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LIST OF ABBREVIATIONS

ATRP	Atom Transfer Radical Polymerization
aq	Aqueous
Boc	Butoxycarbonyl
BPO	Benzoyl peroxide
Bu	Butyl
Bpy	2,2'-Bipyridyl
CuBr	Copper bromide
CRP	Controlled Radical Polymerization
DBU	1,8-diazabicyclo(5.4.0)undecen-7-ene
DMA	2-(dimethylamino)ethyl methacrylate
DMF	*N,N*-dimethylformamide
dNbpy	4,4'-Di(*n*-nonyl)-2,2'-bipyridine
DPA	2-(diisopropylamino)ethyl methacrylate
DP	Degree of polymerization
DPE	Diphenyl ether
E^+	Electrophile
Et	Ethyl
Fmoc	9-fluorenylmethoxycarbonyl group
FTIR	Fourier Transform Infrared Spectrometry
HCl	Hydrochloric acid
HMTETA	1,1,4,7,10,10-hexamethyltriethylenetetramine
hrs	Hours
I	Initiator
KF	Potassium fluoride
L	Ligand
Me_6TREN	Tris[2-(dimethylamino)ethyl]amine
M	Monomer
MBP	Methyl 2-bromopropionate
Me	Methyl
MMA	Methyl methacrylate
MPC	2-(methacryloyloxy)ethyl phosphorylcholine
NMP	Nitroxide Mediated Free Radical Polymerization

NMR	Nuclear Magnetic Resonance Spectrometry
PDI	Polydispersity index
PMMA	Poly(methyl methacrylate)
PMDETA	*N,N,N',N'',N''*-pentamethyldiethylenetriamine
Ph	Phenyl
PS	Polysulfone
RAFT	Reversible Addition-Fragmentation Chain Transfer Polymerization
RT	Room temperature
R	Alkyl
SEC	Size Exclusion Chromatography
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TEMPO	2,2,6,6-tetramethylpiperidiny-1-oxy
TMS	Tetramethylsilane
wt	Weight

CHAPTER 1

INTRODUCTION

Polysulfone and its derivatives are the most important engineering thermoplastic materials used as precursors to fabricate membranes for many industrial applications such as fuel cell technology[1-13] and liquid and gas separation processes[14-34], electrodialysis and polymer electrolyte membrane electrolysis[35-38]. The chemical and physical characteristics of polysulfone, such as good thermal and chemical stability, mechanical strength and excellent oxidative resistance, make polysulfone the material of choice for use as membrane substrates[1-39]. However, due to its hydrophobic nature, polysulfone membranes are susceptible to fouling[40] by various mechanisms that reduce the application of polysulfone membranes in the treatment of food streams and biological separations. Thus, the synthesis of new functionalized polysulfone polymers and its subsequent use as membrane matrix polymers has been the focus of industrial and academic research in order to meet the increased industrial need for polysulfone membranes with increased hydrophilicity, high flux and low fouling[14-40]. In particular, the regiospecific chemical incorporation of bulky amine groups pendant to the polysulfone chain has been a challenge due to deleterious side reactions associated with amination reactions with polysulfone derivatives[41-44]. The present research focuses on the synthesis of dipyridyl functionalized polysulfones with improved hydrophilicity, enhanced membrane morphological characteristics and excellent ATRP polymeric ligand properties. The polymer functionalization process involves the formation of lithiated polysulfone from unmodified polysulfone and the subsequent reaction with 2,2'-vinylidenedipyridine in tetrahydrofuran at -78 ^{o}C under argon atmosphere to afford the corresponding dipyridyl functionalized polysulfone.

Atom transfer radical polymerization[45] (ATRP) is one of the most versatile and powerful synthetic techniques in polymer science. ATRP allows the synthesis of polymers with well defined number average molecular weight, narrow molecular weight distribution, good control of chain end functionality, composition and molecular architecture. The most common ATRP reaction involves the reversible homolytic cleavage of a carbon halogen bond of an alkyl halide initiator derivative by a redox reaction with a transition metal/ligand complex, followed by monomer addition to form well defined polymers. An essential feature of the ATRP process is the equilibrium between a low concentration of active propagating species and a large number of dormant chains via an electron transfer process promoted by a transition metal/ligand complex. In the classical ATRP process, the topology of the polymer chains is such that the • -terminal group is a halogen atom with the initiator fragment at the •-terminus of the polymer chain. Thus, with the selection of an appropriate functionalized initiator molecule or functionalized initiator system, a wide variety of chain end functionalized polymers can be prepared via the ATRP technique[45].

The use of functionalized 1,1-diphenylethylene derivatives in polymer synthesis provides one of the best polymer synthesis methods to produce well defined polymers[46-52]. The synthesis of chain end functionalized polymers utilizes the addition reactions of active polymer chain ends with functionalized 1,1-diphenylethylene derivatives for the following reasons: (a) the addition is simple and quantitative; (b) due to steric factors, only monoaddition occurs, i.e., no oligomerization of the 1,1-diphenylethylene unit is observed; and (c) a variety of substituted 1,1-diphenylethylene derivatives can easily be prepared by standard organic reactions. By ATRP methods, well defined amine functionalized polymers can be prepared using a general, quantitative, one pot, functionalization method, which employs appropriate amine functionalized 1,1-diphenylethylene derivatives as amine functionalized initiator precursors for the polymerization of styrene and methyl methacrylate[53].

The current study outlines the preparation of new amine chain end functionalized polystyrene and poly(methyl methacrylate) by Atom Transfer Radical Polymerization (ATRP) methods by the following synthetic pathways:

(a) The use of a new primary amine functionalized initiator adduct, formed *in situ* by the reaction of 1-(4-aminophenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as catalyst in diethyl ether at 110 ^{o}C, for the polymerization of styrene to provide a new method for the synthesis of •-aminophenyl functionalized polystyrene[54].

(b) The synthesis of new •-bis(aminophenyl) and •,•-tetrakis(aminophenyl) functionalized polymers by ATRP methods using the following synthetic strategy:

(i) the initiation of styrene polymerization with a new primary diamine functionalized initiator adduct, generated *in situ* by the reaction of stoichiometric amounts of 1,1-bis(4-aminophenyl)ethylene with (1-bromo-ethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as catalyst, to afford a unique synthetic route for the preparation of •-bis(aminophenyl) functionalized polystyrene;
(ii) the synthesis of •-bis(aminophenyl) functionalized poly(methyl methacrylate) by ATRP methods using the primary diamine functionalized initiator adduct as initiator for methyl methacrylate polymerization; and
(iii) the preparation of well defined •,•-tetrakis(aminophenyl) functionalized polystyrene by a post ATRP chain end modification reaction of •-bis(aminophenyl) functionalized polystyrene with 1,1-bis(4-aminophenyl)-ethylene at the completion of the polymerization reaction.

(c) A new tertiary diamine functionalized initiator adduct, formed *in situ* by treatment of equimolar amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as the catalyst in diphenyl ether at 110 ^{o}C, can be employed as initiator for styrene polymerization by ATRP methods to provide a new method for the synthesis of •-bis(4-dimethylaminophenyl) functionalized polystyrene. Furthermore, the ATRP of methyl methacrylate, initiated by the new tertiary diamine functionalized initiator adduct, provides a new method for the preparation of •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate). In addition, •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene can be prepared via a post ATRP chain end modification reaction of •-bis(4-dimethylaminophenyl) functionalized polystyrene with equimolar amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene at the completion of the polymerization process.

The current research investigates the polymerization kinetics data of each ATRP reaction to determine the controlled/living character of each ATRP reaction leading to the formation of the different amine chain end functionalized polymers.

Furthermore, one of the limitations of the ATRP process for industrial development is the presence of residual metal catalyst in the final polymer product, which is detrimental to the quality of the polymer product as well as the environment. A potential way to overcome the drawback of contamination, cost and recovery of the catalyst is to immobilize the metal catalyst onto a solid carrier, which could be readily removed from the final product and reused for further ATRP reactions[55]. The present study describes the preparation of a novel dipyridyl functionalized polysulfone/CuBr supported catalyst system and the determination of its efficiency for the ATRP of styrene.

CHAPTER 2

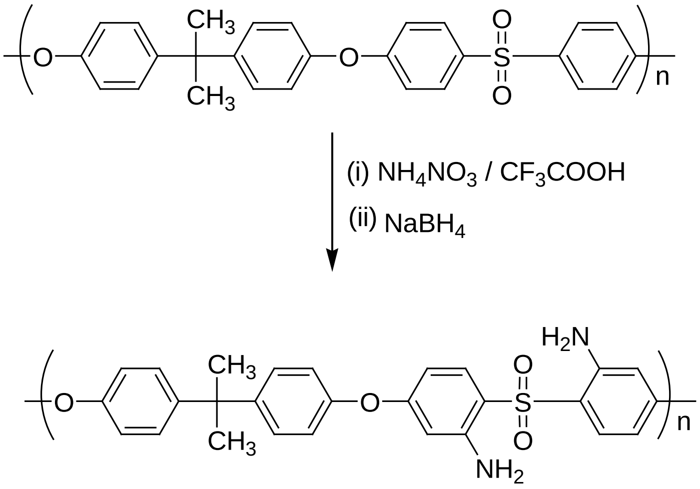
LITERATURE REVIEW

2.1 Chemical Modification of Polysulfone by Anionic Methods

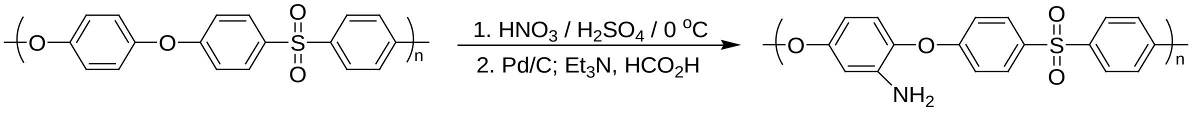
Polysulfone and its derivatives are widely used as engineering thermoplastic materials to fabricate membranes for applications in fuel cell technology[1-13], ultrafiltration, reverse osmosis and liquid and gas separation processes[14-34] such as carbon dioxide stripping from natural gas streams and production of high purity nitrogen from air. In particular, polysulfones are used as ion exchange membranes in electro-membrane processes such as electrodialysis and polymer electrolyte membrane electrolysis[35-38]. The chemical and physical characteristics of polysulfone, such as good thermal and chemical stability, mechanical strength and excellent oxidative resistance, make polysulfone the material of choice for use as membrane substrates[1-39].

However, due to its hydrophobic nature, polysulfone membranes are susceptible to fouling[40] by various mechanisms that reduce the application of the polysulfone membrane in the treatment of food streams and biological separations. Furthermore, it is well known that the incorporation of bulky pendant groups onto the polymer backbone effects significant changes to the gas permeability, permselectivity, mechanical and surface properties of polysulfone membranes. Thus, the synthesis of new functionalized polysulfone polymers and their subsequent use as membrane matrix polymers have been the focus of industrial and academic research in order to meet the increased industrial need for polysulfone membranes with increased hydrophilicity, high flux and low fouling[14-40]. In particular, the regiospecific introduction of amine groups pendant to the polysulfone chain has been a challenge since the rigorous reaction conditions lead to uncontrolled, multiple sites of amination as well as chain scission and cross-linking without any control of the degree of functionalization.

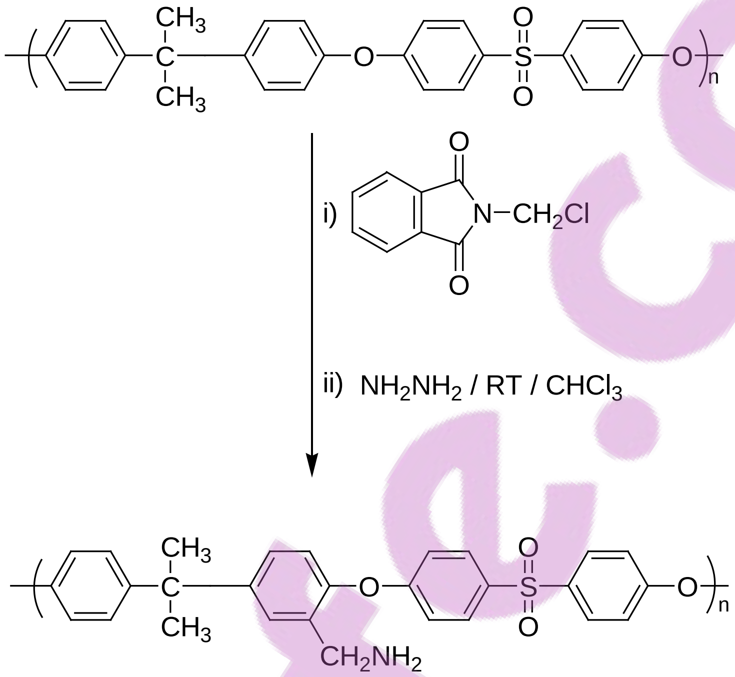
Several reviews on the chemical modification of polysulfone by different chemical mechanisms to effect the facile introduction of the functional groups onto the polysulfone backbone have been reported[1-44]. For example, Daly and coworkers[41] reported the amination of polysulfone by the direct nitration of polysulfone with an ammonium nitrate/trifluoroacetic acid mixture. The intermediate nitro derivative was converted to the amine by reduction with sodium borohydride. However, some degree of polymer degradation was observed without any control of the position and degree of functionalization:



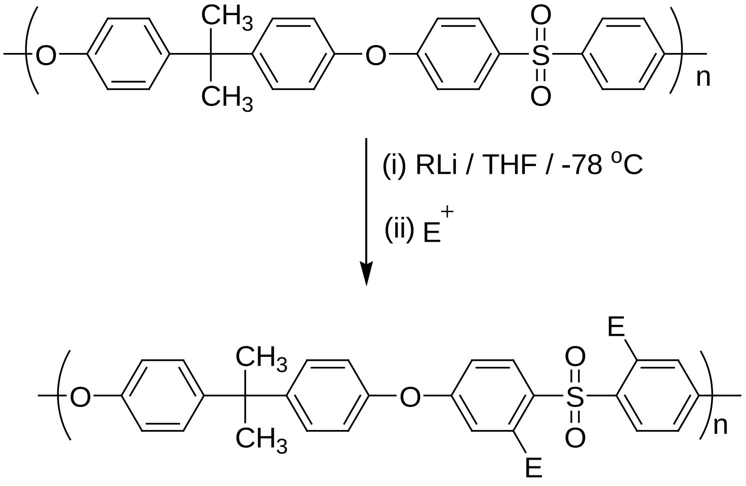
Naik[42] and Conningham[43] reported a more efficient amine functionalization process which involves the nitration-reduction reactions of poly(ether ether sulfones) and poly(ether sulfones), respectively. Each process shows that the polysulfone is nitrated exclusively on the hydroquinone unit. The reduction of the nitro group affords the corresponding amine functionalized polysulfone derivative:



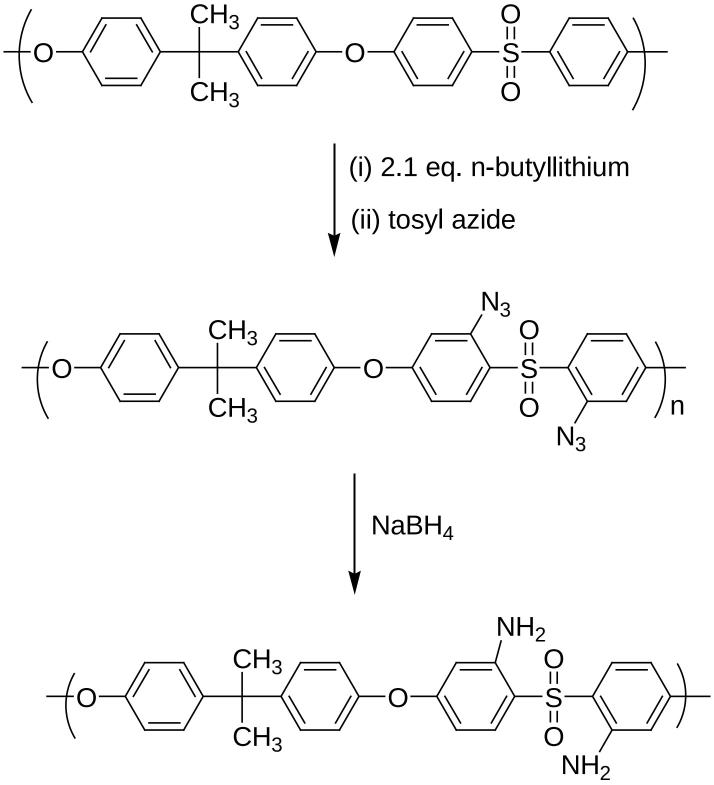
Kahana and coworkers[44] reported the introduction of the amine functionality on the polysulfone backbone using the phthalimido methylation route with N-chloromethyl phthalimide as reagent:



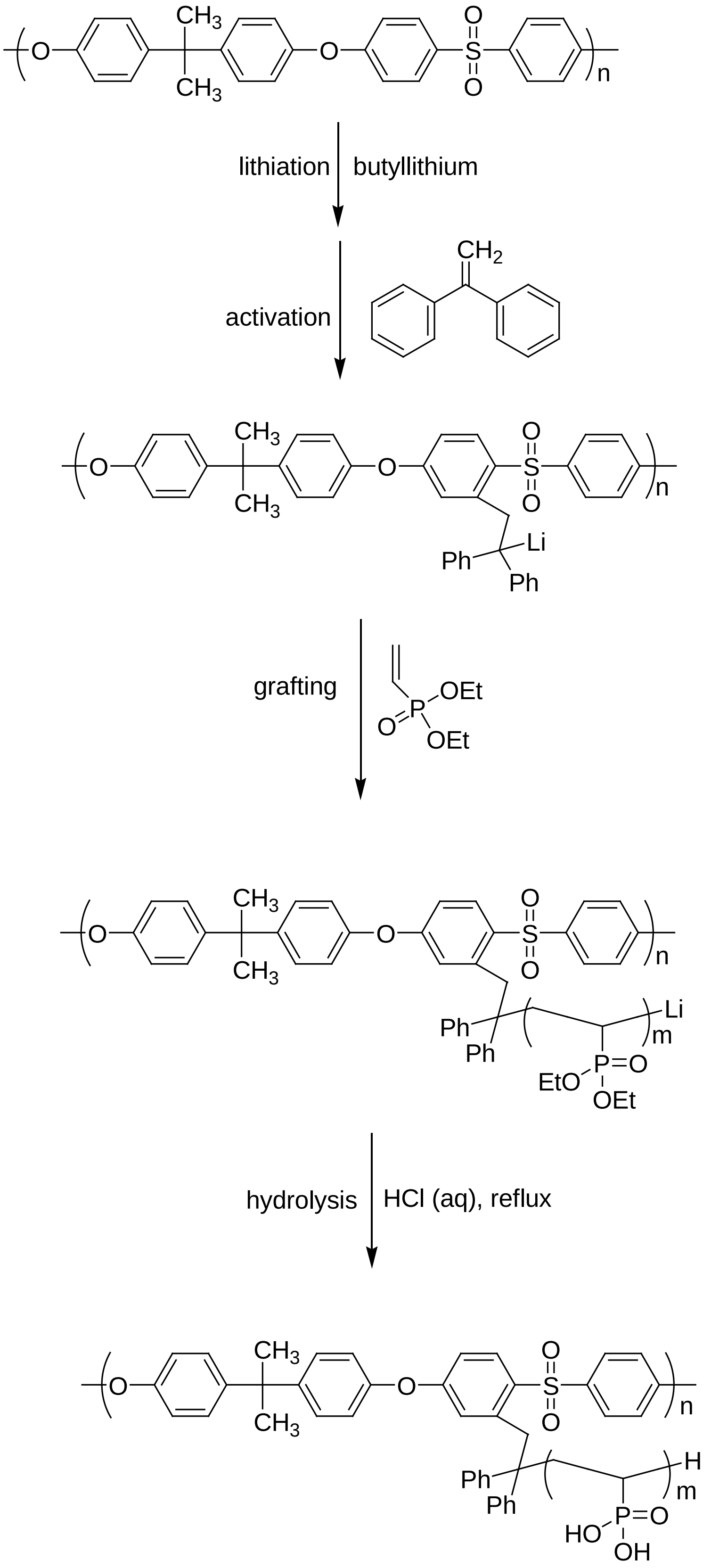
To meet the demand for a regiospecific, well controlled polymer modification reaction, a more attractive, site specific and efficient approach in the chemical modification of polysulfone is required. Guiver and coworkers[14-17,35-37] developed a novel route, which was later exploited by Jannasch and coworkers[1-7] for the regiospecific introduction of functional groups on the polysulfone backbone. The process involves the chemical modification of commercially available polysulfone using carbanion chemistry to introduce functional groups onto the polymer backbone. By the treatment of unmodified polysulfone with an organolithium compound and the subsequent reaction of the lithiated polysulfone derivative with the appropriate electrophiles afforded a wide variety of functionalized polysulfone derivatives in quantitative yields. The lithiation process is well controlled and takes place regiospecifically at the ortho position relative to the sulfone groups of the polymer backbone. The subsequent addition of different electrophilic systems (E^+) leads to the introduction of different functional groups such as the carboxyl, halogen, alkyl, aldehyde, sulfonate, primary amine and silyl groups pendant to the polymer backbone[14-17,35-37], as outlined as follows:



In particular, for the preparation of amine functionalized polysulfone, unmodified polysulfone was reacted directly with *n*-butyllithium at low temperature. The lithiated polysulfone was then converted quantitatively to the azide polysulfone derivative by treatment with tosyl azide. Subsequent reduction of the azide groups to the primary amine groups by the addition of sodium borohydride gave the amine functionalized polysulfone in quantitative yields. The polymeric amine precursors are used extensively in cross-linking or chain extension reactions to achieve reduced brittleness in thermosetting resins:



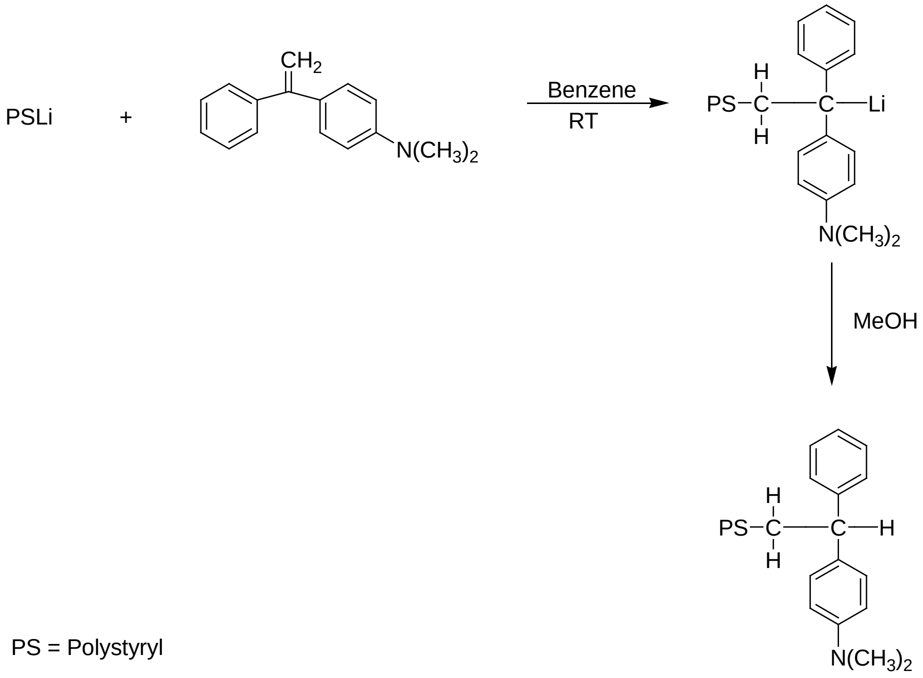
Recently, Jannasch and coworkers[5-7] prepared mechanically strong and flexible polysulfone membrane substrates by grafting poly(vinylphosphonic acid) side chains onto polysulfone. Lithiation of unmodified polysulfone by butyllithium produced lithiated polysulfone which acted as initiator for the anionic polymerization of diethylvinylphosphate from the polysulfone backbone. The direct polymerization from the lithiated sites on polysulfone gave very low yields of the designed product even after long reaction times. Thus, to overcome the inefficient nucleophilic power and the initiating capacity of the lithiated polysulfone, 1,1-diphenylethylene was added to the reaction mixture to form the diphenylalkyllithium anion prior to the addition of the diethylvinylphosphate monomer. Polymerization proceeded *via* a well controlled reaction and, after the quantitative cleavage of the ester function, polysulfone-g-poly(vinylphosphonic acid) copolymers were produced:


lithiation
butyllithium
activation
grafting
hydrolysis
HCl (aq), reflux

The results indicate that the crossover reaction of lithiated polysulfone with the bulky 1,1-diphenylethylene electrophile proceeded quantitatively with the introduction of only one 1,1-diphenylethylene unit pendant to the polymer chain. In the current study, the preparation of dipyridyl functionalized polysulfone is described[39]. The method involves the quantitative lithiation of polysulfone and subsequent addition of 2,2'-vinylidenedipyridine to produce the corresponding dipyridyl functionalized polysulfones with degrees of functionalization ranging between 45% - 95% as determined by proton nuclear magnetic resonance spectrometry. The functionalized polymers were characterized by size exclusion chromatography, ^{1}H NMR, FTIR, differential scanning calorimetry and thermogravimetric analysis. Membranes obtained from unmodified polysulfone as well as dipyridyl functionalized polysulfones were characterized by atomic force microscopy, scanning electron microscopy, pure water permeation measurements and contact angle measurements.

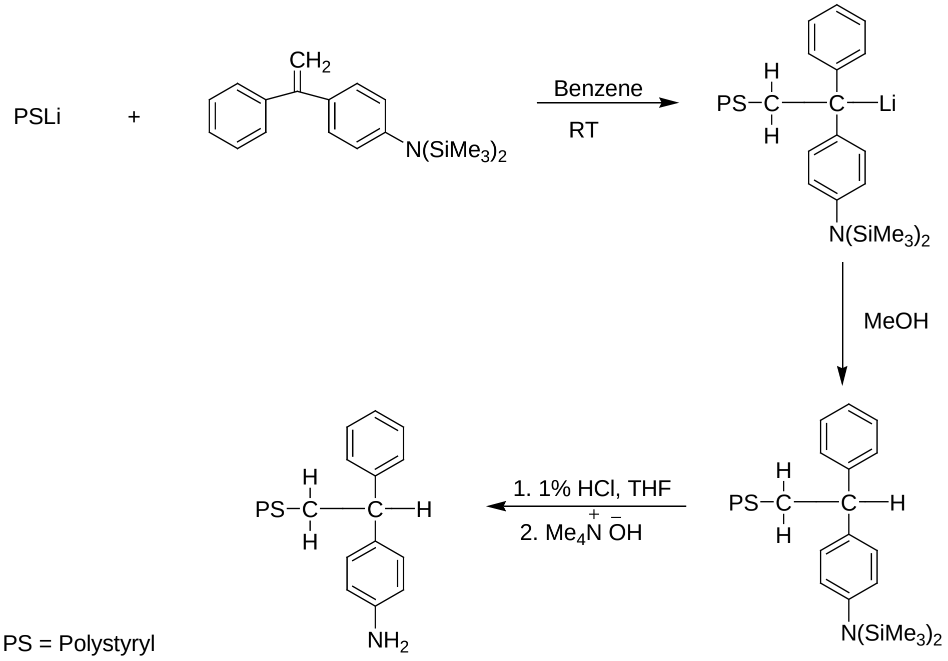
2.2 Functionalization of Polymers with 1,1-Diarylethylene Derivatives

The reaction of polymeric carbanionic centers with functionalized 1,1-diphenylethylene derivatives is one of the most versatile methods for the introduction of functional groups at the polymeric chain end. Quirk and coworkers[46-51] developed a general, quantitative, living, anionic functionalization method, independent of the specific functional group, based on the addition reaction of simple and polymeric organolithium compounds to 1,1-diphenylethylene derivatives. A feature of such reactions is that, due to steric effects, the 1,1-diphenylethylene unit does not homopolymerize and undergo only quantitative monoaddition reactions with the anionic species. Thus, the functionalized 1,1-diphenylethylene unit readily reacts with organolithium compounds to quantitatively produce 1:1 adducts. For example, dimethylamino functionalized polystyrene was prepared by the reaction of polystyryllithium (PSLi) with 1-[4'-(N,N-dimethylaminophenyl)]-1-phenylethylene[46] as outlined below:



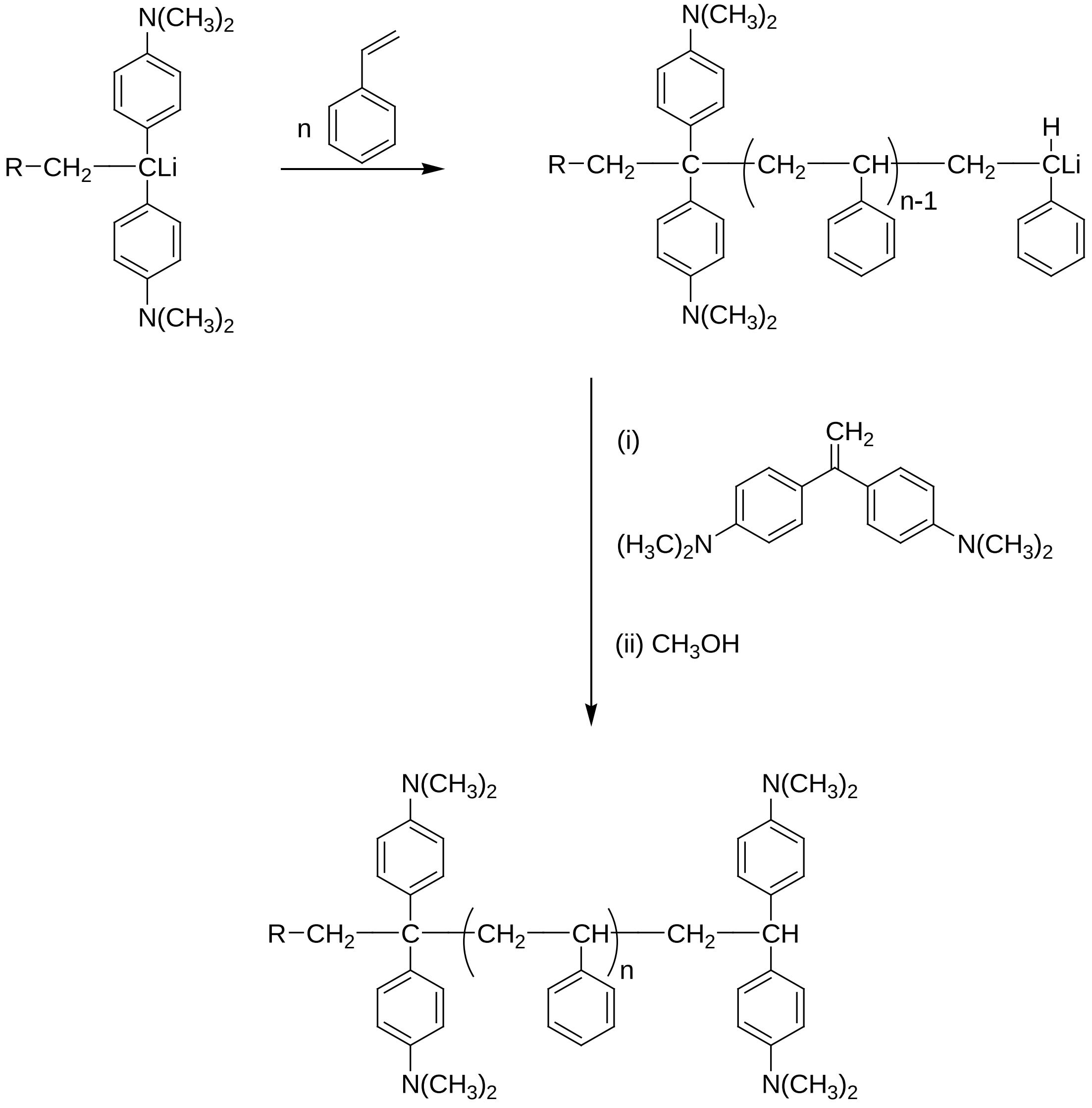
PS = Polystyryl

Similarly, • -aminopolystyrene[51] was prepared in quantitative yields by reacting polystyryllithium with 1-[4'-{N,N-bis(trimethylsilyl)amino}phenyl]-1-phenylethylene in benzene at room temperature, followed by the removal of the silyl protecting group by hydrolysis with 1% concentrated HCl and neutralization with 20 wt% $Me_4N^+OH^-$ in methanol:



PS = Polystyryl

Recently, Kim and coworkers[52] outlined an anionic chain end functionalization reaction whereby tertiary amine groups are introduced at one end or at both ends of the polymer chain using 1,1-bis[(4-dimethylamino)phenyl]ethylene as functionalizing agent. Functionalized polymers with aromatic tertiary amine groups at both the •- and • - termini of the polymer chain were prepared by the crossover reactions of *n*-butyllithium with the diphenylethylene analogue to form an initiator intermediate for styrene polymerization, followed by the chain end functionalization reaction by the addition of 1,1-bis[(4-dimethylamino)phenyl]-ethylene at the end of the polymerization process:



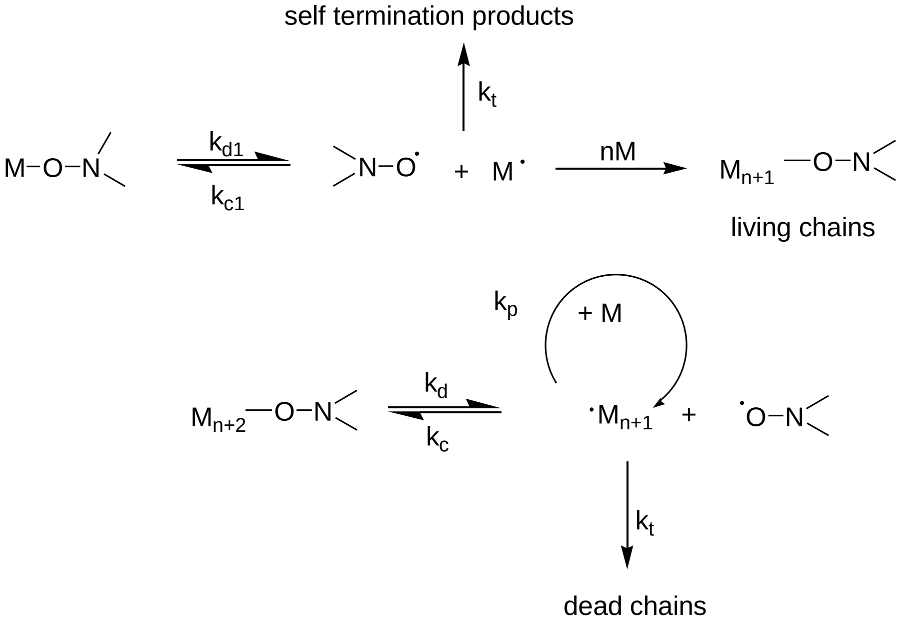
The current research work describes the synthesis of functionalized polymers *via* controlled free radical polymerization using functionalized 1,1-diphenylethylene compounds as amine initiator precursors. The method involves the preparation of well defined primary and tertiary amine functionalized polymers by a general, quantitative, one pot ATRP functionalization process, using appropriate functionalized initiator systems derived from primary and tertiary amine substituted 1,1-diphenylethylenes as well as post ATRP chain end functionalization reactions.

2.3 Free Radical Polymerization

Free radical polymerization is the most widely used industrial method for the preparation of polymers. The advantages of conventional free radical polymerization are its low reactant purity reactions and that a wide variety of monomers can undergo polymerization and copolymerization under simple experimental conditions. However, polymers with no control of the number average molecular weights and molecular weight distributions are obtained. The high concentration of reactive free radicals cause side reactions, such as termination and chain transfer reactions, to take place to a great extent. Hence, more controlled polymerization techniques are needed for the preparation of polymers with well-defined structures. Several new controlled/living free radical polymerization methods (CRP), which allow the preparation of well defined polymers by free radical mechanisms, were developed over the past decade. The most widely used CRP methods for the synthesis of well defined polymeric materials are nitroxide mediated free radical polymerization (NMP)[56], reversible addition-fragmentation chain transfer polymerization (RAFT)[57] and atom transfer radical polymerization (ATRP)[45].

2.3.1 Nitroxide Mediated Free Radical Polymerization

To overcome the deficiencies of uncontrolled polymer growth experienced in the traditional free radical process, the nitroxide mediated free radical polymerization (NMP) method, having characteristics of a living polymerization process, has been developed[58]. The NMP method is the simplest of the various techniques currently used for CRP.[59] The technique is based on the reversible dissociation of a (macro)alkoxyamine[60] species, which decreases the irreversible termination reactions. As a result, a majority of dormant living chains can grow until the monomer is consumed, producing a polymer with equal chain length and with a reactive chain end:

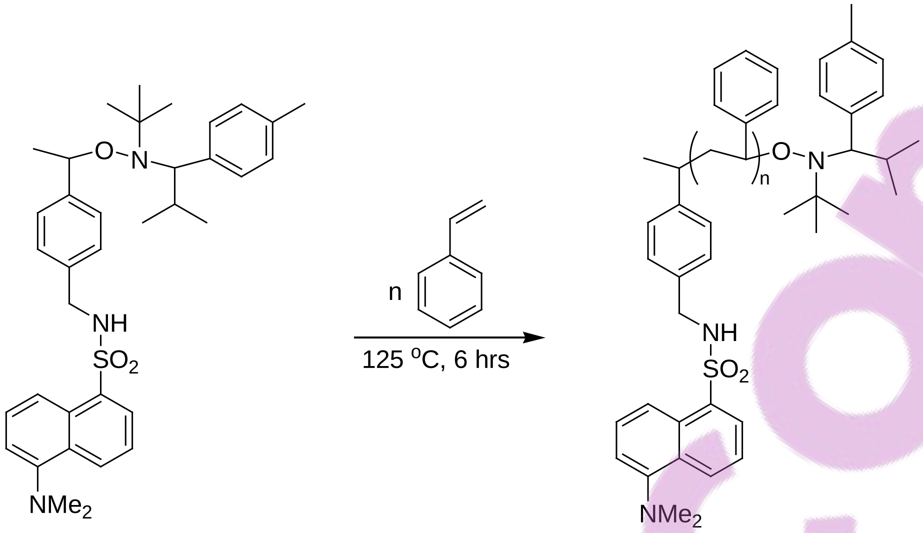


Although the NMP method may not strictly obey the definition of a living polymerization, it does satisfy many of the requirements, hence the use of the terms “living” or “pseudoliving”. The stimulus for the current interest in the NMP process is the report of Georges[61], where it is shown that polystyrene with narrow molecular weight distribution can be prepared using a mixture of benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO) as an initiating system.

The success of the NMP method can be related to the ability of stable nitroxide free radicals, such as TEMPO, to react at near diffusion controlled rates with the carbon centered free radical of the growing polymer chain end in a thermally reversible process. The process dramatically lowers the concentration of free radicals in the polymerization system and, coupled with the inability of the nitroxide free radicals to initiate new chain growth, leads to controlled polymerization. The features of the NMP process have been exploited in the preparation of star and graft polymers[62-65], hyperbranched systems[66] and random and block polymers with narrow molecular weight distributions[63-,66].

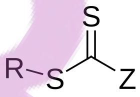
The NMP method has been applied to the polymerization of styrene and its derivatives as well as the copolymerization of styrenics with other monomers such as acrylates, methacrylates and acrylonitriles[67]. However, poor control in the polymerizations of monomers other than styrenics[68] have been obtained by the NMP method.

The NMP method has been exploited for the preparation of chain end functionalized polymers using functionalized unimolecular initiators. For example, Hawker[69] and Braslau[70] prepared amine chain end functionalized polymers by using amine functionalized alkoxyamine initiators for styrene polymerization. Incorporation of the amine chain end functionality of greater than 97% into polymers was achieved and polymers with number average molecular weights up to 70 000 g/mol were obtained:



2.3.2 Reversible Addition-Fragmentation Chain Transfer Free Radical Polymerization

Reversible addition-fragmentation chain transfer free radical polymerization (RAFT) is a versatile and robust controlled free radical polymerization process based on the use of a conventional radical polymerization initiator in the presence of (thiocarbonyl)sulfanyl compounds of general structure S=C(Z)-SR (**i**)[71].



(i)

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

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

iv) Z = Ph, R = CH_2Ph

v) Z = Ph, R = $C(CH_3)(CN)CH_2CO_2Na$

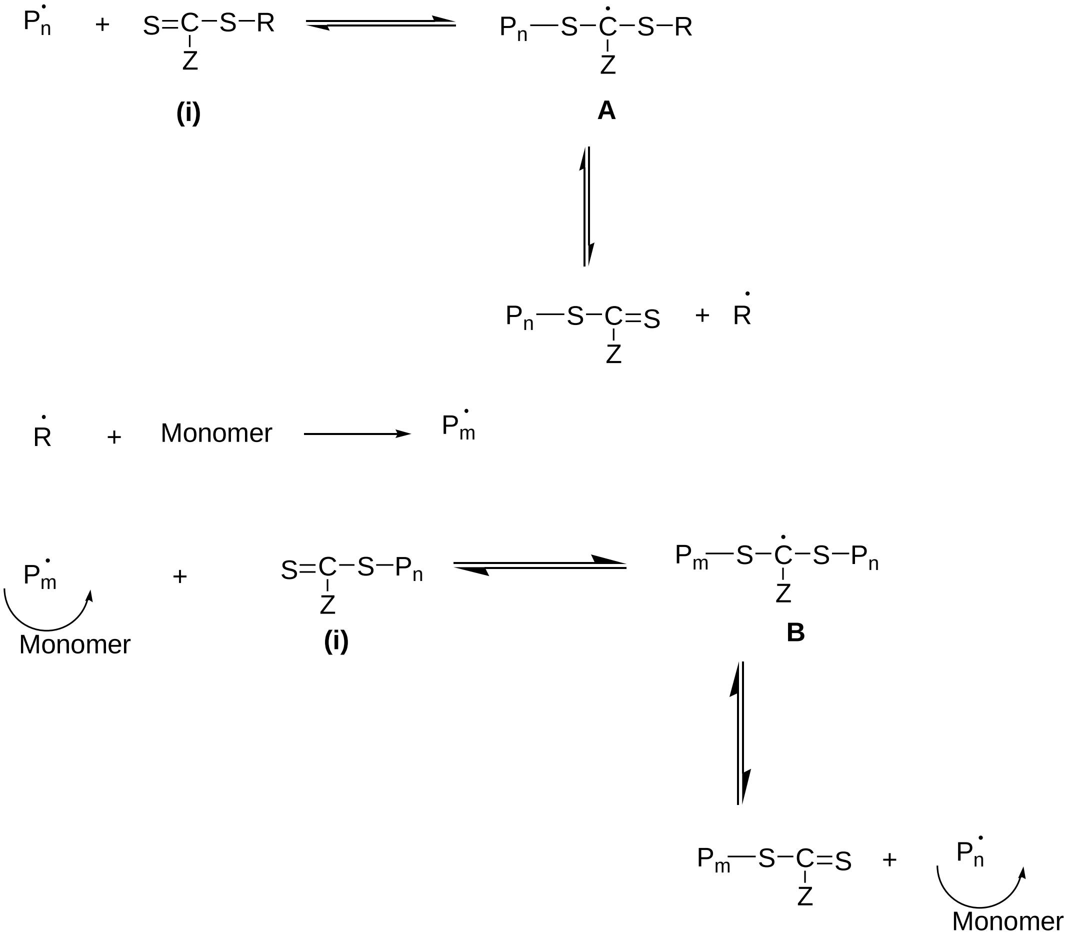
vi) Z = Ph, R = $C(CH_3)(CN)(CH_2)_2CO_2H$

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

viii) Z = CH_3, R = CH_2Ph

ix) Z = Ph, R= $C(CH_3)(CN)CH_2CH_2OH$

The (thiocarbonyl)sulfanyl compound **(i)** acts as an efficient reversible addition fragmentation chain transfer agent and confers living characteristics to the polymerization. RAFT can be distinguished from other controlled/”living” free radical polymerization methods by its use in the polymerization of a wide range of monomers with varying reaction conditions. In each case, RAFT provides polymers with controlled number average molecular weights and narrow molecular weight distributions (usually <1.2). The RAFT process involves free radical polymerization in the presence of reagent **(i)** as shown below:



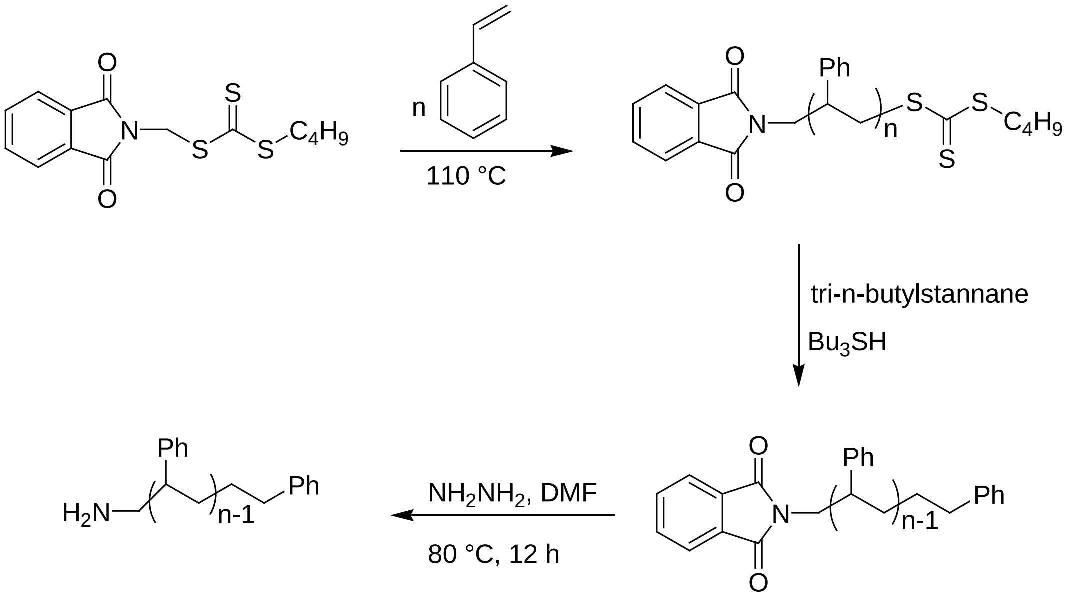
Addition of a propagating radical ($P^{\bullet}_{n}$) to a (thiocarbonyl)sulfanyl compound **(i)** gives an adduct radical **A** which can fragment to form a polymeric (thiocarbonyl)sulfanyl compound P_n-SC(Z)=S and a new radical $R^{\bullet}$. The reaction of $R^{\bullet}$ with a monomer M forms a new propagating radical $P^{\bullet}_{m}$. A dynamic equilibrium is subsequently established between the active propagating radical ($P^{\bullet}_n$ and $P^{\bullet}_m$) and dormant polymeric (thiocarbonyl)sulfanyl compounds (P_n-S-C(Z)=S) such that there is an equal probability of growth for all chains, resulting in polymers with narrow molecular weight distributions[72].

The effectiveness of reagents **(i - ix)** in providing living character to the RAFT process is attributed to their very high transfer constants which ensure a rapid rate of exchange between dormant and living chains. The choice of Z and R in reagent **(i)** is crucial to the success of the RAFT process. To ensure a high transfer constant, Z should activate (or at least not deactivate) the C=S double bond toward radical addition. Suitable Z groups are aryl and alkyl groups. The R group should be a good free radical leaving group (e.g. cumyl, cyanoisopropyl) and the expelled radical should be effective in reinitiating free radical polymerization.

RAFT can be carried out in bulk, solution, emulsion or suspension polymerization processes. The advantage of the RAFT process is its compatibility with a very wide range of monomers including functional monomers containing acid (e.g. acrylic acid), acid salt (e.g. styrene-sulfonic acid sodium salt), hydroxyl (e.g. hydroxyl ethyl methacrylate) or tertiary amine (e.g. dimethylaminoethyl methacrylate) groups. The RAFT process can also be used for the preparation of block copolymers with narrow molecular weight distributions[73].

