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LIST OF ABBREVIATIONS

| | |
|--------|--|
| AIBN | 2,2'-Azobisisobutyronitrile |
| ARGET | Activators Generated by Electron Transfer |
| ATRP | Atom Transfer Radical Polymerization |
| 1-BEB | (1-Bromoethyl)benzene |
| bpy | 2,2'-Bipyridyl |
| CuBr | Copper (I) bromide |
| CuOAc | Copper (II) acetate |
| dNbpy | 4,4'-Di(<i>n</i> -nonyl)-2,2'-bipyridyl |
| DP | Degree of polymerization |
| DPE | Diphenylether |
| FTIR | Fourier Transformer Infrared Spectroscopy |
| hrs | Hours |
| ICAR | Initiators for Continuous Activator Regeneration |
| I | Initiator |
| MAO | Methylaluminoxane |
| M | Monomer |
| MMA | Methyl methacrylate |
| NMP | Nitroxide Mediated Free Radical Polymerization |
| NMR | Nuclear Magnetic Resonance Spectrometry |
| PMMA | Poly(methyl methacrylate) |
| PMDETA | <i>N,N,N',N'',N''</i> -pentamethyldiethylenetriamine |
| RAFT | Reversible Addition Fragmentation Chain Transfer |
| RT | Room temperature |
| SEC | Size Exclusion Chromatography |
| TLC | Thin Layer Chromatography |
| TEMPO | 2,2,6,6-tetramethylpiperidiny-1-oxy |

CHAPTER 1

INTRODUCTION

Atom Transfer Radical Polymerization (ATRP) is one of the most successful methods used for the controlled polymerization of vinylic monomers, such as styrene, (meth)acrylates and acrylonitrile, to produce polymer derivatives with well defined number average molecular weight, narrow molecular weight distribution, controlled chain end functionality and molecular topology.¹⁻¹¹

ATRP is a controlled free radical polymerization method which requires an alkyl halide as an initiator, a transition metal in a lower oxidation state and a ligand that complexes with the metal for styrene and (meth)acrylate polymerization. The equilibrium between active and dormant radicals is formed by the reversible redox reaction between the metal/ligand complex and the alkyl halide.^{6,7} Because of its radical nature, the ATRP method is tolerant to many functional groups in monomers and initiators, leading to the formation of polymers with the functional group at the polymer chain ends as well as along the polymer chains. A wide variety of chain end functionalized polymers have been prepared by atom transfer radical polymerization methods.¹² The structure of the organohalogen initiator used in ATRP reactions determines the nature of the end groups of the polymers, such that the ω -terminus is the halogen atom and the organic portion of the initiator is at the α -terminus of the polymer chain. Thus, the choice of an appropriate functionalized initiator in ATRP reactions results in the formation of a large variety of α -functionalized polymers. When functionalized organohalide initiators substituted by the appropriate functional group, such as the vinyl, carboxyl, epoxide, cyano and amine groups, are used in ATRP reactions, the specific functional group is incorporated at the alpha terminus of the polymer chain, while the ω -terminus of the polymer chain is a halogen atom.¹³⁻¹⁵

A variety of hydroxyl chain end functionalized poly(methyl methacrylate) and polystyrene derivatives have been synthesized by atom transfer radical polymerization methods.¹⁶ For example, hydroxyl functionalized polystyrene has been prepared using 2-hydroxyethyl 2-bromoisobutyrate as a hydroxyl functionalized initiator for styrene polymerization by ATRP methods. However, the preparation of siloxyl and hydroxyl chain end functionalized polymers by ATRP methods using functionalized initiators based on 1,1-diphenylethylene chemistry has not been reported in the literature. The use of substituted 1,1-diphenylethylene derivatives as precursors for the *in situ* formation of functionalized unimolecular initiators for the ATRP of styrene and methyl methacrylates involves a general, quantitative, one-pot ATRP chain end functionalization reaction for the preparation of chain functionalized polymers by atom transfer radical polymerization methods.^{17,18} The functionalized initiator synthesis involves the *in situ* addition reaction between simple organohalide derivatives and functionalized 1,1-diphenylethylene compounds by ATRP methods since the 1,1-diphenylethylene units do not homopolymerize and only undergo monoaddition reactions with the radical species. By employing siloxyl substituted 1,1-diphenylethylene derivatives as precursors for the formation of siloxyl functionalized initiator systems for styrene and methyl methacrylate polymerization, the synthesis of siloxyl chain end functionalized polymers by ATRP methods can be achieved.

The present study describes the synthesis of α -siloxyl functionalized polymers via a one-pot ATRP chain end functionalization process which involves the polymerization of styrene and methyl methacrylate using an appropriate siloxyl functionalized initiator adduct to give quantitative yields of the corresponding well defined α -siloxyl functionalized polymers as follows:

(a) the *in situ* reaction of (1-bromoethyl)benzene with 1-(4-t-butyldimethylsiloxy-phenyl)-1-phenylethylene in the presence of CuBr/bpy or CuBr/PMDETA as the

catalyst system to form the unimolecular siloxyl functionalized initiator adduct;
and

(b) the use of the resultant siloxyl functionalized initiator adduct as initiator for the ATRP of styrene and methyl methacrylate to form the corresponding α -siloxyl functionalized polymers.

Similarly, the ATRP of styrene and methyl methacrylate using a new disiloxyl functionalized initiator adduct in the presence of CuBr/bpy or CuBr/PMDETA as catalyst system provides a unique synthetic method for the quantitative synthesis of α -bis(siloxyl) functionalized polymers. The synthesis pathway involves the following:

(a) the formation of a new unimolecular disiloxyl functionalized initiator adduct prepared *in situ* by the reaction of 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene with (1-bromoethyl)benzene in the presence of the CuBr/bpy or CuBr/PMDETA catalyst complex in solution; and

(b) the utilization of the disiloxyl functionalized initiator adduct as initiator for the polymerization of styrene and methyl methacrylate to form quantitative yields of the corresponding α -bis(siloxyl) functionalized polystyrene and α -bis(siloxyl) functionalized poly(methyl methacrylate), respectively.

The current study investigates the polymerization kinetic parameters to determine the controlled/living character of each ATRP process. For a controlled/living ATRP process, the following experimental features must be observed:

(a) a linear semilogarithmic first order kinetic plot of $\ln([M]_0/[M])$ vs time, indicating the constant radical concentration throughout the polymerization process.

(b) the linear increase in the number average molecular weight with percentage monomer conversion, indicating the absence of any chain transfer or termination reactions.

(c) the formation of polymers with narrow molecular weight distributions, $\overline{M}_w / \overline{M}_n$ values below 1.5.

The present study also describes the preparation of α -hydroxyl and α -bis(hydroxyl) functionalized polystyrene derivatives via post polymerization chain end modification reactions which involves the conversion of the siloxyl group to the hydroxyl group. The acid catalyzed hydrolysis of α -siloxyl and α -bis(siloxyl) functionalized polystyrene provide a facile method for the preparation of α -hydroxyl and α -bis(hydroxyl) functionalized polystyrene, respectively.

CHAPTER 2

HISTORICAL REVIEW

2.1 CONTROLLED FREE RADICAL POLYMERIZATION

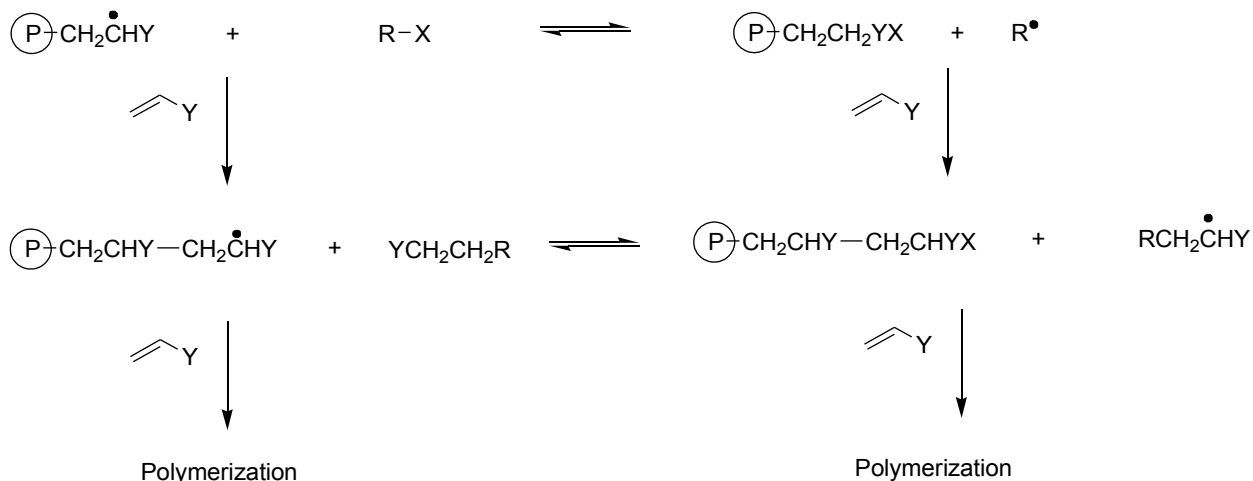
Free radical polymerization is the most widespread polymer synthesis method used to produce organic polymeric materials. The advantages of free radical polymerization, over ionic or coordination polymerization methods, are the large variety of vinyl monomers which can undergo polymerization or copolymerization in aqueous media via suspension or emulsion polymerization methods. In addition, the conventional free radical polymerization is tolerable to different functional groups and to impurities such as dust, air and moisture. Although conventional free radical polymerization has been known for a very long time, it is difficult to control the polymerization process and consequently the polymer structure because of undesirable radical chain transfer and termination reactions. Due to the slow initiation, fast propagation and subsequent chain transfer or termination reactions between growing radicals, polymers with high number average molecular weights and broad molecular weight distributions are generally produced by conventional free radical polymerization processes.¹⁹

The discovery and development of 'living' anionic polymerization by Szwarc^{19,20} as a chain growth process, without chain breaking reaction, allowed for the preparation of well defined macromolecules which have control over major polymer variables, such as the number average molecular weight, molecular weight distribution, chain end functionality and the block and graft copolymer structure.

During the past two decades, several controlled free radical polymerization methods have been reported in the literature. The most common controlled free radical polymerization methods applied to the synthesis of well defined polymers and copolymers include the following:

(a) The Iniferter Method, which utilizes alkyl dithiocarbamates as initiators in free radical polymerization reactions.²¹ For example, tetraethylthiuram disulfide was used as an iniferter since it undergoes photochemical activation to form dithiocarbamate radicals. At low temperatures, the dithiocarbamate radical slowly initiates radical polymerization of the monomer. The propagating polymer radicals can then combine with the dithiocarbamate radical to form the dormant species. The resultant dormant species which forms undergo dissociation when irradiated to form two radicals and thereafter the process repeats itself.²¹

(b) The Degenerative Iodine Transfer Radical Polymerization Method is used to obtain the controlled radical polymerization of styrene and acrylates.^{22,23} The degenerative iodine transfer radical polymerization method is a process which involves the transfer of an atom, or group from a covalent, dormant species, present in large excess, to the initiator to produce free radicals. The overall polymerization consists of all typical elementary reactions such as initiation, propagation and termination, but is additionally supplemented by a degenerative transfer step.^{22,23} In degenerative iodine transfer polymerization, the radical R^\bullet is generated from the transfer agent $R-X$ by abstraction of the group or an atom. The new radical R^\bullet can subsequently react with a monomer to form the radical species $RCH_2CH_2Y^\bullet$. The radical, $R-CH_2CHY^\bullet$ then abstracts the group or atom X from $R-X$ to form the dormant species, $R-CH_2CHY-X$ and R^\bullet . The process can then repeat itself. Only small quantities of the initiator, relative to the transfer agent, are required to drive the reaction to completion.^{24,25} The initiator concentration affects only the polymerization rate without having any effect on the total concentration of chains:



(c) Nitroxide Mediated Free Radical Polymerization (NMP), a free radical polymerization process, involves initiation and reversible termination of growing polymer chains by nitroxides, such as 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). The equilibrium is strongly shifted towards the dormant species such that the capping of the active radical is fast enough to compete with bimolecular termination. Thus, the termination of the polymer chains is reduced over the course of the reaction as compared to conventional free radical polymerization.^{26,27}

(d) Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) is a versatile and robust free radical polymerization process for the synthesis of well defined polymers.²⁸⁻³⁰ The RAFT process is accomplished by performing a conventional radical polymerization in the presence of readily available dithiocarbonyl compounds of the general structure [S=C(Z)-SR]. The RAFT agent acts as an efficient reversible addition fragmentation chain transfer agent and confers living characteristics to the polymerization process.

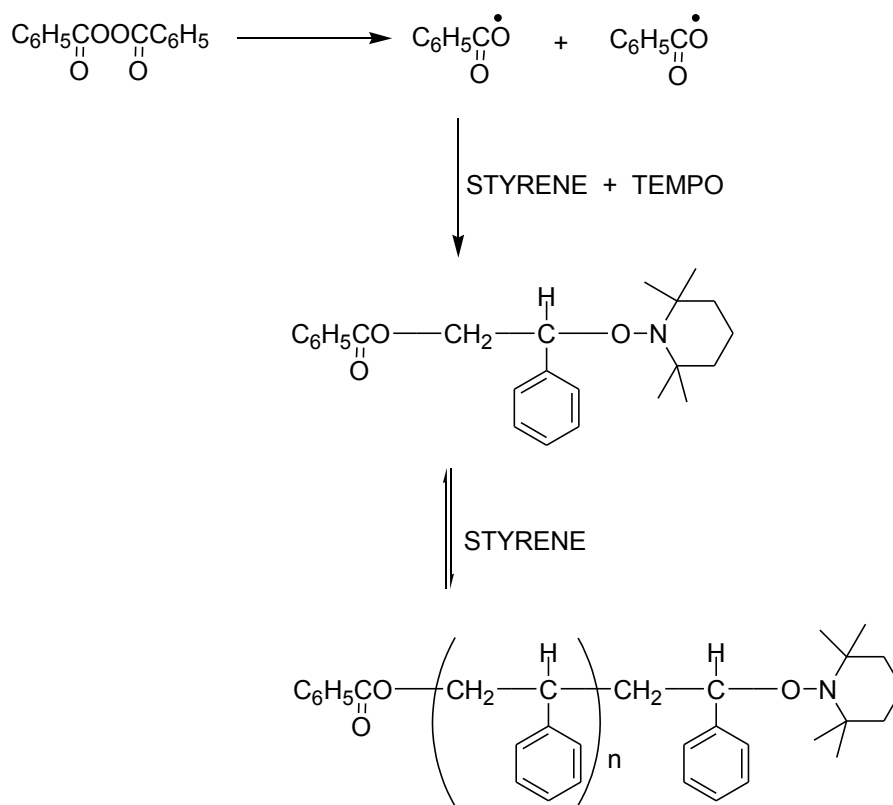
(e) Transition Metal Mediated Controlled Free Radical Polymerization is a free radical polymerization method which requires an alkyl halide as an initiator, a transition metal in a lower oxidation state and a ligand that complexes with the metal for styrene and methacrylate polymerizations.^{6,7} The equilibrium between

active and dormant radicals is formed by the reversible redox reaction between the metal/ligand complex and the alkyl halide. The halogen atom is homolytically cleaved from the alkyl halide (R-X), yielding a carbon centered radical ($R\cdot$) and a metal with an increased oxidation state ($X-M_t^{n-1}$). The resultant stable radical then initiates the polymerization process via a controlled radical polymerization process and allows the facile synthesis of polymers with controlled number average molecular weights, narrow molecular weight distributions, well defined molecular architecture and chain functionality. Due to its similarity to the atom transfer radical addition reaction, the process was named Atom Transfer Radical Polymerization (ATRP) by Wang and Matyjaszewski.^{3,6,13,14,31}

Since the discovery of controlled/living free radical polymerization processes for the preparation of well defined polymer structures, NMP, RAFT and ATRP are the most simple and versatile methods employed by industry and academia for the preparation of a wide variety of well defined chain end functionalized polymers.

2.2 NITROXIDE MEDIATED FREE RADICAL POLYMERIZATION (NMP)

Controlled/living free radical polymerization, mediated by stable nitroxyl radicals, is a simple and robust free radical polymerization method to synthesize homopolymers, random copolymers and block copolymers with controlled end-group functionality, narrow molecular weight distributions and controlled chain architectures.³²⁻³⁵ The use of nitroxyl radicals and alkoxyamines as initiators in a free radical polymerization was first reported by Rizzardo and Solomon,^{26,36} who indicated that an adduct of a nitroxide and an initiator fragment can initiate the polymerization of vinyl monomers to form low molecular weight oligomers:

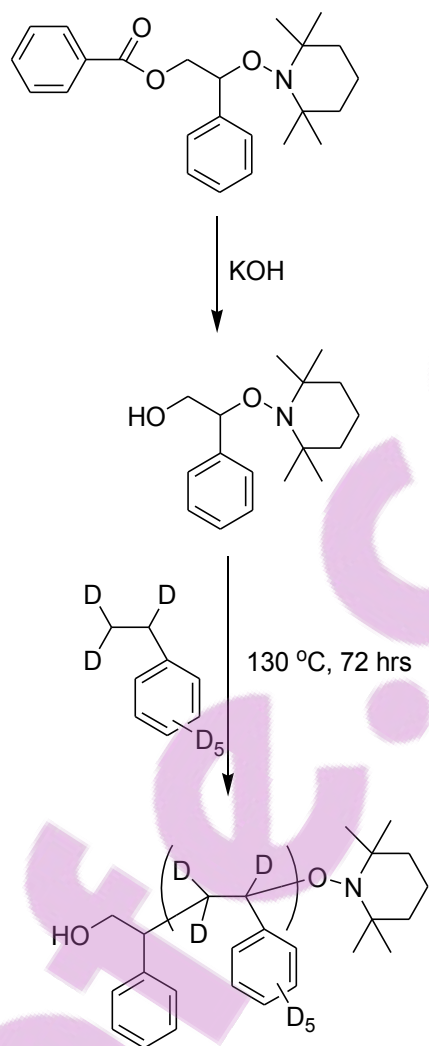


The Nitroxide Mediated Free Radical Polymerization (NMP) process for the polymerization of styrene using benzoyl peroxide as initiator in the presence of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) is typically performed at 125 °C. Initiation begins with the rapid formation of the benzoyloxy primary radical, which undergoes a rapid addition reaction with styrene, followed by the immediate reaction with the TEMPO derivative to form a unimer. The resulting styryl radical can either recombine with TEMPO to regenerate the original molecule, or it can add a monomer before the growing chains recombine with TEMPO. The latter sequence repeats itself to produce a polymer.¹⁴

According to Georges and coworkers,³⁷ the quick initiation of all the chains, the fast exchange between the uncapped and capped polymer chains and the lack of premature termination, all combine to yield polymers with narrow molecular weight distributions. The dissociation reactions for the (PS)-TEMPO adduct is

known to occur at high temperature in a limited number of systems, which restricts the reversible use of NMP to control free radical polymerization. In addition, the irreversible bimolecular termination and chain transfer reactions limits the structural and process control in NMP to relatively short chains.^{38,39}

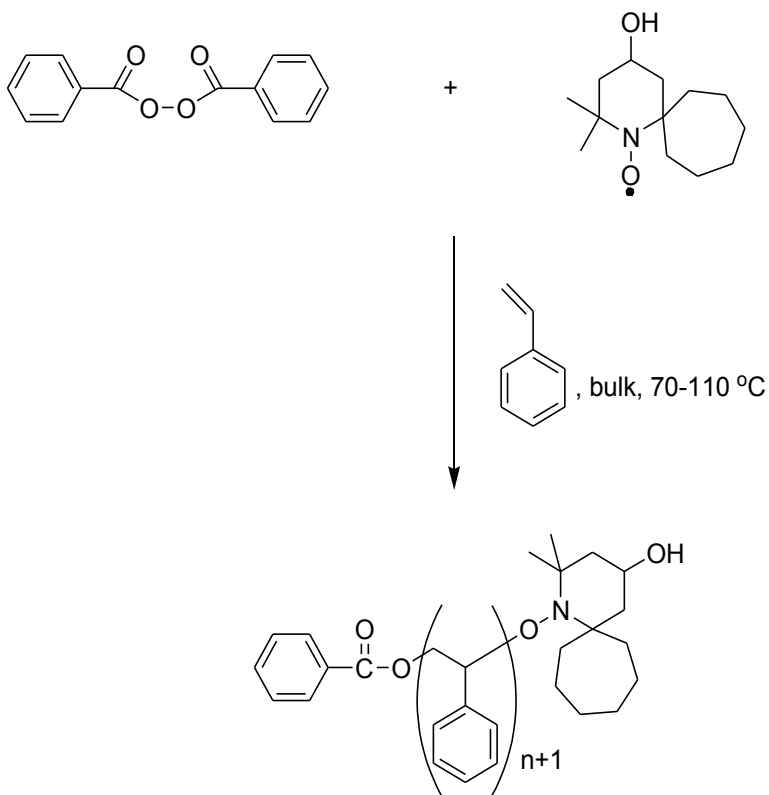
The nitroxide mediated radical polymerization method can be used to prepare functionalized polymers via the use of functionalized monomers⁴⁰⁻⁴⁴ to form functionalized homopolymers and functionalized block copolymers^{45,46} as well as the use of functionalized initiators⁴⁶⁻⁴⁹ to form chain end functionalized polymers. Moreover, nitroxide mediated free radical polymerization (NMP) methods can be utilized for the synthesis of chain end functionalized polymers with predictable number average molecular weights and narrow molecular weight distributions and designed molecular architecture.⁵⁰⁻⁵³ The most efficient synthetic route for the preparation of chain end functionalized polymers by NMP methods involves the use of functionalized initiators.⁵³ In particular, several unimolecular hydroxyl functionalized initiators, such as 2-phenyl-2-(2,2,6,6-tetramethylpiperidin-1-yloxy)ethanol⁵¹ and 2-[N-t-butyl-N-(2-methyl-1-phenylpropyl)-aminoxy]-2-phenylethanol have been used as initiators in NMP processes to form hydroxyl chain end functionalized polymers.^{54,55} The NMP approach depends on the quantitative synthesis of functionalized monoadducts of styrene and TEMPO and their subsequent use as initiators in polymerization reactions. For example, the synthesis of hydroxyl chain end functionalized polymers can be achieved by using functionalized nitroxide initiators, substituted with the hydroxyl group:



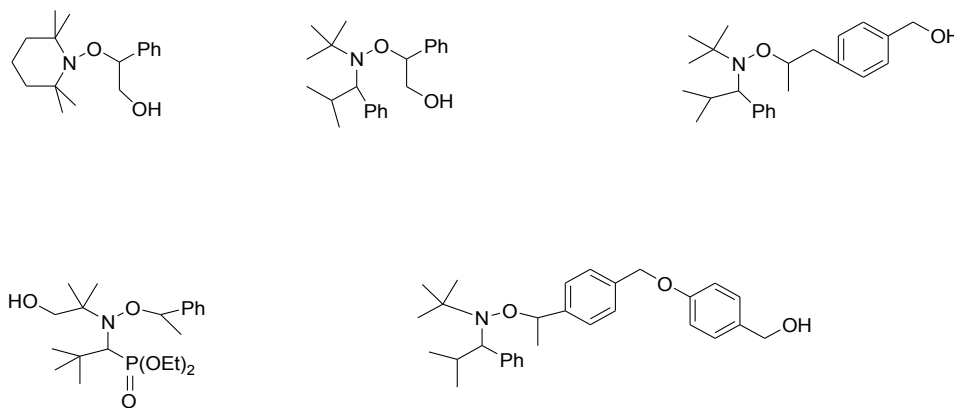
The initiating system was hydrolysed with KOH to give the hydroxyl derivative. The polymerization of the deuterated styrene initiated with hydroxyl functionalized TEMPO at 130 °C for 72 hours afforded the hydroxyl chain end functionalized polystyrene with the hydroxyl group incorporated at the α -terminus of the polymer chain.⁵³

Miura and coworkers⁵⁶ reported the synthesis of hydroxyl chain end functionalized polystyrene in bulk, initiated with benzoyl peroxide in the presence of 1-aza-2,2-dimethyl-4-hydroxyspiro[5.6]dodecane-1-yl-oxyl to afford ω -hydroxyl functionalized polystyrene in quantitative yield. Polymers with narrow molecular

weight distributions $\overline{M}_w / \overline{M}_n$ below 1.3 were obtained, indicating that the polymerization proceeded in a controlled/"living" manner:

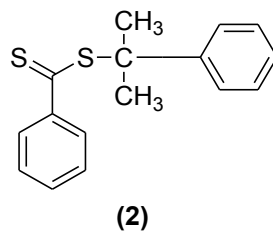
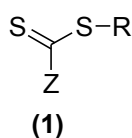


The following hydroxyl functionalized initiators have been employed in nitroxide mediated polymerization of styrene, acrylate and acrylamide polymerization to form the corresponding hydroxyl functionalized polymers:⁵⁷



2.3 REVERSIBLE ADDITION FRAGMENTATION CHAIN TRANSFER POLYMERIZATION (RAFT)

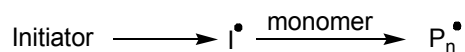
The Reversible Addition Fragmentation Chain Transfer Polymerization (RAFT) method, a versatile and robust free radical polymerization process for the synthesis of well defined polymers, has been developed by Rizzardo and coworkers.^{28,58,59} The RAFT process is accomplished by performing a conventional radical polymerization in the presence of readily available dithiocarbonyl compounds of general structure [S=C(Z)-SR] which acts as an efficient reversible addition fragmentation chain transfer agent and confers living characteristics to the polymerization process. Amongst a host of variable structures, the following dithiocarbonyl compounds have been successfully employed as RAFT agents in the RAFT process:^{60,61}



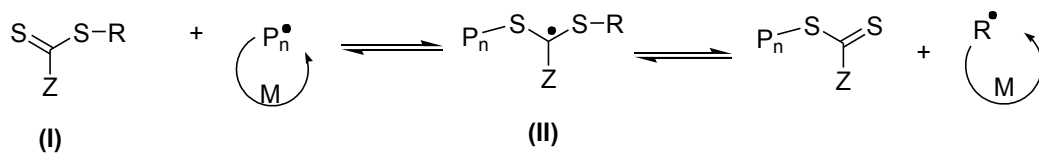
- (3) Z = Ph, R=C(CH₃)(CN)(CH₂)₂CO₂Na (4) Z = Ph, R=C(CH₃)(CN)(CH₂)₃OH
(5) Z = Ph, R = C(CH₃)₂(CN)

The mechanism for the RAFT process is briefly outlined below:

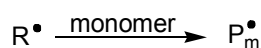
a. Initiation:



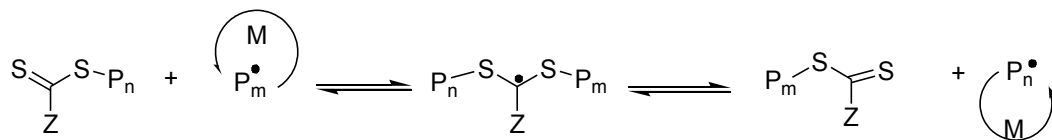
b. Chain transfer:



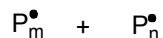
c. Re-initiation:



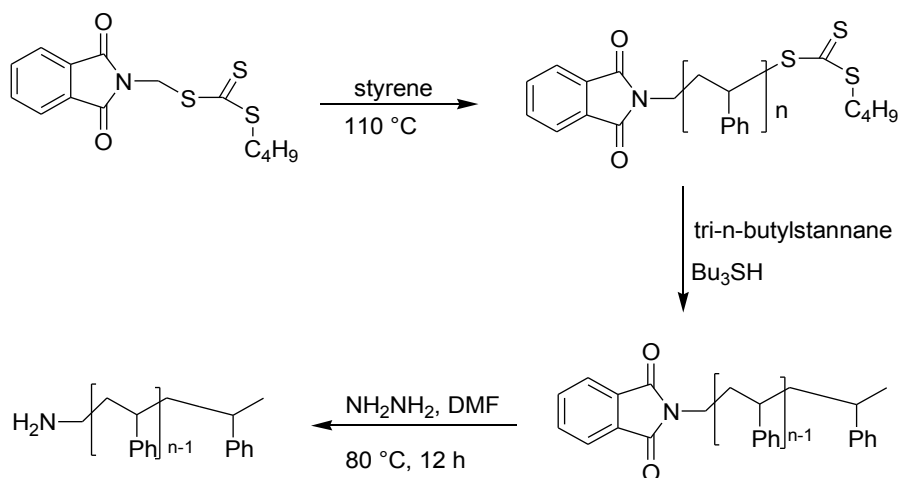
d. Chain equilibration:



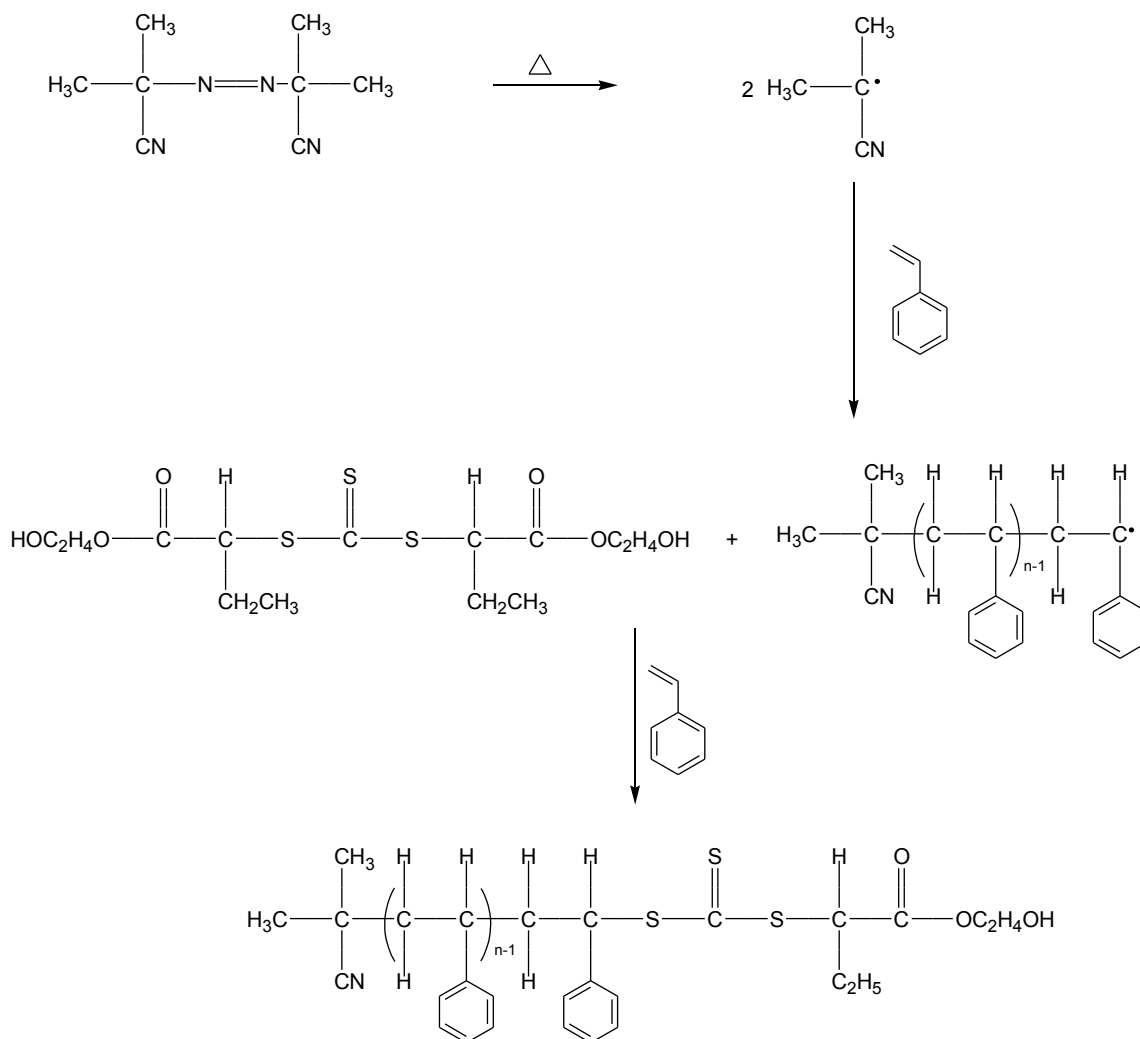
e. Termination:



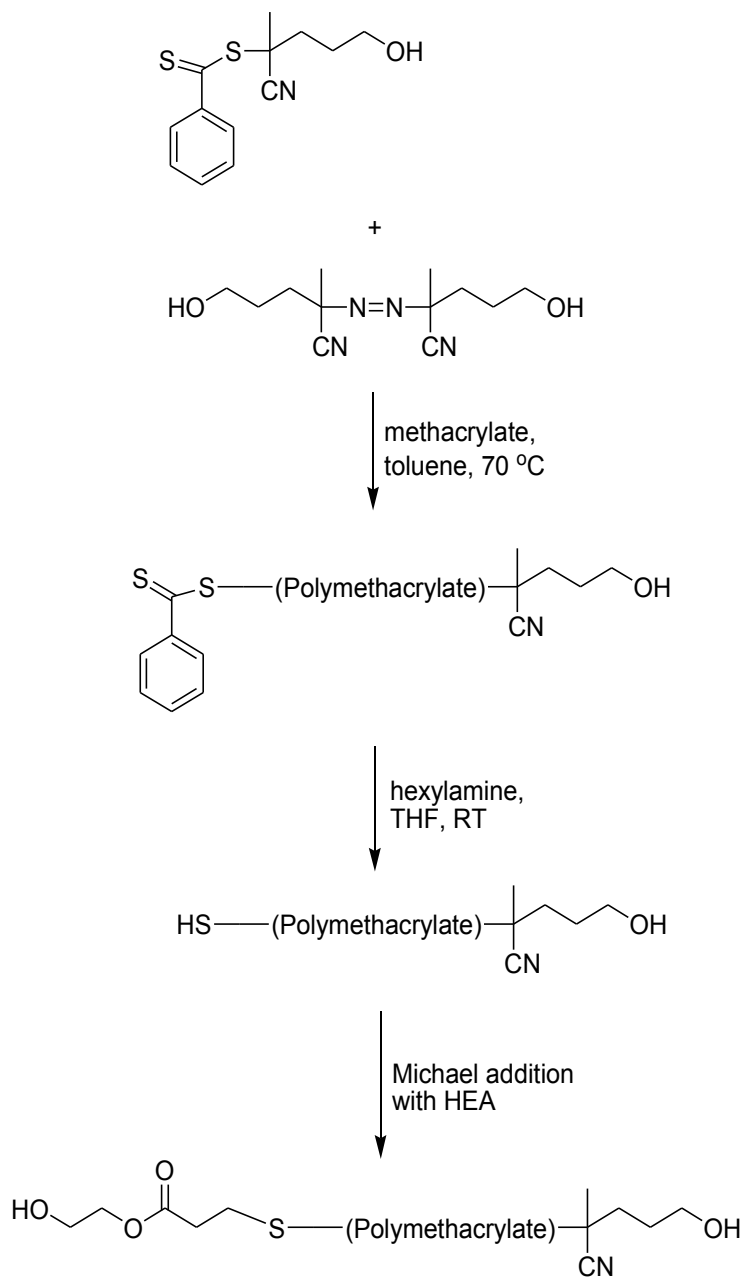
The requirements for a thiocarbonylthio compound to be considered as a RAFT agent are that: (i) the rates of addition and fragmentation must be fast, relative to the rate of propagation, and (ii) the expelled radical must be capable of re-initiating polymerization. The first requirement ensures the rapid consumption of the initial RAFT agent and the fast equilibration of the dormant and active species, while the second requirement ensures the continuity of the chain process. A classical RAFT process is outlined below:



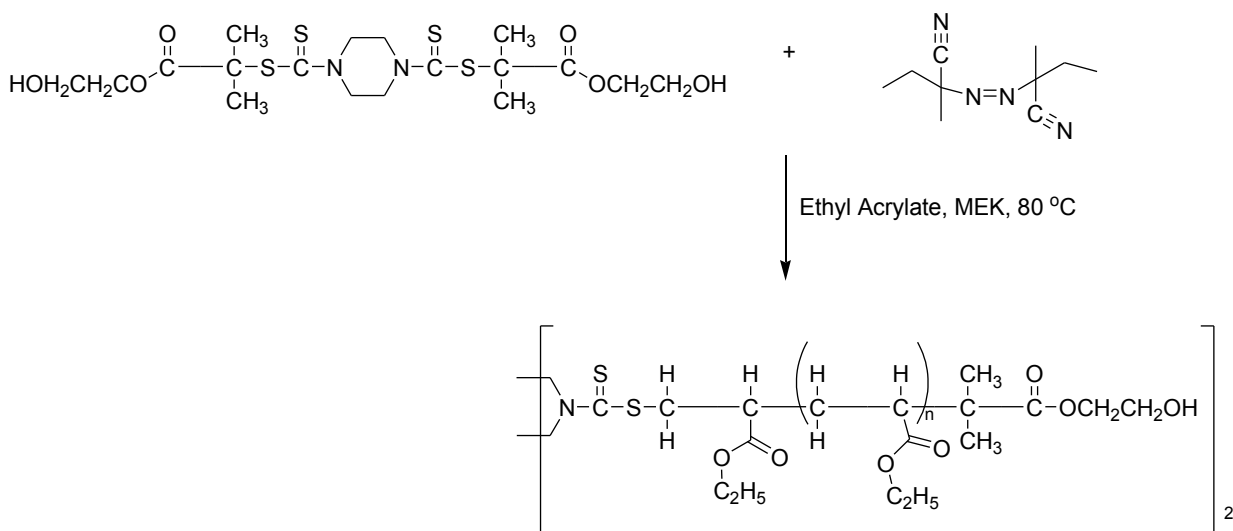
The major advantage of the RAFT polymerization method as a controlled/“living” free radical polymerization reaction is that the method is compatible with a wide range of monomers, including functionalized monomers containing the acid^{62,63} hydroxyl groups.⁶⁴⁻⁶⁷ For example, Liu and coworkers⁶⁷ prepared S,S'-bis(2-hydroxyethyl-2'-butyrate)trithiocarbonate (BHEBT), a novel RAFT agent with two terminal hydroxyl groups, from CS_2 and HEBrB, in the presence of an ion exchange resin. The RAFT polymerization of styrene using BHEBT as the chain transfer agent, yielded ω -hydroxyl functionalized polymers with controlled number average molecular weights and narrow molecular weight distributions:



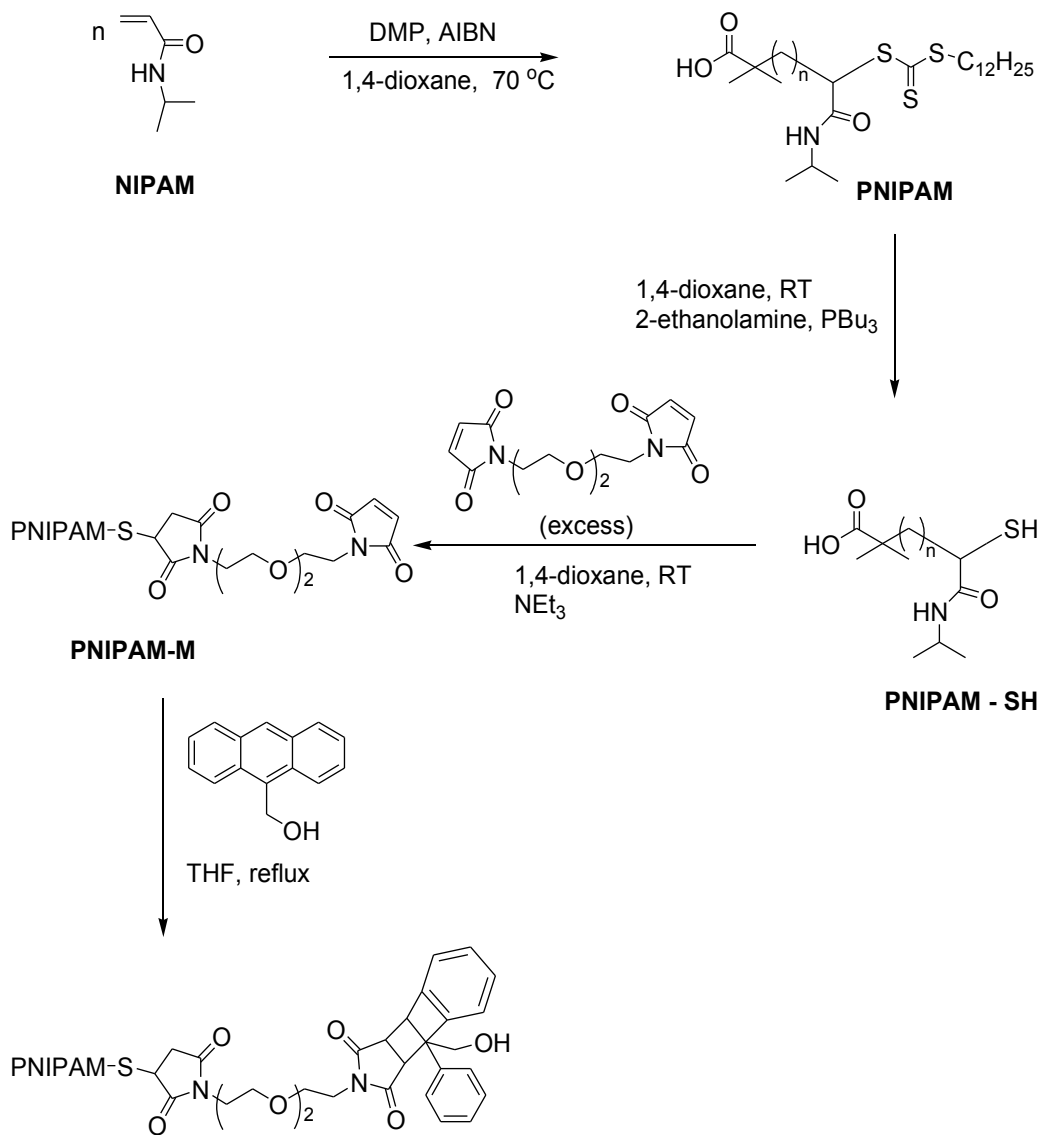
Hydroxyl telechelic poly(methyl acrylate)s were synthesized by the RAFT method using a hydroxyl monofunctional RAFT agent via a two step synthetic process: (a) the RAFT polymerization of methyl acrylate in the presence of the RAFT agent to afford the ω -hydroxyl functionalized poly(methyl acrylate) derivative, and (b) the chain end modification of the dithioester group at the α -chain end to form α,ω -hydroxyl functionalized poly(methyl acrylate) as follows:⁶⁸



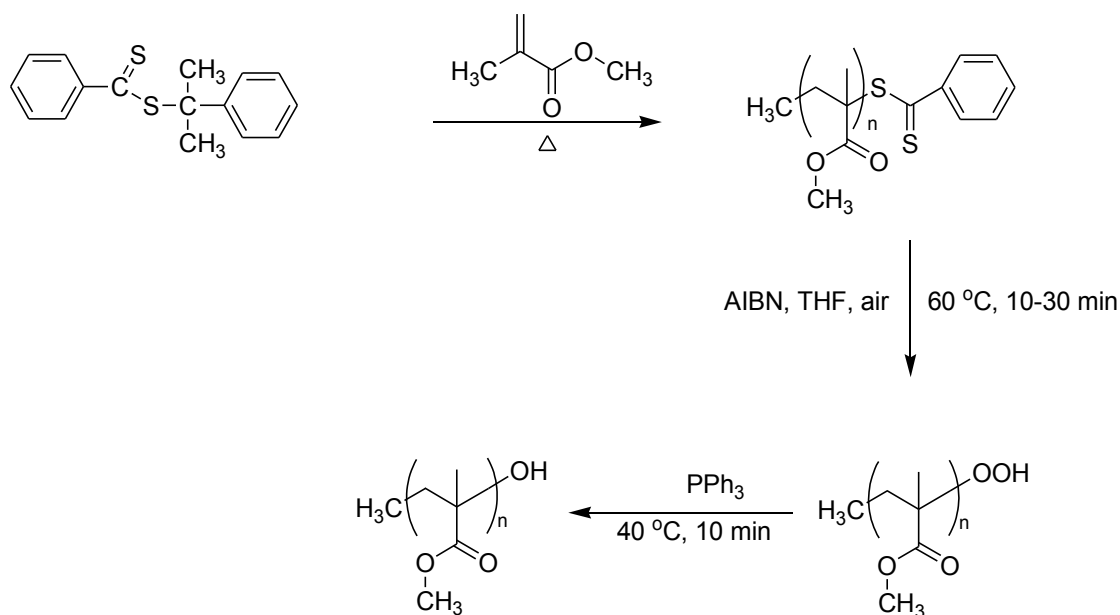
Lai and coworkers⁶⁹ reported the synthesis of a series of carboxyl and hydroxyl substituted dithiocarbamates and xanthates which were used as RAFT agents in RAFT polymerization of different styrenic and meth(acrylate) monomers to form monocarboxyl, dicarboxyl and dihydroxyl functionalized polymers and block copolymers:



Chain end functionalized polymers can also be prepared by the RAFT process via post polymerization chain end transformation reactions.⁶²⁻⁶⁹ Hydroxyl chain end functionalized polymers, prepared by the RAFT polymerization was accomplished by conversion of thiocarbonylthio end groups to the corresponding hydroxyl group by standard organic reactions. For example, ω -hydroxyl functionalized poly(N-isopropylacrylamide) (PNIPAM) was prepared by the RAFT method and subsequent aminolysis led to sulfhydroxyl-terminated polymers. Reaction of the terminal SH group with an excess of 1,8-bis-maleimido-diethyleneglycol gave the corresponding maleimido-terminated macromolecules. Coupling of the maleimide activated PNIPAM derivative with a hydroxyl substituted anthracene derivative via a Diels Alder reaction produced the corresponding ω -hydroxyl chain end functionalized PNIPAM in quantitative yields.⁷⁰



Recently, Gruending and coworkers^{68,71} reported the degradation of dithiobenzoate functional poly(methyl methacrylate) in peroxide containing THF as a method to prepare ω -hydroxyl functionalized poly(methyl methacrylate). The quantitative conversion of vinyl polymers that contain the dithioester functional group at the ω -chain end into the hydroperoxide and hydroxyl derivatives has been performed by the following one-pot chain end modification reaction:

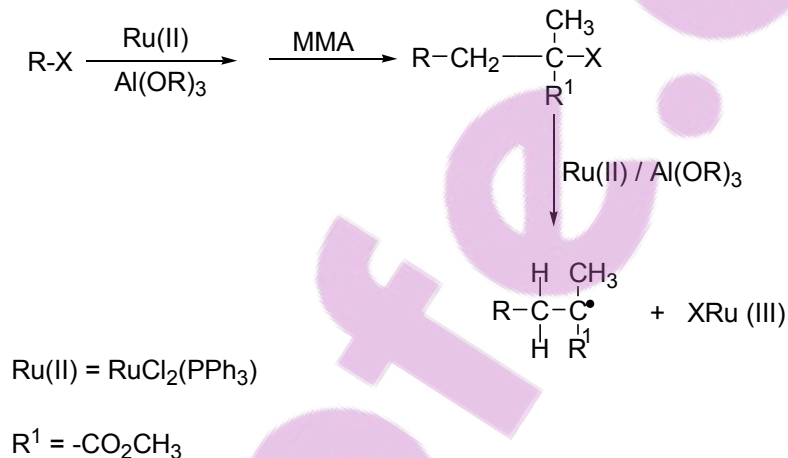


2.4 TRANSITION METAL CATALYZED LIVING RADICAL POLYMERIZATION

The transition metal mediated controlled radical polymerization is one of the most robust and powerful polymer synthesis techniques used for the preparation of polymers with well defined polymer properties. A general feature of the transition metal mediated controlled radical polymerization is that a dynamic equilibrium between dormant species and propagating radicals is obtained via a reversible deactivation procedure in the presence of transition metal catalysts complexed with specific ligands. Sawamoto and coworkers^{2,7} named such polymerization reactions as metal catalyzed living radical polymerization reactions.

The mechanism of transition metal catalyzed radical polymerizations with $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{FeCl}_2(\text{PPh}_3)_3$ and $\text{NiBr}_2(\text{PPh}_3)_2$ involves a reversible and dynamic equilibrium between the dormant species and the carbon radical, mediated by the metal-ligand complex. The initiators employed in transition metal catalyzed radical polymerizations are alkyl halides and their derivatives such as

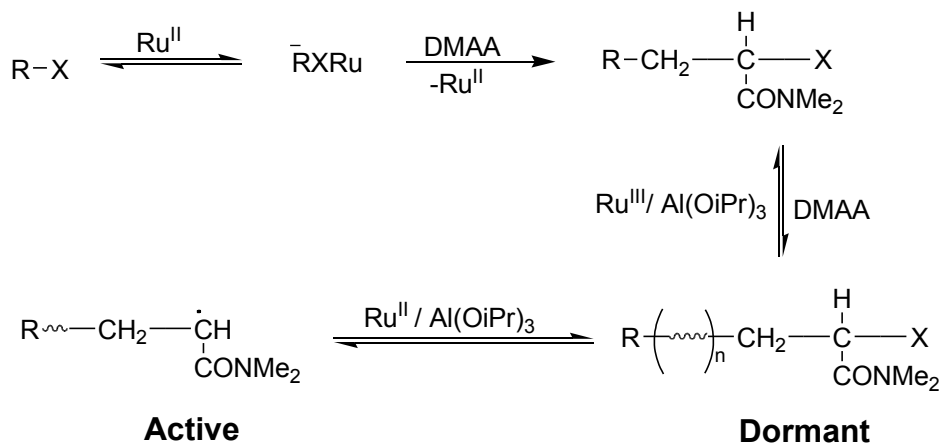
haloketones,⁷² α -haloesters⁷² and carbon tetrachloride,^{73,74} where the carbon-halogen bonds are homolytically cleaved by the metal catalysts. The initiators induce the living radical polymerization of styrenic and methacrylate monomers in the presence of $\text{RuCl}_2(\text{PPh}_3)_3$ or $\text{FeCl}_2(\text{PPh}_3)_3$, along with aluminum compounds, such as $\text{Al}(\text{OiPr})_3$, to yield polymers with controlled number average molecular weights and narrow molecular weight distributions.^{2,72-82} The nature of the metal complex is crucial for the living character of the polymerization process. The terminal C-X bond which originates from the R-X is reversibly and homolytically activated into a radical via the single electron redox reaction of the metal centre and the resulting radical species adds to the monomer:



The use of additives or cocatalysts provides an additional and equally powerful tool for living radical polymerization in the design of initiating systems, consisting of an initiator, a metal catalyst, and a cocatalyst. Sawamoto and coworkers⁷⁸ investigated the effects of additives or cocatalysts, such as water, methanol, galvinoxyl and TEMPO on the Ru (II), Fe (I), Fe (II) and Ni (II) complexes. Cocatalyst interacts with and modifies the metal catalysts *in situ* to generate new metal complexes.

Different metal catalysts for living radical polymerization of a variety of monomers such as methacrylates,^{61,77,83-86} styrenes,⁸⁵⁻⁸⁹ acrylamides,^{78,90} vinyl acetate,⁹¹ olefinic monomers with functional groups⁹²⁻⁹⁴ and acrylates,^{85,95} have been

developed. For example, Sawamoto and coworkers⁷⁹ reported the living radical polymerization of N,N-dimethylacrylamide (DMAA) initiated by an alkyl halide derivative in the presence of RuCl₂(PPh₃)₃/Al(OiPr)₃. Polymers with controlled number average molecular weights, but broad molecular weight distributions, were obtained ($\overline{M}_w / \overline{M}_n = 1.6$):



Chain end functionalized polymers can also be prepared by transition metal catalyzed radical polymerizations using an appropriately functionalized initiator.⁹⁵ For example, Sawamoto and coworkers⁹⁵ reported the synthesis of hydroxyl chain end functionalized polymers using 2-hydroxyethyl 2-bromoisobutyrate as hydroxyl functionalized initiator in the presence of RuCl₂(PPh₃)₃ as catalyst and *n*-Bu₂NH as additive for the polymerization of methyl methacrylate:

2.5 ATOM TRANSFER RADICAL POLYMERIZATION (ATRP)

A specific type of transition metal mediated controlled radical polymerization process, namely, the copper mediated controlled/living free radical polymerization method was developed by Matyjaszewski^{3,96} and called Atom Transfer Radical Polymerization (ATRP). The ATRP method resembles the atom transfer radical addition reaction, which is a modification of the Kharash addition reaction⁹⁷ and associated with the transition metal catalyzed telomerization reactions.⁹⁸ The ATRP process is one of the most efficient controlled radical polymerization methods, allowing the synthesis of polymers with controlled number average molecular weights, narrow molecular weight distributions,^{3,4,13,99-106} chain end functionality^{5,6} and the polymerization of a variety of functionalized monomers.¹⁰⁷⁻¹²⁰ In the absence of any side reactions, the magnitude of the equilibrium constant ($K_{eq} = k_{act}/k_{deact}$) determines the polymerization rate. The mechanism of the ATRP reaction is briefly outlined below:

The ATRP method generally requires an alkyl halide as an initiator in the presence of a transition metal/ligand catalyst complex system for the initiation of vinyl monomers. Initially, the transition metal species, M_t^n abstracts the halogen atom X from the organic halide R-X to form the oxidized species XM_t^{n+1} and the

carbon centered radical $R\cdot$. In the subsequent step, the radical $R\cdot$ reacts with an alkene $CH_2=CHY$, to form an intermediate radical $R-CH_2\dot{C}HY$. The reaction between XM_t^{n+1} and $R-CH_2\dot{C}HY$ results in the target product $R-CH_2CHY-X$ and regenerates the reduced transition metal species M_t^n , which again reacts with $R-X$ and promotes a new redox cycle.

The mechanism consists of phenomenological related initiation and propagation steps. The processes are comprised of an atom transfer equilibrium step in conjunction with a kinetic radical addition to the monomer step. The presence of radical intermediates in the mechanism is consistent with experimental results from trapping experiments,⁶ copolymerization reactivity ratios⁶ as well as the regio-stereochemistry of the polymerization. The best way to determine the living character of such systems experimentally is to follow the kinetics of the polymerization reaction and the evolution of the number average molecular weights and the molecular weight distributions with percentage monomer conversion. For the ATRP reaction to be classified as a controlled/living polymerization reaction, the following experimental parameters must be determined:

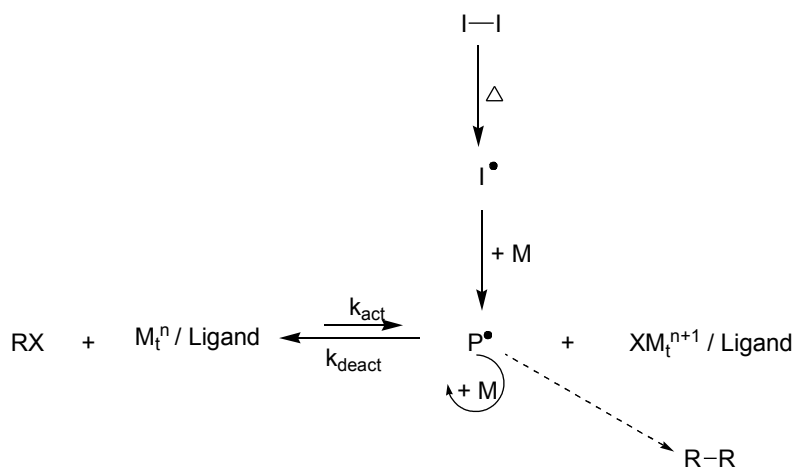
(a) the linear kinetic plots of the semilogarithmic coordinates ($\ln[M]_0/[M]$) vs time, which indicates that the reaction is first order with respect to the monomer concentration. Acceleration on the kinetic plots may indicate that the rate of propagation is much faster than the rate of initiation, while a deceleration may indicate that the rate of propagation is slow.

(b) the number average molecular weights of the polymers should increase linearly with percentage monomer conversion. A lower number average molecular weight than the predicted may indicate that chain transfer reactions occurred, whereas a higher molecular weight indicates either inefficient initiation or chain coupling reactions occurred.

(c) for systems that have rapid initiation and rapid exchange, the molecular weight distributions of the polymers should be below 1.5. In general, atom transfer radical polymerization is more complex than other controlled radical polymerization methods because it often involves a complex, heterogeneous catalytic system. The solubility, structure or effect of ion-pairing may not only change with the overall catalyst composition and preparation, but also for each polymerization reaction. Therefore, the choice of initiator, catalyst, ligand, solvent, temperature and additional additives affects the efficiency of a given ATRP reaction.

(d) the ATRP method has been used to prepare polymers with a variety of functional groups, compositions and topologies. The presence of functional groups within a polymer affects many properties, such as solubility, polarity, biocompatibility, melting and glass transition temperatures. The functional group can be incorporated into the polymer structure by using functionalized monomers, functionalized initiators or post polymerization modification reactions.

