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# GLOSSARY

| | |
|---|---|
| ATRC | Atom transfer radical coupling reactions |
| ATRA | Atom transfer radical addition |
| ATRP | Atom Transfer Radical Polymerization |
| aq | Aqueous |
| 1-BEB | (1-Bromoethyl)benzene |
| Boc | Butoxycarbonyl |
| BPO | Benzoyl peroxide |
| Bu | Butyl |
| bpy | 2,2'-Bipyridine |
| CABSC | p-Carboxybenzene sulfonyl chloride |
| $CCl_4$ | Carbon tetrachloride |
| $CH_2Cl_2$ | Dichloromethane |
| CuBr | Copper(I) bromide |
| $cm^{-1}$ | Wavenumber |
| CRP | Controlled/"living" Free Radical Polymerization |
| DAEM | 2-(dimethylamino)ethyl methacrylate |
| DMAEMA | Dimethylaminoethyl methacrylate |
| DMF | N,N-dimethylformamide |
| DMSO | Dimethylsulfoxide |
| dNbpy | 4,4'-Di(5-nonyl)-2,2'-bipyridine |
| DP | Degree of polymerization |
| DPE | Diphenylether |
| DTBP | Di-tertiary-butylphthalate |
| $Et_2O$ | Diethyl ether |
| $E^+$ | Electrophile |
| Et | Ethyl |
| $Et_6$TREN | Tris[2-(diethylamino)ethyl]amine |
| Fmoc | 9-Fluorenylmethoxycarbonyl group |

| | |
|---|---|
| FTIR | Fourier Transform Infrared Spectroscopy |
| g | Grams |
| HCl | Hydrochloric acid |
| HEMA | 2-hydroxyethyl methacrylate |
| HMTETA | 1,1,4,7,10,10-hexamethyltriethylenetetramine |
| h | Hours |
| INFERTER | Initiator-transfer-agent-termination |
| I | Initiator |
| KF | Potassium fluoride |
| L | Ligand |
| $LiAlH_4$ | Lithium aluminium hydride |
| $M_6$TREN | Tris[2-(dimethylamino)ethyl]amine |
| M | Monomer |
| Me | Methyl |
| MeOH | Methanol |
| $MgSO_4$ | Magnesium sulphate |
| MMA | Methyl methacrylate |
| MeLi | Methyl lithium |
| mol | Mole |
| $NaHCO_3$ | Sodium hydrogen carbonate |
| $NH_4Cl$ | Ammonium chloride |
| NMP | Nitroxide Mediated Free Radical Polymerization |
| NMR | Nuclear Magnetic Resonance Spectrometry |
| NTA | Nitrilotriacetic acid |
| n-Pr-L | N-(n-propyl)-2-pyridylmethanimine |
| PMMA | Poly(methyl methacrylate) |
| PMDETA | N,N,N',N'',N''-pentamethyldiethylenetriamine |
| Ph | Phenyl |
| PS | Polystyrene |
| $P_2O_5$ | Phosphorus pentoxide |

| | |
|---|---|
| RAFT | Reversible Addition Fragmentation Chain Transfer Polymerization |
| SEC | Size Exclusion Chromatography |
| $SOCl_2$ | Thionyl chloride |
| TBAF | tetrabutylammonium fluoride |
| TFA | Trifluoroacetic acid |
| THF | Tetrahydrofuran |
| TLC | Thin Layer Chromatography |
| TsCl | p-Toluenesulfonyl chloride |
| TEMPO | 2,2,6,6-Tetramethylpiperidinyoxy |
| TMS | Tetramethylsilane |
| Titr | Titration |

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Title: AROMATC OXAZOLYL AND CARBOXYL FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION

Novel methods for the preparation of aromatic and carboxyl functionalized polymers by atom transfer radical polymerization were developed. In addition, the application of 1,1-diarylethylene chemistry was extended to free radical polymerization methods by using new mono- and dioxazolyl substituted 1,1-diphenylethylene derivatives as functionalized initiator precursors for the synthesis of well defined α-oxazolyl and α-bis(oxazolyl) functionalized polystyrene by atom transfer radical polymerization, respectively. The polymerization kinetic data for all reactions show that the polymerization reactions follow first order rate kinetics with respect to monomer consumption. The number average molecular weights of the oxazolyl chain end functionalized polymers increase linearly with percentage monomer conversion and polymers with narrow molecular weight distribution were obtained. Furthermore, a new, general, *in situ* post atom transfer radical polymerization chain end modification reaction for the preparation of α,ω-bis(oxazolyl) and α,ω-tetrakis(oxazolyl) polystyrenes was developed using the specific oxazolyl substituted 1,1-diphenylethylene derivative as initiator precursor as well as functionalizing agent. Aromatic carboxyl chain end functionalized polymers were prepared by post polymerization chain end modification reactions by the chemical conversion of the oxazoline groups to the carboxyl groups at the polymer chain ends. The functionalized polymers can be utilized in water purification processes, drug delivery systems and nanotechnology applications.

## KEY WORDS

Atom transfer radical polymerization, oxazolyl functionalized initiator α-oxazolyl functionalized polystyrene, carboxyl functionalized polystyrene, 1,1-diphenylethylene, α,ω-bis(oxazolyl) functionalized polystyrene and α,ω-tetrakis(oxazolyl) functionalized polystyrene.

# CHAPTER 1

# INTRODUCTION

The preparation of new functionalized polymers is the fastest evolving synthesis area in polymer chemistry. Currently, functionalized polymers are of great interest due to their applications in technological areas[1-3] such as nanotechnology, biotechnology, surface modification, adhesion, coatings, polymer compatibilization, block copolymer synthesis and as building blocks in macromolecular design. Consequently, the focus on new synthetic methods for the preparation of well defined functionalized polymers with control of chain functionality, number average molecular weights and molecular weight distributions is desirable[3,4].

One of the traditional polymerization routes towards the synthesis of chain end functionalized polymers is via living anionic polymerization techniques[5]. However, anionic living polymerization suffers from several limitations such as the required absence of impurities, the requirement of high purity of monomers and solvents, the incompatibility of the process with polar monomers and the very low polymerization temperature for acrylate polymerization reactions[4,5].

Recently, controlled/"living" radical polymerization (CRP) methods were developed, which are particularly amenable to the synthesis of functionalized polymers[3,6]. The CRP techniques allow the synthesis of well defined polymers with predictable number average molecular weights, narrow molecular weight distributions and controlled composition, topology and chain end functionality[3]. The controlled/"living" polymerization methods commonly employed in industry and academia include nitroxide mediated free radical polymerization[3] (NMP),

reversible addition fragmentation chain transfer radical polymerization[3] (RAFT) and atom transfer radical polymerization[7-8] (ATRP). In particular, the ATRP method, pioneered by Matyjaszewski[9] in 1995, is the most versatile controlled free radical process employed to prepare a wide range of functionalized polymers with controlled number average molecular weights, molecular weight distributions and chain end functionality due to its tolerance to a wide range of functional groups.[3,7,9,10]. In a typical ATRP reaction, a dynamic equilibrium between the low concentration of active propagating radicals and a large amount of dormant species is established by the use of transition metal complexes, such as copper(I)/nitrogen ligand complexes, and a reversible halogen atom transfer agent. As a result, the concentration of propagating radicals is kept low (approximately $10^{-8}$-$10^{-7}$ M)[10]. Consequently, after monomer addition, negligible radical termination reactions and controlled polymerization reactions are observed.

The end groups of polymers prepared by the ATRP method are determined by the structure of the initiator employed in the ATRP process. In general, alkyl halide initiators are commonly used in ATRP reactions[11]. The alkyl group fragment of the initiator is incorporated at the α-terminus of the polymer chain, with the halogen group at the ω-end of the polymer chain[7-8]. Thus, the use of an appropriate functionalized initiator in ATRP reactions leads to the preparation of a plethora of functionalized polymers with the functional group specifically introduced at the initiating end of the polymer chain[3,4]. For successful chain end functionalized polymer synthesis via ATRP methods, the functional group in the initiator must not interfere with the ATRP process and must therefore be inert towards the catalyst/ligand complex frequently used in ATRP reactions[11].

ATRP is the most convenient method to prepare chain end functionalized polymers using functionalized initiators[11]. Different functional groups such as the hydroxyl, amine, esters, thiols and allyl groups have been readily introduced at

the $\alpha$-terminus of the polymer chain using functionalized initiators based on the functionalized haloalkyl benzene, haloesters and sulfonyl halides[7,11]. However, the synthesis of oxazoline chain end functionalized polymers using oxazoline functionalized initiators is not well documented in the literature. Pionteck and coworkers[12] reported the preparation of α-oxazolyl functionalized polystyrene by employing a series of oxazolyl functionalized initiators such as 4-(1,3-oxazoline-2-yl)phenyl-4-(1-bromoethyl)benzoate and 2-(1-bromoethyl)-1,3-oxazoline in the presence of copper(I) salts and an appropriate nitrogen based ligands in atom transfer radical polymerization processes. Zhang and coworkers[13] employed 2-bromomethyl-4,5-diphenyloxazole as an oxazolyl functionalized initiator for the polymerization of methyl methacrylate in the presence of copper(I) bromide/2,2'-bipyridine catalyst system to produce well defined oxazolyl chain end functionalized poly(methyl methacrylate).

Furthermore, the quantitative synthesis of carboxyl chain end functionalized polymers by ATRP using functionalized initiators has been well documented in the literature[11]. Carboxyl functionalized polymers can be prepared by direct ATRP methods, using carboxyl functionalized initiators with the carboxylic acid group in its free form[14-17]. For example, Matyjaszewski[15] and Haddleton[16] independently prepared carboxyl chain end functionalized polystyrene and poly(methyl ethacrylate) using α-halocarboxylic acid initiators for the ATRP of styrene and methyl methacrylate, respectively. However, the polymerization reactions were not well controlled. Low initiation efficiency reactions due to side reactions, which include poisoning of the catalyst, were observed. However, the use of alkyl halide initiators with remote free carboxylic group has emerged as one of the efficient alternative routes for the preparation of carboxyl functionalized polymers[15-17]. For example, Summers and coworkers[17] prepared well defined carboxyl functionalized polystyrene by ATRP methods using α-bromo-p-toluic acid as functionalized initiator. The use of an initiator with the free carboxylic acid group remote to the initiating halogen resulted in minimal interference of the acid moiety

with the transition metal catalyst, as evidenced by the relatively high initiation efficiency of the carboxylic acid substituted initiator.

Due to the potential complexation of the carboxylic acid moiety with the transition metal catalyst system in the ATRP reactions, many indirect methods, which involve the use of functionalized initiators substituted with carboxylic acid derivative, particularly the α-haloesters, can also be used to prepare α-carboxyl functionalized polymers[7,8,15]. Derivatization of the carboxylic acid group in the initiator led to improved initiator efficiency reactions. After the deblocking of the carboxylic group in a post polymerization reaction, the corresponding well defined α-carboxyl functionalized polymers are obtained[15,18]. For example, Pionteck and coworkers[18] employed the α-chloropropionate derivative containing the t-butyl ester functionality as the functionalized initiator in the ATRP of styrene in the presence of copper(I) bromide/PMDETA catalyst system to prepare well defined ester functionalized polystyrenes. Subsequent quantitative hydrolysis of the resultant ester functionalized polymers by saponification reactions gave the corresponding well defined carboxyl chain end functionalized polystyrene.

The use of substituted 1,1-diphenylethylene derivatives in polymer synthesis provides one of the best methods for the preparation of polymers with predictable, well defined polymer properties, in particular the excellent control of the chain end functionality[5]. The reactions of polymeric anions, cations and free radicals with substituted 1,1-diphenylethylene compounds provides an efficient functionalization method for the preparation of functionalized organic compounds and polymers. Such addition reactions are simple, rapid and without side reactions[5]. In addition, due to steric factors, the stoichiometric reactions of anions, cations and free radical species with substituted 1,1-diphenylethylene derivatives proceed quantitatively with the incorporation of a single 1,1-diphenylethylene unit, that is, no oligomerization or polymerization of the 1,1-diphenylethylene derivative occurs[5,19]. Quirk and coworkers[19-21] developed a

general anionic functionalization methodology for the preparation of functionalized polymers based on the addition reactions involving polymeric organolithium compounds and 1,1-diphenylethylene derivatives. The functionalization reaction proceeds smoothly, irrespective of the nature of substituents. Thus, a variety of 1,1-diphenylethylenes derivatives bearing the oxazoline[19], siloxyl[21], tertiary amine[22], amide[23] and halogen[24] groups were used as functionalizing agents in the chain end functionalization reactions with polymeric anions.

The use of 1,1-diphenylethylene derivatives in the preparation of well defined functionalized polymers was extended to ATRP methods[25-28]. Summers and coworkers[25-28] developed a general, one pot, quantitative ATRP functionalization method which uses a functionalized initiator adduct, prepared from the reaction of a substituted 1,1-diphenylethylene derivative with (1-bromoethyl)benzene in the presence of copper(I) bromide/2,2'-bipyridine as a catalyst system, as the functionalized initiator for preparation of chain end functionalized polymers. For example, the use of the tertiary amine functionalized initiator adduct system, prepared *in situ* by the addition reaction of (1-bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene, as initiator for styrene polymerization by ATRP methods produced well defined α-tertiary amine functionalized polystyrene in quantitative yields[25].

The present research focuses on the preparation of a series of α-oxazolyl functionalized polymers by ATRP methods using different oxazolyl functionalized initiator systems. By ATRP methods, three different oxazoline derivatives were used as oxazolyl functionalized initiators or initiator precursors for styrene or methyl methacrylate polymerization. The research work outlines the synthetic strategy for the preparation of oxazolyl chain end functionalized polymers by the ATRP process according to the following methods:

(a) The synthesis of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole and its use as an oxazolyl functionalized initiator for the synthesis of α-oxazolyl functionalized polystyrene and poly(methyl methacrylate) in the presence of copper(I) bromide/2,2'-bipyridine or PMDETA as a catalyst system.

(b) The synthesis of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole and its utility as an aromatic oxazolyl functionalized initiator precursor for the preparation of $\alpha$-oxazolyl functionalized polystyrene by atom transfer radical polymerization methods. The use of a new oxazolyl initiator adduct, prepared *in situ* by the reaction of (1-bromoethyl)benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, as the initiator for the polymerization of styrene by ATRP methods provides a new method for the synthesis of the corresponding α-oxazolyl functionalized polystyrene.

(c) The novel synthesis of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene and its use as an aromatic dioxazolyl functionalized initiator precursor for the synthesis of α-bis(oxazolyl) functionalized polystyrene by ATRP methods. The utilization of a new dioxazolyl functionalized initiator adduct, obtained by the *in situ* reaction of (1-bromoethyl)benzene with 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, as initiator for the ATRP of styrene provides a unique synthetic route for the preparation of α-bis(oxazolyl) functionalized polystyrene.

For a controlled/"living" atom transfer radical polymerization reaction, the following primary experimental features must be observed[7,8]: (a) a linear semi-logarithmic first order plot of ln ($[M]_o/[M]$) versus time, indicating that the radical concentration is constant throughout the polymerization reaction, (b) a linear evolution of the

number average molecular weight with percentage monomer conversion, which indicates the absence of any side reactions, and (c) the formation of polymers with narrow molecular weight distributions, below 1.5, which are close to Poisson distribution. The current study investigates the controlled/"living" nature of each ATRP reaction leading to the preparation of a series of α-oxazolyl functionalized polymers using three different oxazolyl functionalized initiator systems as initiators for styrene polymerization.

The present study also describes the preparation of α,ω-bis(oxazolyl) and α,ω-tetrakis(oxazolyl) functionalized polystyrene by the post ATRP chain end transformation reactions via the following synthetic pathway:

(a) the atom transfer radical polymerization of styrene initiated by the new oxazolyl functionalized initiator adduct derived from the appropriate oxazolyl functionalized 1,1-diphenylethylene unit.

(b) the addition of the appropriate oxazolyl substituted 1,1-diphenylethylene unit to the ω-terminus of the polymer chain at the end of the polymerization process.

The current research also outlines the preparation of aromatic carboxyl chain end functionalized polymers by the quantitative chemical transformation of the oxazoline group of the appropriate oxazolyl chain end functionalized polymers to the corresponding carboxylic acid group. The successive acid and base hydrolysis of the specific oxazolyl functionalized polystyrene derivative, followed by final acidification, provides a useful method for the synthesis of the corresponding well defined chain end carboxyl functionalized polystyrene.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 CHAIN GROWTH POLYMERIZATION

Polymerization reactions are classified into two major groups based on the polymerization mechanism, namely, step growth and chain growth processes[29-30]. There are a variety of different chain polymerization mechanisms including free radical, ionic, complex and ring opening polymerization. In chain growth polymerization, the growth of the chain is associated with the addition of consecutive monomer units to a single molecule. The features of chain growth polymerization are as follows[29-31]:

(a) The chain growth reaction involves the addition of a monomer at one end of the chain. The polymerization reaction is effected by a kinetic chain of reactions. Thus, different mechanisms operate at different stages of the reaction.

(b) The polymerization rate initially increases and becomes constant with polymerization time.

(c) An initiator is required to start the reaction.

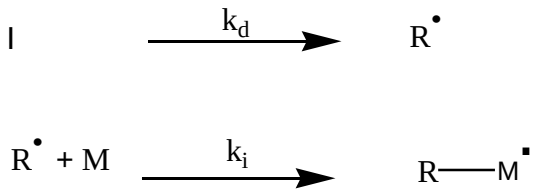
(d) Chain growth polymerization involves the reaction of a monomer with active centers that may be free radicals, ions and polymer-catalyst bonds.

## 2.2 CONVENTIONAL FREE RADICAL POLYMERIZATION

### 2.2.1 Mechanism of Free Radical Polymerization

A typical chain growth polymerization reaction consists of three major kinetic steps, namely, initiation, propagation and termination. The free radical polymerization process is one of the most important chain growth polymerization methods. Conventional free radical polymerization is a rapid chain reaction which proceeds via the following characteristic kinetic steps:

**Initiation**




Organic compounds with a half life $t_{1/2} \approx 10$ hours, such as benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) are commonly employed as initiators for production of free radicals ($R^{\bullet}$) at a rate constant $k_d$[31]. The formation of free radicals is followed by the subsequent one step addition to the monomer molecule (M) to form a new free radical (monomer radical, $R\text{-}M_1^{\bullet}$) at a rate constant of $k_i$. The rate of initiation is given by the following equation:

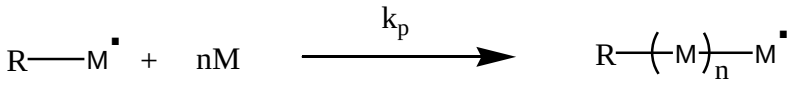
$$R_i = -d[M^{\bullet}]/dt = 2fk_d[I]$$

where $R_i$ is the rate of initiation, 2 represents the two primary radicals formed during the decomposition of the initiating species, $[M^{\bullet}]$ is the radical species

concentration, [I] is the initiator concentration and f is the initiator efficiency, that is, the proportion of radical that initiate polymer chain versus radicals formed from the initiator.

**Propagation**

Chain propagation proceeds rapidly by the consecutive addition of monomer (M) molecules, mainly in a head-to-tail fashion, to produce macroradicals ($R\text{-}(M)_n\text{-}M^{\bullet}$ at a rate constant $k_p$. The propagation rate constant is independent of the chain length and the specific rate constants for all propagation steps are equal.




The rate of monomer consumption is given by:

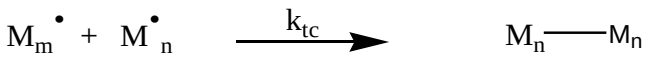
$$R_p = k_p [M][M^{\bullet}]$$

where $[M^{\bullet}]$ is the sum of the concentration of all monomer ended radicals in the reaction system, $k_p$ is the rate constant of propagation and [M] is the concentration of monomer.

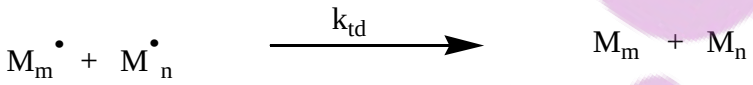
**Termination**

Polymerization stops when the propagating chain ends are destroyed by an appropriate chain termination reaction. In conventional free radical polymerization reactions, the most important chain termination steps involve two possible kinetic steps, namely, combination and disproportionation.

In the combination reaction, two chain ends couple together in a head to head fashion to form one long chain at a rate constant $k_{tc}$ as shown below:



In the disproportionation reaction, an atom such as a hydrogen atom is transferred between two macroradicals with a rate constant $k_{td}$, resulting in two reaction products, one of which is saturated and the other is unsaturated.

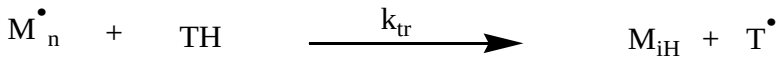


The rate equation for the rate of combination and disproportionation is given by:

$R_{tc} = 2k_{tc}[M^{\bullet}]^2$ and $R_{td} = 2k_{td}[M^{\bullet}]^2$, respectively.

**Chain transfer reactions**

In addition to initiation, propagation and termination reactions, other kinetic processes, such as chain transfer reactions, can occur during the polymerization reaction. In chain transfer reactions, the growth of the polymer chain can be terminated by the abstraction of an atom, such as a hydrogen atom from a neutral saturated molecule which may be a solvent, monomer, initiator or other additives present in the polymerization reaction. As a result, a lower molecular weight polymer is produced and the reactivity of the free radical is transferred to other species. The general equation for the chain transfer process involving a macroradical $M_n^{\bullet}$ and a transfer agent TH is depicted below:



The rate of chain transfer is given as: $R_{tr} = k_{tr}[M^{\bullet}][TH]$

Conventional free radical polymerization is the most widely applied methodology for the industrial production of polymer material. Over 50% of commercial polymers including synthetic plastics, elastomers and some fibers are synthesized via free radical polymerization[29-31]. The advantages of the conventional free radical polymerization process in the industry and academia is due to the following factors[6,29]:

(a) The rigorous purification of monomers, solvents and other reagents is minimal.

(b) The propagating species is compatible with a wide variety of functional groups such as acids, hydroxyl and amine groups. Thus, nearly all vinylic and vinylidene monomers, such as methacrylates, styrenes, methacrylamides, butadiene and vinyl acetate, can undergo free radical polymerization and copolymerization to form an infinite number of polymers with properties determined by the monomer composition.

(c) Free radical polymerizations are characterized by a high rate of polymerization.

In conventional free radical polymerization, the degree of control that can be asserted over polymer structure, particularly the molecular weight distributions, composition and architecture is limited and results in production of polymers with poor control of number average molecular weight, molecular weight distribution

and efficiency of chain end functionalization[6-7,31]. The poor control of the polymerization process is due to the inherent slow initiation relative to fast propagation and the inevitable near diffusion controlled termination reactions of growing radical species[7]. In addition, the life span of a propagating chain is too short for any synthetic manipulation such as chain end functionalization reactions or addition of a second monomer to form a block copolymer[7].

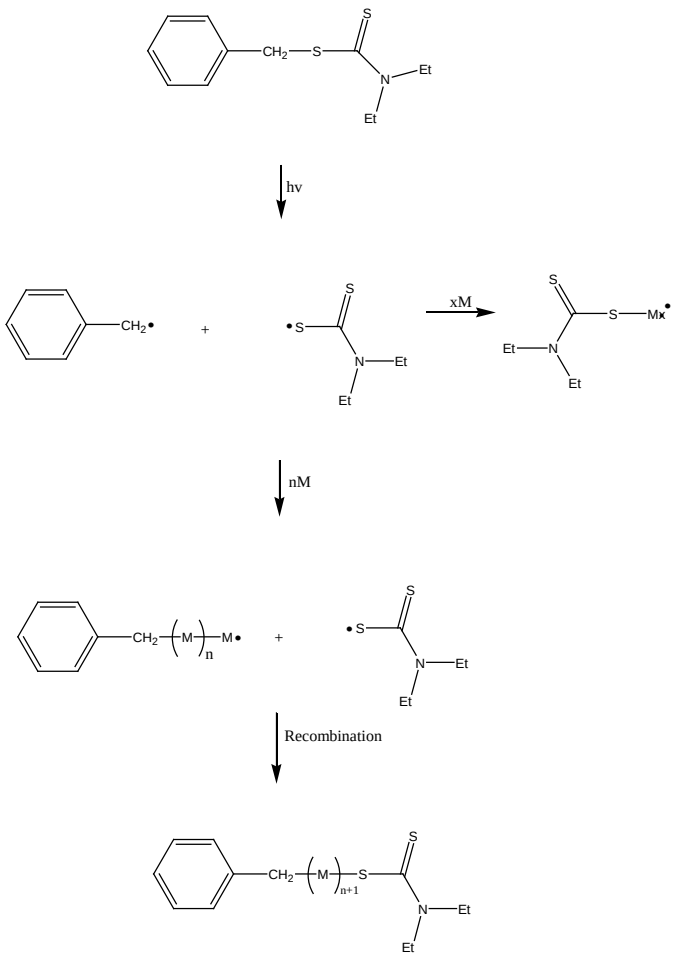
Thus, there is a need for the development of controlled/"living" synthesis methods for the preparation of well-defined polymer structures. Thus, several new controlled/"living" free radical polymerization methods were developed independently by different research groups worldwide. The most powerful controlled/"living" free radical polymerization techniques are nitroxide mediated radical polymerization[3] (NMP), reversible addition fragmentation chain transfer radical polymerization[3] (RAFT) and atom transfer radical polymerization[3,7,8] (ATRP).

## 2.3 CONTROLLED/"LIVING" FREE RADICAL POLYMERIZATION (CRP)

The term controlled/"living" polymerization refers to a polymerization reaction in which termination reactions occur at a minimal rate of less than ten percent. Truly living polymerization cannot be achieved in radical polymerization because of unavoidable fast, irreversible termination reactions of growing radicals induced by a high concentration of highly reactive radicals[7,8]. However, if the ratio of terminated chains to total number of chains is kept minimal, the polymerization reaction can proceed in a controlled manner. The ability to allow the synthesis of well defined polymers with predetermined number average molecular weight, composition, topology and chain end functionality, while retaining much of the

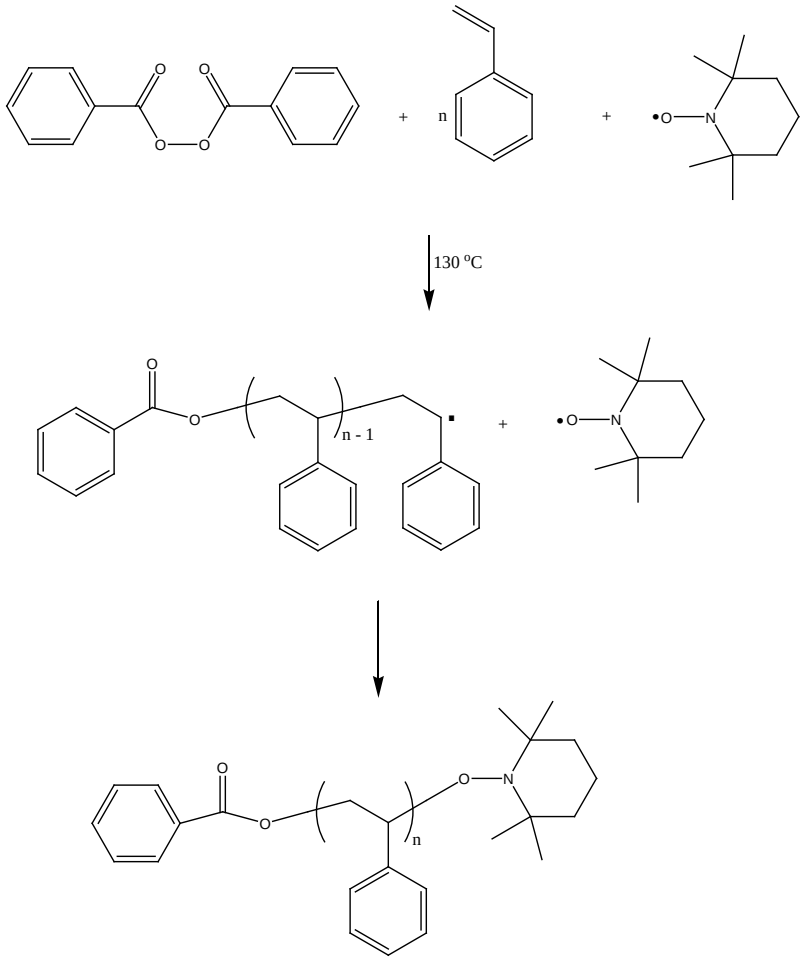
versatility of radical polymerization, has resulted in the widespread adoption of controlled/"living" radical polymerization in research laboratories[7,9].

Several controlled/"living" free radical polymerization methods, which allow the preparation of well defined polymers by free radical mechanism, have been reported in the literature. Otsu and Yoshida[32] first published a report on the controlled free radical polymerization process by outlining a method for the preparation of well defined polymers using the Initiator-Transfer-Agent-Termination (INIFERTER) method:

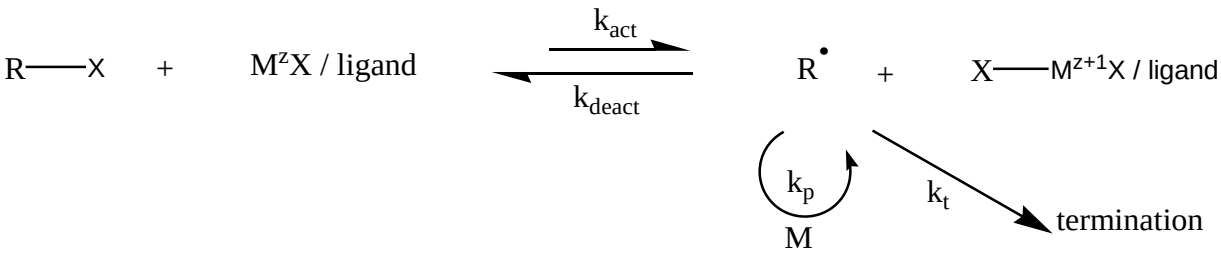


Linear evolution of the number average molecular weight with percentage monomer conversion and the preparation of block copolymers were achieved. However, broad molecular weight distribution polymers were obtained due to multiple initiation steps.

Following the INFERTER work, Georges and coworkers[33] employed a bimolecular system, consisting of 2,2,6,6-tetramethylpiperidinyloxy (TEMPO) as a stable radical and benzoyl peroxide, as an initiator to prepare polystyrenes with predictable number average molecular weights and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.2-1.3) via the nitroxide mediated radical polymerization (NMP) method:

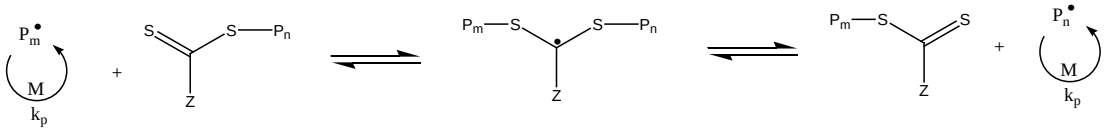


In 1995, Matyjaszewski[9] and Sawamoto[34] independently reported the metal-catalyzed controlled/"living" radical polymerization process as a new versatile method to prepare well defined polymers. The synthesis approach possesses the ability to control the polymerization process by a metal/ligand catalyst complex while retaining all the characteristic of conventional radical polymerization[9,34]. A general mechanism for metal-catalyzed living radical polymerization is depicted below:




Sawamoto[34] reported the living polymerization of methyl methacrylate catalyzed by a ruthenium (II) complex in conjunction with an initiator (R-X) such as carbon tetrachloride. Similarly, the polymerization using a copper based catalyst was reported by Matyjaszewski[9] in the polymerization of styrene and named the polymerization technique as Atom Transfer Radical Polymerization (ATRP).

The reversible addition fragmentation chain transfer polymerization (RAFT) process was introduced by Rizzardo and coworkers[35] as the most robust controlled/"living" polymerization method. The RAFT method utilizes thiocarbamates and thioesters as transfer agents to induce living character to the polymerization process. In the RAFT technique, the monomer unit is inserted into the C-S bond of the thiocarbonylthio compounds as outlined in the following reaction:



A key feature in all controlled free radical polymerizations methods[6] is the fast dynamic equilibrium between the propagating radicals and corresponding dormant species. In NMP and ATRP techniques, the dynamic equilibrium is achieved by reversible termination of the growing polymeric radicals through activation and deactivation process[36]. In RAFT polymerization, the propagating radicals may partake in transfer degenerative exchange process for dynamic equilibrium to occur[35].

Since the outstanding features of the controlled/"living" free radical polymerization is the absence of any chain termination or chain transfer steps, control of the following polymer and experimental parameters can be obtained[36-37]:

(a) **First order rate kinetics with respect to monomer**: Well controlled polymerization systems are characterized by linear semilogarithmic plots of monomer conversion versus time (ln $([M]_o/[M])$ vs time), due to insignificant contribution of bimolecular termination or chain transfer reactions. This feature requires fast quantitative initiation accompanied by fast propagation, achieved by the establishment of a dynamic equilibrium between activation and deactivation processes. As a result, a low steady concentration of propagating radical is generated and an insignificant contribution of radical bimolecular termination reactions is observed. The gradient of the plot should be equal to the pseudo first order rate coefficient ($k_{app}$) which is equivalent to the reaction rate.

(b) **Linear evolution of number average molecular weight with percentage monomer conversion**: For controlled/"living" radical polymerization, a linear relationship exists between the evolution of number average molecular weight and percentage conversion of monomer, which demonstrates the fast, uniform initiation and growth of propagating chains. The equilibrium between the dormant and active species provides a constant concentration of growing chains which results in uniform polymer growth. Moreover, the linear relationship between the increasing number average molecular weight with percentage monomer conversion signifies the absence of chain transfer and termination reactions.

(c) **Control of number average molecular weight**: The degree of polymerization of a polymer can be predetermined by the ratio of concentration of consumed monomer and initiator according to the following relationship: $M_n^{theory}$ = % conversion/100 $[M]_o/[I]_o M_{wm} + M_{wI}$, where $M_{wm}$ and $M_{wI}$ represent the average molecular weight of monomer and initiator, respectively.

(d) **Narrow molecular weight distribution**: By controlling the relative rates of initiation versus propagation, polymers with narrow molecular weight distributions close to Poisson distribution are formed. Due to the fast initiation relative to propagation and the fast exchange between active and dormant species, negligible chain transfer or termination reactions are observed. Thus, polymers with narrow molecular weight distributions are produced. When all the chains are initiated at the same rate and propagation occurs for the same period, a fixed number of polymeric chains with nearly uniform chain lengths are produced. The molecular weight distribution of polymers decreases with increase in the number avarage molecular weight of the polymer chain according to the following relationship; $\overline{M}_w/\overline{M}_n = 1 + 1/\overline{M}_n$.

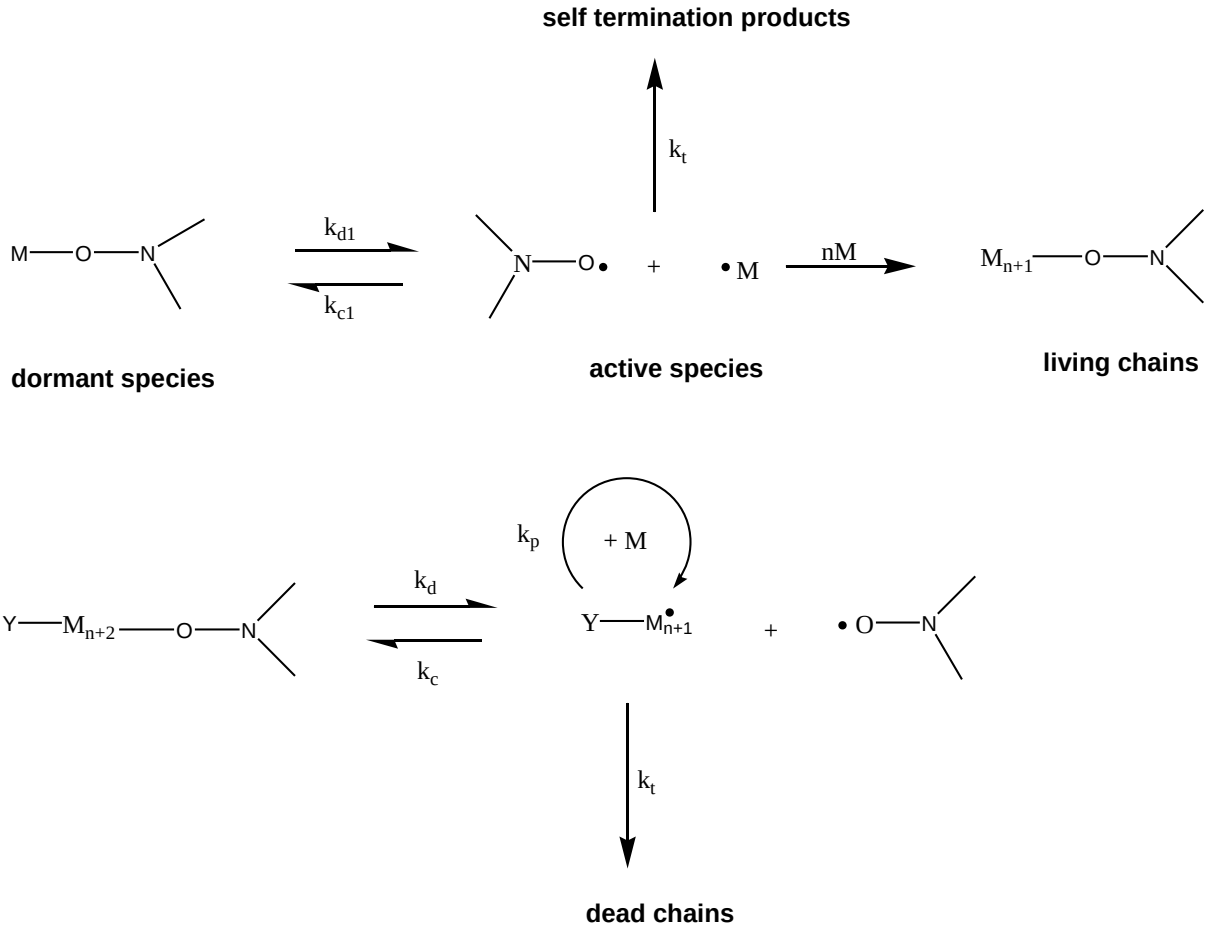
(e) **Chain end functionalization:** In controlled radical polymerization reactions, the use of an appropriate functionalized initiator leads to the preparation of a variety of chain end functionalized polymers with the functional group specifically introduced at the α-terminus of the polymer chain. Moreover, the active species at the ω-terminus of the polymer chain can be subjected to chain end modification reactions such as nucleophilic substitution, elimination, free radical and electrophilic addition reactions[7,8] to give polymers with the desired chain end functionality.

(f) **Block copolymer formation:** Due to negligible chain transfer or termination reactions, a majority of the chain ends are considered as "living". In most controlled free radical polymerization reactions, the propagation reaction resumes upon introduction of an additional monomer. Thus, controlled/"living" polymerization allows preparation of new polymeric material via the sequential monomer addition method by varying the composition of the polymeric chain resulting in the formation of statistical/gradient copolymers and block copolymers.

The most widely used controlled free radical polymerization processes for the synthesis of well defined polymers are nitroxide mediated radical polymerization (NMP)[33], reversible addition fragmentation chain transfer radical polymerization (RAFT)[35] and atom transfer radical polymerization (ATRP)[9].

## 2.4 NITROXIDE MEDIATED RADICAL POLYMERIZATION (NMP)

In 1993, Georges[33] and Solomon[38] developed the nitroxide mediated radical polymerization (NMP) method to prepare well defined polymers by free radical mechanisms. In the NMP method, the control of polymerization is governed by the reversible termination of active species by nitroxides according to the following mechanism:

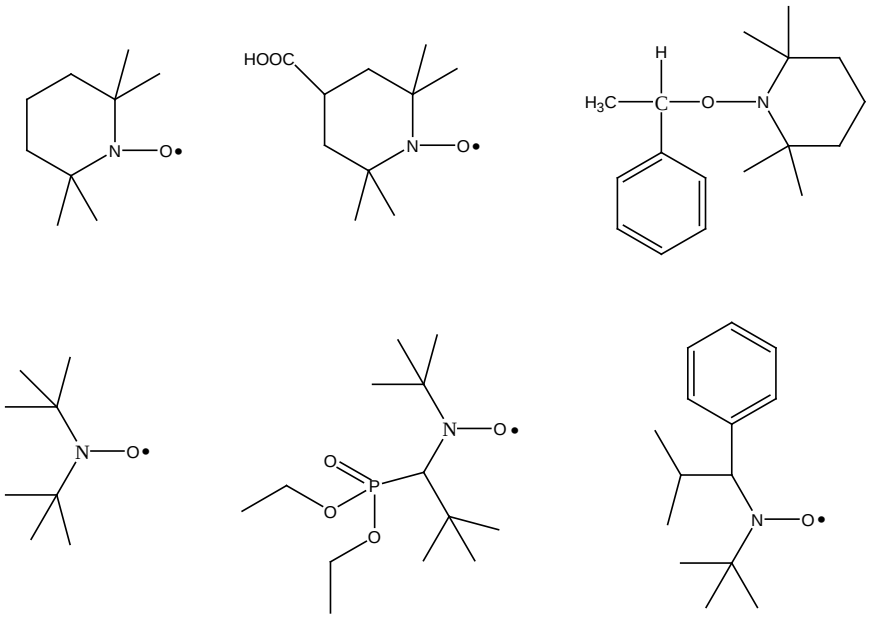



In the NMP process, a stable nitroxide is employed to impart living character to the polymerization process and to ensure the formation of polymers with controlled number average molecular weights and narrow molecular weight

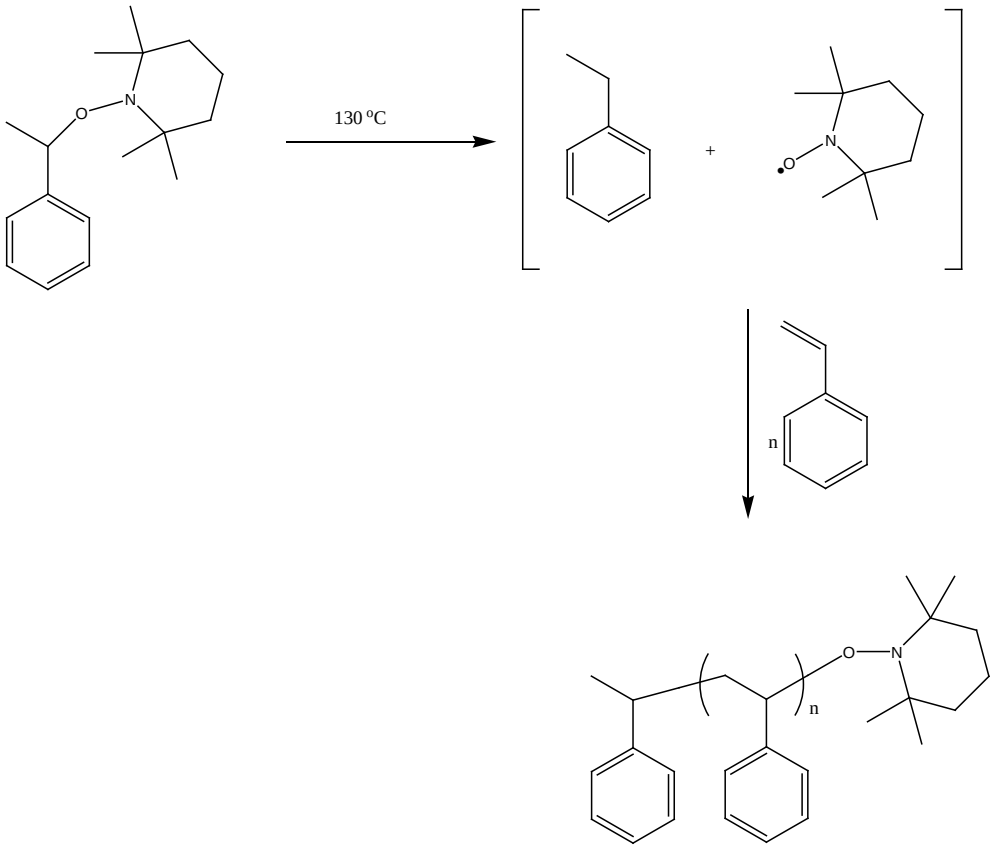
distributions[39-40]. The persistent radical reversibly deactivates the propagating radicals with a rate constant of combination ($k_c$) to form the corresponding dormant (alkoxyamine) species. The activation reaction, at a rate constant of activation $k_d$, follows to give the propagating radicals which propagate at a rate constant $k_p$ before the next cycle. The reversible capping mechanism reduces the concentration of propagating species dramatically. Thus, undesirable termination reactions and other side reactions are prevented. The equilibrium constant ($K = k_c/k_d$) is the main factor leading to the production of well defined polymers at an acceptable polymerization rate[40]. The rate constant, $k_d$ and $k_c$ must be large enough relative to $k_p$ to achieve a well controlled polymerization system[41-42].

The NMP method is attractive for industrial applications since it is a simple, convenient technique for preparation of well defined polymers[39]. However, a great disadvantage of the NMP process is its incompatibility with most families of vinylic monomers[39-43]. Homopolymerization of acrylates is often difficult and sensitive to the structure of nitroxide[39]. Moreover, in the polymerization of methacrylates, side reactions in the NMP method are observed, due to rapid disproportionation reactions which involve β-hydrogen abstraction from a polymeric radical by the nitroxide to give the corresponding hydroxylamine and unsaturation in the polymer chain[40]. In addition, alkoxyamines are relatively expensive and generally difficult to remove from the polymer chain end. Also, the conversion of alkoxyamine to other functional groups is mainly achieved by low yielding radical reactions[42].

An efficient NMP process can be achieved by the use of appropriate monomer/initiator systems[40]. The following nitroxides have been successfully employed in NMP processes[37-44]:




The successful polymerization of styrene and its derivatives by NMP methods was realized using 2,2,6,6-tetramethylpiperidinoxy (TEMPO) in the presence of a suitable initiator[41,43]. The uncertainty in stoichiometric ratios between the initiator and nitroxide, coupled with long induction periods in bimolecular initiating systems, prompted the development of unimolecular initiating system in an effort to improve control in polymerization via NMP methods. Hawker and coworkers[45] synthesized the first TEMPO based unimolecular alkoxyamine to control the structure of functionalized macromolecules and all polymerization variables. Improved control of polymerization based on styrene and its derivatives using the TEMPO based alkoxyamine initiators was obtained. However, the homopolymerization and copolymerization of methacrylates resulted in poorly defined polymers due to side reactions and unfavorable rate constants:




The use of TEMPO and its derivatives as a mediating species necessitate the use of elevated temperature above 20 °C due to high bond dissociation energy associated with the N-O-C bond in the TEMPO end capped dormant species[39,46]. The invention of β-hydrogen bearing acyclic (second generation) nitroxides greatly increased the scope of monomers which can undergo polymerization by NMP reactions[39,47]. Polymerization of vinylic monomers such as styrenic, acrylate, acrylamide, acrylonitrile and 1,3-diene monomers by NMP methods were efficiently mediated in the presence of second generation nitroxides, yielding well defined polymers with narrow molecular weight distributions with $\overline{M}_w/\overline{M}_n \approx 1.05$[39,47-48].

Recently, the development of facile methods for synthesis of alkoxyamine derivatives mimicking the α-end group of the dormant species of vinylic monomers rejuvenated the use of unimolecular initiators in the preparation of

chain end functionalized polymers by the NMP method[42]. The main factors for the renewed interest for the use of unimolecular alkoxyamine initiators in NMP are as follows[39,42]:

(a) Unimolecular initiators are well defined, thus allowing much better control over the polymer parameters such as number average molecular weight, architecture and chain end functionality during the polymerization process.

(b) Alkoxyamine initiates polymerization in its purest form, leading to cleaner chemistry.

(c) Long induction periods observed in bimolecular initiating systems are avoided.

(d) Polymer topologies such as the comb, star, dendrimers, gradient and block copolymer structures can be prepared while maintaining the high degree of control of most polymer variables.

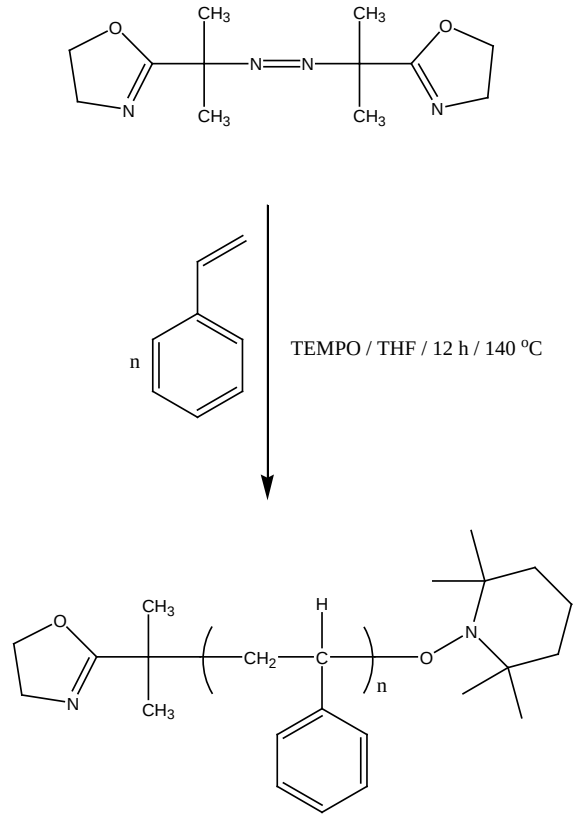
The nitroxide mediated radical polymerization has been employed to prepare different chain end functionalized polymers with a wide range of functional groups such as the amino, carboxyl and hydroxyl groups[39,42]. In the NMP reactions, chain end functionalization can be achieved by the following methods:

(a) Introduction of the functional group at the initiating fragment of the alkoxyamine initiator to give the α-functionalized polymers.

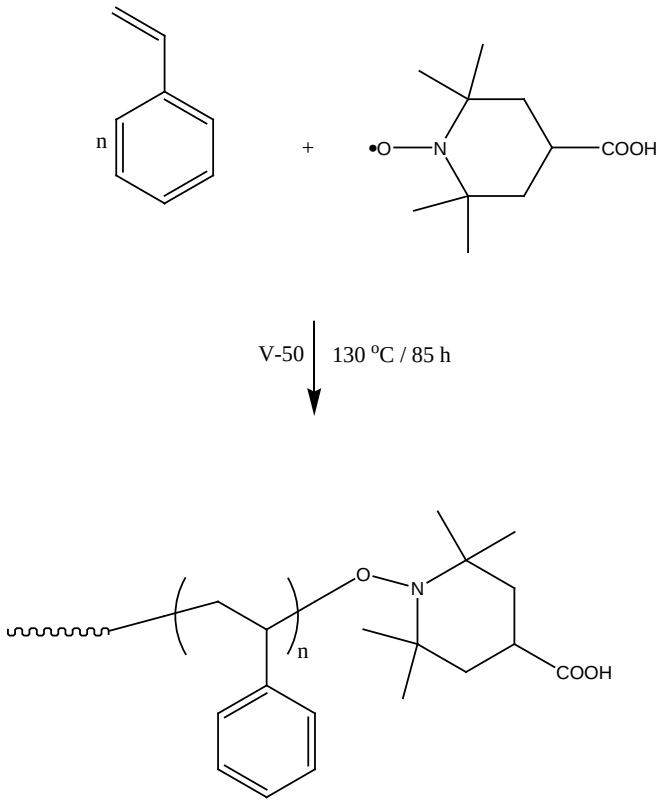
(b) Incorporation of the functionality to the mediating nitroxide radical result to formation of ω-functionalized polymers.

(c) The chemical transformation of the mediating nitroxide in post polymerization reactions has also been employed as an alternative method for incorporating end group functionality at the ω-terminus of the polymer chain.

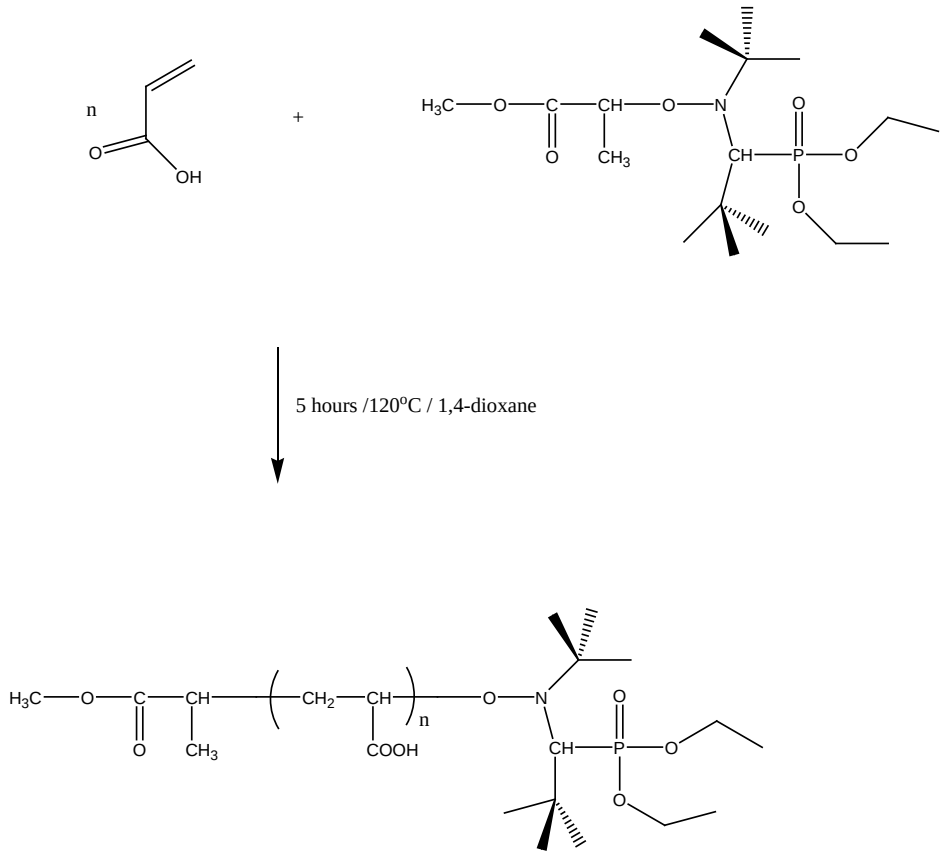
The preparation of functionalized polymers by NMP methods with the functionalized group introduced at the α-terminus of the polymer chain end has been widely reported in the literature[4,46-52]. However, limited reports on the preparation of oxazoline functionalized polymers by NMP methods appear in the literature. Mulhaupt and coworkers[53] prepared oxazoline chain end functionalized polymers by employing 4,4'-azobis(4-cyanopentane carboxylic acid)-[5-pentyl-2-(1,3-oxazoline)]ester as initiator in the bulk polymerization of styrene in the presence of TEMPO. The resultant mono-oxazoline terminated polystyrene derivatives with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.2-1.3) for number average molecular weight values varying between 1000- 50 000 g/mol were obtained:




Limited reports on the preparation of carboxyl functionalized polymers by NMP methods are documented in the literature[44,49-55]. The preparation of ω-functionalized polymers can be achieved by introducing an appropriate substituent to the mediating nitroxide radical[44,49-55]. For example, Claverie and coworkers[44] introduced the carboxyl group at the ω-chain end by using carboxyl functionalized TEMPO derivative as a mediating species in the controlled bulk polymerization of styrene:

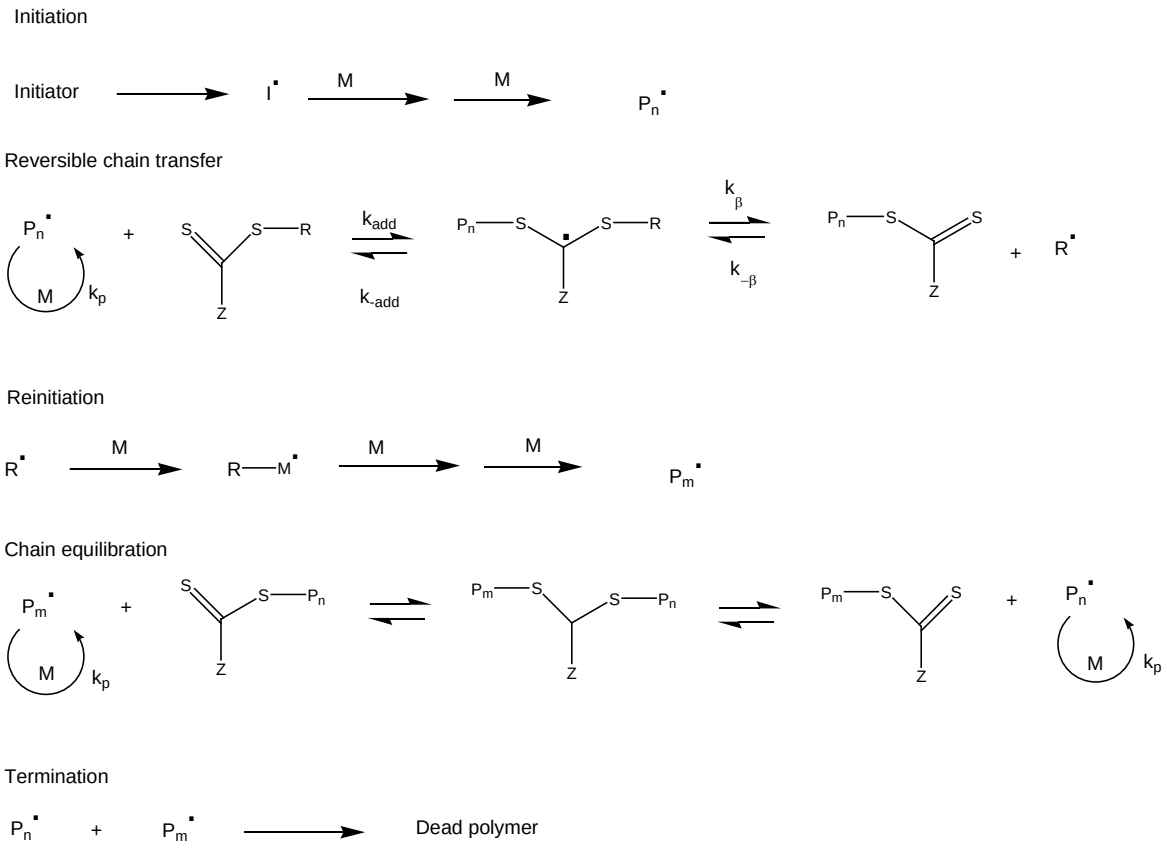



The preparation of α-ester functionalized polymers by NMP methods was obtained by the polymerization of acrylic acid using an ester functionalized alkoxyamine initiator. For example, Charleux and coworkers[55] employed an ester functionalized alkoxyamine initiator based on N-tert-butyl-N-(1-diethylphosphono-2,2-dimethylpropyl)nitroxide (SG1) in NMP reactions to produce α-ester functionalized polymers. High percentage monomer conversions (85-90%) were reported, irrespective of the initiator concentration. Polymerization kinetics studies gave a linear evolution of the number average molecular weight with percentage monomer conversion and polymers with relatively narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.3-1.5) were obtained:




## 2.5 REVERSIBLE ADDITION FRAGMENTATION CHAIN TRANSFER RADICAL POLYMERIZATION (RAFT)

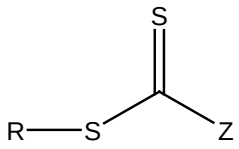
Since its discovery in the late 1990s by researchers at the CSIRO organization in Australia, the reversible addition fragmentation chain transfer radical polymerization (RAFT) process has emerged as one of the most valuable polymer synthesis methods in both academia and industry[35,56-57]. The RAFT process involves the use of a suitable chain transfer agent, such as thiocarbonylthio compound, in conjunction with a conventional free radical initiator for the polymerization of different vinylic monomers according to the following mechanism[35,58-61].




The dithioesters and trithiocarbonates with the general formula S=C(Z)-SR are the most commonly employed chain transfer agents[61]. Because of the ease of synthesis and purification[60], trithiocarbonates are frequently used to confer control in polymerization of a wide range of monomers under reaction conditions amenable to conventional radical polymerization. In RAFT polymerization, an addition reaction involving a conventional initiator such as AIBN and a monomer produces propagating radicals ($P_n^{\bullet}$). During the early stages of polymerization, addition of the propagating radicals to the transfer agent at a rate constant of $k_{add}$ gives an intermediate adduct radical. Fragmentation of the intermediate radical at either of its two arms may result in the formation of polymeric thiocarbonylthio compounds and a new re-initiating species ($R^{\bullet}$) at a rate constant ($k_{\beta}$) or yields back the reactant at a rate constant ($k_{-\beta}$).

A new propagating radical ($P_m^{\bullet}$) is formed through a re-initiation reaction involving the new radical ($R^{\bullet}$) and monomer (M). The rapid equilibration between the propagating radicals $P_n^{\bullet}$ and $P_m^{\bullet}$ and the dormant thiocarbonylthio species ensure an equal opportunity for chain growth[62]. As a result, polymers with narrow molecular weight distributions exhibiting a linear increase of number average molecular weight with percentage monomer conversion are produced[59]. Low concentration of initiator relative to transfer agent ensures that all dormant polymeric thiocarbonylthio compounds are predominant over propagating species which minimizes radical-radical termination reactions[58]. At the end of the RAFT polymerization reaction, both R and $ZCS_2$ group at the chain-ends are retained, enabling synthesis of end functionalized polymers and block copolymers by chain extension reactions.

The choice of the RAFT agent (**i**) is extremely important for the success of controlled/"living" RAFT polymerization reactions[60-61]:




**(i)**

ii) Z = Ph, R = $C(CH_3)_2Ph$

ii) Z = Ph, R = $CH(CH_3)Ph$

iv Z = Ph, R = $CH_2Ph$

v) Z = Ph, R = $C(CH_3)(CN)COONa$

vi) Z = Ph, R = $C(CH_3)(CN)(CH_2)_2COOH$

vii) Z = Ph, R = $C(CH_3)_2CN$

viii) Z = $CH_3$ R = $CH_2Ph$

xi Z = Ph, R = $C(CH_3)(CN)CH_2OH$

An effective RAFT agent is characterized by a reactive C=S bond, which ensures a high rate constant for addition of propagating radicals to the thiocarbonyl species. The nature of the monomer and the property of the R and Z groups determine the effectiveness of the RAFT agent[60].

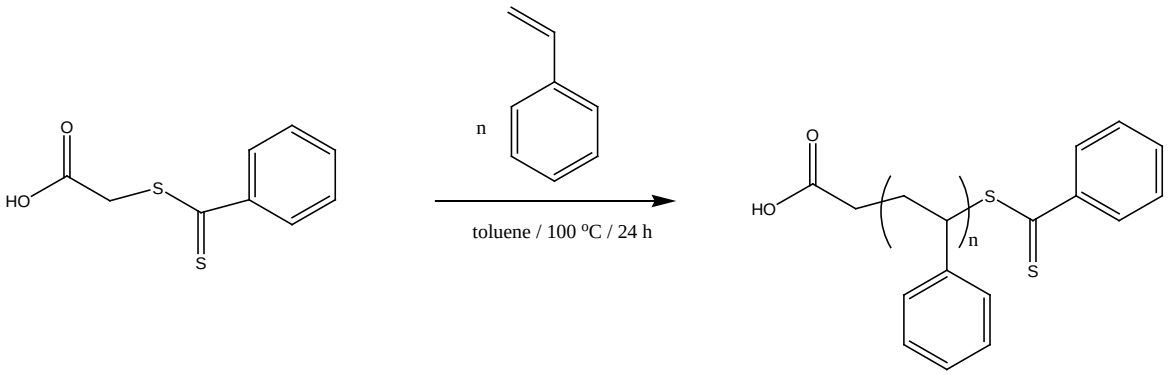
The Z substituent influences the rate of addition of radicals to the C=S bond of the RAFT agent. Groups such as the aryl, alkyl (dithioester or S-alkyl) groups which stabilize radicals, increases the activity of the C=S bond and results in an increased addition rate[63]. However, when Z = O or N, the lone pairs on the heteroatoms conjugate with the C=S bond, thus lowering its reactivity[60]. The magnitude of the rate constant of fragmentation of the intermediate is determined by the R group[61]. Relative to the attacking $P_n^{\bullet}$, the R group must be a good homolytic leaving group[58]. If the R group is bulky and electrophilic, the

corresponding radical is stable (R = cumyl or cyanoisopropyl groups) and the RAFT agent will exhibit a higher transfer constant[58,61]. In addition, the expelled $R^{\bullet}$ radical must effectively reinitiate polymerization.

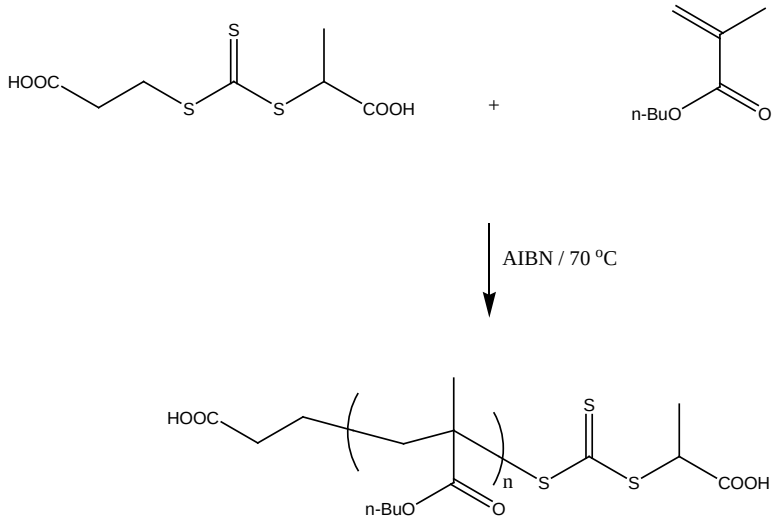
Polymers with high number average molecular weight that are commercially acceptable can be synthesized via the RAFT process using a wide range of monomers such as methacrylates, styrenes, methacrylamides, butadiene and vinyl acetate[56-63]. The RAFT technique is compatible with a wide range of functionality in monomers, solvents and initiators such as the OH, $NR_2$, COOH, $CONR_2$ groups[58-61]. Since active chain ends are retained, complex architectures of polymers such as stars, blocks, microgels, hyperbranched structures and supramolecular assemblies can be prepared in high purity[61]. However, most RAFT agents are relatively expensive and are not commercially available.

The RAFT method can be used for the synthesis of chain end functionalized polymers by using an appropriate functionalized RAFT agent[61]. The synthesis of chain end functionalized polymers with the functional group at the α-terminus of the polymer chain can be conducted by introducing a substituent in the R group of the RAFT agent. Similarly, by incorporating a functional group in the Z group of the RAFT agent, chain end functionalized polymers with the functional group at the ω-terminus are produced[60]. Transformation of the labile thiocarbonylthio end group in post polymerization reactions can also lead to the preparation of polymers with different functional groups at the ω-terminus of the polymer chain[59].

The preparation of carboxyl chain end functionalized polymers via the RAFT process have been widely reported in literature[61-71]. For example, Farmer and Patten[64] employed S-(thiobenzoyl)thioglycolic acid as a RAFT agent in the RAFT polymerization of styrene to afford α-carboxyl functionalized polymers with controlled number average molecular weight and narrow molecular weight distributions as low as 1.38:




Furthermore, the RAFT method was adopted for the preparation of α,ω-carboxyl functionalized polymers. For example, Wang and coworkers[65] illustrated the use of a dicarboxyl functionalized trithiocarbonate compound such as, 2-(2-carboxylethylsulfanylthiocarbonylsulfanyl)propanoic acid as a RAFT agent to prepare well defined α,ω-carboxyl functionalized poly(t-butyl methacrylate) via a controlled/"living" RAFT process:

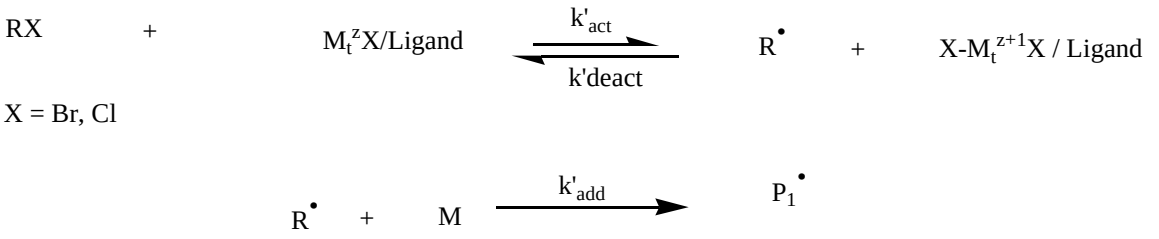


## 2.6 ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

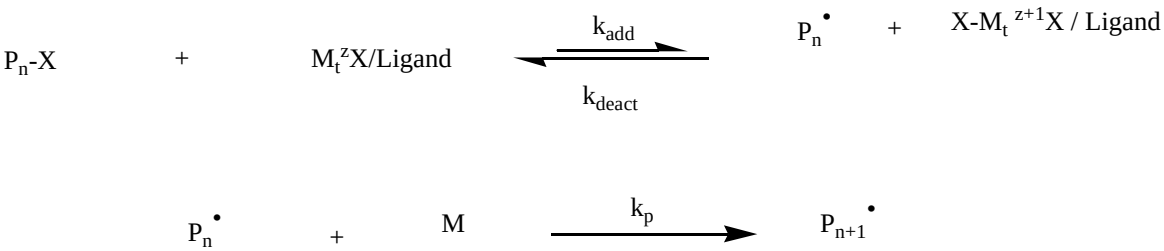
The transition metal mediated controlled free radical polymerization method was developed independently by Matyjaszewski[9] and Sawamoto[34]. The transition metal catalyzed living radical polymerization method involves the use of an initiator radical species, generated from an organo halide derivative in the presence of a metal/ligand catalyst complex to effect the polymerization of vinylic monomers to form well defined polymers[9,34]. The metal catalyst undergoes an oxidation reaction upon the homolytic cleavage of a halogen atom from the initiator molecule to form the corresponding mediating species[3,72,73].

The atom transfer radical polymerization (ATRP) method, a copper mediated controlled/"living" free radical process discovered by Matyjaszewski[9] in 1995, is one of the most powerful controlled free radical processes employed to prepare polymers with well defined polymer properties. The ATRP technique is a modification of the atom transfer radical addition reaction (ATRA) as well as the transition metal catalyzed telomerization process[9,73]. Matyjaszewski reported the controlled/"living" polymerization of styrene catalyzed by a copper/ligand system using (1-bromoethyl)benzene as the initiator. The ATRP mechanism occurs via two distinct kinetic steps, namely, initiation and propagation as follows:

**Initiation**




**Propagation**




**Termination**


The termination reaction occurs to a limited extent because only a negligible amount (< 5%) of the propagating radicals is present in the reaction system during the course of the reaction[7]. In a classical ATRP reaction, the initiation step involves the generation of carbon-centered radical ($R^\bullet$) with a rate constant of activation ($k_{act}$) via reversible homolytic cleavage of the carbon-halogen bond (R-X) by the transition metal in its low oxidation state ($M_t^zX/L$). Consequently, the lower oxidation state metal complex undergoes a one electron oxidation to form the corresponding higher oxidation state metal halide complex ($M_t^{z+1}X/L$) which functions as a persistent radical species.

The second reaction in the initiation step entails the one step addition of the vinylic monomer to the initiating radical to form the corresponding propagating radicals $P_1^{\bullet}$ at rate constant of propagation ($k'_{add}$)

Successive addition of the vinylic monomer (M = $CH_2$=CXY) at a rate constant $k_p$ to the propagating species is mediated by the persistent radical metal complex ($M_t^{z+1}$ X/L). The metal complex induces reversible deactivation at a rate constant $k_{deact}$ to produce the halide end capped polymeric product ($P_n$-X) and the regenerated catalyst ($M_t^{z}$X/L).

To accomplish a low concentration of the propagating radicals at a given time ($10^{-8}$-$10^{-7}$ M)[10], the ATRP equilibrium ($K_{ATRP} = k_{act}/k_{deact}$) must be strongly shifted towards the dormant species. As a results, the rate constant of deactivation must be higher than the rate constant of activation ($k_{act} << k_{deact}$) and both constants must be larger that the rate constant of propagation. If the deactivation process is slower than the rate of activation and propagation, polymers characterized by high molecular weight distribution and higher degree of polymerization (DP) are obtained.

By virtue of its involvement in establishing fast reversible equilibrium between the growing radicals and dormant species, the catalytic transition metal complex controls the overall polymerization rate ($R_p$). In ATRP reactions, the rate of consumption of monomer with time is determined by the following equation[7]:

$$R_p = k_p[M][RX]_o k_a[Cu^{I}]/(k_d[X\text{-}Cu^{II}])$$

The rate constant of polymerization depends directly on the concentration of monomer, initiator and activator and is inversely proportional to the concentration of the deactivator. An increase in initiator concentration coupled with a low ratio

of activation to deactivation rate enhances the polymerization rate. An increase in the percentage monomer conversion is accompanied by a decrease in molecular weight distribution due to inherent increased concentration of deactivator and low $k_p/k_{deact}$ as shown in the following equation[7]:

$$\overline{M}_w/\overline{M}_n = 1 + \{k_p[RX]_o/k_d[X\text{-}Cu^{II}]\}(2/p-1)$$

The advantages of the ATRP process are related to the following factors[6-7]:

(a) The ATRP method allows the controlled polymerization of a large range of vinyl monomers, particularly styrenes, acrylates and methacrylates. Polymerization of monomers such as acrylonitrile, methacrylamides and water soluble 4-vinylpyridines bearing a substituent which can stabilize the generated radical have also been reported.

(b) The ATRP method allows preparation of tailor-made macromolecules with controlled number average molecular weights predetermined by the general ratio of the monomer to initiator concentration, narrow molecular weight distributions ($1.04 < \overline{M}_w/\overline{M}_n < 1.5$) and regiospecific chain functionality due to its tolerance to a wide range of functional groups.

(c) New polymeric materials have been synthesized by varying the topology of polymers (linear, branched, hyperbranched, stars) or composition of polymeric chain (statistical/gradient).

(d) The commercial availability of inexpensive copper catalysts, ligands, initiators and macroinitiators, particularly the alkyl halides and sulfonyl chlorides, makes the ATRP technique attractive to industrial applications.

(e) Copper based catalyst exhibits great tolerance to reaction media (bulk, solution, suspension, dispersion and emulsion polymerization), solvents, trace amount of impurities (oxygen and water) and polar functional groups such as the OH, $NH_2$ and COOH groups.

(f) The ATRP reactions are conducted under a convenient temperature range between -20 and 130 °C.

(g) The ATRP equilibrium can be approached from the other side via the reverse ATRP process using $CuX_2$/L species in the presence of AIBN as the initiator.

(h) The utility of the ATRP technique could be increased by displacing the halogen chain end with useful functional groups based on a wide range of synthetic organic methods such as nucleophilic substitution reactions, radical processes and other standard organic reactions.

(i) The nature of the ATRP mechanism enables faster polymerization and the adjustment of equilibrium is influenced by the choice of the initiator and the metal catalyst complex.

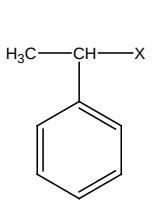
A major limitation of the ATRP method is that the industrial application of the ATRP technique as a versatile synthetic tool for polymer synthesis has not yet been fully realized due to the limited purification methods for the resulting coloured polymers. To reduce the relatively high amounts of residual transition metal complex (0.1-1 %) in the final polymer product[74-75], the current available methods to produce pure polymer product include the use of a supported catalyst in ATRP systems which enables recycling of the catalyst[74-75]. However polymers with poor polymer properties are normally produced in the presence of an additive

such as $Cu^{II}$ species[73]. Another shortcoming of the ATRP method is that polymer tacticity cannot be controlled[9,73]. Furthermore, industrially important monomers such as vinyl acetate and vinyl chloride do not undergo ATRP reactions due to the absence of a stabilizing substituent in the monomer[75]. Also, the use of bipyridines or terpyridines with long alkyl chains have to be synthesized for homogeneous ATRP reactions, otherwise, a co-solvent must be added to most ATRP reactions[11,15,75].

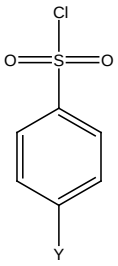
### 2.6.1 Initiators for Atom Transfer Radical Polymerization.

Organohalide compounds are commonly employed as initiators in ATRP reactions due to the presence of a labile, activated C-X bond and its propensity to form stable free radicals after homolysis in the presence of a metal catalyst ligand complex[7,70]. For successful initiation, the organohalogen compounds should contain a substituent, such as an additional halogen, allyl, aryl, carbonyl or cyano group[7], which allows the stabilization of the generated radicals by the inductive or resonance effect.

The following compounds have been employed as initiators in ATRP reactions[6,9,75]:

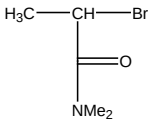


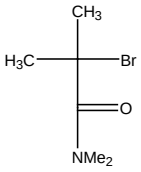

X = Cl, Br

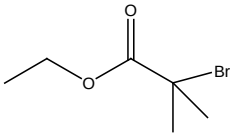


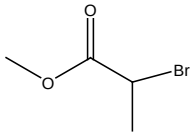

Y = H, $OCH_3$, COOH,

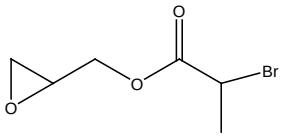
Cl, $NO_2$, F, $CH_3$

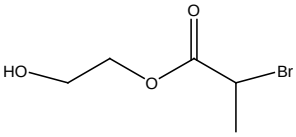


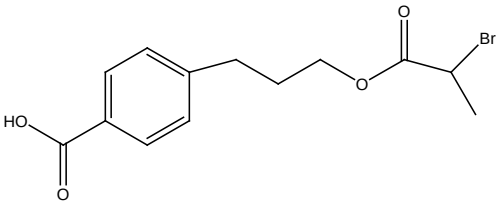




The choice of the initiator molecule must be such that the rate of initiation is equivalent to or faster than rate of propagation in the ATRP reaction in order to accomplish the controlled polymerization for a particular monomer[7]. The structure of the initiator should mimic the structure of propagating chain end, so that initiation and propagation are at least parallel. Under such conditions, the activity of the carbon-halogen bond in the initiator is similar to that of the dormant polymer terminus[11]. Benzylic halides, particularly the bromides and chlorides, were shown to be efficient initiators for the ATRP of styrene and its analogs due to their

structural similarity with the styryl propagating chain end[7,9,75]. For example, Matyjaszewski and Wang[9] used 1-phenylethylchloride as the initiator with copper(I) bromide complexed to 4,4'-di (5-nonyl)-2,2'-bipyridine (dNbpy) to achieve well controlled polymerization of styrene. Polymers with predicted number average molecular weights in the range $\overline{M}_n$ = 4 000-100 000 g/mol were obtained. The number average molecular weights increased linearly with monomer conversion to produce polymers with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n \approx 1.1$). Although similar results were observed when the strong carbon-halogen bond bearing the chloride counterpart was used as initiator with copper(I) chloride/2,2'-bipyridine as a catalyst, polymers with broad molecular weight distributions ($\overline{M}_w/\overline{M}_n \approx 1.5$) were obtained.

The polymerization of monomers having higher equilibrium constants such as methyl methacrylates and acrylates can be effected using α-bromopropionate and 2-bromoisobutyrate as initiators in the presence of an appropriate copper/ligand catalyst system[7].

An efficient initiator should have limited chances of undergoing side reactions. Minimal initiation side effects were reported in ATRP systems based on sulfonyl halides as initiators[7,9,10]. Thus, sulfonyl halides initiators have been used for the controlled polymerization of methyl methacrylate and styrene in the presence of an appropriate copper based catalyst[10]. Termination reactions due to radical coupling reactions were insignificant, despite the extraordinary higher rate of initiation relative to propagation. In addition, substituents attached to the sulfonyl halide initiators, such as the carboxylic acid group, have no effect on the rate of polymerization in ATRP reactions[10].

Tertiary alkyl halides were reported as superior initiators in ATRP reactions in comparison to the secondary and primary counterparts[7,10,76-78]. In addition, the reactivity of the initiator depends on the nature of the leaving atom and thus

activity decreases according to the following order: (I ≥ Br >Cl)[7]. For example, alkyl iodides are light sensitive and the formation of metal iodides is observed and side reactions such as degenerative transfer reactions, usually occur. Polymerization does not take place with fluorine based initiators, due to the strong carbon-fluorine bond which does not easily undergo homolytic fission[10].

There are several ways of increasing the initiator efficiency of alkyl halide initiators[4,9,75-79]:

(a) **The halogen exchange method**: When the halogen exchange method was used for methyl methacrylate polymerization with the α-bromopropionates as initiator in the presence of copper(I) chloride/2,2'-bipyridine[75], well defined poly(methyl methacrylates) with relatively narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.2-1.4) were obtained and the rate of initiation relative to propagation was increased. However, when methyl methacrylate undergoes polymerization with α-bromopropionates as the initiator in the presence of copper(I) bromide/2,2'-bipyridine catalyst complex, poly(methyl methacrylates) with broader molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = ≥ 1.5) were obtained[75].

