plot of M_n against time of PSt by N-ABPN.

2.3c. Analysis of the Structure of the Polystyrene Obtained

The structure of polystyrene obtained with **N-ABPN**/CuBr/Bipyridine catalyst system was investigated by the ^{1}H NMR analysis. The ^{1}H NMR spectrum of polystyrene obtained with **N-ABPN** was displayed in Figure 2.8. In the ^{1}H NMR spectrum of polystyrene, the presence of a double doublet at 5.4 and 4.8 ppm assignable to vinyl protons and a signal at 4.5 ppm assignable to -C**H** proton of α-Br were labeled as b, c and d respectively which indicate that the polymerization was initiated with **N-ABPN**. A broad signal at 7.1 ppm was assigned to aromatic protons (*para*- and *meta*- position) of styrene unit were labeled as m and n, and at 6.51 ppm for *ortho*-proton as o (Figure 2.8). The signals observed at 1.37 and 1.79 ppm were assigned for the -C**H**$_2$ and -C**H** protons of main chain of polystyrene respectively.

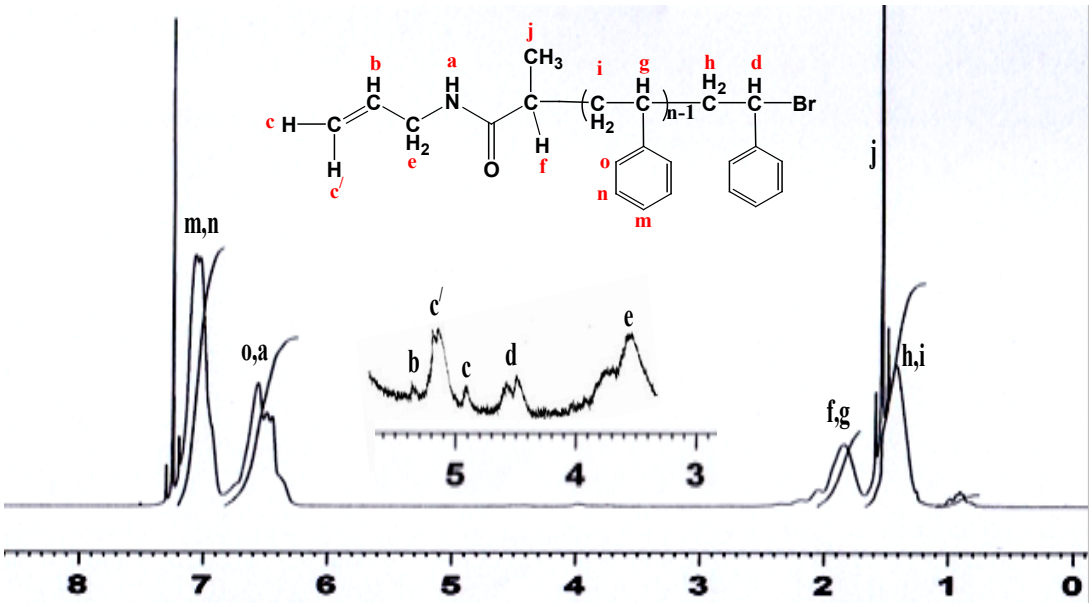


Figure 2.8 ^{1}H NMR spectrum of vinyl end-functional Polystyrene.

2.4. Conclusion

The initiator **N-ABPN** was synthesized in a good yield. The structure of **N-ABPN** was characterized by ^{1}H and ^{13}C NMR analysis. The **N-ABPN** as a initiator was successfully applied for Cu(I)-bipyridine mediated ATRP polymerization of styrene. The polymerization of styrene was investigated at various reaction conditions. At 75 ºC temperature, a trace amount of polymer was obtained where as a good amount of polymer was obtained at 115 ºC. The polymer yield was increased with increasing the feed ratio of styrene and **N-ABPN**. The yield of the polymer linearly increased against time after a certain period of time. This result suggests that the living polymerization of styrene should proceed at 115 ºC by **N-ABPN** /CuBr/BiPy catalyst system with slow initiation.

In the ^{1}H NMR spectrum of the polystyrene obtained with **N-ABPN** /CuBr/BiPy catalyst system, the signals assignable to allyl amino group indicate the allyl amino chain-end structure of the polystyrene, which was formed by the ATRP initiated with **N-ABPN**.

CHAPTER III

Synthesis of Undecenyl-2-bromopropeonate and Its Application as Initiator on the ATRP Polymerization of Styrene

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Synthesis of Undecenyl-2-bromopropeonate and Its Application as Initiator on the ATRP Polymerization of Styrene

3.1. Introduction

Various α-haloesters have been successfully employed to initiate well-controlled ATRP.[46] In general, α-haloisobutyrates produce initiating radicals faster than the corresponding α-halopropionates due to better stabilization of the generated radicals after the halogen abstraction step. Thus, slow initiation will generally occur if α-halopropionates are used to initiate the polymerization of methacrylates. In contrast, α-bromopropionates are good initiations for the ATRP of acrylates due to their structural resemblance. Matyjaszewski *et. al.* reported the ATRP of styrene with vinyl chloroacetate and allyl chloroacetate as initiator using Cu-BiPy catalyst system. The vinyl chloroacetate was found as better initiator for styrene polymerization.[60] Structural adjustment of the initiator provides a handle to fine-tune the rate of initiation in the ATRP system. Often, the structure of initiator is analogous to the structure of the polymer end group.

Among the other end functional epoxy group in the polymer chain is a very interesting one because it is not only a reactive functional group but also a polymerizable functional group that may be classified as "macromonomers".

In the previous chapter (CHAPTER II), N-allyl-2-bromopropionate (N-ABPN) was synthesized and used as initiator in Cu (I) mediated ATRP of styrene at various reaction conditions, and the polystyrene was obtained with allyl propionate chain end. In this chapter, undecenyl-2-bromopropionate (UBP) will be synthesized and the ATRP of styrene will be investigated using UBP as initiator. The initiator efficiency, polymer properties and conversion of vinyl chain end to epoxy end will also be studied.

3.2. Experimental Section

3.2a.Materials. Styrene was purchased from Aldrich and it was purified by passing through an alumina column to remove stabilizer and then stirred with CaH_2 for 8 h and filtered. Finally it was stored at 0 °C under nitrogen prior to use. Copper (I) bromide was purified by recrystalization in methanol and washed with ether. Bipyridine from Fluka, 2-bromopropenyl bromide and 10-undecen-1-ol were purchased from Aldrich and used without further purification. Triethylamine was distilled over CaH_2. All solvents were purified by distillation followed by refluxed with sodium and benzophenone.

3.2b. Polymerization Procedure. Polymerization was carried out in a 50 mL Schelnk type reactor equipped with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuBr and bipyridene. Three freeze-pump-thaw cycles were performed, and the tubes were sealed under vacuum with rubber septum. A required amount of degassed styrene and initiator were added with syringe. The reactor was placed in an oil bath held by a thermostat at the desired temperature and the reaction mixture was stirred for certain time. At certain interval, the polymerization was stopped by added methanol followed by cooling the reactor into ice-water and the polymer was precipitated in methanol by stirring over night. The polymers obtained were filtered, adequately washed with methanol, and dried under vacuum at 60 °C for 6 h.

3.2c. Analytical Methods. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by GPC (Waters 150C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. ^1H and ^{13}C NMR spectra of polymers were recorded at room temperature on a JEOL GX 500 spectrometer operated at 125.65 MHz in pulse Fourier Transform mode with chloroform-*d* as solvent. The peak of chloroform in chloroform-*d* (7.26 ppm for ^1H and 74.47 ppm for ^{13}C) was used as internal

reference. Differential scanning calorimetry (DSC) was studied with a Seiko DSC-220 instrument under a nitrogen atmosphere at heating and cooling rate of 10 °C/min. T_g values were determined from the middle point of the phase transition of the second heating scan.

3.2d. Synthesis of Initiator UBP. A 5 g (29.5 mmol) sample of 10-undecene-1-ol (**1**) and 5 mL (36 mmol) of triethylamine were dissolved in 80 mL of THF. The solution was cooled in an ice-water bath. To this solution was added drop-wise 3.20 mL (30 mmol) of 2-bromopropenyl bromide (**2**) in 20 mL of THF. The mixture was stirred for another 2 h at room temperature (**1** reacted with **2** to yield UBP and HBr; HBr was absorbed by triethylamine). Triethylamine hydrogen bromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolved in $CHCl_3$ and washed with 50 mL of water three times. The aqueous parts were combined and shaken with 50 mL of fresh $CHCl_3$. The total $CHCl_3$ solution was then dried over anhydrous $CaCl_2$ for overnight. After filtering off the drying agent, $CHCl_3$ was distilled out under vacuum. A brown liquid was obtained. A further distillation under high vacuum gave a colorless liquid; yield 7.60 g (82 %).

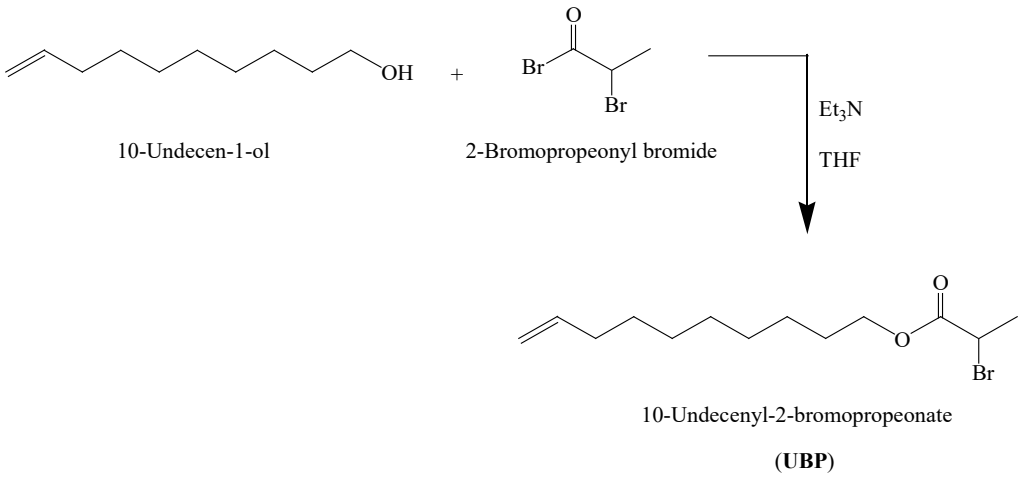
^{1}H NMR ($CDCl_3$): 5.72 ppm (m, 1H, CH_2=C***H***-); 4.85 ppm (dd, 2H, =CH_2); 4.41 ppm (q, 1H, CH_3C***H***(Br)-OC(O)-); 4.1 ppm (t, 2H, -O-C***H***$_2$$CH_2$-); 2.00 ppm (q, 2H, CH_2=CH-C***H***$_2$-); 1.80 ppm (d, 3H –CH(Br)-C***H***$_3$), 1.55 ppm (t, 2H, -O-CH_2C***H***$_2$-); 1.2 – 1.4 ppm (m, 14H, -O-CH_2CH_2-(C***H***$_2$)$_7$-

^{13}C NMR ($CDCl_3$): 167.46 ppm (C-l); 136.34 ppm (C-b); 111.47 ppm (C-a); 63.30 ppm (C-k); 37.48 ppm (C-m); 31.10 ppm (C-c); 25.71 - 26.73 ppm (C-d-h, j); 23.05 ppm (C-i); 18.97 ppm (C-n).

3.3. RESULTS AND DISCUSSION

3.3a. Synthesis and Characterization of Initiator

The initiator UBP was synthesized from the reaction between 10-undecene-1-ol and 2-bromopropenyl bromide in the presence of triethylamine (Scheme 3.1).



Scheme 3.1. Synthesis of UBP.

The product **UBP** obtained was characterized by ^{1}H NMR and ^{13}C NMR analysis. The ^{1}H NMR spectra of 2-bromopropenyl bromide and UBP were compared in Figure 3.1. In the ^{1}H NMR spectrum of 2-bromopropenyl bromide, two signals appeared at 1.8 ppm and 4.3 ppm assignable to (-C**H**$_3$) and (-C**H**Br-) protons, respectively, were labeled as 1 and 2 in Figure 3.1A. In the ^{1}H NMR spectrum of the **UBP**, several signals including the signals of 2-bromopropenyl bromide were observed. All signals correspond to the different protons of UBP were assigned clearly and labeled in Figure 3.1B. In the ^{13}C NMR spectrum of the UBP (Figure 3.2), the signals appeared were clearly assigned to the all carbons of UBP, which indicate the purity of **UBP**.

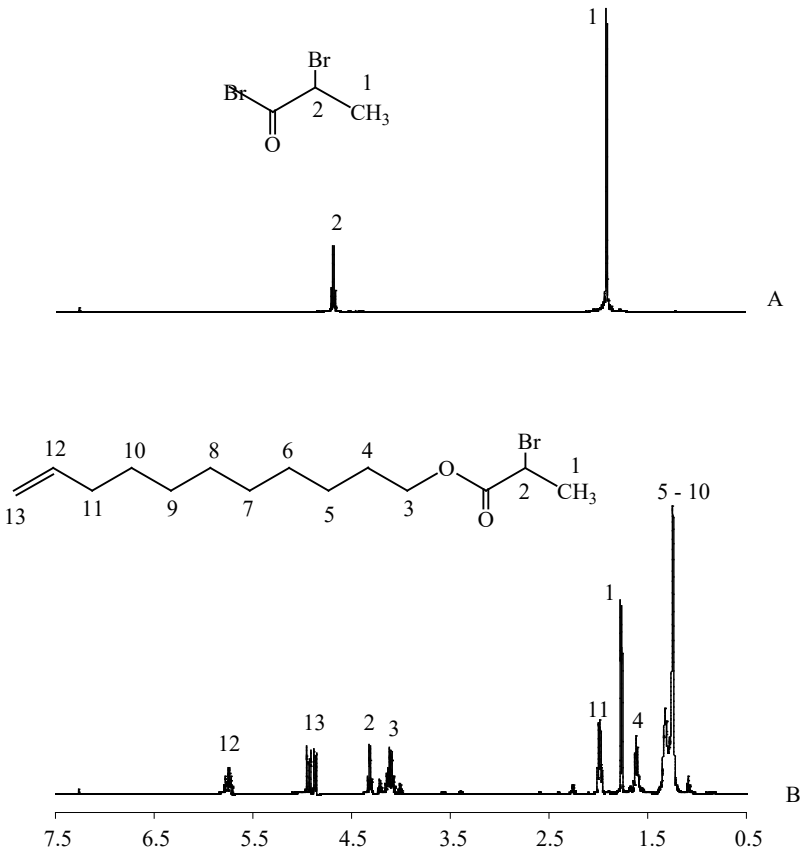


Figure 3.1. ^{1}H NMR spectra of 2-bromopropenyl bromide (A) and UBP (B).

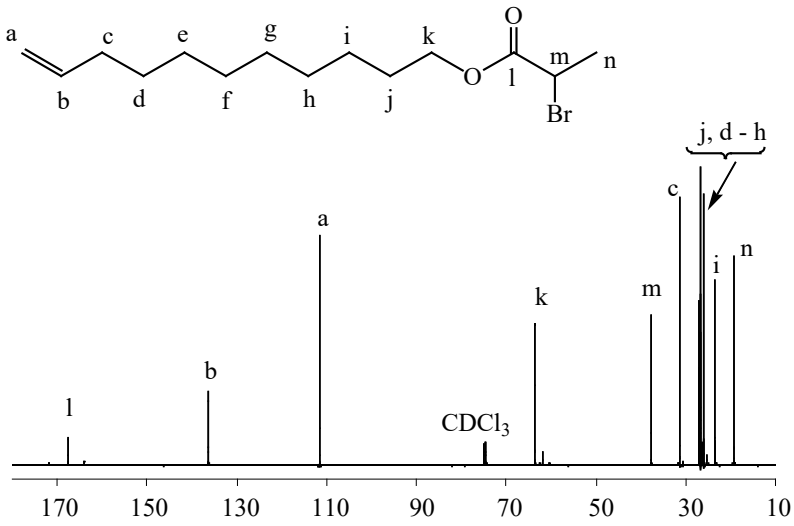


Figure 3.2. ^{13}C NMR spectrum of UBP.

3.3b. Polymerization of Styrene by ATRP using UBP as Initiator

Styrene was polymerized by ATRP at 110 ºC initiated with three different concentration of UBP relative to styrene in conjunction with cupper (I) chloride and bipyridine as a catalyst under nitrogen atmosphere. The results of the polymerization are shown in Table 3.1. The ratio of styrene and UBP (St/UBP) significantly affects on the polymerization. The yield of polymers was almost same at high ratio of styrene and UBP (St/UBP = 1000 and 500) and it was about half at ratio St/UBP = 250. The molecular weight and molecular weight distribution of the polymers obtained were measured with gel permeation chromatography (GPC) and the GPC curves obtained are displayed in Figure 3.3. The polymers obtained with this system showed high molecular weight and narrow molecular weight distribution (M_w/M_n < 1.5). The molecular weight of the polymers obtained was decreased with decreasing St/UBP ratio, whereas the molecular weight distributions were almost constant.

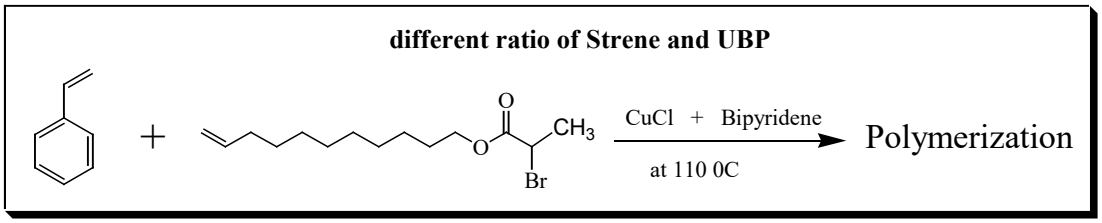


Table 3.1. Effect of the Ratio of Styrene/Initiator on Polymerization of Styrene with CuCl/BiPy.[a]

entry	St/UBP	yield (g)	M_n [b]	M_w [c]	M_w/M_n [d]
1	1000	1.02	18864	27760	1.47
2	500	0.96	9759	14684	1.50
3	250	0.61	4863	7295	1.50

[a]Polymerization conditions; CuCl = 0.08 mmol, BiPy = 0.24 mmol, temperature = 110 ºC, time = 2h. [b]Number average molecular weight, [c]Weight average molecular weight and [d]Molecular weight distribution were measured by GPC analysis using polystyrene standard.