In the reverse atom transfer radical polymerization, the higher oxidation state transition metal complexes are added to the reaction. The initiator (R-X) and activator are generated *in situ* by reactions triggered by decomposition of conventional free radical initiators.^{98,121-124} The initiation step does not proceed by activation of an alkyl halide with a catalyst system, but rather by thermal decomposition of a conventional free radical initiator, such as AIBN. The generated radicals either react with the higher oxidation state transition metal complex to form the reduced transition metal species and a dormant species ($I^\bullet + XM_t^{n+1}/L$ forming I-X), or react with a monomer to form a propagating radical, $I-P_1^\bullet$, which is then quickly deactivated by reaction with $X-M_t^{n+1}/L$ to form M_t^n/L and a dormant species (I-P₁-X). In subsequent steps, the reduced transition metal/ligand species, M_t^n/L , reacts with the newly formed halogen terminated chains, as in the normal ATRP initiation/propagation process:



The development of new catalyst systems with concomitant reduction of the required catalyst concentration have been an active area of the research in ATRP processes. For example, the Activators Regenerated by Electron Transfer (ARGET) ATRP process is similar to simultaneous and reverse¹²⁵⁻¹³⁰ ATRP in that ARGET starts with an alkyl halide as an initiator and a transition metal complex in its oxidatively stable state as catalyst precursor. Instead of employing a conventional radical initiator to activate the catalyst, a non-radical forming reducing agent is employed to generate the activator. Reducing agents such as tin-2-ethylhexanoate,¹³¹ ascorbic acid¹³² and methylaluminoxane (MAO)¹³³ react with the oxidatively stable copper (II) complex to generate the activator, that is, the transition metal complex in its lower oxidation state. The mechanism of the ARGET reaction is briefly as follows:

The concept of Initiators for Continuous Activator Regeneration (ICAR) could be considered a "reverse" ARGET ATRP. In the ICAR ATRP process, a constant source of organic free radicals works to regenerate the Cu (I) activator which is otherwise consumed in termination reactions when catalysts are used at very low concentrations. With the ICAR technique, controlled synthesis of polystyrene and poly(meth)acrylate can be conducted with catalyst concentrations between 10-50 ppm, where its removal or recycling would be unwarranted for many applications and the reaction driven to completion with low concentrations of a standard free radical initiator.¹³⁴

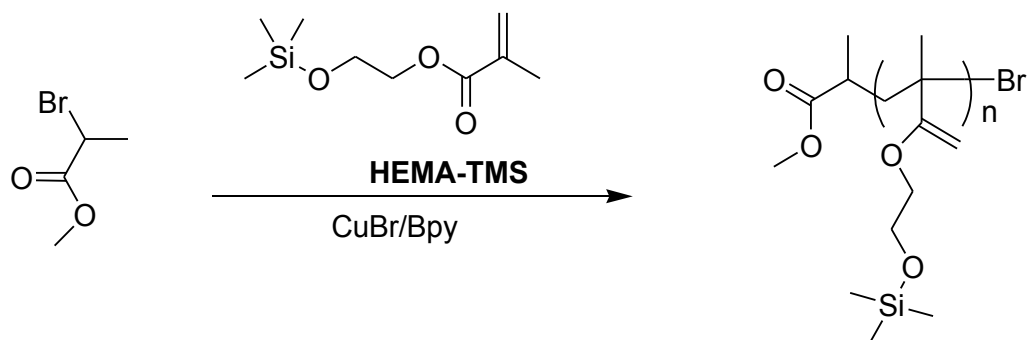
2.5.1 Features of the atom transfer radical polymerization process

For the accurate control and the effective use of the ATRP method in polymer synthetic strategies, the reactivity relationships between the different components of the ATRP reactions need careful evaluation. The synergistic effect between the initiator, monomer, metal catalyst, ligand, solvent and reaction temperature is essential for good control of the polymerization process.

The choice of monomer and initiator and the resultant stability of the halide end group display a pronounced solvent dependence. In general, to choose a good initiator, the structure of the alkyl group of the alkyl halide initiator should be similar to the dormant polymer species, that is, 1-phenylethyl halide derivatives which resemble dormant polystyrene chain ends and α -halopropionates which approximate dormant acrylate end groups. When (1-phenylethyl)bromide is employed as initiator for styrene polymerization, non-polar solvents are recommended, since polar media promote solvent-assisted side reactions, such

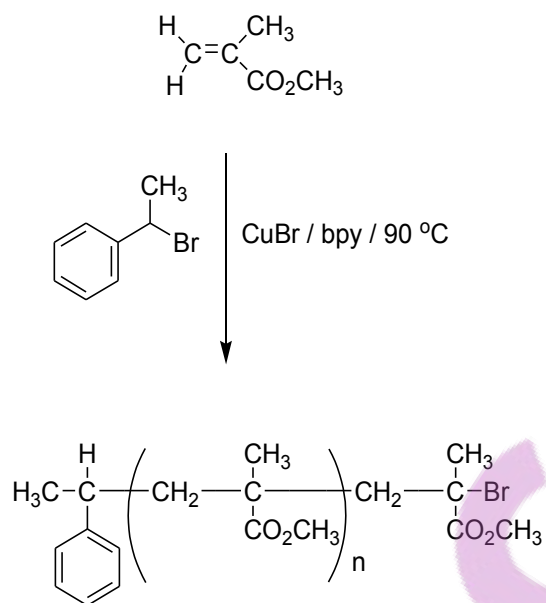
as elimination of HX from polystyryl halides and also catalyst poisoning by the solvent. The copper chloride-mediated polymerization of styrene^{3,4,6,103,135} is usually conducted at 130 °C, whereas the reaction for the copper bromide/bpy polymerization occurs at 110 °C. For a more efficient catalyst, such as CuBr/PMDETA or CuOAc/CuBr/ dNbpy,^{3,6,136,137} the reaction temperature can be lowered to 80-90 °C to produce well defined polystyrene:

In addition, the copper bromide catalyzed ATRP of acrylates has been reported using alkyl bromopropionates as initiators because the initiator structure is similar to the propagating chain end group structure:

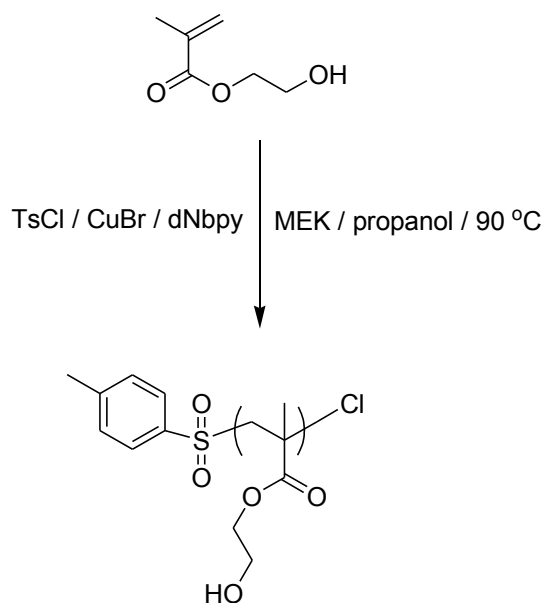


Sulfonyl halides have also been used as initiators in ATRP reactions.⁵ Any alkyl halide derivative with activated substituents on the α -carbon, such as hydroxyl, silyl, amino, cyano, halo, epoxy, acryl, carbonyl or allyl groups can be potentially used as initiators in ATRP reactions.^{3,4,138-140} With alkyl fluorides, the fluorine-carbon bond strength is apparently too strong to undergo homolytic cleavage and induce atom transfer radical polymerization reactions. Organo iodine compounds have been found to work well for acrylate polymerization, leading to controlled polymerization of acrylates in the presence of ruthenium and rhodium based catalysts. However, in styrene polymerizations, the heterolytic elimination of hydrogen iodide is too fast at high temperature.¹⁴¹

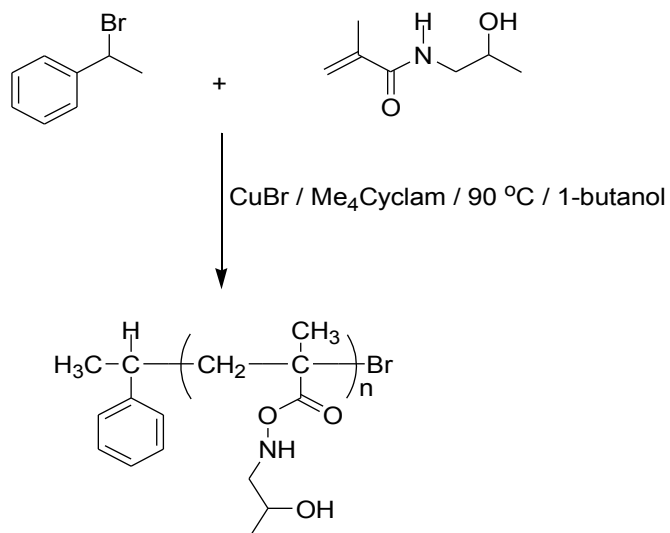
A variety of vinyl monomers undergo polymerization by ATRP methods. Typical monomers include styrenes, (meth)acrylates, (meth)acrylamides and acrylonitrile, which contain substituents that can stabilize the propagating radicals.¹³⁸⁻¹⁴⁴



A number of functionalized (meth)acrylates undergo controlled ATRP reactions. The ATRP of 2-hydroxyethyl acrylate (HEA) provides well defined poly(2-hydroxyethyl acrylate) derivatives with good control of the number average molecular weight and molecular weight distribution values.¹⁴⁵ In addition, the polymerization of 2-hydroxyethyl methacrylate (HEMA) in bulk at room temperature led to the formation of polymers with high molecular weight distribution.^{10,146-149} Well defined poly(HEMA) could be prepared by the tosyl chloride initiated polymerization of 2-hydroxyethyl methacrylate using mixed solvents such as a 70/30 mixture of methyl ethyl ketone and 1-propanol at 90 °C as follows:



A unique amide monomer, N-(2-hydroxypropyl)methacrylamide undergoes ATRP in a controlled manner, using CuBr/Me₄Cyclam as the catalyst system.¹⁵⁰ The polymerization was carried out in 1-butanol to yield relatively well defined polymers:



The main role of the ligand in ATRP reactions is to solubilize the transition-metal salt in the organic media and to adjust the redox potential of the metal center for

appropriate reactivity and dynamics for the atom transfer.¹⁵¹ There are several guidelines for an efficient ATRP catalyst:

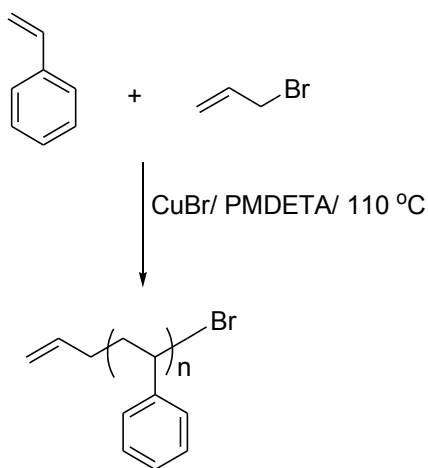
(a) fast and quantitative initiation ensures that all the polymer chains start to grow simultaneously;

(b) the equilibrium between the alkyl halide and the transition metal is strongly shifted toward the dormant species side. The equilibrium position will render most of the growing polymer chains dormant and produce a low radical concentration. As a result, the contribution of radical termination reactions to the overall polymerization is minimized;

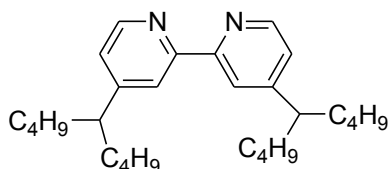
(c) fast deactivation of the active radicals by halogen transfer ensures that all polymer chains are growing at approximately the same rate, leading to the formation of a polymer with a narrow molecular weight distribution;

(d) relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate; and

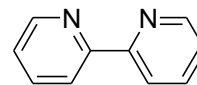
(e) no side reactions such as β -H abstraction or reduction/oxidation of the radicals in the presence of the catalyst/ligand system must occur:



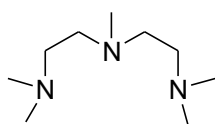
The following nitrogen ligands have been used extensively in copper mediated atom transfer radical polymerization processes:



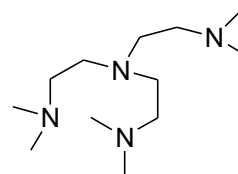
4,4'-di(5-nonyl)-2,2'-bipyridine



2,2'-bipyridyl



N,N,N',N'',N'''-Pentamethyldiethylenetriamine



Me₆TREN

ATRP can be carried out either in bulk, in solution or via heterogeneous systems such as emulsion and suspension polymerization. A variety of solvents, such as benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide (DMF), ethylene carbonate, alcohol and water have been used in the ATRP of different monomers. The choice of solvent must be such that chain transfer reactions to solvent are minimal. Thus, interactions between solvent and the catalytic system should be carefully considered.^{102,152-158}

The rate of polymerization in ATRP reactions increases with increasing temperature. This is due to the increase of both the radical propagation rate constant and the atom transfer equilibrium constant. As a result of higher activation energy for the radical propagation as opposed to the termination, higher k_p/k_t ratios and better control may be observed at higher temperatures. However, chain transfer and other side reactions become more pronounced at elevated temperatures.^{159,160} In general, the solubility of the catalyst increases at higher temperatures, however, the catalyst decomposition may also occur with

the increase in temperature.¹⁶¹ The optimum temperature for a given ATRP reaction depends mainly on the monomer, the catalyst and the targeted number average molecular weight.

2.6 FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION

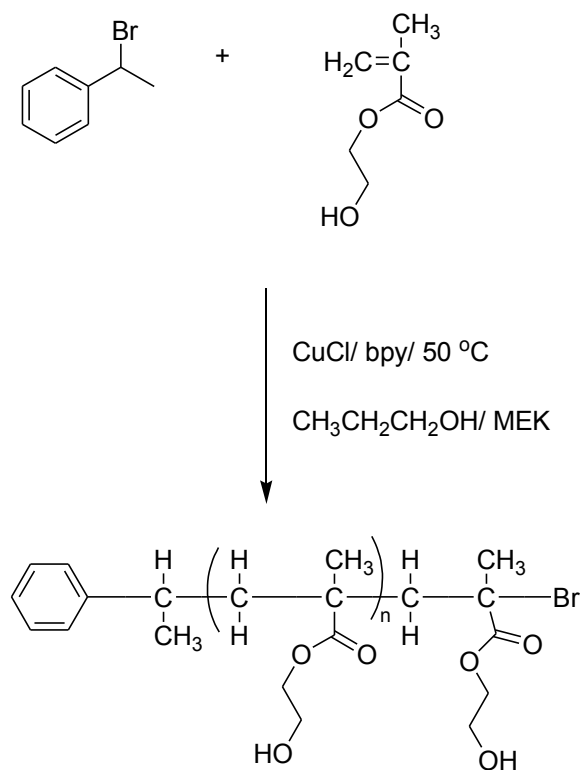
Atom Transfer Radical Polymerization allows the synthesis of polymers and copolymers with predictable number average molecular weights, narrow molecular weight distributions as well as controlled functionality, topology and molecular architectures. In particular, the regiospecific introduction of the functional groups into the polymer chains increases the utility of polymers and its applications in different technological areas. The following ATRP synthetic strategies for the preparation of well defined functionalized polymers with site specific functional groups have been developed:

- (a) The direct polymerization of functionalized monomers.
- (b) The post polymerization modification of monomer units along the polymer chain.
- (c) The post polymerization transformation of the C-Br bond at the ω -terminus of the polymer chain.
- (d) The use of functionalized initiators for the ATRP of vinyl monomers

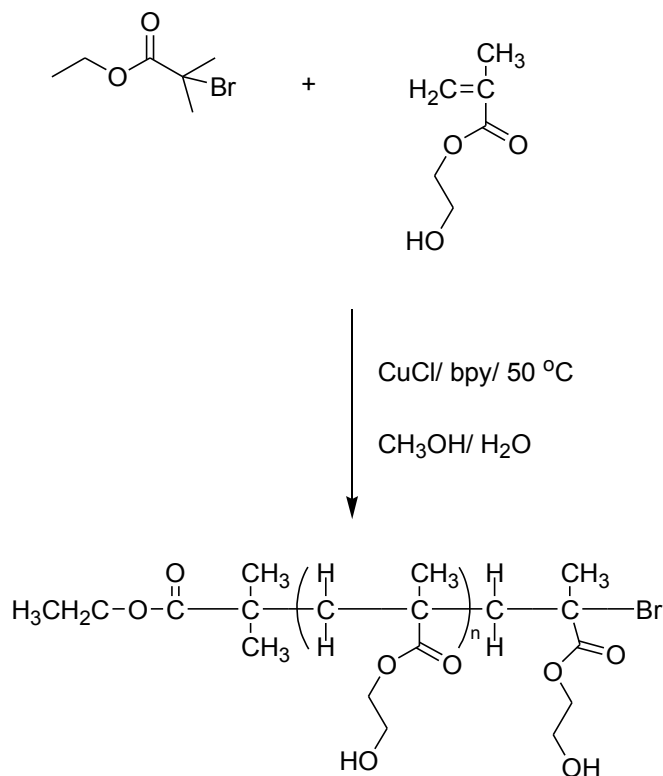
(a) **The direct polymerization of functionalized monomers:** A number of polar monomers containing polar functional groups, such as acrylonitrile,¹⁵⁹⁻¹⁶² meth(acrylamides),^{162,163} 4-vinylpyridine,^{164,165} dimethylaminoethyl methacrylate,¹⁶⁶

2-hydroxyethylacrylate,¹⁶⁶ 2-hydroxyethylmethacrylate,¹⁶⁸ glycidyl acrylate¹⁶⁸ and 4-acetoxystyrene¹⁶⁹ undergo polymerization by atom transfer radical polymerization methods. In addition, a wide range of functionalized random and block copolymers and terpolymers with precise control of the number average molecular weight, composition and functionality can be easily prepared via the sequential ATRP of two or more monomers, respectively.^{145,166,167,171-178}

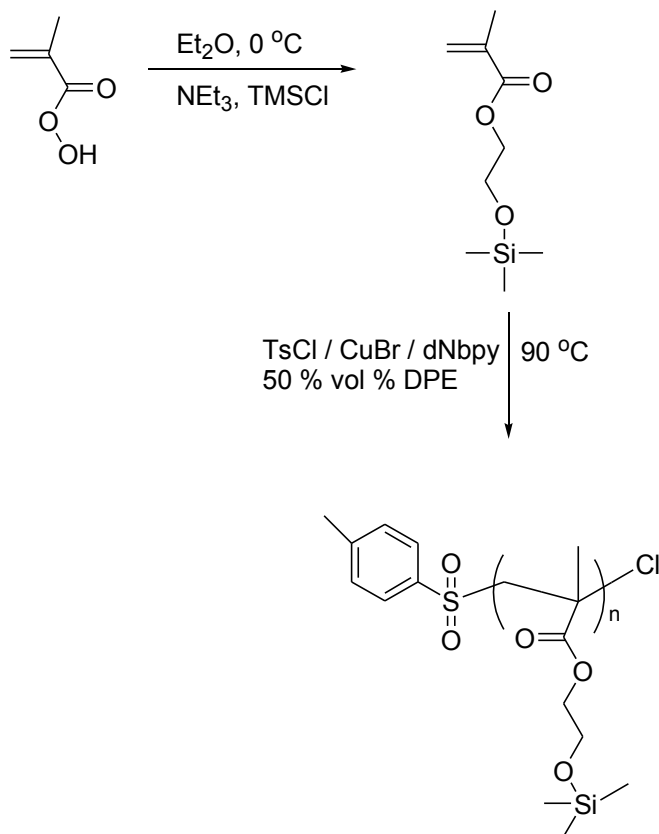
When the ATRP of 2-hydroxyethyl methacrylate (HEMA) was conducted in bulk, a very fast reaction was observed. When a ratio of monomer to initiator of 100:1 was used, the polymerization was completed within 20 minutes, even at room temperature. The number average molecular weights of the polymers were significantly higher than the theoretical number average molecular weights and polymers with broad molecular weight distributions were formed. However, when the polymerization of HEMA was conducted in solution in a mixed solvent system of n-propanol/2-butanone (50% v/v), the polymerization reaction was better controlled and polymers with number average molecular weights up to 4.0×10^4 g/mol and $\overline{M}_w / \overline{M}_n < 1.5$ were obtained.¹⁷⁹



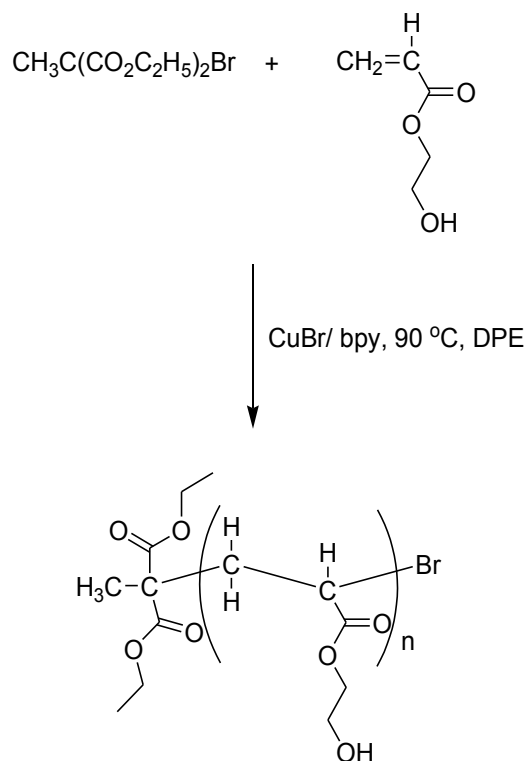
Similarly, Armes and coworkers¹⁰ and Zhung and coworkers¹⁸⁰ demonstrated that HEMA can undergo controlled polymerization reactions under mild conditions in either CH₃OH or CH₃OH/H₂O mixtures at room temperature to produce polymers with high number average molecular weights and with molecular weight distributions ranging from 1.2 to 1.3:



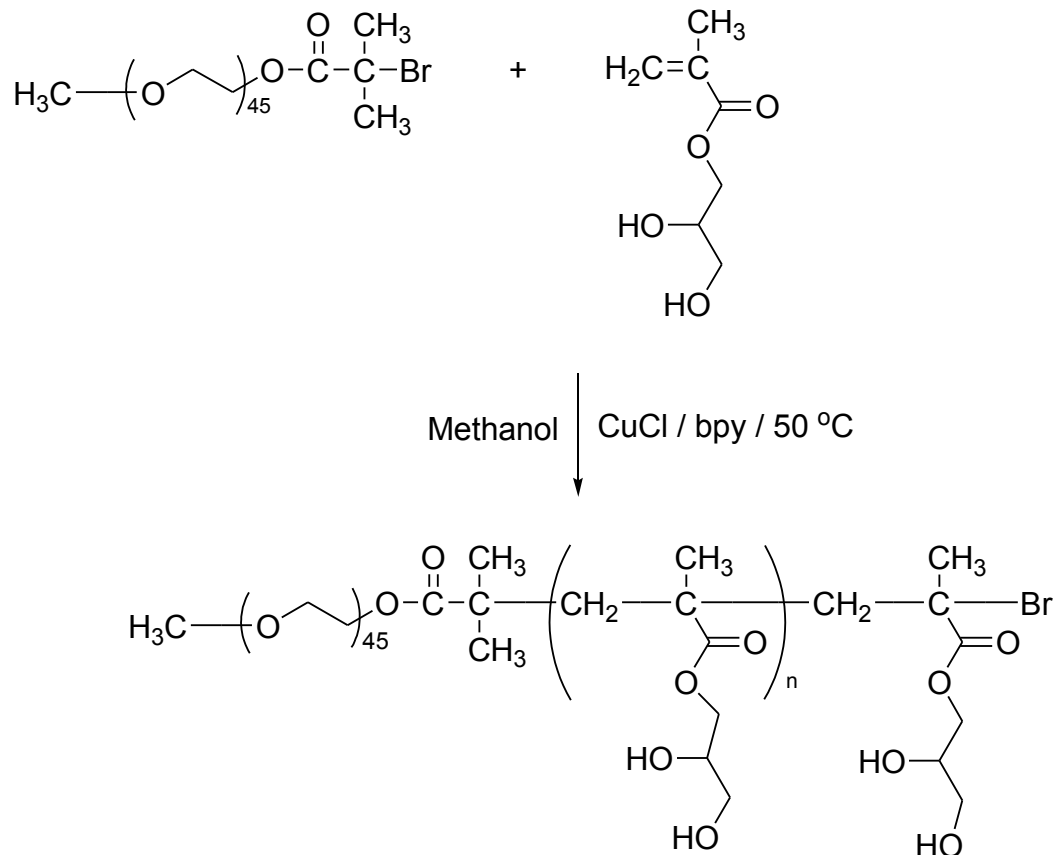
In addition, the atom transfer radical polymerization of a siloxyl protected HEMA derivative proceeds to form well defined siloxyl functionalized polymers.^{179,181,182}



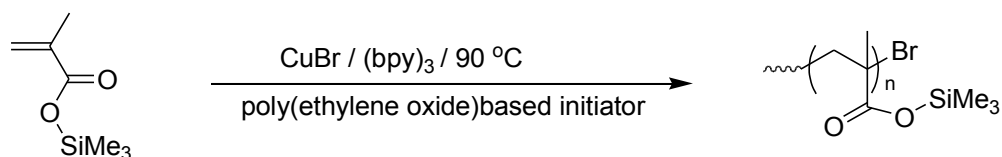
The controlled atom transfer radical polymerization of a hydroxyl functionalized monomer, 2-hydroxyethyl acrylate (HEA), was reported by Coca and coworkers.¹⁴⁵ The polymerization reaction exhibits first order rate kinetics and the number average molecular weights of the polymers increase linearly with percentage monomer conversion. In addition, the molecular weight distributions remain narrow throughout the polymerization process ($\overline{M}_w / \overline{M}_n < 1.2$):



Armes and coworkers¹⁸³ reported the homopolymerization of different hydroxyl functionalized monomers via ATRP methods. For example, glycerol monomethacrylate (GMA) undergoes polymerization by ATRP methods in methanol to produce well defined hydroxyl functionalized polymers with high number average molecular weights and with good control of the molecular weight distributions ($\overline{M}_w / \overline{M}_n = 1.09 - 1.30$):

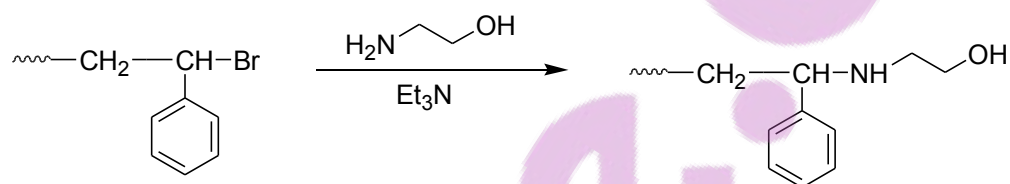


(b) **The post polymerization modification of monomer units along the polymer chain:** Acidic monomers, such as (meth)acrylic acid, isomeric vinylbenzoic acids, unsaturated sulfonic or phosphonic acids cannot undergo polymerization directly via the ATRP methods due to protonation effects and destruction of the transition metal/nitrogen ligand complexes typically used as ATRP catalysts. Thus, monomers substituted with protected acid groups must be employed in the ATRP processes in order to prepare polymers with acidic functional group derivatives¹⁸⁴ as outlined in the following synthesis pathway:

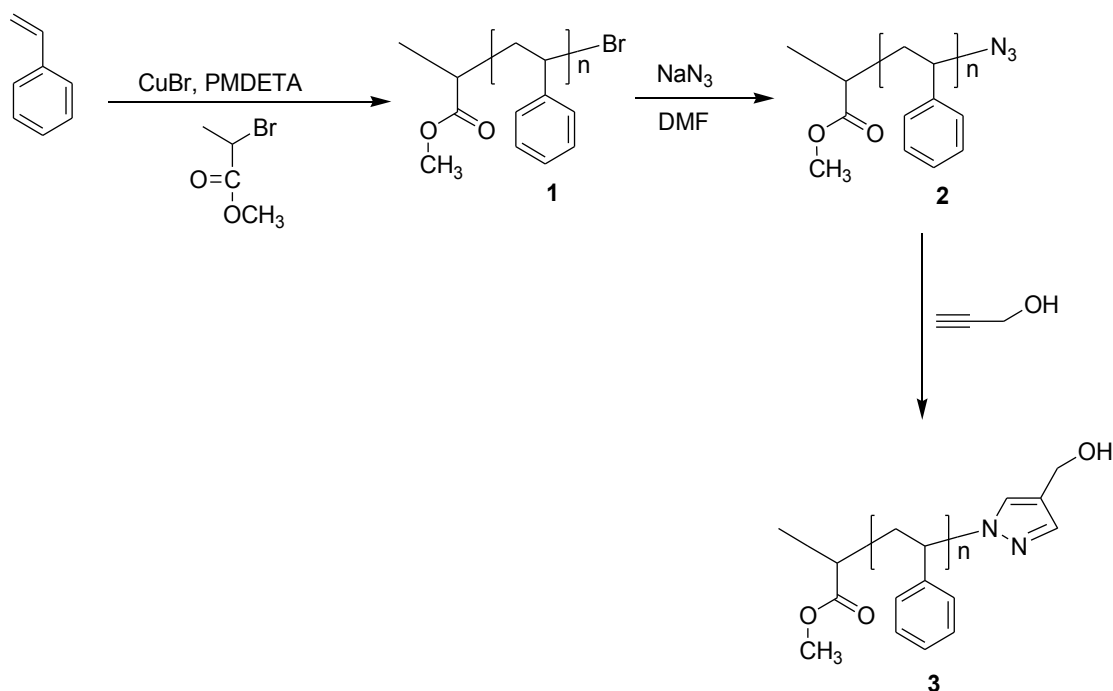


(c) **The post polymerization transformation of the C-Br bond at the**

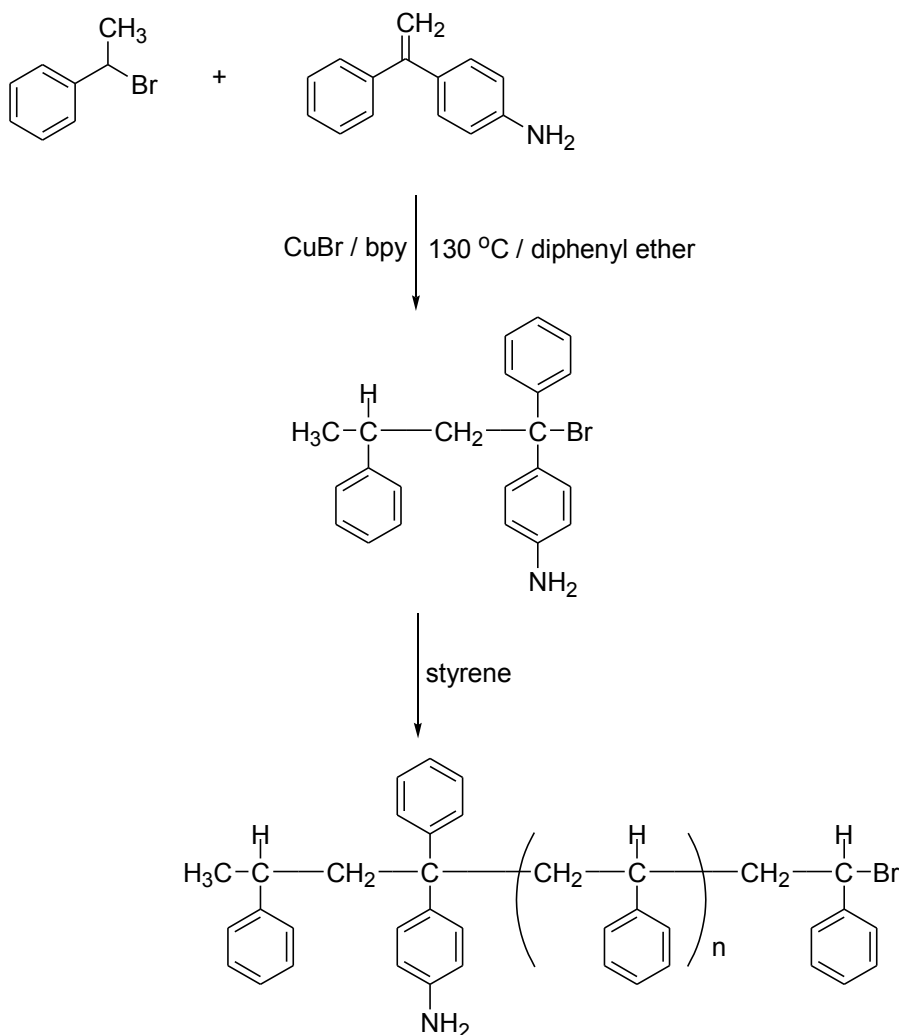
ω -terminus of the polymer chain: Polymers prepared by ATRP methods can be subjected to post polymerization functionalization reactions to form chain end functionalized polymers with the functionality at the omega end of the chain. Coessen and coworkers^{185,186} reported that the carbon-halogen end group of homopolymers prepared by ATRP methods can be converted to other functional groups by nucleophilic substitution, electrophilic substitution and addition reactions. For example, the omega halide chain end of polystyrene, which was prepared by ATRP methods, can be converted to an alcohol functional group by nucleophilic reactions with 2-aminoethanol to form the corresponding ω -hydroxyl functionalized polystyrene:¹⁸⁷



Similarly, the C-Br of the ω -chain ends of polymers prepared by ATRP methods can easily be converted to a wide variety of functional groups using click chemistry methodology.^{188,189} Lutz and coworkers¹⁹⁰ reported the synthesis of ω -hydroxyl, ω -carboxyl and ω -methyl vinyl polystyrenes using a combination of ATRP and click chemistry. For example, the carbon-bromine chain end of polystyrene prepared by ATRP was first transformed into an azide end group and subsequently reacted with propargyl alcohol in the presence of 1,3-dipolar cycloaddition reaction catalyzed by CuBr/dNbpy to form the corresponding ω -hydroxyl chain end functionalized polystyrene:



(e) The use of functionalized initiators for the ATRP of vinyl monomers: The simplest way to obtain chain end functionalized polymers by ATRP methods is to use functionalized initiators that contain the desired functional group for the polymerization of styrenic and (meth)acrylate monomers. The most widely used functionalized initiators to prepare functionalized polymers are activated alkyl or acyl halides and sulfonyl halide compounds. A wide variety of functionalized initiators have been employed in ATRP reactions to produce chain end functionalized polymers with functional groups such as the hydroxyl, cyano and amine groups regiospecifically introduced at the α -terminus of the polymer chain. Matyjaszewski and coworkers¹⁹¹ demonstrated that chain end functionalized polymers with thiol,¹³⁰ phthalic,¹⁹² cyano, allyl, 1,3-bis{1-methyl-1-[2,2,2-trichloroethoxy]carbonylamino}ethyl}benzene ester,¹⁹³ cholesteryl,¹²⁸ amine and carboxyl functional groups can be prepared via ATRP methods using functionalized initiators. In addition, Summers and coworkers¹⁷ prepared α -aminophenyl functionalized polystyrene using an amine functionalized initiator adduct for the polymerization of styrene by ATRP methods:

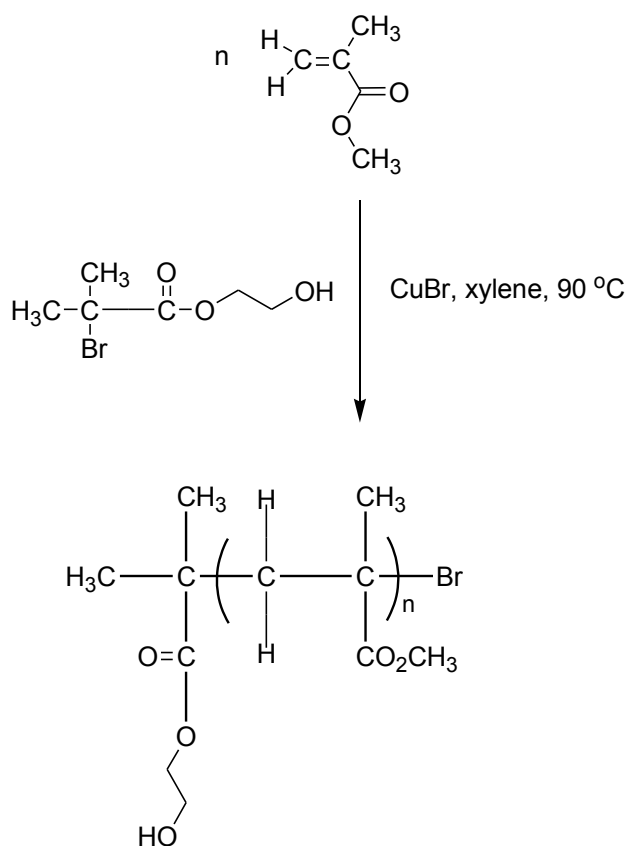


2.7 HYDROXYL CHAIN END FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION: USE OF FUNCTIONALIZED INITIATORS.

In ATRP reactions, the initiator structure determines the nature of the polymer chain ends in the process of preparation of well defined polymers. By using functionalized initiators in ATRP reactions, hetero-telechelic polymers are formed directly, without the need for post-polymerization modification reactions. When functionalized organohalides are used as initiators in ATRP reactions, the functional group is introduced at the α -terminus of the polymer chain. Many hydroxyl functionalized organohalides or organosulfonyl compounds were

employed as initiators in styrene and methyl methacrylate polymerization to form hydroxyl functionalized polymers.

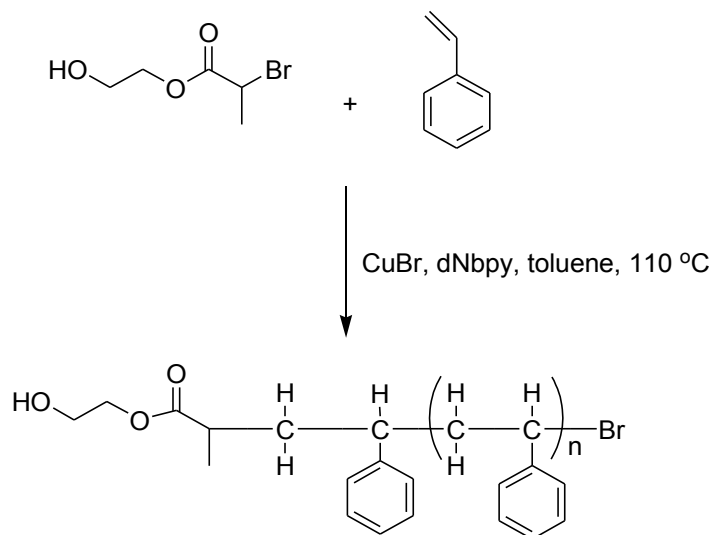
Haddleton and coworkers¹⁰¹ reported the synthesis of hydroxyl chain end functionalized polymers using 2-hydroxyethyl 2-bromoisobutyrate as functionalized initiator for the ATRP of MMA to form well defined α -hydroxyl functionalized poly(methyl methacrylate):



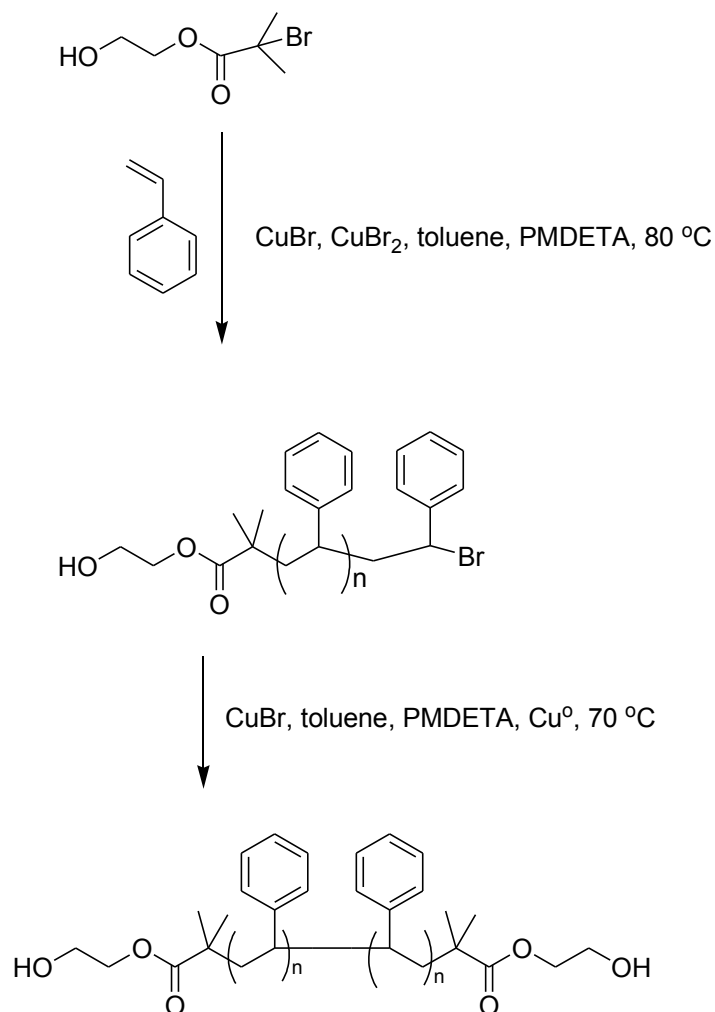
The presence of the hydroxyl group during the polymerization does not interfere with the polymerization reaction and polymers with controlled number average molecular weights and narrow molecular weight distributions were obtained.

A hydroxyl functionalized alkyl bromide derivative, 2-hydroxyethyl 2-bromopropanoate was used as functionalized initiator for the polymerization of

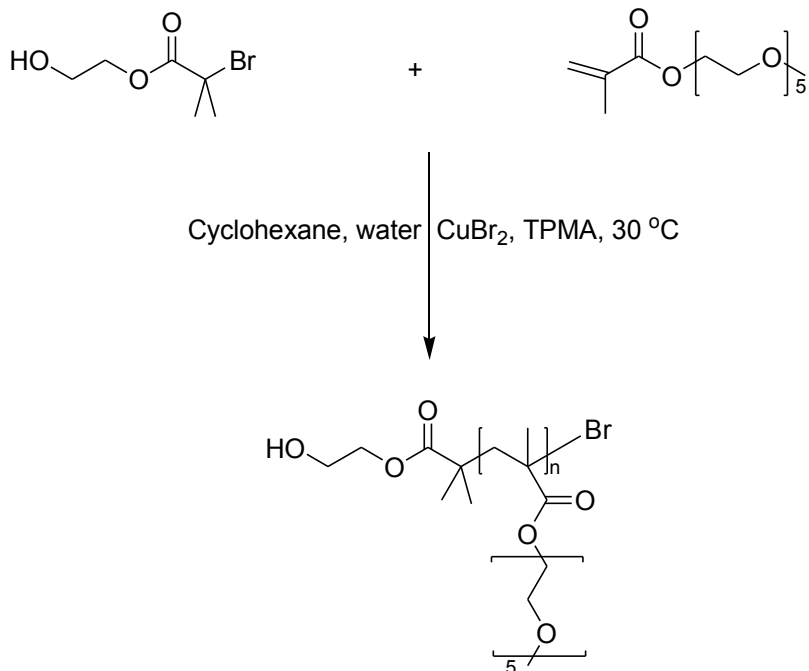
styrene by ATRP methods.¹¹¹ Well defined α -hydroxyl functionalized polystyrene with number average molecular weight ($\overline{M}_n = 4.1 \times 10^3$ g/mol) and molecular weight distribution ($\overline{M}_w / \overline{M}_n = 1.17$) was obtained:



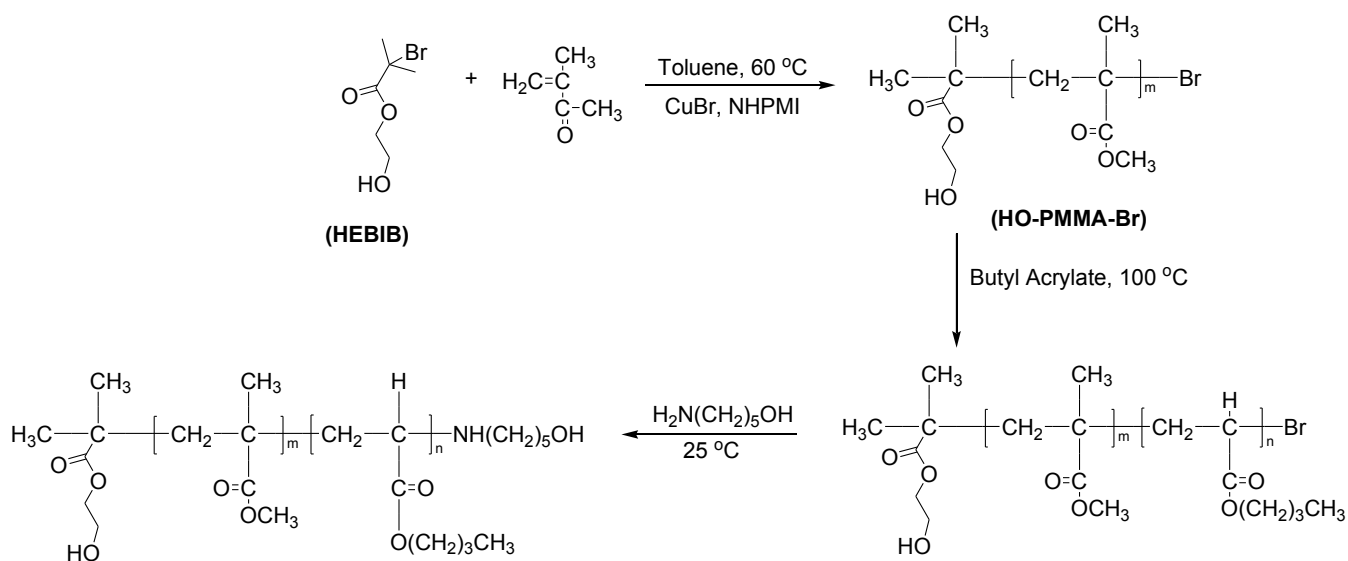
Well defined hydroxyl chain end functionalized polystyrene was prepared by atom transfer radical polymerization, using 2-hydroxyethyl 2-bromoisobutyrate (HEBIB) as a hydroxyl functionalized initiator. Subsequently, α,ω -hydroxyl functionalized polymers were prepared by standard atom transfer radical coupling reactions in the presence of nanosize copper particles as reducing agent.¹¹²



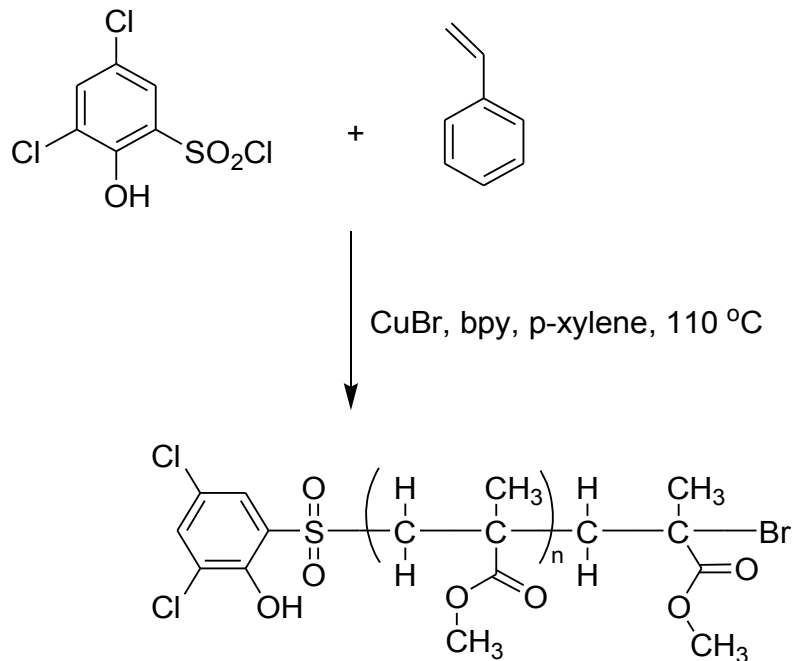
Similarly, Siegwart and coworkers¹⁹⁴ reported the use of HEBIB as an initiator in aqueous ARGET ATRP and inverse mini-emulsion ARGET ATRP as a method to produce linear functionalized polymers and nanogels. Hydroxyl functionalized poly[oligo(ethylene oxide)methacrylate] was prepared by AGET ATRP of oligo(ethylene oxide)methacrylate using HEBIB as an initiator in water or inverse mini-emulsion of water/cyclohexane at ambient temperature:



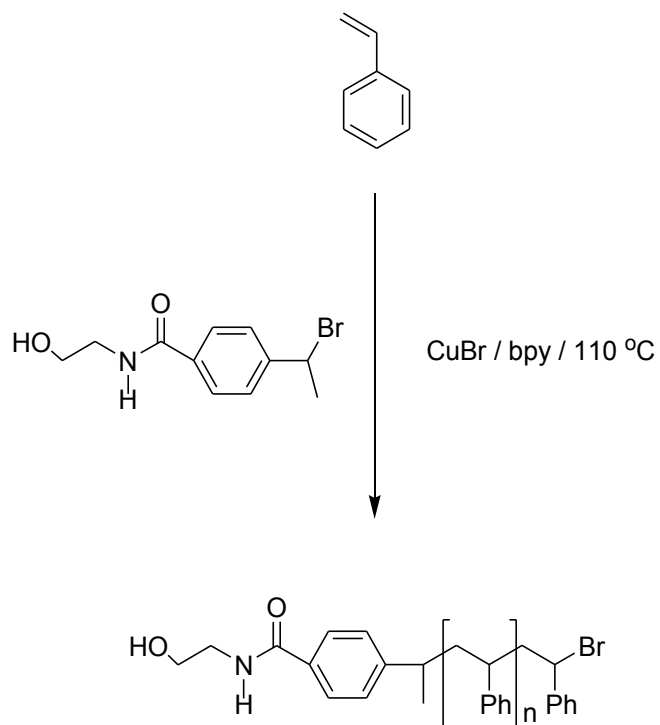
Zhang and coworkers¹⁹⁵ reported the synthesis of hydroxyl end-capped block copolymers of poly(methyl methacrylate) and poly(*n*-butyl acrylate) by ATRP methods. In a one pot reaction at 100 °C, 2-hydroxyethyl 2-bromoisobutyrate was used as a hydroxyl functionalized initiator for the polymerization of methyl methacrylate followed by the sequential addition of butyl acrylate to form HO-PMMA-*b*-PBA-Br in quantitative yields. The terminal C-Br bond was converted to HO-PMMA-*b*-PBA-OH by reaction with 5-amino-1-pentanol at 25 °C to form the α,ω -hydroxyl functionalized poly(methyl methacrylate)-*b*-poly(butyl acrylate) copolymer:



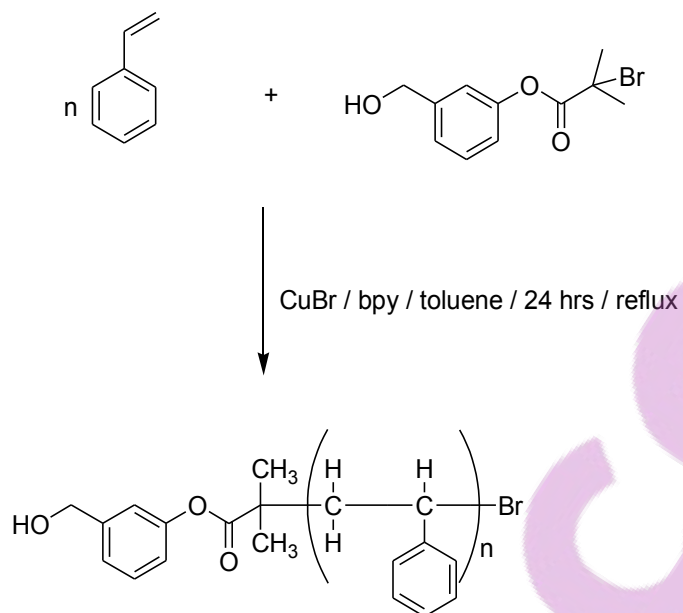
Percec and coworkers¹⁹⁶ reported the synthesis of a variety of functionalized sulfonyl chlorides substituted with the carbonyl, hydroxyl, methoxy and tertiary amine groups and their utility as functionalized initiators in the ATRP of styrene, butyl acrylate and methyl methacrylate. For example, when dichlorohydroxybenzene sulfonyl chloride was used as a functionalized initiator for the polymerization of methyl methacrylate, well defined α -hydroxyl functionalized poly(methyl methacrylate) with narrow molecular weight distribution ($\overline{M}_w / \overline{M}_n < 1.4$) was obtained:



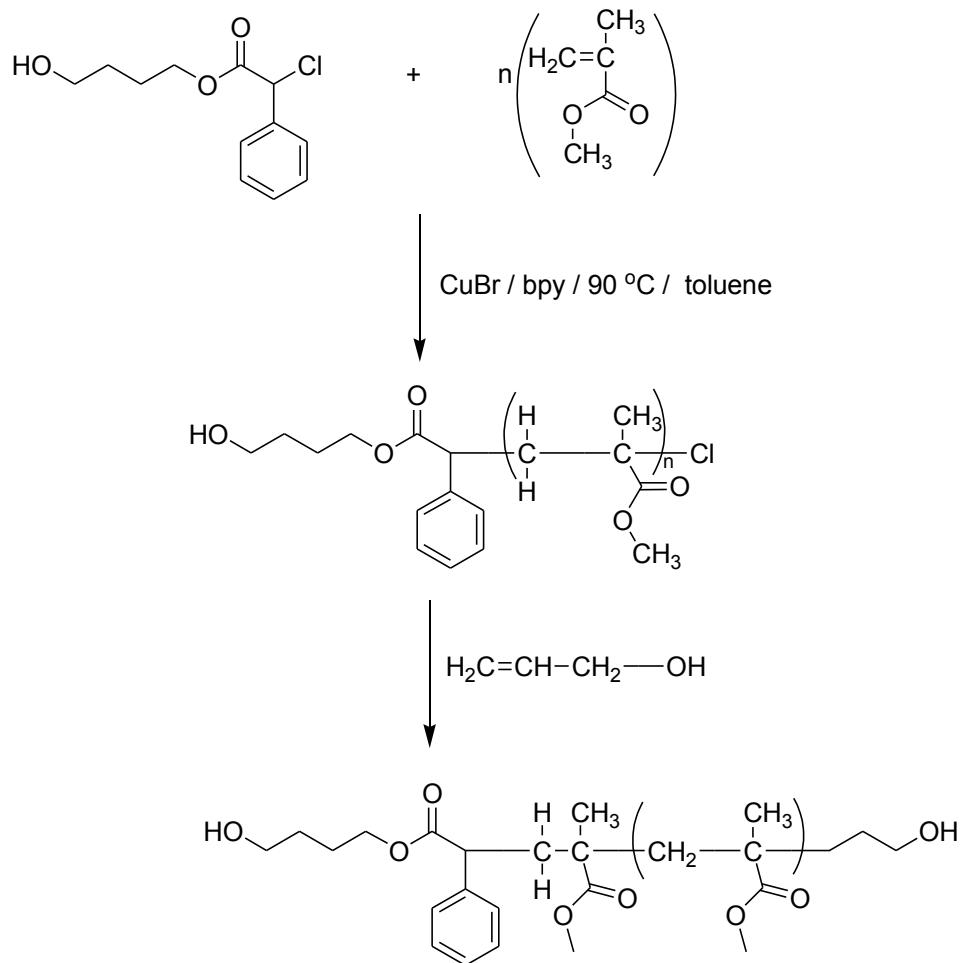
Pionteck and coworkers¹⁹⁷ reported the synthesis of hydroxyl functionalized polymers using N-(2-hydroxyethyl) 4-(1-bromoethyl)benzamide as a functionalized initiator for the ATRP of styrene. In the presence of the CuBr/bpy catalyst system, hydroxyl chain end functionalized polystyrene with $\overline{M}_n = 2.4 \times 10^3$ g/mol and $\overline{M}_w / \overline{M}_n = 1.3$ was obtained:



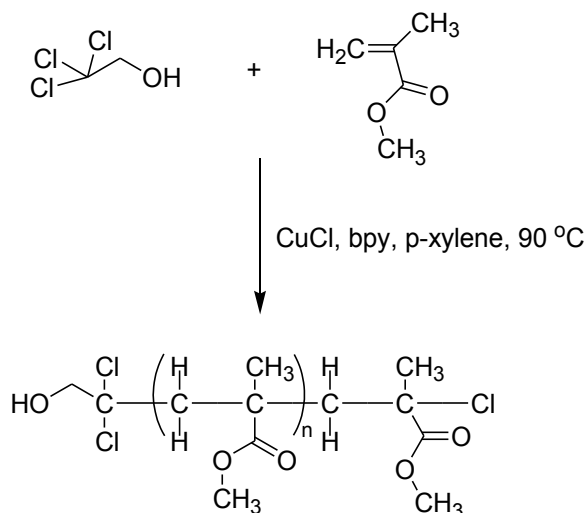
Likhitsup and coworkers¹⁹⁸ reported the ATRP of styrene using functionalized initiators based on hydroxyl benzyl ester derivatives. Polymers with number average molecular weights of $\overline{M}_n = 1.5 \times 10^4 - 2.0 \times 10^4$ g/mol and molecular weight distributions of $\overline{M}_w / \overline{M}_n = 1.2 - 1.23$ were obtained:



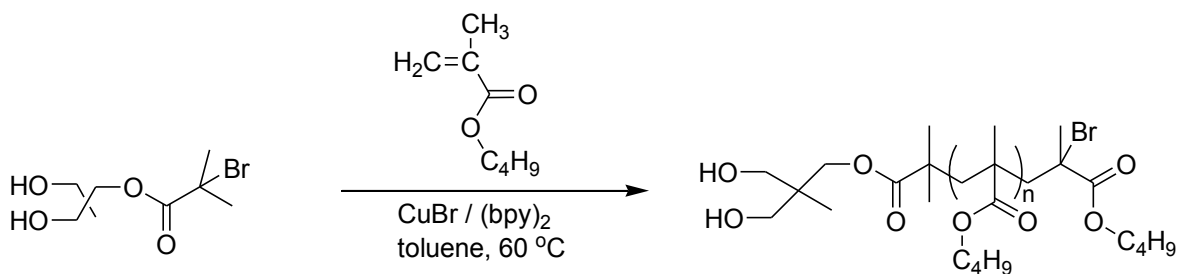
Keul and coworkers¹⁹⁹ prepared telechelic poly(methyl methacrylate)s with hydroxyl end groups by ATRP methods. The ATRP of methyl methacrylate, initiated by 4-hydroxybutyl chlorophenylacetate produced well defined α -hydroxyl functionalized poly(methyl methacrylate). The post modification polymerization chain end modification reaction with allyl alcohol affords α,ω -dihydroxyl functionalized poly(methyl methacrylate) with high degree of chain end functionality ($f_{\text{OH}} = 1.8$):



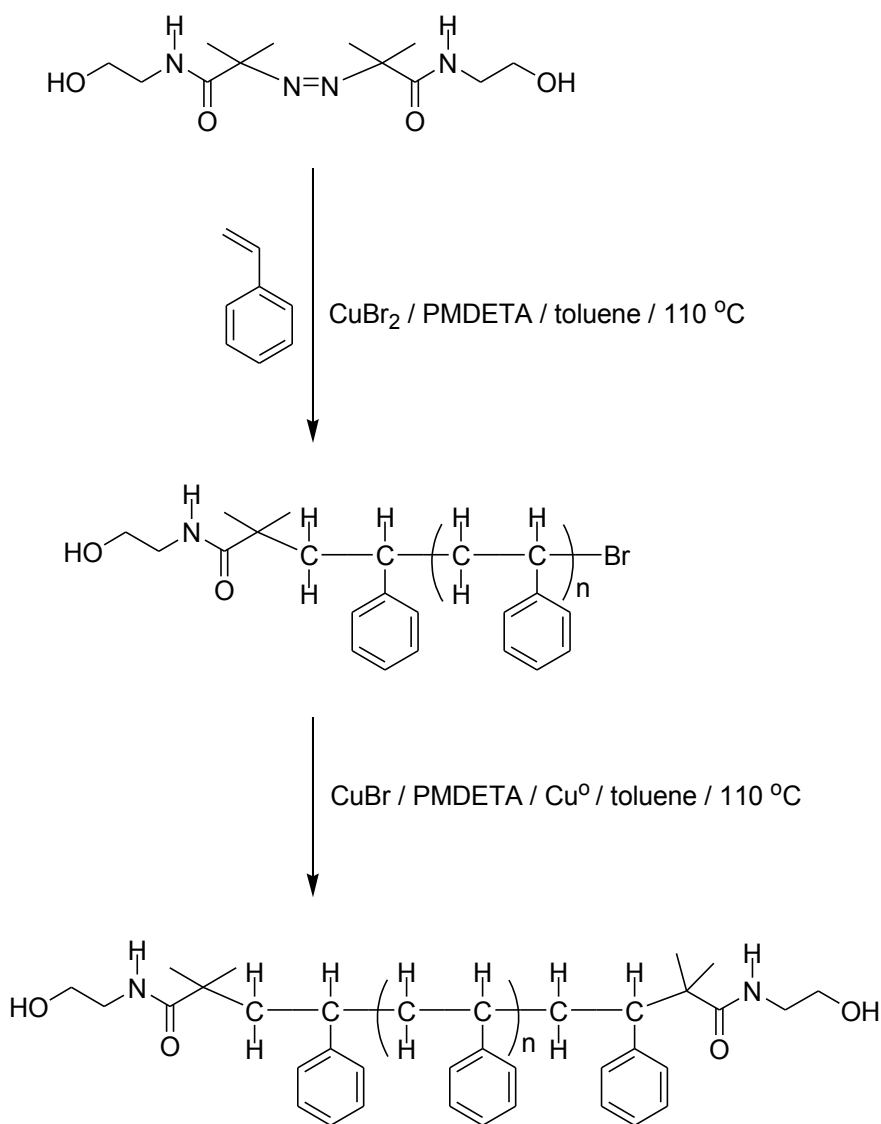
Peters and coworkers²⁰⁰ reported the synthesis of α -hydroxyl functionalized poly(methyl methacrylate) using 2,2,2-trichloroethanol as the hydroxyl functionalized initiator. Low number average molecular weight poly(methyl methacrylate) ($\overline{M}_n = 2.4 \times 10^3 \text{ g/mol}$) with the hydroxyl group introduced at the α -terminus of the polymer chain was obtained.