(b) **The order of reagent addition**: Bimolecular termination reactions are reduced when the reactive benzyhydryl chloride initiator was slowly added into the reaction mixture in polymerization of methyl methacrylate mediated by the CuCl/dNbpy catalyst system. Reduction of the malonyl radical by the copper(I) species was prevented and polymers with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.1-1.2) were obtained[8]. However, polymers with broad molecular weight distributions were obtained upon the once-off addition of the benzyhydryl chloride initiator during the polymerization reaction.

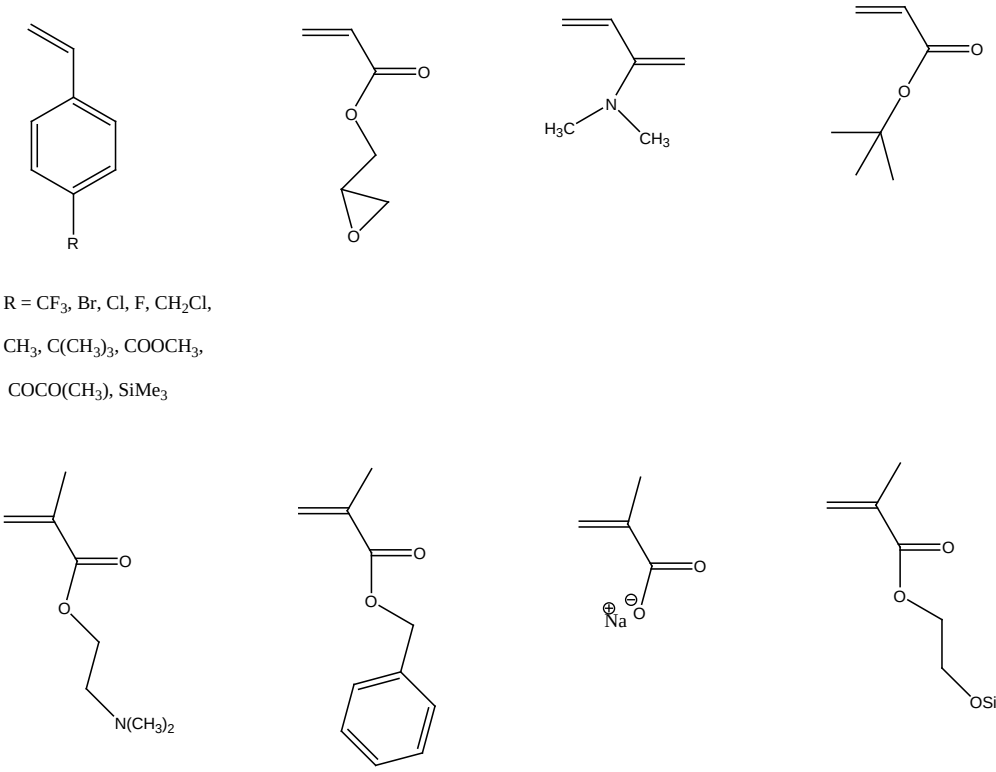
(c) **Slow addition of catalyst**: The slow addition of catalyst was reported to increase the initiator efficiency, particularly in systems involving formation of organic radicals with electron withdrawing groups, such as malonyl radicals[77]. High concentrations of the copper(I) species reduce the malonyl radicals to the corresponding anions, as observed in synthesis of polystyrene in the presence of $CuBr(dNbpy)_2$ catalytic system[78].

(d) **The use of a heterogeneous catalyst system**: The use of a heterogeneous catalytic metal complex may result in efficient initiation when compared with homogeneous systems, especially when used in conjunction with a very reactive alkyl halide[7]. For example, the use of $CCl_4$ initiator in the presence of $CuBr(bpy)_3$ catalyst system provides a good initiation system for styrene polymerization in contrast to the $CCl_4$/CuBr/$(dNbpy)_2$ initiator/catalytic system[77].

### 2.6.2 Monomers for Atom Transfer Radical Polymerization

The ATRP method allows the successful polymerization of a large range of vinylic monomers such as styrenes, acrylates, methacrylates, acrylonitrile, methacrylamides and 4-vinylpyridines[7-8]. Since the presence of a stabilizing substituent in the polymerizable monomers is a major prerequisite, the polymerization of less conjugated monomers such as vinyl acetate, vinyl chloride and olefins by ATRP methods is not possible[7-8]. The concentration and type of catalyst, temperature, solvent and additives that are related to the inherent atom transfer equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) control the success of the ATRP reaction of a specific monomer[7]. Controlled polymerization of styrenic monomers has been reported with copper based systems[7,8,34]. Due to the increased monomer reactivity induced by the labile carbon-halogen bond, faster polymerization rates were observed when styrenic derivatives bearing an electron withdrawing substituents were polymerized by ATRP methods[77]. The following

monomers undergo ATRP reactions to form the corresponding polymers with controlled number average molecular weights and narrow molecular weight distributions[6-8,34,77,79].




### 2.6.3 Catalyst/Ligand Systems for Atom Transfer Radical Polymerization

Many transition metal mediated controlled free radical polymerization methods have been developed successfully using a variety of transition metal complexes based on iron[80-82], molybdenum[83-86], rhodium[87], ruthenium[34,88], cobalt[89], osmium[90], nickel[91] and copper[9]. Most ATRP polymerizations are carried out using copper(I) bromide or copper(I) chloride in the presence of a bidentate or tridentate nitrogen ligand.

For the control of polymer variables such as the number average molecular weight, molecular weight distribution, chain topology and chain end functionality in ATRP reactions, careful selection of catalyst/ligand system in conjunction with the specific initiator is essential[7]. The catalyst ligand system adjusts the dynamic equilibrium between the propagating radicals and a large amount of dormant species by the reversible redox reaction involving halogen exchange by radical methods[7,92]. The active radical species is produced when the metal center abstracts a halogen atom at the propagating chain end, with simultaneous oxidation of the metal center[93].

An efficient metal centre must exhibit the following characteristics[7-8,75,93]:

(a) The catalyst must possess at least two readily accessible oxidation states separated by one electron e.g., Cu(I) and Cu(II). The lower oxidation state of the metal centre should be more stable than its higher counterpart to enable fast deactivation with diffusion controlled rate constants.

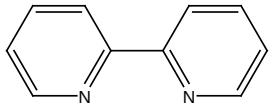
(b) The catalyst should have a high selectivity for halogen transfer reactions and should not participate in side reactions such as ionic coordination and abstraction of the β-hydrogen in methacrylates.

(c) The catalyst must not be a strong Lewis acid, in order to avoid ionization of certain initiators or polymeric end group which leads to chain termination reactions.

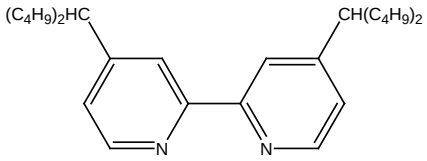
(d) The catalyst center should complex relatively strongly to the ligand.

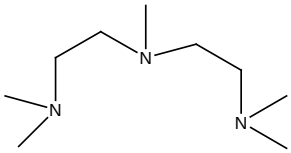
(e) The catalyst must have a reasonable halogenophilicity

Nitrogen based ligands commonly employed in ATRP reactions include bidentate ligands such as 2,2'-bipyridine and its 4,4'-disubstituted derivatives; tridentate ligands such as N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) and tetradendate ligands such as 1,1,4,7,10,10-hexamethyltriethylene-tetramine (HMTETA):

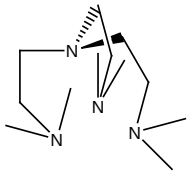


bpy



PMDETA



$Me_6TREN$

A major function of the ligand in ATRP systems is to enhance the solubility of the transition metal complex in organic media[93]. The solubility of the transition metal/ligand complex increases with the length of the alkyl chain present in the ligand structure[7]. For example, the use of copper(I)/2,2'-bipyridine complex in styrene polymerization results in a heterogenous reaction system in non-polar solvents. However, the polymerization of styrene using its corresponding analogue, copper(I)/4,4'-di(5-nonyl)-2,2'-bipyridine (copper(I)/dNbpy) catalyst complex in the same solvent system results in a homogeneous system, thus polymers with well defined number average molecular weights and narrow molecular weight distributions are formed[93]. The ligand also plays a major role in fine-tuning the redox potential ($E_{1/2}$) of the metal center through electronic effects

which ensures that the ATRP equilibrium is shifted towards the dormant species[7]. The ligand confers selectivity on the catalyst through steric hindrance coupled with electronic factors[6]. In ATRP, the activity of nitrogen based ligands decreases with the number of coordination sites and coordination angles. For example, the PMDETA ligand induces a higher rate of styrene polymerization than bpy[7,93]. In addition, the rates of activation and deactivation are influenced by the steric bulk around the metal center. For example, the $Me_6$TREN complex with copper is more active than the corresponding $Et_6$TREN copper complex.

### 2.6.4 Solvents for Atom Transfer Radical Polymerization

The ATRP reactions can be performed in bulk, solution or via heterogeneous techniques such as emulsion and suspension polymerization methods. In general, non-polar solvents are commonly used in ATRP systems[7-8]. The choice of the solvent should be such that potential radical chain transfer to solvent reactions are minimized or avoided[75]. If the preparation of low molecular weight polymers (<20 000 g/mol) is required, the use of aromatic non polar solvents such as toluene and xylene is desirable[71]. Polar solvents such as carboxylic acids or phosphines should be avoided in ATRP reactions, since complexation with the metal and subsequent catalyst poisoning is observed[8]. Certain functional groups at the polymer chain end can also undergo solvolysis or elimination reactions in the presence of polar solvents such as ethylene carbonate[8]. However, polar solvents assist in dissolving the copper catalyst when complexed to unsubstituted 2,2'-bipyridine[7-8]. Solvents employed in ATRP reactions include benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide, ethylene carbonate, alcohol, water and carbon dioxide[8,75].

### 2.6.5 Polymerization Temperature for Atom Transfer Radical Polymerization

In general, an increase in the polymerization temperature increases the polymerization rate in ATRP reactions, due to the higher propagation rate and equilibrium constants[7,74,75]. The optimum polymerization temperature depends on the nature of the monomer, catalyst/ligand system and the targeted number average molecular weight[7]. At elevated temperatures, the ratio of the rate constants of propagation to termination ($k_p/k_t$) is higher which leads to better controlled polymerization[7]. However, although the catalyst solubility is increased at high temperatures, significant catalyst decomposition is observed at higher temperatures[6]. Moreover, chain transfer and other side reactions become more significant at higher temperature[7,74,75]. Also, prolonged polymerization reaction time at elevated temperature leads to loss of end groups, if conversion exceeds 95%[75].

## 2.7 FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION

The ATRP method is the most powerful method to prepare tailor-made macromolecules with controlled number average molecular weights, molecular weight distributions and the desired chain functionality due to its tolerance to a wide range of functional groups[94-101]. Functionalized polymers have been utilized in different applications in technological areas[11] such as nanotechnology, biotechnology, surface modification, adhesion, coatings, polymer compatibilization, block copolymers syntheses and building blocks in macromolecular design. Functionalized polymers can be prepared by ATRP methods using the following synthetic methodologies[7-8,11]:

(a) The polymerization of functionalized monomers.

(b) The post polymerization chemical transformation of functional groups along the polymer backbone.

(c) The chemical transformation of the halogen chain end functionality into different functional groups by different organic reactions.

(d) Post polymerization coupling of chain end functionalized polymers.

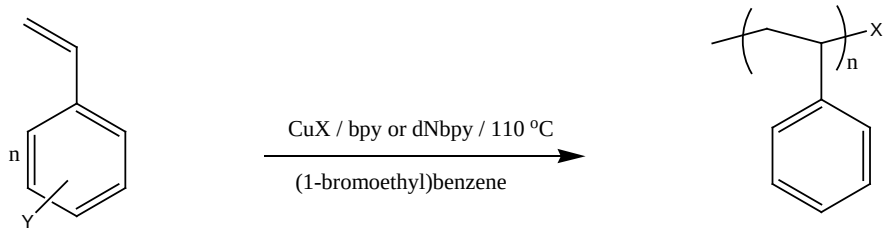
(e) The utilization of functionalized initiators in the polymerization of vinylic monomers.

### 2.7.1 The Polymerization of Functionalized Monomers

The ATRP methodology allows the polymerization of functionalized monomers to produce the corresponding well defined functionalized polymers[102-104]. However, the polymerization of less conjugated monomers such as vinyl acetate, vinyl chloride and olefins has not yielded appreciable results, because the resultant unstabilized radicals promotes many side reactions[7-8,11].

The most general functionalization method associated with polymerization of functionalized monomers is based on the use of substituted styrene monomers. Matyjaszewski and Qiu[102] reported the polymerization of styrenic monomers bearing electron withdrawing and electron donating groups using (1-bromoethyl)benzene as an initiator in the presence of copper(I) bromide and a suitable nitrogen based ligand. The polymerization of styrene bearing an electron withdrawing group produced polymers with predetermined number

average molecular weights at higher polymerization rates. Kinetic studies gave a linear evolution of number avarage molecular weights with percentage monomer conversion and polymers with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ < 1.5) were obtained. However, the polymerization of styrene with an electron donating group was accompanied by side reactions, such as elimination and termination reactions, with resultant formation of poorly defined polymers. In the presence of termination reactions, the decrease in the concentration of the activator [Cu(I)] and subsequent increase in [Cu(II)] decelerate the polymerization rate. The polymerization of styrene derivatives with strong electron donating group such as methoxy group resulted in the formation of oligomers, due to heterolysis or oxidation of radicals to corresponding carbocations:

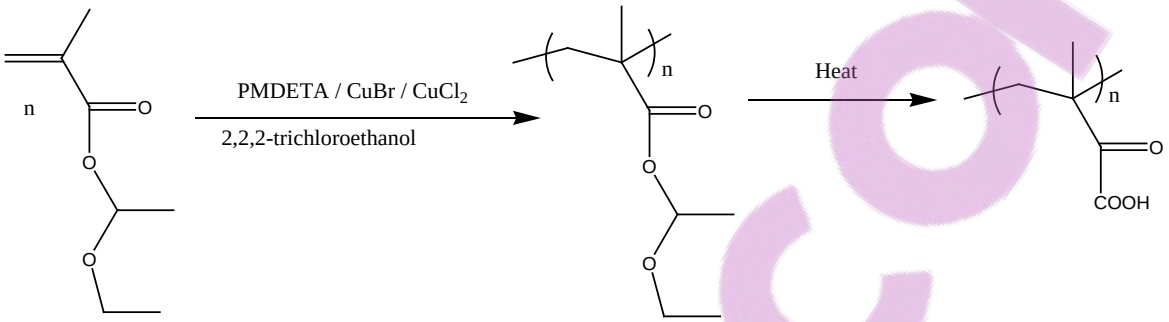



X = Br, Cl

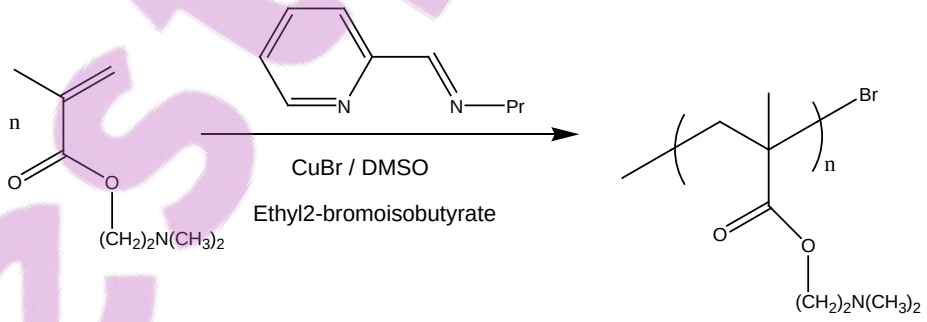
Y = CN, $CF_3$, Br, Cl, I, H, $CH_3$, $OCH_3$

Van Camp and Du Prez[103] proposed a facile route for the ATRP of functionalized monomers such as 1-ethoxyethyl methacrylate and 1-ethoxyethyl acrylate. For example, the polymerization of 1-ethoxyethyl methacrylate was initiated by 2,2,2-trichloroethanol in the presence of copper(I) bromide in conjunction with a nitrogen ligands such as N,N,N',N'',N''-pentamethyldiethylene triamine. The polymerization reaction proceeded at a higher polymerization rate and good control of polymerization was achieved in the presence of a small amount of $CuCl_2$. Water soluble polymers with well controlled number average molecular weights and narrow molecular weight

distributions ($\overline{M}_w/\overline{M}_n$ < 1.2) were obtained. Deprotection of the poly(1-ethoxyethyl methacrylate) by thermolysis gave the corresponding poly(methyl methacrylate) derivative:

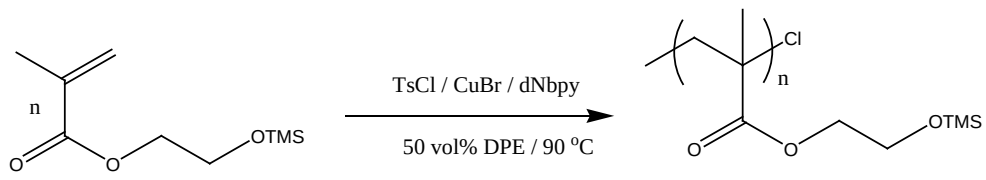



Haddleton and coworkers[105] investigated the ATRP of dimethylaminoethyl methacrylate (DMAEMA) using ethyl2-bromoisobutyrate as the initiator and mediated by the copper(I) bromide/N-(n-propyl)-2-pyridylmethanimine (n-Pr-L) catalyst system, in dimethylsulfoxide (DMSO) at temperatures ranging between 40-90 °C. The number average molecular weights of the resulting functionalized polymers increased linearly with percentage monomer conversion and the molecular weight distributions of the polymers were relatively narrow with $\overline{M}_w/\overline{M}_n$ values between 1.24-1.25. However, side reactions such as termination reactions were observed:



### 2.7.2 Post Polymerization Chemical Transformation of Functional Groups along the Polymer Backbone

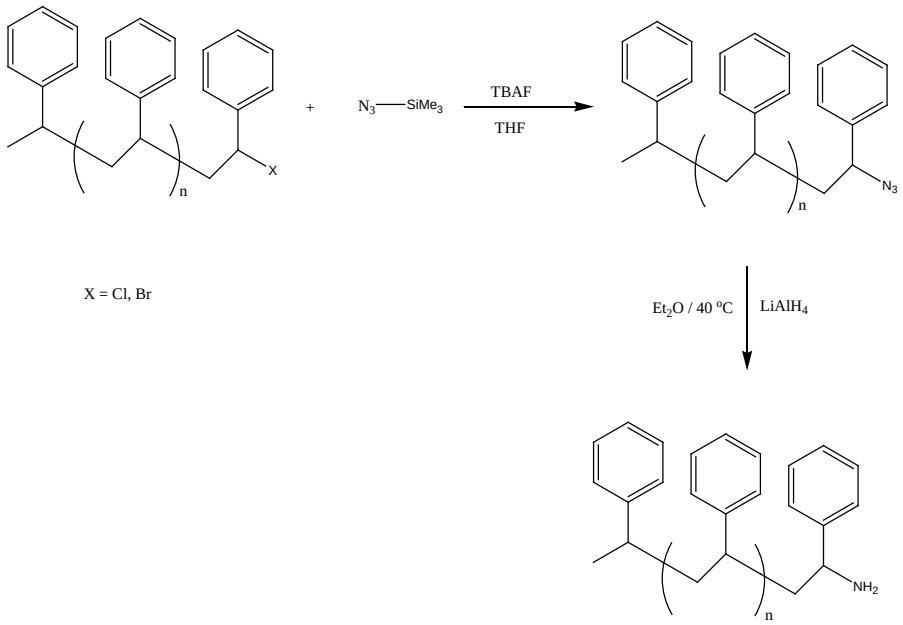
The direct ATRP synthesis of monomers bearing acidic substituents, such as methacrylic acid, vinyl benzoic acid, unsaturated sulfonic acid, acrylic acid and phosphonic acid is challenging due to side reactions such as the interaction of the functional groups with the transition metal complex catalyst[7]. Due to the complexation reactions between the carboxylic acid, sulfonic acid and phosphonic acid groups and the transition metal complex, synthetic routes to organic acid functionalized polymers by ATRP methods employ functionalized monomers with protected functional groups[11]. In carboxylated monomers, the carboxylic acid-coordinated metal complexes, e.g., copper carboxylates, formed from the reaction of the carboxylic acid group with the transition metal complex, inhibit formation of the dormant species[14]. Moreover, the nitrogen-based ligand frequently used in ATRP undergo protonation reactions in the presence of the carboxylic acid group, thus the complexing ability of the metal center is disrupted[7]. However, the controlled ATRP of such monomers can be realized by the polymerization of its derivatives such as trimethyl silyl methacrylate, t-butyl methacrylate and benzyl methacrylate, followed by the removal of the protecting group[11]. For example, the polymerization of TMS-protected 2-hydroxyethyl methacrylate (HEMA) by ATRP methods resulted in the preparation of polymers with predictable number average molecular weights ($\overline{M}_n \approx 100\,000$ g/mol) and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n < 1.2$) in high percentage monomer conversion reactions[106]:



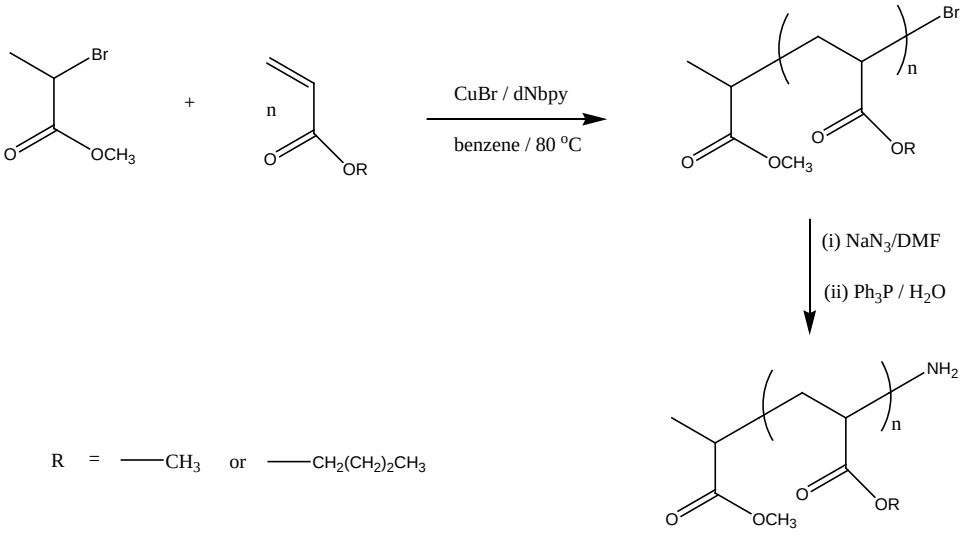
### 2.7.3 The Chemical Transformation of the Halogen Chain End

In general, the organohalide initiated ATRP of styrenic and methacrylate monomers produce a polymer chain where the ω-terminus of the polymer chain is a halogen atom which is derived from the alkyl halide initiator[11]. The chemical transformation of the terminal carbon halogen bond to form other functional groups such as the hydroxyl, allyl, azido, phosphonium, alkenyl and oxazolyl groups can be achieved using standard organic reactions such as nucleophilic substitution, elimination, free radical and electrophilic addition reactions[7,8,107,108].

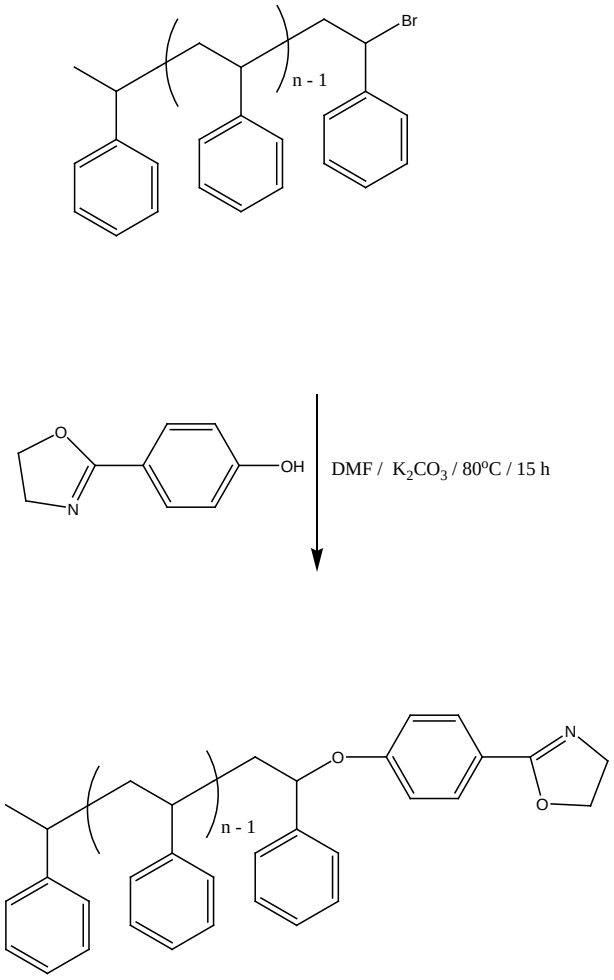
For example, Matyjaszewski and coworkers[107] reported a facile method for azidation of the bromine chain end functionalized polystyrene in the presence of trimethylsilyl azide and tetrabutylammonium fluoride (TBAF) to form the intermediate azide derivative. Reduction of the azide group at the polymer chain end with lithium aluminium hydride ($LiAlH_4$) gave well defined amine chain end functionalized polystyrene:



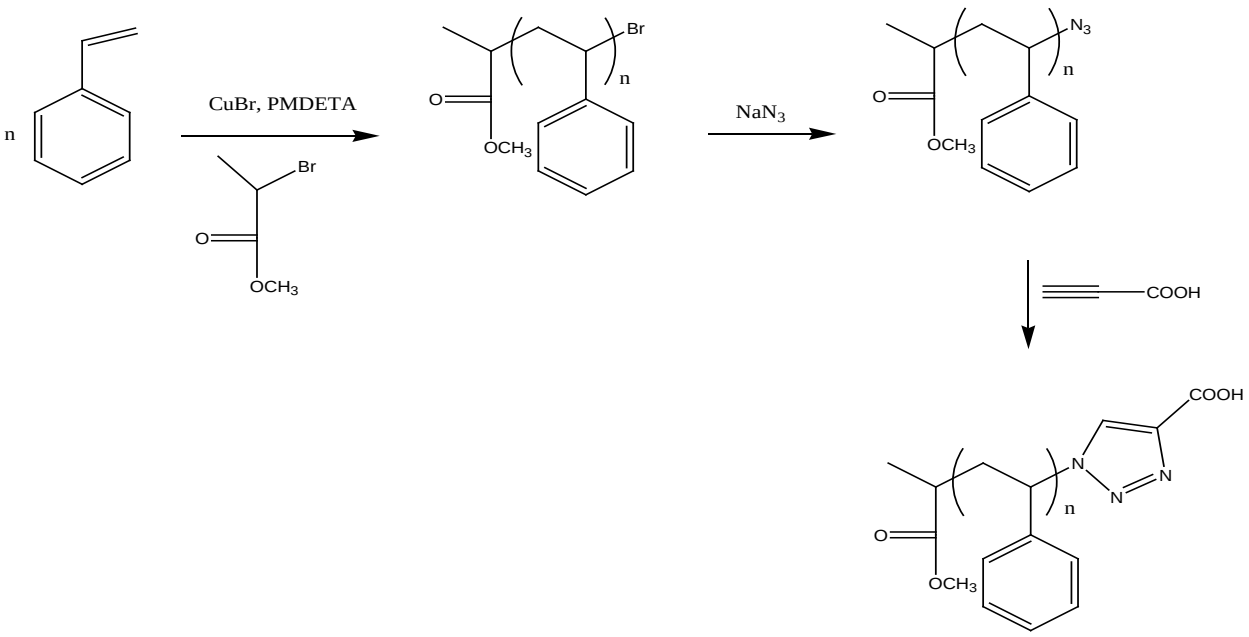
Similarly, Matyjaszewski and coworkers[36] transformed a series of bromine end-capped polystyrene, poly(n-butyl acrylate) and poly(methyl acrylate) derivatives into quantitative yield of the amine end groups by using relatively simple organic reactions. Transformation of the bromine end group to azide groups was performed using sodium azide and DMF as a solvent. The azide groups were subsequently converted to iminophosphorane end groups via Staudinger reaction, which upon hydrolysis afforded the amine chain end functionalized polymers:



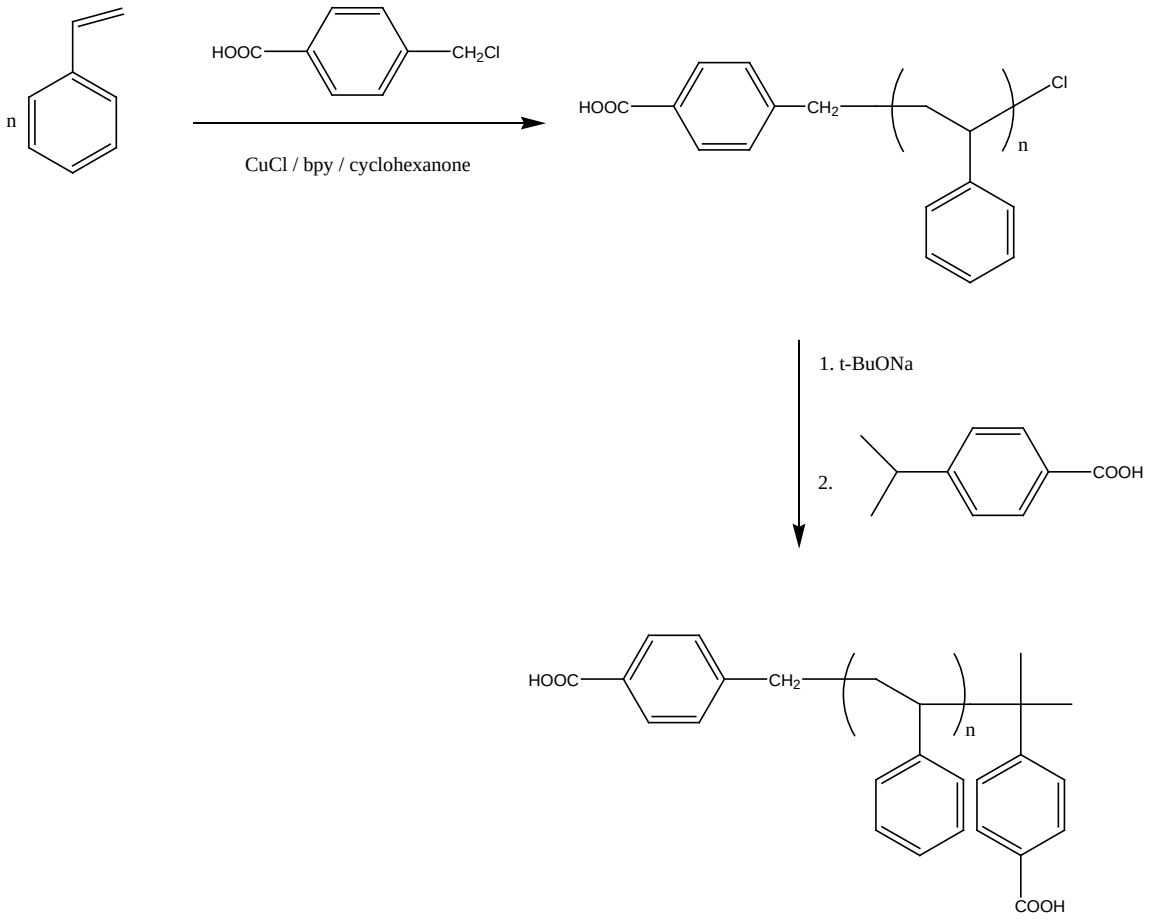

There are limited reports on the chemical transformation of the halogen end group of polymers obtained via ATRP methods to the oxazoline or the carboxyl functionality. Pionteck and coworkers[12] incorporated the oxazoline end functionality at the ω-terminus of the polystyrene chain end via the William ether synthesis method. In the reaction of bromine chain end functionalized polystyrene with 2-(4-hydroxyphenyl)-1,3-oxazoline, low yields of the corresponding ω-oxazolyl functionalized polystyrene were obtained due to side reactions such as elimination reactions which produce vinyl-terminated polystyrene as a by-product:




Recently, Lutz and coworkers[109] reported a high yield, two step method for the chemical transformation of ω-bromo polystyrene to the corresponding polystyrene bearing the carboxyl functionalized triazole group at the omega end of the polymer chain. The first step involved the transformation of the bromide chain end functionalized polystyrene into the azido chain end functionalized polystyrene by azidation of the bromine end-groups of the polystyrene with sodium azide in dimethyl formamide. The azido chain end functionalized polystyrene was coupled with a carboxyl functionalized alkynyl derivative in the presence of copper(I) bromide as a catalyst and 4,4'-di-(5-nonyl)-2,2'-bipyridine (dNbpy) via the click chemistry method to give the corresponding ω-carboxyl functionalized polystyrene.



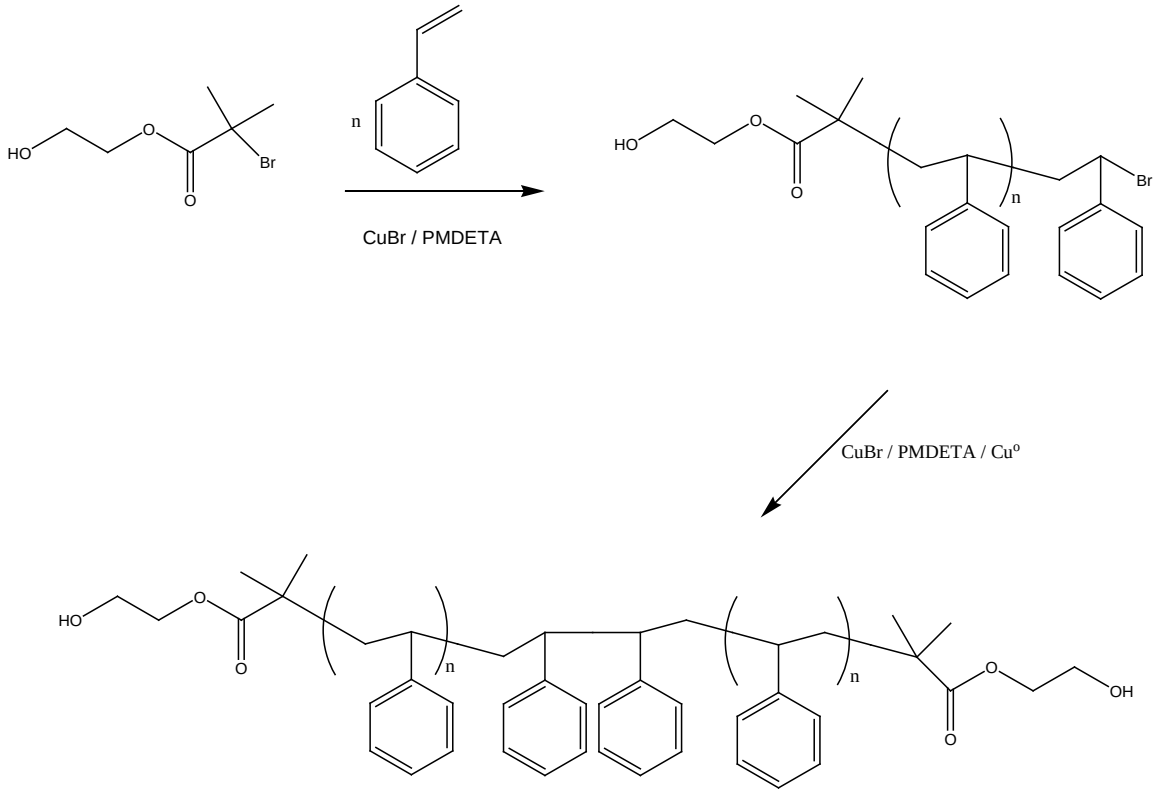

Yagci and coworkers[110] reported a facile route for obtaining α,ω-bis(carboxyl) functionalized polystyrene by transforming the halogen end group of α-carboxyl functionalized polystyrene to an aromatic derivative substituted with a carboxylic acid group in post ATRP reaction. For example, the α-carboxyl functionalized polymers with a chlorine group at the omega end of the polymer chain were synthesized using α-bromo-p-toluic acid as an initiator for styrene polymerization in conjunction with CuCl/bpy metal complex as a catalyst. The ω-chlorine group was transformed to the carboxylic acid group in the presence of cumic acid to form the corresponding α,ω-bis(carboxyl) functionalized polystyrene:



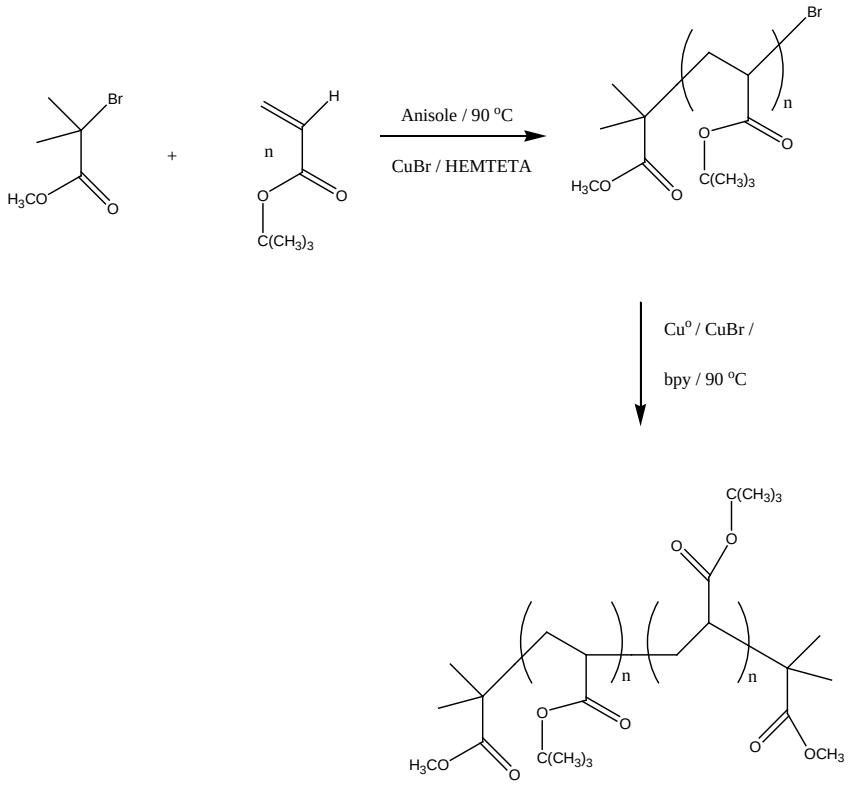

### 2.7.4 Post Polymerization Coupling of Chain End Functionalized Polymers.

Telechelic polymers are useful starting materials for preparation of various polymer materials such as block polymers and composite materials[1-3]. Telechelic polymers have been prepared by exploiting the living nature of the carbon-halogen bond in polymers prepared by the ATRP method. Different telechelic polymers can be prepared by modifying the halide end group of the α-functionalized polymers by means of electrophilic addition, nucleophilic substitution, atom transfer radical addition (ATRA) and atom transfer radical coupling reactions (ATRC)[74,75].

The utility of ATRP coupled with ATRC[111-112] in the preparation of telechelic polymers was demonstrated in the preparation of α,ω-hydroxyl functionalized polymers. For example Matyjaszeswki and coworkers[111] used the ATRP method to prepare α-hydroxyl functionalized polystyrene in the presence of 2-hydroxyethyl2-bromoisobutyrate initiator and copper(I) bromide/ PMDETA as a catalyst system. Subsequently, the synthesis of α,ω-hydroxy functionalized polystyrene was achieved through the ATRC reaction using the CuBr/PMDETA catalytic system in conjunction with copper(0) as a reducing agent:



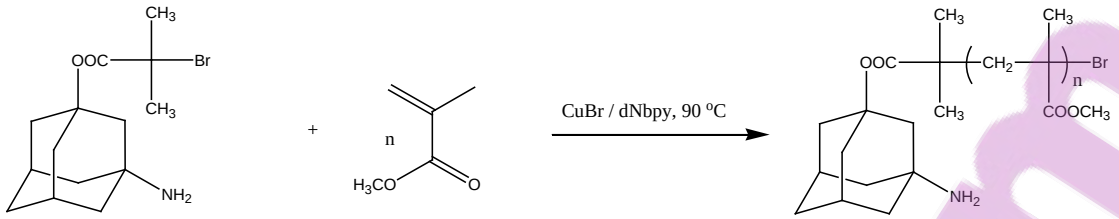
Telechelic poly(t-butylacrylate) bearing ester groups at each end of the polymer chain were synthesized by Otazaghine and coworkers[113]. First, acrylate oligomers were prepared by the ATRP of t-butylacrylate using methyl 2-bromo-2-methylisobutyrate as an initiator and CuBr/HMTETA as the metal complex catalyst. Coupling of the resulting oligomers was effected by using the CuBr/bpy catalyst system in the presence of Cu(0):



### 2.7.5 Functionalized Initiators for Atom Transfer Radical Polymerization

Alkyl halides are frequently utilized as initiators for the ATRP reactions[11]. The ATRP mechanism is characterized by the incorporation of the alkyl group fragment at the α-terminus of the polymer chain, with the halogen atom at the ω-end of the polymer chain[10]. Thus, the use of appropriate functionalized initiators in ATRP reactions leads to the preparation of a plethora of chain end functionalized polymers with the functional group specifically introduced at the initiating end of the polymer chain[7-11]. The selection of the particular functionalized initiator must be such that the functional group of the initiator must not interfere with the ATRP reaction and must therefore be inert towards the catalyst/ligand system employed on ATRP reactions[11].

Different chain end functionalized polymers substituted with the functional groups such as hydroxyl, amine, esters, thiols and allyl groups at the α-terminus of the polymer chain have been prepared by using functionalized halogenated alkanes, benzylic halides, allyl halides, α-haloketones, α-haloesters, α-haloamides, α-halonitriles and functionalized sulfonyl halides as functionalized initiators in ATRP reactions[7-11]. In particular, functionalized benzylic halides, haloesters and sulfonyl halides are frequently used for the polymerization of styrene and methyl methacrylates[7-11]. Recently, Kavitha and Singha[114] employed an amino-adamantyl isobutyryl bromide initiator in the presence of CuBr/dNbpy catalyst system for the polymerization of methyl methacrylate to prepare well defined α-amine functionalized poly(methyl methacrylate) via ATRP methods. Quantitative incorporation of the bromine end group at the ω-terminus of the polymer chain was confirmed by the controlled synthesis of block copolymers using the amino-adamantyl functionalized poly(methyl methacrylate) as macroinitiator:



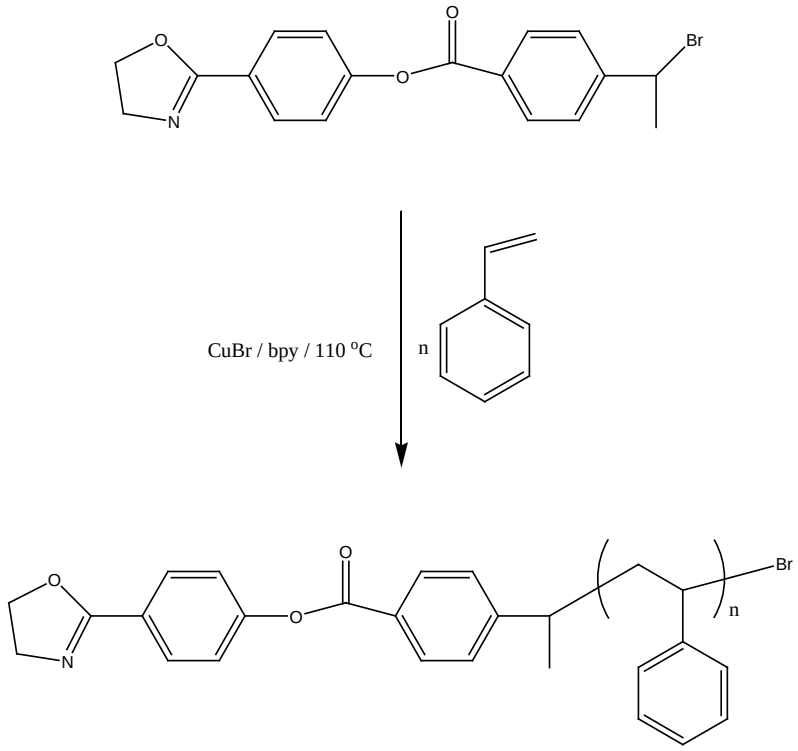

However, the preparation of α-oxazolyl functionalized polymers by ATRP methods have not been well documented in the literature. In addition, the synthesis of α-carboxyl functionalized polymers by ATRP method can be obtained by using appropriate functionalized initiators with the carboxylic acid functional group as the carboxylic acid derivative or in the free carboxylic acid form.

### 2.7.5.1 Oxazolyl Functionalized Initiators for Atom Transfer Radical Polymerization

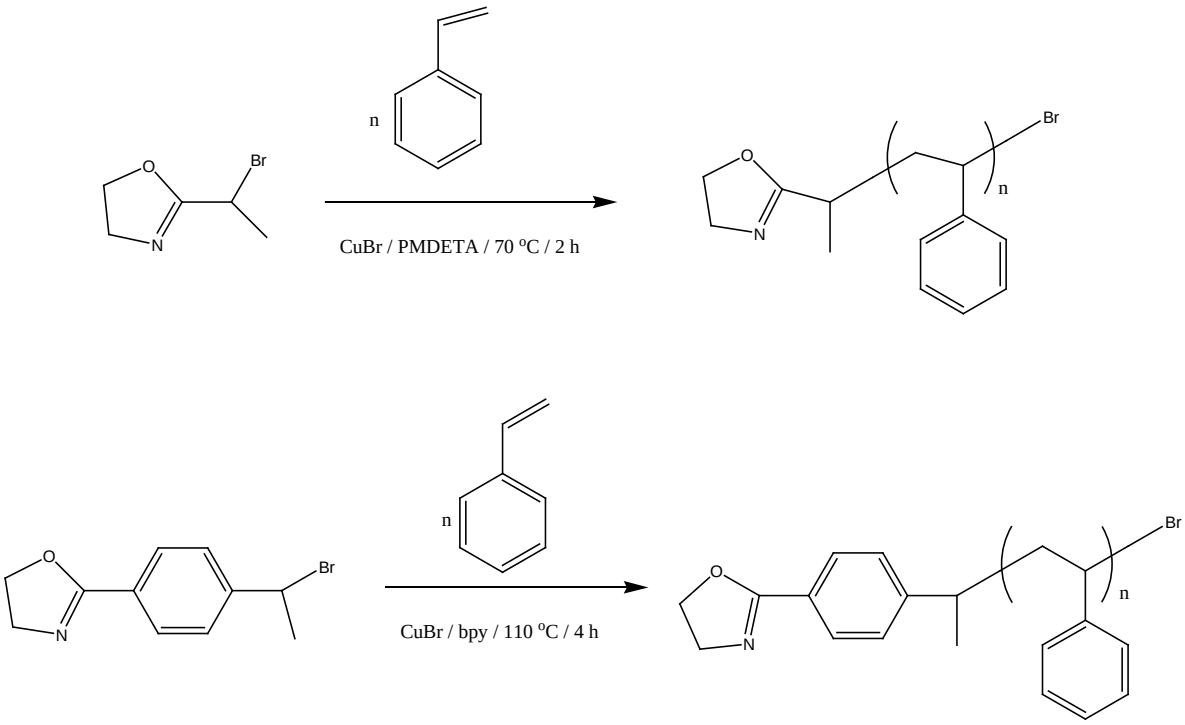
Oxazoline functionalized polymers can be used as catalysts, sensors, separating systems, enzymatic bioconjugates and drug carriers[115-116]. The oxazoline group at the termini of polymers can be used to prepare different polymer architectures such as graft copolymers, block copolymers, star-shaped and hyperbranched cross-linked networks[14-16].

The ATRP method is the most powerful method to prepare chain end functionalized polymers using functionalized initiators[7]. However, there are few reports in the literature which deals with ATRP method to synthesize oxazoline chain end functionalized polymers using oxazoline functionalized initiators. Pionteck and coworkers[12] employed 4-(1,3-oxazoline-2-yl)phenyl-4-(1-bromoethyl)benzoate as a functionalized initiator for the ATRP of styrene. The resultant oxazoline functionalized polystyrene with experimental number average molecular weight of $\overline{M}$ = 2 400 g/mol and $\overline{M}_w/\overline{M}_n$ = 1.31 was obtained in 2 hours. However, the polymerization process was not well characterized.

Moreover, polymerization kinetic data to substantiate the living features of the polymerization process was not recorded:



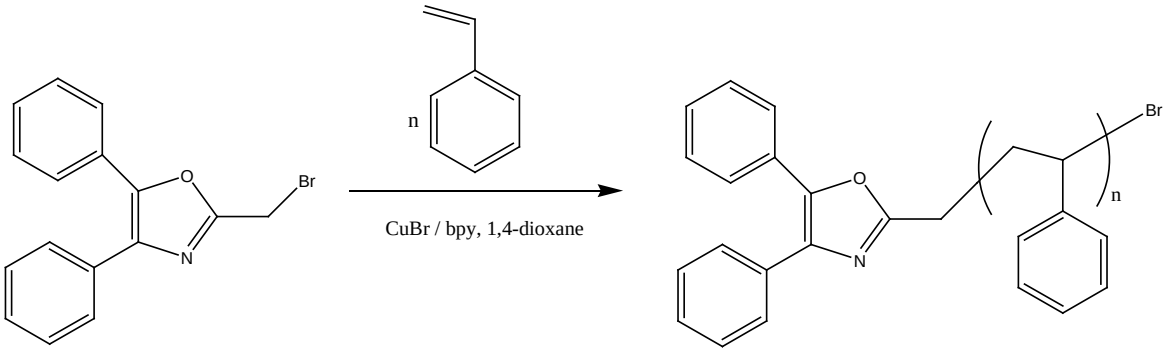

Pionteck and coworkers[117] also investigated the efficiency of different oxazoline functionalized compounds, such as 2-(1-bromoethyl)-1,3-oxazoline and 2-(4-(1-bromoethyl)phenyl)-1,3-oxazoline as oxazoline functionalized initiators in the atom transfer radical polymerization of styrene:




When 2-(1-bromoethyl)-1,3-oxazoline was used as an initiator in the presence of the copper(I) bromide/PMDETA catalyst complex, polystyrene with number average molecular weight value of 2 100 g/ mol with a narrow molecular weight distribution of $\overline{M}_w/\overline{M}_n$ = 1.09 was obtained within 2 hours. In contrast, the use of 2-(4-(1-bromoethyl)phenyl)-1,3-oxazoline as an initiator for styrene polymerization gave polystyrene with a number average molecular weight value of 3 500 g/mol in 4 hours. However, the molecular weight distribution values of the polymers were not recorded and the percentage monomer conversion was low for each reaction. Furthermore, no data of the polymerization kinetics to substantiate the living character of the polymerization process was reported.

Zhang and coworkers[13] reported the preparation of oxazole chain end functionalized polymers by the atom transfer radical polymerization of methyl methacrylate using 2-bromomethyl-4,5-diphenyloxazole as an oxazoline functionalized initiator in the presence of the copper(I) bromide/bpy catalyst

complex. The polymerization process followed first order rate kinetics. A linear increase in number average molecular weight with percentage monomer conversion was observed and polymers with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.10-1.35) were obtained. The initiation efficiency was relatively low, since the experimental number average molecular weights of the resultant polymers were higher than the theoretical values:




The current research work describes the novel synthesis of 2-[(4-bromomethyl)-phenyl]-4,5-dihydro-4,4-dimethyloxazole and its direct use as an oxazolyl functionalized initiator for polymerization of styrene or methyl methacrylate in the presence of copper(I) bromide/bpy or copper(I) bromide/PMDETA as a catalyst system to afford α-oxazolyl functionalized polymers. In addition, the present research investigates controlled/"living" character of the ATRP reaction of styrene initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole in the presence of CuBr/bpy or CuBr/PMDETA catalyst complex.

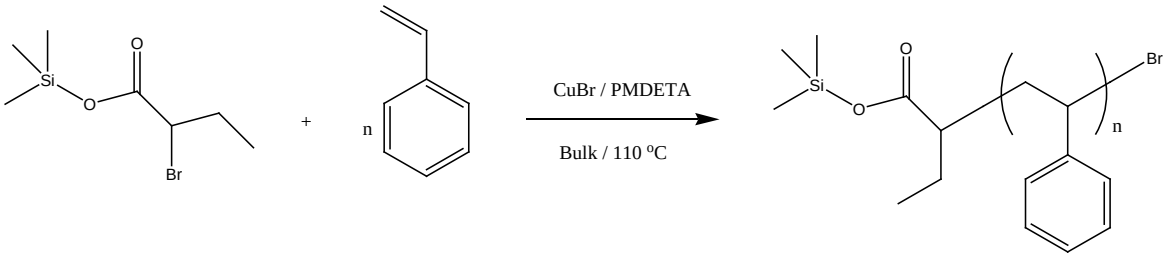
### 2.7.5.2 Carboxyl Functionalized Initiators for Atom Transfer Radical Polymerization

Carboxyl chain end functionalized polymers exhibit unique chemical, physical and mechanical properties[15] and are thus attractive to many industrial applications. Carboxyl chain end functionalized polymers are useful building blocks in the preparation of block copolymers by reactive blending using ring opening polymerization reactions of compounds such as α,α-disubstituted β-propiolactones and oxazolines[15,18,118].

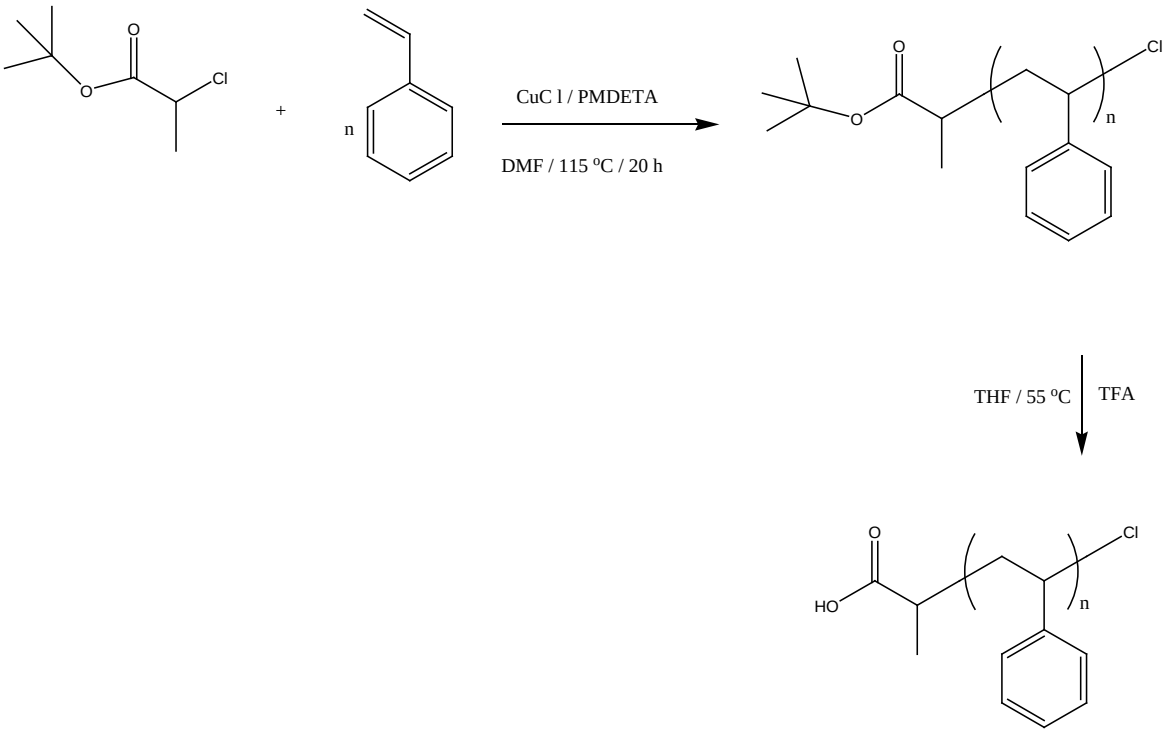
In general, carboxylated polymers have been prepared by living ionic polymerization methods by using functionalized initiators substituted with carboxylic acid group in its protected form. However, the use of protected carboxylic acid initiators such as 4,4-dimethyl-2-oxazoline-2-ylmethyl lithium in anionic polymerization, leads to poor initiation of styrene and methyl methacrylates and the polymers are formed in low percentage conversion[5]. In addition, due to extreme sensitivity of the living anionic polymeric species to the labile proton of the carboxylic acid group as well as the electrophilic carbonyl group, the direct carboxylation of poly(styryl)lithium with carbon dioxide is often complicated by the formation of a significant amount of the corresponding dimer and trimer species[4,5].

The synthesis of α-carboxyl functionalized polymers by ATRP reactions, using different functionalized initiators substituted with a range of carboxylic acid derivatives, have been well documented in the literature. A range of functionalized initiators with carboxylic acid derivatives as functionalized initiators have been used in the atom transfer radical polymerization of monomers such as styrene and methyl methacrylate[7-8]. Due to the potential complexation of the carboxylic acid group with the transition metal catalyst system in the ATRP reactions, many indirect methods, which involve the use of functionalized initiators

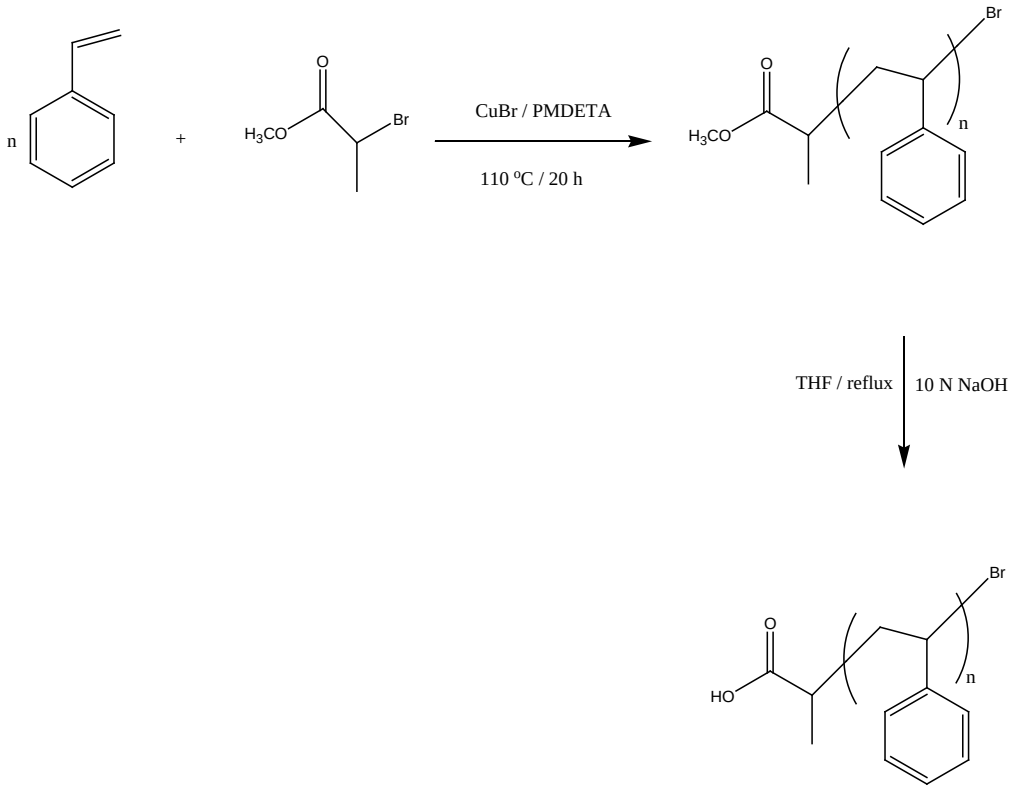
with the carboxylic acid group in the derivatized form, have been used to prepare α-carboxyl functionalized polymers[6]. For example, the ester derivatives of α-haloacids are employed as functionalized initiators in ATRP process for the preparation of carboxyl chain end functionalized polymers[7]. Matyjaszewski and Zhang[15] employed initiators such as trimethylsilyl 2-bromobutyrate as an initiator for styrene polymerization. Although the initiator efficiency was low, the number average molecular weights of the polymers increased linearly with percentage monomer conversion. The low initiator efficiency was attributed to unavoidable side reactions which includes hydrolysis of the trimethylsilyl group and subsequent formation of the γ-butyrolactone compound from the reaction of trimethylsily α-bromocarboxylate and styrene:



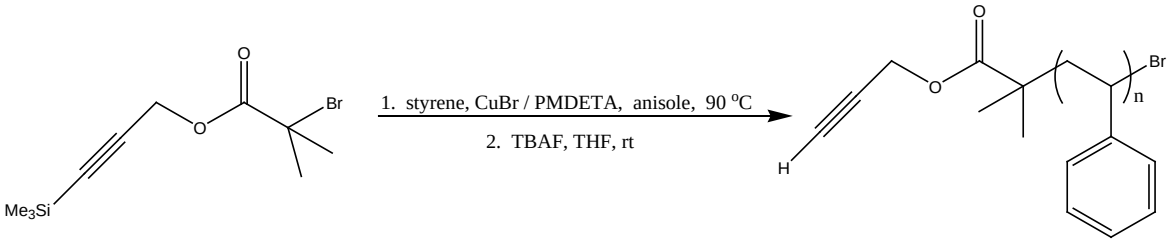

Pionteck and coworkers[18] used a α-chloropropionate derivative containing the t-butyl ester functionality as initiator for the copper(I) chloride/PMDETA-mediated ATRP of styrene to yield the corresponding ester functionalized polystyrene. The polymerization proceeded to low percentage monomer conversion, but polymers with high number average molecular weights of 25 000 g/mol and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n \approx 1.26$) were obtained. Subsequent quantitative hydrolysis of the t-butyl ester chain end functionalized polystyrene in the presence of trifluoro acetic acid (TFA) afforded well defined α-carboxyl functionalized polystyrene:



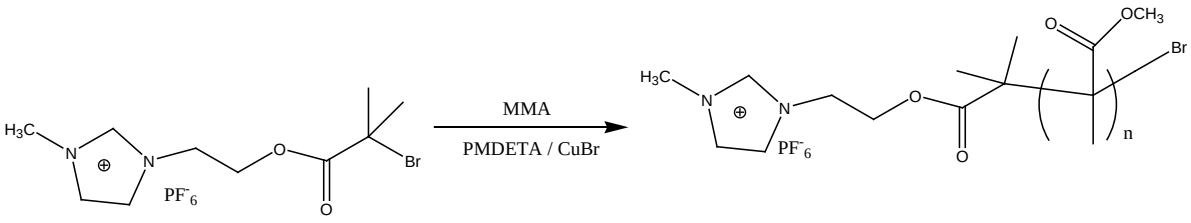

Kallitsis and coworkers[118] reported the methyl 2-bromopropionate initiated bulk polymerization of styrene in the presence of the copper(I) bromide/PMDETA catalyst system to prepare ester chain end functionalized polystyrene with $\overline{M}_n \geq$ 73 000 g/mol and initiator efficiency values ranging between 0.67-0.77. The styrene polymerization in solution proceeded in a controlled manner only for polymers in the low molecular weight range. The carboxyl chain end functionalized polymers were obtained after saponification of the ester derivative with aqueous sodium hydroxide and subsequent acidification reactions:




Hest and Opsteen[119] used 3-(1-trimethylsilyl)-2-propynyl 2-bromo-2-methylpropanoate) as an initiator for the CuBr/PMDETA mediated ATRP of styrene. Well defined α-alkyne functionalized polystyrene with predictable number average molecular weight and narrow molecular distribution ($\overline{M}_w/\overline{M}_n$ = 1.18) was obtained:

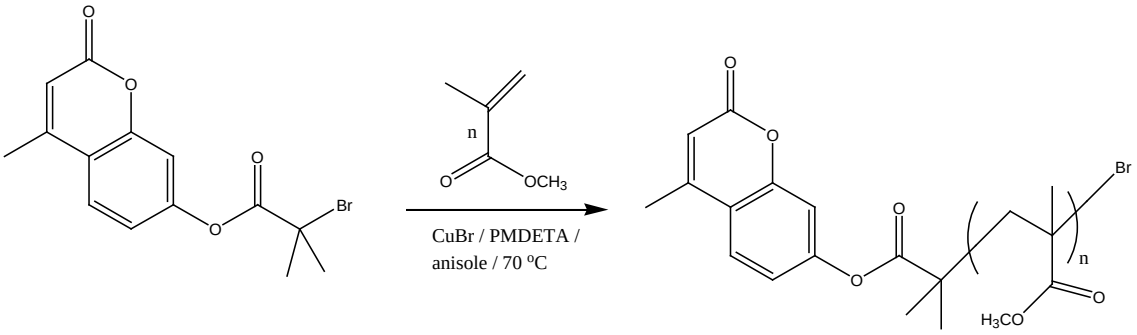


Gong and coworkers[120] extended the versatility of the use of α-haloesters as functionalized initiators to the controlled bulk ATRP polymerization of methyl methacrylate. The polymerization reaction was initiated by 1-(2-bromoiso-butyryloxyethyl)-3-methylimidazolium hexafluorophosphate in the presence of copper(I) bromide /PMDETA catalyst system. The polymerization reaction proceeded in a controlled fashion over a wide temperature range of 0-60 °C. The resulting poly(methyl methacrylate) derivatives with number average molecular weights of $\overline{M}_n$ = 3600-12 440 g/mol were characterized by narrow molecular weight distribution values ($\overline{M}_w/\overline{M}_n$ = 1.28-1.31). In addition, the linear evolution of the number average molecular weight with percentage monomer conversion provided experimental evidence of a controlled free radical polymerization process:

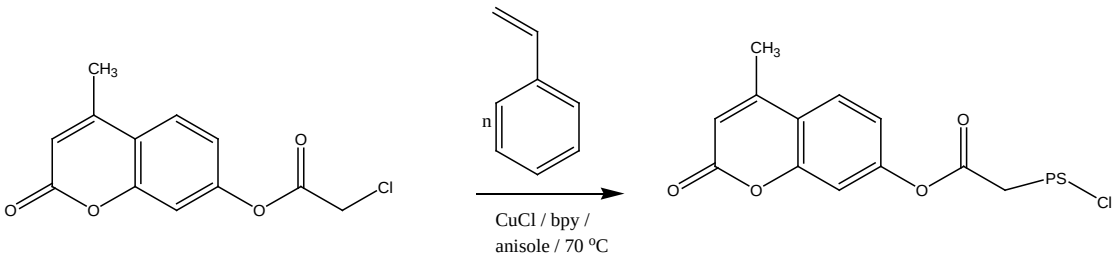



Recently, Sinkel and coworkers[121] and Cheng-Mei and coworkers[122] demonstrated that α-haloesters bearing a coumarin group, when used as an initiator for the ATRP of styrene and methyl methacrylate, do not interfere with the ATRP process. Sinkel and coworkers[121] incorporated a coumarin group at the α-chain end of poly (methyl methacrylate) via the ATRP technique using 7-(2'-bromoisobutyryloxy)-4-methylcoumarin as initiator for methyl methacrylate polymerization in the presence of the copper(I) bromide/PMDETA catalyst system. The polymerization reaction proceeded in a controlled fashion to give poly(methyl methacrylate) derivatives with predictable number average molecular weights and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.1-1.4). The

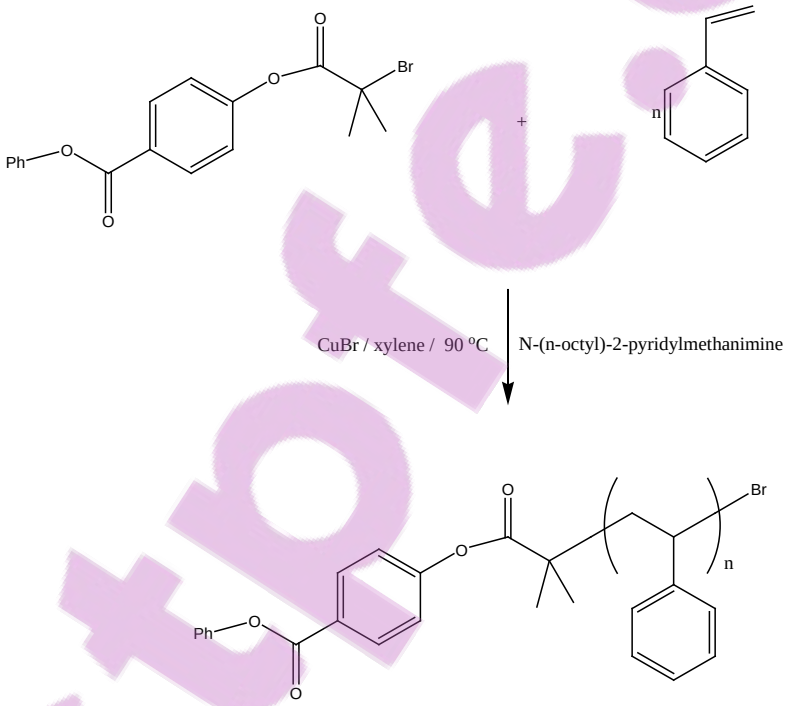
resultant methylcoumarin end functional polymers were subsequently used for photochemical drug loading:



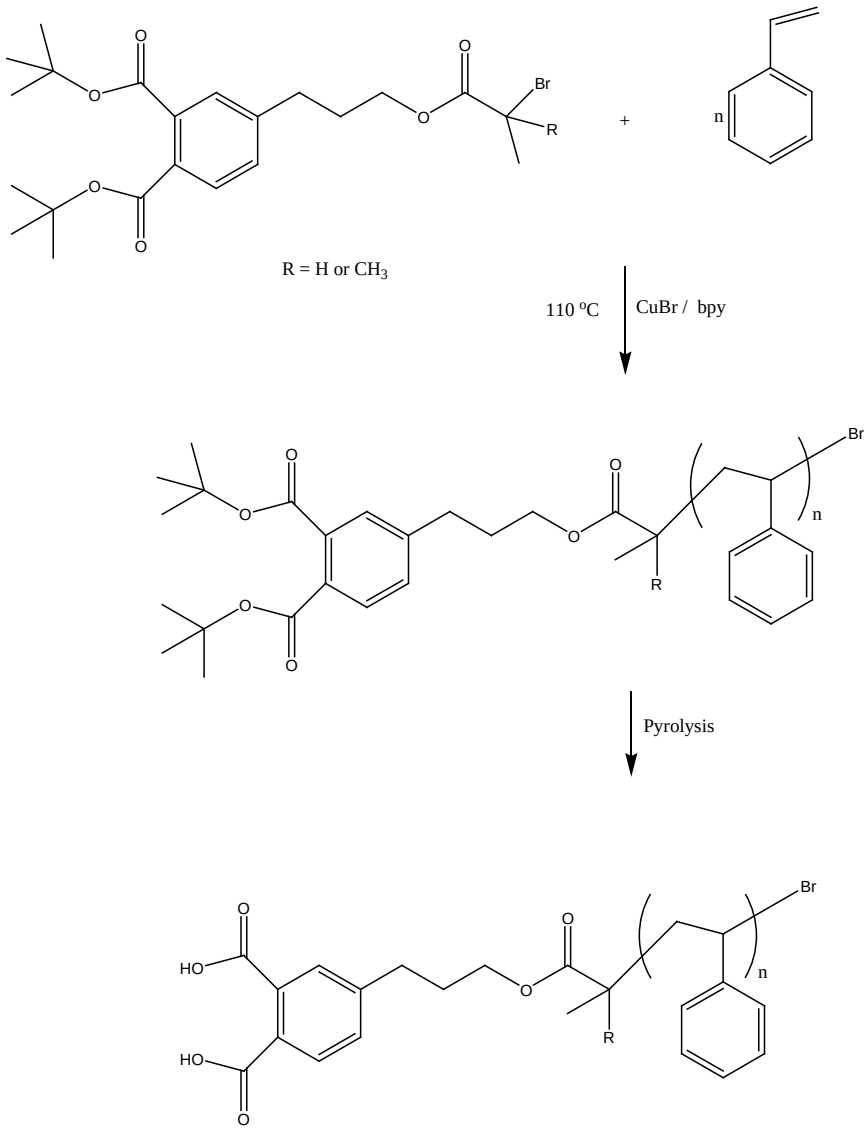

Similarly, Cheng-Mei and coworkers[122] utilized 7-chloroacetoxy-4-methyl-coumarin as functionalized initiator in conjunction with CuCl/bpy for the preparation of photosensitive polystyrene by ATRP methods with the quantitative incorporation of the coumarin group at the α-terminus of the polymer chain. Polymerization kinetic studies depicted a linear increase in the number average molecular weight with percentage monomer conversion for the polymerization reaction. Moreover, polymers with narrow molecular weight distributions as low as 1.40 were obtained at 75% monomer conversion:



Haddleton and Waterson[16] used a wide range of substituted α-haloester initiators such as phenyl-4-(2'-bromo-2'-methylpropionato)benzoate as functionalized initiators for the polymerization of styrene and alkylated methacrylates. Polystyrene with controlled number average molecular weight up to 10 000 g/mol was obtained when phenyl-4-(2'-bromo-2'-methylpropianato)benzoate was used as an initiator for styrene polymerization in the presence of a copper based catalyst and N-(n-octyl)-2-pyridylmethanimine as a ligand. Polymerization studies indicated a linear increase in number average molecular weight with percentage monomer conversion and polymers with narrow molecular weight distributions were obtained:

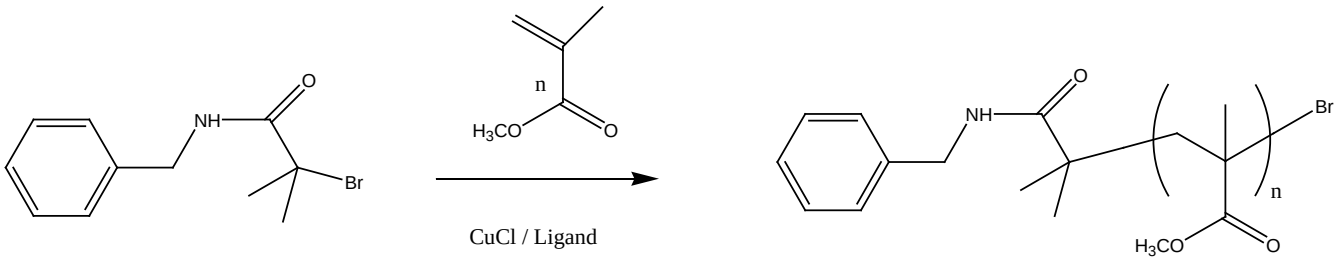



Macosko and coworkers[123] used α-haloester derivatives substituted with the di-t-butylphthalate (DTBP) group as initiators for styrene polymerization in the presence of CuBr/bpy catalyst system. Quantitative yields of α-bis(carboxyl) chain end functionalized polymers were produced after the pyrolysis of the intermediate di-t-butylphthalate end functionalized polymers:

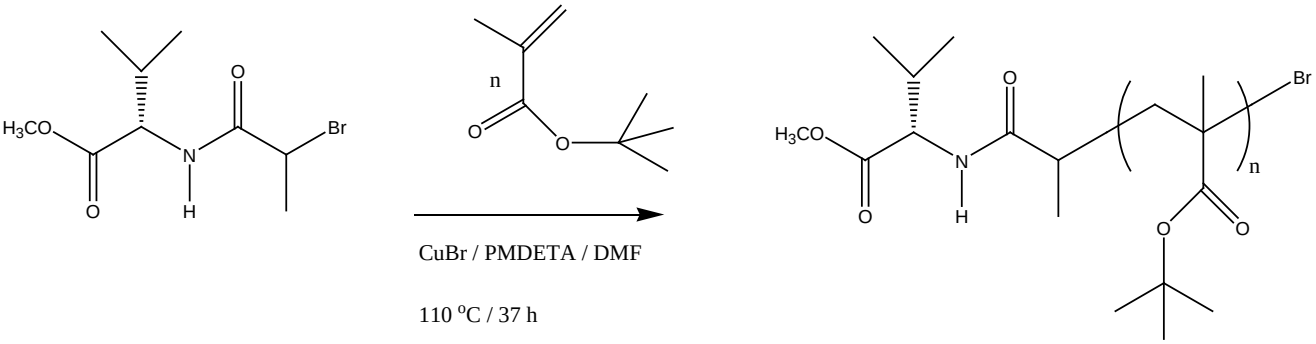



α-Haloamides have been employed as functionalized initiators for the polymerization of styrene and methyl methacrylate by ATRP methods. Haddleton and Limer[124] employed different α-haloamides as functionalized initiators in the controlled ATRP of styrene and a wide range of methacrylate monomers. For example, the initiation of methyl methacrylate using the N-benzyl-2-bromo-2-methylpropanamide initiator in the presence of CuCl/N-(n-octyl)-2-pyridylmethanimine as a metal complex catalyst system proceeded smoothly up to $\overline{M}_n$ = 12 900 g/mol with relatively high percentage monomer conversion of

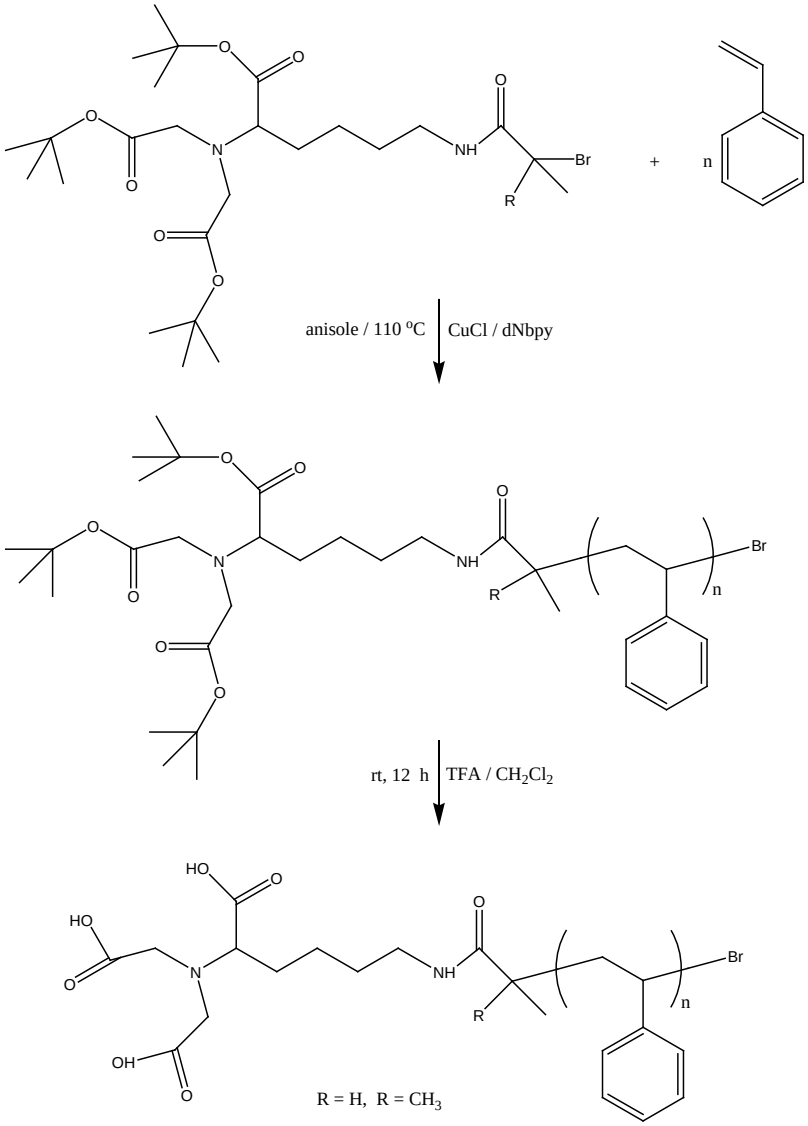
70 %. Polymers with predictable number average molecular weights and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.24) were obtained:



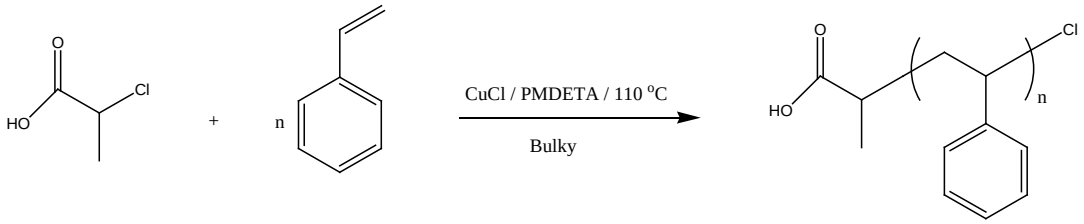

Wooley and Venkataraman[125] extended the utility of α-haloamide initiators to the controlled polymerization of t-butyl acrylate. By using an α-haloamide compound with the valine moeity linked to the nitrogen atom as initiator in the ATRP reactions, well defined polymers, incorporating the valine group at the α-terminus of the polymer chain, were produced. Although, the experimental number average molecular weights of the polymers were higher than the predicted values, the resulting polymers were characterized by narrow molecular weight distributions. The potential modification of the amide group should lead to the formation of the corresponding carboxyl chain end functionalized poly(t-butyl methacrylate):



Cho and coworkers[126] prepared nitrilotriacetic acid (NTA) chain end functionalized polystyrene using α-haloamides substituted with the NTA moiety as initiators for styrene polymerization via ATRP methods. The functionalized initiator, N',N'-bis[(t-butyloxycarbonyl)methyl]-N''-bromoisobutyl-L-Lysine, was used as initiator for the polymerization of styrene. Treatment of the nitriloacetic acid chain end functionalized polystyrenes with triflouroacetic acid gave the corresponding α-tris(carboxyl) chain end functionalized polystyrene in quantitative yields:

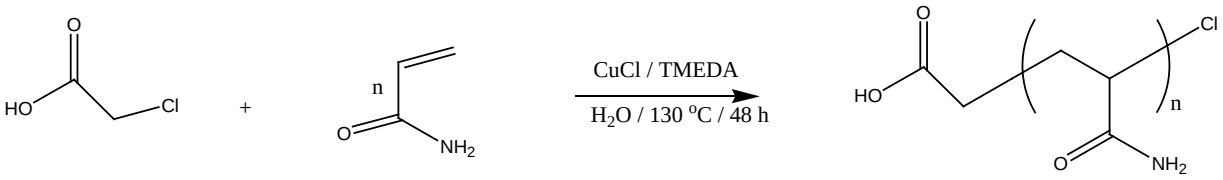


Carboxyl chain end functionalized polymers can also be prepared by direct ATRP methods by using carboxyl functionalized initiators, where the carboxylic acid group occurs in the free acid form. Matyjaszewski[15] and Haddleton[16] used different α-halocarboxylic acid initiators for styrene and methyl methacrylate polymerization by ATRP methods for the preparation of carboxyl chain end functionalized polymers. For example, when 2-chloropropionic acid was used as an initiator for the polymerization of styrene, the polymerization reactions proceeded in a controlled manner. However, poor initiations were observed ($I_{eff}$ = 0.3-0.4) and polymers with broad molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.25-1.75) were obtained. The reaction was accompanied by side reactions involving the formation of butyrolactone in the reaction between the monomer and the initiator.