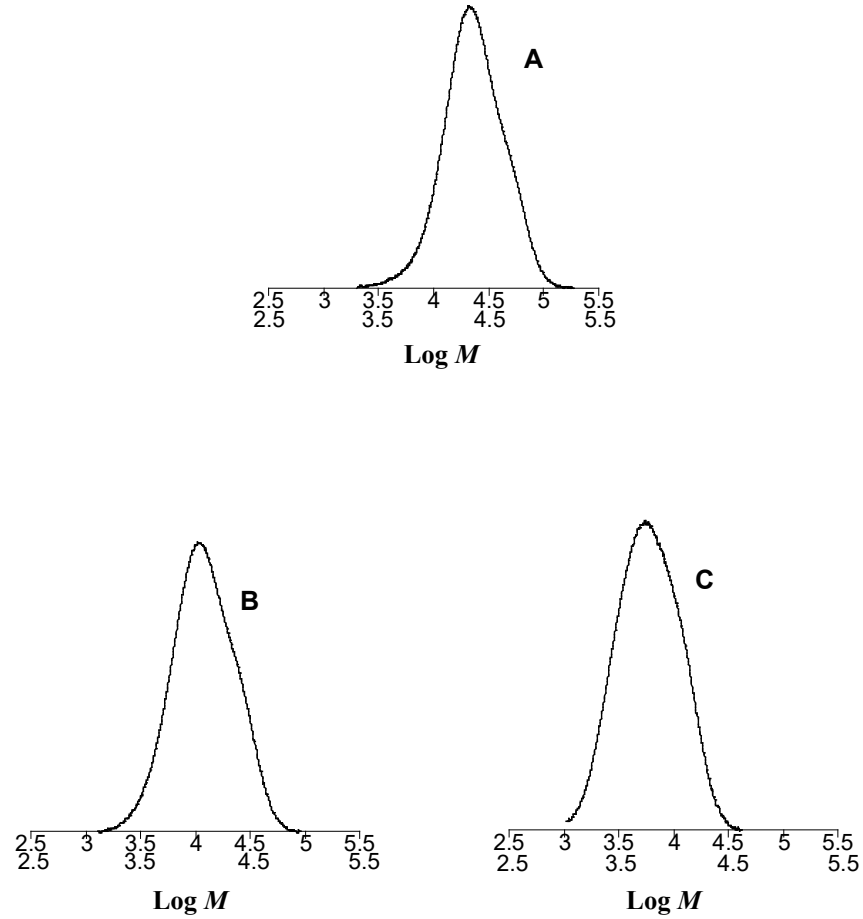


Figure 3.3. GPC curves of polystyrene obtained from entry 1 (A), entry 2 (B), and entry 3 (C).

The effect of temperature on polymerization of styrene with UBP/CuCl/BiPy (1:1:3) was investigated at various temperatures (75, 110 and 130 ºC). The results obtained are listed in Table 3.2. The yield of polymers was increased with raising the temperature of the polymerization. The GPC curve of the polystyrene obtained were displayed in Figure 3.4. The molecular of the polymers was increased and the molecular weight distribution became narrower with raising temperature.

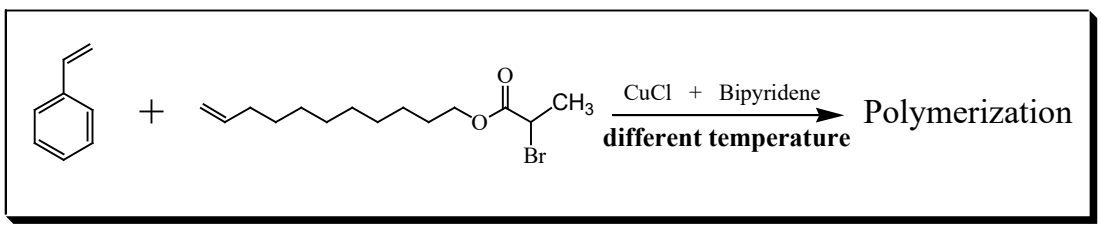


Table 3.2. Effect of Temperature on Polymerization of Styrene with CuCl / Bipyredene / UBP.[a]

Entry	Temperature (ºC)	Yield (g)	M_n [b]	M_w [c]	M_w/M_n [d]
4	75	0.05	8537	15499	1.81
5	110	0.96	9759	14684	1.50
6	130	1.74	14820	21236	1.43

[a]Polymerization conditions; CuCl = UBP = 0.08 mmol, BiPy = 0.24 mmol, Styrene = 5 mL, temperature = 110 ºC, time = 2h. [b]Number average molecular weight, [c]Weight average molecular weight and [d]Molecular weight distribution were measured by GPC analysis using polystyrene standard.

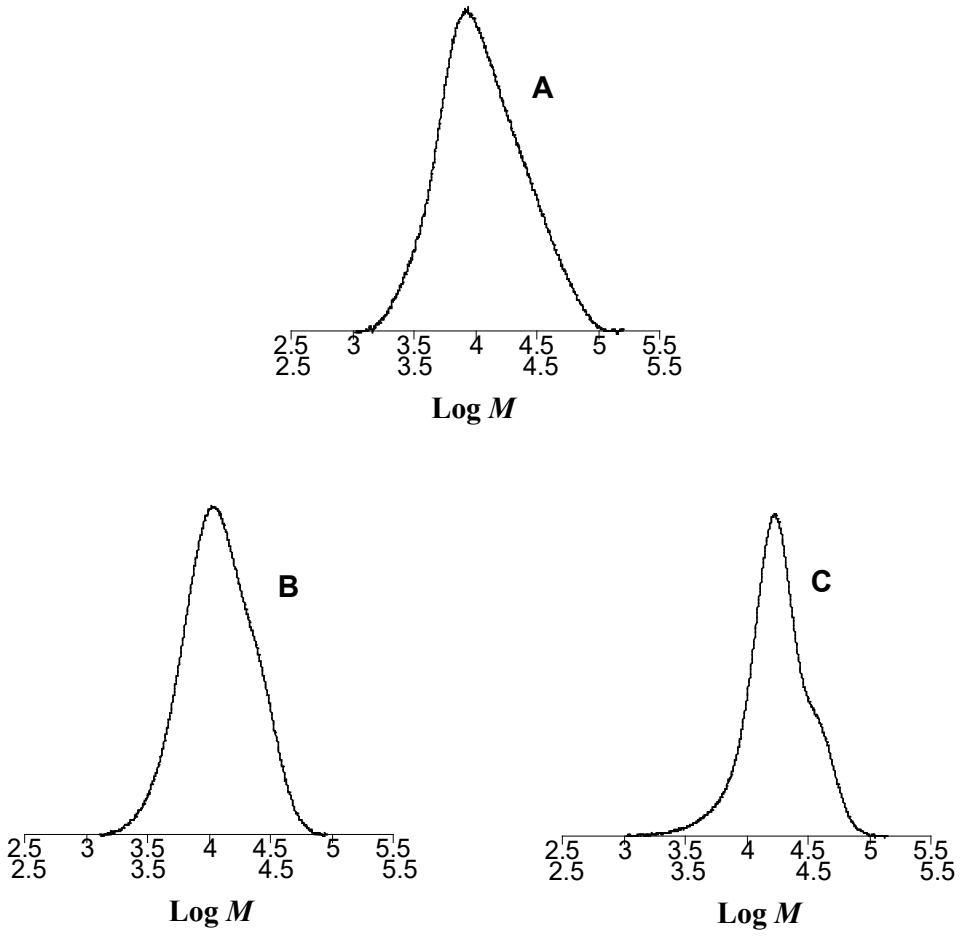


Figure 3.4. GPC curves of polystyrene obtained from entry 4 (A), entry 5 (B), and entry 6 (C).

The narrow polydispersity (M_w/M_n = 1.50) of the polymers obtained at 110 and 130 ºC suggests that the living polymerization of styrene should proceed with these conditions. To confirm the living nature at 110 ºC, the dependence of M_n on polymerization time was investigated by sampling method. 1 mL of reaction mixture was sampled with a syringe at every 30 minutes during polymerization. The molecular weight and molecular weight distribution of the polystyrene obtained by sampling method were measured by GPC. The GPC curves obtained are displayed in Figure 3.5 and the results are summarized in Table 3.3.

Table 3.3. Time Dependence Polymerization of Styrene with CuCl/Bipy/UBP by Sampling Method.[a]

Entry	Time (min.)	Yield (g)	M_n [b]	M_w [c]	M_w/M_n [d]
7	30	0.28	6305	10199	1.62
8	60	0.48	7663	12521	1.62
9	90	0.82	9168	14344	1.56
10	120	1.10	10556	15806	1.49
11	150	1.48	11916	17269	1.45
12	180	1.71	13147	19021	1.45

[a]Polymerization conditions; CuCl = UBP = 8 mmol, BiPy = 24 mmol, Styrene = 5 mL, temperature = 110 ºC, [b]Number average molecular weight, [c]Weight average molecular weight and [d]Molecular weight distribution were measured by GPC analysis using polystyrene standard.

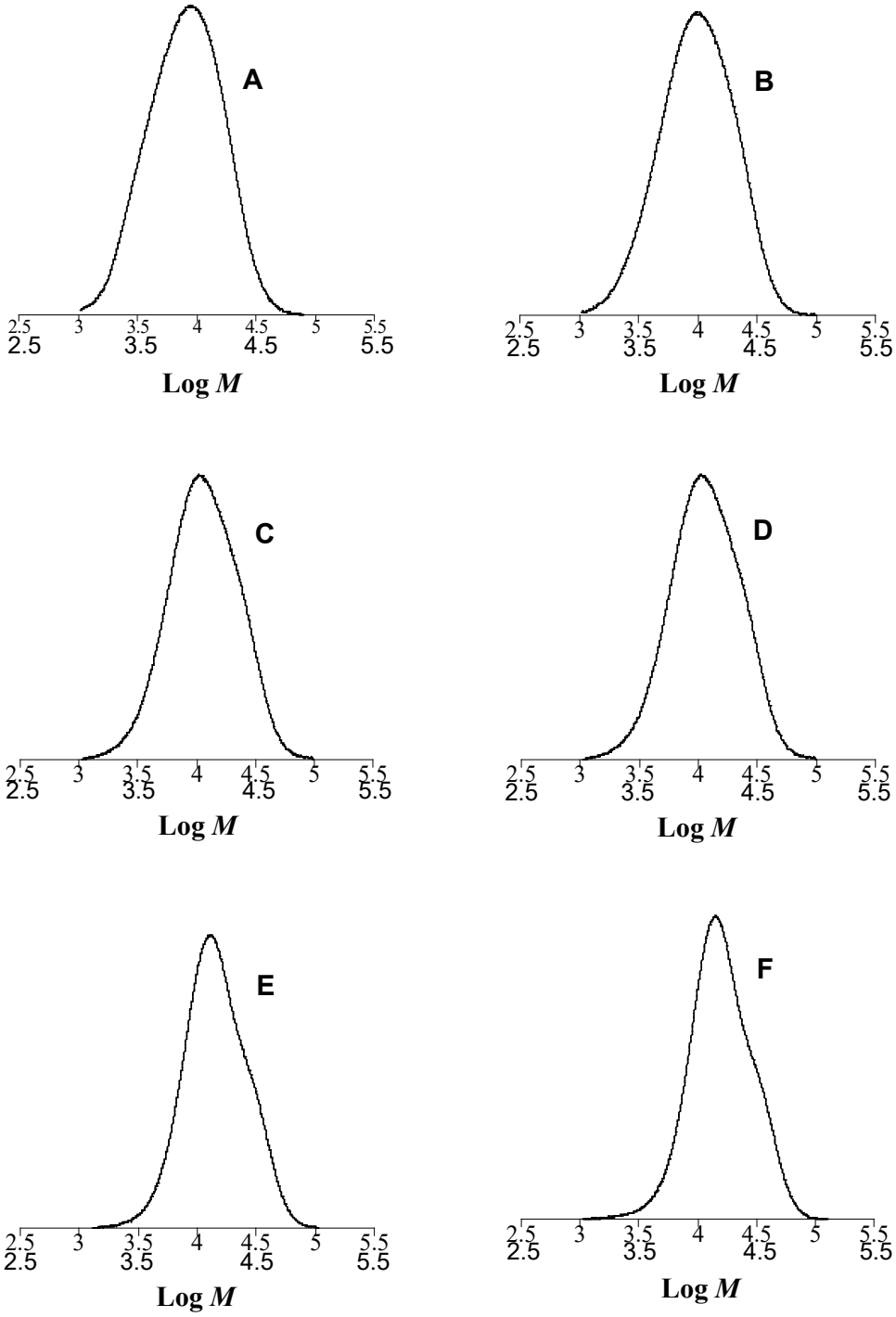


Figure 3.5. GPC curves of polystyrene obtained from entry 7 (A), entry 8 (B), entry 9 (C), entry10 (D), entry 11 (E) and entry 12 (F).

The GPC curves of polymers obtained by sampling were compared in Figure 3.6 and the curves were shifted to the higher molecular weight region with increasing polymerization time keeping narrow M_w/M_n. The M_n and M_w/M_n values vs conversion are plotted in Figure 3.7. The M_n value of the polystyrene linearly increased against conversion. The yield of the sampled polymer also increased linearly with polymerization time (Figure 3.8). These results indicate that the living polymerization of styrene proceeded at 110 ºC using CuCl/BiPy/UBP catalyst system.

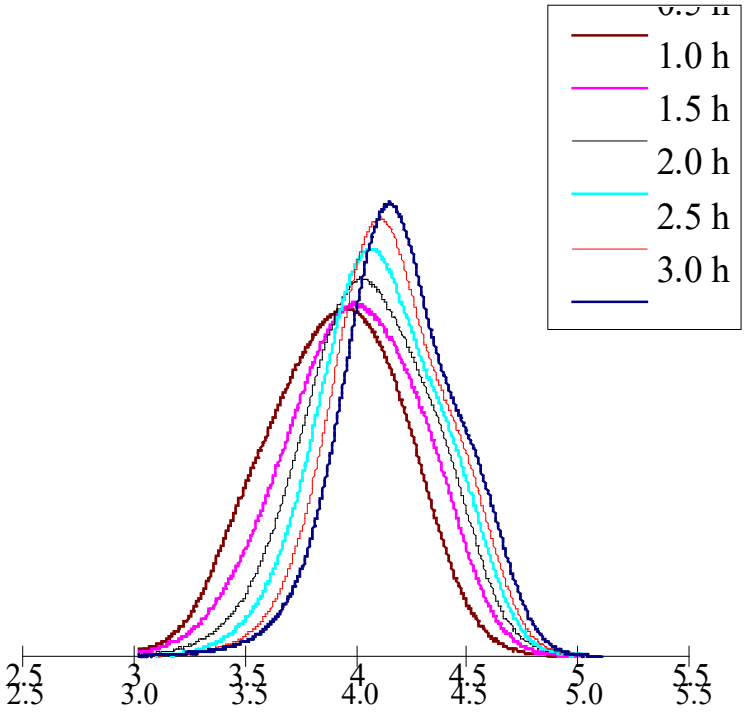


Figure 3.6. Comparison of GPC curves of polystyrene obtained from sampling method.

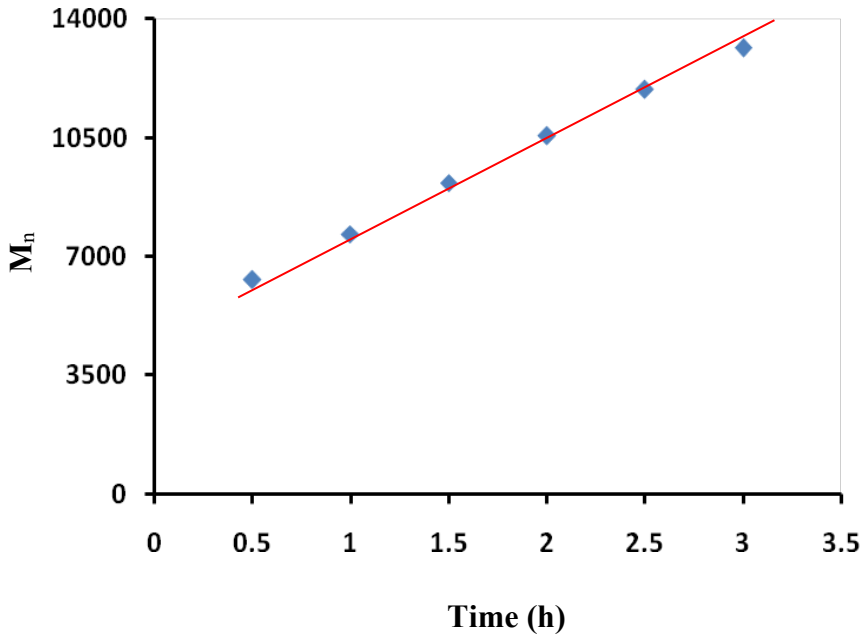


Figure 3.7. Plot of M_n of polystyrene obtained from sampling method against time.

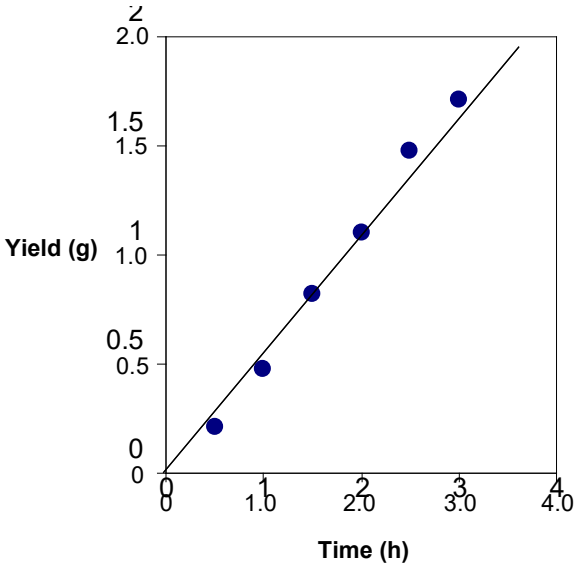


Figure 3.8. Plot of yield against time of polystyrene obtained from the sampling method.

3.3c. Structure of the Polystyrene Initiated with UBP

The structure of polystyrene obtained using UBP initiator was investigated by ^{1}H and ^{13}C NMR analysis of the polymer and comparison with the spectrum of UBP initiator. In Figure 3.9, the ^{1}H NMR spectrum of polystyrene was compared with the ^{1}H NMR spectrum of UBP. In the ^{1}H NMR spectrum of polystyrene, the signals at 5.6 and 6.3 ppm assignable to vinyl protons and a signal at 4.7 ppm assignable to -C**H** proton of α-Br indicates that the polymerization was initiated with UBP. A broad signal at 7.26 ppm assignable to aromatic protons (meta- and para-position) of styrene unit were labeled as t and u, and at 6.75 ppm for ortho-proton as s in Figure 3.9B. The signals observed at 1.50 and 2.00 ppm assignable to -C$\mathbf{H}_2$ and -C**H** protons of main chain of polystyrene were labeled as o and p respectively.

The ^{13}C NMR spectrum of polystyrene was compared with the ^{13}C NMR spectrum of UBP initiator in the Figure 3.10. The signals for UBP unit were clearly observed in the spectrum of the polystyrene. The signals at 136.34 and 111.47 ppm assignable to vinyl carbons indicate the presence of vinyl chain end in the polystyrene. The signals assignable to styrene unit were also observed in the ^{13}C NMR spectrum of the polymer as follows: at 143, 127, 126 ppm for aromatic carbons labeled as t, u, v and w; at 50 ppm for -CH_2 carbon β to Br labeled as r; at 43 ppm -CH carbon α to Br labeled as s; and 38 – 42 ppm for CH_2 and CH carbons of main chain of polystyrene labeled as p and q in Figure 3.10B. These results clearly indicate the presence of vinyl group in the *ω*-end of polystyrene obtained with UBP initiator.