The RAFT polymerization method can be adapted for the synthesis of end functionalized polymers by the careful choice of the RAFT agent[57]. If the R-groups of the RAFT agent contain a functional group, • -functionalized polymers are obtained. For example, Moad and coworkers[74] prepared amine functionalized polymers by introducing the amine functionality *via* a phthalimido methyl RAFT precursor. The synthesis of • -phthalimidomethylpolystyrene involved the use of a phthalimido RAFT agent for the initiation of styrene polymerization at 110 °C. Hydrazinolysis of the phthalimido end group afforded a polymer with the desired

• -amino functionality. The RAFT agent functionality was removed prior to deprotection of the amine group by reaction with tri-n-butylstannane as outlined below:



2.4 Atom Transfer Radical Polymerization

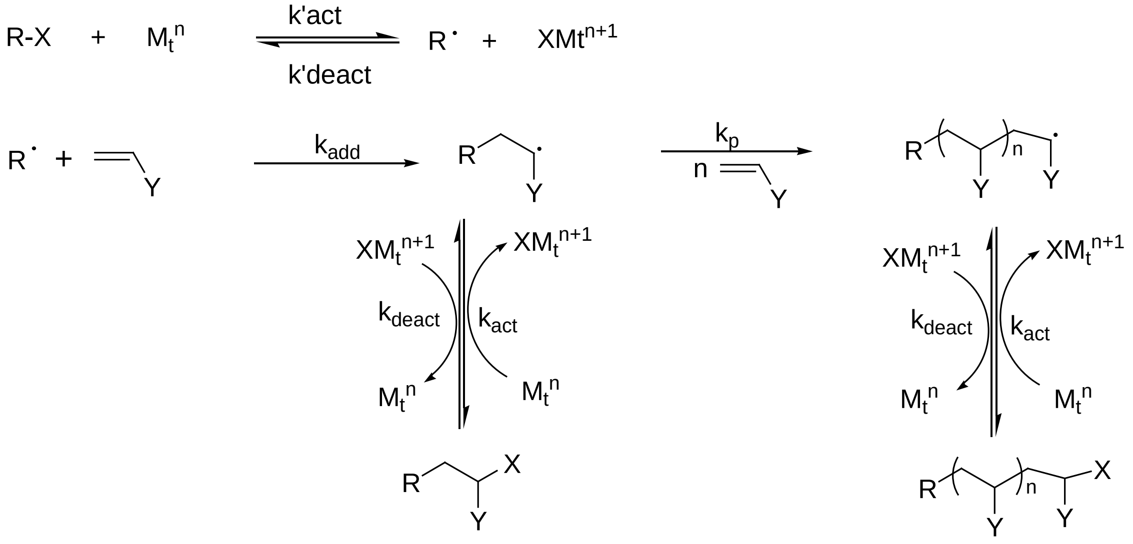
Transition metal catalyzed free radical polymerization was developed independently by Matyjaszewski and Wang[75,76] and Sawamoto and coworkers[77] in 1995. In particular, the copper mediated method, called atom transfer radical polymerization (ATRP) has proven to be more successful for the controlled/"living" (co)polymerization of a wide range of monomers including styrenes, acrylates and methacrylates. In the classical ATRP method, developed from redox catalyzed telomerization reactions[78] as well as atom transfer radical addition reactions (ATRA)[79], a transition metal/ligand complex catalyst acts as a carrier of the halogen atom in a reversible redox process[80,81] during the ATRP method.

The ATRP technique is a powerful tool for the synthesis of polymers with controlled number average molecular weights, narrow molecular weight distributions, controlled chain functionality, composition and morphology[76,82,83].

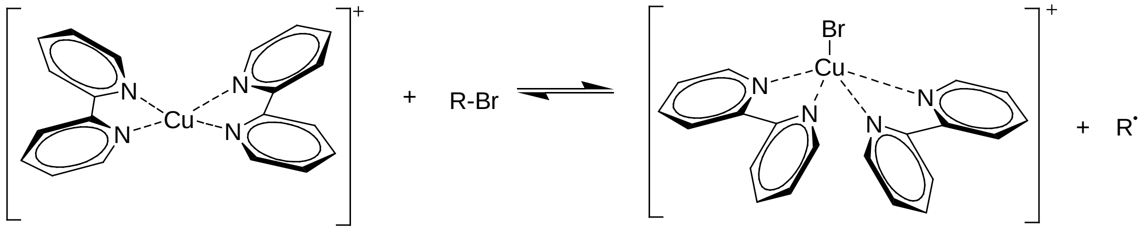
The classical ATRP method encompasses the reversible homolytic cleavage of a carbon-halogen bond of an alkyl halide initiator molecule in the presence of transition metal salt complexed with a suitable bi- or tridentate ligand as catalyst, followed by the addition of the monomer to form a polymer. Controlled radical polymerization is based on the maintenance of a low, stationary concentration of the active free radical species and the establishment of a fast, dynamic equilibrium between the active and dormant species[84,85].

2.4.1 Mechanism of Atom Transfer Radical Polymerization

In the ATRP method, the active species is formed when the halogen in the alkyl halide is abstracted by the metal complex, M_t^n, to form the oxidized species, XM_t^{n+1} and the carbon centered radical, $R^\bullet$. In the subsequent step the radical $R^\bullet$ reacts with an alkene $CH_2{=}CHY$ to form a transient radical $R\text{-}CH_2CHY^\bullet$ species. The reaction between XM_t^{n+1} and $R\text{-}CH_2CHY^\bullet$ results in the target product $R\text{-}CH_2CHY\text{-}X$ and regenerates the reduced transition metal species M_t^n which again reacts with R-X to promote a new redox cycle[76] as illustrated in the following reaction scheme:



In the ATRP process, the deactivation rate must be higher than the activation rate in order to create a low concentration of propagating radicals. Thus, the equilibrium between the dormant and the active species must be greatly shifted towards the dormant species. If deactivation is very slow or non-existent, the polymerization reaction becomes uncontrolled[86]. The overall rate of the reaction is highly dependent on the redox potential of the metal complexes:



The ATRP process in the presence of copper as catalyst takes place in two major kinetic steps: initiation and propagation. Termination reactions also occur, but no more than a few percentages of the growing chains undergo termination in ATRP reactions[76].

Initiation

$\text{R-X} + \text{Cu(I)X/ligand} \rightleftharpoons \text{R}^{\bullet} + \text{X-Cu(II)X/ligand}$

(X=Cl, Br)

$\text{R}^{\bullet} + \text{monomer} \xrightarrow{k_p} \text{P}_1^{\bullet}$

Propagation

$\text{P}_n\text{-X} + \text{Cu(i)X/ligand} \overset{K_{eq}}{\rightleftharpoons} \text{P}_n^{\bullet} + \text{X-Cu(II)X/ligand}$

$\text{P}_n^{\bullet} + \text{monomer} \xrightarrow{k_p} \text{P}_{n+1}^{\bullet}$

Termination

$\text{P}_n^{\bullet} + \text{P}_m^{\bullet} \xrightarrow{k_t} \text{P}_{n+m}$

The following rate laws are derived from the initiation and propagation steps:[87]

$$K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{\left[P^{\bullet}\right]\left[Cu(II)X\right]}{\left[Cu(I)\right]\left[PX\right]}$$

$$R_p = k_p\left[P\right]\left[M\right] = k_p K_{eq}\left[I\right]_0 \frac{\left[Cu(I)X\right]}{\left[Cu(II)X\right]}\left[M\right]$$

R_p is based on the assumption that the termination step can be neglected and that a fast pre-equilibrium is established. The propagating rate (R_p) of the polymerization process is first order with respect to monomer concentration [M], initiator concentration [I] and activator concentration [Cu(I)X]. However, in the beginning, the reaction is negative with respect to deactivator concentration [Cu(II)X]. This is due to the persistent radical effect and the irreversible formation of Cu(II)X in the initial stages of the polymerization[88].

There are three primary experimental features which determine a controlled/”living” free radical polymerization[89] process, namely:

(i) the first order rate plot of $\ln[M]_0/[M]$ versus time should be linear. This is an indication that the concentration of active radical species is constant throughout the reaction. The plot should have a gradient equal to the pseudo first order rate coefficient, K^{app}, which gives an indication of the rate of reaction. K^{app} is defined by:

$$\ln\frac{[M]_0}{[M]} = K_p\left[Pol^{*}\right]_t = K^{app}t$$

where [M] is the monomer concentration, $[M]_0$ is the initial monomer concentration, K_p is the propagation rate coefficient, [Pol*] is the concentration of active propagating species and t is time.

(ii) the molecular weight distributions of the polymers should be below 1.5.

(iii) an observed increase in the number average molecular weight of the polymer as monomer conversion proceeds should be linear, indicating that all the chains are growing at the same rate, described by the equation below:

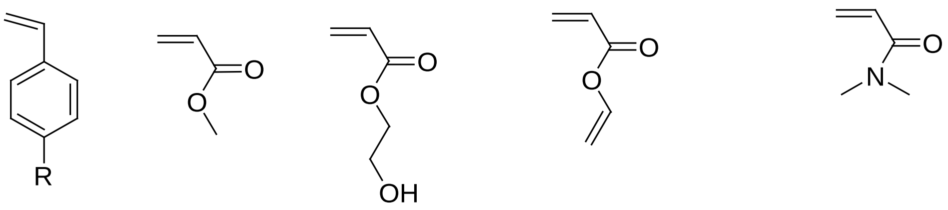
$$M_n^{theory} = \frac{\%conversion}{100} \frac{[M]_0}{[I]_0} MW_m + MW_i$$

where $[M]_0$ and $[I]_0$ are the initial concentrations of monomer and initiator respectively, and MW_M and MW_i are the molecular weights of monomer and initiator, respectively.

2.4.2 Characteristics of the ATRP reaction

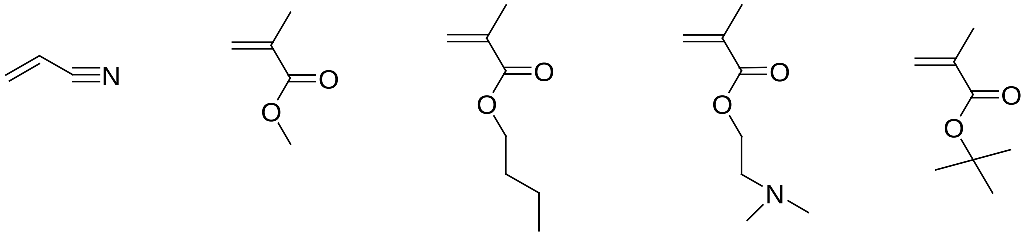
Monomers

A variety of vinyl monomers such as styrenes[76,88-92], acrylates[76,77,93-97] and methacrylates[92,96,98-104] undergo polymerization by ATRP methods. Other monomers such as acrylonitrile[105,106] and (meth)acrylamide[107-109], which contains substituents that can stabilize a propagating radical, also undergo facile ATRP reactions. Some examples of monomers that undergo polymerization by ATRP methods are shown below:



R = H, Me, t-Bu, Br

F, CF_3, OAc



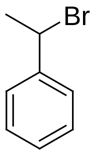
Initiators

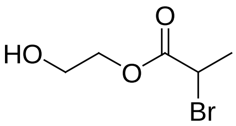
In ATRP reactions, the initiator generates the growing chains. Thus, the initiator concentration determines the molecular weight of the resulting polymer. The theoretical degree of polymerization (DP) can be calculated according to the following equation[110]:

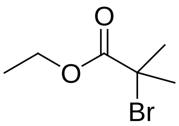
$$DP = \frac{[M]_o}{[I]_o} \text{ x conversion}$$

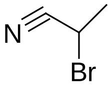
In ATRP reactions, the initiator is typically an alkyl halide (RX). For the formation of polymers with narrow molecular weight distributions, it is important that the initiation rate is higher than the propagating rate, in order to get all the chains growing at the same time. Incomplete initiation leads to polymers with higher number average molecular weights than the targeted values and with broader molecular weight distributions[86]. Another important factor is that the initiator must show little or no tendency to undergo side reactions. It has been shown that tertiary alkyl halides are better initiators than the secondary and primary alkyl halides, respectively.

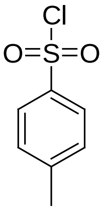
Other variables that are important to take into account when choosing initiators are steric effects, polar properties and redox potentials[111]. One easy rule to follow is that the R-group in the alkyl halide should be similar in structure to that of the monomer. For example, (1-bromoethyl)benzene is usually used for the polymerization of styrene[76]. Compounds such as ethyl-2-bromoisobutyrate and ethyl-2-bromopropionate are used for the polymerization of (meth)acrylates[92] and 2-bromopropionitrile can be used for acrylonitrile polymerization[105,106]. However, other initiators work well for different monomers. The halogen atom in ATRP initiators is usually a bromine or chlorine atom. The ATRP of acrylates[112] and styrene[90,91] with iodine-based initiators has been reported. Organofluorine compounds do not work in ATRP due to the strong C-F bond, which cannot undergo homolytic cleavage. Some examples of ATRP initiators are shown below:

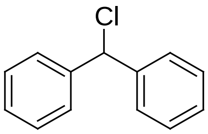


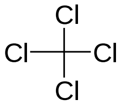










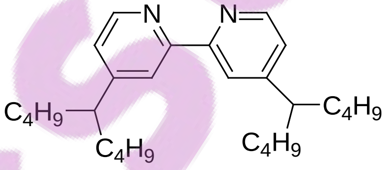


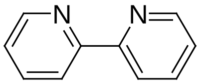
Transition metals

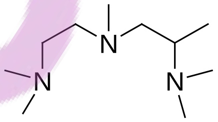
Several transition metal catalysts have been used in transition metal catalyzed free radical polymerization reactions. Catalyst based on copper is by far the most widely used metal catalyst due to its relatively low cost and versatility in ATRP reactions. However, other metals such as iron[92,103,113], ruthenium[77,114-117], nickel[101,118,119], molybdenum[120,121], rhenium[112], rhodium[122] and palladium[123] have also been used as catalysts for the polymerization of a variety of monomers. The requirements of the metal are that it should (a) have an accessible one-electron redox couple, (b) have a reasonable affinity towards a halogen atom, (c) have a coordination sphere around the metal and (d) be able to increase in oxidation state by one in order to selectively accommodate a new ligand. Also, the metal should have a low affinity for other atoms such as hydrogen atoms and alkyl radicals[45].

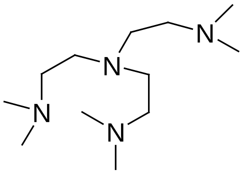
Ligands

A large variety of ligands have been used in conjunction with the different transition metals in ATRP reactions. The ligand is an important part of the ATRP catalyst system and its role is three-fold. First, the ligand solubilizes the metal in the organic media. Second, the ligand controls catalyst selectivity by steric effects and electronic factors. Finally, by their electronic effects, ligands also affect the redox chemistry of the final metal complex. Copper is usually ligated with nitrogen-based ligands. The following scheme shows some examples of bidentate [4,4'-di-5''-nonyl-2,2'-bipyridine, (dNbpy) and 2,2'-bipyridyl, (bpy)], tridentate [pentamethyldiethylenetriamine, (PMDETA)][124] and tetradentate [tris[2-(dimethylamino)ethyl]amine, (Me_6TREN)] [125] ligands that have been used in copper-based ATRP reactions:









Iron is usually ligated by phosphine base ligands such as tributylphosphine or triphenylphosphine[92,103], but can also be used in conjunction with nitrogen based ligands. Phosphorus-based ligands are also used to complex other metals in ATRP reactions such as rhenium, ruthenium, rhodium, nickel and palladium.

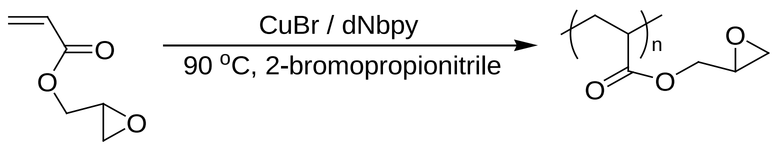
2.5 Functionalized Polymers by ATRP

The synthesis of functionalized polymers with well-controlled architecture and predictable number average molecular weight is currently of great academic and industrial interest. Polymers bearing reactive functional groups have potential applications in several areas such as reactive processing, catalysis, drug delivery and compatibilization of polymer blends[126-129]. Atom transfer radical polymerization (ATRP) is one of the most successful controlled/living free radical polymerization processes employed for the preparation of functionalized polymers[45,130-132]. The preparation of functionalized polymers by ATRP methods can be achieved *via* four different synthetic strategies:

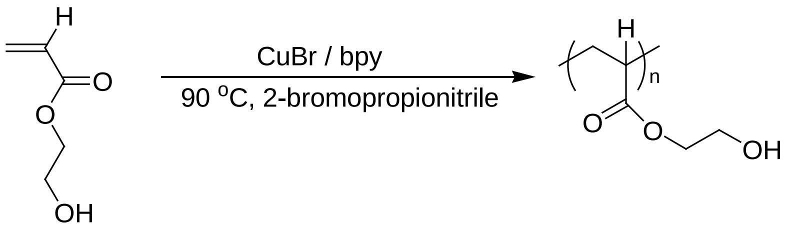
a) the atom transfer radical polymerization of functionalized monomers.
b) the post polymerization modification of monomer units along the polymer chain.
c) the post polymerization chain end functionalization of the carbon-halogen bond.
d) the use of functionalized initiators for the ATRP of vinyl monomers.

a) The atom transfer radical polymerization of functionalized monomers:

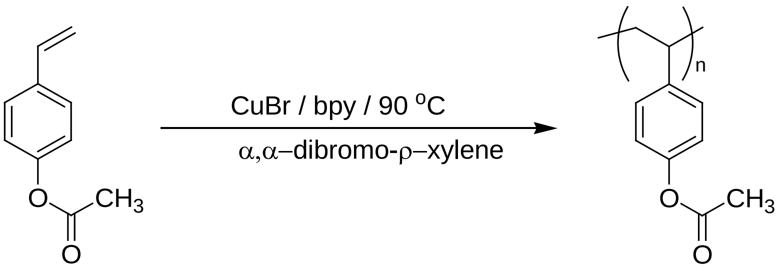
A number of monomers containing different polar functional groups undergo polymerization by the ATRP method[133-140]. However, reactive monomers such as vinyl acetate, vinylchloride and •-olefins[141] do not undergo controlled ATRP reactions. Matyjaszewski and coworkers[142] reported the ATRP of glycidyl acrylate to form well defined polymers with high number average molecular weights and narrow molecular weight distributions containing the reactive glycidyl group. Subsequent modification reactions of poly(glycidyl acrylate) are possible since the pendant oxirane rings can undergo ring opening reactions.



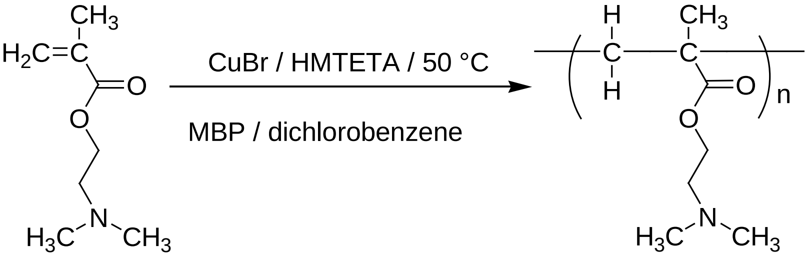
In addition, Matyjaszewski and coworkers[143] prepared hydroxyl functionalized polymers by the ATRP of 2-hydroxyethyl acrylate at 90 °C to give water-soluble polymers with applications in the field of coatings and biomaterials:



Gao and coworkers[144] introduced the ester functionality into a polymer by using a substituted styrene monomer in ATRP reactions. The monomer used was 4-acetoxystyrene. The number average molecular weights of the polymers increased linearly with monomer conversion and the molecular weight distributions of the polymers remained low throughout the polymerization (M_w/M_n = 1.11-1.18):

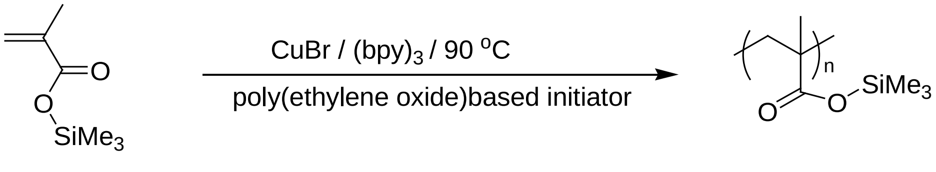


Zhang and coworkers[145] described the synthesis of tertiary amine functionalized polymers by the ATRP of 2-(dimethylamino)ethyl methacrylate to give well defined polymers with number average molecular weights up to M_n = 20 000 g/mol and M_w/M_n = 1.25. The amine functionalized polymers are water-soluble and find applications in the fields of environmental protection, drug delivery and sensors. However, polydentate ligands were used to avoid any interaction between the polar dimethylamino group of the monomer and the catalyst/ligand complex:



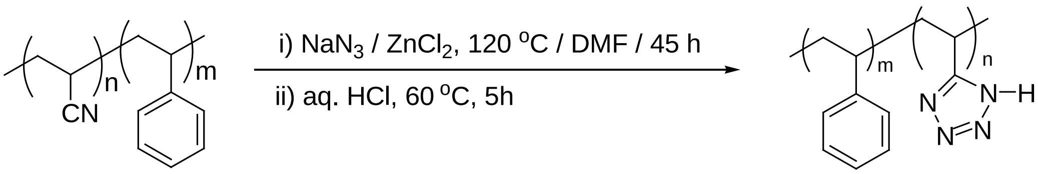
b) The post polymerization modification of monomer units along the polymer chain

Acidic monomers, such as (meth)acrylic acid, isomeric vinylbenzoic acids, unsaturated sulfonic or phosphonic acids cannot undergo direct polymerization *via* the ATRP method due to protonation and subsequent 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 protected acidic functional groups[45] as outlined in the following synthesis pathway:



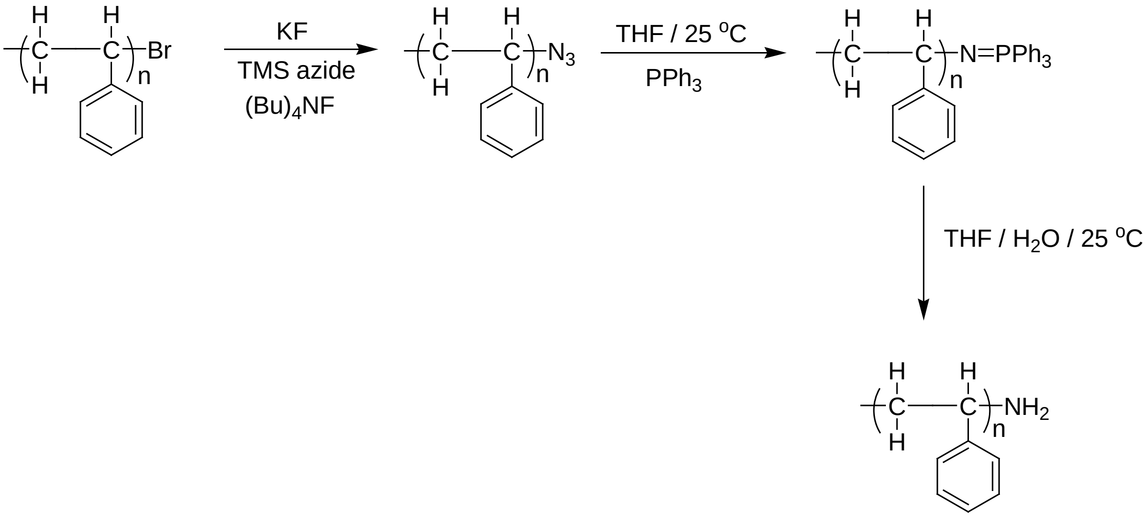
Subsequent removal of the protecting group produces the corresponding polymers with the free acid functional group.

In addition, the ATRP of vinyl tetrazoles has not been reported because of potential interaction of the acidic and coordinating properties of the tetrazole group with the ATRP catalyst system. Therefore, well defined tetrazole containing polymers are prepared by the copolymerization of styrene and acrylonitrile by ATRP methods followed by a “click” chemistry type of chemical modification of the polyacrylonitrile section to yield the desired material[146]:

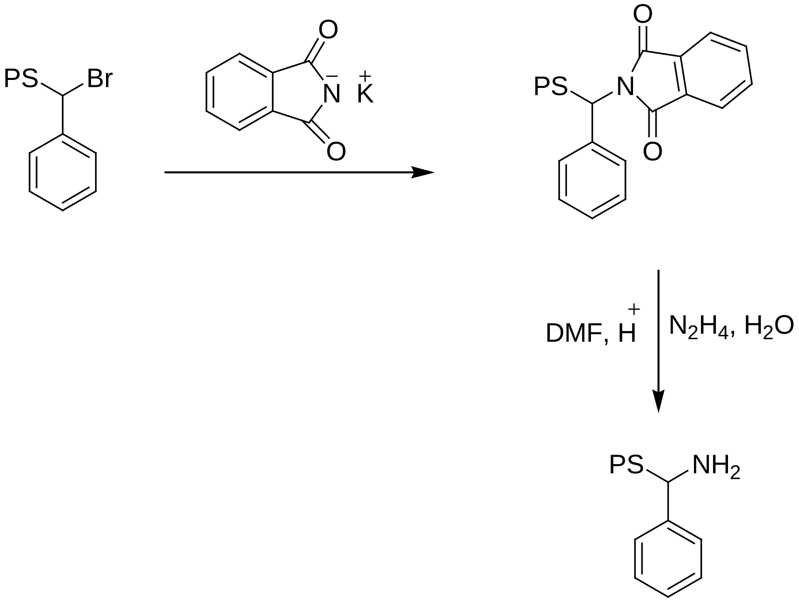


c) Post polymerization chain end functionalization of the carbon-halogen bond

The carbon-halogen end functionality, which is present on the active chain end of polymers prepared by ATRP methods, particularly polystyrene or polyacrylates, can undergo nucleophilic substitution reactions[141,147-153] to form other functional groups such as the hydroxyl, allyl, azido and ammonium or phosphonium groups in excellent yields. Matyjaszewski and coworkers[141,147-150] reported the substitution of the halogen end groups by azides in THF using TMS azide in the presence of potassium fluoride and a catalytic amount of tetrabutylammonium fluoride. The azide group was first converted to the phosphoranimine end group and subsequent hydrolysis leads to the formation of the amino end group:

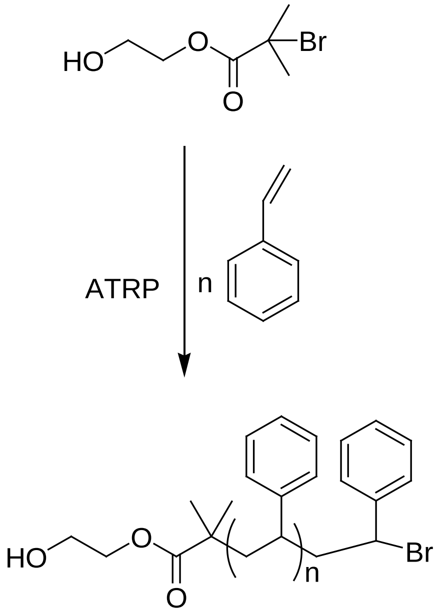


Moad and coworkers[154] reported the synthesis of amine chain end functionalized polystyrene through intermediary phthalimido end-functionalized polystyrene. Pthalimido groups are then converted to amine groups by hydrazinolysis according to an Ing-Manske procedure:



d) The use of functionalized initiators for the ATRP of vinyl monomers

In the ATRP process, the topology of the polymer chain is such that the • -terminal group is a halogen atom with the initiator fragment at the •-terminus of the polymer chain. Thus, with the selection of the appropriate functional group on the initiator molecule, a wide variety of telechelic polymers can be prepared *via* the ATRP technique[155-160]. Initiators bearing functional groups such as the hydroxyl, amine, epoxy, aldehyde and carboxylic acid groups were employed in the initiation of styrene polymerization to afford the corresponding chain end functionalized polystyrenes with the functional group introduced at the • -terminus of the polymer chain[45,147]. To illustrate the efficiency of such reactions, recently, Sarbu and coworkers[161] introduced a hydroxyl functionality at the • -terminus of the polymer chain by using 2-hydroxyethyl 2-bromoisobutyrate as an initiator for the ATRP of styrene to form a well-defined polymer with high end group functionality:

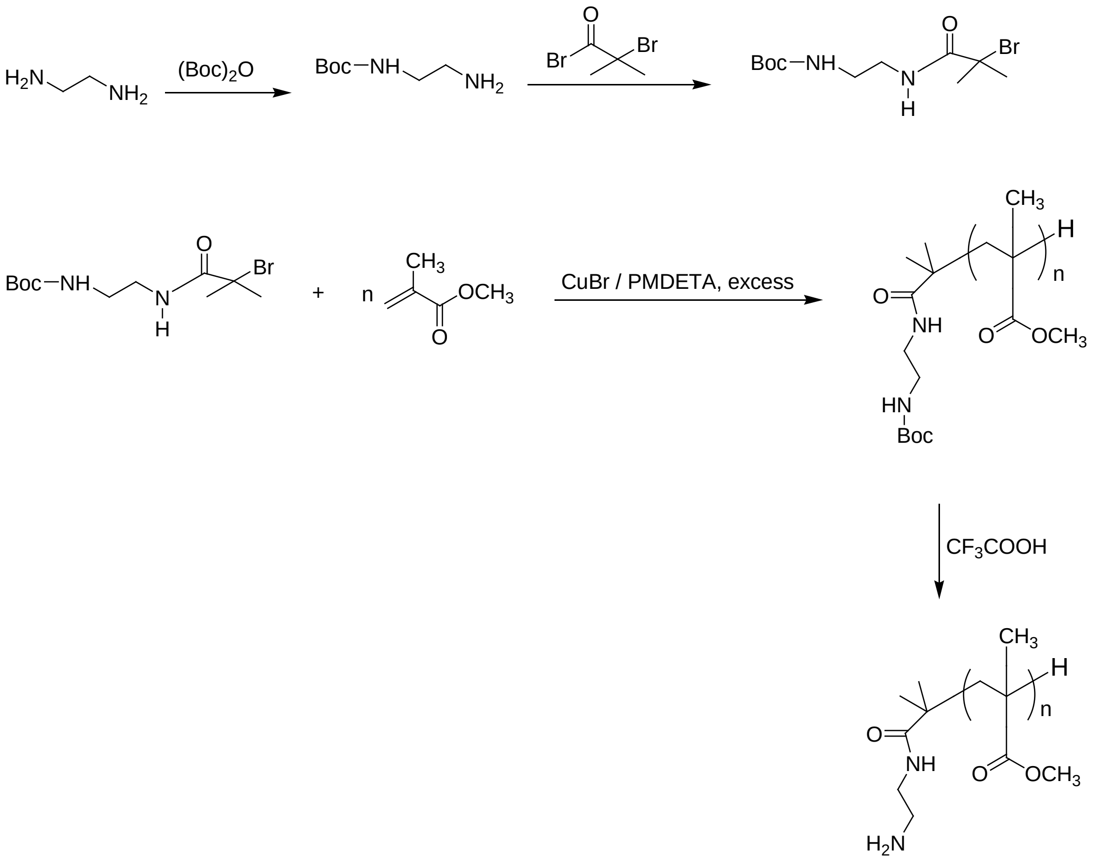


2.5.1 Amine Functionalized Initiators for ATRP

The most common ATRP reaction encompasses the reversible homolytic cleavage of a carbon-halogen bond of an alkyl halide initiator derivative by a redox reaction with a transition metal/ligand complex followed by monomer addition to form well defined polymers. In particular, the control of the initiation step in the ATRP reaction is directly dependant on the initiator reactivity and the rapid formation and stability of the catalyst/ligand system. The ligands used in the ATRP catalyst system are mostly bidentate and multidentate amine molecules. Thus, for the synthesis of well defined amine polymers, appropriately designed amine functionalized initiators are required for successful ATRP reactions whereby the interaction between the amine functionality and the catalyst/ligand system is reduced.

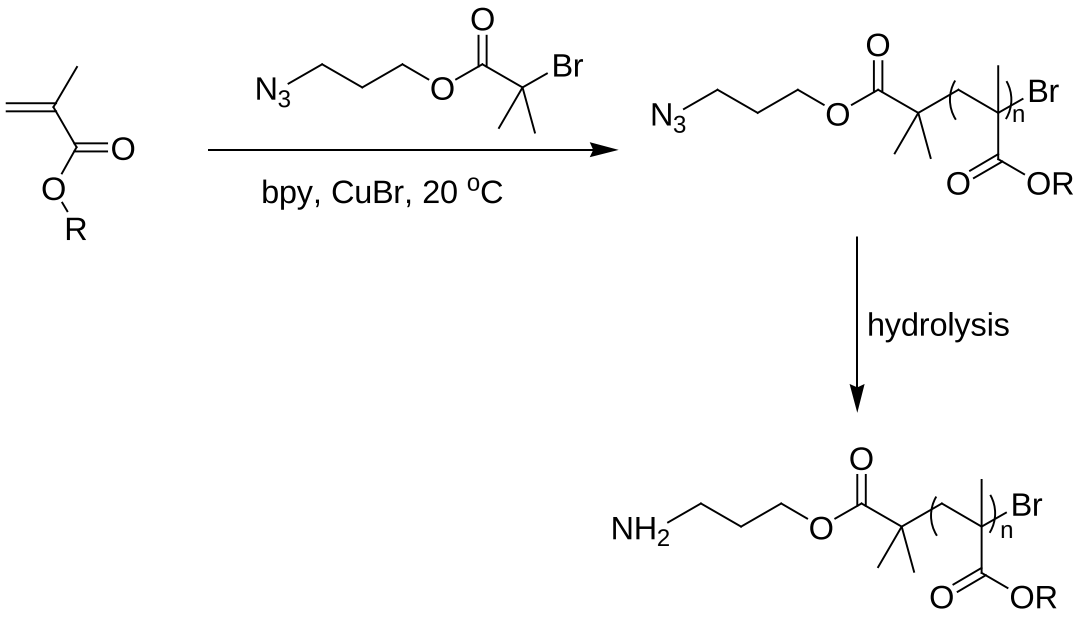
2.5.1.1 Primary Amine Functionalized Initiators for ATRP

Since the ligands which are used to complex with the metal in ATRP reactions are mostly multidentate amine derivatives and to reduce the possible interaction between the amine functional group and the ATRP catalyst system, many indirect methods, which involve the use of protected primary amine unimolecular initiators, has been adopted for the preparation of • -primary amine functionalized polymers by ATRP methods. Recently, Pionteck[162,163] prepared primary amine chain end functionalized poly(methyl methacrylate) by ATRP methods by using a Boc protected amine compound, (N-Boc-ethylamino)-2-bromoisobutanamide, as an initiator of methyl methacrylate polymerization:

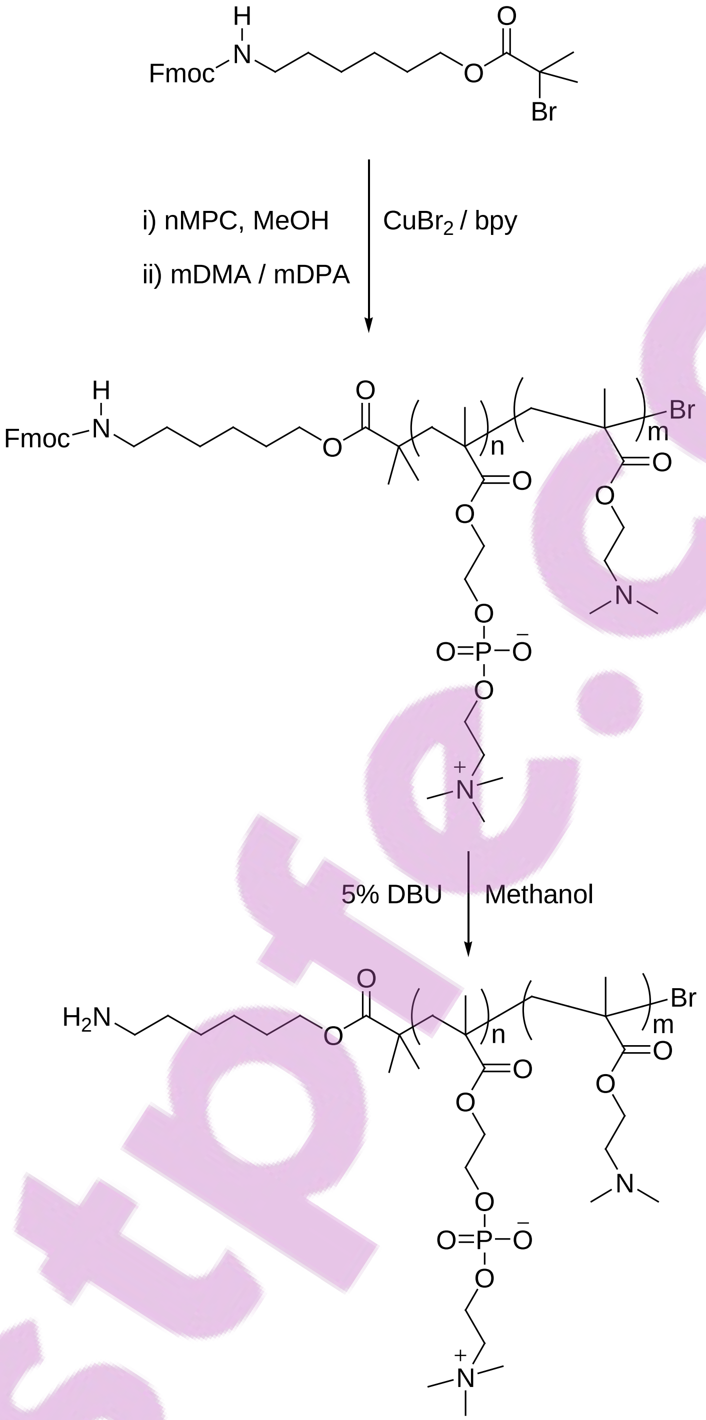


The reactions show that the amine group is first protected to avoid possible side reactions of the amine group with the catalyst system. After complete polymerization, the tert-butyloxycarbonyl (Boc) protecting group is removed by treating the polymer with trifluoroacetic acid in dichloromethane, producing the corresponding •-amine functionalized poly(methyl methacrylate) in quantitative yields and with high degree of chain end purity.

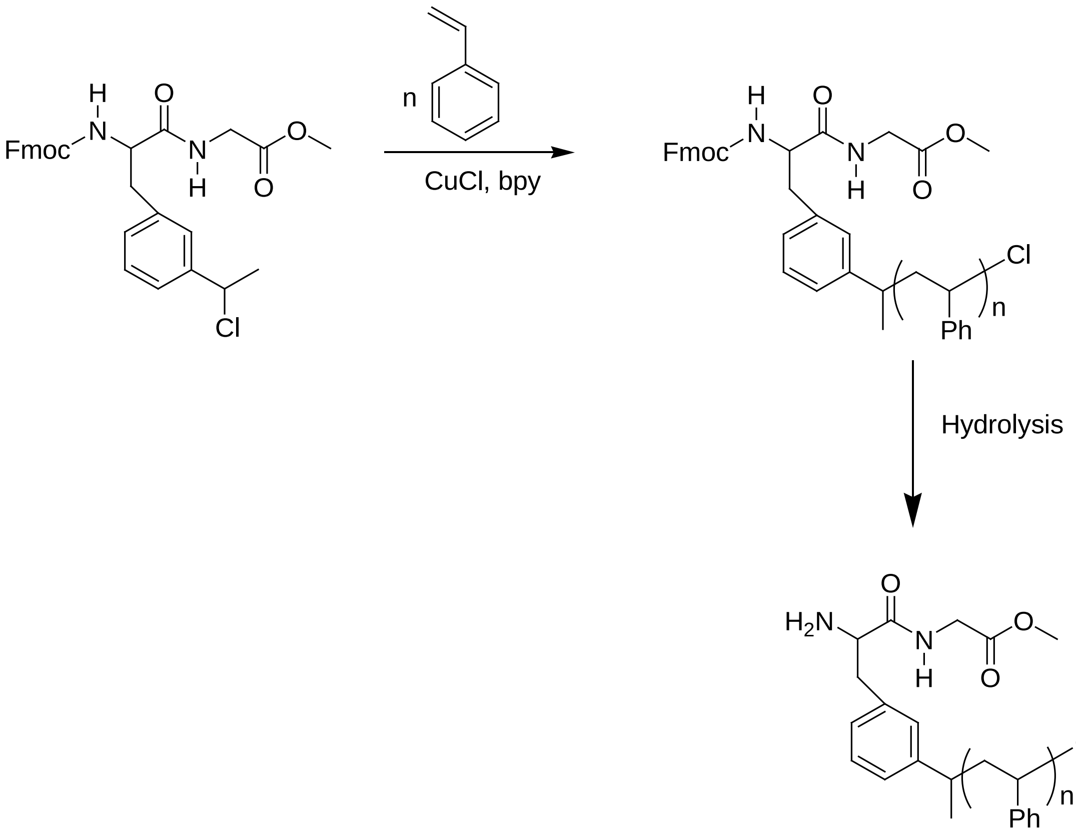
Armes and coworkers[164] utilized an •-azido functionalized initiator in ATRP reactions to produced well-defined azide functionalized homopolymers in protic media at 20 ^{o}C. In principle, the azide group of the •-azide functionalized polymers can, *via* acid catalyzed hydrolysis reactions, be converted to the corresponding well defined amine functionalized polymers:



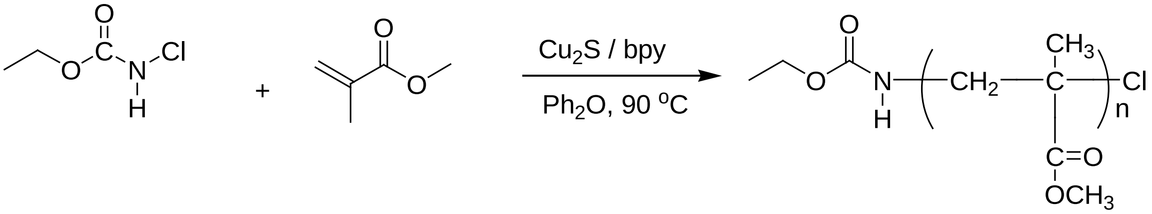
Armes and coworkers[165] also developed an interesting, new synthetic route to • -primary amine functionalized polymers by using a 9-fluorenylmethylchloroformate (Fmoc)-protected hexylamino 2-bromoisobutyrate derivative and folic acid substituted 2-bromoisobutyrate compounds as initiators for the polymerization of styrene by ATRP methods. Deprotection of the Fmoc and folic acid groups produced the terminal primary amine groups.



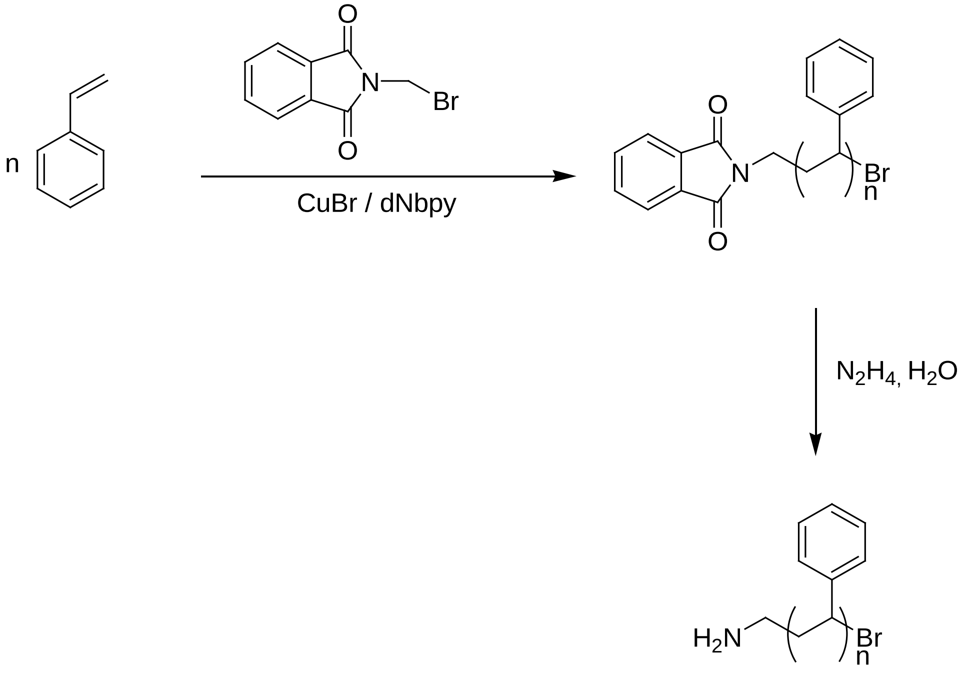
By using the Fmoc protecting group, Broyer and coworkers[166] used an amino acid functionalized initiator for styrene polymerization by ATRP methods to prepare well defined polymers bearing the amine functionality at the •-terminus of the polymer chain. The Fmoc protecting group can be removed by hydrolysis to give the required amine functionality:



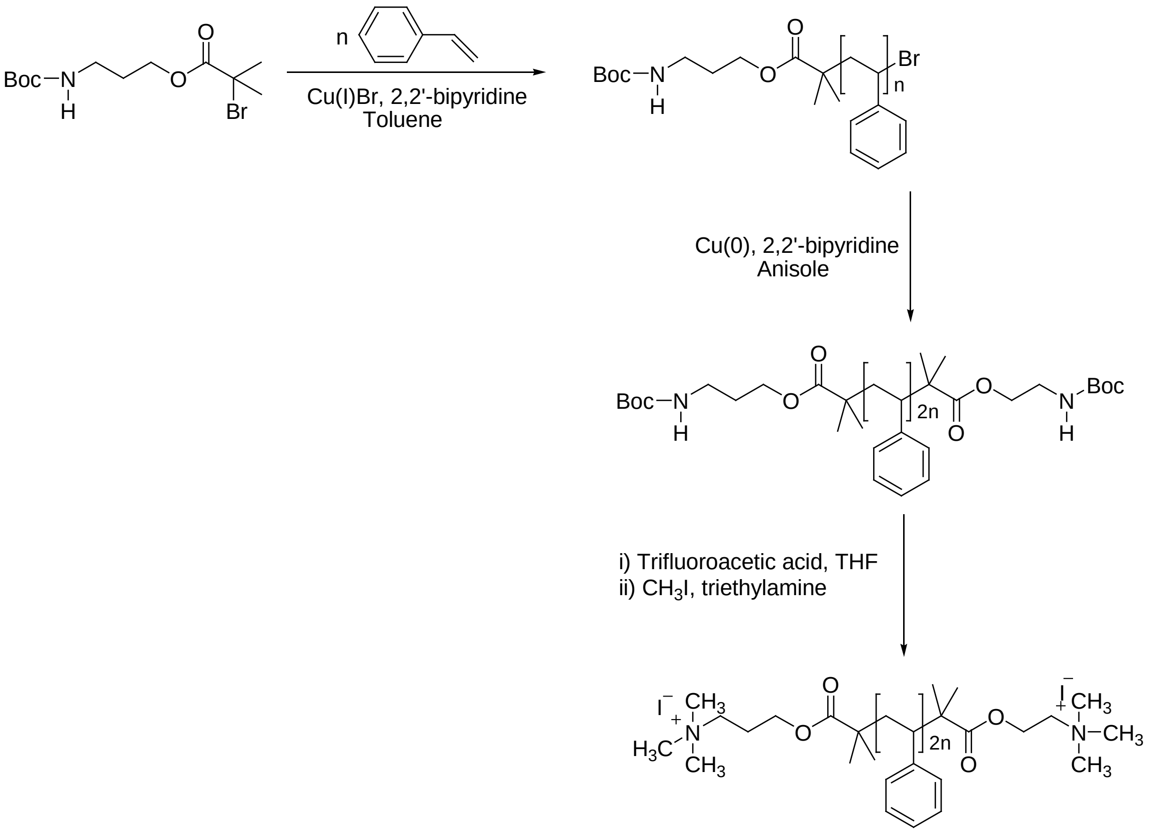
Percec and coworkers[167] reported the synthesis of a series of well defined primary amine chain end functionalized polymers by the ATRP methods using different N-chloro amides, lactams, carbamates and imides as protected amine functionalized initiators. For example, N-chloro ethylcarbamate was used to initiate the metal catalyzed living radical polymerization of methyl methacrylate to give polymers with narrow molecular weight distributions and good control of chain end functionality. Conversion of the precursor end groups to the primary amine groups occurs *via* post polymerization organic reactions:



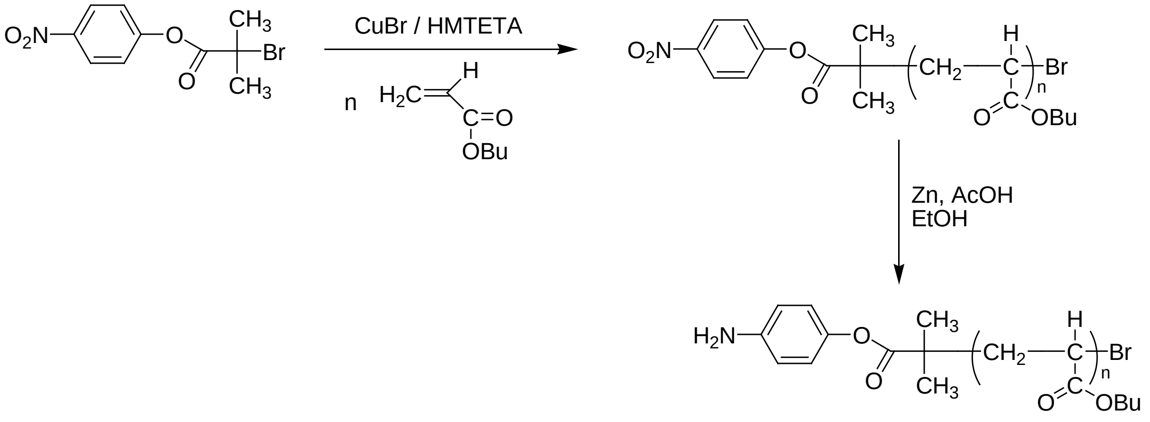
By using phthalimido functionalized initiators, Haddleton[168] and Moad and coworkers[154] synthesized • -amine functionalized polystyrene with N-(bromo-methyl)phthalimide as an initiator in ATRP reactions. Subsequent hydrolysis gave quantitative yields of the amine functionalized polystyrene with narrow molecular weight distributions, high initiator efficiency and with the desired amine end group introduced at the • -terminus of the polymer chain:



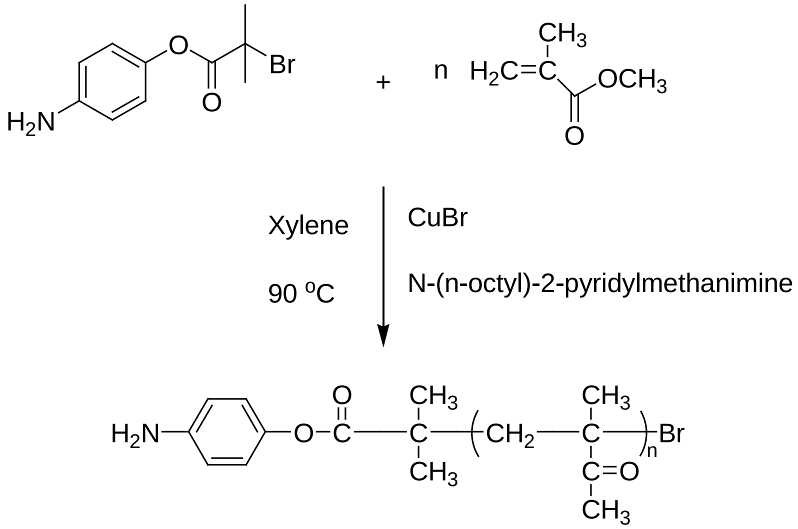
Recently, Monge and coworkers[159] reported the use of the Boc protected amine compound, (N-Boc-propylamino) 2-bromoisobutyrate as an initiator in the preparation of • -amine functionalized polymers *via* the ATRP method. The amine functionality is formed by the methylation of the polymer after the removal of the Boc protection to give (trimethylammonium) chain end functionalized polystyrene:



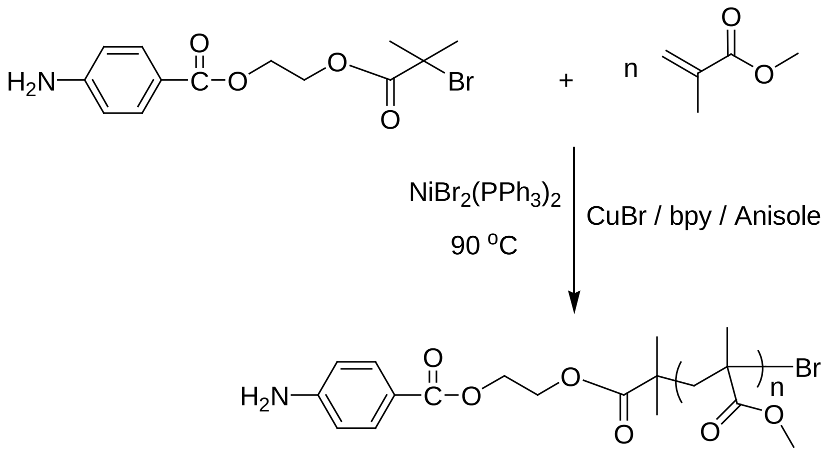
Robin and coworkers[169] prepared • -amine functionalized polymers *via* the ATRP method using an initiator bearing an aromatic nitro group. The nitro group at the • -terminus of the intermediate polymer can easily be reduced in the presence of zinc and acetic acid in ethanol to an aromatic amine after the completion of the polymerization process:



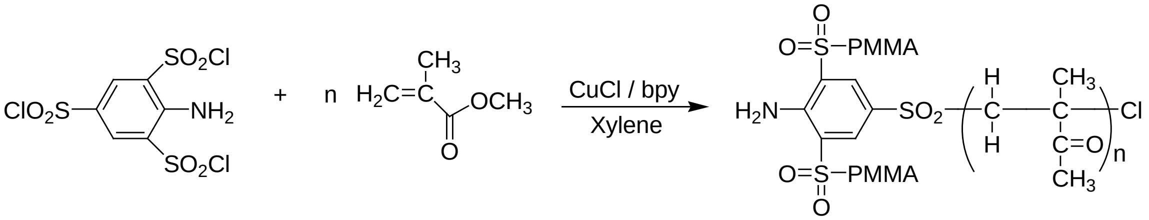
The synthesis of • -primary amine functionalized polymers can also be achieved by using primary amine functionalized initiators in ATRP reactions, where the amine group occurs in the unprotected, free primary amine form. Haddleton and Waterson[170] reported the use of primary amine functionalized phenolic ester derivatives as initiators for the direct preparation of primary amine functionalized polymers by the ATRP methods whereby the aromatic amine moiety is introduced at the • -terminus of the polymer chain. The polymerization proceeded *via* a controlled fashion with good control of the polymer parameters in methyl methacrylate polymerization. The results show that the ATRP reaction is tolerant to aromatic amine functional groups linked to the initiator molecule:



Recently, Blazquez and coworkers[171] reported the preparation of poly(methyl methacrylate) bearing the aromatic primary amine and primary diamine end groups by the ATRP of methyl methacrylate using 4-aminobenzoic acid 2-(2-bromo-2-methylpropionyloxy)ethyl ester and 3,5-aminobenzoic acid 2-(2-methyl-propionyloxy)ethyl ester as primary amine functionalized initiators, respectively. For example:



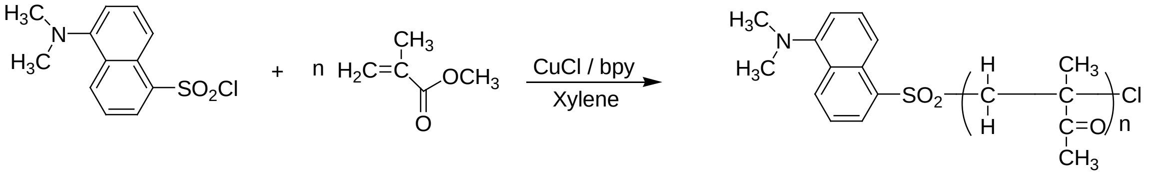
Also, Percec and coworkers[172] prepared perfect primary amine functionalized star polymers using an appropriately designed multifunctional sulfonyl derivative as a functionalized initiator for the ATRP of different monomers:



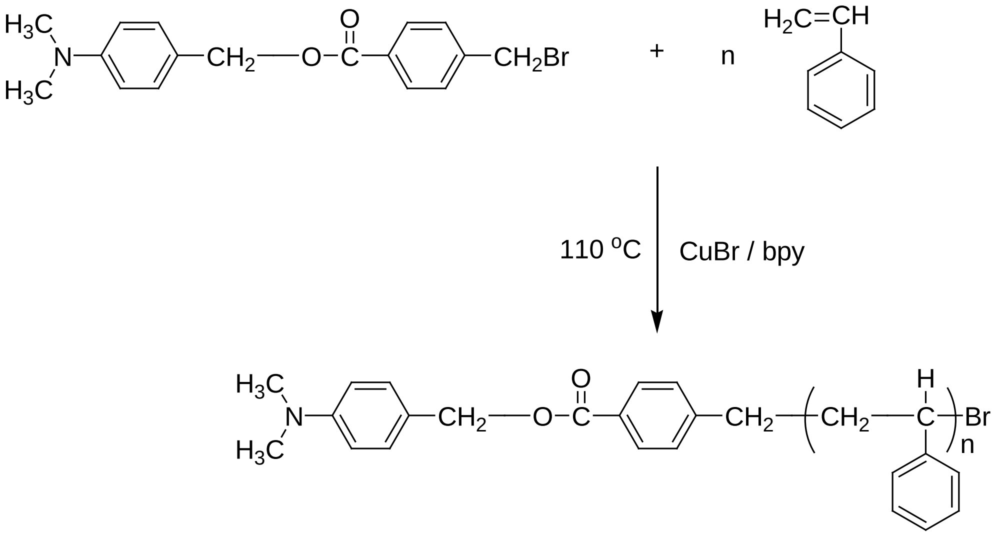
Recently, • -primary amine functionalized polystyrene was prepared by a general quantitative ATRP functionalization method, which is based on the *in situ* formation of a primary amine functionalized initiator adduct upon the reaction of an alkyl halide with a primary amine substituted 1,1-diphenylethylene derivative in the presence of the transition metal-ligand complex catalysts[54], as outlined in the thesis. Primary amine functionalized polystyrene was prepared by the ATRP method using a primary amine functionalized initiator adduct, formed *in situ* by the reaction of 1-(4-aminophenyl)-1-phenylethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system, as initiator for styrene polymerization. The polymerization proceeded *via* a controlled free radical process to afford quantitative yields of • -primary amine functionalized polymers with predictable number average molecular weights, narrow molecular weight distributions, well defined chain end functionality in high initiator efficiency reactions. No evidence of interaction of the primary amine group of the initiator with the catalyst system was apparent. The procedure illustrates a general controlled, quantitative functionalization reaction, independent of the specific functional group. Such reactions are highly efficient for the synthesis of functionalized initiators and polymers because (a) the addition reactions with 1,1-diphenylethylene units are simple and quantitative, and (b) due to steric factors, only monoaddition of the 1,1-diphenylethylene unit occurs during formation of the initiator.

2.5.1.2 Tertiary Amine Functionalized Initiators for ATRP

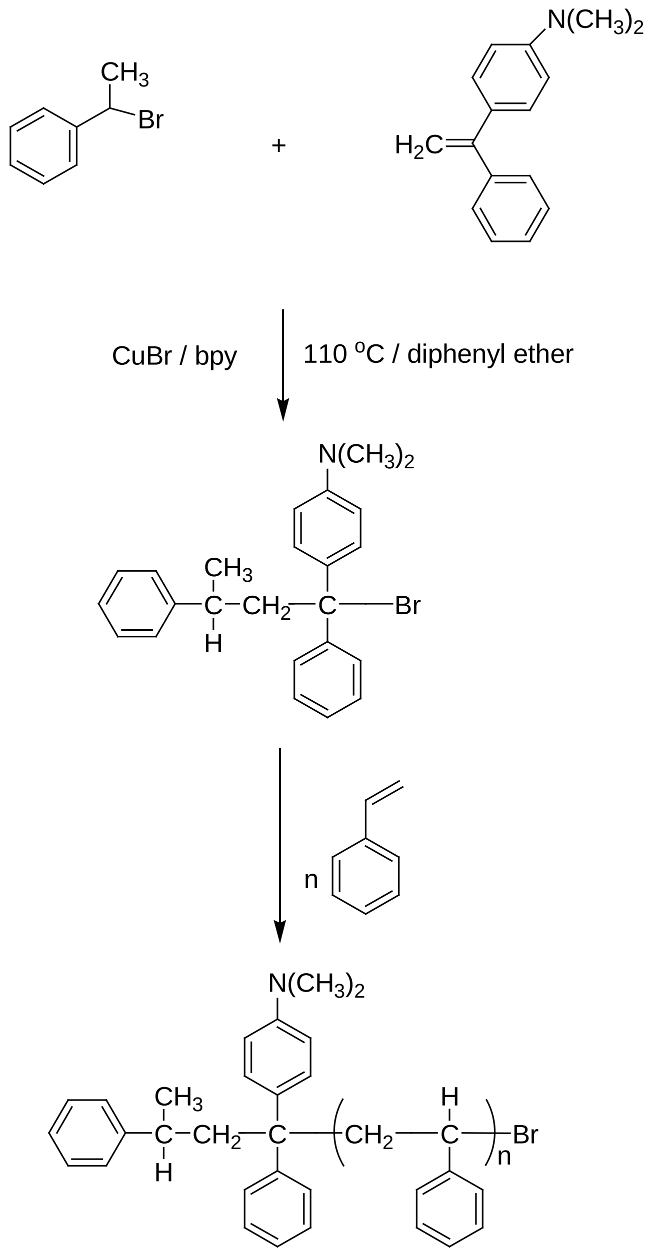
Although a wide variety of functionalized ATRP initiators have been employed for the preparation of heterotelechelic polymers, limited reviews on the synthesis of tertiary amine chain end functionalized polymers using tertiary amine functionalized initiators by ATRP methods have been reported in the literature. Percec and coworkers[173,174] reported a method for the synthesis of tertiary amine functionalized polymers using tertiary amine functionalized sulfonyl chlorides as initiators for the transition metal catalyzed controlled free radical polymerization of styrene and methyl methacrylate. However, with dansyl chloride as initiator, polymers with broad molecular weight distributions were obtained, due to the slow initiation of styrene and methyl methacrylate polymerization by dansyl chloride. For example:



Another route to the ATRP synthesis of tertiary amine functionalized polymers using functionalized alkyl bromide initiators was developed by Yagci and coworkers[155]. The method involves the use of 4-(dimethylamino)benzyl 4-(bromomethyl)benzoate as the ATRP initiator for styrene polymerization to form well defined • -tertiary amine functionalized polymers with narrow molecular weight distributions:



In addition, a general quantitative ATRP functionalization method for the preparation of tertiary amine functionalized polymers, using a tertiary amine substituted 1,1-diphenylethylene derivative as an initiator precursor, has been developed in our laboratories[53]. Using a tertiary amine functionalized initiator adduct, formed *in situ* by the reaction of 1-(4-dimethylaminophenyl)-1-phenylethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system, for styrene polymerization produced the corresponding tertiary amine functionalized polymers with good control of the number average molecular weight, molecular weight distribution and chain end functionality:

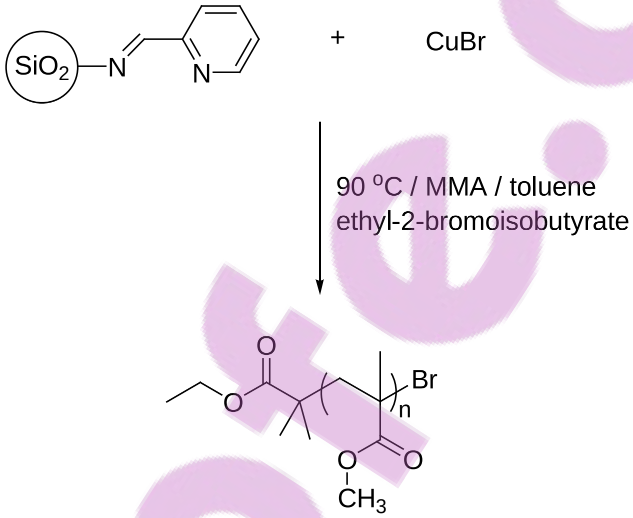


The present study describes the utilization of 1,1-diphenylethylene chemistry in ATRP reactions to prepare aromatic primary and tertiary amine chain end functionalized polymers. The method is based on a general quantitative ATRP initiation process, where initiator adducts are formed by the simple reactions of alkyl halides with functionalized 1,1-diphenylethylene derivatives substituted with the primary and tertiary amine groups. The preparation of •-bis primary and tertiary amine functionalized polymers by the ATRP process involves the use of the specific diamine functionalized unimolecular initiator adduct of (1-bromoethyl)benzene with the appropriate primary or tertiary diamine substituted 1,1-diphenylethylene derivative for styrene and methacrylate polymerization in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system. In addition, •,•-tetrakis(amine) functionalized polystyrenes can be prepared *via* the post ATRP chain end functionalization reactions which involves the addition of equimolar amounts of the respective diamine functionalized 1,1-diphenylethylene derivative to the •-bis(amine)functionalized polymer at the end of the polymerization process. Furthermore, the present research evaluates the polymerization kinetics data for each ATRP reaction leading to the formation of amine chain end functionalized polymers to determine the controlled/living character of each polymerization reaction.

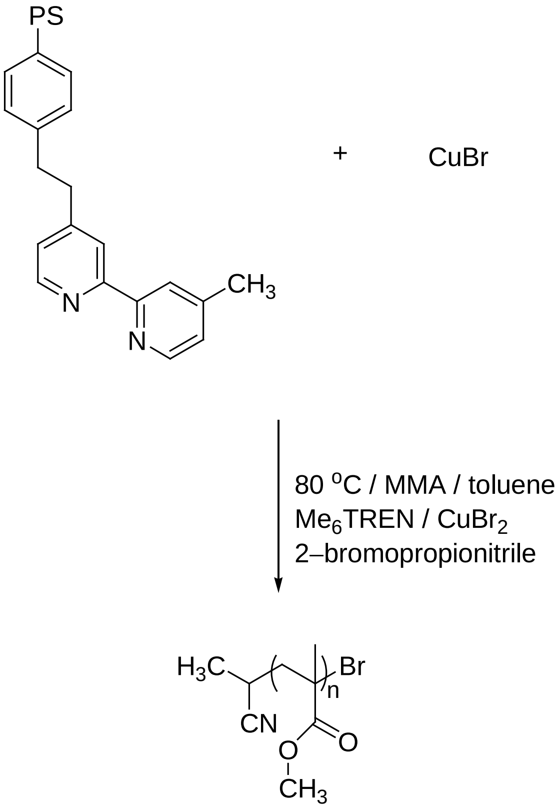
2.6 Supported Catalyst Systems for ATRP

Since 1995, different transition-metal/ligand catalyst systems for the transition metal catalyzed free radical polymerization reactions based on copper[75], nickel[104], iron[106], ruthenium[116], rhodium[175] and rhenium[175] have been developed. However, one of the limitations of the ATRP method for industrial development is the presence of residual copper metal catalyst in the final polymer product. The high catalyst residues cause colouration in the final polymer product and costly additional steps are needed to remove the transition metal salts from the final polymer product. A potential way to overcome this drawback is to support the catalyst onto a solid carrier, which could be readily removed from the final product by simple catalyst recovery methods and ideally be recycled for any further polymerization reactions.

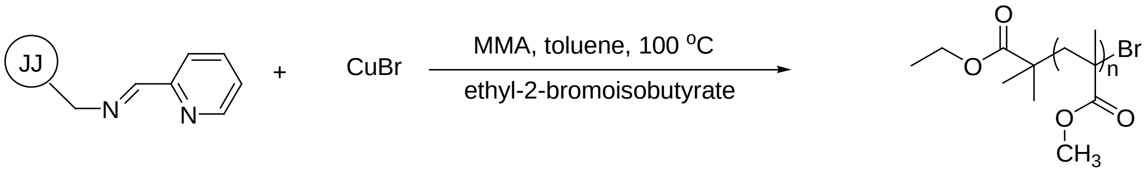
In ATRP reactions, the development of several supported catalytic systems, whereby the copper bromide catalyst was ligated by immobilized nitrogenated ligands, have been reported in the literature[55,176]. However, polymeric or macromolecular nitrogen ligands based on pyridyl groups as catalyst supports have not been extensively employed in ATRP reactions. The first supported catalytic system for the ATRP, based on copper (I) bromide and alkylpyridyl methanimines for the polymerization of methyl methacrylate in toluene, was reported by Haddleton and coworkers[177,178] in 1999:



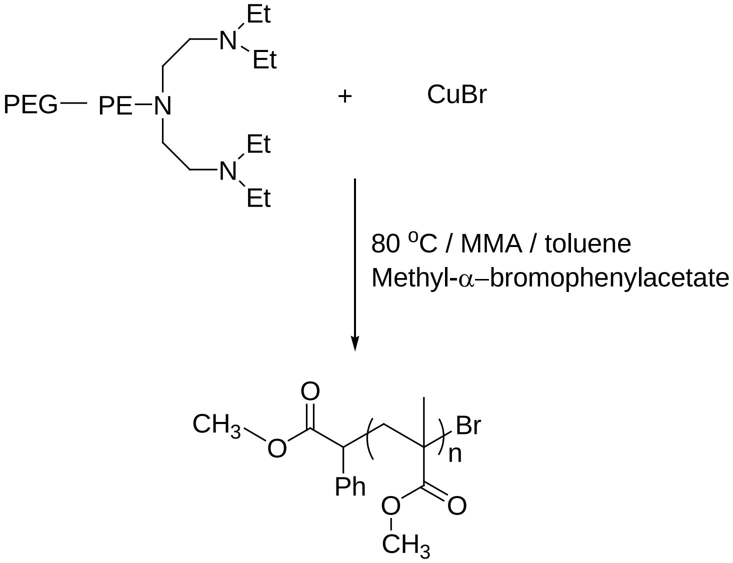
Similarly, Matyjaszewski and coworkers[179,180] reported the controlled polymerization of methyl methacrylate with CuBr immobilized onto 4,4'-dimethyl-2,2'-bipyridine functionalized Merrified resins in the presence of a tiny amount of soluble ligated and oxidized catalyst, $CuBr_2$/tris[2-(dimethylamino)ethyl]amine. Polymers with predictable number average molecular weights and narrow molecular weight distributions were obtained and the immobilized catalyst was removed by simple filtration or sedimentation:



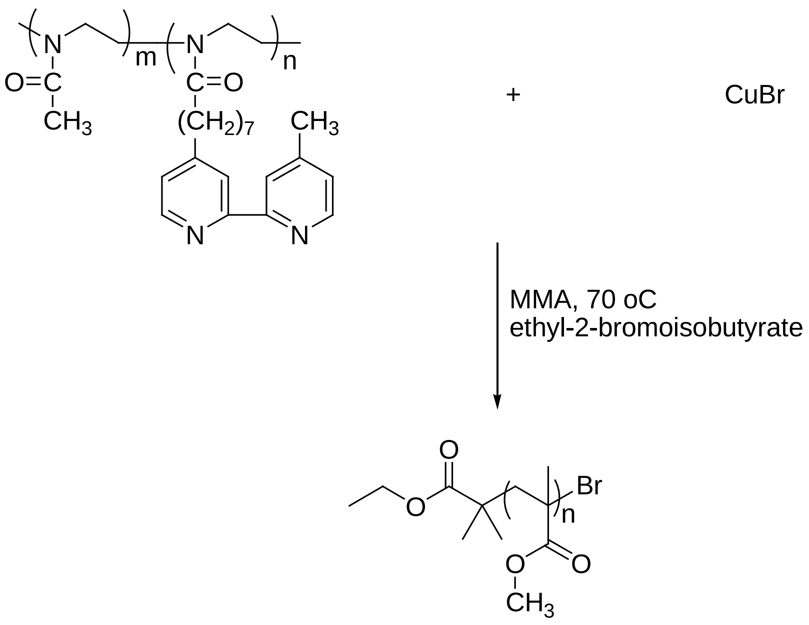
Brittain and coworkers[181] examined the use of a soluble–recoverable catalyst consisting of an ATRP ligand covalently attached to a low molecular weight polyethylene derivative. Polymers with slightly broader molecular weight distributions (M_w/M_n = 1.45) were produced. The catalyst support was easily removed by the crystallization of the polyethylene segment together with the ligand and copper from the polymer solution and the polymer product purified by precipitation into methanol. Brittain and coworkers[182] also used a solid supported catalyst for the polymerization of a wider variety of monomers, such as styrene, methyl methacrylate and 2-(dimethylamino)ethyl methacrylate, under different reaction conditions. The solid support used was the JandaJel resin. The polymerization proceeded *via* a controlled polymerization process in shorter reaction times than the system with the polyethylene supported ligand. The catalyst/ligand complex was easily removed by filtration.



To achieve homogeneous reaction conditions and the ease of catalyst removal, Zhu and coworkers[183,184] used a CuBr/[(diethylamino)ethyl] amine complex attached to a poly(ethylene)-block-poly(ethylene glycol) support as a soluble/recoverable catalyst in ATRP reactions. The system displayed good control in the ATRP reaction affording polymers with molecular weight distributions of 1.2. The catalyst was recovered and 90% of the catalyst activity was retained.



Weberskirsch and coworkers[185] reported that the ATRP of methyl methacrylate in the presence of the copper catalyst supported onto an amphiphilic block copolymer with pendant bipyridine ligands. On average, 96-99% of all copper used in the polymerization was removed by a simple precipitation/washing step due to the different solubility behaviour of the macroligand and poly(methyl methacrylate) particles.



The present study focuses on the synthesis and characterization of new dipyridyl functionalized polysulfone[39] with high degree of functionalization and the evaluation of its efficiency as a supported catalyst system with CuBr for atom transfer radical polymerization of styrene. By using the dipyridyl functionalized polysulfone/CuBr complex as the supported catalyst system in ATRP reactions, the polymerization kinetics data will be evaluated to determine the controlled/living nature of the styrene polymerization reaction.

CHAPTER 3

EXPERIMENTAL

3.1 Materials and Glassware

All chemicals and solvents were purchased from the Sigma Aldrich Chemical Company, unless otherwise stated. Styrene and methyl methacrylate were purified by drying over calcium hydride followed by vacuum distillation and drying over molecular sieves prior to use. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone after stirring at room temperature for few days[39,49]. Distillation of THF was performed when the solution had a purple-blue colour which is an indication of the dryness of the solvent and the absence of reactive impurities. Excess sodium metal was used to ensure the complete conversion of benzophenone to the benzophenone radical anion since traces of unreacted benzophenone would sublime upon subsequent distillation of THF.

Copper (I) bromide, (1-bromoethyl)benzene, 4-aminobenzophenone, diphenyl ether, 2,2'-bipyridyl (99+%), 4,4'-diaminobenzophenone, *n*-butyllithium (1.6M in hexane), methyllithium (1.6M in diethyl ether), methyl triphenylphosphonium bromide, potassium tert-butoxide, calcium hydride and di-2-pyridylketone were used as received. 4,4'-Bis(dimethylamino)benzophenone was recrystallized twice from absolute ethanol before use.

All glassware was oven dried at 120 ^{o}C for 24 hours prior to use and all reactions were carried out under a dry argon or nitrogen atmosphere, where applicable.

3.2 Characterization

Nuclear Magnetic Resonance Spectrometry (NMR)

^{1}H NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer with $CDCl_3$ solvent at ambient temperature. Polymers were dissolved in an appropriate deuterated solvent to give a viscous polymer solution in an NMR tube.

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}. Polymer samples were placed over the ATR crystal and maximum pressure applied using the slip-clutch mechanism.

Size Exclusion Chromatography (SEC)

Molecular weights and molecular weight distributions of polymers were measured by size exclusion chromatography (SEC) on a Waters Alliance SEC autosampler equipped with a Phenogel guard column and a Phenogel column (5 µ, 500 Å pore size, 1K-15K MW range, 300 mm x 7.8 mm) in series with refractive index and dual angle laser light scattering detectors. THF was used as an eluent at a flow rate of 1 mL/min at 30 °C. The lazer light scattering detector of the SEC system was calibrated with monodisperse polystyrene and poly(methyl methacrylate) standards (Aldrich Chemical Company). Polymers were dissolved in THF (4 mg/1.5 mL) before characterization by size exclusion chromatography.

Gas Chromatography (GC)

The monomer conversion was determined by gas chromatography using a Shimadzu Gas Chromatograph 17Å equipped with PB-5 M column (30 m x 0.32 mm; 0.25 µm film) at a constant flow rate of 1.7 mL/min. The initial column temperature was set at 90 ^{o}C with a hold time of 3 minutes, followed by an increase in temperature to 280 ^{o}C at a heating rate of 10 ^{o}C /min. Tetrahydrofuran (THF) was used as the internal standard for the analysis. An aliquot of 1 µL of the test sample was injected *via* a syringe into the injection port for the GC analysis.

Thermogravimetric Analysis (TGA)

Thermogravimetrical curves were generated on a TA instrument Auto Hi-Res Q500 Thermogravimetrical Analyzer at a heating rate of 10 ^{o}C /min under nitrogen atmosphere. Approximately 600 mg of the polymer sample was placed on a preweighed TGA pan for analysis.

Differential Scanning Calorimetry (DSC)

Glass transition temperatures of polymeric samples were determined on a TA Instruments Auto MDSC Q100 Differential Scanning Calorimeter by heating the polymers from 10 ^{o}C to 700 ^{o}C. Polymer sample sizes with masses ranging from 5-10 mg were measured into a DSC sample pan for analysis.

Thin Layer Chromatography (TLC)

Thin layer chromatographic analyses of all the products were performed on Silica gel plates (Merck, Silica Gel 60 F_{254}). Samples were dissolved in suitable solvents. Solutions containing the sample were then spotted on the TLC plates, about one centimeter from the base and developed in a standard chromatography chamber.

Melting point determination

The melting points of the different samples are uncorrected. The melting points of samples were recorded on a Stuart Melting Point Analyser (Barloworld Scientific Limited) with a measuring range of 25 – 400 ^{o}C, accuracy of ± 0.3 ^{o}C (25 – 200 ^{o}C) and ± 0.5 ^{o}C (200 – 400 ^{o}C) and reproducibility of ± 0.2 ^{o}C. The dried samples were loaded into capillary tubes, with sample height between 2.0 mm and 3.0 mm and placed in the melting point apparatus.

Non-Aqueous Titrations

The number average molecular weights of the primary and tertiary amine functionalized polymers were determined by non-aqueous titrations of amine groups[186-191]. The concentrations of primary and tertiary amine end groups in the functionalized polymers were determined by separate non-aqueous titrations of 0.1 g polymer samples in a 1/1 (v/v) mixture of chloroform and glacial acetic acid with standardized perchloric acid (0.01 M) in glacial acetic acid using methyl violet as an indicator.

Contact Angle Tests

Contact angle data was obtained at the University of Stellenbosch with an ERMA G-1 contact angle meter at 20 ^{o}C using pure water as probe liquid.

Water Permeability Tests

Water permeability tests were carried out at 25 ^{o}C at transmembrane pressures ranging between 20 and 100 kPa and membrane surface of 0.0050731 m^2 using pure water obtained by ion exchange and reverse osmosis treatment.

Flux Data

Flux data were obtained by passing pure water under pressure through the flat sheet membranes and collecting permeate on a Mettler balance to determine the water permeability of the membranes.

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images of unmodified and dipyridyl functionalized polysulfone membranes were obtained at the University of Stellenbosch with an Explorer TMX 2000 AFM from Topometrix operated in the low amplitude non-contact mode. The resonance frequency of the low frequency non-contact silicon cantilevers (Nanosensors GmbH) was 35-65 N/m. The low resonance cantilever was 220 µm long and 40 µm wide. The average roughness of the membrane surface, R_a was determined using the following equation:

$$R_a = \left(\frac{1}{N}\right)\sum_{i=0}^{N}\left|Z_i - \overline{Z}\right|$$

where N is the total number of points in the image matrix and Z_i is the height of the *i*th point of reference value. AFM analyses were performed at different scan ranges for each polysulfone sample at different places on the sample. At least three interpore regions of each membrane were analyzed to obtain average R_a values.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) photographs were obtained at the University of Pretoria with a JEOL 6000F in-lens field emission SEM and a

JEOL 840 scanning electron microscope as follows:

(a) Freeze drying

To prevent the collapse of the polysulfone membrane pores, the membranes were kept in distilled water. The wet membranes were cut into 0.4 cm^2 (0.4 cm x 1 cm) samples and freeze-dried in liquid propane at -180 ^oC with a Riechert KF 80 freeze plunger. The frozen samples were transferred under liquid nitrogen into slots in a copper block (63 mm x 63 mm x 15 mm). The copper block was kept completely immersed in liquid nitrogen in a plastic container, thus keeping the material under nitrogen atmosphere and preventing the condensation of moisture onto the sample. The copper block was thereafter transferred to a Fisons high vacuum unit where the evacuation started immediately. The temperature of the copper block was below -130 ^oC when the vacuum reached 1.33 Pa (1×10^{-2} Torr). Freeze-drying was carried out over 2 days, during which the temperature steadily increased back to room temperature.

(b) Sample preparation

Samples of the membrane were cut and placed flat and upright onto the polished side of graphite stubs to view the surface and cross-section, respectively of the membrane. The stubs were made from spectrographic rods turned down to a diameter of 5 mm with a lathe. Disks of 1 mm thickness were cut from the rod and subsequently polished. Double-sided carbon tape was used to secure the samples onto the stub. Furthermore, carbon dag (Leit C, Neubauer Chemikalien) was applied to the edges of the sample for additional support and to reduce the charging of the specimen surface.

(c) Coating and sample viewing

Samples were coated with chromium (ca. 3-4 nm) in a Gatan Ion beam coater, model 681. The samples were viewed at a minimum magnification of 5000x. To obtain lower magnification photos the samples were gold spurred in a Polaron E5200 sputter coater for viewing.

3.3 Anionic Synthesis of Functionalized Polysulfone

3.3.1 Purification of Polysulfone, (1)

Commercially available polysulfone, (**1**) (Ultrason S, BASF, $M_n = 47 \times 10^3$ g/mol, $M_w/M_n = 1.05$) was dissolved in THF and precipitated in methanol, filtered and vacuum dried at 120 ^oC prior to the chemical modification reactions.

3.3.2 The synthesis of 2,2'-vinylidenedipyridine, (2)

The synthesis of 2,2'-vinylidenedipyridine, (**2**) according to the procedures outlined by Eckard and Summers[192] and Summers and coworkers[193] afforded the desired product in low yields. Thus, a new method to synthesize 2,2'-vinylidenedipyridine, (**2**) was developed using the synthetic route outlined by Subramanyam[194], with modifications.

Under an argon atmosphere, potassium tert-butoxide (27.51 mL of a 1.0 M solution, 0.027 mol) was added to methyltriphenylphosphonium bromide (9.7 g, 0.027 mol) in freshly distilled anhydrous THF (200 mL) at 0 ^oC and the reaction stirred for 1.5 hours. After complete reaction, di-2-pyridylketone (5.0 g, 0.027 mol) in dry THF (100 mL) was added to the freshly prepared phosphorous ylide at 0 ^oC. The resultant dark orange solution was stirred for 12 hours at room temperature to achieve complete reaction. The colour of the reaction mixture

changed from dark-orange to orange-green to brown. The reaction was quenched by the addition of methanol (2 mL). The triphenylphosphine oxide salt which precipitated from the solution was removed by vacuum filtration. The filtrate was concentrated on a rotary evaporator and the resultant brown oil purified by silica gel chromatography using toluene as eluent to give 4.21g (92%) of pure 2,2'-vinylidenedipyridine as a light brown oil: ^{1}H NMR ($CDCl_3$): • 6.05 ppm [s, 2H, C$\underline{H}_2$], 6.97-7.70 ppm [m, 6H, aromatic H], 8.50-8.60 ppm [d, 2H, aromatic H]; FTIR (oil): 1634 cm^{-1} (C=N); TLC (Silica Gel 60F_{254}, Merck),
R_f (acetonitrile) = 0.35.

3.3.3 Synthesis of Dipyridyl Functionalized Polysulfone, (3)

The synthesis of dipyridyl functionalized polysulfone with 45% degree of functionalization (PFPS-45) was conducted according to the procedure of Summers and coworkers[39,193]. To improve the degree of functionalization, the preparation of dipyridyl functionalized polysulfone with 80% (PFPS-80) and 95% (PFPS-95) degree of functionalization were effected using 10% and 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) respectively. In a typical procedure, for the preparation of dipyridyl functionalized polysulfone, PFPS-80, dry, unmodified polysulfone, (**1**) (1.0 g, 0.0023 mol, $M_n = 47 \times 10^3$ g/mol; $M_w/M_n = 1.05$) was transferred into a clean, dry 250 mL round bottomed flask under an argon atmosphere. Freshly distilled, dry THF (40 mL) was added to dissolve the polymer. The reaction mixture was cooled to -78 ^oC using a dry ice/isopropanol bath. *n*-Butyllithium (2.2 mL of a 1.6 M solution in hexane, 0.0035 mol) was added to the reaction mixture. The reaction mixture was stirred for 2 hours at -78 ^oC to effect complete metalation. Freshly prepared 2,2'-vinylidenedipyridine, (**2**) (1.03 g, 0.0057 mol) in THF (20 mL) was then added to the viscous deep-red lithiated polymer *via* a cannula, whereupon the reaction mixture turned to a deep orange colour. The reaction mixture was allowed to stir at -78 ^oC for 4 hours. The colour and the viscosity of the reaction mixture remained unchanged. Upon quenching the reaction mixture with methanol (2 mL), a homogenous orange solution was obtained. The mixture was concentrated on a rotary evaporator and the functionalized polysulfone was precipitated in excess methanol, filtered off and dried at 120 ^{o}C to afford 1.35 g (96% yield) of dipyridyl functionalized polysulfone, (**3**), PFPS-80, as a white solid: ^{1}H NMR ($CDCl_3$): • 3.78-3.91 ppm [broad m, 2H, C$\underline{H_2}$], 4.68-4.85 ppm [broad m, 1H, H,C$\underline{H}$], 6.43-8.62 ppm [m, aromatic H]; FTIR (film): 1634 cm^{-1} (C=N); SEC: M_n = 56.87 x 10^{3} g/mol, M_w/M_n = 1.22.

The preparation of dipyridyl functionalized polysulfone, (**3**), PFPS-95 was conducted *via* a similar procedure by adding 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the corresponding lithiated polysulfone derivative.

3.3.4 Membrane Preparation

Membranes were prepared from 15% (w/w) polymer (PS, PFPS-45, PFPS-80 and PS-1-80) solutions in N-methyl-2-pyrrolidone. Sample PS-1-80 is a blend of 1% PFPS-80 in PS. Solutions were cast at 25 ^{o}C on a glass plate to form thin films with thickness of 150 µm. After exposure to air for 15 seconds at 20 ^{o}C and 60% relative humidity, the thin films were immersed in water at 15 ^{o}C. After an immersion period of 5 minutes in distilled water, the membranes detached from plate and were leached for an additional 3 hours under running water before use.

3.4 Atom Transfer Radical Polymerization: Synthesis of Amine Chain End Functionalized Polymers

3.4.1 Primary Amine Functionalized Initiator Precursor: Synthesis of 1-(4-Aminophenyl)-1-phenylethylene, (4)

Freshly distilled tetrahydrofuran (100 mL) was added to a three necked round bottom flask containing methyltriphenylphosphonium bromide (10.81 g; 0.0303 mol). The mixture was purged with argon for 15 minutes. Methyllithium (18.91 mL of a 1.6 M solution in diethyl ether, 0.0303 mol) was added dropwise to the reaction flask *via* a syringe at 0 ^{o}C to form a ylide. The mixture turned yellow upon addition of methyllithium. After stirring for 4 hours at room temperature, the resultant phosphorous ylide was transferred via a cannula into the solution of 4-aminobenzophenone (5.0 g, 0.0254 mol) and dry THF (100 mL) at 0 ^{o}C with stirring. The reaction mixture immediately turned orange in colour. After stirring the reaction mixture at room temperature for 12 hours, methanol (2 mL) was added to quench the reaction. The triphenylphosphine oxide salt, which precipitated from solution, was removed by vacuum filtration. The filtrate was concentrated and the crude product was purified by column chromatography using toluene as eluent. After removing the solvent *via* a rotary evaporator, yellow-white crystals were formed. Recrystallization of the product from 80% aqueous ethanol gave 4.47 g (90%) of 1-(4-aminophenyl)-1-phenylethylene, (**4**) as light yellow crystals: mp = 81.2-82.6 ^{o}C (lit. mp[51] = 80-81 ^{o}C); ^{1}H NMR ($CDCl_3$): • = 3.67 ppm [broad s, 2H, NH_2], 5.19 ppm [s, 2H, $C\underline{H}_2$], 6.62 and 7.18 ppm [m, 6H and 5H respectively, aromatic H]; FTIR (solid): 3468 cm^{-1} (N-H); TLC: R_f (toluene) = 0.44.

3.4.2 Synthesis of • -Aminophenyl Functionalized Polystyrene, (6)

All polymerization reactions were performed in Schlenk flasks and under dry argon atmosphere.

In a typical procedure, copper (I) bromide (0.0735 g, 0.5122 x 10^{-3} mol) and 2,2'-bipyridyl (0.2401 g, 1.5366 x 10^{-3} mol) were added to a Schlenk flask, followed by the successive addition of (1-bromoethyl)benzene (0.095 g, 0.07 mL, 0.5122 x 10^{-3} mol), 1-(4-aminophenyl)-1-phenylethylene, (**4**) (0.1 g, 0.5122 x 10^{-3} mol) and diphenyl ether (1.7 mL). The reaction mixture was stirred at room temperature for 5 minutes. The heterogenous mixture was degassed by three freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 110 ^{o}C for 60 minutes with stirring. The disappearance of 1-(4-aminophenyl)-1-

phenylethylene, (**4**) was monitored by TLC analysis. Freshly distilled styrene (1.86 mL, 1.6903 g, 0.0162 mol) was added to the resultant green reaction mixture *via* a stainless steel syringe at room temperature and the reaction mixture was heated at 110 ^{o}C for 12 hours. Upon cooling and addition of tetrahydrofuran (10 mL), the resultant green solution was purified by passage through a short silica gel column to remove copper and ligand impurities. The polymer solution was concentrated on a rotary evaporator and precipitated from THF solution into excess methanol to afford 1.94 g of the corresponding •-aminophenyl functionalized polystyrene, (**6**) as a white solid: ^{1}H NMR: • = 1.20 – 2.39 ppm [m, polystyrene CH_2 and CH], 3.69 ppm [broad s, 2H, NH_2], 6.26 - 7.41 ppm [aromatic H]; FTIR (solid): 3469 cm^{-1} (N-H); $M_{n,\ theory}$ = 3.30 x 10^{3} g/mol; SEC: M_n = 3.10 x 10^{3} g/mol, M_w/M_n = 1.08; $M_{n,\ titration}$ = 3.35 x 10^{3} g/mol.

3.4.3 Primary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis(4-aminophenyl)ethylene, (7)

Under an argon atmosphere, freshly distilled tetrahydrofuran (100 mL) was added to a dry three necked round bottom flask containing methyltriphenyl-phosphonium bromide (10.05 g; 0.0281 mol). The mixture was degassed with argon for 15 minutes. Methyllithium (17.60 mL of a 1.6 M solution in diethyl ether, 0.0281 mol) was added dropwise to the reaction flask *via* a syringe at 0 ^{o}C. The mixture turned yellow upon addition of methyllithium. After stirring for 4 hours at room temperature, the resulting ylide was transferred *via* a cannula into a solution of 4,4'-diaminobenzophenone (5.0 g; 0.0236 mol) in dry THF (100 mL) at 0 ^{o}C, with stirring. The reaction mixture was heated to reflux for 12 hours. Methanol (2 mL) was then added to quench the reaction. The triphenylphosphine oxide salt, which precipitated from solution, was removed by vacuum filtration. The filtrate was concentrated and the crude product was purified by column chromatography using hexane/ethyl acetate (*v/v*, 20/80) to give a dark brown solid. Recrystallization of the solid from 80% aqueous ethanol solution gave

3.98 g (80%) of pure 1,1-bis(4-aminophenyl)ethylene, (**7**) as pale yellow crystals: mp = 160.5 - 162.0 ^{o}C (lit. mp[194,195] = 159-160 ^{o}C); ^{1}H NMR ($CDCl_3$): • = 3.69 ppm [broad s, 4H, 2 x NH_2], 5.21 ppm [s, 2H, $=C\underline{H_2}$], 6.63 and 7.20 ppm [d x d, 8H, aromatic H]; FTIR (solid): 3443 cm^{-1} (N-H); TLC: R_f (hexane/ethyl acetate, v/v, 20/80) = 0.71.

3.4.4 Synthesis of • -Bis(aminophenyl) Functionalized Polystyrene, (9)

In a typical experiment, under argon atmosphere, copper (I) bromide (0.0493 g, 0.3433 x 10^{-3} mol), 2,2'-bipyridyl (0.1609 g, 1.030 x 10^{-3} mol), (1-bromoethyl)benzene (0.0640 g, 0.047 mL, 0.3433 x 10^{-3} mol), 1,1-bis(4-aminophenyl)ethylene, (**7**) (0.072 g, 0.3433 x 10^{-3} mol) and diphenyl ether (1.70 mL) were added to the Schlenk tube. The tube was tightly sealed with a rubber septum and degassed by three freeze-pump-thaw cycles. The Schlenk tube was then immersed in an oil bath, preset at 110 ^{o}C, for an hour. The disappearance of 1,1-bis(4-aminophenyl)ethylene, (**7**) was monitored by TLC. Subsequently, freshly distilled styrene (1.70 mL, 1.545 g, 0.0135 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was heated at 110 ^{o}C for 12 hours. The tube was withdrawn from the oil bath and THF (10 mL) was added to the reaction flask. The reaction mixture was then passed through an silica gel column to remove the metal/ligand impurities. The polymer product was isolated by precipitation from a THF solution into excess methanol and dried under vacuum at 60 ^{o}C to give 1.89 g of • -bis(aminophenyl) functionalized polystyrene, (**9**) as a white solid: ^{1}H NMR: • = 1.22 – 2.45 ppm [m, polystyrene CH_2 and CH], 3.62 ppm [broad s, 4H, 2 x NH_2], 6.28 - 7.45 ppm [aromatic H]; FTIR (solid): 3412 cm^{-1} (N-H); $M_{n,theory}$ = 4.5 x 10^{3} g/mol; SEC: M_n = 4.10 x 10^{3} g/mol, M_w/M_n = 1.11;
$M_{n,\ titration}$ = 4.35 x 10^{3} g/mol.

3.4.5 Synthesis of •-Bis(aminophenyl) Functionalized Poly(methyl methacrylate), (10)

In a typical experiment, under argon atmosphere, copper (I) bromide (0.0504 g, 0.3510 x 10^{-3} mol), 2,2'-bipyridyl (0.1645 g, 1.0530 x 10^{-3} mol), (1-bromoethyl)-benzene (0.0650 g, 0.048 mL, 0.3510 x 10^{-3} mol), 1,1-bis(4-aminophenyl)-ethylene, (**7**) (0.074 g, 0.3510 x 10^{-3} mol) and diphenyl ether (1.0 mL) were added to a Schlenk tube. The tube was tightly sealed with a rubber septum and degassed by three freeze-pump-thaw cycles. The Schlenk tube was then immersed in an oil bath, preset at 90 ^{o}C. After 1 hour, freshly distilled methyl methacrylate (1.50 mL, 1.404 g, 0.0140 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe and the reaction mixture was heated at 90 ^{o}C for 12 hours. The tube was then withdrawn from the oil bath and THF (10 mL) was added to the reaction flask. The reaction mixture was passed through a silica gel column to remove the metal/ligand impurities. The polymeric product was isolated by precipitation from THF solution into excess methanol. The polymer product was filtered and dried under vacuum at 60 ^{o}C to give 1.76 g of •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) as a white solid: ^{1}H NMR: • = 3.69 ppm [broad s, 4H, 2 x NH_2], 6.50 - 7.22 ppm [aromatic H]; FTIR (solid): 3469 cm^{-1} (N-H); $M_{n,\ theory}$ = 4.0 x 10^3 g/mol; SEC: M_n = 3.60 x 10^3 g/mol, M_w/M_n = 1.18;
$M_{n,\ titration}$ = 3.85 x 10^3 g/mol.

3.4.6 Synthesis of •,• -Tetrakis(aminophenyl) Functionalized Polystyrene, (11)

A Schlenk tube was charged with copper (I) bromide (0.0525 g, 0.3660 x 10^{-3} mol), 2,2'-bipyridyl (0.1715 g, 1.098 x 10^{-3} mol), (1-bromoethyl)benzene (0.068 g, 0.050 mL, 0.3660 x 10^{-3} mol), 1,1-bis(4-aminophenyl)ethylene, (**7**) (0.80 g, 0.3660 x 10^{-3} mol) and diphenyl ether (1.7 mL). The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove

oxygen. Under argon atmosphere, the Schlenk tube was then immersed in a thermostatically controlled oil bath at 110 ^{o}C. After 60 minutes, freshly distilled styrene (1.7 mL, 1.537 g, 0.0148 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was heated at 110 ^{o}C for 24 hours. An aliquot of the reaction mixture was removed and subjected to GC analysis to determine the presence of styrene in the reaction mixture. After complete consumption of styrene, as evidenced by GC analysis, 1,1-bis(4-aminophenyl)ethylene, (**7**) (0.1 g, 0.4756 x 10^{-3} mol) was added to the reaction mixture in the solid form at room temperature. The resultant reaction mixture was heated at 110 ^{o}C for 2 hours. The tube was then withdrawn from the oil bath, 10 mL THF was added to dissolve the reaction mixture and passed through a silica gel column to remove the catalyst and ligand impurities. The polymer product was isolated by precipitation from THF solution into excess methanol, filtered and dried under vacuum at 60 ^{o}C to give 1.90 g of • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) as a white solid: ^{1}H NMR: • = 1.23 – 2.46 ppm [m, polystyrene CH_2 and CH], 3.65 ppm [broad s, 8H, 4 x NH_2], 6.24 - 7.44 ppm [aromatic H]; FTIR (solid): 3469 cm^{-1} (N-H); $M_{n,\ theory}$ = 4.20 x 10^{3} g/mol;
SEC: M_n = 3.80 x 10^{3} g/mol, M_w/M_n = 1.13; $M_{n,\ titration}$ = 4.17 x 10^{3} g/mol.

3.4.7 Tertiary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis[(4-dimethylamino)phenyl]ethylene, (12)

4,4'-Bis(dimethylamino)benzophenone (98%) was purified by recrystallization from absolute ethanol. In a dry three-necked round bottom flask, methyltriphenyl-phosphonium bromide (5.25 g; 0.0147 mol) in freshly distilled, dry THF (100 mL) was degassed with argon for 15 minutes. Methyllithium (10.5 mL of a 1.4M solution in diethyl ether, 0.0147 mol) was added dropwise to the reaction flask *via* a syringe at 0 ^{o}C to form the corresponding phosphorous ylide. After stirring for 4 hours at room temperature, the resulting ylide was transferred *via* a cannula into a solution of 4,4'-bis(dimethylamino)benzophenone (3.30 g; 0.0123 mol) in dry

THF (100 mL) at 0 ^{o}C, with stirring. The reaction mixture immediately turned orange in colour. After stirring the reaction at room temperature for 12 hours, methanol (2 mL) was added to quench the reaction. Using hexane/ethyl acetate (*v/v,* 20/80) mixture as eluent, the product was purified by column chromatography. Recrystallization of the resultant orange solid from absolute ethanol gave 2.92 g (89%) of pure 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) as light green crystals: mp = 126.8 - 127.9 ^{o}C (lit. mp[196] = 120-121 ^{o}C);
^{1}H NMR ($CDCl_3$): • = 2.96 ppm [s, 12H, 2 x $N(C\underline{H}_3)_2$], 5.20 ppm [s, 2H, $=CH_2$], 6.71 and 7.29 ppm [d x d, 8H, aromatic H]; FTIR (solid): 1334 cm^{-1} (N-C);
TLC: R_f (hexane/ethyl acetate, v/v, 20/80) = 0.88.