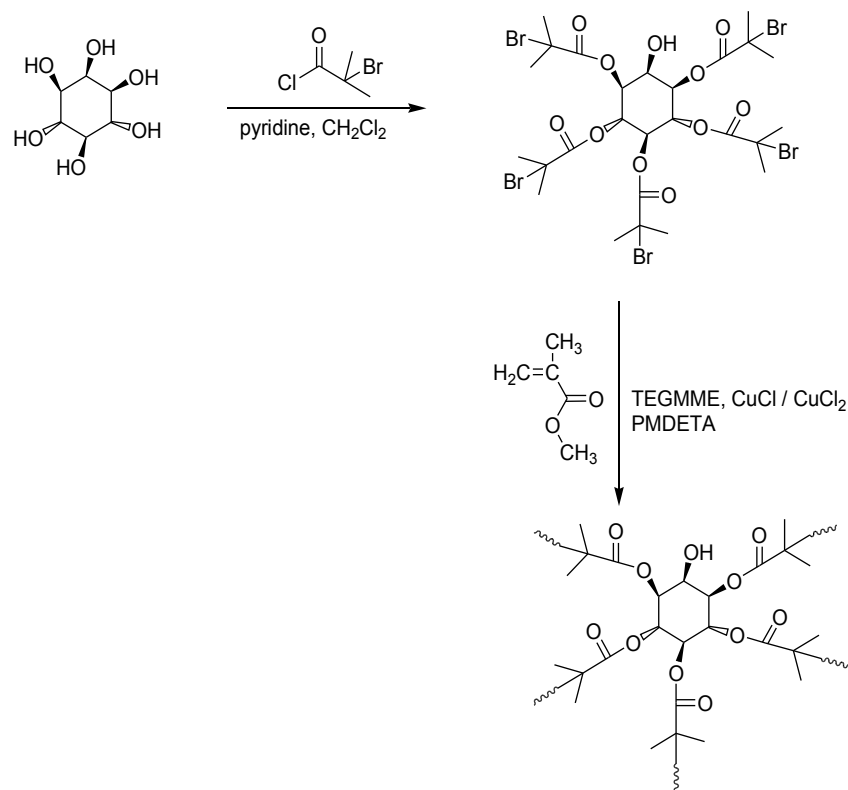
Glaied and coworkers²⁰¹ reported the synthesis of well defined α -bis(hydroxyl) functionalized poly(*t*-butyl methacrylate) by ATRP methods using 2,2-bis-(hydroxymethyl)propyl 2-bromoisobutyrate as a dihydroxyl functionalized initiator. α -Bis(hydroxyl) functionalized poly(*t*-butyl methacrylate) with number average molecular weight ($\overline{M}_n = 9 \times 10^3$ g/mol) and the molecular weight distribution ($\overline{M}_w / \overline{M}_n = 1.39$) was obtained:



Yagci and coworkers²⁰² reported the synthesis of α,ω -dihydroxyl functionalized polymers by ATRP methods using hydroxyl substituted azo initiators. By using 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide] as the initiator for styrene polymerization, α -hydroxyl functionalized polystyrene with high number average molecular weights and narrow molecular weight distributions were obtained. Subsequent radical coupling reactions produced the corresponding α,ω -dihydroxyl functionalized polystyrene:

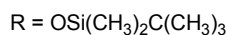
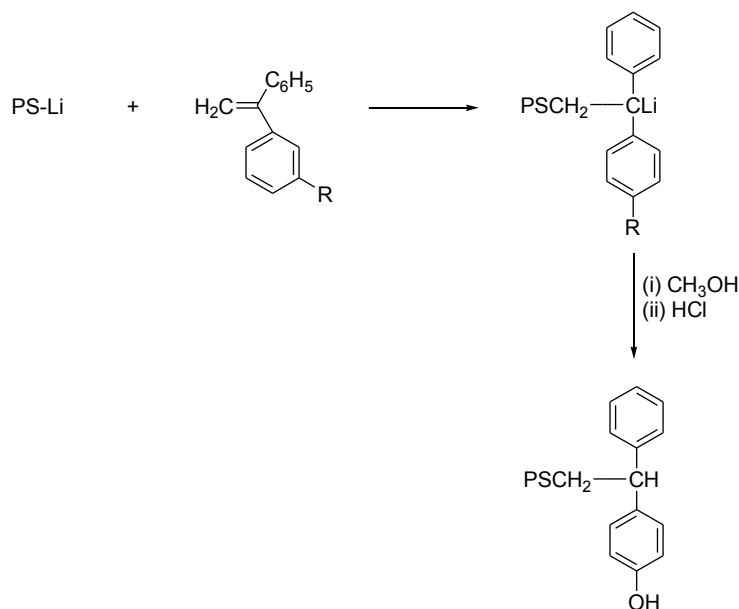


The synthesis of a novel hydroxyl functionalized initiator for ATRP reactions was reported by Kimani and coworkers.²⁰³ The initiator was prepared by esterification of a non-reducing sugar, meso-inositol, to the corresponding 2-bromoisobutyrate derivative. The resultant hydroxyl functionalized initiator was employed in the ATRP of methyl methacrylate (MMA) in tri(ethylene glycol)monoethyl ether (TEGMME) solvent and $\text{CuCl}/\text{CuCl}_2/\text{PMDETA}$ as the catalytic system at room temperature to form the corresponding well defined five arm star polymers with the hydroxyl group at the center of the star polymer:



2.8 THE PREPARATION OF CHAIN END FUNCTIONALIZED POLYMERS USING FUNCTIONALIZED 1,1-DIPHENYLETHYLENE DERIVATIVES

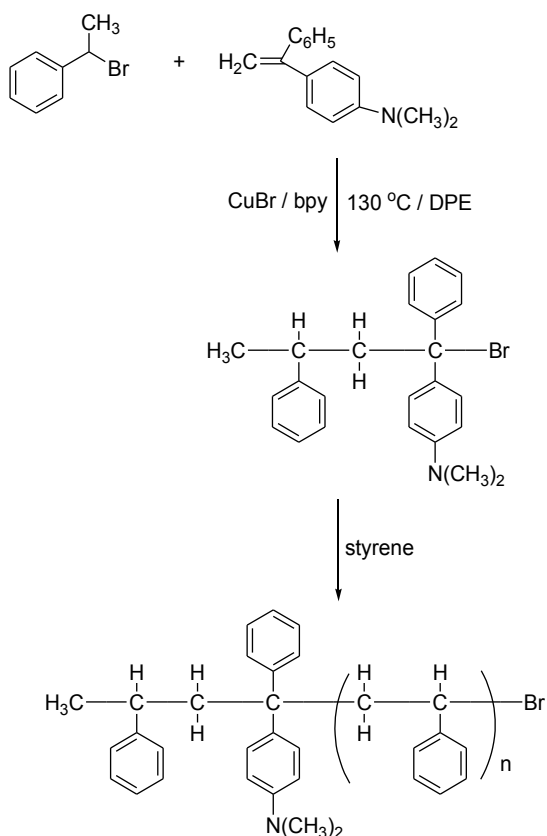
In 1989, Quirk and Zhu²⁰⁴ developed a general, quantitative living anionic functionalization method for the preparation of functionalized polymers, using substituted 1,1-diphenylethylene derivatives as functionalization agents. The chain end functionalization method is based on the addition reactions of polymeric organolithium compounds to 1,1-diphenylethylene derivatives to produce functionalized polymers in reactions which proceed quantitatively and independent of the specific functional group. For example, phenol-terminated polystyrene was prepared by the reaction of poly(styryl)lithium with 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene to form the corresponding phenol chain end functionalized polystyrene in >99 % yields, after acid hydrolysis:



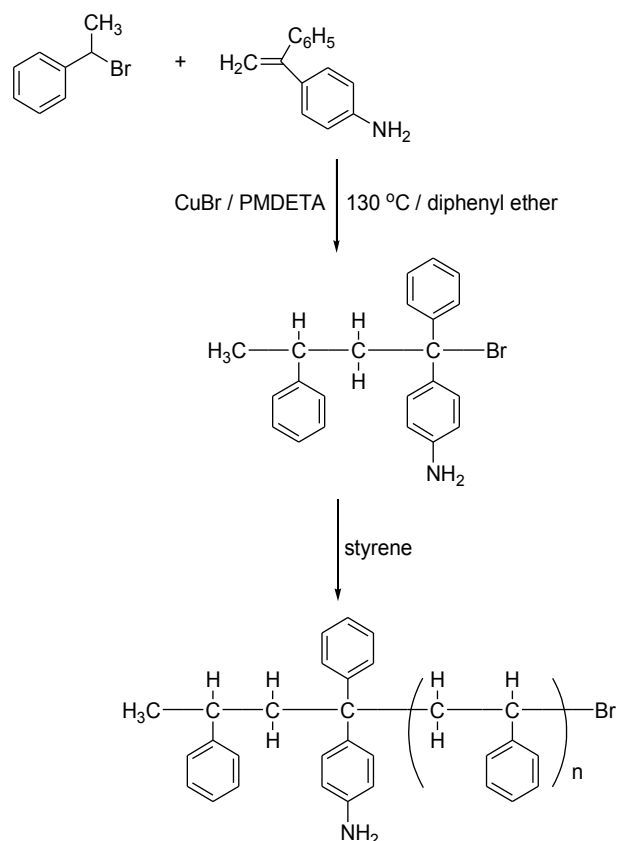
Similarly, the synthesis of siloxyl,²⁰⁵ tertiary amine,²⁰⁶ primary amine,²⁰⁷ oxazolyl,²⁰⁸ carboxyl²⁰⁸ and amide²⁰⁹ functionalized polymers by anionic mechanisms using 1,1-diphenylethylene chemistry has been reported by Quirk and coworkers.

Summers and coworkers^{17,18} have extended the application of 1,1-diphenylethylene chemistry to free radical polymerization methods using substituted 1,1-diphenylethylene derivatives as functionalized initiator precursors for the synthesis of chain end functionalized polymers in atom transfer radical polymerization reactions. The efficiency of the ATRP method using functionalized initiators based on 1,1-diphenylethylene precursors was demonstrated by the preparation of tertiary amine chain end functionalized polystyrene. The initiator adduct, prepared *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene in the presence of the CuBr/bpy catalyst system at 110 °C was employed as the unimolecular tertiary amine functionalized initiator in the ATRP of styrene to produce tertiary amine chain end functionalized polymers in quantitative yields. The polymerization proceeded via a controlled free radical polymerization process to afford tertiary amine chain end

functionalized polystyrenes with well defined structures and chain end functionality:¹⁷



Similarly, primary amine chain end functionalized polymers¹⁸ with well defined polymer structure and chain end functionality were prepared by ATRP methods using the appropriate primary amine 1,1-diphenylethylene derivative as initiator precursor:



The present study explores the use of siloxyl and disiloxyl substituted 1,1-diphenylethylene derivatives as precursors for the formation of functionalized unimolecular initiators in the preparation of siloxyl and disiloxyl functionalized polymers by ATRP methods. In particular, the research work describes the synthetic routes for the preparation of siloxyl chain end functionalized polymers by the ATRP process according to the following methods:

(a) the synthesis of 1-(4-t-butyl dimethyl siloxyphenyl)-1-phenylethylene and its use as a siloxyl functionalized initiator precursor for the preparation of α -siloxyl functionalized polymers by atom transfer radical polymerization.

(b) the use of a new siloxyl initiator adduct, generated *in situ* by the reaction of 1-(4-t-butyl dimethyl siloxyphenyl)-1-phenylethylene with (1-bromoethyl)benzene in the presence of CuBr/bpy or CuBr/PMDETA, as initiator for the polymerization of styrene and methyl methacrylate to provide a new method for the synthesis of

α -siloxyl functionalized polystyrene and α -siloxyl functionalized poly(methyl methacrylate), respectively.

Similarly, the current research outlines the preparation of α -bis(siloxyl) functionalized polymers by ATRP methods using the following synthetic strategy:

(a) the synthesis of 1,1-bis(4-t-butyl dimethyl siloxyphenyl)ethylene and its utility as a disiloxyl functionalized initiator precursor for the preparation of α -bis(siloxyl) functionalized polymers by atom transfer radical polymerization.

(b) the utilization of a new disiloxyl initiator adduct, prepared *in situ* by the reaction of 1,1-bis(4-t-butyl dimethyl siloxyphenyl)ethylene with (1-bromoethyl)benzene in the presence of CuBr/bpy or CuBr/PMDETA, as initiator for the ATRP of styrene and methyl methacrylate to provide a new synthesis method for the preparation of α -bis(siloxyl) functionalized polystyrene and α -bis(siloxyl) poly(methyl methacrylate), respectively.

The current research also investigates the controlled/living character of each ATRP reaction leading to the formation of α -siloxyl and α -bis(siloxyl) functionalized polymers.

In addition, the present study describes the synthesis of hydroxyl chain end functionalized polymers by the quantitative post polymerization chain end transformation of the siloxyl groups of the appropriate siloxyl chain end functionalized polymers to the corresponding hydroxyl groups.

CHAPTER 3

EXPERIMENTAL

3.1 MATERIALS AND GLASSWARE

3.1.1 Chemicals and solvents

Unless otherwise stated, the following chemicals and solvents were used as received:

N,N-dimethylformamide (BDH Chemicals, bp = 153-155 °C).

Methylithium (1.4 M in diethyl ether, Sigma - Aldrich Chemical Company).

Methyltriphenylphosphonium bromide (Sigma - Aldrich Chemical Company, mp = 230-234 °C).

4,4'-Dihydroxybenzophenone (Sigma - Aldrich Chemical Company, 98%).

Diphenyl ether (Sigma - Aldrich Chemical Company, bp = 258 °C).

(1-Bromoethyl)benzene (Sigma - Aldrich Chemical Company, bp = 94 °C, 97%).

2,2'-Bipyridyl (Sigma - Aldrich Chemical Company, mp = 70-73 °C, 99%).

Copper (I) bromide (Sigma - Aldrich Chemical Company, 98%).

t-Butyldimethyl silylchloride (Sigma - Aldrich Chemical Company, 97%).

Imidazole (Sigma - Aldrich Chemical Company, 99%).

Methanol (Saarchem, Pty Ltd), bp = 65 °C).

Tetrabutylammonium fluoride (Fluka, 1.0 M in THF).

3.1.2 Purification of Reagents

4-Hydroxybenzophenone: (Sigma - Aldrich Chemical Company, 98%) was recrystallized from a mixture of ethanol and water (80/20), mp = 133-136 °C.²¹⁰

Tetrahydrofuran: Tetrahydrofuran (THF, Saarchem, Pty Ltd) was freshly distilled from Na/benzophenone after stirring at room temperature for 24 hours. Distillation was conducted when the solution had a purple-blue color which is an indication of the dryness of the solvent and absence of reactive impurities. Sodium metal was added in excess to ensure the complete conversion of benzophenone to the benzophenone radical anion since traces of unreacted benzophenone would sublime upon distillation of THF.^{18,210}

Styrene: Styrene (Sigma - Aldrich Chemical Company, bp = 145-146 °C) was stirred over freshly ground calcium hydride for 12 hours, followed by vacuum distillation into a flask containing molecular sieves and purged with argon before use.²¹⁰

Methyl methacrylate: Methyl methacrylate (Sigma - Aldrich Chemical Company, bp = 100 °C) was stirred over freshly ground calcium hydride for 12 hours and then vacuum distilled into a flask containing molecular sieves and purged with argon before use.²¹⁰

3.1.3 Glassware

All glassware was oven dried at 120 °C for 24 hours prior to use. All reactions were carried out under dry argon atmosphere.

3.2 CHARACTERIZATION

3.2.1 Gas Chromatography (GC)

The percentage monomer conversion with time was determined by gas chromatography using a Shimadzu Gas Chromatograph 17A, equipped with a SPB-5 M column (30 m x 0.32 mm, 0.25 μm film) at a constant flow rate of 1.7 mL/min. The ramp temperature was set at 90 $^{\circ}\text{C}$ with a hold of 3 minutes, followed by an increase in temperature to 280 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$.

3.2.2 Size Exclusion Chromatography (SEC)

Size exclusion chromatography (SEC) was used for the determination of the number average molecular weights and molecular weight distributions of polymers. SEC analyses were conducted using a Waters Alliance SEC autosampler equipped with a Phenogel guard column and a Phenogel column (5 μm , 500 \AA pore size, 1K-150 K MW range, 300 x 7.8 mm) in series with Refractive Index and Dual Angle Laser Light Scattering Detectors. Polystyrene (Aldrich Chemical Company) and poly(methyl methacrylate) standards (Sigma - Aldrich Chemical Company) were used for the calibration of the dual angle laser light scattering detector of the SEC instrument, where applicable.

3.2.3 Thin Layer Chromatography (TLC)

Functionalized and unfunctionalized polymers as well as initiator derivatives were characterized by thin layer chromatography (TLC). TLC analyses were carried out on silica gel plates (Silica Gel 60 F₂₅₄) using toluene as mobile phase. The mobile phase was specifically chosen to provide maximum resolution for the separation of the samples into individual components.

3.2.4 Nuclear Magnetic Resonance Spectrometry (NMR)

^1H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz NMR spectrometer or a Varian 300 MHz NMR spectrometer. Spectra were acquired using deuterated chloroform as solvent. The chemical shifts for the ^{13}C and ^1H NMR are reported in ppm relative to the chloroform resonance at $\delta = 77.00$ ppm and 7.24 ppm, respectively. Polymer samples, with concentrations of 40 mg of polymer in 5 mL of CDCl_3 were prepared directly in an NMR tube prior to NMR analysis.

3.2.5 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were recorded on a Perkin Elmer 883 Infrared spectrophotometer or on a Digilab FTS-700 FTIR Spectrometer equipped with a UMA 600 ATR Microscope attachment and a germanium Crystal ATR at wave numbers from 4000 to 600 cm^{-1} . The solid samples were placed over the ATR crystal and maximum pressure applied using the slip-clutch mechanism.

3.2.6 Non - Aqueous Titrations

The number average molecular weights of the hydroxyl functionalized polymers were determined by non-aqueous titration measurements. The concentrations of hydroxyl end groups in the functionalized polymers were determined by the non-aqueous titrations of a 0.1 g polymer sample in a 1/1 (v/v) mixture of chloroform and glacial acetic acid with standardized perchloric acid 0.1 M in glacial acetic acid using methyl violet as an indicator.

3.2.7 Melting Point Determination

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

3.2.8 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.

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

3.3.1 Synthesis of Siloxyl Functionalized Polymers by ATRP using a Siloxyl Functionalized Initiator Precursor

3.3.1.1 Siloxyl Functionalized Initiator Precursor: Synthesis of 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene, (1).

The preparation of 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene, (**1**) was conducted according to the method outlined by Quirk and Zhu²⁰⁴, with modifications.

4-(t-Butyldimethylsiloxy)benzophenone: 4-Hydroxybenzophenone was recrystallized from ethanol-water solution (20/80 v/v), mp = 133 -136 °C, literature mp = 132-135 °C.²¹⁰ Under an argon atmosphere, pure 4-hydroxy-benzophenone (6.73 g, 32.54 mmol) in dry N,N-dimethylformamide (30 mL) was added to a 250 mL round bottom flask, followed by the addition of t-butyldimethylsilyl chloride (7 g, 45 mmol) and imidazole (10.5 g, 150 mmol). The resultant reaction mixture was heated at 45 °C for 4 hours. The product was extracted with 300mL of 5% NaHCO₃ and hexane (60 mL), followed by solvent removal using a rotary evaporator. The residue was purified by column

chromatography on silica gel using toluene as eluent to produce 5.86 g (58%) of 4-(t-butyltrimethylsilyloxy)benzophenone as a clear, viscous liquid:

TLC (SiO₂, toluene): R_f = 0.4; ¹H NMR (CDCl₃): δ 0.21 [s, 6H, Si-(CH₃)₂], 1.0 [s, 9H, Si-C-(CH₃)₃], 6.9-7.2 ppm (m, 9H, aromatic C-H); FTIR: 1656 cm⁻¹ (vs, C=O) and 1272 cm⁻¹ (vs, Si-CH₃).

1-(4-t-Butyltrimethylsilyloxyphenyl)-1-phenylethylene, (1): The siloxyl functionalized initiator precursor, 1-(4-t-butyltrimethylsilyloxyphenyl)-1-phenylethylene (**1**) was synthesized according to the procedure outlined by Quirk and Zhu.²⁰⁴ Under an argon atmosphere, methyltriphenylphosphonium bromide (10.06 g, 29.0 mmol) and dry THF (250 mL) was added to a 500 mL round bottom flask. Methylolithium (17.9 mL of a 1.4 M solution in diethyl ether, 29.0 mmol) was added to the reaction flask at 0 °C. The reaction mixture was stirred for two hours to form a phosphorus ylide. To the solution of the phosphorus ylide, a solution of 1-(4-t-butyltrimethylsilyloxyphenyl)benzophenone (7.91g, 21.0 mmol) in THF (100 mL) was added dropwise at 0 °C. The contents of the flask were then stirred for 12 hours at room temperature. The reaction was quenched by the addition of methanol (10 mL). The triphenylphosphine oxide, which precipitated from solution, was removed by filtration. The crude product was purified by silica gel column chromatography followed by vacuum distillation to yield 4.02 g (64%) of pure 1-(4-t-butyltrimethylsilyloxyphenyl)-1-phenylethylene, (**1**) as a clear liquid: TLC (SiO₂, toluene): R_f = 0.9; ¹H NMR (CDCl₃): δ 0.25 [s, 6H, Si-(CH₃)₂], 1.0 [s, 9H, Si-C-(CH₃)₃], 5.4 (d, 2H, C=CH₂), 6.9 - 7.2 ppm (m, 9H, aromatic C-H); ¹³C NMR (CDCl₃): δ -4.4 [Si-(CH₃)₂], 18.2 [Si-C-(CH₃)₃], 25.5 [Si-C-(CH₃)₃], 150 ppm (aromatics C-H); FTIR: 1654 cm⁻¹ (vs, C=O) and 1260 cm⁻¹ (vs, Si-CH₃).

3.3.1.2 Synthesis of α-Siloxyl Functionalized Polystyrene, (3):

A series of α -siloxy functionalized polystyrene derivatives, (**3**) were prepared using a new siloxy functionalized initiator adduct, (**2**) as initiator for the ATRP of styrene, in bulk or solution in the presence of CuBr/bpy or CuBr/PMDETA as catalyst systems.

In a typical procedure and under an argon atmosphere, copper (I) bromide (46 mg, 0.322 mmol), 2,2'-bipyridyl (151 mg, 0.966 mmol) was added to a dry Schlenk flask, followed by the successive addition of (1-bromoethyl)benzene (59 mg, 0.044 mL, 0.322 mmol), diphenyl ether (1 mL) and 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene (100 mg, 0.322 mmol). The heterogeneous mixture was degassed by three freeze-pump-thaw cycles. The mixture was then heated at 110 °C for one hour with stirring. Upon cooling to room temperature, freshly distilled styrene (1.818 g, 2 mL, 17.48 mmol) was added to the flask via a syringe and the reaction mixture was heated at 110 °C for 12 hours. After cooling, the reaction mixture was quenched with tetrahydrofuran (2 mL). The polymer was purified by passage through a short column of silica gel, using THF as eluent, to remove the catalyst/ligand impurities. The filtrate was then concentrated *in vacuo* and the polymer product was precipitated from THF into excess methanol, filtered and vacuum dried to afford α -siloxy functionalized polystyrene, (**3**) as a white solid: TLC: (SiO₂, toluene): R_f = 0.77; \overline{M}_n (SEC) = 4.9 x 10³; $\overline{M}_w / \overline{M}_n$ = 1.30; ¹H NMR (CDCl₃): δ 0.2 [m, 6H, Si-(CH₃)₂], 1.0 [m, 9H, SiC(CH₃)₃], 6.3 – 7.3 ppm [m, aromatic C-H]; ¹³C NMR (CDCl₃): δ 26.2 [SiC(CH₃)₃], 120 – 145 ppm [aromatic C=C]; FTIR: 1261 cm⁻¹ (Si-CH₃), 600 cm⁻¹ (C-Br).

The experimental data for the preparation of different α -siloxy functionalized polystyrene derivatives (**3**) is given in the following table:

Experimental Data for the Synthesis of α -Siloxyl Functionalized Polystyrene, (3) using 1-(4-t-Butyldimethylsiloxyphenyl)-1-phenylethylene, (1) as Siloxyl Functionalized Initiator Precursor:

| Sample | R-X | Catalyst system | Solvent | \overline{M}_n (th) (g/mol) | \overline{M}_n (SEC) (g/mol) | $\overline{M}_w / \overline{M}_n$ | I_{eff} |
|--------|-------|-----------------|---------|-------------------------------|--------------------------------|-----------------------------------|------------------|
| A | 1-BEB | CuBr/Bpy | - | 8.4×10^3 | 8.3×10^3 | 1.21 | 0.99 |
| B | 1-BEB | CuBr/Bpy | DPE | 5.6×10^3 | 4.9×10^3 | 1.30 | 0.98 |
| C | 1-BEB | CuBr/PMDETA | - | 5.7×10^3 | 5.9×10^3 | 1.27 | 0.97 |
| D | 1-BEB | CuBr/PMDETA | DPE | 5.7×10^3 | 6.5×10^3 | 1.19 | 0.98 |

3.3.1.3 Synthesis of α -Siloxyl Functionalized Poly(methyl methacrylate), (4):

The ATRP of methyl methacrylate was initiated by a new siloxyl substituted initiator adduct, (2) in bulk or solution in the presence of CuBr/2,2'-bipyridyl or CuBr/PMDETA as catalyst systems to afford α -siloxyl functionalized poly(methyl methacrylate), (4). In a typical procedure and under an argon atmosphere, copper (I) bromide (59 mg, 0.044 mL, 0.322 mmol), PMDETA (167 mg, 0.966 mmol) and (1-bromoethyl)benzene (59 mg, 0.044 mL, 0.322 mmol), 1-(4-t-butylsilyloxyphenyl)-1-phenylethylene (100 mg, 0.322 mmol) and xylene (2 mL) were added to a Schlenk flask equipped with a magnetic stirrer. The flask was sealed with rubber septa. The homogeneous mixture was degassed by three freeze-pump-thaw cycles. The mixture was stirred at 90 °C for 60 minutes. Upon cooling to room temperature, freshly distilled methyl methacrylate (1.896 g, 2 mL, 18.96 mmol) was added to the flask via a syringe. The flask was then placed in a thermostated oil bath and heated at 90 °C for 12 hours. After cooling, the sample was dissolved in THF (2 mL) and filtered through a short silica gel column to remove catalyst impurities. The filtrate was concentrated and the polymer product was precipitated from THF into methanol, filtered and vacuum dried to afford α -siloxyl functionalized poly(methyl methacrylate), (4): TLC: (SiO₂,

toluene): $R_f = 0.77$; \overline{M}_n (SEC) = 5.3×10^3 , $\overline{M}_w / \overline{M}_n = 1.41$; $^1\text{H NMR}$ (CDCl_3): δ 1.0 [s, 9H, $\text{SiC}(\underline{\text{C}}\text{H}_3)_3$], 3.5 [s, 3H, OCH_3], 7.0 – 7.3 ppm [m, aromatic C-H]; $^{13}\text{C NMR}$ (CDCl_3): δ 26.2 [$\text{SiC}(\underline{\text{C}}\text{H}_3)_3$], 176 – 178 ppm [aromatic C=C]; FTIR: 1270 cm^{-1} ($\text{Si}-\underline{\text{C}}\text{H}_3$), 1750 cm^{-1} (C=O), 3080 cm^{-1} (C-H), 1495 cm^{-1} (C-H).

The detailed experimental data for the synthesis of α -siloxy functionalized poly(methyl methacrylate), (**4**), is listed in the following table:

Experimental Data for the Synthesis of α -Siloxy Functionalized Poly(methyl methacrylate), (4**) using 1-(4-*t*-Butyldimethylsiloxyphenyl)-1-phenylethylene, (**1**) as Siloxy Functionalized Initiator Precursor:**

| Sample | R-X | Catalyst system | Solvent | \overline{M}_n (th) (g/mol) | \overline{M}_n (SEC) (g/mol) | $\overline{M}_w / \overline{M}_n$ | l_{eff} |
|--------|-------|-----------------|---------|-------------------------------|--------------------------------|-----------------------------------|------------------|
| A | 1-BEB | CuBr / Bpy | DPE | 5.8×10^3 | 5.7×10^3 | 1.30 | 0.98 |
| B | 1-BEB | CuBr/PMDETA | Xylene | 5.4×10^3 | 5.3×10^3 | 1.41 | 0.98 |

3.3.1.4 Synthesis of α -Hydroxyl Functionalized Polystyrene, (5**)**

The preparation of α -hydroxyl functionalized polystyrene, (**5**) by the hydrolysis of α -siloxy functionalized polystyrene, (**3**) was effected by the method outlined by Weisberg and coworkers,²¹¹ with modifications. In a typical procedure, tetrabutyl ammonium fluoride (3 mL, 1.72×10^{-4} mol) was added to α -siloxy functionalized polystyrene, (**3**) (1.45 g, \overline{M}_n (SEC) = 4.9×10^3 g/mol) in THF (10 mL) at room temperature. The reaction mixture was then heated to reflux for 24 hours. The reaction was monitored by thin layer chromatography (TLC) with toluene as eluent by observing the disappearance of α -siloxy functionalized polystyrene, (**3**) at $R_f = 0.9$ with the concomitant formation of the corresponding α -hydroxyl functionalized polystyrene, (**5**) at $R_f = 0$. The resulting mixture was concentrated *in vacuo* and the polymer product precipitated in methanol to afford 0.9 g of the

corresponding α -hydroxyl functionalized polystyrene, (**5**) as a white solid: TLC: (SiO₂, toluene): R_f = 0; ¹H NMR (CDCl₃): δ 3.7 [bs, 1H, O-H]; FTIR: 3443 cm⁻¹ (bs, 1H, O-H), \overline{M}_n (titr) = 5.0 x 10³ g/mol

3.3.2 Synthesis of Bis(siloxyl) Functionalized Polymers by ATRP using a Disiloxyl Functionalized Initiator Precursor

3.3.2.1 Disiloxyl Functionalized Initiator Precursor: Synthesis of 1,1-bis(4-t-butyl dimethylsiloxyl)ethylene, (**6**):

The synthesis of 1,1-bis(4-t-butyl dimethylsiloxyl)ethylene, (**6**) was performed according to the method outlined by Quirk and Wang,²⁰⁵ with modifications.

4,4'-Bis(4-t-butyl dimethylsiloxyl)benzophenone: Under an argon atmosphere, 4,4'-dihydroxybenzophenone (33.36 g, 155.87 mmol), N,N-dimethylformamide (30 mL), t-butyl dimethylsilyl chloride (21.8 g, 144.66 mmol) and imidazole (14 g, 65.04 mmol) were added to a 250 mL round bottom flask equipped with a reflux condenser and a magnetic stirrer bar. The mixture was heated at 40 °C for 3 hours. After the addition of hexane (120 mL), the solution was washed three times with 5% aqueous NaHCO₃ (3 x 10 mL), dried over anhydrous MgSO₄ and concentrated on a rotary evaporator. The residue was purified by SiO₂ column chromatography, using toluene as eluent to produce the crude product as a clear, viscous liquid, which solidified on standing. Recrystallization of the solid from ethanol gave 28.78 g (90%) of pure 4,4'-bis(4-t-butyl dimethylsiloxyl)benzophenone as white crystals: mp = 53-56 °C. TLC (SiO₂, toluene): R_f = 0.6; ¹H NMR (CDCl₃): δ 0.21 [s, 12H, 2 x Si-(CH₃)₂], 1.0 [s, 18H, 2 x Si-C-(CH₃)₃], 6.9 and 7.7 (d x d, 8H, C=CH₂); FTIR: 1654 cm⁻¹ (vs, C=O) and 1260 cm⁻¹ (vs, Si-CH₃); FTIR: 1275 cm⁻¹ (vs, Si-(CH₃), 1656 cm⁻¹ (vs, C=O).

1,1-Bis-(4-t-butyldimethylsiloxyphenyl)ethylene, (6): Under an argon atmosphere, methyllithium (29.1 mL of a 1.4 M solution in diphenyl ether, 43.2 mmol) was added to methyltriphenylphosphonium bromide (15.32 g, 43.2 mmol) in dry THF (250 mL) in a 500 mL round bottom flask. The reaction mixture was stirred at room temperature for 2 hours. A solution of 1,1-bis(4-t-butyldimethylsiloxyphenyl)benzophenone (18.04 g, 40,75 mmol) in THF (100 mL) was then added dropwise at 0 °C to the resultant phosphorus ylide. The reaction mixture was stirred at room temperature for 12 hours. The reaction was terminated by the addition of acetone (10 mL). The triphenylphosphine oxide, which precipitated from solution, was removed by filtration. After solvent removal *in vacuo*, the clear residue was extracted with petroleum ether (1 x 120 mL). After removal of the petroleum ether *in vacuo*, the crude product was obtained as a white solid. Recrystallization of the solid three times from ethanol gave 13.01 g (73%) of pure 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene (**6**) as clear, colorless crystals: mp = 55.9-59.4 °C; TLC (SiO₂, toluene): R_f = 0.95; ¹H NMR (CDCl₃): δ 0.1 [s, 12H, 2 x Si-(CH₃)₂], 0.8 [s, 18H, 2 x Si-C-(CH₃)₃], 5.2 (s, 2H, C=CH₂), 6.6 - 7.0 ppm (d x d, 8H, aromatic C-H); ¹³C NMR (CDCl₃): δ 25.5 [Si-C-(CH₃)₃], 120 – 148 ppm (aromatics C-H); FTIR: 1654 cm⁻¹ (vs, C=O) and 1260 cm⁻¹ (vs, Si-CH₃).

3.3.2.2 Synthesis of α-Bis(siloxy) Functionalized Polystyrene, (8):

In a typical procedure and under argon atmosphere, copper (I) bromide (0.033 g, 0.227 mmol), PMDETA (0.118 g, 0.681 mmol), (1-bromoethyl)benzene (0.042 g, 0.031 mL, 0.227 mmol), 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene (0.1 g, 0.227 mmol) and diphenyl ether (1.5 mL) were added to a Schlenk flask equipped with a magnetic stirrer bar. The flask was sealed with rubber septa and degassed by three freeze-pump-thaw cycles. Under argon atmosphere, the mixture was then stirred at 110 °C for one hour. Freshly distilled, deoxygenated

styrene (2 g, 2.2 mL, 19.23 mmol) was then added into the flask via a syringe. The reaction flask was immersed in an oil bath and heated to 110 °C for 12 hours. After cooling, the reaction mixture was quenched with THF (2 mL). The resulting polymer product was purified by passage through a short column of silica gel to remove catalyst impurities. The filtrate was then concentrated *in vacuo* and the polymer product was precipitated from THF into excess methanol. The polymer product was filtered and vacuum dried to afford α -bis(siloxy) functionalized polystyrene (**8**), as a white solid: TLC: (SiO₂, toluene): R_f = 0.86; \overline{M}_n (SEC) = 8.0 x 10³ g/mol, $\overline{M}_w / \overline{M}_n$ = 1.16; ¹H NMR (CDCl₃): δ = 0.3 [s, 12H, 2 x Si-(CH₃)₂], 1.2 [s, 18H, 2 x SiC(CH₃)₃], 6.5 – 7.5 ppm [bs, aromatic C-H]; ¹³C NMR (CDCl₃): δ 26.2 [SiC(CH₃)₃]; FTIR: 1265 cm⁻¹ (Si-CH₃).

The following table depicts the experimental data for the preparation of the different α -bis(siloxy) functionalized polystyrene, (**8**) derivatives:

Experimental Data for the Synthesis of α -Bis(siloxy) Functionalized Polystyrene, (8**) using 1,1-Bis-(4-t-butyl dimethylsiloxy-phenyl)ethylene, (**6**) as the Disiloxy Functionalized Initiating Precursor:**

| Sample | Initiator | Catalyst system | Solvent | \overline{M}_n (theo) (g/mol) | \overline{M}_n (SEC) (g/mol) | $\overline{M}_w / \overline{M}_n$ | I_{eff} |
|--------|-----------|-----------------|---------|---------------------------------|--------------------------------|-----------------------------------|------------------|
| A | 1-BEB | CuBr/bpy | DPE | 6.0 x 10 ³ | 6.1 x 10 ³ | 1.18 | 0.98 |
| B | 1-BEB | CuBr/ PMDETA | DPE | 8.8 x 10 ³ | 8.0 x 10 ³ | 1.16 | 0.89 |

3.3.2.3 Synthesis of α -Bis(siloxy) Functionalized Poly(methyl methacrylate), (9**).**

In a general procedure and under argon atmosphere, copper (I) bromide (0.032 g, 0.227 mmol), 2,2'-bipyridyl (0.106 g, 0.681 mmol), (1-bromoethyl)benzene

(0.042 g, 0.031 mL, 0.227 mmol), xylene (2 mL) and 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene (0.1 g, 0.227 mmol) were added in a Schlenk tube equipped with a magnetic stirrer bar. The flask was sealed with rubber septa and degassed by three freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was then heated in an oil bath at 90 °C. After an hour, the contents of the flask were cooled at room temperature and methyl methacrylate (1.1 g, 1.2 mL, 10.99 mmol) was added into the Schlenk flask. Subsequently, the flask was heated at 90 °C in an oil bath for 12 hours. After cooling, the sample was dissolved in THF (1 mL) and filtered through a short silica gel column to remove catalyst impurities. The filtrate was then concentrated and the polymer product was precipitated from THF into excess methanol, filtered and vacuum dried to afford α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**) as a white solid: TLC: (SiO₂, toluene): R_f = 0.77; \overline{M}_n (SEC) = 5.5 × 10³ g/mol, $\overline{M}_w / \overline{M}_n$ = 1.07; ¹H NMR (CDCl₃): δ 0.05 [m, 12H, 2 x Si-(CH₃)₂], 0.8 [s, 18H, 2 x SiC(CH₃)₃], 3.4 [s, 3H, OCH₃], 6.5 – 7.1 ppm [bs, aromatic C-H]; ¹³C NMR (CDCl₃): δ 26.2 [SiC(CH₃)₃], 176 – 178 ppm [aromatic C=C]; FTIR: 1270 cm⁻¹ (Si-CH₃), 1750 cm⁻¹ (C=O), 2800-3000 cm⁻¹ (C-H).

The following table depicts the experimental data for the preparation of the different α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**) derivatives:

Experimental Data for the Synthesis of α -Bis(siloxy) Functionalized Poly(methyl methacrylate), (9**) using 1,1-Bis-(4-t-butyldimethylsiloxyphenyl)ethylene, (**6**) as the Disiloxy Functionalized Initiator Precursor:**

| Sample | Initiator | Catalyst system | Solvent | \overline{M}_n (theo) (g/mol) | \overline{M}_n (SEC) (g/mol) | $\overline{M}_w / \overline{M}_n$ | I _{eff} |
|--------|-----------|-----------------|---------|------------------------------------|-----------------------------------|-----------------------------------|------------------|
| | | | | | | | |

| | | | | | | | |
|---|-------|--------------|--------|---------------------|--------------------|------|------|
| A | 1-BEB | CuBr/bpy | xylene | 10.35×10^3 | 7.78×10^3 | 1.18 | 0.98 |
| B | 1-BEB | CuBr/ PMDETA | DPE | 10.87×10^3 | 5.5×10^3 | 1.16 | 0.89 |

3.3.2.4 Synthesis of α -Bis(hydroxyl) Functionalized Polystyrene, (10):

The conversion of α -bis(siloxy) functionalized polystyrene, (8) to the corresponding α -bis(hydroxyl) functionalized polystyrene, (10) was effected by a standard acid catalysed hydrolysis reaction as outlined by Quirk and Wang²⁰⁵ In a typical procedure, concentrated hydrochloric acid (2 mL) was added to α -bis(siloxy) functionalized polystyrene, (8) (1.5 g, \overline{M}_n (SEC) = 8×10^3 g/mol) in THF (10 mL). The reaction mixture was heated to reflux for 12 hours. The reaction was monitored by thin layer chromatography (TLC) using toluene as eluent to determine the extent of consumption of α -bis(siloxy) functionalized polystyrene, (8) with $R_f = 0.86$. The resulting mixture was concentrated *in vacuo*. The polymer product was precipitated from THF into methanol, filtered and vacuum and dried to afford 1.2 g of the corresponding α -bis(hydroxyl) functionalized polystyrene, (10) as a white solid: TLC (SiO₂, toluene): $R_f = 0$; ¹H NMR (CDCl₃): $\delta = 3.7$ [s, 1H, O-H]; FTIR: 3500 cm⁻¹ (O-H), 1263 cm⁻¹ (s, Si-CH₃); \overline{M}_n (titr) = 8.1×10^3 g/mol)

3.4 ATOM TRANSFER RADICAL POLYMERIZATION: POLYMERIZATION KINETIC STUDIES

A series of polymerization kinetic experiments for the preparation of α -siloxy and α -bis(siloxy) functionalized polystyrene and poly(methyl methacrylate) derivatives by ATRP methods were conducted at different initial concentrations of

the initiator system with $[M]_0/[I]_0$ ratios of 50:1, 100:1 and 200:1 in the presence of different catalyst systems such as CuBr/bpy or CuBr/PMDETA.

For a typical polymerization kinetic experiment, the synthesis of α -siloxyl functionalized polystyrene, **(3)** catalyzed by CuBr/bpy, is outlined as follows: A Schlenk tube was charged with copper (I) bromide (0.25 g, 1.745 mmol), 2,2'-bipyridyl (0.817 g, 5.235 mmol), (1-bromoethyl)benzene (0.323 g, 0.238 mL, 1.745 mmol), 1-(4-t-butyl dimethyl siloxyphenyl)-1-phenylethylene (0.542 g, 1.745 mmol) and diphenyl ether (10 mL). The heterogeneous mixture was degassed by three freeze-pump-thaw cycles. The mixture was stirred at 110 °C for one hour. The reaction mixture was then cooled to room temperature and freshly distilled styrene (9.09 g, 10 mL, 87.4 mmol) was added to the flask via a syringe. An aliquot (1 mL) of the sample was withdrawn from the reaction vessel using a syringe and dissolved in THF (9 mL). The initial styrene concentration was measured by gas chromatography at time, $t = 0$. After purging the mixture with argon, the reaction vessel was immersed in an oil bath at 110 °C. At different time intervals, different aliquots (1 mL) were taken from the solution and dissolved in THF (9 mL) to determine the percentage monomer conversion with time by gas chromatographic analysis.

For the different polymerization kinetic experiments, the experimental data for the preparation of the different α -siloxyl and α -bis(siloxyl) functionalized polystyrene and poly(methyl methacrylate) derivatives in the presence of CuBr/bpy or CuBr/PMDETA catalyst system is given in the following tables:

Synthesis of α -Siloxyl Functionalized Polystyrene, (3).

| | | | | | | |
|---------------|---------|-------|------|-----|------------|-----|
| $[M]_0/[I]_0$ | Styrene | 1-BEB | CuBr | bpy | (1) | DPE |
|---------------|---------|-------|------|-----|------------|-----|

| | | | | | | |
|-------|---------------|-------------------|------------|------------|------------|--------------|
| 50:1 | 9.09 g, 10 mL | 0.323 g, 0.238 mL | 0.25 g | 0.818 g | 0.542 g | 9.72 g, 9 mL |
| | 87.4 mmol | 1.745 mmol | 1.745 mmol | 5.235 mmol | 1.745 mmol | 57.11 mmol |
| 100:1 | 9.09 g, 10 mL | 0.162 g, 0.119 mL | 0.125 g | 0.4085 g | 0.271 g | 9.72 g, 9 mL |
| | 87.4 mmol | 0.873 mmol | 0.873 mmol | 2.618 mmol | 0.873 mmol | 57.11 mmol |
| 200:1 | 9.09 g, 10 mL | 0.081 g, 0.059 mL | 0.063 g | 0.202 g | 0.136 g | 9.72 g, 9 mL |
| | 87.4 mmol | 0.436 mmol | 0.436 mmol | 1.309 mmol | 0.436 mmol | 57.11 mmol |

Synthesis of α -Siloxyl Functionalized Polystyrene, (3).

| [M] ₀ /[I] ₀ | Styrene | 1-BEB | CuBr | PMDETA | (1) | DPE |
|------------------------------------|---------------|-------------------|------------|------------|------------|--------------|
| 50:1 | 9.09 g, 10 mL | 0.323 g, 0.238 mL | 0.25 g | 0.908 g | 0.542 g | 9.72 g, 9 mL |
| | 87.4 mmol | 1.745 mmol | 1.745 mmol | 5.235 mmol | 1.745 mmol | 57.11 mmol |
| 100:1 | 9.09 g, 10 mL | 0.162 g, 0.119 mL | 0.125 g | 0.454 g | 0.271 g | 9.72 g, 9 mL |
| | 87.4 mmol | 0.873 mmol | 0.873 mmol | 2.618 mmol | 0.873 mmol | 57.11 mmol |
| 200:1 | 9.09 g, 10 mL | 0.081 g, 0.059 mL | 0.063 g | 0.227 g | 0.136 g | 9.72 g, 9 mL |
| | 87.4 mmol | 0.436 mmol | 0.436 mmol | 1.309 mmol | 0.436 mmol | 57.11 mmol |

Synthesis of α -Siloxyl Functionalized Poly(methyl methacrylate), (4).

| [M] ₀ /[I] ₀ | MMA | 1-BEB | CuBr | bpy | | DPE |
|------------------------------------|-----|-------|------|-----|--|-----|
| | | | | | | |

| | | | | | (1) | |
|-------|----------------------------|---------------------------------|-----------------------|-----------------------|-----------------------|-------------------------------|
| 50:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.21 g, 0.154 mL 1.610 mmol | 0.230 g 1.61 mmol | 0.754 g 4.830 mmol | 0.5 g 1.610 mmol | 6.48 g, 6.0 mL, 38.07 mmol |
| 100:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.11 g, 0.077 mL 0.805 mmol | 0.115 g 0.805 mmol | 0.419 g 2.415 mmol | 0.25 g 0.805 mmol | 6.48 g, 6.0 mL, 38.07 mmol |
| 200:1 | 5.9 g, 10 mL 56.7 mmol | 0.051 g, 0.039 mL 0.403 mmol | 0.058 g 0.403 mmol | 0.209 g 1.208 mmol | 0.125 g 0.403 mmol | 6.48 g, 6.0 mL, 38.07 mmol |

Synthesis of α -Siloxyl Functionalized Poly(methyl methacrylate), (4).

| [M] ₀ /[I] ₀ | MMA | 1-BEB | CuBr | PMDETA | (1) | DPE |
|------------------------------------|----------------------------|---------------------------------|-----------------------|------------------------|-----------------------|-------------------------------|
| 50:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.21 g, 0.154 mL 1.610 mmol | 0.230 g, 1.61 mmol | 0.837 g, 4.830 mmol | 0.5 g 1.610 mmol | 6.48 g, 6.0 mL, 38.07 mmol |
| 100:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.11 g, 0.077 mL 0.805 mmol | 0.115 g 0.805 mmol | 0.419 g 2.415 mmol | 0.25 g 0.805 mmol | 6.48 g, 6.0 mL, 38.07 mmol |
| 200:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.051 g, 0.039 mL 0.403 mmol | 0.058 g 0.403 mmol | 0.209 g, 1.208 mmol | 0.125 g 0.403 mmol | 6.48 g, 6.0 mL, 38.07 mmol |

Synthesis of α -Bis(siloxyl) Functionalized Polystyrene, (8).

| [M] ₀ /[I] ₀ | Styrene | 1-BEB | CuBr | bpy | (6) | DPE |
|------------------------------------|---------------|------------------|---------|---------|-------|-----------------|
| 50:1 | 5.9 g, 6.5 mL | 0.21 g, 0.154 mL | 0.163 g | 0.532 g | 0.5 g | 6.48 g, 6.0 mL, |

| | | | | | | |
|-------|----------------------------|---------------------------------|-----------------------|-----------------------|-----------------------|-------------------------------|
| | 56.7 mmol | 1.135 mmol | 1.135 mmol | 3.405 mmol | 1.135 mmol | 38.07 mmol |
| 100:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.105 g, 0.077 mL 0.568 mmol | 0.081 g 0.568 mmol | 0.266 g 2.415 mmol | 0.25 g 0.568 mmol | 6.48 g, 6.0 mL, 38.07 mmol |
| 200:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.051 g, 0.039 mL 0.284 mmol | 0.041 g 0.284 mmol | 0.133 g 1.208 mmol | 0.125 g 0.284 mmol | 6.48 g, 6.0 mL, 38.07 mmol |

Synthesis of α -Bis(siloxy) Functionalized Polystyrene, (8).

| [M] ₀ /[I] ₀ | Styrene | 1-BEB | CuBr | PMDETA | (6) | DPE |
|------------------------------------|----------------------------|---------------------------------|-----------------------|-----------------------|-----------------------|-------------------------------|
| 50:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.21 g, 0.154 mL 1.135 mmol | 0.163 g 1.135 mmol | 0.590 g 3.405 mmol | 0.5 g 1.135 mmol | 6.48 g, 6.0 mL, 38.07 mmol |
| 100:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.105 g, 0.077 mL 0.568 mmol | 0.081 g 0.568 mmol | 0.295 g 2.415 mmol | 0.25 g 0.568 mmol | 6.48 g, 6.0 mL, 38.07 mmol |
| 200:1 | 5.9 g, 6.5 mL 56.7 mmol | 0.051 g, 0.039 mL 0.284 mmol | 0.041 g 0.284 mmol | 0.148 g 1.208 mmol | 0.125 g 0.284 mmol | 6.48 g, 6.0 mL, 38.07 mmol |

Synthesis of α -Bis(siloxy) Functionalized Poly(methyl methacrylate), (9).

| [M] ₀ /[I] ₀ | MMA | 1-BEB | CuBr | bpy | (6) | DPE |
|------------------------------------|-----------------------------|--------------------------------|-----------------------|------------------------|-----------------------|----------------------------|
| 50:1 | 6.363 g, 7 mL 63.55 mmol | 0.171 g, 0.126 mL 0.924 mol | 0.133 g 0.924 mmol | 0.397 g, 2.772 mmol | 0.407 g 0.924 mmol | 7.56 g, 7 mL 44.48 mmol |
| 100:1 | 6.363 g, 7 mL | 0.086 g, 0.063 mL | 0.067 g | 0.199 g | 0.204 g | 7.56 g, 7 mL |

| | | | | | | |
|-------|-----------------------------|---------------------------------|-----------------------|-----------------------|----------------------|----------------------------|
| | 63.55 mmol | 0.655 mmol | 0.462 mmol | 1.386 mmol | 0.462 mmol | 44.48 mmol |
| 200:1 | 6.363 g, 7 mL 63.55 mmol | 0.043 g, 0.032 mL 0.328 mmol | 0.034 g 0.231 mmol | 0.108 g 0.693 mmol | 0.102 g 0.231mmol | 7.56 g, 7 mL 44.48 mmol |

Synthesis of α -Bis(siloxy) Functionalized Poly(methyl methacrylate), (9).

| [M] ₀ /[I] ₀ | MMA | 1-BEB | CuBr | PMDETA | (6) | DPE |
|------------------------------------|-----------------------------|---------------------------------|-----------------------|------------------------|-----------------------|----------------------------|
| 50:1 | 6.363 g, 7 mL 63.55 mmol | 0.171 g, 0.126 mL 0.924 mol | 0.133 g 0.924 mmol | 0.480 g, 2.772 mmol | 0.407 g 0.924 mmol | 7.56 g, 7 mL 44.48 mmol |
| 100:1 | 6.363 g, 7 mL 63.55 mmol | 0.086 g, 0.063 mL 0.462 mmol | 0.067 g 0.462 mmol | 0.240 g 1.386 mmol | 0.204 g 0.462 mmol | 7.56 g, 7 mL 44.48 mmol |
| 200:1 | 6.363 g, 7 mL 63.55 mmol | 0.043 g, 0.032 mL 0.231mmol | 0.034 g 0.231mmol | 0.120 g 0.693 mmol | 0.102 g 0.231mmol | 7.56 g, 7 mL 44.48 mmol |

CHAPTER 4

RESULTS AND DISCUSSION

Atom transfer radical polymerization (ATRP) is one of the most successful methods for the controlled polymerization of vinylic monomers such as styrene, (meth)acrylates and acrylonitrile yielding polymers with predictable degrees of polymerization, narrow molecular weight distributions, regiospecific functionalization and microstructures.¹⁸⁶ The success of the ATRP method is dependent on the establishment of equilibrium between the active and dormant centres during the radical polymerization of vinyl monomers. The initiation

process involves a reversible homolytic cleavage of an atom, or group from an initiator molecule, such as (1-phenylethyl)chloride which is catalyzed by a transition metal complex, such as copper (I) bromide/2,2'-bipyridyl, to afford low concentrations of a stable free radical for subsequent monomer addition reactions. Successive monomer insertion into the carbon-halogen bond at the propagating chain-end generates the resultant polymer chain.⁹⁶

The use of functionalized initiators in ATRP reactions is a useful method to prepare functionalized polymers with the functional group introduced at the α -terminus of the polymer chain. A variety of functionalized initiators with functional groups such as the hydroxyl, epoxy, aromatic carboxyl, tertiary amine and primary amine groups were successfully employed in the initiation of styrene and methyl methacrylate polymerization by ATRP methods.^{96,108} In particular, the use of functionalized 1,1-diphenylethylene derivatives as initiator precursors in ATRP reactions provides an efficient method for the preparation of functionalized polymers with the functional group introduced quantitatively at the alpha terminus of the polymer chain. Summers and coworkers¹⁷ reported the synthesis of tertiary amine functionalized polystyrene by using the adduct of (1-bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene as an amine functionalized initiator for the polymerization of styrene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system. Tertiary amine functionalized polystyrene derivatives with predictable number average molecular weights ($\overline{M}_n = 1.6 \times 10^3 - 4.4 \times 10^3$ g/mol) and narrow molecular weight distributions ($\overline{M}_w / \overline{M}_n = 1.09 - 1.3$) with controlled chain end functionality were obtained.