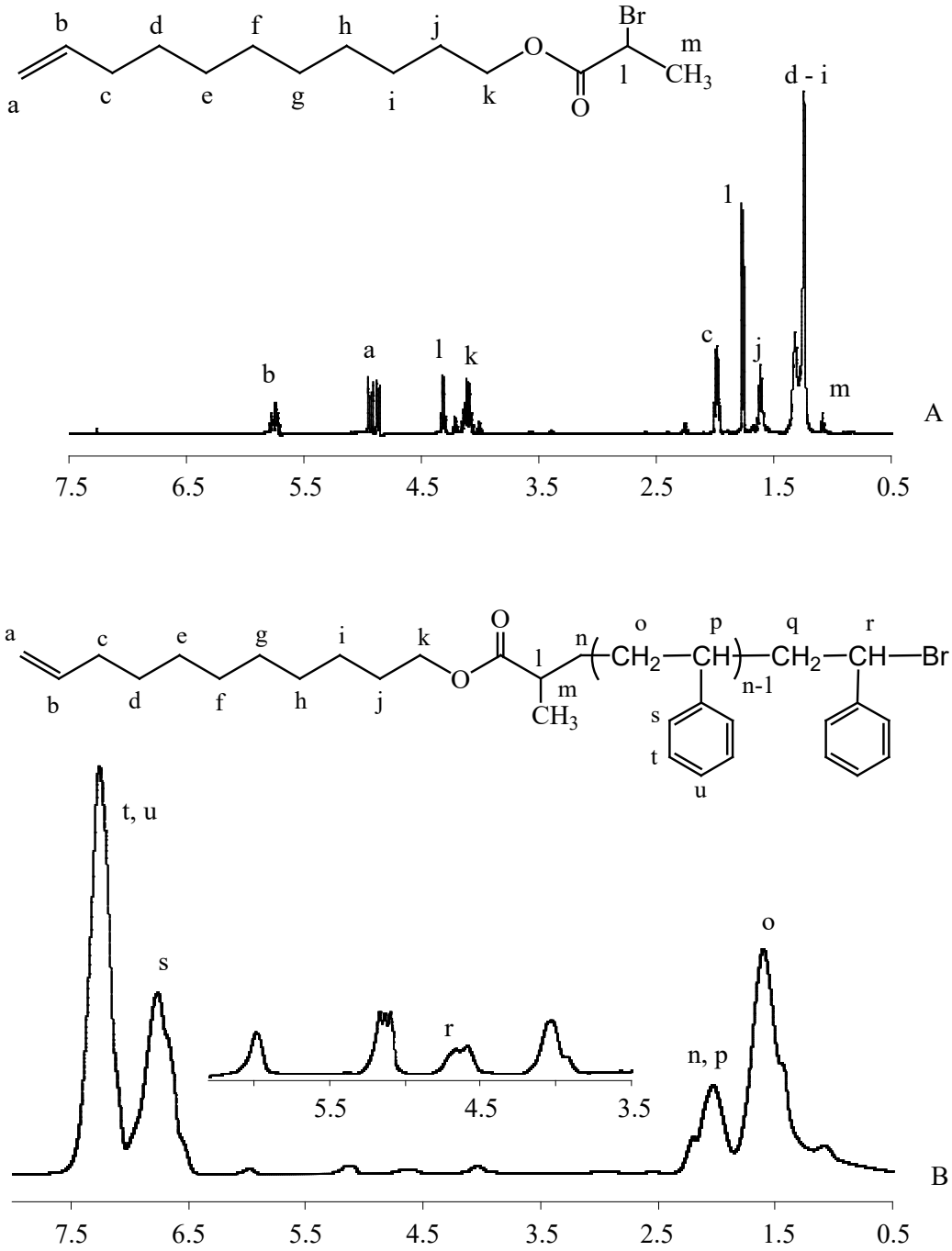


Figure 3.9. ^{1}H NMR spectra of UBP (A) and polystyrene (B) obtained by using UBP as initiator.

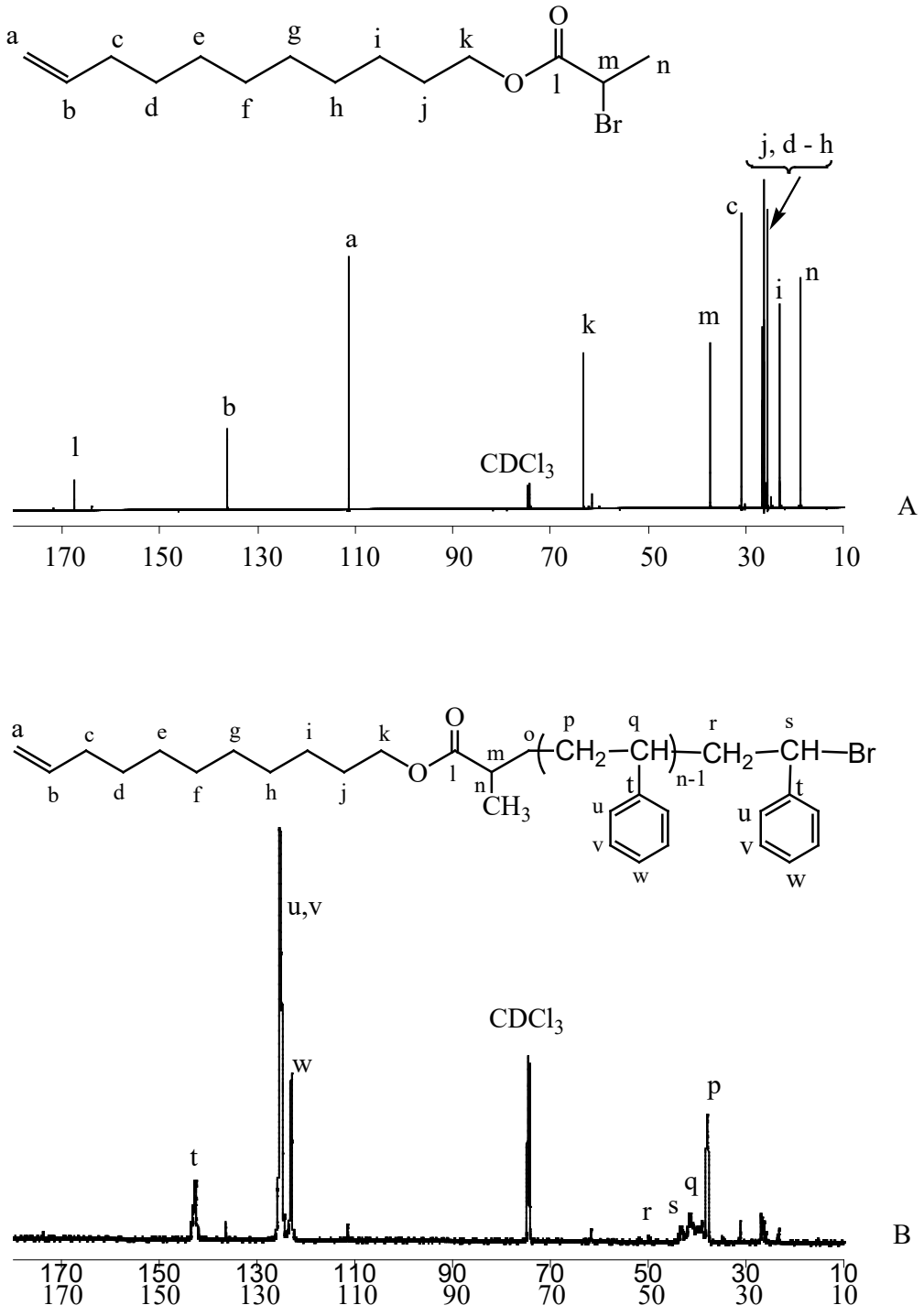


Figure 3.10. ^{13}C NMR spectra of UBP (A) and polystyrene (B) obtained by using as initiator.

3.3d. Thermal Properties of Polystyrene Obtained

The thermal properties of the polystyrene obtained by ATRP using UBP as initiator was measured by differential scanning calorimetry (DSC) with a Seiko DSC-220 instrument under a nitrogen atmosphere at heating and cooling rate of 10 °C/min at range from 10 to 150 ºC. The DSC thermogram of the polystyrene obtained was displayed in Figure 3.11. The glass transition temperature (T_g) value was determined from the middle point of the phase transition of the second heating scan. The T_g value of the polystyrene was 96.5 ºC.

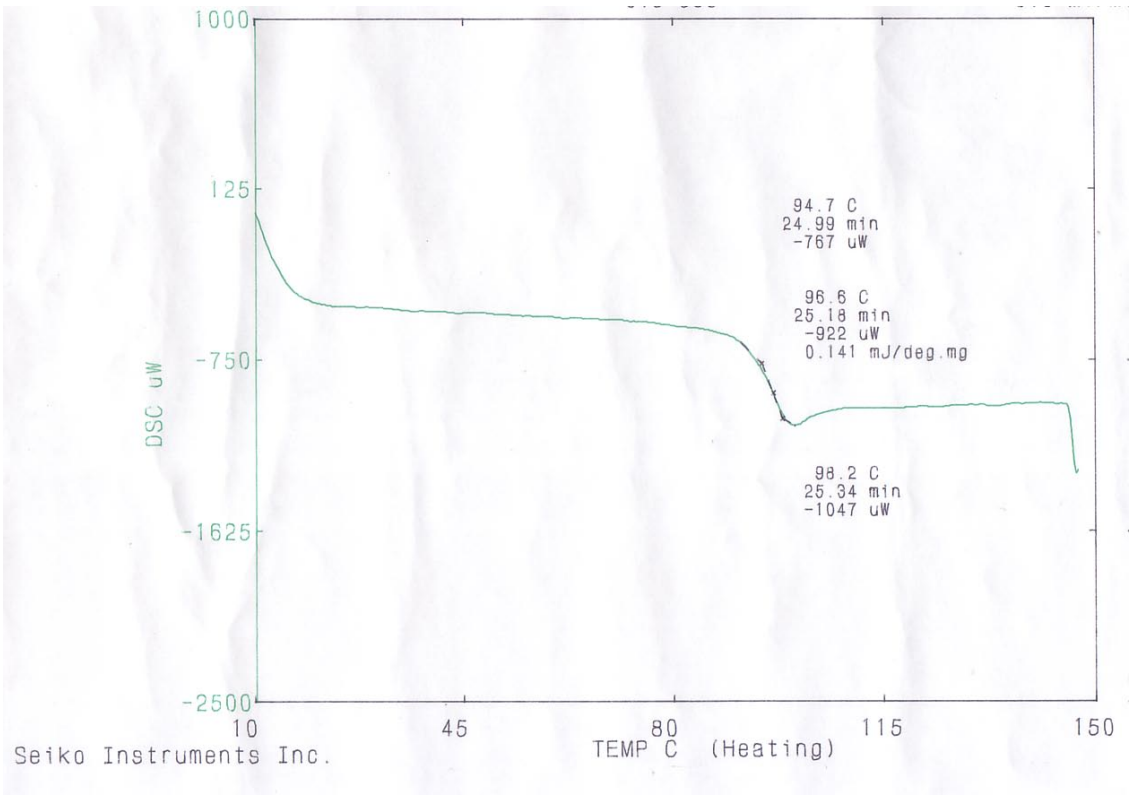


Figure 3.11. DSC thermogram of the polystyrene obtained by ATRP using UBP as initiator.

3.4. Epoxidation of the Polystyrene Initiated with UBP

The epoxidation of the vinyl group at the chain end of the polystyrene obtained with UBP initiator was carried out at 65 ºC in toluene for 4 h using *m*-chloroperbenzoic acid. The quantitative conversion vinyl group to epoxy group was confirmed by the ^{1}H NMR analysis of the product.

The ^{1}H NMR spectra of the polystyrene before and after epoxidation are compared in Figure 3.12. Complete epoxidation was rationalized from the disappearance of the peak of **H**$_2$C=C**H**- protons at 4.98 and 5.22 ppm in the spectrum of the polystyrene after epoxidation. On the other hand, two broad peaks at 3.62 and 3.77 ppm assignable to epoxy protons (-C**H**-O-C**H**$_2$-) were appeared in the ^{1}H NMR spectrum of the epoxidized polymer.

The ^{13}C NMR spectra of the polystyrene before and after epoxidation are compared in Figure 3.13. No signal was appeared at 136.34 to 111.47 ppm assignable to vinyl carbons in the spectrum of the epoxidised polystyrene which confirm the quantitative conversion of vinyl group to epoxy group. The signals for epoxy carbons (-**C**H-O-**C**H$_2$) were not detected clearly due to the overlap with other signals.

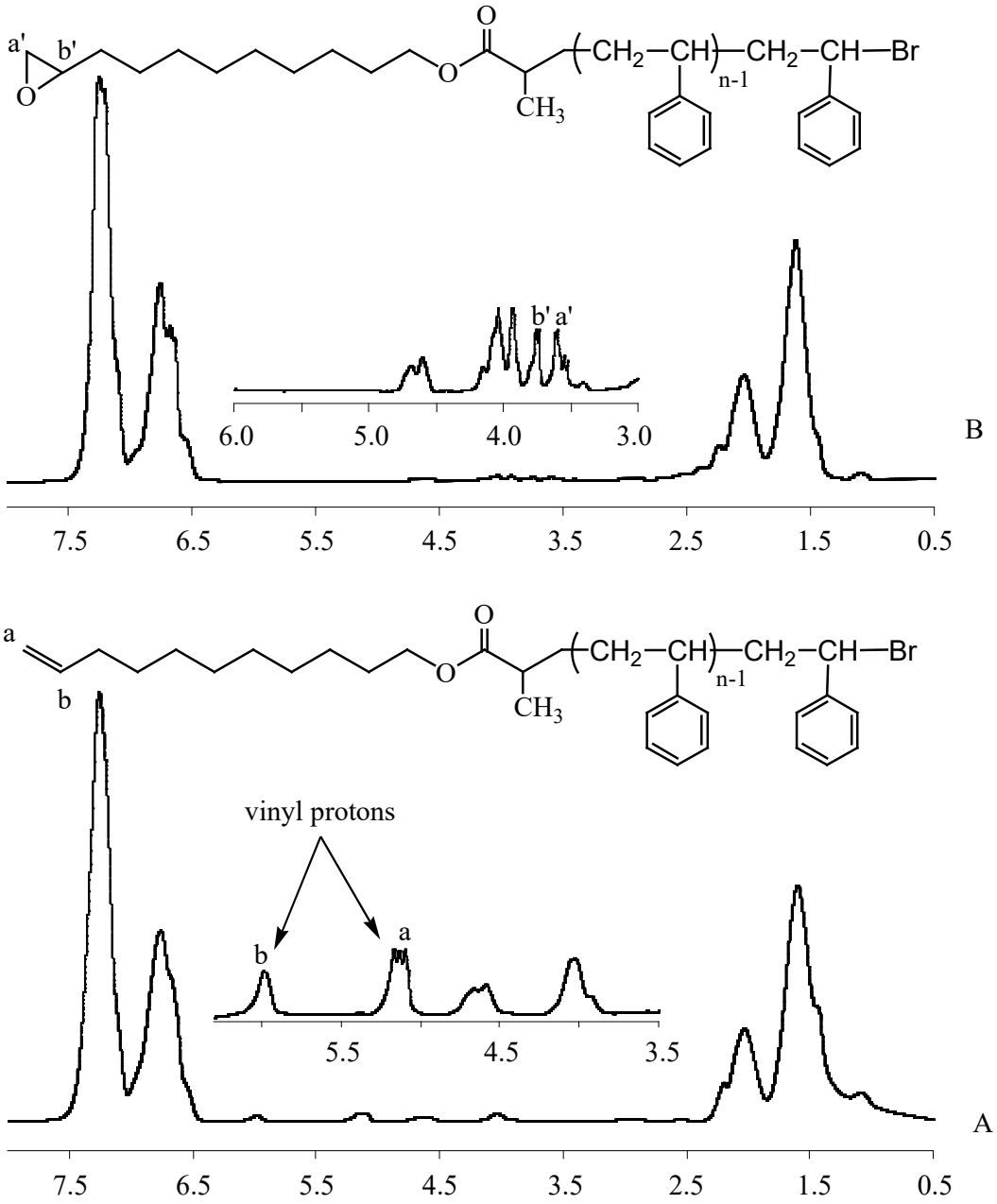


Figure 3.12. ^{1}H NMR spectra of polystyrenes (A) before and (B) after epoxidation.

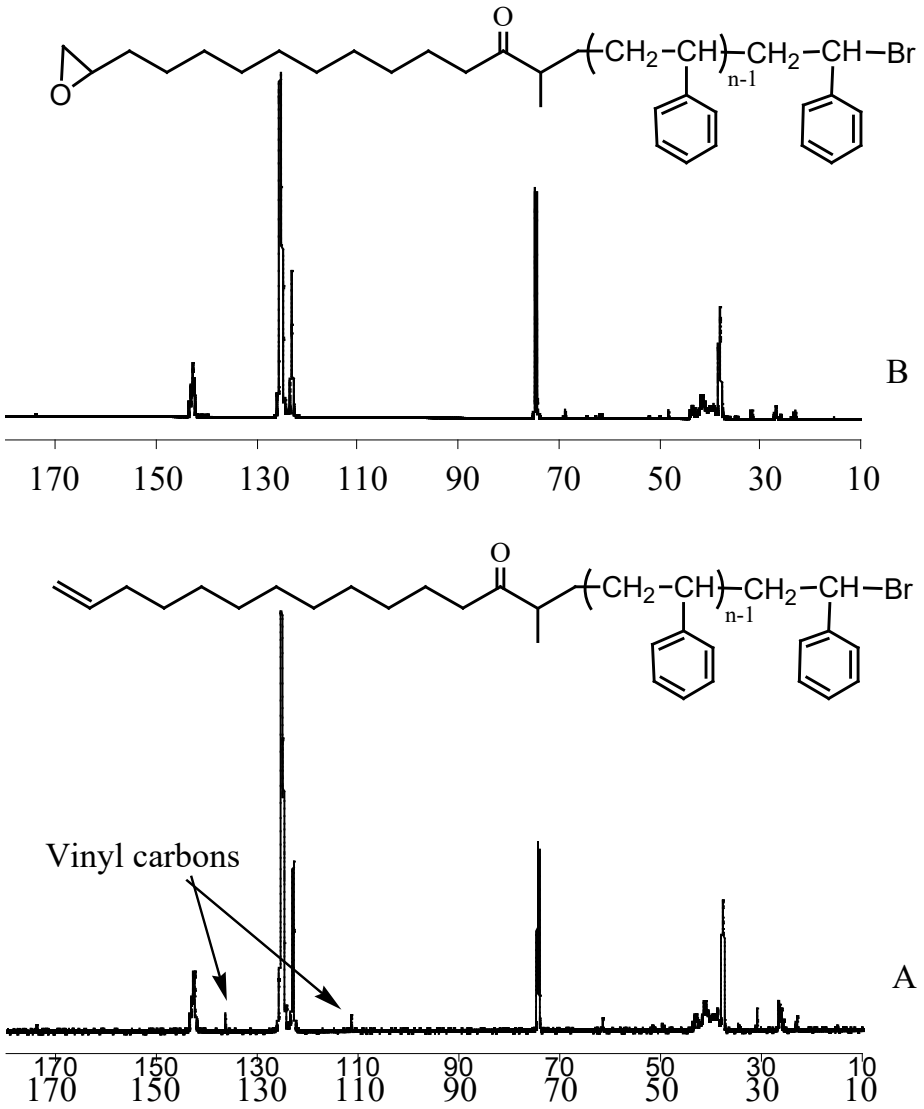


Figure 3.13. ^{13}C NMR spectra of polystyrenes (A) before and (B) after epoxidation.