3.4.8 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Polystyrene, (14)

A Schlenk tube was charged with copper (I) bromide (0.0449 g, 0.3128 x 10^{-3} mol), 2,2'-bipyridyl (0.1466 g, 0.9384 x 10^{-3} mol), (1-bromoethyl)benzene (0.05790 g, 0.043 mL, 0.3128 x 10^{-3} mol), 1,1-bis[(4-dimethylamino)phenyl]-ethylene, (**12**) (0.083 g, 0.3128 x 10^{-3} mol) and diphenyl ether (1.7 mL). The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. Under argon atmosphere, the flask was then immersed in a thermostated oil bath at 110 ^{o}C. The consumption of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was monitored by TLC analysis. After 60 minutes, freshly distilled styrene (1.90 mL, 1.6893 g, 0.0162 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was then heated at 110 ^{o}C for 12 hours. The tube was withdrawn from the oil bath, followed by the addition of THF (10 mL) to the reaction mixture. The reaction mixture was then passed through a silica gel column to remove copper-catalyst impurities. The polymer product was purified by precipitation from THF solution into excess methanol, filtered and dried under vacuum at 60 ^{o}C to give 2.03 g of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) as a white solid:

^{1}H NMR: • = 1.22 – 2.46 ppm [m, polystyrene CH$_2$ and CH], 3.02 ppm [2 x s, 12H, 2 x N(CH$_{3)2}$], 6.28 - 7.79 ppm [aromatic H]; FTIR (solid): 1350 cm^{-1} (N-C); $M_{n,\ theory}$ = 5.40 x 10^3 g/mol; SEC: M_n = 5.10 x 10^3 g/mol, M_w/M_n = 1.14;
$M_{n,\ titration}$ = 5.21 x 10^3 g/mol.

3.4.9 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Poly(methyl methacrylate), (15)

A Schlenk flask was charged with copper (I) bromide (0.0397 g, 0.2730 x 10^{-3} mol), 2,2'-bipyridyl (0.1280 g, 0.8190 x 10^{-3} mol), (1-bromoethyl)benzene (0.0506 g, 0.038 mL, 0.2730 x 10^{-3} mol), 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) (0.73 g, 0.2730 x 10^{-3} mol) and diphenyl ether (1.0 mL). The Schlenk tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. Under argon atmosphere, the Schlenk tube was then immersed in a thermostated oil bath at 110 ^{o}C. The disappearance of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was monitored by TLC. After 1 hour, freshly distilled methyl methacrylate (1.60 mL, 1.5016 g, 0.0150 mol) was added to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was then heated at 90 ^{o}C for 12 hours. The tube was withdrawn from the oil bath and THF (10 mL) was added to the reaction mixture. The reaction mixture was passed through a silica gel column to remove the copper/ligand impurities. The functionalized polymer product was isolated by precipitation from the THF solution into excess methanol. The polymer was filtered, dried under vacuum at 60 ^{o}C to give 1.80 g of •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) as a white solid: ^{1}H NMR: • = 3.01 ppm [broad s, 12H, 2 x N(CH$_3$)$_2$], 6.26 - 7.41 ppm [aromatic H];
FTIR (solid): 1349 cm^{-1} (N-C); $M_{n,\ theory}$ = 5.50 x 10^3 g/mol; SEC:
M_n = 5.23 x 10^3 g/mol, M_w/M_n = 1.03; $M_{n,\ titration}$ = 5.35 x 10^3 g/mol.

3.4.10 Synthesis of •,• -Tetrakis(4-dimethylaminophenyl) Functionalized Polystyrene, (16)

A Schlenk tube was charged with copper (I) bromide (0.0429 g, 0.2956 x 10^{-3} mol), 2,2'-bipyridyl (0.1385 g, 0.8868 x 10^{-3} mol), (1-bromoethyl)benzene (0.0547 g, 0.041 mL, 0.2956 x 10^{-3} mol), 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) (0.079 g, 0.2956 x 10^{-3} mol) and diphenyl ether (1.7 mL). The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. Under argon atmosphere, the Schlenk tube was then immersed in a thermostated oil bath at 110 ^{o}C. After 1 hour, freshly distilled styrene (1.7 mL, 1.537 g, 0.0148 mol) was added to the resultant green reaction mixture using a degassed stainless steel syringe. The reaction mixture was heated at 110 ^{o}C for 24 hours. An aliquot of the reaction mixture was removed and subjected to GC analysis to determine the presence of styrene in the reaction mixture. After complete consumption of styrene, as evidenced by GC analysis, the reaction tube was cooled to room temperature and 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) (0.1 g, 0.3754 x 10^{-3} mol), in its solid form, was added to the reaction mixture. The Schlenk tube was then heated at 110 ^{o}C for 2 hours, with stirring. The Schlenk tube was withdrawn from the oil bath and THF (10 mL) was added to the reaction mixture. The resultant reaction mixture was then passed through a silica gel column to remove copper-catalyst impurities. The polymer product was isolated by precipitation from the THF phase into excess methanol. The tetrafunctional polymer product was filtered, vacuum dried at 60 ^{o}C to give 1.84 g of •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) as a white solid: ^{1}H NMR: • = 1.20 – 2.42 ppm [m, polystyrene CH_2 and CH], 3.16 ppm [broad s, 24H, 4 x $N(CH_3)_2$], 6.38 - 7.27 ppm [aromatic H]; FTIR (solid): 1349 cm^{-1} (N-C); $M_{n,\ theory}$ = 5.20 x 10^{3} g/mol; SEC: M_n = 4.93 x 10^{3} g/mol, M_w/M_n = 1.16; $M_{n,\ titration}$ = 5.13 x 10^{3} g/mol.

3.5 A New Supported Catalyst System for the Atom Transfer Radical Polymerization of Styrene

Dipyridyl functionalized polysulfone, (**3**), (PFPS-95), which was used as the polymeric ligand in the reaction, was prepared by the addition of 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the lithiated polysulfone according to the procedure outlined in Section 3.3.3 of the experimental work. In a typical ATRP experiment for the polymerization of styrene in the presence of the new supported catalyst system, a Schlenk flask was charged with PFPS-95 (0.2 g, 0.3343 mmol), CuBr (0.0240 g, 0.1672 mmol) and diphenyl ether (1.0 mL) to give a yellow-green solution. On addition of (1-bromoethyl)benzene (0.0309 g, 0.023 mL, 0.1672 x 10^{-3} mol) to the reaction mixture, the mixture turned green. The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. The Schlenk flask was then immersed in an oil bath at 110 ^{o}C for 5 minutes. Upon cooling the reaction mixture to room temperature, freshly distilled styrene (1.5 mL, 1.3635 g, 0.0131 mol) was then added to the resultant green reaction mixture by using a degassed stainless steel syringe. The reaction mixture was subsequently heated at 110 ^{o}C for 12 hours. Upon cooling, THF (10 mL) was added to the reaction mixture to dissolve the polystyrene product. The resultant mixture was added to toluene (500 mL) to remove the PFPS-95 catalyst support, which precipitated from toluene solution. The polysulfone derivative, PFPS-95 was filtered and the toluene filtrate was passed through a short silica gel column. The toluene was removed in vacuo and the polymer product was precipitated into excess methanol, filtered, dried under vacuum at 60 ^{o}C to give 1.2 g of pure polystyrene, (**17**) as the final product: ^{1}H NMR: • = 1.10 – 2.22 ppm [m, polystyrene CH$_2$ and CH], 6.46 - 7.49 ppm [aromatic H]; $M_{n,\ theory}$ = 8.15 x 10^{3} g/mol; SEC: M_n = 8.13 x 10^{3} g/mol,
M_w/M_n = 1.14.

3.6 Amine Functionalized Polymers by Atom Transfer Radical Polymerization: Polymerization Kinetics Studies

A series of polymerization kinetics experiments were conducted using each amine functionalized initiator system with monomer: initiator ratios of 50:1, 100:1 and 200:1 for each reaction sequence. Polymerization kinetics experiments for the following three systems were performed:

(a) Synthesis of •-aminophenyl functionalized polystyrene, (**6**) by ATRP
(b) Synthesis of •-bis(aminophenyl) functionalized polystyrene, (**9**) by ATRP
(c) Synthesis of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) by ATRP

In a typical experiment, the procedure for the synthesis of •-aminophenyl functionalized polystyrene, (**6**) by ATRP methods is outlined as follows:

A Schlenk flask was charged with copper (I) bromide (0.1488 g, 1.0244 x 10^{-3} mol), 2,2'-bipyridyl (0.44 g, 3.0732 x 10^{-3} mol), (1-bromoethyl)benzene (0.1896 g, 0.14 mL, 1.0244 x 10^{-3} mol), 1-(4-aminophenyl)-1-phenylethylene (0.2 g, 1.0244 x 10^{-3} mol) and diphenyl ether (5 mL). The mixture was degassed by three freeze-pump-thaw cycles to remove the oxygen and then purged with argon for 15 minutes. The reaction mixture was stirred at room temperature for 5 minutes. The flask was immersed in an oil bath thermostated at 110 ^{o}C for 60 minutes, with stirring. Upon cooling the reaction mixture, freshly distilled and degassed styrene (5.86 mL, 5.3344 g, 51.218 x 10^{-3} mol) was added to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature. An aliquot (1 mL) of the sample was withdrawn from the reaction mixture, diluted with THF (9 mL) and subjected to gas chromatography analysis to determine the amount of styrene in the sample at t = 0. Under an argon atmosphere, the mixture was then heated to 110 ^{o}C. At different time intervals, aliquots of 1 mL sample were withdrawn from the reaction flask under argon and diluted with a known amount of THF (9 mL). The residual styrene content was determined by gas chromatographic analysis. At the completion of the analysis, the polymer samples were purified by passage through a short silica gel column to remove catalyst impurities and then precipitated from THF solution into excess methanol. The different •-aminophenyl functionalized polystyrene, (**6**) samples were precipitated several times from THF solution into methanol, filtered off and vacuum dried in preparation for size exclusion chromatography analyses to determine the number average molecular weights and molecular weight distributions of the polymers.

Experimental data for the different polymerization kinetics experiments for [M]/[I] ratio of 50:1, 100:1 and 200:1 is given below:

Synthesis of • -aminophenyl functionalized polystyrene, (6)

[M]/[I]	**(4)**	Styrene	(1-bromo-ethyl)-benzene	Copper (I) Bromide	2,2'-Bipyridyl	DPE (mL)
50:1	0.2 g; 1.0244 mmol	5.33 g; 5.87 mL; 0.0512 mol	0.1896 g; 0.1404 mL; 1.0244 mmol	0.1488 g; 1.0244 mmol	0.480 g; 3.0732 mmol	5.0
100:1	0.15 g; 0.7683 mmol	8.0 g; 8.8 mL; 0.0768 mol	0.1422 g; 0.1053 mL; 0.7683 mmol	0.1102 g; 0.7683 mmol	0.360 g; 2.3049 mmol	7.0
200:1	0.1 g; 0.5122 mmol	10.67 g; 11.7mL; 0.1024 mol	0.0948 g; 0.0702 mL; 0.5122 mmol	0.0735 g; 0.5122 mmol	0.240 g; 1.5366 mmol	8.0

Synthesis of • -bis(aminophenyl) functionalized polystyrene, (9)

[M]/[I]	**(7)**	Styrene	(1-bromoethyl)benzene	Copper (I) Bromide	2,2'-Bipyridyl	DPE (mL)
50:1	0.20 g; 0.9512 mmol;	4.95 g; 5.5 mL; 0.0476 mol	0.1760 g; 0.1304 mL; 0.9512 mmol	0.1365 g; 0.9512 mmol	0.4457 g; 2.8278 mmol	3.0
100:1	0.16 g; 0.7610 mmol	7.93 g; 8.7 mL; 0.0761 mol	0.1408 g; 0.1043 mL; 0.7610 mmol	0.1092 g; 0.7610 mmol	0.3566 g; 2.283 mmol	7.0
200:1	0.11 g; 0.5232 mmol	10.90 g; 12.0 mL; 0.1046 mol	0.0968 g; 0.0717 mL; 0.5232 mmol	0.0751 g; 0.5232 mmol	0.2452 g; 1.5696 mmol	8.0

Synthesis of • -bis(4-dimethylaminophenyl) functionalized polystyrene, (14)

[M]/[I]	**(12)**	Styrene	(1-bromoethyl)benzene	Copper (I) Bromide	2,2'-Bipyridyl	DPE (mL)
50:1	0.26 g; 0.9761 mmol	5.08 g; 5.6 mL; 0.0488 mol	0.1806 g; 0.1338 mL; 0.9761 mmol	0.140 g; 0.9761 mmol	0.4574 g; 2.9283 mmol	3.0
100:1	0.20 g; 0.7509 mmol	7.82 g; 8.6 mL; 0.0751 mol	0.1390 g; 0.1030 mL; 0.7509 mmol	0.1077 g; 0.7509 mmol	0.3518 g; 2.2527 mmol	7.0
200:1	0.15 g; 0.5631 mmol	11.73 g; 13.0 mL; 0.1126 mol	0.1050 g; 0.0778 mL; 0.5631 mmol	0.0808 g; 0.5631 mmol	0.2638 g; 1.6893 mmol	8.0

3.7 Synthesis of Polystyrene, (17) using Dipyridyl Functionalized Polysulfone, (3) as Ligand: Polymerization Kinetics Studies

In a typical experiment, a Schlenk flask was charged with dipyridyl functionalized polysulfone, (**3**) (PFPS-95, 0.4088 g, 0.6555 mmol), CuBr (0.0313 g, 0.2185 mmol) and diphenyl ether (5 mL) to give a yellow-green solution. On addition of (1-bromoethyl)benzene (0. 0313 g, 0.0232 mL, 0.2185 x 10^{-3} mol) to the reaction mixture, the mixture turned green. The flask was then degassed by three freeze-pump-thaw cycles to remove the oxygen. After purging with argon for 15 minutes, freshly distilled styrene (5.0 mL, 4.545 g, 0.0437 mol) was introduced by syringe and stirred for 5 minutes to ensure dispersion of the PFPS-95 support. The polymerization was monitored by gravimetric analysis. At different intervals, 1 mL aliquot was withdrawn from the solution and diluted with a known amount of THF (2 mL). The product was then precipitated into excess toluene to remove the PFPS-95/CuBr catalyst complex. The toluene filtrate was passed through a silica gel column, transferred into a flask and concentrated on the rotary evaporator. The polystyrene was precipitated into excess methanol, filtered and vacuum dried to constant mass. Each polystyrene sample was subjected to size exclusion chromatography analysis to determine its number average molecular weight and molecular weight distribution.

CHAPTER 4

RESULTS AND DISCUSSION

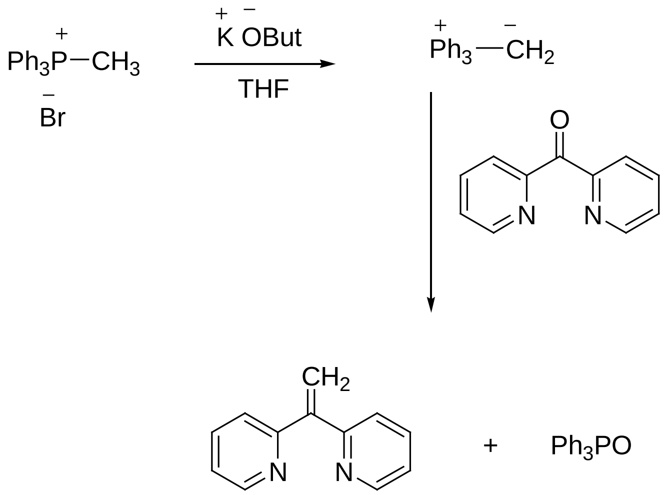
4.1 Chemical Modification of Polysulfone by Anionic Methods

Several reviews on the chemical modification of polysulfone by different chemical methods to effect the introduction of functional groups onto the polysulfone backbone have been reported in the literature. The most efficient method, which has been developed by Guiver and coworkers[35], involves the treatment of unmodified polysulfone with an organolithium compound and the subsequent reaction of lithiated polysulfone with different electrophiles which introduced different functional groups onto the polymer backbone. For example, for the preparation of amine functionalized polysulfones, Guiver and coworkers[35] reported an efficient methodology for quantitatively introducing amine groups onto commercially available Udel P3500 polysulfone and Radel R5000 poly(aryl sulfone) by the azidation of lithiated polysulfone followed by sodium borohydride reduction of the azide derivative. The process provided amine functionalized polysulfone having a high degree of functionality with site specificity to either the sulfone aromatic ring or the bisphenol ring.

The present study focused on the development of a new synthetic method for the preparation of novel dipyridyl functionalized polysulfones[39]. The anionic functionalization process involves the formation of lithiated polysulfone from unmodified polysulfone, (**1**) and subsequent reaction with 2,2'-vinylidenedipyridine, (**2**) in THF at -78 ^{o}C under argon atmosphere to afford the corresponding dipyridyl functionalized polysulfone, (**3**). In addition, the unmodified polysulfone, (**1**) as well as the different dipyridyl functionalized polysulfone, (**3**) samples were used as membrane substrates for membrane formation to determine the membrane characteristics of each sample by standard membrane characterization methods.

4.1.1 Synthesis of 2,2'-vinylidenedipyridine, (2)

The method for the synthesis of 2,2'-vinylidenedipyridine, (**2**) outlined by Eckard and Summers[192] and Summers and coworkers[193] afforded the desired product in low yields. Thus, a new synthetic strategy[39], using the experimental design of Subramanyam[194] was adopted, with modifications, for the preparation of 2,2'-vinylidenedipyridine, (**2**). 2,2'-Vinylidenedipyridine, (**2**) was obtained as a light brown oil in 80% yield by the classical Wittig reaction of di-2-pyridylketone with the phosphorous ylide, an intermediate which was generated from the reaction of potassium tert-butoxide and methyltriphenylphosphonium bromide in THF:



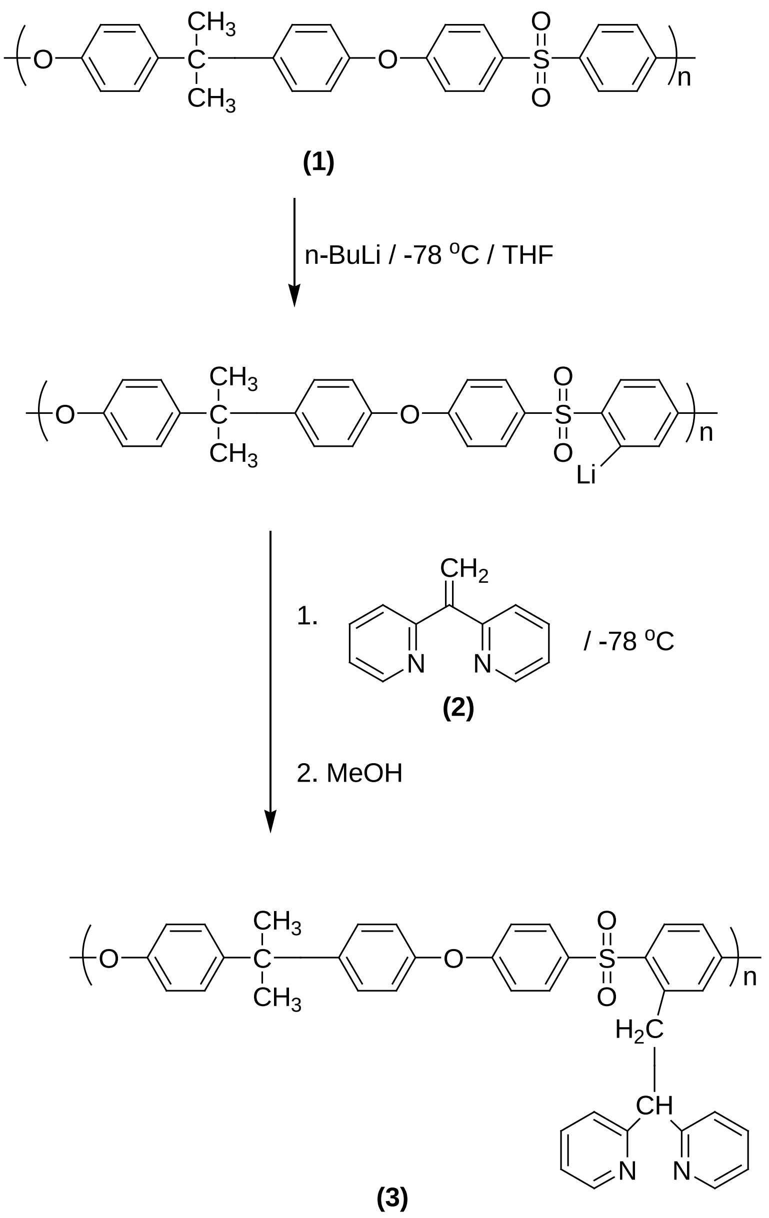
(2)

The ^{1}H NMR spectrum **(**Figure 1**)** of 2,2'-vinylidenedipyridine, (**2**) exhibits a singlet at • = 6.05 ppm, due to the resonances of equivalent alkene protons and a multiplet between • = 6.97 – 8.61 ppm, attributed to the resonances of the aromatic protons of the pyridyl groups. The FTIR spectrum (Figure 2) of 2,2'-vinylidenedipyridine, (**2**) shows a strong C=N absorption frequency at 1634 cm^{-1}, typical of the presence of pyridyl groups[192,197].

4.1.2 Synthesis of Dipyridyl Functionalized Polysulfone, (3)

The reactions of lithiated polysulfone with different electrophiles provide efficient synthetic routes for the preparation of polysulfones with different functional groups pendant to the polysulfone backbone[14-17,35-38]. Such synthetic procedures were adopted for the preparation of polysulfone derivatives substituted with pyridyl groups. The reaction of living polymeric carbanions with 2,2'-vinylidene-dipyridine, (**2**) provides a novel method for the synthesis of dipyridyl functionalized polysulfone, (**3**). The functionalization of polysulfone, (**1**) with 2,2'-vinylidenedipyridine, (**2**) involves two steps: (a) the regiospecific lithiation of polysulfone, (**1**) with *n*-butyllithium at low temperature, and (b) the reaction of lithiated polysulfone with 2,2'-vinylidenedipyridine, (**2**) at low temperature.

Upon lithiation of unmodified polysulfone, (**1**) with *n*-butyllithium, formation of a homogenous red-brown viscous solution, which indicates the formation of the lithiated polysulfone, was observed at low temperature. However, precipitation of the lithiated species occured at room temperature[14,15]. The stoichiometry of the reaction affects the degree of pyridyl substitution of the product. When equimolar amounts of lithiated polysulfone and 2,2'-vinylidenedipyridine, (**2**) were employed in the reaction, dipyridyl functionalized polysulfone, (**3**) PFPS-45, with degree of functionalization as high as 45% was obtained. However, higher degrees of functionalization were effected by the treatment of lithiated polysulfone with excess of 2,2'-vinylidenedipyridine, (**2**) in THF at -78 ^{o}C to afford the corresponding dipyridyl functionalized polysulfones, (**3**). With the addition of 10% and 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the corresponding lithiated polysulfone, the corresponding dipyridyl functionalized polysulfones, (**3**) PFPS-80 and PFPS-95, with degrees of functionalization of 80% and 95%, respectively, were obtained according to the following synthetic pathway:



The different dipyridyl functionalized polysulfones, (**3**) were characterized by ^{1}H NMR, FTIR, DSC and thermogravimetric analysis. Using sample PFPS-80, the spectroscopic characterization data for dipyridyl functionalized polysulfone, (**3**) is provided to confirm the structure of the functionalized polysulfones. The ^{1}H NMR spectrum (Figure 3) of dipyridyl functionalized polysulfone, (**3**) (PFPS-80) exhibits signals at • = 3.78 and • = 4.65 ppm, due to the resonances of CH_2 and CH protons, respectively, indicating the incorporation of the functionalizing agent onto the polysulfone backbone. Furthermore, the signals between • = 6.3 – 6.7

ppm, 7.4 – 7.8 ppm and 8.1 – 8.4 ppm are attributed to the resonances of the aromatic protons of the pyridine groups[194]. The resonances for pyridine protons are absent in the proton NMR spectrum of unfunctionalized polysulfone. The FTIR spectrum (Figure 4) of dipyridyl functionalized polysulfone (**3**), (PFPS-80) shows the presence of a strong absorption band at 1634 cm^{-1}, which is characteristic of the C=N stretching mode of the pyridine group of dipyridyl derivatives such as 2,2'-vinylidenedipyridine[192,197].

The thermal stabilities of the unfunctionalized polysulfone and the different dipyridyl functionalized polysulfones, (**3**) were determined by thermogravimetric analysis (TGA). The TGA thermograms (Figure 5) show that the PFPS-45 and PFPS-80 samples are thermally less stable than the parent unfunctionalized polysulfone, most probably due to the introduction of the bulky groups along the polymer backbone. With the onset of weight loss at 250 ^{o}C, PFPS-45 exhibits a two phase degradation pattern with a distinct weight loss of 8% observed at 350 ^{o}C, with a total weight of 56% at 534 ^{o}C. The initial weight loss in PFPS-45 is believed to be due to the loss of pyridine functional groups as well as the removal of water which is associated with the dipyridine groups. In contrast, the PFPS-80 is thermally more stable with the degradation pattern showing the onset of weight loss at 307 ^{o}C, with 25% weight loss at 404 ^{o}C, followed by the major weight loss of 38% at 537 ^{o}C. The presence of more polar dipyridyl pendant groups on the PFPS-80 polysulfone sample accounts for its higher thermal stability as compared to the PFPS-45 sample.

The glass transition temperatures of each polysulfone sample were obtained from differential scanning calorimetry and the data is listed below:

Sample	T_g (^{o}C)
PS	189
PFPS-45	185
PFPS-80	161

For the PFPS-45 and PFPS-80 derivatives with pendant dipyridyl substituents, a decrease in the glass transition temperature is observed when compared to the parent polysulfone sample. However, the largest decrease in the glass transition temperature was observed for the PFPS-80 sample. The introduction of more pendant dipyridyl groups along the polymer backbone increases polymer mobility which ultimately lowers the glass transition temperature value.

Membranes obtained from unmodified as well as the dipyridyl functionalized polysulfones, (**3**) were characterized by atomic force microscopy, scanning electron microscopy, pure water permeation measurements and contact angle analysis.

The three dimensional AFM images for the different polysulfone membranes, PS, PFPS-45 and PFPS-80 are displayed in Figure 6. The topographic images of PS show a distinct difference between the top and bottom surfaces of the membrane. The top or skin side of the membrane has larger nodules than the bottom, indicated by the higher roughness values obtained. The diameters of the nodules range from 1.02 to 1.26 µm, with nodule diameter sizes on the bottom side ranging from 0.35 to 0.42 µm. The diameter of the pores on the bottom side of the PS membrane vary between 0.13 to 0.21 µm compared to the pore size diameters on the top of the membrane of 0.24 – 0.42 µm.

For sample PFPS-45, the roughness values for the skin surface were much larger than that of the PS membrane, while the bottom surface of PFPS-45 was much smoother than that of the PS membrane. The top of the PFPS-45 membrane was much smoother than that of the PS membrane. The top of the PFPS-45 has more densely packed nodules than the bottom. Nodules in the membrane skin surface range from 0.83 µm to 1.39 µm and 0.24 µm to 1.13 µm in the bottom surface. The bottom surface has rod-like structures that are 2.97 µm long and 1.37 µm wide. Thus, the nodule size of the PS sample seems to be larger than the PFPS-45 sample, which has a larger range of nodule size diameters. The diameter of the pores on the bottom of the PFPS-45 sample varies between 0.51 and 1.31 µm. The pore sizes on the top were between 166 and 167 nm in diameter. Thus, the pore sizes of PFPS-45 are significantly smaller than those in the PS membrane.

Similarly, for example PFPS-80, the surface roughness was significantly greater than the unmodified polysulfone sample. Cross-section profiles show that average nodule size of PFPS-80 is 347 nm, which is slightly larger than the nodules present in the PS sample. Also, the average pore size of the PFPS-80 sample was 390 nm, whereas, the average pore size of the PS sample was 254 nm. Analysis shows that pore size distribution of the PFPS-80 sample is larger than that of the PS sample.

In general, the rough surface structures observed for the dipyridyl functionalized polysulfones should produce a looser surface fouling layer in applications of the membrane substrate in separation technologies, consistent with data reported in literature[14-17,35-38,198,199].

SEM photographs reveal distinctly different morphological patterns for each of the membranes. Figure 7 shows the cross-section photographs of the PS, PFPS-45 and PFPS-80 membrane samples and indicates that each polymer membrane structure is composed of a thin, dense layer at the top of the membrane, with a porous sublayer in the middle and porous architecture at the bottom. However, the membrane prepared from the PFPS-45 sample was more brittle and the PFPS-80 sample was thicker and denser on the top.

Figure 8 shows the SEM analysis of the top view of different membranes. The PS sample reveals a smooth human skin-like upper layer with tiny pores on the surface. However, the top view of PFPS-45 shows an irregular wave-like orientation of polymer rods with the pores oriented on the side of the polymer rod. The topology of PFPS-80 exhibits an irregular, fibrous orientation of polymer material on the surface.

Figure 9 shows the SEM analysis of the bottom view of the different polysulfone membranes. The photograph for the unmodified polysulfone membrane shows Swiss-cheese like structures with well defined smooth areas between pore openings as well as pores of different sizes. In the PFPS-80 sample, the Swiss-cheese morphology is more pronounced with smooth areas between pore openings, but with more pores of different sizes and shapes. In contrast, a bottom view of the PFPS-45 sample shows more particulate structures with jig-saw-like aggregates or discs fragments of different sizes and shapes as well as variable pore sizes between the polymer fragments.

Figure 10 shows the plot of pure water flux as a function of pressure at 25 ^{o}C for the different polysulfone membranes. For all membrane substrates, the rate of permeate production increases linearly with pressure. The unmodified polysulfones exhibits a lower pure-water flux at a given pressure as compared to the dipyridyl functionalized polysulfones, PFPS-45 and PFPS-80 and the polysulfone blend. Both PS and PFPS-45 produce linear flux-pressure plots, with relatively small amount of permeate flux at a given pressure. In contrast, the PFPS-80 sample exhibits a linear flux-pressure plot, but a non-linear flux-pressure plateau is observed at higher pressures, probably due to membrane compaction. Furthermore, the variations in permeate flux data could be attributed to the degree of functionalization, surface roughness, pore sizes and pore size distribution. Thus, for the dipyridyl functionalized polysulfone with higher degree of functionalization, PFPS-80, the pure water flux is the highest, most probably as a result of increased hydrophilicity and larger pore sizes and pore density which makes the PFPS-80 sample the most suitable precursor to prepare membranes with anti-fouling properties and improved permeability.

Nevertheless, the PFPS-80 sample exhibits greater permeation rates at a given pressure value, even though it is more expensive to prepare as evidenced by the methods of synthesis. More significantly, the PS-1-80 sample, the blend of 1% PFPS-80 in a polysulfone matrix, show larger pure water flux values as compared to the unfunctionalized polysulfone at a given pressure, but smaller values than the PFPS-80 sample, which indicates that the introduction of polar groups such as the dipyridyl group onto the polysulfone backbone does improve membrane permeability properties.

The flat sheet asymmetric membranes as well as dense films were prepared and characterized by contact angle measurements to evaluate the hydrophilic character of each membrane. Contact angle data was obtained at 20 ^{o}C with an ERMA G-1 contact angle meter using pure water as probe liquid. The contact angle data for PS and PFPS-80 is given below:

Sample	Asymmetric membrane (^{o})	Dense film (^{o})
PS	78	74
PFPS-80	87	84

Results show that the dipyridyl functionalized polysulfone sample PFPS-80 is more hydrophilic than the unmodified polysulfone sample. The increased contact angle value for PFPS-80 is most probably influenced by the introduction of the hydrophilic dipyridyl groups on the surface as well as the surface roughness and porosity of the asymmetric membranes and dense films.

The detailed spectroscopic, chromatographic, thermal and microscopic data and contact angle measurements provide evidence for the synthesis of well defined dipyridyl functionalized polysulfones, (**3**) with improved hydrophilicity and excellent thermal and membrane properties.

4.2 Atom Transfer Radical Polymerization: Synthesis of Chain End Functionalized Polymers

The process of Atom Transfer Radical Polymerization (ATRP), which was developed by Matyjaszewski in 1995, provides the most versatile method for the synthesis of well defined polymers with high regiospecificity with respect to chain end functionality. One of the best synthetic strategies for the introduction of a functional group at the •-terminus of the polymer chain is *via* the use of functionalized initiators during the ATRP polymerization process. However, limited work on the ATRP preparation of polymers with the amine group at the •-terminus of the polymer using functional initiators has been documented[159-166]. Since the ligands used in ATRP systems are mostly bidentate and multidentate amine molecules, appropriately designed functionalized initiators are required for the successful ATRP reactions whereby the interaction between the amine functionality of the functionalized initiator and the catalyst/ligand system is reduced.

The current research focuses on the synthesis of well defined primary and tertiary amine functionalized polymers based on a general, quantitative ATRP chain end functionalization method using different functionalized unimolecular initiator systems[53]. The study outlines the synthetic pathways for different amine functionalized 1,1-diphenylethylene compounds and the determination of their utility as amine functionalized initiator precursor compounds in ATRP reactions. The *in situ* formation of the specific unimolecular functionalized initiator adduct is based on a simple reaction of alkyl halides with functionalized amine or diamine 1,1-diphenylethylene derivatives substituted with the primary and tertiary amine groups. Different •-amine and •-bis(amine) functionalized polymers can be prepared using the specific amine or diamine functionalized initiator adducts as initiators for the ATRP of styrene and methyl methacrylate.

The synthesis of different amine chain end functionalized polymers by ATRP methods were conducted by using the following methods:

a) the synthesis of 1-(4-aminophenyl)-1-phenylethylene, (**4**) and its use as a primary amine functionalized initiator precursor for the preparation of •-aminophenyl functionalized polystyrene, (**6**) by ATRP methods. The use of a new primary amine initiator adduct, (**5**), generated *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene, (**4**), as the initiator for the ATRP of styrene provides a new method for the synthesis of the corresponding •-aminophenyl functionalized polystyrene, (**6**).

b) the preparation of 1,1-bis(4-aminophenyl)ethylene, (**7**) and its utility as a primary diamine functionalized initiator precursor for the synthesis of •-bis(aminophenyl) functionalized polymers by ATRP methods. The utilization of a new primary diamine functionalized initiator adduct, (**8**), obtained *in situ* by the reaction of (1-bromoethyl)benzene with 1,1-bis (4-aminophenyl)ethylene, (**7**), as the initiator for the styrene and methyl methacrylate polymerization by ATRP methods provides a unique synthetic route for the preparation of the corresponding •-bis(aminophenyl) functionalized polystyrene, (**9**) and •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**), respectively.

c) the synthesis of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**), and its use as a tertiary diamine functionalized initiator precursor for the preparation of •-bis(4-dimethylaminophenyl) functionalized polymers. The use of a new tertiary diamine functionalized initiator adduct, (**13**), prepared *in situ* by the reaction of (1-bromoethyl)benzene with 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) in the presence of copper (I) bromide/2,2'-bipyridyl as the catalyst system, for the styrene and methyl methacrylate polymerization by ATRP methods affords a new method for the preparation of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) and •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**), respectively.

The current study investigates the controlled/living nature of each ATRP reaction leading to the preparation of the different amine chain end functionalized polymers by evaluating the polymerization kinetics data for each polymerization reaction.

The preparation of •,•-tetrakis(aminophenyl) functionalized polystyrene, (**11**) and •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) can be prepared by post ATRP chain end modification reactions according to the following synthesis strategy:

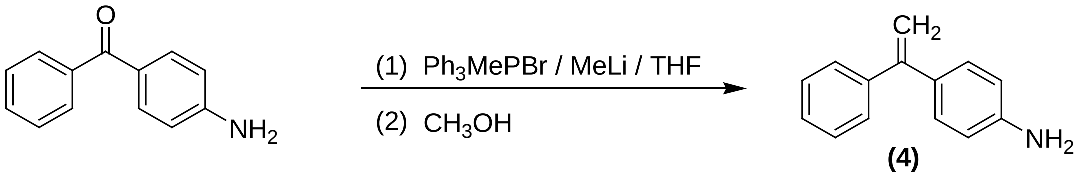
a) the atom transfer radical polymerization of styrene initiated by the appropriate new diamine functionalized initiator adduct, derived from the specific diamine functionalized 1,1-diphenylethylene derivative.
b) the addition of the appropriate diamine functionalized 1,1-diphenylethylene compound to the •-terminus of the specific •-bis(amine) functionalized polystyrene after the completion of the polymerization process.

4.3 Synthesis of Primary Amine Functionalized Polymers by Atom Transfer Radical Polymerization

In general, direct and indirect methods, which involve unimolecular organohalide compounds with free and protected primary amine groups, respectively, have been employed as initiators for the polymerization of different styrenic and acrylate monomers in the ATRP reactions to produce •-primary amine functionalized polymers[147]. To reduce the possible interaction between the primary amine functional group and the amine-ligand catalyst system used in the ATRP reactions, the careful selection of the amine substituted initiator molecule or initiator system is essential for a well controlled ATRP functionalization reaction. The present work describes the preparation of primary amine and diamine functionalized 1,1-diphenylethylene derivatives and the determination of their utility as unimolecular, primary amine functionalized initiator precursor compounds for the ATRP of styrene and methyl methacrylate in ATRP functionalization reactions to form •-primary amine and •-primary diamine functionalized polymers.

4.3.1 Primary Amine Functionalized Initiator Precursor: Synthesis of 1-(4-Aminophenyl)-1-phenylethylene, (4)

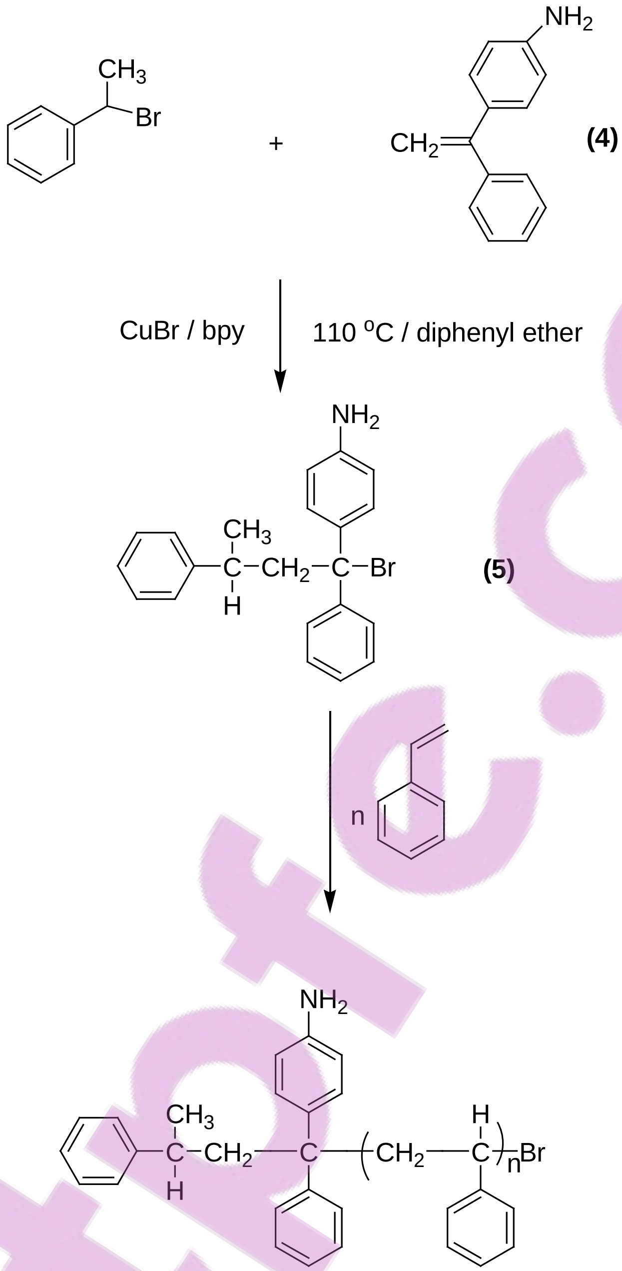
The synthesis of 1-(4-aminophenyl)-1-phenylethylene was performed according to the methodology outlined by Quirk and Lynch[51]. The preparation sequence for 1-(4-aminophenyl)-1-phenylethylene, (**4**) involved the classical Wittig reaction of 4-aminobenzophenone with a ylide, generated *in situ* from the reaction of methyllithium and methyltriphenylphosphonium bromide in freshly distilled tetrahydrofuran (THF) at room temperature. The following pathway outlines the synthesis route for the preparation of 1-(4-aminophenyl)-1-phenylethylene, (**4**):



Purification of the final product was achieved by column chromatography on silica gel using toluene as an eluent. Recrystallization of the product from 80% aqueous ethanol afforded 4.47 g (90%) of 1-(4-aminophenyl)-1-phenylethylene, (**4**) as light yellow crystals with a melting point of 81.2-82.6 ^{o}C. The ^{1}H NMR (Figure 11) of 1-(4-aminophenyl)-1-phenylethylene, (**4**) exhibits a singlet at • = 5.19 ppm, which is attributed to the resonance of equivalent vinyl protons (=CH$_2$) and a singlet at • = 3.67 ppm, due to the resonance of the NH$_2$ protons. Figure 12 depicts the FTIR spectrum of 1-(4-aminophenyl)-1-phenylethylene, (**4**) and shows the structurally significant absorption bands at 3468 cm^{-1}, which corresponds to the N-H stretching vibrations of the primary amine groups.

4.3.2 Synthesis of • -Aminophenyl Functionalized Polystyrene, (6)

The general synthetic pathway for the preparation of •-aminophenyl functionalized polystyrene, (**6**) by the ATRP method employs a new primary amine functionalized initiator adduct, (**5**) as unimolecular, primary amine functionalized initiator for the polymerization of styrene. Prior to the addition of styrene, the primary amine functionalized initiator adduct, (**5**) was prepared *in situ* by reacting stoichiometric amounts of 1-(4-aminophenyl)-1-phenylethylene, (**4**) with (1-bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3. The completion of the reaction was determined by TLC analysis by monitoring the disappearance of 1-(4-aminophenyl)-1-phenylethylene, (**4**) [R_f = 0.44, toluene]. The rapid initiation of styrene polymerization occurred after the addition of styrene monomer as evidenced by the rapid increase in the viscosity of the reaction medium, which indicates that the free radical generated from the adduct was reactive enough to initiate the polymerization of styrene. The polymerization proceeded *via* a controlled free radical polymerization process to afford quantitative yields of the corresponding •-aminophenyl functionalized polystyrene, (**6**) according to the following reaction pathway:



(6)

After polymer purification, TLC analysis of •-aminophenyl functionalized polystyrene, (**6**) [R_f = 0.89, toluene] shows only one spot on the chromatogram, consistent with the formation of the primary amine functionalized polymer in quantitative yields and the absence of any unfunctionalized polystyrene.

The size exclusion chromatogram (Figure 13) of •-aminophenyl functionalized polystyrene, (**6**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 3.10 x 10^3 g/mol and M_w/M_n = 1.08. The SEC value compares favourably with a theoretical $M_{n,theory}$ value of 3.30 x 10^3 g/mol and corresponds to 94% monomer conversion during the polymerization reaction.

The ^{1}H NMR spectrum (Figure 14) of •-aminophenyl functionalized polystyrene, (**6**) exhibits a broad peak in the region of • = 3.7 ppm, due to the resonance of amine protons[51] as well as a broad resonance at • = 4.3 ppm, due to the resonance of the terminal –CHPhBr proton[76]. The amine group functionality value for •-aminophenyl functionalized polystyrene, (**6**) was 0.99, as determined by end-group titration[54,200] and corresponds to a number average molecular weight value of 3.10 x 10^3 g/ mol.

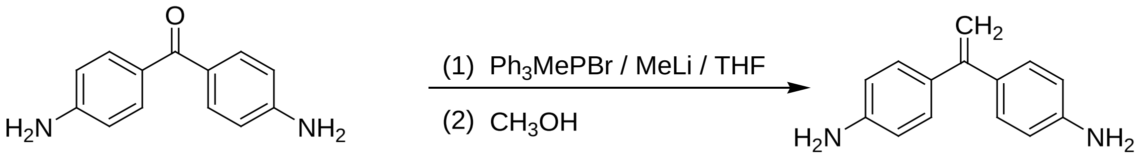
The FTIR spectrum (Figure 15) of •-aminophenyl functionalized polystyrene, (**6**) shows an absorption band at 3469 cm^{-1}, characteristic of the N-H stretching vibration of the NH_2 group. A sharp absorption band at 696 cm^{-1} is due to the stretching vibrations of the C-Br bond at the omega terminus of the polymer chain.

Initiation of the atom transfer radical polymerization of styrene by a new primary amine functionalized initiator adduct, (**5**), obtained *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene, (**4**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system afforded quantitative yields of •-aminophenyl functionalized polystyrene, (**6**). All polymer characterization data is consistent with the incorporation of the aminophenyl group of the initiator molecule at the •-terminus of the polymer chain[51,91].

4.3.3 Primary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis(4-aminophenyl)ethylene, (7)

Different synthetic strategies for the preparation of symmetrical diamine 1,1-diphenylethylene derivatives were reported in the literature[52,194]. Bencze[201] outlined the synthesis method for 1,1-bis(4-aminophenyl)ethylene, (**7**) by the reaction of 3,3-di(4-aminophenyl)-2-butanone with polyphosphoric acid. In addition, Sudalai and coworkers[195] prepared 1**,**1-bis(4-aminophenyl)ethylene, (**7**) in excellent yields by treatment of 1,1,1-trichloroethane with the appropriate aromatic substrate under Friedel-Craft reaction conditions.

A new synthetic method is used for the preparation of 1,1-bis(4-aminophenyl)-ethylene, (**7**), *via* the classical Wittig reaction, which involves the treatment of 4,4'-diaminobenzophenone with a phosphorous ylide, generated *in situ* from the reaction of methyllithium and methyltriphenylphosphonium bromide in freshly distilled tetrahydrofuran at room temperature according to the following reaction:



(7)

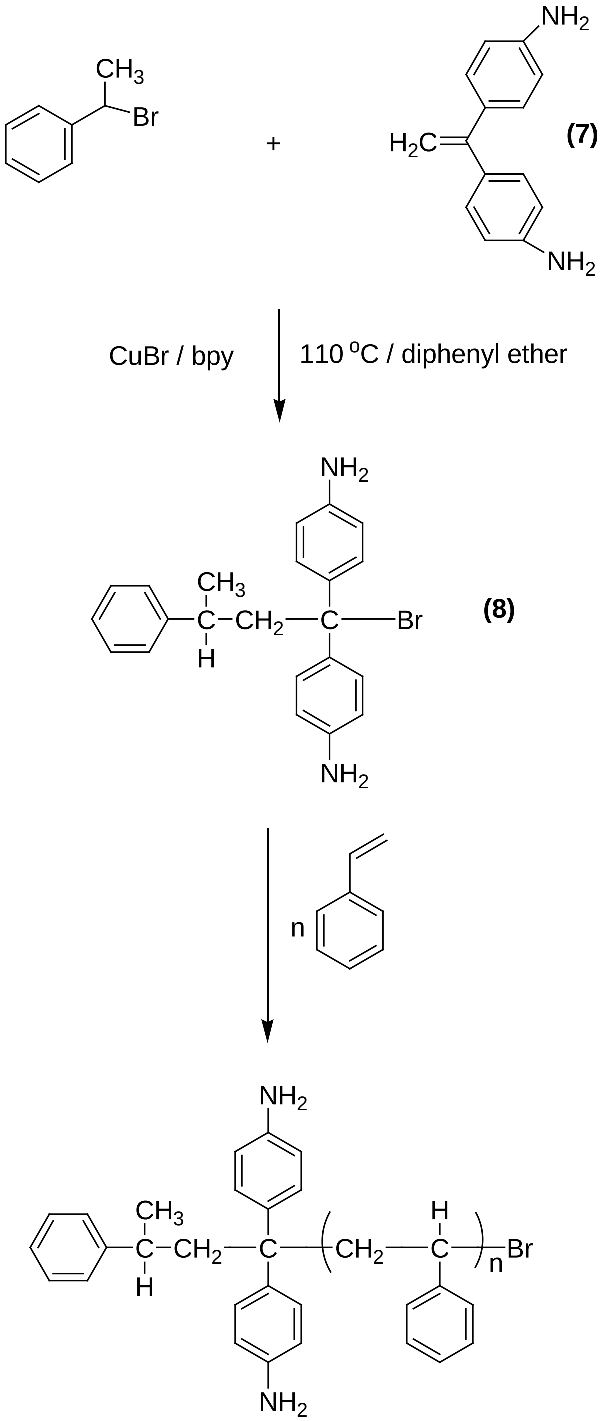
Purification of the crude product by column chromatography on silica gel using a hexane/ethyl acetate (*v/v*, 20/80) mixture as eluent and subsequent recrystallization from 80% aqueous ethanol solution gave 3.98 g (80.21%) of pure 1,1-bis(4-aminophenyl)ethylene, (**7**) as pale yellow crystals with a melting point of 160.5-162.0 ^{o}C.