The present study focused on the synthesis of α -siloxyl and α -bis(siloxyl) functionalized polymers by the ATRP of styrene and methyl methacrylate using siloxyl functionalized 1,1-diphenylethylenes as precursor initiator compounds. By employing a new siloxyl functionalized initiator adduct, prepared *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-t-butyl dimethylsiloxylphenyl)-1-

phenylethylene, for the ATRP of styrene or methyl methacrylate afforded the corresponding α -siloxyl functionalized polymers. Similarly, well defined α -bis(siloxyl) functionalized polymers were prepared by using a new disiloxyl functionalized initiator adduct for styrene and methyl methacrylate polymerization by ATRP methods. The disiloxyl functionalized initiator adduct was generated *in situ* by the reaction of (1-bromoethyl)benzene with 1,1-bis(4-t-butyl dimethylsiloxyphenyl)ethylene in the presence of CuBr/bpy or CuBr/PMDETA catalyst systems. The different siloxyl functionalized polymers were converted to the corresponding hydroxyl functionalized polymers by post polymerization chain end modification reactions which involved the acid catalyzed hydrolysis of the siloxyl chain end groups to the hydroxyl groups.

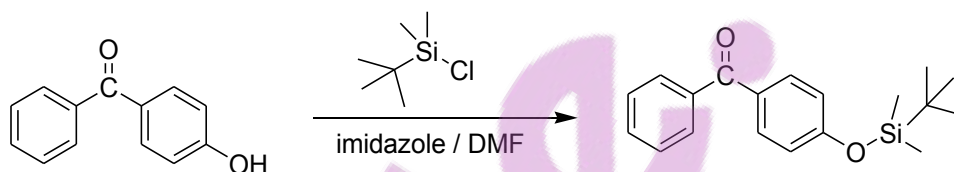
4.1 ATOM TRANSFER RADICAL POLYMERIZATION: SYNTHESIS OF SILOXYL CHAIN END FUNCTIONALIZED POLYMERS.

4.1.1 Siloxyl Functionalized Initiator Precursor: Synthesis of 1-(4-t-butyl dimethylsiloxyphenyl)-1-phenylethylene, (1)

Recently, Summers and coworkers^{17,18} have extended the application of 1,1-diphenylethylene chemistry to free radical polymerization methods, by using substituted 1,1-diphenylethylene derivatives as functionalized initiator precursors for the synthesis of chain end functionalized polymers in atom transfer radical polymerization reactions.

The siloxyl functionalized initiator precursor, 1-(4-t-butyl dimethylsiloxyphenyl)-1-phenylethylene, (**1**) was synthesized according to the procedure as outlined by Quirk and Zhu²⁰⁴ as follows:

4-(t-Butyldimethylsiloxy)benzophenone: The intermediate compound, 4-(t-butyl dimethylsiloxy)benzophenone was prepared by the reaction of 4-hydroxybenzophenone with t-butyl dimethylsilyl chloride in the presence of N,N-dimethylformamide for 4 hours at 45 °C. After column chromatographic analysis, 5.86 g (58%) of 4-(t-butyl dimethylsiloxy)benzophenone was isolated as a clear, viscous liquid.

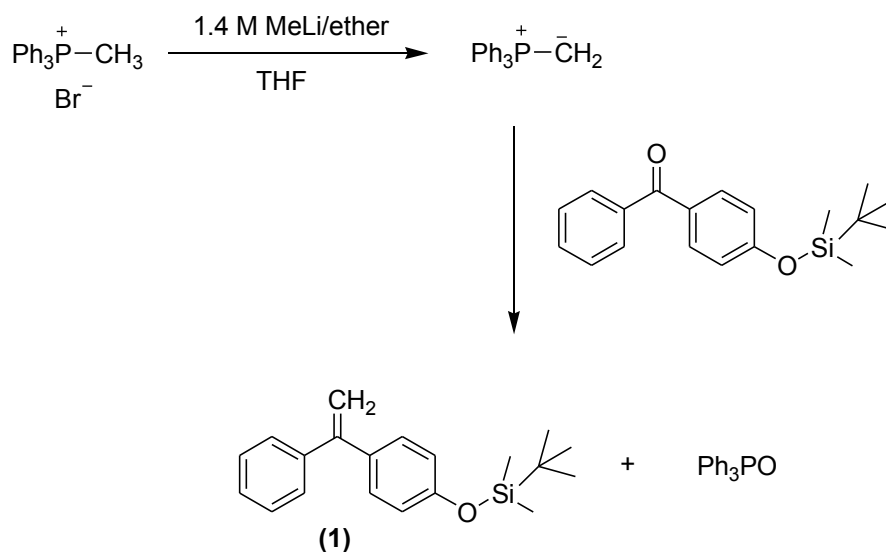


Thin layer chromatography of the product using toluene as eluent produced only one spot on the chromatogram ($R_f = 0.4$, toluene).

The ¹H NMR spectrum (Figure 1) of 4-(t-butyl dimethylsiloxy)benzophenone exhibits characteristic peaks at $\delta = 0.21$ and 1.0 ppm, due to the proton resonances of the methyl groups in the Si-(CH₃)₂ and Si-C(CH₃)₃ groups, respectively. The multiplet between 6.9-7.8 ppm is attributed to the resonances of the aromatic protons of the phenyl rings.

The FTIR spectrum (Figure 2) of 4-(t-butyl dimethylsiloxy)benzophenone shows a very strong absorption band at 1656 cm⁻¹, due to the stretching band vibration of the C=O group. In addition, the observed absorption band at 1270 cm⁻¹, is due to Si-C stretching vibrations.

1-(4-t-Butyldimethylsiloxyphenyl)-1-phenylethylene, (1): The synthetic pathway for the preparation of 1-(4-t-butylidimethylsiloxyphenyl)-1-phenylethylene, (**1**) involved the Wittig reaction using 1-(4-t-butylidimethylsiloxy)-benzophenone as a precursor. Treatment of 1-(4-t-butylidimethylsiloxy)-benzophenone with a phosphorus ylide, generated *in situ* from the reaction of methyllithium with methyltriphenylphosphonium bromide in freshly distilled THF for 12 hours at room temperature, produced a yellow intermediate product. The reaction was quenched by the addition of methanol. The triphenylphosphine oxide, which precipitated from solution, was removed by filtration. After purification of the crude residue by column chromatography on silica gel using toluene as eluent, 4.02 g (64%) of 1-(4-t-butylidimethylsiloxyphenyl)-1-phenylethylene, (**1**), was obtained as a clear viscous liquid:



The TLC analysis of 1-(4-t-butylidimethylsiloxyphenyl)-1-phenylethylene, (**1**) with toluene as eluent ($R_f = 0.9$) shows only one spot on the chromatogram, indicating the absence of any precursor compound and the complete conversion of the carbonyl group to the alkene group via the Wittig reaction.

Figure 3 shows the ^1H NMR spectrum of 1-(4-t-butyltrimethylsilyloxyphenyl)-1-phenylethylene, (**1**) with the following characteristic peaks: a singlet at 0.25 ppm, attributed to the resonances of the protons of the $[\text{Si}-\text{CH}_3]$ group; a singlet at 1.1 ppm, assigned to the resonances of $[\text{Si}-\text{C}(\text{CH}_3)_3]$ protons; a doublet at 5.4 ppm, which corresponds to the resonances of the vinyl protons, $\text{C}=\text{CH}_2$ and a multiplet between 6.9-7.9 ppm, attributed to the resonances of the aromatic protons of the phenyl rings.

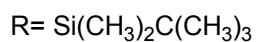
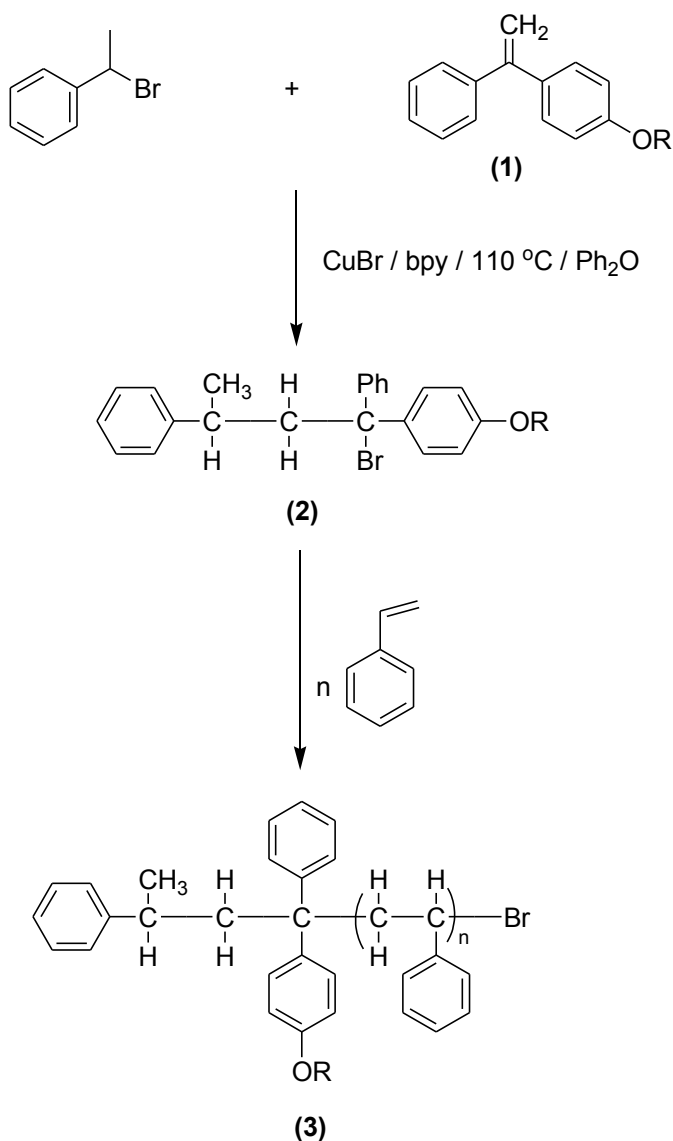
The ^{13}C NMR spectrum (Figure 4) of 1-(4-t-butyltrimethylsilyloxyphenyl)-1-phenylethylene, (**1**) exhibits peaks at -4.4 and 25.5 ppm, which is attributed to the resonances of the methyl carbons of the $[\text{Si}-\text{CH}_3]$ and $[\text{Si}-\text{C}(\text{CH}_3)_3]$ groups, respectively. The peak at 18.2 ppm is due to the resonance of the tertiary carbon in the $[\text{Si}-\text{C}(\text{CH}_3)_3]$ group.

The FTIR spectrum of 1-(4-t-butyltrimethylsilyloxyphenyl)-1-phenylethylene, (**1**) is depicted in Figure 5. The absence of a strong $\text{C}=\text{O}$ absorption band at 1654 cm^{-1} , indicates the complete conversion of the $\text{C}=\text{O}$ group to the $\text{C}=\text{CH}_2$ group. In addition, the absence of the O-H stretching frequency at 3228 cm^{-1} , coupled with the presence of an absorption band at 1260 cm^{-1} due to the Si-CH₃ stretching mode, indicates the retention of the siloxyl group during the Wittig reaction.

4.1.2 Synthesis of α -Siloxyl Functionalized Polystyrene, (**3**).

The ATRP of styrene using a new siloxyl functionalized initiator adduct, (**2**) in the presence of $\text{CuBr}/2,2'$ -bipyridyl as catalyst, produces α -siloxyl functionalized polystyrene, (**3**) in quantitative yields. The siloxyl functionalized initiator adduct is generated *in situ* by the reaction 1-(4-t-butyltrimethylsilyloxyphenyl)-1-phenylethylene, (**1**) with (1-bromoethyl)benzene in the presence of the $\text{CuBr}/2,2'$ -bipyridyl catalyst system in diphenyl ether at $110\text{ }^\circ\text{C}$. After 12 hours, the

polymerization reaction was quenched with THF and the reaction mixture was passed through a short 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 afford α -siloxy functionalized polystyrene, **(3)** as a white solid. The following pathway outlines the synthetic strategy for the preparation of α -siloxy functionalized polystyrene, **(3)**:



Thin layer chromatographic analysis of α -siloxy functionalized polystyrene, **(3)**

($R_f = 0.77$, toluene) shows one spot on the chromatogram, which corresponds to the absence of any unfunctionalized base polystyrene ($R_f = 0.99$, toluene), indicating the formation of functionalized polymer in quantitative yields.

Figure 6 shows a monomodal size exclusion chromatogram of α -siloxy functionalized polystyrene, (**3**), which corresponds with a number average molecular weight of 4.9×10^3 g/mol and a molecular weight distribution value of $\overline{M_w} / \overline{M_n} = 1.30$. The number average molecular weight value obtained by SEC analysis is in good agreement with the $\overline{M_n}$ (theory) = 5.6×10^3 g/mol as determined from the stoichiometry of the polymerization reaction.

The ^1H NMR spectrum (Figure 7) of α -siloxy functionalized polystyrene, (**3**), exhibits characteristic peaks at $\delta = 0.1$ ppm and 0.9 ppm, due to the proton resonances of the $\text{Si}-(\text{CH}_3)_2$ and $\text{Si}-\text{C}(\text{CH}_3)_3$ groups, respectively.

The ^{13}C NMR spectrum (Figure 8) of α -siloxy functionalized polystyrene, (**3**), exhibits a peak at $\delta = 26.2$ ppm, characteristic of the resonances of the methyl carbons of the $[\text{Si}-\text{C}(\text{CH}_3)_3]$ group. The presence of peaks at $\delta = 120$ -145 ppm, due to aromatic $\text{C}=\text{C}$ resonances,

The FTIR spectrum (Figure 9) of α -siloxy functionalized polystyrene, (**3**) shows the presence of an absorption band at 1261 cm^{-1} , due to $\text{Si}-\text{C}$ stretching vibration of the $\text{Si}-\text{CH}_3$ group. Furthermore, the strong absorption band at 600 cm^{-1} , corresponds to the $\text{C}-\text{Br}$ bond at the omega end of the polymer chain.

The spectroscopic and chromatographic data is consistent with the structure of α -siloxy functionalized polystyrene, (**3**). The initiation of the polymerization of styrene by the siloxy functionalized initiator adduct (**2**), formed by the *in situ* reaction of 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene, (**1**) with (1-bromoethyl)benzene in the presence of CuBr/bpy as catalyst, produces the corresponding well defined α -siloxy functionalized polystyrene, (**3**) in high yields.

4.1.3 Synthesis of α -Siloxyl Functionalized Poly(methyl methacrylate), (**4**).

Well defined α -siloxyl functionalized poly(methyl methacrylate), (**4**) was prepared using siloxyl functionalized initiator adduct (**2**) as initiator for the polymerization of methyl methacrylate by ATRP methods. The siloxyl functionalized initiator adduct (**2**) was prepared *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-t-butyl dimethylsiloxylphenyl)-1-phenylethylene, (**1**) in the presence of copper (I) bromide/PMDTA in xylene at 90 °C. After 12 hours, the polymerization reaction was quenched with THF and the reaction mixture was passed through a short silica gel column to remove catalyst impurities. The polymer product was purified by precipitation from THF into excess methanol, filtered and vacuum dried to afford α -siloxyl functionalized poly(methyl methacrylate), (**4**) as a white solid according to the following pathway:

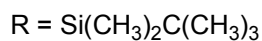
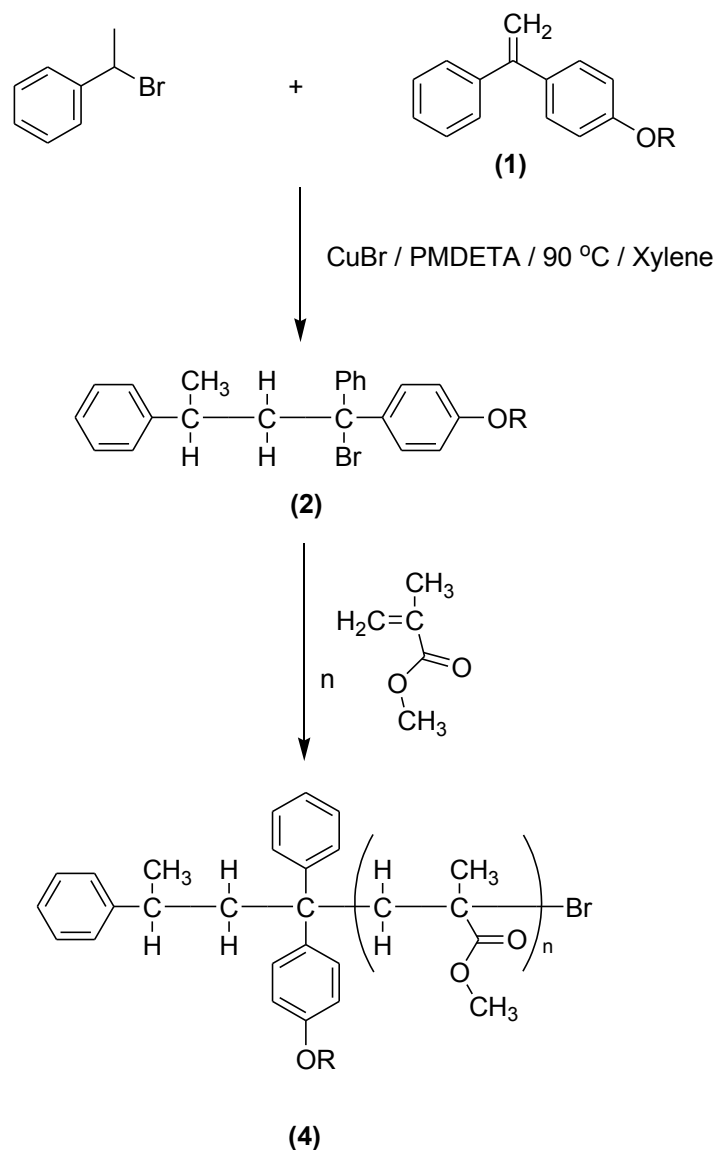


Figure 10 shows a monomodal size exclusion chromatogram of α -siloxy functionalized poly(methyl methacrylate), **(4)**. The experimental number average molecular weight value of $\overline{M}_n = 5.3 \times 10^3$ g/mol corresponds well with the number average molecular weight value of $\overline{M}_n = 5.4 \times 10^3$ g/mol obtained from the stoichiometry of the polymerization reaction. In addition, α -siloxy functionalized poly(methyl methacrylate) with narrow molecular weight distribution, $\overline{M}_w / \overline{M}_n = 1.41$ was obtained.

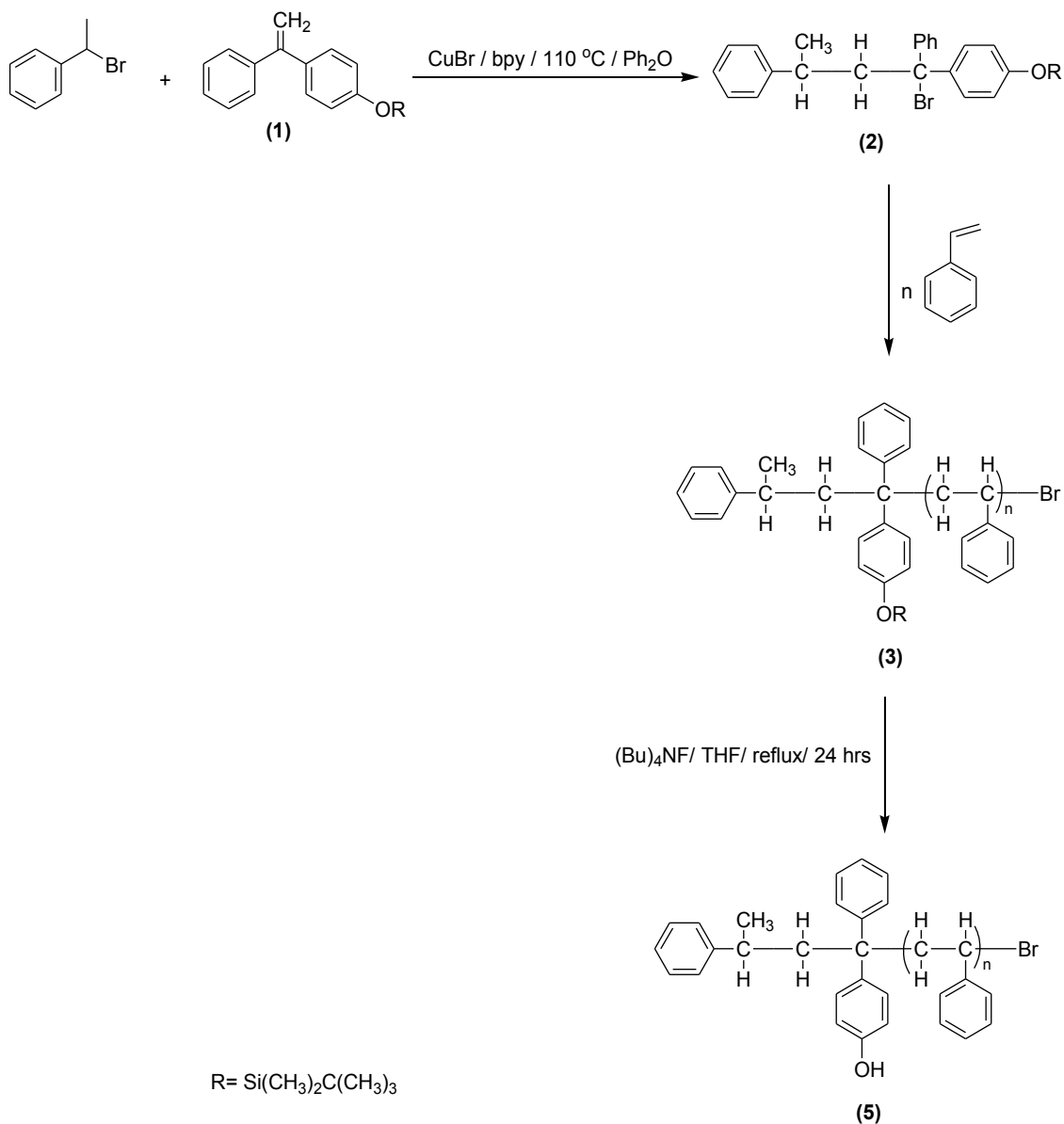
The ^1H NMR spectrum of α -siloxy functionalized poly(methyl methacrylate), **(4)** is shown in Figure 11. The characteristic peak at 1.0 ppm is due to the resonances of the protons of the $\text{Si-C}(\text{CH}_3)_3$ group. The signals at 0.7-0.9 ppm and 1.4-2 ppm are due to the resonances of methyl and methylene groups of the polymer chain, respectively. The peak at 3.5 ppm is attributed to the resonance of the methyl protons of the CH_3O group. A multiplet between 7.0-7.3 ppm, is assigned to the resonances of the aromatic protons of the phenyl rings, consistent with the introduction of the initiator fragment at the α -terminus of the polymer chain.

The ^{13}C NMR spectrum (Figure 12) of α -siloxy functionalized poly(methyl methacrylate), **(4)** exhibits a peak at 26.02 ppm, corresponding to the carbon resonance of the $\text{Si-C}(\text{CH}_3)_3$ group. The peaks at 175-178 ppm are assigned to resonances of the carbonyl carbon atoms of the methacrylate ester groups.

The FTIR spectrum (Figure 13) of α -siloxy functionalized poly(methyl methacrylate), **(4)** shows the following spectral features: an absorption band at 1270 cm^{-1} , due to the Si-C stretching vibrations of the Si-CH_3 group, an absorption band at 1750 cm^{-1} , attributed to the stretching vibrations of the C=O group of the ester; an absorption at 3080 cm^{-1} , due to the stretching vibrations of the C=C-H groups; and an absorption bands at 1495 cm^{-1} , which corresponds to the bending modes of the C-C group along the polymer chain.

4.1.4 Synthesis of α -Hydroxyl Functionalized Polystyrene, (5).

The acid catalyzed hydrolysis of α -siloxy functionalized polystyrene, **(3)** provide a facile method for the preparation of α -hydroxyl functionalized polystyrene, **(5)**. The hydroxyl functionalized polymers were prepared by post ATRP modification reactions according to the following synthesis pathway:²¹¹



A sample of α -siloxyl functionalized polystyrene, **(3)** ($\overline{M}_n = 4.9 \times 10^3 \text{ g/mol}$) was subjected to acid catalyzed hydrolysis in the presence of tetrabutylammonium fluoride in THF at reflux for 24 hours. The resulting mixture was concentrated and the polymer product precipitated into excess methanol, filtered and vacuum dried to afford the corresponding α -hydroxyl functionalized polystyrene **(5)**.

Thin layer chromatographic analysis of α -hydroxyl functionalized polystyrene, **(5)** with toluene as eluent gave one spot on the chromatogram ($R_f = 0$, in toluene).

The absence of any α -siloxyl functionalized polystyrene, **(3)** ($R_f = 0.77$, toluene), indicates complete removal of the silyl group.

The ^1H NMR spectrum (Figure 14) of α -hydroxyl functionalized polystyrene **(5)** exhibits a broad peak at 3.7 ppm, due to the resonance of the proton of the hydroxyl group and the concomitant absence of the proton resonances at 0.1 ppm and 0.9 ppm which are attributed to the proton resonances of $[\text{Si}-\text{CH}_3]$ and $[\text{Si}-\text{C}(\text{CH}_3)_3]$ groups of the α -siloxyl functionalized polystyrene, **(3)** precursor.

The FTIR spectrum (Figure 15) of α -hydroxyl functionalized polystyrene **(5)**, shows a broad absorption band at 3443 cm^{-1} , due to the presence of the OH group. The absence of an absorption band at 1263 cm^{-1} , attributed to $[\text{Si}-\text{CH}_3]$ groups, confirms the quantitative conversion of the siloxyl group to the hydroxyl group.

Non - aqueous titration measurements of α -hydroxyl functionalized polystyrene **(5)** with standardized perchloric acid in glacial acetic acid gave a value of $\overline{M}_n = 5.0 \times 10^3\text{ g/mol}$ and confirms the quantitative incorporation of the hydroxyl group at the α -terminus of the polymer chain.

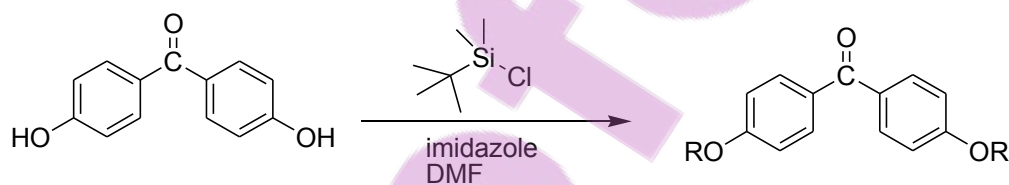
4.2.1 Disiloxyl Functionalized Initiator Precursor: Synthesis of 1,1-bis(4-t-butyl dimethylsiloxylphenyl)ethylene, (6).

The disiloxyl functionalized initiator precursor, 1,1'-bis(4-t-butyl dimethylsiloxylphenyl)ethylene, **(6)** was prepared from 4,4'-dihydroxybenzophenone according to the procedure reported by Quirk and Wang.²⁰⁵ The synthesis process involved the following key steps:

(a) the treatment of 4,4'-dihydroxybenzophenone with t-butyldimethylsilyl chloride to form 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone.

(b) the conversion of 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone to 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene, (**6**) via the Wittig reaction.

4,4'-bis(4-t-butyldimethylsiloxy)benzophenone: The disiloxy substituted benzophenone derivative, 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone was prepared by the treatment of 4,4'-dihydroxybenzophenone with t-butyldimethylsilyl chloride in the presence of imidazole for 3 hours. After purification of the crude product by silica gel column chromatography, 28.78 g (90%) of pure 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone was isolated as fine white crystals with a melting point of 53-56 °C. In addition, thin layer chromatography of 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone in toluene as eluent produced only one spot on the chromatography with $R_f = 0.6$.



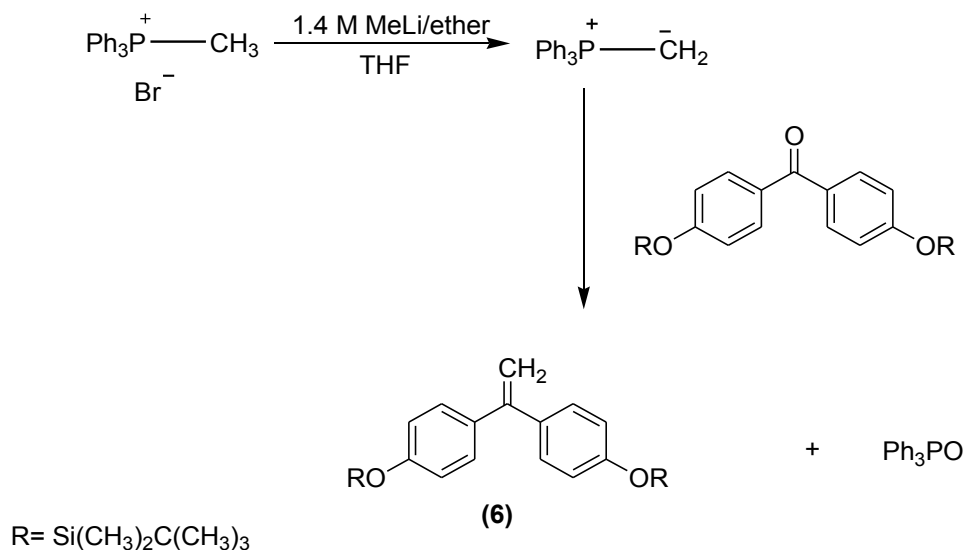
$R = \text{Si}(\text{CH}_3)_2\text{C}(\text{CH}_3)_3$

The ^1H NMR spectrum (Figure 16) of 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone exhibits characteristic peaks at $\delta = 0.21$ and 1.0 ppm, due to the proton resonances of the methyl groups of the $\text{Si}(\text{CH}_3)_2$ and $\text{Si}-\text{C}(\text{CH}_3)_3$ silyl substituents, respectively. The doublet of doublets between 6.9-7.8 ppm corresponds to the resonances of the aromatic protons of the p-substituted phenyl rings.

Figure 17 shows the FTIR spectrum of 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone with a very strong absorption band at 1656 cm^{-1} , due to the

stretching band vibration of the C=O group. In addition, the observed absorption band at 1270 cm⁻¹ corresponds to Si-C stretching vibrations of the alkyl siloxyl group.

1,1-Bis(4-t-butyl dimethyl siloxy phenyl) ethylene, (6): The siloxyl functionalized initiator precursor, 1,1-bis(4-t-butyl dimethyl siloxy phenyl) ethylene, **(6)** was prepared by the Wittig reaction of 4,4'-bis(4-t-butyl dimethyl siloxy) benzophenone with a phosphorus ylide. The phosphorus ylide was generated *in situ* from the reaction of methyltriphenyl phosphonium bromide and methyllithium in THF at 0 °C. After silica gel column chromatography and recrystallization from ethanol, 13.01 g (73%) of 1,1-bis(4-t-butyl dimethyl siloxy phenyl) ethylene, **(6)** was isolated as clear, colourless crystals with a melting point of 55.9-59.4 °C. The purity of 1,1-bis(4-t-butyl dimethyl siloxy phenyl) ethylene, **(6)** was confirmed by TLC analysis using toluene as the eluent (R_f = 0.95).



The ¹H NMR spectrum (Figure 18) of 1,1-bis(4-t-butyl dimethyl siloxy phenyl) ethylene, **(6)** shows characteristic singlets at 0.01 ppm and 0.8 ppm, which corresponds to the resonances of the protons of the Si-(CH₃)₂ and Si-C(CH₃)₃ groups, respectively. The singlet at 5.1 ppm is assigned to the proton resonance

of the olefin [C=CH₂] group. The doublet of doublets multiplet at 6.6-7.2 ppm corresponds to the aromatic proton resonances of the p-substituted phenyl rings.

The ¹³C NMR spectrum (Figure 19) of 1,1-bis(4-t-butyldimethylsiloxyphenyl)-ethylene, **(6)** exhibits a peak at 26.08 ppm, due to the carbon resonances for the [Si-C(CH₃)₃] group. The peaks at 149.5 ppm and 119.9 ppm are due to the characteristic carbon resonances for the carbon atoms of the olefin group, [C=C-(C₂)] and [C=CH₂], respectively.

The FTIR spectrum (Figure 20) of 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene, **(6)** exhibits a characteristic absorption band at 1265 cm⁻¹, due to the Si-CH₃ stretching mode.

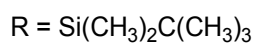
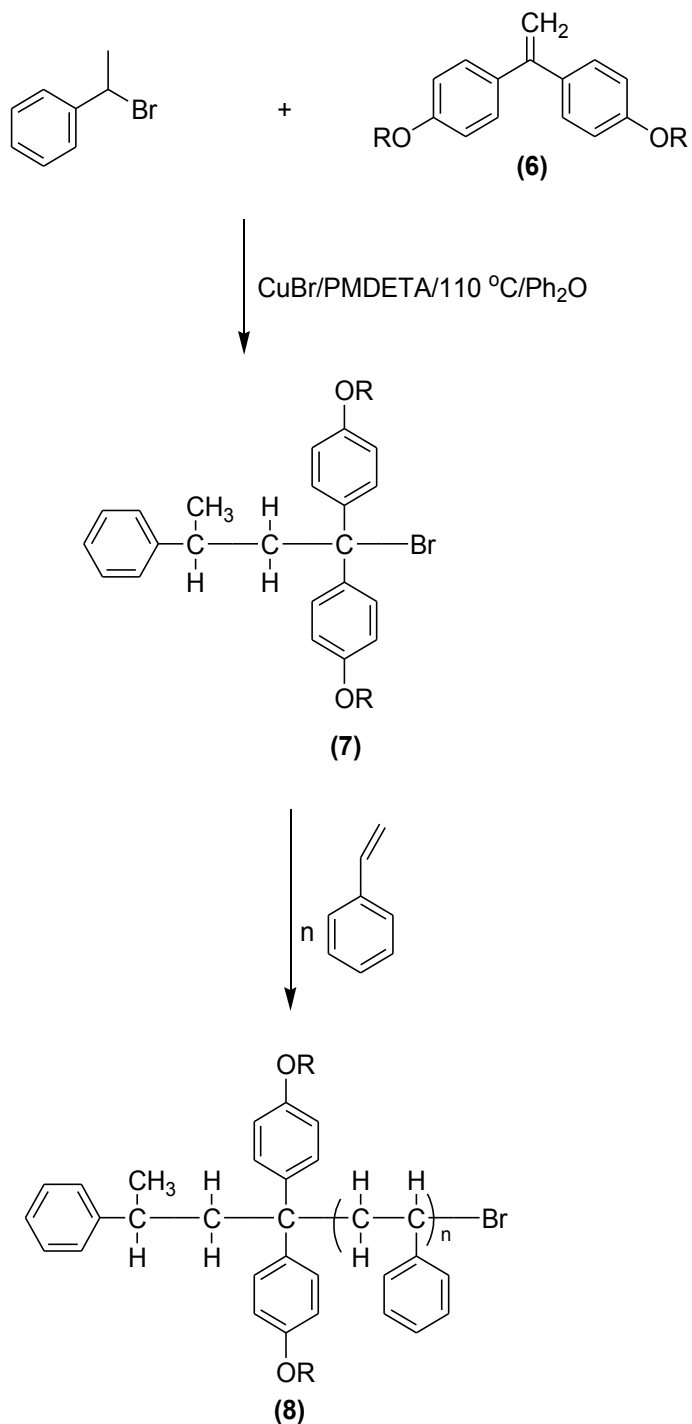
The detailed spectroscopic analysis data provides evidence for the high yield, high purity synthesis of 1,1-bis(4-t-butyldimethylsiloxyphenyl)ethylene, **(6)** from 4,4'-bis(4-t-butyldimethylsiloxy)benzophenone via the Wittig reaction.

4.2.2 Synthesis of α-Bis(siloxy) Functionalized Polystyrene, (8).

The ATRP of styrene, initiated by a new disiloxy functionalized adduct, **(7)** in the presence of CuBr/bpy or CuBr/PMDETA, produces quantitative yields of the corresponding α-bis(siloxy) functionalized polystyrene, **(8)**.

The new disiloxy functionalized initiator adduct, **(7)** was prepared *in situ* by the reaction of (1-bromoethyl)benzene with 1,1-bis(4-t-butyldimethylsiloxyphenyl)-ethylene, **(6)** in the presence of CuBr/PMDETA catalyst system in diphenyl ether at 110 °C in the mole ratio of [CuBr]₀ : [R-X]₀ : [PMDETA]₀ = 1:1:3. The disiloxy functionalized adduct, **(7)** was employed as a functionalized initiator for styrene polymerization to produce α-bis(siloxy) functionalized polystyrene, **(8)**. After 12 hours, the polymer product was isolated by precipitation from THF solution into excess methanol, filtered and vacuum dried to give quantitative yields of

α -bis(siloxy) polystyrene, **(8)** as a white solid, according to the following reaction pathway:



Thin layer chromatographic analysis of α -bis(siloxy) functionalized polystyrene, **(8)** ($R_f = 0.86$, toluene) shows only one spot on the chromatogram, consistent

with the quantitative formation of α -bis(siloxy) functionalized polystyrene, **(8)** and the absence of any unfunctionalized base polystyrene ($R_f = 0.99$, toluene).

Figure 21 shows a monomodal size exclusion chromatogram of α -bis(siloxy) functionalized polystyrene, **(8)** with a number average molecular weight value of 8.0×10^3 g/mol, which is in good agreement with the number average molecular weight value of 8.8×10^3 g/mol obtained from the stoichiometry of the polymerization reaction. In addition, α -bis(siloxy) functionalized polystyrene, **(8)** with narrow molecular weight distributions ($\overline{M}_w / \overline{M}_n = 1.16$) was formed.

The ^1H NMR spectrum (Figure 22) of α -bis(siloxy) functionalized polystyrene, **(8)** exhibits the characteristic peaks at 0.3 ppm and 1.2 ppm, which correspond to the proton resonances of the $\text{Si}-(\text{CH}_3)_2$ and $\text{Si}-\text{C}(\text{CH}_3)_3$ groups, respectively.

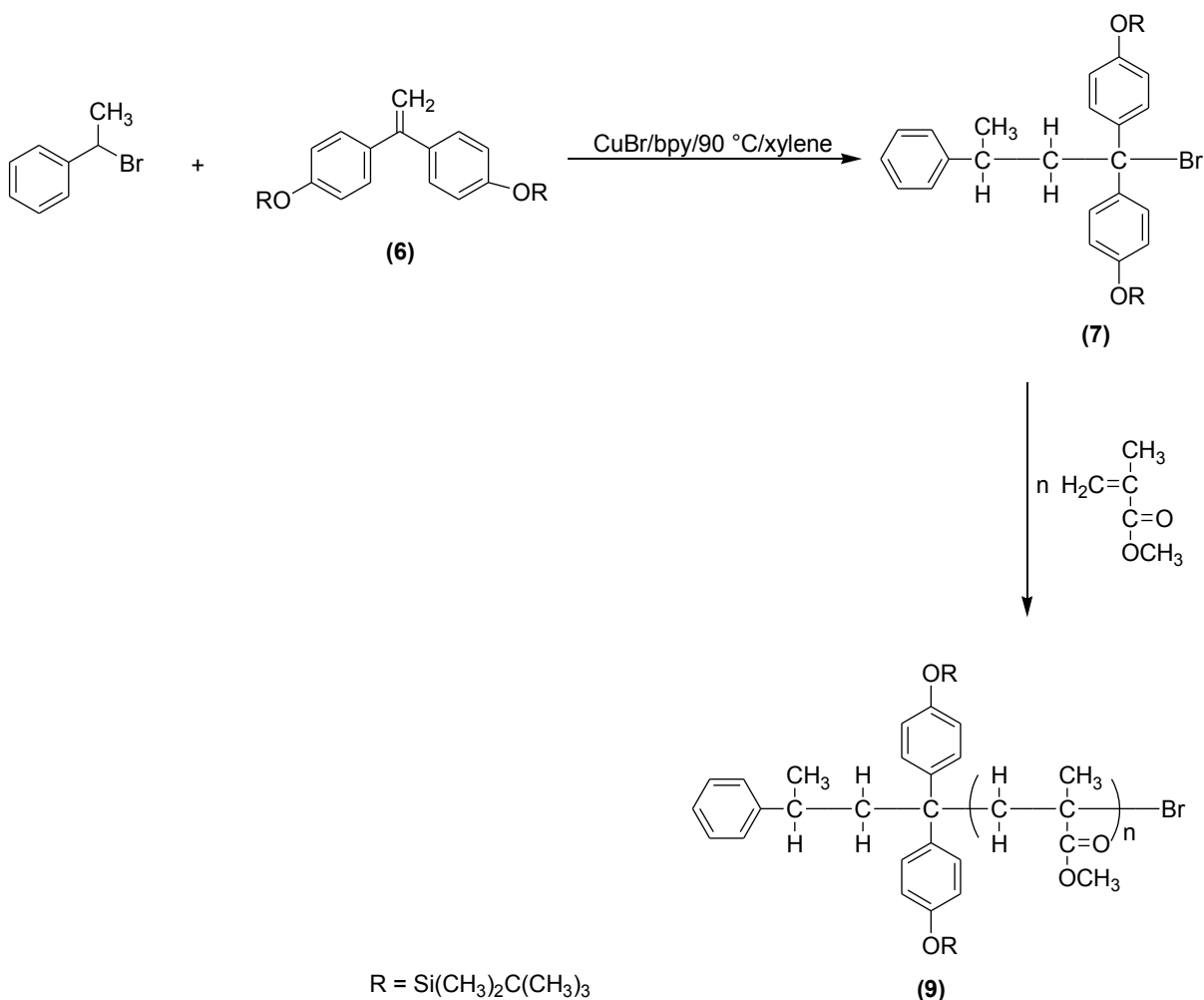
The ^{13}C NMR spectrum (Figure 23) of α -bis(siloxy) functionalized polystyrene, **(8)**, exhibits peaks at 26.2 ppm, which is due to the resonances for the methyl carbons of the $[\text{Si}-\text{C}(\text{CH}_3)_3]$ groups.

Figure 24 shows the FTIR spectrum of α -bis(siloxy) functionalized polystyrene, **(8)**, which exhibits a characteristic absorption band at 1265 cm^{-1} , due to the $\text{Si}-\text{CH}_3$ stretching modes of the alkyl siloxy groups.

The results obtained from spectroscopic analysis are consistent with the incorporation of the α -bis(siloxy) group of the initiator molecule at the α -terminus of the α -bis(siloxy) functionalized polystyrene **(8)**.

4.2.3 Synthesis of α -Bis(siloxy) Functionalized Poly(methyl methacrylate), **(9).**

The preparation of α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**) by ATRP methods was conducted by using a new disiloxy functionalized initiator adduct, (**7**) as initiator for the polymerization of methyl methacrylate in the presence of CuBr/bpy complex at 90 °C in xylene. The disiloxy functionalized initiator adduct, (**7**) was prepared *in situ* by the reaction of 1,1-bis(4-t-butyl dimethylsiloxyphenyl)ethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in xylene at 110 °C in the mole ratio of [CuBr]₀ : [R-X]₀ : [bpy]₀ = 1:1:3. After 12 hours, the polymer product was isolated by the precipitation from THF solution into excess methanol. The polymer product was filtered and vacuum dried to give α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**) in quantitative yields. The following pathway outlines the route for the preparation of α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**):



Thin layer chromatographic analysis of α -bis(siloxy) functionalized poly(methyl methacrylate), **(9)** using toluene as eluent produced only one spot on the chromatogram ($R_f = 0$, toluene), indicating the quantitative formation of α -bis(siloxy) functionalized poly(methyl methacrylate), **(9)**.

Figure 25 shows a monomodal size exclusion chromatogram of α -bis(siloxy) functionalized poly(methyl methacrylate), **(9)**. The monomodal chromatogram corresponds to a number average molecular weight value of $\overline{M}_n = 5.5 \times 10^3$ g/mol, and a narrow molecular weight distribution ($\overline{M}_w / \overline{M}_n = 1.07$). In addition the experimental \overline{M}_n value is comparable with the \overline{M}_n (theory) = 4.9×10^3 g/mol.

The ^1H NMR spectrum (Figure 26) of α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**) exhibits characteristic peaks at 0.05 ppm and 1.1 ppm, due to the proton resonances of Si-CH₃ and Si-C(CH₃)₃ groups, respectively. The proton resonances at 0.7-0.9 ppm and 1.4-2.0 ppm are due to the methyl and methylene groups of the poly(methyl methacrylate) chain, respectively. The peak at 3.5 ppm is assigned to the proton resonances of the CH₃O groups. A multiplet between 6.5-7.2 ppm, which corresponds to the resonances of the aromatic protons of the phenyl rings, confirms the incorporation of the initiator portion at the α -terminus of the polymer chain.

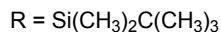
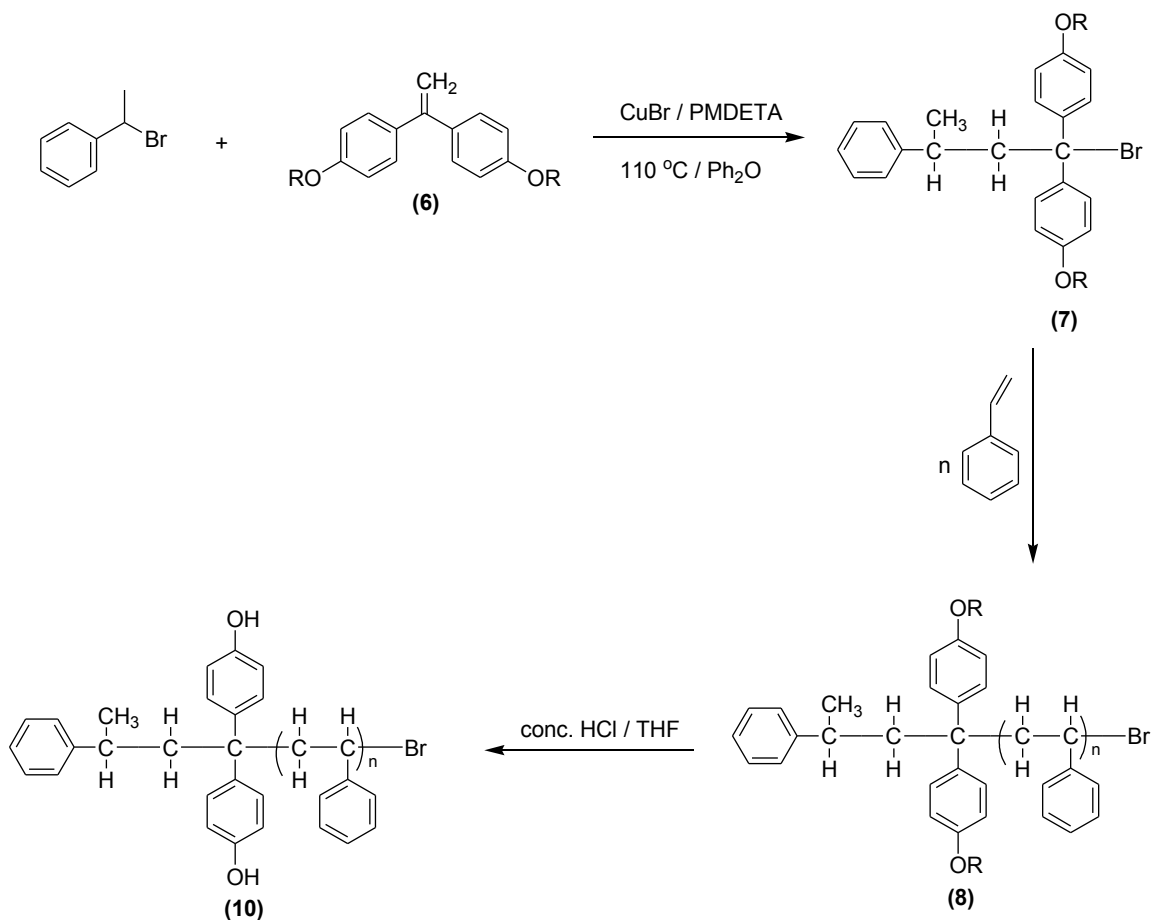
The ^{13}C NMR spectrum of α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**) is shown in Figure 27. The peak at 26.04 ppm is attributed to the carbon resonance of the Si-C(CH₃)₃ group. The carbon resonances at 175-178 ppm are assigned to the resonance of carbonyl carbon atoms of the methacrylate ester groups of the poly(methyl methacrylate) chain.

The FTIR spectrum (Figure 28) of α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**) shows an absorption band at 1270 cm⁻¹, which is characteristic of the stretching vibrations of the Si-CH₃ group. The strong absorption band at 1750 cm⁻¹ corresponds to the C=O stretching vibrations of the ester linkages along the poly(methyl methacrylate) backbone. The absorption bands between 2800 - 3000 cm⁻¹ are assigned to the stretching bands of the C-H bonds along the polymer backbone.

4.2.4 Synthesis of α -Bis(hydroxyl) Functionalized Polystyrene, (**10**).

Treatment of α -bis(siloxy) functionalized polystyrene, (**8**) with a strong acid affords the corresponding α -bis(hydroxyl) functionalized polystyrene, (**10**) according to the standard acid catalysed hydrolysis reaction as outlined by Quirk

and Wang.²⁰⁵ The acid catalyzed hydrolysis reaction was effected by the addition of hydrochloric acid to α -bis(siloxy) functionalized polystyrene, **(8)** (\overline{M}_n (SEC) = 8.0×10^3 g/mol) in THF and heated to reflux for 12 hours. The polymer product was purified by precipitation from THF into excess methanol to afford the corresponding α -bis(hydroxyl) functionalized polystyrene, **(10)**, (\overline{M}_n (titr) = 8.1×10^3 g/mol) according to the following reaction scheme:



Thin layer chromatographic analysis of α -bis(hydroxyl) functionalized polystyrene, **(10)** with toluene as eluent gives one spot on the chromatogram

($R_f = 0$, toluene). The purity of the polymer sample is confirmed by the absence of any α -bis(siloxy) functionalized polystyrene, (**8**), ($R_f = 0.86$, toluene).

Non - aqueous titration measurements of α -bis(hydroxyl) functionalized polystyrene (**10**) with standardized perchloric acid in glacial acetic acid afforded a value of $\overline{M}_n = 8.1 \times 10^3$ g/mol, which confirms the quantitative incorporation of two hydroxyl group at the α -terminus of the polymer chain.

The ^1H NMR spectrum of α -bis(hydroxyl) functionalized polystyrene, (**10**), is shown in Figure 29 and exhibits a broad resonance at 3.7 ppm, due to the resonance of the two hydroxyl group protons. The absence of any peaks at 0.3 and 1.1 ppm, which corresponds to the proton resonances of the $[\text{Si}-\text{CH}_3]$ and $[\text{Si}-\text{C}(\text{CH}_3)_3]$ groups, respectively, confirms the complete conversion of the siloxyl groups to the hydroxyl groups at the α -terminus of the polymer chain .

The FTIR spectrum (Figure 30) of α -bis(hydroxyl) functionalized polystyrene, (**10**) shows a broad absorption band at 3443 cm^{-1} , assigned to the presence of the hydroxyl group (O-H) stretching vibrations. The absence of absorption band at 1263 cm^{-1} , attributed to $[\text{Si}-\text{CH}_3]$ group, confirms the complete removal of the silyl group.

4.3 Atom Transfer Radical Polymerization: Polymerization Kinetic Studies

The controlled/living polymerization method is a powerful polymer synthesis method to produce polymers with the degree of polymerization predetermined by the ratio of the concentration of consumed monomer to the initiator ($\text{DP} = [\text{M}]_0/[\text{I}]_0$). In addition, polymers with molecular weight distribution close to Poisson

distribution ($DP_w/DP_n = 1+1/DP_n$) and controlled chain end functionality are formed. In order to classify a polymerization process as a living/controlled polymerization process, the kinetics of the polymerization reaction should show the following characteristics:

- (i) Linear kinetic plots of semilogarithmic coordinates $\ln([M]_0/[M])$ versus time;
- (ii) the linear increase in the number average molecular weight of the polymer with percentage monomer conversion; and
- (iii) the molecular weight distribution should decrease with percentage monomer conversion and should be below 1.5.

The polymerization kinetic profiles for the synthesis of different siloxyl functionalized polystyrene and poly(methyl methacrylate) derivatives were evaluated to determine the controlled/living character of each polymerization process.