3.5. Conclusion

The initiator UBP was synthesized in a good yield. The structure of UBP was characterized by ^{1}H and ^{13}C NMR analysis. The UBP as initiator was successfully applied for Cu(I)-bipyridine mediated ATRP polymerization of styrene. The polymerization of styrene was investigated at various reaction conditions.

The polymer yield obtained at high feed ratio of styrene and UBP (St/UBP = 1000 and 500) was double than the feed ratio of styrene and UBP (St/UBP = 250). The polymers obtained with this system showed high molecular weight and narrow molecular weight distribution ($M_w/M_n < 1.5$). The molecular weight of the polymers obtained was decreased with decreasing St/UBP ratio, whereas the molecular weight distributions were almost constant.

The yield of polymers and the molecular of the polymers were increased, and the molecular weight distribution became narrower with raising polymerization temperature from 70 ºC to 130 ºC. Living ATRP polymerization of styrene with Cu(I)/Bipy/UBP catalyst system was successfully confirmed by sampling method at 110 ºC.

In the ^{1}H and ^{13}C NMR spectra of the polystyrene obtained with this catalyst system, the signals assignable to vinyl group indicate the vinyl chain-end structure of the polystyrene which formed that the ATRP was initiated by UBP. Finally, the end vinyl group of the polystyrene was converted to epoxy group quantitatively by chemical reaction.

CHAPTER

IV

One Pot Synthesis of 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester and 2-bromo-2-methyl-propionic acid but-2-ynyl diester

CHAPTER IV

One Pot Synthesis of 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester and 2-bromo-2-methyl-propionic acid but-2-ynyl diester

4.1. Introduction

Well-defined functional polymers are most important materials due to their application in chemistry, physics, medicine, biology and nanotechnology. Conventional free radical polymerization techniques are not able to produce polymers with well-defined or controlled molecular weights and molecular weight distributions due to large amount of chain transfer and termination reactions. Atom Transfer Radical Polymerization (ATRP), a polymerization technique combined with a suitable initiator has overcome these drawbacks.[43,50] Since its inception, ATRP also known as transition metal mediated living radical polymerization has proven to be robust for the design of polymers of complex architecture and precise molar mass.[181] ATRP tolerates many functional groups present in monomers or solvents, impurities present in solvents and monomers and also allows for the facile synthesis of many polymers of novel structure and topology.[182]

Various α-haloesters, as initiator, have been successfully employed for well-controlled ATRP to synthesize end-functional polymers. Structural adjustment of the initiator provides a handle to fine-tune the rate of initiation in the ATRP system. For instance, α-haloisobutyrates produce initiating radicals faster than the corresponding α-halopropionates due to better stabilization of the generated radicals after the halogen abstraction step. Thus slow addition will generally occur if α-halopropionates are used to initiate the polymerization of methacrylates. In contrast, α-bromopropionates are good initiators for the ATRP of acrylates due to their structural resemblance. Matyjaszewski et.al. reported the ATRP of styrene with vinyl chloroacetate and allyl chloroacetate as initiator using CuBr-bipyridine catalyst system. The vinyl chloroacetate was found as better initiator for styrene polymerization. Hassan et. al. reported the ATRP of styrene with undecenyl propionyl acetate and the alkene group of α-

end of the polystyrene was converted to epoxy group by post polymerization modification.[183] Various functional α-haloesters have been successfully employed for Cu(I)-mediated ATRP process to synthesize polymers with halo group at ω-end and functional ester group at α-end. Alkyne functionalized bromoester initiated ATRP that produced polymers with halo group at ω-end and alkyne group at α-end.[184] Alkyne end-functionalized polymers are precursors to obtain well defined block copolymers by ligated with well defined azide bearing homopolymers via azide−alkyne click chemistry.[185] Although end-alkyne functional polymers produced by ATRP have been reported, the mid-alkyne functional polymers are rare. Mid-alkyne functional polymers could be used as precursors to obtain well defined star polymers by ligated with well defined azide bearing homopolymers via suitable azide-alkyne click chemistry. Therefore, to synthesis end- and mid-alkyne functional polymers has a great impotency to the new generation synthetic polymer researchers.

In this chapter, end- and mid-alkyne functional two α-bromoesters, namely, 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester **(BPE)** and 2-bromo-2-methyl-propionic acid but-2-ynyl diester **(BPDE)** were synthesized. These two esters will be used as initiators of ATRP method that might give end- and mid-alkyne functional polymers.

4.2. Experimental Section

4.2.a. Materials: 2-Bromo-2-methyl-propionylbromide was purchased from Sigma Aldrich and used without further purification. Pyridine was purified by distillation followed by stirring with CaH_2 for 24 hrs. 2-Butyn-1, 4-diol was purchased from Fluka and was purified as follows: 40 mL of ethyl acetate was added to 10 g of crude 2-butyn-1,4-diol and the mixture was refluxed until the 2-butyn-1,4-diol dissolved. The flask was cooled to 40 °C, and 40 mL of ether was added with stirring. In so doing, 2-butyn-1,4-diol precipitated as snow-

white crystals. For complete precipitation, the flask was cooled for 2-3 hr at 0 °C with intermittent stirring of the contents, so as to prevent agglutination of the crystals. The crystals of 2-butyn-1,4-diol were then filtered off on a Buchner funnel and washed with 10 mL of ether. The product was dried in a vacuum oven at room temperature.

4.2b. Analytical Methods: ^{1}H NMR analysis of organic products were carried out with BRUKER Spectrometer operated at 400 MHz in pulse Flourier Transform mode using chloroform-*d* as solvent. The peak of chloroform-*d* (7.26 ppm) was used as internal reference.

4.2c. Synthesis of End- and Mid-Alkyne Functional Bromoesters: 2-Butyn-1,4-diol (6.36 gm, 73.84 mmol) was dissolved in CH_2Cl_2 (15 mL). Dried pyridine (8.10 gm, 102.33 mmol) was added to the solution of 2-butyn-1,4-diol. The mixture was then cooled to 0 °C. To the mixture 2-bromo-2-methylpropionylbromide (16.98 gm, 73.84 mmol) was added by using syringe. The reaction mixture was stirred for 48 hrs at room temperature using magnetic stirrer. The progress of the reaction was investigated by Thin Layer Chromatography (TLC) using EtOAc/Petroleum ether = 1 : 50 as solvent mixture. The reaction mixture was quenched with 10% HCl solution. The organic layer was separated by using a separating funnel. The aqueous layer was extracted with CH_2Cl_2 (3×50 mL) and the extract was combined to organic layer. The combined organic layer was then washed with water (50 mL), dried with $MgSO_4$, filtered and concentrated in vacuo. The residue was separated by (silica gel) column chromatography (EtOAc/ Petroleum ether = 1 : 50) and two products were isolated as yellowish liquid. The purity of the separated products was investigated by TLC using same solvent mixture. The expected products **BPE** (2.72 gm) and **BPDE** (4.23 gm) were obtained as yellowish liquid followed by evaporation of solvent from each eluent under vacuum. Finally, the structure of the products were confirmed by ^{1}H NMR analysis.

4.2.d. NMR Analysis of BPE initiator.

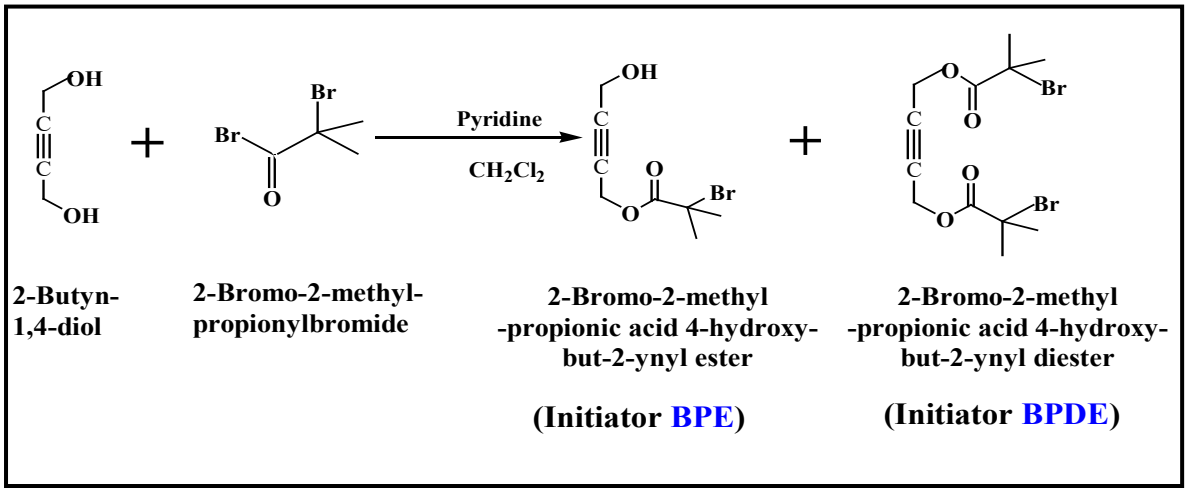
^{1}H NMR ($CDCl_3$): 1.85 ppm (S, 6H, -C(Br)(CH_3)$_2$, at 3.84 ppm (broad , 1H, -*OH*)), 4.28 ppm (S , 2H, -CH_2-OH), 4.77 ppm (S, 2H, -CH_2O-(C=O)-).

4.2.e. NMR Analysis of BPDE initiator.

^{1}H NMR ($CDCl_3$): 1.84 ppm (S, 12H, -C(Br)(CH_3)$_2$), 4.72 ppm (S, 4H, -CH_2O-(C=O)-).

4.3. Result and Discussion:

4.3a. Characterization of Initiators: The expected initiators, **BPE** and **BPDE** were synthesized from the reaction between 2-butyn-1,4-diol and 2-bromo-2-methylpropionylbromide in the presence of pyridine and methylene chloride as following scheme 4.1.



Scheme 4.1. Synthesis of BPE and BPDE.

The two expected products **BPE** and **BPDE** were separated by (silica gel) column chromatography (EtOAc/ Petroleum ether = 1 : 50) and the R_f values calculated from TLC plate were 0.82 and 0.24 respectively (Figure 4.1). The higher R_f value 0.82 indicated the presence of less polar compound which might be **BPDE** and the lower R_f value 0.24 indicated the presence of higher polar compound which might be **BPE**. Finally, the structure of the products, **BPE** and **BPDE** were confirmed by ^{1}H NMR analysis.

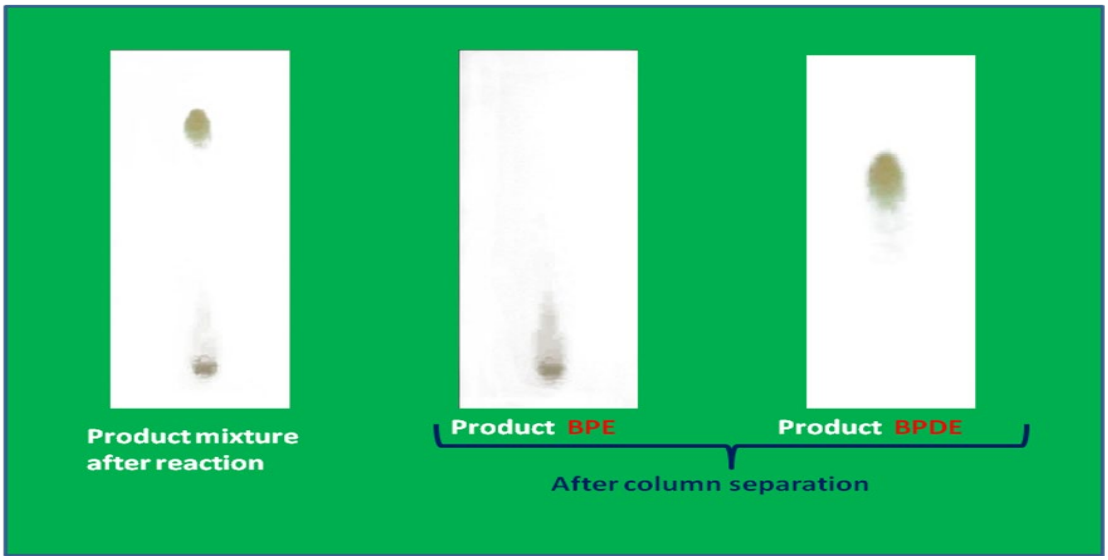


Figure 4.1. TLC performance of the crude and pure products.

The ^{1}H NMR spectrum of **BPDE** was displayed in Figure 4.2. In the ^{1}H NMR spectrum**,** two singlets appeared at 1.84 ppm and 4.72 ppm for -C(Br)(C**H**$_3$)$_2$ and -C**H**$_2$O-(C=O)- protons, respectively. In both signals, the presence of two additional weak peaks suggested the presence of the conformers of this product. All these different types of protons and their corresponding signals are indicated in the following figure 4.2.

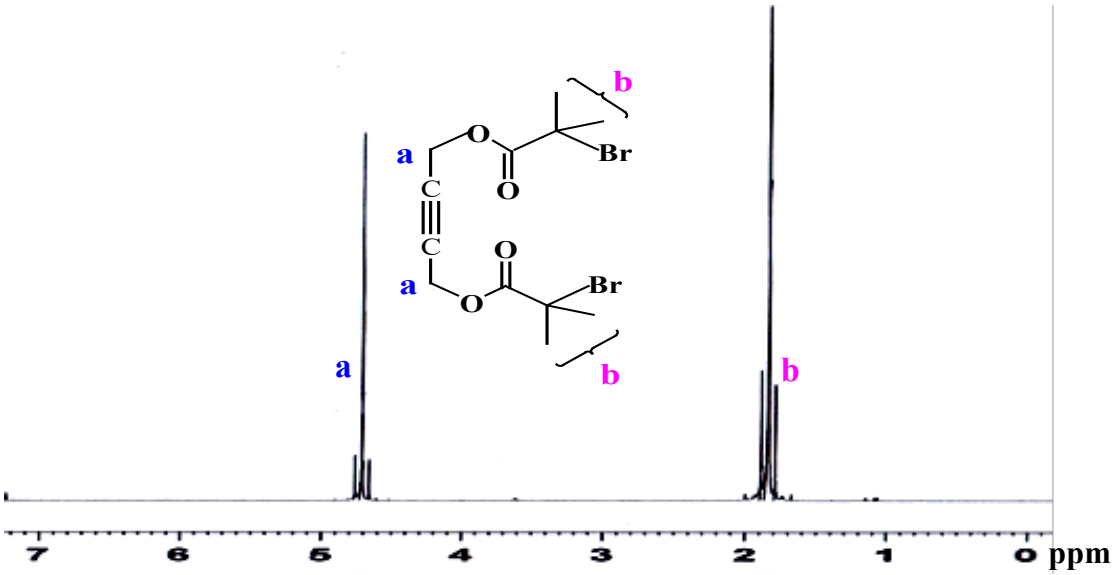


Figure 4.2. ^{1}H NMR spectrum of initiator BPDE.

The ^{1}H NMR spectrum of **BPE**, was displayed in Figure 4.3. In the ^{1}H NMR spectrum, three singlets appeared at 1.85 ppm , 4.72 ppm, 4.28 ppm for -C(Br)(C**H**$_3$)$_2$, -C**H**$_2$O-(C=O)- 2H, -C**H**$_2$-OH protons and a broad peak appeared at 3.84 ppm for –O**H** protons respectively. The presence of two additional weak peaks with main peak suggested the presence of the conformers of this product. All these different types of protons and their corresponding ^{1}H NMR signals are indicated in the following figure 4.3.

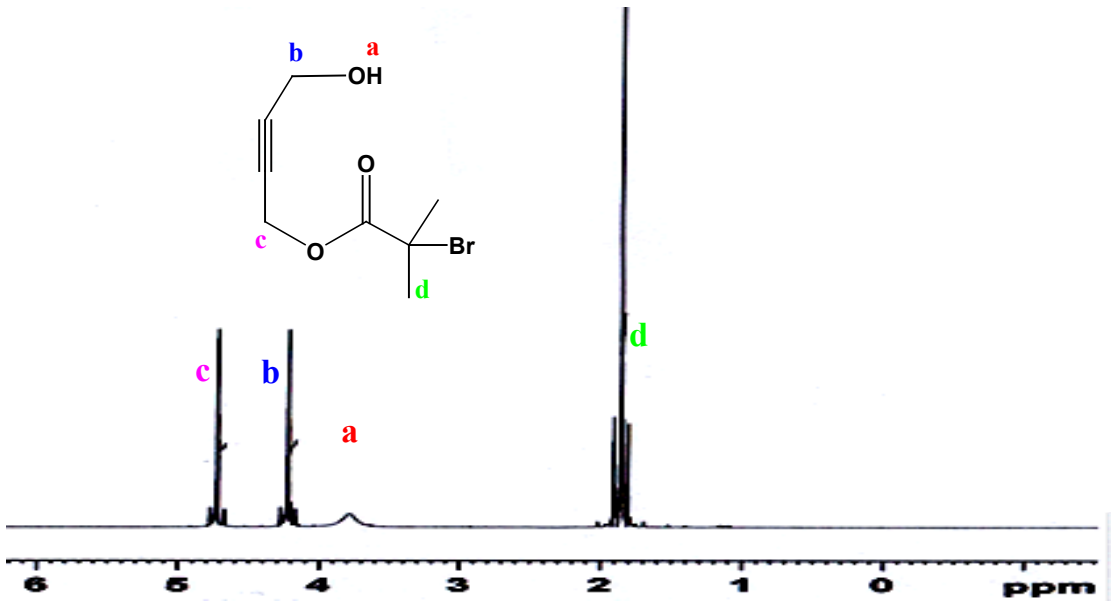


Figure 4.3. ^{1}H NMR spectrum of initiator **BPE**.

4.4. Conclusion

Two new bromoesters i.e. **BPE** and **BPDE** were synthesized in a good yield. The product mixture was separated by column chromatography. The structures of these two initiators were characterized by ^{1}H NMR analysis.

These two bromoesters **BPE** and **BPDE** will be used as initiator for the Atom Transfer Radical Polymerization of styrene and the results will be discussed in the following Chapter V and VI respectively.

CHAPTER V

Polymerization of Styrene using 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester as Initiator by ATRP Method

CHAPTER V

Polymerization of Styrene using 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester as Initiator by ATRP Method

5.1. Introduction

A number of functional initiators were used for the ATRP of styrene and methyl acrylate.[158,159] The general rules for the selection of the appropriate initiators is that the production of the apparent equilibrium constant and the rate constant of the addition to monomer for the initiation step should be similar to or larger than that for the propagation step. In addition, any functionalities in the initiator should not interfere with ATRP (i.e. should be inert toward both the catalyst and the alkyl halide).

Various α-haloesters have been successfully employed to initiate well-controlled ATRP. A variety of functionalities, such as hydroxyl, epoxy, allyl, vinyl, lactone, and carboxylic acid have been introduced onto the α-end of the polymer by use of a functional initiator.[61,89,185,] α-Haloesters with various functional groups attached can easily be prepared through a straightforward esterification reaction of the appropriate acid halides. Since ATRP can tolerate various functional groups, well-defined end-functional polymers have been conveniently prepared without the need for additional protecting reactions.