The ^{1}H NMR spectrum (Figure 16) of 1,1-bis(4-aminophenyl)ethylene, (**7**) shows a singlet at • = 5.21 ppm, which is attributed to the resonance of the equivalent methylene protons [=C$\underline{H_2}$]. In addition, the broad peak at • = 3.69 ppm corresponds to the resonance of primary amine protons of the NH_2 groups.

The FTIR spectrum (Figure 17) of 1,1-bis(4-aminophenyl)ethylene, (**7**) shows the absorption band of C=C stretching vibrations at 1605 cm^{-1}, due to the presence of the $C=CH_2$ group. In addition, the strong absorption band at 3402 cm^{-1} is attributed to the N-H stretching vibrations of NH_2 groups. The absence of the strong C=O absorption band at 1669 cm^{-1} implies the quantitative conversion of the precursor benzophenone derivative to the olefin compound, which is consistent with the data of pure 1,1-bis(4-aminophenyl)ethylene, (**7**).

4.3.4 Synthesis of • -Bis(aminophenyl) Functionalized Polystyrene, (9)

The preparation of • -bis(aminophenyl) functionalized polystyrene, (**9**) by ATRP methods was conducted by using a new primary diamine functionalized initiator adduct, (**8**) for styrene polymerization. Quantitative yields of • -bis(aminophenyl) functionalized polystyrene, (**9**) was obtained according to the following reaction pathway:



(7) **(8)** **(9)**

The primary diamine functionalized initiator adduct, (**8**) was prepared *in situ* by the reaction of stoichiometric amounts of 1,1-bis(4-aminophenyl)ethylene, (**7**) with (1-bromoethyl)benzene in the presence of copper(I) bromide complexed with 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of

$[CuBr]_0$: [(1-bromoethyl)benzene]$_0$: $[bpy]_0$ = 1:1:3. Rapid initiation of styrene polymerization occurred after the addition of styrene monomer, as observed by the increase in the viscosity of the reaction medium. The polymerization proceeded *via* a controlled free radical polymerization process which indicates that the free radical generated from the primary diamine functionalized initiator adduct, (**8**) was reactive enough to initiate polymerization of styrene.

Thin layer chromatography was utilized to monitor the polymerization reaction and to determine the presence of functionalized and unfunctionalized polymer as well as unreacted initiator precursor in the polymerization reaction. Only one spot [R_f = 0.78, toluene], corresponding to •-bis(aminophenyl) functionalized polystyrene, (**9**), was observed on the thin layer chromatogram at the completion of the polymerization reaction.

The size exclusion chromatogram (Figure 18) of •-bis(aminophenyl) functionalized polystyrene, (**9**) shows a monomodal molecular weight distribution curve corresponding to the M_n value of 4.10 x 10^3 g/mol and M_w/M_n = 1.11. By comparison with the theoretical $M_{n,theory}$ value of 4.5 x 10^3 g/mol, the extent of polymerization corresponds to 91% monomer conversion during the polymerization reaction. The $M_{n,\ titration}$ value of 4.35 x 10^3 g/mol obtained from non-aqueous titration of the primary amine end groups of •-bis(aminophenyl) functionalized polystyrene, (**9**) shows a good comparison with M_n (SEC) and $M_{n,theory}$ values and indicates the quantitative incorporation of the bis(aminophenyl) group at the •-terminus of the polymer chain.

The chemical structure of •-bis(aminophenyl) functionalized polystyrene, (**9**) was determined by proton nuclear magnetic resonance spectrometry. The ^1H NMR spectrum (Figure 19) of •-bis(aminophenyl) functionalized polystyrene, (**9**) shows a broad peak at • = 3.65 ppm, due to the resonance of the amine protons of two NH_2 groups[51], as well as a broad peak at • = 4.5 ppm, due to the resonance of the terminal –CHPhBr proton[76].

FTIR spectroscopy was used to determine the presence of the amine functionality in the functionalized polystyrene sample. The FTIR spectrum (Figure 20) of • -bis(aminophenyl) functionalized polystyrene, (**9**) exhibits an absorption band at 3412 cm^{-1}, characteristic of the N-H stretching vibrations of the NH_2 groups.

Well defined • -bis(aminophenyl) functionalized polystyrene, (**9**) with good control of major polymer characteristics was prepared by ATRP methods using a new primary diamine functionalized initiator adduct, (**8**) as an initiator for styrene polymerization in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system.

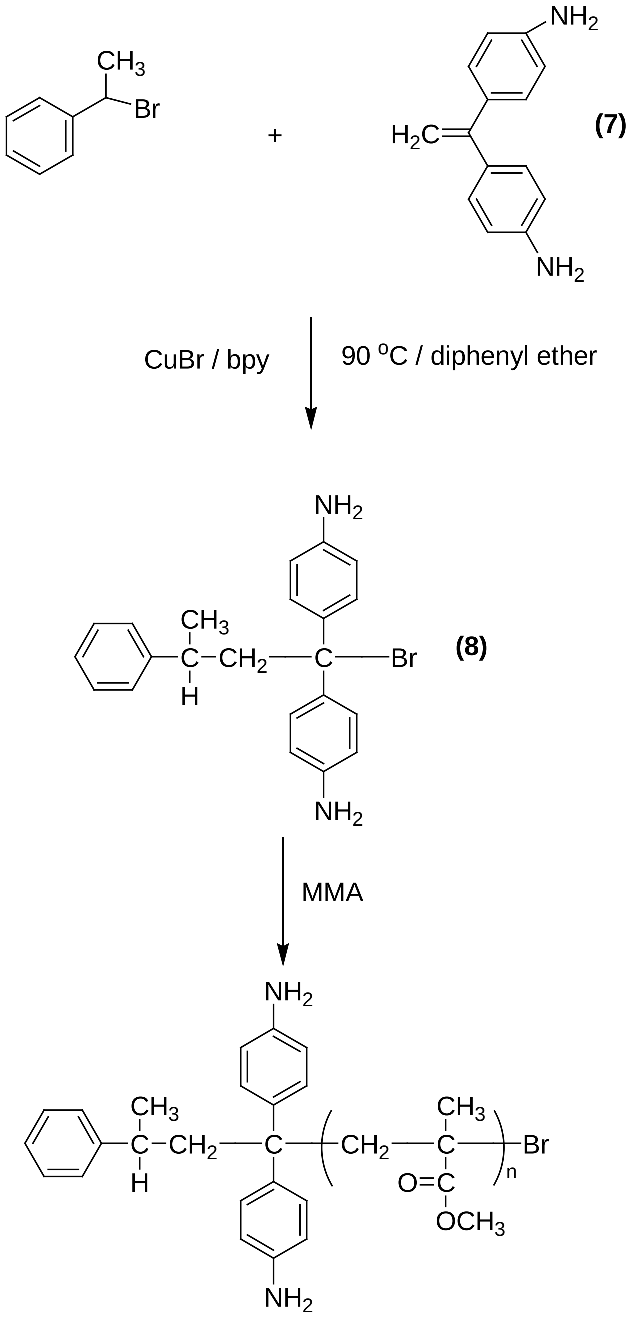
4.3.5 Synthesis of • -Bis(aminophenyl) Functionalized Poly(methyl methacrylate), (10)

• -Bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) was prepared by the ATRP of methyl methacrylate using a primary diamine functionalized initiator adduct, (**8**) as initiator. The new primary diamine functionalized initiator adduct, (**8**) was prepared *in situ* by the reaction of 1,1-bis(4-aminophenyl)ethylene, (**7**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 90 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3.

The size exclusion chromatogram (Figure 21) of • -bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) shows a monomodal molecular weight distribution curve, which corresponds with the number average molecular weight of $M_n = 3.6 \times 10^3$ g/mol and narrow molecular weight distribution of $M_w/M_n = 1.18$. By comparison to the theoretical M_n value of 4.0×10^3 g/mol, the SEC analysis indicates that although polymerization only proceeded to 90% monomer conversion, good chain length control and essentially controlled initiation and polymerization process was observed, especially for the formation of low molecular weight functionalized polymers.

The ^{1}H NMR spectrum (Figure 22) of •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) shows a broad peak at • = 3.8 ppm, corresponding to the resonance of the protons of the NH_2 groups. The presence of multiplets between • = 6.50-7.22 ppm, attributed to aromatic proton resonances, confirms the incorporation of the bis(aminophenyl) moiety of the initiator fragment at the •-terminus of the poly(methyl methacrylate) chain.

The extent of incorporation of •-bis(aminophenyl) groups at the •-terminus of the poly(methyl methacrylate) chain was determined by non-aqueous titrations of the primary diamine groups. The M_n value of 3.85 x 10^3 g/mol obtained by non-aqueous titration measurements is consistent with the M_n values obtained by SEC data. The detailed spectroscopic, chromatographic and non-aqueous titration data provide evidence for the quantitative incorporation of the bis(aminophenyl) group at the •-terminus of the polymer chain according to the following synthetic pathway:



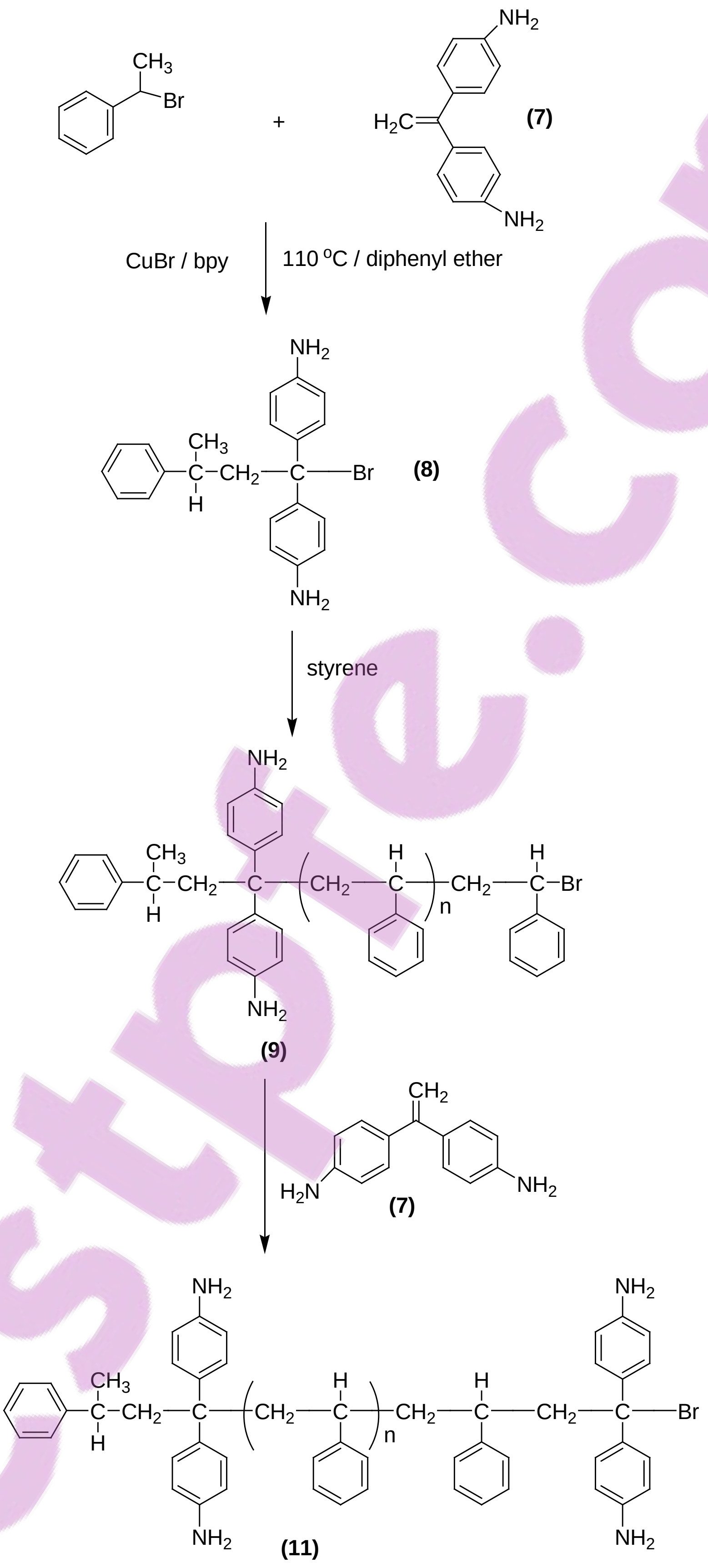
(7)

(8)

(10)

4.3.6 Synthesis of • ,• -Tetrakis(aminophenyl) Functionalized Polystyrene, (11)

The preparation of • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) was performed *via* a post ATRP chain end functionalization reaction using a primary diamine functionalized initiator adduct, (**8**) as functionalized initiator for the ATRP of styrene followed by the chain end functionalization reaction by the addition of 1,1-bis(4-aminophenyl)ethylene, (**7**) at the end of the polymerization reaction. Under argon atmosphere, the primary diamine functionalized initiator adduct, (**8**) was prepared by the reaction of stoichiometric amounts of 1,1-bis(4-aminophenyl)ethylene, (**7**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0 = 1:1:3$. Since styrene undergoes copolymerization reactions with 1,1-diphenylethylene derivatives, the success of the chain end functionalized reaction is dependant on the completion of the polymerization reaction prior to the addition of 1,1-bis(4-aminophenyl)ethylene, (**7**). The completion of the polymerization process was determined by the absence of styrene in the reaction mixture as evidenced by GC analysis. After 24 hours, 1,1-bis(4-aminophenyl)ethylene, (**7**) was added to the reaction mixture which contains the • -bis(aminophenyl) functionalized polystyrene precursor, (**9**) to form • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) according to the following synthetic pathway:


CH3
Br
+
NH2
H2C
(7)
NH2
CuBr / bpy
110 °C / diphenyl ether
NH2
CH3
C
CH2
C
Br
H
(8)
NH2
styrene
NH2
CH3
C
CH2
C
H
CH2
C
n
CH2
H
C
Br
H
NH2
(9)
CH2
H2N
(7)
NH2
NH2
CH3
C
CH2
C
H
CH2
C
n
CH2
H
C
CH2
C
NH2
Br
H
NH2
(11)
NH2

The size exclusion chromatogram (Figure 23) of • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 3.80 x 10^3 g/mol and M_w/M_n = 1.13. The SEC analysis also shows that no side reactions such as polymeric dimer or trimer formation occurred during the ATRP chain end functionalization reaction. The M_n values obtained by SEC analysis compares favourably with the theoretical M_n value of 4.20 x 10^3 g/mol for 100% monomer conversion during the polymerization process. The SEC analysis indicates that the polymerization proceeded *via* a controlled free radical polymerization process and that the subsequent chain end functionalization reaction affords quantitative yields of the corresponding • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**).

Non-aqueous titration data with standardized perchloric acid indicate the quantitative incorporation of the bis(aminophenyl) groups at both ends of the polystyrene chain. The value of the number average molecular weight, $M_{n,\ titration}$ = 4.17 x 10^3 g/mol, calculated from titration measurements, assuming the presence of four amine groups per polymer chain, is in good agreement with the M_n value obtained from SEC data.

The ^{1}H NMR spectrum (Figure 24) of • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) exhibits a broad peak in the region • = 3.65 ppm, due to the resonance of amine protons of four primary amine groups[68].

By post ATRP chain end modification reactions, well defined • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) was prepared in quantitative yields and high chain end functionality by ATRP methods. Using a primary diamine functionalized initiator adduct, (**8**) in the presence of CuBr/2,2'-bipyridyl catalyst system for styrene polymerization and the subsequent addition of 1,1-bis(4-aminophenyl)ethylene, (**7**) at the end the polymerization reaction gave • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) in an efficient chain end functionalization reaction.

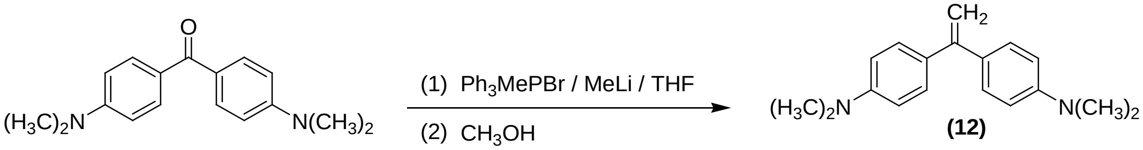
4.4 Synthesis of Tertiary Amine Functionalized Polymers by Atom Transfer Radical Polymerization

In the general ATRP process, the reversible homolytic cleavage of a carbon halogen bond of an alkyl halide initiator derivative by a redox reaction with a transition metal/amine ligand complex is essential to effect the rapid, efficient initiation of the polymerization of vinyl monomers. One of the most efficient methods for the preparation of chain end functionalized polymers by the ATRP methods is by the utilization of functionalized alkyl halide compounds as initiators for the polymerization of styrene and acrylates. Limited reports on the preparation of tertiary amine functionalized polymers by the ATRP methods using functionalized initiators bearing the tertiary amine group have been reported in the literature. Percec[173] and Yagci[155] reported the preparation of well-defined amine functionalized polymers with narrow molecular weight distributions and the incorporation of the tertiary amine group at the • -terminus of the polymer chain. In addition, tertiary amine functionalized polymers were prepared in quantitative yields by ATRP methods using an adduct of (1-bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene as an initiator for styrene polymerization in the presence of copper (I) bromide/2,2'-dipyridyl catalyst system[53]. All the polymerization reactions proceeded in a controlled manner without evidence of interaction between the tertiary amine functional group of the initiator molecule and the amine-ligand catalyst system used in ATRP reactions.

The present work describes the preparation of a tertiary diamine functionalized 1,1-diphenylethylene derivative and the determination of its utility as a unimolecular, tertiary diamine functionalized initiator precursor compound for the ATRP of styrene and methyl methacrylate as well as a functionalizing agent in post ATRP functionalization reactions to form different tertiary amine functionalized polymers.

4.4.1 Tertiary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis[(4-dimethylamino)phenyl]ethylene, (12)

In general, the synthetic route for the preparation of symmetrical disubstituted 1,1-diphenylethylene derivatives involves the conversion of the appropriate benzophenone derivative to the corresponding carbinol, followed by the spontaneous thermal or acid catalyzed dehydration of the intermediate carbinol[196,202,203]. Another method for the direct conversion of disubstituted benzophenones to the corresponding disubstituted 1,1-diphenylethylene derivatives is *via* the classical Wittig reaction with phosphoryl ylides or the Tebbe reagent[52]. The synthetic sequence for the preparation of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) *via* the Wittig reaction, involved the treatment of 4,4'-bis(dimethylamino)benzophenone with a phosphorous ylide, generated *in situ* from the reaction of methyllithium and methyltriphenylphosphonium bromide in freshly distilled tetrahydrofuran at room temperature:



The target molecule, 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was purified by silica gel column chromatography using hexane/ethyl acetate (*v/v*, 20/80) mixture as the eluent. Recrystallization of the product from 80% aqueous ethanol solution gave 2.92 g (89.1%) of pure 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) as light green crystals with a melting point of 126.8 - 127.9 ^{o}C.

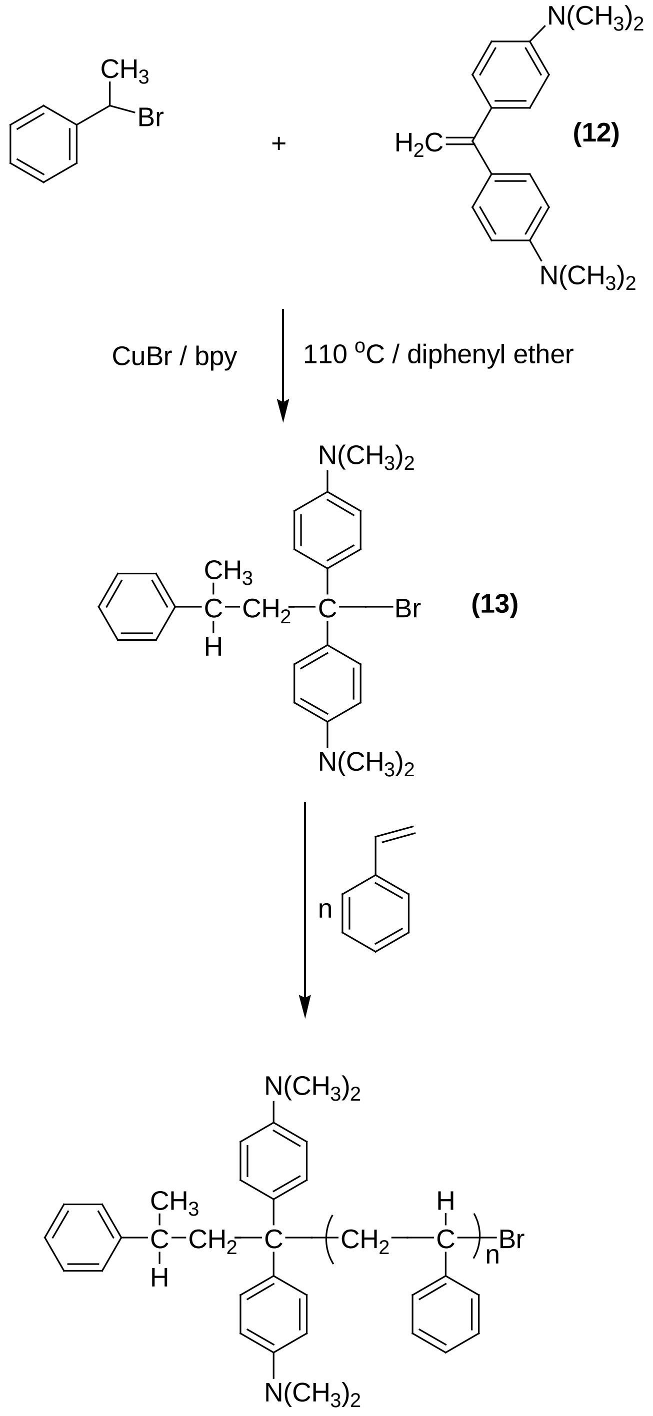
The ^{1}H NMR spectrum (Figure 25) of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) shows a singlet at • = 5.20 ppm, attributed to the resonance of equivalent methylene protons [$=C\underline{H}_2$] and a singlet at • = 2.96 ppm, attributed to the resonance of twelve hydrogens of the dimethylamino groups [2 x $-N(C\underline{H}_3)_2$]. The doublet of doublets at • = 6.71 - 7.29 ppm, corresponding to the resonance of the protons of the phenyl rings, is characteristic of p-substituted benzene rings.

The FTIR spectrum (Figure 26) of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) shows an absorption band at 1605 cm^{-1}, due to the C=C stretching vibrations of the $C=CH_2$ group and an absorption band at 1334 cm^{-1}, due to the N-C stretching vibrations of the $N(CH_3)_2$ groups.

The spectroscopic data provides evidence of the synthesis of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) by the classical Wittig reaction using 4,4'-bis(dimethylamino)benzophenone as precursor.

4.4.2 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Polystyrene, (14)

The atom transfer radical polymerization of styrene, initiated by a new tertiary diamine functionalized initiator adduct, (**13**) afforded •-bis(4-dimethylamino-phenyl) functionalized polystyrene, (**14**) in quantitative yields. The tertiary diamine functionalized initiator adduct, (**13**) was prepared *in situ* by the reaction of stoichiometric amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3. After 12 hours, the polymer product was isolated by precipitation from THF solution into excess methanol, filtered and vacuum dried to give •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) in quantitative yields according to the following synthetic pathway:



(12)

(13)

(14)

Thin layer chromatography analysis of the purified polymer product shows only one spot on the chromatogram [R_f = 0.79, toluene] which corresponds to the formation of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) in quantitative yields.

The size exclusion chromatogram (Figure 27) of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 5.10 x 10^3 g/mol and M_w/M_n = 1.09, compared with the $M_{n,theory}$ value of 5.40 x 10^3 g/mol at 94% monomer conversion. The $M_{n,\ titration}$ value of 5.21 x 10^3 g/mol obtained from non-aqueous titration of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) corresponds with the number average molecular weight data of M_n = 5.10 x 10^3 obtained from SEC analysis and is consistent with the incorporation of two dimethylamino groups per polymer chain.

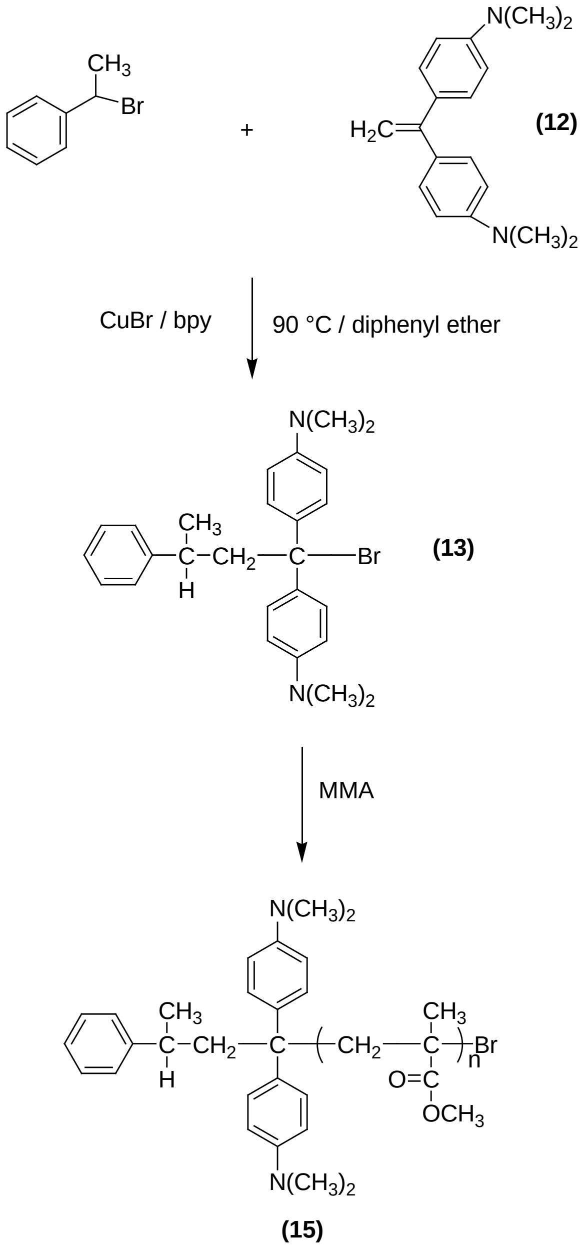
The ^{1}H NMR spectrum (Figure 28) of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) shows a signal at • = 3.02 ppm, due to the resonance of the protons of the tertiary amine groups[53,155] of the functionalized initiator fragment. The peak at • = 4.5 ppm corresponds to the proton resonance of the CHPhBr end group at the •-terminus of the polymer chain[76].

The FTIR spectrum (Figure 29) of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) shows a strong absorption band at 1350 cm^{-1}, characteristic of the N-C stretching vibrations of the $N(CH_3)_2$ groups. A sharp absorption band at 697 cm^{-1} is due to the C-Br bond vibrations at the •-terminus of the polymer chain.

The atom transfer radical polymerization of styrene, initiated by a new tertiary diamine functionalized initiator adduct, (**13**) afforded quantitative yields of well defined •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**). The spectroscopic and end group analysis data provide detailed evidence for the incorporation of the bis(4-dimethylaminophenyl) group at the •-terminus of the polymer chain[52,53,105,173,174].

4.4.3 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Poly(methyl methacrylate), (15)

The preparation of •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) by ATRP methods was effected by the initiation of methyl methacrylate polymerization using a new tertiary diamine functionalized initiator adduct, (**13**) as outlined in the following synthetic pathway:



The tertiary diamine functionalized initiator adduct, (**13**) was prepared *in situ* by treatment of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) with (1-bromoethyl)-benzene in the presence of copper(I) bromide/ 2,2'-bipyridyl catalyst system in diphenyl ether at 90 ^{o}C, in the molar ratio of [CuBr]$_0$: [(1-bromoethyl)benzene]$_0$: [bpy]$_0$ = 1:1:3. The polymer product was purified by precipitation from THF solution into excess methanol, filtered and vacuum dried to give • -bis(4-dimethyl-aminophenyl) functionalized poly(methyl methacrylate), (**15**) as a white solid.

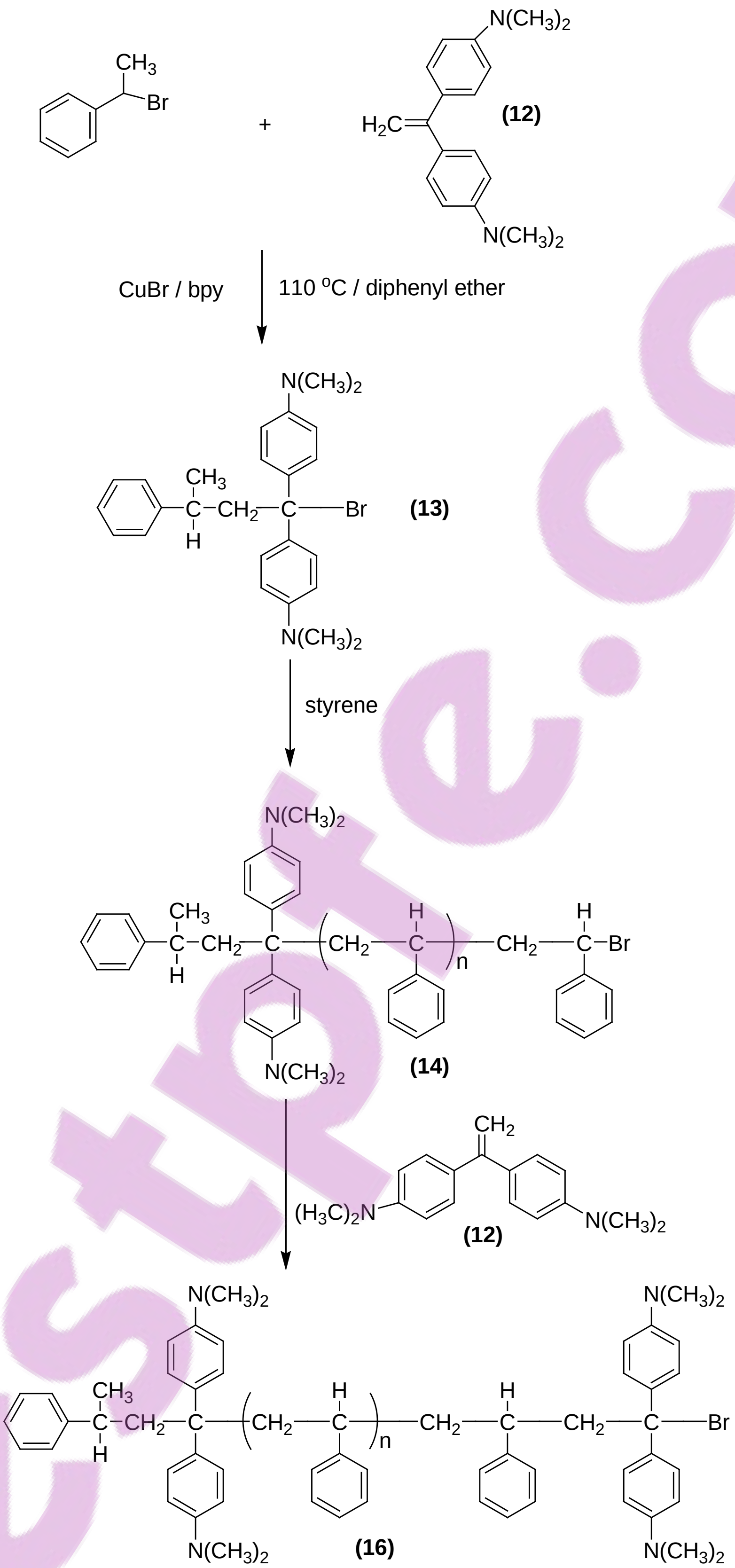
The size exclusion chromatogram (Figure 30) of • -bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) shows a monomodal molecular weight distribution curve, with the number average molecular weight of M_n = 5.23 x 10 ^{3} g/mol and narrow molecular weight distribution of M_w/M_n = 1.03. The M_n value obtained from SEC analysis compared favourably with the $M_{n,theory}$ = 5.50 x 10^3 g/mol obtained from the stoichiometry of the reaction for 95% monomer conversion during the polymerization process. The M_n value of 5.35 x 10^3 g/mol, obtained from the non-aqueous titration of • -bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) is in agreement with the number average molecular weight data of M_n = 5.23 x 10^3 g/mol obtained from SEC analysis for a polymer chain with two dimethylamino groups per chain.

The ^{1}H NMR spectrum (Figure 31) of • -bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) shows a signal between 2.85 ppm and 2.96 ppm**,** corresponding to the proton resonance of the $N(CH_3)_2$ groups. The presence of peaks at • = 6.58-7.24 ppm, due to aromatic proton resonances, confirms the incorporation of the • -bis(4-dimethylaminophenyl) moiety at the end of the poly(methyl methacrylate) chain.

The chromatographic, spectroscopic and non-aqueous titration analysis data indicate that the polymerization of methyl methacrylate, initiated by a tertiary diamine functionalized initiator adduct, (**13**), proceeded *via* a controlled atom transfer radical polymerization process with the quantitative incorporation of the bis(4-dimethylaminophenyl) group at the •-terminus of the •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) chain.

4.4.4 Synthesis of •,• -Tetrakis(4-dimethylaminophenyl) Functionalized Polystyrene, (16)

The preparation of •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) was conducted by the ATRP of styrene initiated by a tertiary diamine functionalized initiator adduct, (**13**), followed by the post ATRP chain end modification reaction by the addition of 1,1-bis[(4-dimethylamino)phenyl]-ethylene, (**12**) to the polymer chain end of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) at the completion of the polymerization process. Under argon atmosphere, the tertiary diamine functionalized initiator adduct, (**13**) was prepared by the reaction of stoichiometric amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3. The styrene polymerization proceeded for 24 hours to ensure complete monomer consumption during the polymerization process, as evidenced by GC analysis. To effect the chain end functionalization reaction, 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was added to the reaction mixture in the solid form after completion of the polymerization process. After passage of the crude product through a silica gel column to remove catalyst impurities, the polymer product was isolated by precipitation from THF solution into excess methanol, filtered and vacuum dried to afford •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) as a white powder. The synthesis pathway for the preparation of •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) is outlined as follows:


CH3
Br
+
N(CH3)2
H2C
(12)
N(CH3)2
CuBr / bpy
110 °C / diphenyl ether
N(CH3)2
CH3
C
CH2
C
Br
H
(13)
N(CH3)2
styrene
N(CH3)2
CH3
C
CH2
C
CH2
H
C
n
CH2
H
C
Br
H
N(CH3)2
(14)
CH2
(H3C)2N
N(CH3)2
(12)
N(CH3)2
CH3
C
CH2
C
CH2
H
C
n
CH2
H
C
CH2
C
Br
H
N(CH3)2
(16)
N(CH3)2
N(CH3)2

The size exclusion chromatogram (Figure 32) of • ,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 4.93 x 10^3 g/mol and M_w/M_n = 1.16, consistent with the theoretical $M_{n,theory}$ value of 5.20 x 10^3 g/mol for 100% monomer conversion during the styrene polymerization process. The M_n value of 5.13 x 10^3 g/mol obtained from non-aqueous titration analysis of • ,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) for the incorporation of four dimethylamino groups per polymer chain is consistent with the number average molecular weight data of M_n (SEC) = 4.93 x 10^3 g/mol obtained from SEC analysis.

The ^{1}H NMR spectrum (Figure 33**)** of • ,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) exhibits a signal at • = 3.16 ppm, due to the resonance of protons of the four dimethylamino groups at the polymer chain ends[52,53]. The absence of a broad peak at • = 4.4 – 4.6 ppm, which is due to the resonance of the proton of the CHPhBr end group[76] of the precursor polymer molecule, indicates the complete addition of the 1,1-diphenylethylene unit during the chain end modification reaction. In addition, the quantitative incorporation of four dimethylamino groups at the end of the polymer chain provides evidence that no styrene was present to undergo copolymerization reactions with 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) during the ATRP chain end functionalization reaction.

The ATRP method allows the preparation of well-defined polymers with high end group functionality. By post ATRP chain end modification reactions, well defined • ,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) was prepared in quantitative yields and high chain end functionality by the addition of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) to the polymer chain end of • -bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**).

4.5 Synthesis of Amine Chain End Functionalized Polymers by Atom Transfer Radical Polymerization: Polymerization Kinetics Studies

For an effective and well controlled ATRP reaction, three primary experimental features must be established, namely, (i) the first order rate plot of $\ln[M]_0/[M]$ versus time should be linear, indicating that the concentration of active radical species is constant throughout the reaction; (ii) the molecular weight distributions of polymers should be below 1.5; and (iii) the increase in the number average molecular weight of the polymers with respect to percentage monomer conversion should be linear, indicating that all chains are growing concomitantly with consumption of monomer and the absence of any chain transfer and termination reactions[126].

4.5.1 Syntheses of • -Aminophenyl Functionalized Polystyrenes, (6)

A series of • -aminophenyl functionalized polystyrenes, (**6**) were prepared by ATRP methods using the primary amine functionalized initiator adduct, (**5**), formed by the reaction of 1-(4-aminophenyl)-1-phenylethylene, (**4**) with (1-bromo-ethyl)benzene, as the initiator in the solution polymerization of styrene. Experiments were performed in the presence of copper (I) bromide/2,2'-bipyridyl with ratios of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0 = 1:1:3$ in diphenyl ether at 110 ^oC at different monomer to initiator concentration ratios. The ATRP reactions proceeded under heterogeneous conditions in high initiator efficiency reactions.

Figure 34 shows the plots of percentage monomer conversion versus time for each polymerization reaction. Results indicate that at the lower $[M]_0/[I]_0$ ratio, the reaction was the fastest and 98% monomer conversion was reached in 4.5 hours. When the $[M]_0/[I]_0$ ratio is increased to 100, the percentage monomer conversion with time decreases slightly to 83% after 5 hours of polymerization time. A retardation in the reaction is observed at the higher $[M]_0/[I]_0$ ratio = 200, whereby only 10% monomer consumption occurs after one hour of reaction time and a percentage monomer conversion value of 61% was recorded after 5.5 hours of reaction.

Figure 35 shows the semilogarithmic kinetic plots of $\ln[M]_0/[M]$ as a function of polymerization time at different $[M]_0/[I]_0$ ratios for the heterogenous synthesis of •-aminophenyl functionalized polystyrene, (**6**) using the primary amine functionalized initiator adduct, (**5**) as the initiator system for styrene polymerization by ATRP methods. The kinetic plots show that the ratio of the concentration of monomer to initiator affects the rate of polymerization. Linear relationships were obtained for the kinetic plots of $\ln[M]_0/[M]$ versus polymerization time, indicating that fast initiation has occurred and that the radical concentration remains constant throughout the polymerization process. The linearity of the semilogarithmic plots of $\ln[M]_0/[I]$ versus time indicates that the polymerizations were first order with respect to monomer consumption. At the lower $[M]_0/[I]_0$ ratio, the reaction rate is the fastest and the reaction rate drops significantly with decreasing initiator concentration. The linear behaviour of the kinetic plots is further confirmed by the observed linear regression coefficient values of 0.97 or greater:

$[M]_0/[I]_0$	Linear Regression Coefficient R^2	Slope
50 : 1	0.9962	0.01374
100 : 1	0.9721	0.00711
200 : 1	0.9778	0.00189

Figure 36 shows the plots of the experimental number average molecular weights and molecular weight distributions with percentage monomer conversion for the different ATRP reactions for the preparation of •-aminophenyl functionalized polystyrenes, (**6**). The number average molecular weights of •-aminophenyl functionalized polystyrenes, (**6**) increase linearly with percentage monomer conversion and are consistent with the theoretical values. Polymers with narrow molecular weight distributions were obtained. The linear increase of number average molecular weight with percentage monomer conversion suggests that no significant chain transfer or termination reactions occurred once the initiation step is complete. Primary amine chain end functionalized polymers with predictable number average molecular weights ($M_n = 1.89 \times 10^3$ g/mol to 13.43×10^3 g/mol) and molecular weight distributions ranging from 1.03 to 1.25 were obtained, indicating the occurrence of a fast initiation process which involves the rapid equilibrium exchange between active and dormant species during the polymerization reaction.

Experimental results show that good control of the number average molecular weight, molecular weight distributions and high initiator efficiency reactions in the solution ATRP synthesis of • -aminophenyl functionalized polystyrenes, (**6**) was observed using the primary amine functionalized initiator adduct, (**5**) as initiator for styrene polymerization. The quantitative incorporation of the functionalized 1,1-diphenylethylene fragment at the polymer chain end in the ATRP of styrene and the control of major polymer properties, such as the number average molecular weight, molecular weight distribution and degree of functionalization is attributed to the *in situ* formation of the amine functionalized initiator adduct, (**5**) by the stoichiometric addition reaction of (1-bromoethyl)benzene to 1-(4-aminophenyl)-1-phenylethylene, (**4**) and the subsequent efficient and rapid reaction with the styrene to initiate styrene polymerization by ATRP methods.

4.5.2 Syntheses of • -Bis(aminophenyl) Functionalized Polystyrenes, (9)

A series of • -bis(aminophenyl) functionalized polystyrenes, (**9**) were prepared by the ATRP of styrene using a new primary diamine functionalized initiator system. The primary diamine functionalized initiator adduct, (**8**) was prepared by the reaction of 1,1-bis(4-aminophenyl)ethylene, (**7**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 °C with the stoichiometry of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3. In a typical experiment, starting at t = 0, aliquots of 1 mL were removed at

30 minute intervals, diluted with THF (9 mL) and subjected to gas chromatographic analysis to determine the percentage monomer conversion of styrene with time.

Figure 37 shows the plots of percentage monomer conversion with polymerization time for the ATRP of styrene, initiated by the adduct of 1-bis(4-aminophenyl)ethylene, (**7**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C. The syntheses of • -bis(aminophenyl) functionalized polystyrenes, (**9**) were carried out under different molar ratios of monomer to initiator. The conversion of monomer during the polymerization process increased as the molar ratios of monomer to initiator decreased. At the lower $[M]_0/[I]_0$ ratio = 50, the reaction was the fastest and 89% monomer conversion was reached in 4 hours. When the $[M]_0/[I]_0$ ratio is increased to 100, the extent of monomer conversion reduced slightly to 76% within 4 hours. At monomer to initiator ratio of 200, a lower percentage monomer conversion value to 61% was recorded after 4 hours.

Figure 38 shows the first order kinetic plots of $\ln[M]_0/[M]$ as a function of polymerization time for the ATRP of styrene using the primary diamine functionalized initiator adduct, (**8**) as initiator for styrene polymerization. In all plots, linear relationships between $\ln[M]_0/[M]$ versus time are observed, indicating that the radical concentration stays constant throughout the course of the polymerization reaction and that rapid exchange between the active and dormant species occurs, i.e. fast initiation of styrene polymerization. Furthermore, considering the slope of the plots, the reaction is the fastest for the lower $M]_0/[I]_0$ ratio = 50 and the polymerization time decreases as the $M]_0/[I]_0$ ratio increases. The observed linear regression coefficients of the reactions are close to or greater than 0.98, which indicates the linearity of the first order kinetic plots:

$[M]_0/[I]_0$	Linear Regression Coefficient R^2	Slope
50 : 1	0.9890	0.01434
100 : 1	0.9994	0.00764
200 : 1	0.9827	0.00357

Figure 39 shows the plots of the number average molecular weights and molecular weight distributions as a function of percentage monomer conversion for the different ATRP reactions. The solution atom transfer radical polymerization of styrene was initiated by the primary diamine functionalized initiator adduct, (**8**) in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C. The M_n values increases linearly with percentage monomer conversion, which suggests that no significant chain transfer or termination reactions occured once the initiation step is complete. For the $[M]_0/[I]_0$ ratio of 200, polymers with number average molecular weights up to 13.42 x 10^3 g/mol are obtained, whereas low molecular weight polymers ranging from 1.1 x 10^3 to 4.2 x 10^3 g/mol are obtained when the $[M]_0/[I]_0$ ratio = 50. Furthermore, the molecular weight distributions of the resultant •-bis(aminophenyl) functionalized polystyrenes, (**9**) are relatively narrow, ranging from 1.03 to 1.25.

The polymerization kinetics data shows that a series of different •-bis(aminophenyl) functionalized polystyrenes, (**9**) 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 styrene using a primary diamine functionalized initiator adduct, (**8**) as initiator for the styrene polymerization. The primary diamine functionalized initiator adduct, (**8**), prepared *in situ* from the reaction of 1,1-bis(4-aminophenyl)ethylene, (**7**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C, is a good primary diamine functionalized initiator for the ATRP of styrene and affords •-bis(aminophenyl) functionalized polystyrenes, (**9**) in quantitative yields.

4.5.3 Syntheses of •-Bis(4-dimethylaminophenyl) Functionalized Polystyrenes, (14)

The copper-mediated ATRP of styrene, initiated by the tertiary diamine functionalized initiator adduct, (**13**) produces •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) in quantitative yields. Styrene polymerization was initiated by the tertiary diamine functionalized initiator adduct, (**13**), prepared *in situ* by the stoichiometric reaction of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst in diphenyl ether at 110 ^{o}C. Different experiments were conducted by varying the monomer to initiator concentration ratios from 50:1, 100:1 to 200:1 for the different experiments. Starting at t = 0, aliquots of 1 mL were removed at 30 minute intervals, diluted with THF (9 mL) and subjected to gas chromatographic analysis to determine the percentage monomer conversion of styrene as a function of polymerization time.

Figure 40 shows the plots of percentage monomer conversion versus polymerization time for the synthesis of the different •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) derivatives. When the $[M]_0/[I]_0$ ratio = 50, the polymerization reaction was the fastest and a monomer conversion of 94% was reached within 4 hours. The percentage monomer conversion decreased considerably on increasing the monomer to initiator ratio from 100 to 200, where the respective percentage monomer conversions values of 80% and 63% were obtained within the same polymerization time.

Figure 41 shows a linear relationship between $\ln[M]_0/[M]$ and time for the different experiments where the $[M]_0/[I]_0$ ratios range from 50 to 200. Styrene polymerization was initiated by the tertiary diamine functionalized initiator adduct, (**13**), derived from the reaction of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst in diphenyl ether at 110 ^{o}C. The experimental data shows that the polymerization kinetics for each reaction was first order with respect to monomer consumption and that the concentration of the propagating radicals in each reaction remains constant throughout the polymerization process. The linear behaviour of each reaction kinetics plot is further confirmed by the observed linear regression coefficients values of 0.98 for each polymerization process:

$[M]_0/[I]_0$	Linear Regression Coefficient R^2	Slope
50 : 1	0.9896	0.01088
100 : 1	0.9783	0.00632
200 : 1	0.9773	0.00366

Figure 42 shows the plots of the experimental number average molecular weight and molecular weight distribution with percentage monomer conversion for the different ATRP reactions for the preparation of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**). The number average molecular weights of the different •-bis(4-dimethylaminophenyl) functionalized polystyrenes, (**14**), obtained by SEC, increases linearly with the percentage monomer conversion. The linearity of the plots indicates the polymerization proceeded by normal ATRP mechanisms which involves a fast exchange between active and dormant species, that is, fast initiation of styrene polymerization and no measurable 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. Also, polymers with narrow molecular weight distributions were obtained, indicating that the rate of initiation was at least equal to or greater than the rate of propagation for each reaction. The molecular weight distribution values of the •-bis (4-dimethylaminophenyl) functionalized polystyrenes, (**14**) ranged from 1.03 to 1.44.