4.3.1 Synthesis of α -Siloxyl Functionalized Polystyrene, (3).

(a) With CuBr/2,2'-bipyridyl as the catalyst/ligand system:

The syntheses of the different α -siloxyl functionalized polystyrene derivatives were conducted using a new siloxyl functionalized initiator adduct, (2) for the initiation of the polymerization of styrene by ATRP methods. The initiator adduct, (2) was formed by the *in situ* reaction of (1-bromoethyl)benzene with 1-(4-t-butyl)dimethylsiloxylphenyl-1-phenylethylene, (1) in the presence of CuBr/2,2'-bipyridyl at 110 °C using diphenyl ether as a solvent. After the addition of styrene, an aliquot (1 mL) was removed from the reaction mixture and diluted with THF (9 mL) to measure the initial styrene concentration by gas chromatography at time, $t=0$. Similarly, at different 1 hour time intervals, aliquots (1 mL) were taken from

the solution and dissolved in THF (9 mL) to determine the extent of monomer consumption with time by gas chromatographic analysis. The number average molecular weight and molecular weight distribution of each polymer sample was determined by size exclusion chromatography. The following table shows the polymerization kinetic data for the ATRP of styrene, initiated by a new siloxyl functionalized initiator adduct (**2**), formed by the reaction of (1-bromoethyl)benzene and 1-(4-t-butyl dimethylsiloxylphenyl)-1-phenylethylene in the presence of CuBr/bpy in diphenyl ether at 110 °C:

Synthesis of α -Siloxyl Functionalized Polystyrene, (3**).**

| [M] ₀ /[I] ₀ | Catalyst system | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) (x10 ³) g/mol | $\overline{M}_w / \overline{M}_n$ |
|------------------------------------|-----------------|------------|----------------------|---|-----------------------------------|
| 50:1 | CuBr/bpy | 1 | 36.7 | 1.9 | 1.11 |
| | | 2 | 44.9 | 2.8 | 1.09 |
| | | 3 | 50.6 | 3.2 | 1.11 |
| | | 4 | 55.6 | 3.7 | 1.05 |
| | | 5 | 59.03 | 4.0 | 1.06 |
| 100:1 | CuBr/bpy | 1 | 19.4 | 2.2 | 1.15 |
| | | 2 | 30.6 | 3.6 | 1.12 |
| | | 3 | 33.97 | 4.0 | 1.14 |
| | | 4 | 40.01 | 4.9 | 1.05 |
| | | 5 | 50.3 | 6.3 | 1.07 |
| 200:1 | CuBr/bpy | 1 | 16.5 | 3.1 | 1.11 |
| | | 2 | 25.57 | 4.2 | 1.12 |
| | | 3 | 29.03 | 4.9 | 1.18 |
| | | 4 | 35.3 | 5.7 | 1.12 |
| | | 5 | 38.79 | 6.9 | 1.12 |

Figure 31 shows the plots of percentage monomer conversion versus time for the ATRP reactions with different initial monomer to initiator ratios of 50:1, 100:1 and 200:1. When the ratio of $([M]_0/[I]_0) = 50$, the polymerization reaction is the fastest and the percentage monomer conversion of 59% was reached within 5 hours. By increasing the ratio of $([M]_0/[I]_0) = 100$, the percentage monomer conversion decreased to 50% within 5 hours. Upon reduction of the initiator concentration at $([M]_0/[I]_0) = 200$, a significant decrease in the extent of polymerization was observed and only 39% monomer conversion was obtained within 5 hours. For each reaction, a rapid decrease in monomer concentration with subsequent polymerization is observed within 1 hour. Thereafter a gradual increase in monomer consumption relative to time was observed.

Figure 32 shows the semilogarithmic linear first order kinetic plots of $\ln([M]_0/[M])$ vs time for the ATRP reactions with different $[M]_0/[I]_0$ ratios. During the initial stages of the $[M]_0/[I]_0 = 50:1$ polymerization reaction, a rapid increase in polymerization is observed within 1 hour. For the polymerization of $[M]_0/[I]_0 = 200:1$, an induction period is observed before the controlled radical polymerization process occurs. For all the polymerization reactions, after complete formation of the initiator species, a linear relationship between $\ln([M]_0/[M])$ and time is observed, indicating that the concentration of the radical species is constant throughout the propagation step. When the ratio of $[M]_0/[I]_0 = 50:1$, that is, at higher initiator concentration, the polymerization reaction is the fastest, but the rate of polymerization decreases significantly when the initiator concentration is reduced to $[M]_0/[I]_0 = 100:1$ and $[M]_0/[I]_0 = 200:1$, respectively.

Figure 33 shows the plots of the experimentally observed number average molecular weights and molecular weight distribution values versus percentage monomer conversion. For all the polymerization reactions, after completion of the initiation process, the number average molecular weights increase linearly with percentage monomer conversion, indicating the absence of side reactions during the propagation step. However, the experimental number average molecular weight values are

significantly higher than the theoretical values predicted from reaction stoichiometry, indicating reduction of the initiator concentration during the formation of the siloxyl functionalized initiator adduct. α -Siloxyl functionalized polystyrene derivatives with number average molecular weights ($\overline{M}_n = 1.9 \times 10^3 - 8.0 \times 10^3$ g/mol) and narrow molecular weight distributions ($\overline{M}_w / \overline{M}_n = 1.03 - 1.16$) were obtained. The deviation of the experimental number average molecular weight values from the theoretically predicted values may indicate side reactions during the initiation step, such as radical termination reactions, leading to the reduction in initiator concentrations before the onset of the propagation process.

(b) With CuBr/PMDETA as the catalyst/ligand system:

The effect of the catalyst/ligand system on the polymerization process for the preparation of α -siloxyl functionalized polystyrene, **(3)** was also evaluated. The initiation of styrene polymerization by a new siloxyl functionalized initiator adduct **(2)**, formed by the reaction of (1-bromoethyl)benzene and 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene in the presence of copper (I) bromide/PMDETA catalyst system, affords α -siloxyl functionalized polystyrene **(3)** with controlled number average molecular weight and narrow molecular weight distributions. The following table shows the polymerization kinetic data for the ATRP of styrene, initiated by a new siloxyl functionalized initiator adduct **(2)**, formed by the reaction of (1-bromoethyl)benzene and 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene in the presence of CuBr/PMDETA in diphenyl ether at 110 °C for three different reaction sequences at initial monomer to initiator concentration ratios of 50:1; 100:1 and 200:1:

Synthesis of α -Siloxyl Functionalized Polystyrene, (3).

| [M] ₀ /[I] ₀ | Catalyst/Ligand | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) (x 10 ³) g/mol | $\overline{M}_w / \overline{M}_n$ |
|------------------------------------|-----------------|------------|----------------------|--|-----------------------------------|
| 50:1 | CuBr/PMDETA | 1 | 49.7 | 4.1 | 1.10 |
| | | 2 | 58.2 | 5.4 | 1.13 |
| | | 3 | 61.4 | 6.1 | 1.11 |
| | | 4 | 65.3 | 6.9 | 1.10 |
| | | 5 | 68.1 | 7.7 | 1.11 |
| | | 6 | 73.26 | 8.5 | 1.11 |
| | | 7 | 80.66 | 9.5 | 1.11 |
| 100:1 | CuBr/PMDETA | 1 | 25.39 | 4.7 | 1.10 |
| | | 2 | 30.23 | 5.5 | 1.18 |
| | | 3 | 41.56 | 6.3 | 1.104 |
| | | 4 | 53.06 | 8.7 | 1.11 |
| | | 5 | 56.71 | 9.2 | 1.05 |
| | | 6 | 61.16 | 10.6 | 1.15 |
| | | 7 | 69.62 | 11.9 | 1.03 |
| 200:1 | CuBr/PMDETA | 1 | 12.3 | 4.0 | 1.11 |
| | | 2 | 15.42 | 4.5 | 1.12 |
| | | 3 | 25.55 | 7.3 | 1.11 |
| | | 4 | 40.00 | 9.6 | 1.19 |

| | | | | | |
|--|--|---|-------|------|------|
| | | 5 | 50.11 | 11.9 | 1.15 |
| | | 6 | 56.9 | 12.9 | 1.29 |
| | | 7 | 62.84 | 14.5 | 1.03 |

Figure 34 illustrates the plots of the percentage monomer conversion with time for the ATRP reactions leading to the preparation of α -siloxy functionalized polystyrene, (3). The polymerization reaction is affected by the concentration of the initiator system. At high initiator concentration, $[M]_0/[I]_0 = 50:1$, after an initial rapid monomer conversion of 50% after 1 hour, the overall percentage monomer conversion of 81% was reached after 7 hours. When the $[M]_0/[I]_0$ ratio was increased to 100:1, a slight reduction in the percentage monomer conversion to 70% was observed after 7 hours. At low initiator concentration, when $[M]_0/[I]_0$ was increased to 200:1, the extent of monomer conversion of 63% was recorded after 7 hours. For the reaction at low initiator concentration, $[M]_0/[I]_0 = 200:1$, a linear relationship between the consumption of monomer with time was observed throughout the reaction.

Figure 35 depicts the different first order kinetic plots for the ATRP of styrene, initiated by the siloxy functionalized initiator adduct, (2) at different monomer to initiator concentrations of $[M]_0/[I]_0 = 50:1$, 100:1 and 200:1. The siloxy functionalized initiator adduct (2) was formed *in situ* by the reaction of 1-(4-t-butyl)dimethylsiloxyphenyl)-1-phenylethylene (1) with (1-bromoethyl)benzene in the presence of CuBr/PMDETA in diphenyl ether at 110 °C. The rate of polymerization is influenced by the initial concentration of the initiator system. The polymerization rate was the fastest at higher initiator concentration $[M]_0/[I]_0 = 50:1$. The linearity of the relationship between $\ln([M]_0/[M])$ and time indicates that the concentration of the propagating radicals remained constant during the propagation step for each polymerization reaction. Furthermore, a large reduction in the polymerization rate was observed when the initiator concentrations were reduced to $[M]_0/[I]_0 = 100:1$ and $[M]_0/[I]_0 = 200:1$, respectively.

Figure 36 shows the plots of the experimental number average molecular weight and molecular weight distribution versus percentage monomer conversion for the different ATRP reactions for the preparation of α -siloxy functionalized polystyrene, **(3)** in the presence of the CuBr/PMDETA catalyst system. A linear increase in the number average molecular weight with percentage monomer conversion is observed for each polymerization reaction, indicating the absence of any chain transfer and termination reactions after completion of the initiation process. However, the experimental number average molecular weight values were slightly higher than the theoretical values obtained from the stoichiometry of the polymerization reaction. The higher \overline{M}_n (SEC) values could be attributed to the reduction of the concentration of initiator species due to side reactions during initiation formation and the concomitant inefficient initiation. In addition, the observed narrow molecular weight distribution values of 1.03 to 1.29 indicates that, after the complete *in situ* initiator formation of the initiator adduct, **(2)**, the rate of initiation is equal to or greater than the rate of propagation for each polymerization reaction.

The atom transfer radical polymerization of styrene, initiated by the adduct of 1-(4-t-butyl dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene, in the presence of CuBr/2,2'-bipyridyl or CuBr/PMDETA proceeds via a controlled free radical polymerization process to form α -siloxy functionalized polystyrene, **(3)** with good control of the number average molecular weights and molecular weight distributions.

4.3.2 Synthesis of α -Bis(siloxy) Functionalized Polystyrene, (8).

(a) With CuBr/bpy as the catalyst/ligand system:

The controlled/living character of the ATRP reaction for the preparation of

α -bis(siloxy) functionalized polystyrene, (**8**) was evaluated by considering the polymerization kinetics of the polymerization reaction. The different α -bis(siloxy) functionalized polystyrene derivatives, (**8**) were prepared by standard ATRP methods. The polymerization of styrene was initiated by a new disiloxy functionalized initiator adduct, (**7**), generated *in situ* by the reaction of 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)ethylene with (1-bromoethyl)benzene in the presence of CuBr/bpy at 110 °C in diphenyl ether as a solvent in different reactions with initial monomer to initiator ratios of 50:1, 100:1 and 200:1. After the addition of styrene, an aliquot (1 mL) was removed from the reaction mixture and diluted with THF (9 mL) to measure the initial styrene concentration by gas chromatography at time, $t=0$. Similarly, at different 1 hour time intervals, aliquots (1 mL) were taken from the solution and dissolved in THF (9 mL) to determine the extent of monomer consumption with time by gas chromatographic analysis. The number average molecular weight and molecular weight distribution of each sample was determined by size exclusion chromatography. The following table shows the polymerization kinetic data for the ATRP of styrene, initiated by a new disiloxy functionalized initiator adduct, (**7**), formed by the reaction of (1-bromoethyl)benzene and 1,1-bis(4-*t*-butyl-dimethylsiloxyphenyl)ethylene, (**6**) in the presence of CuBr/bpy in diphenyl ether at 110 °C:

Synthesis of α -Bis(siloxy) Functionalized Polystyrene, (**8**).

| $[M]_0/[I]_0$ | Catalyst/Ligand | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) ($\times 10^3$) g/mol | $\overline{M}_w / \overline{M}_n$ |
|---------------|-----------------|------------|----------------------|--|-----------------------------------|
| 50:1 | CuBr/bpy | 1 | 42.03 | 1.4 | 1.26 |
| | | 2 | 48.40 | 1.6 | 1.24 |
| | | 3 | 55.11 | 3.6 | 1.24 |
| | | 4 | 64.53 | 5.4 | 1.21 |
| | | 5 | 75.10 | 6.9 | 1.13 |
| 100:1 | CuBr/bpy | 1 | 33.5 | 6.2 | 1.39 |
| | | 2 | 40.4 | 7.4 | 1.24 |
| | | 3 | 47.7 | 8.3 | 1.25 |

| | | | | | |
|-------|----------|---|------|------|------|
| | | 4 | 54.1 | 10.2 | 1.20 |
| | | 5 | 67.6 | 11.6 | 1.21 |
| 200:1 | CuBr/bpy | 1 | 15.2 | 5.9 | 1.36 |
| | | 2 | 22.3 | 7.8 | 1.31 |
| | | 3 | 27.7 | 9.9 | 1.27 |
| | | 4 | 31.9 | 11.6 | 1.20 |
| | | 5 | 46.2 | 14.6 | 1.16 |

Figure 37 shows the different plots of percentage monomer conversion versus time for the different ATRP reactions leading to the preparation of α -bis(siloxy) functionalized polystyrene (**8**). The polymerization reactions are influenced by the initial concentration of the initiator system. For each reaction, after an initial rapid increase in monomer consumption within 1 hour, a gradual increase in the monomer consumption is observed over a period of five hours. For the $[M]_0/[I]_0 = 50:1$ reaction, the polymerization reaction was the fastest and the percentage monomer conversion value of 75% was observed within 5 hours. With the reduction in the initial initiator concentration from $[M]_0/[I]_0 = 100:1$ to $[M]_0/[I]_0 = 200:1$, a gradual reduction in the percentage monomer conversion values is observed, with values of 68% and 46% recorded, respectively.

Figure 38 shows the plots of $\ln([M]_0/[M])$ versus time for the three different ATRP reactions. The plots of the semilogarithmic coordinates of $\ln[M]_0/[I]_0$ versus time shows a linear relationship for each polymerization reaction, indicating that each polymerization is first order with respect to monomer consumption. At $[M]_0/[I]_0 = 50:1$, the rate of polymerization is the fastest, but the rate of polymerization gradually decreases with decreasing concentration of the initiator system from $[M]_0/[I]_0 = 100$ to $[M]_0/[I]_0 = 200:1$. Moreover, the linear relationship between $\ln([M]_0/[M])$ versus time indicates that the concentration of the propagating radicals remain constant during the polymerization process.

Figure 39 depicts the plots of the number average molecular weight and molecular weight distribution as a function of percentage monomer conversion for each polymerization reaction. After the completion of the initiation process, a

linear evolution of the number average molecular weight with percentage monomer conversion was observed for each polymerization reaction at the different initial monomer to initiator concentration ratios of 50:1, 100:1 and 200:1, indicating the absence of chain transfer and termination reactions during the propagation step. However, the slightly higher experimental number average molecular weight values relative to the \overline{M}_n (theory) values could be attributed to a reduction in the initiator concentration due to unavoidable irreversible radical termination reactions at the early stages of the polymerization process. Side reactions observed during formation of the initiator species lead to inefficient initiation and the formation of polymers with higher number average molecular weight values as compared to the theoretical values obtained from the stoichiometry of the reaction.

The formation of polymers with narrow molecular weight distributions indicates that, after the complete *in situ* formation of the initiator species, the rate of initiation is equal to or greater than the rates of propagation for each reaction. The fast exchange between dormant and active species and the absence of any side reactions afforded a fixed number of chains of nearly equal lengths and consequently the formation of polymers narrow molecular weight distributions.

(b) With CuBr/PMDETA as the catalyst/ligand system:

In order to study the effect of the catalyst/ligand system on the polymerization kinetics for the synthesis of α -bis(siloxy) functionalized polystyrene, **(8)** by ATRP methods, the different ATRP reactions were conducted in the presence of the CuBr/PMDETA catalyst system. The initiation of styrene polymerization was effected by the disiloxy functionalized initiator adduct, **(7)** prepared *in situ* by the reaction of stoichiometric amounts of 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)-ethylene, **(6)** with (1-bromoethyl)benzene in the presence of CuBr/PMDETA in diphenyl ether at 110 °C at different initial monomer to initiator ratios of 50:1,

100:1 and 200:1. The following table shows the polymerization kinetic data for the ATRP of styrene, initiated by a new disiloxy functionalized initiator adduct (**7**), formed by the reaction of (1-bromoethyl)benzene and 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene in the presence of CuBr/PMDETA in diphenyl ether at 110 °C:

Synthesis of α -bis(siloxy) Functionalized Polystyrene, (8**).**

| [M] ₀ /[I] ₀ | Catalyst/Ligand | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) (x 10 ³) g/mol | $\overline{M}_w / \overline{M}_n$ |
|------------------------------------|-----------------|------------|----------------------|---|-----------------------------------|
| 50:1 | CuBr/PMDETA | 1 | 50.47 | 2.2 | 1.24 |
| | | 2 | 56.49 | 5.1 | 1.23 |
| | | 3 | 62.89 | 6.9 | 1.16 |
| | | 4 | 71.37 | 7.9 | 1.14 |
| | | 5 | 78.05 | 10.5 | 1.06 |
| 100:1 | CuBr/PMDETA | 1 | 11.81 | 5.2 | 1.17 |
| | | 2 | 23.31 | 7.5 | 1.15 |
| | | 3 | 34.57 | 9.3 | 1.16 |
| | | 4 | 48.26 | 10.5 | 1.14 |
| | | 5 | 60.26 | 11.8 | 1.12 |
| 200:1 | CuBr/PMDETA | 1 | 8.09 | 9.8 | 1.27 |
| | | 2 | 17.21 | 10.9 | 1.17 |
| | | 3 | 26.67 | 12.3 | 1.12 |
| | | 4 | 37.89 | 13.7 | 1.19 |
| | | 5 | 45.36 | 14.8 | 1.19 |

Figure 40 shows the plots of percentage monomer conversion versus time for the different ATRP reactions. The rates of polymerization increased with increasing concentration of the initiator system. However, at a specific [M]₀/[I]₀ ratio, the polymerization rate was slightly higher in the CuBr/PMDETA system when compared to the CuBr/bpy system. For example, for the [M]₀/[I]₀ = 50:1 reaction,

the percentage monomer conversion value of 78% was observed within 5 hours for the CuBr/PMDETA compared to the recorded value of 75% for the CuBr/bpy after the same reaction time. The faster rate of polymerization is due to the lower redox potentials associated with the coordination complex of the more soluble CuBr/PMDETA system in diphenyl ether. Thus, the k_a value for the CuBr/PMDETA system increased, resulting in the rapid rate of formation of radicals, which ensures faster rates of polymerization. When $[M]_0/[I]_0$ was increased to 100:1, the extent of reaction linearly reached 60% after 5 hours. However, when $[M]_0/[I]_0$ was increased to 200, the percentage monomer consumption was 45% occurred after 5 hours.

Figure 41 shows the plots of $\ln([M]_0/[M])$ against polymerization time for the three different ATRP reactions. The observed linear relationship between $\ln([M]_0/[M])$ and polymerization time indicates that the polymerization reactions proceeded in a controlled manner. After completion of the initiation process, the radical concentration was constant during the propagation process, and no evidence of chain transfer and termination reactions was observed.

Figure 42 shows the plots of the number average molecular weight and molecular weight distribution as a function of percentage monomer conversion. For all polymerization reactions, after complete formation of the initiator species, linear evolution of the number average molecular weight with percentage monomer conversion is observed. The linear relationship of number average molecular weight versus percentage monomer conversion is only observed between 50-78% monomer conversions for the $[M]_0/[I]_0 = 50:1$ reaction, which suggests the unavoidable side reactions during the early stages of percentage monomer consumption. The side reactions during the initial stages of the polymerization could be attributed to the high Cu (I) concentration which induces high radical formation with concomitant high radical termination reactions, hence the nonzero intercepts for all the polymerization reactions.

For each polymerization reaction, polymers with narrow molecular weight distributions, ranging from $\overline{M}_w / \overline{M}_n = 1.27$ to 1.05, were obtained, which suggests that all polymer chains were initiated at the same time when compared to the propagation step and that the number of active chains remained constant throughout the polymerization process.

Polymerization kinetic studies show that good control of molecular weight, molecular weight distributions and high initiator efficiencies in the solution ATRP synthesis of α -bis(siloxy) functionalized polystyrenes, **(8)** can be obtained by using the α -bis(siloxy) functionalized initiator adduct **(7)** as initiator for the polymerization of styrene. The quantitative incorporation of the functionalized 1,1-diphenylethylene fragment into the polymer chain end in the ATRP of styrene and the control of major polymer properties, such as number average molecular weight, molecular weight distribution and degree of functionalization is attributed to (a) the quantitative formation of the initiator adduct **(7)** *in situ* by the stoichiometric addition reaction of (1-bromoethyl)benzene with 1,1-bis(4-t-butyl)dimethylsiloxyphenyl)ethylene, **(6)** and (b) the subsequent efficient and rapid reaction of the diphenylethylene radical chain end with the styrene to initiate the polymerization of styrene.

4.3.3 Synthesis of α -Siloxy Functionalized Poly(methyl methacrylate), **(4):**

(a) With CuBr/bpy as the catalyst/ligand system:

The different polymerization kinetic experiments for the preparation of α -siloxy functionalized poly(methyl methacrylate), **(9)** were performed by using 1-(4-t-butyl)dimethylsiloxyphenyl)-1-phenylethylene, **(1)** as a siloxy functionalized initiator precursor for the polymerization of methyl methacrylate in the presence of CuBr/bpy as the catalyst system by varying the initial initiator concentration using different monomer to initiator precursor ratios of 50:1, and 100:1 and 200:1. The polymerization of methyl methacrylate was initiated by a new siloxy functionalized initiator adduct, **(2)** which was prepared *in situ* by the reaction of

1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene, **(1)** and (1-bromoethyl)-benzene by standard ATRP methods. After the addition of methyl methacrylate, an aliquot (1 mL) was removed from the reaction mixture and diluted with THF (9 mL) to measure the initial methyl methacrylate concentration by gas chromatography at time, $t=0$. Similarly, at 30 minutes time intervals, aliquots (1 mL) were taken from the solution and dissolved in THF (9 mL) to determine the extent of monomer consumption with time by gas chromatographic analysis. The number average molecular weight and molecular weight distribution of each polymer sample was determined by size exclusion chromatography. The following table shows the polymerization kinetic data for the ATRP of methyl methacrylate, initiated by a new siloxyl functionalized initiator adduct, **(2)** formed by the reaction of (1-bromoethyl)benzene and 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene, **(1)** in the presence of CuBr/bpy in diphenyl ether at 90 °C:

Synthesis of α -Siloxyl Functionalized Poly(methyl methacrylate), (4).

| $[M]_0/[I]_0$ | Catalyst/Ligand | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) ($\times 10^3$) g/mol | $\overline{M}_w / \overline{M}_n$ |
|---------------|-----------------|------------|----------------------|---|-----------------------------------|
| 50:1 | CuBr/bpy | 0.5 | 35.20 | 3.2 | 1.17 |
| | | 1 | 47.10 | 3.9 | 1.28 |
| | | 1.5 | 55.98 | 4.6 | 1.53 |
| | | 2 | 67.46 | 5.5 | 1.09 |
| | | 2.5 | 78.12 | 6.4 | 1.02 |
| | | 3 | 85.25 | 7.0 | 1.02 |
| 100:1 | CuBr/bpy | 0.5 | 27.90 | 4.6 | 1.21 |
| | | 1 | 35.71 | 5.6 | 1.17 |
| | | 1.5 | 42.35 | 6.1 | 1.17 |
| | | 2 | 52.58 | 6.7 | 1.11 |
| | | 2.5 | 55.91 | 7.1 | 1.10 |
| | | 3 | 66.35 | 7.6 | 1.11 |
| 200:1 | CuBr/bpy | 0.5 | 11.69 | 5.6 | 1.13 |
| | | 1 | 13.71 | 6.4 | 1.25 |
| | | 1.5 | 17.08 | 7.2 | 1.10 |
| | | 2 | 24.06 | 8.6 | 1.19 |
| | | 2.5 | 30.81 | 9.4 | 1.17 |
| | | 3 | 36.09 | 9.8 | 1.17 |

Figure 43 shows the plots of percentage monomer conversion versus time for the respective ATRP reactions catalyzed by the CuBr/bpy system. The rate of monomer consumption is rapid for each reaction. When the ratio of $[M]_0/[I]_0 =$

50:1, after the initial rapid monomer conversion of 35% after 30 minutes, the overall percentage monomer conversion of 85% was recorded after 3 hours. When the initial concentration of the initiator system was reduced to $[M]_0/[I]_0 = 100$, the extent of percentage monomer consumption reached only 66% after 3 hours. However, at low initial initiator concentration of $[M]_0/[I]_0 = 200$, only 36% monomer consumption was observed after 3 hours.

Figure 44 depicts the semilogarithmic plots of $\ln[M]_0/[M]$ versus time for the different methyl methacrylate polymerization reactions by ATRP methods. The polymerization of methyl methacrylate was initiated by the adduct formed *in situ* by the reaction of 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene, (**1**) with (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst system in diphenyl ether at 90 °C. The linearity of the semilogarithmic plots of $\ln[M]_0/[M]$ versus time for each reaction indicates that each polymerization reaction is first order with respect to monomer consumption and that, after formation of the initiator species, the concentration of the active radicals remains constant from the onset of the polymerization and also throughout the propagation process.

Figure 45 shows the plots of the number average molecular weight and molecular weight distributions as a function of percentage monomer conversion for each ATRP of methyl methacrylate polymerization reaction that was initiated by the adduct of 1-(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene, (**1**) and (1-bromoethyl)benzene and catalyzed by CuBr/bpy in diphenyl ether at 90 °C. A linear evolution of the number average molecular weight with percentage monomer conversion for each polymerization reaction was observed, especially after the complete formation of the initiator system and completion of the initiation step. The linear relationship between the number average molecular weight values and percentage monomer conversion indicates that chain transfer and termination reactions were insignificant during the propagation step. However, the observed number average molecular weight values are higher than the theoretical calculated from the stoichiometry of the reaction. The higher

experimental number average molecular weight values could be attributed to side reactions during formation of the initiator adduct species, which ultimately reduces the initiator concentration and leads to polymers with high number average molecular weights. In addition, the observed molecular weight distribution values between 1.2 and 1.02 for the polymers formed in the different polymerization reactions imply that the rates of initiation were rapid and equal to or greater than the rates of propagation.

(b) With CuBr/PMDETA as the catalyst/ligand system:

In order to study the effect of the catalyst/ligand system on the preparation of α -siloxyl functionalized poly(methyl methacrylate), **(4)** by ATRP methods, the polymerization kinetic experiments were performed by using 1-(4-*t*-butyl-dimethylsiloxylphenyl)-1-phenylethylene, **(1)** as a siloxyl functionalized initiator precursor for the polymerization of methyl methacrylate in the presence of CuBr/PMDETA as catalyst system in diphenyl ether at 90 °C. The following table depicts the polymerization kinetic raw data for the preparation of different α -siloxyl functionalized poly(methyl methacrylate) derivatives, **(4)**.

Synthesis of α -Siloxyl Functionalized Poly(methyl methacrylate), (4).

| [M] ₀ /[I] ₀ | Catalyst/Ligand | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) (x 10 ³) g/mol | $\overline{M}_w / \overline{M}_n$ |
|------------------------------------|-----------------|------------|----------------------|--|-----------------------------------|
| 50:1 | CuBr/PMDETA | 0.5 | 45.39 | 4.5 | 1.43 |
| | | 1 | 53.77 | 6.3 | 1.29 |
| | | 1.5 | 67.89 | 7.5 | 1.22 |
| | | 2 | 77.7 | 9.3 | 1.27 |
| | | 2.5 | 85.35 | 10.1 | 1.10 |
| | | 3 | 96.1 | 11.5 | 1.09 |
| 100:1 | CuBr/PMDETA | 0.5 | 28.24 | 7.9 | 1.09 |
| | | 1 | 38.04 | 8.8 | 1.09 |
| | | 1.5 | 44.57 | 9.6 | 1.19 |
| | | 2 | 56.38 | 10.3 | 1.13 |
| | | 2.5 | 68.65 | 11.4 | 1.19 |
| | | 3 | 72.23 | 12.2 | 1.12 |
| 200:1 | CuBr/PMDETA | 0.5 | 13.7 | 9.1 | 1.25 |
| | | 1 | 17.5 | 10.7 | 1.19 |
| | | 1.5 | 30.8 | 12.7 | 1.15 |
| | | 2 | 36.4 | 14.2 | 1.09 |
| | | 2.5 | 47.6 | 15.5 | 1.03 |
| | | 3 | 58.01 | 17.4 | 1.17 |

Figure 46 outlines the plots of percentage monomer conversion versus time for the polymerization of methyl methacrylate by using the adduct of 1-(4-*t*-butyl-dimethylsiloxylphenyl)-1-phenylethylene, (**1**) and (1-bromoethyl)benzene as a siloxyl functionalized initiator precursor in the presence of the CuBr/PMDETA catalyst system. The polymerization reactions proceeded rapidly at higher initial

initiator concentration. At higher initiator concentration, when $[M]_0/[I]_0 = 50:1$, a high percentage monomer consumption of 96% was reached after 3 hours, indicating a very fast reaction when compared to a similar reaction which was conducted in the presence of the CuBr/bpy catalyst system. When the initial concentrations of the initiator systems were reduced to $[M]_0/[I]_0 = 100:1$ and $[M]_0/[I]_0 = 200:1$, the overall percentage monomer conversion values reduced to 72% and 58%, respectively. At lower initiator concentration, a linear relationship between percentage monomer consumption with time was observed.

Figure 47 depicts the linear plots for the relationship between $\ln[M]_0/[M]$ versus time for each ATRP reaction. The polymerization kinetic data shows that each polymerization reaction follows first order rate kinetics with respect to monomer consumption and that the radical concentration was constant throughout the propagation process for each reaction. The observed non-zero intercepts for the reactions conducted at higher initiator concentrations suggests that side reactions occur during the formation of the initiator system.

Figure 48 depicts the plots of \overline{M}_n and $\overline{M}_w / \overline{M}_n$ versus percentage monomer conversion for the polymerization of methyl methacrylate using a siloxyl functionalized adduct formed by the reaction of (1-bromoethyl)benzene with 1-(4-t-butyl dimethyl siloxyphenyl)-1-phenylethylene, (**1**) in the presence of CuBr/PMDETA in diphenyl ether at 90 °C. The linear evolution of the number average molecular weights with percentage monomer conversion indicates that, after complete initiation, the propagation step occurred without chain transfer or termination steps and the number of growing chains were constant throughout the polymerization reaction. However, the experimental number average molecular weights were higher than the theoretical values obtained from the stoichiometry of the polymerization reaction. The higher \overline{M}_n (SEC) values could be attributed to the reduction of the concentration of the initiator species due to side reactions. In addition, rapid initiation reactions relative to the propagation steps

were observed, as evidenced by the formation of polymers with narrow molecular weight distributions $\overline{M}_w / \overline{M}_n = 1.03$ to 1.43.

The polymerization kinetic data shows that a series of α -siloxyl functionalized poly(methyl methacrylate) derivatives with good control of polymer variables such as number average molecular weight, molecular weight distribution and chain end functionality are obtained by the ATRP of methyl methacrylate using siloxyl functionalized initiator adduct (**2**) as initiator in the presence of CuBr/bpy or CuBr/PMDETA as the catalyst systems

4.3.4 Synthesis of α -Bis(siloxyl) Functionalized Poly(methyl methacrylate), (9).

(a) With CuBr/bpy as the catalyst/ligand system:

The polymerization kinetic experiments for the ATRP of methyl methacrylate were conducted and α -bis(siloxyl) functionalized poly(methyl methacrylate), (**9**) derivatives were produced in quantitative yields. By utilizing a disiloxyl substituted 1,1-diphenylethylene derivative as functionalized initiator precursor in ATRP reactions, a series of different α -bis(siloxyl) functionalized poly(methyl methacrylate) derivatives were prepared by standard ATRP methods. The polymerization of methyl methacrylate was initiated by the disiloxyl functionalized initiator adduct, (**7**) which was prepared in situ by the reaction of (1-bromoethyl)benzene with 1,1-bis(4-t-butyl dimethylsiloxypheyl)-1-phenylethylene, (**6**) in the presence of the CuBr/bpy catalyst system in diphenyl ether at 90 °C. The different polymerization reactions were conducted by standard ATRP methods by varying the initial concentrations of the monomer to initiator, $[M]_0/[I]_0$ from 50:1, 100:1 to 200:1 and the general ratio of reactants $[R-X]:[CuBr]:[Ligand] = 1:1:3$. After the addition of methyl methacrylate, an aliquot (1 mL) was removed

from the reaction mixture and diluted with THF (9 mL) to measure the initial methyl methacrylate concentration by gas chromatography at time, $t=0$. Similarly, at 30 minutes time intervals, aliquots (1 mL) were taken from the solution and dissolved in THF (9 mL) to determine the extent of monomer consumption with time by gas chromatographic analysis. The number average molecular weight and molecular weight distribution of each polymer sample was determined by size exclusion chromatography. The following table depicts the raw ATRP kinetic data for the synthesis of α -bis(siloxy) functionalized poly(methyl methacrylate) in the presence of the CuBr/bpy catalyst system:

Synthesis of α -Bis(siloxy) Functionalized Poly(methyl methacrylate), (9).

| [M] ₀ /[I] ₀ | Catalyst/Ligand | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) (x 10 ³) g/mol | $\overline{M}_w / \overline{M}_n$ |
|------------------------------------|-----------------|------------|----------------------|---|-----------------------------------|
| 50:1 | CuBr/bpy | 0.5 | 29.10 | 2.37 | 1.16 |
| | | 1 | 37.74 | 2.8 | 1.15 |
| | | 1.5 | 53.49 | 4.6 | 1.14 |
| | | 2 | 64.70 | 6.2 | 1.26 |
| | | 2.5 | 74.90 | 7.0 | 1.22 |
| | | 3 | 85.11 | 8.1 | 1.19 |
| 100:1 | CuBr/bpy | 0.5 | 19.21 | 4.1 | 1.16 |
| | | 1 | 30.30 | 5.6 | 1.28 |
| | | 1.5 | 41.17 | 6.5 | 1.27 |
| | | 2 | 48.58 | 7.3 | 1.19 |
| | | 2.5 | 62.05 | 8.9 | 1.09 |
| | | 3 | 68.01 | 9.9 | 1.15 |
| 200:1 | CuBr/bpy | 0.5 | 14.47 | 5.2 | 1.17 |
| | | 1 | 18.21 | 6.3 | 1.15 |
| | | 1.5 | 30.79 | 8.2 | 1.22 |
| | | 2 | 40.91 | 9.3 | 1.16 |
| | | 2.5 | 55.69 | 10.5 | 1.07 |
| | | 3 | 64.46 | 11.6 | 1.08 |

Figure 49 shows the plots of percentage monomer conversion versus polymerization time for the ATRP of methyl methacrylate, initiated by a new disiloxy functionalized initiator adduct (**7**) in the presence of the CuBr/bpy catalyst system in diphenyl ether at 90 °C. The initial initiator concentration

affects the overall rate of monomer consumption. The rate of monomer consumption was the fastest at $[M]_0/[I]_0 = 50:1$ and the percentage monomer conversion value of 85% was observed after 3 hours. A slight decrease in the extent of monomer consumption was obtained when the initial initiator concentration were reduced to $[M]_0/[I]_0 = 100:1$ and $200:1$, where percentage monomer conversion values of 68% and 64% were recorded after 3 hours, respectively.

Figure 50 shows the first order kinetic plots for the ATRP of methyl methacrylate initiated by the disiloxy functionalized initiator adduct, **(7)** in the presence of the CuBr/bpy catalyst system. The disiloxy functionalized initiator adduct, **(7)** was prepared by the reaction of (1-bromoethyl)benzene with 1,1-bis(4-t-butyl dimethylsiloxyphenyl)ethylene, **(6)** catalyzed by CuBr/bpy in diphenyl ether at 90 °C. The polymerization reaction was fastest at higher concentration of the initiator system. The linear relationship between $\ln([M]_0/[M])$ versus reaction time indicates that the concentration of the propagating radicals remained constant during the polymerization process for each reaction, irrespective of the initial initiator concentration.

Figure 51 shows the plots of \overline{M}_n and $\overline{M}_w / \overline{M}_n$ versus percentage monomer conversion for the different ATRP reactions for the preparation of α -bis(siloxy) functionalized poly(methyl methacrylate) derivatives, **(9)**. The methyl methacrylate polymerization was initiated by the disiloxy functionalized initiator adduct, **(7)** prepared by the reaction of (1-bromoethyl)benzene with 1,1-bis(4-t-butyl dimethylsiloxyphenyl)ethylene, catalyzed by CuBr/bpy in diphenyl ether at 90 °C. After completion of the initiator step, a linear increase in the number average molecular weights with percentage monomer conversion is observed for each reaction. The linear relationship between number average molecular weight and percentage monomer conversion implies that, after complete *in situ* formation of the initiator adduct **(7)**, the initiation of methyl

methacrylate was rapid and efficient and the concomitant propagation step proceeded without any side reactions.

However, the experimental number average molecular weight values are significantly higher than the theoretical values predicted from reaction stoichiometry, indicating the reduction of the initiator concentration during initiator adduct formation. The deviation of the experimental number average molecular weight values from values obtained by the reaction stoichiometry may indicate the prevalence of side reactions, such as radical termination, leading to the reduction in initiator concentrations before the onset of the propagation process. The formation of polymers with narrow molecular weight distributions, in the range of 1.07-1.28, indicates that each polymerization reaction proceeded by a controlled free radical polymerization mechanism.

(b) With CuBr/PMDETA as the catalyst/ligand system:

In general, the choice of the catalyst/ligand system affects the polymerization kinetics for a particular ATRP reaction. The initiation of methyl methacrylate polymerization by a new disiloxy functionalized initiator adduct (**7**), formed by the reaction of (1-bromoethyl)benzene and 1,1-bis(4-t-butyl)dimethylsiloxyphenyl)ethylene in the presence of CuBr/PMDETA catalyst system in diphenyl ether at 90 °C, affords α -bis(siloxy) functionalized poly(methyl methacrylate), (**9**). The following table shows the polymerization kinetic data for the ATRP of methyl methacrylate, initiated by a new disiloxy functionalized initiator adduct, (**7**) in the presence of CuBr/PMDETA in diphenyl ether at 90 °C for three different polymerization reactions at initial monomer to initiator concentration ratios of 50:1, 100: and 200:1.

Synthesis of α -Bis(siloxy) Functionalized Poly(methyl methacrylate), (9).

| $[M]_0/[I]_0$ | Catalyst/Ligand | Time (hrs) | % Monomer Conversion | \overline{M}_n (SEC) ($\times 10^3$) g/mol | $\overline{M}_w / \overline{M}_n$ |
|---------------|-----------------|------------|----------------------|---|-----------------------------------|
| 50:1 | CuBr/PMDETA | 0.5 | 27.58 | 2.4 | 1.07 |
| | | 1 | 45.52 | 2.8 | 1.05 |
| | | 1.5 | 55.21 | 3.3 | 1.08 |
| | | 2 | 73.45 | 3.8 | 1.05 |
| | | 2.5 | 85.01 | 4.2 | 1.05 |
| | | 3 | 95.10 | 5.5 | 1.01 |
| 100:1 | CuBr/PMDETA | 0.5 | 16.29 | 3.4 | 1.21 |
| | | 1 | 30.59 | 4.7 | 1.27 |
| | | 1.5 | 45.98 | 6.8 | 1.10 |
| | | 2 | 53.38 | 8.1 | 1.13 |
| | | 2.5 | 68.98 | 10.8 | 1.13 |
| | | 3 | 73.76 | 11.8 | 1.09 |
| 200:1 | CuBr/PMDETA | 0.5 | 10.55 | 6.1 | 1.21 |
| | | 1 | 22.76 | 7.5 | 1.17 |
| | | 1.5 | 30.07 | 8.2 | 1.03 |
| | | 2 | 44.36 | 9.8 | 1.31 |
| | | 2.5 | 58.34 | 11.6 | 1.13 |
| | | 3 | 67.96 | 12.9 | 1.02 |

Figure 52 shows the plots of the percentage monomer conversion versus time for the respective polymerization reactions for the preparation of α -bis(siloxy) functionalized poly(methyl methacrylate), (9). At high initiator concentration, $[M]_0/[I]_0 = 50:1$, after an initial rapid monomer conversion of 27% after 0.5 hours, the

overall percentage monomer conversion of 95% was reached after 3 hours. The polymerization reaction is affected by the concentration of the initiator system. With the reduction in initiator concentration to $[M]_0/[I]_0 = 100:1$, a reduction in the percentage monomer conversion to 74% was observed after 3 hours. At low initiator concentration, when $[M]_0/[I]_0$ was increased to 200:1, the extent of monomer consumption of 68% was recorded after 3 hours. For all three polymerization reactions, a linear relationship between the percentage monomer conversion with time was observed after an initial rapid monomer consumption within 0.5 hours.

Figure 53 depicts a linear relationship for the plots of $\ln([M]_0/[M])$ versus time for the different ATRP reactions which involved the initiation of the polymerization of methyl methacrylate by the disiloxyl functionalized initiator adduct, **(7)**. The disiloxyl functionalized initiator adduct, **(7)** was formed *in situ* by the reaction of 1,1-bis(4-t-butyl dimethylsiloxyphenyl)ethylene, **(6)** with (1-bromoethyl)benzene in the presence of CuBr/PMDETA in diphenyl ether at 90 °C. The polymerization reactions were conducted at different monomer to initiator concentrations of $[M]_0/[I]_0 = 50:1$, 100:1 and 200:1. The rate of polymerization is influenced by the initial concentration of the initiator system. The polymerization rate was the fastest at higher initiator concentration of $[M]_0/[I]_0 = 50:1$. The linearity of the relationship between $\ln([M]_0/[M])$ and time implies that each polymerization reaction followed first order rate kinetic with respect to monomer consumption and indicates that the concentration of the propagating radicals remained constant during the polymerization process for each polymerization reaction. Furthermore, a large reduction in the polymerization rate was observed when the initiator concentrations were reduced to $[M]_0/[I]_0 = 100:1$ and $[M]_0/[I]_0 = 200:1$, respectively.

Figure 54 depicts the plots of number average molecular weight and molecular weight distribution versus percentage monomer conversion for the ATRP of methyl methacrylate using a new disiloxyl functionalized initiator adduct, **(7)** as

initiator. The siloxyl functionalized initiator adduct, **(7)** was prepared by the reaction of 1,1-bis(4-t-butyl(dimethyl)siloxy)phenyl)ethylene, **(6)** with (1-bromoethyl)benzene in the presence of CuBr/PMDETA in diphenyl ether at 90 °C. The linear increase in the average number molecular weight values as a function of percentage monomer conversion indicates that, after completion of the initiation step, the propagation step proceeded without chain transfer and termination reactions. However, the observed number average molecular weight values are higher than the expected values. The prevalence of side reactions during formation of the initiator adduct species reduces the initiator concentration and leads to polymers with high number average molecular weights. The linearity of the plots indicates the polymerization proceeded by normal ATRP mechanisms which involves a fast exchange between an active dormant species, that is, fast initiation of the polymerization of methyl methacrylate and no contribution of chain transfer and termination reactions. The significant increase in the number average molecular weight indicates that all chains grew in direct relation with the disappearance of the monomer, typical of a controlled living free radical polymerization process.

For each polymerization reaction, polymers with narrow molecular weight distributions, ranging from $\overline{M}_w / \overline{M}_n = 1.02-1.27$, were obtained for the different polymerization reactions implying that the rates of initiation were rapid and equal to or greater than the rates of propagation.

Polymerization kinetic studies show that the synthesis of α -bis(siloxyl) functionalized poly(methyl methacrylate) via the ATRP of methyl methacrylate using the disiloxyl functionalized initiator adduct, **(7)** in the presence of CuBr/bpy or CuBr/PMDETA as the catalyst system proceeds via a controlled polymerization process to afford functionalized polymers with good control of all polymer parameters.

CHAPTER 5

SUMMARY

The copper mediated ATRP of styrene and methyl methacrylate, using siloxyl functionalized initiators based on the adducts derived from siloxyl substituted 1,1-diphenylethylene precursors proceeded via a controlled living polymerization process to afford chain end functionalized polymers with controlled number average molecular weights and narrow molecular weight distributions and high chain end functionality. Siloxyl chain end functionalized polymers were prepared by the ATRP of styrene and methyl methacrylate using new well defined siloxyl functionalized initiator adducts as initiators.

α -Siloxyl functionalized polymers were prepared by ATRP methods using the following synthesis strategy:

(a) The siloxyl substituted 1,1-diphenylethylene derivative, 1-(4-t-butyldimethyl-siloxyphenyl)-1-phenylethylene (**1**) was used as a siloxyl functionalized initiator precursor for the preparation of a α -siloxyl functionalized initiator in ATRP reactions.

(b) A new siloxyl functionalized initiator adduct, (**2**), generated *in situ* by the reaction of 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene (**1**) with (1-bromoethyl)benzene, in the presence of CuBr/2,2'-bipyridyl or CuBr/PMDETA was used as initiator for the polymerization of styrene or methyl methacrylate by ATRP methods.

(c) Well defined α -siloxy functionalized polymers with predictable number average molecular weights ($\overline{M}_n = 1.8 \times 10^3 - 1.7 \times 10^4$ g/mol) and narrow molecular weight distributions were obtained in quantitative yields.

Similarly, α -bis(siloxy) functionalized polymers were synthesized by ATRP processes via the following synthesis method:

(a) The disiloxy substituted 1,1-diphenylethylene compound, 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene, (**6**) was employed as a disiloxy functionalized initiator precursor in the preparation of a α -bis(siloxy) functionalized initiator in ATRP reactions:

(b) A new disiloxy functionalized initiator adduct, (**7**), prepared *in situ* by the stoichiometric reaction of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene (**6**) with (1-bromoethyl)benzene in the presence of CuBr/bpy or CuBr/PMDETA catalyst system, was used as initiator for the polymerization of styrene and methyl methacrylate by ATRP methods to form quantitative yields of the corresponding α -bis(siloxy) functionalized polymers with controlled number average molecular weights ($\overline{M}_n = 1.4 \times 10^3 - 1.5 \times 10^4$ g/mol) and narrow molecular weight distributions ($\overline{M}_w / \overline{M}_n = 1.02 - 1.27$).

The polymerization processes were monitored by gas chromatographic analysis. Polymerization kinetic measurements show that each polymerization reaction followed first order rate kinetic with respect to monomer consumption. The number average molecular weight increased linearly with percentage monomer consumption with the concomitant formation of polymers with narrow molecular weight distributions.

Well defined hydroxyl functionalized polymers were prepared by post ATRP chain end modification reactions. The acid catalysed hydrolysis of α -siloxy functionalized polystyrene, (**3**) and α -bis(siloxy) functionalized polystyrene, (**8**) in

the presence of concentrated hydrochloric acid or tetrabutyl ammonium fluoride afforded the corresponding α -hydroxyl functionalized polystyrene, **(5)** and α -bis(hydroxyl) polystyrene **(10)** in quantitative yields, respectively.

The organic compounds, the siloxyl substituted 1,1-diphenylethylene derivatives and the chain end functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, spectroscopy and non-aqueous titration measurements .

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APPENDIX

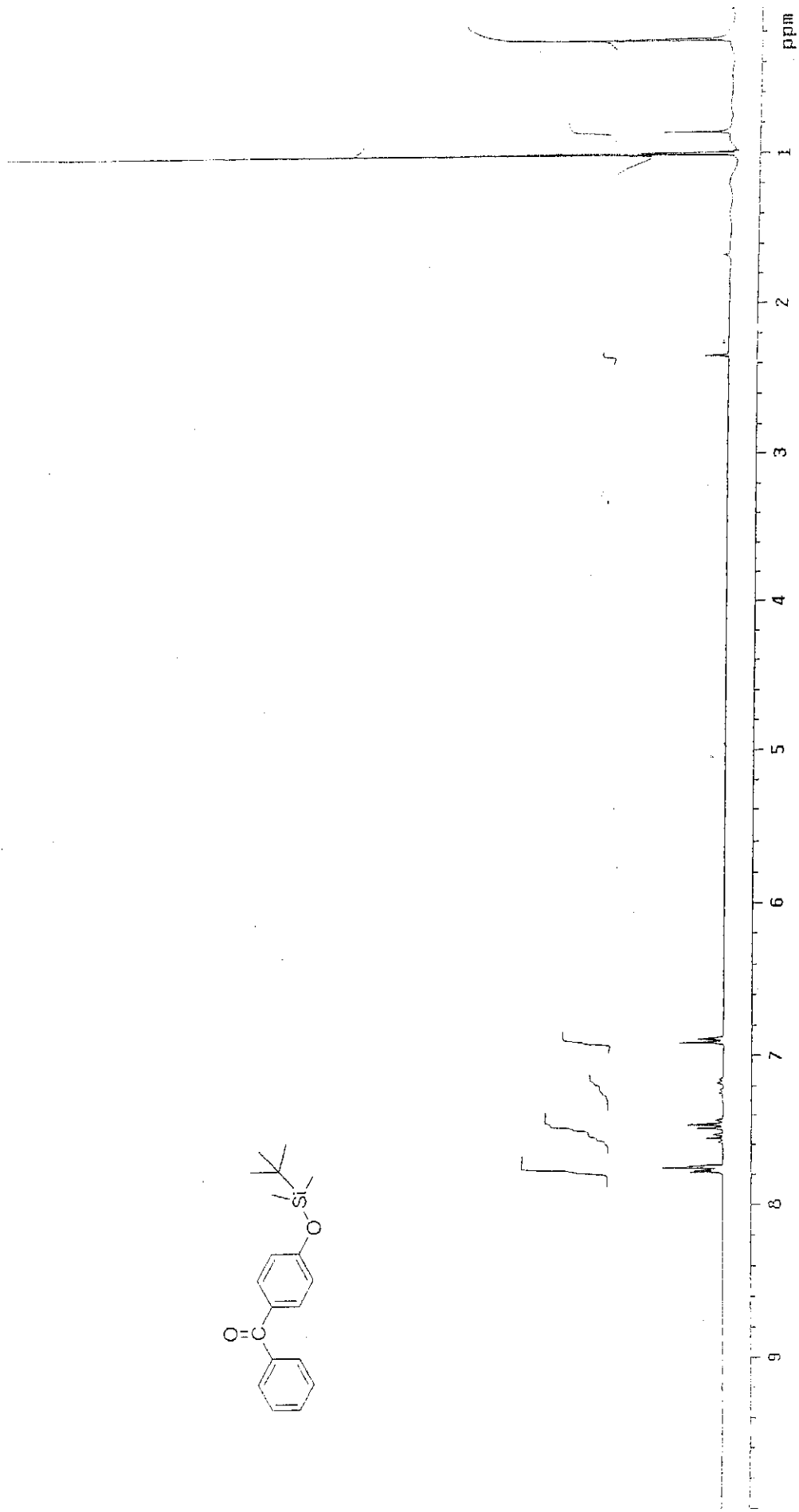
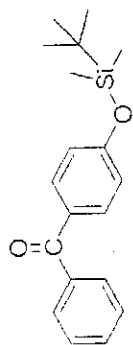


Figure 1. ¹H NMR spectrum of 4-(t-butyl(dimethylsiloxy)benzophenone).

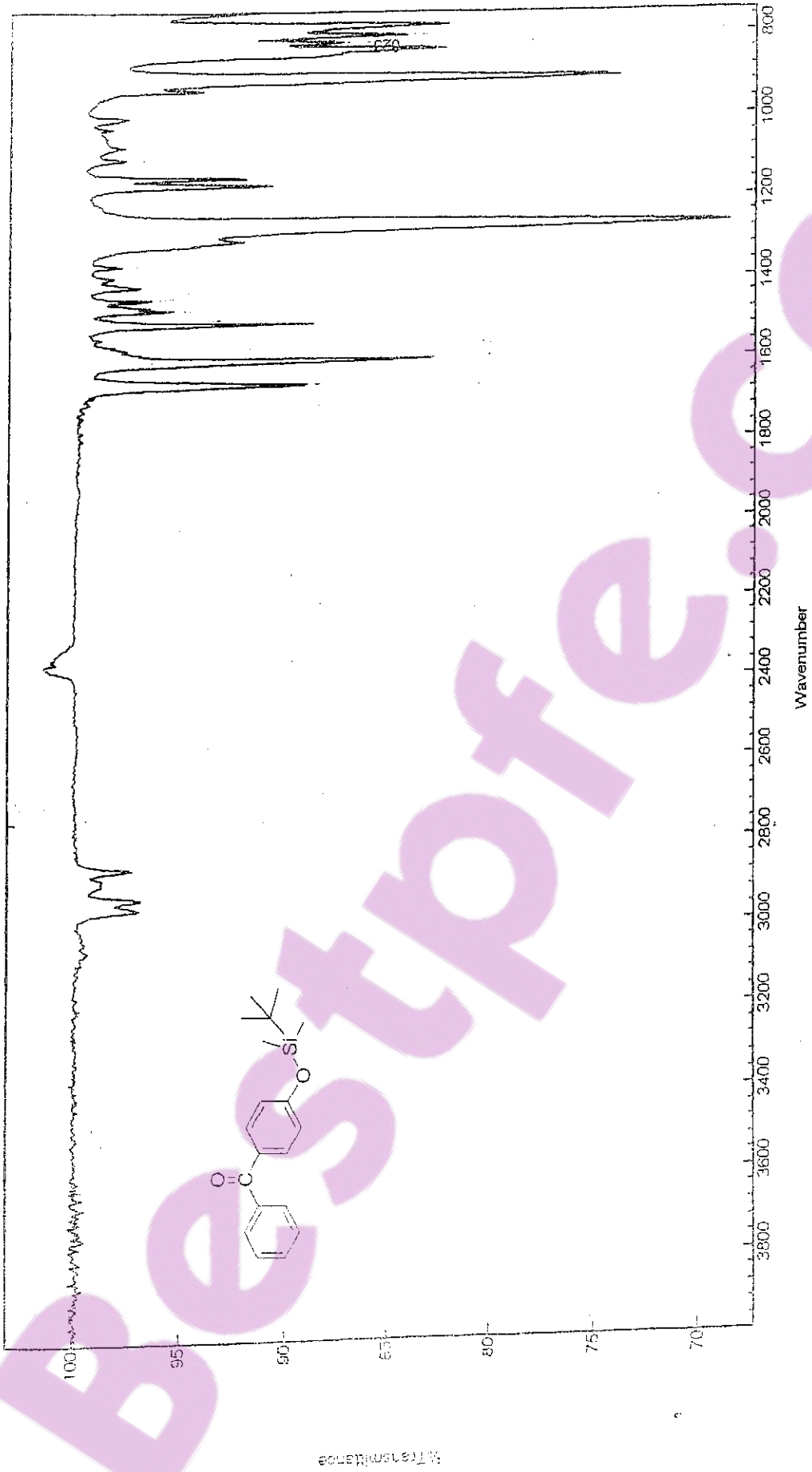


Figure 2. FTIR spectrum of 4-(t-butylidimethylsiloxy)benzophenone.