Recently, alkyne functionalized polymers have achieved much attraction to the synthetic polymer researchers. These alkyne-functionalized polymers are very much interesting because the alkyne group is a clickable functional group. These alkyne-functionalized polymers can act as precursors for the synthesis of macrocyclic polymers,[160] semiconductor polymers,[187] dendritic and hyperbranched polymers,[188] for surface modification via click reaction,[189] and for the synthesis of star polymers,[190] polymer capsules,[191] block copolymers.[192]

In this chapter, an alkyne group containing α-bromoester i.e. 2-bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl ester (**BPE)** synthesized in chapter IV**)** was applied as initiator for synthesis of end-alkyne functionalized polystyrene by Cu(I) mediated ATRP. The polymerization results and the structure of the polymer were also discussed in this chapter.

5.2. Experimental

5.2a. Polymerization Procedure. Polymerization was carried out in a 50 mL Schelnk type reactor equipped with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuBr, bipyridene and a tiny magnetic capsule. Three cycles of vacuum-evacuation of reactor and fill-up with nitrogen gas were performed, and the reactor was then sealed with rubber septum. A required amount of degassed styrene and initiator were added with a syringe. The reactor was placed in an oil bath at the desired temperature controlled by a thermostat and the reaction mixture was stirred for certain time. At timed intervals, the polymerizations were stopped by addition of methanol followed by cooling the reactor into ice-water and the polymer was precipitated in methanol by stirring over night. The polymers obtained were filtered, adequately washed with methanol, and dried under vacuum at 60 °C for 6 h.

5.2b. Analytical Methods. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by GPC (Waters 150 C) at 140 °C using *o*-dichlorobenzene as solvent and calibrated by polystyrene standards. ^{1}H NMR spectrum of polymer was recorded at room temperature on a BRUKER spectrometer operated at 400 MHz in pulse Fourier Transform mode with chloroform-*d* as solvent. The peak of chloroform-*d* (7.23 ppm) was used as internal reference.

5.3. Results and Discussion:

5.3a. Polymerization of Styrene by ATRP using BPE as an Initiator

Styrene was polymerized by ATRP initiated by **BPE** at 115 ^{0}C using three different time duration in conjugation with cupper(I) bromide and bipyridine as a catalyst under nitrogen atmosphere (Scheme 1). The results of the polymerization are shown in the **Table 5.1**. The yield and the molecular weight of polymers affected with the polymerization time. Both the yield and molecular weight of the polymers were increased with increasing polymerization time. The GPC curves of polymers obtained were compared in **Figure 5.1** and the curves were shifted to the higher molecular weight region with increasing polymerization time with narrow molecular weight distributions (M_w/M_n). The M_n values vs time are plotted in **Figure 5.2**. The M_n value of the polystyrene increased against time. The yield of polymer also increased with polymerization time. These results indicate that the controlled polymerization of styrene proceeded at 115 ^{0}C using CuBr/BiPy/BPE catalyst system and the length of the polymer chain was controlled by changing the polymerization time.

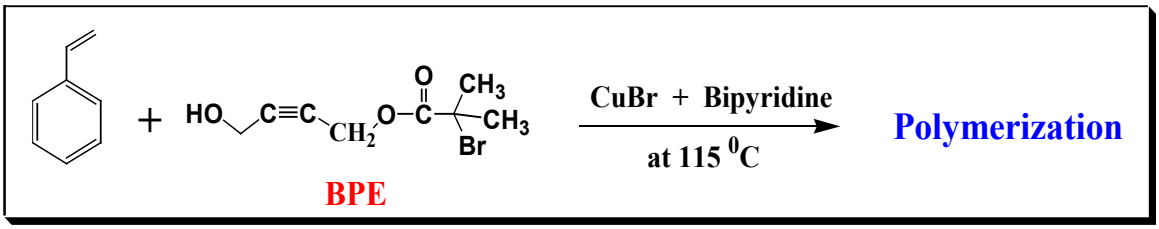


Table 5.1. Effect of Time on Polymerization of Styrene using BPE as Initiator.

Entry	Time (h)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
1	2	0.39	7.8	9.7	1.23
2	4	0.72	15.9	21.0	1.32
3	6	0.99	51.7	67.2	1.30

Polymerization conditions; **BPE** = 0.11 mmol, CuBr = 0.11 mmol, BiPy = 0.21 mmol, Styrene = 3.0 mL, Temperature = 115 ^{0}C, Styrene/**BPE** = 250.

The GPC curves of polymers obtained from different period of time (0.5, 1 and 2 hours) were compared in Figure 5.1. The GPC curves were shifted to the higher molecular weight region with increasing polymerization time. The plot of time vs M_n showed linear relationship with a slop at initial period in Figure 5.2.

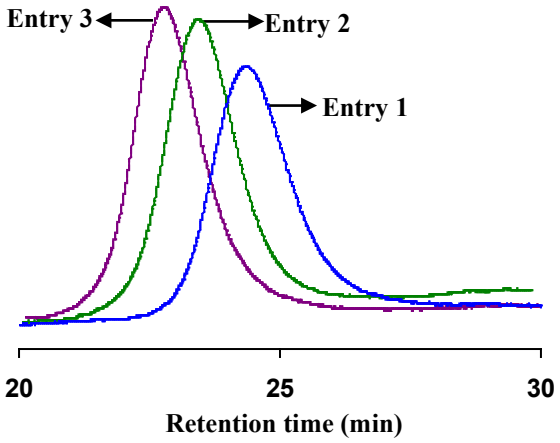


Figure 5.1: GPC curves of PSt by BPE.

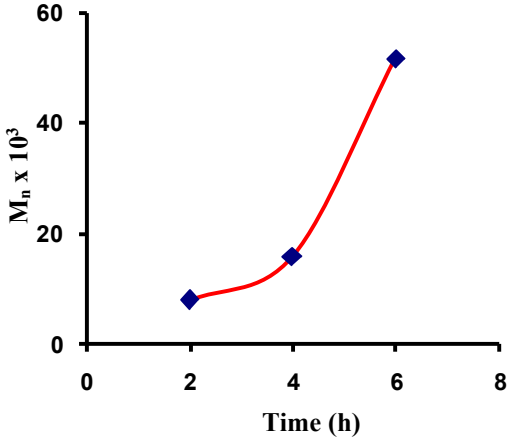


Figure 5.2: Plot of M_n against time of PSt by BPE.

5.3b. Structure of the Polystyrene Initiated with BPE.

The structure of polystyrene obtained by using **BPE**/CuBr/Bipyridine was investigated by the ^{1}H NMR analysis. The ^{1}H NMR spectrum of polystyrene obtained with **BPE** was displayed in **Figure 5.3**.

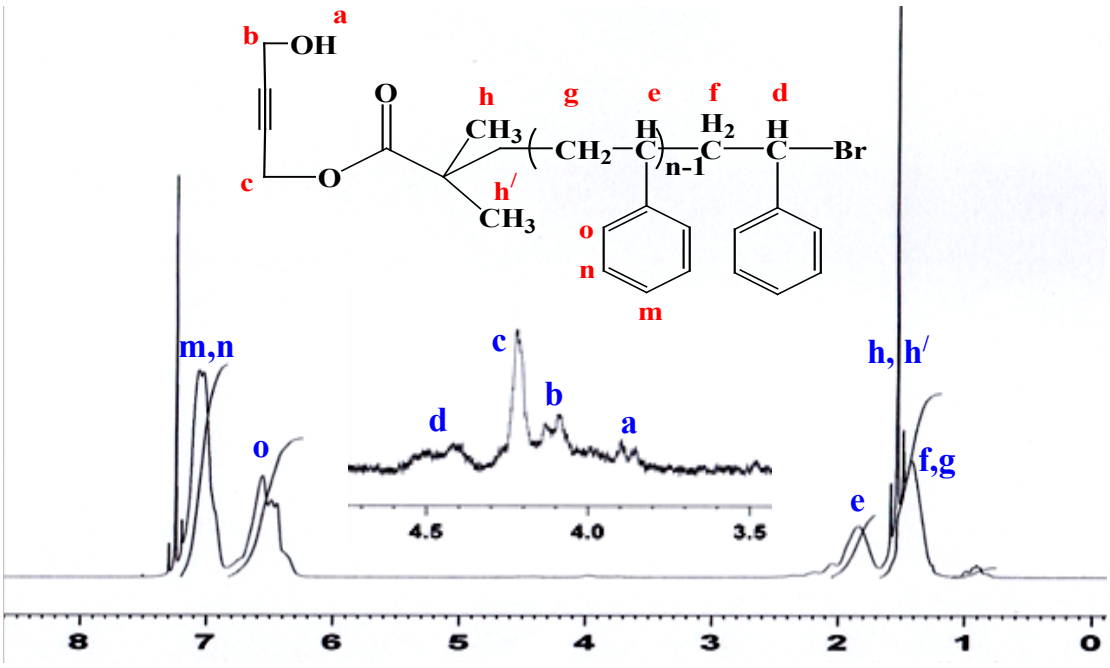


Figure 5.3: ^{1}H NMR spectra of polystyrene obtained by BPE.

In the ^{1}H NMR spectrum of polystyrene, the signal at 1.54 ppm was assigned to the same -C**H**$_3$ protons denoted by h, h$^{/}$ in the structure of the polystyrene in Figure 5.3. Due to the presence of electron withdrawing effect of Br, the signal for C**H**$_3$ protons of –(C**H**$_3$)$_2$Br group of initiator was shifted to that of the downfield compared to the –O-CO–(C**H**$_3$)$_2$- group of polystyrene obtained. The signals for protons of HO-C**H**$_2$-C≡C-C**H**$_2$-O- group in the polymer chain (denoted by b and c) were also observed at 4.13 ppm and 4.27 ppm (which were clearly seen in the expanded region 3.4- 4.7 ppm) of the spectrum of the polymer. A broad peak appeared at 4.5 ppm which was assigned to -C**H** proton (denoted by d) of α-Br at ω- end of the polymer chain. All these facts indicated that the polymerization was initiated with **BPE** initiator. A broad signal at 7.0 ppm was assigned to aromatic protons (para- and meta-position) of styrene unit

labeled as m and n and at 6.5 ppm for ortho-protons labeled as o in **Figure 5.3**. The signals observed at 1.48 ppm and 1.83 ppm was assigned for the -C**H**$_2$ and -C**H** protons of main chain of polystyrene labeled as f, g, and e respectively.

5.4. Conclusion: Atom Transfer Radical Polymerizations of styrene were carried-out using **BPE** initiator by Cu(I)/bipyridine catalyst at 115 ^{0}C successfully. The yield and molecular weight of polymers were increased with increasing the reaction time. The molecular weight distribution of polymer was narrow. The M_n values of the polymers obtained by the **BPE**/CuBr/bipyridine catalyst system could be controlled by changing the polymerization time.

The ^{1}H NMR spectra of the polystyrene obtained by using **BPE** clearly indicated that the polymerization proceeded with **BPE** initiator by ATRP method.

CHAPTER VII

Synthesis of 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4-ylmethyl]ester and Its Application as Initiator on the ATRP Polymerization of Styrene

CHAPTER VII

Synthesis of 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4-ylmethyl]ester and Its Application as Initiator on the ATRP Polymerization of Styrene

7.1. Introduction

Controlled radical polymerization, atom transfer radical polymerization (ATRP) is a technique whereby a catalytic amount of a Cu(I) coordination complex reversibly abstracts a halogen atom (Cl or Br) from the polymer chain ends, switching them from a dormant to an active propagating state.

The ATRP process exhibits all of the experimental characteristics of a living polymerization, can be used for a large variety of monomers,[68,69] allows facile control of chain topology, composition and functionality and can employ a wide range of halogenated initiators and macroinitiators. Since it is a catalytic process, the proportion of radicals and consequently the polymerization rate can be easily controlled, based on the amount and activity of the transition metal compounds used as redox catalyst. Moreover, experimental conditions are rather simple and Matyjaszewski and coworkers have showed that polymerization can be carried out in water, in a particular case in the presence of oxygen and even at room temperature.

A further feature of polymers obtained by ATRP is that they possess an ω-halogen end-group that can be converted to other functional groups. Formation of azides, amines, double bonds and even sulfide have been shown to be feasible,[16] however, Among the various functional group dioxolane end group in the polymer chain is a very interesting one because dioxolane end-functional group containing polymer can be converted to dihydroxy end-functional polymer. Which could be used as “microinitiator” for synthesis of various graft, block, two or three armed copolymer.[193] Therefore a dioxolane group containing initiator 2-bromopropionic [2,2-dimethyl-1,3-dioxolane-4-ylmethyl]

ester (**BPDME**) was synthesized and the ATRP of styrene was investigated using BPDME as initiator.[163] The initiator efficiency and polymer properties will also be studied. Finally the dioxolane ring was opened by the chemical reaction.[194]

7.2. Experimental Section

7.2a. Materials. Styrene was purchased from Aldrich and it was purified by passing through an alumina column to remove stabilizer and then stirred with CaH_2 for 8 hrs and filtered. Finally it was stored at 0 ºC under nitrogen prior to use. Copper (I) bromide was purified by recrytalization in methanol and washed with ether. Bipyridine from Fluka and 2-bromopropionyl bromide were purchased from Aldrich. 2,2-dimethyl-1,3-dioxolane was synthesize in our laboratory. Triethylamine was distilled over CaH_2. All solvent were purified by distillation followed by refluxed with sodium and benzophenone for 6 hrs.

7.2b. Polymerization Procedure. Polymerization was carried out in a 25 mL Schelnk tube with magnetic stirrer in nitrogen atmosphere. The reactor was charged with prescribed amount of CuBr, bipyridine and a tiny magnetic capsule. Three cycles of vacuum-evacuation of reactor and fill-up with nitrogen gas were performed, and the reactor was then sealed with rubber septum. A required amount of degassed styrene and initiator were added with syringe. The rector was placed in an oil bath to keep desired temperature by tuning thermostat and the reaction mixture was stirred for certain time using magnetic stirrer. At certain interval, the polymerization was stopped by added methanol followed by cooling the tube into ice-water and the polymer was precipitated in methanol by stirring for overnight. The polymers obtained were filtered, adequately washed with methanol and dried under vacuum at 60 ºC for 6 h.

7.2c. Analytical Methods. Molecular weight (M_n) and molecular weight distribution (M_w/M_n) of polymer were measured by gel permeation chromatography (Toyo soda HLC-802; Column, GMH6 × 2 + G4000H8;) and eluent, $CHCl_3$ as solvent and calibrated by polystyrene standards. ^1H and ^{13}C NMR spectra of polymers were recorded at room temperature on a JEOL GX 500 spectrometer operated at 400 MHz in pulse Fourier transform mode with chloroform-*d* as solvent. The peak of chloroform in chloroform-*d* (7.26 ppm for ^1H and 77 ppm for ^{13}C) was used as internal reference.

7.2d. (i) Synthesis of 2,2-dimethyl-1,3-dioxolane-4-methanol. A 1,000 mL two-necked round bottomed flask fitted with a mechanical stirrer and a condenser was taken. To this flask 50 g of glycerol, 150 mL of acetone and 150 mL of toluene were added. Then 1.5 g of *p*-toluenesulphonic acid and 150 g of dry molecular sieves (5Å) were added. Water at 0 ºC was circulated through the condenser during reaction. The reaction mixture was heated under gentle reflux for 33 hrs using a heating mantle with stirring. The condenser was then disconnected and excess acetone was allowed to evaporate. The acidic reaction mixture was neutralized with 1.5 g sodium acetate. The molecular sieves were separated by filtration using a Buchner funnel. The resulting liquid was distilled under vacuum. The colorless organic product was collected by distillation at 80-82 ºC under 10 mm Hg. The yield of product was 86 %.

^1H NMR ($CDCl_3$) for 2,2-dimethyl-1,3-dioxolane-4-methanol: 4.10 ppm (p, 1H, -CH_2-***CH***-O-); 3.9 and 3.6 ppm (dd, 2H, -***CH***$_2$-O-); 3.5 and 3.4 ppm (dd, 2H, HO-***CH***$_2$-CH-); 3.0 ppm (s, 1H, -***OH***); 1.43 and 1.35 ppm (s, 6H, (-***CH***$_3$)$_2$);

^{13}C NMR ($CDCl_3$) for 2,2-dimethyl-1,3-dioxolane-4-methanol: 109ppm (-O-***C***-O-); 76 ppm (-CH_2-***CH***-O-);); 65 ppm (-***CH***$_2$-O-); 62 ppm (-***CH***$_2$-OH);26 ppm (-C-***CH***$_3$);

(ii) Synthesis of BPDME: To a 100 mL R.B. flask, 5.3 mL (40 mmol) of 2,2-dimethyl-1, 3-dioxolane-4-methanol (**1**), 11.1 mL (40 mmol) of triethylamine and 40 mL of THF were taken. The reaction mixture was cooled in an ice-water bath. To this solution, 4.65 ml (40 mmol) of 2-bromopropionyl bromide (**2**) in 20 mL of THF was added drop-wise. The mixture was stirred for another 2 hrs at room temperature (**1** reacted with **2** to yield **BPDME** and HBr was absorbed by triethylamine). Triethylamine hydrogenbromide salt was filtered out. THF in the filtrate was removed under vacuum at room temperature. The residual was dissolve in diethyl ether and washed with 50 mL of cold water. The organic layer was separated, washed with a saturated solution of sodium carbonate, acidified with HCl (pH = 4.5) and a second aliquot was washed with sodium carbonate. The organic layer was dried over anhydrous sodium sulphate, filtered and solvent was removed under vacuum. The product was finally isolated by vacuum distillation as slightly yellowish oil. The product yield was 61%.

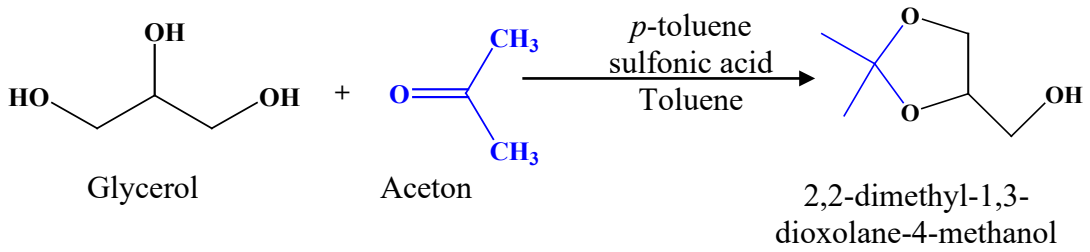
^{1}H NMR ($CDCl_3$) of BPDME: 4.4 ppm (p, 1H, -CH_2-***CH***-O-); 4.3 ppm (q, 1H, Br-***CH***(CH_3)-); 4.2 ppm (d, 2H, -O-***CH_2***-CH-); 4.0 and 3.8 ppm (dd, 2H, -***CH_2***-O-); 1.8 ppm (d, 3H, Br-CH(***CH_3***)-); 1.40 and 1.35 ppm (s, 6H, -C(***CH_3***)$_2$);

^{13}C NMR ($CDCl_3$) of BPDME: 170 ppm (-***C***=O); 109 ppm –O-***C***-O-) 73 ppm (-CH_2-***CH***-O-); 65 ppm (-O-CH_2-CH-***CH_2***-O-); 65 ppm (-O-***CH_2***-CH-O-); 39 ppm (Br-***CH***(CH_3)-); 26 and 25 ppm (-C(***CH_3***)$_2$); 21 ppm (Br-CH(***CH_3***)).