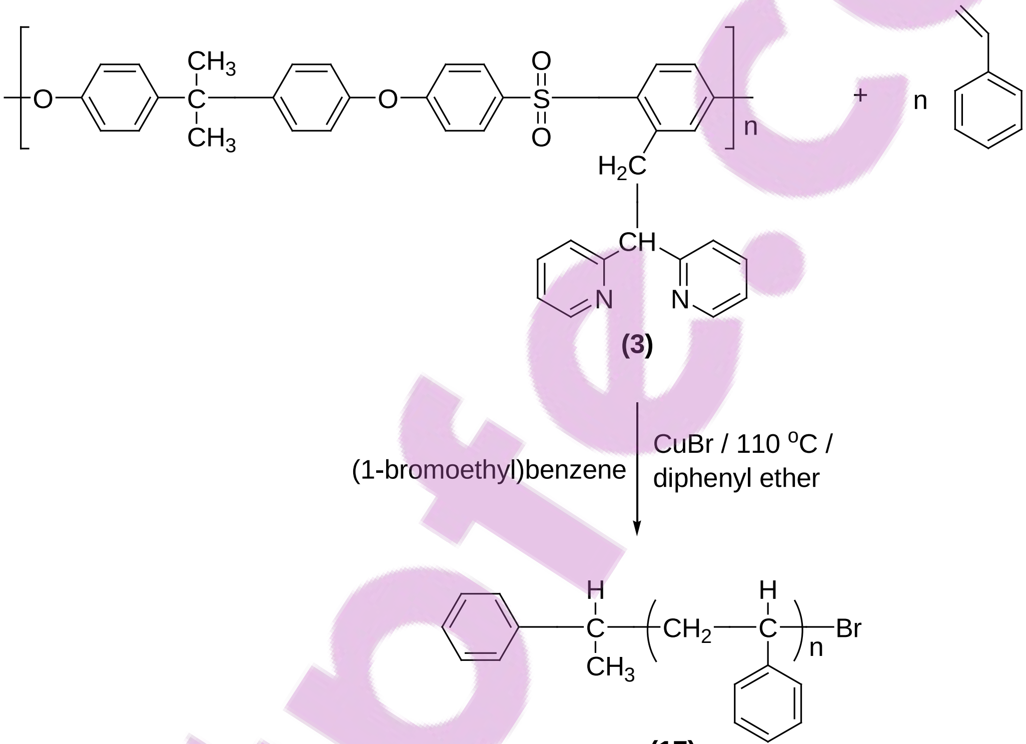
The polymerization kinetics data shows that a series of different •-bis(4-dimthylaminophenyl) functionalized polystyrenes, (**14**) with good control of polymer characteristics such as the number average molecular weight, molecular weight distribution and chain end functionality are obtained by the ATRP of styrene using a tertiary diamine functionalized initiator adduct, (**13**) as initiator for the styrene polymerization. The tertiary diamine functionalized initiator adduct, (**13**), prepared *in situ* from the reaction of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C, is a good tertiary diamine functionalized initiator for the ATRP of styrene and affords • -bis(4-dimethylaminophenyl) functionalized polystyrenes, (**14**) in quantitative yields.

4.6 A New Supported Catalyst System for the Atom Transfer Radical Polymerization of Styrene

The ATRP process is a powerful technique for the laboratory synthesis of well-defined polymers. However, the purification steps involved after the polymerization process have prevented the extensive application of the ATRP method for polymer production at the industrial scale. Thus, the current industrial research work is centered on the development of new synthetic procedures to make the ATRP technique more amenable to commercialization processes. To overcome the industrial limitations of polymer purification during the ATRP process, three approaches[55] to the reduction of residual catalyst in the final polymer product have been used, namely, (a) the development of a more active catalyst system for catalyst reduction and elimination of the purification step; (b) the utilization of catalyst supports to facilitate catalyst recovery and recycling; and (c) more facile and effective polymer purification methods. Although all these approaches have shown successes, only the first two have been accepted by industry, since the methods allow a reduction in the raw catalyst cost while minimizing the need for post polymerization purification work. Thus, a new polymeric supported catalyst system, based on dipyridyl functionalized polysulfones, was developed for the ATRP of styrene.

4.6.1 Synthesis of Polystyrene, (17) using Dipyridyl Functionalized Polysulfone, (3) as Ligand

A new polymer supported catalyst system, prepared *in situ* by the complexation of dipyridyl functionalized polysulfone, (**3**) (PFPS-95) as ligand with CuBr, was evaluated as a polymeric supported catalyst system for the ATRP of styrene according to the following synthetic pathway.



The polymerization of styrene was initiated by (1-bromoethyl)benzene in the presence of the PFPS-95/CuBr supported catalyst complex in diphenyl ether at 110 °C with a mole ratio of $[\text{CuBr}]_0$: $[\text{(1-bromoethyl)benzene}]_0$: $[\text{dipyridyl functionalized polysulfone}]_0$ = 1:1:3. Upon the addition of CuBr to dipyridyl functionalized polysulfone, (**3**) a yellow-green reaction mixture was formed and the CuBr/PFPS-95 complex was soluble in diphenyl ether. At the beginning of the reaction, the observed instantaneous green colouration of the mixture indicates the formation of standard ATRP reaction conditions and the strong anchoring of the transition-metal catalyst on the ligand to form a stable complex. After completion of the polymerization process, the crude polymer mixture was concentrated and precipitated into toluene to remove the polymeric ligand/copper (I) bromide system. The dipyridyl functionalized polysulfone, (**3**), which precipitated in toluene, was filtered and vacuum dried. The ^{1}H NMR spectrum (Figure 43) of dipyridyl functionalized polysulfone, (**3**) shows signals at • = 3.78 and • = 4.65 ppm, due to the proton resonances of CH_2 and CH groups, respectively. Furthermore, the multiplets between • = 6.3 – 6.7 ppm, 7.4 – 7.8 ppm and 8.1 – 8.4 ppm are attributed to the aromatic proton resonances of the pyridyl groups[194], indicating the complete recovery of the polymeric ligand from the ATRP reaction.

The toluene filtrate, which contained polystyrene, (**17**) was passed through a short silica gel column to remove additional copper catalyst/ligand impurities. The toluene phase was concentrated in vacuo and the polymer product was added to excess methanol. The white polymer solid which precipitated was filtered and vacuum dried to give well defined polystyrene, (**17**). The size exclusion chromatogram (Figure 44) of polystyrene, (**17**) shows a monomodal molecular weight distribution curve with M_n = 8.13 x 10^3 g/mol and M_w/M_n = 1.14, consistent with the theoretical value of M_n = 8.15 x 10^3 g/mol. The ^{1}H NMR spectrum (Figure 45) of polystyrene, (**17**) shows the classical peaks between • = 1.10 - 2.22 ppm, due to the resonances of the protons of the CH and CH_2 groups of the polystyrene backbone and the peaks at • = 6.46 -7.49 ppm which corresponds to the aromatic proton resonances of the pendant phenyl groups of the polystyrene chain.

Experimental results show that a new polymer supported catalyst system, PFPS-95/CuBr was efficient in promoting the controlled atom transfer radical polymerization of styrene using (1-bromoethyl)benzene as the initiator in diphenyl ether at 110 ^{o}C. Polystyrene, (**17**) with good control of the number average molecular weight and molecular weight distribution was obtained.

4.6.2 Synthesis of Polystyrene, (17) using Dipyridyl Functionalized Polysulfone, (3) as Ligand: Polymerization Kinetics Studies

The polymerization kinetics studies of the atom transfer polymerization of styrene, initiated by (1-bromoethyl)benzene in the presence of a new polymer supported catalyst system of CuBr complexed with dipyridyl functionalized polysulfone, (**3**), (PFPS-95) were performed in diphenyl ether at 110 ^{o}C. The stoichiometry of the reaction was initiator: catalyst: ligand = [(1-bromoethyl)benzene]$_0$: [CuBr] : [PFPS-95] = 1: 1: 3 and the monomer: initiator ratio of $[M]_0/[I]_0$ = 200. The dipyridyl functionalized polysulfone/CuBr complex was completely soluble in the reaction mixture. Upon the addition of CuBr to dipyridyl functionalized polysulfone, (**3**), (PFPS-95) in diphenyl ether, a yellow-green reaction mixture was formed. With the addition of the initiator, the homogenous reaction mixture turned green. After the addition of the styrene monomer, starting at t = 0, aliquots of 1 mL were removed at 30 minute intervals, followed by the addition of THF (2 mL). The aliquots were subjected to gravimetric analysis to determine the percentage monomer conversion of styrene with time by evaluating the mass of each polymer sample as a function of time.

Figure 46 shows the plot of percentage monomer conversion versus polymerization time for the ATRP of styrene in the presence of the CuBr/PFPS-95 supported catalyst system in diphenyl ether at 110 ^{o}C. The polymerization proceeded slowly and only reached 54% conversion after 3 hours.

Figure 47 shows the semilogarithmic plot of $\ln[M]_0/[M]$ versus time for the ATRP of styrene in the presence of the CuBr/PFPS-95 supported catalyst system. The first order kinetic plot is linear with a slope of 0.00598 and a linear regression coefficient of R^2 = 0.9896, suggesting constant radical concentration throughout the polymerization process.

Figure 48 shows the plot of the experimental number average molecular weights and molecular weight distributions with percentage monomer conversion for the ATRP synthesis of polystyrene in the presence of CuBr/PFPS-95 supported catalyst system. The number average molecular weights of the polystyrene samples increased linearly with percentage monomer conversion and are close to the theoretical values. The molecular weight distributions are less than 1.2, which is comparable to values obtained in the presence of CuBr/bpy catalyst system[55,147].

Polymerization kinetics data shows that first order rate kinetics was observed during the ATRP of styrene in the presence of a new polymer supported catalyst system derived from PFPS-95 and CuBr. The number average molecular weights of styrene, (**17**), increase linearly with percentage monomer conversion and polymers with narrow molecular weight distributions were obtained. Experimental data demonstrates that the new PFPS-95/CuBr catalyst complex is an efficient catalytic system for the ATRP of styrene.

CHAPTER 5

CONCLUSION

5.1 Chemical Modification of Polysulfone by Anionic Methods

Dipyridyl functionalized polysulfones, (**3**) with improved hydrophilicity, enhanced membrane morphological properties and excellent ATRP polymeric ligand properties were prepared by the chemical modification of polysulfone by anionic methods. Modification of aromatic polysulfone was achieved by the direct lithiation of the unmodified polysulfone, (**1**), followed by the addition of 2,2'-vinylidenedipyridine, (**2**) to give the corresponding dipyridyl functionalized polysulfones, (**3**) with different degrees of substitution, depending on the stoichiometry of the reactions. A reduced temperature was necessary during the lithiation step to prevent polymer cross-linking. When equimolar amounts of 2,2'-vinylidenedipyridine, (**2**) are added to the lithiated polysulfone, the degree of functionalization obtained was 45%. However, the addition of 10% and 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the corresponding lithiated polysulfone, produce dipyridyl functionalized polysulfones, (**3**) with degrees of functionalization of 80% and 95%, respectively.

Detailed spectroscopic analyses of dipyridyl functionalized polysulfone, (**3**) indicated that the reaction was regiospecific in that functionalization occurred solely on the aromatic rings ortho to the sulfone linkage. The dipyridyl functionalized polysulfones, (**3**) are thermally less stable than the parent polysulfone. The glass transition temperature of the modified polysulfones decreased with higher degree of substitution because of increased chain mobility. Furthermore, the dipyridyl modified polysulfones exhibit improved hydrophilic characteristics with excellent membrane properties and therefore can be considered as suitable polymeric substrate precursors for the preparation of membranes with anti-fouling properties. The membrane obtained from dipyridyl functionalized polysulfone, (**3**) with the higher degree of substitution (PFPS-80) exhibits higher water permeate flux with better structural integrity of the membrane as determined by scanning electron microscopy and atomic force microscopic analysis.

5.2 Atom Transfer Radical Polymerization: Synthesis of Amine Chain End Functionalized Polymers

Amine chain end functionalized polymers with controlled number average molecular weights and narrow molecular weight distributions were prepared by ATRP methods using amine or diamine functionalized unimolecular initiator adducts as initiators for styrene and methyl methacrylate polymerization. The preparation of the specific amine or diamine functionalized initiator adduct was based on the reaction of the appropriate amine or diamine functionalized 1,1-diphenylethylene derivative with (1-bromoethyl)benzene in the presence of CuBr/2,2-bipyridyl catalyst. In addition, telechelic amine functionalized polymers were prepared by a facile post ATRP chain end modification reaction which involve the addition of the specific diamine functionalized 1,1-diphenylethylene derivative to the • -bis(amine) functionalized polymer precursor at the completion of the ATRP process.

A general one-pot atom transfer radical polymerization method was adopted for the synthesis of • -aminophenyl functionalized polystyrene, (**6**) according to the following synthesis pathway:

(a) the preparation of 1-(4-aminophenyl)-1-phenylethylene, (**4**) using 4-aminobenzophenone as a starting material.
(b) the *in situ* synthesis of a new primary amine functionalized initiator adduct, (**5**), obtained from the reaction of (1-bromoethyl)benzene with 1-(4-

aminophenyl)-1-phenylethylene, (**4**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C.

(c) the use of the new primary amine functionalized initiator adduct, (**5**) as initiator for the ATRP of styrene afforded the corresponding •-aminophenyl functionalized polystyrene, (**6**) with predictable number average molecular weights (M_n = 1.62 x 10^3 g/mol to 13.21 x 10^3 g/mol) and narrow molecular weight distributions (M_w/M_n = 1.09 – 1.26) in high initiator efficiency reactions.

A series of well defined •-bis(aminophenyl) and •,• -tetrakis(aminophenyl) functionalized polymers were prepared using the following synthesis strategy:

(a) the synthesis of 1,1-bis(4-aminophenyl)ethylene, (**7**) using 4,4'-diamino-benzophenone as precursor.

(b) the *in situ* synthesis of a new primary diamine functionalized initiator adduct, (**8**), generated by the stoichiometric reaction of (1-bromoethyl)benzene with 1,1-bis(4-aminophenyl)ethylene, (**7**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C.

(c) the utilization of the new primary diamine functionalized initiator adduct, (**8**) as initiator for the ATRP of styrene and methyl methacrylate in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system afforded quantitative yields of •-bis(aminophenyl) functionalized polystyrene, (**9**) and •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**), respectively.

(d) •-bis(aminophenyl) functionalized polymers with number average molecular weights of M_n = 1.09 x 10^3 g/mol to 15.32 x 10^3 g/mol and narrow molecular weight distributions (M_w/M_n = 1.01 – 1.42) were obtained.

(e) •,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**), with M_n = 3.80 x 10^3 g/mol and M_w/M_n = 1.13 and high chain end functionality was prepared in quantitative yields by the post ATRP chain end modification reaction of •-bis(aminophenyl) functionalized polystyrene, (**9**) with excess 1,1-bis(4-aminophenyl)ethylene, (**7**) in a one-pot chain end functionalization reaction.

Similarly, well defined •-bis(4-dimethylaminophenyl) and •,•-tetrakis(4-dimethylaminophenyl) functionalized polymers were prepared according to the following synthesis strategy:

(a) the preparation of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) using 4,4'-bis(dimethylamino)benzophenone as starting material.

(b) the *in situ* preparation of a new tertiary diamine functionalized initiator adduct, (**13**) by the reaction of (1-bromoethyl)benzene and 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C.

(c) the use of the new tertiary diamine functionalized initiator adduct, (**13**) as initiator for styrene and methyl methacrylate polymerization by ATRP methods gave quantitative yields of the corresponding •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) and •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**), respectively.

(d) •-bis(4-dimethylaminophenyl) functionalized polymers with number average molecular weights of $M_n = 1.23 \times 10^3$ g/mol to 16.78×10^3 g/mol and narrow molecular weight distributions (M_w/M_n =1.05 – 1.23) were obtained.

(e) •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) with $M_n = 4.93 \times 10^3$ g/mol and $M_w/M_n = 1.16$ was prepared in quantitative yields and with high chain end functionality by the post ATRP chain end modification reaction of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) and excess of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) in a one-pot chain end functionalization reaction.

The polymerization processes were monitored by gas chromatographic analyses. For all polymerization reactions, polymerization kinetics data shows that the polymerization process for each reaction follows first order rate kinetics with respect to monomer consumption. In addition, polymerization reactions leading to the formation of tertiary amine chain end functionalized polymers proceeded at a faster rate when compared to similar reactions for the preparation of primary amine functionalized polymers. The number average molecular weights of the polymers ($M_n = 1.3 \times 10^3 – 16.4 \times 10^3$ g/mol) increased linearly with percentage monomer conversion and polymers with narrow molecular weight distributions ($M_w/M_n = 1.03 – 1.29$) were obtained.

The organic compounds, amine and diamine substituted 1,1-diphenylethylene initiator precursor derivatives and the functionalized polymers were characterized by nuclear magnetic resonance spectrometry, fourier transform infrared spectroscopy, size exclusion chromatography and non-aqueous titration analysis.

Experimental results show that good control of the number average molecular weight, molecular weight distributions in high initiator efficiency reactions in the solution ATRP syntheses of •-aminophenyl, •-bis(aminophenyl) and •-bis(4-dimethylaminophenyl) functionalized polymers can be obtained using the respective amine functionalized initiator adducts as initiators. The quantitative incorporation of the functionalized 1,1-diphenylethylene fragment into the polymer chain end in the ATRP of styrene and methyl methacrylate and the control of major polymer properties, such as the number average molecular weight, molecular weight distribution and degree of functionalization, is attributed to the formation of the appropriate amine functionalized initiator adduct *in situ* from the specific amine substituted 1,1-diphenylethylene precursor and the subsequent efficient and rapid initiation of styrene and methyl methacrylate to afford the corresponding amine chain end functionalized polymers.

5.3 A New Supported Catalyst System for the Atom Transfer Radical Polymerization of Styrene

One of the limitations of the ATRP process for industrial development is the presence of residual metal catalyst in the final polymer which is detrimental to the quality of the polymer product as well as the environment. A potential way to overcome the drawback of contamination, cost and recovery of the catalyst, is to immobilize the metal catalyst onto a solid carrier, which could be readily removed from the final product and reused for further ATRP reactions.

Well defined polystyrene, (**17**) with predictable number average molecular weight and narrow molecular weight distribution was prepared by ATRP methods using a new polymer supported catalyst system according to the following synthesis process:

(a) the novel synthesis of a new polymeric ligand, dipyridyl functionalized polysulfone, (**3**) by the reaction of lithiated polysulfone with 20% excess of 2,2'-vinylidenedipyridine, (**2**) in THF at -78 °C.

(b) the *in situ* formation of the CuBr/dipyridyl functionalized polysulfone supported catalyst system in diphenyl ether at 110 °C.

(c) the ATRP of styrene in the presence of the CuBr/dipyridyl functionalized polysulfone supported catalyst gave well defined polystyrene, (**17**) with number average molecular weight of 8.13 x 10^3 g/mol and molecular weight distribution of M_w/M_n = 1.14.

The polymerization kinetics data for the styrene polymerization reaction shows first order rate kinetics with respect to monomer consumption and a linear increase in the number average molecular weight as a function of percentage monomer conversion (M_n = 5.1 x 10^3 to 11.3 x 10^3 g/mol). Polymers with narrow molecular weight distributions (M_w/M_n = 1.25 to 1.31) were obtained.

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APPENDIX

PYRIDINE AND AMINE FUNCTIONALIZED POLYMERS BY ANIONIC AND CONTROLLED FREE RADICAL POLYMERIZATION METHODS

by

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SUPERVISOR: PROFESSOR G J SUMMERS

JULY 2009

Student number: 3199-480-6

I declare that PYRIDINE AND AMINE FUNCTIONALIZED POLYMERS BY ANIONIC AND CONTROLLED FREE RADICAL POLYMERIZATION METHODS is my work and that all the sources that I have used or quoted have been indicated and acknowledged by means of complete references.

………………………………… ………………………

SIGNATURE DATE

(MR M.P. NDAWUNI)

The exact wording of the title as it appears on the copies of your dissertation, submitted for examination purposes, should be indicated in the open space

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ABSTRACT

The synthesis of dipyridyl functionalized polysulfones with improved hydrophilicity, enhanced membrane morphology and excellent ATRP polymeric ligand properties was conducted by the following method:

(a) the formation of lithiated polysulfone from unmodified polysulfone and the subsequent reaction with 2,2'-vinylidenedipyridine in tetrahydrofuran at -78 ^{o}C under argon atmosphere to afford the corresponding dipyridyl functionalized polysulfone. The stoichiometry of the reaction affects the degree of functionalization of the product. When equimolar amounts of 2,2'-vinylidenedipyridine are added to the lithiated polysulfone, the degree of functionalization obtained was 45%. However, the addition of 10% and 20% molar excess of 2,2'-vinylidenedipyridine to the corresponding lithiated polysulfone produced dipyridyl functionalized polysulfones with degrees of functionalization of 80% and 95%, respectively; and

(b) the membranes obtained from unmodified polysulfone as well as dipyridyl functionalized polysulfones were characterized by atomic force microscopy, scanning electron microscopy, pure water permeation measurements and contact angle measurements.

Amine chain end functionalized polystyrene and poly(methyl methacrylate) were prepared by Atom Transfer Radical Polymerization (ATRP) methods as follows:

(a) • -Aminophenyl functionalized polystyrene was prepared in quantitative yields by ATRP methods using a new primary amine functionalized initiator adduct, formed *in situ* by the reaction of 1-(4-aminophenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as catalyst in diethyl ether at 110 ^{o}C, for the polymerization of styrene.

(b) New •-bis(aminophenyl) and •,•-tetrakis(aminophenyl) functionalized polymers were prepared in quantitative yields by the ATRP method using the following synthetic strategy:

(i) the initiation of styrene polymerization with a new primary diamine functionalized initiator adduct, generated *in situ* by the reaction of stoichiometric amounts of 1,1-bis(4-aminophenyl)ethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as catalyst, afforded •-bis(aminophenyl) functionalized polystyrene; and
(ii) •-bis(aminophenyl) functionalized poly(methyl methacrylate) was prepared by the ATRP method using the primary diamine functionalized initiator adduct as initiator for methyl methacrylate polymerization; and
(iii) well defined •,•-tetrakis(aminophenyl) functionalized polystyrene was prepared by the post ATRP chain end modification reaction of •-bis(aminophenyl) functionalized polystyrene with 1,1-bis(4-aminophenyl)-ethylene at the completion of the polymerization reaction.

(c) Similarly, •-bis(4-dimethylaminophenyl) functionalized polystyrene was prepared by using a new tertiary diamine functionalized initiator adduct, formed *in situ* by treatment of equimolar amounts of 1,1-bis[(4-dimethylamino)phenyl]-ethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as the catalyst in diphenyl ether at 110 ^{o}C for the initiation of styrene polymerization by the ATRP method. Furthermore, the ATRP of methyl methacrylate, initiated by the new tertiary diamine functionalized initiator adduct, produced •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate). In addition, •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene was synthesized *via* a post ATRP chain end modification reaction of •-bis(4-dimethylaminophenyl) functionalized polystyrene with equimolar amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene at the completion of the polymerization process.

Quantitative yields of the different amine functionalized polymers with predictable number average molecular weights (M_n = 1.3 x 10^3 – 16.4 x10^3 g/mol), narrow molecular weight distributions (M_w/M_n = 1.03 – 1.29) and controlled chain end functionality were obtained.

Polymerization kinetics data was employed to determine the controlled/living character of each ATRP reaction leading to the formation of the different amine chain end functionalized polymers. The polymerization processes were monitored by gas chromatographic analyses. Polymerization kinetics measurements for all reactions show that the polymerizations follow first order rate kinetics with respect to monomer consumption. The number average molecular weight of the amine functionalized polymers increases linearly with percentage monomer conversion and polymers with narrow molecular weight distribution were obtained.

The ATRP of styrene, catalyzed by a novel dipyridyl functionalized polysulfone/CuBr supported catalyst system, afforded well defined polystyrene with predictable number average molecular weight and narrow molecular weight distribution in a controlled/living free radical polymerization process.

The substituted 1,1-diphenylethylene initiator precursor derivatives and the functionalized polymers were characterized by nuclear magnetic resonance spectrometry, fourier transform infrared spectroscopy, thin layer chromatography, column chromatography, size exclusion chromatography, non-aqueous titrations, differential scanning calorimetry and thermogravimetrical analysis.

***Keywords**:* Anionic polymerization, polysulfone, polymer membranes, controlled/living polymerization, atom transfer radical polymerization, amine functionalized polymers, telechelic polymers, amine substituted 1,1-diphenyl-ethylene derivatives, supported catalyst.

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LIST OF FIGURES

LIST OF ABBREVIATIONS

ATRP	Atom Transfer Radical Polymerization
aq	Aqueous
Boc	Butoxycarbonyl
BPO	Benzoyl peroxide
Bu	Butyl
Bpy	2,2'-Bipyridyl
CuBr	Copper bromide
CRP	Controlled Radical Polymerization
DBU	1,8-diazabicyclo(5.4.0)undecen-7-ene
DMA	2-(dimethylamino)ethyl methacrylate
DMF	*N,N*-dimethylformamide
dNbpy	4,4'-Di(*n*-nonyl)-2,2'-bipyridine
DPA	2-(diisopropylamino)ethyl methacrylate
DP	Degree of polymerization
DPE	Diphenyl ether
E^+	Electrophile
Et	Ethyl
Fmoc	9-fluorenylmethoxycarbonyl group
FTIR	Fourier Transform Infrared Spectrometry
HCl	Hydrochloric acid
HMTETA	1,1,4,7,10,10-hexamethyltriethylenetetramine
hrs	Hours
I	Initiator
KF	Potassium fluoride
L	Ligand
Me_6TREN	Tris[2-(dimethylamino)ethyl]amine
M	Monomer
MBP	Methyl 2-bromopropionate
Me	Methyl
MMA	Methyl methacrylate
MPC	2-(methacryloyloxy)ethyl phosphorylcholine
NMP	Nitroxide Mediated Free Radical Polymerization

NMR	Nuclear Magnetic Resonance Spectrometry
PDI	Polydispersity index
PMMA	Poly(methyl methacrylate)
PMDETA	*N,N,N',N'',N''*-pentamethyldiethylenetriamine
Ph	Phenyl
PS	Polysulfone
RAFT	Reversible Addition-Fragmentation Chain Transfer Polymerization
RT	Room temperature
R	Alkyl
SEC	Size Exclusion Chromatography
THF	Tetrahydrofuran
TLC	Thin Layer Chromatography
TEMPO	2,2,6,6-tetramethylpiperidiny-1-oxy
TMS	Tetramethylsilane
wt	Weight

CHAPTER 1

INTRODUCTION

Polysulfone and its derivatives are the most important engineering thermoplastic materials used as precursors to fabricate membranes for many industrial applications such as fuel cell technology[1-13] and liquid and gas separation processes[14-34], electrodialysis and polymer electrolyte membrane electrolysis[35-38]. The chemical and physical characteristics of polysulfone, such as good thermal and chemical stability, mechanical strength and excellent oxidative resistance, make polysulfone the material of choice for use as membrane substrates[1-39]. However, due to its hydrophobic nature, polysulfone membranes are susceptible to fouling[40] by various mechanisms that reduce the application of polysulfone membranes in the treatment of food streams and biological separations. Thus, the synthesis of new functionalized polysulfone polymers and its subsequent use as membrane matrix polymers has been the focus of industrial and academic research in order to meet the increased industrial need for polysulfone membranes with increased hydrophilicity, high flux and low fouling[14-40]. In particular, the regiospecific chemical incorporation of bulky amine groups pendant to the polysulfone chain has been a challenge due to deleterious side reactions associated with amination reactions with polysulfone derivatives[41-44]. The present research focuses on the synthesis of dipyridyl functionalized polysulfones with improved hydrophilicity, enhanced membrane morphological characteristics and excellent ATRP polymeric ligand properties. The polymer functionalization process involves the formation of lithiated polysulfone from unmodified polysulfone and the subsequent reaction with 2,2'-vinylidenedipyridine in tetrahydrofuran at -78 ^{o}C under argon atmosphere to afford the corresponding dipyridyl functionalized polysulfone.

Atom transfer radical polymerization[45] (ATRP) is one of the most versatile and powerful synthetic techniques in polymer science. ATRP allows the synthesis of polymers with well defined number average molecular weight, narrow molecular weight distribution, good control of chain end functionality, composition and molecular architecture. The most common ATRP reaction involves the reversible homolytic cleavage of a carbon halogen bond of an alkyl halide initiator derivative by a redox reaction with a transition metal/ligand complex, followed by monomer addition to form well defined polymers. An essential feature of the ATRP process is the equilibrium between a low concentration of active propagating species and a large number of dormant chains via an electron transfer process promoted by a transition metal/ligand complex. In the classical ATRP process, the topology of the polymer chains is such that the • -terminal group is a halogen atom with the initiator fragment at the •-terminus of the polymer chain. Thus, with the selection of an appropriate functionalized initiator molecule or functionalized initiator system, a wide variety of chain end functionalized polymers can be prepared via the ATRP technique[45].

The use of functionalized 1,1-diphenylethylene derivatives in polymer synthesis provides one of the best polymer synthesis methods to produce well defined polymers[46-52]. The synthesis of chain end functionalized polymers utilizes the addition reactions of active polymer chain ends with functionalized 1,1-diphenylethylene derivatives for the following reasons: (a) the addition is simple and quantitative; (b) due to steric factors, only monoaddition occurs, i.e., no oligomerization of the 1,1-diphenylethylene unit is observed; and (c) a variety of substituted 1,1-diphenylethylene derivatives can easily be prepared by standard organic reactions. By ATRP methods, well defined amine functionalized polymers can be prepared using a general, quantitative, one pot, functionalization method, which employs appropriate amine functionalized 1,1-diphenylethylene derivatives as amine functionalized initiator precursors for the polymerization of styrene and methyl methacrylate[53].

The current study outlines the preparation of new amine chain end functionalized polystyrene and poly(methyl methacrylate) by Atom Transfer Radical Polymerization (ATRP) methods by the following synthetic pathways:

(a) The use of a new primary amine functionalized initiator adduct, formed *in situ* by the reaction of 1-(4-aminophenyl)-1-phenylethylene and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as catalyst in diethyl ether at 110 ^{o}C, for the polymerization of styrene to provide a new method for the synthesis of •-aminophenyl functionalized polystyrene[54].

(b) The synthesis of new •-bis(aminophenyl) and •,•-tetrakis(aminophenyl) functionalized polymers by ATRP methods using the following synthetic strategy:

(i) the initiation of styrene polymerization with a new primary diamine functionalized initiator adduct, generated *in situ* by the reaction of stoichiometric amounts of 1,1-bis(4-aminophenyl)ethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as catalyst, to afford a unique synthetic route for the preparation of •-bis(aminophenyl) functionalized polystyrene;
(ii) the synthesis of •-bis(aminophenyl) functionalized poly(methyl methacrylate) by ATRP methods using the primary diamine functionalized initiator adduct as initiator for methyl methacrylate polymerization; and
(iii) the preparation of well defined •,•-tetrakis(aminophenyl) functionalized polystyrene by a post ATRP chain end modification reaction of •-bis(aminophenyl) functionalized polystyrene with 1,1-bis(4-aminophenyl)-ethylene at the completion of the polymerization reaction.

(c) A new tertiary diamine functionalized initiator adduct, formed *in situ* by treatment of equimolar amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl as the catalyst in diphenyl ether at 110 ^{o}C, can be employed as initiator for styrene polymerization by ATRP methods to provide a new method for the synthesis of •-bis(4-dimethylaminophenyl) functionalized polystyrene. Furthermore, the ATRP of methyl methacrylate, initiated by the new tertiary diamine functionalized initiator adduct, provides a new method for the preparation of •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate). In addition, •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene can be prepared via a post ATRP chain end modification reaction of •-bis(4-dimethylaminophenyl) functionalized polystyrene with equimolar amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene at the completion of the polymerization process.

The current research investigates the polymerization kinetics data of each ATRP reaction to determine the controlled/living character of each ATRP reaction leading to the formation of the different amine chain end functionalized polymers.

Furthermore, one of the limitations of the ATRP process for industrial development is the presence of residual metal catalyst in the final polymer product, which is detrimental to the quality of the polymer product as well as the environment. A potential way to overcome the drawback of contamination, cost and recovery of the catalyst is to immobilize the metal catalyst onto a solid carrier, which could be readily removed from the final product and reused for further ATRP reactions[55]. The present study describes the preparation of a novel dipyridyl functionalized polysulfone/CuBr supported catalyst system and the determination of its efficiency for the ATRP of styrene.

CHAPTER 2

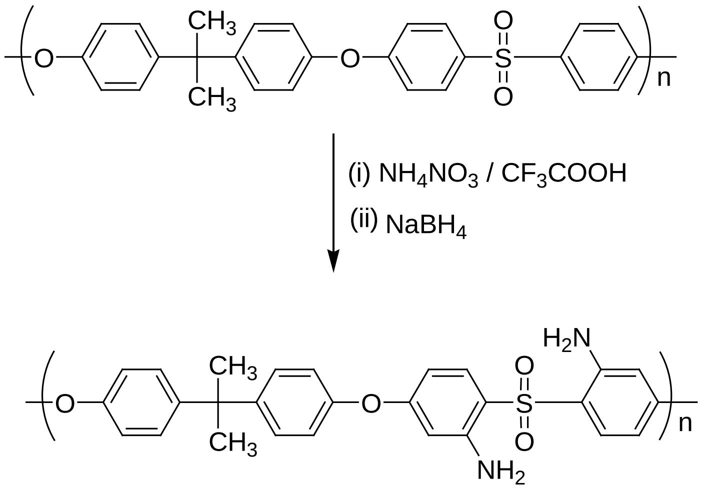
LITERATURE REVIEW

2.1 Chemical Modification of Polysulfone by Anionic Methods

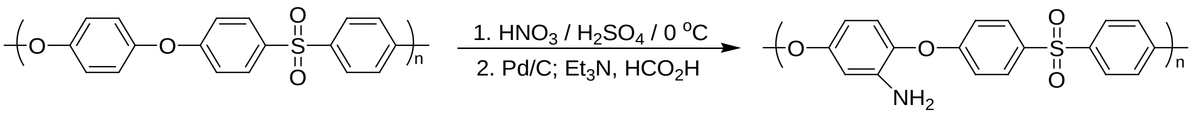
Polysulfone and its derivatives are widely used as engineering thermoplastic materials to fabricate membranes for applications in fuel cell technology[1-13], ultrafiltration, reverse osmosis and liquid and gas separation processes[14-34] such as carbon dioxide stripping from natural gas streams and production of high purity nitrogen from air. In particular, polysulfones are used as ion exchange membranes in electro-membrane processes such as electrodialysis and polymer electrolyte membrane electrolysis[35-38]. The chemical and physical characteristics of polysulfone, such as good thermal and chemical stability, mechanical strength and excellent oxidative resistance, make polysulfone the material of choice for use as membrane substrates[1-39].

However, due to its hydrophobic nature, polysulfone membranes are susceptible to fouling[40] by various mechanisms that reduce the application of the polysulfone membrane in the treatment of food streams and biological separations. Furthermore, it is well known that the incorporation of bulky pendant groups onto the polymer backbone effects significant changes to the gas permeability, permselectivity, mechanical and surface properties of polysulfone membranes. Thus, the synthesis of new functionalized polysulfone polymers and their subsequent use as membrane matrix polymers have been the focus of industrial and academic research in order to meet the increased industrial need for polysulfone membranes with increased hydrophilicity, high flux and low fouling[14-40]. In particular, the regiospecific introduction of amine groups pendant to the polysulfone chain has been a challenge since the rigorous reaction conditions lead to uncontrolled, multiple sites of amination as well as chain scission and cross-linking without any control of the degree of functionalization.

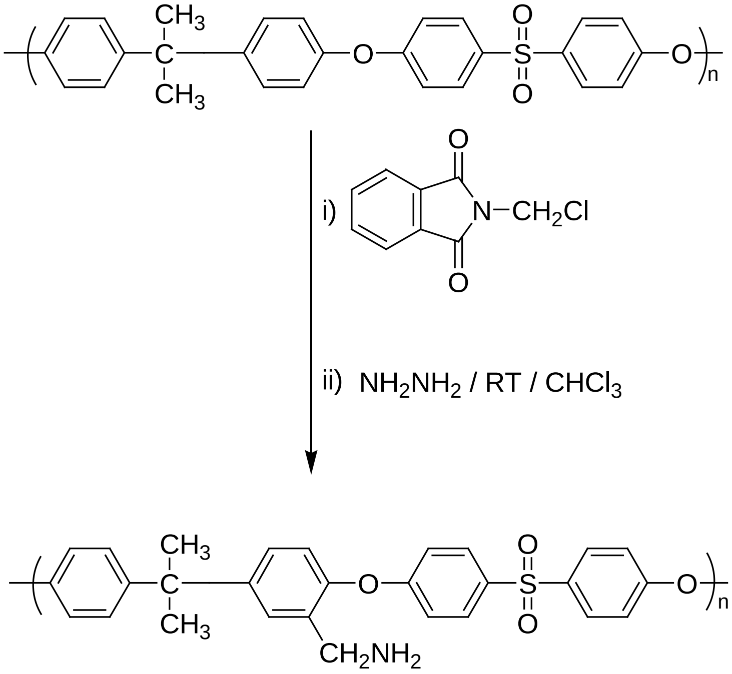
Several reviews on the chemical modification of polysulfone by different chemical mechanisms to effect the facile introduction of the functional groups onto the polysulfone backbone have been reported[1-44]. For example, Daly and coworkers[41] reported the amination of polysulfone by the direct nitration of polysulfone with an ammonium nitrate/trifluoroacetic acid mixture. The intermediate nitro derivative was converted to the amine by reduction with sodium borohydride. However, some degree of polymer degradation was observed without any control of the position and degree of functionalization:



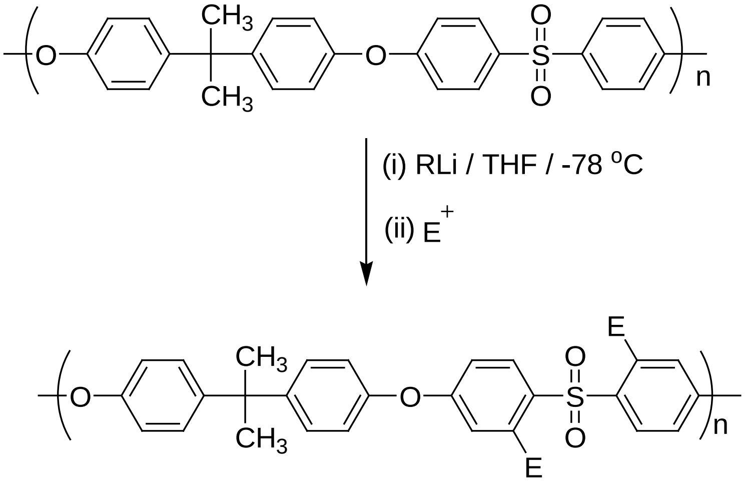
Naik[42] and Conningham[43] reported a more efficient amine functionalization process which involves the nitration-reduction reactions of poly(ether ether sulfones) and poly(ether sulfones), respectively. Each process shows that the polysulfone is nitrated exclusively on the hydroquinone unit. The reduction of the nitro group affords the corresponding amine functionalized polysulfone derivative:



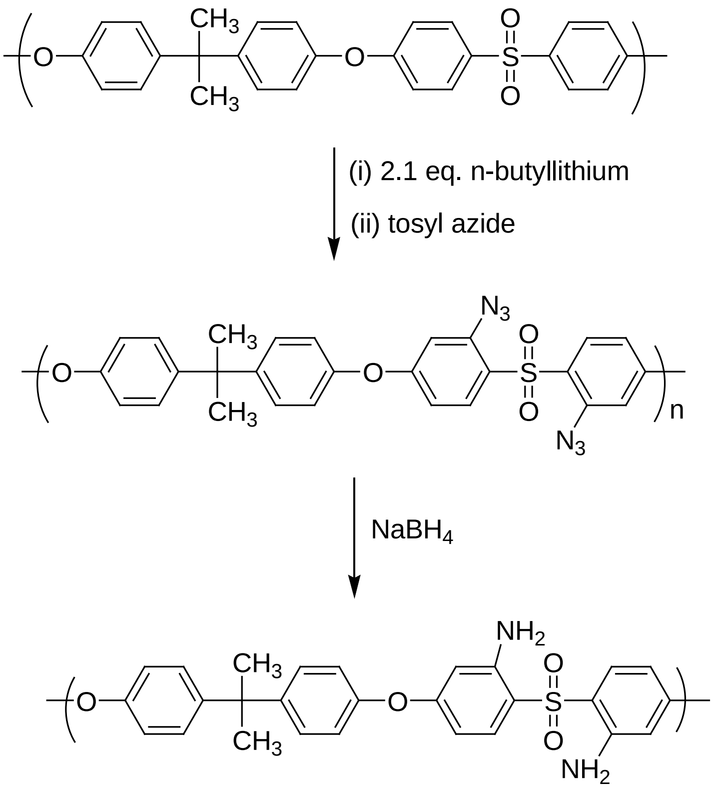
Kahana and coworkers[44] reported the introduction of the amine functionality on the polysulfone backbone using the phthalimido methylation route with N-chloromethyl phthalimide as reagent:



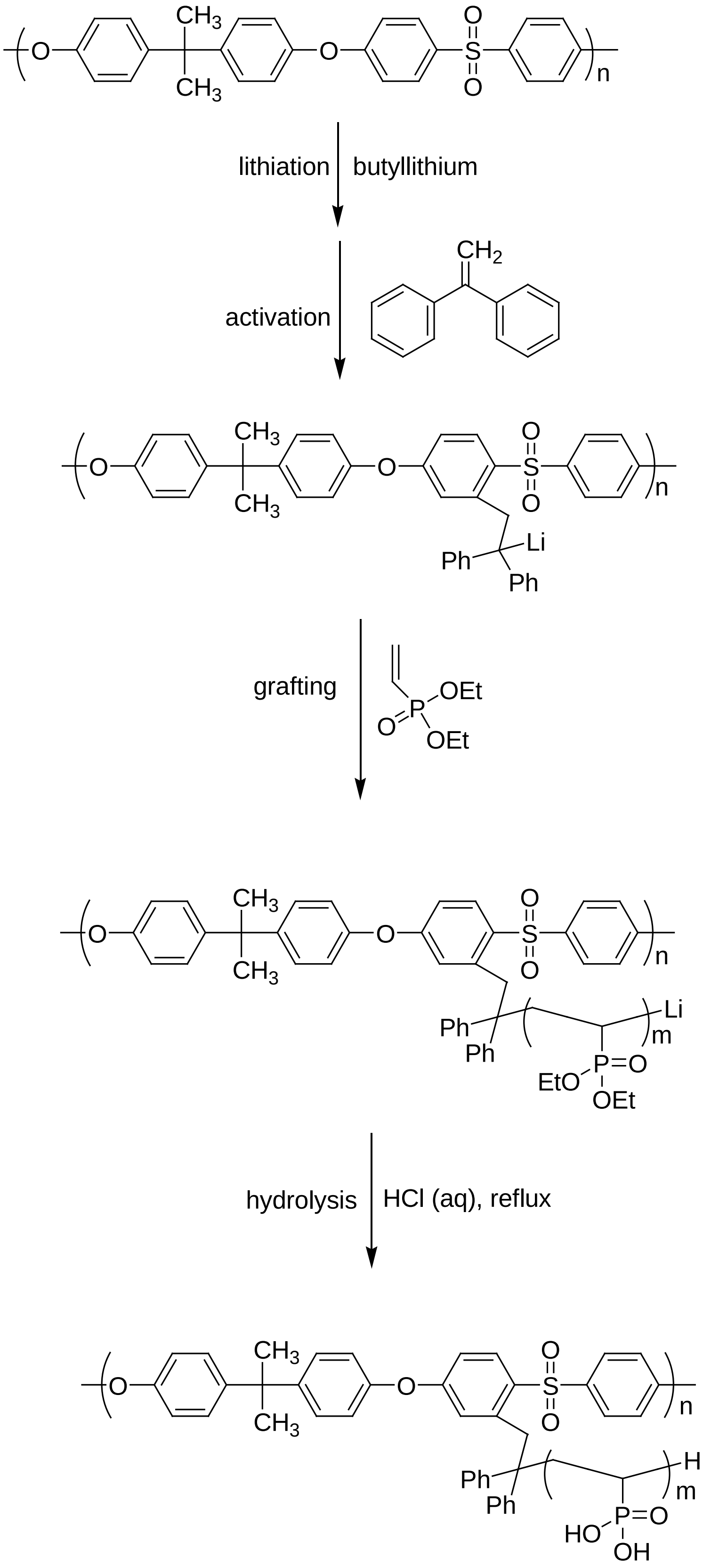
To meet the demand for a regiospecific, well controlled polymer modification reaction, a more attractive, site specific and efficient approach in the chemical modification of polysulfone is required. Guiver and coworkers[14-17,35-37] developed a novel route, which was later exploited by Jannasch and coworkers[1-7] for the regiospecific introduction of functional groups on the polysulfone backbone. The process involves the chemical modification of commercially available polysulfone using carbanion chemistry to introduce functional groups onto the polymer backbone. By the treatment of unmodified polysulfone with an organolithium compound and the subsequent reaction of the lithiated polysulfone derivative with the appropriate electrophiles afforded a wide variety of functionalized polysulfone derivatives in quantitative yields. The lithiation process is well controlled and takes place regiospecifically at the ortho position relative to the sulfone groups of the polymer backbone. The subsequent addition of different electrophilic systems (E^+) leads to the introduction of different functional groups such as the carboxyl, halogen, alkyl, aldehyde, sulfonate, primary amine and silyl groups pendant to the polymer backbone[14-17,35-37], as outlined as follows:



In particular, for the preparation of amine functionalized polysulfone, unmodified polysulfone was reacted directly with *n*-butyllithium at low temperature. The lithiated polysulfone was then converted quantitatively to the azide polysulfone derivative by treatment with tosyl azide. Subsequent reduction of the azide groups to the primary amine groups by the addition of sodium borohydride gave the amine functionalized polysulfone in quantitative yields. The polymeric amine precursors are used extensively in cross-linking or chain extension reactions to achieve reduced brittleness in thermosetting resins:



Recently, Jannasch and coworkers[5-7] prepared mechanically strong and flexible polysulfone membrane substrates by grafting poly(vinylphosphonic acid) side chains onto polysulfone. Lithiation of unmodified polysulfone by butyllithium produced lithiated polysulfone which acted as initiator for the anionic polymerization of diethylvinylphosphate from the polysulfone backbone. The direct polymerization from the lithiated sites on polysulfone gave very low yields of the designed product even after long reaction times. Thus, to overcome the inefficient nucleophilic power and the initiating capacity of the lithiated polysulfone, 1,1-diphenylethylene was added to the reaction mixture to form the diphenylalkyllithium anion prior to the addition of the diethylvinylphosphate monomer. Polymerization proceeded *via* a well controlled reaction and, after the quantitative cleavage of the ester function, polysulfone-g-poly(vinylphosphonic acid) copolymers were produced:

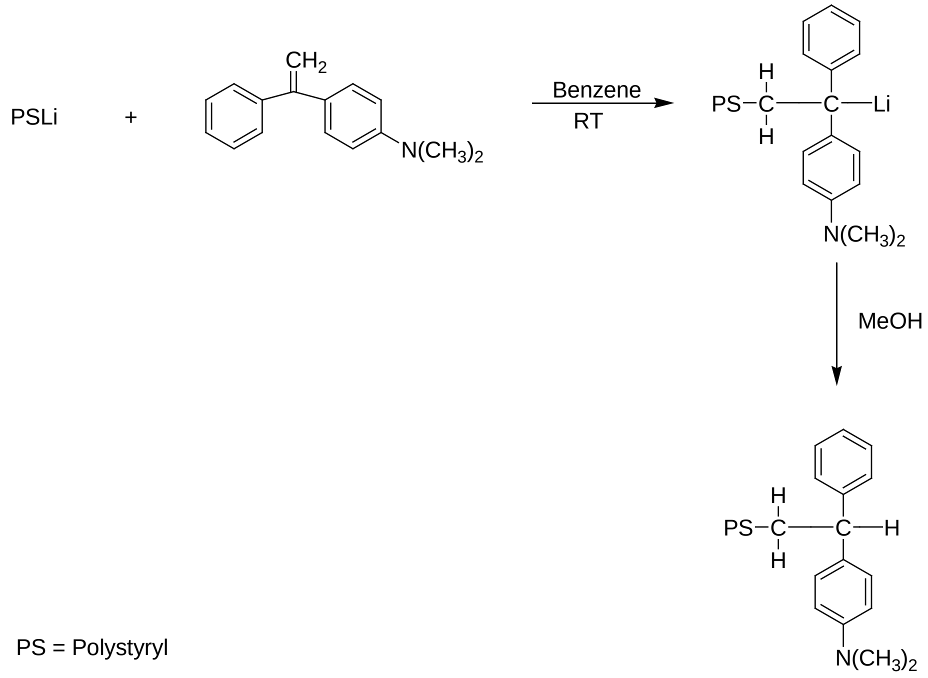


lithiation
butyllithium
activation
grafting
hydrolysis
HCl (aq), reflux

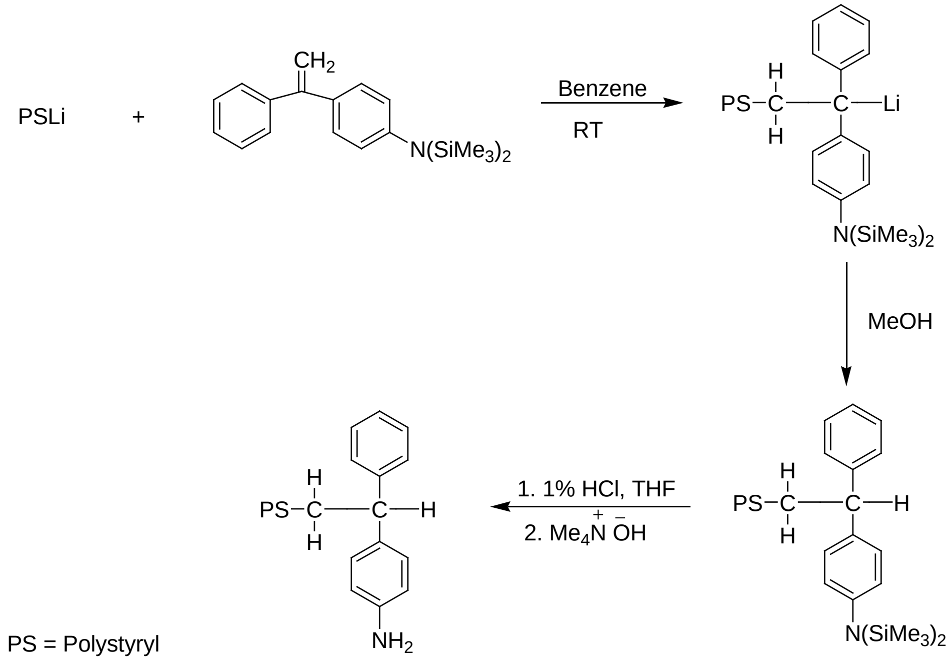
The results indicate that the crossover reaction of lithiated polysulfone with the bulky 1,1-diphenylethylene electrophile proceeded quantitatively with the introduction of only one 1,1-diphenylethylene unit pendant to the polymer chain. In the current study, the preparation of dipyridyl functionalized polysulfone is described[39]. The method involves the quantitative lithiation of polysulfone and subsequent addition of 2,2'-vinylidenedipyridine to produce the corresponding dipyridyl functionalized polysulfones with degrees of functionalization ranging between 45% - 95% as determined by proton nuclear magnetic resonance spectrometry. The functionalized polymers were characterized by size exclusion chromatography, ^{1}H NMR, FTIR, differential scanning calorimetry and thermogravimetric analysis. Membranes obtained from unmodified polysulfone as well as dipyridyl functionalized polysulfones were characterized by atomic force microscopy, scanning electron microscopy, pure water permeation measurements and contact angle measurements.