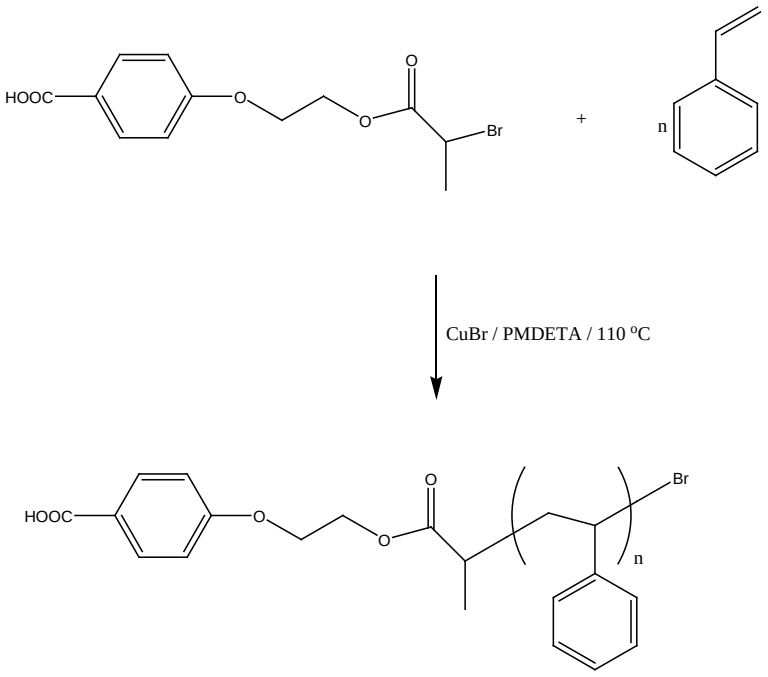



Jiang and coworkers[127] reported the α-haloacid initiated polymerization of acrylamide in the presence of copper(I) chloride/N,N,N',N'-tetramethyl-ethylenediamine catalyst system to prepare carboxyl chain end functionalized polyacrylamide under aqueous acidic conditions induced by the α-chloroacetic acid initiator. The reactions proceeded in a controlled fashion, although low percentage monomer conversion reactions were observed. Moreover, a linear increase in number average molecular weight with percentage monomer conversion was observed and polymers with narrow molecular weight distributions (1.03-1.44) were obtained. It was reported that unavoidable side reactions such as the formation of γ-butyrolactone by intermolecular cyclization reactions between chloroacetic acid and the monomer could have resulted in the

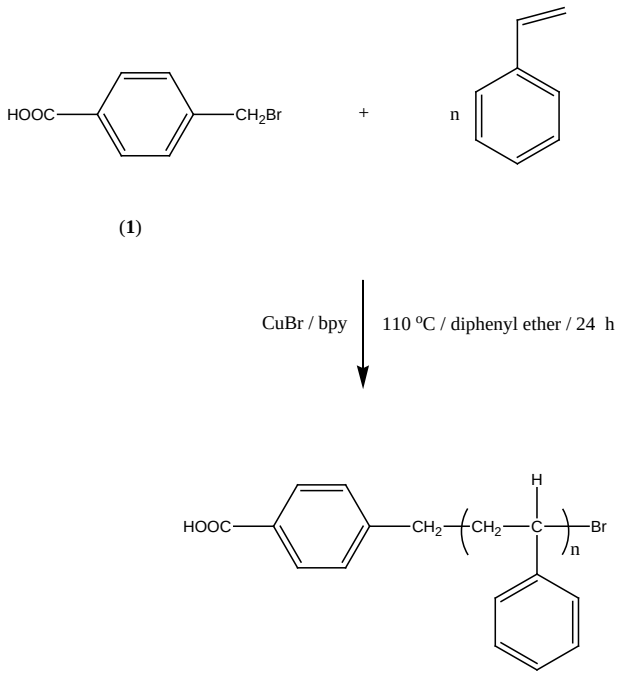
limited initiator efficiency. Moreover, the possible interaction between the initiator and the ligand was also reported:




The use of alkyl halide or α-haloacid initiators with remote free carboxylic acid groups has emerged as one of the efficient alternative routes for preparation of carboxyl chain end functionalized polymers by ATRP methods. Matyjaszewski and Zhang[15] demonstrated that initiators with the carboxylic acid group remote to the initiating halogen can enforce control in the ATRP of styrene. By using 4-(1-bromoethyl)-benzoic acid and 4-(2-bromopropionyloxy)ethoxy)benzoic acid as an initiator for styrene polymerization in the presence of copper(I) bromide/PMDETA as a catalyst system, controlled ATRP processes were reported without noticeable coordination reactions between the carboxylic acid group and the transition metal complex. The number average molecular weights of the polymers increased linearly with percentage monomer conversion in high initiator efficiency reactions ($I_{eff}$ = 70). The molecular weight distributions of the polymers were narrow throughout the reactions ($\overline{M}_w/\overline{M}_n \approx 1.1$). For example:



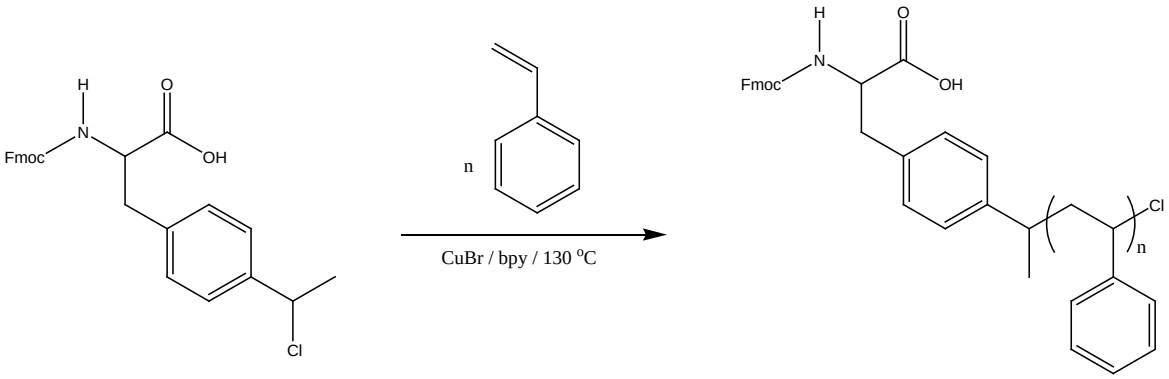

Independently, Summers and coworkers[17] prepared aromatic carboxyl chain end functionalized polymers by ATRP methods using α-bromo-p-toluic acid as the initiator in the presence of copper(I) bromide/bpy as a catalyst for the quantitative synthesis of α-carboxyl functionalized polystyrene. α-Carboxyl functionalized polystyrenes with predictable number average molecular weights for $\overline{M}_n$ = 1 600-25 900 g/mol and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.1-1.4) were obtained. Initially, the polymer product was isolated as the copper carboxylate as evidenced by FTIR analysis. The desired carboxyl functionalized polymer was obtained by acidification of the polymeric carboxylate salt:



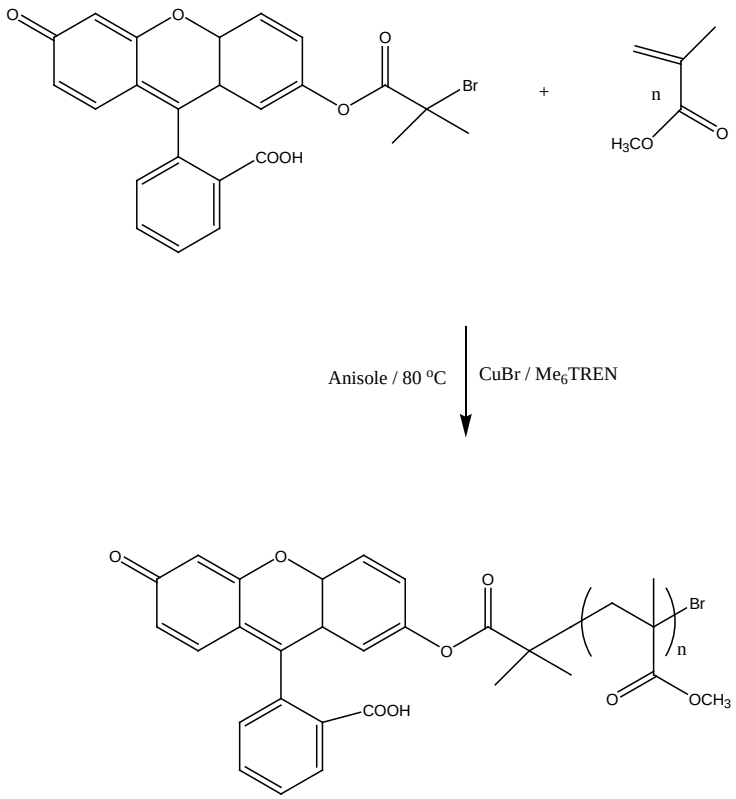

(**1**)

Similarly, Xia and coworkers[128] utilized α-bromo-p-toluic acid as an initiator for the ATRP of styrene in the presence of CuBr/bpy catalytic system to form the α-carboxyl functionalized polymers. Polymers with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.19-1.55) were obtained. The resultant polymers were used for the formation of polymeric europium (III) complex which exhibit emission of polymer and Eu(III) ion.

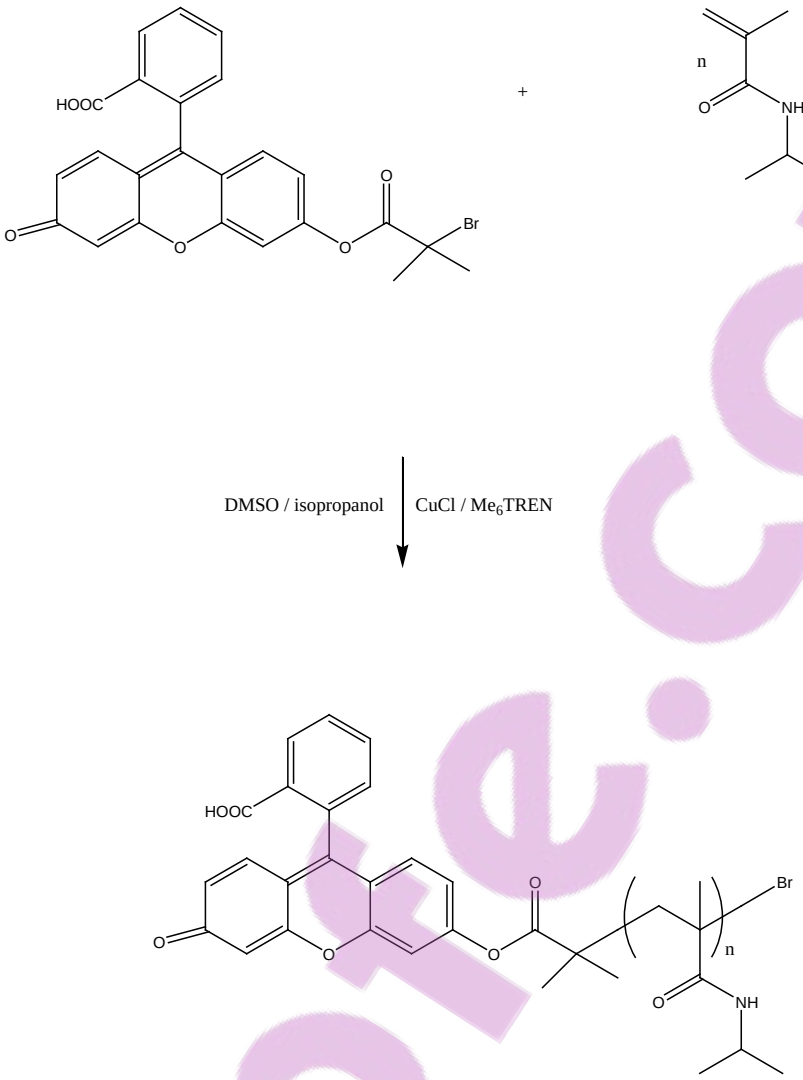
Recently, Broyer and coworkers[129] performed the bulk polymerization of styrene in a high percentage monomer conversion ATRP reaction using a benzyl chloride derivative bearing an amino acid, Fmoc-4-(1-chloroethyl)phenylalanine as initiator in the presence of the CuBr/bpy catalyst system. Well defined carboxyl chain end functionalized polystyrene with $\overline{M}_n$ = 13 x $10^3$ g/mol and narrow molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = 1.27) was obtained:




Aromatic carboxyl chain end functionalized poly(methyl methacrylate) was prepared via an ATRP reaction by Li and coworkers[130] Using 3-(2'-bromo-2'-methylpropionic acid) fluorescein ester as initiator for the polymerization of methyl methacrylate in the presence of CuBr/$Me_6$TREN as a metal complex catalyst, the polymerization proceeded in a controlled manner with the number average molecular weights of the polymers increasing linearly with increasing percentage monomer conversion. Polymers with relatively narrow molecular weight distributions were obtained for reactions up to 90% monomer conversion. However, the number average molecular weights were significantly higher than the theoretically determined values based on reaction stoichiometry, indicating low initiator efficiency ($I_{eff} \approx 0.5$):

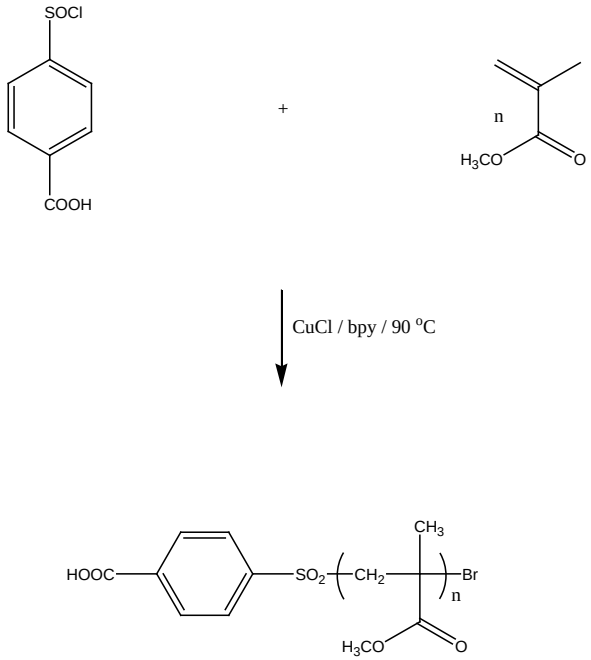



Similarly, Lu and coworkers[131] used flourescein 2-bromoisobutyrate as an initiator for the polymerization of N-isopropylacrylamide by ATRP methods in the presence of copper(I) chloride and $Me_6$TREN as the catalyst system. Controlled polymerization reactions were observed and polymers with predictable number average molecular weights up to 65% monomer conversion and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.15-1.28) were obtained:




In the process of preparing aromatic carboxyl chain end functionalized polymers by ATRP methods, arene sulfonyl halides bearing a carboxylic acid group have also been widely utilized as functionalized initiators for the polymerization of styrene, acrylates and methacrylates[132]. Sulfonyl halides exhibit fast and quantitative initiation, without significant effect on initiation rate imposed by the presence of a substituent such as the carboxylic acid group[10]. Percec and coworkers[133] employed a functionalized arene sulfonyl chloride initiator bearing a carboxylic acid group at the para-position for the metal catalyzed polymerization of methyl methacrylate and butyl methacrylate. Well defined polymers were obtained in quantitative yields. Controlled polymerization reactions with high

initiation efficiency and high percentage monomer conversion (88%) were observed when p-carboxybenzene sulfonyl chloride (CABSC) was used as an initiator for methyl methacrylate polymerization in the presence of the copper(I) chloride/2,2'-bipyridine complex. Polymerization kinetic data gave plots of the linear increase of the number average molecular weight with percentage monomer conversion and polymers with relatively narrow molecular weight distributions, ranging between 1.2-1.8, were produced:



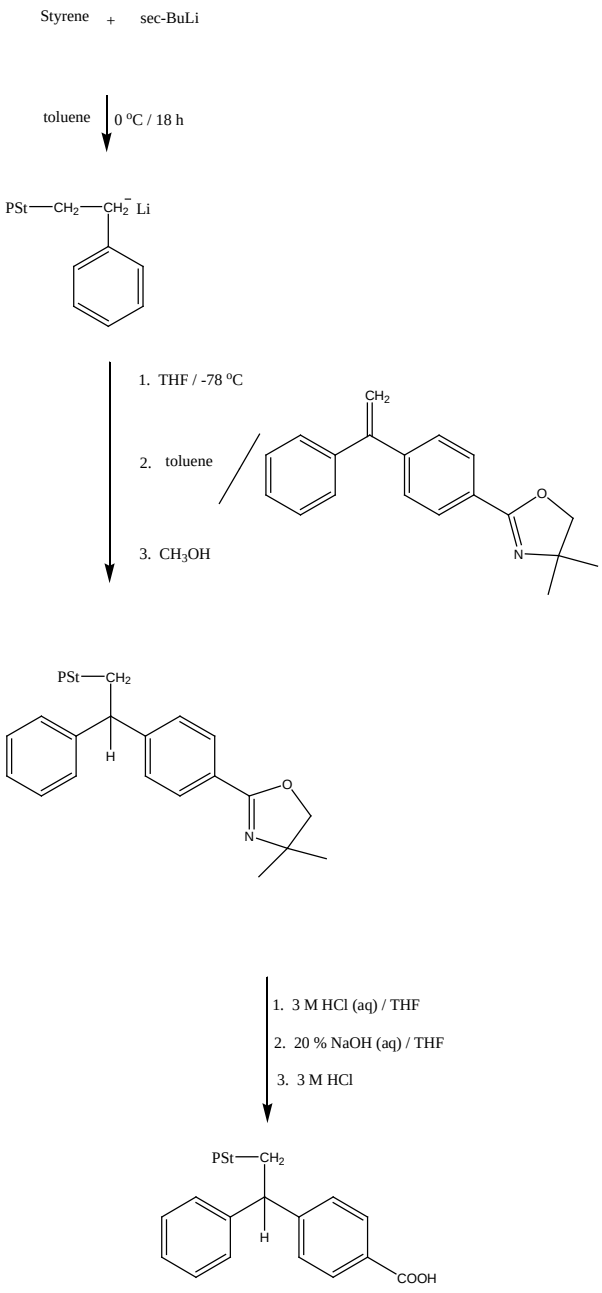

The current research work entails the preparation of a series of α-oxazolyl, α-bis(oxazolyl), α,ω-bis(oxazolyl) and α,ω-tetrakis(oxazolyl) functionalized polymers by ATRP methods. The post polymerization chemical transformation of the oxazolyl chain end groups of the oxazolyl functionalized polymers to the carboxylic acid moiety, forms the corresponding aromatic carboxyl chain end functionalized polymers.

## 2.8 FUNCTIONALIZED POLYMERS VIA 1,1-DIPHENYLETHYLENE DERIVATIVES

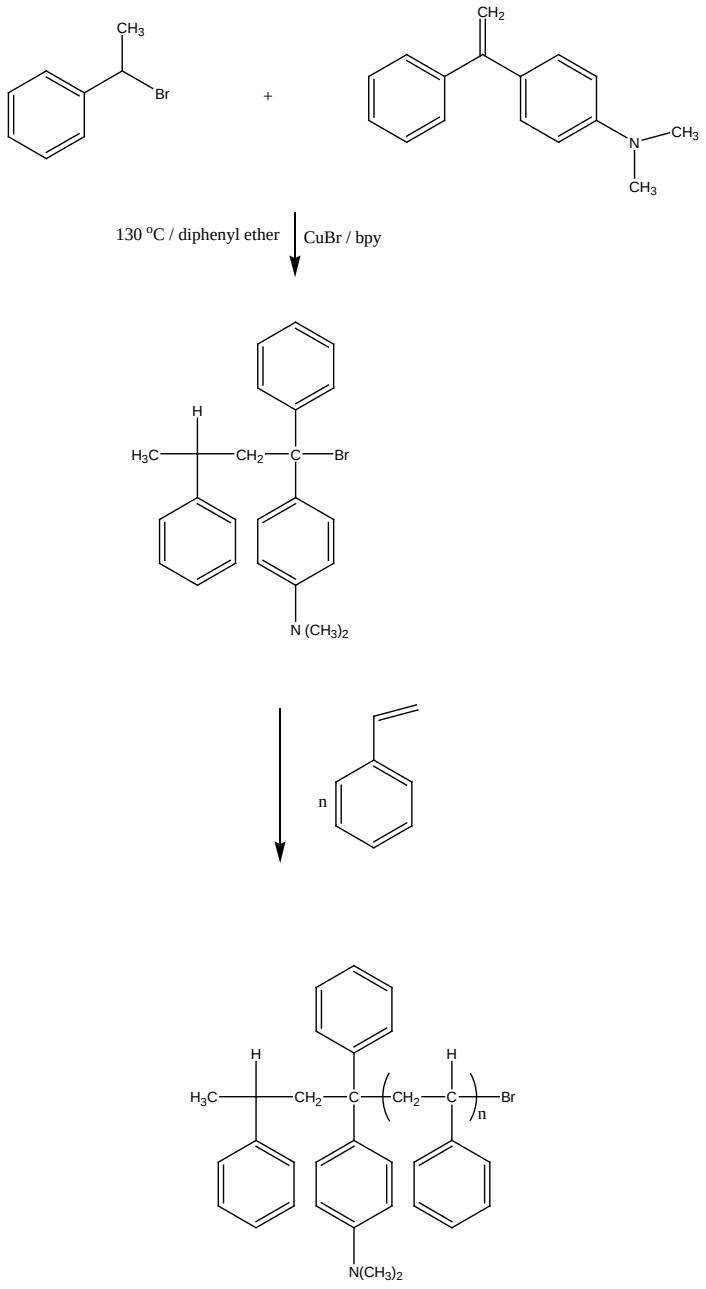
The use of substituted 1,1-diphenylethylene derivatives in polymer synthesis provides one of the best methods for the preparation of polymers with well defined polymer structures, in particular, the excellent control of the chain end functionality[5]. The reactions of simple or polymeric anions, cations and free radicals with substituted 1,1-diphenylethylene compounds provides an efficient functionalization method for the preparation of functionalized organic compounds and polymers, respectively. Such addition reactions are simple, rapid and without side reactions[5,25-26]. In addition, due to steric factors, the stoichiometric reactions of anions, cations and free radical species with substituted 1,1-diphenylethylene derivatives proceed quantitatively with incorporation of a single 1,1-diphenyl-ethylene unit, that is, no oligomerization or polymerization of the 1,1-diphenyl-ethylene derivative occurs[19]. A plethora of functionalized polymers can be prepared by anionic, cationic and free radical mechanisms, since many substituted 1,1-diphenylethylene derivatives can easily be prepared by simple organic reactions[19-26].

Quirk and coworkers[19,21,23] developed a general anionic functionalization methodology for the preparation of functionalized polymers based on the addition reactions of polymeric organolithium compounds with 1,1-diphenylethylene derivatives. The functionalization reactions proceed smoothly irrespective of the nature of substituents. Thus, a variety of 1,1-diphenylethylene derivatives bearing the oxazolyl[19], siloxyl[21], tertiary amine[22], amide[23] and halogen[24] groups were used as functionalizing agents in the chain end functionalization reactions via anionic methods. For example, Summers and Quirk[19,23] prepared aromatic carboxyl functionalized polymers via the anionic chain end functionalization reactions of polymeric anions with 1,1-diphenylethylene derivatives. The reactions of poly(styryllithium) with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethyl)phenyl]-

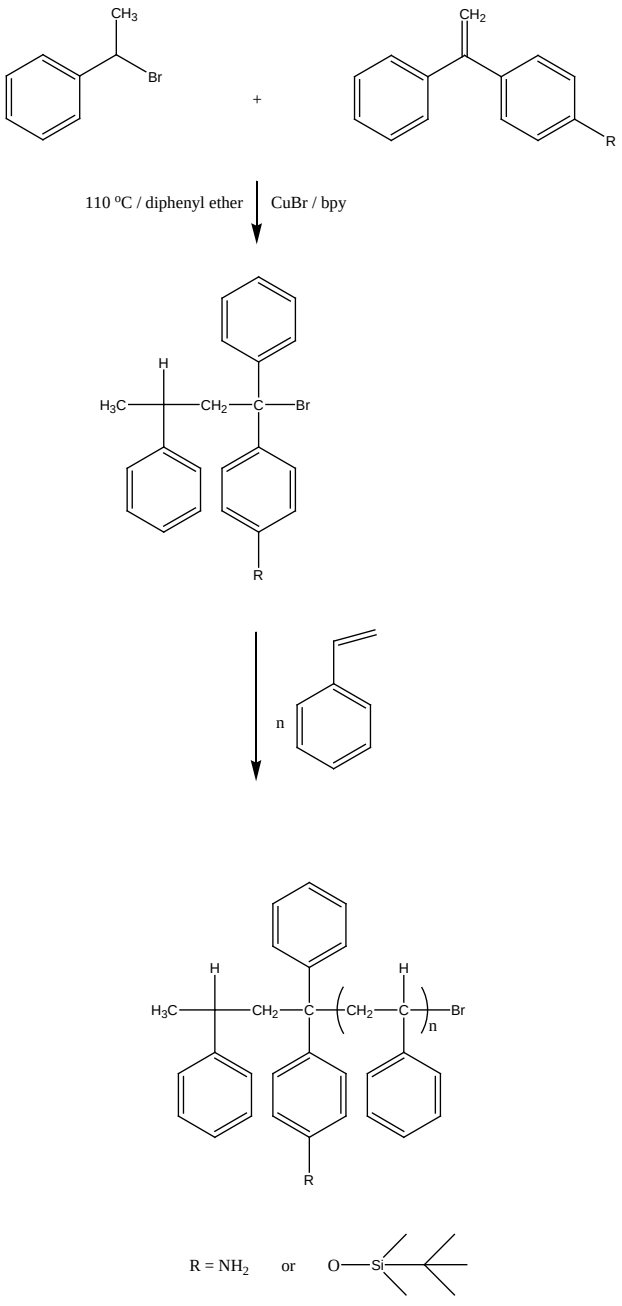
oxazole produced the corresponding ω-oxazolyl functionalized polymers in quantitative yields. The ω-oxazolyl functionalized polymers were subjected to successive acid and base hydrolysis, resulting in the quantitative formation of the corresponding well defined carboxyl functionalized polystyrenes with predetermined number avarage molecular weights of $\overline{M}_n^{GPC}$ = 2 100-14 001 g/mol and narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.03-1.05):



The use of 1,1-diphenylethylene derivatives in polymer synthetic methods was extended to the preparation of well defined functionalized polymers by ATRP methods. Summers and coworkers[25-28] developed a general, one pot, quantitative ATRP functionalization reaction using substituted 1,1-diphenyl-ethylene derivatives as initiator precursors. Different unimolecular functionalized initiator systems, prepared *in situ* by the reaction of organohalogen compounds with substituted 1,1-diphenylethylene derivatives in the presence of copper(I) bromide/2,2'-bipyridine catalyst, were used as functionalized initiators for styrene polymerization to produce the corresponding chain end functionalized polymers in quantitative yields. For example, by using a tertiary amine functionalized initiator adduct system, prepared *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene, as an initiator for the ATRP of styrene, the corresponding well defined α-tertiary amine functionalized polystyrene was produced in quantitative yields[25].


CH3
Br
+
CH2
N
CH3
CH3
130 °C / diphenyl ether
CuBr / bpy
H
H3C
CH2
C
Br
N (CH3)2
n
H
H3C
CH2
C
CH2
C
Br
n
N(CH3)2

Similarly, the primary amine[26-27] and siloxyl[28] chain end functionalized polymers can be prepared by ATRP methods using a similar synthetic strategy which involves the selection of the appropriate substituted 1,1-diphenylethylene derivative as initiator precursor:



By using 1,1-diphenylethylene chemistry, the current research work describes the preparation of oxazolyl chain end functionalized polystyrene using two different oxazolyl functionalized initiator systems according to the following method:

(a) the synthesis of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]-oxazole and its subsequent use as an aromatic oxazolyl functionalized initiator precursor for the solution ATRP of styrene to afford $\alpha$-oxazolyl functionalized polystyrene. A new oxazolyl initiator adduct, prepared *in situ* by the reaction of (1-bromoethyl)benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole in the presence of CuBr/bpy and xylene, can be employed as initiator for the ATRP of styrene to give the corresponding α-oxazolyl functionalized polystyrene.

(b) the novel synthesis of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]-ethylene and its utilization as an aromatic dioxazolyl functionalized initiator precursor for the synthesis of α-bis(oxazolyl) functionalized polystyrene by ATRP methods. The utilization of a new dioxazolyl functionalized initiator adduct, obtained *in situ* by the reaction of (1-bromoethyl)benzene with the 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, as initiator for the ATRP of styrene provides a facile method for the preparation of the corresponding α-bis(oxazolyl) functionalized polystyrene.

The current study investigates the controlled/"living" nature of each ATRP reaction leading to the preparation of the different oxazolyl chain end functionalized polymers using two different functionalized 1,1-diphenylethylene initiator systems as initiators for the polymerization of styrene.

The present study also describes the preparation of α,ω-bis(oxazolyl) and α,ω-tetrakis(oxazolyl) functionalized polystyrene by the post ATRP chain end transformation reactions via the following synthetic pathway:

(c) the atom transfer radical polymerization of styrene initiated by a new oxazolyl functionalized initiator adduct derived from the appropriate oxazolyl functionalized 1,1-diphenylethylene unit.

(d) the addition of the appropriate oxazolyl substituted 1,1-diphenylethylene derivative to the ω-terminus of the polymer chain at the end of the polymerization process.

The current research also outlines the preparation of aromatic carboxyl functionalized polymers by the quantitative chemical transformation of the oxazoline group of the appropriate oxazolyl chain end functionalized polymers to the corresponding carboxylic acid group. The successive acid and base hydrolysis of the specific oxazolyl functionalized polystyrene derivative, followed by final acidification, provides a useful method for the synthesis of the corresponding well defined carboxyl functionalized polystyrene.

# CHAPTER 3

# EXPERIMENTAL

## 3.1 MATERIALS AND GLASSWARE

### 3.1.1 Glassware

All reactions were conducted in oven-dried glassware which was subsequently purged with argon. Air and moisture sensitive solutions were transferred via a cannula or an argon purged glass syringe equipped with a stainless steel needle.

### 3.1.2 Reagents and Solvents

All chemicals were purchased from the Sigma Aldrich Chemicals Company, unless otherwise stated. The following chemicals and solvents were used as received: thionyl chloride ($SOCl_2$), 2-amino-2-methyl-1-propanol, sodium hydroxide (NaOH), magnesium sulphate ($MgSO_4$), triethylamine ($Et_3N$), ethyl acetate, hexane, copper(I) bromide (CuBr), diphenyl ether (DPE), tetrahydrofuran (THF), methanol (MeOH), N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), 32 % hydrochloric acid (HCl), 4-benzoylbenzoic acid, methyltriphenylphosphonium bromide, methyl lithium (1.4 M in diethyl ether), (1-bromoethyl)benzene, 4-bromobenzoic acid, iodine ($I_2$), anhydrous ethyl acetate, ammonium chloride ($NH_4Cl$), sodium hydrogen carbonate ($NaHCO_3$), calcium hydride ($CaH_2$), phosphorus pentoxide ($P_2O_5$), deuterated chloroform ($CDCl_3$), distilled water and dry argon (UHP CYL from AFROX).

The following chemicals and solvents were purified as follows:

(i) α-bromo-ρ-toluic acid was recrystallized from acetone[134]; mp = 229.5-230.6 °C (lit mp: 228-232 °C)[135].

(ii) Toluene, dichloromethane ($CH_2Cl_2$) and sulphur free xylene were dried over phosphorus pentoxide ($P_2O_5$) at room temperature for 12 hours, heated to reflux for 2 hours and then distilled from $P_2O_5$ and stored over molecular sieves[135,136].

(iii) Diethyl ether ($Et_2O$) and tetrahydrofuran (THF) were distilled from a sodium benzophenone ketyl[135].

(iv) 2,2'-bipyridine (bpy) was recrystallized from petroleum ether[134] ; mp = 70.2-72.3 °C (lit mp = 70-73 °C)[135].

(v) Magnesium (Mg) for use in the formation of a Grignard reagent was oven dried at 150 °C for 24 hours.

### 3.1.3 Monomers

(i) Styrene was stirred over freshly ground calcium hydride for 24 hours and freshly distilled under vacuum prior to use.

(ii) Methyl methacrylate (MMA) was passed through a column of activated alumina (WOELM), dried over calcium chloride for 24 hours and was freshly distilled under vacuum prior to use.

## 3.2 CHARACTERIZATION

### 3.2.1 Thin Layer Chromatography

Thin Layer Chromatography (TLC) was used for identification, separation and purification of initiators, initiator precursors and functionalized polymers. TLC analysis was performed on pre-coated silica gel plates (MERCK, Aluminium sheets 20 x 20 silica gel 60 F 254). The chromatograms were developed under UV (254 nm) light.

### 3.2.2 Column Chromatography

Column Chromatography was used for the purification of the initiators, initiator precursors and polymeric products using silica gel 60 (0.063-0.2 mm / 230-400 mesh) as a stationary phase. Solvents used for column chromatography were analytical grade and their selection was determined by TLC analysis results. Organic solutions were concentrated by solvent evaporation under reduced pressure on a rotary evaporator and then under vacuum.

### 3.2.3 Fourier Transform Infrared Spectroscopy

Infrared spectra of solid samples were recorded on a Digilab Fourier-Transform Infrared Spectrometer over the region of 4 000-600 $cm^{-1}$. The solid samples were placed on the ATR crystal (Germanium: $n_1 = 4.0$; ATR range = 5 500-780 $cm^{-1}$) under pressure.

### 3.2.4 Nuclear Magnetic Resonance Spectrometry

$^{1}H$ NMR spectrometry and $^{13}C$ NMR spectrometry were used to determine the structure of the initiators, initiator precursors and the functionalized polymers. Proton ($^{1}H$) and carbon-13 ($^{13}C$) nuclear magnetic resonance spectra were recorded at 25 °C using a VARIAN VXR 300 Pulsed Fourie Transform NMR spectrometer at 300 MHz and 75 MHz, respectively. The chemical shifts are given in parts per million (ppm) on the delta scale (δ). The following solvent peaks were used as a reference value: $^{1}H$ NMR: $CDCl_3$ = 7.26 ppm, $^{13}C$ NMR: $CDCl_3$ = 77.00 ppm.

For $^{1}H$ NMR analyses, 10 mg of the sample were dissolved in 0.5 mL of deuterated chloroform, $CDCl_3$. For $^{13}C$ NMR analyses of polymer products, 40 mg of the polymer were dissolved in 0.7 mL of $CDCl_3$. Spectra were recorded at 25 °C, with each analysis taking 10 minutes for $^{1}H$ NMR and approximately 24 hours for $^{13}C$ NMR.

Data for $^{1}H$ NMR are reported as follows: s = singlet; d = doublet; t = triplet; q = quartet; dd = doublet of doublets; m = multiplet; b = broad.

### 3.2.5 Melting Point Determination

The melting points of organic compounds are reported as uncorrected. Melting points were determined using a Stuart Melting point (SMP 10) apparatus.

### 3.2.6 Size Exclusion Chromatography

The number average and weight average molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and molecular weight distributions ($\overline{M}_w/\overline{M}_n$) of polymers were determined by size exclusion chromatography (SEC). Size exclusion chromatographic analyses of polymers were performed using a Water 2690 GPC autosampler equipped with a refractive index detector and a dual angle laser scattering detectors in series. The SEC component system was equipped with a 5 µ Phenogel guard column (50 x 7.8 mm) and Phenogel column (5 µ, 500 A° pore size, 1K-15K MW range, 300 mm x 7.8 mm). The concentration of each polymer sample for SEC analysis was set at 2 mg/2 mL in tetrahydrofuran. All polymer solutions were filtered through a prefilter-filter combination system before SEC analysis:

| | |
|---|---|
| Mobile phase: | Tetrahydrofuran |
| Flow rate: | 1 mL/min |
| Detector Temperature: | 30°C |
| Injection volume: | 1µL |
| Calibration: | SEC system equipped with the dual angle laser light scattering detector was calibrated by using polystyrene and poly(methyl methacrylate) (Aldrich Chemical Company) as polymer standards. |
| Chromatogram: | Varian Star version 5.5 software |

dn/dc values: 0.186 (polystyrene) and 0.098 poly(methyl methacrylate)

### 3.2.7 Gas Chromatography

Polymerization kinetic data, which involved the measurement of the disappearance of monomer with time, was obtained by gas chromatographic analysis using a Shimadzu Graph Chromatograph 17A. The column specifications were: SPB-5 M (30 m, diameter: 0.32 mm x 0.25 µm film thickness). The oven temperature was set at 90 °C for 3 min rising to 280 °C at 10 °C/min, the injector temperature was set at 200 °C, and the FID detector was set at 300 °C. The injection volume was 1µL, 1.5 split and the flow rate was kept at 1.7 mL/min. Analyses of results were performed by using the Star Chromatography Work Station (version 6.00).

### 3.2.8 Non-Aqueous Titrations

The concentrations of carboxyl end groups in polymers were determined by non-aqueous acid-base titrations according to the method outlined by Anand and coworkers[137]. A solution of standardized potassium hydroxide in methanol was used as a titrant. Polymers were dissolved in toluene and phenolphthalein was used as an indicator. Sulphamic acid was employed as a primary standard for the standardization of potassium hydroxide.

### 3.2.9 Elemental Analyses

Microanalyses for C, H and N were carried out at the University of Cape Town using a Thermo Flash 1112 Series CHNS-O Analyser.

## 3.3 ATOM TRANSFER RADICAL POLYMERIZATION: SYNTHESIS OF CHAIN END FUNCTIONALIZED POLYMERS.

### 3.3.1 Synthesis of Aromatic Oxazolyl Functionalized Polymers by ATRP using an Oxazolyl Functionalized Initiator.

#### 3.3.1.1 Oxazolyl Functionalized Initiator: Synthesis of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (1).

The oxazolyl functionalized initiator, 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole (**1**) was synthesized according to the general method for synthesis of oxazolines as outlined by Meyers and coworkers[138] and Shchepinov and coworkers[139], with modifications. Under an argon atmosphere, α-bromo-p-toluic acid (25.02 g, 0.1163 mol) was added to a two-necked round bottom flask equipped with a reflux condenser and a $CaCl_2$ tube. Thionyl chloride ($SOCl_2$) (27 mL, 45.01 g, 0.3750 mol) was then added in a single portion and the resultant reaction mixture was heated to reflux for 6 h. Excess $SOCl_2$ was removed by distillation and the remaining brown residue of the acid chloride was dissolved in dry toluene. The residual $SOCl_2$ was removed by forming an azeotrope with toluene to give 27.13 g of the desired acid chloride in quantitative yields. The acid chloride was used for the next reaction without further purification.

Under argon atmosphere, the acid chloride (25.00 g, 0.1071 mol) was dissolved in dry dichloromethane (100 mL) and added to a two-necked round bottom flask equipped with an addition funnel, a reflux condenser and a calcium chloride tube. The acid chloride solution was then cooled to 0 °C. A solution of 2-amino-2-methyl-1-propanol (19.07.g, 0.2212 mol) in dry dichloromethane (100 mL) was then added to the reaction mixture over a period of 30 minutes. After complete addition, the reaction mixture was stirred for 1 h at room temperature. The resultant salt which precipitated from a clear solution was removed by filtration

and then washed repeatedly with $CH_2Cl_2$ (3 x 50 mL). The different $CH_2Cl_2$ aliquots were combined and washed with distilled water (2 x 100 mL) and dried with anhydrous magnesium sulphate. Evaporation of the dichloromethane solvent gave N-(2,2-dimethyl-3-hydroxypropyl)-p-bromomethylbenzamide (29.91 g, 98%), as an intermediate product.

Cyclization of the amide to the corresponding oxazoline was achieved by the gentle addition of $SOCl_2$ (19 mL, 31.19 g, 0.2621 mol) in a single portion to the solid amide (25.01 g, 0.0874 mol) at 0 °C under inert atmosphere. When the vigorous reaction had subsided, the yellow solution was stirred at room temperature for 3 h. The yellow solution was added to cold diethyl ether (300 mL). The resulting white hydrochloride salt which precipitated upon stirring was filtered. Cold 20% NaOH (150 mL) was added dropwise to the hydrochloride salt in water (100 mL) to neutralize the acidic salt solution. The product was extracted from the cloudy solution with diethyl ether (3 x 200 mL) and the diethyl ether solution was dried with anhydrous magnesium sulphate. Removal of the diethyl ether on a rotary evaporator gave a white solid as the crude product. Recrystallization of the crude product from toluene gave 22.02 g (94%) of pure 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as white crystals. $R_f$ = 0.56 (80% ethyl acetate-hexane); mp = 77-78.5 °C (lit mp = 77-78 °C)[140]. FTIR: 1647 $cm^{-1}$ (C=N). $^1H$ NMR ($CDCl_3$): δ = 1.36 (s, 6H, $(C\underline{H}_3)_2$-C); 4.09 (s, 2H, $CH_2$-O); 4.58 (s, 2H, $C\underline{H}_2$-Br); 7.39-7.41 (dd, 2H, aromatic C-H); 7.90-7.92 ppm (dd, 2H, aromatic C-H). $^{13}C$ NMR ($CDCl_3$): δ = 28.26 [$(\underline{C}H_3)_2$-]; 45.44 ($\underline{C}H_2$-Br); 67.50 ($\underline{C}$-$(CH_3)$; 78.97 ($\underline{C}H_2$-O); 127.94-128.80 (aromatic carbons, 6C); 161.35 ppm ($\underline{C}$=N)

### 3.3.1.2 Synthesis of α-Oxazolyl Functionalized Polystyrene, (2).

All polymerization reactions were performed in Schlenk flasks under dry argon atmosphere. α-Oxazolyl functionalized polystyrene, (**2**) was synthesized by the polymerization of styrene, initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of copper(I) bromide catalyst and 2,2'-bipyridine (bpy) or N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA) as a ligand.

In a typical procedure, a Schlenk tube was successively charged with copper(I) bromide (0.0473 g, 0.3297 mmol), 2,2'-bipyridine (0.1546 g, 0.9898 mmol) and diphenyl ether (0.5 mL) and the reaction mixture was stirred at room temperature. After 5 minutes, 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) (0.0885 g, 0.3300 mmol) and degassed styrene (1.001 g, 1.1 mL, 9.601 mmol) were added successively to the reaction flask. The heterogeneous mixture was then subjected to three freeze-pump-thaw cycles to remove oxygen. Under an argon atmosphere, the reaction vessel was heated to 110 °C with stirring. Within 30 minutes period, the colour of the reaction mixture turned green and then light brown. After 12 h and upon cooling to room temperature, the resultant viscous brown reaction mixture was then quenched with THF (10 mL). The resultant green solution of the crude product was passed through a short column of silica gel to remove the catalyst and ligand impurities. The filtrate was then concentrated under reduced pressure and the polymer product was precipitated from THF solution into excess methanol. The polymer product was collected by filtration and vacuum dried under 50 °C to constant weight to give 0.9601 g, (96%) of α-oxazolyl functionalized polystyrene, (**2**) as a white solid: Percentage monomer conversion = 91%; $R_f$ = 0.21 (toluene); $M_n^{theory}$ = 3.0 x $10^3$ g/mol; $\overline{M}_n^{SEC}$ = 3.7 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.22; $I_{eff}$ = 0.89. FTIR: 1650 $cm^{-1}$ (C=N). $^1$H NMR ($CDCl_3$): δ 1.39-2.25 (m, ($C\underline{H}_3)_2$ -oxazoline, polystyryl-$C\underline{H}_2$- and -$C\underline{H}$-); 4.09-4.08; (bs, $C\underline{H}_2$-O, oxazoline) 4.25-4.42 (bs, -$C\underline{H}$Br at chain end); 6.52-7.34

(m, polystyryl aromatic –C<u>H</u>); 7.37-7.77 ppm (m, initiator aromatic -C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 28.26 [(<u>C</u>$H_3$)$_2$-]; 40.23-46.24 (polystyryl -<u>C</u>$H_2$- and –<u>C</u>H-); 67.35 (<u>C</u>-($CH_3$); 78.82 (<u>C</u>$H_2$-O); 125.56-129.46 (polystyryl aromatic carbons); 145.19-145.87 (aromatic –<u>C</u>H); 161.73 ppm (<u>C</u>=N).

Similarly, α-oxazolyl functionalized polystyrene, (**2**) was prepared in the presence of CuBr/PMDETA as the catalyst/ligand system using the following reaction stoichiometry: copper(I) bromide (0.0472 g, 0.3290 mmol), PMDETA (0.1711 g, 0.9873 mmol), diphenyl ether (0.5 mL), 2-[(4-bromomethyl)phenyl]-4, 5-dihydro-4,4-dimethyloxazole, (**1**) (0.0882 g, 0.3289 mmol) and degassed styrene (1.1 mL, 1.001 g, 9.602 mmol). The polymer product was isolated by precipitation from THF into methanol, filtered and vacuum dried to give 0.9801 g (98%) of α-oxazolyl chain end functionalized polystyrene, (**2**) as a white solid. $R_f$ = 0.21 (toluene); Percentage monomer conversion = 97%; $M_{n,}^{theory}$ = 3.0 x $10^3$ g/mol; $\overline{M}_n^{SEC}$ = 5.9 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.32; $I_{eff}$ = 0.51

### 3.3.1.3 Synthesis of α-Oxazolyl Functionalized Poly(methyl methacrylate), (3)

Similarly, the oxazolyl functionalized initiator, 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) was used as an oxazoline functionalized unimolecular initiator for methyl methacrylate polymerization in the presence of CuBr/bpy or CuBr/PMDETA as the catalyst/ligand system to afford α-oxazolyl functionalized poly(methyl methacrylate), (**3**).

In a typical reaction, copper(I) bromide (0.0429 g, 0.2991 mmol), 2,2'-bipyridine (0.1401 g, 0.8970 mmol) and xylene (0.5 mL) were added to a Schlenk flask. The reaction mixture was stirred at room temperature. After 5 minutes, 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) (0.0802 g, 0.2991

mmol) and degassed methyl methacrylate (0.9350 g, 1 mL, 9.339 mmol) were then added successively to the reaction mixture. The Schlenk reactor was subjected to three freeze-pump-thaw cycles. Under argon atmosphere, the flask was then heated at 90 °C, with stirring. The colour of the reaction mixture changed to light brown within 5 minutes. After 12 h, the polymerization was terminated by cooling the reaction flask to room temperature under argon atmosphere. The mixture was diluted with THF (10 mL) and the catalyst and ligand impurities were removed by passing the resultant green solution through a short silica gel column. The polymer was concentrated by removal of the solvent under reduced pressure. The polymer was isolated by precipitation from THF solution into hexane, filtered and vacuum dried at 50 °C to give 0.8110 g (87%) of α-oxazolyl functionalized poly(methyl methacrylate), (**3**) as a white solid: $R_f$ = 0.07 ($CH_2Cl_2$), Percentage monomer conversion = 88%; $M_n^{theory}$, = 3.1 x $10^3$; $\overline{M}_n^{SEC}$ = 7.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 2.12; $I_{eff}$ = 0.45. FTIR: 1726 (COOCH$_3$); 1645 $cm^{-1}$ (C=N). $^1$H NMR ($CDCl_3$): δ 0.81-0.99 (bs, –CCH$_3$COOCH$_3$); 1.22 (bs C-CH$_3$ oxazoline); 1.79-1.10 (m, -CH$_2$-, polymer chain); 3.32 (bs, PhCH$_2$-); 3.57 (bs, COOCH$_3$); 7.09-7.24 ppm (m, oxazoline aromatic -CH). $^{13}$C NMR ($CDCl_3$): δ 28.31 [(CH$_3$)$_2$-]; 54.36 [(CH$_3$)$_2$-C-]; 77.43 (CH$_2$-O); 128.22-129.67 (initiator aromatic -CH); 157.15 (C=N); 176.13-178.35 ppm (COOH).

### 3.3.2 Syntheses of Aromatic Carboxyl Functionalized Polymers

#### 3.3.2.1 Synthesis of α-Carboxyl Functionalized Polystyrene, (4)

The chemical conversion of α-oxazolyl functionalized polystyrene, (**2**) to the corresponding α-carboxyl polystyrene derivative, (**4**) was effected by the method outlined by Nakahama and coworkers[141].

In a typical procedure, the acid hydrolysis of α-oxazoyl functionalized polystyrene, (**2**) ($M_n$ = 3.7 x $10^3$ g/mol, 0.5501 g, 1.493 mmol) in THF (55 mL) was effected by treatment with 3 M HCl (30 mL) at reflux for 6 h. The resultant amino ester hydrochloride in THF (50 mL) was hydrolyzed by the reaction with 40 mL of 20% NaOH solution (MeOH/$H_2O$ = 1/1) and heated to reflux for 6 h. The reaction mixture was then concentrated on a rotary evaporator and the residue was added into a large excess of 3 M HCl. The white powder which precipitated was filtered, dissolved in THF and precipitated into excess methanol. The polymer product was filtered and dried in *vacuo* at 30 °C to give 0.4001 g (79%) of α-carboxyl functionalized polystyrene, (**4**) as a white solid: $R_f$ = 0 (toluene). $\overline{M}_n^{SEC}$= 3.6 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.31; $\overline{M}_n^{titr}$= 3.5 x $10^3$ g/mol. FTIR: 1691 $cm^{-1}$ (C=O). $^1$H NMR ($CDCl_3$): δ 1.28-2.27 (m, polystyryl-C<u>H</u>$_2$- and -C<u>H</u>-); 4.22-4.55 (bs -C<u>H</u>Br) at chain end); 6.54-7.33 (m, polystyryl aromatic –C<u>H</u>); 7.39 ppm (m, initiator aromatic -C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 33.73 (<u>C</u>$H_2$-); 39.22-45.80 (polystyryl -<u>C</u>$H_2$- and –<u>C</u>H-); 125.66-130.20 (polystyryl aromatic carbons); 145.28-145.59 (aromatic –<u>C</u>H); 171.17 ppm (<u>C</u>OOH)

### 3.3.3 Synthesis of Aromatic Oxazolyl Functionalized Polymers by ATRP using an Aromatic Oxazolyl Functionalized Initiator Precursor.

#### 3.3.3.1 Aromatic Oxazolyl Functionalized Initiator Precursor: Synthesis of 4,5-Dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]-oxazole, (5).

**4-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)benzophenone**: The preparation of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone from 4-benzolylbenzoic acid was carried out according to the procedures outlined by Quirk and Summers[19], Meyers and coworkers[138] and Shchepinov and coworkers[139], with modifications. In a typical procedure, under argon atmosphere, 4-benzoylbenzoic acid (15.01 g, 0.0664 mol) in dry $CH_2Cl_2$ (150 mL) was added to a three-necked round bottom flask equipped with a reflux condenser and a calcium chloride tube. Thionyl chloride (45 mL, 27.59 g, 0.6204 mol) was added in a single portion to the reaction flask. The reaction mixture was heated to reflux for 12 h, with stirring. The resulting clear solution was concentrated by the removal of $SOCl_2$ and $CH_2Cl_2$ by distillation. Removal of the residual amount of $SOCl_2$ as an azeotrope with toluene (100 mL) gave quantitative yields of the corresponding acid chloride mp = 94.0-94.5°C (lit mp = 93.0-93.5°C)[19]

Under an argon atmosphere, a solution of 4-benzoylbenzoyl chloride (15.51 g, 0.0634 mol) in dry dichloromethane (150 mL) was added into a 500 mL two-necked round bottom flask. The solution was cooled to 0 °C, followed by the dropwise addition of 2-amino-2-methyl-1-propanol (11.27 g, 0.1270 mol) solution in $CH_2Cl_2$ (50 mL) over a period of 30 min. After complete addition, the reaction mixture was stirred at room temperature for 1 hour. The white precipitate which formed was filtered and the residue was washed with dichloromethane (3 x 100 mL). The different $CH_2Cl_2$ fractions were combined and washed with $H_2O$ and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave quantitative yields

of N-(2-hydroxy-1,1-dimethylethyl)-4-benzoylbenzamide as white crystals. mp = 151.5-152.7 0 °C.

To cyclize the amide, thionyl chloride (16.1 mL, 9.910 g, 0.1378 mol) was gently added in a single portion to the solid amide (18.02 g, 0.0605 mol) in a 250 mL round bottom flask. When the vigorous reaction had subsided, the light yellow solution was stirred at room temperature for 6 h and then poured into cold diethyl ether (300 mL). The resulting white hydrochloride salt which precipitated upon stirring was filtered. The hydrochloride salt was dissolved in water (150 mL). Cold 20% aqueous sodium hydroxide (100 mL) was added dropwise to the aqueous solution of the hydrochloride salt at 0 °C until neutralization was complete. The product was extracted with diethyl ether (3 x 100 mL) and dried over anhydrous $MgSO_4$. Evaporation of the solvent gave the crude product as a white crystalline solid. Recrystallization of the crude product from diethyl ether:hexane (4:1) gave 14.50 g (86%) of pure 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone as white needle-like crystals. $R_f$ = 0.33 (20% ethyl acetate-hexanes); mp = 99.5-100.5 °C (lit mp = 99.3-100.8 °C)[19]. FTIR: 161.69 (C=O), 1641 $cm^{-1}$ (C=N); $^1$H NMR ($CDCl_3$): δ = 1.39 (s, 6H, ($CH_3$)$_2$-C); 4.14 (s, 2H, $CH_2$-O); 7.24-8.05 (m, 6H, aromatic C-H); 7.89-7.92 ppm (m, 3H, aromatic C-H). $^{13}$C NMR ($CDCl_3$): δ = 29.40 [($CH_3$)$_2$-]; 69.57 [C-($CH_3$)$_2$]; 79.77 ($CH_2$-O); 129.29-130.54 (aromatic carbons, 6C); 144.28 (CHPhPhR, aromatic carbon); 161.85 $cm^{-1}$ (C=N); 181.81 ppm (C=O).

**4,5-Dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole,** (**5**): The direct conversion of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone to 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) was effected by the classic Wittig reaction[142]. Under an argon atmosphere, freshly distilled dry THF (200 mL) was added into a 500 mL three-necked round bottom flask charged with methyltriphenylphosphonium bromide (18.36 g, 0.0136 mol) and a stirrer bar. The reaction mixture was degassed with argon for 5 min and then cooled to 0 °C.

Upon the addition of methyl lithium (32 mL, 0.0136 mol, 1.4 M solution in diethyl ether) via a syringe, the reaction mixture changed to a yellow colour. The mixture was then stirred at room temperature for 4 hours to complete the formation of the corresponding ylide. The resulting ylide solution was subsequently added dropwise via a cannula to a solution of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)-benzophenone (12.01 g, 0.0429 mol) in freshly distilled, dry THF (50 mL). The resulting milky white reaction mixture was allowed to stir at room temperature. After 15 min, the white milky reaction mixture was quenched with methanol (20 mL). After removal of the solvent in *vacuo*, the viscous residue was purified by silica gel column chromatography using ethyl acetate:hexane (1:9) as an eluent in the presence of small amounts of triethylamine ($Et_3N$). The solvent was removed in *vacuo* to give the crude product as a white solid. Recrystallization of the crude product from hexane gave 10.51 g (88%) of pure 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) as fine white crystals. $R_f$ = 0.45, ethyl acetate-hexanes (1.4); mp = 77.2-77.7°C (lit mp = 77.1-78.8 °C)[19]; FTIR ($cm^{-1}$): 1641 (C=N); $^1$H NMR ($CDCl_3$): δ = 1.38 (s, 6H, [C<u>H</u>$_3$)$_2$-C]; 4.10 (s, 2H, C<u>H</u>$_2$-O); 5.50 (s, 2H, C<u>H</u>$_2$=C-); 7.32-7.38 (m, 6H, aromatic C-<u>H</u>); 7.89-7.92 ppm (m, 3H, aromatic C-<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ = 28.40 [(<u>C</u>H$_3$)$_2$-]; 67.58 (<u>C</u>-(CH$_3$); 79.07 (<u>C</u>H$_2$-O); 115.27 (H$_2$<u>C</u>=C-); 127.29-128.54 (aromatic carbons, 6C); 140.96 (-<u>C</u>-CON, aromatic); 144.28 (<u>C</u>HPhPhR, aromatic); 149.40 (-<u>C</u>=CH$_2$); 161.81 ppm (<u>C</u>=N).

### 3.3.3.2 Synthesis of α-Oxazolyl Functionalized Polystyrene, (7).

α-Oxazolyl functionalized polystyrene, (**7**) was prepared by using an oxazolyl functionalized initiator adduct, (**6**) formed *in situ* by the reaction of 1-(bromomethyl)benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) in the presence of CuBr/2,2'-bipyridine as a catalyst system, as initiator for styrene polymerization by ATRP methods.

In a typical procedure, a Schlenk flask was successively charged with copper(I) bromide (0.0560 g, 0.3904 mmol), 2,2'-bipyridine (0.1830 g, 0.1172 mmol), 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) (0.1083 g, 0.3905 mmol), (1-bromoethyl)benzene (0.0723 g, 0.3907 mmol) and freshly distilled xylene (0.5 mL). The reaction mixture was stirred for 5 minutes at room temperature and then subjected to three freeze-pump-thaw cycles. The reaction flask was purged with argon and heated at 110 °C for 1 h, with stirring. The green reaction mixture which formed was cooled to room temperature. Freshly distilled, dry, degassed styrene (1.182 g, 1.3 mL, 11.35 mmol) was added to the reaction mixture, followed by heating for an additional 24 hours at 110°C. The reaction mixture was cooled to room temperature and quenched with THF (10 mL). The crude polymer product was purified by passing the resultant green solution through a short silica gel column to remove catalyst and ligand impurities. The resultant solution was concentrated in *vacuo* and the polymer was precipitated into excess methanol, filtered and vacuum dried to give 1.230 g (73%) of α-oxazolyl functionalized polystyrene, (**7**): $R_f$ = 0.22 (toluene); Percentage monomer conversion = 85%; $M_n^{theory}$ = 3.0 x $10^3$ g/mol; $\overline{M}_n^{SEC}$ = 3.9 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ =1.42; $I_{eff}$ = 0.78. FTIR: 1648 $cm^{-1}$ (C=N). $^1$H NMR ($CDCl_3$): δ 1.21 [C-($C\underline{H}_3$)$_2$- oxazoline]; 1.22-2.45 (m, polystyryl -$C\underline{H}_2$- and -C<u>H</u>-); 4.08-4.09 (bs, 2H, oxazoline, $C\underline{H}_2$-O); 4.24-4.56 (bs, -C<u>H</u>Br at chain end); 6.52-7.34 (m, polystyryl aromatic –C<u>H</u>); 7.81-8.78 ppm (m, initiator aromatic -C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 28.26 [C-($\underline{C}H_3$)$_2$, oxazoline ring]; 31.36 [(-$\underline{C}H_3$)- initiator]; 40.23-46.24

(polystyryl -$\underline{C}H_2$- and –$\underline{C}$H-); 67.35 [$\underline{C}$-$(CH_3)_2$]; 78.82 ($\underline{C}H_2$-O); 125.56-129.46 (polystyryl aromatic carbons); 145.19-145.87 (aromatic carbons); 161.73 ppm ($\underline{C}$=N).

However, similar synthesis of α-oxazolyl functionalized polystyrene, (**7**) in the presence of CuBr/PMDETA as a ligand, produced no polymer product, even after reaction time of 24 h in both diphenyl ether or xylene as solvents.

#### 3.3.3.3 Synthesis of α,ω-Bis(oxazolyl) Functionalized Polystyrene, (8)

The preparation of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) was achieved by the *in situ* post ATRP chain end transformation reaction between α-oxazolyl functionalized polystyrene, (**7**) and 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethyl)-phenyl]oxazole, (**5**).

In a typical procedure, a Schlenk flask, containing stirrer bar, was charged with copper(I) bromide (0.0496 g, 0.3458 mmol), 2,2'-bipyridine (0.1620 g, 1.037 mol), 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) (0.0959 g, 0.3458 mmol), (1-bromoethyl)benzene (0.0640 g, 0.3458 mmol) and xylene (0.5 mL). The flask was degassed by three freeze-pump thaw cycles. Under an argon atmosphere, the reaction mixture was heated at 110 °C for 1 h. The reaction was monitored by TLC analysis by monitoring the disappearance of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethyl)phenyl]oxazole, (**5**). The reaction mixture was then cooled to room temperature. Freshly distilled styrene (1.091 g, 1.2 mL, 10.47 mmol) was added to the green reaction mixture under positive argon pressure using a degassed stainless steel syringe. The reaction mixture was heated at 110 °C for 24 h to ensure complete monomer conversion, as determined by GC analysis. The Schlenk flask was withdrawn from the oil bath and cooled to room temperature. Under argon atmosphere, an excess of 4,5-dihydro-4,4-dimethyl-2-

[4-(1-phenylethenyl)phenyl]oxazole, (**5**) (0.1101 g, 0.3970 mmol) in xylene (1 mL) was added to the reaction mixture. The reaction mixture was further heated at 110 °C for 24 h. The flask was then cooled to room temperature and the contents were dissolved in THF (10 mL). The resulting green solution was passed through a column of neutral alumina to remove the metal-ligand complex impurities. Evaporation of the solvent in *vacuo* gave a viscous product which was dissolved in a small amount of THF. The polymer product was precipitated from THF into an excess of methanol, filtered and dried at 30 °C under vacuum for 24 hours to give 0.7210 g (72%) of pure α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) as a white solid: Percentage monomer conversion = 91%; $R_f$ = 0.21 (toluene); $M_n^{theory}$ = 3.0 x $10^3$ g/mol; $\overline{M}_n^{SEC}$ = 4.3 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.45; $I_{eff}$ = 0.69;. FTIR: 1649 $cm^{-1}$(C=N). $^1$H NMR ($CDCl_3$): δ 1.02-1.26 (bs, -C<u>H</u>$_3$, initiator); 1.43-2.25 (m, (C<u>H</u>$_3$)$_2$- oxazoline, polystyryl-C<u>H</u>$_2$- and -C<u>H</u>-); 4.10-4.12 (bs, 4H, oxazoline $CH_2$-O); 7.82-8.25 ppm (m, polystyryl aromatic –C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 28.25 [(<u>C</u>H$_3$)$_2$-, oxazoline group]; 30.12 (-<u>C</u>H$_3$, initiator); 40.23-46.23 (polystyryl -<u>C</u>H$_2$- and –<u>C</u>H-); 68.34 [<u>C</u>-(CH$_3$)$_2$]; 78.92 (<u>C</u>H$_2$-O); 125.56-129.46 (polystyryl aromatic carbons); 145.18-145.87; 161.74 ppm (<u>C</u>=N).

### 3.3.4 Syntheses of Aromatic Carboxyl Functionalized Polymers

The chemical transformations of α-oxazolyl functionalized polystyrenes, (**7**) and α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) to the corresponding carboxyl functionalized polymers were performed using a method outlined by Nakahama and coworkers[141].

### 3.3.4.1 Synthesis of α-Carboxyl Functionalized Polystyrene, (9)

In a typical procedure, α-carboxyl functionalized polystyrene, (**9**) was prepared as follows: A solution of α-oxazolyl functionalized polystyrene, (**7**) ($M_n$ = 4.0 x $10^3$ g/mol, 1.001 g, 0.2497 mmol) in THF (55 mL) was added into a 250 mL round bottomed flask equipped with a reflux condenser. Aqueous hydrochloric acid (3 M, 50 mL) was then added in a single portion and the reaction mixture was heated to reflux for 6 h. The reaction mixture was then concentrated under reduced pressure. The crude polymer product was then dissolved in THF (5 mL), precipitated into excess methanol and isolated as the polymeric amino ester derivative. To hydrolyze the resultant polymeric ester derivative, a solution of 20% aqueous NaOH in methanol/water =1:1 (60 mL) was added to the solution of the polymeric amino ester derivative in THF (50 mL) and the reaction mixture was heated to reflux for 6 h. The reaction mixture was then concentrated on a rotary evaporator and the resultant residue was poured into a large excess of 3 M aqueous hydrochloric acid. The resulting white polymer product was filtered, dissolved in a small amount of THF and precipitated in excess methanol. The resultant polymer product which precipitated from the solution was filtered and dried in *vacuo* at 30 °C to give 0.8101 g (81 %) of α-carboxyl functionalized polystyrene, (**9**) as a white solid: $R_f$ = 0 (toluene); $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.47; $\overline{M}^{titr}$ = 3.7 x $10^3$ g/mol. FTIR: 1692 $cm^{-1}$ (C=O). $^1$H NMR ($CDCl_3$): δ 0.81-0.99 (bs, C<u>H</u>$_3$-, initiator); 1.22-2.61 (m, polystyryl -C<u>H</u>$_2$- and -C<u>H</u>-); 4.24-4.56 (bs, -C<u>H</u>Br at chain end); 6.54-7.26 (m, polystyryl aromatic –C<u>H</u>); 7.41-7.81 (m, initiator aromatic -C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 30.55 (<u>C</u>H$_3$-, initiator); 40.29-46.35 (polystyryl -<u>C</u>H$_2$- and –<u>C</u>H-); 125.45-130.07 (polystyryl aromatic carbons); 145.04-145.97 (aromatic –<u>C</u>H); 171.86 ppm (<u>C</u>OOH)

### 3.3.4.2 Synthesis of α,ω-Bis(carboxyl) Functionalized Polystyrene, (10)

Similarly, α,ω-bis(carboxyl) functionalized polystyrene, (**10)** was prepared according to the method of Nakahama and coworkers[141]: The acid hydrolysis of α,ω-dioxazolyl functionalized polystyrene, (**8**) ($M_n$ = 4.4 x $10^3$ g/mol, 0.8101 g, 0.1843 mmol) solution in THF (50 mL) was achieved by heating the oxazolyl functionalized polystyrene with 3 M HCl (35 mL) under reflux for 12 h. A solution of 20% NaOH (100 mL) was added to the resulting polymeric amino ester in THF (30 mL) to effect the base hydrolysis reaction. After acidification, the resultant polymer was obtained by precipitation of the mixture into methanol, filtered and dried in *vacuo* at 30 °C to give 0.7102 g (91%) of α,ω-bis(carboxyl) functionalized polystyrene, (**10**) as a white solid: $R_f$ = 0 (toluene); $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.51; $\overline{M}_n^{titr}$ = 3.9 x $10^3$ g/mol; FTIR: 1690 $cm^{-1}$ (C=O). $^1$H NMR ($CDCl_3$): δ 1.15-1.20 (bs, C-C<u>H</u>$_3$, initiator), 1.29-2.45 (m, polystyryl -C<u>H</u>$_2$- and -C<u>H</u>-); 6.54-7.33 ppm (m, polystyryl aromatic –C<u>H</u>, initiator aromatic -C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 30.56 (<u>C</u>$H_3$- initiator); 30.27 (<u>C</u>$H_2$); 38.99-46.36 (polystyryl -<u>C</u>$H_2$- and –<u>C</u>H-); 125.44-130.11 (polystyryl aromatic carbons); 145.14-145.89 (aromatic –<u>C</u>H); 172.02 ppm (<u>C</u>OOH).

### 3.3.5 Synthesis of Aromatic Oxazolyl Functionalized Polymers by ATRP using an Aromatic Dioxazoyl Functionalized Initiator Precursor.

#### 3.3.5.1 Aromatic Dioxazolyl Functionalized Initiator Precursor: Synthesis of of 1,1-Bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (11).

**2-(4-Bromophenyl)-4,4-dimethyl-2-oxazoline**: The intermediate oxazoline derivative, 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline, was synthesized according to the general method for synthesis of oxazolines as outlined by Meyers and coworkers[138] and Shchepinov and coworkers[139], with modifications. Under an inert atmosphere, 4-bromobenzoic acid (25.01 g, 0.1250 mol) in thionyl chloride (28 mL, 45.01 g, 0.3750 mol) was heated to reflux for 6 h. The excess $SOCl_2$ was removed by distillation and the remaining dark oil was dissolved in toluene. After removal of the remainder of $SOCl_2$ by forming an azeotrope with toluene, the resultant 4-bromobenzoyl chloride (27.13 g) was obtained in quantitative yields as a light brown solid. The acid chloride was then used for the next reaction without further purification.

Under an argon atmosphere, 4-bromobenzoyl chloride (24.81 g, 0.1100 mol) was dissolved in dry $CH_2Cl_2$ (100 mL) and the reaction was cooled to 0 °C. A solution of 2-amino-2-methyl-1-propanol (19.07.g, 0.2212 mol) in $CH_2Cl_2$ (100 mL) was then added dropwise using an addition funnel to the reaction mixture over a period of 35 minutes. The solution was stirred at room temperature for 1 h. The white precipitate which formed was filtered and washed with $CH_2Cl_2$ (3 x 50 mL). The combined $CH_2Cl_2$ aliquots were washed with distilled water (2 x 100 mL) and dried with anhydrous $MgSO_4$. Evaporation of the dichloromethane gave 29.91 g (98%) of N-(2,2-dimethyl-3-hydroxypropyl)-p-bromomethylbenzamide as a white solid.

To convert the amide to the corresponding oxazoline derivative, $SOCl_2$ (19 mL, 31.19 g, 0.2621 mol) was added gently in a single portion to the solid amide (27.01 g, 0.2263 mol) at 0 °C. The yellow solution, which formed after the vigorous reaction had subsided, was stirred at room temperature for 3 h. Cold diethyl ether (300 mL) was then added to the yellow solution at 0 °C. The resulting white hydrochloride salt which formed was filtered and then dissolved in water (200 mL) and cooled to 0 °C. A portion of cold aqueous 5 M NaOH (150 mL) was then added dropwise, with stirring to neutralize the acidic salt solution. The product was extracted with diethyl ether (3 x 150 mL) and the organic phase was dried over anhydrous magnesium sulphate. Removal of the diethyl ether under reduced pressure gave the crude product as a white solid. Recrystallization of the crude product from hexane gave 19.11 g (82%) of pure 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline as white needle-like crystals: mp = 37.2-38.3 °C (lit mp = 37-38 °C)[138]; $R_f$ = 0.5 (80% ethyl acetate-hexane. FTIR: 1649 $cm^{-1}$ (C=N). $^1H$ NMR ($CDCl_3$): δ = 1.35 [s, 6H, ($C\underline{H}_3)_2$-C]; 4.08 (s, 2H, $C\underline{H}_2$-O); 7.50-7.53 (dd, 2H, aromatic C-H,); 7.76-7.79 ppm (dd, 2H, aromatic C-H). $^{13}C$ NMR ($CDCl_3$): δ = 28.26 [($\underline{C}H_3)_2$-]; 45.44 ($\underline{C}H_2$-Br); 67.50 ($\underline{C}$-($CH_3$); 78.97 ($\underline{C}H_2$-O); 127.94-128.80 (aromatic carbons, 6C); 161.35 ppm ($\underline{C}$=N)

**1,1-Bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol**: The general methods outlined by Quirk and coworkers[143] for the preparation of carbinol derivatives from carbonyl precursors was used to prepare 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethanol. In a typical procedure, magnesium turnings (1.150 g, 0.4792 mol) was transferred to a 500.0 mL three-necked round bottom flask equipped with an addition funnel and a reflux condenser and dried at 150 °C for 24 h and then cooled to room temperature under argon atmosphere. Dry THF (20 mL) and two granules of iodine were added to the reaction flask. Via the addition funnel, a solution of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline (10.01 g, 0.0394 mol) in dry THF (50 mL) was then added dropwise with stirring until a gently reflux was observed. The colour of the reaction mixture changed from brown to a cloudy white mixture within 5 minutes. The remaining oxazoline was then added to the

reaction mixture over a period of 30 minutes. The reaction mixture was heated to reflux for 4 hours to allow complete formation of the corresponding Grignard reagent. Upon cooling the reaction mixture to 0 °C, anhydrous ethyl acetate (1.731 g, 1.9 mL, 0.197 mmol) was added dropwise to the solution of the Grignard reagent via a degassed syringe. An exothermic reaction was observed upon addition of ethyl acetate and the colour of the reaction mixture changed to a light yellow colour. The resultant reaction mixture was heated to reflux for 4 hours and then stirred overnight at room temperature. Hydrolysis of the reaction mixture was performed by the addition of aqueous saturated ammonium chloride solution (20 mL). The reaction mixture was concentrated in *vacuo* and the product was extracted with diethyl ether (3 x 150 mL). The combined organic layers were dried over anhydrous magnesium sulphate. Removal of the solvent in *vacuo* gave a yellow residue. Purification of the crude product by silica gel chromatography using ethyl acetate:hexanes (4:1) gave 8.551 g (55%) of pure 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol as white, fluffy crystals. $R_f$ = 0.45 (ethyl acetate:hexane = 1:4); mp = 218.7-219.9 °C; FTIR ($cm^{-1}$): 3235 (-OH); 1643 (C=N). $^1$H NMR ($CDCl_3$): δ = 1.34 (s, 12H, 4 x C<u>H</u>$_3$); 1.94 (s, 3H, -COHC<u>H</u>$_3$); 2.74 (s, H, -O<u>H</u>); 4.06 (s, 4H, C<u>H</u>$_2$-O); 7.40-7.42 (dd, 4H, aromatic C-<u>H</u>); 7.83-7.86 ppm (dd, 4H, aromatic C-<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ = 28.37 [(<u>C</u>H$_3$)$_2$-]; 30.58(-COH<u>C</u>H$_3$); 67.55 [<u>C</u>-(CH$_3$)$_2$]; 79.06 (<u>C</u>H$_2$-O); 125.79-128.17 (aromatic carbons, -<u>C</u>H); 150.70 (<u>C</u>COHCH$_3$PhR, aromatic); 161.76 ppm (<u>C</u>=N). Anal: Calcd for $C_{24}H_{28}N_2O_3$: C, 73.44; H, 7.19; N, 7.14%. Found: C, 73.36; H, 6.83; N, 6.89%.

**1,1-Bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene,** (**11**). The conversion of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol to 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene was effected by the Lewis acid catalyzed dehydration reaction as outlined by Furniss and coworkers[144]. In a typical procedure, a solution of bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol (5.0 g, 0.0127 mol) in $CH_2Cl_2$ (20 mL) was added to a two-necked round-bottomed flask. Thionyl chloride (10 mL, 3.330 g, 0.0280 mol) was added to the reaction flask in a

single portion. The reaction mixture was stirred at room temperature for 1 h. After the removal of excess thionyl chloride by distillation, saturated sodium hydrogen carbonate (100 mL) was added dropwise to the reaction mixture to neutralize excess acid. The product was extracted with $CH_2Cl_2$ (3 x 100 mL) and dried with anhydrous $MgSO_4$. Evaporation of dichloromethane under reduced pressure gave a yellow, viscous residue. Purification of the viscous product by silica gel chromatography using ethyl acetate:hexanes (1:19) as eluent gave the crude product as a white solid. Recrystallization of the crude product from hexane gave 3.201 g (67%) of pure 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) as white, fluffy crystals. $R_f$ = 0.61 (ethyl acetate:hexanes = 1.4; mp = 159.2-160.9. FTIR ($cm^{-1}$): 3086, 2966, 2929, 2893 ($CH_3$-, $CH_2$-); 1641 (C=N); $^1$H NMR ($CDCl_3$): δ = 1.38 (s, 12H, 4 x -C<u>H</u>$_3$); 4.10 (s, 4<u>H</u>, $CH_2$-O); 5.55 (s, 2H, C<u>H</u>$_2$=C-); 7.32-7.35 (dd, 4H, aromatic C-<u>H</u>); 7.88-7.91 ppm ( dd, 4H, aromatic C-<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ = 28.40 [(2 x <u>C</u>H$_3$)$_2$-]; 67.61 (2 x <u>C</u>-($CH_3$); 79.10 (2 x <u>C</u>H$_2$-O); 116.23 ($H_2$<u>C</u>=C-); 127.50-128.18 (ethelylene carbon, -<u>C</u>H); 143.77 (-<u>C</u>-CON); 148.80 (-<u>C</u>=$CH_2$, ethylene carbon) and 161.28 ppm (C=N). Anal: Calcd for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48%. Found: C, 76.87; H, 7.13; N, 7.24%.

### 3.3.5.2 Synthesis of α-Bis(oxazolyl) Functionalized Polystyrene, (13)

A dioxazolyl functionalized adduct, prepared *in situ* by the reaction of (1-bromoethyl)benzene and 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (**11**) in the presence of CuBr/bpy catalyst system, was used as a dioxazolyl functionalized initiator for the polymerization of styrene to produce α-bis(oxazolyl) functionalized polystyrene, (**13**) by ATRP methods.

In a typical procedure, under an argon atmosphere, a Schlenk flask was charged with copper(I) bromide (0.0510 g, 0.3555 mmol), 2,2'-bipyridine (0.1958 g, 1.254 mmol), 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) (0.1565 g,

0.4179 mmol), (1-bromoethyl)benzene (0.0773 g, 0.4179 mmol) and freshly distilled xylene (1 mL). The reaction mixture was stirred at room temperature for 5 minutes and then subjected to three freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated at 110 °C for 1 h, with stirring. The resultant green reaction mixture was then cooled to room temperature under argon. Freshly distilled, degassed styrene (1.273 g, 1.4 mL, 12.19 mmol) was added and the reaction mixture was heated for an additional 24 hours at 110 °C. The Schlenk tube was then removed from the oil bath and cooled to room temperature. The green solution of the crude product in THF (10 mL) was passed through a short silica gel column to remove catalyst impurities. The resultant solution was concentrated in *vacuo* and the polymer product was precipitated into methanol, filtered and vacuum dried to give 1.230 g (73%) of α-bis(oxazolyl) functionalized polystyrene, (**13**) as a white solid: $R_f$ = 0.20 (toluene).

Percentage monomer conversion = 82%; $M_n^{theory}$ = 3.0 x $10^3$ g/mol; $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.47; $I_{eff}$ = 0.76. FTIR: 1649 (C=N). $^1$H NMR ($CDCl_3$): δ 0.87-122 [(bs, ($CH_3$)$_2$-] oxazoline)]; 1.22-2.19 (m, polystyrene-$CH_2$- and -CH-); 4.11-4.13; (bs, 2H, oxazoline -$CH_2$-O-); 4.25-4.62 (bs, -CHBr at chain end); 7.61-8.02 ppm (m, polystyryl aromatic –CH). $^{13}$C NMR ($CDCl_3$): δ 28.38 [($CH_3$)$_2$-, oxazoline ring]; 29.98 ($CH_3$-, initiator); 40.29-45.87 (polystyryl -$CH_2$- and –CH-); 67.35 (C-($CH_3$)$_2$]; 79.22 ($CH_2$-O); 125.45-127.90 (polystyryl aromatic carbons); 145.04-145.97 (aromatic carbons); 161.91 ppm (C=N).

### 3.3.5.3 Synthesis of α,ω-Tetrakis(oxazolyl) Functionalized Polystyrene, (14)

The synthesis of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) was effected by the *in situ* post ATRP chain end modification reaction of α-bis(oxazolyl) functionalized polystyrene, (**13**) with 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl)phenyl]ethylene, (**11**).