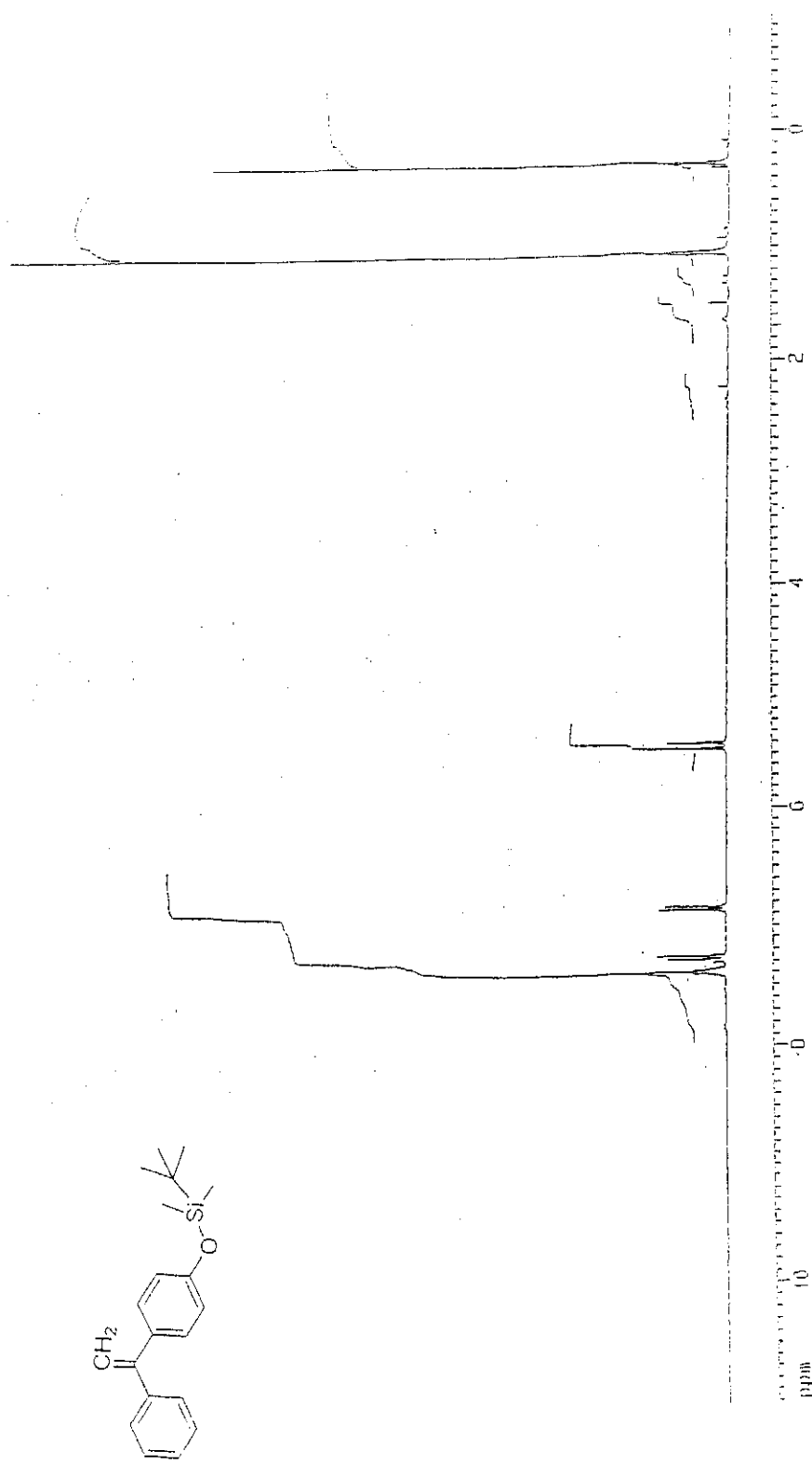


Figure 3. ¹H NMR spectrum of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene, (1).

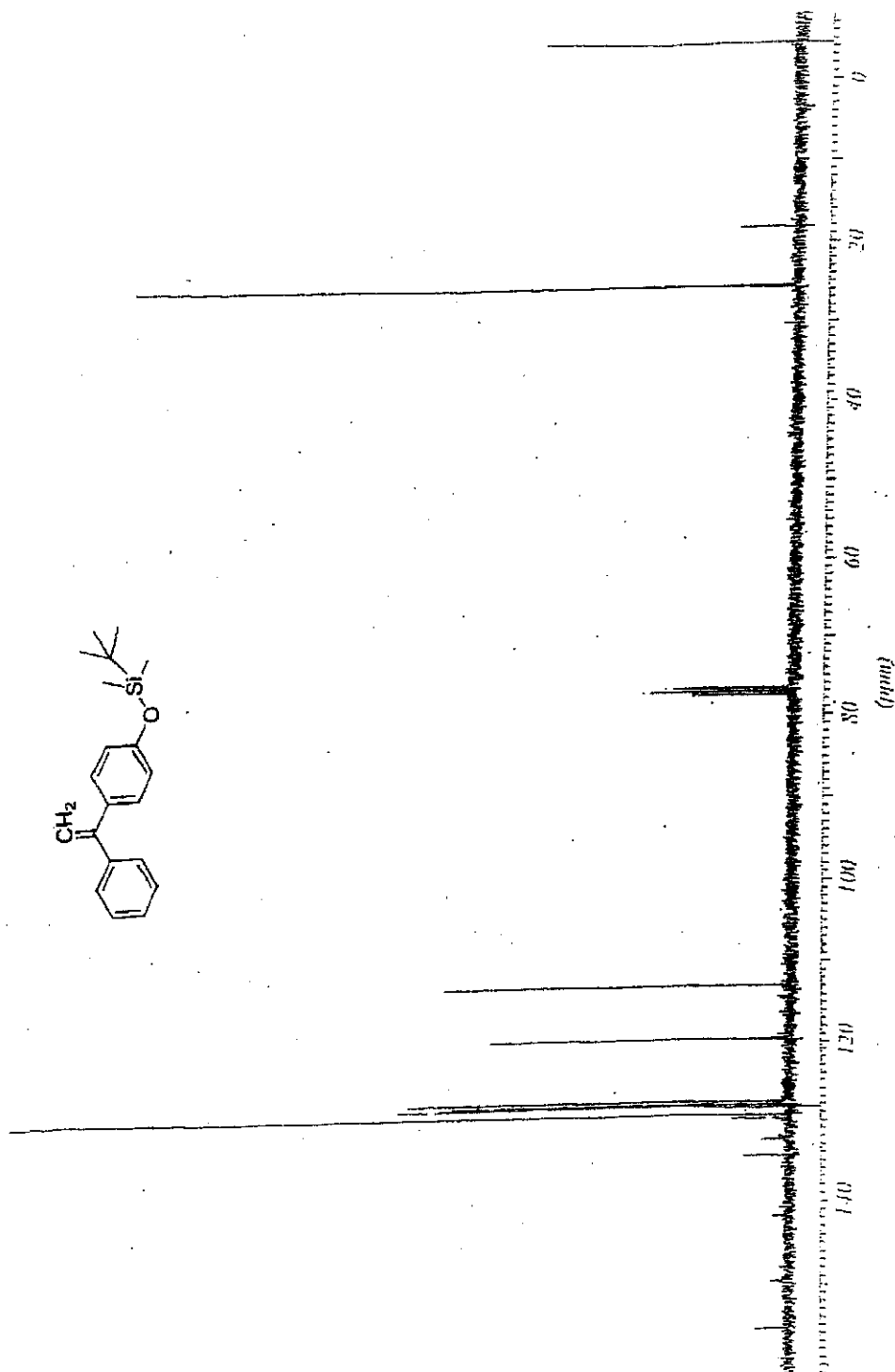


Figure 4. ^{13}C NMR spectrum of 1-(4-t-butyltrimethylsilyloxyphenyl)-1-phenylethylene, (1).

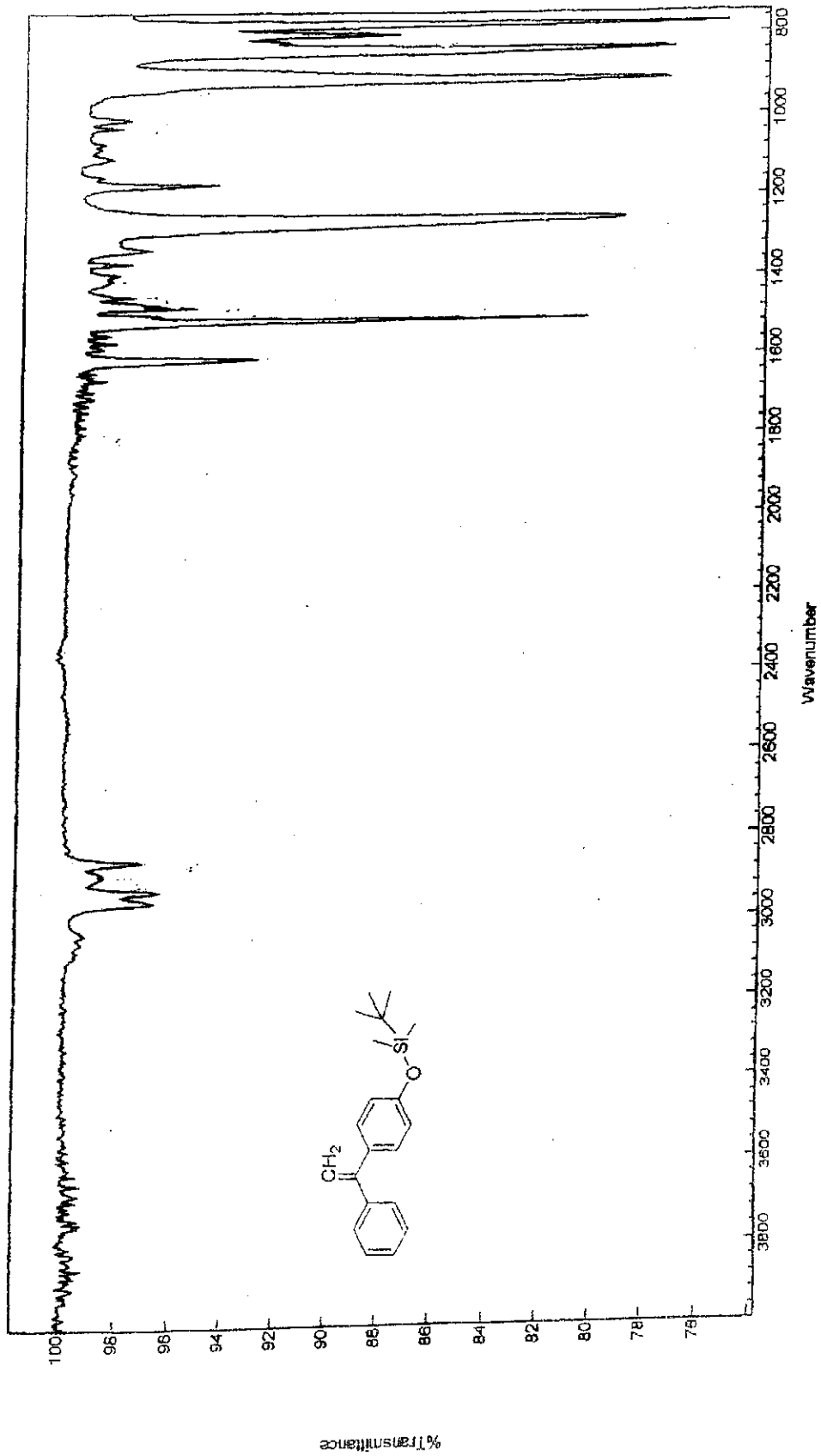
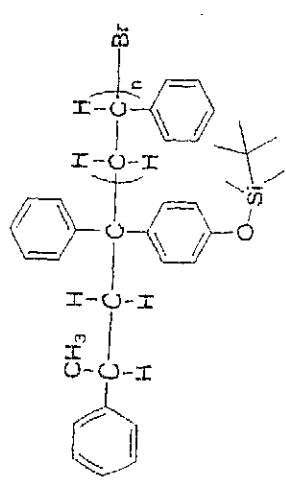
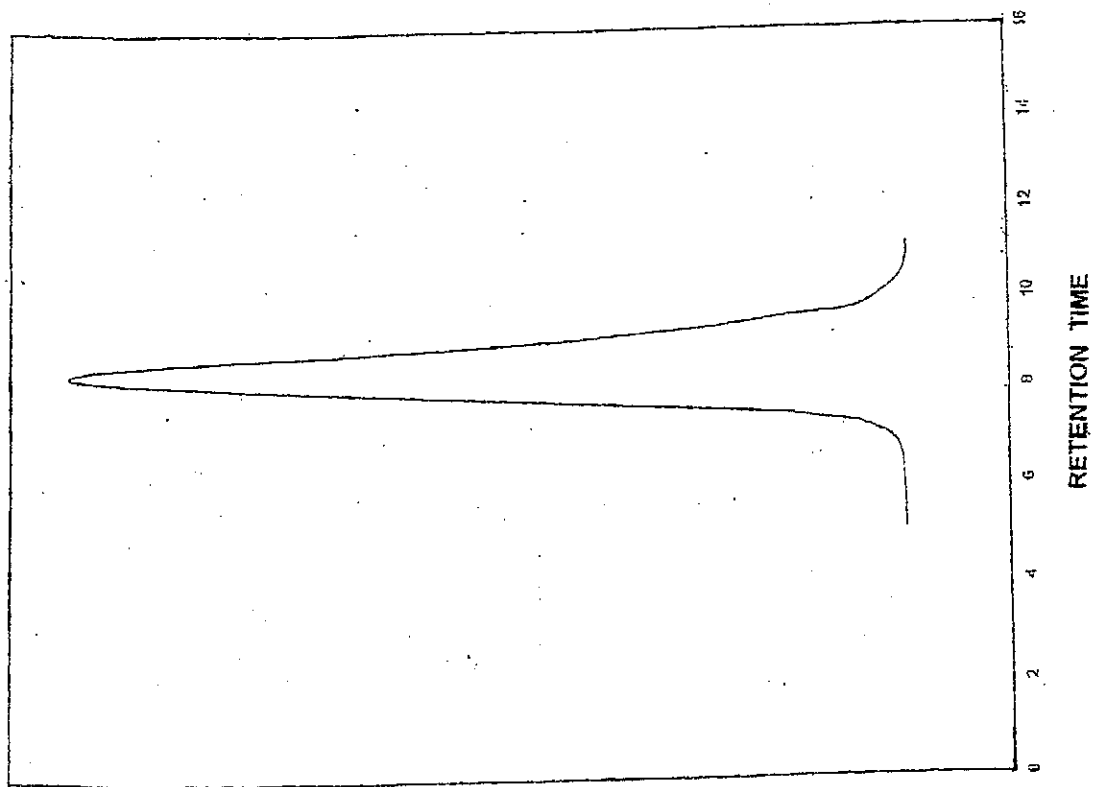


Figure 5. FTIR spectrum of 1-(4-t-butyl(dimethyl)siloxyphenyl)-1-phenylethylene, (1).



DETECTOR RESPONSE (mV)

RETENTION TIME

Figure 6. Size exclusion chromatogram of α -siloxy functionalized polystyrene, (3).

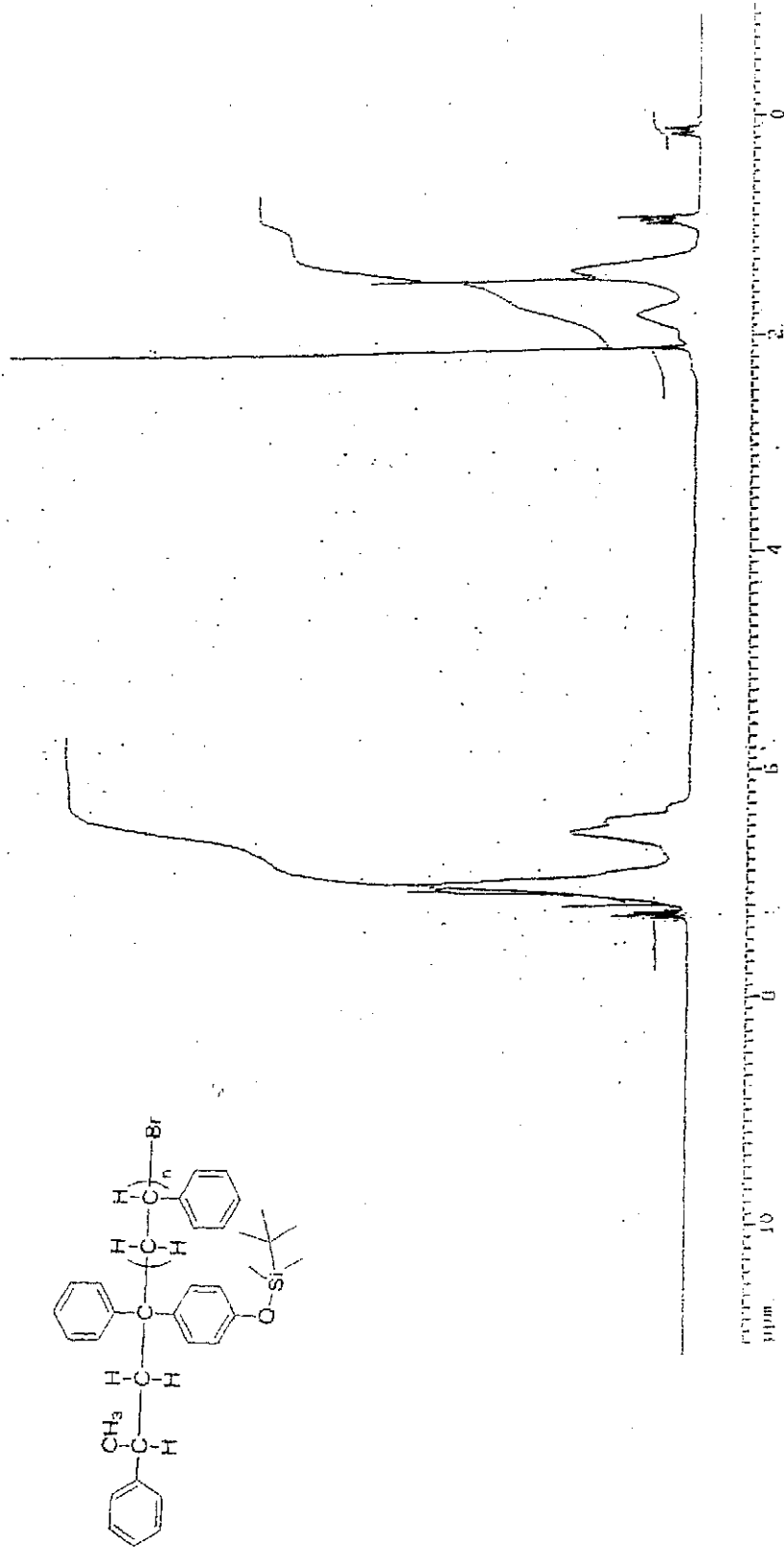


Figure 7. ^1H NMR spectrum of α -siloxy functionalized polystyrene, (3).

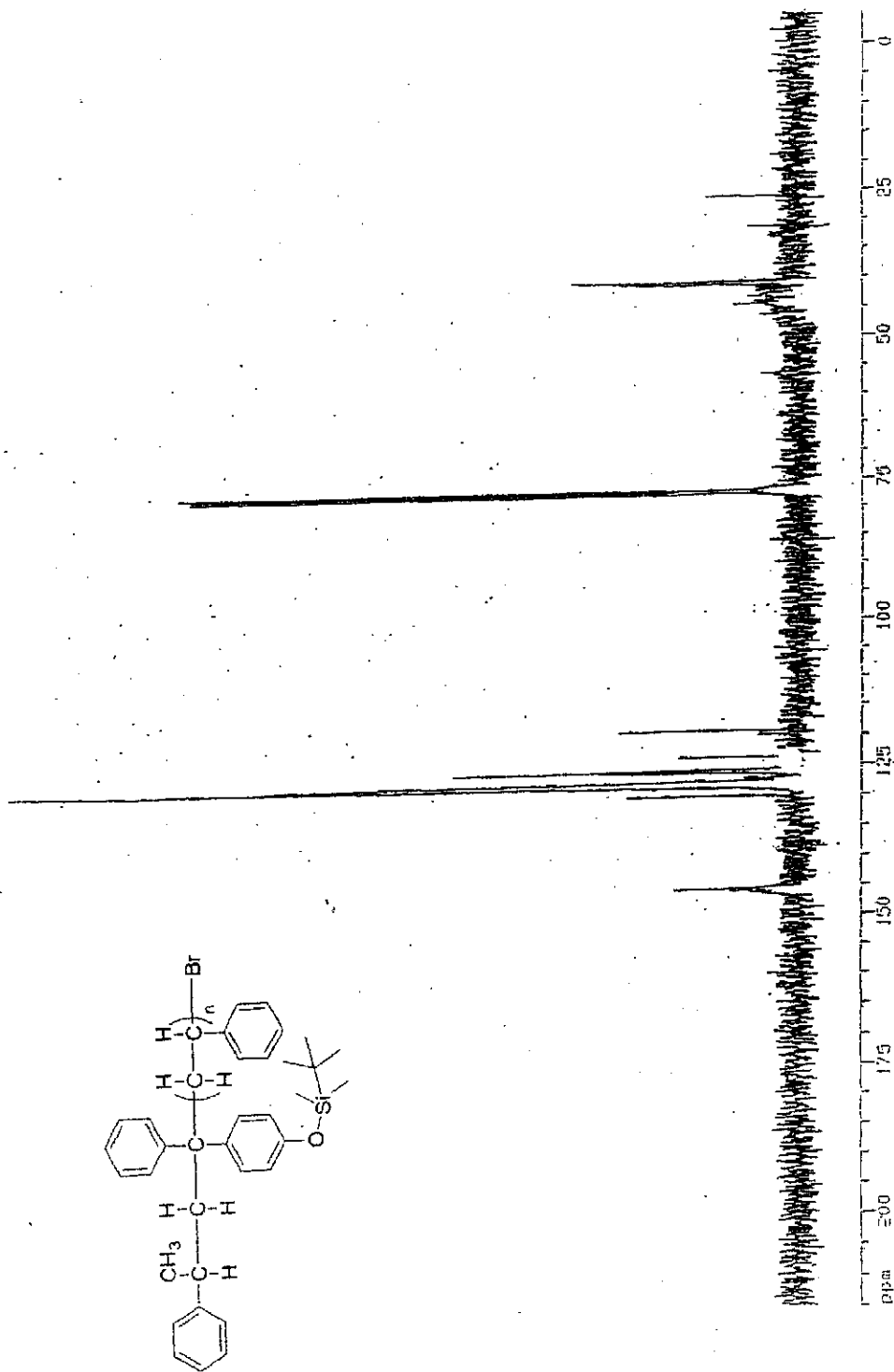


Figure 8. ^{13}C NMR spectrum of α -siloxy functionalized polystyrene, (3).

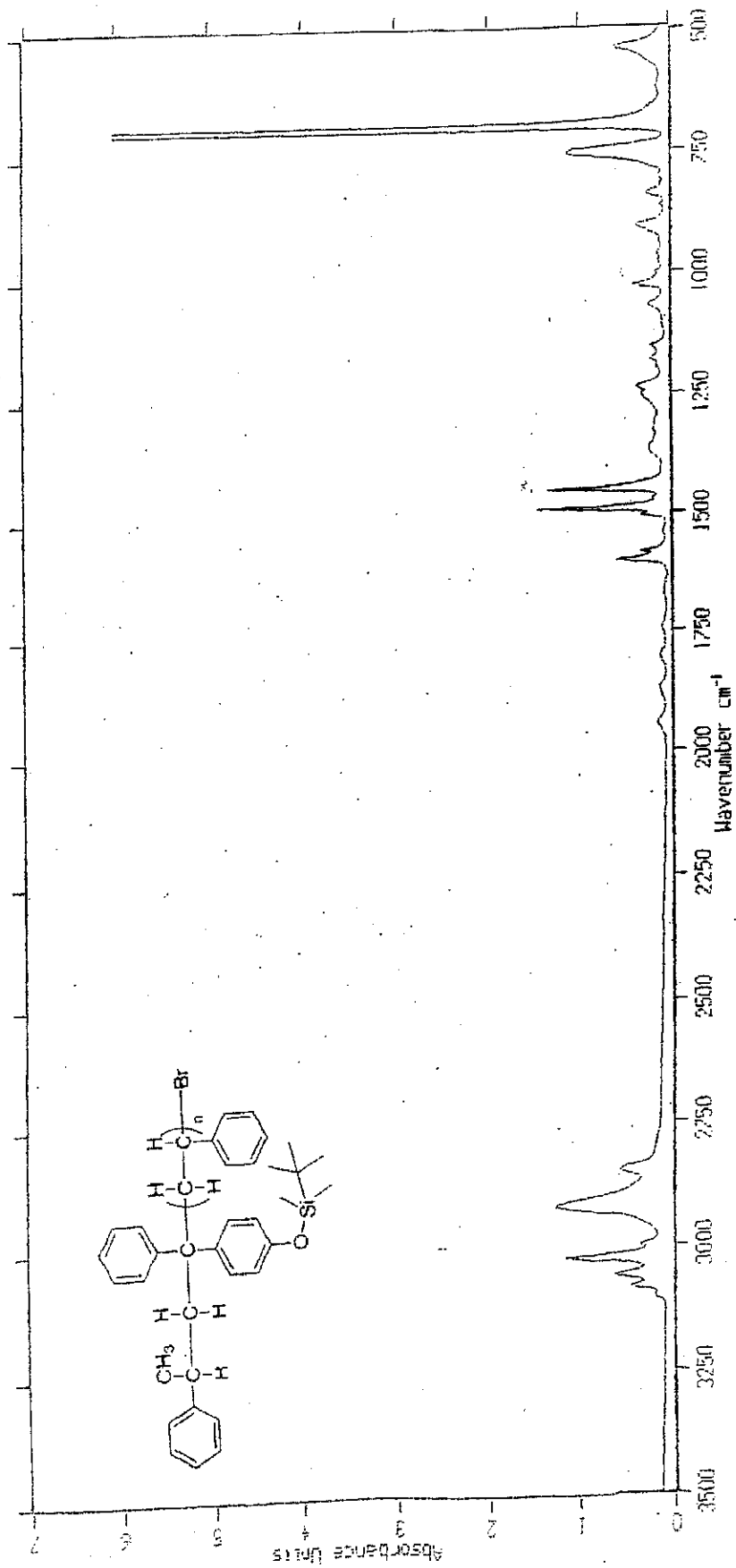


Figure 9. FTIR spectrum of α -siloxy functionalized polystyrene, (3).

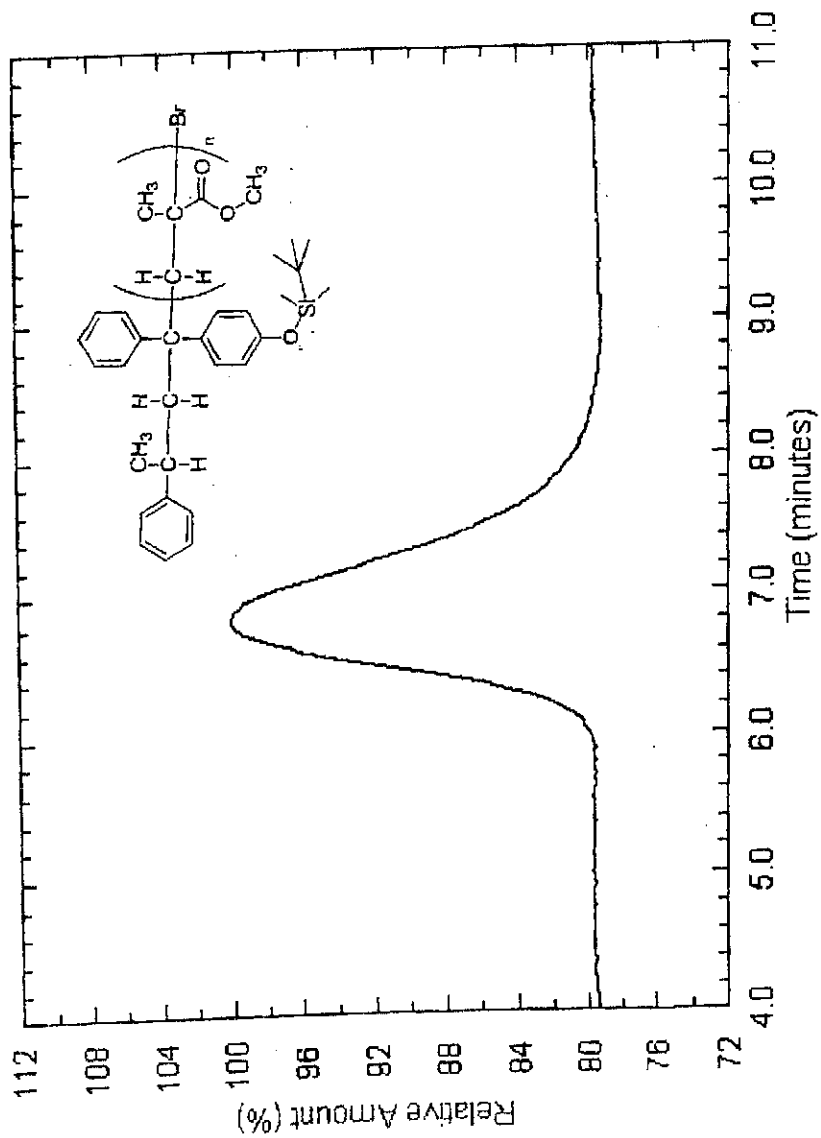


Figure 10. Size exclusion chromatogram of α -siloxy functionalized poly(methyl methacrylate), (4).

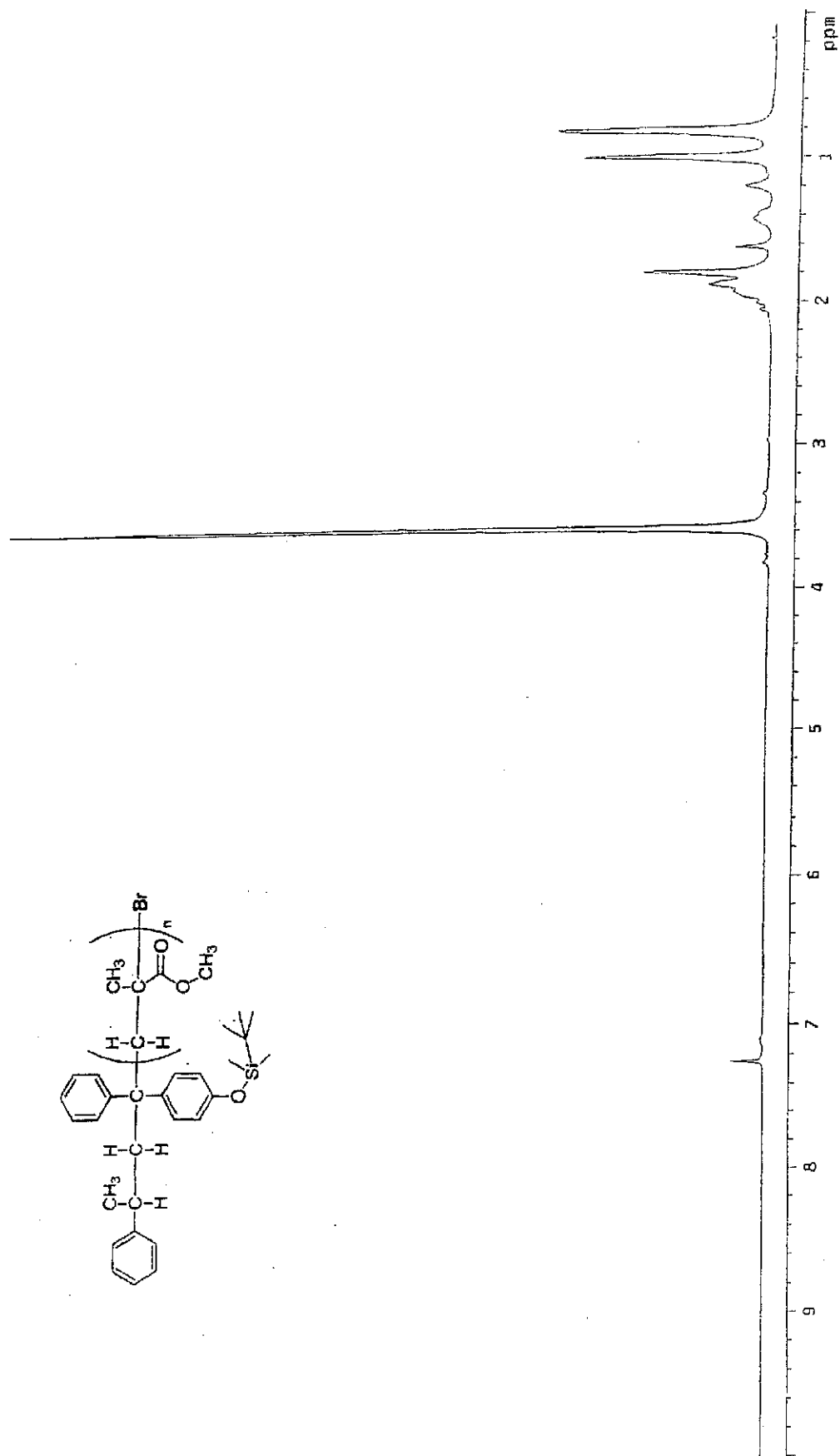


Figure 11. ¹H NMR spectrum of α -siloxy functionalized poly(methyl methacrylate), (4).

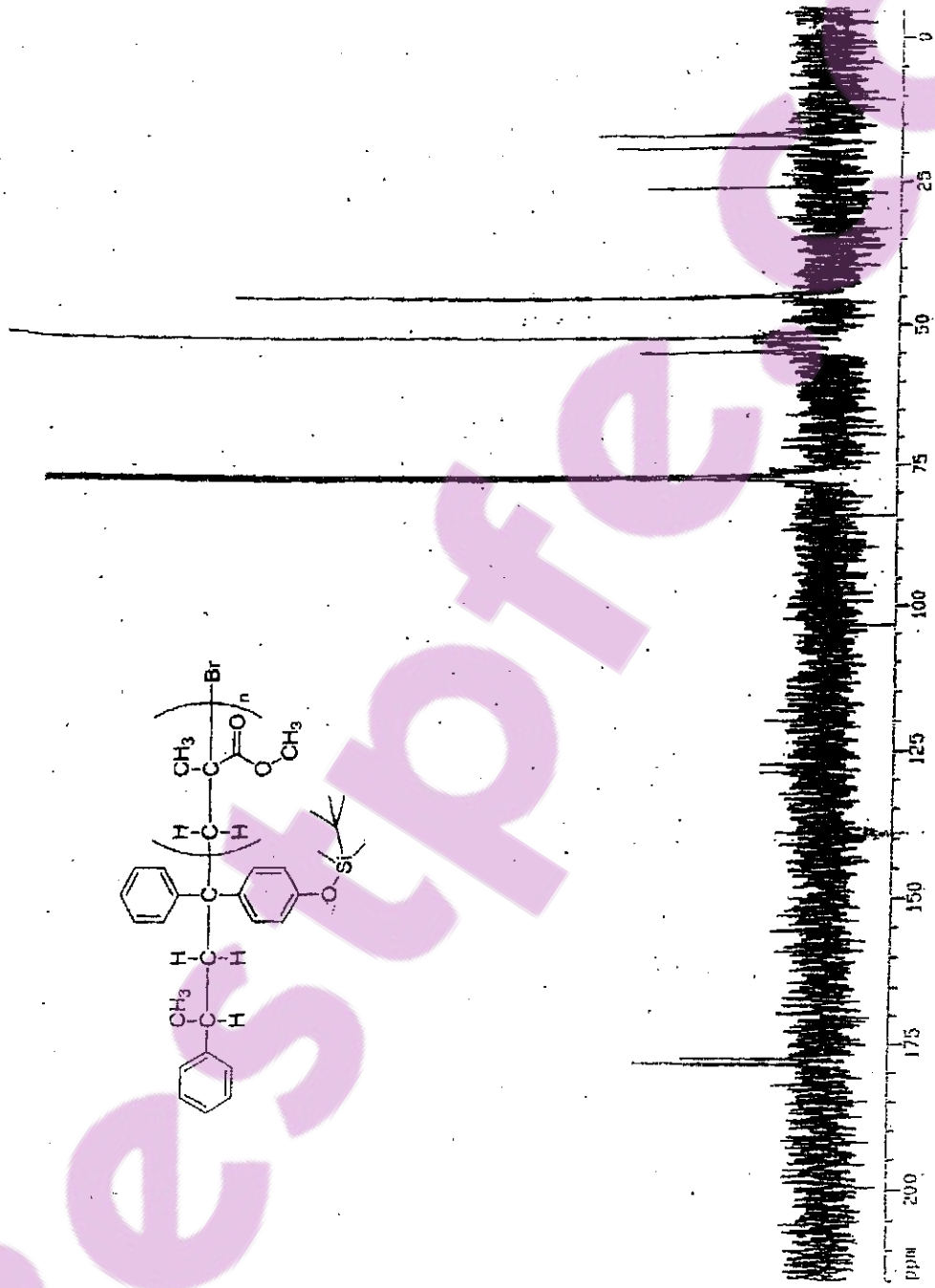
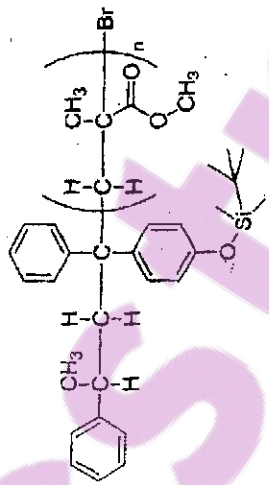


Figure 12. ^{13}C NMR spectrum of α -siloxy functionalized poly(methyl methacrylate), (4).

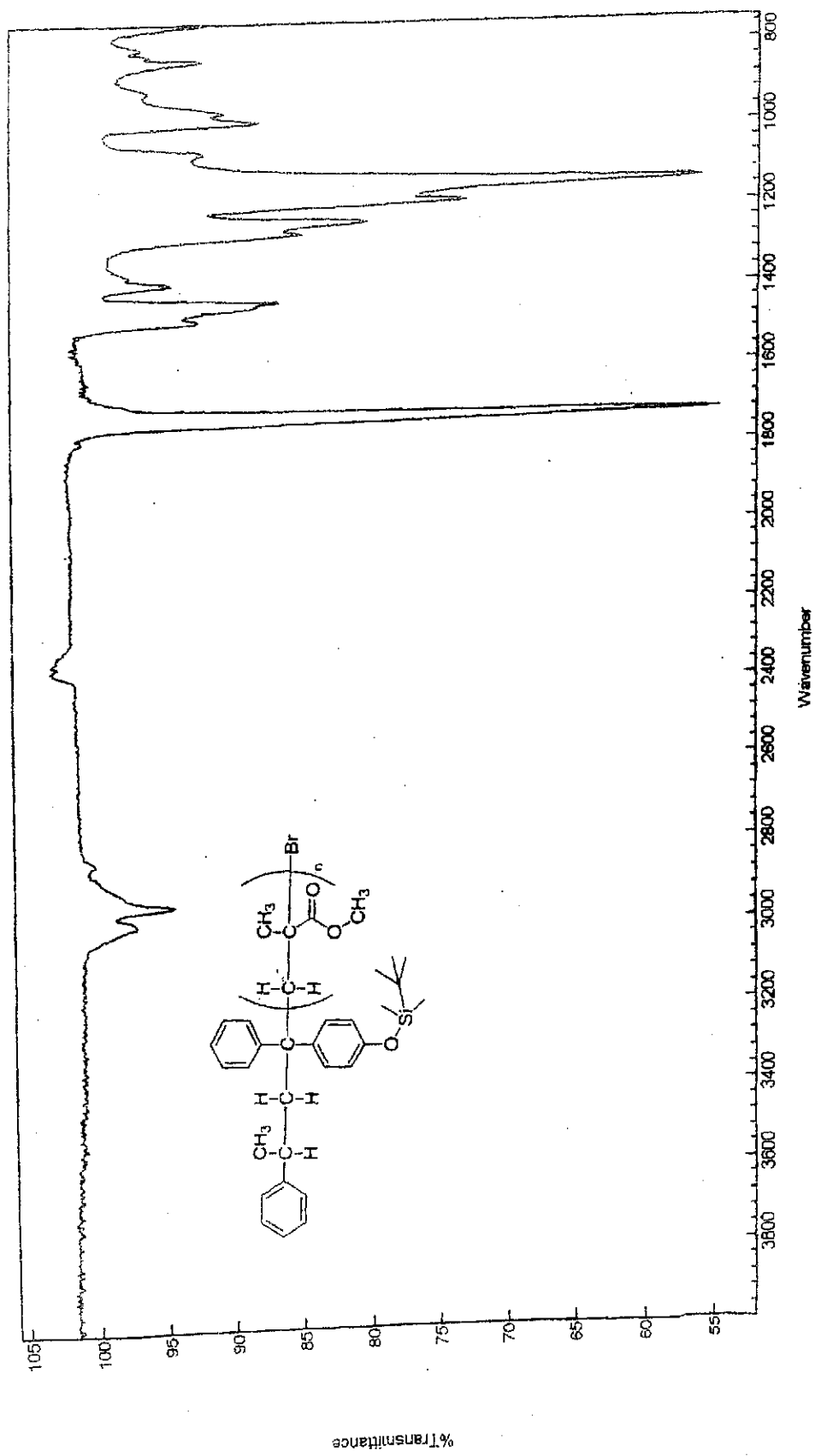


Figure 13. FTIR spectrum of α -siloxy functionalized poly(methyl methacrylate), (4).

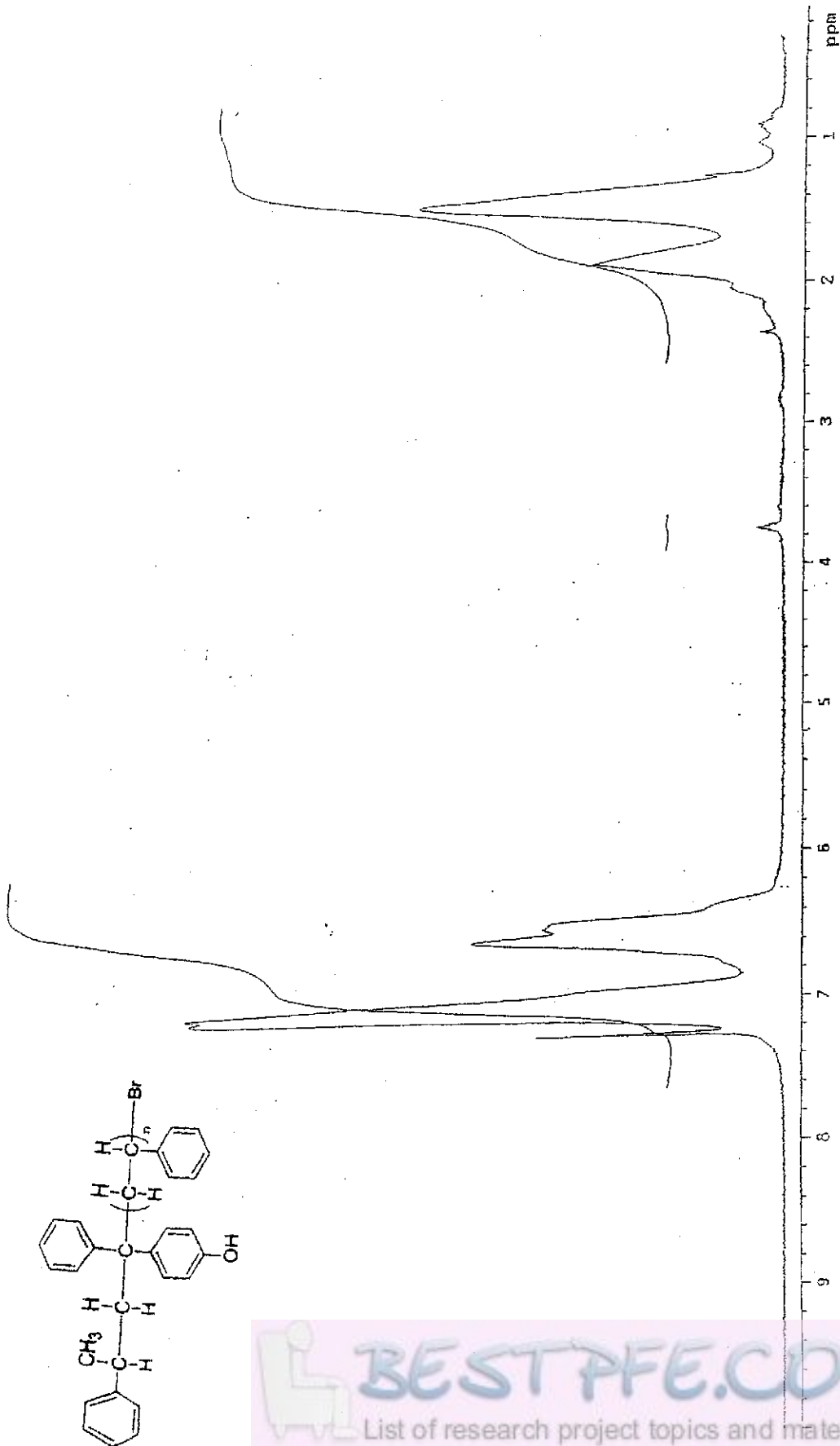


Figure 14. ^1H NMR spectrum of α -hydroxyl functionalized polystyrene, (5).

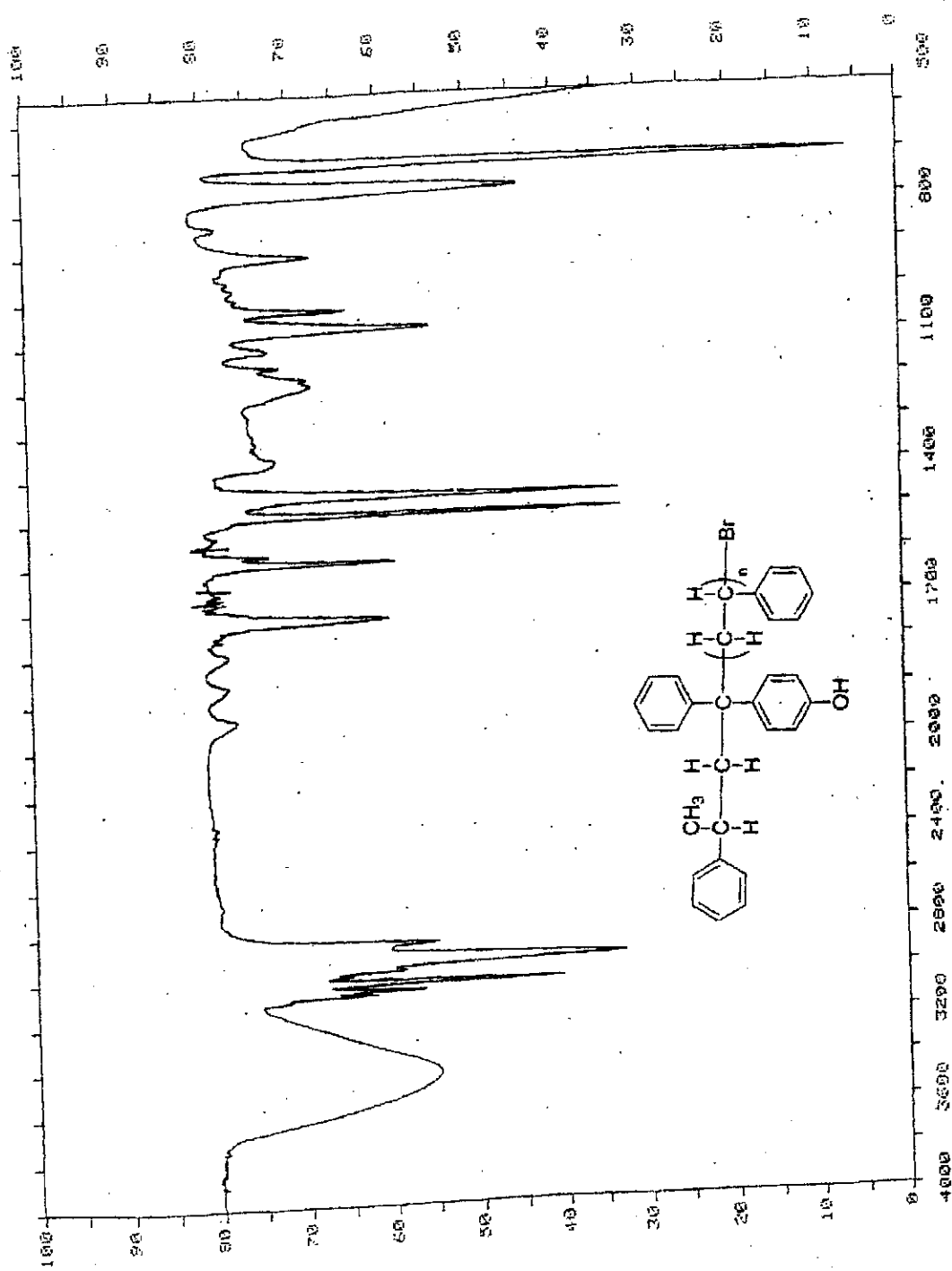


Figure 15. FTIR spectrum of α -hydroxyl functionalized polystyrene, (5).

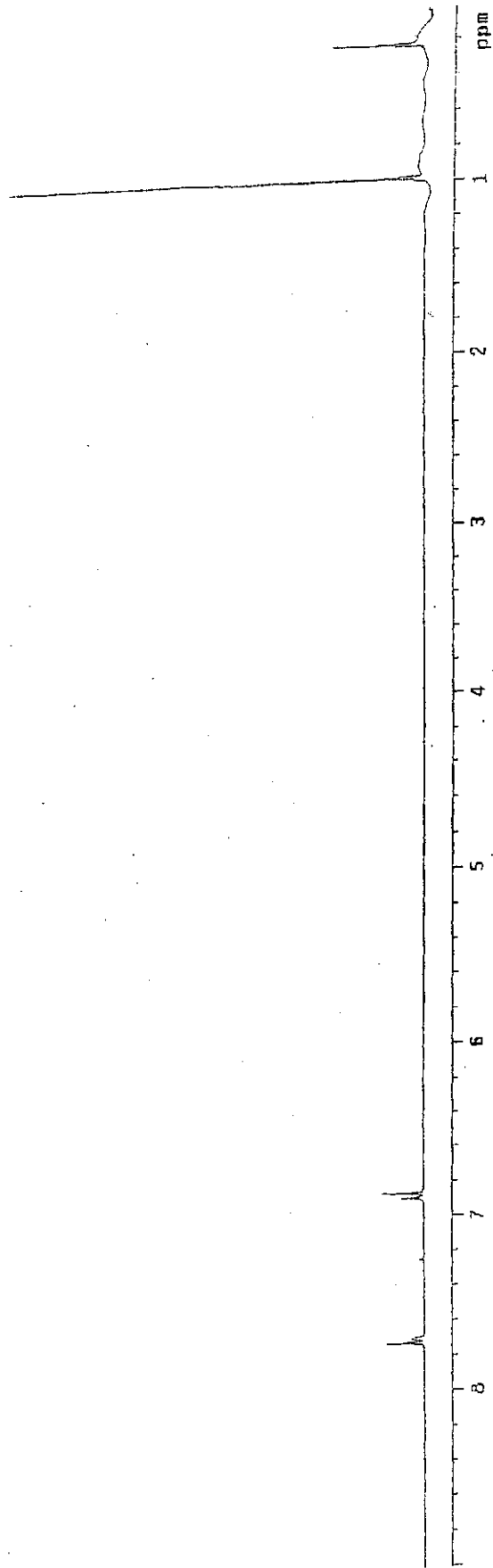
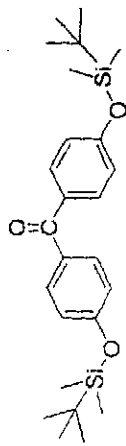


Figure 16. ¹H NMR spectrum of 4,4'-(t-butylidimethylsiloxy)benzophenone.

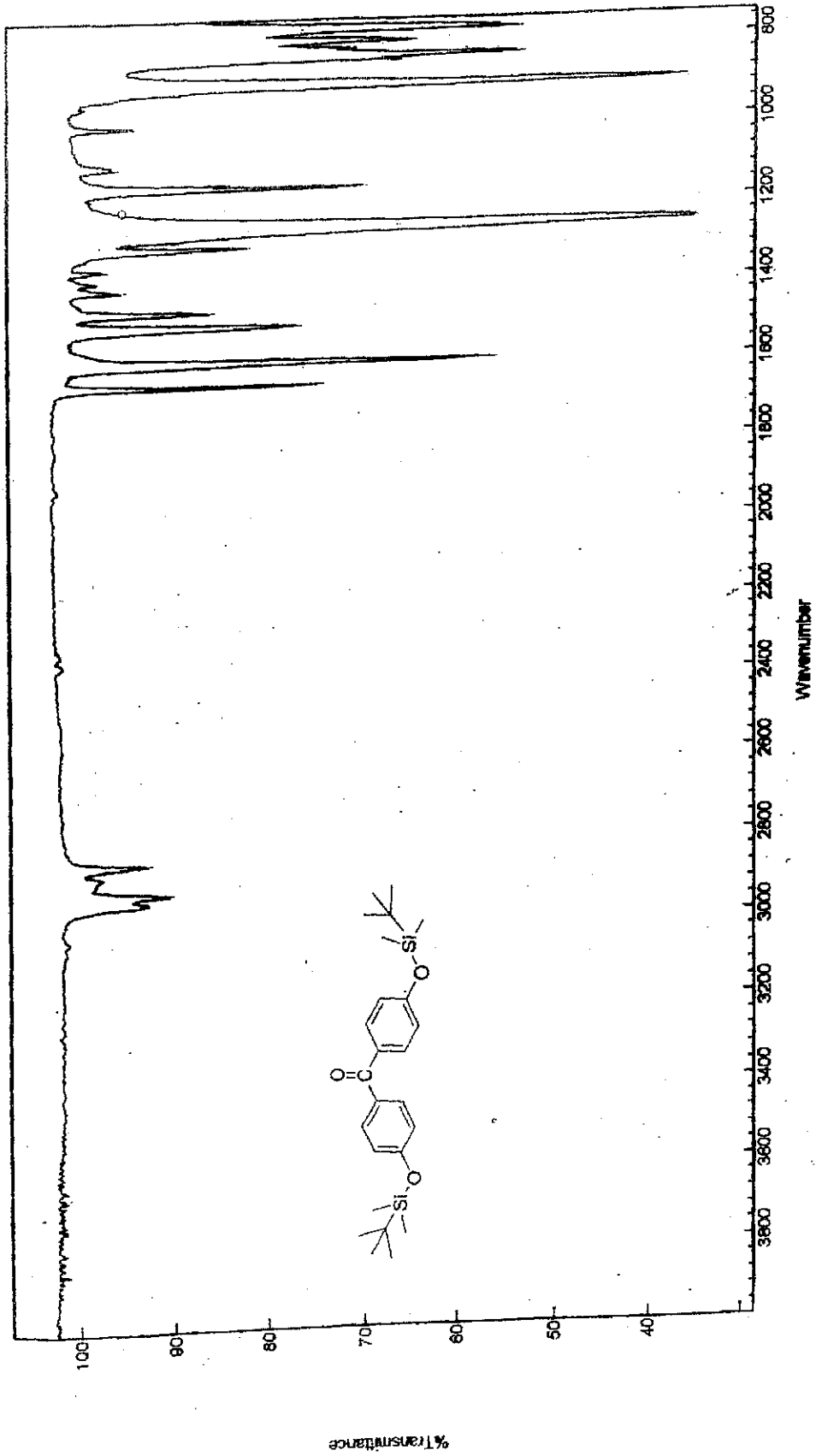


Figure 17. FTIR spectrum of 4,4'-(t-butylidimethylsiloxy)benzophenone.

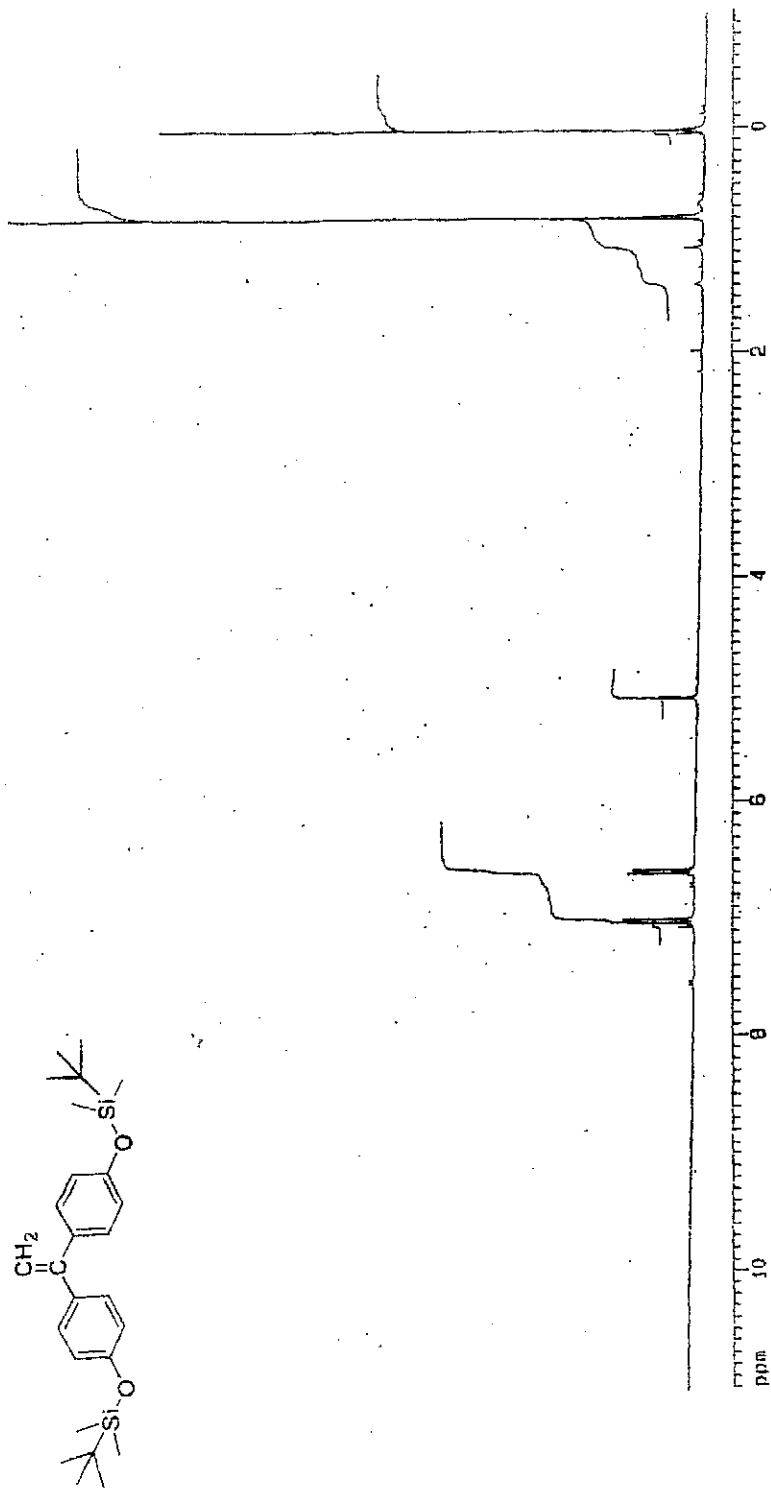


Figure 18. ¹H NMR spectrum of 1,1-bis(4-t-butylmethoxysilyloxyphenyl)ethylene, (6).