2.2 Functionalization of Polymers with 1,1-Diarylethylene Derivatives

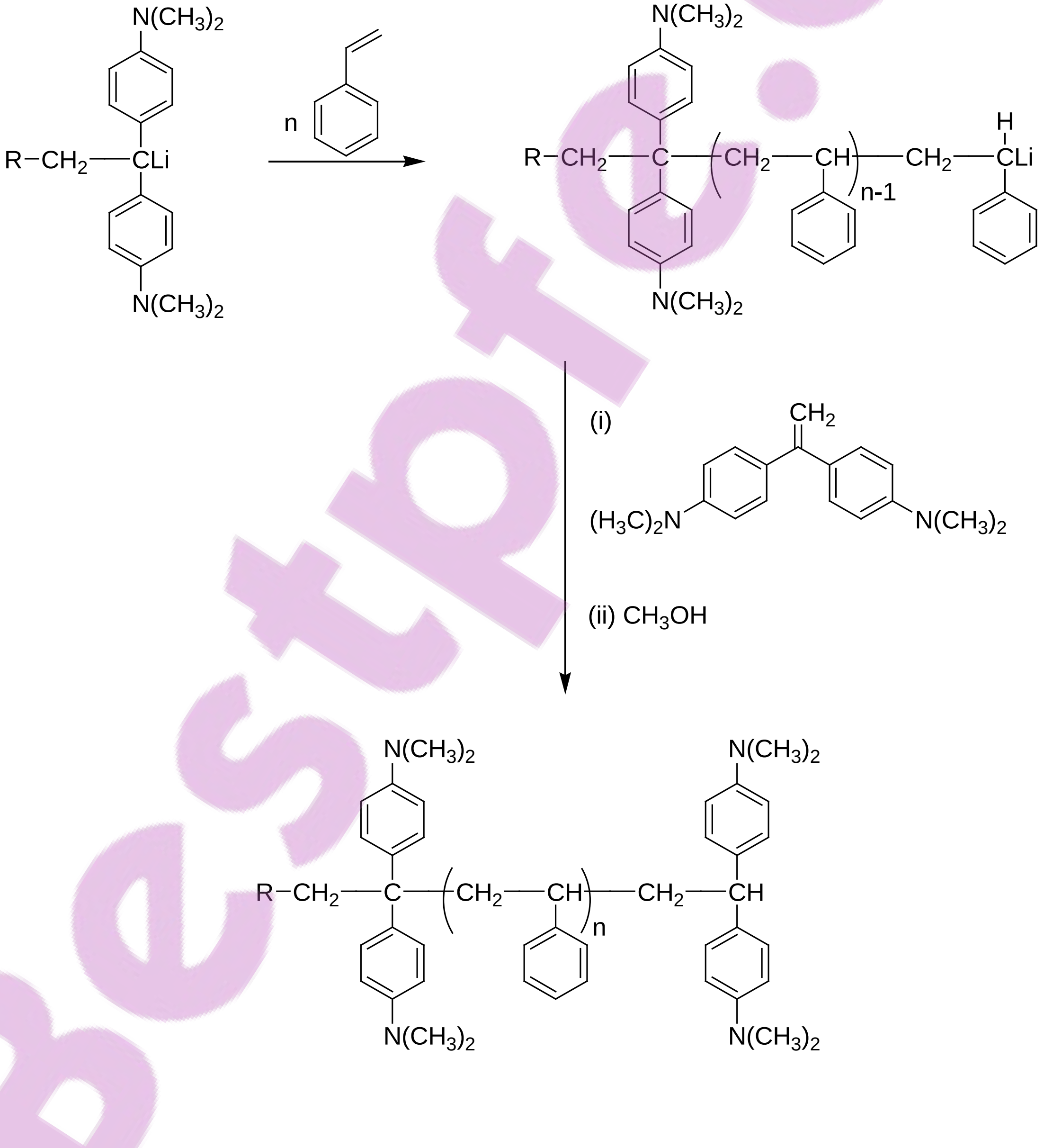
The reaction of polymeric carbanionic centers with functionalized 1,1-diphenylethylene derivatives is one of the most versatile methods for the introduction of functional groups at the polymeric chain end. Quirk and coworkers[46-51] developed a general, quantitative, living, anionic functionalization method, independent of the specific functional group, based on the addition reaction of simple and polymeric organolithium compounds to 1,1-diphenylethylene derivatives. A feature of such reactions is that, due to steric effects, the 1,1-diphenylethylene unit does not homopolymerize and undergo only quantitative monoaddition reactions with the anionic species. Thus, the functionalized 1,1-diphenylethylene unit readily reacts with organolithium compounds to quantitatively produce 1:1 adducts. For example, dimethylamino functionalized polystyrene was prepared by the reaction of polystyryllithium (PSLi) with 1-[4'-(N,N-dimethylaminophenyl)]-1-phenylethylene[46] as outlined below:



Similarly, • -aminopolystyrene[51] was prepared in quantitative yields by reacting polystyryllithium with 1-[4'-{N,N-bis(trimethylsilyl)amino}phenyl]-1-phenylethylene in benzene at room temperature, followed by the removal of the silyl protecting group by hydrolysis with 1% concentrated HCl and neutralization with 20 wt% $Me_4N^+OH^-$ in methanol:



Recently, Kim and coworkers[52] outlined an anionic chain end functionalization reaction whereby tertiary amine groups are introduced at one end or at both ends of the polymer chain using 1,1-bis[(4-dimethylamino)phenyl]ethylene as functionalizing agent. Functionalized polymers with aromatic tertiary amine groups at both the • - and • - termini of the polymer chain were prepared by the crossover reactions of *n*-butyllithium with the diphenylethylene analogue to form an initiator intermediate for styrene polymerization, followed by the chain end functionalization reaction by the addition of 1,1-bis[(4-dimethylamino)phenyl]-ethylene at the end of the polymerization process:



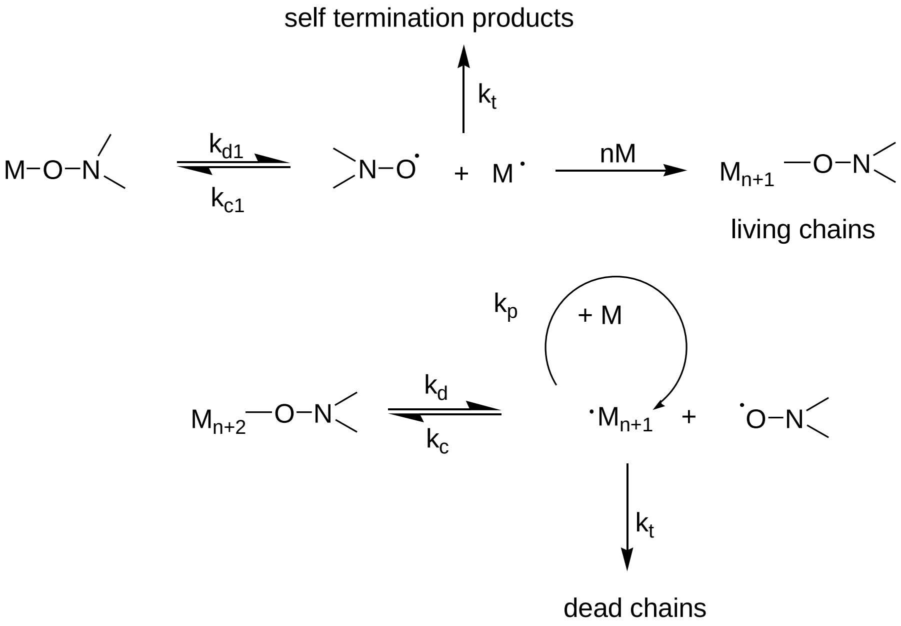
The current research work describes the synthesis of functionalized polymers *via* controlled free radical polymerization using functionalized 1,1-diphenylethylene compounds as amine initiator precursors. The method involves the preparation of well defined primary and tertiary amine functionalized polymers by a general, quantitative, one pot ATRP functionalization process, using appropriate functionalized initiator systems derived from primary and tertiary amine substituted 1,1-diphenylethylenes as well as post ATRP chain end functionalization reactions.

2.3 Free Radical Polymerization

Free radical polymerization is the most widely used industrial method for the preparation of polymers. The advantages of conventional free radical polymerization are its low reactant purity reactions and that a wide variety of monomers can undergo polymerization and copolymerization under simple experimental conditions. However, polymers with no control of the number average molecular weights and molecular weight distributions are obtained. The high concentration of reactive free radicals cause side reactions, such as termination and chain transfer reactions, to take place to a great extent. Hence, more controlled polymerization techniques are needed for the preparation of polymers with well-defined structures. Several new controlled/living free radical polymerization methods (CRP), which allow the preparation of well defined polymers by free radical mechanisms, were developed over the past decade. The most widely used CRP methods for the synthesis of well defined polymeric materials are nitroxide mediated free radical polymerization (NMP)[56], reversible addition-fragmentation chain transfer polymerization (RAFT)[57] and atom transfer radical polymerization (ATRP)[45].

2.3.1 Nitroxide Mediated Free Radical Polymerization

To overcome the deficiencies of uncontrolled polymer growth experienced in the traditional free radical process, the nitroxide mediated free radical polymerization (NMP) method, having characteristics of a living polymerization process, has been developed[58]. The NMP method is the simplest of the various techniques currently used for CRP.[59] The technique is based on the reversible dissociation of a (macro)alkoxyamine[60] species, which decreases the irreversible termination reactions. As a result, a majority of dormant living chains can grow until the monomer is consumed, producing a polymer with equal chain length and with a reactive chain end:

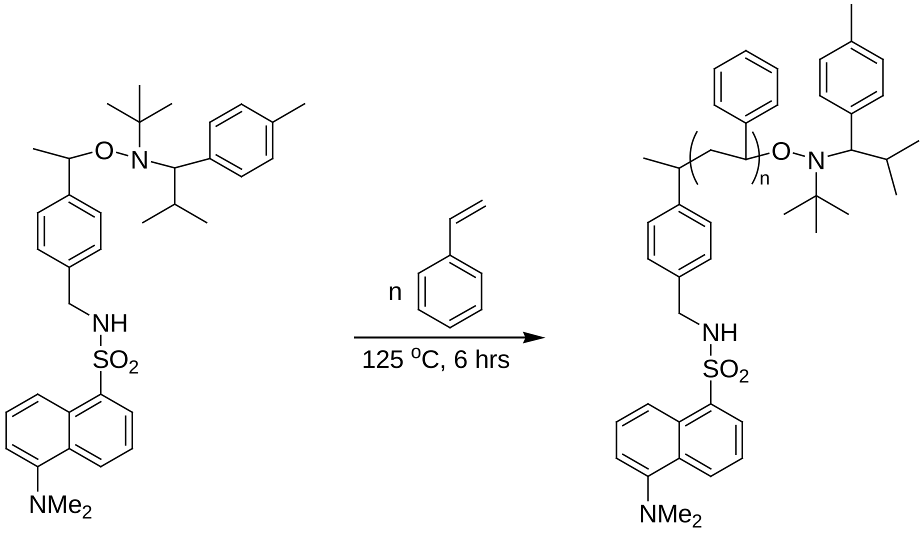


Although the NMP method may not strictly obey the definition of a living polymerization, it does satisfy many of the requirements, hence the use of the terms “living” or “pseudoliving”. The stimulus for the current interest in the NMP process is the report of Georges[61], where it is shown that polystyrene with narrow molecular weight distribution can be prepared using a mixture of benzoyl peroxide (BPO) and 2,2,6,6-tetramethylpiperidiny-1-oxy (TEMPO) as an initiating system.

The success of the NMP method can be related to the ability of stable nitroxide free radicals, such as TEMPO, to react at near diffusion controlled rates with the carbon centered free radical of the growing polymer chain end in a thermally reversible process. The process dramatically lowers the concentration of free radicals in the polymerization system and, coupled with the inability of the nitroxide free radicals to initiate new chain growth, leads to controlled polymerization. The features of the NMP process have been exploited in the preparation of star and graft polymers[62-65], hyperbranched systems[66] and random and block polymers with narrow molecular weight distributions[63-,66].

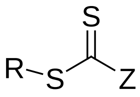
The NMP method has been applied to the polymerization of styrene and its derivatives as well as the copolymerization of styrenics with other monomers such as acrylates, methacrylates and acrylonitriles[67]. However, poor control in the polymerizations of monomers other than styrenics[68] have been obtained by the NMP method.

The NMP method has been exploited for the preparation of chain end functionalized polymers using functionalized unimolecular initiators. For example, Hawker[69] and Braslau[70] prepared amine chain end functionalized polymers by using amine functionalized alkoxyamine initiators for styrene polymerization. Incorporation of the amine chain end functionality of greater than 97% into polymers was achieved and polymers with number average molecular weights up to 70 000 g/mol were obtained:



2.3.2 Reversible Addition-Fragmentation Chain Transfer Free Radical Polymerization

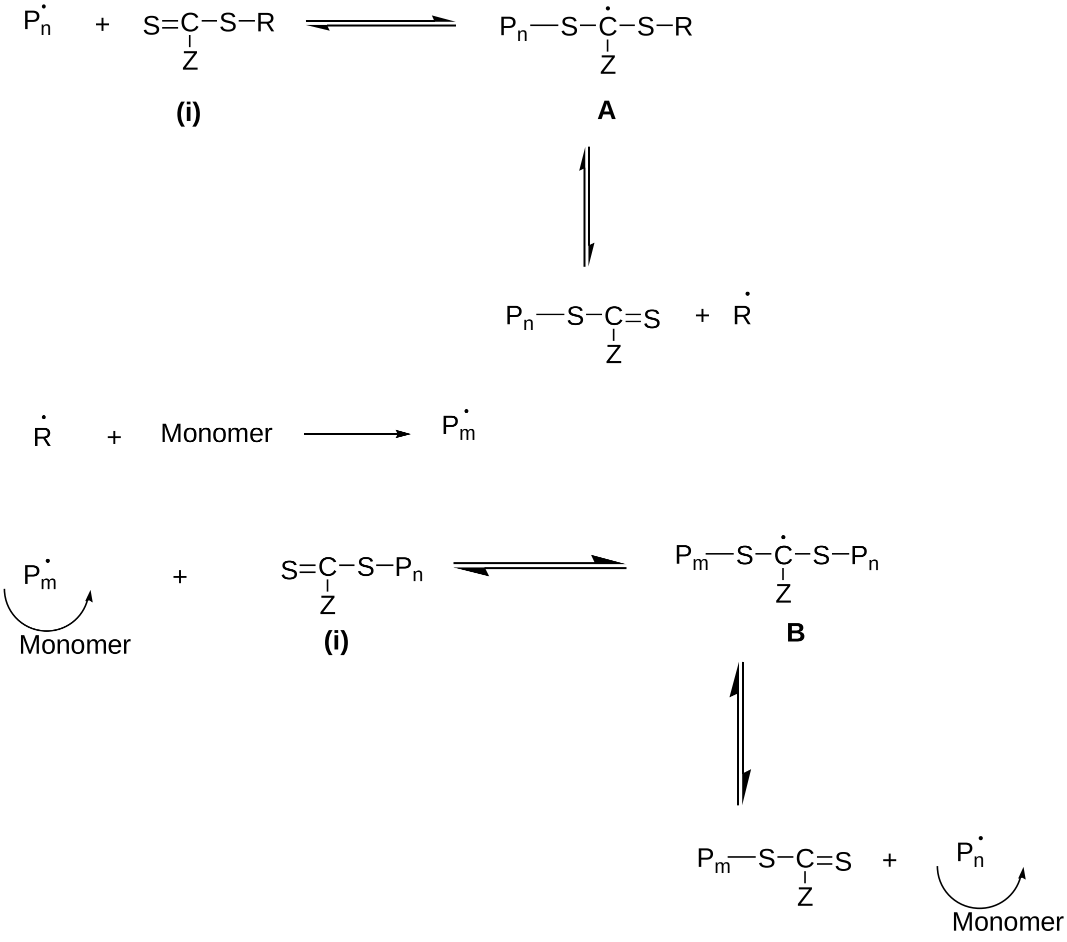
Reversible addition-fragmentation chain transfer free radical polymerization (RAFT) is a versatile and robust controlled free radical polymerization process based on the use of a conventional radical polymerization initiator in the presence of (thiocarbonyl)sulfanyl compounds of general structure S=C(Z)-SR (**i**)[71].



(i)

ii) Z = Ph, R = $C(CH_3)_2Ph$
iii) Z = Ph, R = $CH(CH_3)Ph$
iv) Z = Ph, R = CH_2Ph
v) Z = Ph, R = $C(CH_3)(CN)CH_2CO_2Na$
vi) Z = Ph, R = $C(CH_3)(CN)(CH_2)_2CO_2H$
vii) Z = Ph, R = $C(CH_3)_2CN$
viii) Z = CH_3, R = CH_2Ph
ix) Z = Ph, R= $C(CH_3)(CN)CH_2CH_2OH$

The (thiocarbonyl)sulfanyl compound **(i)** acts as an efficient reversible addition fragmentation chain transfer agent and confers living characteristics to the polymerization. RAFT can be distinguished from other controlled/"living" free radical polymerization methods by its use in the polymerization of a wide range of monomers with varying reaction conditions. In each case, RAFT provides polymers with controlled number average molecular weights and narrow molecular weight distributions (usually <1.2). The RAFT process involves free radical polymerization in the presence of reagent **(i)** as shown below:



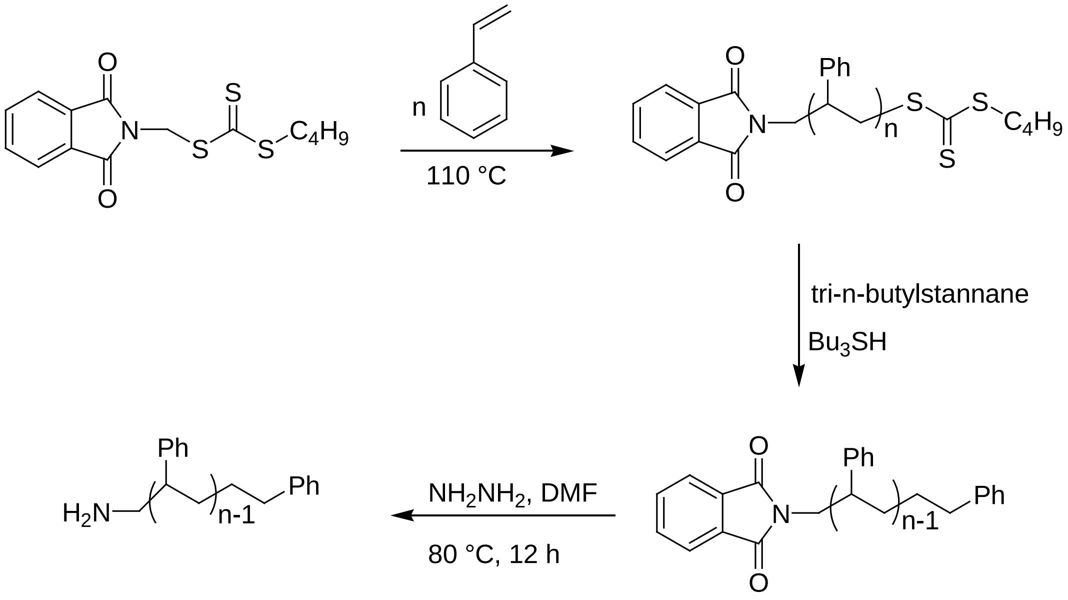
Addition of a propagating radical ($P^\bullet_n$) to a (thiocarbonyl)sulfanyl compound **(i)** gives an adduct radical **A** which can fragment to form a polymeric (thiocarbonyl)sulfanyl compound P_n-SC(Z)=S and a new radical $R^\bullet$. The reaction of $R^\bullet$ with a monomer M forms a new propagating radical $P^\bullet_m$. A dynamic equilibrium is subsequently established between the active propagating radical ($P^{\bullet}_{n}$ and $P^{\bullet}_{m}$) and dormant polymeric (thiocarbonyl)sulfanyl compounds (P_n-S-C(Z)=S) such that there is an equal probability of growth for all chains, resulting in polymers with narrow molecular weight distributions[72].

The effectiveness of reagents **(i - ix)** in providing living character to the RAFT process is attributed to their very high transfer constants which ensure a rapid rate of exchange between dormant and living chains. The choice of Z and R in reagent **(i)** is crucial to the success of the RAFT process. To ensure a high transfer constant, Z should activate (or at least not deactivate) the C=S double bond toward radical addition. Suitable Z groups are aryl and alkyl groups. The R group should be a good free radical leaving group (e.g. cumyl, cyanoisopropyl) and the expelled radical should be effective in reinitiating free radical polymerization.

RAFT can be carried out in bulk, solution, emulsion or suspension polymerization processes. The advantage of the RAFT process is its compatibility with a very wide range of monomers including functional monomers containing acid (e.g. acrylic acid), acid salt (e.g. styrene-sulfonic acid sodium salt), hydroxyl (e.g. hydroxyl ethyl methacrylate) or tertiary amine (e.g. dimethylaminoethyl methacrylate) groups. The RAFT process can also be used for the preparation of block copolymers with narrow molecular weight distributions[73].

The RAFT polymerization method can be adapted for the synthesis of end functionalized polymers by the careful choice of the RAFT agent[57]. If the R-groups of the RAFT agent contain a functional group, •-functionalized polymers are obtained. For example, Moad and coworkers[74] prepared amine functionalized polymers by introducing the amine functionality *via* a phthalimido methyl RAFT precursor. The synthesis of •-phthalimidomethylpolystyrene involved the use of a phthalimido RAFT agent for the initiation of styrene polymerization at 110 °C. Hydrazinolysis of the phthalimido end group afforded a polymer with the desired

• -amino functionality. The RAFT agent functionality was removed prior to deprotection of the amine group by reaction with tri-n-butylstannane as outlined below:



2.4 Atom Transfer Radical Polymerization

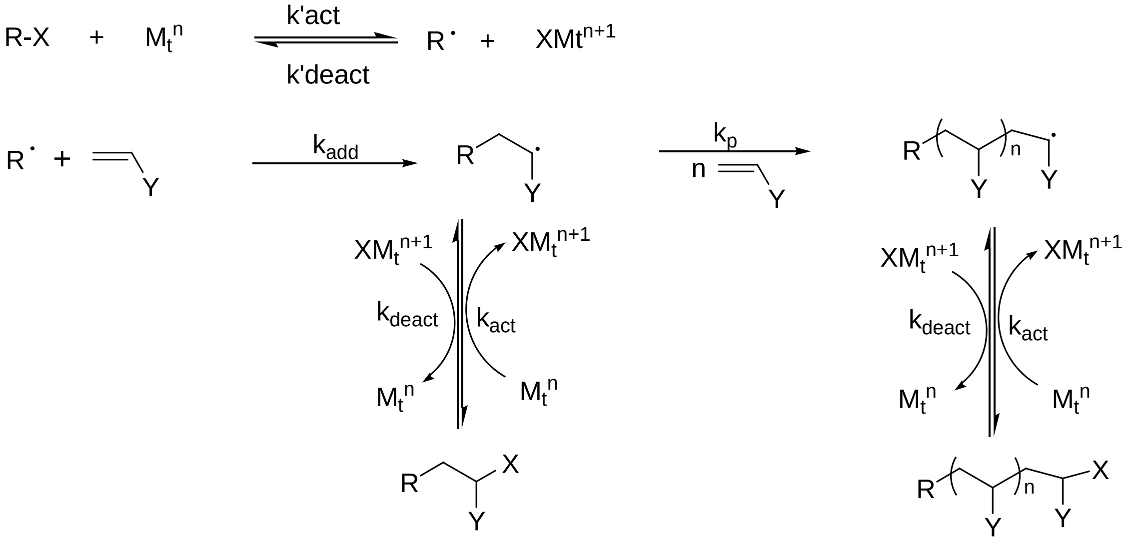
Transition metal catalyzed free radical polymerization was developed independently by Matyjaszewski and Wang[75,76] and Sawamoto and coworkers[77] in 1995. In particular, the copper mediated method, called atom transfer radical polymerization (ATRP) has proven to be more successful for the controlled/"living" (co)polymerization of a wide range of monomers including styrenes, acrylates and methacrylates. In the classical ATRP method, developed from redox catalyzed telomerization reactions[78] as well as atom transfer radical addition reactions (ATRA)[79], a transition metal/ligand complex catalyst acts as a carrier of the halogen atom in a reversible redox process[80,81] during the ATRP method.

The ATRP technique is a powerful tool for the synthesis of polymers with controlled number average molecular weights, narrow molecular weight distributions, controlled chain functionality, composition and morphology[76,82,83].

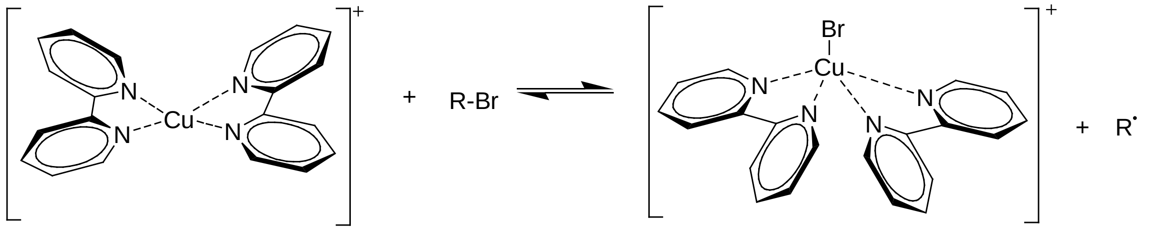
The classical ATRP method encompasses the reversible homolytic cleavage of a carbon-halogen bond of an alkyl halide initiator molecule in the presence of transition metal salt complexed with a suitable bi- or tridentate ligand as catalyst, followed by the addition of the monomer to form a polymer. Controlled radical polymerization is based on the maintenance of a low, stationary concentration of the active free radical species and the establishment of a fast, dynamic equilibrium between the active and dormant species[84,85].

2.4.1 Mechanism of Atom Transfer Radical Polymerization

In the ATRP method, the active species is formed when the halogen in the alkyl halide is abstracted by the metal complex, M_t^n, to form the oxidized species, XM_t^{n+1} and the carbon centered radical, $R^\bullet$. In the subsequent step the radical $R^\bullet$ reacts with an alkene $CH_2=CHY$ to form a transient radical $R\text{-}CH_2CHY^\bullet$ species. The reaction between XM_t^{n+1} and $R\text{-}CH_2CHY^\bullet$ results in the target product $R\text{-}CH_2CHY\text{-}X$ and regenerates the reduced transition metal species M_t^n which again reacts with R-X to promote a new redox cycle[76] as illustrated in the following reaction scheme:



In the ATRP process, the deactivation rate must be higher than the activation rate in order to create a low concentration of propagating radicals. Thus, the equilibrium between the dormant and the active species must be greatly shifted towards the dormant species. If deactivation is very slow or non-existent, the polymerization reaction becomes uncontrolled[86]. The overall rate of the reaction is highly dependent on the redox potential of the metal complexes:



The ATRP process in the presence of copper as catalyst takes place in two major kinetic steps: initiation and propagation. Termination reactions also occur, but no more than a few percentages of the growing chains undergo termination in ATRP reactions[76].

Initiation

$$\text{R-X} \quad + \quad \text{Cu(I)X/ligand} \quad \rightleftharpoons \quad \text{R}^{\bullet} \quad + \quad \text{X-Cu(II)X/ligand}$$

(X=Cl, Br)

$$\text{R}^{\bullet} \quad + \quad \text{monomer} \quad \xrightarrow{k_p} \quad \text{P}_1^{\bullet}$$

Propagation

$$\text{P}_n\text{-X} \quad + \quad \text{Cu(i)X/ligand} \quad \overset{K_{eq}}{\rightleftharpoons} \quad \text{P}_n^{\bullet} \quad + \quad \text{X-Cu(II)X/ligand}$$

$$\text{P}_n^{\bullet} \quad + \quad \text{monomer} \quad \xrightarrow{k_p} \quad \text{P}_{n+1}^{\bullet}$$

Termination

$$\text{P}_n^{\bullet} \quad + \quad \text{P}_m^{\bullet} \quad \xrightarrow{k_t} \quad \text{P}_{n+m}$$

The following rate laws are derived from the initiation and propagation steps:[87]

$$K_{eq} = \frac{k_{act}}{k_{deact}} = \frac{\left[P^{\bullet}\right]\left[Cu(II)X\right]}{\left[Cu(I)\right]\left[PX\right]}$$

$$R_p = k_p\left[P\right]\left[M\right] = k_p K_{eq}\left[I\right]_0 \frac{\left[Cu(I)X\right]}{\left[Cu(II)X\right]}\left[M\right]$$

R_p is based on the assumption that the termination step can be neglected and that a fast pre-equilibrium is established. The propagating rate (R_p) of the polymerization process is first order with respect to monomer concentration [M], initiator concentration [I] and activator concentration [Cu(I)X]. However, in the beginning, the reaction is negative with respect to deactivator concentration [Cu(II)X]. This is due to the persistent radical effect and the irreversible formation of Cu(II)X in the initial stages of the polymerization[88].

There are three primary experimental features which determine a controlled/”living” free radical polymerization[89] process, namely:

(i) the first order rate plot of $\ln[M]_0/[M]$ versus time should be linear. This is an indication that the concentration of active radical species is constant throughout the reaction. The plot should have a gradient equal to the pseudo first order rate coefficient, K^{app}, which gives an indication of the rate of reaction. K^{app} is defined by:

$$\ln\frac{[M]_0}{[M]} = K_p\left[Pol^{*}\right]_t = K^{app}t$$

where [M] is the monomer concentration, $[M]_0$ is the initial monomer concentration, K_p is the propagation rate coefficient, [Pol*] is the concentration of active propagating species and t is time.

(ii) the molecular weight distributions of the polymers should be below 1.5.

(iii) an observed increase in the number average molecular weight of the polymer as monomer conversion proceeds should be linear, indicating that all the chains are growing at the same rate, described by the equation below:

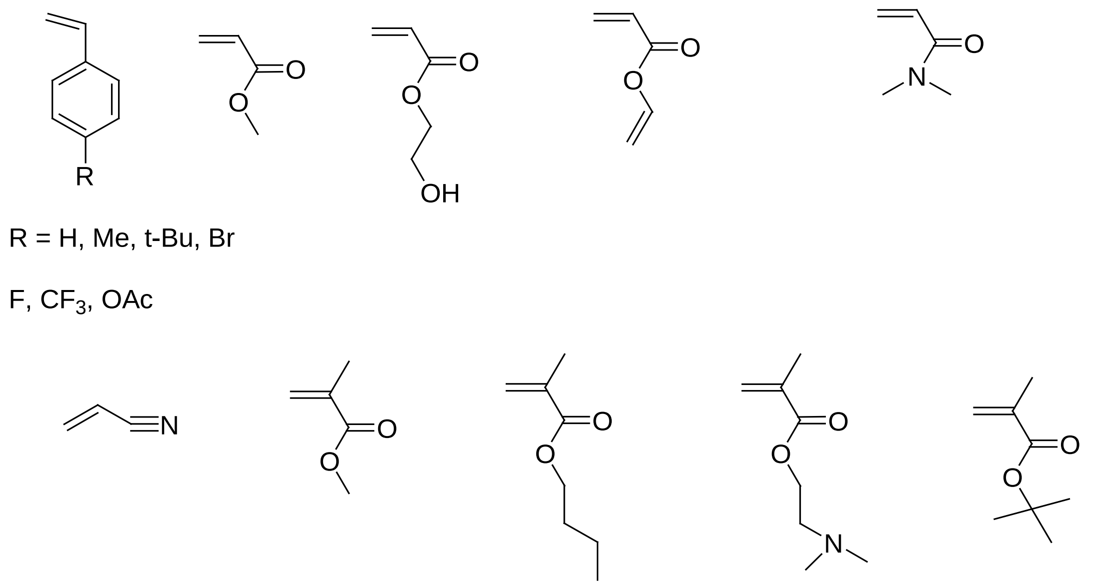
$$M_n^{theory} = \frac{\%conversion}{100} \frac{[M]_0}{[I]_0} MW_m + MW_i$$

where $[M]_0$ and $[I]_0$ are the initial concentrations of monomer and initiator respectively, and MW_M and MW_i are the molecular weights of monomer and initiator, respectively.

2.4.2 Characteristics of the ATRP reaction

Monomers

A variety of vinyl monomers such as styrenes[76,88-92], acrylates[76,77,93-97] and methacrylates[92,96,98-104] undergo polymerization by ATRP methods. Other monomers such as acrylonitrile[105,106] and (meth)acrylamide[107-109], which contains substituents that can stabilize a propagating radical, also undergo facile ATRP reactions. Some examples of monomers that undergo polymerization by ATRP methods are shown below:



R = H, Me, t-Bu, Br

F, CF_3, OAc

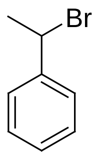
Initiators

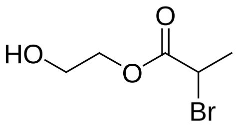
In ATRP reactions, the initiator generates the growing chains. Thus, the initiator concentration determines the molecular weight of the resulting polymer. The theoretical degree of polymerization (DP) can be calculated according to the following equation[110]:

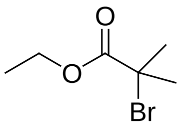
$$DP = \frac{[M]_o}{[I]_o} \text{ x conversion}$$

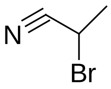
In ATRP reactions, the initiator is typically an alkyl halide (RX). For the formation of polymers with narrow molecular weight distributions, it is important that the initiation rate is higher than the propagating rate, in order to get all the chains growing at the same time. Incomplete initiation leads to polymers with higher number average molecular weights than the targeted values and with broader molecular weight distributions[86]. Another important factor is that the initiator must show little or no tendency to undergo side reactions. It has been shown that tertiary alkyl halides are better initiators than the secondary and primary alkyl halides, respectively.

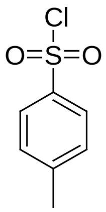
Other variables that are important to take into account when choosing initiators are steric effects, polar properties and redox potentials[111]. One easy rule to follow is that the R-group in the alkyl halide should be similar in structure to that of the monomer. For example, (1-bromoethyl)benzene is usually used for the polymerization of styrene[76]. Compounds such as ethyl-2-bromoisobutyrate and ethyl-2-bromopropionate are used for the polymerization of (meth)acrylates[92] and 2-bromopropionitrile can be used for acrylonitrile polymerization[105,106]. However, other initiators work well for different monomers. The halogen atom in ATRP initiators is usually a bromine or chlorine atom. The ATRP of acrylates[112] and styrene[90,91] with iodine-based initiators has been reported. Organofluorine compounds do not work in ATRP due to the strong C-F bond, which cannot undergo homolytic cleavage. Some examples of ATRP initiators are shown below:

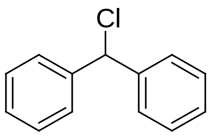


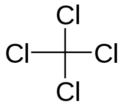










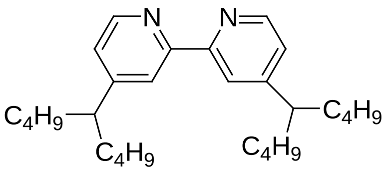


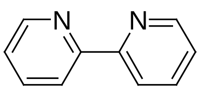
Transition metals

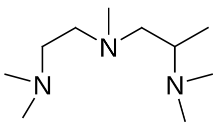
Several transition metal catalysts have been used in transition metal catalyzed free radical polymerization reactions. Catalyst based on copper is by far the most widely used metal catalyst due to its relatively low cost and versatility in ATRP reactions. However, other metals such as iron[92,103,113], ruthenium[77,114-117], nickel[101,118,119], molybdenum[120,121], rhenium[112], rhodium[122] and palladium[123] have also been used as catalysts for the polymerization of a variety of monomers. The requirements of the metal are that it should (a) have an accessible one-electron redox couple, (b) have a reasonable affinity towards a halogen atom, (c) have a coordination sphere around the metal and (d) be able to increase in oxidation state by one in order to selectively accommodate a new ligand. Also, the metal should have a low affinity for other atoms such as hydrogen atoms and alkyl radicals[45].

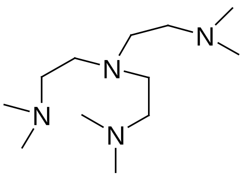
Ligands

A large variety of ligands have been used in conjunction with the different transition metals in ATRP reactions. The ligand is an important part of the ATRP catalyst system and its role is three-fold. First, the ligand solubilizes the metal in the organic media. Second, the ligand controls catalyst selectivity by steric effects and electronic factors. Finally, by their electronic effects, ligands also affect the redox chemistry of the final metal complex. Copper is usually ligated with nitrogen-based ligands. The following scheme shows some examples of bidentate [4,4'-di-5''-nonyl-2,2'-bipyridine, (dNbpy) and 2,2'-bipyridyl, (bpy)], tridentate [pentamethyldiethylenetriamine, (PMDETA)][124] and tetradentate [tris[2-(dimethylamino)ethyl]amine, (Me_6TREN)] [125] ligands that have been used in copper-based ATRP reactions:









Iron is usually ligated by phosphine base ligands such as tributylphosphine or triphenylphosphine[92,103], but can also be used in conjunction with nitrogen based ligands. Phosphorus-based ligands are also used to complex other metals in ATRP reactions such as rhenium, ruthenium, rhodium, nickel and palladium.

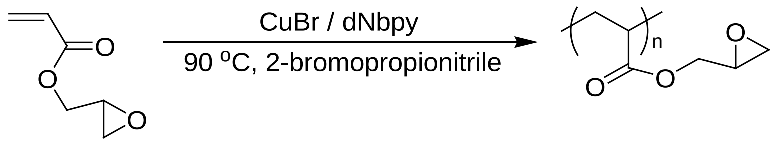
2.5 Functionalized Polymers by ATRP

The synthesis of functionalized polymers with well-controlled architecture and predictable number average molecular weight is currently of great academic and industrial interest. Polymers bearing reactive functional groups have potential applications in several areas such as reactive processing, catalysis, drug delivery and compatibilization of polymer blends[126-129]. Atom transfer radical polymerization (ATRP) is one of the most successful controlled/living free radical polymerization processes employed for the preparation of functionalized polymers[45,130-132]. The preparation of functionalized polymers by ATRP methods can be achieved *via* four different synthetic strategies:

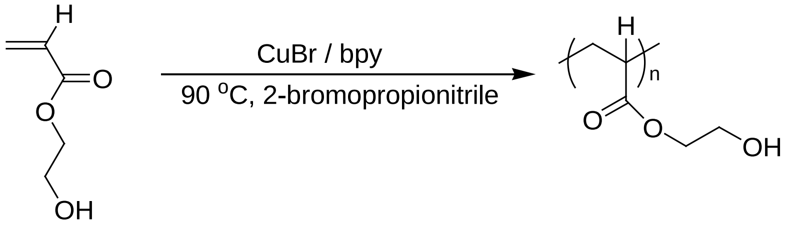
a) the atom transfer radical polymerization of functionalized monomers.
b) the post polymerization modification of monomer units along the polymer chain.
c) the post polymerization chain end functionalization of the carbon-halogen bond.
d) the use of functionalized initiators for the ATRP of vinyl monomers.

a) The atom transfer radical polymerization of functionalized monomers:

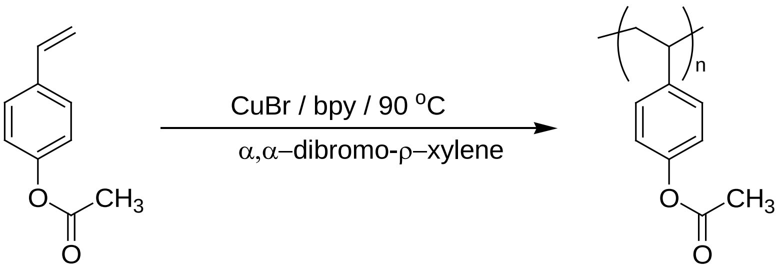
A number of monomers containing different polar functional groups undergo polymerization by the ATRP method[133-140]. However, reactive monomers such as vinyl acetate, vinylchloride and •-olefins[141] do not undergo controlled ATRP reactions. Matyjaszewski and coworkers[142] reported the ATRP of glycidyl acrylate to form well defined polymers with high number average molecular weights and narrow molecular weight distributions containing the reactive glycidyl group. Subsequent modification reactions of poly(glycidyl acrylate) are possible since the pendant oxirane rings can undergo ring opening reactions.



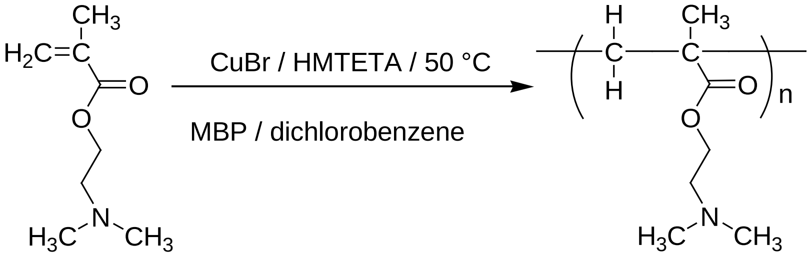
In addition, Matyjaszewski and coworkers[143] prepared hydroxyl functionalized polymers by the ATRP of 2-hydroxyethyl acrylate at 90 °C to give water-soluble polymers with applications in the field of coatings and biomaterials:



Gao and coworkers[144] introduced the ester functionality into a polymer by using a substituted styrene monomer in ATRP reactions. The monomer used was 4-acetoxystyrene. The number average molecular weights of the polymers increased linearly with monomer conversion and the molecular weight distributions of the polymers remained low throughout the polymerization
(M_w/M_n = 1.11-1.18):

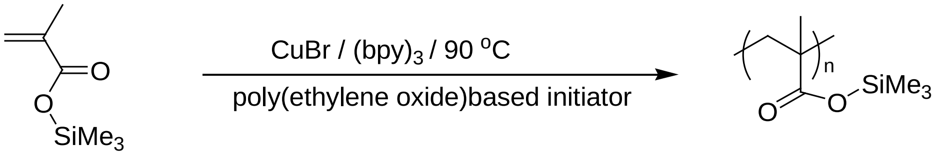


Zhang and coworkers[145] described the synthesis of tertiary amine functionalized polymers by the ATRP of 2-(dimethylamino)ethyl methacrylate to give well defined polymers with number average molecular weights up to M_n = 20 000 g/mol and M_w/M_n = 1.25. The amine functionalized polymers are water-soluble and find applications in the fields of environmental protection, drug delivery and sensors. However, polydentate ligands were used to avoid any interaction between the polar dimethylamino group of the monomer and the catalyst/ligand complex:



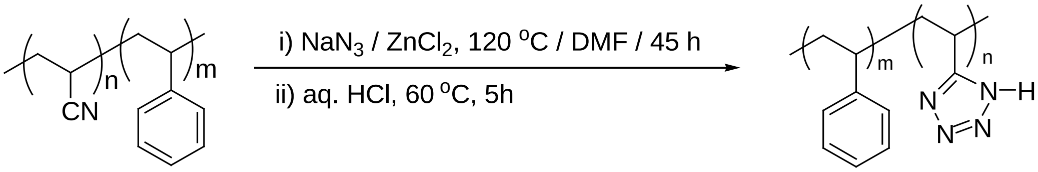
b) The post polymerization modification of monomer units along the polymer chain

Acidic monomers, such as (meth)acrylic acid, isomeric vinylbenzoic acids, unsaturated sulfonic or phosphonic acids cannot undergo direct polymerization *via* the ATRP method due to protonation and subsequent 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 protected acidic functional groups[45] as outlined in the following synthesis pathway:



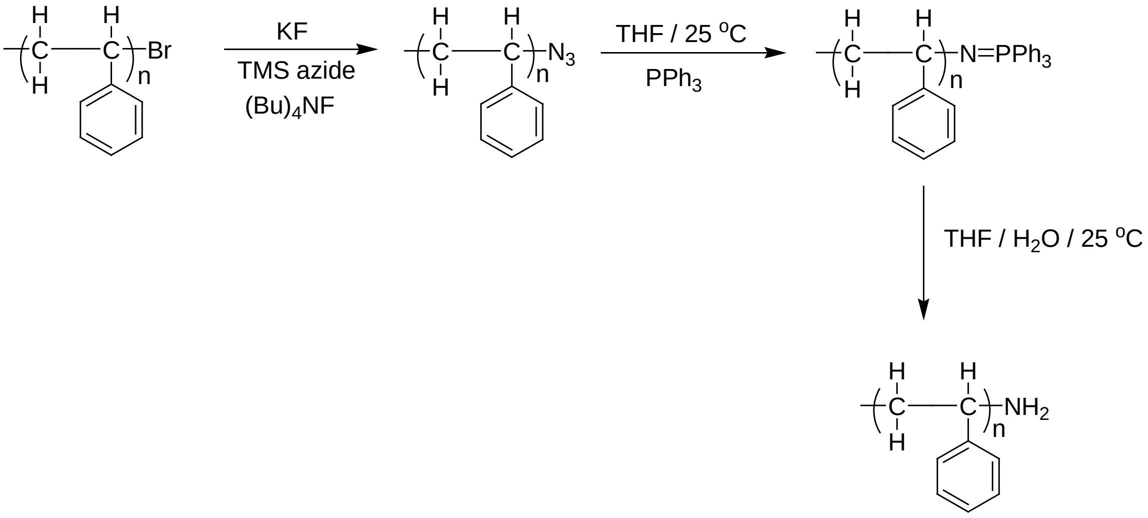
Subsequent removal of the protecting group produces the corresponding polymers with the free acid functional group.