Under an argon atmosphere, copper(I) bromide (0.0477 g, 0.3116 mmol), 2,2'-bipyridine (0.1558 g, 0.9975 mmol), 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (**11**) (0.1245 g, 0.3325 mmol), (1-bromoethyl)benzene (0.0615 g, 0.3323 mmol) and xylene (1 mL) were added successively into a Schlenk flask. The flask was then degassed by three freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated for 1 hour in an oil bath thermostated at 110 °C. Complete consumption of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) was monitored by TLC analysis. After 1 hour, the Schlenk flask was withdrawn from the oil bath and then cooled to room temperature. Freshly distilled, degassed styrene (1.001 g, 1.1 mL, 9.602 mmol) was then added via a degassed syringe to the green reaction mixture. The reaction mixture was then heated to 110 °C for 24 hours. Upon completion of styrene consumption as evidenced by GC analysis, the reaction mixture was cooled to room temperature under argon atmosphere. An excess of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) (0.1295 g, 0.3458 mmol) in xylene (1 mL) was then added to the reaction mixture. The reaction mixture was then heated to 110 °C for 24 hours. The reaction mixture was cooled to room temperature, followed by the addition of THF (20 mL). The polymer product was separated from the catalyst impurities by passing the green solution through a short neutral alumina column. Evaporation of the solvent gave an oily product which was then dissolved in a small amount of THF. The polymer product was precipitated from THF into excess methanol, filtered and dried at 30 °C under vacuum for 24 hours to give 1.11 g (65%) of pure α,ω-tetrakis (oxazolyl)

functionalized polystyrene, (**14**) as a white solid: $R_f$ = 0.18 (toluene); Percentage monomer conversion = 94%; $M_n^{theory}$ = 3.0 x $10^3$ g/mol; $\overline{M}_n^{SEC}$ = 4.4 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48; $I_{eff}$ = 0.69. FTIR: 1651 $cm^{-1}$ (C=N). $^1$H NMR ($CDCl_3$): δ 1.09-1.12 (bs, -C<u>H</u>$_3$, initiator); 1.23-1.89 (m, (C<u>H</u>$_3$)$_2$- oxazoline, polystyryl-C<u>H</u>$_2$- and -C<u>H</u>-); 4.10-4.12; (bs, 4H, oxazoline C<u>H</u>$_2$-O); 6.56-7.38 ppm (m, polystyryl aromatic –C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 28.40 [(<u>C</u>H$_3$)$_2$-, oxazoline ring]; 30.02 (<u>C</u>H$_3$-, initiator); 40.31-46.38 (polystyryl -<u>C</u>H$_2$- and –<u>C</u>H-); 67.50 [<u>C</u>-(CH$_3$)$_2$]; 79.09 (<u>C</u>H$_2$-O); 125.45-127.92 (polystyryl aromatic carbons); 145.05-145.98 9aromatic carbons); 161.88 ppm (<u>C</u>=N).

### 3.3.6 Syntheses of Aromatic Carboxyl Functionalized Polymers.

The conversion of α-bis(oxazolyl) functionalized polystyrene, (**13**) and α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) to the corresponding α-bis (carboxyl) functionalized polystyrene, (**15**) and α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**), respectively, was effected according to a method reported by Nakahama and coworkers[141].

#### 3.3.6.1 Synthesis of α-Bis(carboxyl) Functionalized Polystyrene, (15)

In a typical procedure, a solution of α-bis(oxazolyl) functionalized polystyrene, (**13**) ($M_n$ = 3.9 g/mol, 1.002 g, 0.2458 mmol), 3 M aqueous hydrochloric acid (50 mL) and THF (55 mL) was heated to reflux for 12 h. The reaction mixture was then concentrated under reduced pressure. The resultant mixture was concentrated in vacuo, dissolved in a small amount of THF, precipitated in methanol, filtered and then vacuum dried to afford the polymeric amine ester hydrochloride derivative. A solution of 20% aqueous NaOH solution in methanol/water =1:1 (60 mL) was then added to the polymeric amine ester derivative in THF (50 mL). The reaction mixture was heated to reflux for 12 h.

After concentration of the reaction mixture in *vacuo*, the polymeric residue was poured into a large excess of 3 M aqueous hydrochloric acid. The resulting white precipitate was filtered and then precipitated from THF into excess methanol. The polymer product were filtered and dried in *vacuo* at 30 °C to give 0.8101 g (76%) of α-bis(carboxyl) functionalized polystyrene, (**15**) as a white solid: $R_f$ = 0 (toluene); $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.49; $\overline{M}_n^{titr}$ = 3.8 x $10^3$ g/mol; FTIR: 1689 $cm^{-1}$ (C=O). $^1$H NMR ($CDCl_3$): δ 1.11-1.23 (bs, C-C<u>H</u>$_3$, initiator); 1.13-2.78 (m, polystyryl-C<u>H</u>$_2$- and -C<u>H</u>-); 4.21-4.54 (bs, -C<u>H</u>Br at chain end); 6.54-7.26 (m, polystyryl aromatic –C<u>H</u>); 7.82-8.17 ppm (m, initiator aromatic -C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 30.27 (<u>C</u>H$_3$-, initiator); 40.29-46.35 (polystyryl -<u>C</u>H$_2$- and –<u>C</u>H-); 125.45-130.07 (polystyryl aromatic carbons); 145.04-145.97 (aromatic –<u>C</u>H); 171.86 ppm (<u>C</u>OOH).

### 3.3.6.2 Synthesis of α,ω-Tetrakis(carboxyl) Functionalized Polystyrene, (16)

In a typical procedure, α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) ($M_n$ = 4.4 x $10^3$ g/mol, 0.81 g, 0.1848 mmol) was dissolved in THF (50 mL) in a round bottomed flask. Upon the addition of 3 M aqueous HCl (35 mL), the reaction mixture was heated to reflux for 12 h to effect the acid catalyzed hydrolysis process. The resulting polymeric amine ester derivative was isolated and then dissolved in THF (30 mL). A portion of 20% aqueous NaOH (45 mL) was added to the reaction flask. The reaction flask was heated to reflux for 12 h to complete the saponification process. The polymer product was isolated by precipitation of the polymer residue from THF into methanol containing 3 M aqueous hydrochloric acid (200 mL). The polymer product was filtered and dried in *vacuo* at 30 °C to give 0.7101 g (91%) of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**): $R_f$ = 0 (toluene); $\overline{M}_n^{SEC}$ = 4.1 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48; $\overline{M}_n^{titr}$ = 4.0 x $10^3$ g/mol; FTIR: 1690 $cm^{-1}$ (C=O). $^1$H NMR ($CDCl_3$): δ 0.91-1.02 (bs, C-C<u>H</u>$_3$, initiator); 1.55-2.39 (m, polystyryl-C<u>H</u>$_2$- and -C<u>H</u>-); 7.61-7.78 ppm (m, polystyryl

aromatic –C<u>H</u>, initiator aromatic -C<u>H</u>). $^{13}$C NMR ($CDCl_3$): δ 30.35 (<u>C</u>$H_3$- initiator); 40.31-46.37 (polystyryl -<u>C</u>$H_2$- and –<u>C</u>H-); 125.48-130.12 (polystyryl aromatic carbons); 145.07-146.02 (aromatic –<u>C</u>H); 171.26 ppm (<u>C</u>OOH).

### 3.3.7 ATOM TRANSFER RADICAL POLYMERIZATION: POLYMERIZATION KINETIC STUDIES.

#### 3.3.7.1 Synthesis of α-Oxazolyl Functionalized Polystyrene, (2) using 2-[(4-Bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (1) as an Oxazolyl Functionalized Initiator.

Using 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as an oxazolyl unimolecular initiator, the different polymerization kinetic experiments for synthesis of α-oxazolyl functionalized polystyrene, (**2**) were conducted at different initiator concentrations with monomer to initiator concentration ratios of 50:1, 100:1 and 200:1 in the presence of CuBr/bpy or CuBr/PMDETA as the catalyst/ligand systems.

A typical procedure for the polymerization reaction which involves the monomer to initiator ratio of 50:1 is outlined as follows: Under an argon atmosphere, copper(I) bromide (0.2675 g, 1.865 mmol), 2,2'-bipyridine (0.8737 g, 5.594 mmol) and diphenyl ether (5 mL) were introduced into a Schlenk reactor. The reaction mixture was stirred for five minutes at room temperature. 2-[(4-Bromomethyl)-phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) (0.5001 g, 1.865 mmol) and styrene (9.726 g, 10.7 mL, 93.39 mmol) were then added sequentially to the reaction flask. The Schlenk flask was degassed by three freeze-pump-thaw cycles. The reaction mixture was purged with argon for 10 minutes and stirred at ambient

temperature for 5 minutes. A 1 mL aliquot was withdrawn from the reaction mixture, diluted with THF (9 mL) and subjected to gas chromatographic analysis to determine the concentration of styrene at time t = 0. The reaction flask was then heated at 110 °C. Aliquots of 1 mL samples were then withdrawn at 30 minutes intervals from the flask under positive argon pressure and diluted with THF (9 mL). The ratio of the concentration of styrene relative to THF was determined by gas chromatography (GC). After GC analysis, catalyst impurities were removed from the samples by passing the crude polymer solutions through a short alumina column. Precipitation of the different polymers from THF solution into methanol, followed by vacuum drying, gave pure α-oxazolyl functionalized polystyrene, (**2**) samples. The polymer samples were subjected to size exclusion chromatography (SEC) analyses to determine the number average molecular weight and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) for each polymer sample. Stoichiometric data for the polymerization kinetic experiments for the different ATRP reactions with $[M]_o/[I]_o$ ratios of 50:1, 100:1 and 200:1 is depicted in the following table:

**Synthesis of α-Oxazolyl Functionalized Polystyrene, (2) using CuBr/bpy as the Catalyst/Ligand System**

| $[M]_o/[I]_o$ | **1** | CuBr | bpy | Diphenyl ether | Styrene |
|---|---|---|---|---|---|
| 50:1 | 0.5001 g, 1.865 mmol | 0.2675 g, 1.865 mmol | 0.8737 g, 5.594 mmol | 5.1 mL | 9.726 g, 10.7 mL, 93.40 mmol |
| 100:1 | 0.2499 g, 0.9319 mmol | 0.1337g, 0.9320 mmol | 0.4368 g, 2.797 mmol | 5.2 mL | 9.620 g, 10.4 mL 93.38 mmol |
| 200:1 | 0.1250 g, 0.4662 mmol | 0.0669 g, 0.4664 mmol | 0.2185 g, 1.399 mmol | 5.1 mL | 9.726 g, 10.7 mL, 93.40 mmol |

Similarly, the polymerization kinetic experiments for the synthesis α-oxazolyl functionalized polystyrene, (**2**) were performed in the presence of CuBr/PMDETA as catalyst/ligand system using the following experimental data:

**Synthesis of α-Oxazolyl Functionalized Polystyrene, (2) using CuBr/PMDETA as the Catalyst/Ligand System.**

| $[M]/_o[I]_o$ | **1** | CuBr | PMDETA | Diphenyl ether | Styrene |
|---|---|---|---|---|---|
| 50:1 | 0.5051 g, 1.867 mmol | 0.2680 g, 1.868 mmol | 0.9699 g, 5.597 mmol | 5.1 mL | 9.726 g, 10.7 mL 93.40 mmol |
| 100:1 | 0.2491 g, 0.9290 mmol | 0.1340, 0.9289 | 0.4846 g, 2.796 mmol | 5.2 mL | 9.726 g, 10.7 mL 93.40 mmol |
| 200:1. | 0.1250 g, 0.4664 mmol | 0.0669 g, 0.4664 mmol | 0.2424 g, 1.399 mmol | 5.1 mL | 9.726 g, 10.7 mL, 93.40 mmol |

### 3.3.7.2. Synthesis of α-Oxazolyl Functionalized Polystyrene, (7) using 4,5-Dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (5) as an Oxazolyl Functionalized Initiator Precursor.

The polymerization kinetic experiments for the preparation of α-oxazolyl functionalized polystyrene using 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) as an oxazolyl functionalized initiator precursor in the presence of CuBr/bpy catalyst system was conducted at different monomer to initiator precursor concentration ratios of 50:1, 100:1 and 200:1. A new oxazolyl functionalized initiator adduct, (**6**), prepared *in situ* by the reaction of 1-(bromoethyl)benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) in the presence of CuBr/bpy as the catalyst system, was used as initiator for styrene polymerization by standard ATRP methods.

A typical procedure for the polymerization reaction involving monomer to initiator ratio of 50:1 is depicted as follows: Under an argon atmosphere, copper(I) bromide (0.2551 g, 1.778 mmol), 2,2'-bipyridine (0.8336 g, 5.337 mmol), (1-bromoethyl)benzene (0.3292 g, 1.779 mmol), 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethyl)phenyl]oxazole, (**5**) (0.4937 g, 1.780 mmol) and freshly distilled xylene (5 mL) were introduced into a Schlenk flask. The reaction mixture was stirred for 5 minutes at ambient temperature. The reaction mixture was then subjected to three freeze-pump-thaw cycles. Under argon atmosphere, the reaction flask was heated at 110 °C. Upon complete consumption of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethyl)phenyl]oxazole, (**5**) after 1 hour, as evidenced by the TLC analysis, the reaction mixture was cooled to room temperature. Styrene (9.264 g, 10.2 mL, 88.95 mmol) was then added via a degassed glass syringe. A 1 mL aliquot was then withdrawn from the reaction mixture and was added to THF (9 mL) to determine the amount of styrene in the sample at time t = 0 by gas chromatographic analysis. After heating the reaction mixture at 110 °C, aliquots of 1 mL sample were then withdrawn at 60 minutes intervals from the flask under

positive argon pressure and dissolved in THF (9 mL). The concentrations of residual styrene per aliquot were determined by gas chromatography (GC) using THF as a standard. Catalyst impurities were then removed by passing the solution of the crude polymer through a short alumina column after completion of GC analysis. The solution of the crude polymer was concentrated under reduced pressure, precipitated into excess methanol and vacuum dried to give pure α-oxazolyl functionalized polystyrene, (**7**) samples. The number average ($\overline{M}_n$) and weight average ($\overline{M}_w$) molecular weights and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of each polymer sample were determined by size exclusion chromatography (SEC).

The stoichiometric data for the polymerization kinetic experiments for the different ATRP reactions with $[M]_o/[I]_o$ ratios of 50:1, 100:1 and 200:1, is shown in the following table:

**Synthesis of α-Oxazolyl Functionalized Polystyrene, (7) using CuBr/bpy as the Catalyst/Ligand System**

| $[M]_o/[I]_o$ | (1-bromoethyl)-benzene | CuBr | bpy | **5** | Xylene | Styrene |
|---|---|---|---|---|---|---|
| 50:1 | 0.3478 g, 1.780 mmol | 0.2551 g, 1.779 mmol | 0.8336, 5.337 mmol | 0.4937 g, 1.780 mmol | 5 mL | 9.264 g, 10.2 mL, 88.95 mmol |
| 100:1 | 0.1736 g, 0.9382 mmol | 0.1346 g, 0.9383 mmol | 0.4396g, 2.8145 mmol | 0.2602 g, 0.9381 mmol | 5 mL | 9.726 g, 10.7 mL, 93.40 mmol, |
| 200:1 | 0.0869 g, 0.4698 mmol | 0.0674 g, 0.4699 mmol | 0.2201, 1.409 mmol | 0.1303 g, 0.4698 mmol | 5 mL | 9.726 g, 10.7 mL, 93.40 mmol |

### 3.3.7.3 Synthesis of α-Bis(oxazolyl) Functionalized Polystyrene, (13) using 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (11) as a Dioxazolyl Functionalized Initiator Precursor.

The polymerization kinetic experiments for the synthesis of α-bis(oxazolyl) functionalized polystyrene, (**13**) were effected by using 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) as a dioxazolyl functionalized initiator precursor in the presence of CuBr/bpy as a catalyst system at different monomer to initiator precursor concentration ratios of 50:1, 100:1 and 200:1. The polymerization of styrene was initiated by a new dioxazolyl functionalized initiator adduct, (**12**) which was generated *in situ* by the reaction of (1-bromoethyl)-benzene with 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl)phenyl]ethylene, (**11**) by the standard ATRP methods.

In a typical procedure, the polymerization reaction involving monomer to initiator of 50:1 reaction is outlined as follows: Under an argon atmosphere, copper(I) bromide (0.2460 g, 1.715 mmol), 2,2'-bipyridine (0.8036 g, 5.145 mmol), (1-bromoethyl)benzene (0.3478 g, 1.714 mmol), 1,1-bis[(2-(4,4-dimethyl-1,3-oxazolyl))phenyl)ethylene, (**11**) (0.6419 g, 1.715 mmol) and freshly distilled xylene (5 mL) were added sequentially into a Schlenk flask. The reaction mixture was stirred for 5 minutes at ambient temperature and then degassed by three freeze-pump-thaw cycles. The reaction flask was heated at 110 °C for 1 hour, under argon atmosphere. The reaction mixture was then cooled to room temperature. Upon complete consumption of 1-bis[(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl)ethylene, (**11**), as evidenced by TLC analysis, dry, degassed styrene (8.923 g, 9.8 mL, 85.67 mmol) was then added using a degassed glass syringe. The reaction mixture was stirred at room temperature for 5 minutes. A 1 mL aliquot was withdrawn from the reaction mixture, diluted with THF (9mL) and the resultant mixture was subjected to gas chromatographic analysis to determine the concentration of styrene at time t = 0. The reaction mixture was then heated at

110 °C. Under argon atmosphere, 1 mL aliquots of sample were withdrawn in 60 minutes intervals from the Schlenk flask and dissolved in THF (9 mL). The concentrations of residual styrene per aliquot were determined by gas chromatography (GC). The catalyst impurities were removed by passing the resultant green solution of the crude polymer product through a short alumina column. The solution of each crude polymer product was concentrated in *vacuo*, precipitation from THF into excess methanol and vacuum dried to give pure α-bis(oxazolyl) functionalized polystyrene, (**13**). Size exclusion chromatography (SEC) was employed to determine the number and weight avarage molecular weights ($\overline{M}_n$ and $\overline{M}_w$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) of each polymer sample. The following table depicts the polymerization kinetic data for the different ATRP reactions with $[M]_o/[I]_o$ ratios of 50:1, 100:1 and 200:1:

**Synthesis of α-Bis(oxazolyl) Functionalized Polystyrene, (13) using CuBr/bpy as the Catalyst/Ligand System.**

| $[M]_o/[I]_o$ | 1-(bromoethyl)-benzene | CuBr | bpy | **11** | Xylene | Styrene |
|---|---|---|---|---|---|---|
| 50:1 | 0.3170 g, 1.714 mmol | 0.2460 g, 1.715 mmol | 0.8036 g, 5.145 mmol | 0.6419 g, 1.714 mmol | 4 mL | 8.923 g, 9.8 mL, 85.67 mmol, |
| 100:1 | 0.1291 g, 0.6976 mmol | 0.1001 g, 0.6977 mmol | 0.3268 g, 2.093 mmol | 0.2612 g, 0.6975 mmol | 4 mL | 7.286 g, 8.0 mL, 69.76 mmol, |
| 200:1 | 0.0647 g, 0.3496 mmol | 0.0516 g, 0.3497 mmol | 0.1639 g, 1.049 mmol | 0.1310 g, 0.3498 mmol | 4 mL | 7.286 g, 8.0 mL, 69.76 mmo1 |

# CHAPTER 4

# RESULTS AND DISCUSSION

## 4.1 ATOM TRANSFER RADICAL POLYMERIZATION: SYNTHESES OF CHAIN END FUNCTIONALIZED POLYMERS.

The heterogeneous polymerization of styrenic, acrylate, methacrylate, acrylonitrile, methacrylamide and 4-vinylpyridine monomers by the atom transfer radical polymerization (ATRP) method permits the synthesis of well defined polymers with controlled number average molecular weight, molecular weight distribution, chain functionality, polymer architecture and composition[11]. In a typical reaction, ATRP entails the reversible homolytic cleavage of a carbon-halogen bond of the organo halide initiator molecule, catalyzed by the transition metal salt complexed with a multidentate nitrogen ligand, followed by the successive monomer insertion into the carbon halogen bond to form the desired polymer[7-11].

Functionalized polymers have been used for different applications in technological areas[1,2,11] such as nanotechnology, biotechnology, surface modification, adhesion, coatings, polymer compatibilization and block copolymer synthesis. ATRP has emerged as the most robust controlled radical polymerization method to prepare chain end functionalized polymers with controlled number average molecular weight ($\overline{M}_n$), molecular weight distribution ($\overline{M}_w/\overline{M}_n$), chain end functionality, topology and architecture[4,11]. In ATRP reactions, the $\overline{M}_n$ value for each polymer sample can be predetermined using the following equation[4,11]:

$M_n^{theory}$ = % conversion/100 $[M]_o/[I]_o M_{wm} + M_{wI}$, where $M_{wm}$ and $M_{wI}$ represent the average molecular weight of monomer and initiator, respectively.

Different ATRP methods are documented for the preparation of functionalized polymers, namely:

(a) The polymerization of functionalized monomers.

(b) Post polymerization chemical transformation of functional groups along the polymer backbone.

(c) The chemical transformation of the halogen chain end functionality into different functional groups by different organic reactions.

(d) Post polymerization coupling of chain end functionalized polymers.

(e) The use of functionalized initiators for the polymerization of styrenic, acrylate, methacrylate, acrylonitrile, methacrylamide and 4-vinylpyridine monomers.

In the ATRP method, the use of an organohalogen compound as the initiator results in the incorporation of the alkyl group fragment at the α-terminus of the polymer chain, with the halogen atom at the ω-end of the chain[7]. Thus, by using an appropriate functionalized initiator, the preparation of a wide range of chain end functionalized polymers, with the functional group specifically introduced at the α-terminus of the polymer chain is possible by ATRP methods[4,7-11]. For successful ATRP reactions, the functional group on the initiator must not interfere with any aspect of the polymerization process[7]. In particular, the initiator functional group must not complex with the catalyst. Many alkyl halides and organosulfonyl halides bearing functional groups such as the hydroxyl, amine, esters, thiols and allyl groups have been employed readily as functionalized initiators in ATRP reactions to form chain end functionalized polymers with the

functional groups regiospecifically introduced at the α-terminus of the polymer chain end[7-11].

The current thesis research work outlines the synthesis of a series of α-oxazolyl functionalized polymers by ATRP methods using three different oxazolyl functionalized initiator systems. The different oxazoline derivatives were used as oxazolyl functionalized initiators or initiator precursors for the ATRP of styrene or methyl methacrylate. The preparation of oxazolyl chain end functionalized polymers by ATRP methods were conducted using the following synthesis strategies:

(a) The synthesis of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyl-oxazole, (**1**) and its direct use as an oxazolyl functionalized initiator for the synthesis of α-oxazolyl functionalized polystyrene, (**2**) and poly(methyl methacrylates), (**3**) in the presence of copper(I) bromide/bpy or copper(I) bromide/PMDETA as the catalyst system.

(b) The synthesis of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]-oxazole, (**5**) and its utility as an aromatic oxazolyl functionalized initiator precursor for the preparation of α-oxazolyl functionalized polystyrene, (**7**) by atom transfer radical polymerization methods. The use of a new oxazolyl initiator adduct, (**6**), prepared *in situ* by the reaction of (1-bromoethyl) benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) as the initiator for the ATRP of styrene, provides a new method for the synthesis of the corresponding α-oxazolyl functionalized polystyrene, (**7**).

(c) The novel synthesis of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]-ethylene, (**11**) and its use as an aromatic dioxazolyl functionalized initiator precursor for the synthesis of α-bis(oxazolyl) functionalized polystyrene,

(**13**) by ATRP methods. The utilization of the new dioxazolyl functionalized initiator adduct, (**12**), obtained by the *in situ* reaction of (1-bromoethyl)-benzene with 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**), as initiator for the ATRP of styrene provides a unique synthetic route for the preparation of α-bis(oxazolyl) functionalized polystyrene, (**13**).

The controlled/"living" nature of each ATRP reaction leading to the preparation of the different oxazolyl chain end functionalized polystyrenes was also investigated by evaluating the polymerization kinetic data for each polymerization reaction.

The preparation of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) and α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) by post ATRP chain end transformation reactions was conducted via the following synthetic pathway:

(a) The atom transfer radical polymerization of styrene initiated by the appropriate new oxazolyl functionalized initiator adduct derived from an appropriate oxazolyl functionalized 1,1-diphenylethylene derivative.

(b) The addition of the appropriate oxazolyl substituted 1,1-diphenylethylene compound to the ω-terminus of the polymer chain at the end of the polymerization process.

The preparation of aromatic carboxyl chain end functionalized polystyrenes from the appropriate oxazolyl chain end functionalized polystyrene precursors was achieved in quantitative yields by using successive acid and base catalyzed hydrolysis methods, followed by the final acidification reactions.

### 4.1.1 Syntheses of Aromatic Oxazolyl Functionalized Polymers by ATRP using an Oxazolyl Functionalized Initiator.

In industry and academia, oxazoline functionalized polymers can be used as catalysts, sensors, separating systems, enzymatic bioconjugates and drug carriers in many technological applications[145-147]. The oxazoline termini on polymers can be incorporated into many different polymer architectures such as graft copolymers, block copolymers, star-shaped and hyperbranched crosslinked networks[148-149]. Well defined oxazolyl chain end functionalized polymers have been readily prepared by anionic polymerization processes[19] and nitroxide mediated free radical polymerization[53] methods. However, there are few papers in the literature which cover the synthesis of well defined oxazolyl chain end functionalized polymers by ATRP methods, using the oxazolyl functionalized initiator method. Recently, Pionteck and coworkers[12] prepared oxazolyl chain end functionalized polystyrene using 4-(1,3-oxazoline-2-yl)phenyl-4-(1-bromoethyl)-benzoate and 2-(1-bromoethyl)-1,3-oxazoline as oxazolyl functionalized initiators for the styrene polymerization by the ATRP methods. Zhang and coworkers[13] employed 2-bromomethyl-4,5-diphenyloxazole as an initiator for the preparation of $\alpha$-oxazole functionalized poly(methyl methacrylate) in the presence of copper bromide/bpy catalyst complex.

The present study outlines the synthesis of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) and its direct use as an oxazolyl functionalized initiator for the styrene polymerization by ATRP methods to produce well defined α-oxazolyl functionalized polystyrene.

#### 4.1.1.1 Oxazolyl Functionalized Initiator: Synthesis of 2-[(4-bromo-methyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (1).

The synthesis of the oxazoline compounds from carboxylic acid derivatives using the classical method outlined by Meyers and coworkers[138] proceeds in three steps:

(a) The conversion of the carboxylic acid derivative to the corresponding acid chloride by treatment with thionyl chloride ($SOCl_2$).

(b) The reaction of the acid chloride precursor with an appropriate amino alcohol to afford the hydroxy amide intermediate.

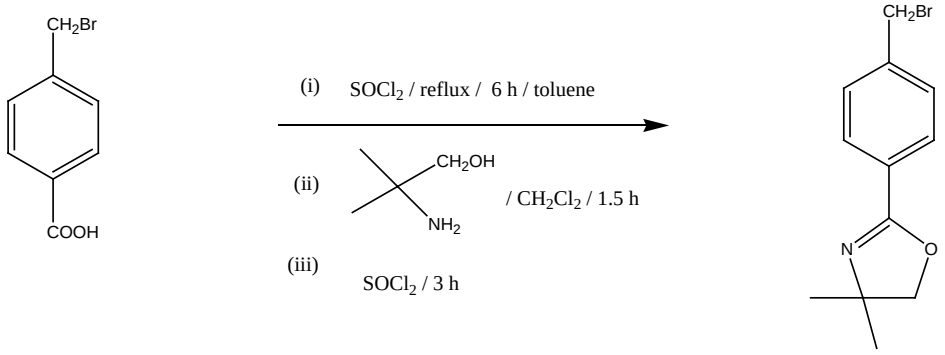
(c) Cyclization of the intermediate hydroxy amide compound by the reaction with thionyl chloride to form the desired oxazoline derivative.

In general, the use of thionyl chloride as a reagent for the conversion of the carboxylic acid moiety to the more reactive acyl chloride as well as the cyclization of the intermediate hydroxy amide compound has limitations such as the difficulty in removing excess $SOCl_2$ and the instability of the chloride group towards neutral oxygen nucleophiles such as water and methanol[150], which ultimately leads to the reduction in the yields of the desired oxazoline compounds.

The synthesis of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) was first reported by Beebeejaun[140]. However, low yields of the desired oxazoline derivative were obtained when α-bromo-p-toluic acid was used as the precursor for the oxazoline formation via the method outlined by Meyers[138]. In an attempt to reduce the deleterious effects of the $SOCl_2$ impurity during the oxazoline synthesis pathway and to increase the yield of the product, the synthesis of 2-[(4-

bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) was conducted in the absence of thionyl chloride. Using a one pot, direct synthesis method for the preparation of the intermediate hydroxyl amide derivative via the reaction of the carboxylic acid precursor with the specific amino alcohol in toluene under reflux conditions with subsequent azeotropic removal of water[139], low yields of the hydroxylamide intermediate product (10%) were obtained, even after three days of reaction. Thus, to improve the yield, the synthesis of 2-[(4-bromomethyl)-phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) was conducted using the combined methods outlined by Meyers and coworkers[138]and Shchepinov and coworkers[139], with modifications. Improvement to the synthesis method involved the quantitative removal of the thionyl chloride contamination by using toluene as cosolvent to ensure the complete azeotropic removal of thionyl chloride during each specific reaction step.

The reaction pathway for the efficient synthesis of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) is shown as follows:




(**1**)

Under an argon atmosphere, treatment of the commercially available α-bromo-p-toluic acid with $SOCl_2$ at reflux for 6 h, followed by distillation of the excess $SOCl_2$ and the azeotropic removal of the residual amounts of the $SOCl_2$ in toluene, gave quantitative yields of the corresponding acid chloride as a brown solid. A solution

of 2-amino-2-methyl-1-propanol in dichloromethane was subsequently reacted with the acid chloride at ambient temperature to give the corresponding N-(2,2-dimethyl-3-hydroxypropyl)-p-bromomethylbenzamide as white crystals in high yields (98%). The reaction of the benzamide intermediate with thionyl chloride afforded the final product as a white solid. Recrystallization of the crude product from toluene gave a high yield (94%) of pure 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as fine white crystals with a melting point of 77-78.5 °C, which is consistent with literature reported values[140].

The FTIR spectrum of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) is shown in Figure 1. The FTIR spectrum shows an absorption band at 1647 $cm^{-1}$, characteristic of the C=N bond vibrations of the oxazoline group.

The structure of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) was confirmed by $^{1}H$ NMR analysis. The $^{1}H$ NMR spectrum (Figure 2) of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) shows singlets at 1.36 and 4.09 ppm, due to the resonances of the six methyl protons $–C(C\underline{H}_3)_2$ and the two methylene protons ($C\underline{H}_2$-O) of the oxazoline functional group, respectively. The singlet at 4.58 ppm is attributed to the resonance of the methylene protons of the $C\underline{H}_2Br$ group. The doublet of doublets at 7.39-7.41 and 7.90-7.92 ppm correspond to the resonances of aromatic protons and are characteristic of p-substituted benzene rings.

The $^{13}C$ NMR spectrum (Figure 3) of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) shows the presence of a signal at 161.35 ppm, due to the carbon resonance of the C=N moiety of the oxazoline functionality. The signals at 78.97, 67.50 and 28.26 ppm are due to the resonances of the methylene carbon (-$\underline{C}H_2$-O-), quaternary carbon ($\underline{C}$-($CH_3$) and methyl carbons [-$C(\underline{C}H_3)_2$) of the oxazoline ring, respectively. The signal at 45.44 ppm is attributed to the

resonance of the methylene carbon of the –$\underline{C}H_2Br$ group. The signals between 127.94-128.80 ppm correspond to the resonances of the carbon atoms of the phenyl ring.

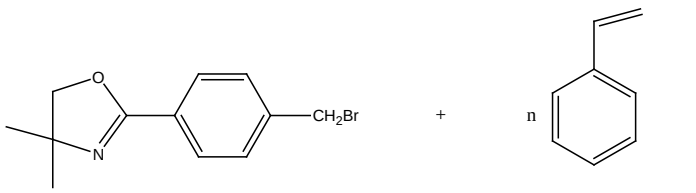
The modified synthetic route for the preparation of oxazolines is a very efficient method for the preparation of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**). High yields of the desired oxazoline product was obtained without the need for exhaustive purification techniques, such as column chromatograghy, which may lead to decomposition of product through ring opening reactions of the oxazoline. Spectroscopic evidence confirms the formation of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) which was subsequently employed as an oxazolyl functionalized initiator in the preparation of α-oxazolyl functionalized polystyrene, (**2**) and α-oxazolyl functionalized poly(methyl methacrylate), (**3**), respectively.

#### 4.1.1.2 Synthesis of α-Oxazolyl Functionalized Polystyrene, (2).

Preliminary results by Beebeejaun[140] described the initiation of styrene and methyl methacrylate polymerization using 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as a useful ATRP method for the synthesis of well defined α-oxazolyl functionalized polymers. However, the complete synthesis reactions and polymerization kinetic data were not fully reported. The present research describes a detailed study of a series of ATRP reactions leading to the preparation of α-oxazolyl functionalized polymers using 2-[(4-bromomethyl)-phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as an oxazolyl functionalized initiator for the solution polymerization of styrene and methyl methacrylate in the presence of CuBr/bpy or CuBr/PMDETA catalyst systems.

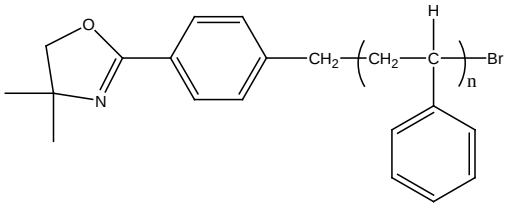
The synthesis of α-oxazolyl functionalized polystyrene, (**2**) was performed by the polymerization of styrene using 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-

dimethyloxazole, (**1**) as the oxazolyl functionalized initiator in the presence of CuBr/bpy catalyst system in diphenyl ether according to the following reaction scheme:




(**1**)

CuBr / bpy | 110 °C / diphenyl ether / 12 h




(**2**)

Quantitative yields of α-oxazolyl functionalized polystyrene, (**2**) were obtained, as evidenced by TLC analysis ($R_f$ = 0.21, toluene). No unfunctionalized polystyrene ($R_f$ = 0.99, toluene) was detected in the polymer product.

Figure 4 depicts a monomodal size exclusion chromatogram of α-oxazolyl functionalized polystyrene, (**2**) which corresponds to a number average molecular weight value of $\overline{M}_n^{SEC}$ = 3.7 x $10^3$ g/mol and a narrow molecular weight distribution of $\overline{M}_w/\overline{M}_n$ = 1.22. However, the number average molecular weight was higher than the theoretically predicted values ($M_n^{theory}$ = 3.0 x $10^3$ g/mol), calculated by the following equation: $M_n^{theory}$ = % conversion/100 $[M]_o/[I]_o M_{wm}$ + $M_{wI}$, where $M_{wm}$ and $M_{wI}$ represent the average molecular weight of monomer and

initiator, respectively. The slight deviation of the experimental $\overline{M}_n$ value from the theoretical $M_n$ value could be attributed to side reactions, such as the complexation reaction between the nitrogen atom of the oxazolyl moiety and the transition metal catalyst complex, which ultimately reduces the concentration of the initiating radicals[3],[151-152]. However, the electronic factors conferred by the electron withdrawing oxazoline group did not have any significant effects on the control of the polymerization reaction, as evidenced by the narrow molecular weight distribution of the resultant polystyrene ($\overline{M}_w/\overline{M}_n$ = 1.22).

The FTIR spectrum (Figure 5) of α-oxazolyl functionalized polystyrene, (**2**) shows the presence of an absorption band at 1650 $cm^{-1}$, due to the C=N absorption of the oxazoline group, indicating the incorporation of the oxazoline ring at the end of the polymer chain.

The $^1H$ NMR of α-oxazolyl functionalized polystyrene, (**2**) is depicted in Figure 6. The presence of a broad singlet at 4.08-4.09 is attributed to the resonance of two methylene protons (-C<u>H</u>$_2$-O-) of the oxazoline moiety. The broad signal at 4.25-4.42 ppm, is due to the resonance of the methine proton (-C<u>H</u>Br) at the ω-terminus of the polymer chain[107]. The signals between 7.37-7.77 ppm is due to resonance of the aromatic protons of the initiator molecule at the α-terminus of the α-oxazolyl functionalized polystyrene, (**2**)[107].

The $^{13}C$ NMR spectrum of α-oxazolyl functionalized polystyrene, (**2**) is shown in Figure 7 and is characterized by the presence of the signals at 28.26, 67.35, 78.82 and 161.73 ppm, due to the carbon resonances of the [-C(<u>C</u>H$_3$)$_2$], (-<u>C</u>-(CH$_3$)$_2$, (-<u>C</u>H$_2$-O-) and (<u>C</u>=N) moieties of the oxazoline ring, respectively, which confirms the incorporation of the oxazoline group at the $\alpha$-end of the polymer chain.

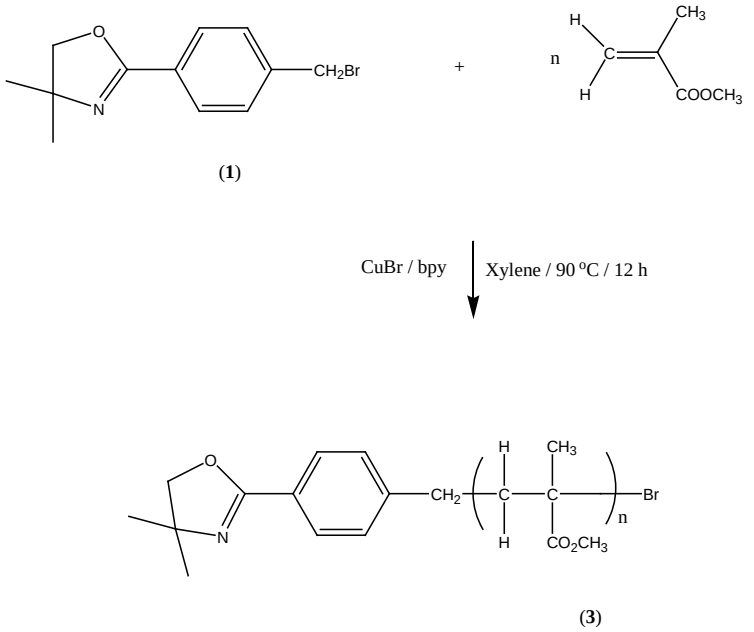
The oxazoline derivative, 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyl oxazole, (**1**) in the presence of CuBr/bpy, is an effective initiator for the ATRP of styrene to form α-oxazolyl functionalized polystyrene, (**2**). However, results show that the potential complexation reaction between the oxazoline initiator and the Cu(I) or Cu(II) species[74] is possible, which disrupts the coordination of the nitrogen ligand with the copper catalyst as shown by the reduced initiator efficiency of 0.89.

Similarly, α-oxazolyl functionalized polystyrene, (**2**) was also prepared by using 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as oxazolyl functionalized initiator in the presence of CuBr/PMDETA catalyst complex. The polymerization reaction was rapid as evidenced by the instant thickening of the reaction mixture within 4 h. The increased polymerization rate can be attributed to the higher activity of the catalyst complex formed from copper(I) bromide and the multidentate PMDETA ligand relative to the CuBr/bpy catalyst complex[151-152]. The spectroscopic data of the $\alpha$-oxazolyl functionalized polystyrene, (**2**) formed in the presence of the CuBr/PMDETA catalyst system, shows similar FTIR and $^{1}$H NMR spectroscopic features as the product formed in the presence of CuBr/bpy catalyst system. However, the presence of a peak at 35.34 ppm in the $^{13}$C NMR spectrum of $\alpha$-oxazolyl functionalized polystyrene, (**2**) prepared in the presence of CuBr/PMDETA catalyst system is consistent with the formation of the terminal methylene carbon in ATRP reactions[152].

#### 4.1.1.3 Synthesis of α-Oxazolyl Functionalized Poly(methyl methacrylate), (3)

The solution ATRP reaction of methyl methacrylate was initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of the CuBr/bpy catalyst complex and xylene as a solvent to form the corresponding

α-oxazolyl functionalized poly(methyl methacrylate), (**3**) according to the following reaction scheme:




(**1**)

(**3**)

The size exclusion chromatogram (Figure 8) of the α-oxazolyl functionalized poly(methylmethacrylate), (**3**) shows a monomodal molecular weight distribution with number average molecular weight value of $\overline{M}_n^{SEC}$ = 7.0 x $10^3$ g/mol, which is significantly higher than the theoretical $M_n$ value of 3.1 x $10^3$ g/mol, calculated at 100% monomer conversion. The significant tailing observed in the low molecular weight region in the size exclusion chromatogram indicates that a poor initiation process occurred. The high experimental number average molecular weight value implies the presence of side reactions which reduced the initiator concentration. Moreover, the molecular weight distribution of the polymer product was very broad ($\overline{M}_w/\overline{M}_n$ = 2.12). The high molecular weight distribution value could be attributed to poor initiation due to the low initiator reactivity of the oxazoline molecule, 2-[(4-bromomethyl) phenyl]-4,5-dihydro-4,4-dimethyloxazole (**1**), relative to the high reactivity of the growing poly(methyl methacrylate) propagating chain end.

The FTIR spectrum (Figure 9) of α-oxazolyl functionalized poly(methyl-methacrylate), (**3**) was characterized by the presence of an absorption band at 1645 $cm^{-1}$, due to the absorption of the C=N group of the oxazoline ring. The weak absorption is attributed to the high number average molecular weight of α-oxazolyl functionalized poly(methyl methacrylate), (**3**) relative to the presence of the initiating species at the α-terminus of the polymer chain.

The $^{1}H$ NMR spectrum (Figure 10) of α-oxazolyl poly(methyl methacrylate), (**3**) shows the presence of the signals between 7.09-7.24 ppm, due to the resonances of the aromatic protons of the initiator molecule, indicating the incorporation of the initiating species at the α-terminus of α-oxazolyl poly(methyl methacrylate), (**3**). The signal at 4.08-4.10 ppm is due to the resonance of the methylene protons (-C$\underline{H}_2$-) in the oxazoline ring[12].

The $^{13}C$ NMR spectrum (Figure 11) of α-oxazolyl functionalized poly(methyl methacrylate), (**3**), exhibits signals at δ = 28.31, 54.36, 77.43 and 157.15, due to the resonances of the [-C($\underline{C}H_3)_2$], (-$\underline{C}$-$(CH_3)_2$, (-$\underline{C}H_2$-O-) and ($\underline{C}$=N) carbons of the oxazoline ring, respectively. The signals attributed to the presence of the oxazoline group provide experimental evidence that the oxazoline group of the initiator molecule was incorporated at the α-terminus of the α-oxazolyl poly(methyl methacrylate), (**3**).

The preparation of α-oxazolyl functionalized poly(methyl methacrylate), (**3**) using 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as an initiator in the presence of CuBr/PMDETA catalyst system produced functionalized polymers with better control of the molecular weight distribution when compared to the synthesis of α-oxazolyl functionalized poly(methyl methacrylate), (**3**) using the CuBr/bpy catalyst system. Significant improvement in molecular weight distribution values ($\overline{M}_w/\overline{M}_n \approx 1.72$) of α-oxazolyl functionalized poly(methyl methacrylate), (**3**) was observed. However, the number average molecular

weights of the polymer product were consistently higher than the theoretical number average molecular weight values.

Furthermore, 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyl oxazole, (**1**) is a poor initiator for ATRP polymerization of methyl methacrylate in the presence of CuBr/bpy or CuBr/PMDETA as the catalyst system for the different polymerization reactions. The initiation of methyl methacrylate polymerization using 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyl oxazole, (**1**) in the presence of CuBr/bpy or CuBr/PMDETA afforded low initiator efficiency values of 0.45 and 0.29, respectively. The inability of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyl oxazole, (**1**) to initiate the polymerization of methyl methacrylate in a controlled manner could be attributed to the difference in the structure and reactivity of the oxazoline initiator molecule relative to the propagating poly(methyl methacrylate) chain end, where the reactivity of the C-Br bond in the propagating chain is higher than the C-Br bond in the initiator[7-11].

### 4.1.2 Syntheses of Aromatic Carboxyl Functionalized Polymers

Polymers containing carboxylic acid groups at the chain ends are employed in a wide range of industrial applications, such as in the preparation of a wide range of block copolymers by reactive blending and the ring opening polymerization of α,α-disubstituted β-propiolactones and oxazolines[15,18,118]. Because of their unique chemical, physical and mechanical properties, polymers bearing the carboxylic groups can be utilized as ligands to form polymeric complexes for applications in nanotechnology and biotechnology[110,118].

Atom transfer radical polymerization provides a convenient protocol for the synthesis of carboxyl functionalized polymers[7,11,15,74]. Because of potential complexation of the carboxylic acid moiety with the transition metal catalyst system in the ATRP reactions, indirect ATRP methods, which involve the use

of functionalized initiators substituted with carboxylic acid derivatives, have been used to prepare α-carboxyl functionalized polymers[118]. For example, a variety of derivatives of α-haloesters initiators have been employed successful[7,8,15-16,18,114-126] for the ATRP of styrene and methacrylates to form the corresponding α-carboxyl functionalized polymers which are produced after post polymerization conversion of the ester derivatives to the carboxylic acid group[7,8,15-16,18,114-126]. Carboxyl chain end functionalized polymers can also be prepared by using carboxyl functionalized initiators, where the carboxylic acid group occurs in the free acid form[15-17]. For example, initiators bearing a free carboxylic group were utilized for efficient preparation of α-carboxyl functionalized polymers. The use of alkyl halide or α-haloacids initiators with remote free carboxylic group has emerged as one of the most efficient alternative methodology for synthesis of α-carboxyl functionalized polymers. Matyjaszewski and Zhang[15] demonstrated that initiators with the carboxylic acid group remote to the initiating halogen can confer control in ATRP polymerization of styrene. Similar studies by Summers and coworkers[17], Xia and coworkers[128], Broyer and coworkers[129], and Li and coworkers[130] led to the synthesis of α-carboxyl functionalized polymers with well defined number average molecular weights, narrow molecular weight distributions and chain end functionality. In the process of preparing aromatic carboxyl chain end functionalized polymers by ATRP methods, arene sulfonyl halides bearing a carboxylic acid group have also been utilized widely as functionalized initiators in styrene, acrylates and methacrylate polymerization[132]. Percec and Barboiu[133] employed a functionalized arene sulfonyl chloride initiator bearing a carboxyl group in the para-position for the metal catalyzed polymerization of methyl methacrylate and butyl methacrylate to form the corresponding α-carboxyl functionalized polymers.

In the current study, the chemical transformation of α-oxazolyl functionalized polystyrene, (**2**) to the corresponding α-carboxyl functionalized polystyrene, (**4**) was performed by the successive acid catalyzed hydrolysis, saponification and final acidification processes[19,141].

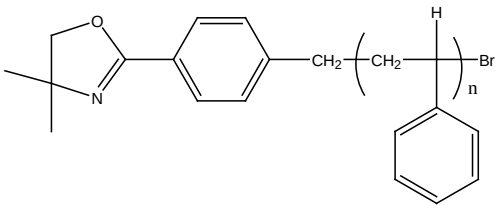
#### 4.1.2.1 Synthesis of α-Carboxyl Functionalized Polystyrene, (4)

The standard hydrolysis method outlined by Nakahama and coworkers[141] provides a versatile route for the chemical transformation of the oxazoline functionality to the corresponding carboxyl moiety via two major steps:

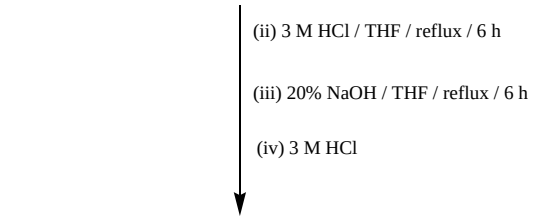
(a) the acid catalyzed hydrolysis of the oxazoline compound to the corresponding amino ester hydrochloride derivative.

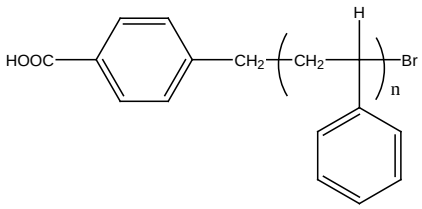
(b) Subsequent saponification of the ester amino derivative followed by acidification, to form the corresponding carboxylic acid.

α-Oxazolyl functionalized polystyrene, (**2**), prepared in the presence of the CuBr/bpy catalyst system, was used as a precursor for the preparation of the corresponding α-carboxyl functionalized polystyrene analogue, (**4**) according to the following reaction scheme:




(**2**)




(**4**)

The chemical transformation of the oxazoline moiety at the α-terminus of α-oxazolyl functionalized polystyrene, (**2**) ($M_n$ = 3.7 x $10^3$ g/mol) to the corresponding α-carboxyl functionalized polystyrene, (**4**) ($\overline{M}_n^{SEC}$ = 3.6 x $10^3$ g/mol) was achieved by successive hydrochloric acid catalyzed hydrolysis and saponification reactions. Final acidification of the polymer product gave the α-carboxyl functionalized polystyrene, (**4**) ($R_f$ = 0, toluene) in quantitative yields, as evidenced by the TLC analysis.

The size exclusion chromatography analysis of α-carboxyl functionalized polystyrene, (**4**) gave a monomodal chromatogram (Figure 12) with number average molecular weight, $\overline{M}_n^{SEC}$= 3.6 x $10^3$ g/mol and molecular weight distribution of $\overline{M}_w/\overline{M}_n$ of 1.31. The size exclusion chromatography results show that chemical transformation of the oxazolyl group to the corresponding carboxyl

group proceeded smoothly without degradation of the polymer chain. Quantitative deblocking of the oxazoline ring was further confirmed by non-aqueous titration measurements of α-carboxyl functionalized polystyrene, (**4**) with standardized methanolic potassium hydroxide. The value of the number average molecular weight obtained by non-aqueous titrations, $\overline{M}_n^{titr}$ = 3.5 x $10^3$ g/mol corresponds well with the SEC value, $\overline{M}_n^{SEC}$ = 3.6 x $10^3$ g/mol.

The FTIR spectrum of α-carboxyl functionalized polystyrene, (**4**) is shown in Figure 13. The absence of the absorption band at 1650 $cm^{-1}$, due to the C=N bond vibrations of the oxazoline group and the presence of a new absorption band at 1689 $cm^{-1}$, due to C=O bond vibration of the carboxyl group indicates the quantitative removal of the oxazoline group.

The $^1$H NMR spectrum (Figure 14) of α-carboxyl functionalized polystyrene, (**4**) shows the absence of a signal at 4.08-4.09 ppm, due to the resonance of the methylene protons (-C<u>H</u>$_2$-O) of the oxazoline group. The resonance of the methine proton (C<u>H</u>-Br) at the ω-terminus of the polymer chain[107] is observed at 4.22-4.55 ppm. The experimental data provides evidence that the chemical transformation of the oxazoline group to the carboxyl derivative does not interfere with the C-Br bond at the ω-terminus of the polymer chain.

The complete removal of the oxazoline group was further confirmed by evaluation of the $^{13}$C NMR spectrum (Figure 15) of α-carboxyl functionalized polystyrene, (**4**). A new signal at 171.17 ppm, due to the resonance of the carbon atom of the <u>C</u>OOH group, was observed. The signals at 161.73, 78.82, 67.35 and 28.26 ppm, due to the carbon resonances of <u>C</u>=N, -<u>C</u>H$_2$-O, (CH$_3$)$_2$<u>C</u>-and -C(<u>C</u>H$_3$)$_2$ groups respectively, are not present in the $^{13}$C NMR of α-carboxyl functionalized polystyrene, (**4**), indicating the complete conversion of the oxazoline group to the carboxylic acid group at the α-terminus of the polymer chain.

The treatment of α-oxazolyl functionalized polystyrene, (**2**) by successive acid and base hydrolysis reaction, followed by final acidification, produced α-carboxyl functionalized polystyrene, (**4**) in quantitative yields. The size exclusion chromatography data, non-aqueous titration measurements and spectroscopic data confirms the quantitative conversion of the oxazolyl group to the carboxylic acid group.

### 4.1.3 Syntheses of Aromatic Oxazolyl Functionalized Polymers by ATRP using an Aromatic Oxazolyl Functionalized Initiator Precursor.

The initiation of the polymerization of styrene by ATRP methods, using a functionalized initiator adduct, prepared *in situ* by the reaction of functionalized 1,1-diphenylethylene derivatives with an appropriate organohalogen compound, outlines a facile synthesis route for the quantitative incorporation of a specific functional group at the α-termini of polymer chains. Earlier, Summers and coworkers[25-28] developed a general ATRP functionalization method focusing on the use of the tertiary amine[25], primary amine[26] and siloxyl[28] functionalized 1,1-diphenylethylene initiator adduct systems, prepared *in situ* by the independent reactions of (1-bromoethyl)benzene with the tertiary amine, primary amine or siloxyl functionalized 1,1-diphenylethylene derivatives as initiators for the polymerization of styrene to afford the corresponding well defined α-tertiary amine, α-primary amine and α-siloxyl functionalized polystyrene derivatives in quantitative yields, respectively. The current study investigates the initiation of the polymerization of styrene by an oxazolyl functionalized initiator adduct, prepared *in situ* by the reaction of (1-bromoethyl)benzene and 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) in the presence of CuBr/bpy catalyst system, as a method for the preparation of α-oxazolyl functionalized polystyrene.

#### 4.1.3.1 Aromatic Oxazolyl Functionalized Initiator Precursor: Synthesis of 4,5-Dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl] oxazole, (5).

The preparation of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) was first reported by Summers and Quirk[19]. The synthetic process involved three steps, namely:

(a) The synthesis of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone from 4-benzoylbenzoic acid by the standard oxazoline synthesis method outlined by Meyers and coworkers[138].

(b) The coupling of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone with methyl magnesium bromide according to the method of Pfeiffer and Wizinger[153] to give 1-[-4(4,5-dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-1-phenylethanol.

(c) The rapid dehydration of 1-[-4(4,5-dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-1-phenylethanol with 20% sulfuric acid in glacial acetic acid according to a method by Gharbisch[154] to afford 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**).

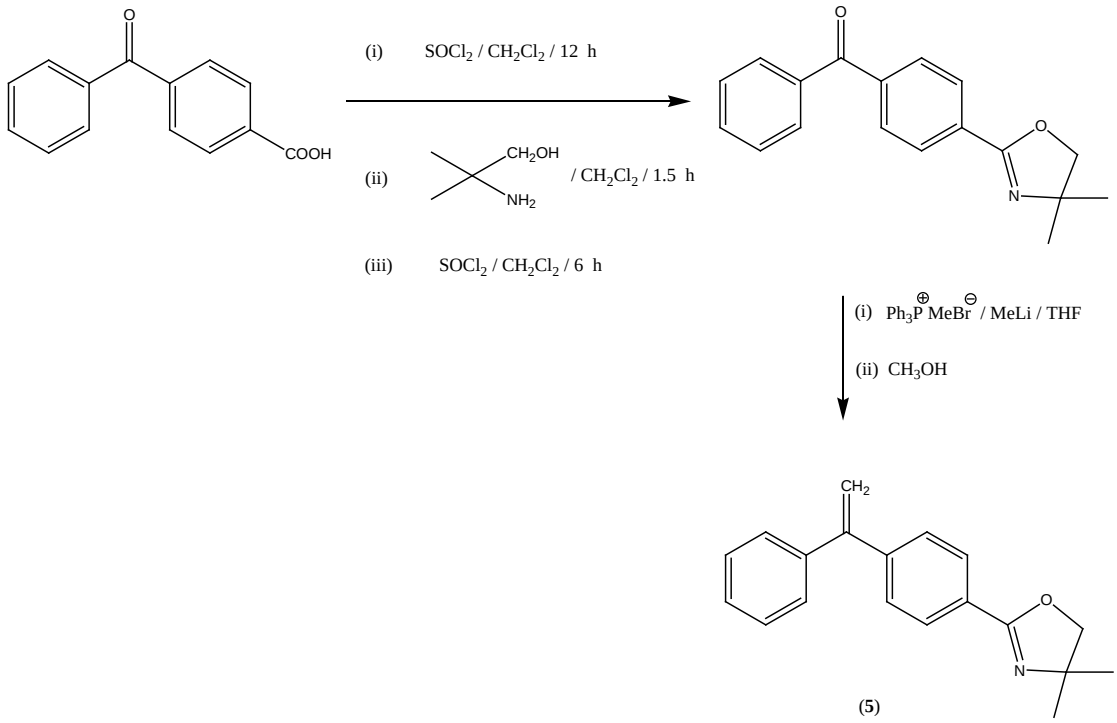
Low yields of the desired oxazoline product were obtained when 20% sulfuric acid in glacial acetic acid was used for the dehydration step. Side reactions, such as the opening of the oxazoline ring, were observed. Thus, the need for a high yield synthesis method for the preparation of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenyl-ethenyl)phenyl]oxazole, (**5**) was desirable.

Initial attempts to repeat the synthesis method of Summers and Quirk[19] for preparation of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) using 4-benzoylbenzoic acid as a starting material afforded the final product in only 10% yield. Dehydration of the intermediate carbinol product, 1-[4(4,5-dihydro-4,4-dimethyl-2-oxazolyl)phenyl]-1-phenylethanol with 20% sulfuric acid in glacial acetic acid led to many side reactions.

The current research work reports a new high yield synthesis pathway for the preparation of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) via a synthesis route which involves two steps:

(a) The preparation of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone from 4-benzoylbenzoic acid.

(b) The direct conversion of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)-benzophenone to 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]-oxazole, (**5**) using the classic Wittig reaction[142] as depicted in the following reaction scheme:




The synthesis of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone using 4-benzoylbenzoic acid as a starting material was effected by the general methods outlined by Meyers and coworkers[138] and Shchepinov and coworkers[139]. The intermediate product, 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone, was obtained in 86% yield with a melting point of 99.5-100.5 °C, which corresponds with the literature melting point of 99.3-100.8 °C[19]. The spectroscopic data of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone was in good agreement with the data reported by Summers and Quirk[19].

The direct conversion of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone to the desired compound, 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]-oxazole, (**5**) was effected using the classic Wittig reaction[142]. The rapid treatment of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone with triphenyl-phosphonium ylide, generated *in situ* by the reaction of methyltriphenyl-phosphonium bromide with methyl lithium in THF at 0 °C, gave 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) as fine white crystals in 88%

yield. The melting point of 77.2-77.7°C for 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) corresponds with the literature value of 77.1-77.8 °C[19].

The FTIR spectrum of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]-oxazole, (**5**) is depicted in Figure 16. The FTIR spectrum shows an absorption band at 1641 $cm^{-1}$, due to the bond vibrations of the C=N group of the oxazoline ring. No evidence of the C=O absorption band at 1669 $cm^{-1}$, associated with the 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone precursor molecule, was observed, indicating the complete Wittig reaction.

The $^{1}H$ NMR spectrum (Figure 17) of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) exhibits the presence of two singlets at 1.38 and 4.10 ppm, due to resonances of the methyl protons ($C\underline{H}_3)_2$-C) and methylene protons (-$C\underline{H}_2$-O-) of the oxazoline ring, respectively. The singlet at 5.50 ppm is attributed to the resonance of the equivalent methylene protons of the olefinic bond ($C\underline{H}_2$=C-) of the 1,1-diphenylethylene unit. The signals at 7.32-7.38 and 7.89-7.92 ppm are due to the resonances of aromatic protons of the phenyl rings.

Analysis of the $^{13}C$ NMR spectrum (Figure 18) of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) shows peaks at 28.40, 67.58, 79.07 and 161.81 ppm, due to the resonances of the methyl carbon ($\underline{C}H_3)_2$-C), the methylene carbon (-$\underline{C}H_2$-O-), the quaternary carbon $(CH_3)_2$-$\underline{C}$) and the $\underline{C}$=N carbon of the oxazoline group, respectively. The signals at 115.27 and 149.40 ppm are attributed to the resonances of the two carbon atoms of the double bond, ($\underline{C}H_2$=C-) and ($H_2C$=$\underline{C}$-) of the ethylene group, respectively. Signals due to the resonances of the aromatic carbon atoms of the benzene rings are observed at 127.29-128.54, 140.96 and 144.28 ppm.

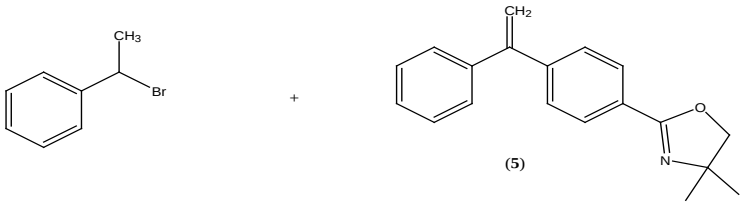
The experimental data provide evidence of the high yield synthesis of a pure sample of the target compound, 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) by: (a) a modified synthesis pathway for the preparation of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone from 4-benzolylbenzoic acid, and (b) the direct conversion of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzo-phenone to 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) using the classical Wittig reaction[142].

### 4.1.3.2 Synthesis of α-Oxazolyl Functionalized Polystyrene, (7).

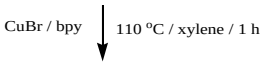
The use of a unimolecular functionalized initiator system, derived from substituted 1,1-diphenylethylene precursors, for the polymerization of styrene and methyl methacrylate by ATRP methods has emerged as a facile route for the quantitative preparation of functionalized polymers. Summers and coworkers[25-26] recently prepared amine chain end functionalized polymers in quantitative yields, using the appropriate amine functionalized 1,1-diphenylethylene based initiator adduct for the ATRP of styrene. The amine functionalized initiator adduct was prepared *in situ* by the reaction of the specific amine substituted 1,1-diphenylethylene derivative with (1-bromoethyl)benzene in the presence of copper(I) bromide/ 2,2'-bipyridine catalyst system in diethyl ether.

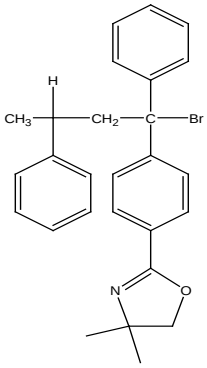
The present study describes the use of the ATRP method for the synthesis of α-oxazolyl functionalized polymers using an oxazolyl functionalized 1,1-diphenyl-ethylene derivative as the initiator precursor compound to prepare an oxazolyl functionalized initiator adduct species which is subsequently used as an initiator for styrene polymerization. The oxazolyl functionalized initiator adduct was formed *in situ* by the reaction of an alkyl halide with the oxazolyl substituted 1,1-diphenylethylene derivative in the presence of a copper(I) bromide/nitrogen ligand catalyst system. By the ATRP mechanism,initiation of the polymerization of styrene by a new oxazolyl functionalized initiator adduct, (**6**), generated *in situ*

by the reaction of (1-bromoethyl)benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) in the presence of CuBr/bpy catalyst system in xylene, afforded the corresponding α-oxazolyl functionalized polystyrene, (**7**) according to the following synthetic pathway:

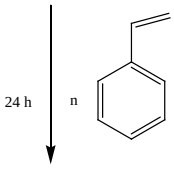


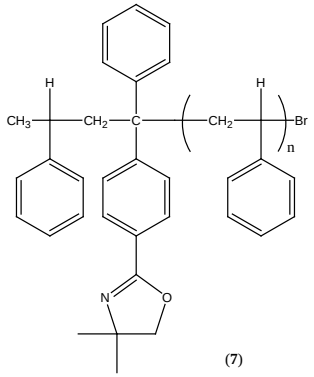

(**5**)




(**6**)




(**7**)

The oxazolyl functionalized initiator adduct, (**6**) was formed *in situ* after 1 h at 110 °C. After the addition of freshly distilled styrene to the resultant, vigorously stirred green solution, initiation with concomitant propagation was evident as the solution became viscous after a period of 24 hours. After cooling to 25 °C followed by the addition of THF, the polymer solution was passed through a silica gel column to remove the catalyst impurities. The polymer product was purified by precipitation from THF into excess methanol, filtered and vacuum dried to give α-oxazolyl functionalized polystyrene, (**7**). TLC analysis shows that α-oxazolyl functionalized polystyrene, (**7**) ($R_f$ = 0.22, toluene) was obtained in quantitative yields, with no evidence of the formation of unfunctionalized polystyrene ($R_f$ = 0.99, toluene) .

The monomodal size exclusion chromatogram (Figure 19) of α-oxazolyl functionalized polystyrene, (**7**) exhibits a broad molecular weight distribution ($\overline{M}_w/\overline{M}_n$ =1.42) which implies unequal growth of the polymer chains. This could be attributed to the heterogeneous polymerization reaction medium, characteristic of copper(I) bromide/bpy in non polar solvents such as xylene[42,93,94,155-156]. Thus, there was slow exchange between species of different reactivities and initiation might have occurred at different stages of the polymerization, consequently, polystyrene with slightly broader molecular weight distribution[42,155-156] was produced. The concentration of the functionalized initiator adduct, (**6**) is reduced due to the formation of resonance stabilized species of the resultant oxazolyl free radicals. Furthermore, the observed number average molecular weight, ($\overline{M}_n^{SEC}$ = 3.9 x $10^3$ g/mol), is significantly higher than the corresponding theoretical value ($\overline{M}_n^{theory}$ = 3.0 x $10^3$ g/mol), based on a simple ratio of monomer to initiator at 100% monomer conversion. It is also possible that the deviation in number average molecular weight accompanied by broad molecular distribution, could be be due to the fact that during the early stages of the polymerization reaction, the persistent cupric complex concentration is not sufficiently large enough to confer control of the polymerization process[155-156]. The initiator efficiency is also reduced presumably due to side reactions during coupling reaction of the initiating radical

formed from (1-bromoethyl)benzene and the sterically hindered 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**)[11], which limits quantitative formation of the oxazolyl functionalized initiator adduct, (**6**), thus the formation of polymers with higher number average molecular weights.

The FTIR spectrum (Figure 20) of α-oxazolyl functionalized polystyrene, (**7**) shows the presence of an absorption band at 1648 $cm^{-1}$, characteristic of the C=N bond vibrations of the oxazoline ring and consistent with the incorporation of the functionalized initiator fragment at the α-terminus of the polymer chain.

The $^{1}H$ NMR spectrum (Figure 21) of α-oxazolyl functionalized polystyrene, (**7**) exhibits a broad signal at 4.08-4.09 ppm, which is attributed to the resonance of two methylene protons (-C$\underline{H}_2$-O-) of the oxazoline group of the initiator fragment. The observed signal at 4.50-4.61 ppm is due to the resonance of the methine proton (-C$\underline{H}$Br) at the ω-terminus of the polymer chain[107]. The presence of the initiator fragment at the α-terminus of α-oxazolyl functionalized polystyrene, (**7**) was confirmed by the presence of a signal at 1.21 ppm due to the methyl protons (2 x -C$\underline{H}_3$) of the oxazolyl initiator molecule. The signals at 7.81-8.78 ppm corresponds to the resonances of the aromatic protons of the initiator at the α-terminus of α-oxazolyl functionalized polystyrene, (**7**)[19]

The $^{13}C$ NMR spectrum (Figure 22) of α-oxazolyl functionalized polystyrene, (**7**) shows the following peaks of the oxazoline group: a peak at 28.26 ppm, due to the resonance of the carbon atom [($\underline{C}H_3)_2$-]; a signal at 67.35 ppm, which corresponds to the carbon resonance of the ($\underline{C}$-($CH_3$) group; a peak at 78.82 ppm attributed to the carbon resonance of the ($\underline{C}H_2$-O) group. The peak downfield at 161.73 ppm is characteristic of the carbon resonance of the $\underline{C}$=N of the oxazoline group. The resonance of the carbon atom of the methyl group in the initiator molecule at the α-terminus of $\alpha$-oxazolyl functionalized polystyrene, (**7**) is

observed at 31.36 ppm, whereas the resonances of the secondary carbon at the ω-chain end is observed between 40.23-46.24 ppm[3].

Initiation of the atom transfer radical polymerization of styrene by an oxazolyl functionalized initiator adduct, (**6**), generated *in situ* by the reaction of (1-bromoethyl)benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) in the presence of CuBr/bpy, gave quantitative yields of α-oxazolyl functionalized polystyrene, (**7**). All polymer characterization data are consistent with the quantitative incorporation of the oxazolyl group at the α-terminus of the polymer chain.

#### 4.1.3.3 Synthesis of α,ω-Bis(oxazolyl) Functionalized Polystyrene, (8)

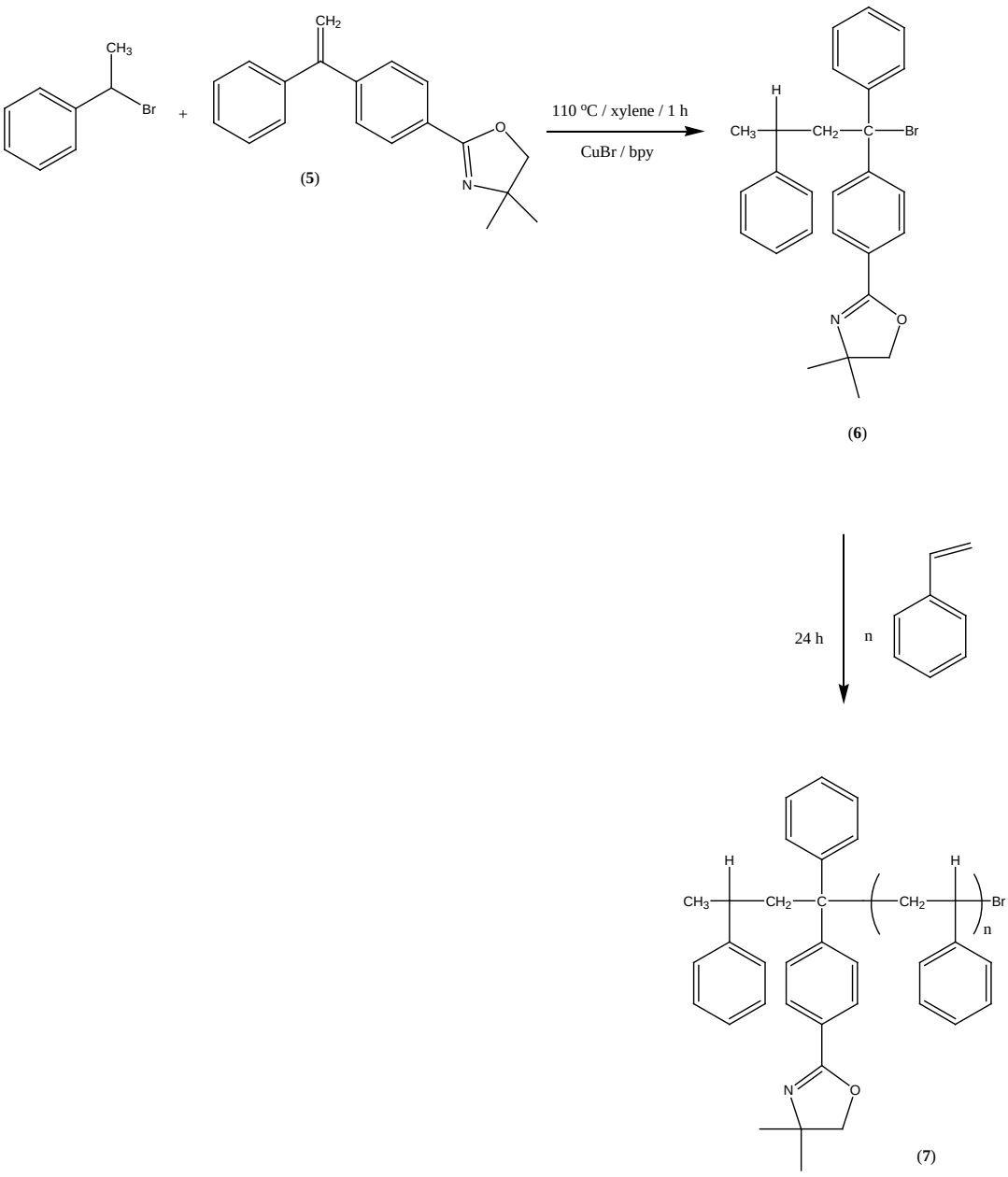
Telechelic polymers are useful starting materials for preparation of a variety of polymeric materials such as block copolymers and composite materials[94-95] Traditionally, telechelic polymers containing different functional groups have been prepared by controlled/"living" polymerization methods, particularly the living ionic polymerization techniques[5,22]. For example, α,ω-tertiary amine functionalized polystyrene were prepared by the crossover reaction of the appropriate α-tertiary amine functionalized polystyryl derivative with 1,1-bis[4-dimethylaminophenyl]-ethylene at ambient temperatures as outlined by Kim and coworkers[22].

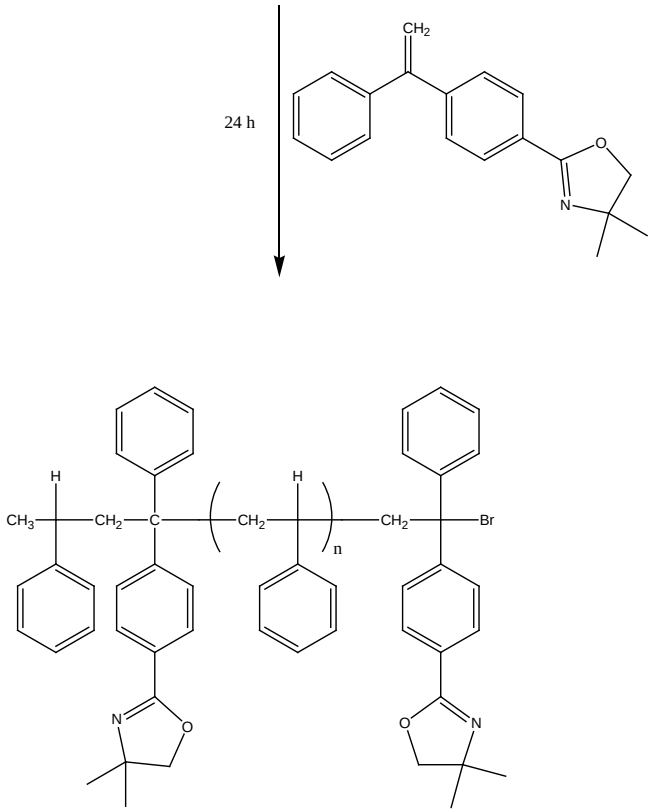
The ATRP method is the most versatile free radical polymerization technique for preparation of chain end functionalized polymers. For example, by using a functionalized organohalogen compound as initiator for the polymerization of styrene by ATRP methods, telechelic polymers are produced with the initiator functional group introduced at the α-terminus of the polymer chain and the carbon-halogen functional group incorporated at the ω-terminus of the polymer chain.

Different telechelic polymers can be prepared by exploiting the reactivity of the ω-carbon-halogen bond in polymers prepared by ATRP reactions. The carbon halogen bond at the ω-terminus of the polymer chain can undergo chemical transformation reactions such as electrophilic addition, nucleophilic substitution, atom transfer radical addition and atom transfer radical coupling reactions. For example, Matyjaszewski and coworkers prepared α,ω-hydroxyl functionalized poly(methyl methacrylate) and polystyrene by ATRP methods, followed by atom transfer radical coupling reactions[111]. The utility of the ATRP process coupled with post ATRP reactions was extended to the preparation of telechelic polymers bearing either a derivatized carboxylic acid or a free carboxylic acid group. Well defined α,ω-carboxyl functionalized polymers were recently prepared by Yagci and coworkers[110] by post polymerization chemical transformation of the carbon-bromine bond at the ω-terminus of the α-carboxyl functionalized polystyrene precursor. α-Carboxyl functionalized polystyrene was prepared using α-bromo-p-toluic acid as a carboxyl functionalized initiator, followed by transformation of the carbon-bromine bond at the ω-end of the polymer chain to the carboxylic acid group using cumic acid.

The preparation of telechelic poly(acrylate) polymers bearing a carboxylic acid derivative at the chain ends was reported by Otazaghine and coworkers[113]. The first step involved the synthesis of polyacrylate oligomers under ATRP conditions, followed by the coupling of the oligomers in the presence of Cu(0), to give the corresponding telechelic poly(acrylate) with an ester group at the chain ends.

No papers on preparation of α,ω-oxazolyl functionalized polymers by direct ATRP methods have been reported in the literature. As part of the present study, a quantitative, one-pot ATRP chain end modification method for the efficient incorporation of the oxazolyl group at the ω-chain end of α-oxazolyl functionalized polystyrene derivative to form the corresponding α,ω-bis(oxazolyl) functionalized polystyrene derivatives was developed according to the following pathway:


CH3
Br
+
CH2
O
N
(5)
110 ºC / xylene / 1 h
CuBr / bpy
H
CH3
CH2
C
Br
N
O
(6)
24 h
n
H
CH3
CH2
C
CH2
H
Br
n
N
O
(7)




(**8**)

α-Oxazolyl functionalized polystyrene, (**7**) was prepared by the ATRP of styrene, initiated by the oxazolyl functionalized initiator adduct, (**6**) in the presence of the CuBr/bpy catalyst complex in xylene. The presence of residual unreacted styrene monomer at the completion of the ATRP process was monitored by GC analysis. After complete monomer consumption, as determined by GC analysis, excess 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) in xylene was added in a one-pot process to the reaction mixture and stirred at 110 °C for an additional 24 hours to effect the quantitative ω-chain end functionalization reaction.

The TLC analysis of the resultant α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) gave one spot on the chromatogram with a $R_f$ value of 0.21 as compared with $R_f$ = 0.22 value of the α-oxazolyl functionalized polystyrene, (**7**) precursor.

The size exclusion chromatogram of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) is shown in Figure 23. The monomodal chromatogram and the absence of any bimodal peaks in the chromatogram of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) implies that the chain end functionalization reaction proceeded without any polymeric radical coupling reactions. An experimental number average molecular weight of $\overline{M}_n^{SEC}$ = 4.3 x $10^3$ g/mol was obtained for α,ω-bis(oxazolyl) functionalized polystyrene, (**8**), with a molecular weight distribution value of $\overline{M}_w/\overline{M}_n$ = 1.45. The higher number average molecular weight of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) relative to the α-oxazolyl functionalized polystyrene, (**7**) precursor is consistent with the addition of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) unit at the ω-end of the polymer chain.

The FTIR spectrum (Figure 24) of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) shows a strong absorption band at 1649 $cm^{-1}$, due to the C=N stretching mode of two oxazoline functional groups at the polymer chain ends.

The $^1$H NMR spectrum of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) is shown in Figure 25. The presence of a strong broad signal at 4.10-4.12 ppm is attributed to the resonance of four methylene protons (-C$\underline{H}_2$-O-), due to the introduction of the oxazoline rings at each end of the polymer chain. The complete chain end modification reaction is confirmed by the $^1$H NMR spectrum (Figure 25) which shows the absence of a signal at 4.24-4.56 ppm, due to the resonances of the terminal methine proton (-C$\underline{H}$Br) of the ω-chain end structure of the α-oxazolyl functionalized polystyrene, (**7**) precursor. The presence of the initiator fragment at the α-terminus of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) is confirmed by the presence of signals between 1.02-1.26 ppm and 7.82-8.25 ppm, due to the resonances of methyl protons and aromatic protons in the initiator molecule, respectively.

The $^{13}C$ NMR spectrum of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) is depicted in Figure 26. The signals of the carbon atoms of the oxazoline group are observed at the following chemical shifts: 28.25, 68.34, 78.92 and 161.74 ppm, attributed to the resonances of the carbon atoms, [-C($\underline{C}H_3)_2$-], $\underline{C}(CH_3)_2$, (-$\underline{C}H_2$-O-) and ($\underline{C}$=N) of the oxazoline ring, respectively. The resonance of the methyl carbon atom of the initiator fragment at the α-chain end of the polymer is observed at 30.12 ppm.

The oxazolyl functionalized initiator adduct, (**6**), formed by the reaction of 4-(4,5-dihydro-4,4-dimethyl-2-[4-(phenylethenyl)phenyl]oxazole, (**5**) with (1-bromoethyl)-benzene in the presence of CuBr/bpy, can be used for the polymerization of styrene to form the corresponding α-oxazolyl functionalized polystyrene, (**7**) in quantitative yields. The α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) can be readily obtained by the post ATRP chemical transformation reaction of the ω-terminus of the α-oxazolyl functionalized polystyrene, (**7**) by the addition of excess amounts of 4-(4,5-dihydro-4,4-dimethyl-2-[4-(phenylethenyl)-phenyl]oxazole, (**5**).