7.3 RESULT AND DISCUSSION

7.3a. Synthesis and Characterization of BPDME

The starting material 2,2-dimethyl-1,3-dioxolane-4-methanol was synthesized from the reaction between glycerol and acetone in presence of *p*-toluene sulfonic acid (Scheme 7.1)



Glycerol Aceton 2,2-dimethyl-1,3-dioxolane-4-methanol

Scheme 7.1. Synthesis of 2,2-dimethyl-1,3-dioxolane-4-methanol.

The structure of the starting material 2,2-dimethyl-1,3-dioxolane-4-methanol was characterized by ^{1}H NMR and ^{13}C NMR analysis. In the ^{1}H NMR spectrum, a pentate at 4.1 ppm was appeared for assumable to ring -CH_2 –C**H**–O- proton. Two double doublets at 3.9 and 3.6 ppm assignable to ring –CH-C**H**$_2$-O- proton and two double doublets at 3.5 and 3. 4 ppm assignable to -C**H**$_2$-OH protons, respectively, indicates the presence of dioxolane group.

All signals correspond to the different protons of 2,2-dimethayl-1,3-dioxolane were assigned clearly and labeled in Figure 7.1. In the ^{13}C NMR spectrum of the 2,2-dimethayl-1,3-dioxolane (Figure 7.2), the signals appeared were clearly assigned to the all carbons of 2,2-dimethayl-1,3-dioxolane, which indicate the purity of 2,2-dimethayl-1,3-dioxolane.

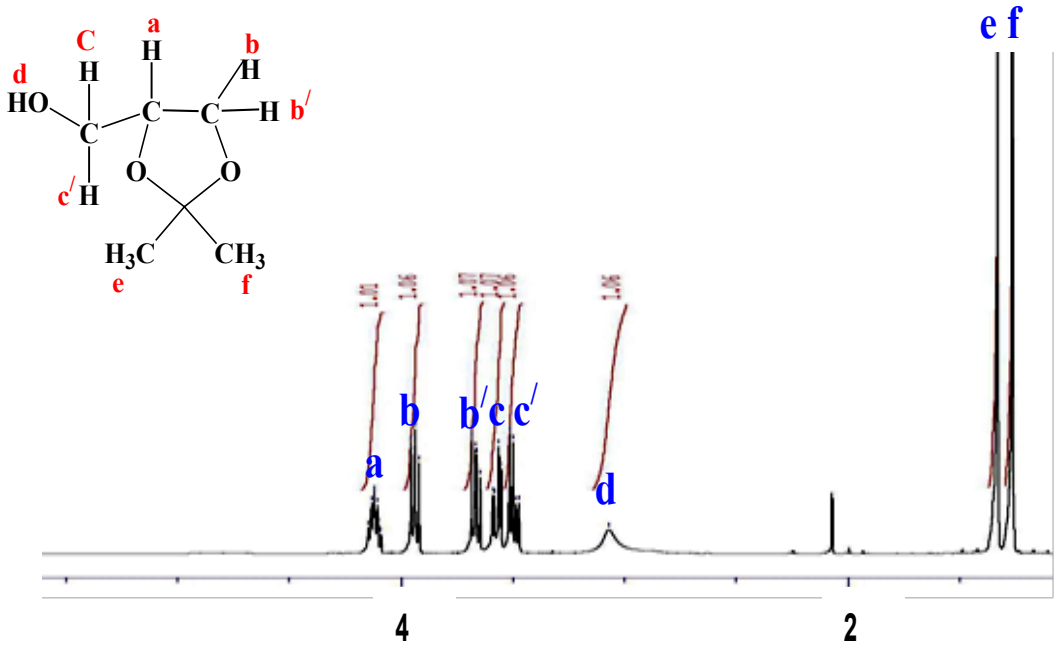


Figure 7.1 ^{1}H NMR spectrum of 2,2-dimethyl-1,3-dioxolane-4-methanol.

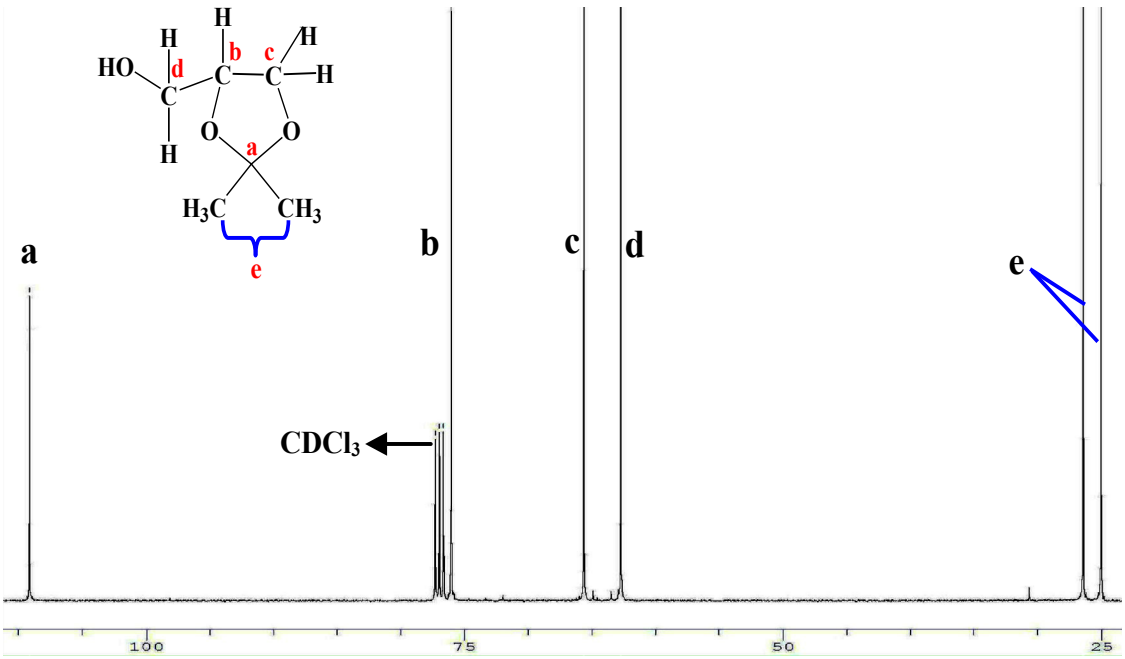
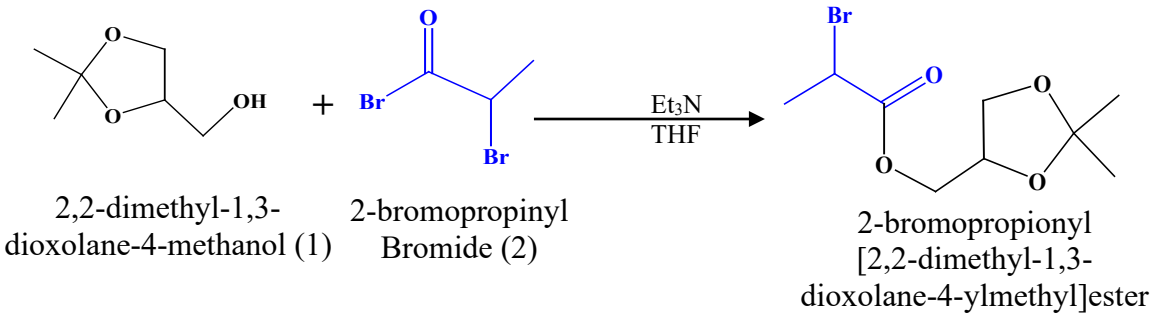


Figure 7.2 ^{13}C NMR spectrum of 2,2-dimethyl-1,3-dioxolane-4-methanol.

The initiator **BPDME** was synthesized from the reaction between 2,2-dimethyl-1,3-dioxolane-4-methanol and 2-bromopropinyl bromide in presence of triethylamine (Scheme 7.2).



Scheme 7.2. Synthesis of **BPDME.**

The structure of the initiator **BPDME** obtained was characterized by ^{1}H NMR analysis. In the ^{1}H NMR spectrum of the **BPDME**, several signals including the signals of 2-bromopropionyl bromide were observed. All signals correspond to the different protons of **BPDME** were assigned clearly and labeled in Figure 7.3 which indicate the purity of **BPDME**.

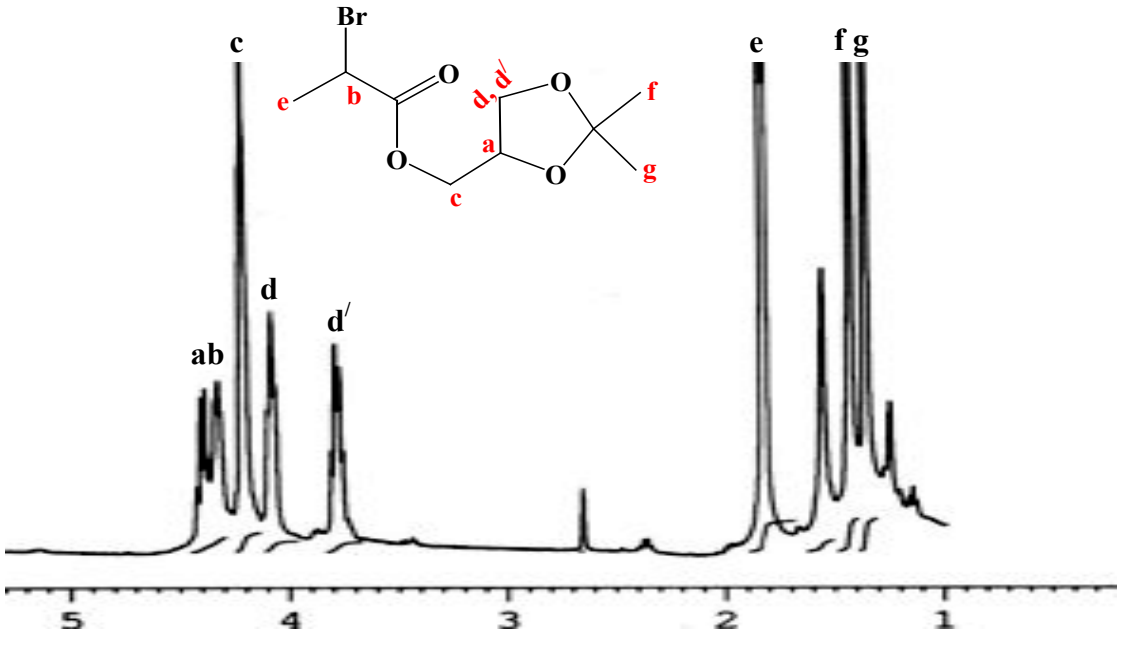


Figure 7.3 ^{1}H NMR spectrum of **BPDME.**

7.3b. Polymerization of Styrene by ATRP using BPDME as Initiator

Styrene was then polymerized by ATRP at 115 ºC initiated with **BPDME** at different styrene/initiator ratio in conjunction with cupper (I) bromide and bipyridine as a catalyst under nitrogen atmosphere. The ratio of styrene and **BDPME** (St/BPDME) significantly affect on the polymerization. The results obtained were listed in **Table 7. 1**. The yield of polymers was increased with increasing the ratio of styrene and **BDPME**. The molecular weight and molecular weight distribution of the polymers obtained were measured with gel permeation chromatography (GPC). The polymers obtained with high molecular weight (M_n). The M_n value of the polymers was increased with the increasing St/BPDME ratio. The molecular weight distribution of polymer was narrow (M_w/M_n ~1.2). The GPC curves of the polymers obtained from the feed ration St/BPDME = 1000, St/BPDME = 500 and St/BPDME = 250 are displayed in **Figure 7.4**.

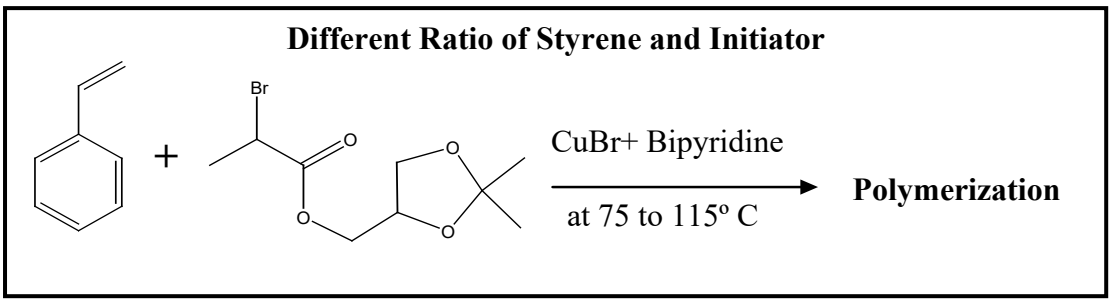


Table 7.1. Effect of the Ratio of Styrene/BPDME on Polymerization of Styrene with CuBr/BiPy.

Entry	St/BDPME	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
1	250	0.51	3.667	4.389	1.19
2	500	0.75	15.42	20.20	1.31
3	1000	1.36	38.20	52.81	1.38

polymerization conditions; CuBr = 0.108 mmol, Bipy = 0.216 mmol, Styrene = 3.1 mL, time = 5 hrs.

The GPC curve of the polymer obtained from higher monomer concentration (St/BPDME = 1000) shifted to the higher molecular weight region than that of the polymer obtained from lower monomer concentration (St/ BPDME = 500). The M_n value (38.2 x 10^3) of the polymer obtained from the higher feed ration (St/ BPDME = 1000) was more than double than the M_n value (15.4 x 10^3) of the polymer obtained from the lower feed ration (St/ BPDME = 500). These results suggest that the higher propagation rate occurred at higher monomer concentration. The linear relationship of molecular weight of the polymers with ratio (**Figure 7.5**) also supports the above results.

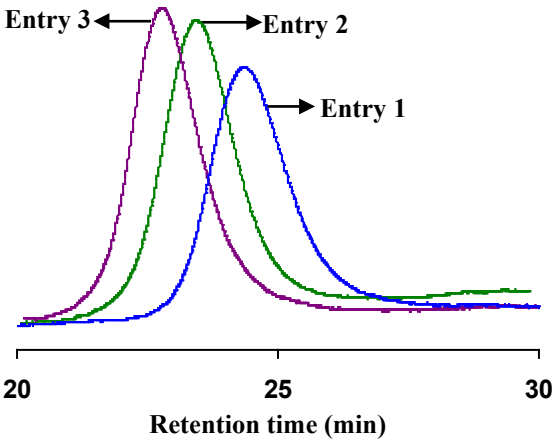


Figure 7.4: GPC curves of PSt by BPDME.

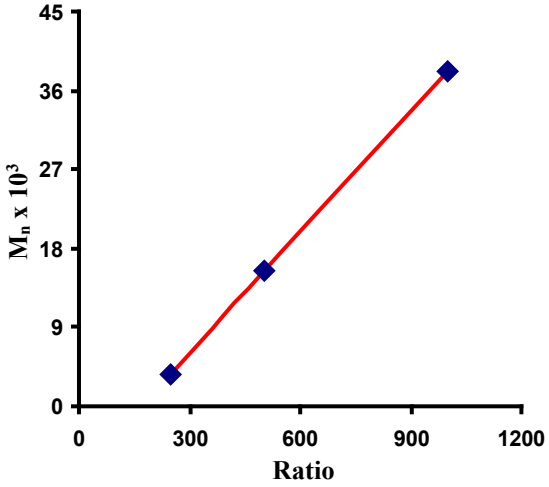


Figure 7.5: Plot of M_n against ratio of PSt by BPDME.

To produce polymer with narrow polydispersity is one of the main criteria for a living polymerization system. The initiator BPDME combined with CuBr/bipyridene catalyst system gave the polymers with narrow polydispersity (M_w/M_n = 1.14) at 115 ºC (entry 6). This result therefore promotes us to make sure the living nature of BDPME/CuBr/bipyridene catalyst system at 115 ºC. The dependence of polymer yield and M_n on polymerization time was investigated by batch method to check the living nature of this catalyst system. The molecular weight and molecular weight distribution of the polymers

obtained by different polymerization time were measured by GPC and the results are summarized in **Table 7.2** and **Table 7.3.**

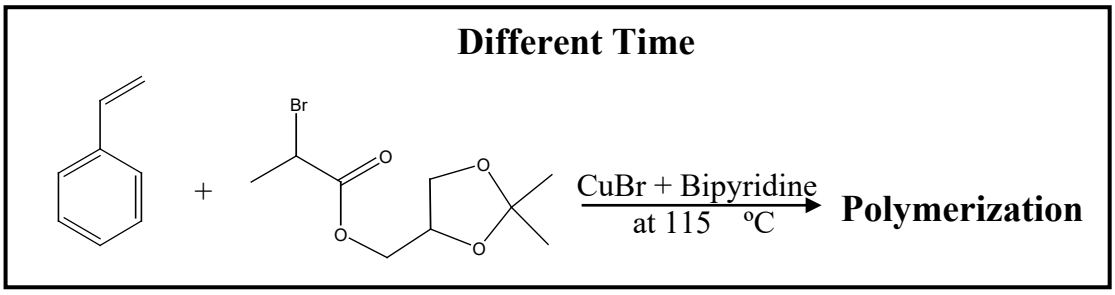


Table 7.2. Time Dependence Polymerization of Styrene with CuBr/BiPy/BDPME using Batch Method.

Entry	Time (h)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
4	5	0.51	3.66	4.38	1.19
5	6.5	0.62	5.56	6.46	1.16
6	8.5	0.92	10.58	12.06	1.14

Polymerization conditions [CuBr = 0.108 mmol, Bipy = 0.216 mmol, Styrene = 3.1 mL, temperature = 115 ºC]

Table 7.3. Time Dependence Polymerization of styrene with CuBr/BiPy/BDPME using Batch Method.

Entry	Time (hours)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
7	5	0.75	15.42	20.20	1.31
8	7	0.92	16.40	20.60	1.26
9	9	1.20	25.60	31.59	1.23
10	10.5	1.53	33.28	44.17	1.32

Polymerization conditions [CuBr = 0.054 mmol, Bipy = 0.108 mmol, Styrene = 3.1 mL, temperature = 115 ºC]

The GPC curves of polymers obtained from different period of time (5, 6.5 and 8.5 hours) at 250:1 ratio and time (5, 7, 9 and 10.5 hours) at 500:1 ratio were

compared in **Figure 7.6 and 7.8**. The GPC curves were shifted to the higher molecular weight region with increasing polymerization time with keeping narrow $M_w/M_{n..}$ The plot of M_n vs time showed linear relationship with a slop at initial period in **Figure 7.7 and Figure 7.9**. The plot of yield vs time also showed linear relationship. These results suggest that the living polymerization **Table 7.2** and **Table 7.3** of styrene proceeded at 115 ºC by **BPDME**/CuBr/BiPy catalyst system with slow initiation.

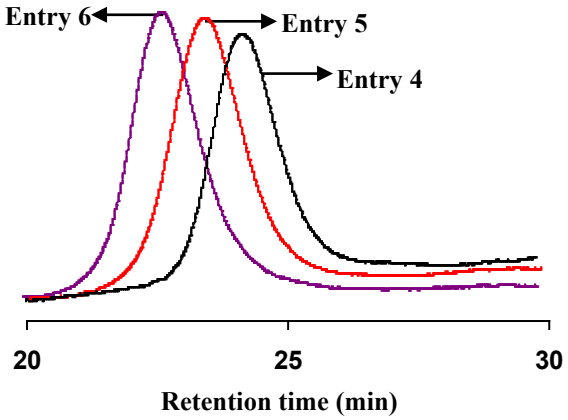


Figure 7.6: GPC curves of PSt by BPDME.