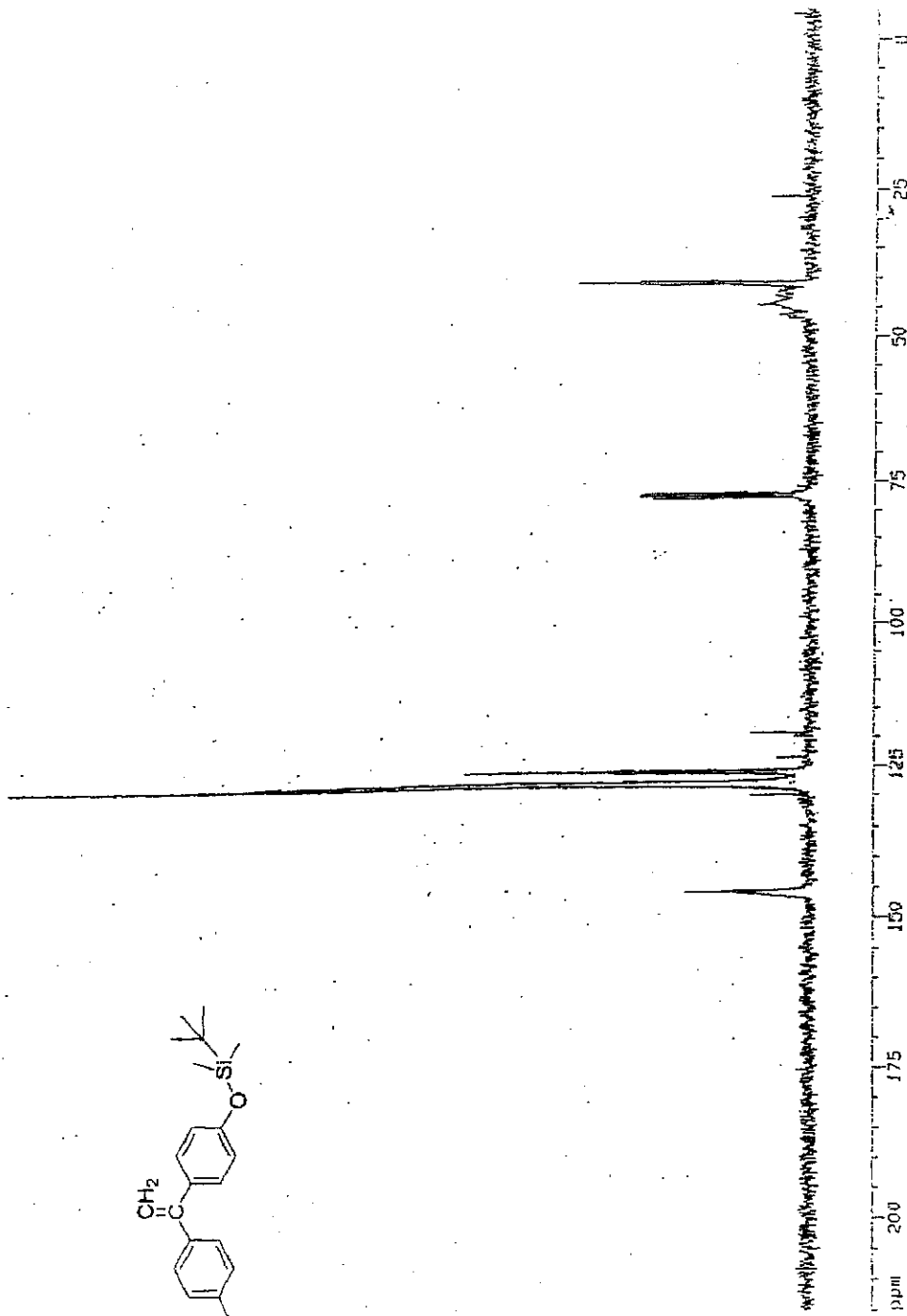
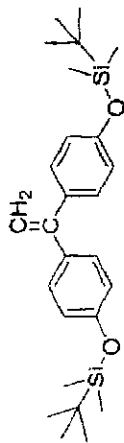


Figure 19. ^{13}C NMR spectrum of 1,1-bis(4-t-butylphenyl)ethylene, (6).

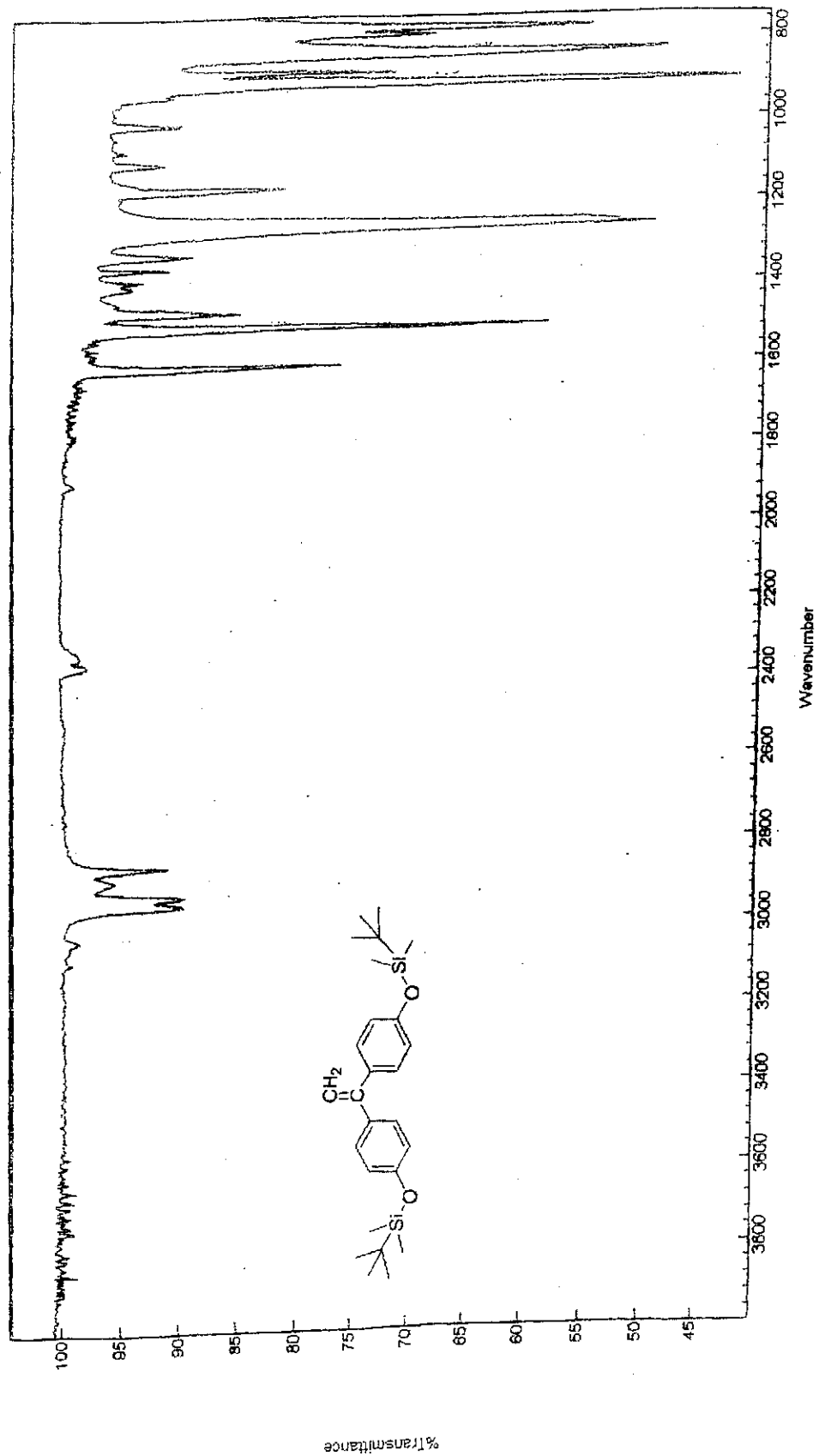


Figure 20. FTIR spectrum of 1,1-bis(4-t-butyl(dimethyl)siloxyphenyl)ethylene, (6).

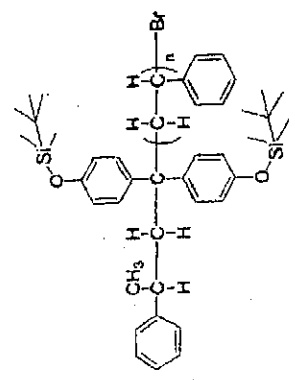
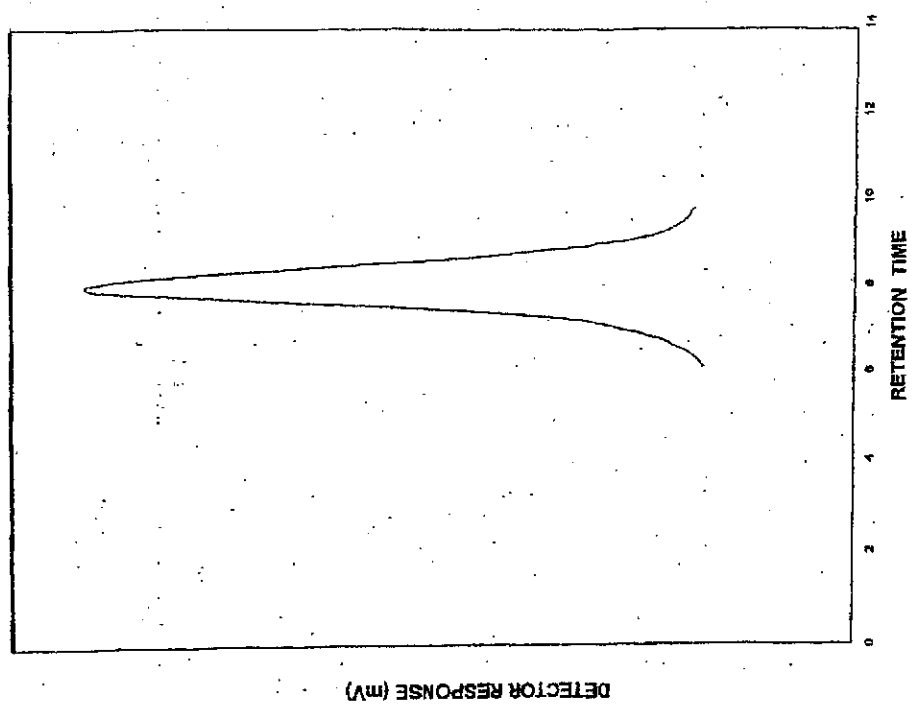


Figure 21. Size exclusion chromatogram of α -bis(siloxy) functionalized polystyrene, (8).

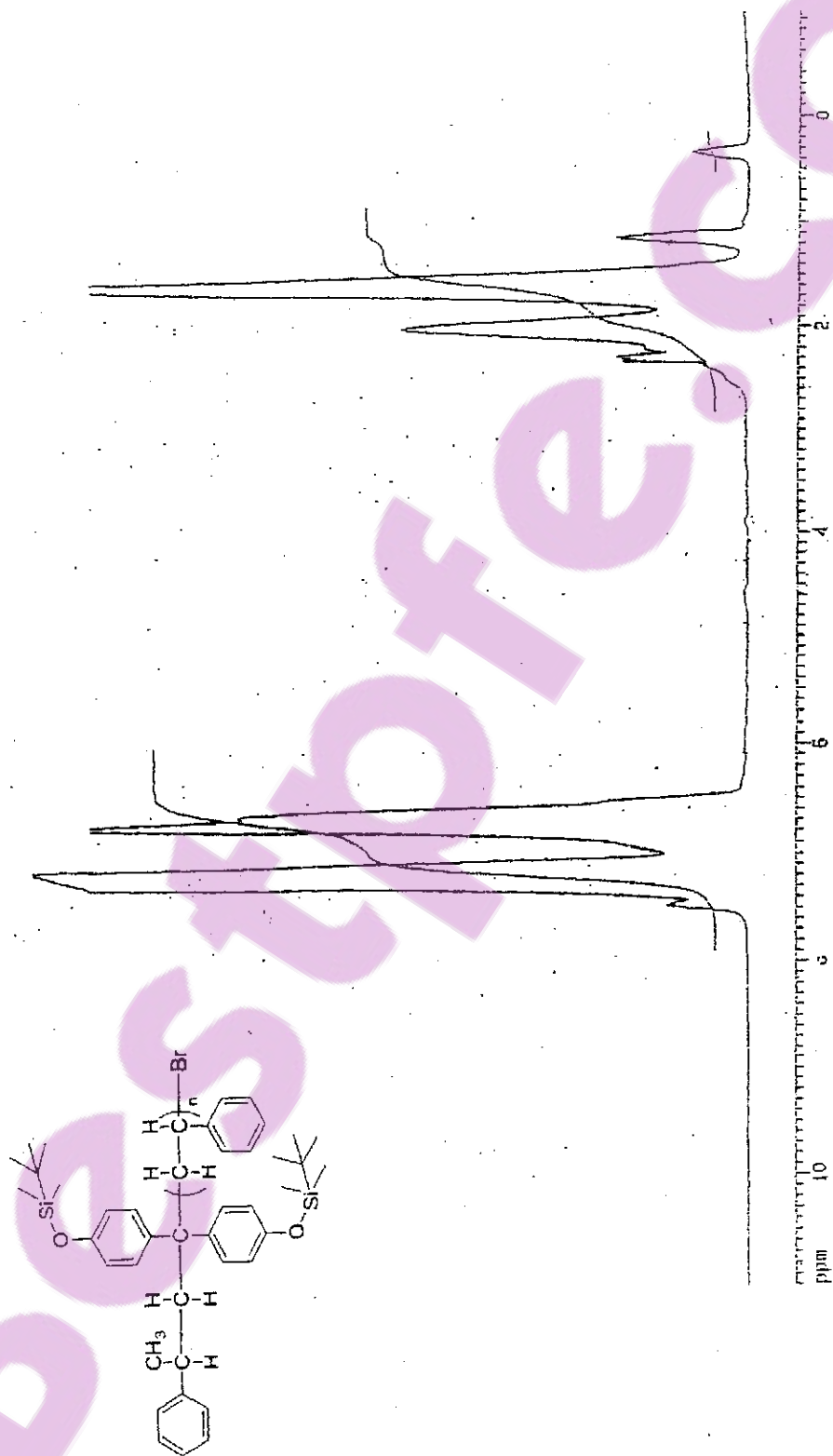


Figure 22. ^1H NMR spectrum of α -bis(siloxy) functionalized polystyrene, (8).

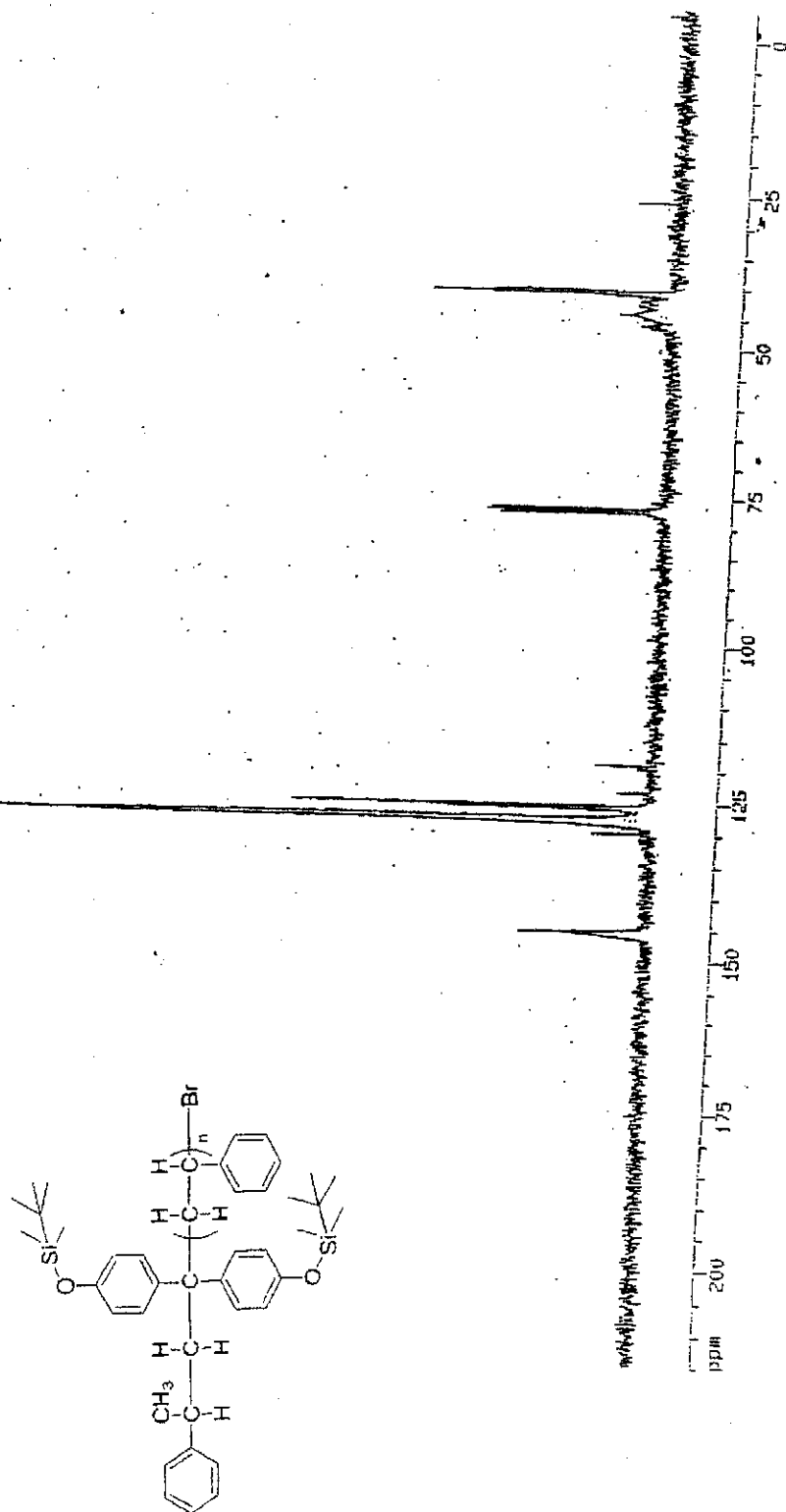


Figure 23. ^{13}C NMR spectrum of α -bis(siloxy) functionalized polystyrene, (8).

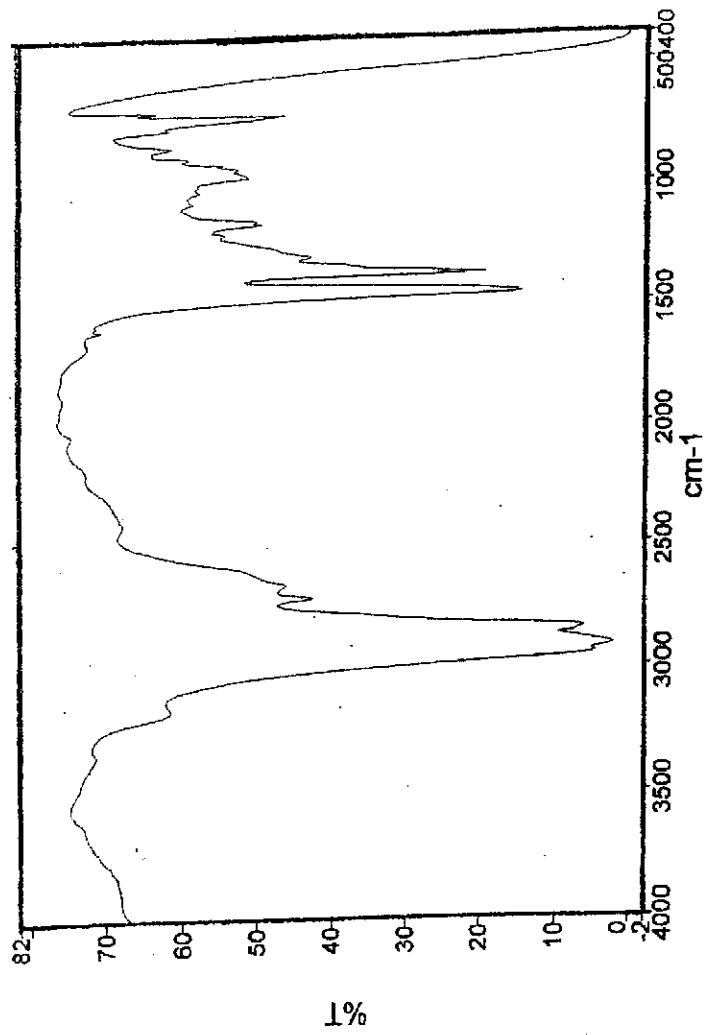
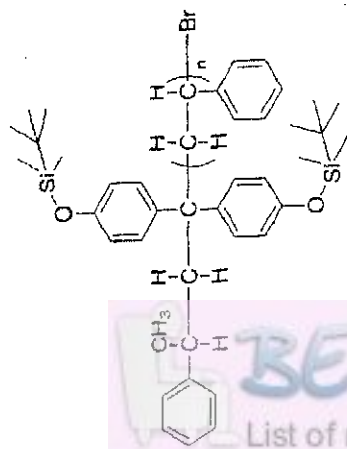


Figure 24. FTIR spectrum of α -bis(siloxy) functionalized polystyrene, (8).

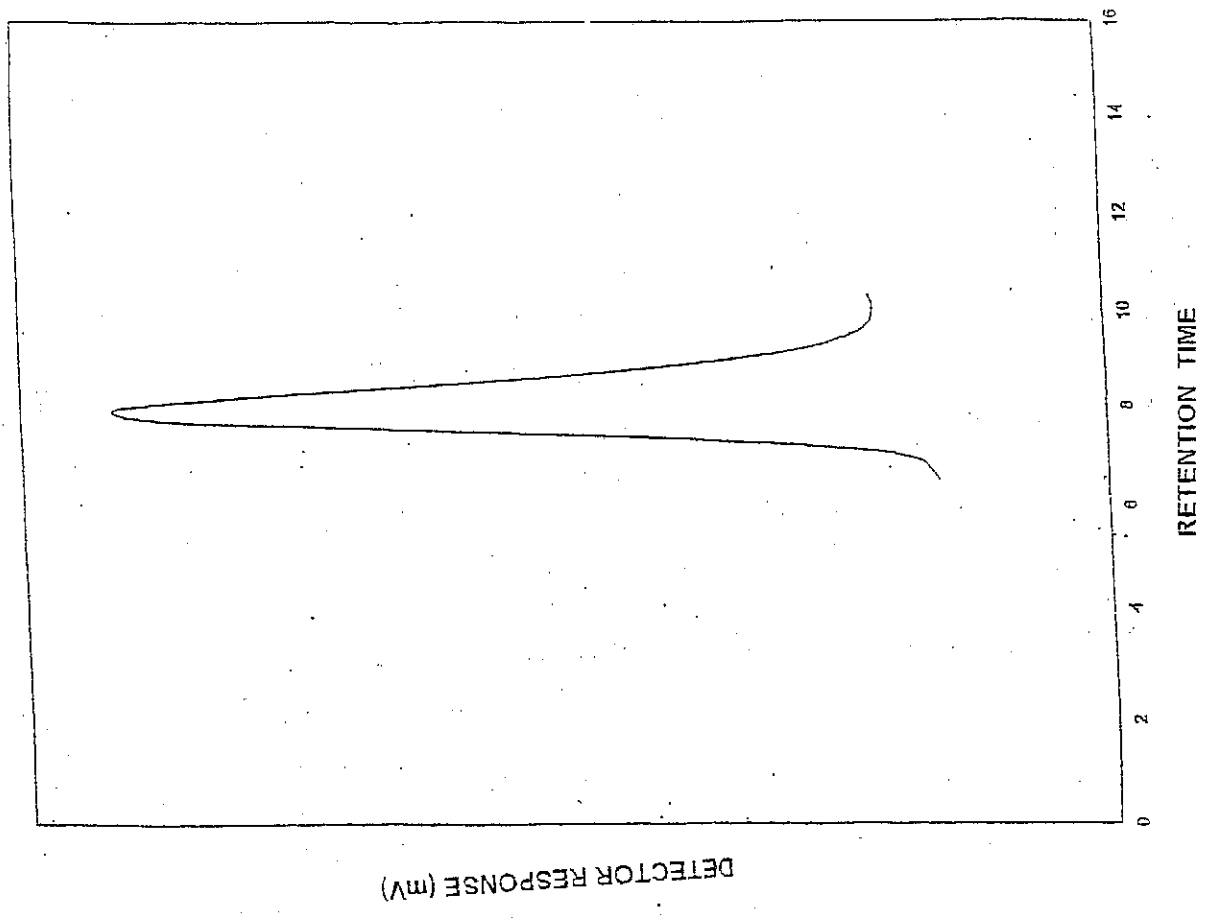


Figure 25. Size exclusion chromatogram of α -bis(siloxy) functionalized poly(methyl methacrylate), (9).

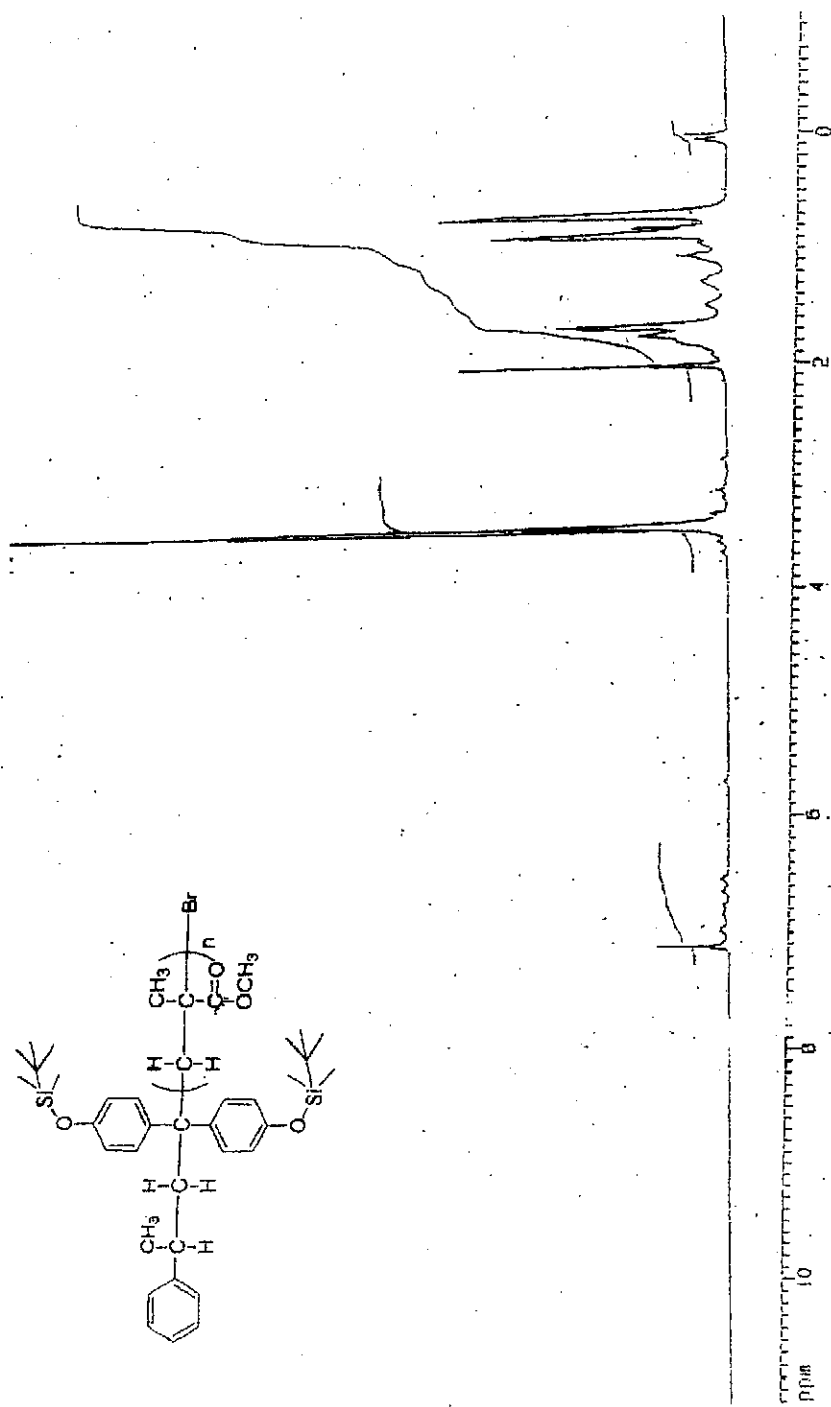


Figure 26. ¹H NMR spectrum of α -bis(siloxy) functionalized poly(methyl methacrylate), (9).

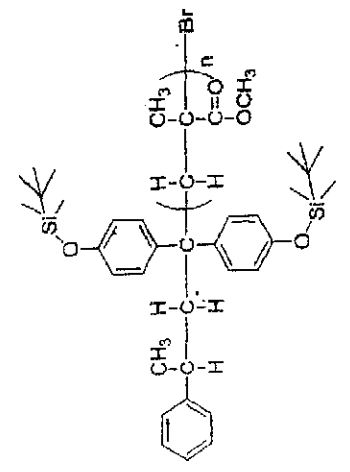
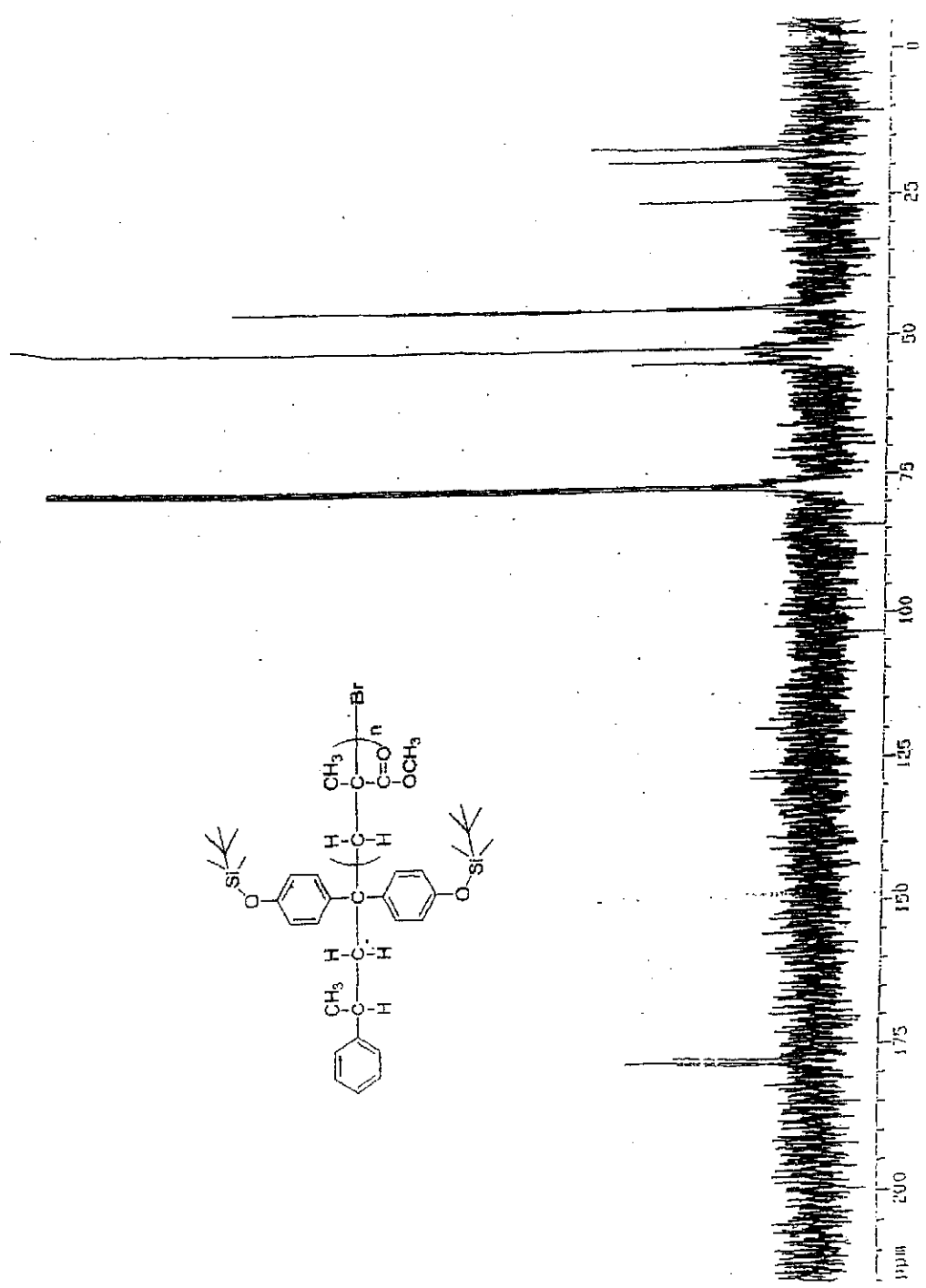


Figure 27 ¹³C NMR spectrum of α-bis(siloxy) functionalized poly(methyl methacrylate), (9).

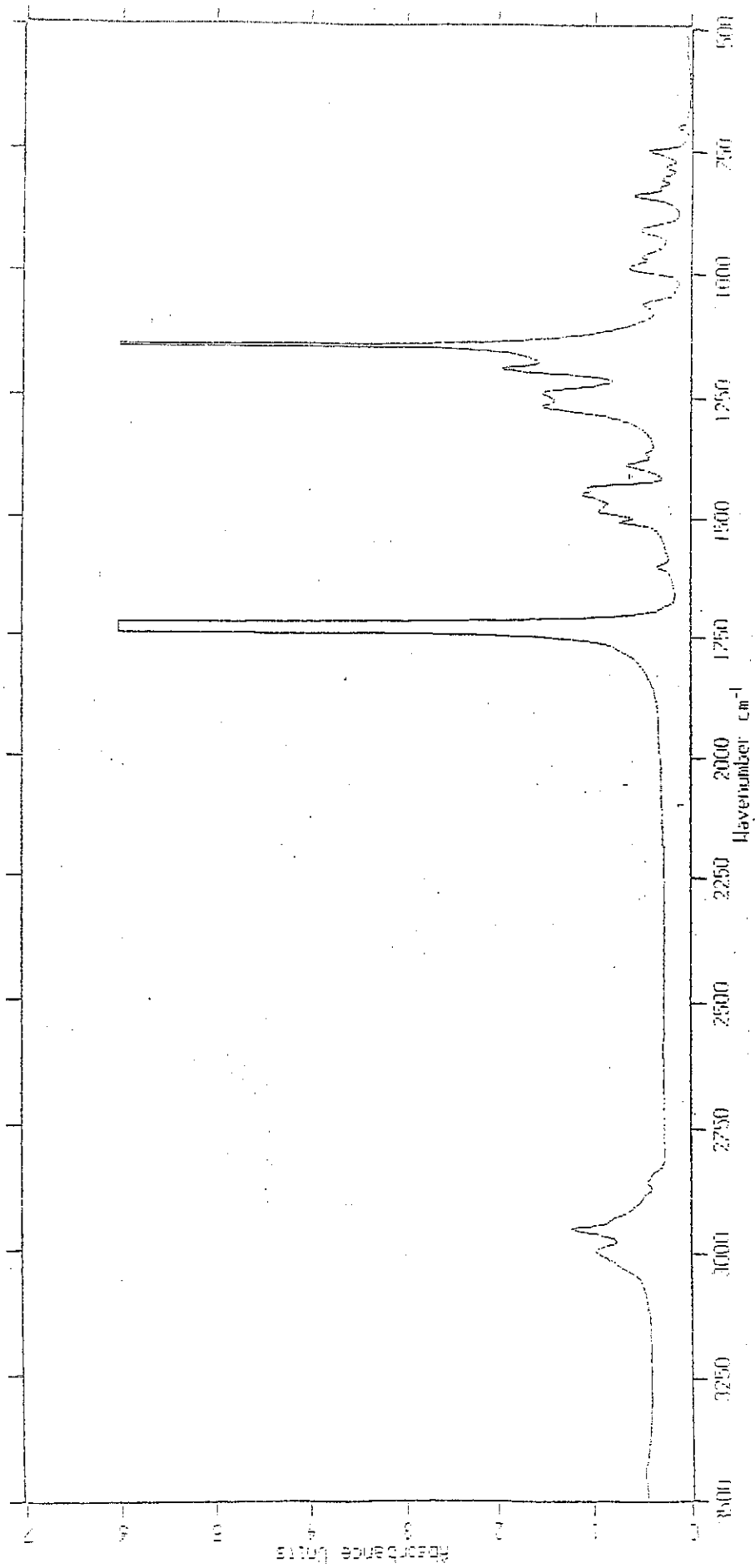


Figure 28. FTIR spectrum of α -bis(siloxy) functionalized poly(methyl methacrylate), (9).

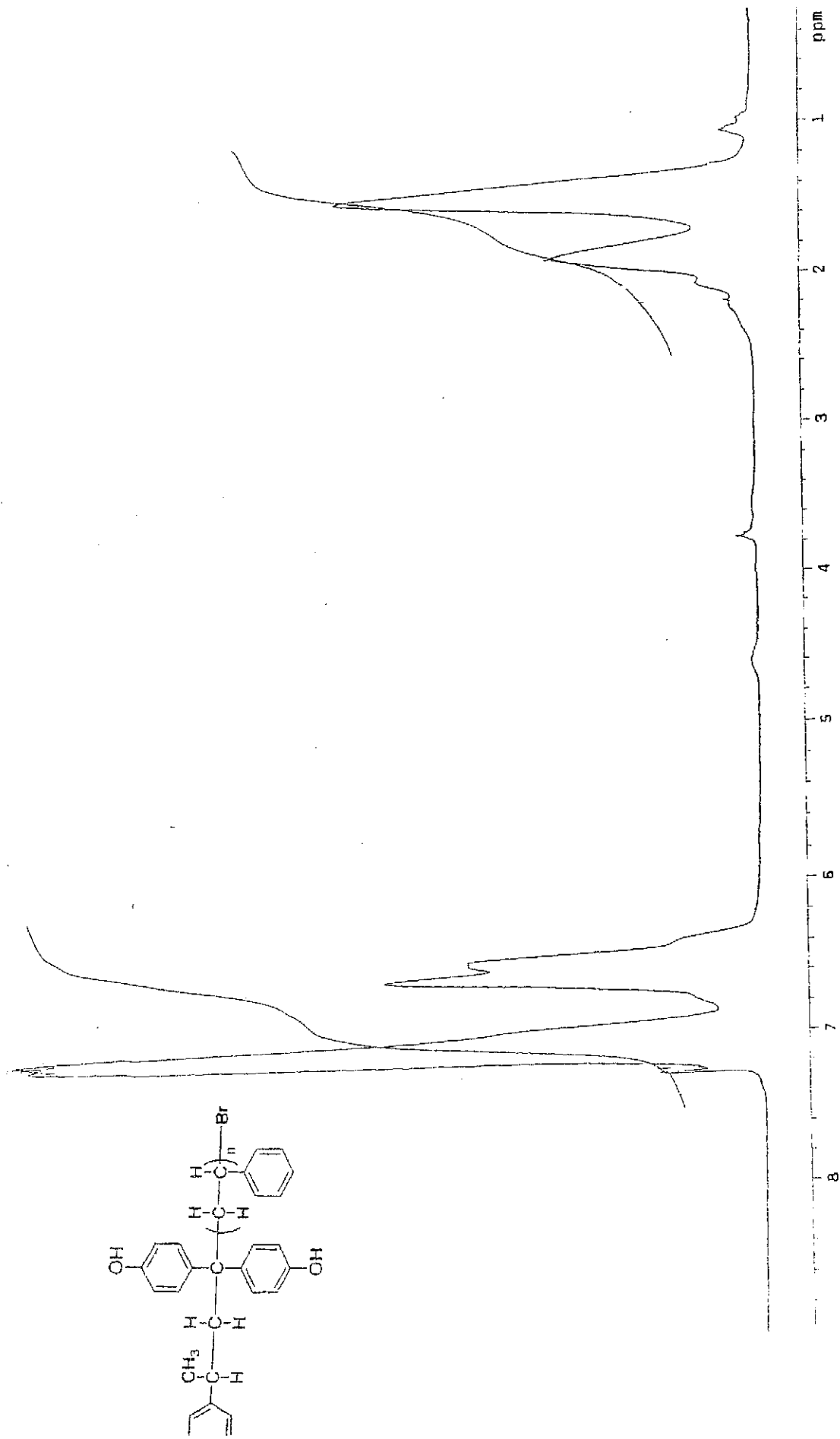


Figure 29. ^1H NMR spectrum of α -bis(hydroxyl) functionalized polystyrene, (10).

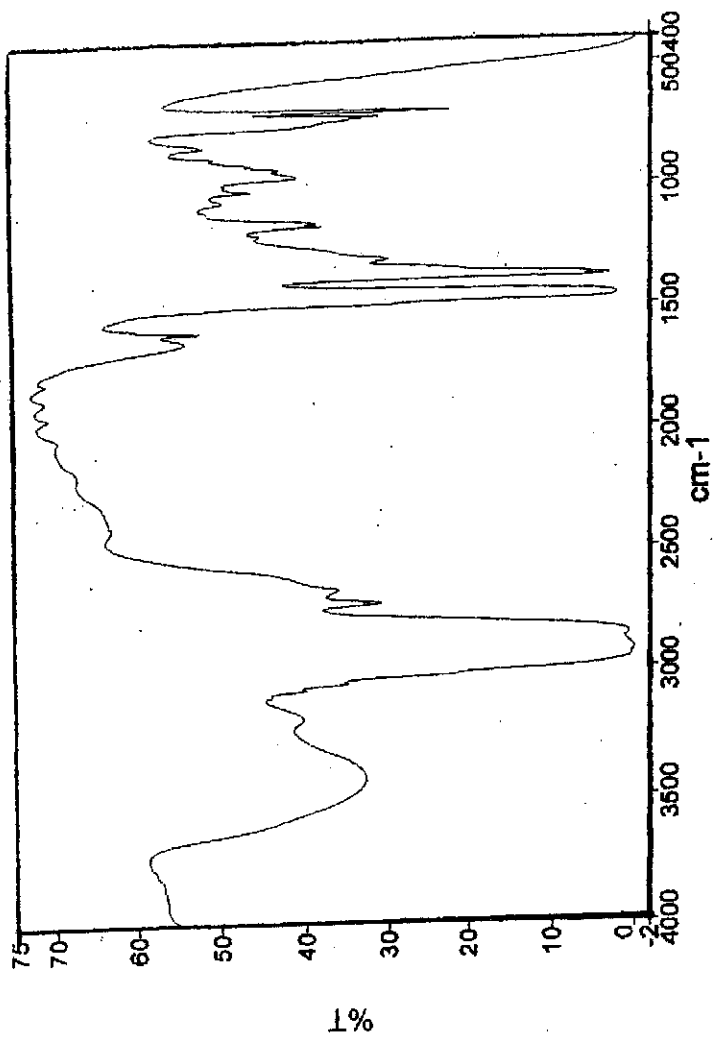
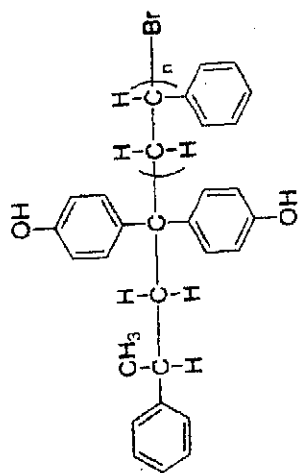


Figure 30. FTIR spectrum of α -bis(hydroxyl) functionalized polystyrene, (10).

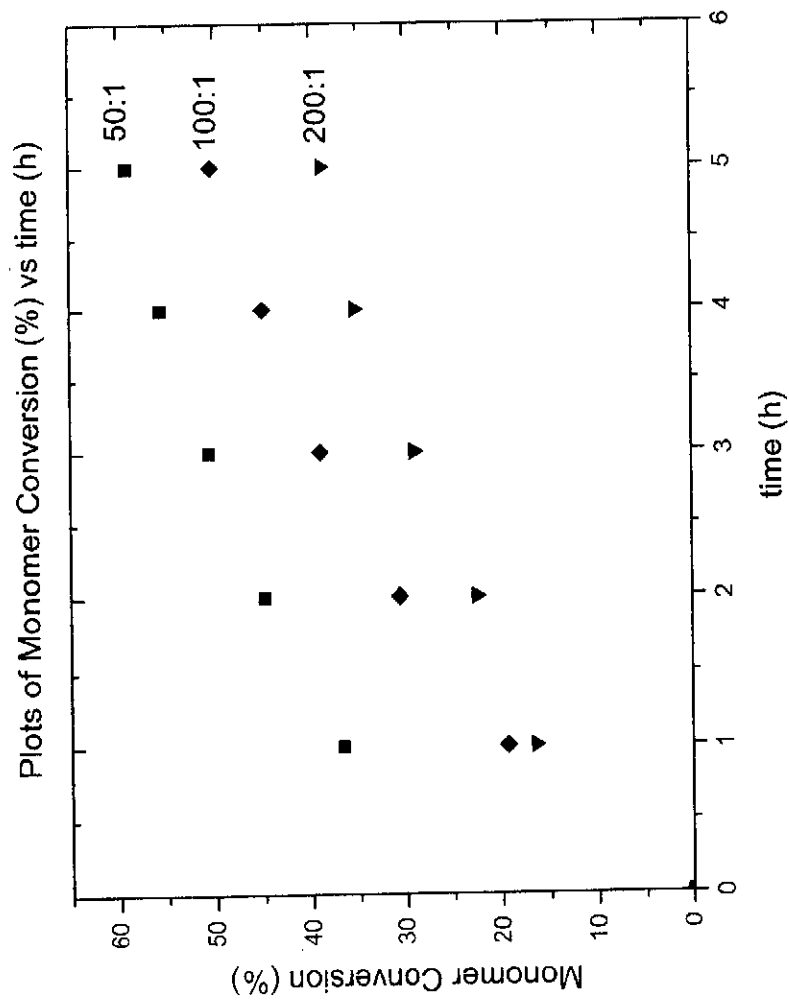


Figure 31. Plots of percentage monomer conversion versus time for the ATRP of styrene initiated by the adduct of 1-(4-t-butylidimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 110 °C in diphenyl ether.

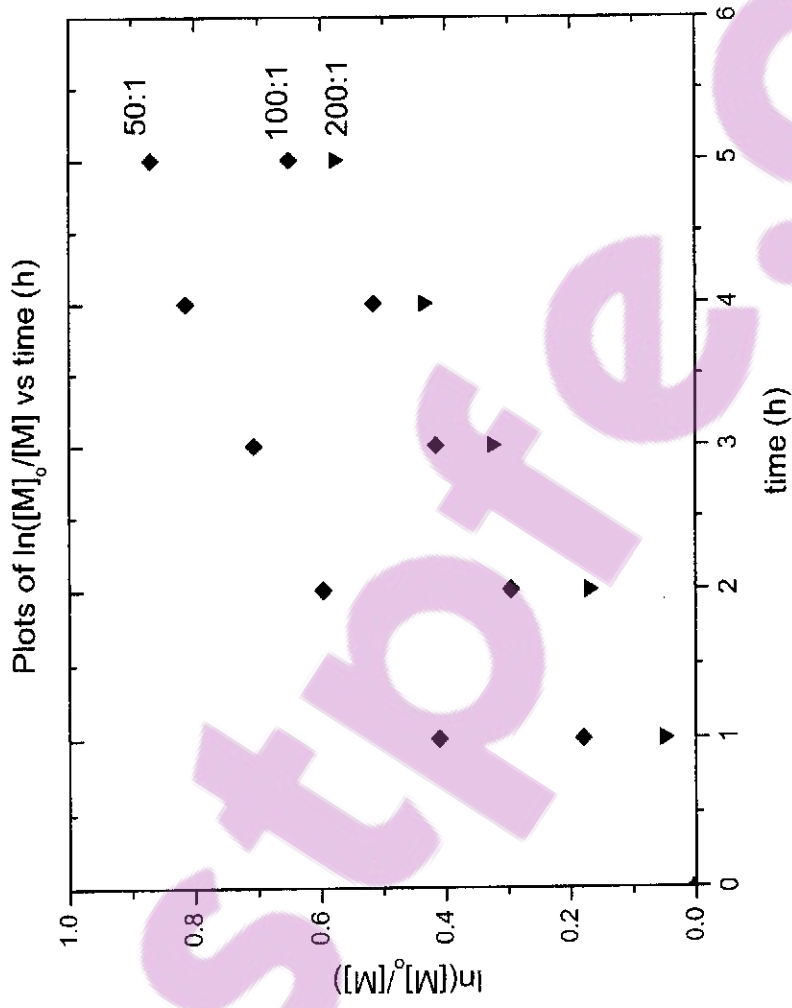


Figure 32. First order kinetic plots for the ATRP of styrene initiated by the adduct of 1-(4-t-butylidimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence CuBr/bpy catalyst at 110 °C in diphenyl ether.

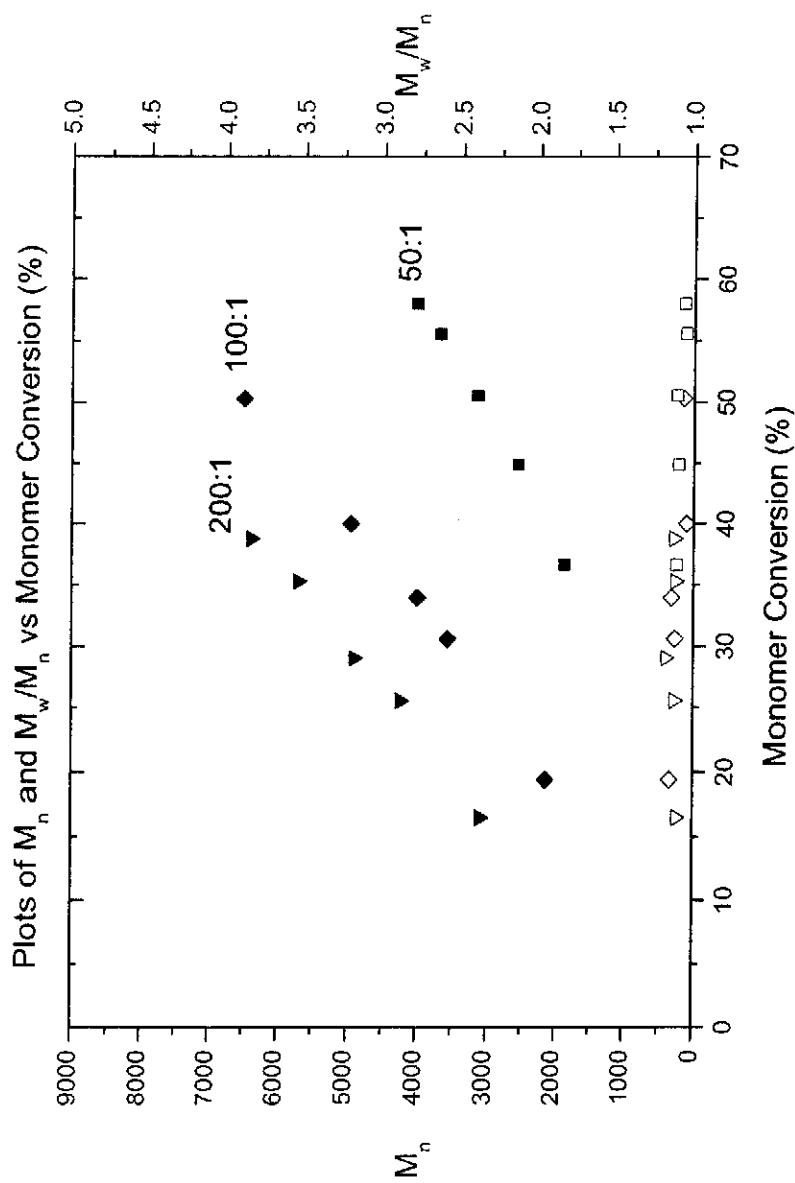


Figure 33. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of styrene initiated by the adduct of 1-(4-*t*-butyldimethylsilyloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 110 °C in diphenyl ether.

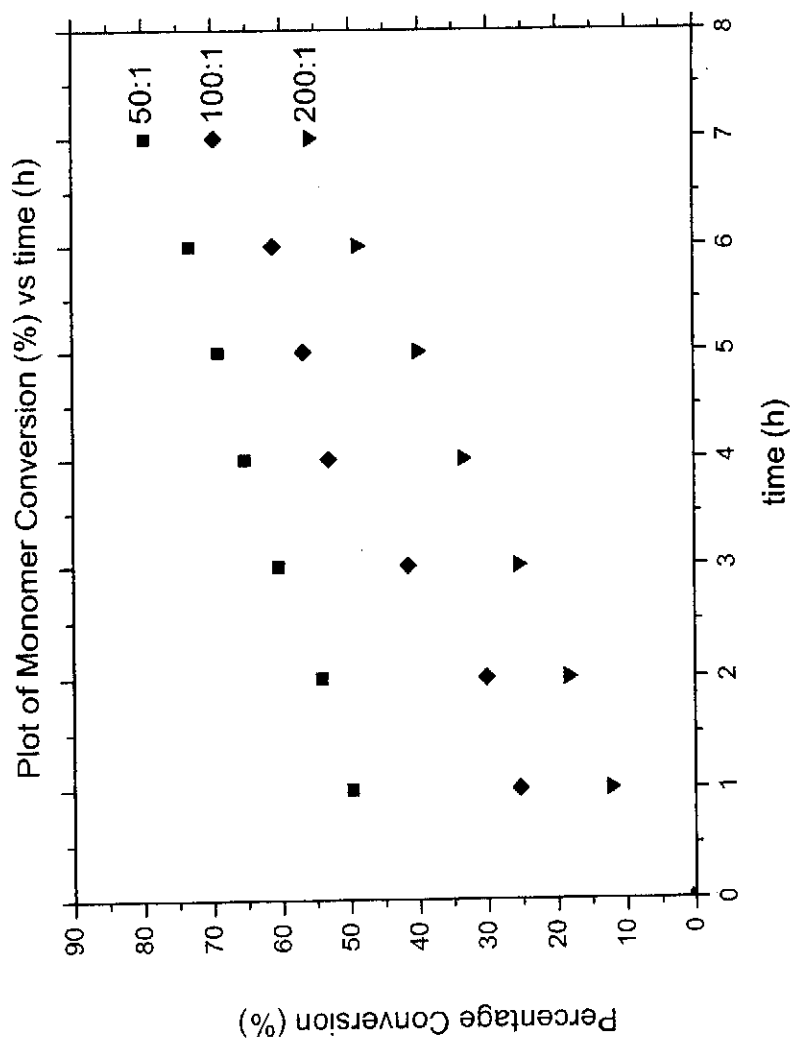


Figure 34. Plots of percentage monomer conversion versus time for the ATRP of styrene initiated by the adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of copper (I) bromide/PMDETA catalyst at 110 °C in diphenyl ether.