### 4.1.4 Syntheses of Aromatic Carboxyl Functionalized Polymers

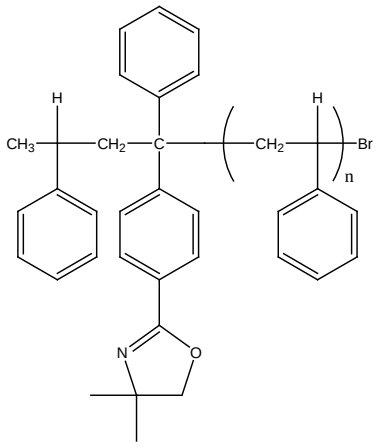
Carboxyl chain end functionalized polymers, which are valuable intermediates for the preparation of block copolymers, can be synthesized by the ATRP technique via the functionalized initiator method, using two major synthetic pathways: The first method entails the use of initiators with derivatized carboxylic acid groups as initiators in ATRP reactions for the preparation of functionalized polymers, followed by deblocking of the carboxylic acid derivative. For example, Pionteck and coworkers[18] used the α-chloropropionate derivative containing the t-butyl ester functionality and alkyl 2-bromopropionates as initiators to prepare ester functionalized polystyrenes. Subsequent demasking of the ester group under appropriate basic conditions gave the corresponding well defined α-carboxyl

functionalized polystyrene. The second method entails the use of organohalogen compounds substituted with the free carboxylic acid group remote to the initiating carbon-halogen end, as functionalized initiators in ATRP reactions to produce well defined α-carboxyl functionalized polymers[15-17]. For example, Matyjaszewski[15] reported the preparation of well defined α-carboxyl functionalized polystyrene using 4-(1-bromoethyl)benzoic acid and 4-(2-bromopropionyloxy)ethoxy)benzoic acid as initiators with the carboxylic acid group remote to the halogen atom. An independent study by Summers and coworkers[17] led to the preparation of well defined α-carboxyl functionalized polystyrene by ATRP methods using α-bromo-p-toluic acid as initiator for the polymerization of styrene.

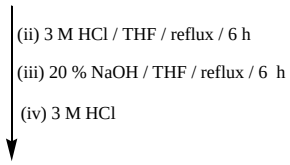
Although initiators bearing the carboxylic acid groups and its derivatives have been used successfully for the direct preparation of carboxyl functionalized polymers by ATRP methods, the indirect preparation of carboxyl functionalized polymers by ATRP using 1,1-diphenylethylene chemistry has not been reported in literature. Carboxyl chain end functionalized polystyrenes have been prepared by anionic polymerization method by Summers and Quirk[19,23] by the reactions of poly(styryl)lithium with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]-oxazole, (**5**) or N,N-diisopropyl-4-(1-phenyl)benzamide, followed by the deblocking of the appropriate functional group. The current study reports the preparation of carboxyl functionalized polymers by the chemical modification of the polymer chain ends of α-oxazolyl functionalized polystyrene, (**7**) and α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) to form the corresponding α-carboxyl functionalized polystyrene, (**9**) and α,ω-bis(carboxyl) functionalized polystyrene, (**10**), respectively by using successive acid catalyzed hydrolysis, saponification, and final acidification reactions.

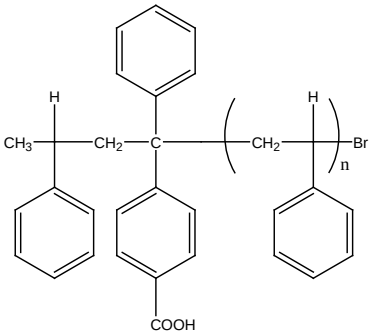
### 4.1.4.1 Synthesis of α-Carboxyl Functionalized Polystyrene, (9)

The chemical transformation of the aromatic oxazoline moiety to the corresponding aromatic carboxylic acid can be realized by successive acid and base hydrolysis reactions, followed by final acidification[141]. The conversion of the oxazoline group at the α-terminus of α-oxazolyl functionalized polystyrene, (**7**) to the corresponding carboxyl acid group at the α-terminus of α-carboxyl functionalized polystyrene, (**9**) was effected by the following reaction pathway:




(**7**)




(**9**)

In a typical reaction, α-oxazolyl functionalized polystyrene, (**7**) was subjected to acid catalyzed hydrolysis in the presence of aqueous hydrochloric acid and THF under reflux for 6 hours. Base hydrolysis of the resulting amino ester intermediate with aqueous hydrochloric acid in THF proceeded for 6 hours under reflux. Subsequent acidification of the polymeric product with hydrochloric acid produced α-carboxyl functionalized polystyrene, (**9**). The extent of hydrolysis of α-oxazolyl functionalized polystyrene, (**7**) was monitored by TLC analysis. The polymer was precipitated in methanol, filtered and vacuum dried. α-Carboxyl functionalized polystyrene, (**9**) was obtained in quantitative yield as evidenced by the TLC analysis ($R_f$ = 0, toluene). The absence of any α-oxazolyl functionalized polystyrene, (**7**) ($R_f$ = 0.2, toluene) is consistent with the complete conversion of the oxazoline group to the carboxylic acid without the occurrence of decarboxylation reactions.

The size exclusion chromatogram (Figure 27) of α-carboxyl functionalized polystyrene, (**9**) gave a monomodal molecular weight distribution curve with $\overline{M}_w/\overline{M}_n$ = 1.47 and $\overline{M}_n^{SEC}$= 3.8 x $10^3$ g/mol, indicating that no polymer chain degradation reactions occurred during the hydrolysis reactions.

The quantitative conversion of the oxazoline ring to the carboxylic acid group was further confirmed by non-aqueous titration measurements. Titration of α-carboxyl functionalized polystyrene, (**9**) with standardized methanolic potassium hydroxide using phenolphthalein as indicator gave a number average molecular weight value of $\overline{M}_n^{titr}$ = 3.7 x $10^3$ g/mol, which is in good agreement with the number average molecular weight value of $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol obtained by SEC analysis.

The FTIR spectrum (Figure 28) of α-carboxyl functionalized polystyrene, (**9**) exhibits an absorption band at 1692 $cm^{-1}$, characteristic of the C=O bond vibration of the carboxyl group. The complete absence of an absorption band at 1648

$cm^{-1}$, due to the C=N stretching mode of the oxazoline group, provides evidence of the quantitative conversion of the aromatic oxazoline group to the corresponding aromatic carboxylic acid group.

Figure 29 shows the $^{1}H$ NMR spectrum of α-carboxyl functionalized polystyrene, (**9**). The resonance of the methylene protons (-C<u>H</u>$_2$-O-) at 4.08-4.09 ppm, which is due to the presence of the oxazoline group, is absent. The resonance of the methine proton at the ω-terminus of the polymer chain at 4.30-4.48 ppm as well as the the signals at 0.99 ppm and between 7.41-7.89 ppm, due to the protons of the initiator fragment are still observed in the $^{1}H$ NMR spectrum of α-carboxyl functionalized polystyrene, (**9**). The presence of the signals at 4.30-4.48 ppm confirms that the chemical transformation of the oxazoline group to the carboxylic acid group does not interfere with the C-Br bond at the ω-terminus of the polymer chain. The experimental results are consistent with the complete transformation of the oxazoline group to the carboxylic acid group.

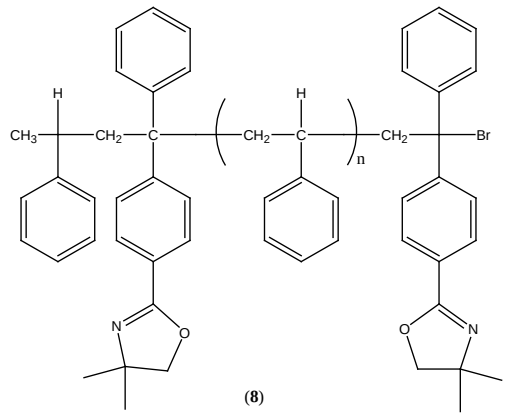
The $^{13}C$ NMR spectrum (Figure 30) of α-carboxyl functionalized polystyrene, (**9**) shows a signal at 171.86 ppm, due to the resonance of the carbon atom of the <u>C</u>OOH group of α-carboxyl functionalized polystyrene, (**9**). The absence of signals at 161.73, 78.82, 67.35 and 28.26 ppm, due to the resonances of the carbon atoms of <u>C</u>=N, -<u>C</u>H$_2$-O, (CH$_3$)$_2$<u>C</u>- and -C(<u>C</u>H$_3$)$_2$ of the oxazoline ring, respectively, indicates the complete removal of the oxazoline ring at the α-terminus of the polymer chain. The presence of the initiator fragment at the α-chain end of α-carboxyl functionalized polystyrene, (**9**), is confirmed by the presence of a signal at 30.55 ppm, due to the resonance of the methyl carbon atom, (-<u>C</u>H$_3$).

Well defined α-carboxyl functionalized polystyrene, (**9**) was prepared *in situ* in quantitative yields using α-oxazolyl functionalized polystyrene, (**7**) as precursor. The spectroscopic and non-aqueous titration data were consistent with

quantitative chemical conversion of the oxazoline group to the carboxylic acid group, with retention of the carbon-bromine bond at the α-terminus of the polymer chain.

#### 4.1.4.2 Synthesis of α,ω-Bis(carboxyl) Functionalized Polystyrene, (10)

Simple aromatic oxazoline precursors are easily converted to the corresponding aromatic carboxylic acids by the general method outlined by Nakahama and coworkers[141]. Similarly, the acid catalyzed hydrolysis of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) with aqueous hydrochloric acid in THF, followed by the saponification of the resulting amino ester intermediate and final acidification, gave α,ω-bis(carboxyl) functionalized polystyrene, (**10)** according to the following pathway:

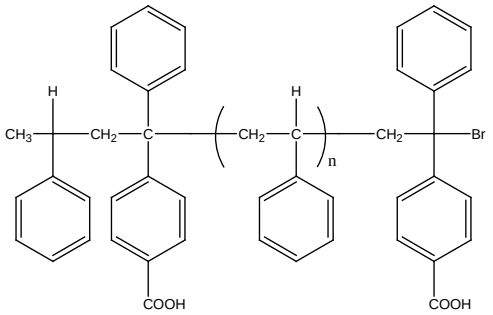


(**8**)

(i) 3 M HCl / THF / reflux / 12 h

(ii) 20 % NaOH / THF/reflux / 12 h

(iii) 3 M HCl



(**10**)

TLC analysis of α,ω-bis(carboxyl) functionalized polystyrene, (**10)** in toluene gave one spot on the chromatogram with $R_f$ = 0, which indicates the quantitative transformation of the oxazoline group to the carboxylic acid group.

The size exclusion chromatogram of α,ω-bis(carboxyl) functionalized polystyrene, (**10**), as shown in Figure 31, exhibits a monomodal molecular weight distribution curve with $\overline{M}_w/\overline{M}_n$ = 1.51 and $\overline{M}_n^{SEC}$= 4.0 x $10^3$ g/mol, indicating that the hydrolysis reaction proceeded without polymer chain degradation or coupling reactions.

The non-aqueous titration data of α,ω-bis(carboxyl) functionalized polystyrene, (**10**) with standardized methanolic potassium hydroxide as a titrant in the presence of phenolphthalein indicator, indicates the quantitative incorporation of two carboxylic acid groups at the polymer chain ends. The observed value of the number average molecular weight of $\overline{M}_n^{titr}$ = 3.9 x $10^3$ g/mol corresponds well with the value of $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol obtained by SEC analysis for α,ω-bis(carboxyl) functionalized polystyrene, (**10**) and indicates the absence of homopolymerization and copolymerization of the 1,1-diphenylethylene unit during post polymerization ATRP chain end modification reaction.

The FTIR spectrum (Figure 32) of α,ω-bis(carboxyl) functionalized polystyrene, (**10**) depicts the presence of a strong absorption band at 171.62 $cm^{-1}$, due to the stretching modes of the C=O moiety of the carboxylic acid group. The absorption band at 1649 $cm^{-1}$, which corresponds with the C=N bond vibrations in the oxazoline group, was not observed, implying the complete conversion of the oxazoline group to the carboxylic acid functionality.

The $^1$H NMR spectrum of α,ω-bis(carboxyl) functionalized polystyrene, (**10**) is shown in Figure 33. The absence of a signal at 4.10-4.12 ppm, due to the four methylene protons (-C$\underline{H}_2$-O-) of the two oxazoline groups, clearly indicates that the oxazoline groups were completely converted to the carboxylic acid groups. In addition, the resonance of the terminal methine proton (-C$\underline{H}$-Br) was not observed in the $^1$H NMR spectrum of α,ω-bis(carboxyl) functionalized polystyrene, (**10**) confirming the conversion of the CHBr end group to the $CPh_2Br$ end group as well as the presence of the 1,1-diphenylethylene unit substituted with the carboxylic functionality at the ω-terminus of the polymer chain. The peak at 1.15-1.20 ppm is due to the resonance of the methyl protons of the initiator fragment, whereas the signal for the resonances which corresponds to aromatic protons of the initiator species is observed between 8.06-8.15 ppm.

The $^{13}C$ NMR spectrum (Figure 34) of α,ω-bis(carboxyl) functionalized polystyrene, (**10**) exhibits a strong signal at 172.02, characteristic of the carbon resonances of the carbonyl carbon atoms of the COOH groups at both the α-and ω-termini of the polymer chain. The $^{13}C$ NMR spectrum of α,ω-bis(carboxyl) functionalized polystyrene, (**10**) is further characterized by the absence of the signals at 161.74, 78.42, 68.34 and 28.25 ppm, due to the resonances of the C=N, -$CH_2$-O-, $(CH_3)_2C$- and -$C(CH_3)_2$ carbon atoms of the oxazoline functionality at the polymer chain ends. The signal at 30.56 ppm is due to the resonance of the methyl carbon of the initiator fragment. The presence of the peak at 47.75 ppm, corresponding to the resonance of the carbon atom at the ω-chain end (PS-CBr), provides evidence of the introduction of the 1,1-diphenylethylene unit at the ω-terminus of the polymer chain.

α,ω-Bis(carboxyl) functionalized polystyrene, (**10**) was prepared in quantitative yields by subjecting α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) to successive acid and base hydrolysis reactions[141]. All spectroscopic and non-aqueous titration data were consistent with the quantitative conversion of the oxazolyl group to the carboxylic acid group.

### 4.1.5 Syntheses of Aromatic Oxazolyl Functionalized Polymers by ATRP using an Aromatic Dioxazoyl Functionalized Initiator Precursor.

Difunctionalized initiator adducts, obtained by reacting an appropriate organolithium compound with a symmetrically substituted 1,1-diphenylethylene derivative, have been utilized for the introduction of two functional groups at the α-terminus of the polymer chain by anionic polymerization methods. For example, Kim and coworkers[22] used an amine initiator adduct, formed by the crossover reaction between n-butyllithium and 1,1-bis(4-dimethylaminophenyl)-ethylene, as the initiator for the polymerization of styrene in the preparation of aromatic tertiary amine chain end functionalized polystyrene.

Similarly, by the ATRP process, the preparation of chain end functionalized polymers carrying two functional groups at the α-terminus of the polymer chain was achieved by using a specific difunctionalized initiator adduct, derived from the reaction of an appropriate disubstituted 1,1-diphenylethylene derivative with (1-bromoethyl)benzene in the presence of CuBr/bpy as the metal complex catalyst, for the polymerization of vinyl monomers by ATRP methods. Recently, Ndawuni[27] used the ATRP method to prepare α-bis(amine) functionalized polystyrene by using an amine functionalized initiator adduct, derived from a specific amine disubstituted 1,1-diphenylethylene precursor derivative, as initiator for the ATRP of styrene. For example, a diamine functionalized initiator adduct, prepared *in situ* by reaction of 1,1-bis(4-dimethylaminophenyl)ethylene with (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst, was utilized as a diamine functionalized initiator for the polymerization of styrene to prepare well defined α-bis(amine) functionalized polystyrene.

The current study describes the one-pot ATRP chain end functionalization using a new dioxazolyl functionalized initiator adduct, (**12**), prepared *in situ* by the reaction of (1-bromo- ethyl)benzene with 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]-ethylene, (**13**), as an initiator for the ATRP of styrene to produce α-bis(oxazolyl) functionalized polystyrene, (**13**). In addition, the *in situ* post ATRP chain end modification reaction of α-bis(oxazolyl) functionalized polystyrene, (**13**) with 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene affords α,ω-tetrakis-(oxazolyl) functionalized polystyrene, (**14**). Moreover, the quantitative chemical transformation of the oxazoline groups of α-bis(oxazolyl) functionalized polystyrene, (**13**) and α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) to the carboxylic acid group by successive acid and base hydrolysis and final acidification provides the corresponding well defined carboxyl functionalized polymers.

#### 4.1.5.1 Aromatic Dioxazolyl Functionalized Initiator Precursor: Synthesis of 1,1-Bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]-ethylene, (11).

The most efficient method for the preparation of 2-aryl-2-oxazoline derivatives involves the conversion of the aromatic carboxylic acids or their acid chlorides to the corresponding hydroxy amides by treatment with an appropriate amino alcohol and subsequent cyclization of the hydroxy amide intermediate with thionyl chloride to give the desired oxazoline compound.

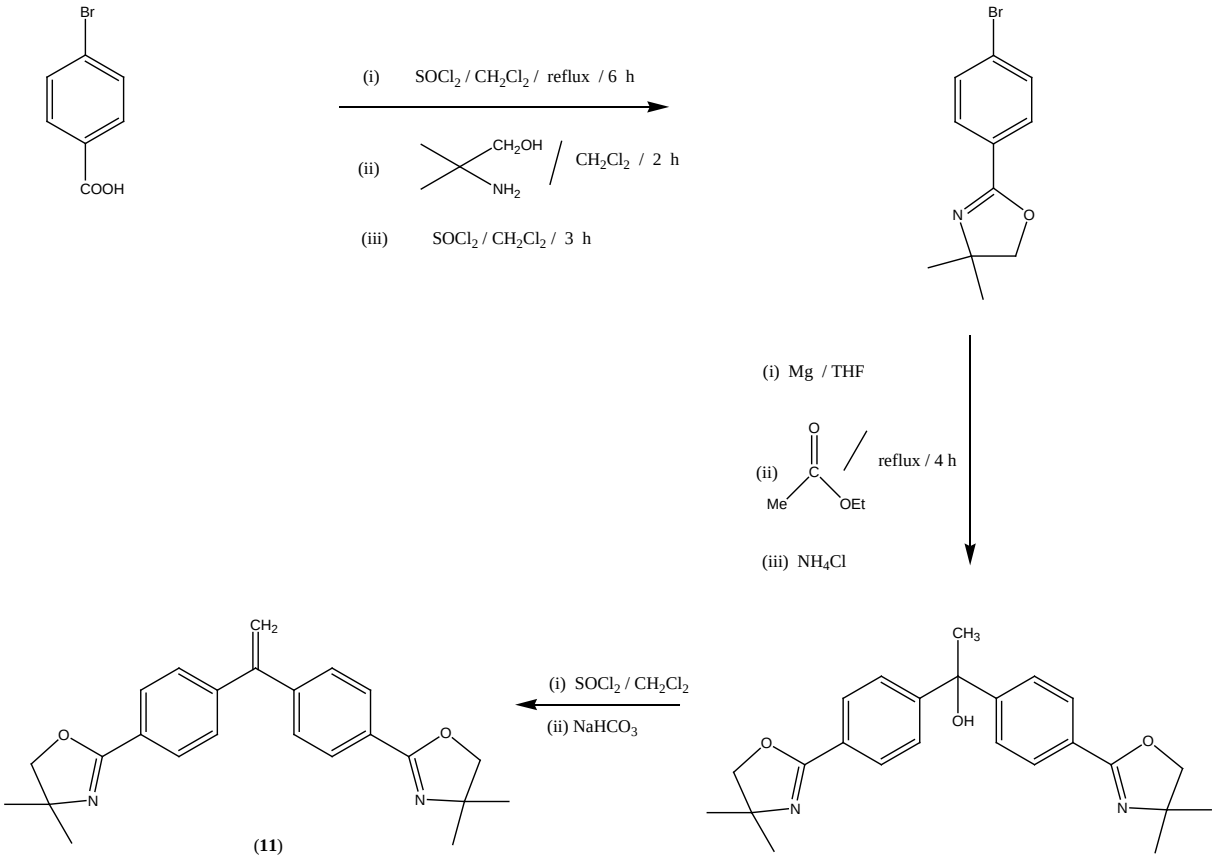
The synthesis of a new 1,1-diphenyethylene derivative, 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) was achieved in three major steps:

(a) The synthesis of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline from 4-bromobenzoic acid, according to the modified method reported by Meyers and coworkers[138]and Shchepinov and coworkers[140].

(b) The synthesis of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol by coupling of ethyl acetate with the Grignard reagent derived from 2-[(4-bromophenyl)-4,4-dimethyl-2-oxazoline.

(c) The dehydration of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol using thionyl chloride to form 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl)-phenyl]ethylene, (**11**).

The following pathway outlines the synthetic route for the preparation of 1,1-bis[4-2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**):




(**11**)

**2-(4-Bromophenyl)-4,4-dimethyl-2-oxazoline**: The synthesis of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline in low yields was reported by Meyers and coworkers[138] using the commercially available 4-bromobenzoic acid as the starting material. However, by adopting a modified method by Meyers[138]and Shchepinov[139], the preparation of 2-(4-bromo-phenyl)-4,4-dimethyl-2-oxazoline was obtained in high yield. Treatment of 4-bromobenzoic acid with $SOCl_2$ at reflux followed by the addition of 2-amino-2-methyl-1-propanol and the subsequent cyclization of the corresponding amide in the presence of thionyl chloride afforded 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline in 82% yield. Recrystallization of the crude product from hexane gave pure 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline as fine white crystals with a melting point of 37.2-38.4

°C, in good agreement with the literature value of 37-38 °C reported by Meyers and coworkers[138].

The FTIR spectrum (Figure 35) of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline shows an absorption band at 1649 $cm^{-1}$, which corresponds to the C=N stretching mode of the oxazoline group.

The $^{1}H$ NMR spectrum (Figure 36) of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline, exhibits the following spectral data: Singlets at 1.35 and 4.08 ppm due to the resonances of six equivalent methyl protons ($C\underline{H}_3)_2C$- and two methylene protons (-$C\underline{H}_2$-O-), respectively; doublets of doublets at 7.40-7.82 ppm and 7.83-7.86 ppm, attributed to the resonances of the aromatic protons of the phenyl ring, characteristic of a p-substituted benzene ring.

The $^{13}C$ NMR spectrum (Figure 37) of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline compounds exhibit signals at 161.35, 78.97, 67.50 and 28.26 ppm, due to the resonances of the carbon atom of the $\underline{C}$=N group, the methylene carbon ($\underline{C}H_2$-O), the quaternary carbon ($\underline{C}$-$(CH_3)_2$ and the methyl carbons [C($\underline{C}H_3$)] of the oxazoline group, respectively.

**1,1-Bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol**: Different synthetic pathways for the preparation of 1,1-diphenylethanol derivatives have been reported in the literature[19,143]. The reaction of an appropriate Grignard reagent with a specific carbonyl compound provides a facile route for preparation of alcohols. Meyers and co-workers[138] utilized the Grignard reagent, formed from 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline as a precursor compound, in reactions with a range of ketone derivatives leading to the formation of a series of hydroxyl compounds. Summers and Quirk[19] described the synthesis of 1-[4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl))phenyl]-1-phenylethanol by the treatment of 4-(4,5-dihydro-4,4-dimethyl-2-oxazolyl)benzophenone with methyl magnesium

bromide. Similarly, Quirk and coworkers[143] used methyl magnesium iodide to convert 4-bromobenzophenone to 1-(4-bromophenyl)-1-phenylethanol.

A new compound, 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol was prepared by the treatment of anhydrous ethyl acetate with a Grignard reagent, formed by the reaction of 2-(4-(bromophenyl)-4,4-dimethyl-2-oxazoline with magnesium in anhydrous THF. After addition of ammonium chloride solution, the crude product was obtained as a white solid. Recrystallization of the crude product from hexane gave pure 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]-ethanol as white fluffy crystals in 55% yield with a melting point of 218.7-219.9 °C.

The FTIR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol is shown in Figure 38. The absorption bands at 3235 and 1643 $cm^{-1}$ correspond to the O-H group frequency of the hydroxyl group and the C=N bond vibrations in the oxazoline group, respectively.

The structure of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol was further confirmed by the NMR spectrometry. The $^{1}H$ NMR spectrum (Figure 39) of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol was characterized by the presence of the following signals: (a) a singlet at 1.34 ppm, due to the resonance of twelve equivalent methyl protons [2 x -C($C\underline{H}_3)_2$] of the two oxazoline rings; (b) a singlet at 1.94 ppm, assigned to the resonance of the three equivalent methyl protons adjacent to the hydroxyl group [C(OH)$C\underline{H}_3$]; (c) a singlet at 2.73 ppm, attributed to the resonance of the hydroxyl proton [-C($O\underline{H}$)$CH_3$] of the carbinol group; (d) a singlet at 4.06 ppm, due to the resonance of the four methylene protons (2 x -$C\underline{H}_2$-O-) of the two oxazoline rings, and (e) signals between 7.40-742 ppm and 7.83-7.86 ppm, due to the resonances of the aromatic protons of the phenyl rings.

The $^{13}C$ NMR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol is given in Figure 40. The $^{13}C$ NMR spectrum shows the following characteristic peaks: (a) a signal at 30.58 ppm, attributed to the resonance of the methyl carbon atom adjacent to the OH group (b) a signal at 28.37 ppm, due to the resonance of the primary carbon atoms of the methyl groups [2 x C($\underline{C}H_3)_2$-] in the two oxazoline groups; (c) a peak at 67.55 ppm, due to the resonance of two quaternary carbon atoms (2 x $\underline{C}(CH_3)_2$ of the oxazoline group; (d) a signal at 79.06 ppm, which corresponds to the resonance of the two methylene carbon atoms, (2 x -$\underline{C}H_2$-O-); (e) a signal at 161.76 ppm is assigned to the resonance of two $\underline{C}$=N groups of the two oxazoline rings; (f) signals between 125.79-128.17 ppm, due to the resonances of aromatic carbon atoms of the benzene rings and (g) a signal at 150.70 ppm, due to the resonance of the quaternary carbon of the carbinol group adjacent to the phenyl rings.

**1,1-Bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (11)**: In general, the synthetic route for the preparation of symmetrically substituted 1,1-diphenyl-ethylene derivatives involves the direct conversion of the symmetrically disubstituted benzophenone derivative to the corresponding 1,1-diphenylethylene compound via the classical Wittig reaction with phosphoryl ylides[142] or the Tebbe reagent[22]. Another synthesis method for the preparation of symmetrical 1,1-diphenylethylene derivatives entails the conversion of the symmetrical benzophenone precursor to the corresponding carbinol, followed by spontaneous thermal or acid catalyzed dehydration of the intermediate carbinol[19].

The synthesis of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) was effected by the dehydration of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethanol in the presence of a weak Lewis acid such as $SOCl_2$[144]. Recrystallization of the crude product from hexane gave pure 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) as white crystals in 55% yield, with a melting point of 259.5-261.1 °C.

The FTIR spectrum (Figure 41) of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]-ethylene, (**11**) shows an absorption band at 1641 $cm^{-1}$, attributed to the absorption of the C=N groups of the oxazoline rings. The absence of an absorption band at 3235 $cm^{-1}$, due to the hydroxyl group absorption of the precursor molecule, implies that the dehydration reaction proceeded without any side reactions.

The $^{1}H$ NMR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) is shown in Figure 42. The singlets at 1.38 and 4.10 ppm are assigned to the resonances of the twelve equivalent methyl protons [2 x -C(C$\underline{H}_3)_2$] and four methylene protons (2 x -C$\underline{H}_2$O-) in the oxazoline moiety, respectively. The absence of the resonance of the hydroxyl proton at 2.73 ppm and the presence of a new singlet downfield at 5.55 ppm, due to the resonance of the two methylene olefinic protons (C$\underline{H}_2$=C-), confirms the completion of the dehydration reaction. The signals between 7.32-7.35 and 7.88-7.91 ppm are attributed to the resonances of the aromatic protons of the para substituted phenyl rings.

The $^{13}C$ NMR spectrum (Figure 43) of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) is characterized by the presence of signals at 28.40, 67.61, 79.10, 161.28 ppm, due to the resonances of the carbon atoms of the 2 x C($\underline{C}H_3)_2$, 2 x $\underline{C}(CH_3)_2$, 2 x -$\underline{C}H_2$-O- and 2 x $\underline{C}$=N groups of the oxazoline ring, respectively. The presence of a signal at 116.23 ppm confirms the presence of the carbon resonance of the olefin group ($H_2\underline{C}$=C-) of the 1,1-diphenylethylene derivative, consistent with literature reports[19]. In addition, the resonance at 148.80 ppm is assigned to the carbon resonance of the ($H_2C$=$\underline{C}$-) group. The signals at 127.50-128.18 and 143.77 ppm are due to the resonances of the carbon atoms of the two phenyl rings.

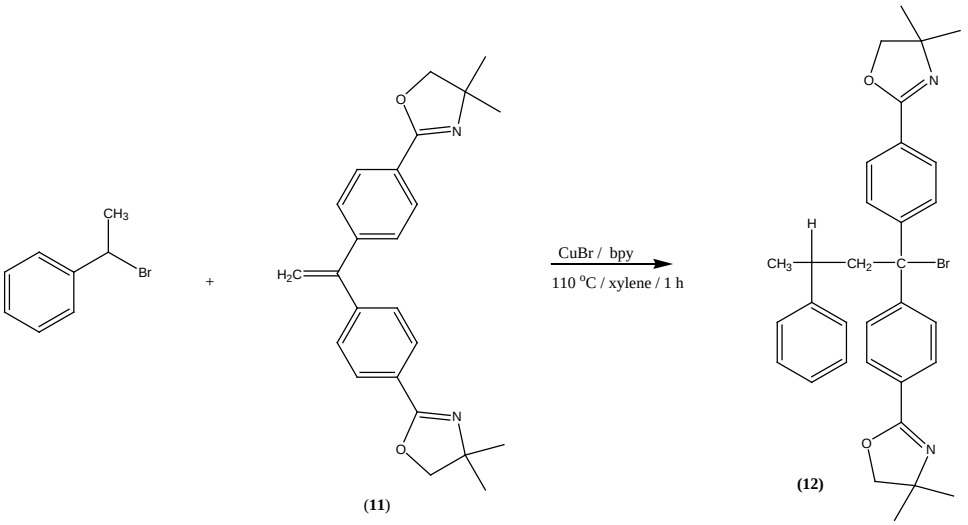
A new compound, 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) was prepared by the following synthesis steps: (a) the high yield synthesis of

2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline using 4-bromobenzoic acid as the starting material, (b) the coupling reaction between anhydrous ethyl acetate and the Grignard reagent, derived from 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline, to afford 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol, and (c) the subsequent dehydration of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol using $SOCl_2$ to give the corresponding 1,1-diphenylethylene compound, 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) in high yield, as evidenced by the spectroscopic and chromatographic data.

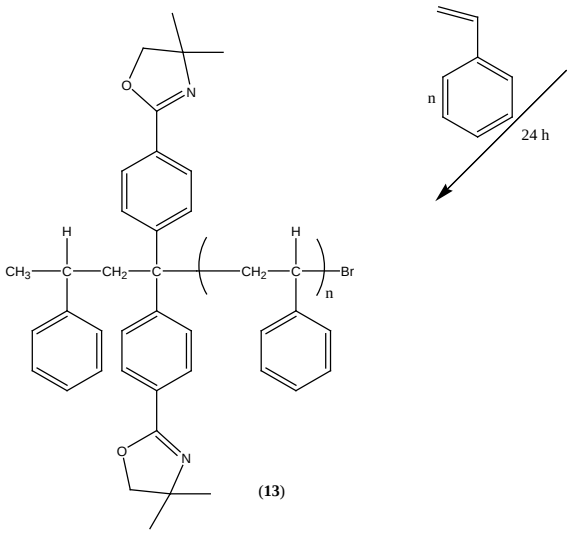
#### 4.1.5.2 Synthesis of α-Bis(oxazolyl) Functionalized Polystyrene, (13)

A difunctionalized initiator adduct, prepared by the reaction of an appropriate symmetrically difunctionalized 1,1-diphenylethylene compound and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst complex, can be employed as a difunctionalized initiator for the polymerization of styrene to prepare α-bis functionalized polymers by ATRP methods[27-28]. For example, Mputumana[28] reported the synthesis of well defined α-disiloxyl functionalized polystyrene using a disiloxyl functionalized 1,1-diphenylethylene as functionalized initiator precursor in ATRP reactions.

Similarly, the ATRP functionalization reaction which involves the use of a dioxazolyl functionalized 1,1-diphenylethylene derivative as an initiator precursor in the ATRP of styrene provides a novel route for the preparation of α-bis(oxazolyl) functionalized polystyrene, (**13**). A dioxazolyl initiator adduct, (**12**), generated *in situ* by the reaction of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (**11**) with (1-bromoethyl)benzene in the presence of the CuBr/bpy catalyst system, was employed as initiator for the polymerization of styrene by ATRP methods to produce well defined α-bis(oxazolyl) functionalized polystyrene, (**13**) according to the following pathway:




(**11**) (**12**)




(**13**)

The most efficient chain end functionalization reaction was effected by using the ratio of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) to styrene of 32:1 and (1-bromoethyl)benzene:CuBr:bpy = 1:1:3 for the polymerization of styrene at 110°C for 24 hours. After complete *in situ* formation of the dioxazolyl functionalized initiator adduct, (**12**) after 1 h, styrene was then added to the green reaction mixture, followed by heating for 24 h. The polymer was precipitated from THF into excess methanol, filtered and vacuum dried to give α-bis(oxazolyl) functionalized polystyrene, (**13**) as a white solid.

Thin layer chromatographic analysis of α-bis(oxazolyl) functionalized polystyrene, (**13**) shows one spot on the chromatogram ($R_f$ = 0.20, toluene) with the absence of any unfunctionalized polystyrene ($R_f$ = 0.99, toluene), indicating the formation of α-bis(oxazolyl) functionalized polystyrene, (**13**) in quantitative yields.

The size exclusion chromatogram (Figure 44) of α-bis(oxazolyl) functionalized polystyrene, (**13**) shows a monomodal molecular weight distribution with $\overline{M}_w/\overline{M}_n$ = 1.47 and $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol which corresponds to 82% monomer conversion. Furthermore, a tailing of the size exclusion chromatogram curve on the low molecular weight side is observed, implying unequal growth of the propagating polymer chains and consequently, the production of a polymer with a broad molecular weight distribution. The use of the copper(I) bromide/bpy catalyst complex in a non polar xylene solvent could lead to a heterogenous polymerization reaction medium and thus reducing the concentration of the deactivating copper(II) species[42,155-156]. This results in different rates of initiation and the subsequent uneven growth of the polymer chain, producing a polymer with a slightly broad molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = 1.47)[7-8]. Resonance stabilization of the initiating radical in conjunction with the electron withdrawing effect of the C=N and C-O groups of the oxazoline ring, reduces the reactivity of the active initiator radicals and consequently the initiation efficiency of the dioxazolyl initiator adduct, (**12**)[7-11]. Moreover, the experimental number average molecular weight value is higher than the $M_n^{theory}$ value of 3.0 x $10^3$ g/mol at 100% monomer conversion. Due to possible side reactions associated with the formation of the initiator adduct, the concentration of the initiator is reduced leading to the formation of higher number average molecular weight values. In addition, the use of toluene, a less polar solvent, could result to the precipitation of the $CuBr_2$/bpy metal complex and incomplete initiator formation. Thus, the $K_{ATRP}$ was shifted towards the propagating radicals and subsequent production of high molecular weight polymer[7-8,157]. Moreover, the two oxazoline group per initiator adduct could enhance the coordination reactions with the copper species,

leading to significant reduction in the concentration of the initiator and consequent production of a polymer with a higher number average molecular weight[7,8].

The FTIR spectrum of α-bis(oxazolyl) functionalized polystyrene, (**13**) is shown in Figure 45. A strong absorption band, due to the C=N stretching mode of the oxazoline groups of α-bis(oxazolyl) functionalized polystyrene, (**13**), was observed at 1649 $cm^{-1}$, confirming the presence of the oxazoline end groups.

The $^{1}H$ NMR spectrum (Figure 46) of α-bis(oxazolyl) functionalized polystyrene, (**13**) confirms the incorporation of the oxazoline functionality at the α-terminus of the polymer chain. The characteristic peaks at 4.10-4.12 ppm are attributed to the presence of the resonance of four methylene protons (2 x -C$\underline{H}_2$-O-) in the oxazoline ring. The signals at 4.35-4.62 ppm corresponds to the resonance of the (-C$\underline{H}$Br) group[107] at the ω-terminus of α-bis(oxazolyl) functionalized polystyrene, (**13**). The signal at 0.81-1.22 ppm is due to the resonance of the methyl protons in the initiator fragment at the α-terminus of the polymer chain. The resonances of the aromatic protons of the initiator fragment, (**12**) are observed between 7.61-8.02 ppm, indicating the presence of the initiator species at the α-terminus of the polymer chain.

The presence of two oxazoline end groups in α-bis(oxazolyl) functionalized polystyrene, (**13**) was confirmed by the $^{13}C$ NMR spectrometry. The $^{13}C$ NMR spectrum (Figure 47) of α-bis(oxazolyl) functionalized polystyrene, (**13**) shows the following characteristic signals for the carbon atoms of the oxazoline rings: (a) a peak at 28.38 ppm, due to the resonance of 2x -C($\underline{C}H_3)_2$- groups; (b) the signal at 67.35 ppm is attributed to the resonance of the 2 x $\underline{C}(CH_3)_2$ groups; (c) a peak at 79.22 ppm, corresponds to the resonance of the 2 x -$\underline{C}H_2$-O- groups and (d) a signal at 161.91 ppm, assigned to the two $\underline{C}$=N groups in the oxazoline rings. The signal due to the resonance of the methyl carbon atom of the initiating species is observed at 29.98 ppm. The signal at 45.87 ppm is due to the

resonance of the secondary carbon atom (CHBr)[3] at the ω-terminus of α-bis(oxazolyl) functionalized polystyrene, (**13**).

A new dioxazolyl functionalized initiator adduct, (**12**) prepared *in situ* by the reaction of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) with (1-bromoethyl)benzene in the presence of the CuBr/bpy catalyst system in xylene, was used as a dioxazolyl functionalized initiator for the ATRP of styrene to afford α-bis(oxazolyl) functionalized polystyrene, (**13**) in quantitative yields. Well defined polystyrene with good control of the number average molecular weight, molecular weight distribution and chain end functionality was obtained in a controlled/"living" polymerization process.

#### 4.1.5.3 Synthesis of α,ω-Tetrakis(oxazolyl) Functionalized Polystyrene, (14)

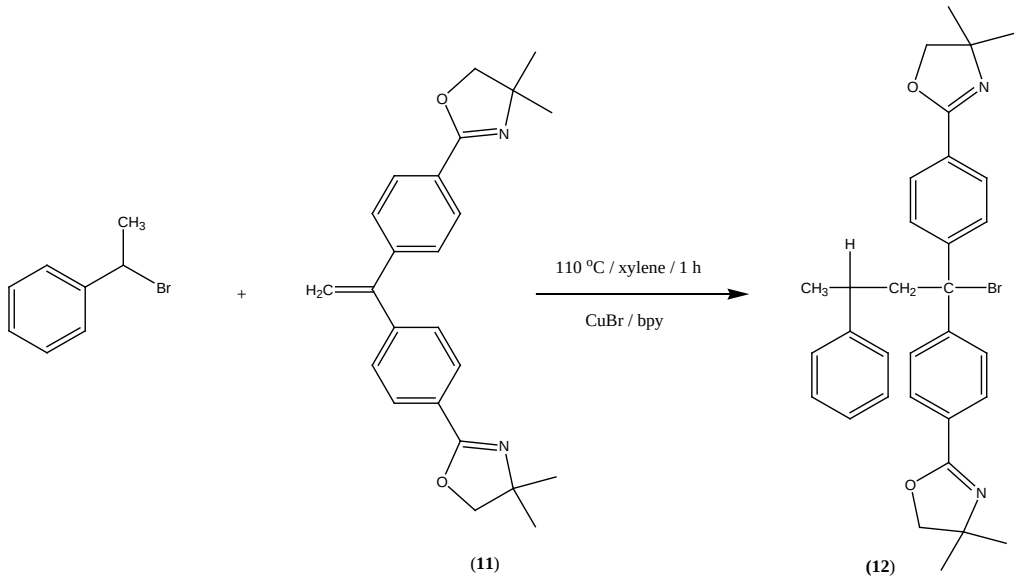
The preparation of telechelic polymers can be achieved by post ATRP chain end transformation reactions by conversion of the terminal CH-Br end group of an α-functionalized polymer derivative to another functional group by the standard organic reactions. Ndawuni[27] outlined a novel *in situ* chain end modification reaction for the synthesis of α,ω-tetrakis(amine) functionalized polymers by post ATRP chain end transformation reactions via the following method:

(a) The atom transfer radical polymerization of styrene initiated by a diamine functionalized initiator adduct derived from the appropriate diamine functionalized 1,1-diphenylethylene derivative, followed by

(b) The addition of an appropriate diamine functionalized 1,1-diphenyl ethylene molecule to the ω-terminus of the polymer chain at the end of the ATRP process.

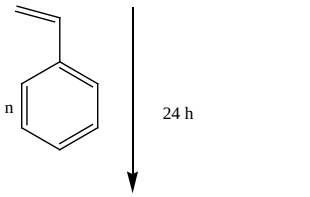
Similarly, α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) was prepared by the *in situ* chain end modification reaction of α-bis(oxazolyl) functionalized polystyrene, (**13**) with 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**), after completion of the ATRP reaction.

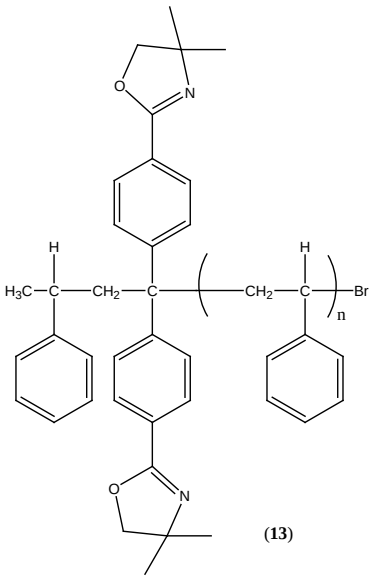
The ATRP of styrene, initiated with a dioxazolyl functionalized initiator adduct, (**12**) produces α-bis(oxazolyl) functionalized polystyrene, (**13**). The dioxazolyl functionalized initiator adduct was obtained by the reaction of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (**11**) with (1-bromoethyl)benzene in the presence of the CuBr/bpy catalyst system. An aliquot of the green reaction mixture was analyzed by gas chromatography in order to determine the presence of unreacted styrene. Upon complete styrene consumption within 24 h and in a one-pot process, excess 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (**11**) in xylene was then added to the reaction mixture to afford α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) in quantitative yields according to the following pathway:



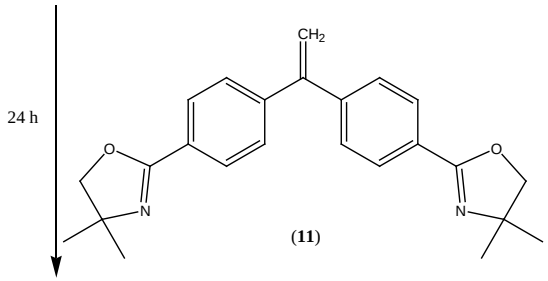

(**11**)

(**12**)

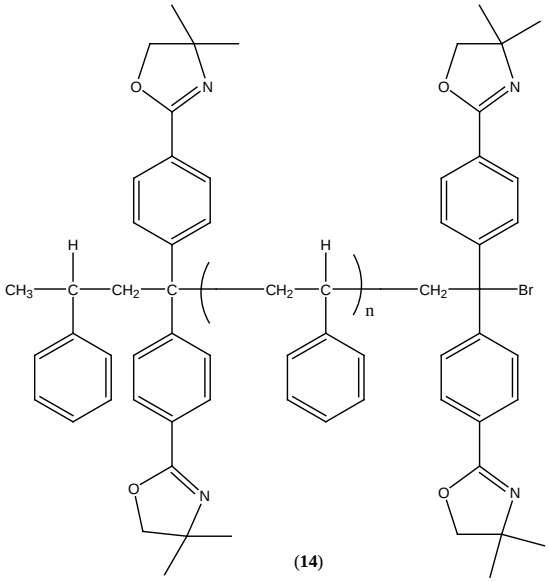



(**13**)




(**11**)




(**14**)

TLC analysis of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) using toluene as an eluent gave one spot on the chromatogram with the $R_f$ value of 0.18, consistent with the quantitative formation of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**). The $R_f$ value of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) differs slightly with the $R_f$ = 0.20 of α-bis(oxazolyl) functionalized polystyrene, (**13**).

Figure 48 shows a monomodal size exclusion chromatogram of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) indicating the absence of any polymer coupling reactions during the post ATRP chain end modification reaction. α,ω-Tetrakis(oxazolyl) functionalized polystyrene, (**14**) with number

average molecular weight value of $\overline{M}_n^{SEC}$ = 4.4 x $10^3$ g/mol and broad molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = 1.48) was obtained. The tailing effect on the high molecular end of the size exclusion chromatogram indicates unequal growth of polymer chains due to sparingly solubility of the copper(I) bromide catalyst complex in xylene, which could results to initiation at different stages of the polymerization reaction[42,155]. Moreover, the presence of the electron withdrawing oxazoline groups relative to the propagating radicals reduces the reactivity of the reactive oxazolyl initiator radicals, resulting in the formation of polymers with broader molecular weight distributions[6].

The FTIR spectrum (Figure 49) of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) shows a strong absorption band at 1651 $cm^{-1}$, which corresponds to the C=N bond vibration of the oxazoline rings.

The $^1$H NMR spectrum of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) is shown in Figure 50. The characteristic broad signal at 4.10-4.12 ppm, is assigned to the resonance of eight methylene protons (4 x -C<u>H</u>$_2$-O-) of the oxazoline rings at the polymer chain ends of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**). The absence of a signal at 4.25-4.62 ppm, which corresponds to the resonance of the terminal proton of the (-C<u>H</u>Br) group at the polymer chain end of α-bis(oxazolyl) functionalized polystyrene, (**13**) precursor, confirms the incorporation of a 1,1-diphenylethylene precursor at the ω-terminus of the polymer chain of α-bis(oxazolyl) functionalized polystyrene, (**13**) by post ATRP chain modification reactions. The signals between 1.04-1.19 ppm and 7.61-7.86 ppm are due to the resonances of methyl protons and the aromatic protons of the initiator fragment, respectively.

The $^{13}$C NMR spectrum of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) is shown in Figure 51 and depicts the following characteristic signals: the peaks at 28.40, 67.50, 79.09 and 161.88 ppm, due to the resonances of the carbon atoms

of the 2 x -C($\underline{C}H_3)_2$, 2 x $\underline{C}(CH_3)_2$, (2 x -$\underline{C}H_2$-O-) and (2 x $\underline{C}$=N) groups of the oxazoline ring, respectively. The signal due to the resonance of the methyl carbon atom of the initiator fragment is observed at 30.02 ppm.

Well defined α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) was prepared *in situ* by the post ATRP chain end functionalization reaction using α-bis(oxazolyl) functionalized polystyrene, (**13**) obtained by standard ATRP methods, as precursor in a one-pot chain end functionalization process. The *in situ* addition of excess 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) to freshly prepared α-bis(oxazolyl) functionalized polystyrene, (**13**) produces the corresponding α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) in quantitative yields.

### 4.1.6 Syntheses of Aromatic Carboxyl Functionalized Polymers.

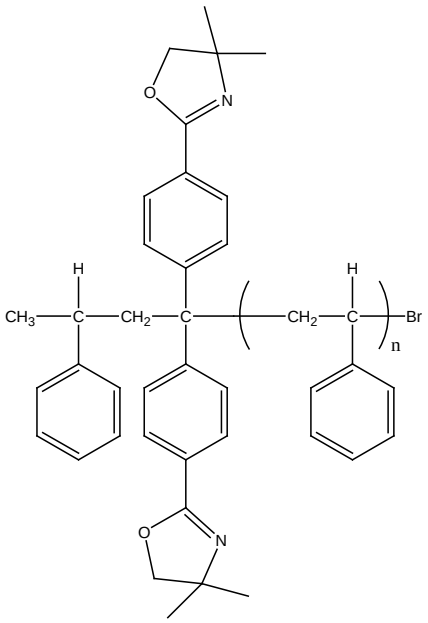
The reactions of poly(styryl)lithium with 1,1-diphenylethylene derivatives substituted with protected carboxylic acid groups, followed by removal of the carboxylic acid protecting group, provides a useful method for the synthesis of chain end functionalized polymers by anionic polymerization methods[19]. Summers and Quirk[19] reported the preparation of ω-carboxyl functionalized polystyrene by the reaction of poly(styryl)lithium with 5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**). The resultant oxazolyl functionalized polystyrene was subjected to acid and base hydrolysis, followed by final acidification reactions, to afford quantitative yields of ω-carboxyl functionalized polystyrene.

The ATRP method is the most versatile controlled radical polymerization method for the synthesis of well defined functionalized polymers and allows the control of the number average molecular weights, molecular weight distributions, molecular architecture, copolymer composition and microstructure of polymers during the

ATRP process[6-11]. By utilizing carboxyl functionalized initiators, with the carboxylic acid group in its free form in ATRP reactions, α-carboxyl functionalized polymers with well defined polymer properties are obtained. In addition, α-carboxyl functionalized polymers can also be prepared by ATRP methods using indirect methods[11]. To avoid the complexation reaction between the transition metal complex and the free carboxylic acid group[15-17], functionalized initiators, bearing derivatives of carboxylic acid group are frequently employed in the synthesis of α-carboxyl functionalized polymers. No reports on the ATRP preparation of α-bis(carboxyl) and α,ω-tetrakis(carboxyl) functionalized polymers by ATRP methods have been reported in the literature. In the current study, the quantitative chemical transformation of the oxazoline groups in α-bis(oxazolyl) functionalized polystyrene, (**13**) and α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) to the corresponding carboxylic acid groups by successive acid and base hydrolysis and final acidification reactions, affords the corresponding well defined carboxyl functionalized polymers.

#### 4.1.6.1 Synthesis of α-Bis(carboxyl) Functionalized Polystyrene, (15)

The α-bis(oxazolyl) functionalized polystyrene, (**13**) was subjected to successive acid and base hydrolysis, followed by acidification, to afford the corresponding α-bis(carboxyl) functionalized polystyrene, (**15**) via the quantitative method reported by Nakahama and coworkers[141], outlined in the following reaction pathway:

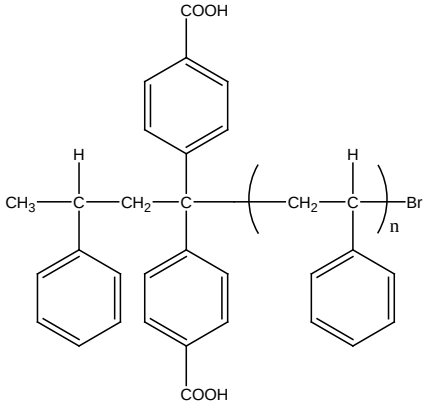


(**13**)

(i) 3 M HCl / THF / reflux / 12 h

(ii) 20 % NaOH / THF / reflux / 12 h

(iii) 3 M HCl



(**15**)

TLC analysis of α-bis(carboxyl) functionalized polystyrene, (**15**) in toluene gave a $R_f$ value of 0, which indicated the quantitative transformation of the oxazoline group to the carboxyl analogue without the occurrence of decarboxylation reactions. The absence of a spot on the chromatogram at $R_f$ = 0.21 (toluene) confirms the complete conversion of the α-bis(oxazoyl) functionalized polystyrene, (**13**) precursor to α-bis(carboxyl) functionalized polystyrene, (**15**) during the hydrolysis process.

The size exclusion chromatogram (Figure 52) of α-bis(carboxyl) functionalized polystyrene, (**15**) shows a monomodal molecular weight distribution curve with $\overline{M}_n^{SEC}$ of 3.8 x $10^3$ g/mol and a $\overline{M}_w/\overline{M}_n$ value of 1.49, indicating that the hydrolysis reaction proceeded without polymer decomposition and crosslinking reactions.

Moreover, the presence of the carboxylic acid groups at the α-terminus of α-bis(carboxyl) functionalized polystyrene, (**15**) was confirmed by non-aqueous titration measurements with standardized methanolic potassium hydroxide in the presence of phenolphthalein as indicator. The observed $\overline{M}_n^{titr}$ value of 3.8 x $10^3$ g/mol is in good agreement with the $\overline{M}_n^{SEC}$ value of = 3.8 x $10^3$ g/mol, which is consistent with the introduction of two carboxylic acid units at the α-terminus of the polymer chain.

The FTIR spectrum (Figure 53) of α-bis(carboxyl) functionalized polystyrene, (**15**) shows the presence of an absorption band at 1689 $cm^{-1}$, assigned to the C=O bond vibrations of the carboxyl functionality at the polymer chain ends. The absence of the characteristic absorption band at 1649 $cm^{-1}$, due to the C=N stretching modes of the oxazoline precursor, is consistent with a quantitative hydrolysis reaction to produce the corresponding carboxylic acid group.

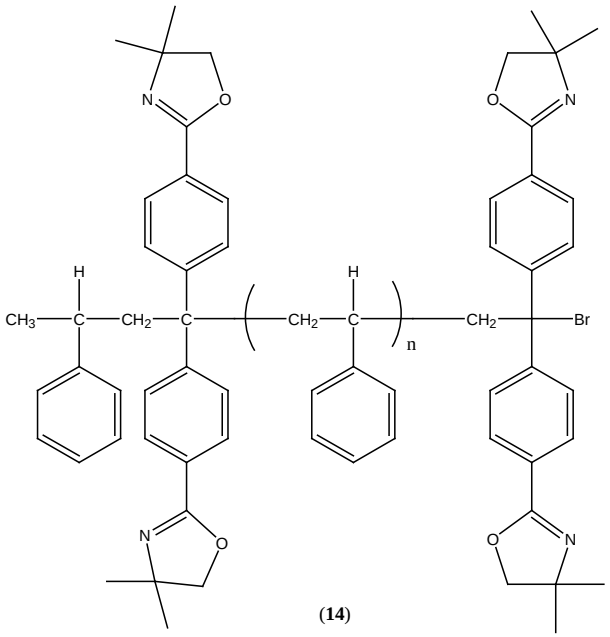
The $^{1}$HNMR spectrum (Figure 54) of α-bis(carboxyl) functionalized polystyrene, (**15**) indicates the presence of a broad peak at 4.21-4.54 ppm, which confirms that the acid and the base hydrolysis reactions occurred without modification of the –CHBr group at the ω-terminus[107]. Furthermore, the absence of a signal between 4.11 and 4.13 ppm, corresponding to the resonance of the methylene protons of -C$\underline{H}_2$O- group of the α-bis(oxazoyl) functionalized polystyrene, (**13**) precursor, confirms the complete chemical conversion of the oxazoline group to the carboxylic acid functional group. The signals at 1.11-1.23 ppm and 7.82-8.17 ppm due to the resonances of the methyl and aromatic protons of the initiator fragment, respectively, are observed in the $^{1}$H NMR spectrum.

The $^{13}$C NMR spectrum (Figure 55) of α-bis(carboxyl) functionalized polystyrene, (**15**) provides evidence for the complete deblocking of the oxazoline group to the corresponding carboxylic acid moiety. The signal at 171.86 ppm due to the resonances of the carbon atoms of the $\underline{C}$OOH groups as well as the absence of the characteristic signals at 28.38, 67.35, 79.22 and 161.91 ppm, due to the respective resonances of the carbon atoms of the 2x [-C($\underline{C}H_3)_2$-], 2 x [$\underline{C}(CH_3)_2$], 2 x -$\underline{C}H_2$-O- and 2 x $\underline{C}$=N groups of the oxazoline ring of the α-bis(oxazolyl) functionalized polystyrene, (**13**) precursor, confirms the complete conversion of the oxazoline group to the carboxylic acid group. The signal at 30.27 ppm is assigned to the methyl carbon atom resonance of the initiator fragment at the α-end of α-bis(carboxyl) functionalized polystyrene, (**15**). The peak at 45.54 ppm corresponds to the resonance of the carbon atom of the CHBr group[3] at the ω-chain end of the polymer.

Spectroscopic, chromatographic and non-aqueous titration measurements provide evidence for the quantitative synthesis of α,bis(carboxyl) functionalized polystyrene, (**15**) by subjecting α,bis functionalized polystyrene, (**13**) to successive acid catalyzed hydrolysis and saponification and acidification reactions.

#### 4.1.6.2 Synthesis of α,ω-Tetrakis(carboxyl) Functionalized Polystyrene, (16)

The conversion of the oxazolyl chain ends of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) to the corresponding carboxylic acid groups was conducted by the method of Nakahama and coworkers[141]. The acid and base catalyzed hydrolysis of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) was performed successively in the presence of 3 M HCl and 20% of NaOH in THF at reflux. After final acidification, the corresponding α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**) was obtained in quantitative yield according to the following pathway:

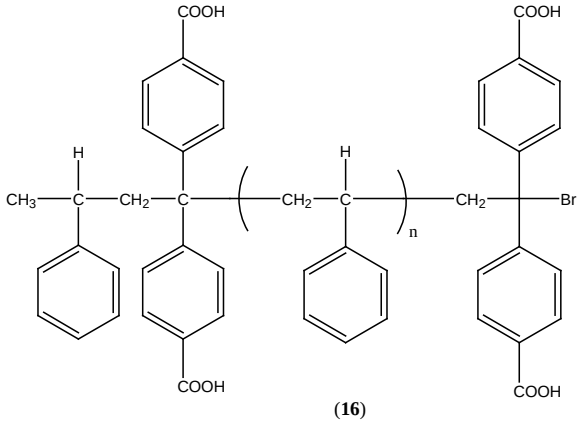


(**14**)

(i) 3 M HCl / THF / reflux / 12 h

(ii) 20 % NaOH / THF / reflux / 12 h

(iii) 3 M HCl



(**16**)

TLC analysis of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**) in toluene shows a single spot on the chromatogram with the $R_f$ value of 0, indicating the quantitative conversion of the oxazoline group to the carboxylic acid group.

The size exclusion chromatogram (Figure 56) of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16)** shows a monomodal molecular weight distribution curve with $\overline{M}_w/\overline{M}_n$ = 1.48 and tailing on the low molecular weight side. The number average molecular weight value of ($\overline{M}_n^{SEC}$) = 4.1 x $10^3$ g/mol compares favourably with the number average molecular weight value determined by non-aqueous titration measurements. Titration of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**) with standardized methanolic potassium hydroxide in the presence of phenolphthalein as indicator gave a $\overline{M}_n^{titr}$ value of 4.0 x $10^3$ g/mol, which corresponds to the introduction of four carboxylic acid groups at the polymer chain ends.

The FTIR spectrum of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**) is shown in Figure 57. The absence of an absorption band at 1649 $cm^{-1}$, due to the C=N bond vibrations of the oxazoline group in the α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) precursor shows the quantitative chemical conversion of the oxazoline group to the corresponding carboxyl acid group. The presence of an absorption band at 1690 $cm^{-1}$, attributed to the C=O bond vibrations of carboxylic acid groups, implies the complete hydrolysis reaction.

The $^1$H NMR spectrum of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**) is shown in Figure 58. The signal between 4.08 and 4.09 ppm, attributed to the resonance of the oxazoline methylene protons (4 x -$CH_2$O-), are absent which confirms the complete removal of the oxazoline group. The signals at 0.91-1.02 ppm and 7.61-7.85 ppm correspond to the proton resonances of the methyl and aromatic protons in the initiator fragment, respectively.

The $^{13}$C NMR spectrum of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**) is shown in Figure 59. The signal at 171.26 ppm is attributed to the resonance of the carbonyl carbons of the carboxylic acid groups at the polymer chain ends of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**). In addition, the absence of

signals at 161.88, 79.09, 67.50 and 28.40 ppm, due to the respective carbon atom resonances of <u>C</u>=N, -<u>C</u>$H_2$-O-, $(CH_3)_2$<u>C</u>- and -C(<u>C</u>$H_3)_2$ of the oxazoline ring, provides evidence for the quantitative conversion of the oxazolyl group to the corresponding carboxylic acid group. The signal at 30.35 ppm is due to resonances of the methyl carbon atom of the initiator fragment.

Spectroscopic, chromatographic and non-aqueous titration measurements provide evidence for the quantitative synthesis of α,ω-tetrakis(carboxyl) functionalized polystyrene, (**16**) by treatment of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) with successive acid and base hydrolysis reactions.

## 4.2 ATOM TRANSFER RADICAL POLYMERIZATION: POLYMERIZATION KINETIC STUDIES.

To evaluate the controlled/"living" character of a polymerization reaction, the polymerization kinetics should exhibit three primary experimental features[7-11]:

(a) A linear semilogarithmic first order plot of ln $([M]_o/[M])$ versus time must be obtained, indicating a constant concentration of radicals throughout the polymerization reaction.

(b) A linear evolution of the number average molecular weight ($M_n$) with percentage monomer conversion should occur according to the following equation; $M_n^{theory}$ = % conversion/100 $[M]_o/[I]_o M_{wm} + M_{wl}$, where $M_{wm}$ and $M_{wl}$ represent the average molecular weight of monomer and initiator, respectively.

(c) Polymers with narrow molecular weight distributions, $\overline{M}_w/\overline{M}_n$, below 1.5, which are close to Poisson distribution, must be produced.

### 4.2.1 Synthesis of α-Oxazolyl Functionalized Polystyrene, (2) by ATRP using 2-[(4-Bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (1) as an Oxazolyl Functionalized Initiator.

Few reports on the polymerization kinetic studies of the ATRP of styrene, initiated by oxazoline functionalized initiators, have been reported in the literature. Zhang and coworkers[13] recently demonstrated that the ATRP of methyl methacrylate, initiated with 2-bromomethyl-4,5-diphenyloxazole in the presence of CuBr/bpy catalyst complex, proceeds via a controlled polymerization process. The polymerization reaction followed first order rate kinetics. A linear increase in the number average molecular weight with percentage monomer conversion was observed and poly(methyl methacrylate) with relatively narrow molecular weight distributions of $M_w/M_n$ = 1.10-1.35 were obtained.

The current work describes the polymerization kinetic study of the ATRP reaction of styrene, initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyl-oxazole, (**1**) in the presence of CuBr/bpy or CuBr/PMDETA at different initial monomer to initiator concentration ratios of 50:1, 100:1 and 200:1 for each reaction sequence to produce $\alpha$-oxazolyl functionalized polystyrene, (**2**). The stoichiometry of the relevant reactions was set at [CuBr]: [ligand]: [initiator] = 1:3:1 in diphenyl ether at 110 °C. In a typical experiment, starting at time t = 0, different aliquots (1 mL) were removed from the reaction mixture at 30 min intervals, diluted with THF (9 mL) and subjected to gas chromatography analysis to determine the percentage monomer conversion of styrene with time. The number average molecular weights and molecular weight distributions of the different polymer samples were determined by size exclusion chromatography.

Figure 60 illustrates the plots of percentage monomer conversion versus time for the preparation of α-oxazolyl functionalized polystyrene, (**2**) effected by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) as the oxazolyl functionalized initiator for the ATRP of styrene in the presence of CuBr/bpy and diphenyl ether as a solvent. The rate of the polymerization reaction is dependent on the ratio of monomer to initiator concentration. The polymerization rate decreased with reduced amount of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**). At $[M]_o/[I]_o$ = 50/1, the polymerization reaction proceeded at a very fast rate with 93% monomer conversion observed after 4.5 h of polymerization time. Upon increasing the $[M]_o/[I]_o$ to 100/1 and 200/1, a significant decrease in the speed of the reaction was observed after the reaction time of 4.5 h and the percentage monomer conversion decreased to 76% and 44%, respectively.

The plots of the semilogarithmic coordinates of ln ($[M]_o/[M]$) vs time (Figure 61) for the polymerization reactions shows a linear relationship for each reaction sequence ($[M]_o/[I]_o$ = 50:1, 100:1 and 200:1), indicating that each polymerization reaction is first order with respect to monomer consumption[7]. The results show that the polymerization rate is affected by the concentration of the initiator, with the highest rate of polymerization at higher initiator concentrations. The linearity of the relationship between ln ($[M]_o/[M]$) and time indicates that the concentration of the propagating radicals remained constant during the polymerization process[157]

Figure 62 shows the relationship between $M_n$ and the molecular weight distribution as a function of percentage monomer conversion for each reaction. Linear evolution of the number average molecular weight with percentage monomer conversion was observed for the different reactions at initial monomer to initiator concentration ratios of 50:1, 100:1 and 200:1, suggesting the absence of termination and chain transfer reactions during the propagation steps. The $M_n$

values determined by SEC were higher than the theoretical values, except at high percentage monomer conversion. Deviation from the predetermined number average molecular weight could be due to lower initial initiator concentration, induced by side reactions such as the coordination of the nitrogen in the oxazoline group with the transition metal catalyst[11,74,158], reducing the formation of a stable initiator/CuBr/bpy complex[151,158]. In addition, the deviation from the predetermined number average molecular weight was more pronounced at low initiator concentrations, especially for the $[M]_o/[I]_o$ = 100/1 and 200/1 reactions. Moreover, the poor control of the reaction could be attributed to the low concentration of the deactivating Cu(II) species at the early stages of the polymerization reaction[156]. At high percentage monomer conversion for $[M]_o/[I]_o$ = 50/1 and $[M]_o/[I]_o$ = 100/1 reactions, an apparent decrease in added monomer units before the next deactivation cycle was observed, as evidenced by the experimental $\overline{M}_n$ values, which are comparable with the predicted $\overline{M}_n$ values, which could be attributed to the decrease in the concentration of monomer as the reaction progresses. In addition, the high viscosity of the reactions at high percentage monomer conversion limited the rate of diffusion of the monomers and the propagating radicals, and thus the rate of collision between the reacting molecules could be dramatically reduced[7-8,151]. The change in the molecular weight distribution values versus percentage monomer conversion at low initiator to monomer concentration followed the expected trend and decreased with increase in percentage monomer conversion with the final $\overline{M}_w/\overline{M}_n$ of 1.02 obtained for all polymerization reaction sequences[5,77]. The formation of polymers with narrow molecular weight distributions indicates that the rates of initiation were equal to or greater than the rates of propagation. Fast exchange between active and dormant species occurred and a fixed number of polymer chains have nearly uniform chain length. Moreover, negligible chain transfer reactions occurred after complete formation of the initiator system as well as during the propagation reactions[77].

In order to study the effect of the catalytic system on the 2-[(4-bromomethyl)-phenyl]-4,5-dihydro-4,4-dimethyl oxazole, (**1**) initiated polymerization of styrene, different reactions were conducted at different monomer to initiator concentration ratios of $[M]_o/[I]_o$ = 50:1, 100:1 and 200:1 in the presence of the more reactive CuBr/PMDETA catalyst system. Figure 63 shows the plots of percentage monomer conversion of styrene polymerization initiated by 2-[(4-bromomethyl)-phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of the more reactive CuBr/PMDETA catalyst system. The polymerization rate increased with increased concentration of the initiator. However, at a specific $[M]_o/[I]_o$ ratio, the polymerization rate was higher for the CuBr/PMDETA catalytic system than in the CuBr/bpy catalytic system. For example, at $[M]_o/(I)o$ = 50:1, the percentage monomer conversion value of 95% was obtained within 4 h for the CuBr/PMDETA system, compared with 93% monomer conversion recorded for CuBr/bpy system. The faster reaction and higher percentage monomer conversion are due to lower redox potentials of the coordination complex of copper(I) and PMDETA, since it could be more soluble in diphenyl ether than the CuBr/bpy complex[155]. The experimental results further confirm that, in the presence of PMDETA as ligand, the value of $k_a$ for the ATRP reaction is increased, which implies that radicals are formed at a higher rate which results in faster rates of polymerization[159]. When the monomer to initiator concentration ratios were increased to 100/1 and 200/1, a noticeable decrease in speed of reactions were observed, as evidenced by the lower percentage monomer conversion values of 87% for $[M]_o/[I]_o$ = 100/1 and 66% for $[M]_o/[I]_o$ = 200/1, respectively.

The linear relationship obtained in the plots of ln ($[M]_o/[M]$) versus time for the three different ATRP reactions (Figure 64), catalyzed by the CuBr/PMDETA system, is due to negligible amount of termination and chain transfer reactions, hence the concentration of propagating radicals is constant through out the polymerization process[36,37,155]. The rate of the polymerization reaction is affected by the concentration of the initiator with significantly higher polymerization rates

observed for the reactions at higher monomer to initiator concentration ratios of 50:1 than 100:1 and 200:1, respectively.

Figure 65 represents the plots of the number average molecular weight versus percentage monomer conversion for each polymerization reaction, catalyzed by the CuBr/PMDETA system. A linear evolution of $\overline{M}_n$ with percentage monomer conversion was observed for each polymerization reaction, especially after completion of the initiation process and during the propagation process. However, contrary to the CuBr/bpy system, at higher initial initiator concentration and at higher percentage monomer conversion, a slight deviation from the linear relationship between $\overline{M}_n$ and percentage monomer conversion was observed. Due to the high viscosity of the reaction mixture at high percentage monomer conversion, limited diffusion rates of the different species, including the metal complex catalyst, the monomer and the propagating radicals are observed[159]. The significantly higher value of experimental number average molecular weight ($\overline{M}_n$) in the polymerization reaction of styrene mediated by CuBr/PMDETA catalytic system could be due to unavoidable irreversible radical termination reactions induced by a high concentration of radicals at the early stages of polymerization[159].

In the reaction catalyzed by CuBr/bpy, a fairly good agreement is observed between the theoretical and experimental $\overline{M}_n$ values, whereas in the CuBr/PMDETA mediated polymerization reaction, the experimental number average molecular weights were significantly higher than the theoretical number average molecular weights. The high activity of the CuBr/PMDETA induces formation of dead chains due to abstraction of the bromine atom which lowers the concentration of the initiator and consequently the production of polymers with high number average molecular weights[151]

The molecular weight distribution ($\overline{M}_w/\overline{M}_n$) values of the polymers decreased from a value of 1.81 at 8% monomer conversion to 1.19 at 95% monomer conversion for the different polymerization reactions. The results suggest that a constant number of active chains were present, particularly at high monomer conversion[5].

The polymerization kinetic results show that the ATRP equilibrium ($K_{ATRP}$) is rapidly established for each catalyst/ligand system and suggests that the 2-[(4-bromomethyl) phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) initiated polymerization of styrene in the presence of the CuBr/bpy catalyst system in solution ATRP proceeded in controlled/living manner to produce the corresponding α-oxazolyl functionalized polystyrene, (**2**) in quantitative yields.

### 4.2.2 Synthesis of α-Oxazolyl Functionalized Polystyrene, (7) by ATRP using 4,5-Dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (5) as an Oxazolyl Functionalized Initiator Precursor.

The current study describes the polymerization kinetics of the syntheses of a series of α-oxazolyl functionalized polystyrene derivatives by ATRP methods using oxazoline substituted 1,1-diphenylethylene derivatives as initiator precursors. The different α-oxazolyl functionalized polystyrene derivatives, (**7**) were prepared by standard solution ATRP methods. The polymerization of styrene was initiated by an oxazoline functionalized initiator adduct, (**6**), prepared *in situ* by the reaction of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) with (1-bromomethyl)benzene in the presence of a CuBr/bpy catalytic system and xylene as a solvent at different initial monomer to initiator concentration ratios of 50:1, 100:1 and 200:1 for each reaction sequence.

After complete consumption of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)-phenyl]oxazole, (**5**) after 1 h, styrene was added to the reaction mixture. Starting at t = 0, aliquots (1 mL) were removed at 1 h intervals and THF (9 mL) was added to each aliquot. The aliquots were subjected to gas chromatography analysis to determine the percentage monomer conversion with time. The number average molecular weight and molecular weight distribution of each polymer sample were determined by size exclusion chromatography.

Figure 66 shows the plots of percentage monomer conversion versus polymerization time for the ATRP of styrene, initiated by the adduct of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene at 110 °C. The polymerization reaction is affected by the initial ratio of the concentration of the monomer to initiator. The polymerization reaction was the fastest at $[M]_o/[I]_o$ = 50/1 and the percentage monomer conversion value of 79% was observed within 8 h. A dramatically decrease in the extent of consumption of monomer was observed when the monomer to initiator concentration ratios were increased to 100/1 and 200/1 and the respective percentage monomer conversions of 47% and 36%, were recorded after 8 h. Furthermore, at $[M]_o/[I]_o$ = 200, rapid monomer consumption was only observed after an induction period of one hour.

Figure 67 shows the first order kinetic plots for the ATRP of styrene polymerization at 110 °C at different monomer to initiator concentrations of $[M]_o/[I]_o$ = 50/1, 100/1 and 200/1. The polymerization of Styrene was initiated by the initiator adduct, (**6**), derived from the reaction of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene. The polymerization reaction proceeded more rapidly at higher initiator concentrations. Moreover, at the lower initiator concentration of $[M]_o/[I]_o$ = 200, polymerization was only observed after an induction period of one

hour. The linearity of the relationship between ln ($[M]_o/[M]$) and time indicates that the concentration of the propagating radicals remained constant during the polymerization process for each polymerization reaction[7].

Figure 68 shows the plots of the change in the experimental number average molecular weight ($\overline{M}_n^{SEC}$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with percentage monomer conversion for the different ATRP reactions for the preparation of $\alpha$-oxazolyl functionalized polystyrene, (**7**). The initiation of styrene polymerization was effected by the oxazolyl functionalized initiator adduct, (**6**) formed *in situ* by the reaction of stoichiometric amounts of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) and (1-bromoethyl)benzene in the presence of CuBr/bpy at different monomer to initiator adduct concentration of 50:1; 100:1 and 200:1. A linear increase in the number average molecular weight with percentage monomer conversion is observed for each polymerization reaction. The linear relationship between $\overline{M}_n$ and percentage monomer conversion implies that, after the *in situ* formation of the oxazolyl functionalized initiator adduct, (**6**), initiation of styrene polymerization was effective, without any significant side reactions during the polymerization process. In addition, the linear plots indicated that fast exchange between dormant species and growing radicals occurred during the polymerization process for each polymerization reaction[7-11,129-130]. Also, the linear increase in the experimental number average molecular weight indicates that all polymer chains grew in direct relation with the disappearance of monomer, a characteristic of a controlled, free radical polymerization process. However, for all the polymerization reactions, the observed experimental number average molecular weights were higher than the predetermined theoretical values. Moreover, the deviation in $\overline{M}_n$ values relative to the theoretical values was more noticeable at lower initial concentration of the initiator. In addition, the higher number average molecular weight could suggest that the primary radicals derived from the less sterically hindered (1-bromoethyl)benzene undergo termination reactions before addition to 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) to form a low

concentration of initiator adduct, (**6**). Due to the electron withdrawing effects of the oxazoline functionality in the oxazolyl functionalized initiator adduct, (**6**), the C-Br bond undergoes rapid homolytic cleavage to form a resonance stabilized species and reduces the reactivity of the initiating radicals[11]. The viscous reaction mixture could be accountable for the less significant increase in number average molecular weight observed at higher percentage monomer conversion, since the rate of collision of reacting species decreases with increase in viscosity of the reaction[4].

Polymers with broad molecular weight distribution were produced. The molecular weight distribution values ($\overline{M}_w/\overline{M}_n$) decreases with the increase in percentage monomer conversion and number average molecular weight of different polymers. At the low initiator concentration, high molecular weight distribution values were obtained. The molecular weight distribution value drops from a relatively high initial value of $\overline{M}_w/\overline{M}_n$ = 1.56 to 1.29 for the $[M]_o/[I]_o$ = 50/1 polymerization reaction. A similar dependence of $\overline{M}_w/\overline{M}_n$ on percentage monomer conversion was observed for the different monomer to initiator concentration ratio reactions. At $[M]_o/[I]_o$ = 100/1, the $\overline{M}_w/\overline{M}_n$ values ranged between 1.76-1.22, whereas at $[M]_o/[I]_o$ = 200/1, the $\overline{M}_w/\overline{M}_n$ values of 1.83-1.24 were obtained. The experimental data implies that the effects of termination reactions and chain transfer reactions were insignificant during each polymerization process. In addition, the rates of initiation were at least equal to the rate of propagation, irrespective of the presence of the electron withdrawing oxazolyl group which reduces the initiator reactivity.

Polymerization kinetic profiles show that the polymerization of styrene, initiated by the oxazolyl functionalized initiator adduct, (**6**), formed by the reaction of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole (**5**) with (1-bromoethyl)benzene in the presence of CuBr/bpy as a catalyst in xylene, proceeds via controlled/"living" polymerization process and affords α-oxazolyl

functionalized polystyrene, (**7**) in quantitative yields. However, the initiator efficiency values for each reaction was reduced, which could be attributed to side reactions such as (a) the potential ability of the oxazoline compounds to function as a complexing agent in the presence of some metals and (b) the occurrence of unavoidable irreversible radical termination and chain transfer reactions of the primary radicals formed during the reaction of (1-bromoethyl)benzene with 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole (**5**), at the early stages of the polymerization process.

### 4.2.3 Synthesis of α-Bis(oxazolyl) Functionalized Polystyrene, (13) by ATRP using 1,1-Bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (11) as a Dioxazolyl Functionalized Initiator Precursor.

The current research describes a detailed polymerization kinetic study of the polymerization of styrene, initiated by a new dioxazolyl functionalized initiator adduct, (**12**) in the presence of CuBr/bpy catalyst system in xylene at 110 °C to form $\alpha$-bis(oxazolyl) functionalized polystyrene, (**13**). The dioxazolyl functionalized initiator adduct, (**12**) was prepared *in situ* by the reaction of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) with (1-bromoethyl)-benzene in the presence of CuBr/bpy catalytic system in xylene at 110 °C for the different polymerization reactions at initial monomer to initiator concentration ratios of 50:1, 100:1 and 200:1. Each polymerization reaction was effected by using the reaction stoichiometry of CuBr/bpy/initiator/(**11**) of 1: 3: 1: 1 in xylene. Upon complete consumption of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (**11**) after 1 h, styrene was added to the reaction mixture. Starting at time t = 0, aliquots (1 mL) were removed at 1 h intervals and THF (9 mL) was added to each aliquot. The aliquots were subjected to gas chromatographic analysis to determine the percentage monomer conversion with time. The number average molecular weight and molecular weight distribution of each polymer sample were determined by size exclusion chromatography.

Figure 69 shows the plots of percentage monomer conversion versus polymerization time for the ATRP of styrene initiated by the adduct of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) and (1-bromoethyl)benzene in xylene at 110 °C. The shapes of the curves indicate that, after an induction period of one hour, a rapid increase in the percentage monomer conversion was observed. The experimental results show that at lower $[M]_o/[I]_o$ ratio, the polymerization reaction was the fastest and the percentage monomer conversion reached a value of 71% within 8 hours. However, the percentage monomer consumption was reduced to 57%, as the initiator concentration decreases to $([M]_o/[I]_o = 100$. For the $[M]_o/[I]_o = 200/1$ polymerization reaction, a low percentage monomer conversion value of only 29% was recorded after 8 hours.

Figure 70 depicts the polymerization kinetic plots for the ATRP of styrene initiated by a new dioxazolyl functionalized initiator adduct, (**12**). The dioxazolyl functionalized initiator adduct, (**12**) was formed by the reaction of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) with (1-bromoethyl)benzene, in the presence of CuBr/bpy catalyst system in xylene at 110 °C. The linearity of the semilogarithmic plots of ln $([M]_o/[M])$ vs time for each polymerization reaction indicates that polymerization process is first order with respect to monomer consumption and that the concentration of active radicals remain constant throughout each polymerization reaction[146]. After an induction period of one hour, the polymerization reactions proceeded in a controlled manner with the concentration of the initiator affecting the rate of polymerization. At higher initial concentration, the rate of polymerization is the fastest. When the monomer to initiator ratio was increased from $[M]_o/[I]_o = 50/1$ to $[M]_o/[I]_o = 200/1$, the polymerization rate decreases with decreasing initiator concentration.

Figure 71 depicts the plots of the relationship between the evolution of experimental number average molecular weight ($\overline{M}_n^{SEC}$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with percentage monomer conversion for the different

ATRP reactions. The solution atom transfer radical polymerizations of styrene was initiated by the dioxazolyl functionalized initiator adduct, (**12**) in the presence of CuBr/bpy in xylene at 110 °C. A linear increase in the number average molecular weight with percentage monomer conversion was observed for all three polymerization reactions, indicating that termination and chain transfer reactions were insignificant during each polymerization process[7-11,105]. However, the presence of the electron withdrawing oxazoline moiety reduces initiator reactivity as well as promoting possible complexation with the catalyst ligand system which ultimately reduces initiator concentration in the ATRP reactions. Reduced initiator concentration results in the production of polymers with higher number average molecular weight relative to the theoretical $M_n$ values. In addition, the observed molecular weight distribution values between 1.61 and 1.29 for the different polymerization reactions imply that the polymerization reaction is controlled, especially at high monomer conversion[6]. The results also suggest that the high molecular weight distribution observed at the beginning of the polymerization reaction implies that the concentration of the deactivating species was low to confer control to polymerization reaction[7].

Polymerization kinetic data show that the dioxazolyl functionalized initiator adduct, (**12**), prepared *in situ* from the reaction of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) with (1-bromoethyl)benzene in the presence of the CuBr/bpy catalyst system in xylene at 110 °C, is a good dioxazolyl functionalized initiator for the ATRP of styrene to afford α-bis(oxazolyl) functionalized polystyrene, (**13**) in quantitative yields. The polymerization reaction proceeded via a controlled free radical polymerization process to give quantitative yields of α-bis(oxazolyl) functionalized polystyrenes, (**13**) with predictable number average molecular weights, narrow molecular weight distributions and initiator efficiency values as high as 0.98.