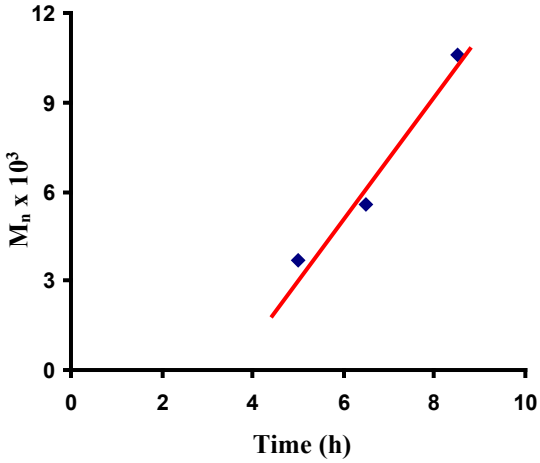


Figure 7.7: Plot of M_n against time of PSt by BPDME.

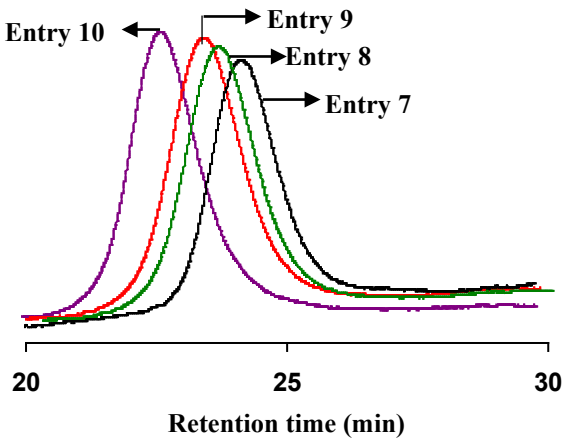


Figure 7.8: GPC curves of PSt by BPDME.

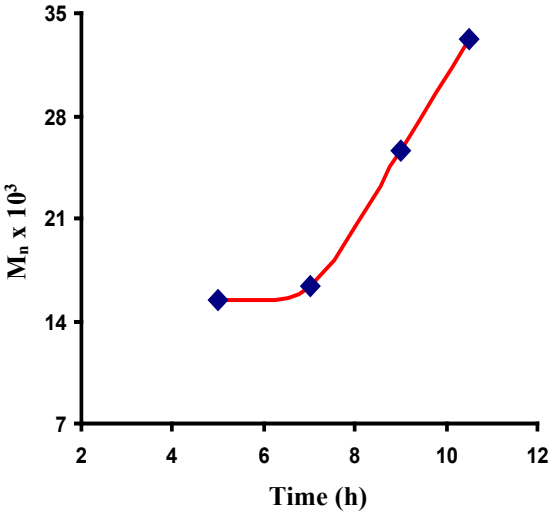


Figure 7.9: Plot of M_n against time of PSt by BPDME.

The dependence of polymer yield and M_n on polymerization temperature was investigated by batch method to check the living nature of this catalyst system. The yield of the polymers was increased with the increasing temperature. The molecular weight and molecular weight distribution of the polymers obtained by different polymerization time were measured by GPC and the results are summarized in **Table 7.4.** The GPC curves of the polymers obtained from different temperature are displayed in **Figure 7.10**.

Table 7.4. Effect of the Temperature on Polymerization of Styrene with CuBr/BiPy

Entry	St/BDPME	Temp (° C)	Yield (g)	M_n (10^3)	M_w (10^3)	M_w/M_n
11	**250**	75	trace	-	-	-
12	**250**	100	0.277	6.043	9.078	1.50
13	**250**	115	0.511	3.667	4.389	1.19

Polymerization conditions; CuBr = 0.108 mmol, Bipy = 0.216 mmol, Styrene = 3.1 mL, time = 5 hrs

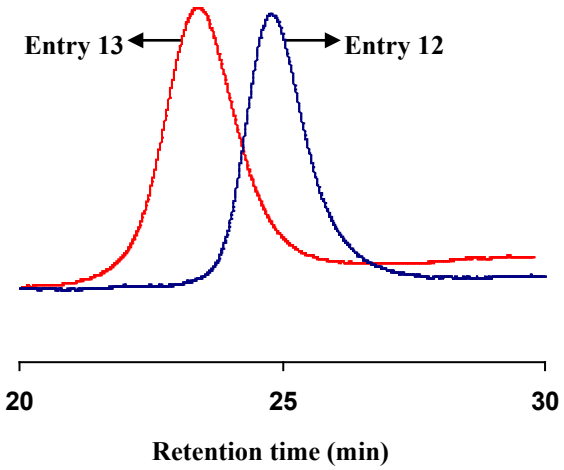
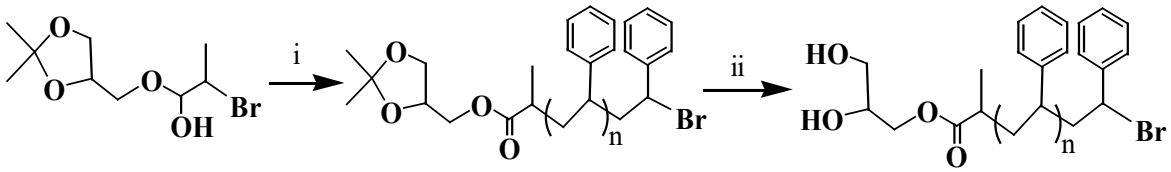


Figure 7.10 GPC curves of polystyrene obtained by BPDME.

Styrene was then polymerized by ATRP with **BPDME** at different condition in conjunction with cupper (I) bromide and bipyridine as a catalyst under nitrogen

atmosphere. The hydroxylation of the dioxolane group of polystyrene (**PS)** was carried out using glacial acetic acid, water and anisole at 80 ºC in THF for 1hour (Scheme 7.3).The quantitative conversion of dioxolane group to dihydroxyl group was confirmed by the ^{1}H NMR analysis.



BPDME **PS-DX** **PS-OH**

i = CuBr, Bipridine, 115 ºC; ii = glacial aceticacid, water, anisole, 80 ºC

Scheme 7. 3. The hydroxylation of the dioxolane group of PS-DX.

7.3c. Analysis of the Structure of the Polystyrene Obtained Initiated with BPDME/CuBr/Bypridene Catalyst System.

The structure of polystyrene obtained using **BPDME** initiator was investigated by ^{1}H NMR analysis of the polymer and comparison with the spectrum of **BPDME** initiator. The ^{1}H NMR spectrum of poly styrene obtained with **BPDME** was displayed in **Figure 7.11**. In the ^{1}H NMR spectrum of polystyrene, the signals at 4.6 ppm and 3.7 ppm assignable to (-O-C**H**-CH_2- and –CH-C**H**$_2$-O-) dioxolane ring protons and a signal at 4.4 ppm assignable to CH proton α to Br indicates that the polymerization was initiated with **BPDME**. A broad signal at 7.2 ppm assignable to aromatic protons (meta- and para-position) of styrene unit labeled as m and n and at 6.5 ppm for ortho-proton labeled as o in **Figure 7.11**. The signals observed at 1.35 and 1.77 ppm assignable to -C**H**$_2$ and -C**H** protons of main chain of polystyrene, respectively. These results clearly indicate the presence of dioxolane group in the ω-end of polystyrene obtained with **BPDME** initiator.

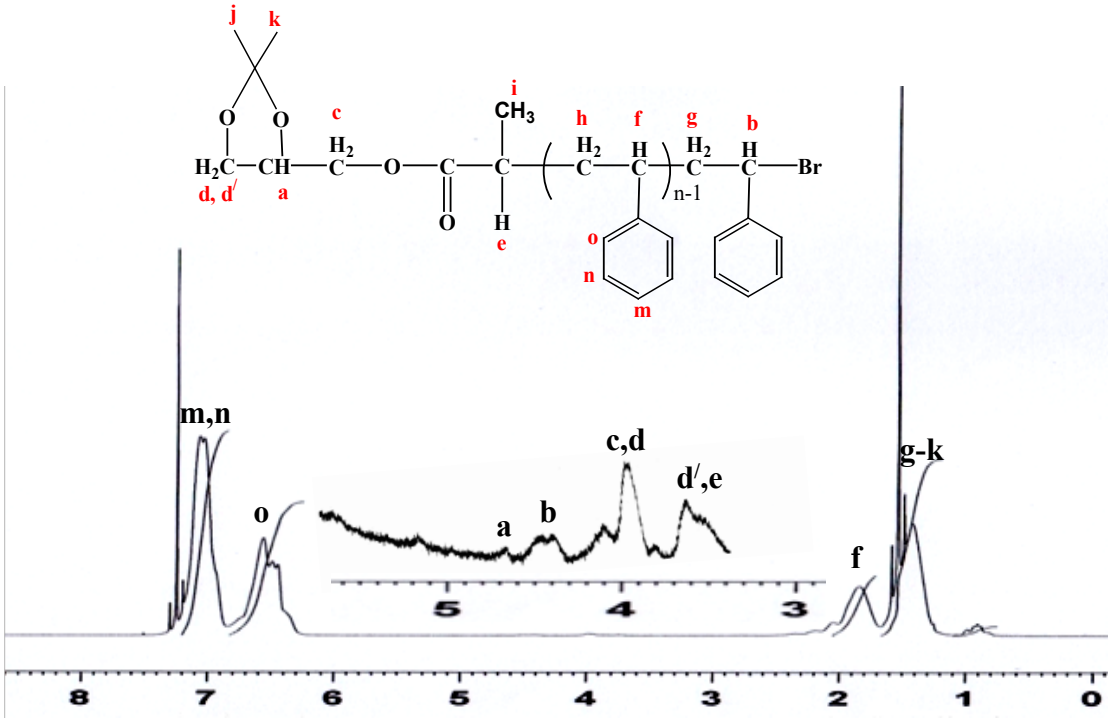


Figure 7.11 ^{1}H NMR spectrum of polystyrene was obtained by using **BPDME** as initiator.

7.3d. Dihydroxylation of the Polystyrene Obtained Initiated with BPDME.

The dihydroxylation of the dioxolane group at the chain end of the polystyrene obtained with **BPDME** initiator was carried out at 80 ºC in THF for 1h using glacial acetic acid, water and anisole. The quantitative conversion of dioxolane group to dihydroxyl group was confirmed by the ^{1}H NMR analysis of the product.

The ^{1}H NMR spectrum of the polystyrene after dihydroxylation was displayed in **Figure 7.12**. The peaks at 5.66 and 5.19 ppm assigned for two -O**H** groups denoted by a, b in the structure of the polystyrene and the signals assignable for main polystyrene chain were also appeared. This observation indicated the dihydroxyl end-functional structure of polystyrene.

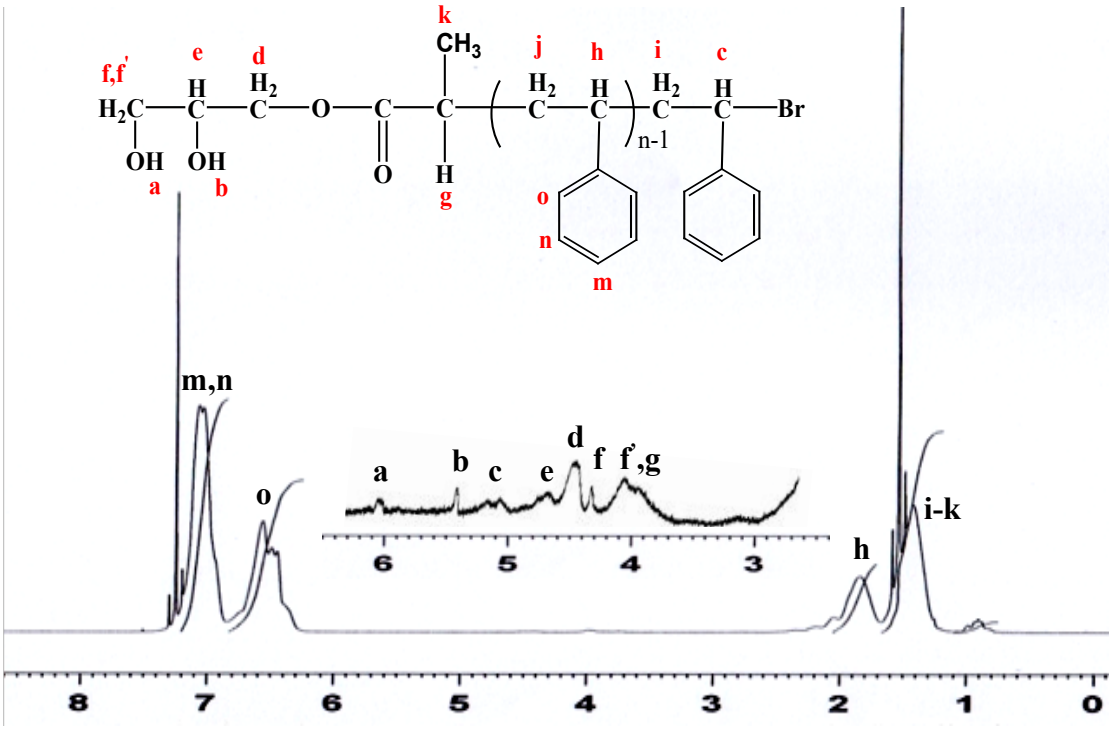


Figure 7.12. ^{1}H NMR spectrum of polystyrenes after dihydrooxylation.

7.4. Conclusion

The initiator **BPDME** was synthesized in a good yield. The structure of **BPDME** was characterized by ^{1}H and ^{13}C NMR analysis. The **BPDME** as initiator was successfully applied for Cu(I)-bipyridine mediated ATRP polymerization of styrene. The polymerization of styrene was investigated at various reaction conditions.

The polymerization of styrene with **BDPME**/CuBr/BiPy (1:1:2) was investigated at various temperatures (75, 100 and 115 ºC) under nitrogen atmosphere. A trace amount of polymer was obtained at 75 ºC. The yield of polymers was increased with raising the temperature of the polymerization and the better yield was obtained at 115 ºC.

The yield and molecular weight of polymers were increased linearly with increasing the ratio of styrene and **BDPME**. These results suggest that the propagation rate was increased with increasing of monomer concentration. The molecular weight distribution of polymer was narrow (M_w/M_n = 1.19). In time dependence polymerization, yield vs time plot showed linear relationship whereas the M_n values of the polymer linearly increased against time after a certain period. The molecular weight distribution was very narrow (M_w/M_n = 1.14). These results suggest that the living polymerization of styrene proceeded at 115 ºC by **BPDME**/CuBr/BiPy catalyst system with slow initiation.

In the ^{1}H NMR spectrum of the polystyrene obtained with **BPDME** initiator, the signals appeared for assignable to dioxolane group indicated the dioxolane chain-end structure of the polystyrene. Finally, the dioxolane end group of the polystyrene was converted to dihydroxy group by treatment of acetic acid, water and anisole at 80 °C. the structure of dihydroxyl end-group was confirmed by ^{1}H NMR spectrum of the polymer.

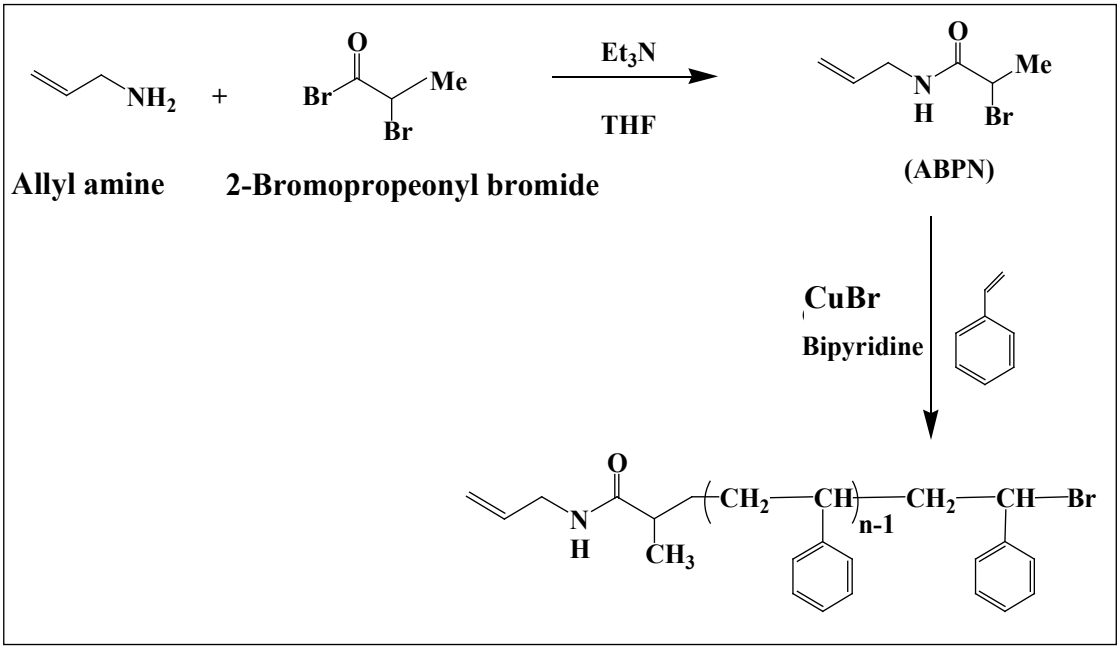
CHAPTER

VIII

Conclusions and Future Prospect

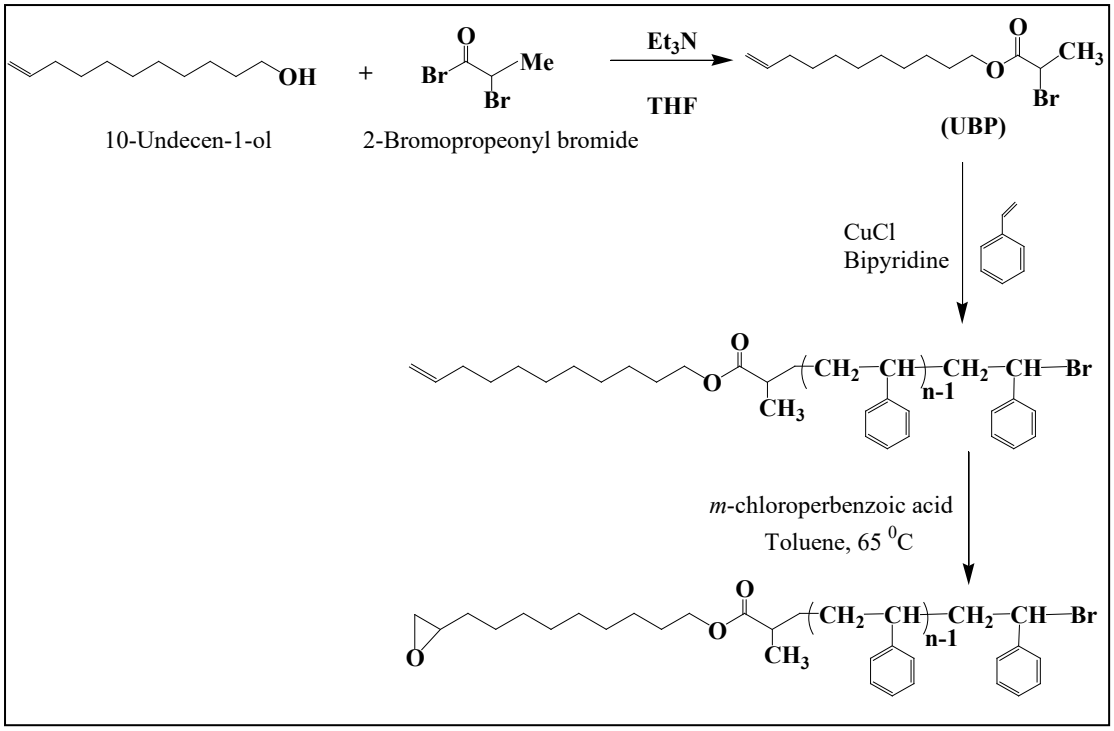
End- and mid-functionality plays an important role in the polymer's property and it allows the polymer to couple with other functionalities forming graft, blocks, cross-linking. Control over the synthesis of blocks and grafts the polymer architectures has become increasingly important in producing high value added materials for nanotechnology, biomaterials, blend modifiers and improving particular polymer properties by self-assembly. The end-functional polymers can be prepared by modifying end group of polymers or most conveniently by using functional initiators in living/controlled polymerization. Recently a method of living/controlled radical polymerization, atom-transfer radical polymerization (ATRP) is versatile enough to synthesize end-functional polymers by using functional initiator method. Among the various functional groups vinyl, alkyne and dioxalane end-group containing polymers are very interesting because of there conjugation of thiol group of any compounds, polymers and protein. Alkyne functionalized polymers are very much important materials because of these polymers contain a clickable alkyne group. On the other hand, dioxalane end-group could be converted to dihydroxy group that could be used as macroinitiator to synthesis of block or three-armed copolymer or dendrimer. On these point of view, five new α-bromoester initiators containing allyl, alkyne and dioxalane groups were synthesized and the polymerization of styrene was carried out using those initiators with Cu(I)-mediated ATRP method in this study. The initiator efficiency, effect of polymerization condition and properties of end-functional polystyrene obtained were also studied.