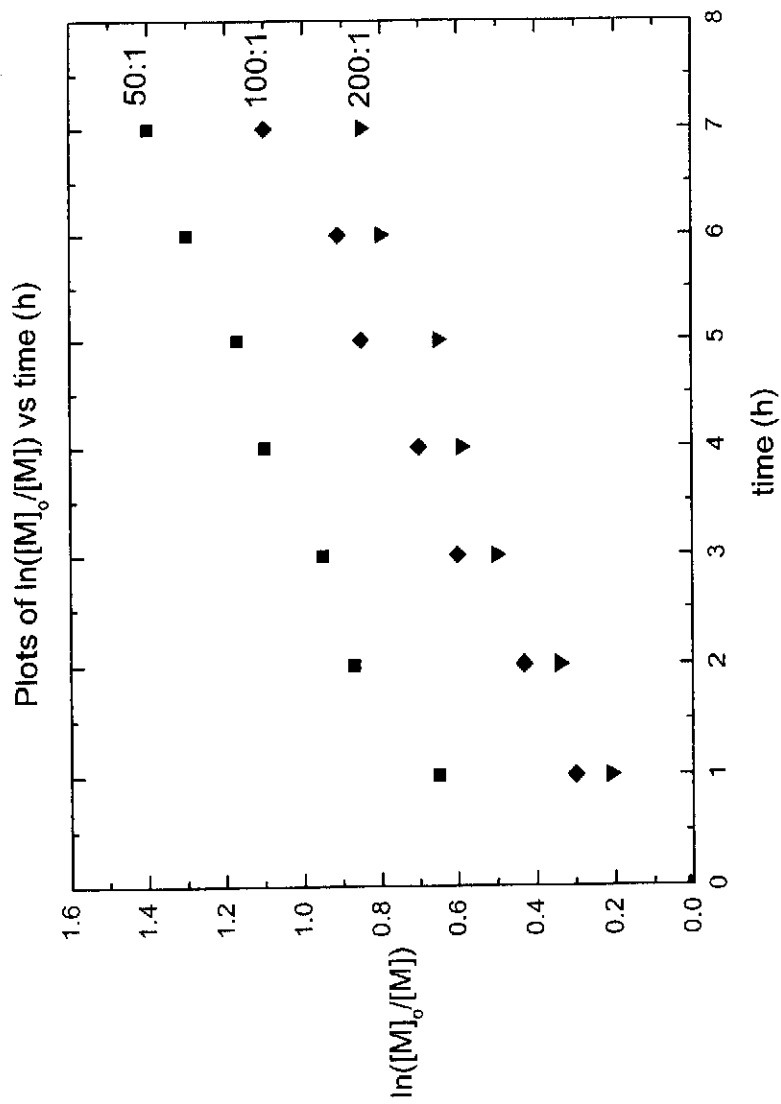


Figure 35. First order kinetic plots for the ATRP of styrene initiated by the adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 110 °C in diphenyl ether.

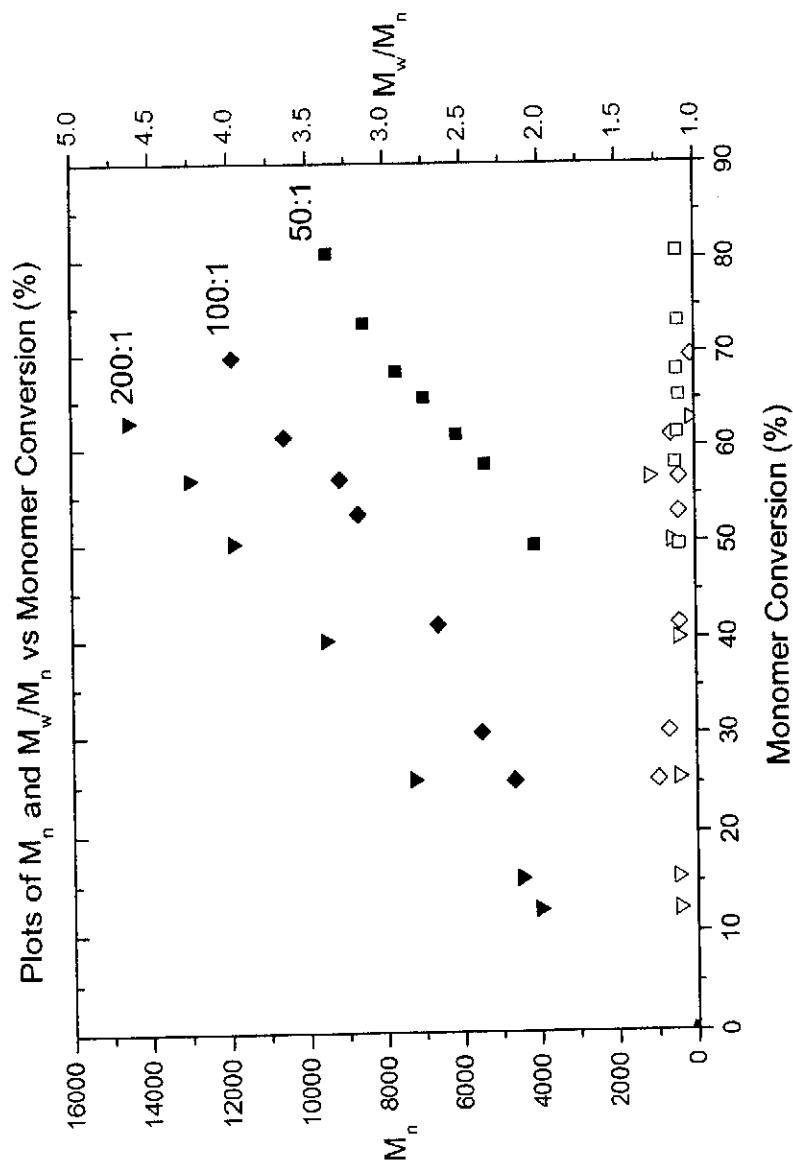


Figure 36. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of styrene initiated by the adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 110 °C in diphenyl ether.

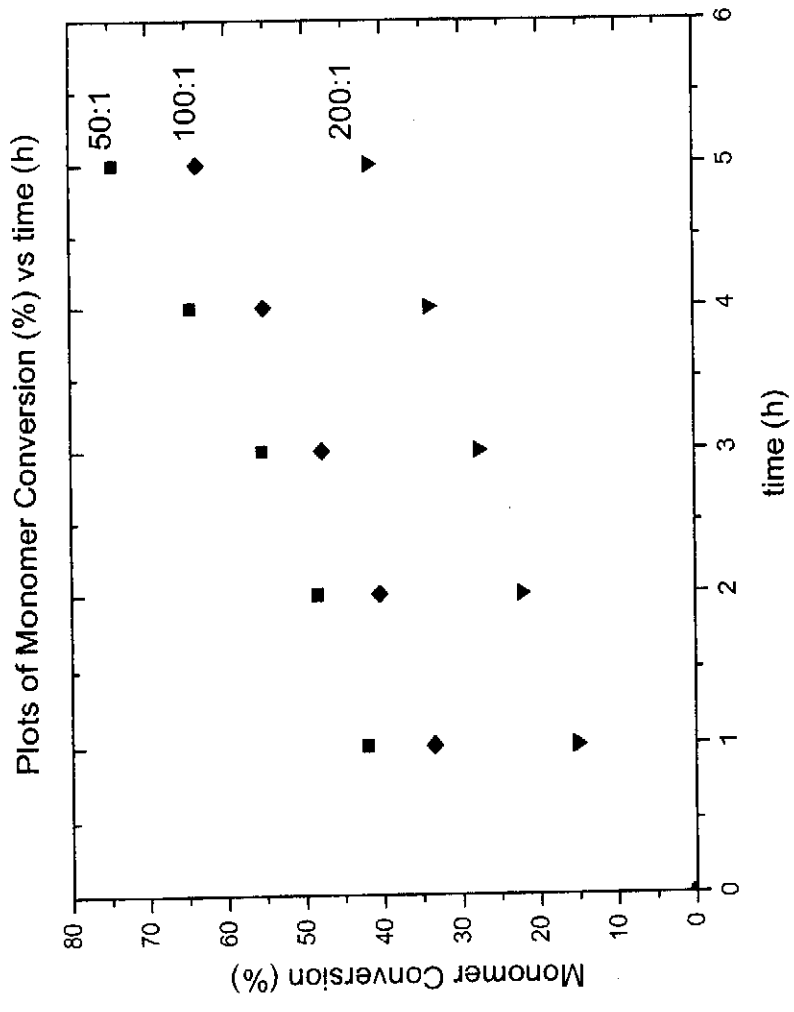


Figure 37. Plots of percentage monomer conversion vs time for the ATRP of styrene initiated by the adduct of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 110 °C in diphenyl ether.

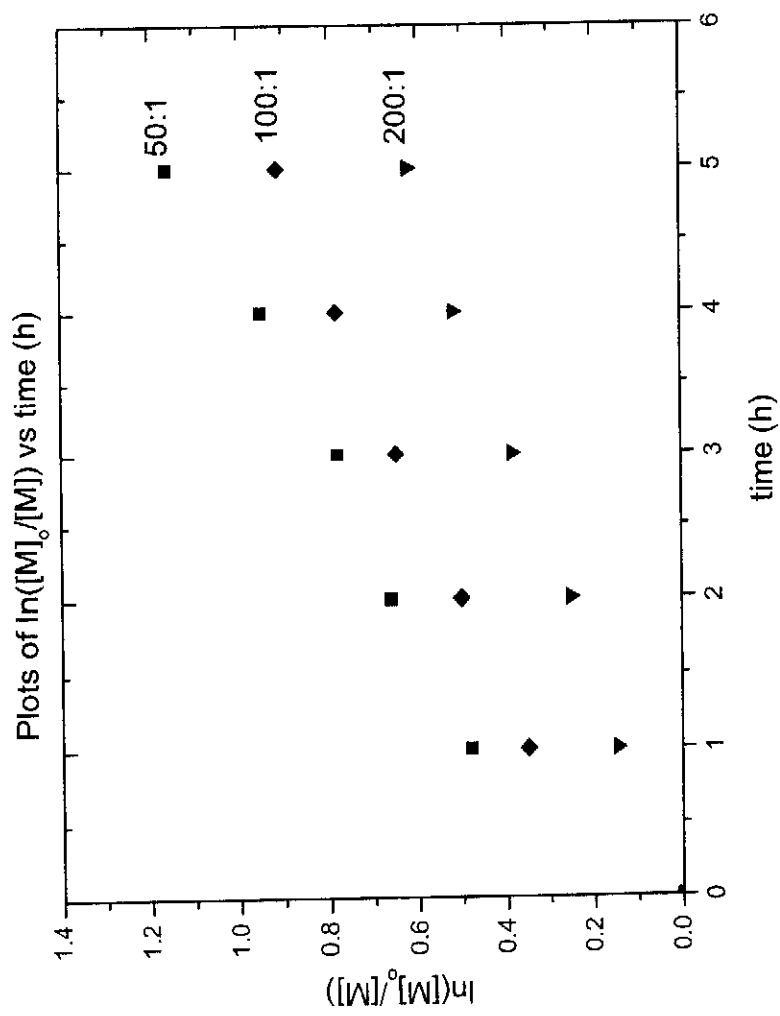


Figure 38. First order kinetic plots for the ATRP of styrene initiated by the adduct of 1,1-bis(4-t-butylidimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 110 °C in diphenyl ether.

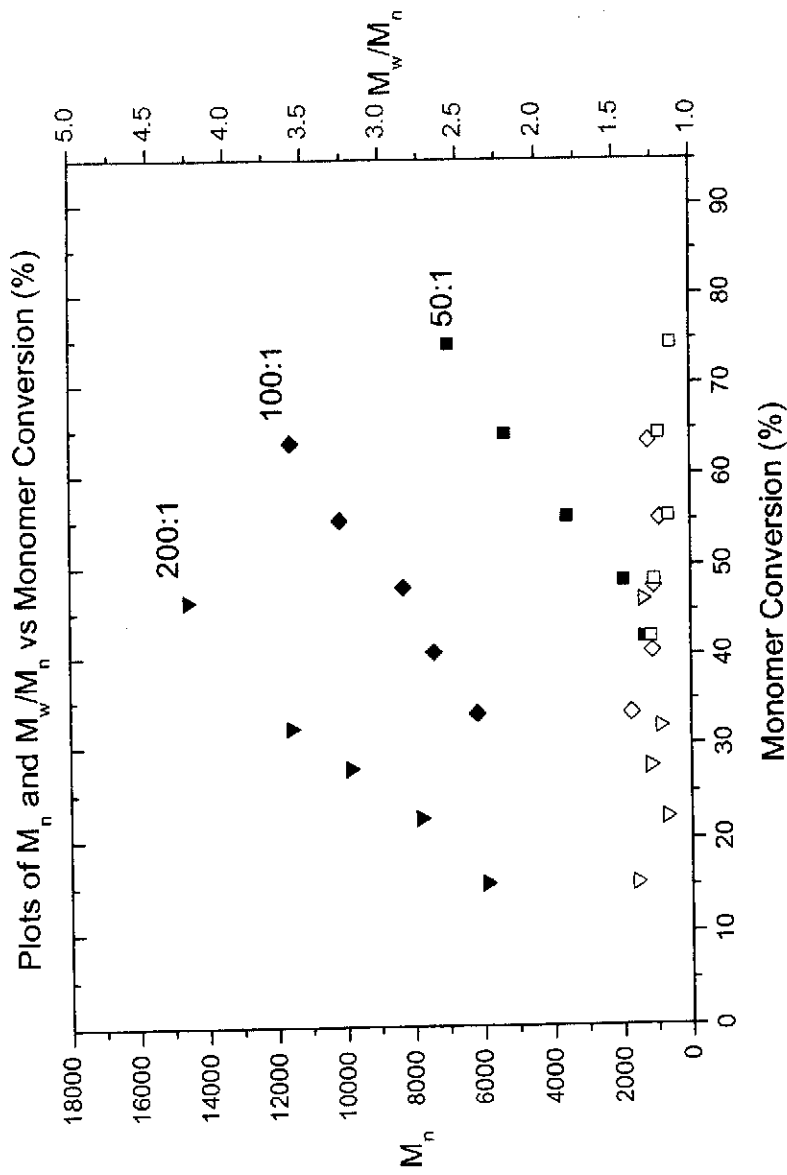


Figure 39. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of styrene initiated by the adduct of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 110 °C in diphenyl ether.

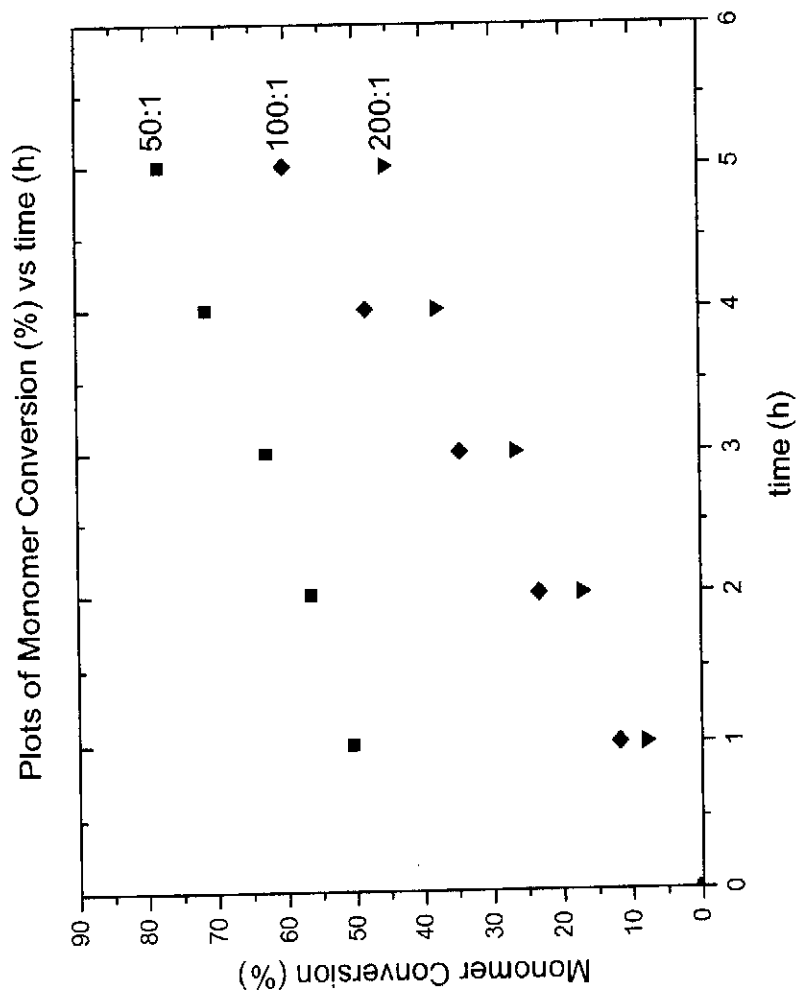


Figure 40. Plots of percentage monomer conversion versus time for the ATRP of styrene initiated by the adduct of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 110 °C in diphenyl ether.

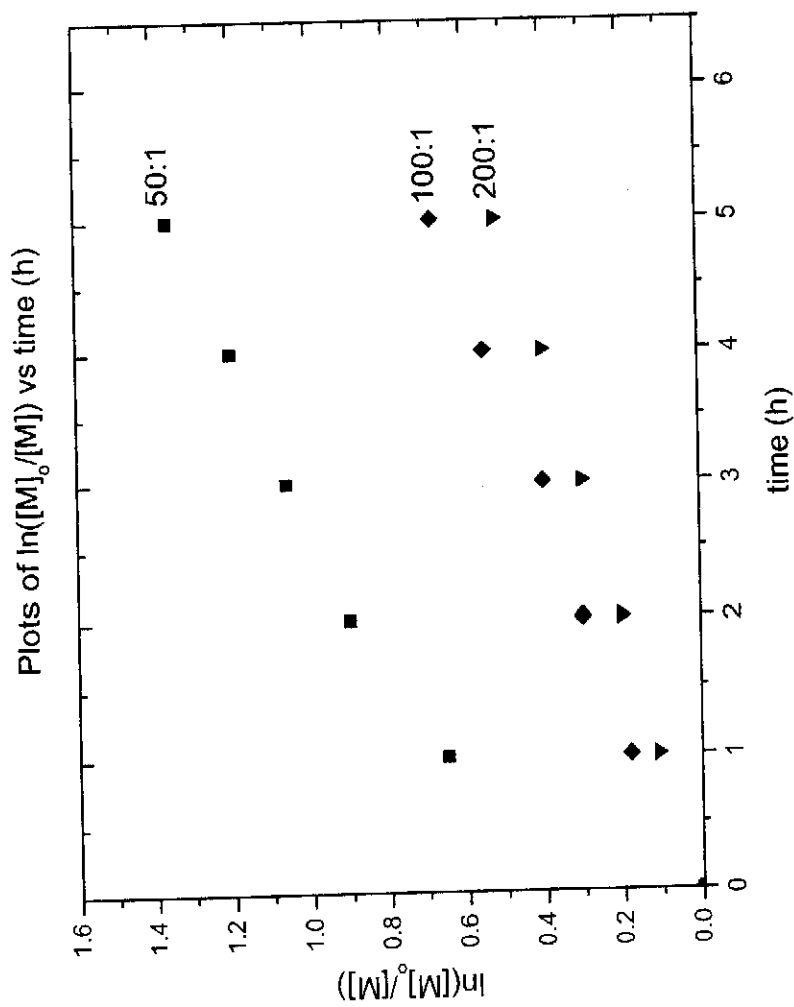


Figure 41. First order kinetic plots for the ATRP of styrene initiated by the adduct of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 110 °C in diphenyl ether.

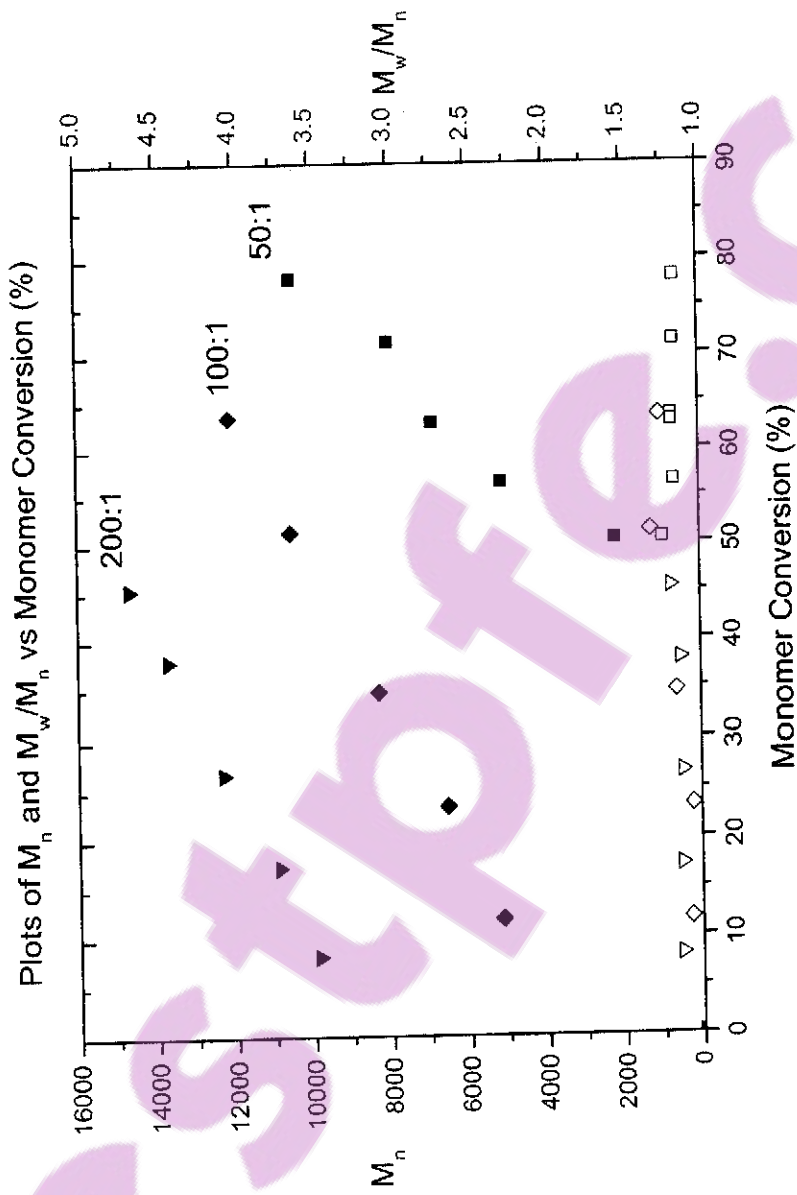


Figure 42. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of styrene initiated by the adduct of 1,1-bis(4-t-butyl-dimethyl-siloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 110 °C in diphenyl ether.

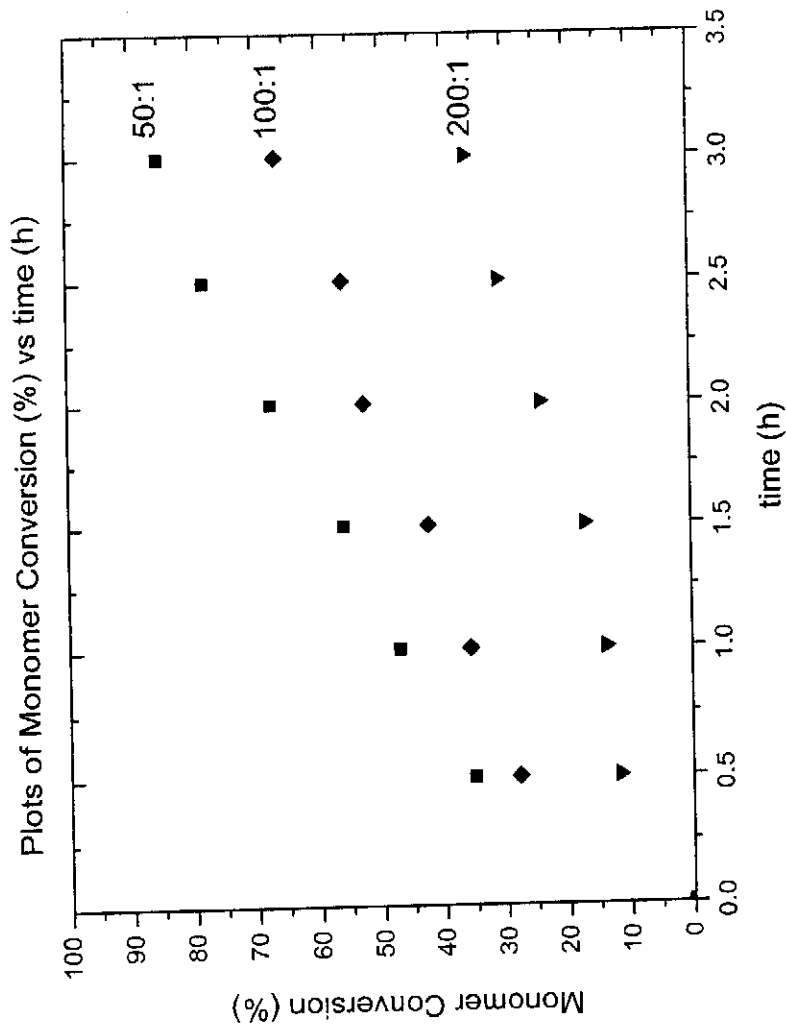


Figure 43. Plots of percentage monomer conversion versus time for the ATRP of methyl methacrylate) initiated by the adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of the CuBr/bpy catalyst at 90 °C in diphenyl ether.

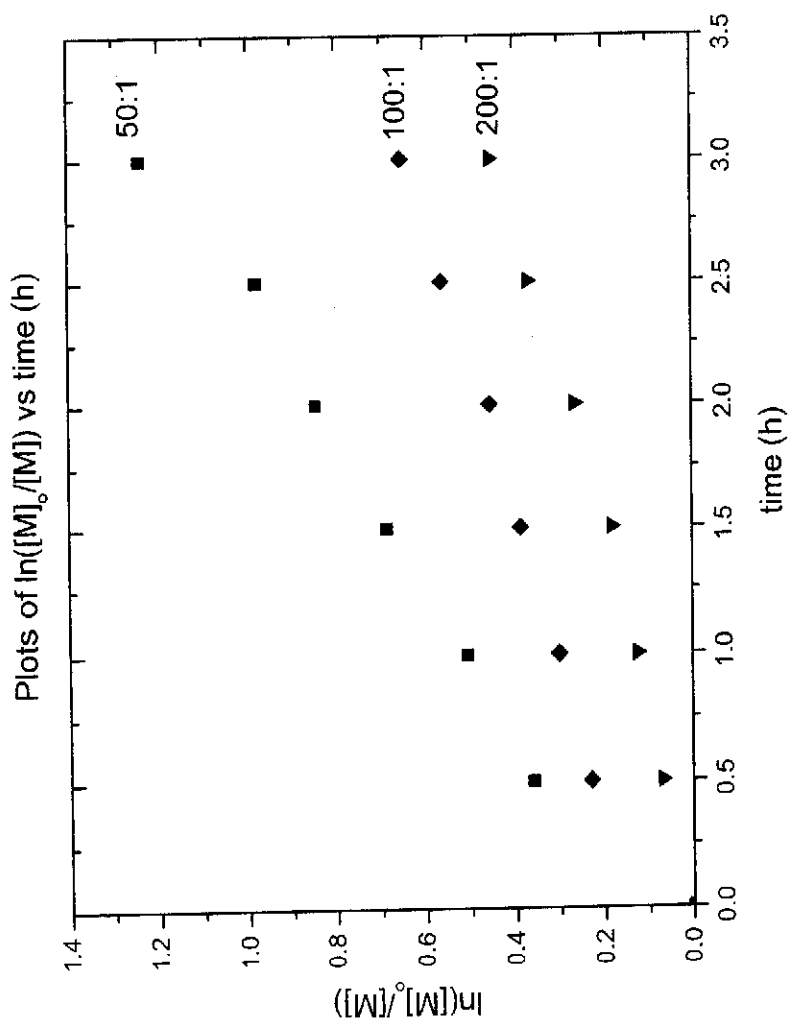


Figure 44. First order kinetic plots for the ATRP of methyl methacrylate initiated by the adduct of 1-(4-t-butylidimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 90 °C in diphenyl ether.

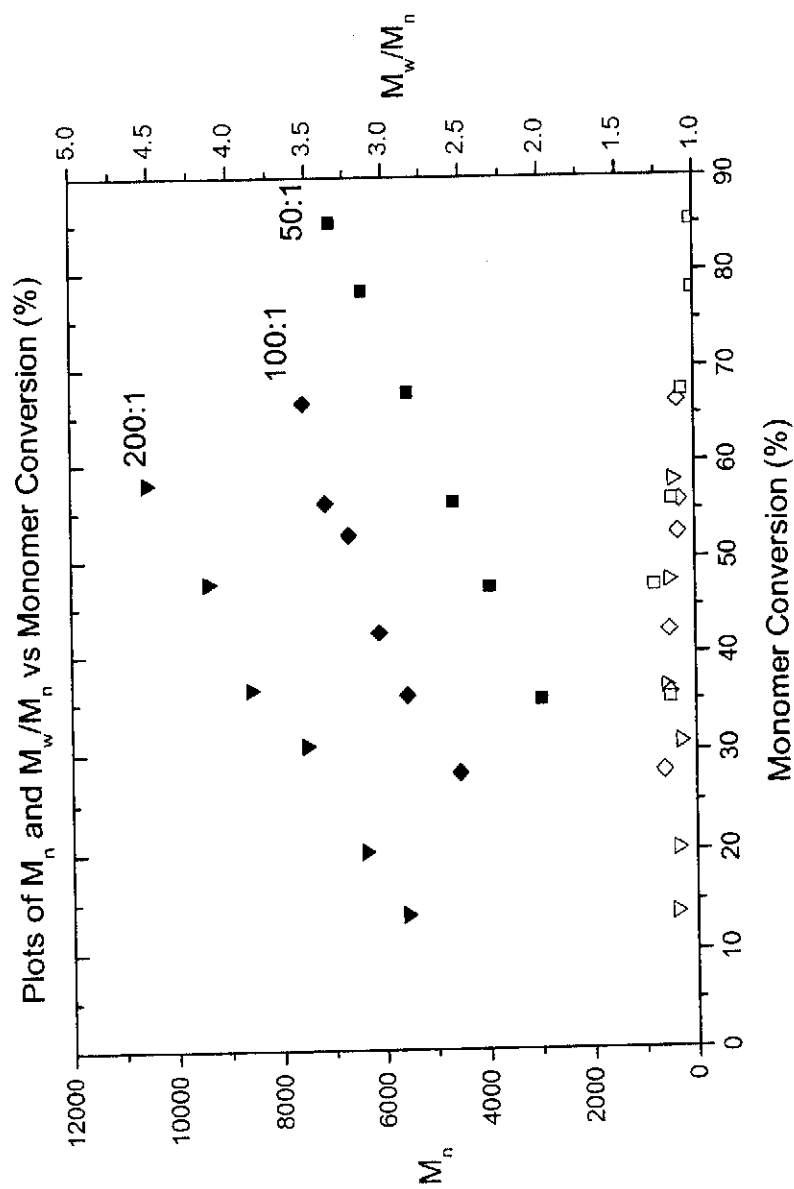


Figure 45. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of methyl methacrylate initiated by the adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 90 °C in diphenyl ether.

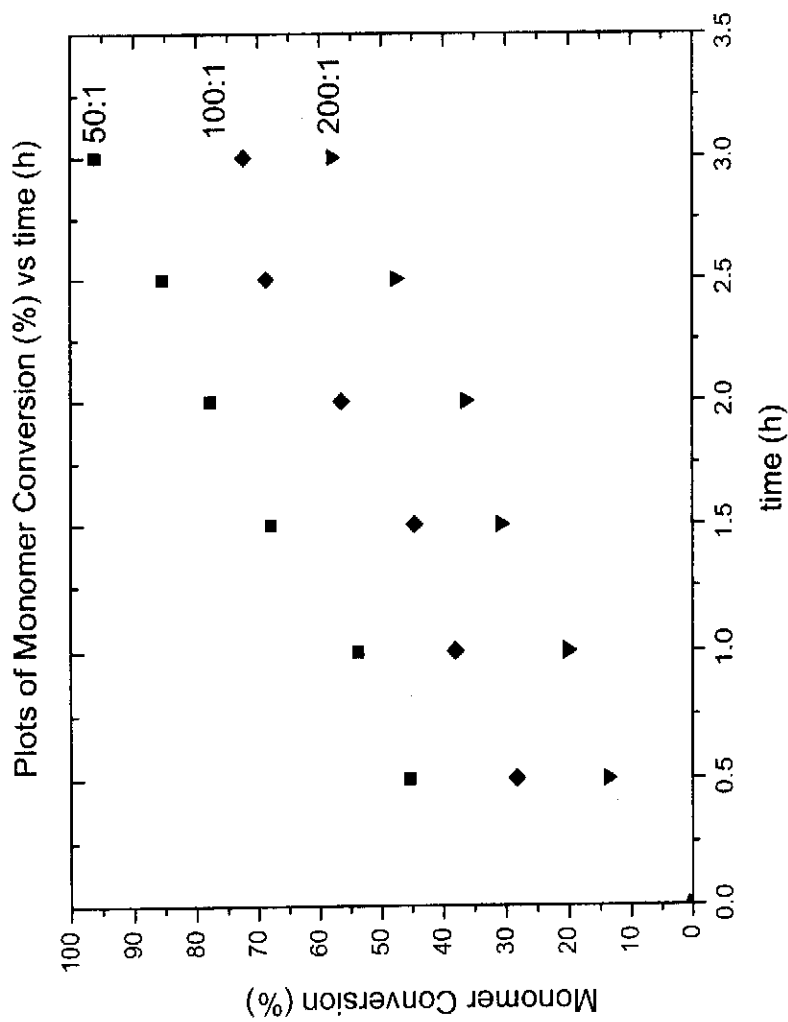


Figure 46. Plots of percentage monomer conversion versus time for the ATRP of methyl methacrylate initiated by the adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene with CuBr/PMDETA catalyst at 90 °C in diphenyl ether.

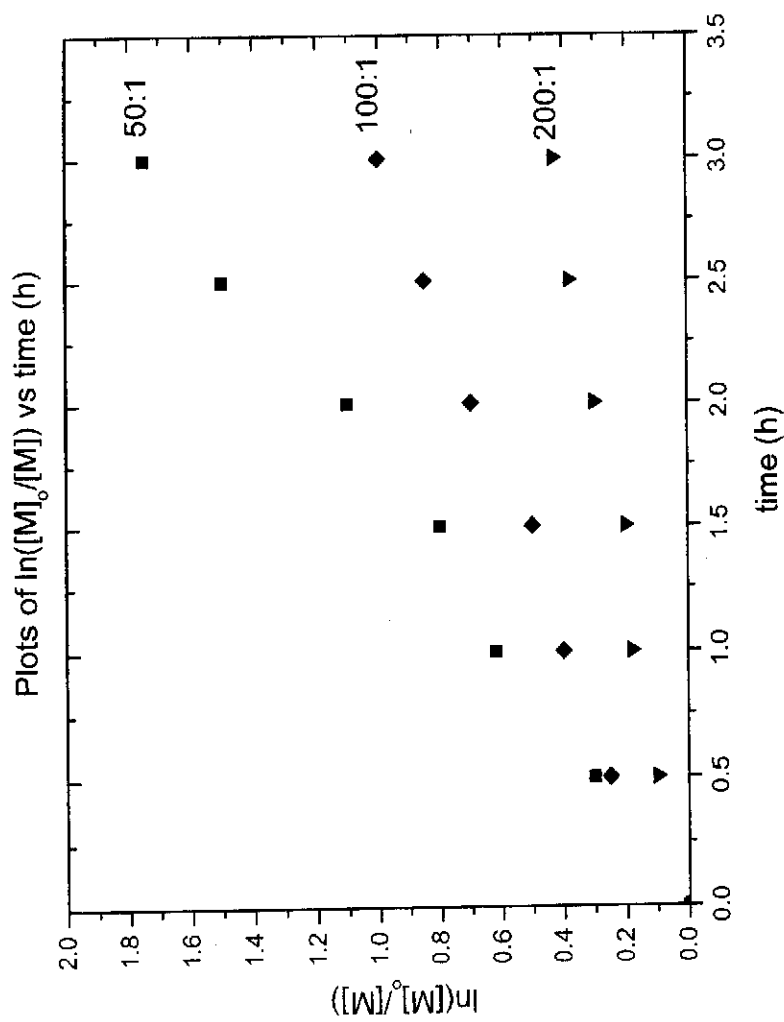


Figure 47. First order kinetic plots for the ATRP of methyl methacrylate initiated by the adduct of 1-(4-t-butylidimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene with CuBr/PMDETA catalyst at 90 °C in diphenyl ether.

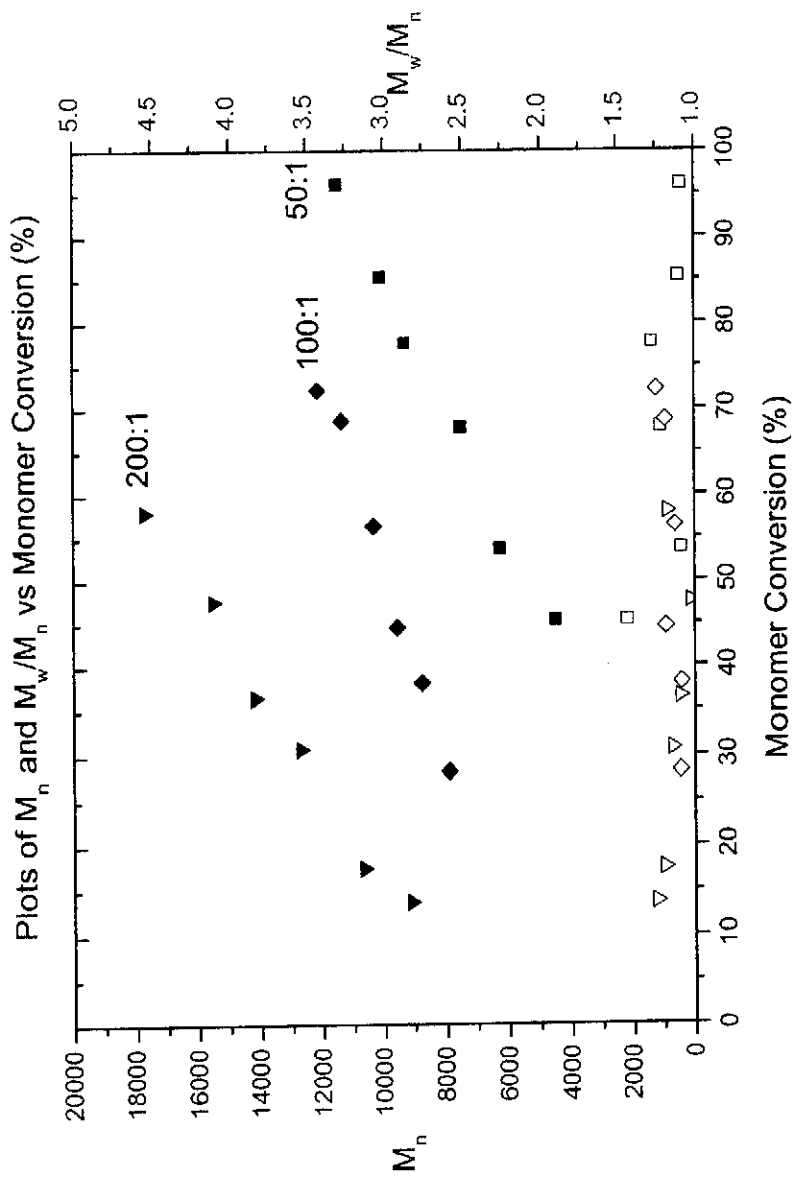


Figure 48. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of methyl methacrylate initiated by the adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene with CuBr/PMDETA catalyst at 90 °C in diphenyl ether.

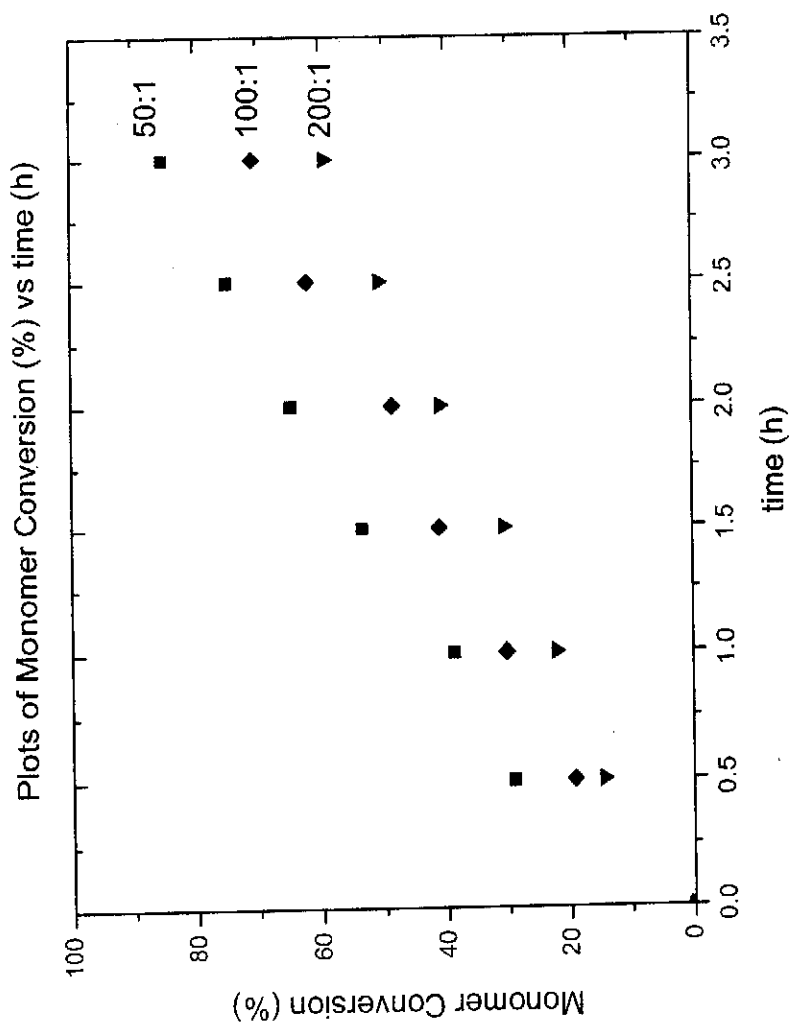


Figure 49. Plots of percentage monomer conversion versus time for the ATRP of methyl methacrylate initiated by the adduct of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 90 °C in diphenyl ether.

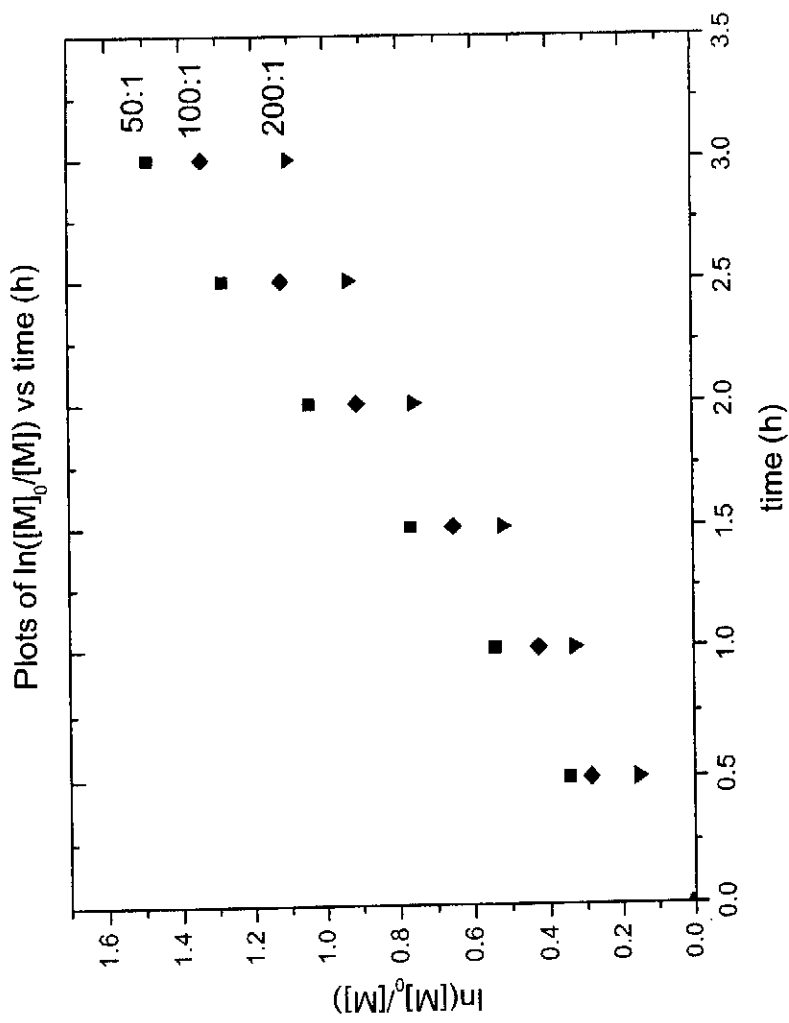


Figure 50. First order kinetic plots for the ATRP of methyl methacrylate initiated by the adduct of 1,1-bis(4-*t*-butyldimethylsiloxyphenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 90 °C in diphenyl ether.

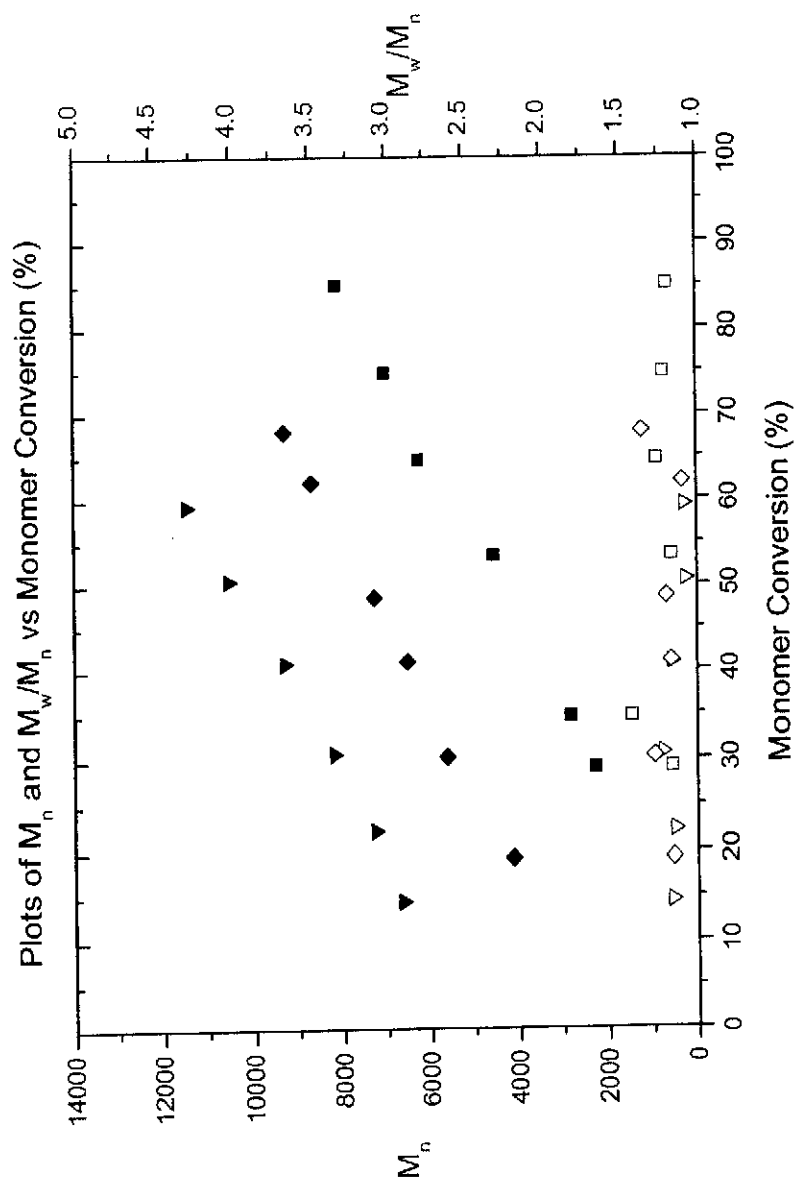


Figure 51. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of methyl methacrylate initiated by the adduct of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/bpy catalyst at 90 °C in diphenyl ether.

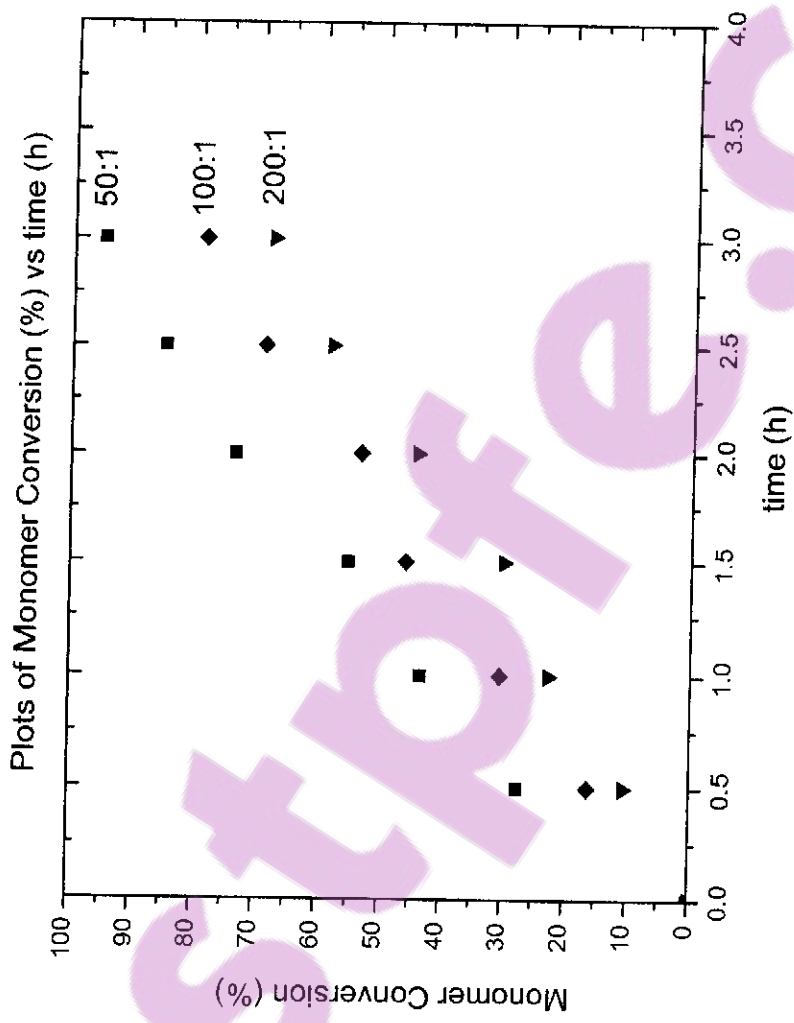


Figure 52. Plots of percentage monomer conversion versus time for the ATRP of methyl methacrylate initiated by the adduct of 1,1-bis(4-t-butyl-dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 90 °C in diphenyl ether.

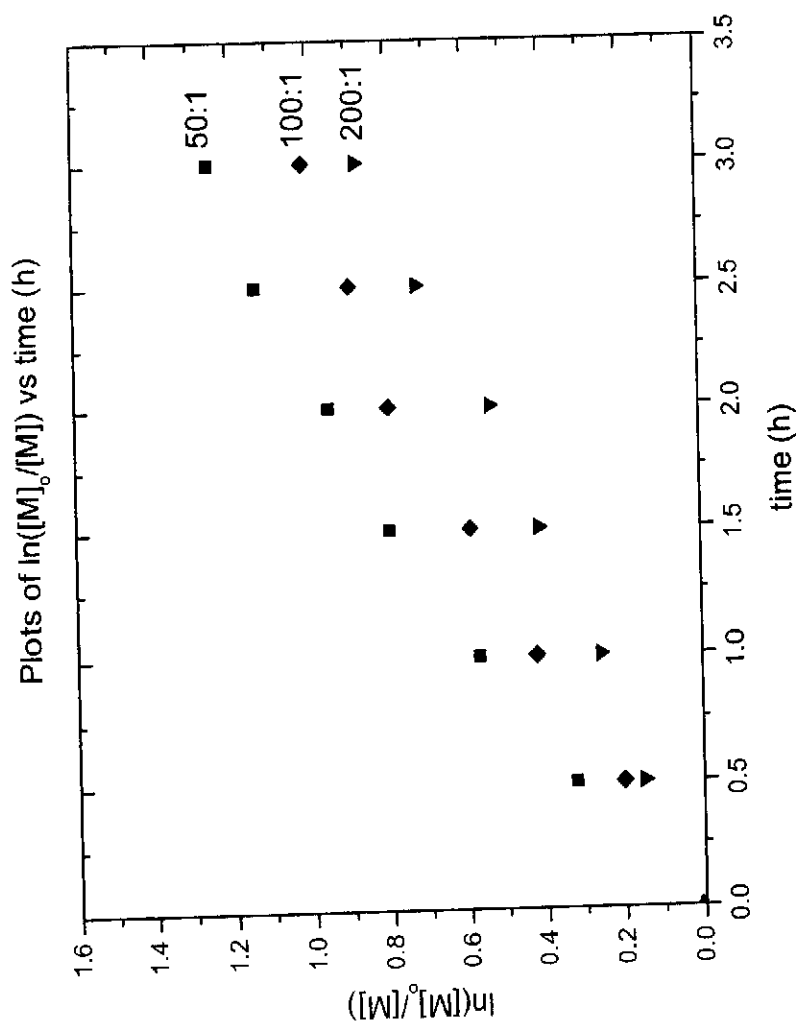


Figure 53. First order kinetic plots for the ATRP of methyl methacrylate initiated by the adduct of 1,1-bis(4-t-butylidimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 90 °C in diphenyl ether.

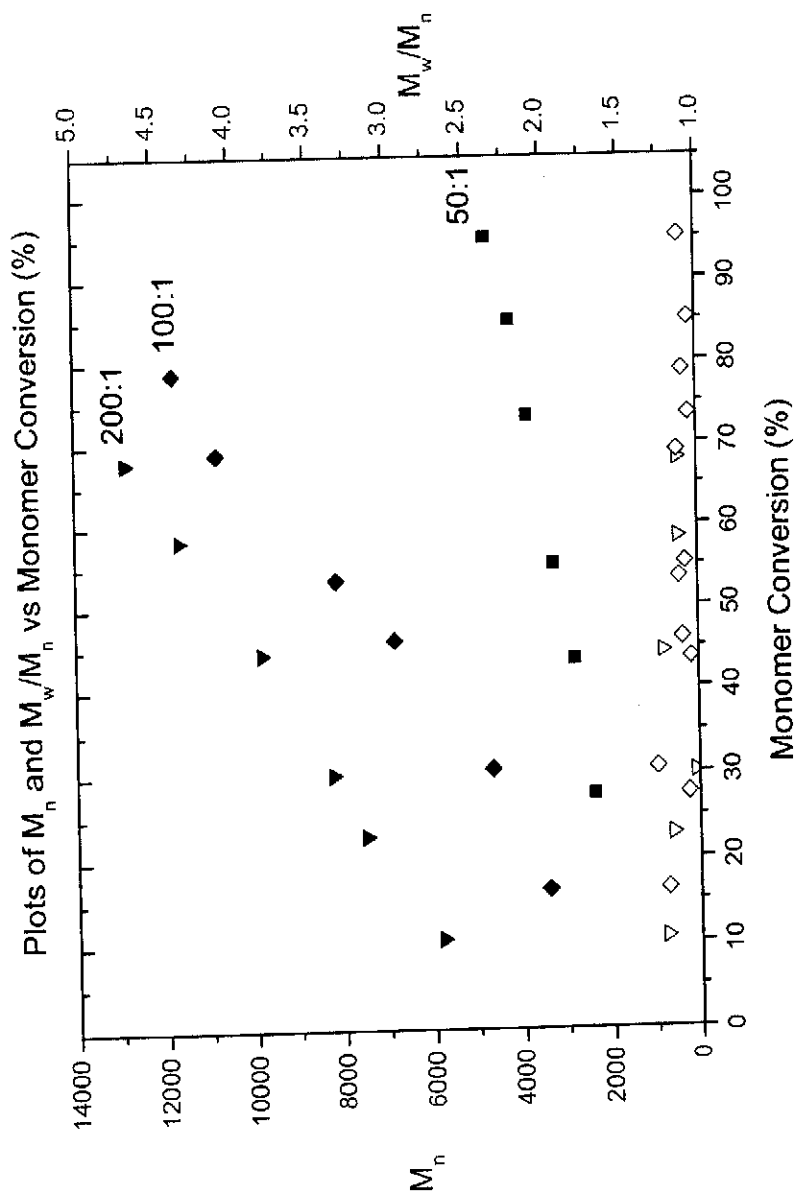


Figure 54. Plots of M_n and M_w/M_n versus percentage monomer conversion for the ATRP of methyl methacrylate initiated by the adduct of 1,1-bis(4-t-butyl(dimethylsiloxyphenyl)ethylene and (1-bromoethyl)benzene in the presence of CuBr/PMDETA catalyst at 90 °C in diphenyl ether.