# CHAPTER 5

## SUMMARY

Well defined α-oxazolyl functionalized polymers with controlled number average molecular weights, narrow molecular weight distributions and regiospecific chain end functionality were prepared by the following synthesis processes:

(a) The synthesis of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in high yields using α-bromo-p-toluic acid as precursor.

(b) The utilization of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyl-oxazole, (**1**) as an oxazolyl functionalized initiator for the atom transfer radical polymerization of styrene and methyl methacrylate, in the presence of CuBr/bpy or CuBr/PMDETA, afforded quantitative yields of α-oxazolyl functionalized polystyrene, (**2**) and poly(methyl methacrylate), (**3**), respectively.

(c) Well defined α-oxazolyl functionalized polystyrenes with number average molecular weight ($\overline{M}_n^{SEC}$ = 3.7 x $10^3$ g/mol - 4.4 x $10^3$ g/mol) and molecular weight distributions of $\overline{M}_w/\overline{M}_n$ = 1.22-1.51 were obtained. However, poly(methyl methacrylate) with $\overline{M}_n^{SEC}$ = 7.0 x $10^3$ g/mol and slightly broader molecular weight distribution ($\overline{M}_w/\overline{M}_n$ = 2.12) was obtained.

Oxazolyl chain end functionalized polymers with predictable number average molecular weights and narrow molecular weight distributions were prepared by

atom transfer radical polymerization methods using oxazolyl functionalized initiator adducts based on 1,1-diphenylethylene precursors. In addition, telechelic oxazolyl functionalized polymers were synthesized by facile *in situ* post ATRP functionalization reactions which involved the addition of the appropriate oxazolyl functionalized 1,1-diphenylethylene derivative at the completion of the atom transfer radical polymerization process.

By employing a general, one-pot atom transfer radical polymerization method, the syntheses of α-oxazolyl functionalized polystyrene, (**7**) as well as α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) were effected using the following synthesis strategy:

(a) The novel, two step synthesis of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) from 4-benzoylbenzoic acid as the starting material.

(b) The *in situ* preparation of a new oxazolyl initiator adduct, (**6**) by the reaction of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) with (1-bromoethyl)benzene in the presence of CuBr/bpy at 110 °C in xylene.

(c) The use of a new oxazolyl functionalized initiator adduct, (**6**) as an initiator for the atom transfer radical polymerization of styrene gave the corresponding α-oxazolyl functionalized polystyrene, (**7**) with predictable number average molecular weight, ($\overline{M}_n^{SEC}$ = 3.9 x $10^3$ g/mol) and $\overline{M}_n/\overline{M}_w$ = 1.42 in a high initiator efficiency reaction.

(d) In addition, well defined α,ω-bis(oxazolyl) functionalized polystyrene, (**8**) of $\overline{M}_n^{SEC}$ = 4.3 x $10^3$ g/mol and $\overline{M}_w/\overline{M}_n$ = 1.45 with a high degree of chain end functionality was prepared *in situ* via a one-pot, post ATRP chain end

modification reaction which involved the addition of excess 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole to $\alpha$-oxazolyl functionalized polystyrene, (**7**), after completion of the ATRP reaction.

Similarly, α-bis(oxazolyl) and α,ω-tetrakis(oxazolyl) functionalized polymers were prepared according to the following synthesis pathway:

(a) The novel, high yield synthesis of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) by: (i) the synthesis of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline using 4-bromobenzoic acid as precursor; (ii) the coupling reaction between anhydrous ethyl acetate and a Grignard reagent, prepared from the reaction of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline with anhydrous magnesium in dry ether; and (iii) the acid catalyzed dehydration of the resultant 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol using $SOCl_2$.

(b) The *in situ* preparation of a new dioxazolyl functionalized initiator adduct, (**12**) from the reaction of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))-phenyl]ethylene, (**11**) with (1-bromoethyl)benzene in the presence of CuBr/bpy at 110 °C in xylene.

(c) The utilization of the new dioxazolyl functionalized initiator, (**12**) as initiator for styrene polymerization afforded quantitative yields of well defined α-bis(oxazolyl) functionalized polystyrene, (**13**) ($\overline{M}_n$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.47).

(d) In addition, well defined α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**) ($\overline{M}_n$ = 4.4 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48) with a high degree of chain end functionality was prepared in quantitative yields by the *in situ* post

ATRP chain end functionalization reaction of α-bis(oxazolyl) functionalized polystyrene, (**13**) with excess 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) in a one-pot chain end functionalization process.

A series of different aromatic carboxyl functionalized polymers were prepared by subjecting the respective oxazolyl functionalized polymer precursors to the following chemical transformation process:

(a) the treatment of the specific oxazolyl functionalized polystyrene with 3 M aqueous hydrochloric acid to give the intermediate polymeric ester derivative.

(b) saponification of the intermediate polymeric ester derivative with aqueous sodium hydroxide to form the polymeric carboxylate derivative.

(c) the final acidification of the polymeric carboxylate to give the corresponding aromatic carboxyl functionalized polystyrene in high yields.

Upon evaluation of the controlled/"living" character of the different polymerization reactions for the syntheses of oxazolyl functionalized polymers, the polymerization kinetic data for all reactions show that the polymerization process for each reaction follows first order rate kinetic with respect to monomer consumption. The number average molecular weight ($\overline{M}_n^{SEC}$ = 0. 61 x $10^3$ g/mol-9.8 x $10^3$ g/mol) increased linearly with percentage monomer conversion and polymers with narrow molecular weight distributions ($\overline{M}_w/\overline{M}_n$ = 1.83-1.22) were obtained. The polymerization processes were monitored by gas chromatographic analyses to determine the extent of monomer consumption as function of time.

The organic compounds, 1,1-diphenylethylene derivatives and functionalized polymers were characterized by proton nuclear magnetic resonance spectrometry, carbon nuclear magnetic resonance spectrometry, fourier transform infrared spectrometry, size exclusion chromatography, non-aqueous titration measurements and elemental analysis.

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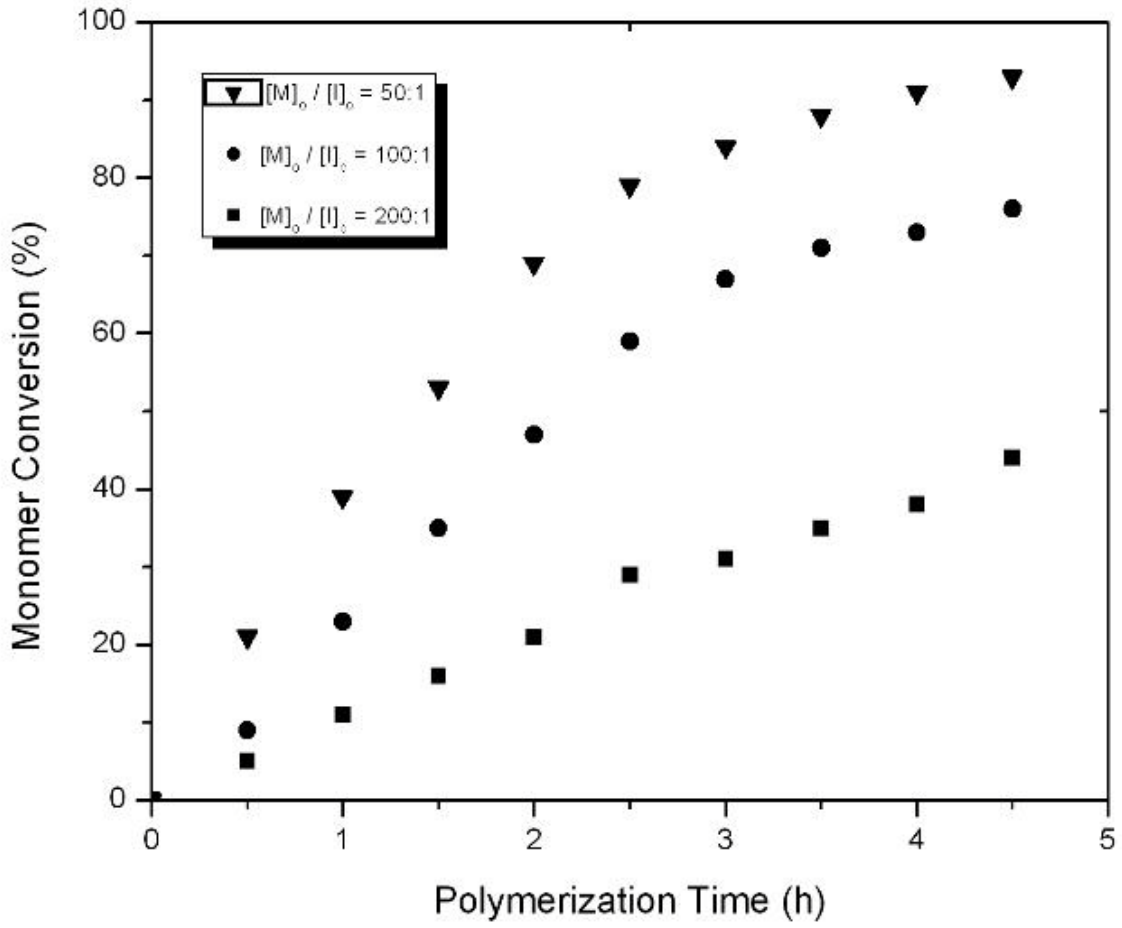


**Figure 60**. Plots of the percentage monomer conversion versus polymerization time for the ATRP of styrene initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of the CuBr/bpy catalyst system in diphenyl ether at 110°C.

▼= [styrene]:[CuBr]:[bpy]:[**1**] = 50:1:3:1

● = [styrene]:[CuBr]:[bpy]:[**1**] = 100:1:3:1

■ = [styrene]:[CuBr]:[bpy]:[**1**] = 200:1:3:1

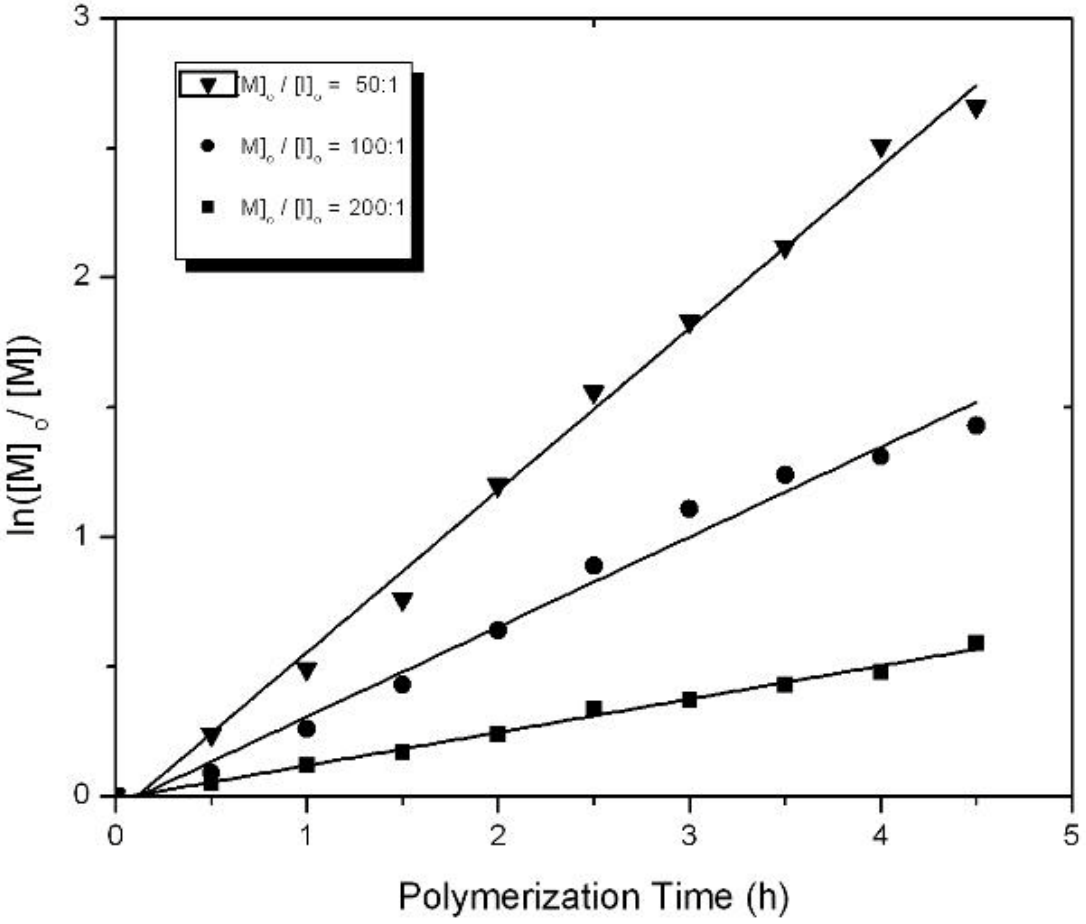


**Figure 61**. Polymerization Kinetic plots for the ATRP of styrene, initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of the CuBr/bpy catalyst system in diphenyl ether at 110°C.

▼= [styrene]:[CuBr]:[bpy]:[**1**] = 50:1:3:1

● = [styrene]:[CuBr]:[bpy]:[**1**] = 100:1:3:1

■ = [styrene]:[CuBr]:[bpy]:[**1**] = 200:3:1

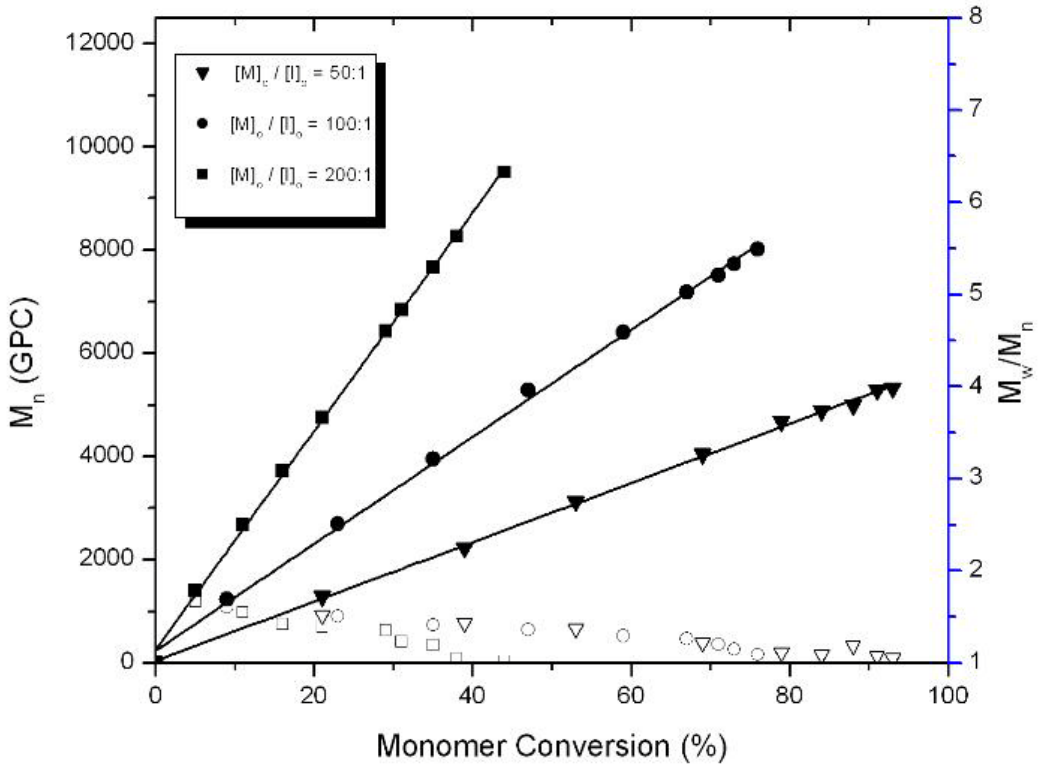


**Figure 62**. Evolution of experimental number average molecular weight ($\overline{M}_n^{SEC}$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with percentage monomer conversion for the ATRP of styrene, initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of the CuBr/bpy catalyst system in diphenyl ether at 110°C.

▼= [styrene]:[CuBr]:[bpy]:[**1**] = 50:1:3:1

● = [styrene]:[CuBr]:[bpy]:[**1**] = 100:1:3:1

■ = [styrene]:[CuBr]:[bpy]:[**1**] = 200:1:3:1

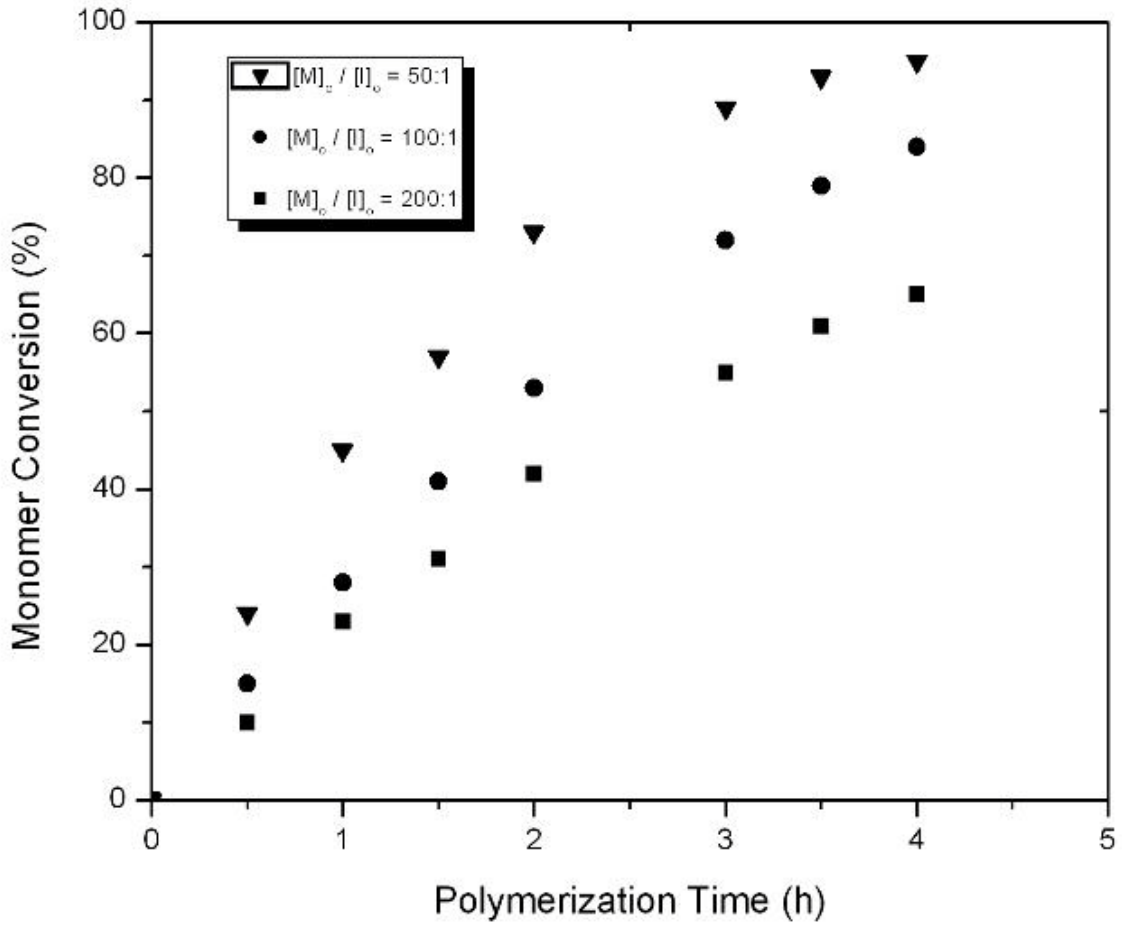


**Figure 63**. Plots of percentage monomer conversion versus polymerization time for the ATRP of styrene initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of the CuBr/PMDETA catalyst system in diphenyl ether at 110 °C.

▼= [styrene]:[CuBr]:[PMDETA]:[**1**] = 50:1:3:1

● = [styrene]:[CuBr]:[PMDETA]:[**1**] = 100:1:3:1

■ = [styrene]:[CuBr]:[PMDETA]:[**1**] = 200:1:3:1

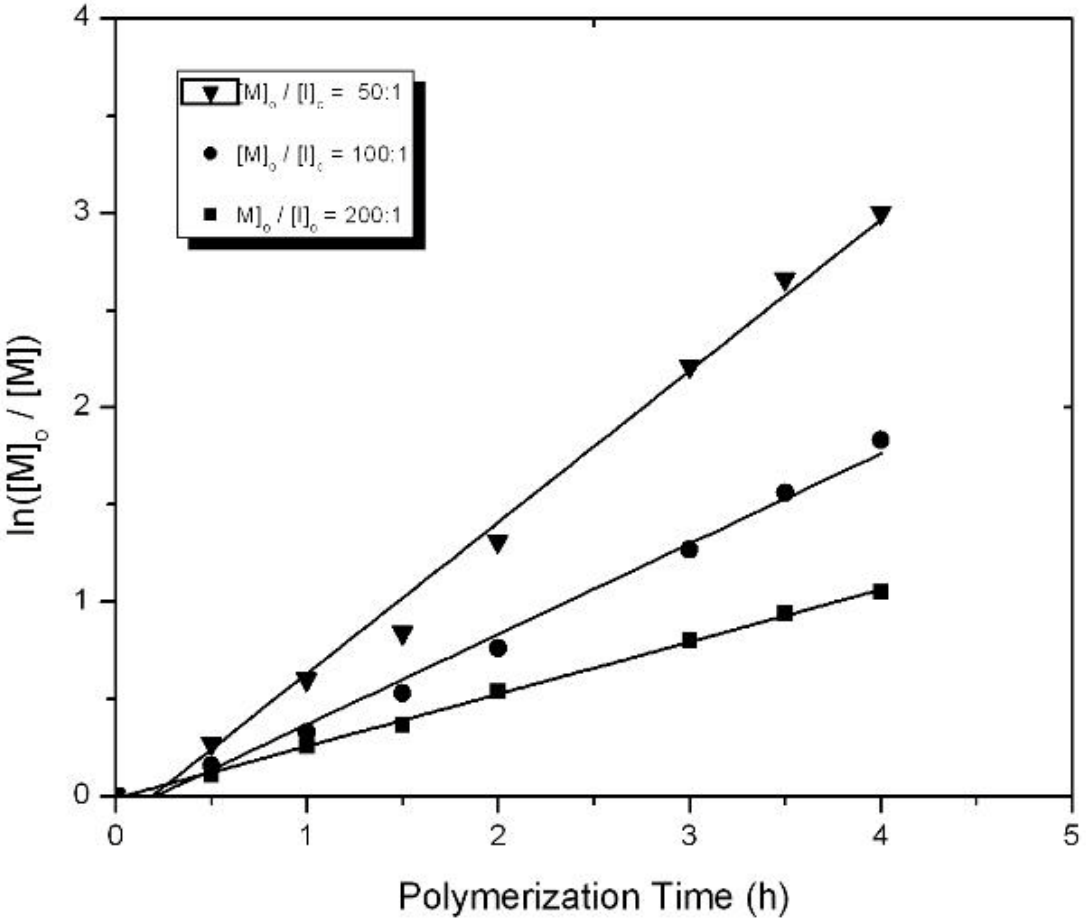


**Figure 64**. Polymerization kinetic plots for the ATRP of styrene initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of the CuBr/PMDETA catalyst system in diphenyl ether at 110 °C.

▼= [styrene]:[CuBr]:[PMDETA]:[**1**] = 50:1:3:1

● = [styrene]:[CuBr]:[PMDETA]:[**1**] = 100:1:3:1

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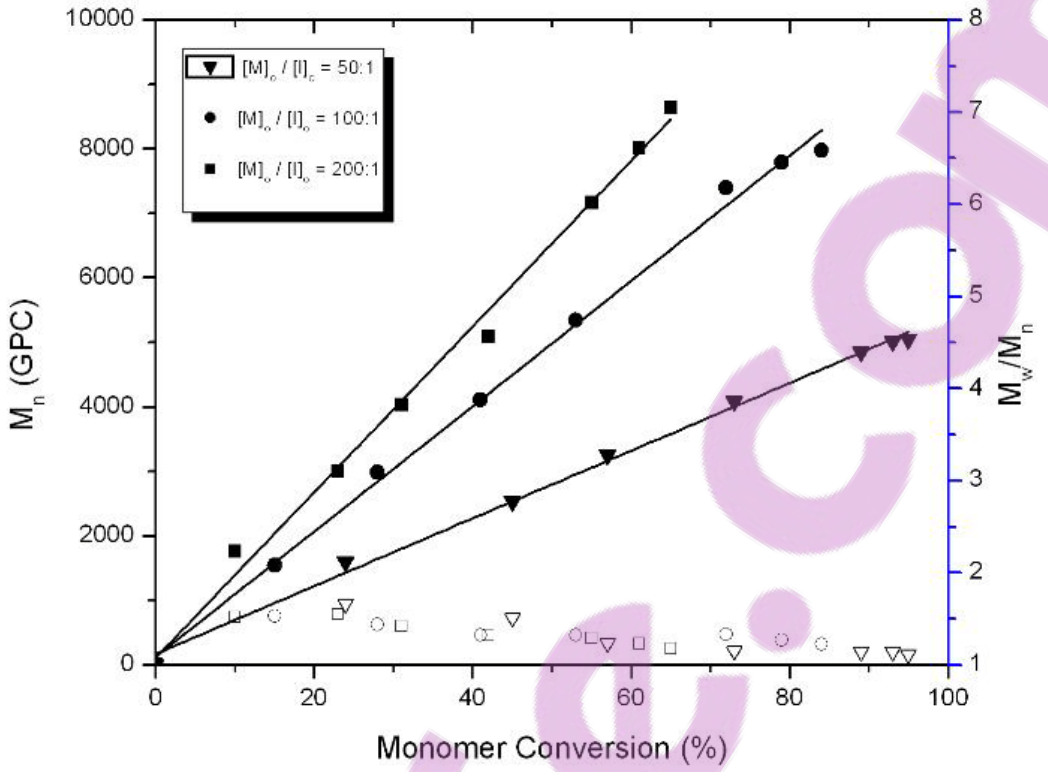


**Figure 65**. Evolution of experimental molecular weight ($\overline{M}_n^{SEC}$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with percentage monomer conversion for the ATRP of styrene initiated by 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**) in the presence of CuBr/PMDETA catalyst system in diphenyl ether at 110 °C.

▼= [styrene]:[CuBr]:[PMDETA]:[**1**] = 50:1:3:1

● = [styrene]:[CuBr]:[PMDETA]:[**1**] = 100:1:3:1

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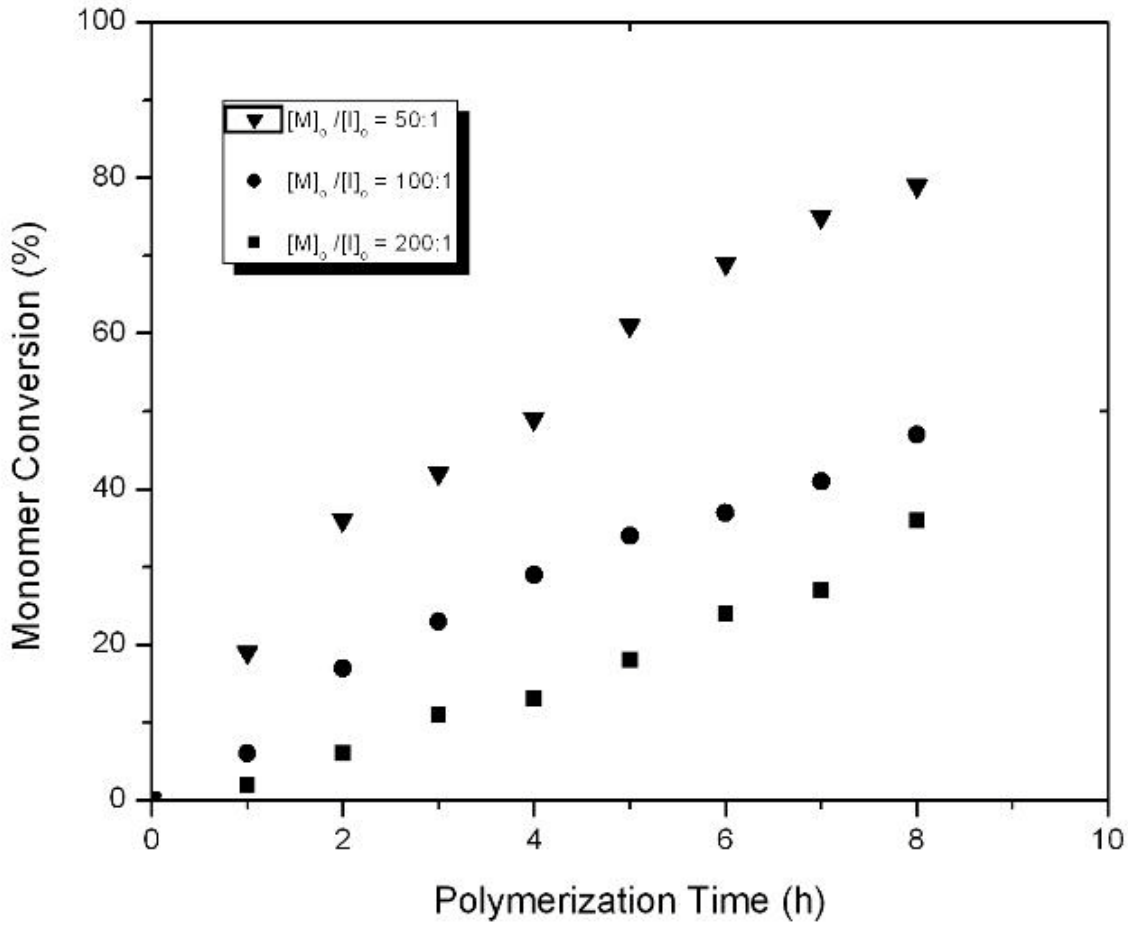


**Figure 66**. Plots of percentage monomer conversion versus polymerization time for the ATRP of styrene, initiated by the adduct of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene at 110 °C.

▼= [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**5**] = 50:1:1:3:1

● = [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**5**] = 100:1:1:3:1

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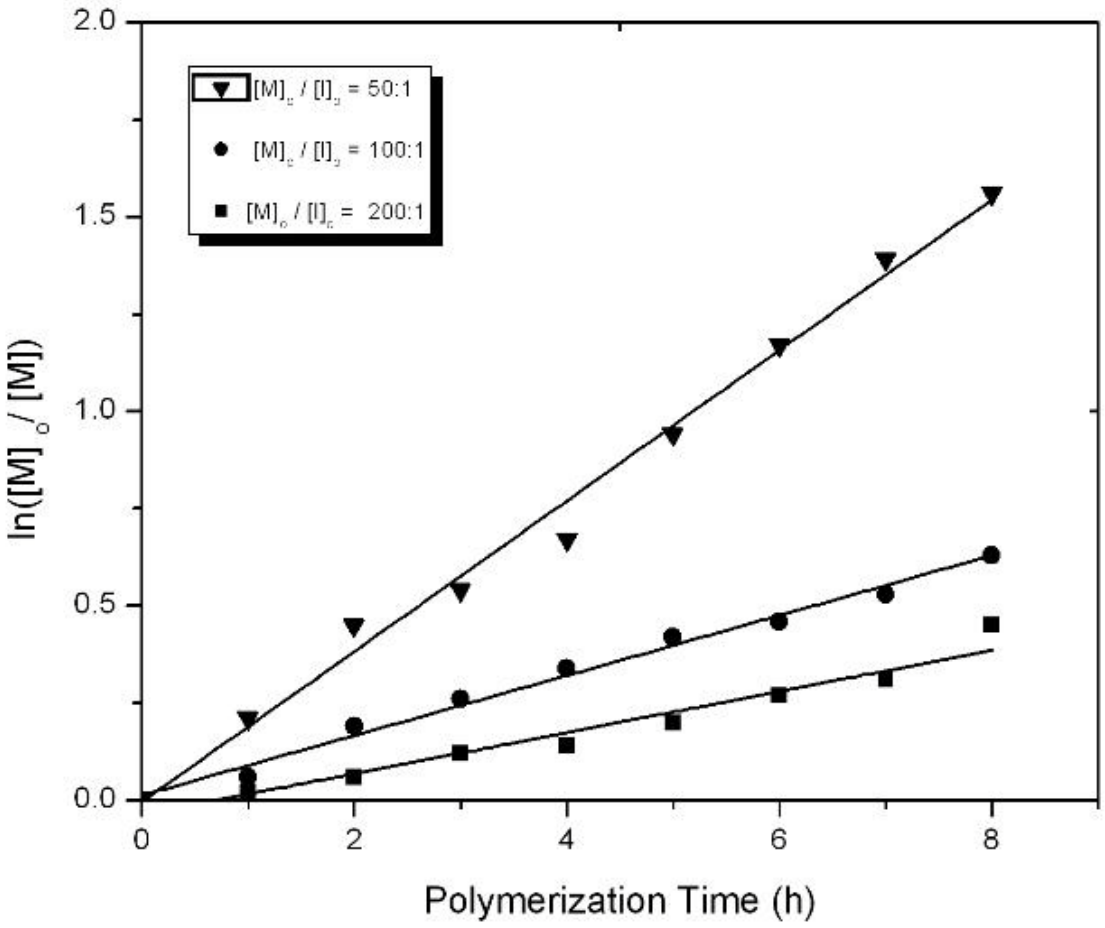


**Figure 67**. Polymerization kinetic plots for the ATRP of styrene initiated by the adduct of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene at 110 °C.

▼= [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**5**] = 50:1:1:3:1

● = [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**5**] = 100:1:1:3:1

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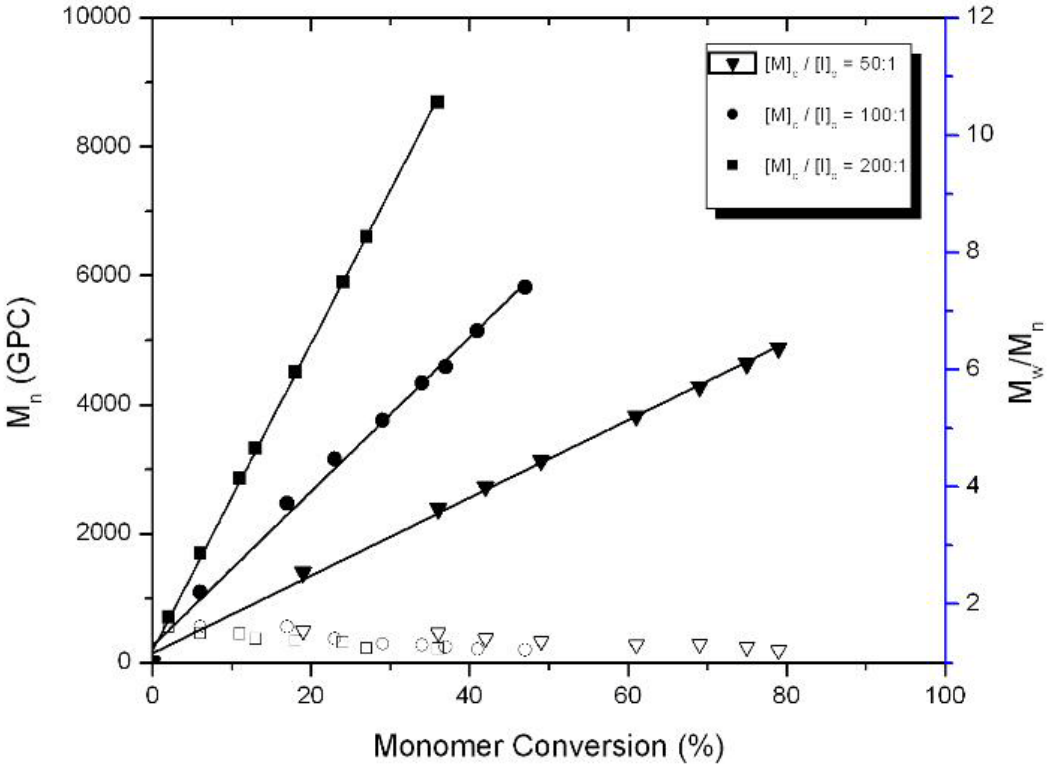


**Figure 68**. Evolution of experimental number average molecular weight ($\overline{M}_n^{GPC}$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with percentage monomer conversion for the ATRP of styrene, initiated by the adduct of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene at 110 °C.

▼= [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**5**] = 50:1:1:3:1

● = [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**5**] = 100:1:1:3:1

■ = [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**5**] = 200:1:1:3:1

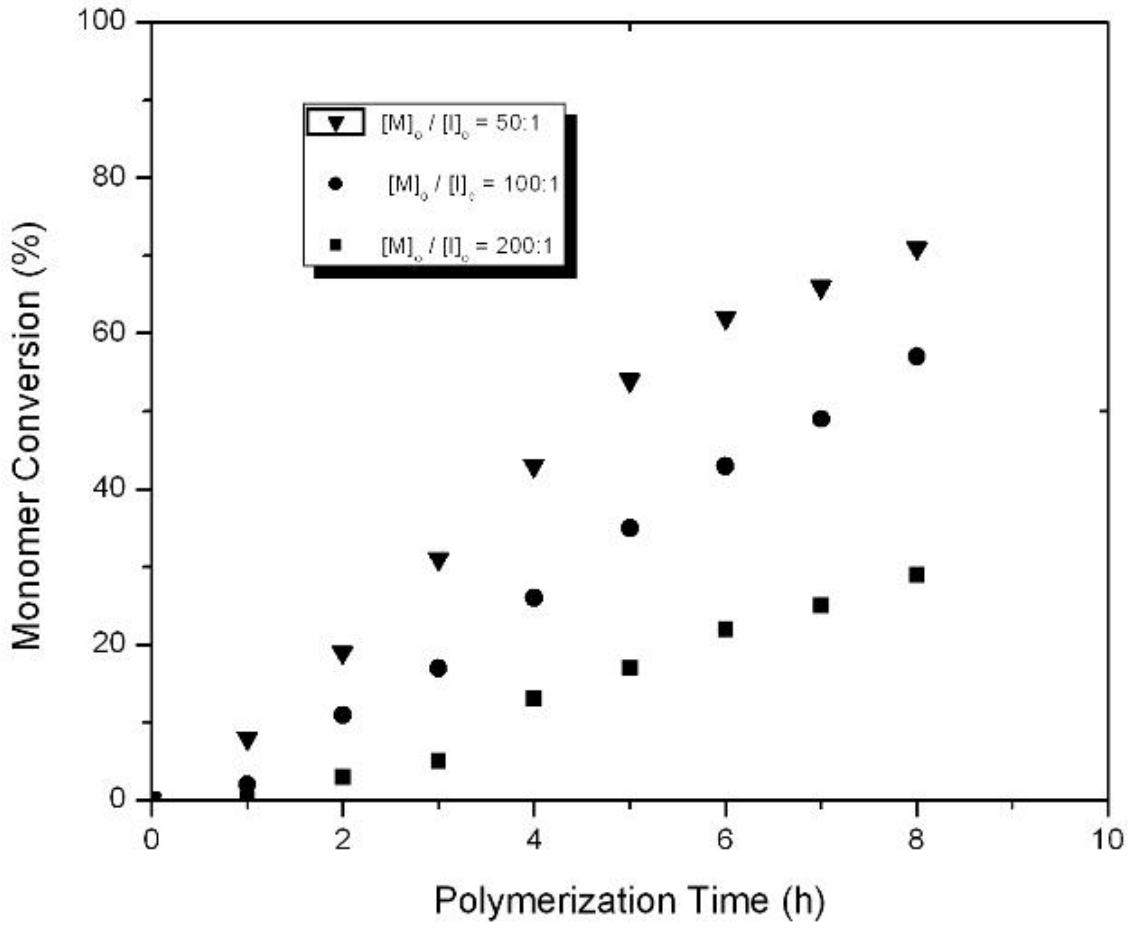


**Figure 69**. Plots of percentage monomer conversion versus polymerization time for the ATRP of styrene, initiated by the adduct of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene at 110 °C.

▼= [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**11**] = 50:1:1:3:1

● = [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**11**] = 100:1:1:3:1

■ = [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**11**] = 200:1:1:3:1

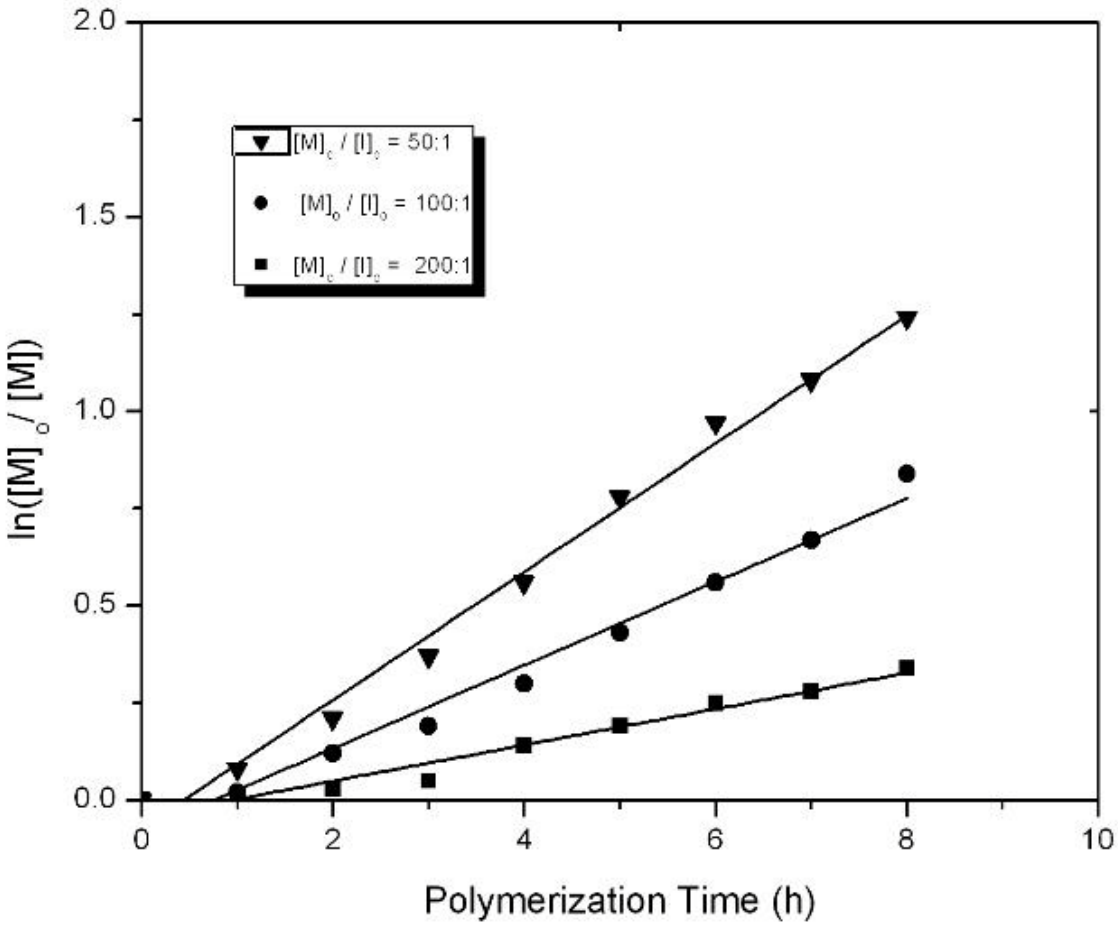


**Figure 70**. Polymerization kinetic plots for the ATRP of styrene, initiated by the adduct of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene at 110 °C.

▼= [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**11**] = 50:1:1:3:1

● = [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**11**] = 100:1:1:3:1

■ = [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**11**] = 200:1:1:3:1

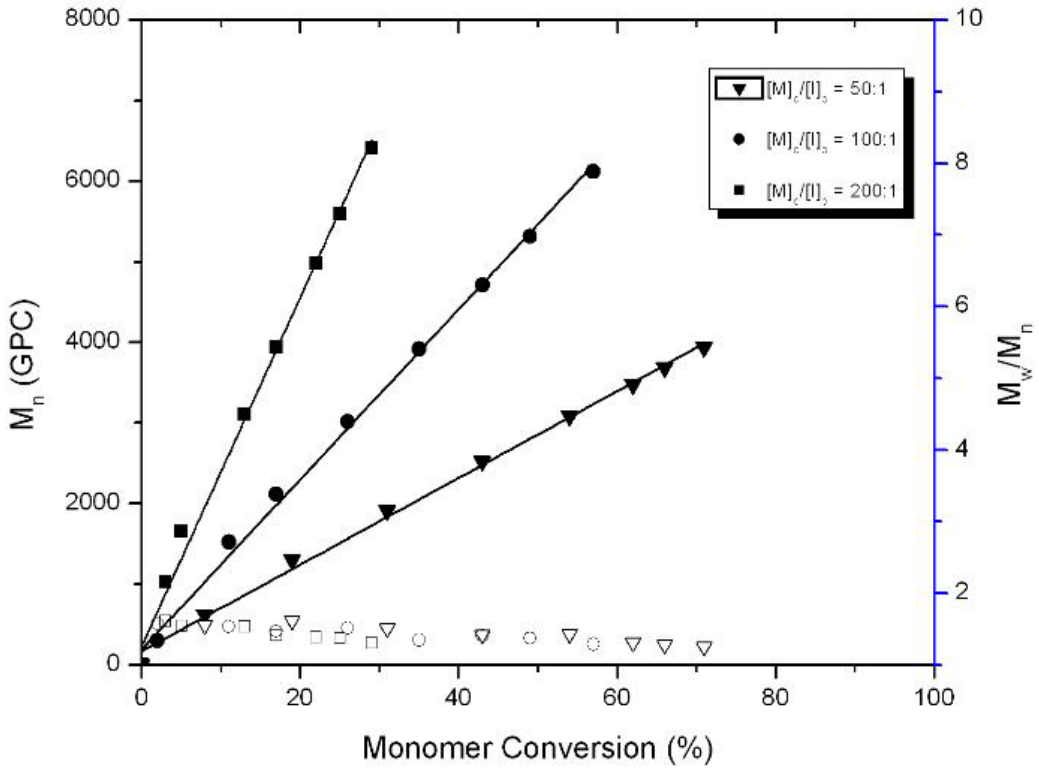


**Figure 71**. Evolution of the experimental number average molecular weight ($\overline{M}_n^{SEC}$) and molecular weight distribution ($\overline{M}_w/\overline{M}_n$) with percentage monomer conversion for the ATRP of styrene, initiated by the adduct of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**) and (1-bromoethyl)benzene in the presence of CuBr/bpy in xylene at 110 °C.

▼= [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**11**] = 50:1:1:3:1

● = [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**11**] = 100:1:1:3:1

■ = [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**11**] = 200:1:1:3:1

# APPENDIX

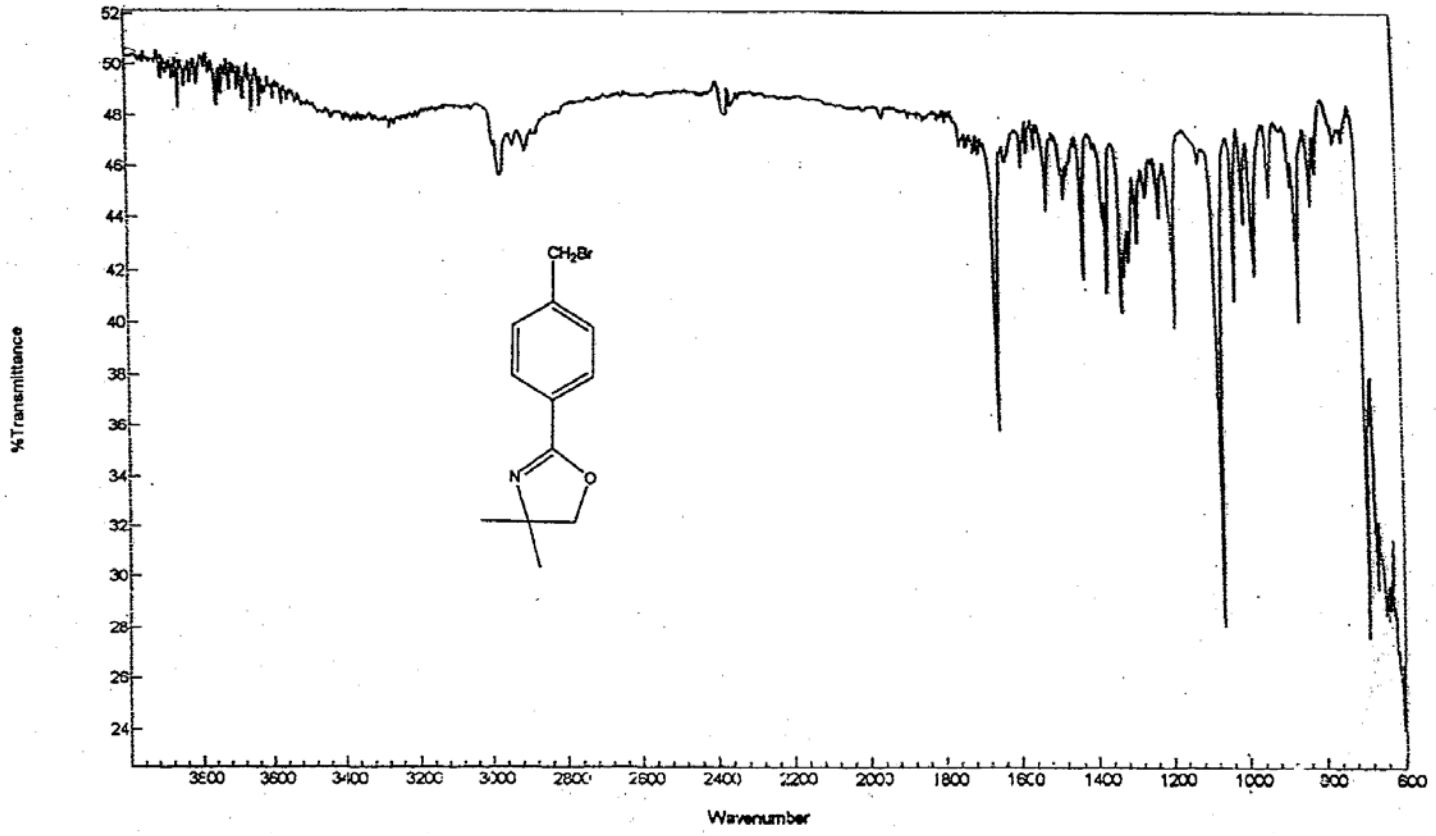


Figure 1: FTIR spectrum of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**).

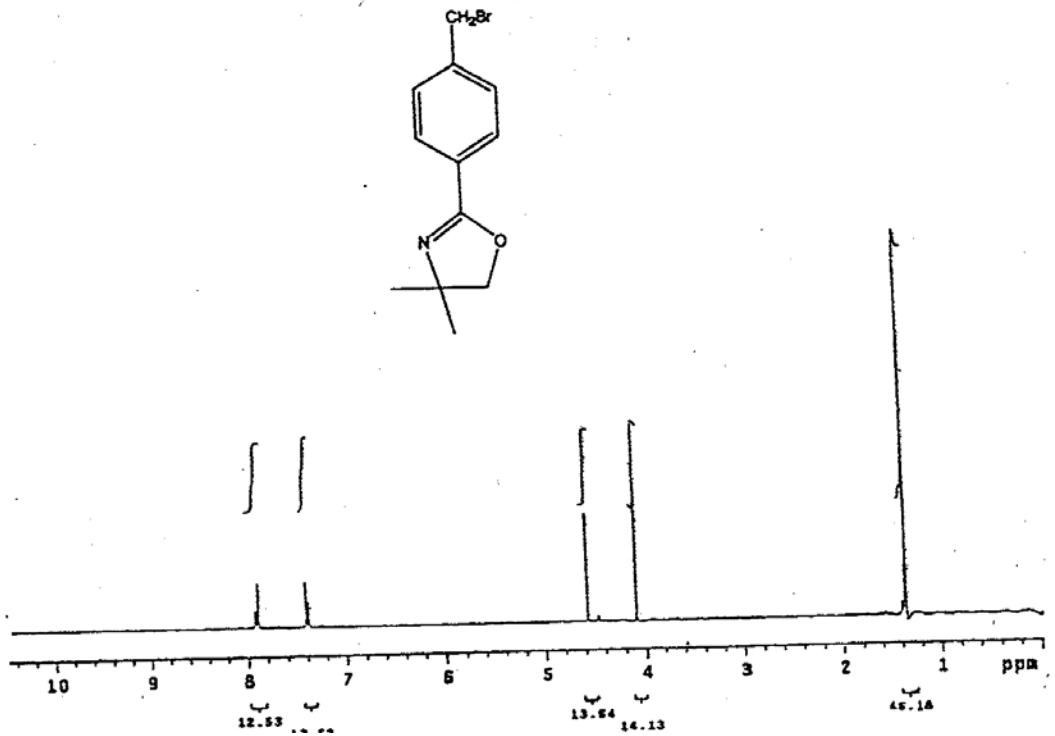


Figure 2: $^{1}$H NMR spectrum of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**).

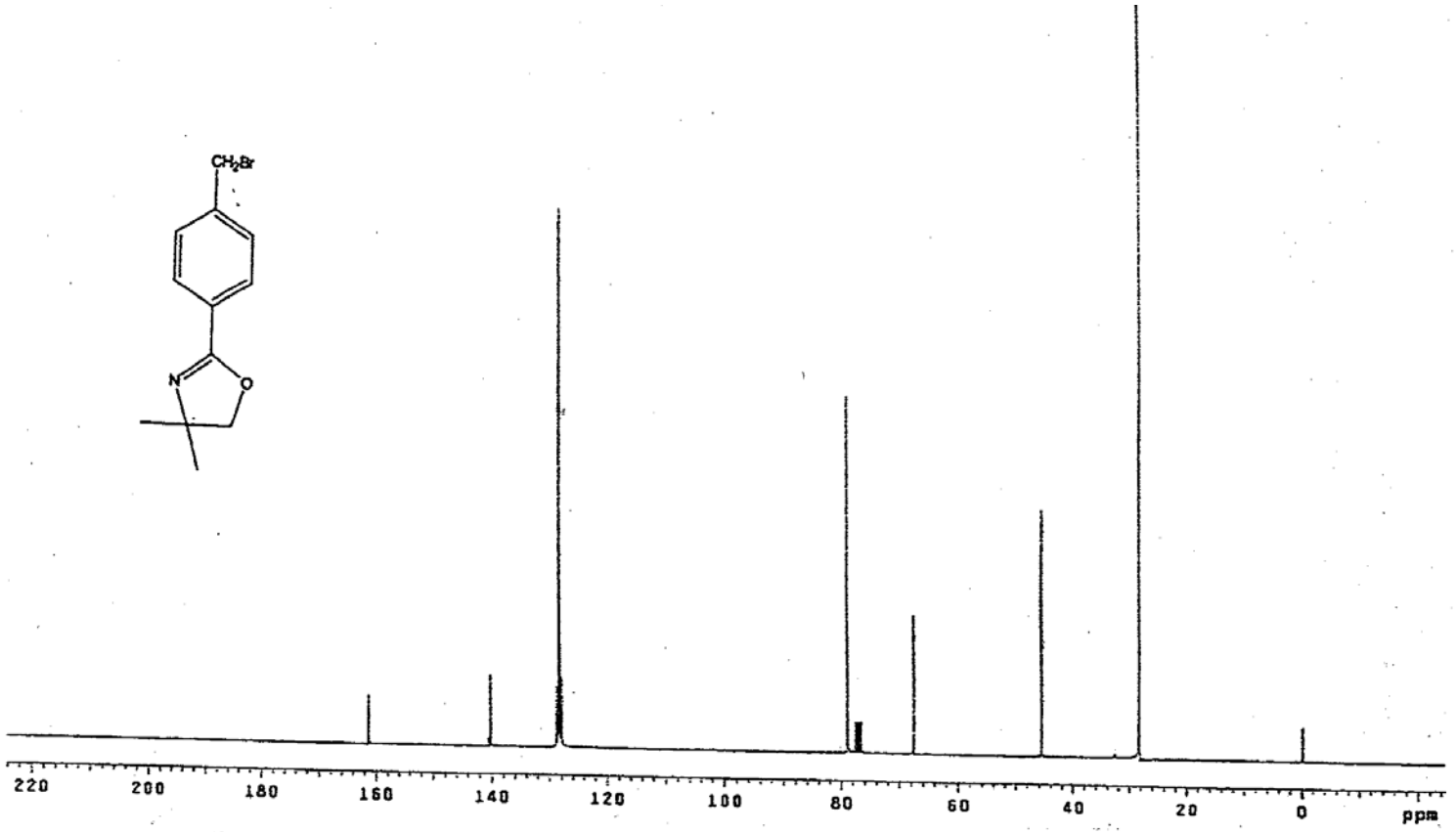


Figure 3: $^{13}C$ NMR spectrum of 2-[(4-bromomethyl)phenyl]-4,5-dihydro-4,4-dimethyloxazole, (**1**).

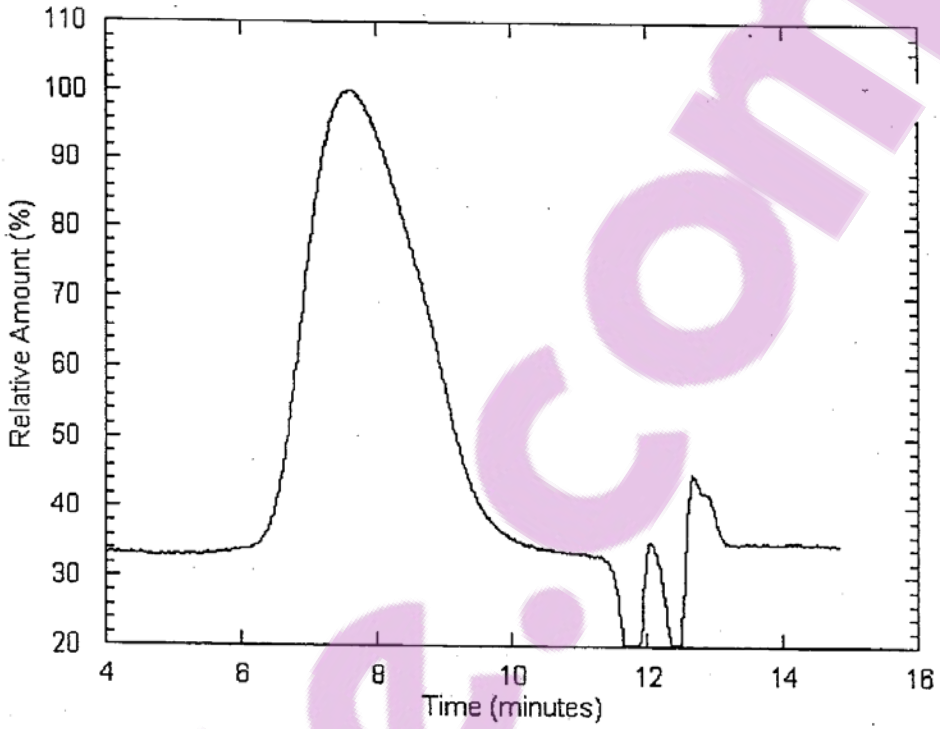


Figure 4: Size exclusion chromatogram of α-oxazolyl functionalized polystyrene, (**2**): [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**1**] = 29:1:1:3:1; solvent: diphenyl ether; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 3.7 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.22.

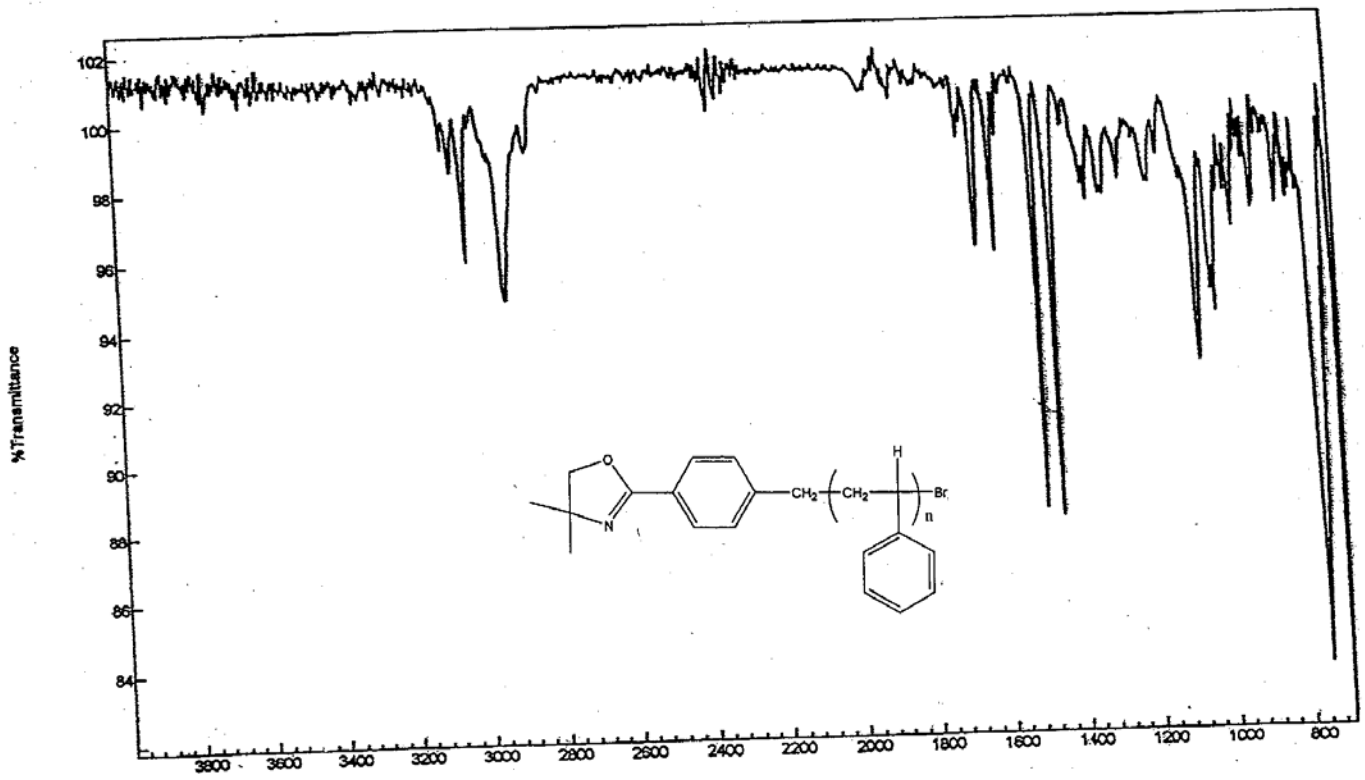


Figure 5: FTIR spectrum of α-oxazolyl functionalized polystyrene, (**2**). [styrene]:[(1-bromoethyl)-benzene]:[CuBr]: [bpy]:[**1**] = 29:1:1:3:1; solvent: diphenyl ether; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 3.7 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.22.

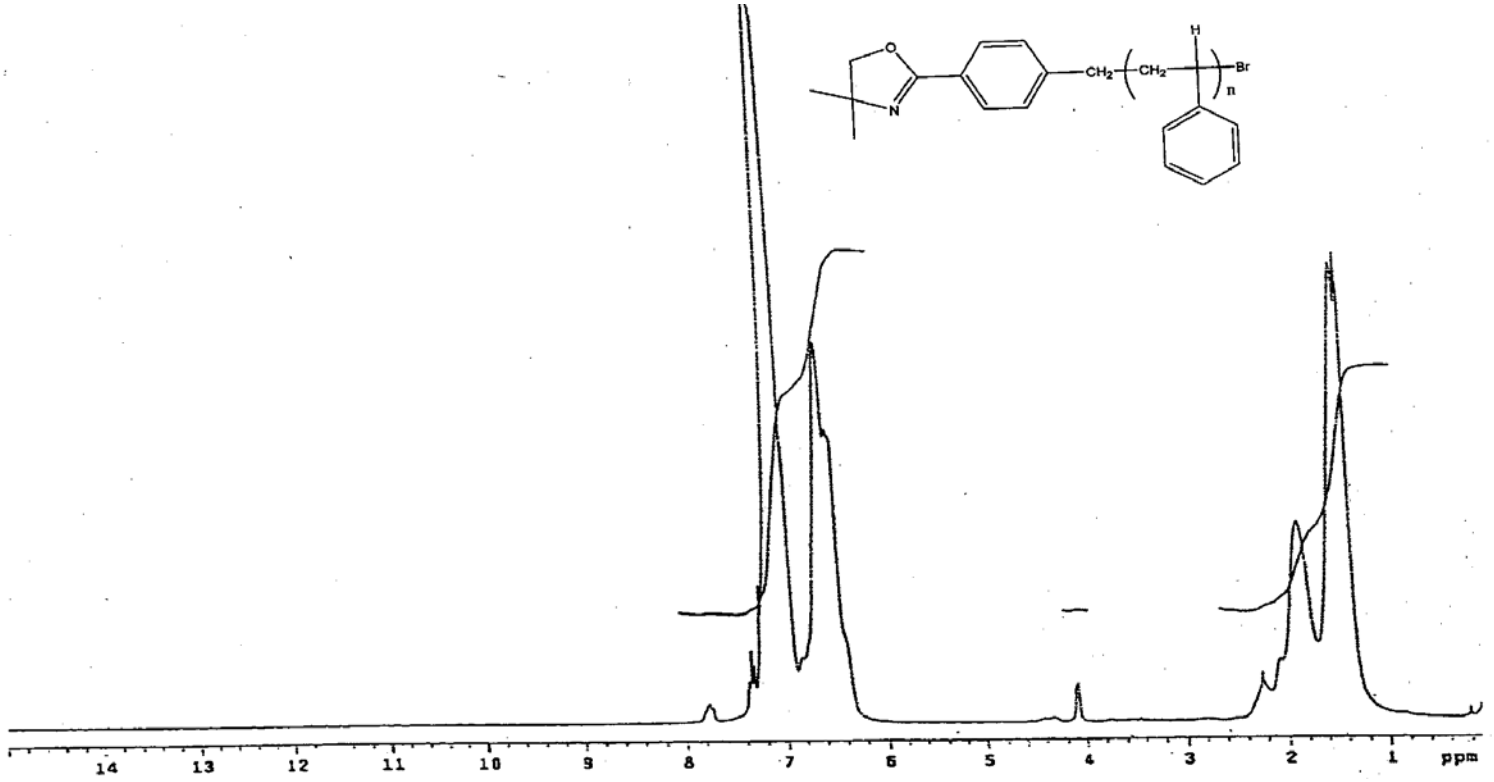


Figure 6: $^{1}$H NMR spectrum of α-oxazolyl functionalized polystyrene, (**2**). [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**1**] = 29:1:1:3:1; solvent: diphenyl ether; temperature: 110 °C. $\overline{M}_{n}^{SEC}$ = 3.7 x $10^3$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.22.

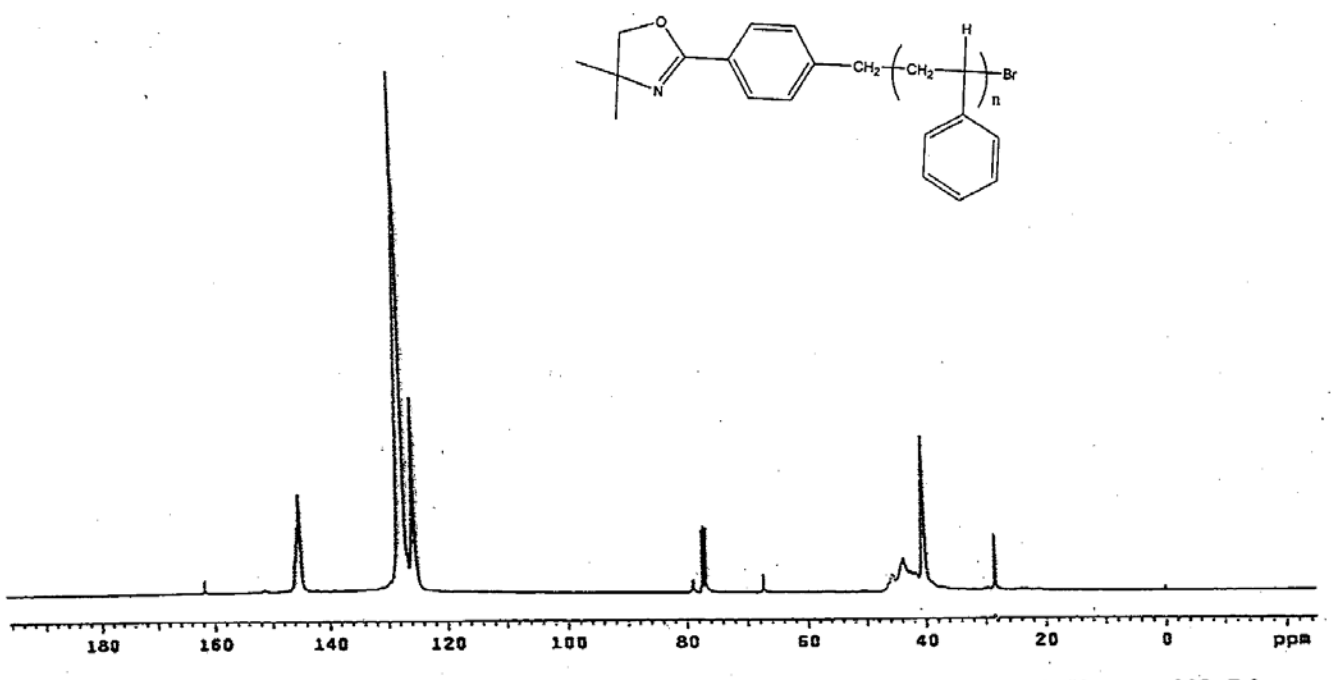


Figure 7: $^{13}$C NMR spectrum of α-oxazolyl functionalized polystyrene, (**2**). [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**1**] = 29:1:1:3:1; solvent: diphenyl ether; temperature: 110 °C. $\overline{M}_{n}^{SEC}$ = 3.7 x $10^3$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.22.

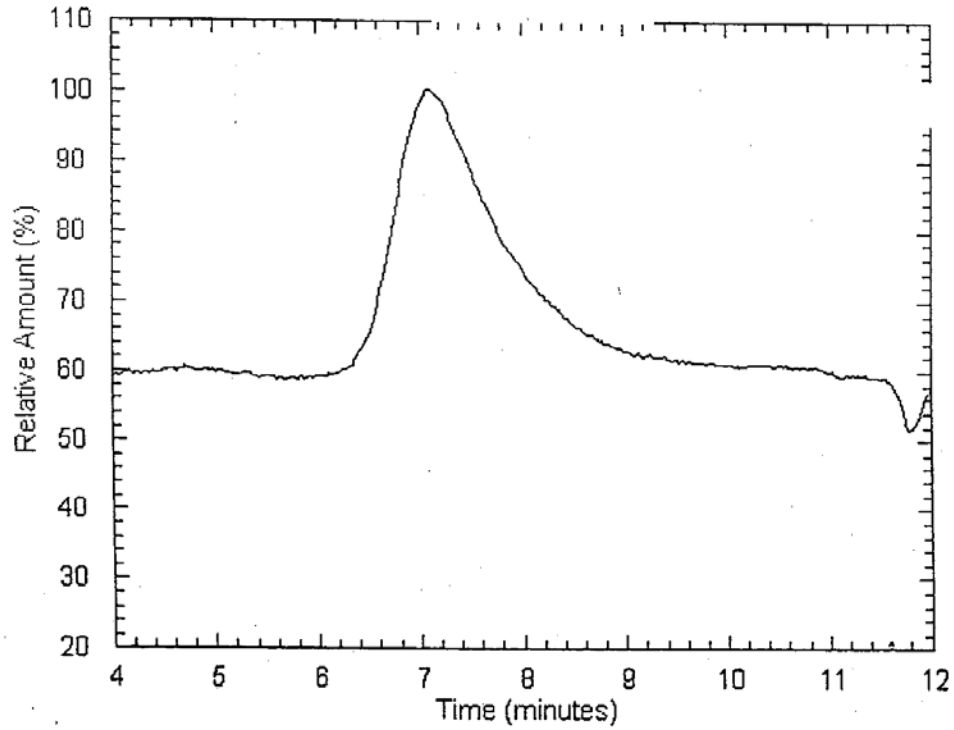


Figure 8: Size exclusion chromatogram of α-oxazolyl functionalized poly(methyl methacrylate), (**3**). [MMA]:[CuBr]: [bpy]:[**1**] = 31:1:3:1; solvent: xylene; temperature: 90 °C. $\overline{M}_n^{SEC}$ = 7.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 2.12.

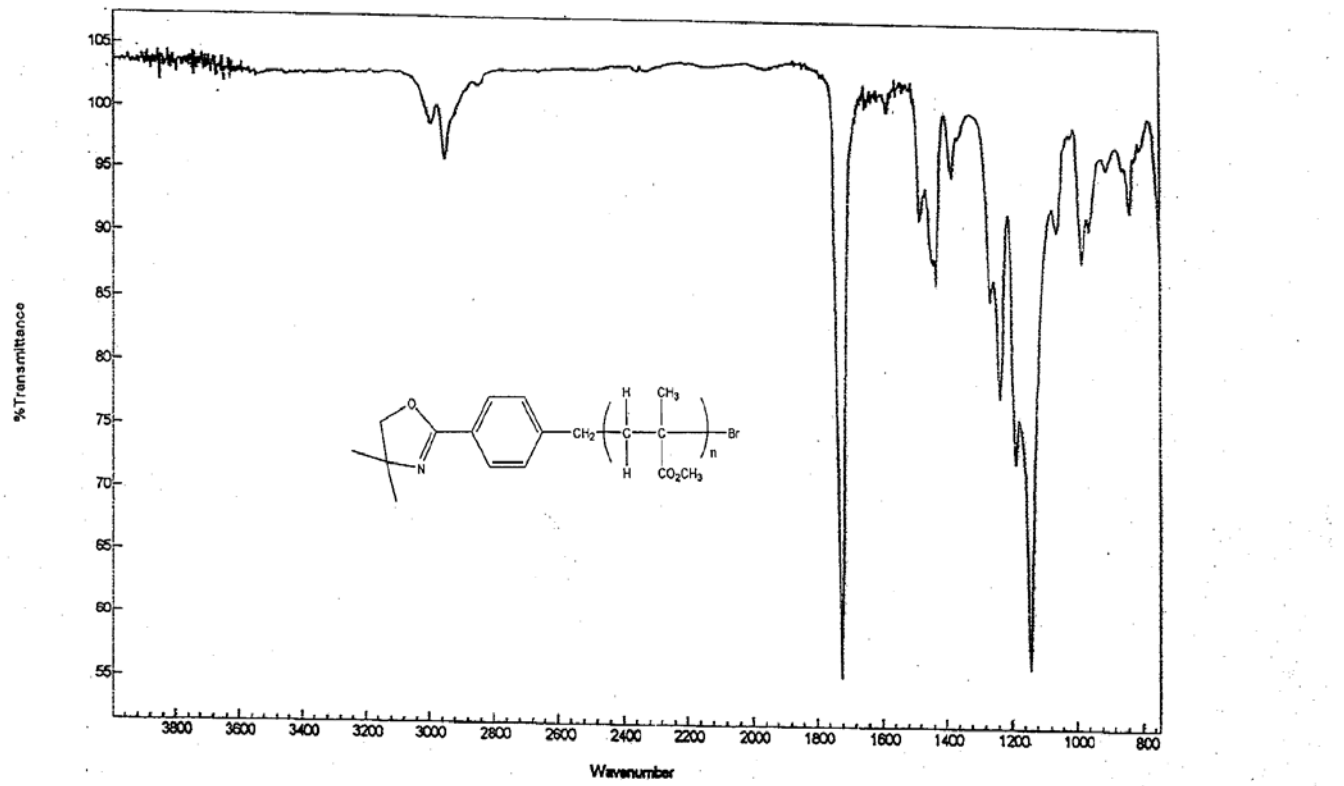


Figure 9: FTIR spectrum of α-oxazolyl functionalized poly(methyl methacrylate), (**3**). [MMA]:[CuBr]: [bpy] :[**1**] = 31:1:3:1; solvent: xylene; temperature: 90 °C. $\overline{M}_n^{SEC}$ = 7.0 x $10^3$ g/mol; $M_w/M_n$ = 2.12.

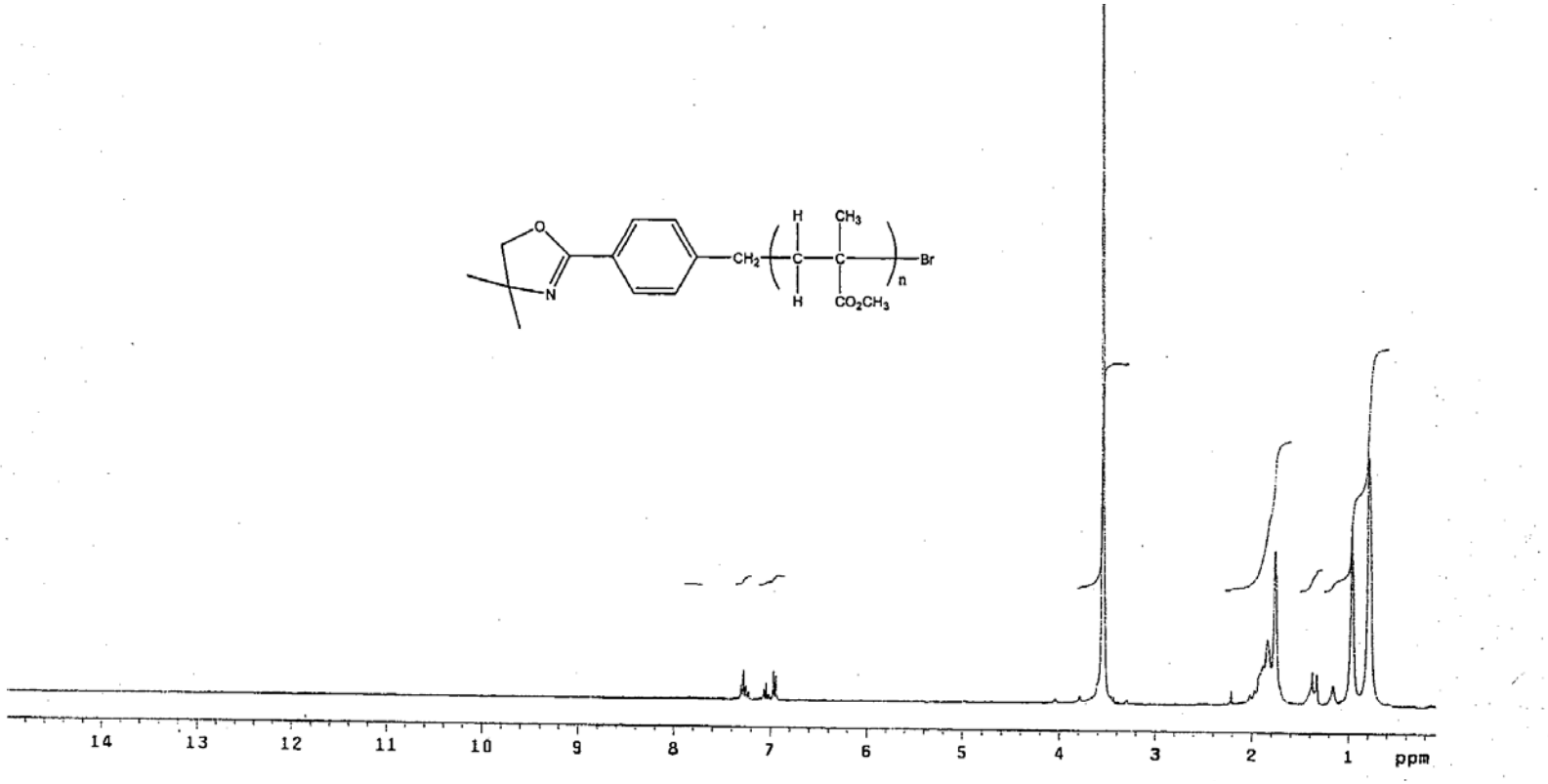


Figure 10: $^{1}$H NMR spectrum of α-oxazolyl functionalized poly(methyl methacrylate), (**3**). [MMA]:[CuBr]:[bpy]:[**1**] = 31:1:3:1; solvent: xylene; temperature: 90 °C. $\overline{M}_{n}^{SEC}$ = 7.0 x $10^{3}$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 2.12.