In chapter II, N-allyl-2-bromopropinamide (**N-ABPN**) was synthesized in a good yield. The structure of **N-ABPN** was characterized by ^{1}H and ^{13}C NMR analysis. The polymerization of styrene was carried out by Cu(I)-bipyridine mediated ATRP method using **N-ABPN** as initiator at various reaction conditions.



The ratio of styrene and **N-ABPN** (St/**N-ABPN**) significantly affects the results of polymerization. The temperature dependent experiments show that the yield of polymers was increased with raising the temperature of the polymerization. At high reaction temperature (115 ºC), the initiator efficiency was high. On the other hand, a trace of polymer was obtained at 75º C. The initiator efficiency was high at high feed ratio of styrene and **N-ABPN** (St/ **N-ABPN** = 1000 and 500). The yield of polymers was increased with the increasing of ratio of styrene and **N-ABPN**. The GPC curves of the polymer were shifted to the higher molecular weight region with increasing polymerization time keeping narrow M_w/M_n. The signals assignable to vinyl group was appeared in the ^1H and ^{13}C NMR spectra of polystyrene obtained with **N-ABPN** which indicate the vinyl chain-end structure of the polystyrene formed by ATRP initiated with **N-ABPN**.

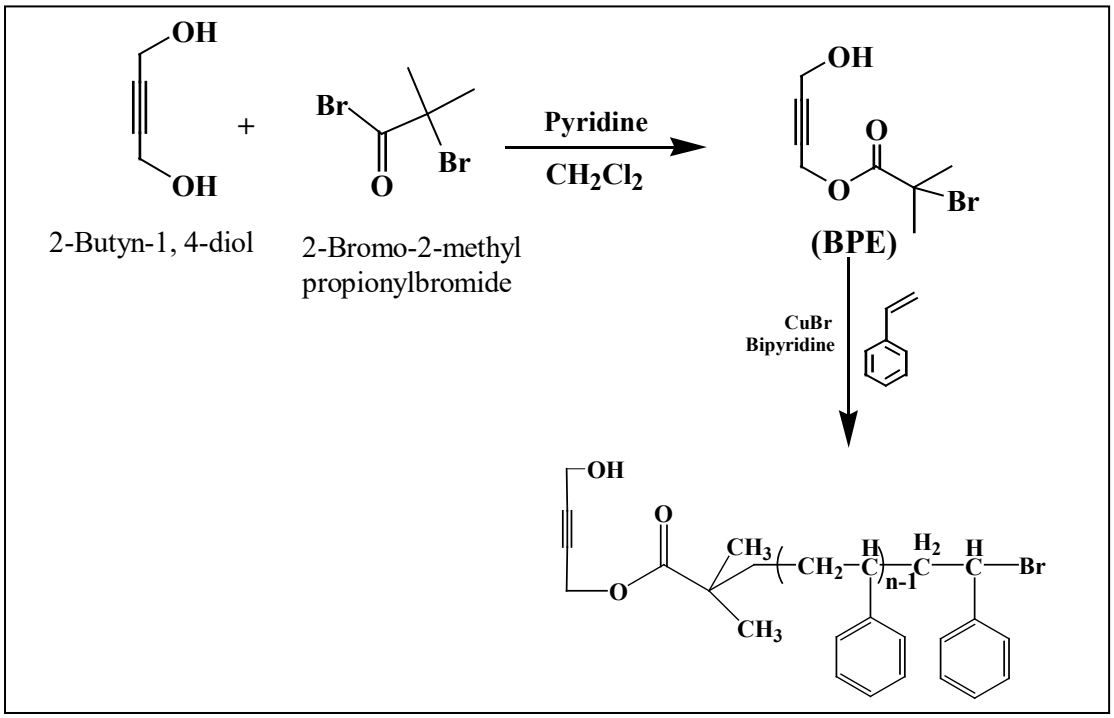
In chapter III, Undecen-2-bromopropionate (UBP) was synthesized in a good yield. The structure of UBP was characterized by ^1H and ^{13}C NMR analysis. The polymerization of styrene was investigated by Cu(I)-bipyridine mediated ATRP using UBP as initiator at various reaction conditions.



The effect of St/UBP ratio and reaction temperature on the styrene polymerization was studied and the similar trend was observed as in chapter II. The yield and the molecular of the polymers were increased, and the molecular weight distribution became narrower with raising reaction temperature from 70 ºC to 130 ºC. The narrow polydispersity (M_w/M_n = 1.50) of the polymers obtained at 110 and 130 ºC suggests that the living polymerization of styrene should proceed with these conditions. To confirm the living nature at 110 ºC, the dependence of M_n on polymerization time was investigated by sampling method. The GPC curves of the polymer were shifted to the higher molecular weight region with increasing polymerization time keeping narrow M_w/M_n. The M_n value of the polystyrene linearly increased against conversion. These results indicate the living ATRP polymerization of styrene with this catalyst system at 110 ºC. In the ^1H and ^{13}C NMR spectra of the polystyrene obtained with this catalyst system, the signals assignable to vinyl group indicate the vinyl chain-end structure of the polystyrene which was formed by ATRP initiated with UBP. Finally, the vinyl end group of the polystyrene was converted to epoxy group by chemical reaction and the quantitative conversion of vinyl group to

epoxy group was confirmed by the disappearance of the vinyl signal in the ^{1}H and ^{13}C NMR spectra of the polystyrene after epoxidation.

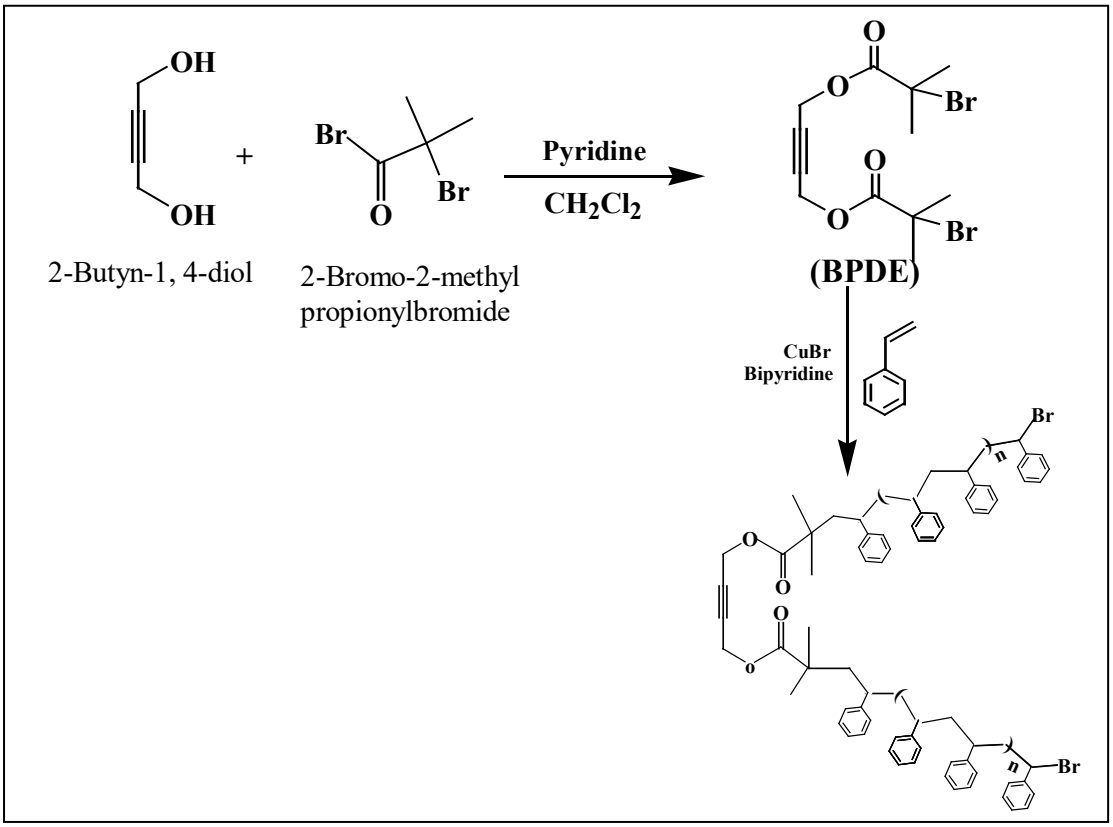
In chapter V, 2-Bromo-2-methyl-propionic acid-but-2-ynyl diester (BPE) was synthesized in a good yield. The structure of BPE was characterized by ^{1}H NMR analysis. The polymerization of styrene was carried out by Cu(I)-bipyridine mediated ATRP method using BPE as initiator at different duration of time.



The polymerization time of styrene and BPE (St/ BPE) significantly affects the results of polymerization. The initiator efficiency was high with increasing polymerization time of styrene and BPE (St/**BPE** = 2, 4 and 6). The yield of polymers was increased with the increasing polymerization time of styrene and **BPE**. The signals assignable to alkyne group was appeared in the ^{1}H NMR spectra of polystyrene obtained with **BPE** which indicate the Alkyne chain-end structure of the polystyrene formed by ATRP initiated with **BPE**.

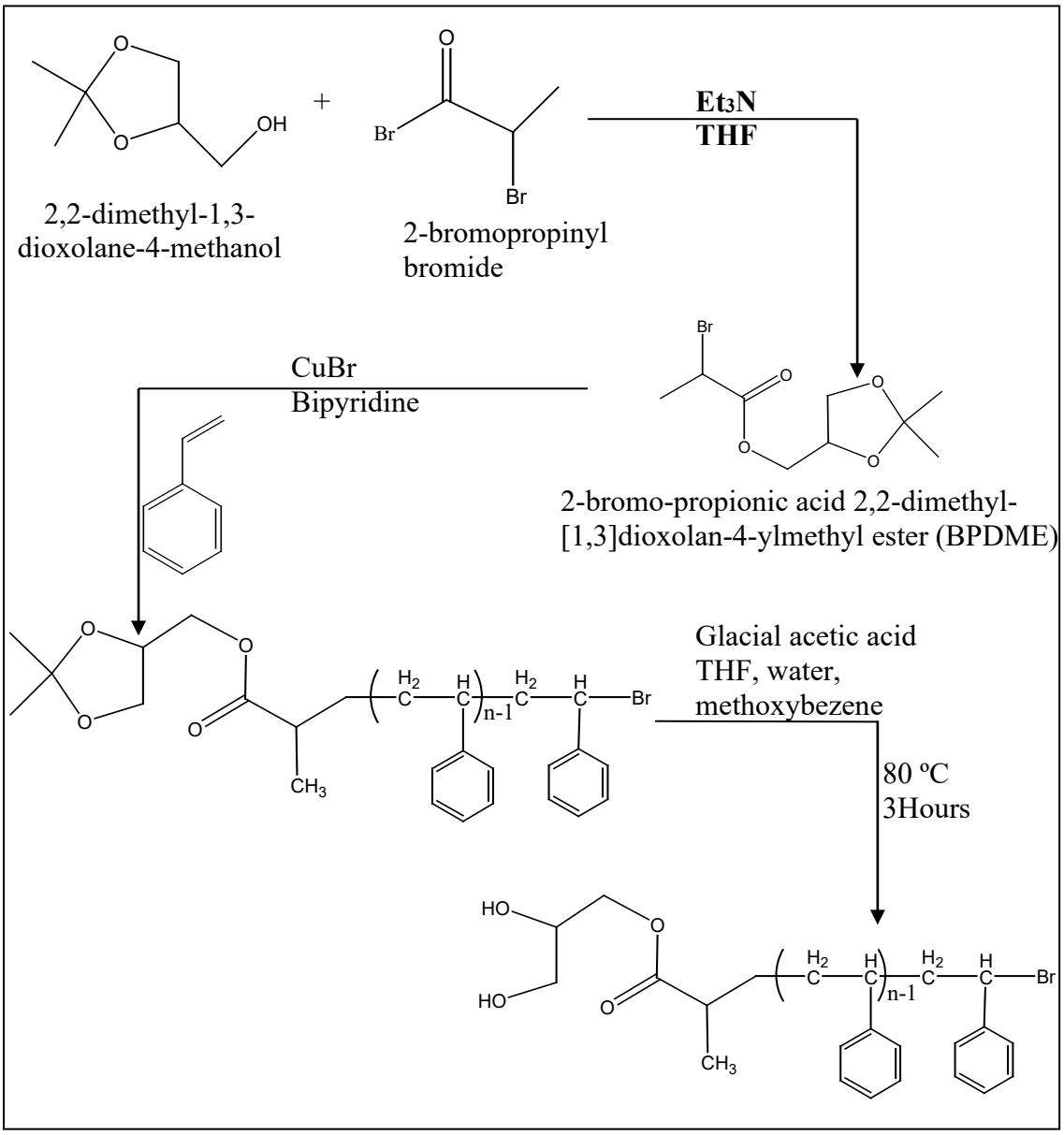
In chapter VI, 2-Bromo-2-methyl-propionic acid 4-hydroxy-but-2-ynyl diester **(BPDE)** was synthesized in a good yield. The structure of **BPDE** was characterized by ^{1}H NMR analysis. The polymerization of styrene was carried

out by Cu(I)-bipyridine mediated ATRP method using **BPDE** as initiator at different duration of time.



The polymerization time of styrene and **BPDE** (St/ BPDE) significantly affects the results of polymerization. The initiator efficiency was high with increasing polymerization time of styrene and BPE (St/ **BPDE** =0.5, 1 and 2). The yield of polymers was increased with the increasing polymerization time. The signals assignable to alkyne group was appeared in the ^{1}H NMR spectra of polystyrene obtained with **BPDE** which indicate the mid-alkyne chain structure of the polystyrene formed by ATRP initiated with **BPDE**.

In chapter VII, 2-bromopropionyl[2,2-dimethyl-1,3-dioxolane-4-ylmethyl] ester (**BPDME**) was synthesized. The structure of **BPDME** was characterized by ^{1}H and ^{13}C NMR analysis. The polymerization of styrene was investigate by Cu(I)-bipyridine mediated ATRP using **BPDME** as initiator at various reaction conditions.



The initiator **BPDME** was synthesized in a good yield. The structure of **BPDME** was characterized by ^{1}H and ^{13}C NMR analysis. The **BPDME** as initiator was successfully applied for Cu(I)-bipyridine mediated ATRP polymerization of styrene. The polymerization of styrene was investigated at various reaction conditions.

The polymerization of styrene with **BDPME**/CuBr/BiPy (1:1:2) was investigated at various temperatures (75, 100 and 115 ºC) under nitrogen atmosphere. A trace amount of polymer was obtained at 75 ºC. The yield of

polymers was increased with raising the temperature of the polymerization and the better yield was obtained at 115 ºC.

In the polymerization at various St/**BDPME** ratios, the yield and molecular weight of polymers obtained were increased linearly with increasing St/**BDPME** ratio. These results suggest that the propagation rate was increased with increasing of monomer concentration. The molecular weight distribution of polymer was narrow. At time dependence polymerization, a linear relationship was observed between polymer yield and time. On the other hand, the M_n value linearly increased with keeping narrow molecular weight distribution (M_w/M_n = 1.14) against time after a certain period. These results suggest that the living polymerization of styrene proceeded at 115 ºC by CuBr/BiPy/**BPDME** catalyst system with slow initiation. In the ^{1}H NMR spectrum of the polystyrene obtained with **BPDME** initiator, the signals were assigned for the presence of dioxolane group, which indicates the dioxolane chain-end structure of the polystyrene. Finally, the dioxolane end group of the polystyrene was converted to dihydroxyl group by treatment of acetic acid, water and anisole at 80 °C. the structure of dihydroxy end-group was confirmed by ^{1}H NMR spectrum of the polymer.

In this research work end-allyl, alkyne and dioxolane functional and mid-alkyne functinal polystyrenes were synthesized by Atom Transfer Radical Polymerization technique using five new initiators. These five end and mid-functional polystyrenes could be used as precursor to synthesis of functional polymers with various architectures as follows:

Allyl end-functional polystyrene can be modified by thiol-ene click reactions which are used to generate block copolymers and telechelic polymers. Biofunctionalisation of polymers by thiol–ene reactions can impart beneficial properties.

Epoxy end functionalized polystyrene obtained in this study could be used as "reactive macromonomer" for synthesis of various graft or block copolymers. Alkyne end-functional polystyrene can be further modified by conversion of alkyne group to other functional group for suitable applications. On the other hand, by the Alkyne-Azide click reaction the terminal alkyne group of polystyrene could be ligated with azide terminal group of different polymer chain to give block copolymer.

Alkyne mid-functional polystyrene could be liagted with azide terminal of other polymer chain to give star polymer by a suitable alkyne-azide click reaction. This mid-alkyne functional polystyrenes have –Br group at both end of the chain. Therefore these both end could be modified to other functional group by suitable reaction to obtain various telechelic polymers.

The functionalization of hydroxyl-group terminated polystyrene could be anchored to magnetite nanoparticles. Dioxolane end-functional polystyrene can be further modified by chemical conversion to produce free two hydroxyl group which can be used as "reactive macroinitiator" for synthesis of tri-arm block copolymers, ABC star block copolymer, Miktoarm star block copolymers and dendrimers. Thefore, reactive functional polymer synthesized in this study could be used as presursore to prepare various type of block or star polymer with well-defined architecture.

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