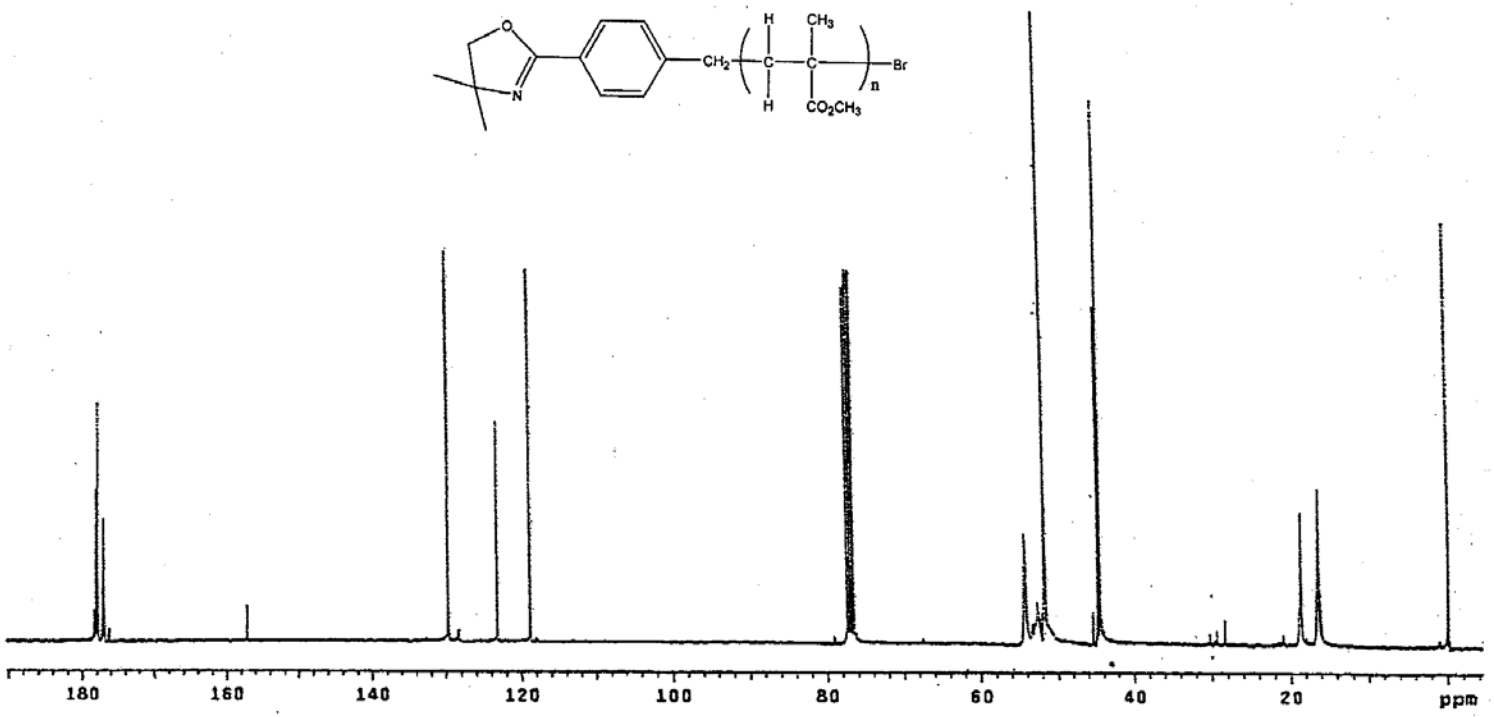


Figure 11: $^{13}$C NMR spectrum of α-oxazolyl functionalized poly(methyl methacrylate), (**3**). [MMA]:[CuBr]:[bpy]:[**1**] = 31:1:3:1; solvent: xylene; temperature: 90 °C. $\overline{M}_n^{SEC}$ = 7.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 2.12.

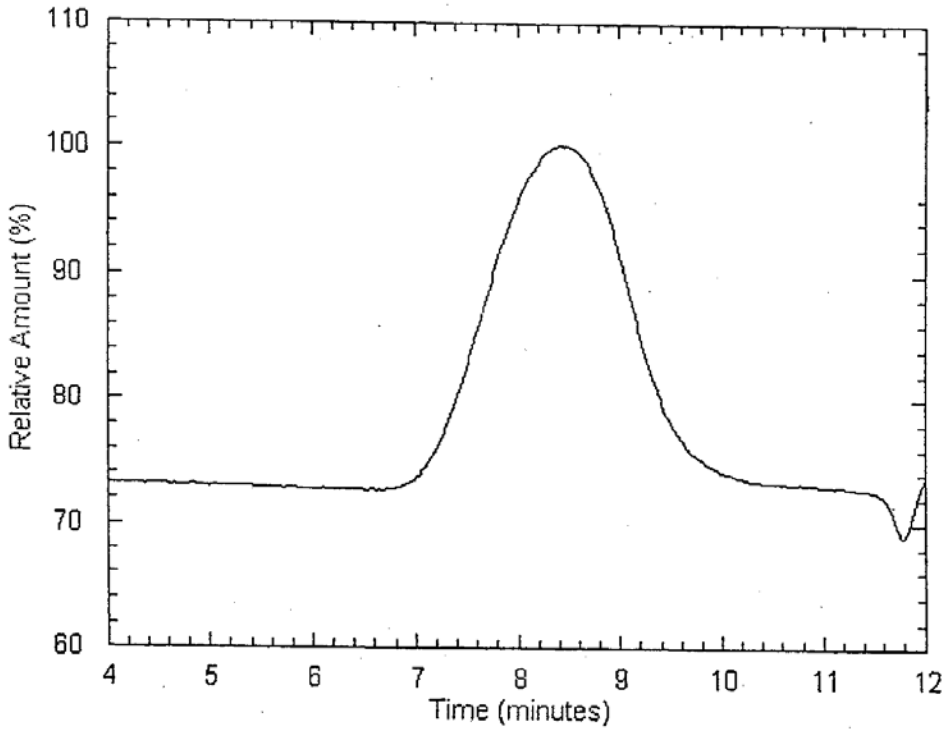


Figure 12: Size exclusion chromatogram of α-carboxyl functionalized polystyrene, (**4**). $\overline{M}_n^{SEC}$ = 3.6 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.31.

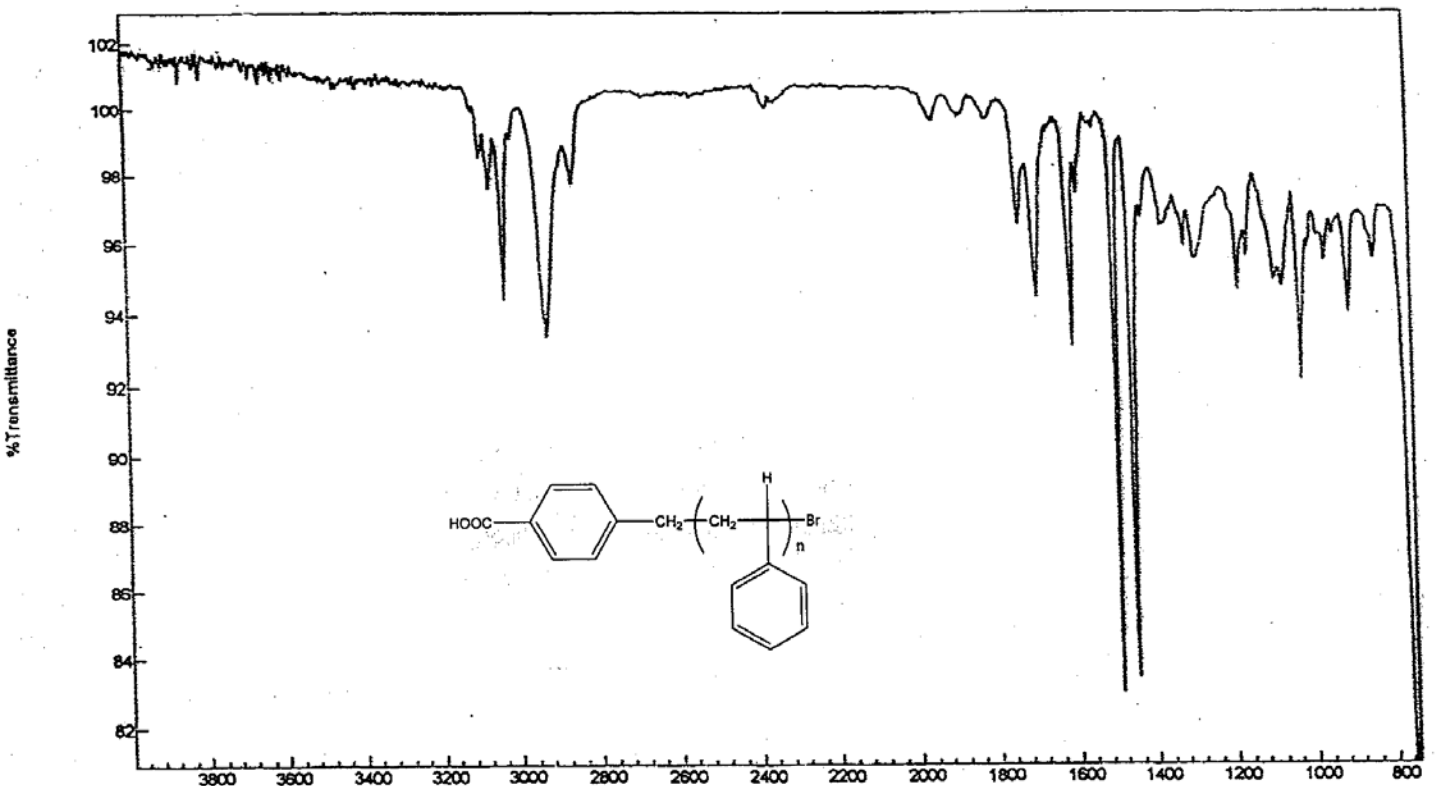


Figure 13: FTIR spectrum of α-carboxyl functionalized polystyrene, (**4**). $\overline{M}_n^{SEC}$ = 3.6 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.31.

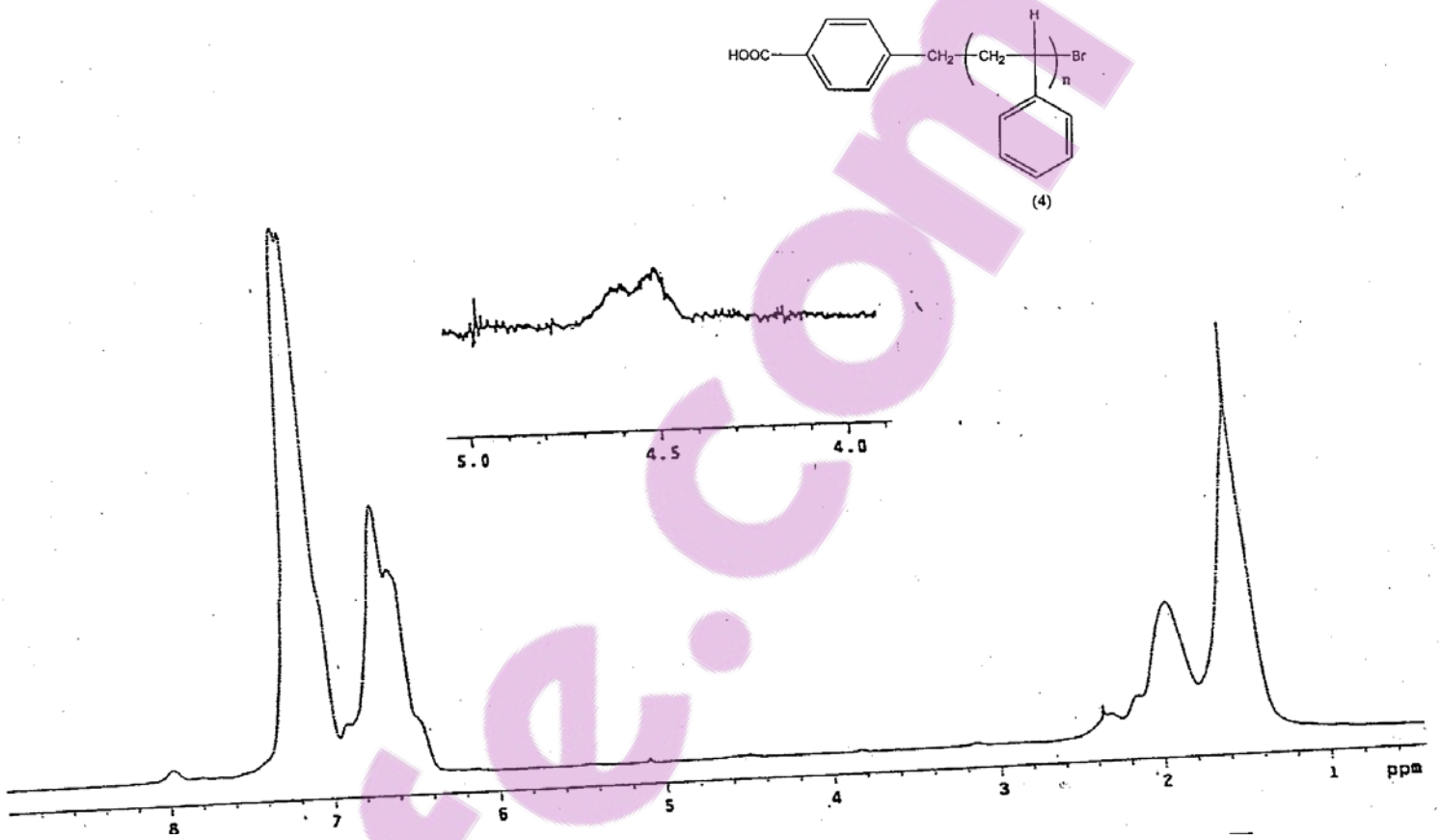


Figure 14: $^{1}$H NMR spectrum of α-carboxyl functionalized polystyrene, (**4**). $\overline{M}_{n}{}^{SEC}$= 3.6 x $10^{3}$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.31.

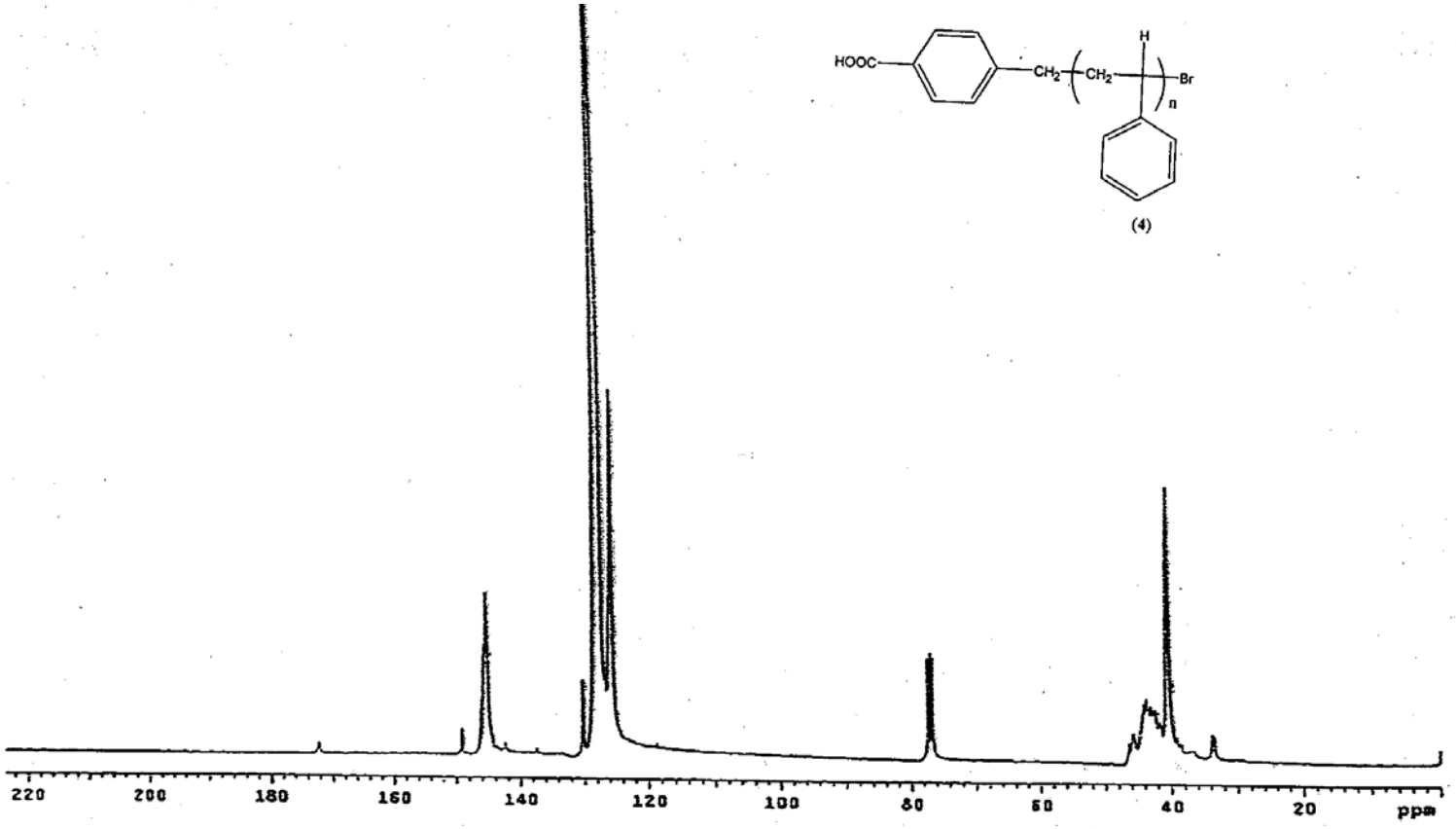


Figure 15: $^{13}C$ NMR spectrum of α-carboxyl functionalized polystyrene, (**4**). $M_n^{SEC} = 3.6 \times 10^3$ g/mol; $M_w/M_n = 1.31$.

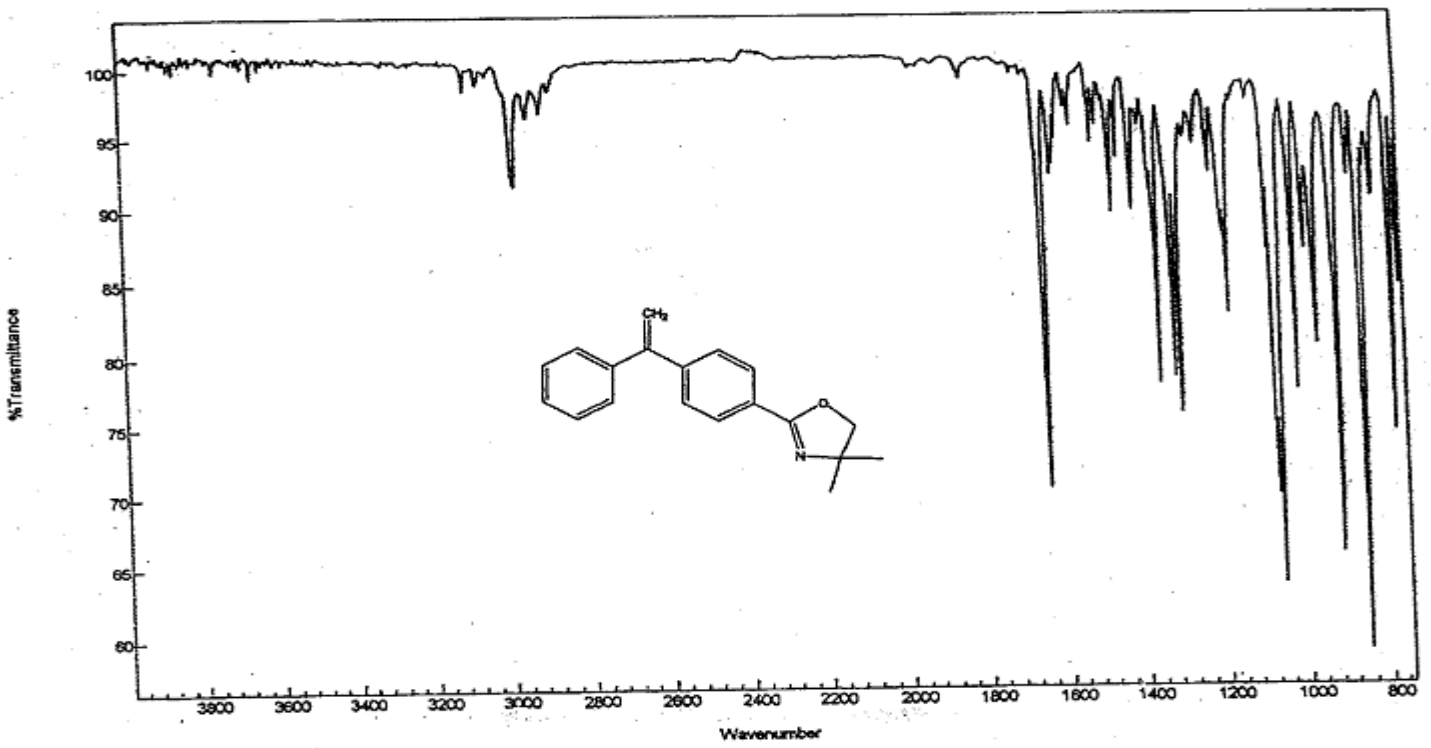


Figure 16: FTIR spectrum of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**).

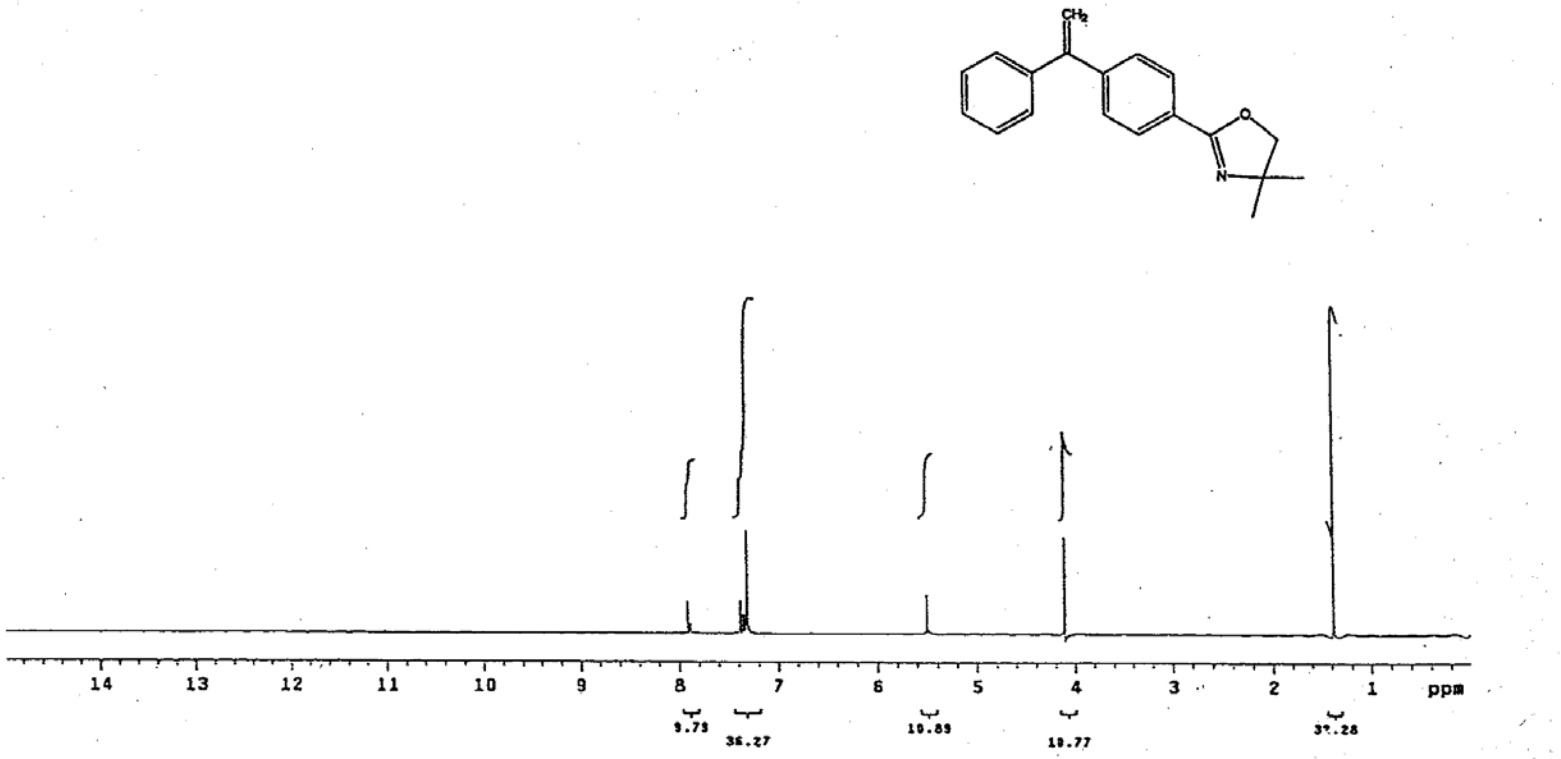


Figure 17: $^{1}$H NMR spectrum of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**).

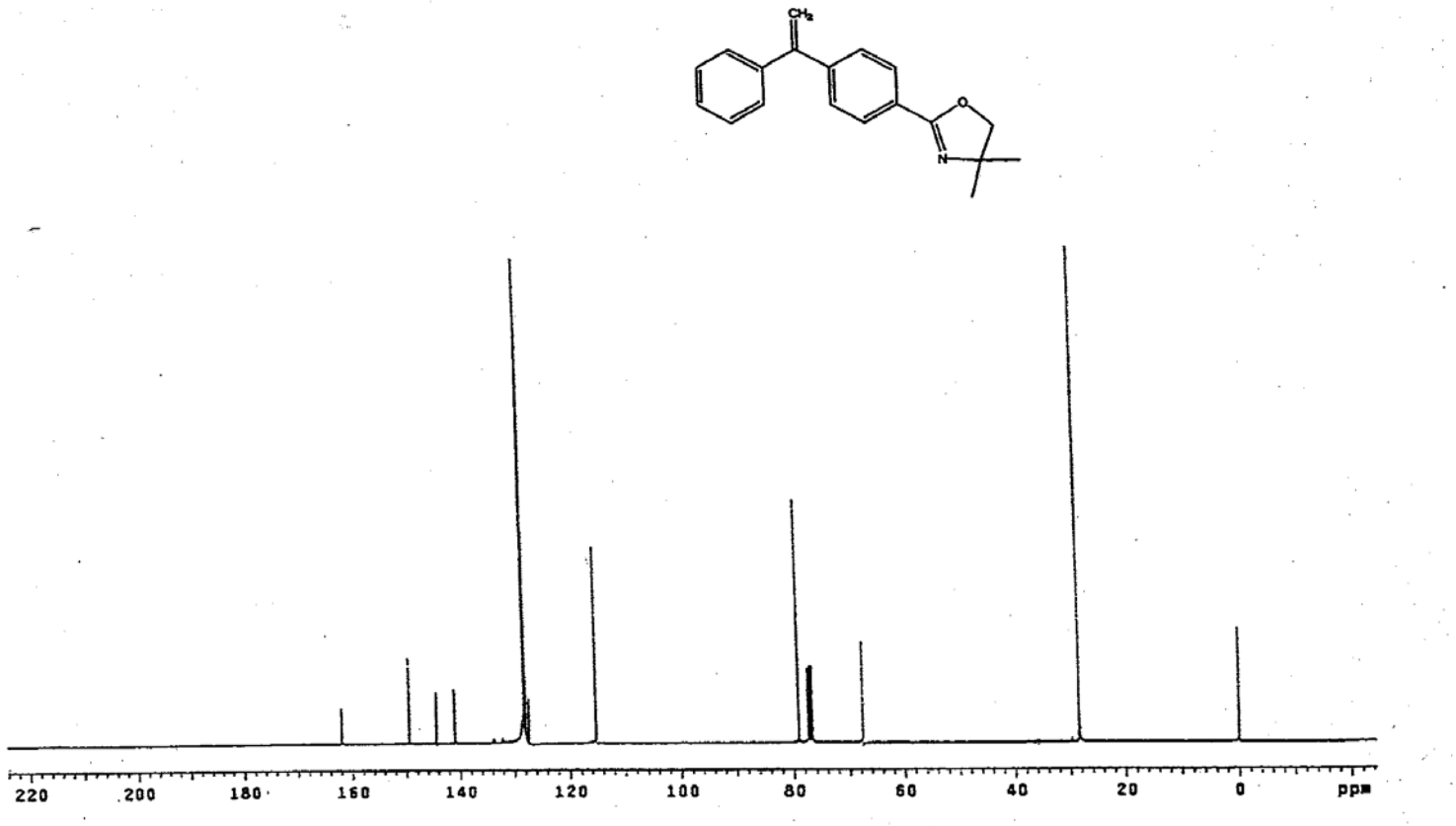


Figure 18: $^{13}$C NMR spectrum of 4,5-dihydro-4,4-dimethyl-2-[4-(1-phenylethenyl)phenyl]oxazole, (**5**).

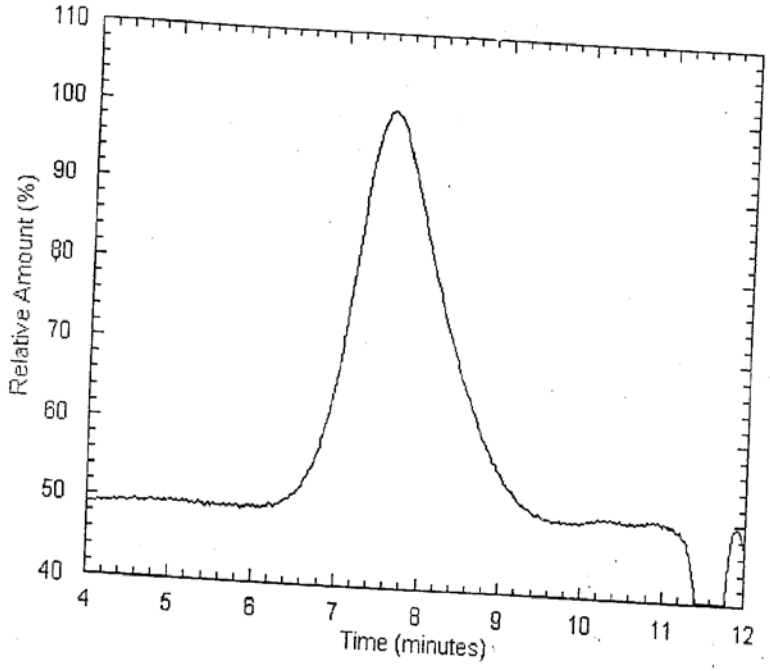


Figure 19: Size exclusion chromatogram of α-oxazolyl functionalized polystyrene, (**7**). [styrene]:[(1-bromoethyl)- benzene]:[CuBr]: [bpy]:[**5**] = 29:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 3.9 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.42.

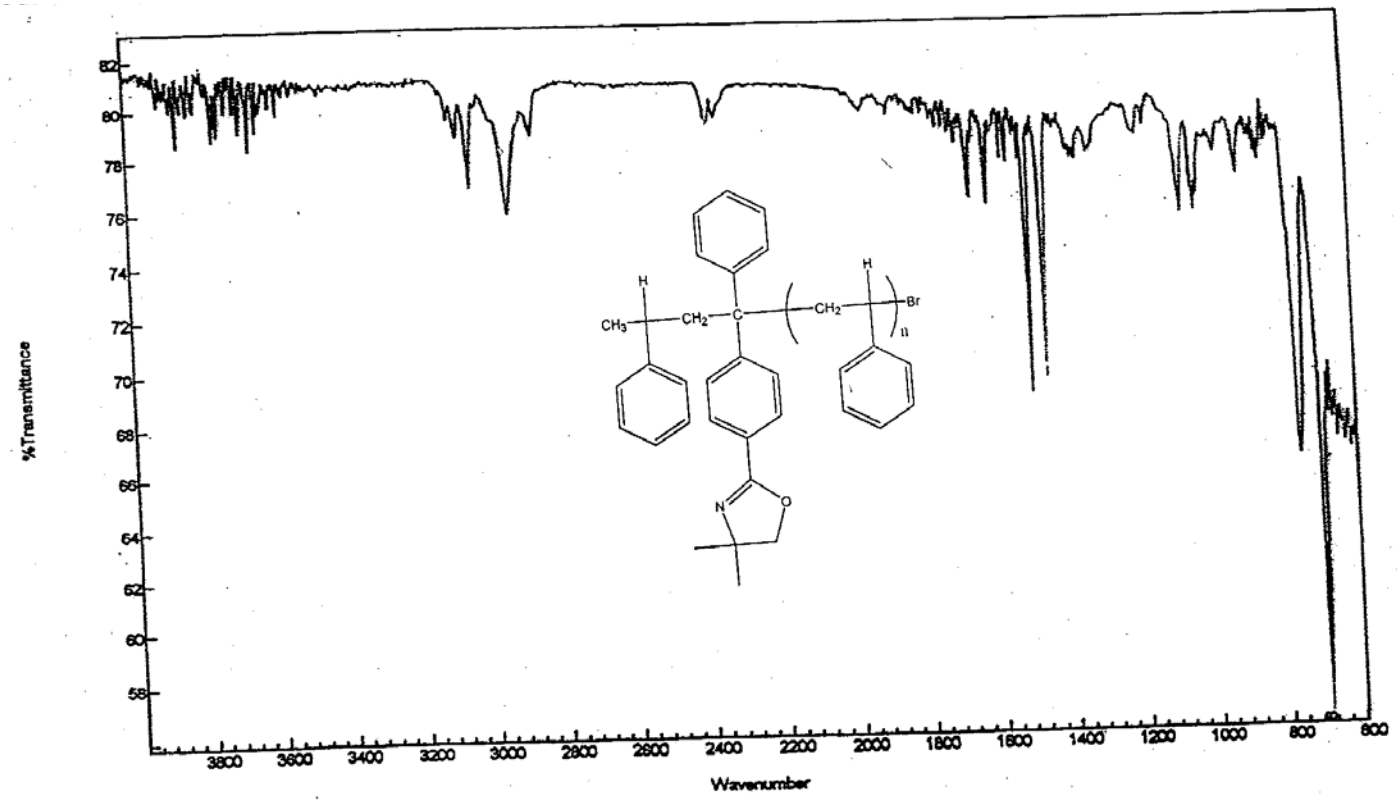


Figure 20: FTIR spectrum of α-oxazolyl functionalized polystyrene, (**7**). [styrene]:[(1-bromoethyl)-benzene]:[CuBr]: [bpy]:[**5**] = 29:1:1:3:1; solvent: xylene: 110 °C. $\overline{M}_n^{SEC}$ = 3.9 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.42.

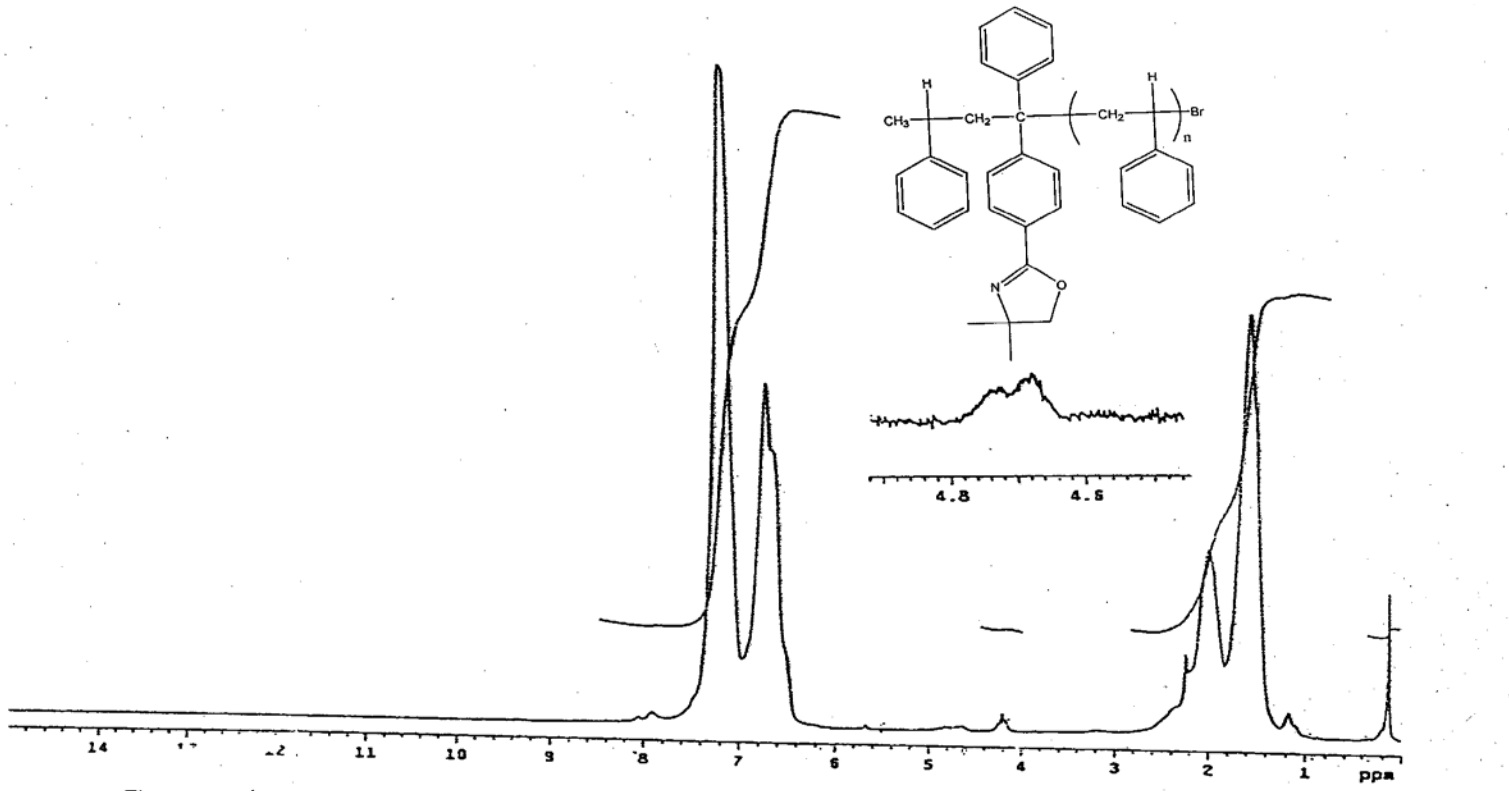


Figure 21: $^{1}$H NMR spectrum of α-oxazolyl functionalized polystyrene, (**7**). [styrene]:[(1-bromoethyl)benzene]:[CuBr]:[bpy]:[**5**] = 29:1:1:3:1;solvent: xylene; temperature: 110 °C. $\overline{M}_{n}^{SEC}$ = 3.9 x $10^3$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.42.

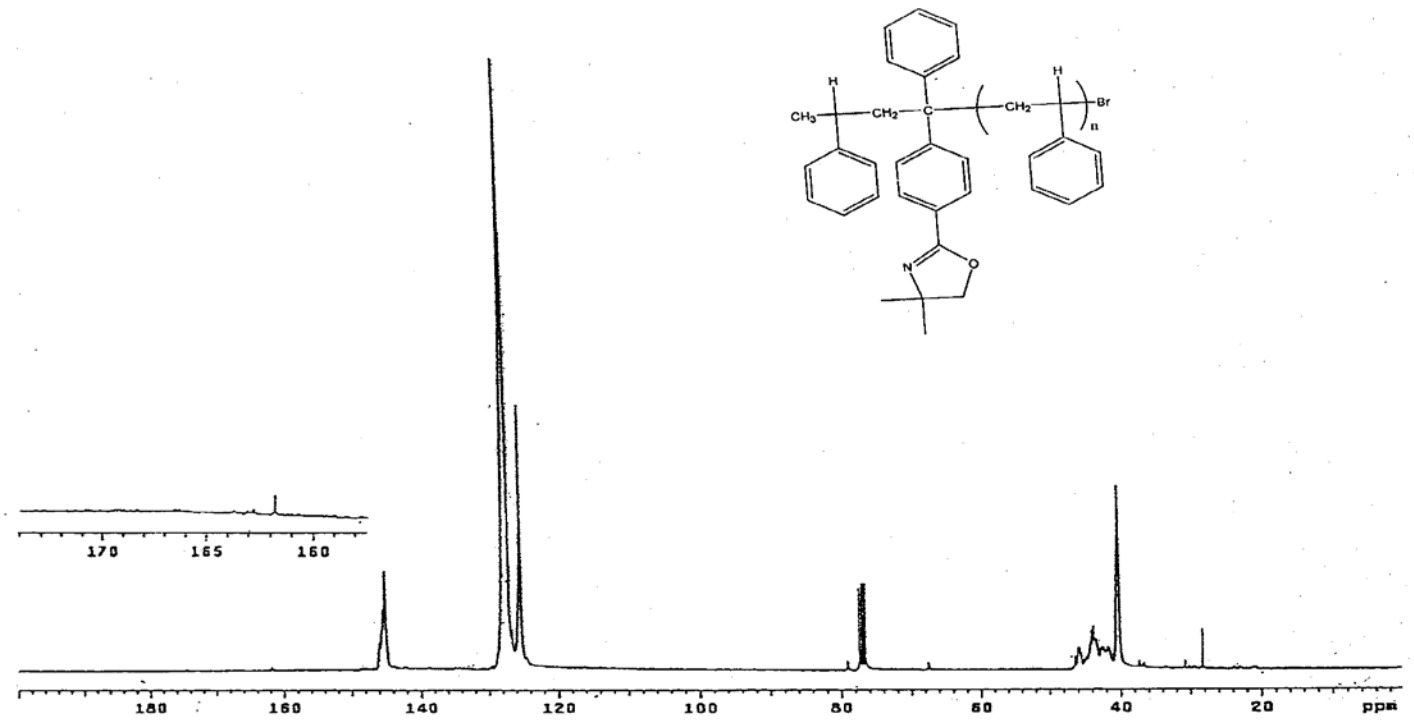


Figure 22: $^{13}$C NMR spectrum of α-oxazolyl functionalized polystyrene, (**7**). [styrene]:[(1-bromoethyl)-benzene]:[CuBr]: [bpy]:[**5**] = 29:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 3.9 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.42.

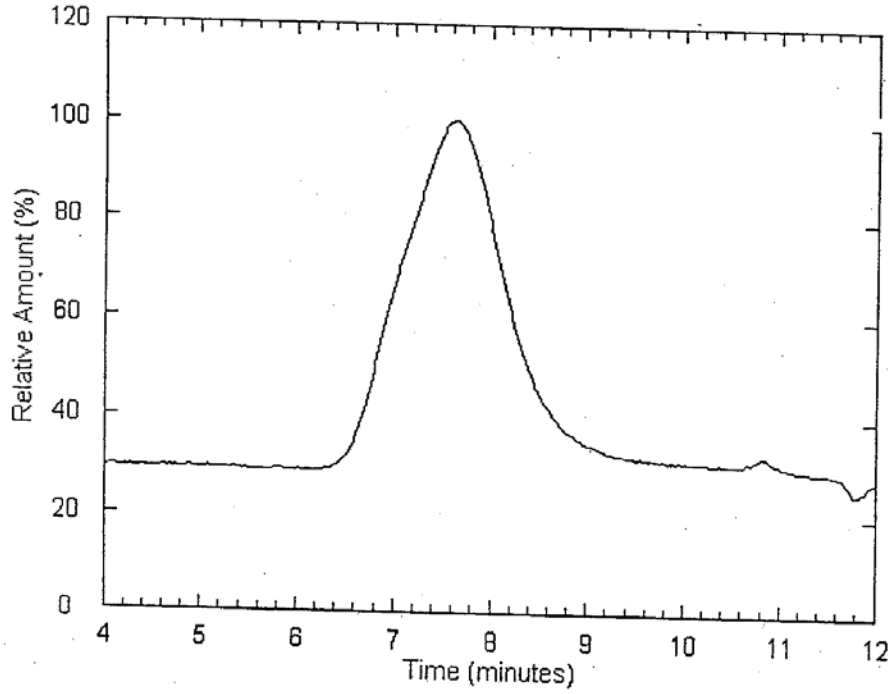


Figure 23: Size exclusion chromatogram of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**). [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**5**] = 30:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 4.3 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.45.

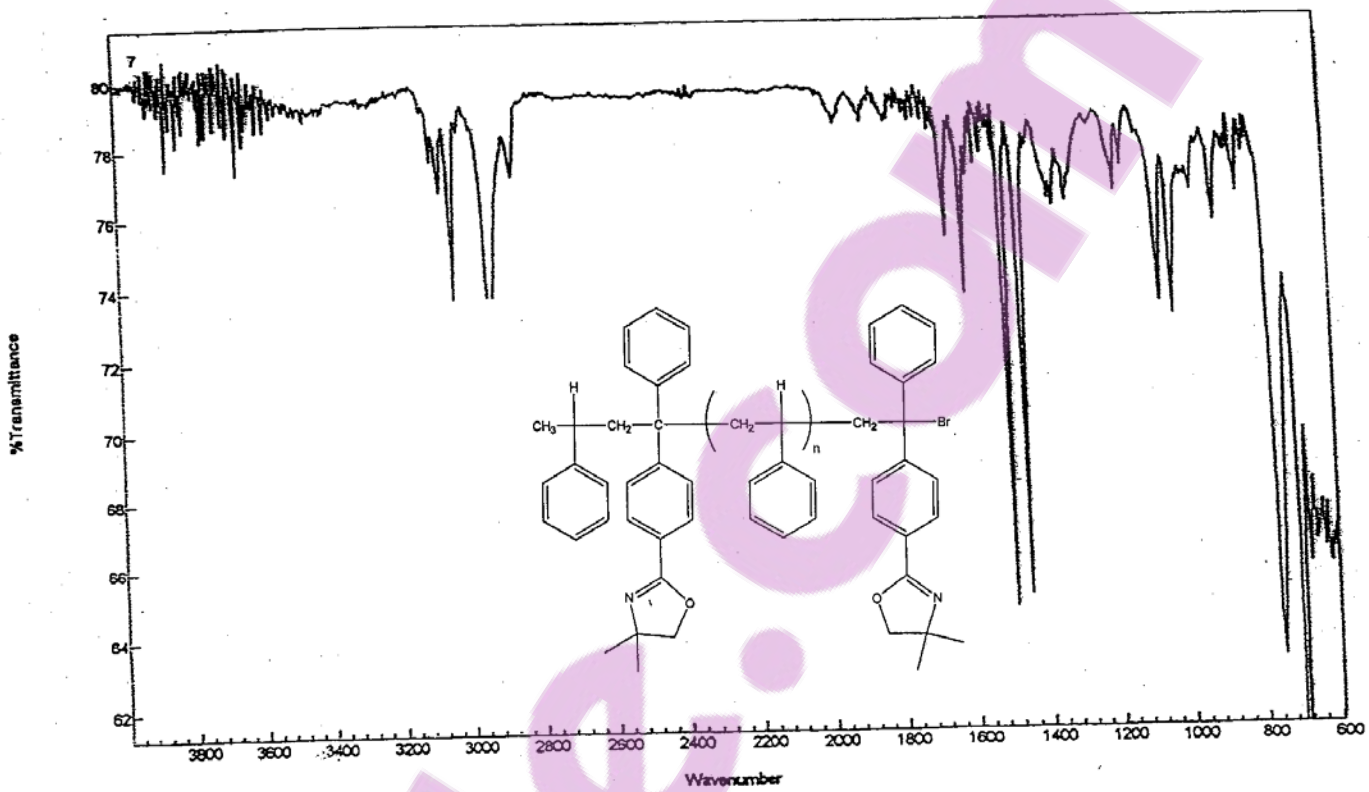


Figure:24 FTIR spectrum of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**). [styrene]:[(1-bromoethyl)-benzene]:[CuBr]: [bpy]:[**5**] = 30:1:1:3:1; solvent: xylene: 110 °C. $\overline{M}_{n}^{SEC}$ = 4.3 x $10^3$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.45.

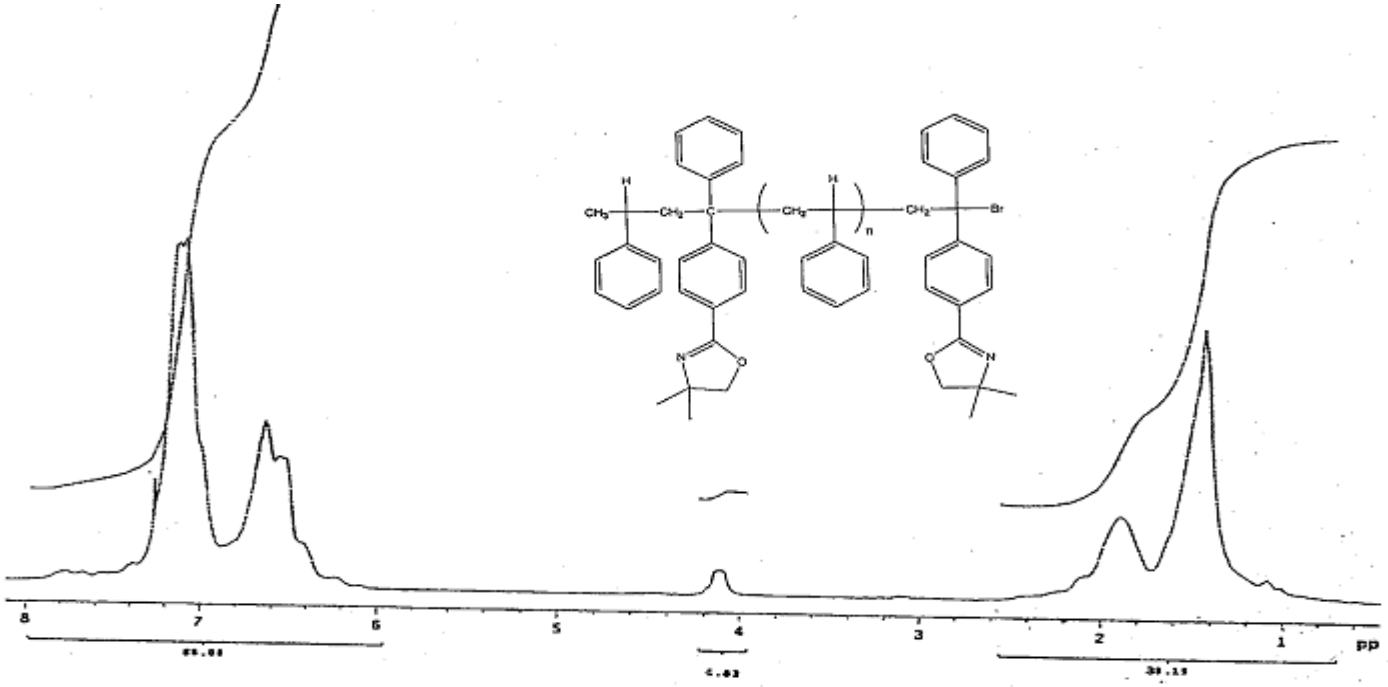


Figure 25: $^{1}$H NMR spectrum of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**). [styrene]:[(1-bromoethyl)benzene] :[CuBr]: [bpy]:[**5**] = 50:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_{n}^{SEC}$ = 4.3 x $10^3$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.45.

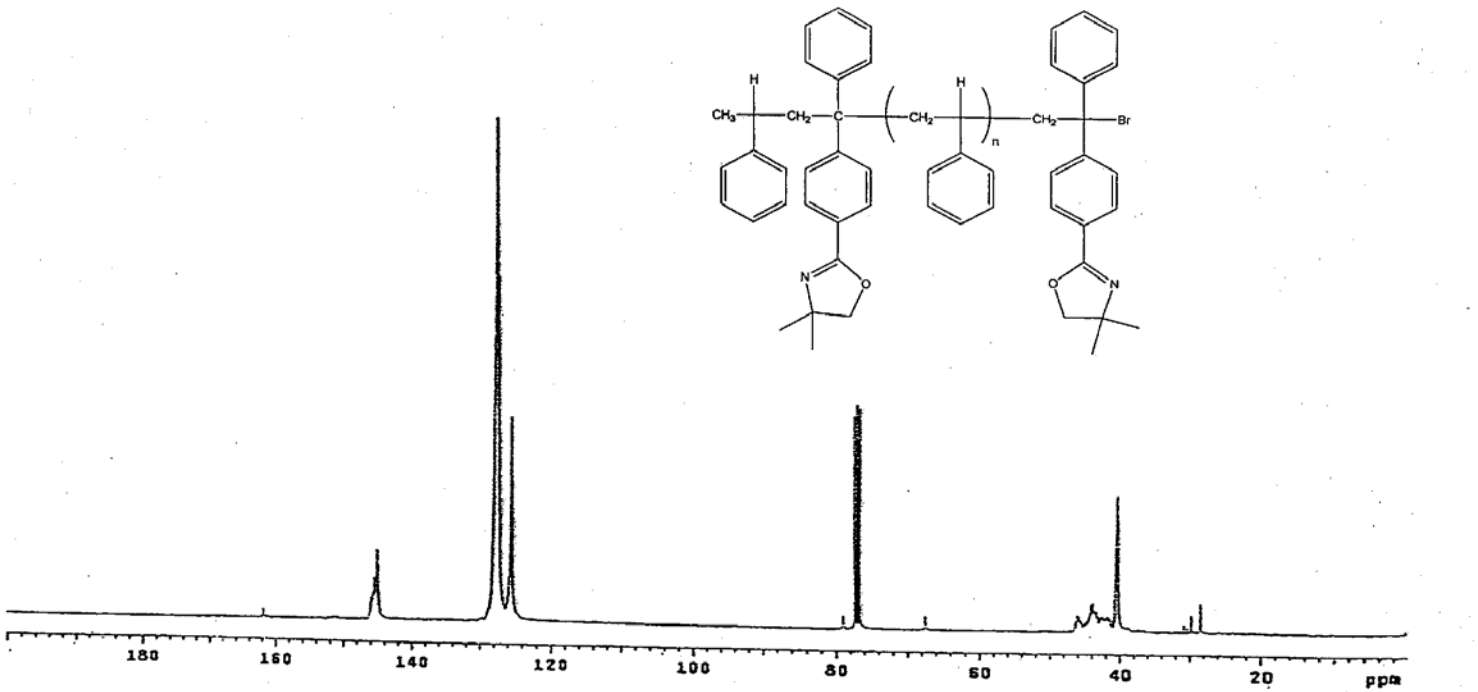


Figure 26: $^{13}$C NMR spectrum of α,ω-bis(oxazolyl) functionalized polystyrene, (**8**). [styrene]:[(1-bromoethyl)benzene] :[CuBr]: [bpy]:[**5**] = 30:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 4.3 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.45.

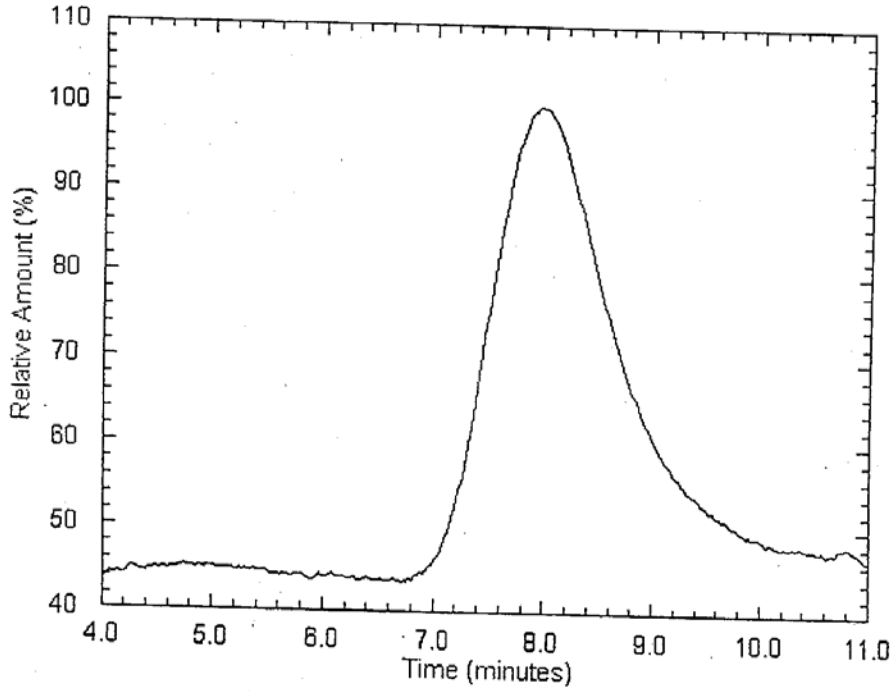


Figure 27: Size exclusion chromatogram of α-carboxyl functionalized polystyrene, (**9**). $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.47.

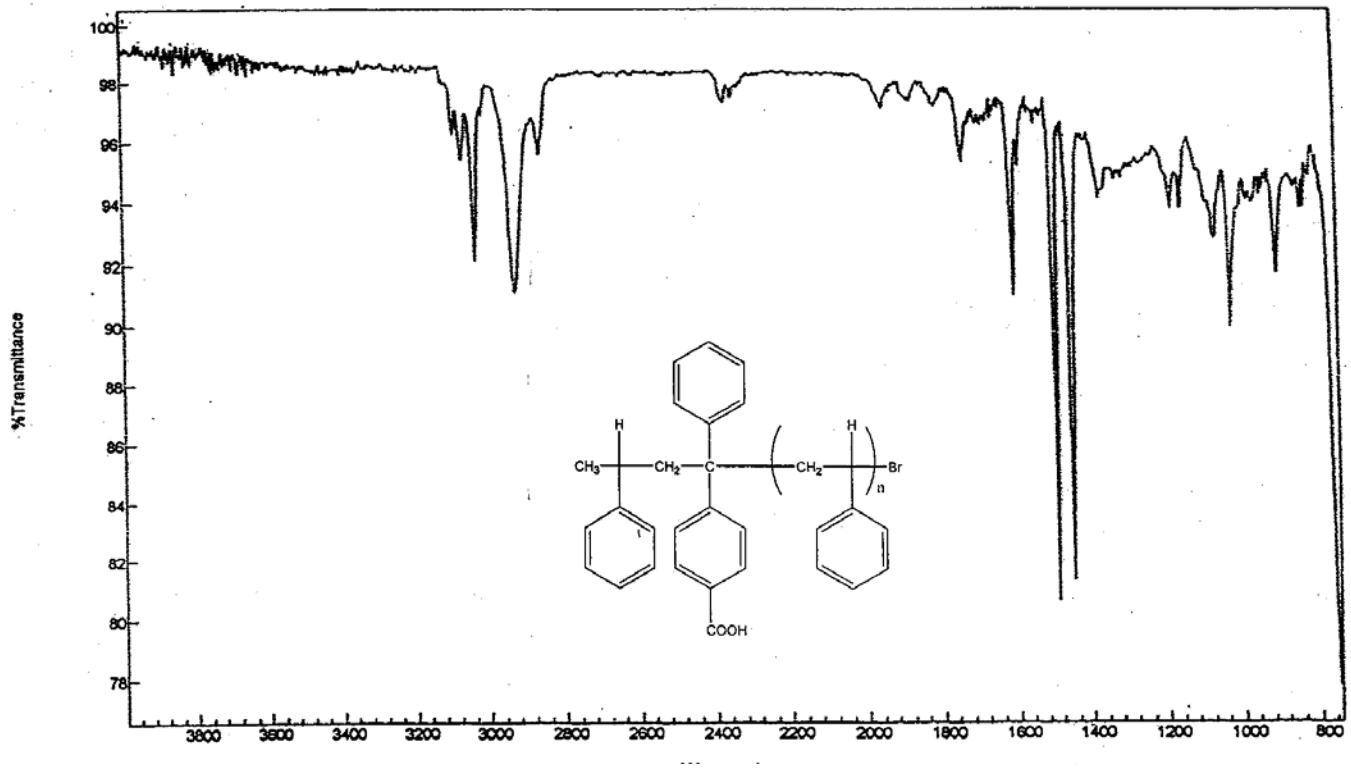


Figure 28: FTIR spectrum of α-matic carboxyl functionalized polystyrene, (**9**). $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.47.

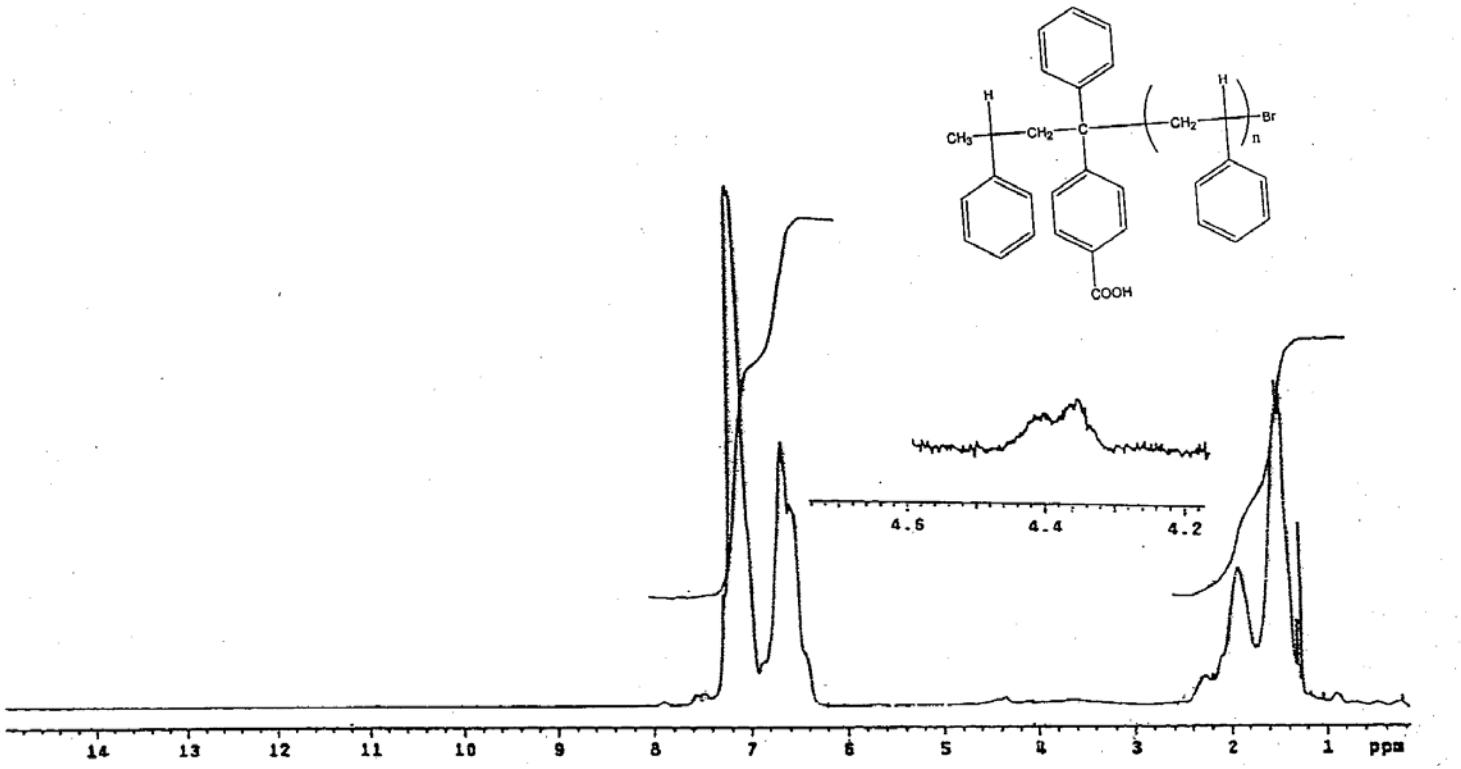


Figure 29: $^{1}$H NMR spectrum of α-carboxyl functionalized polystyrene, (**9**). $\overline{M}_{n}^{SEC}$ = 3.8 x $10^{3}$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.47.

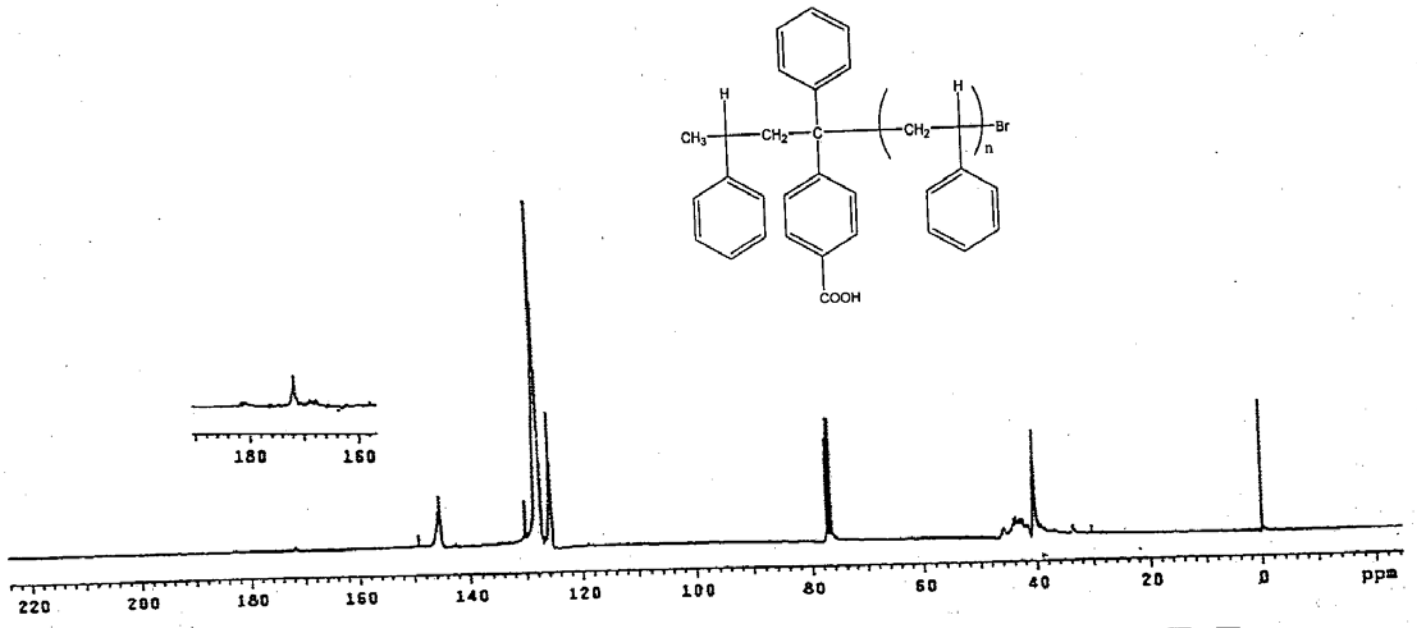


Figure 30: $^{13}$C NMR spectrum of α-carboxyl functionalized polystyrene, (**9**). $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.47.

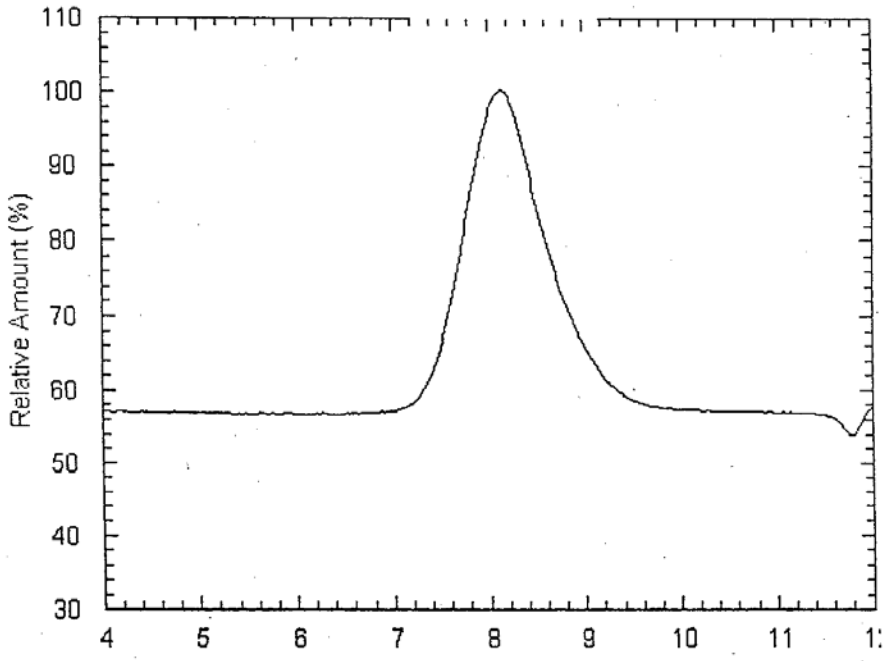


Figure 31: Size exclusion chromatogram of α,ω-bis(carboxyl) functionalized polystyrene, (**10**). $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.51.

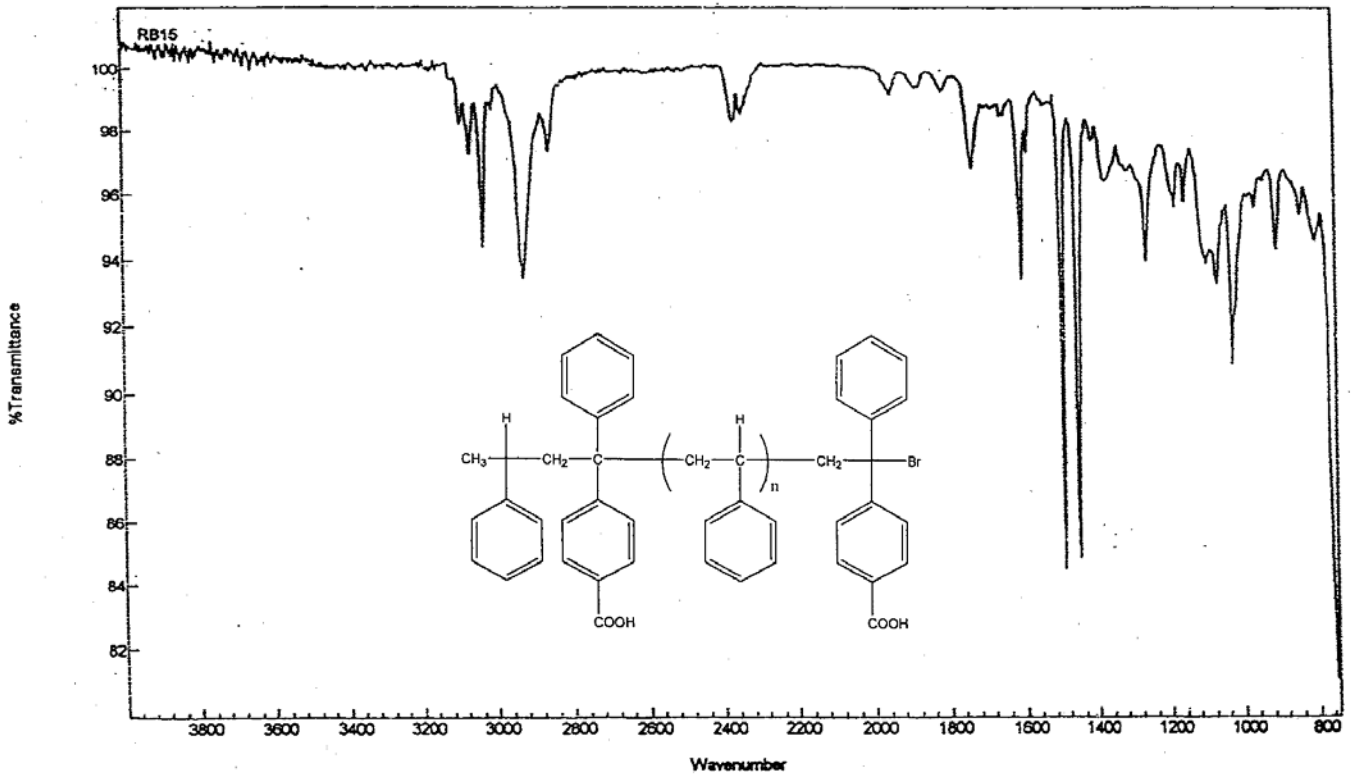


Figure 32: FTIR spectrum of α,ω-bis(carboxyl) functionalized polystyrene, (**10**). $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.51.

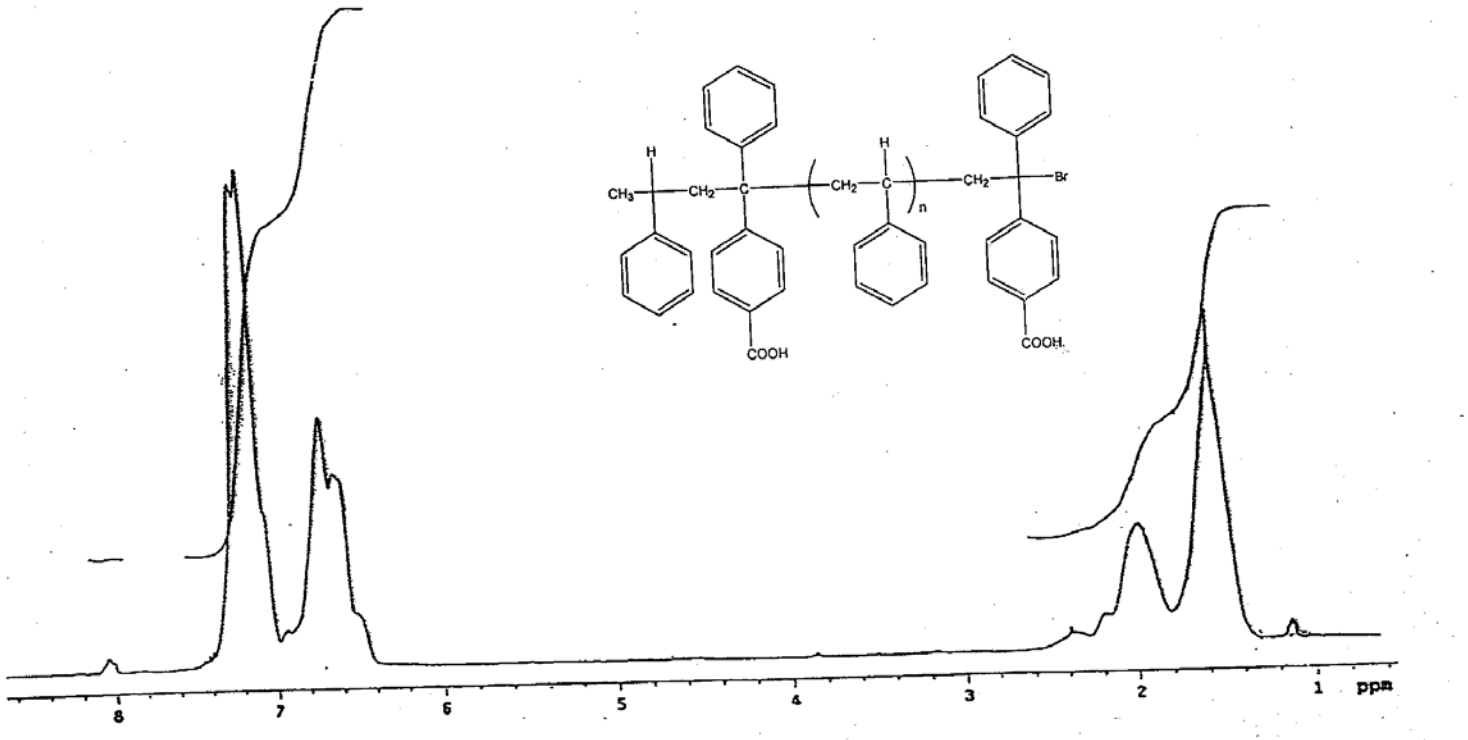


Figure 33: $^{1}$H NMR spectrum of α,ω-bis(carboxyl) functionalized polystyrene, (**10**). $\overline{M}_{n}^{SEC}$ = 4.0 x $10^{3}$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.51.

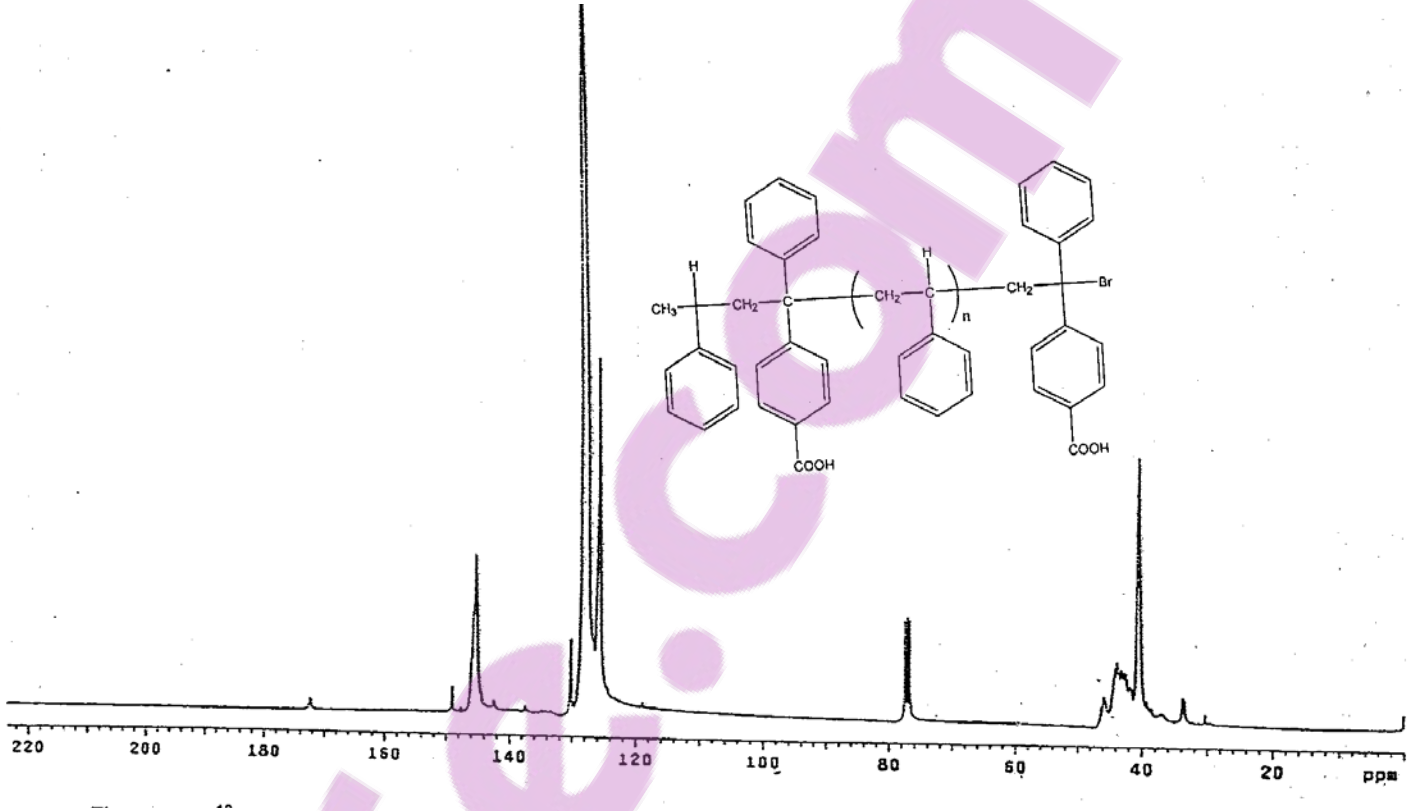


Figure 34: $^{13}$C NMR spectrum of α,ω-bis(carboxyl) functionalized polystyrene, (**10**). $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.51.

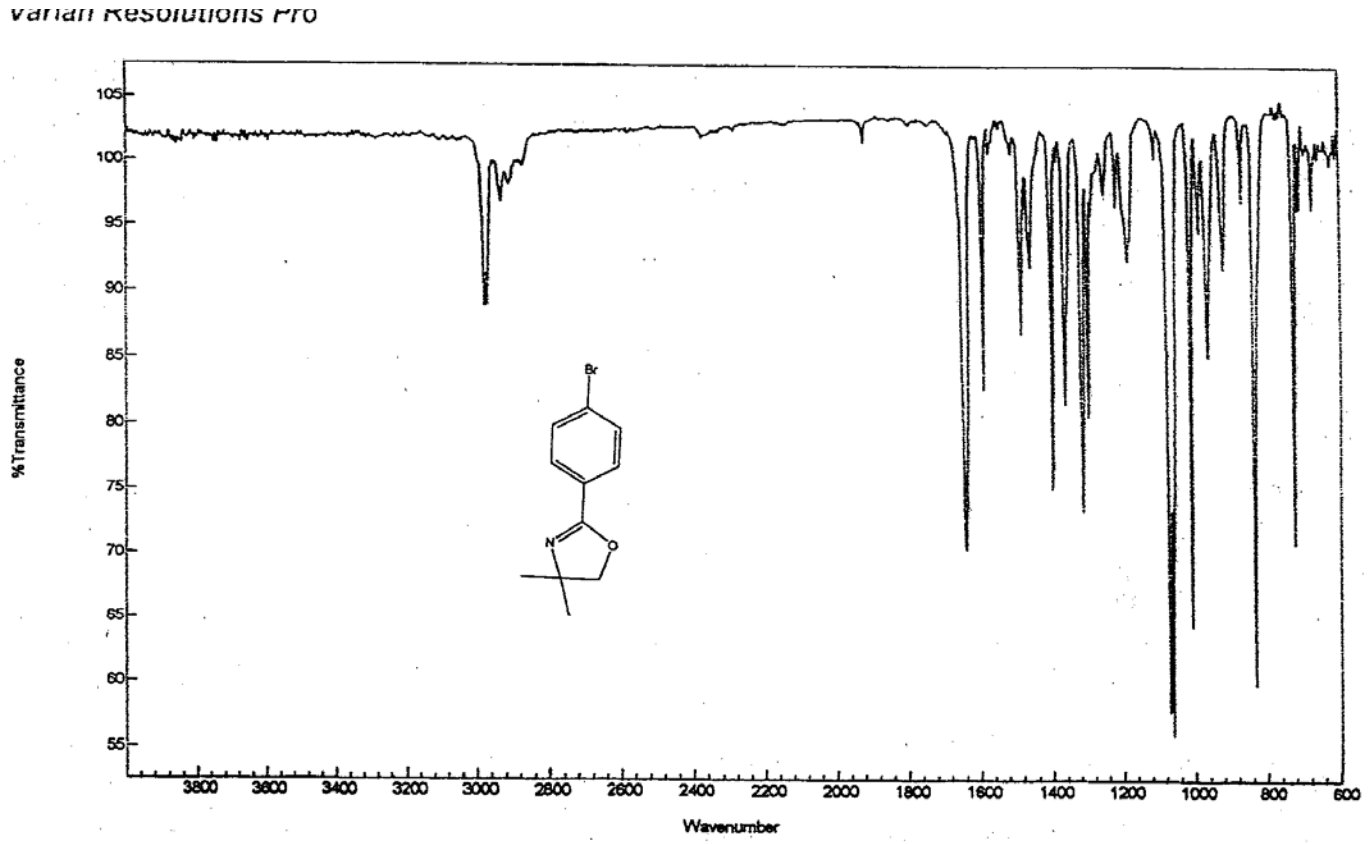


Figure 35: FTIR spectrum of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline.

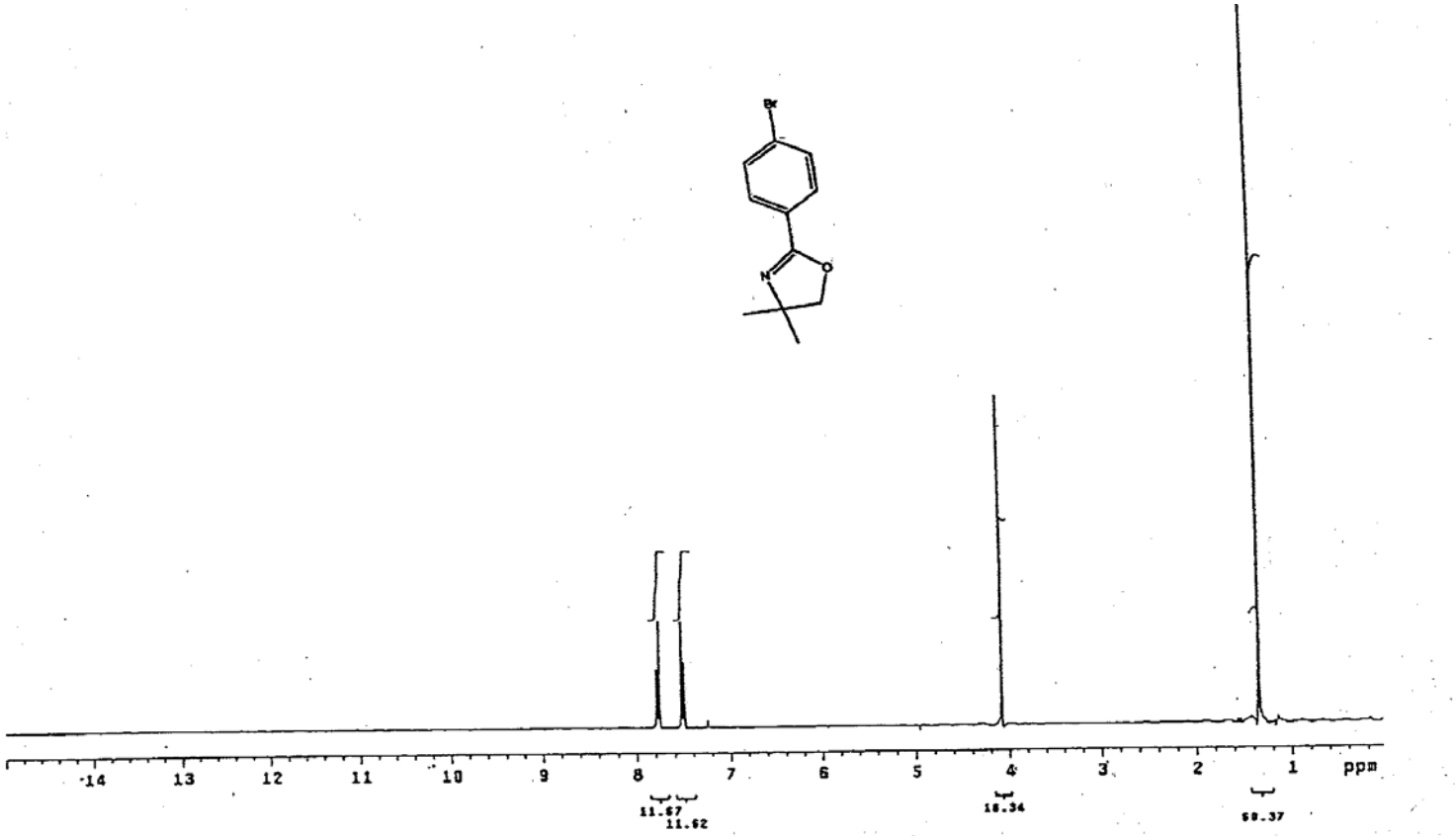


Figure 36: $^{1}$H NMR spectrum of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline.

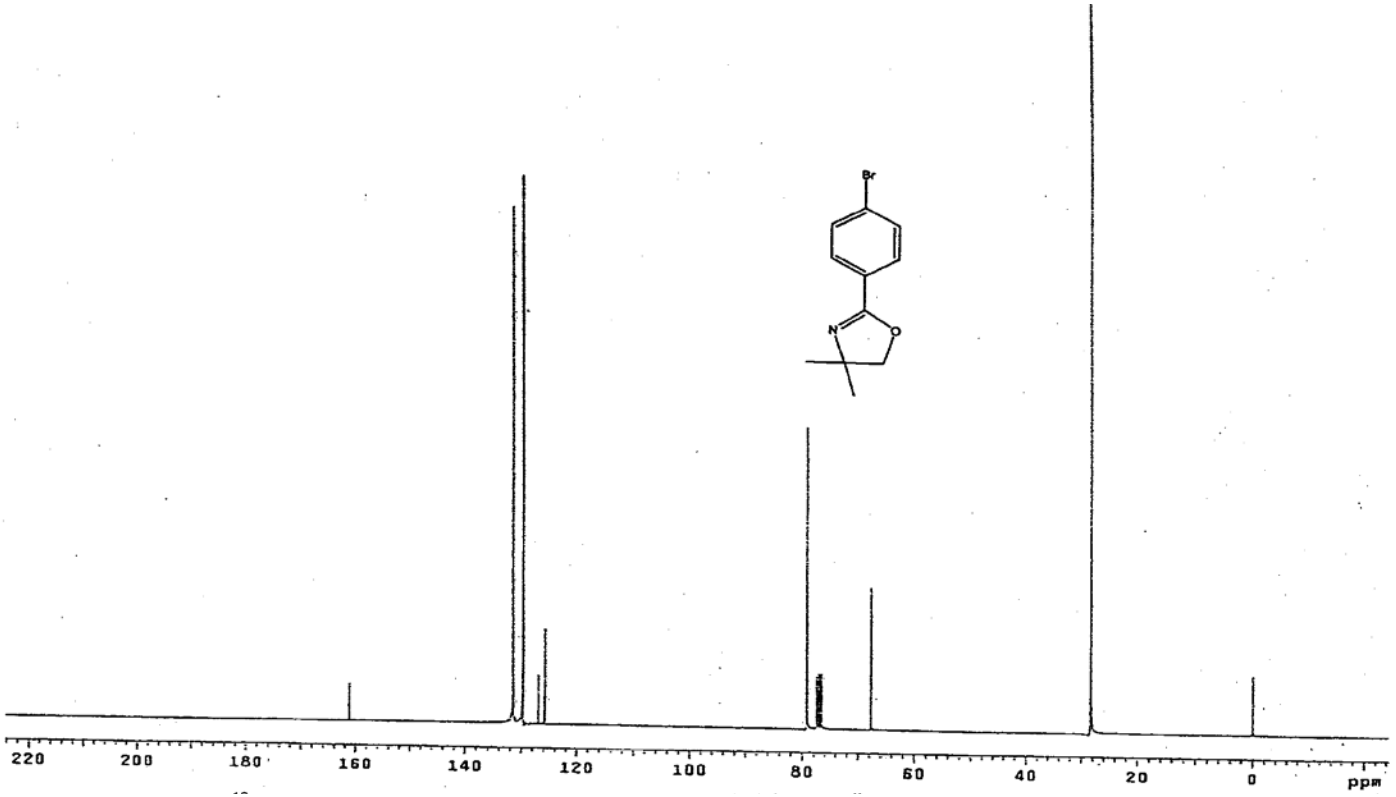


Figure 37: $^{13}C$ NMR spectrum of 2-(4-bromophenyl)-4,4-dimethyl-2-oxazoline.

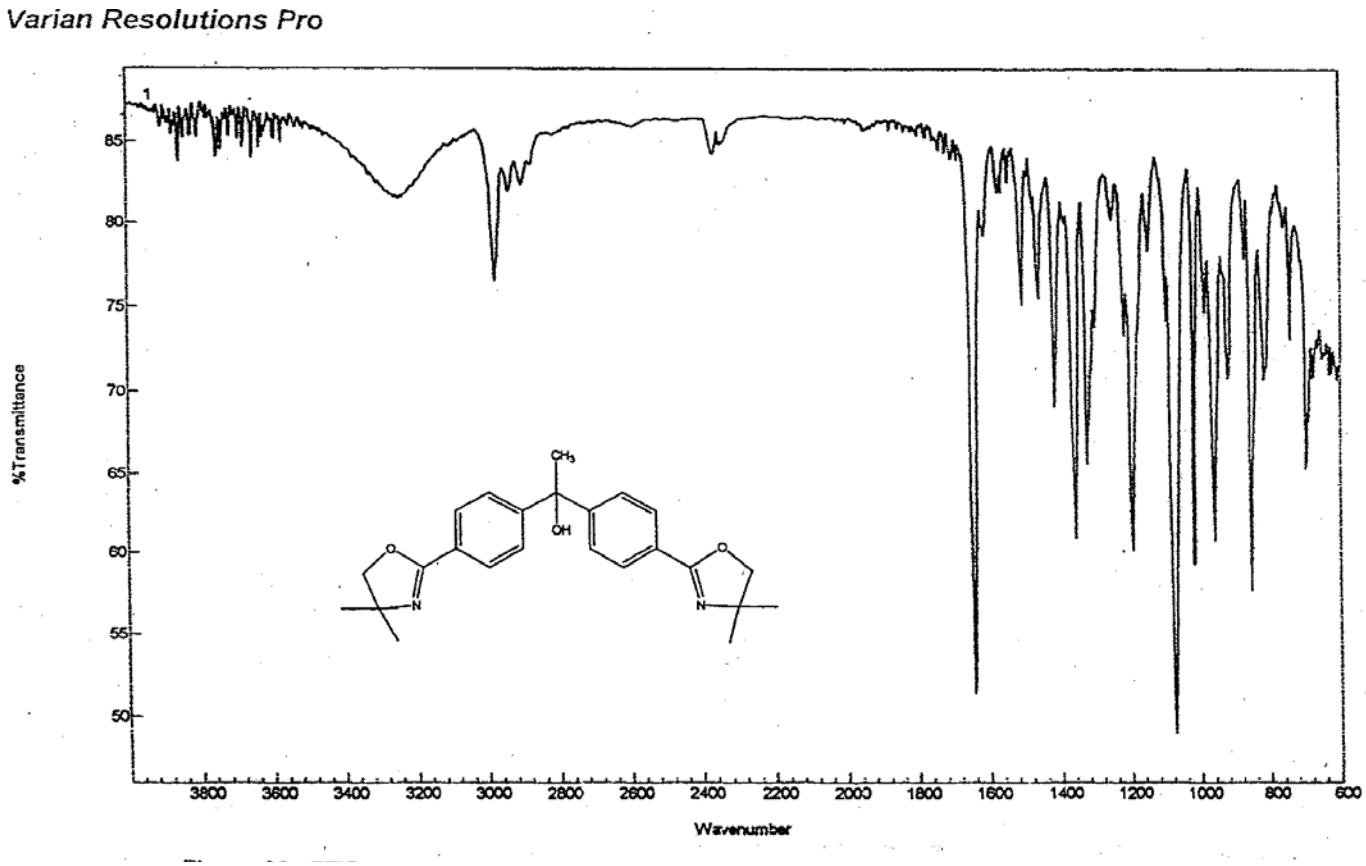


Figure 38: FTIR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol.

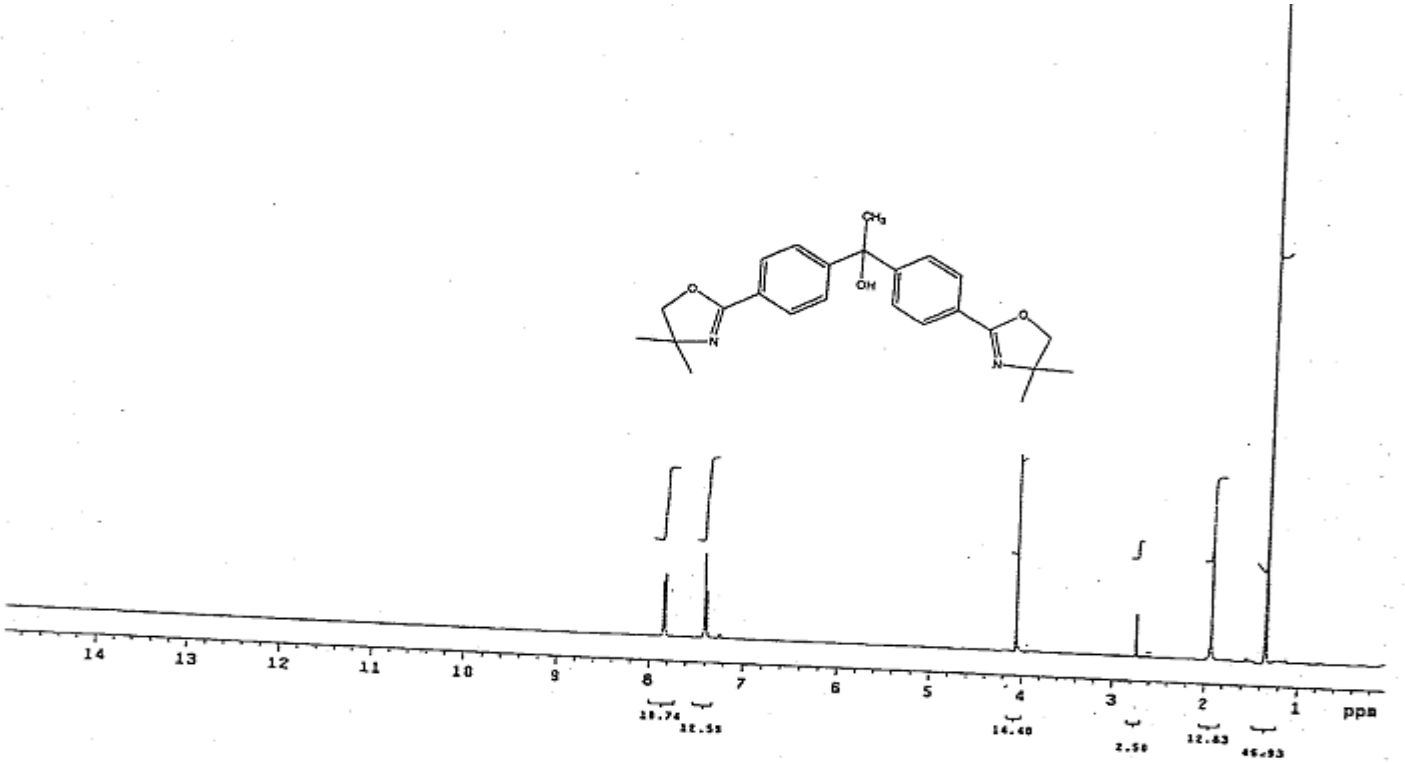


Figure 39: $^{1}$H NMR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol.

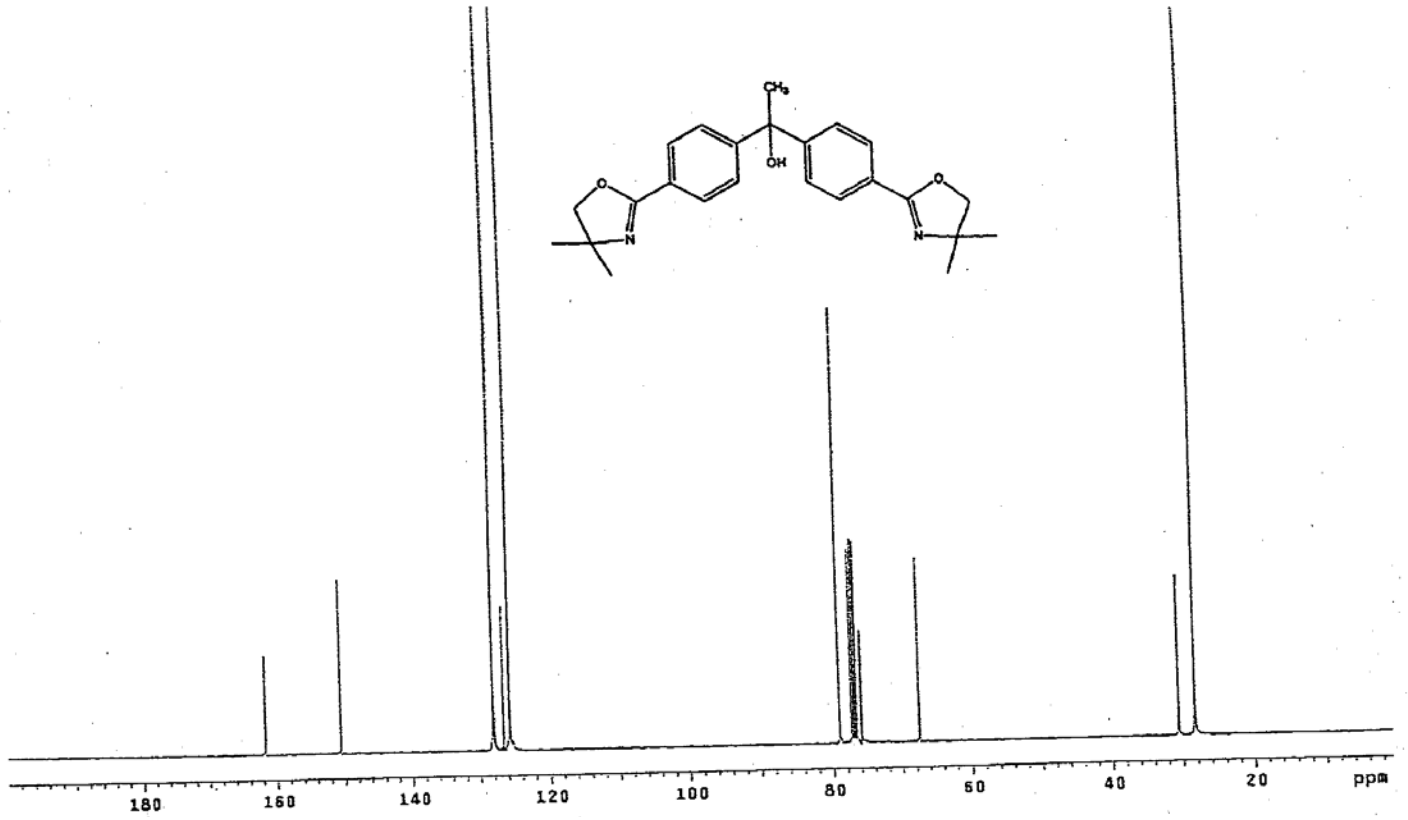


Figure 40: $^{13}C$ NMR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethanol.

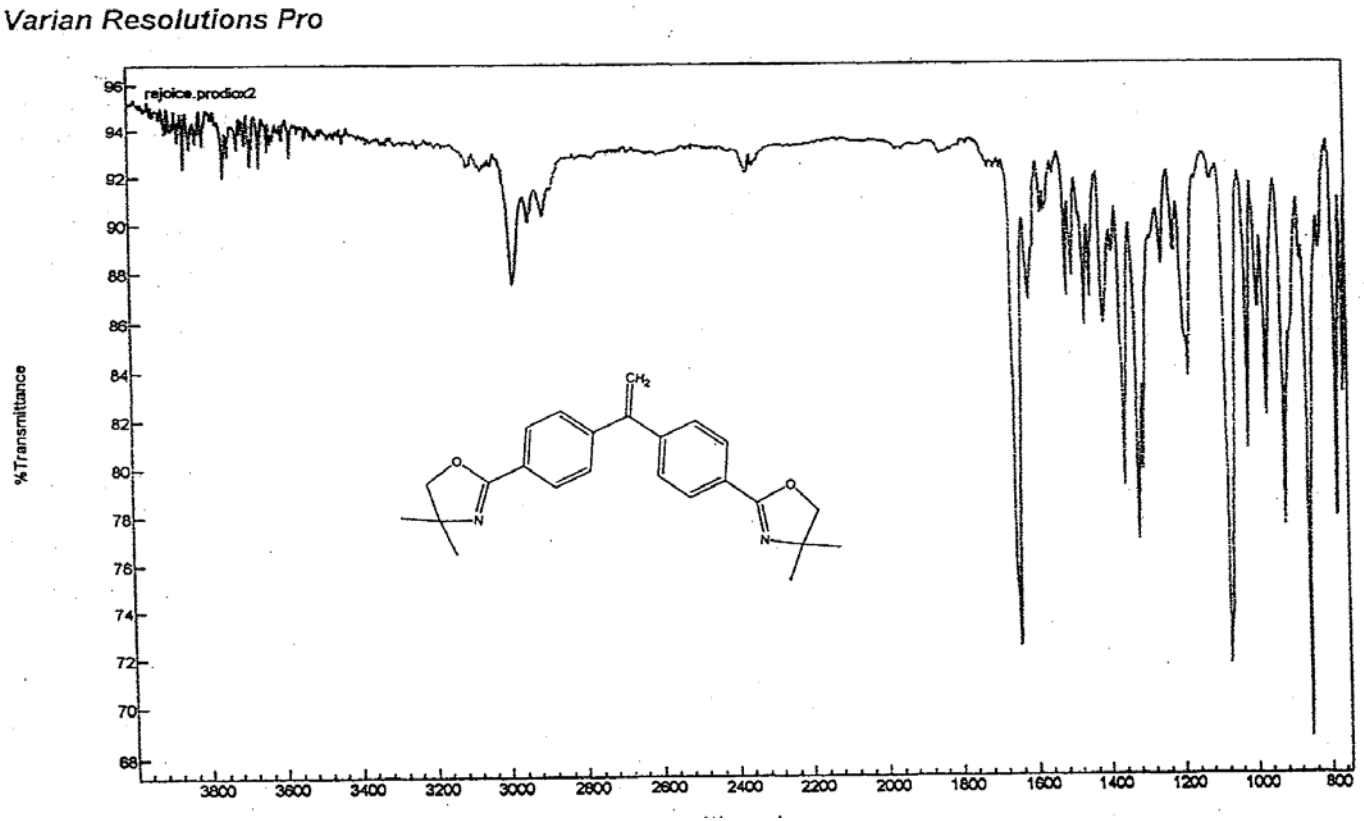


Figure 41: FTIR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**)

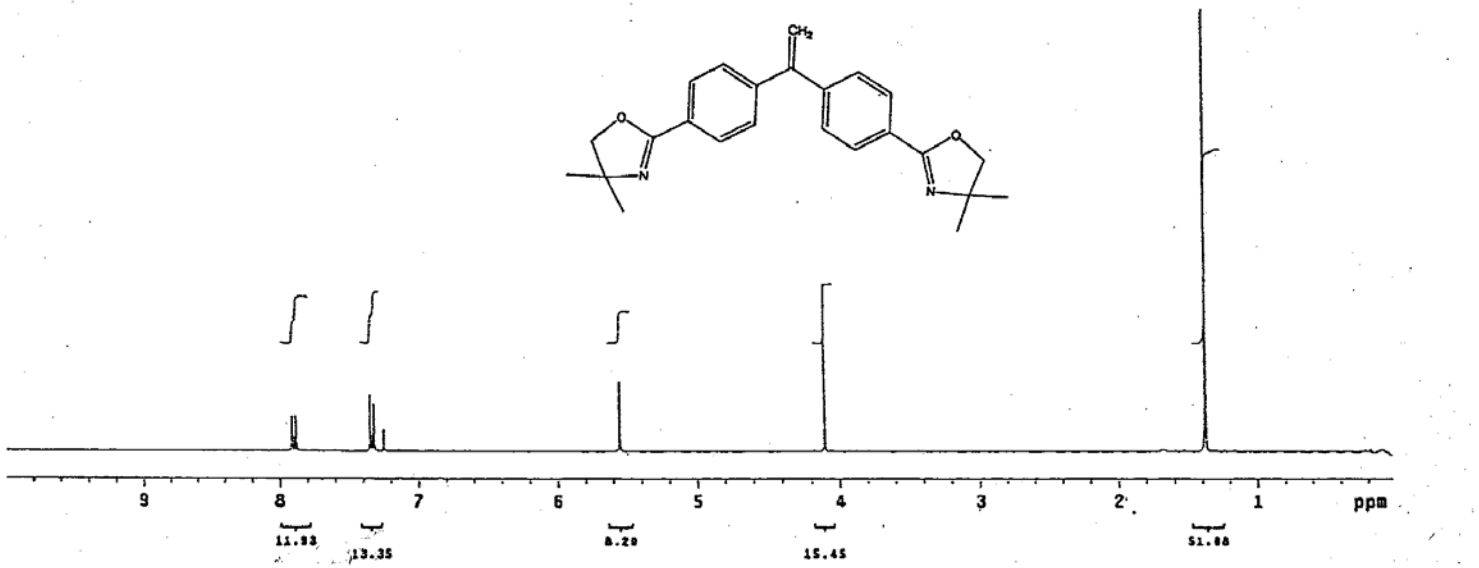


Figure 42: $^{1}$H NMR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**)

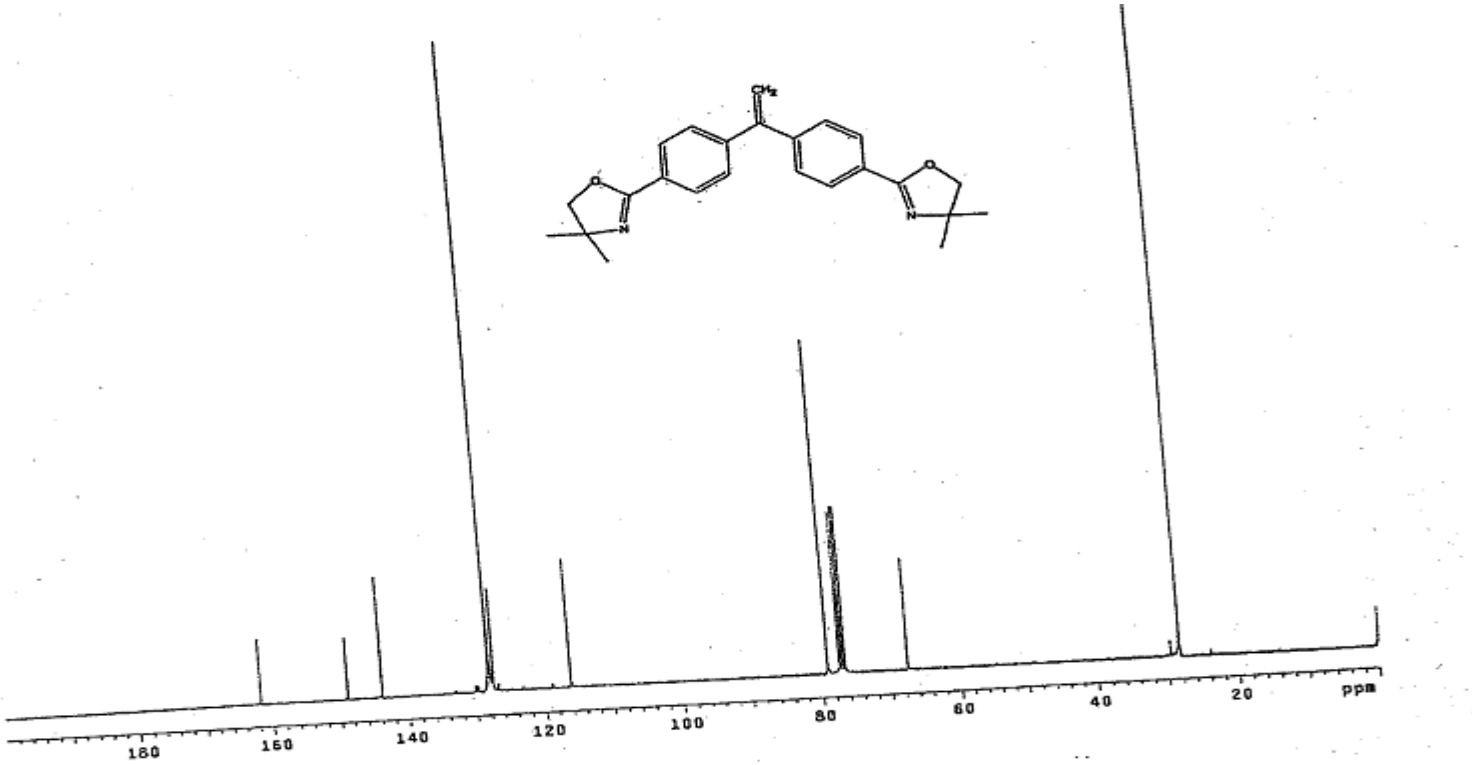


Figure 43: $^{13}$C NMR spectrum of 1,1-bis[4-(2-(4,4-dimethyl-1,3-oxazolyl))phenyl]ethylene, (**11**)

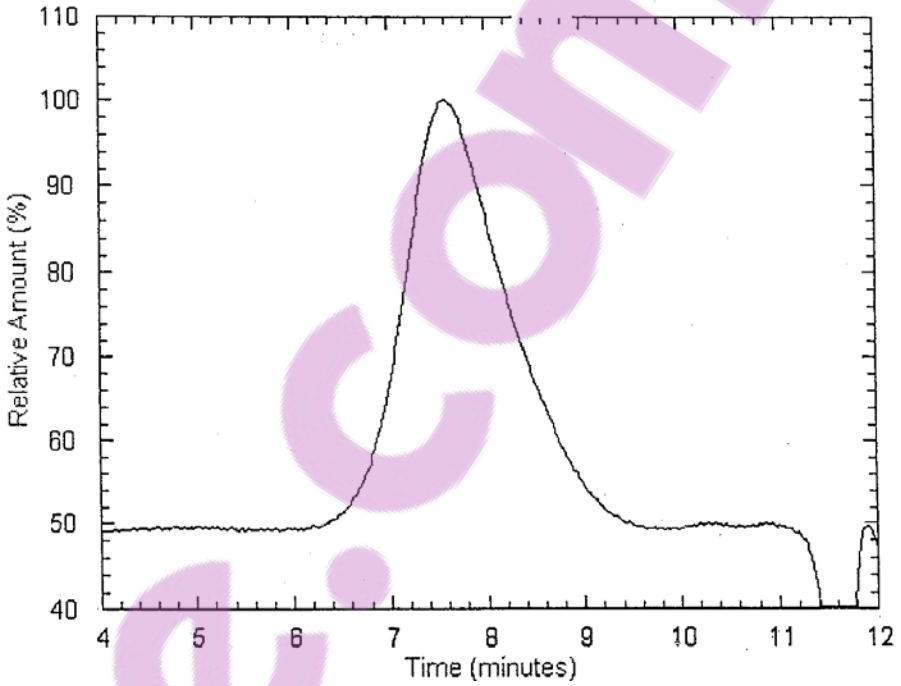


Figure 44: Size exclusion chromatogram of α-bis(oxazolyl) functionalized polystyrene, (**13**). [styrene]:[(1-bromoethyl)- benzene]:[CuBr]: [bpy]:[**11**] = 50:1:1:3:1;solvent: xylene: 110 °C. $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ =1.47.

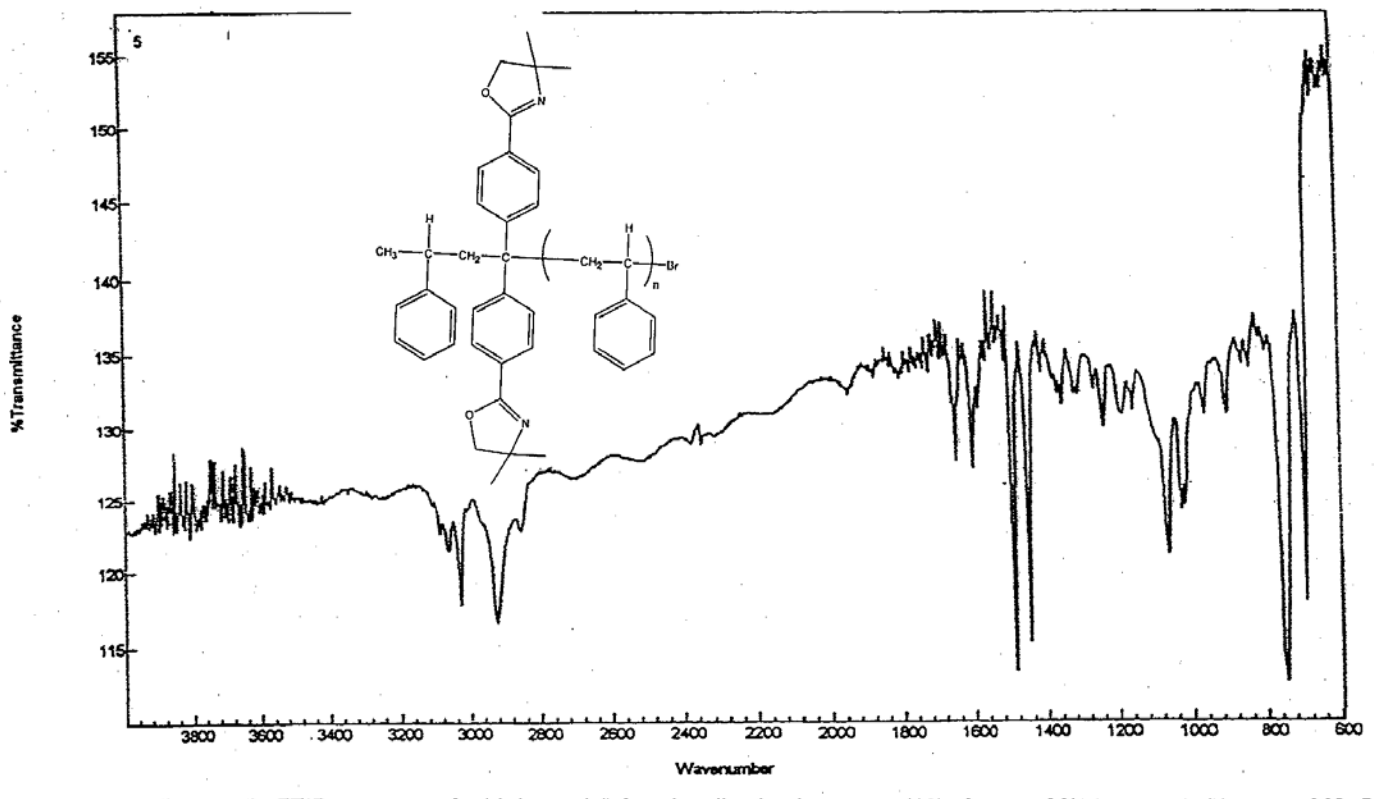


Figure 45: FTIR spectrum of α-bis(oxazolyl) functionalized polystyrene, (**13**). [styrene]: [(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**11**] = 29:1:1:3:1; solvent: xylene: 110 °C. $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ =1.47

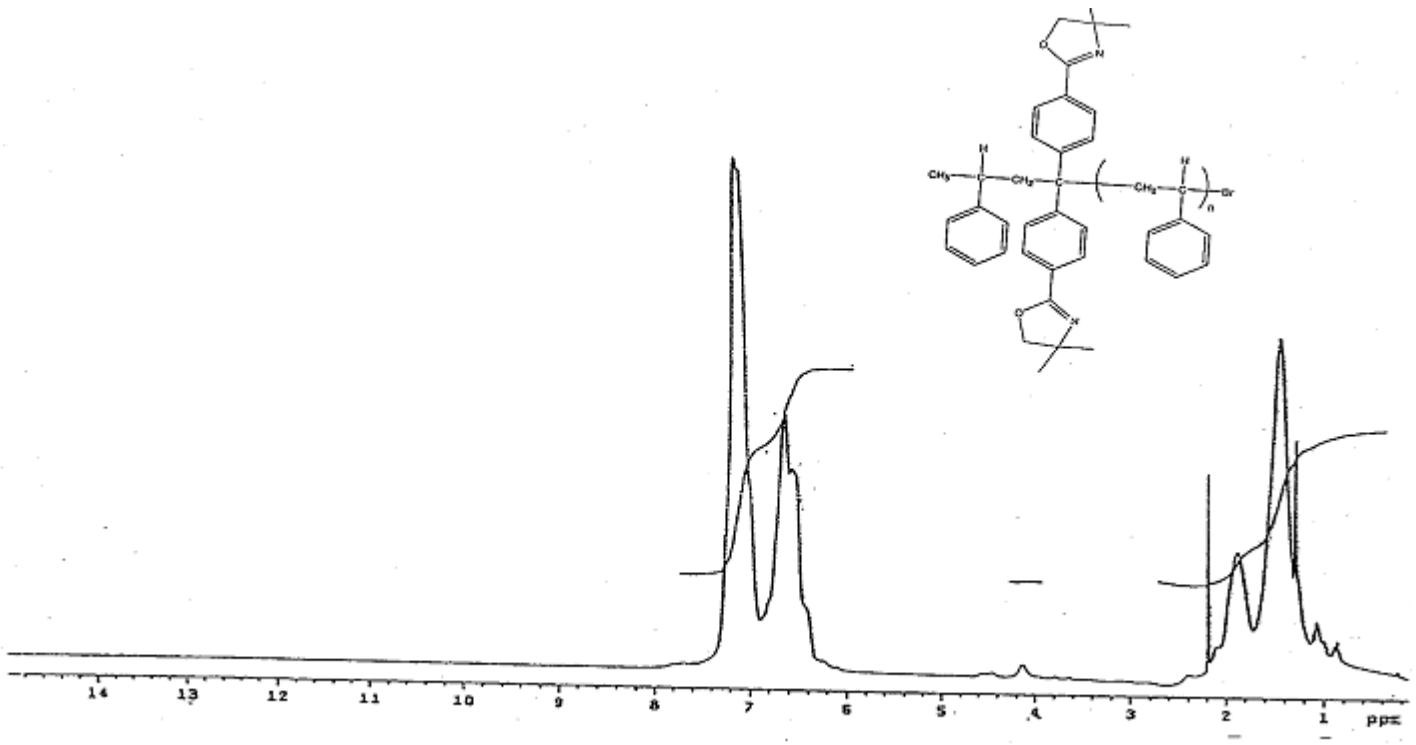


Figure 46: $^{1}$H NMR spectrum of α-bis(oxazolyl) functionalized polystyrene, (**13**). [styrene]:[(1-bromoethyl)benzene] :[CuBr]: [bpy]:[**11**] = 29:1:1:3:1; solvent: xylene: 110 °C. $\overline{M}_{n}^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ =1.47.

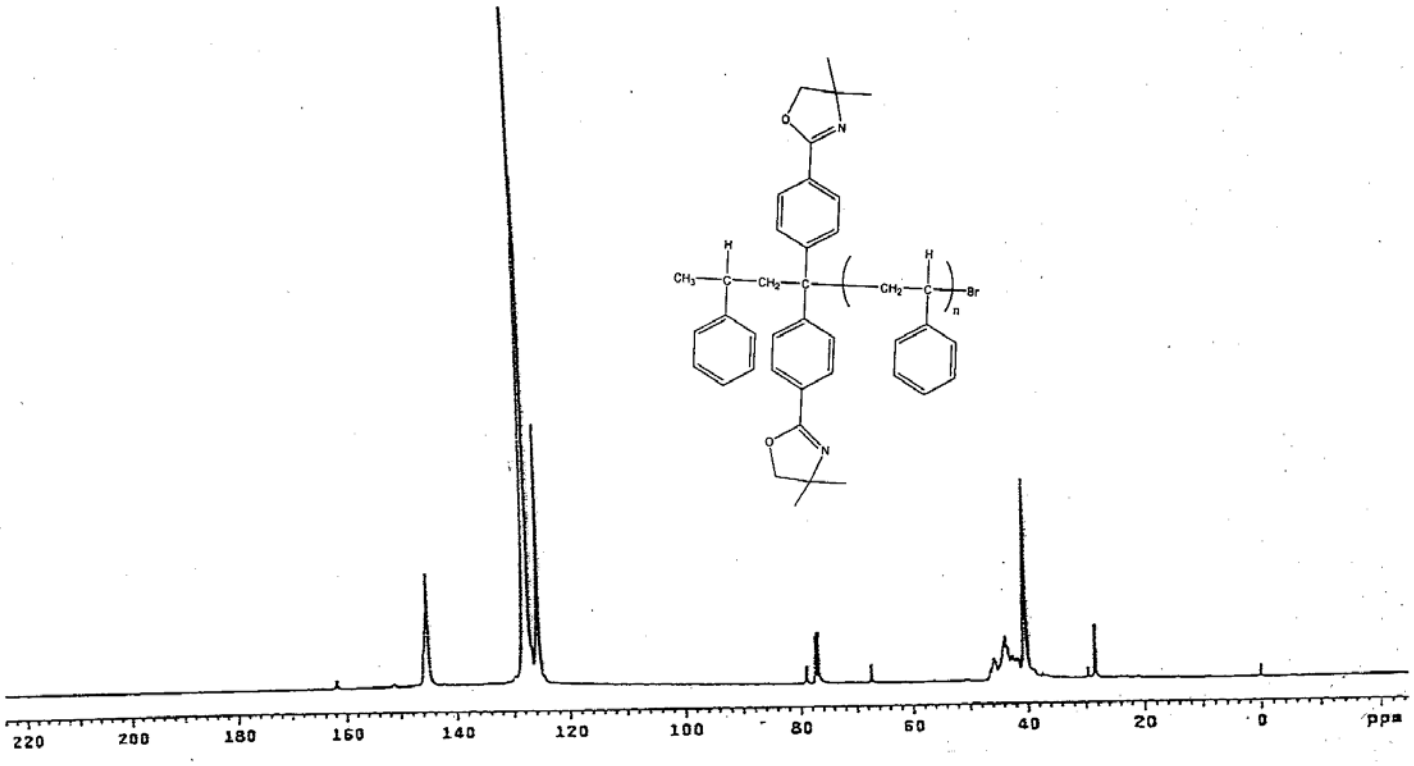


Figure 47: $^{13}$C NMR spectrum of α-bis(oxazolyl) functionalized polystyrene, (**13**). [styrene]: [(1-bromoethyl)benzene] :[CuBr]: [bpy]:[**11**] = 29:1:1:3:1; solvent: xylene: 110 °C. $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ =1.47

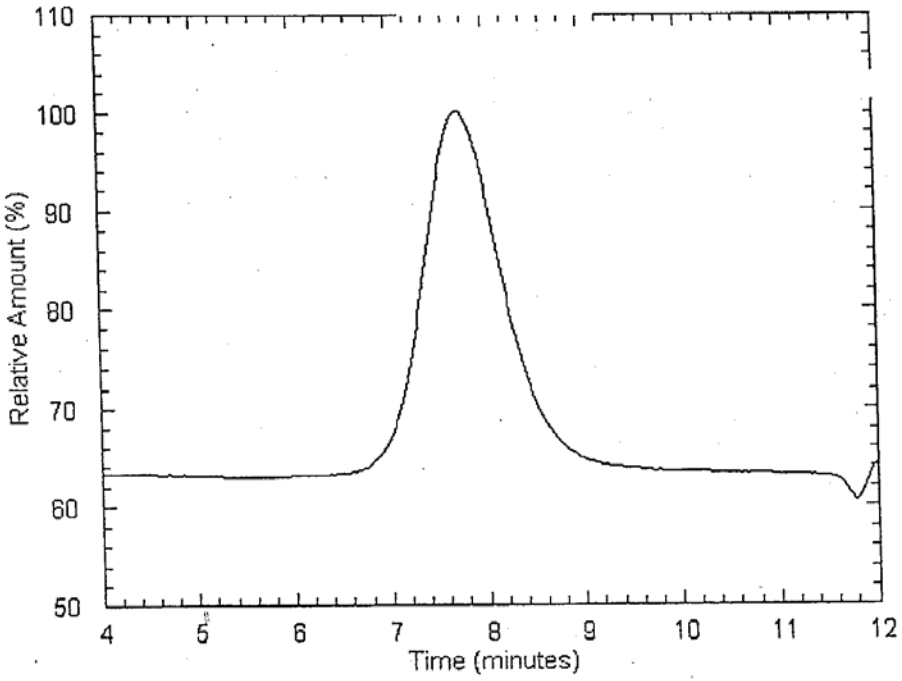


Figure 48: Size exclusion chromatogram of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**). [styrene]:[(1-bromoethyl)benzene]:[CuBr]: [bpy]:[**11**] = 29:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 4.4 x $10^3$ g/moll; $\overline{M}_w/\overline{M}_n$ = 1.48.

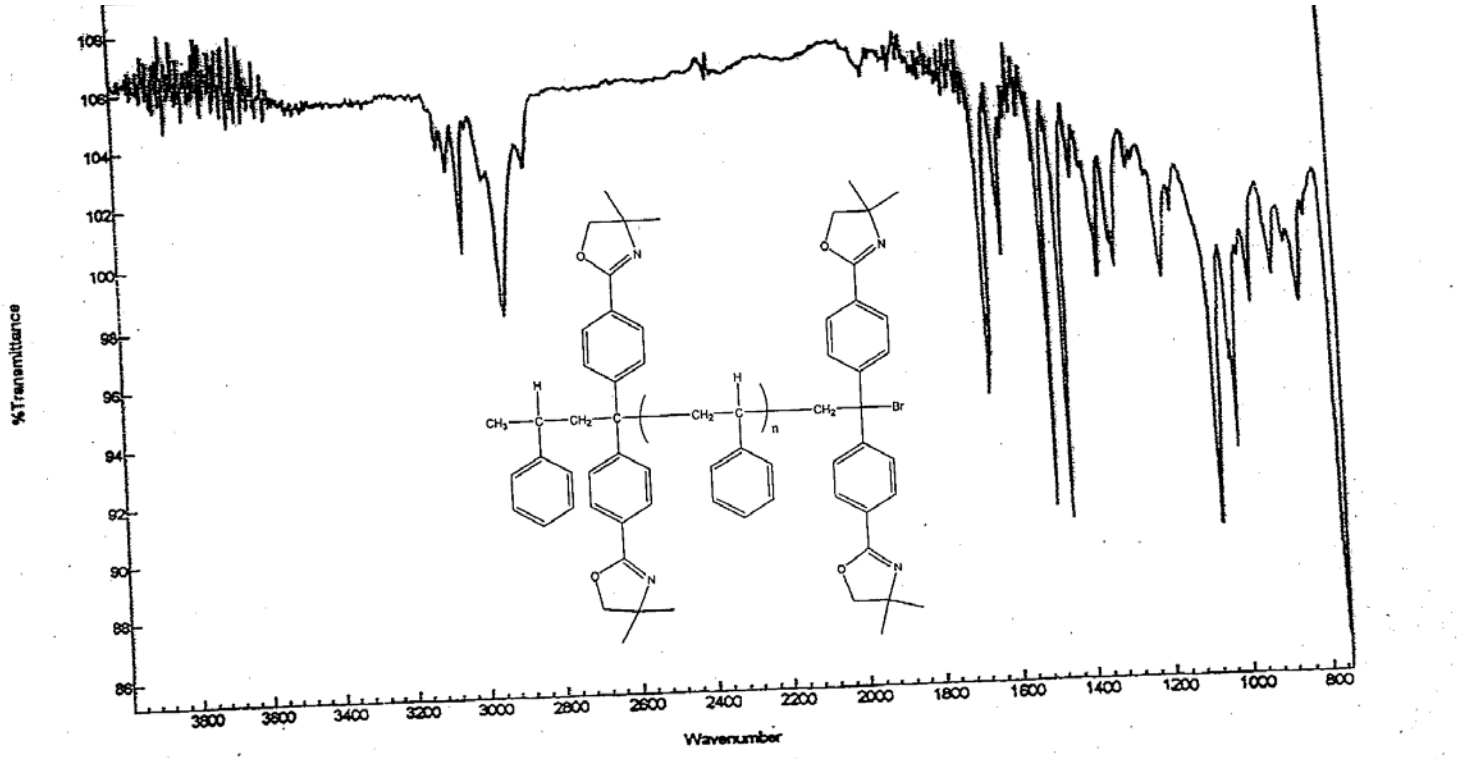


Figure 49: FTIR spectrum of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**). [styrene]:[(1-bromoethyl)-benzene]:[CuBr]: [bpy]:[**11**] = 29:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 4.4 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48.

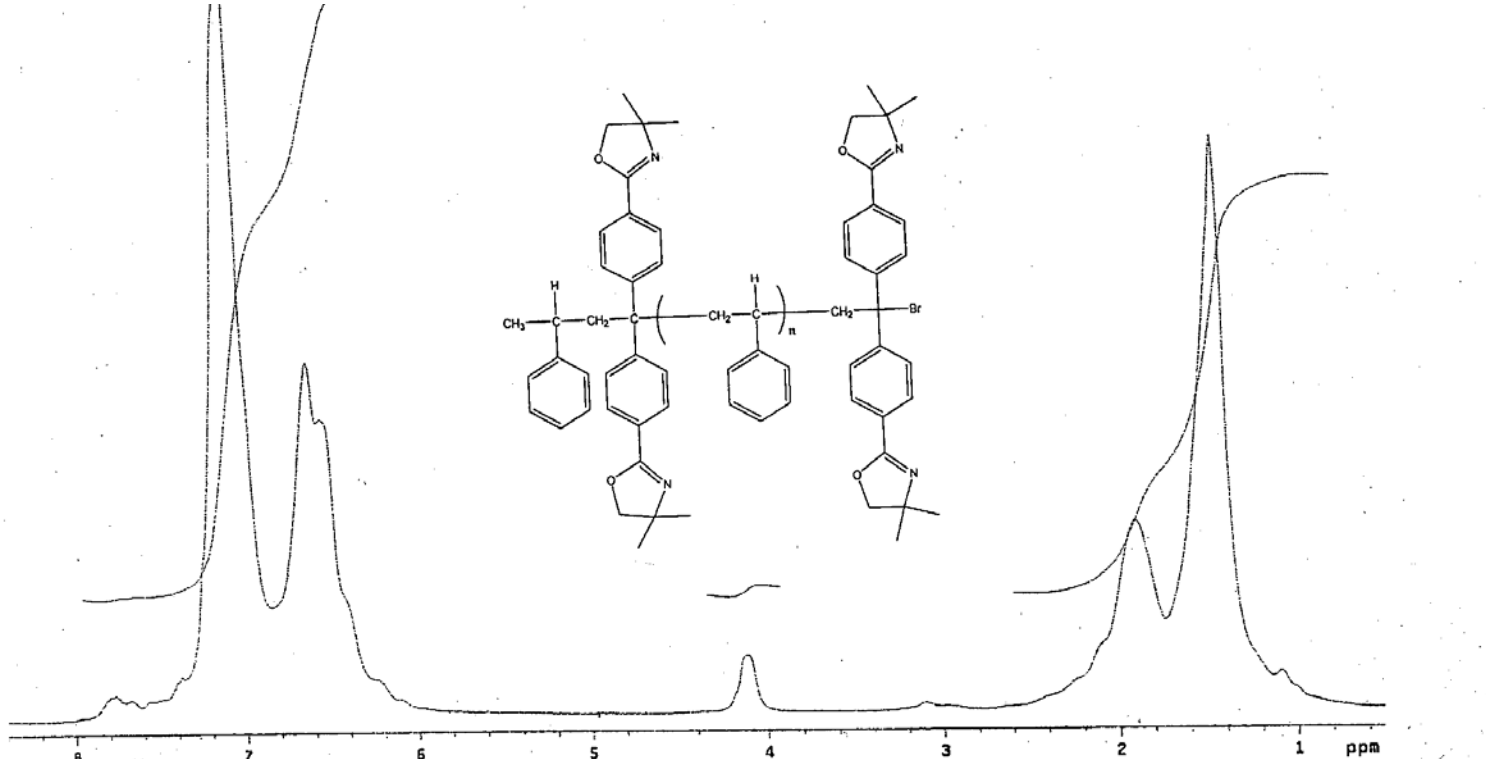


Figure 50: $^{1}$H NMR spectrum of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**). [styrene]:[(1-bromoethyl)- benzene]:[CuBr]: [bpy]:[**11**] = 29:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_{n}^{SEC}$ = 4.4 x $10^3$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.48.

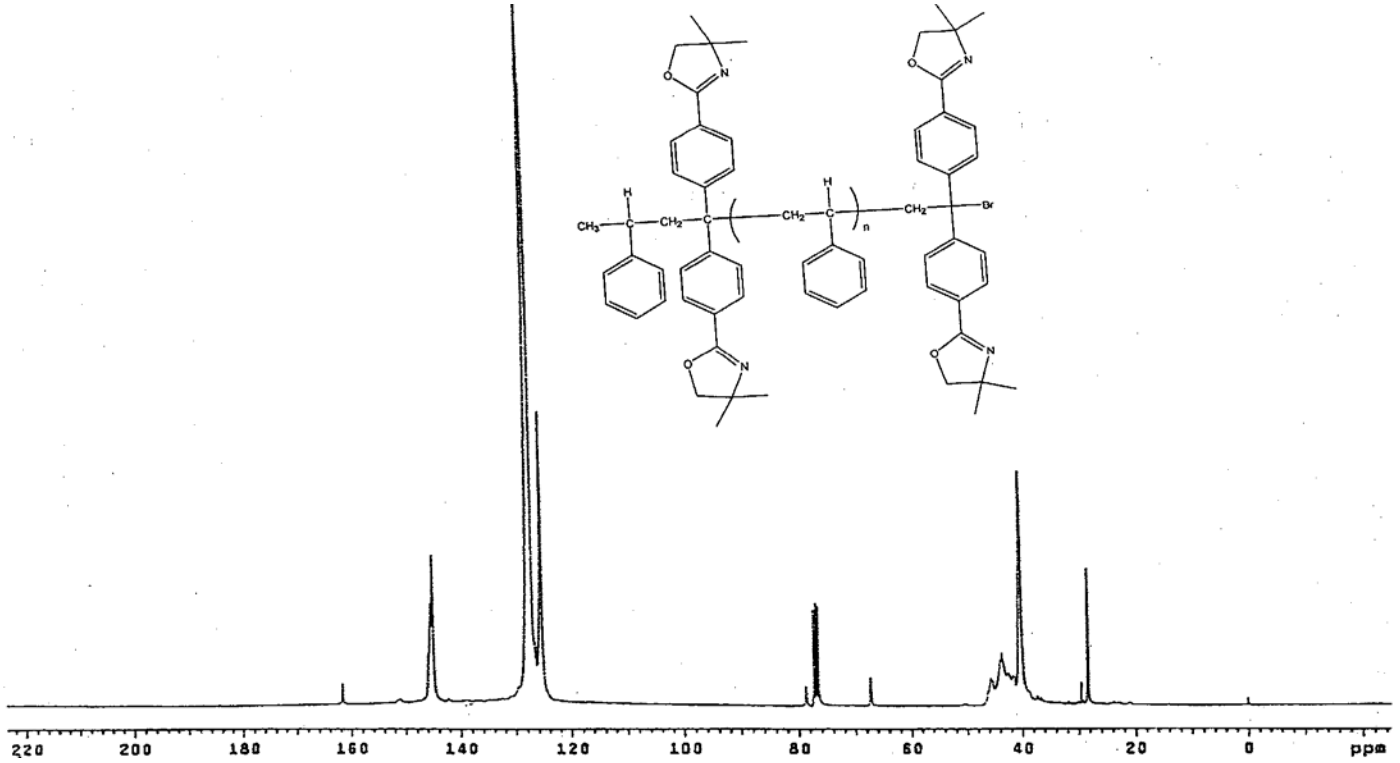


Figure 51: $^{13}C$ NMR spectrum of α,ω-tetrakis(oxazolyl) functionalized polystyrene, (**14**). [styrene]:[(1-bromoethyl)-benzene]:[CuBr]: [bpy]:[**11**] = 29:1:1:3:1; solvent: xylene; temperature: 110 °C. $\overline{M}_n^{SEC}$ = 4.4 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48.

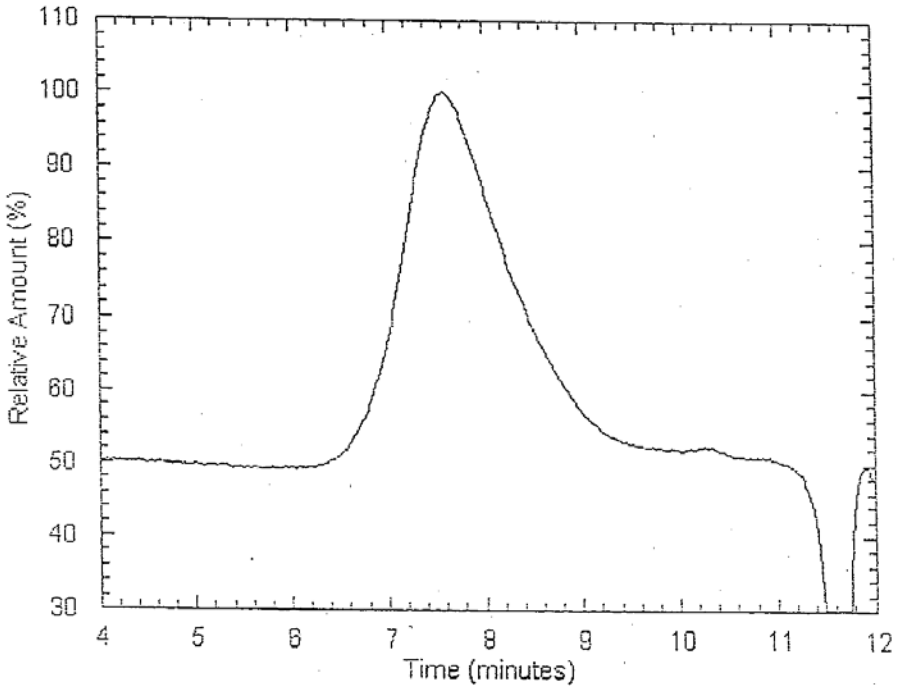


Figure 52: Size exclusion chromatogram of α-bis(carboxyl) functionalized polystyrene, (**15**). $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.49.

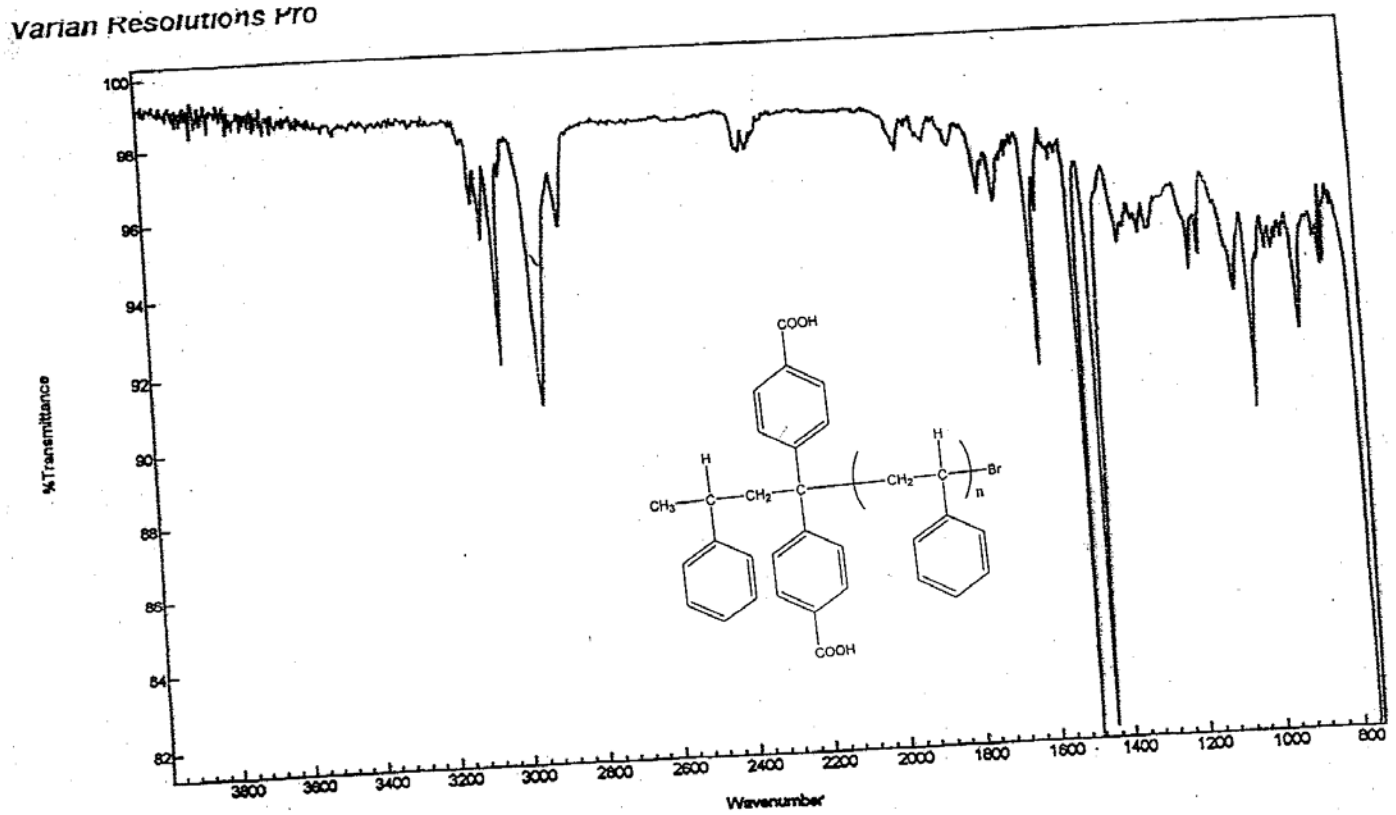


Figure 53: FTIR spectrum of α-bis(carboxyl) functionalized polystyrene, (**15**). $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.49.

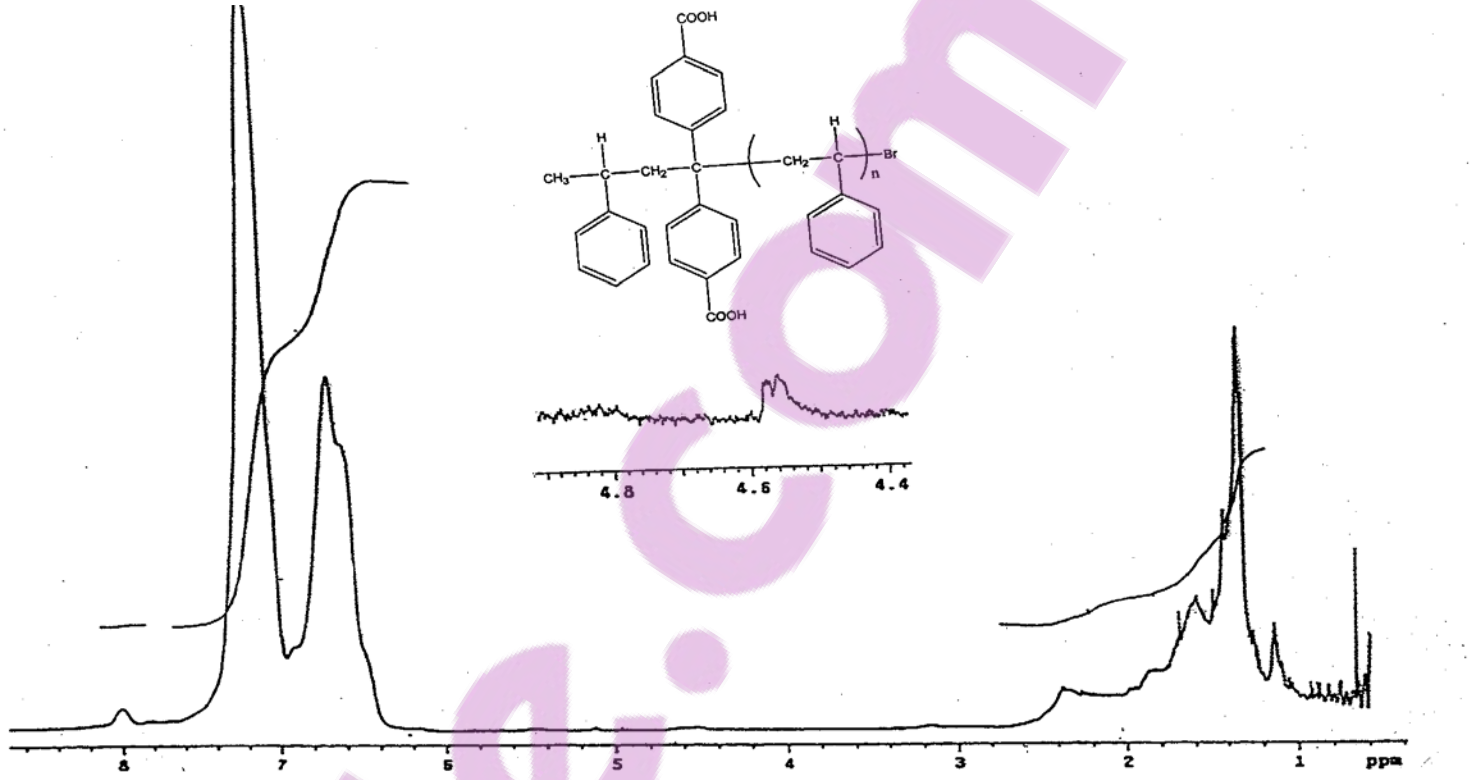


Figure 54: $^{1}$H NMR spectrum of α-bis(carboxyl) functionalized polystyrene, (**15**). $\overline{M}_{n}^{SEC}$ = 3.8 x $10^{3}$ g/mol;. $\overline{M}_{w}/\overline{M}_{n}$ = 1.49.

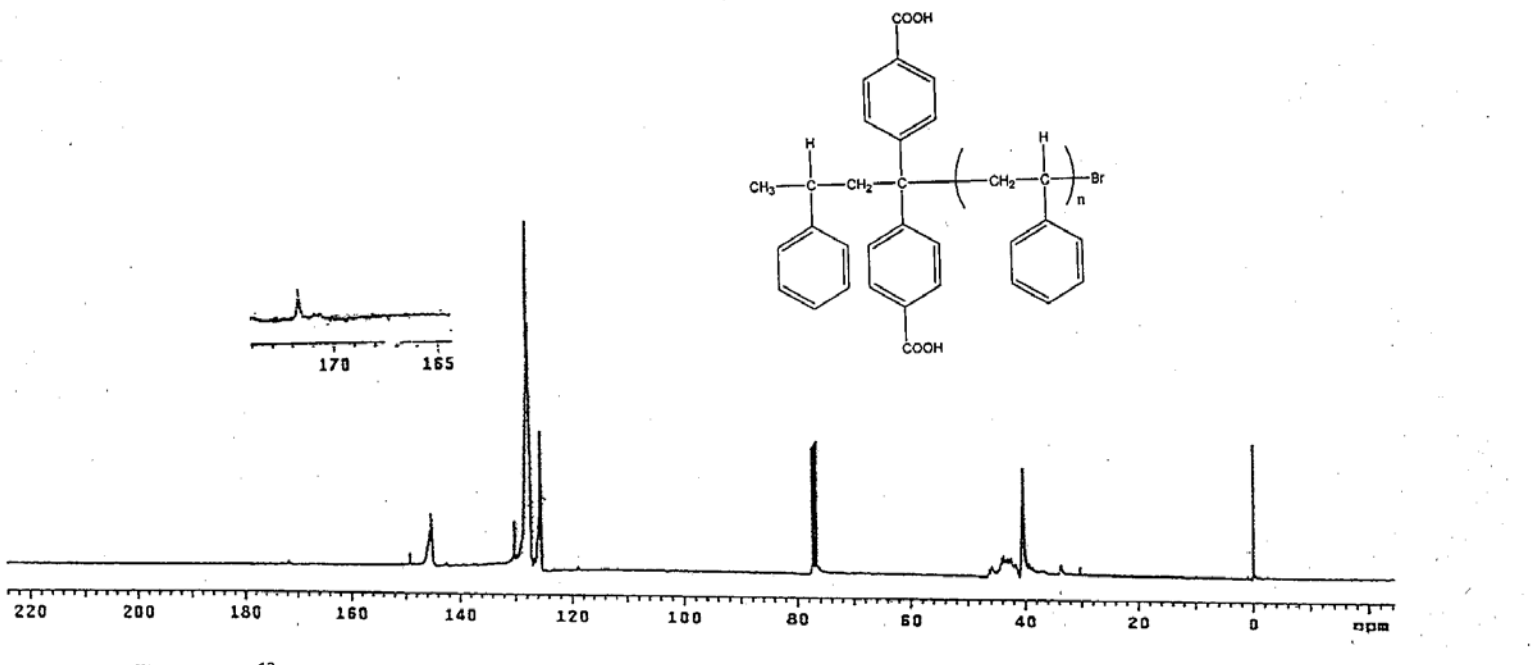


Figure 55: $^{13}$C NMR spectrum of α-bis(carboxyl) functionalized polystyrene, (**15**). $\overline{M}_n^{SEC}$ = 3.8 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.49.

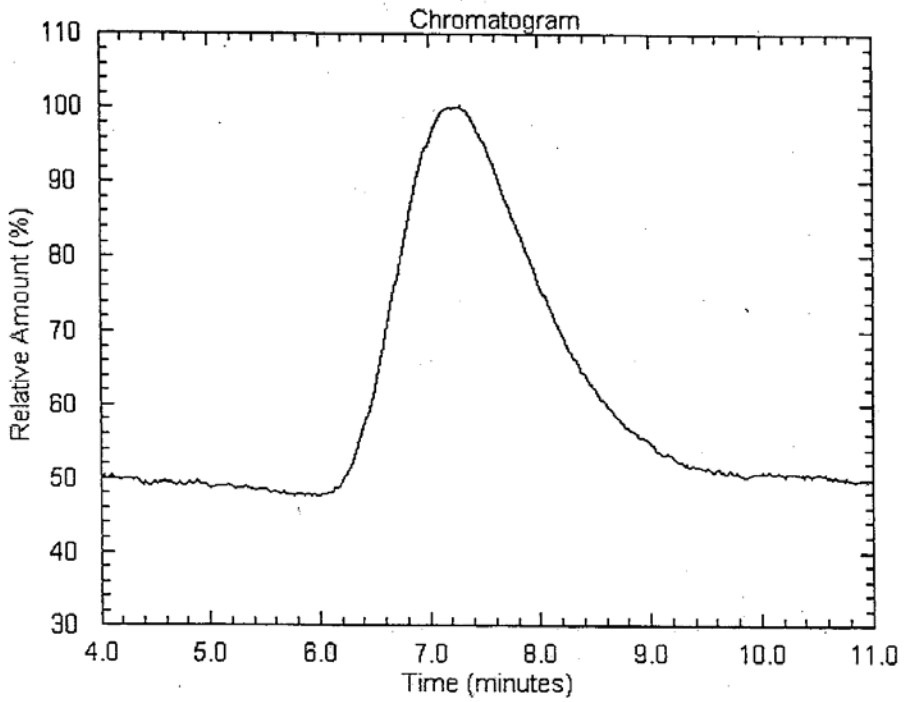


Figure 56: Size exclusion chromatogram of α-ω-tetrakis(carboxyl) functionalized polystyrene, (**16)**. $\overline{M}_n^{SEC}$= 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48.

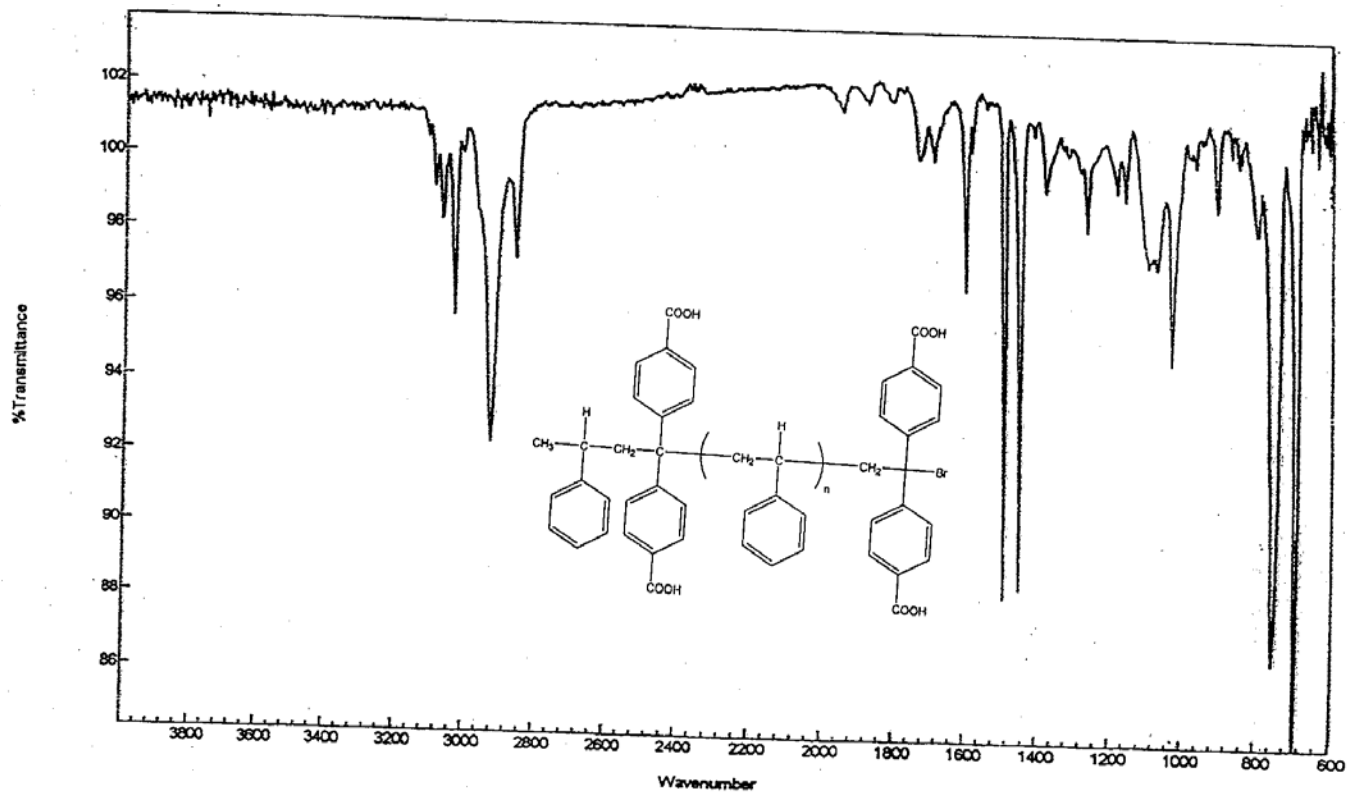


Figure 57: FTIR spectrum of α-ω-tetrakis(carboxyl) functionalized polystyrene, (**16)**. $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48.

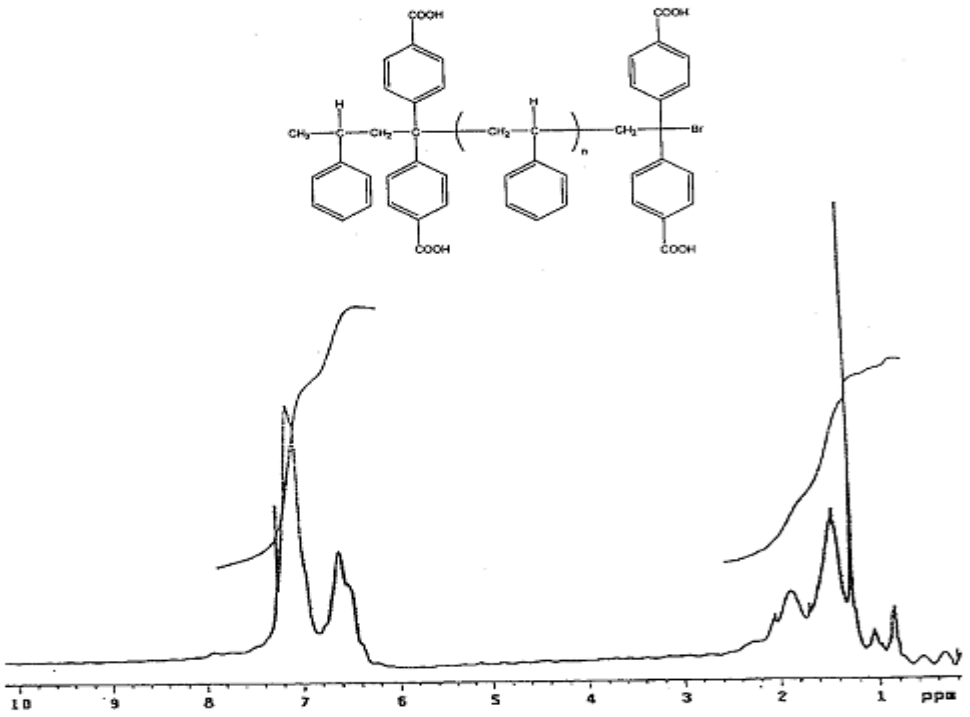


Figure 58: $^{1}$H NMR spectrum of α-ω-tetrakis(carboxyl) functionalized polystyrene, (**16)**. $\overline{M}_{n}^{SEC}$ = 4.0 x $10^{3}$ g/mol; $\overline{M}_{w}/\overline{M}_{n}$ = 1.48.

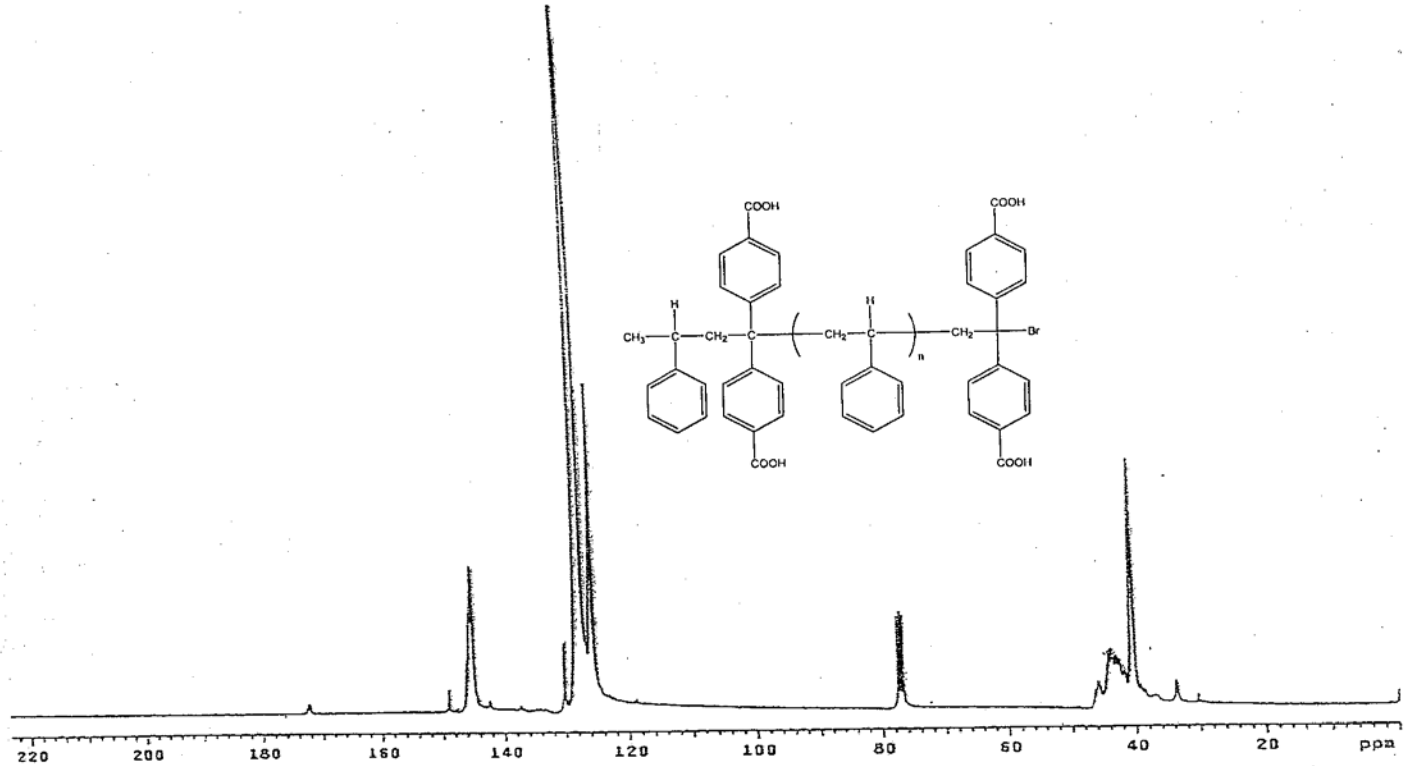


Figure 59: $^{13}C$ NMR spectrum of α-ω-tetrakis(carboxyl) functionalized polystyrene, (**16)**. $\overline{M}_n^{SEC}$ = 4.0 x $10^3$ g/mol; $\overline{M}_w/\overline{M}_n$ = 1.48.