In addition, the ATRP of vinyl tetrazoles has not been reported because of potential interaction of the acidic and coordinating properties of the tetrazole group with the ATRP catalyst system. Therefore, well defined tetrazole containing polymers are prepared by the copolymerization of styrene and acrylonitrile by ATRP methods followed by a "click" chemistry type of chemical modification of the polyacrylonitrile section to yield the desired material[146]:

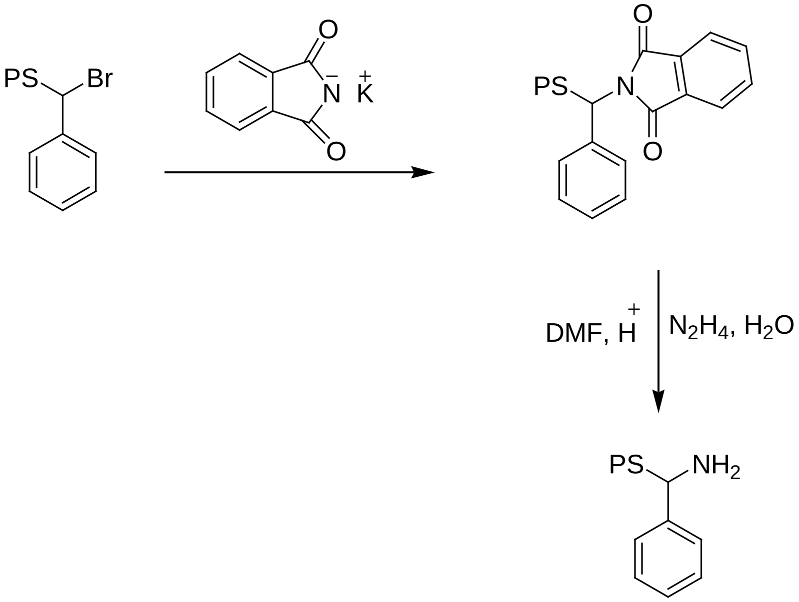


c) Post polymerization chain end functionalization of the carbon-halogen bond

The carbon-halogen end functionality, which is present on the active chain end of polymers prepared by ATRP methods, particularly polystyrene or polyacrylates, can undergo nucleophilic substitution reactions[141,147-153] to form other functional groups such as the hydroxyl, allyl, azido and ammonium or phosphonium groups in excellent yields. Matyjaszewski and coworkers[141,147-150] reported the substitution of the halogen end groups by azides in THF using TMS azide in the presence of potassium fluoride and a catalytic amount of tetrabutylammonium fluoride. The azide group was first converted to the phosphoranimine end group and subsequent hydrolysis leads to the formation of the amino end group:

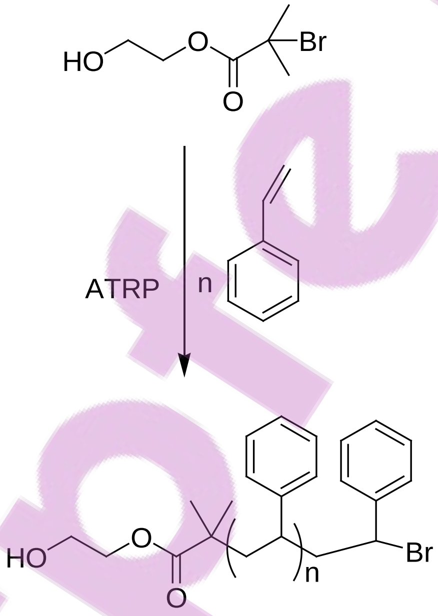


Moad and coworkers[154] reported the synthesis of amine chain end functionalized polystyrene through intermediary phthalimido end-functionalized polystyrene. Pthalimido groups are then converted to amine groups by hydrazinolysis according to an Ing-Manske procedure:



d) The use of functionalized initiators for the ATRP of vinyl monomers

In the ATRP process, the topology of the polymer chain is such that the • -terminal group is a halogen atom with the initiator fragment at the •-terminus of the polymer chain. Thus, with the selection of the appropriate functional group on the initiator molecule, a wide variety of telechelic polymers can be prepared *via* the ATRP technique[155-160]. Initiators bearing functional groups such as the hydroxyl, amine, epoxy, aldehyde and carboxylic acid groups were employed in the initiation of styrene polymerization to afford the corresponding chain end functionalized polystyrenes with the functional group introduced at the •-terminus of the polymer chain[45,147]. To illustrate the efficiency of such reactions, recently, Sarbu and coworkers[161] introduced a hydroxyl functionality at the •-terminus of the polymer chain by using 2-hydroxyethyl 2-bromoisobutyrate as an initiator for the ATRP of styrene to form a well-defined polymer with high end group functionality:

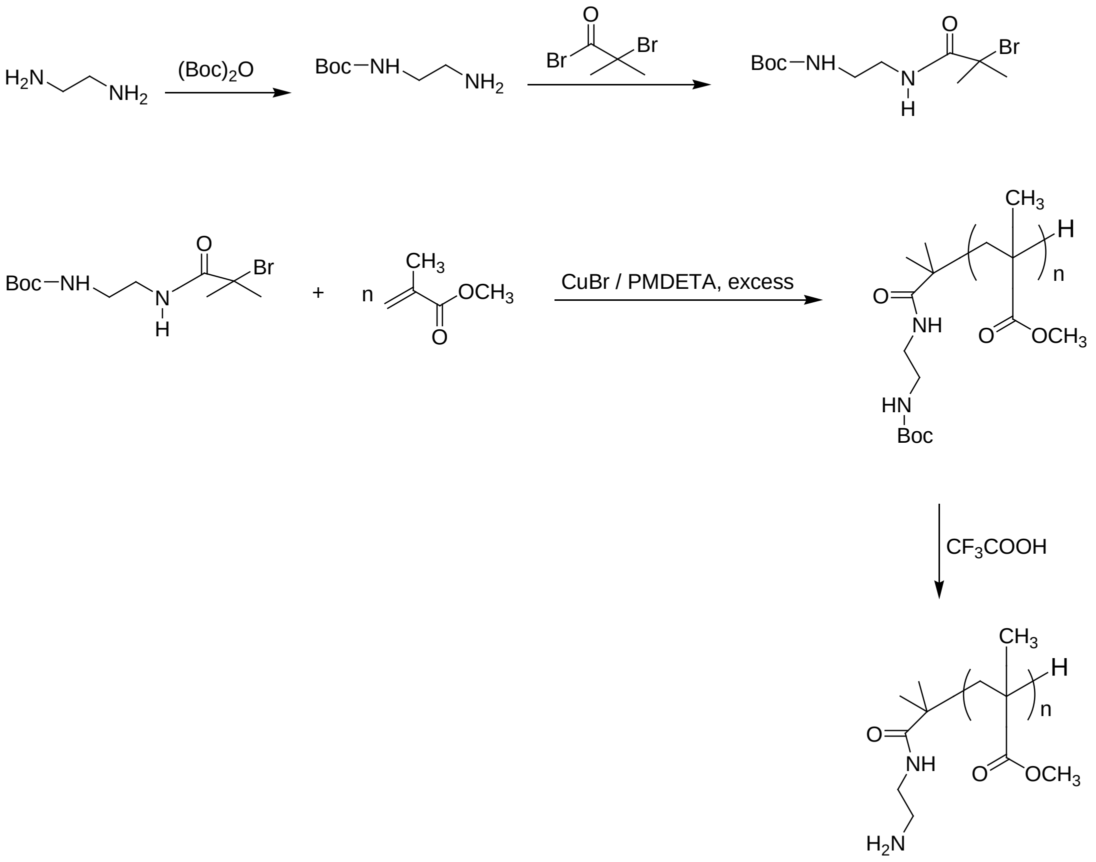


2.5.1 Amine Functionalized Initiators for ATRP

The most common ATRP reaction encompasses the reversible homolytic cleavage of a carbon-halogen bond of an alkyl halide initiator derivative by a redox reaction with a transition metal/ligand complex followed by monomer addition to form well defined polymers. In particular, the control of the initiation step in the ATRP reaction is directly dependant on the initiator reactivity and the rapid formation and stability of the catalyst/ligand system. The ligands used in the ATRP catalyst system are mostly bidentate and multidentate amine molecules. Thus, for the synthesis of well defined amine polymers, appropriately designed amine functionalized initiators are required for successful ATRP reactions whereby the interaction between the amine functionality and the catalyst/ligand system is reduced.

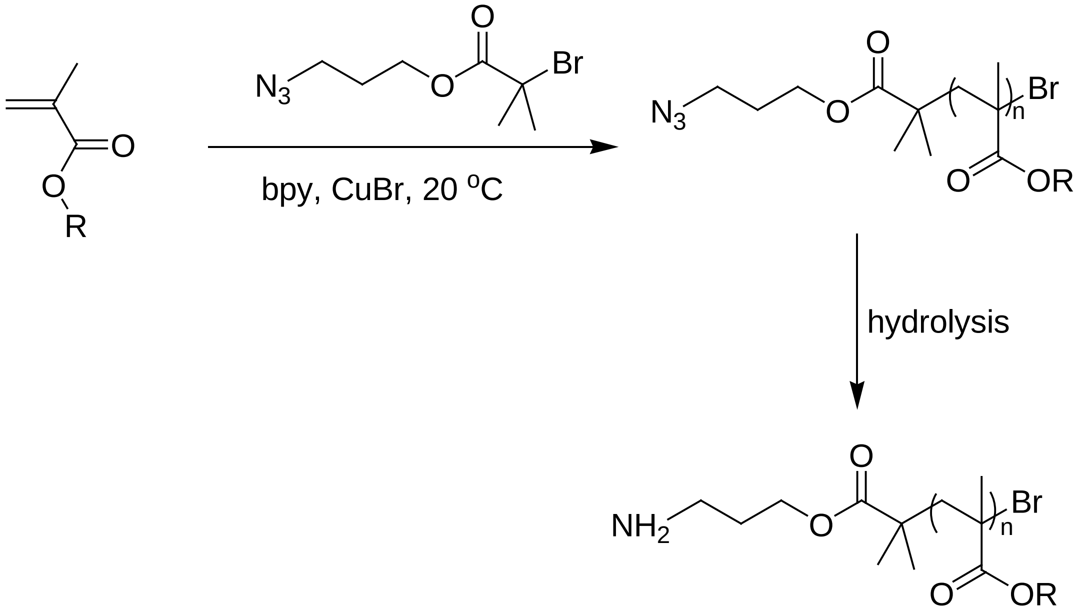
2.5.1.1 Primary Amine Functionalized Initiators for ATRP

Since the ligands which are used to complex with the metal in ATRP reactions are mostly multidentate amine derivatives and to reduce the possible interaction between the amine functional group and the ATRP catalyst system, many indirect methods, which involve the use of protected primary amine unimolecular initiators, has been adopted for the preparation of • -primary amine functionalized polymers by ATRP methods. Recently, Pionteck[162,163] prepared primary amine chain end functionalized poly(methyl methacrylate) by ATRP methods by using a Boc protected amine compound, (N-Boc-ethylamino)-2-bromoisobutanamide, as an initiator of methyl methacrylate polymerization:

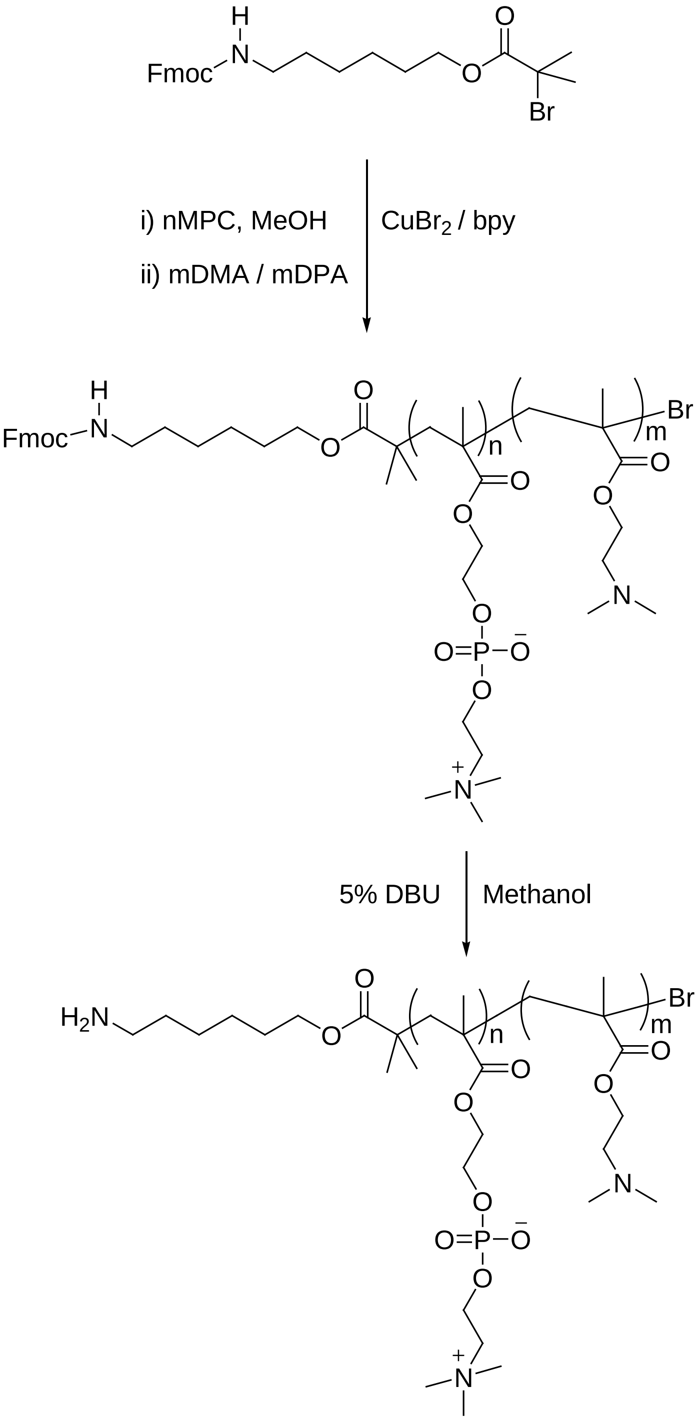


The reactions show that the amine group is first protected to avoid possible side reactions of the amine group with the catalyst system. After complete polymerization, the tert-butyloxycarbonyl (Boc) protecting group is removed by treating the polymer with trifluoroacetic acid in dichloromethane, producing the corresponding •-amine functionalized poly(methyl methacrylate) in quantitative yields and with high degree of chain end purity.

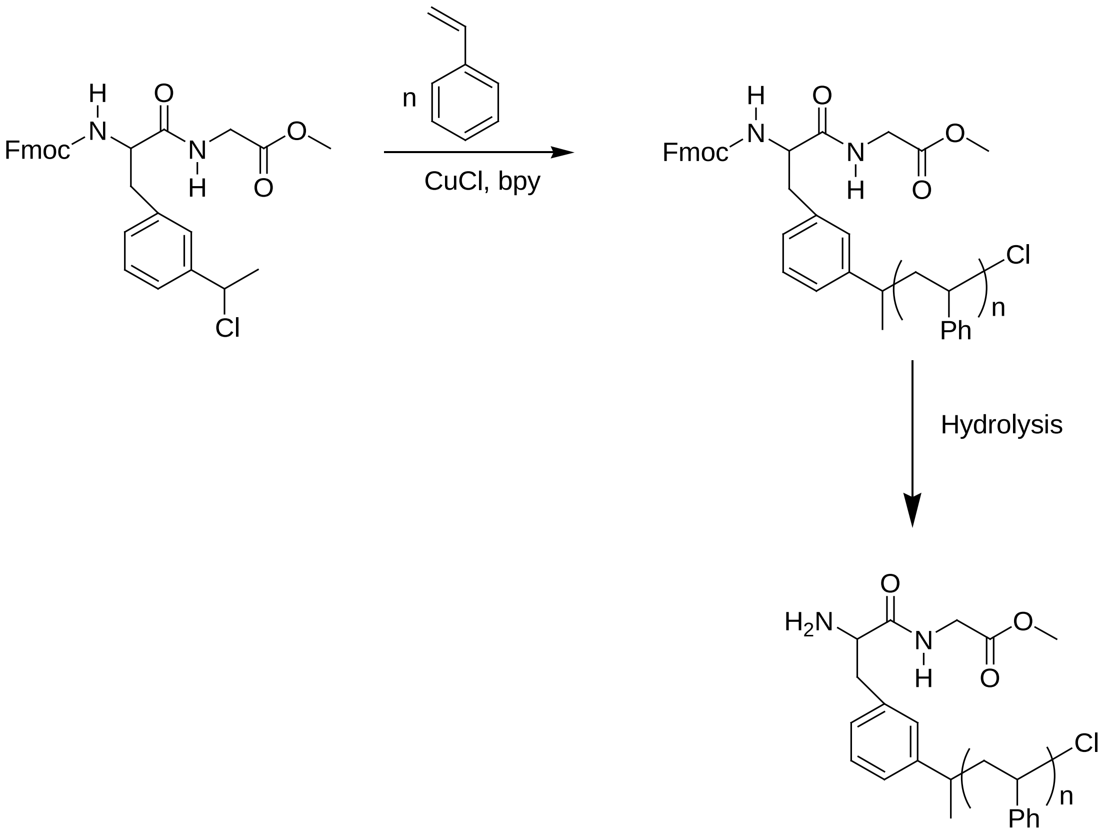
Armes and coworkers[164] utilized an •-azido functionalized initiator in ATRP reactions to produced well-defined azide functionalized homopolymers in protic media at 20 ^{o}C. In principle, the azide group of the •-azide functionalized polymers can, *via* acid catalyzed hydrolysis reactions, be converted to the corresponding well defined amine functionalized polymers:



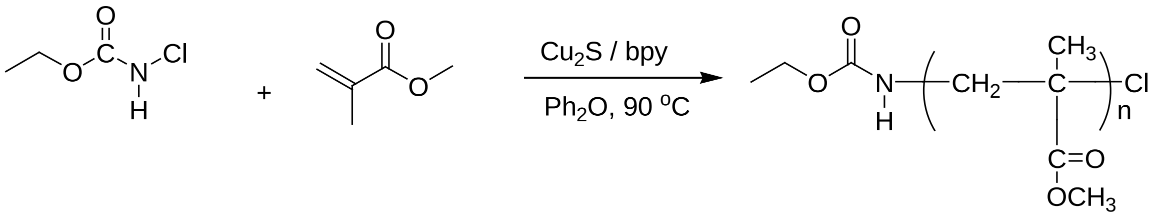
Armes and coworkers[165] also developed an interesting, new synthetic route to • -primary amine functionalized polymers by using a 9-fluorenylmethylchloroformate (Fmoc)-protected hexylamino 2-bromoisobutyrate derivative and folic acid substituted 2-bromoisobutyrate compounds as initiators for the polymerization of styrene by ATRP methods. Deprotection of the Fmoc and folic acid groups produced the terminal primary amine groups.



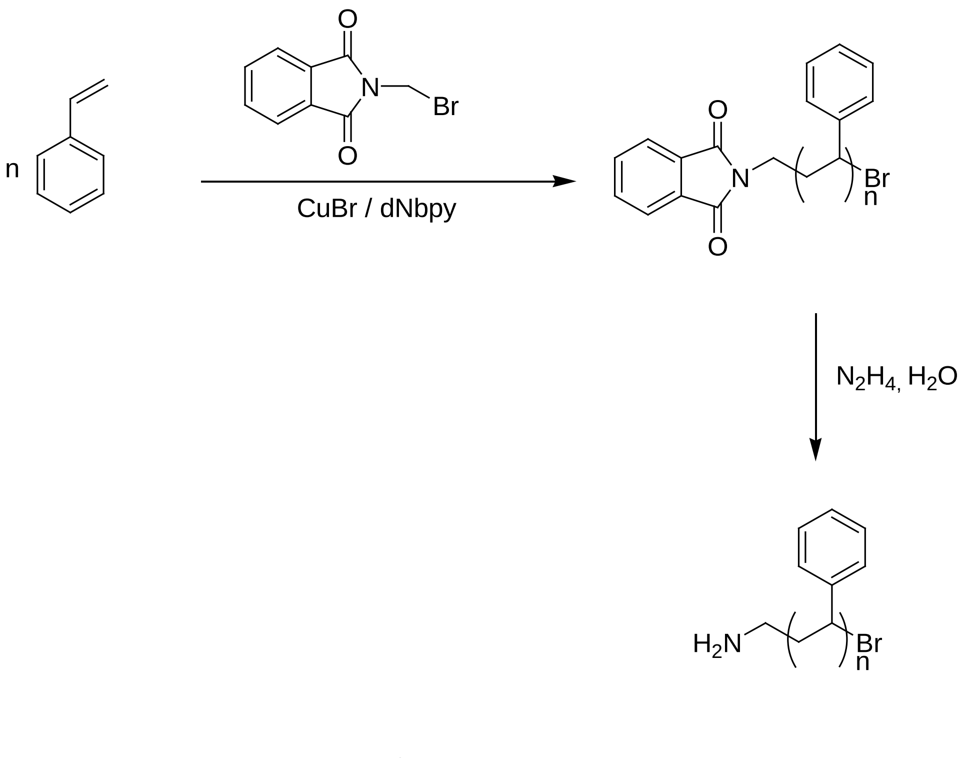
By using the Fmoc protecting group, Broyer and coworkers[166] used an amino acid functionalized initiator for styrene polymerization by ATRP methods to prepare well defined polymers bearing the amine functionality at the • -terminus of the polymer chain. The Fmoc protecting group can be removed by hydrolysis to give the required amine functionality:



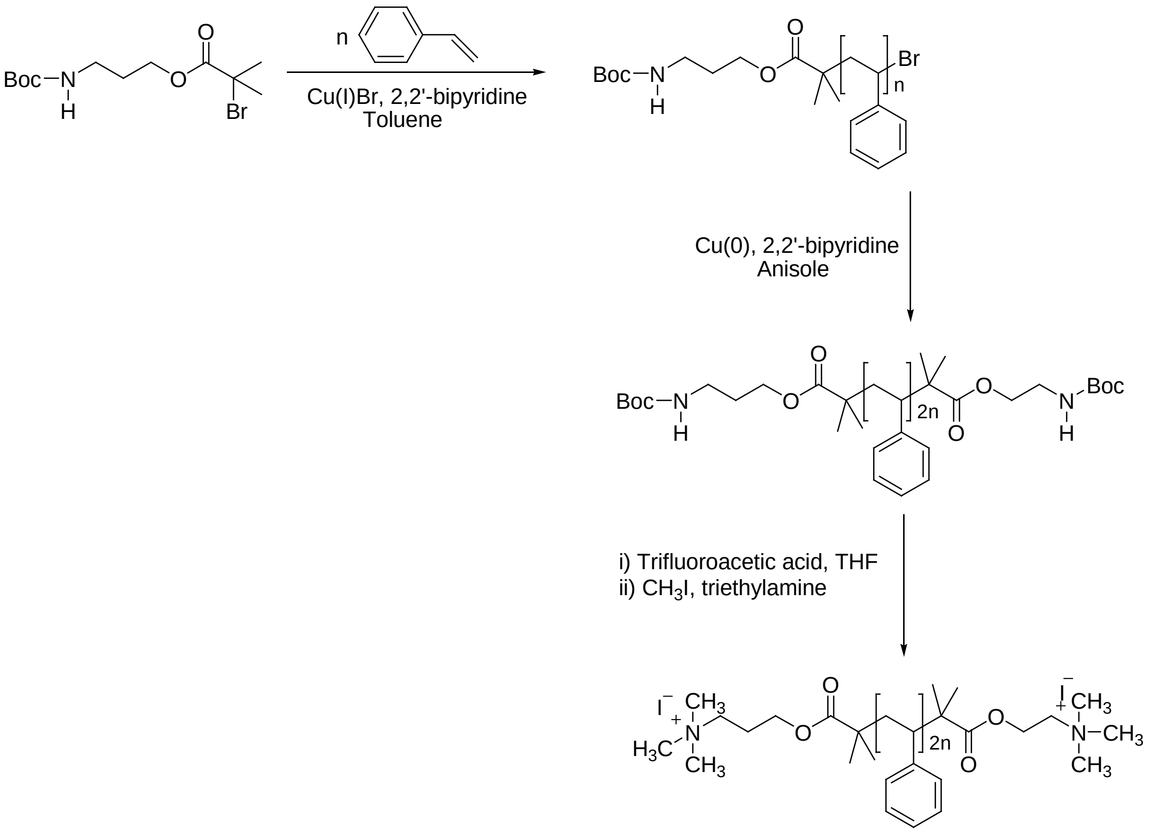
Percec and coworkers[167] reported the synthesis of a series of well defined primary amine chain end functionalized polymers by the ATRP methods using different N-chloro amides, lactams, carbamates and imides as protected amine functionalized initiators. For example, N-chloro ethylcarbamate was used to initiate the metal catalyzed living radical polymerization of methyl methacrylate to give polymers with narrow molecular weight distributions and good control of chain end functionality. Conversion of the precursor end groups to the primary amine groups occurs *via* post polymerization organic reactions:



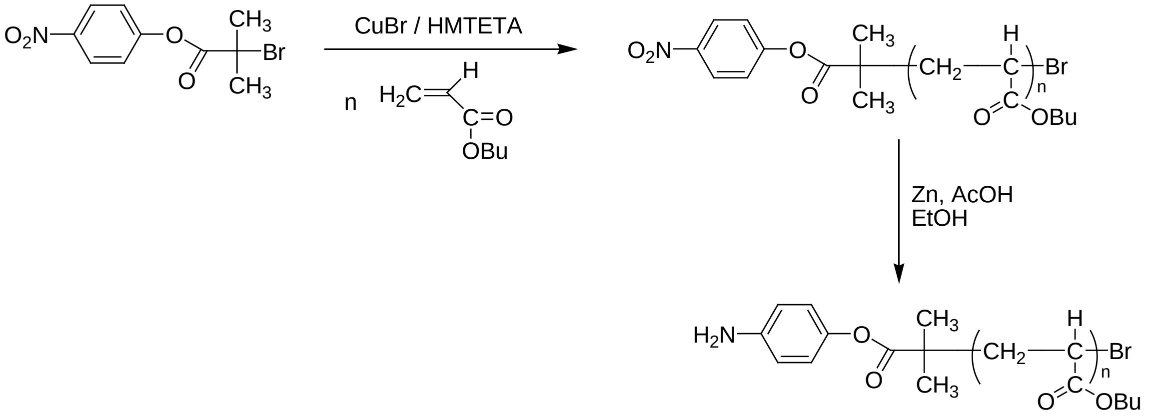
By using phthalimido functionalized initiators, Haddleton[168] and Moad and coworkers[154] synthesized •-amine functionalized polystyrene with N-(bromomethyl)phthalimide as an initiator in ATRP reactions. Subsequent hydrolysis gave quantitative yields of the amine functionalized polystyrene with narrow molecular weight distributions, high initiator efficiency and with the desired amine end group introduced at the •-terminus of the polymer chain:



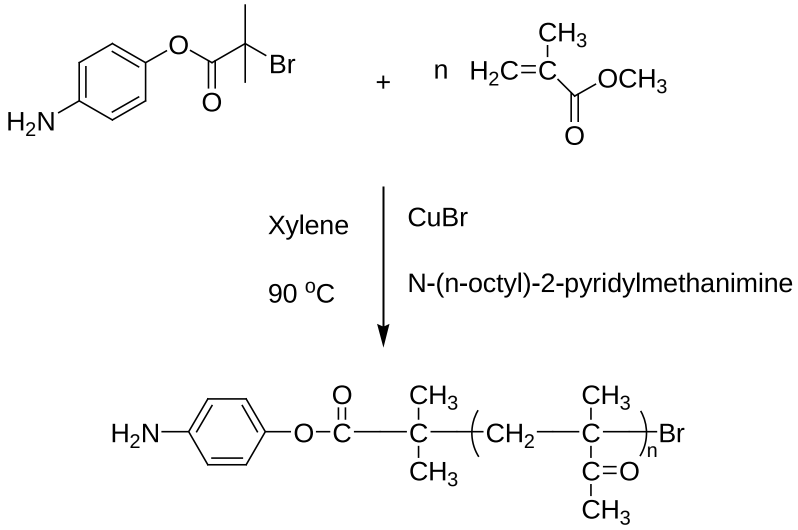
Recently, Monge and coworkers[159] reported the use of the Boc protected amine compound, (N-Boc-propylamino) 2-bromoisobutyrate as an initiator in the preparation of •-amine functionalized polymers *via* the ATRP method. The amine functionality is formed by the methylation of the polymer after the removal of the Boc protection to give (trimethylammonium) chain end functionalized polystyrene:



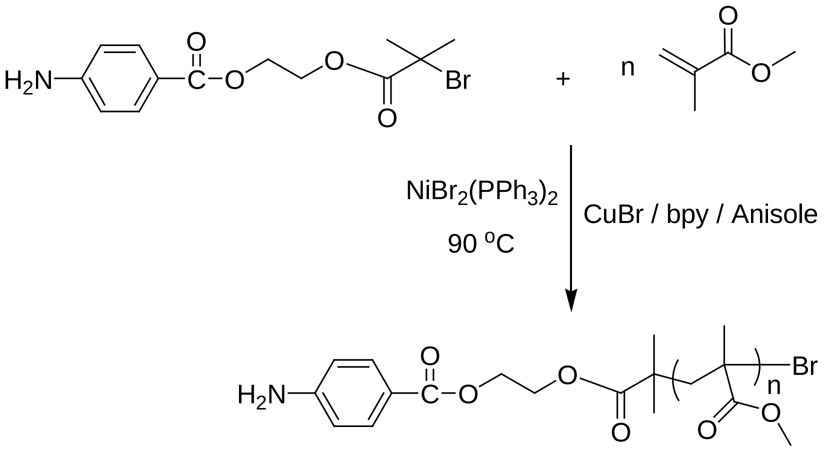
Robin and coworkers[169] prepared • -amine functionalized polymers *via* the ATRP method using an initiator bearing an aromatic nitro group. The nitro group at the • -terminus of the intermediate polymer can easily be reduced in the presence of zinc and acetic acid in ethanol to an aromatic amine after the completion of the polymerization process:



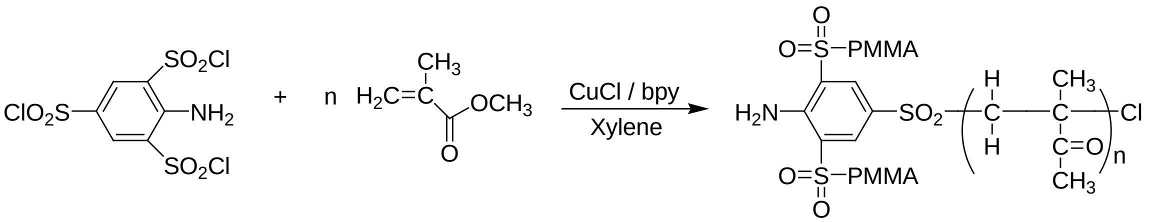
The synthesis of • -primary amine functionalized polymers can also be achieved by using primary amine functionalized initiators in ATRP reactions, where the amine group occurs in the unprotected, free primary amine form. Haddleton and Waterson[170] reported the use of primary amine functionalized phenolic ester derivatives as initiators for the direct preparation of primary amine functionalized polymers by the ATRP methods whereby the aromatic amine moiety is introduced at the • -terminus of the polymer chain. The polymerization proceeded *via* a controlled fashion with good control of the polymer parameters in methyl methacrylate polymerization. The results show that the ATRP reaction is tolerant to aromatic amine functional groups linked to the initiator molecule:



Recently, Blazquez and coworkers[171] reported the preparation of poly(methyl methacrylate) bearing the aromatic primary amine and primary diamine end groups by the ATRP of methyl methacrylate using 4-aminobenzoic acid 2-(2-bromo-2-methylpropionyloxy)ethyl ester and 3,5-aminobenzoic acid 2-(2-methyl-propionyloxy)ethyl ester as primary amine functionalized initiators, respectively. For example:



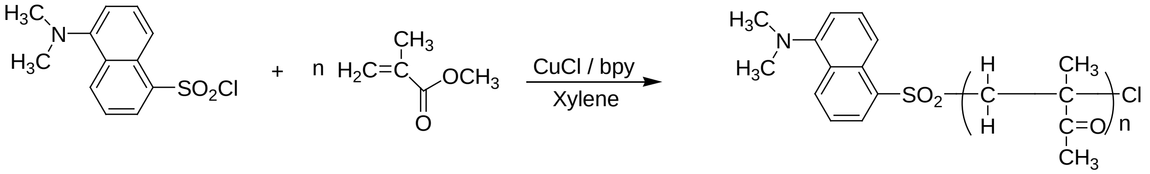
Also, Percec and coworkers[172] prepared perfect primary amine functionalized star polymers using an appropriately designed multifunctional sulfonyl derivative as a functionalized initiator for the ATRP of different monomers:



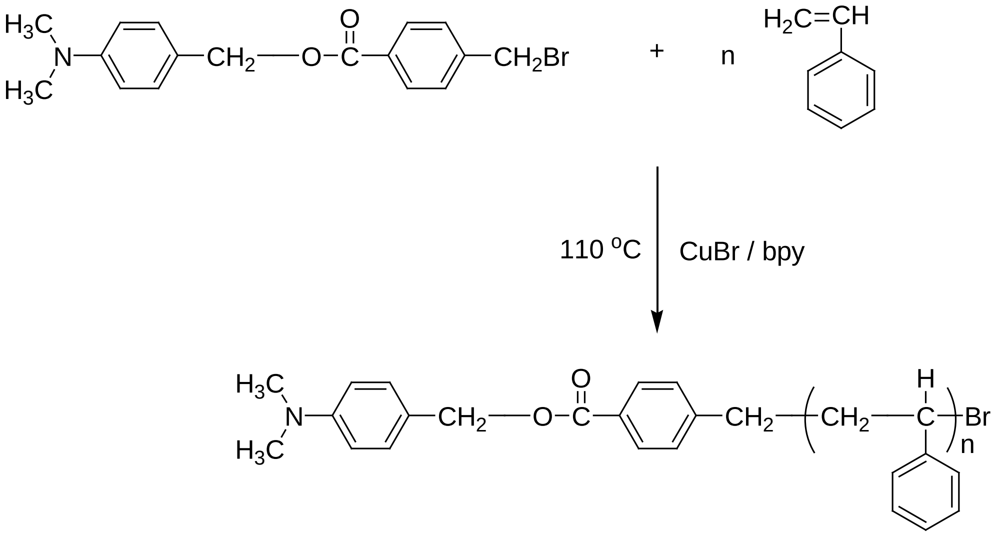
Recently, • -primary amine functionalized polystyrene was prepared by a general quantitative ATRP functionalization method, which is based on the *in situ* formation of a primary amine functionalized initiator adduct upon the reaction of an alkyl halide with a primary amine substituted 1,1-diphenylethylene derivative in the presence of the transition metal-ligand complex catalysts[54], as outlined in the thesis. Primary amine functionalized polystyrene was prepared by the ATRP method using a primary amine functionalized initiator adduct, formed *in situ* by the reaction of 1-(4-aminophenyl)-1-phenylethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system, as initiator for styrene polymerization. The polymerization proceeded *via* a controlled free radical process to afford quantitative yields of • -primary amine functionalized polymers with predictable number average molecular weights, narrow molecular weight distributions, well defined chain end functionality in high initiator efficiency reactions. No evidence of interaction of the primary amine group of the initiator with the catalyst system was apparent. The procedure illustrates a general controlled, quantitative functionalization reaction, independent of the specific functional group. Such reactions are highly efficient for the synthesis of functionalized initiators and polymers because (a) the addition reactions with 1,1-diphenylethylene units are simple and quantitative, and (b) due to steric factors, only monoaddition of the 1,1-diphenylethylene unit occurs during formation of the initiator.

2.5.1.2 Tertiary Amine Functionalized Initiators for ATRP

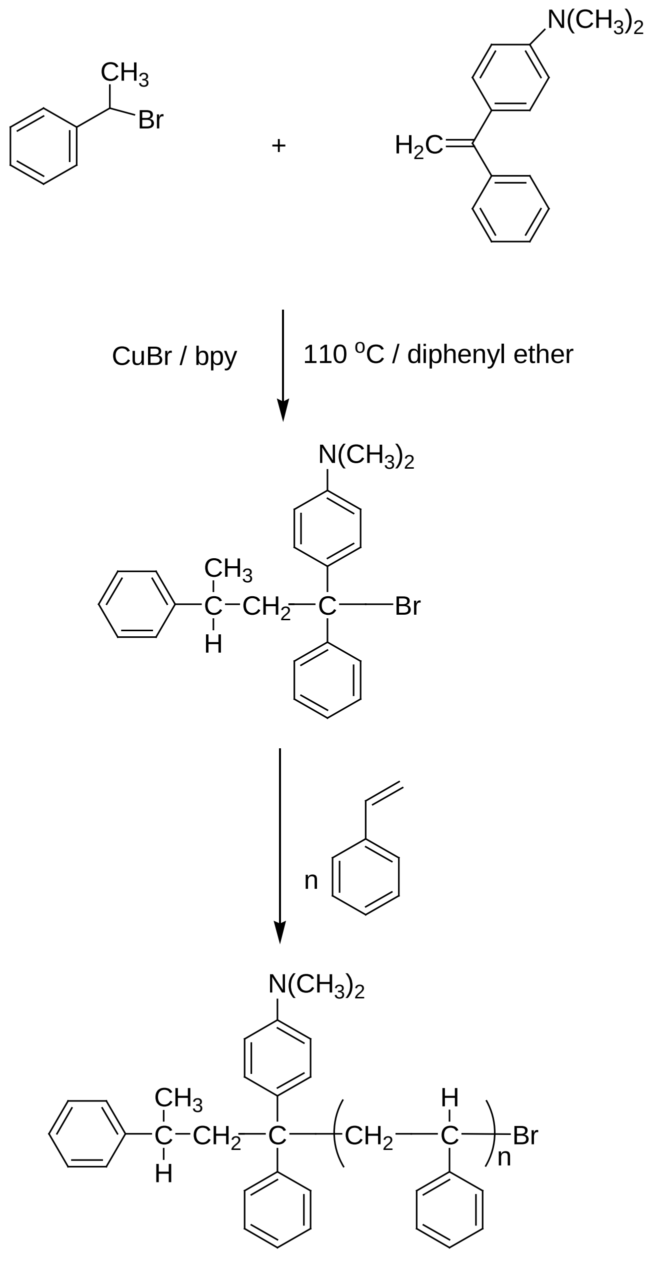
Although a wide variety of functionalized ATRP initiators have been employed for the preparation of heterotelechelic polymers, limited reviews on the synthesis of tertiary amine chain end functionalized polymers using tertiary amine functionalized initiators by ATRP methods have been reported in the literature. Percec and coworkers[173,174] reported a method for the synthesis of tertiary amine functionalized polymers using tertiary amine functionalized sulfonyl chlorides as initiators for the transition metal catalyzed controlled free radical polymerization of styrene and methyl methacrylate. However, with dansyl chloride as initiator, polymers with broad molecular weight distributions were obtained, due to the slow initiation of styrene and methyl methacrylate polymerization by dansyl chloride. For example:



Another route to the ATRP synthesis of tertiary amine functionalized polymers using functionalized alkyl bromide initiators was developed by Yagci and coworkers[155]. The method involves the use of 4-(dimethylamino)benzyl 4-(bromo-methyl)benzoate as the ATRP initiator for styrene polymerization to form well defined • -tertiary amine functionalized polymers with narrow molecular weight distributions:



In addition, a general quantitative ATRP functionalization method for the preparation of tertiary amine functionalized polymers, using a tertiary amine substituted 1,1-diphenylethylene derivative as an initiator precursor, has been developed in our laboratories[53]. Using a tertiary amine functionalized initiator adduct, formed *in situ* by the reaction of 1-(4-dimethylaminophenyl)-1-phenylethylene with (1-bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system, for styrene polymerization produced the corresponding tertiary amine functionalized polymers with good control of the number average molecular weight, molecular weight distribution and chain end functionality:

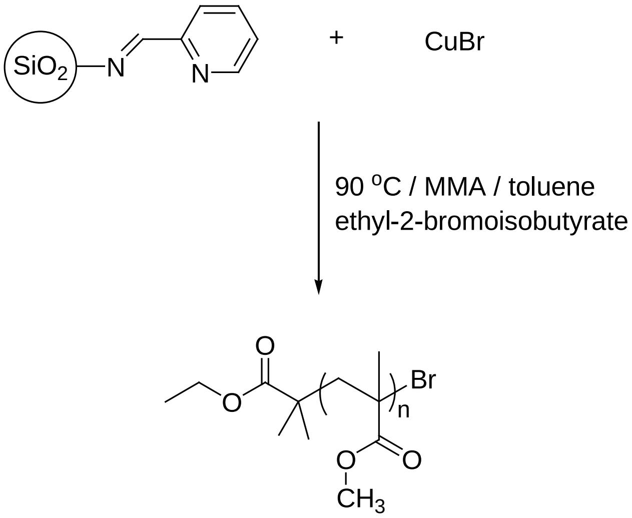


The present study describes the utilization of 1,1-diphenylethylene chemistry in ATRP reactions to prepare aromatic primary and tertiary amine chain end functionalized polymers. The method is based on a general quantitative ATRP initiation process, where initiator adducts are formed by the simple reactions of alkyl halides with functionalized 1,1-diphenylethylene derivatives substituted with the primary and tertiary amine groups. The preparation of •-bis primary and tertiary amine functionalized polymers by the ATRP process involves the use of the specific diamine functionalized unimolecular initiator adduct of (1-bromo-ethyl)benzene with the appropriate primary or tertiary diamine substituted 1,1-diphenylethylene derivative for styrene and methacrylate polymerization in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system. In addition, •,•-tetrakis(amine) functionalized polystyrenes can be prepared *via* the post ATRP chain end functionalization reactions which involves the addition of equimolar amounts of the respective diamine functionalized 1,1-diphenylethylene derivative to the •-bis(amine)functionalized polymer at the end of the polymerization process. Furthermore, the present research evaluates the polymerization kinetics data for each ATRP reaction leading to the formation of amine chain end functionalized polymers to determine the controlled/living character of each polymerization reaction.

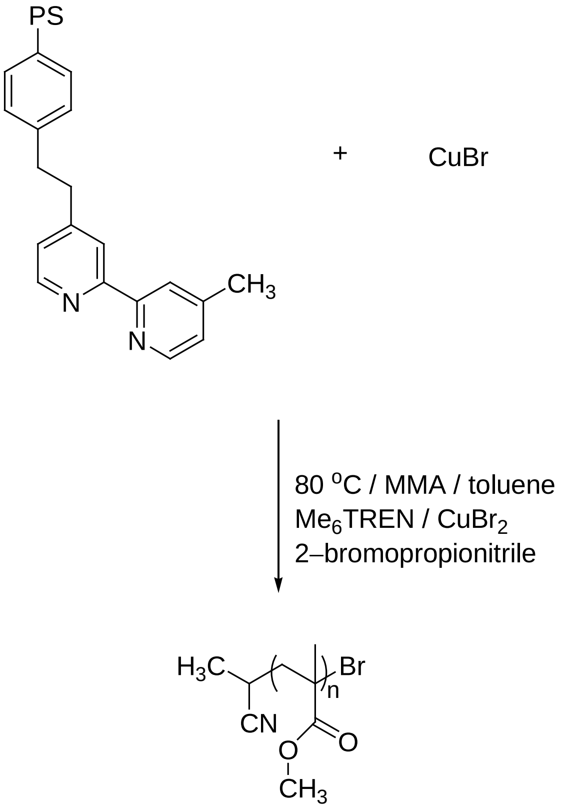
2.6 Supported Catalyst Systems for ATRP

Since 1995, different transition-metal/ligand catalyst systems for the transition metal catalyzed free radical polymerization reactions based on copper[75], nickel[104], iron[106], ruthenium[116], rhodium[175] and rhenium[175] have been developed. However, one of the limitations of the ATRP method for industrial development is the presence of residual copper metal catalyst in the final polymer product. The high catalyst residues cause colouration in the final polymer product and costly additional steps are needed to remove the transition metal salts from the final polymer product. A potential way to overcome this drawback is to support the catalyst onto a solid carrier, which could be readily removed from the final product by simple catalyst recovery methods and ideally be recycled for any further polymerization reactions.

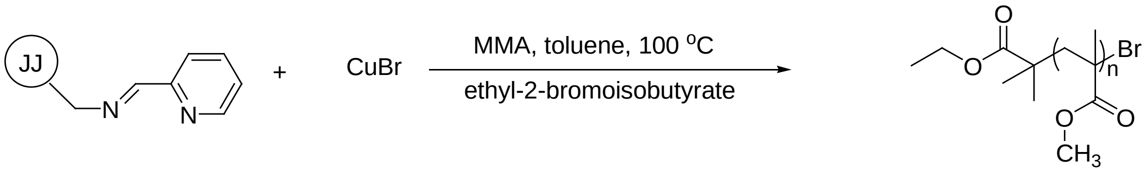
In ATRP reactions, the development of several supported catalytic systems, whereby the copper bromide catalyst was ligated by immobilized nitrogenated ligands, have been reported in the literature[55,176]. However, polymeric or macromolecular nitrogen ligands based on pyridyl groups as catalyst supports have not been extensively employed in ATRP reactions. The first supported catalytic system for the ATRP, based on copper (I) bromide and alkylpyridyl methanimines for the polymerization of methyl methacrylate in toluene, was reported by Haddleton and coworkers[177,178] in 1999:



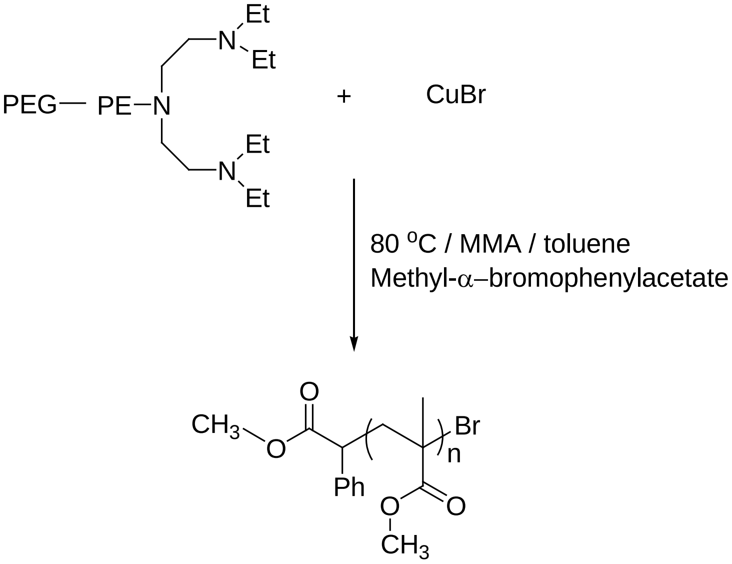
Similarly, Matyjaszewski and coworkers[179,180] reported the controlled polymerization of methyl methacrylate with CuBr immobilized onto 4,4'-dimethyl-2,2'-bipyridine functionalized Merrified resins in the presence of a tiny amount of soluble ligated and oxidized catalyst, $CuBr_2$/tris[2-(dimethylamino)ethyl]amine. Polymers with predictable number average molecular weights and narrow molecular weight distributions were obtained and the immobilized catalyst was removed by simple filtration or sedimentation:



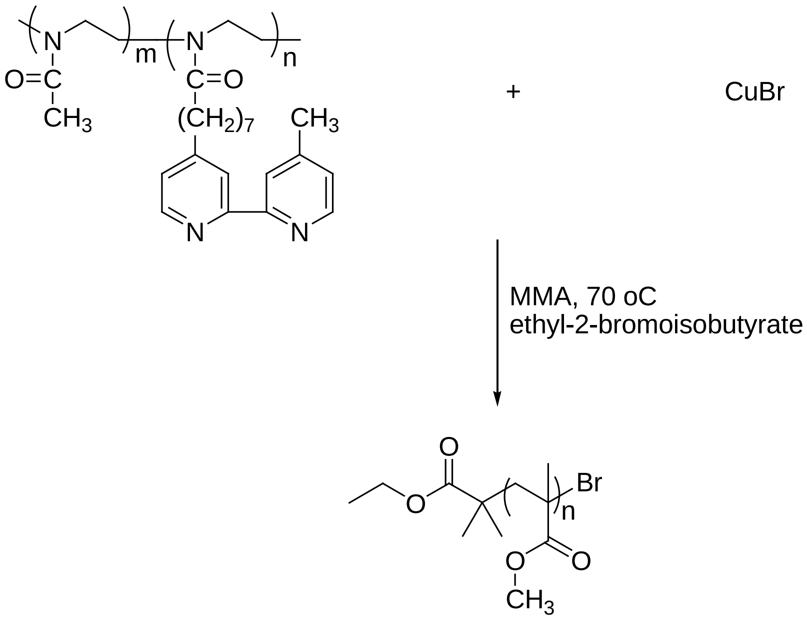
Brittain and coworkers[181] examined the use of a soluble–recoverable catalyst consisting of an ATRP ligand covalently attached to a low molecular weight polyethylene derivative. Polymers with slightly broader molecular weight distributions (M_w/M_n = 1.45) were produced. The catalyst support was easily removed by the crystallization of the polyethylene segment together with the ligand and copper from the polymer solution and the polymer product purified by precipitation into methanol. Brittain and coworkers[182] also used a solid supported catalyst for the polymerization of a wider variety of monomers, such as styrene, methyl methacrylate and 2-(dimethylamino)ethyl methacrylate, under different reaction conditions. The solid support used was the JandaJel resin. The polymerization proceeded *via* a controlled polymerization process in shorter reaction times than the system with the polyethylene supported ligand. The catalyst/ligand complex was easily removed by filtration.



To achieve homogeneous reaction conditions and the ease of catalyst removal, Zhu and coworkers[183,184] used a CuBr/[(diethylamino)ethyl] amine complex attached to a poly(ethylene)-block-poly(ethylene glycol) support as a soluble/recoverable catalyst in ATRP reactions. The system displayed good control in the ATRP reaction affording polymers with molecular weight distributions of 1.2. The catalyst was recovered and 90% of the catalyst activity was retained.



Weberskirsch and coworkers[185] reported that the ATRP of methyl methacrylate in the presence of the copper catalyst supported onto an amphiphilic block copolymer with pendant bipyridine ligands. On average, 96-99% of all copper used in the polymerization was removed by a simple precipitation/washing step due to the different solubility behaviour of the macroligand and poly(methyl methacrylate) particles.



The present study focuses on the synthesis and characterization of new dipyridyl functionalized polysulfone[39] with high degree of functionalization and the evaluation of its efficiency as a supported catalyst system with CuBr for atom transfer radical polymerization of styrene. By using the dipyridyl functionalized polysulfone/CuBr complex as the supported catalyst system in ATRP reactions, the polymerization kinetics data will be evaluated to determine the controlled/living nature of the styrene polymerization reaction.

CHAPTER 3

EXPERIMENTAL

3.1 Materials and Glassware

All chemicals and solvents were purchased from the Sigma Aldrich Chemical Company, unless otherwise stated. Styrene and methyl methacrylate were purified by drying over calcium hydride followed by vacuum distillation and drying over molecular sieves prior to use. Tetrahydrofuran (THF) was freshly distilled from Na/benzophenone after stirring at room temperature for few days[39,49]. Distillation of THF was performed when the solution had a purple-blue colour which is an indication of the dryness of the solvent and the absence of reactive impurities. Excess sodium metal was used to ensure the complete conversion of benzophenone to the benzophenone radical anion since traces of unreacted benzophenone would sublime upon subsequent distillation of THF.

Copper (I) bromide, (1-bromoethyl)benzene, 4-aminobenzophenone, diphenyl ether, 2,2'-bipyridyl (99+%), 4,4'-diaminobenzophenone, *n*-butyllithium (1.6M in hexane), methyllithium (1.6M in diethyl ether), methyl triphenylphosphonium bromide, potassium tert-butoxide, calcium hydride and di-2-pyridylketone were used as received. 4,4'-Bis(dimethylamino)benzophenone was recrystallized twice from absolute ethanol before use.

All glassware was oven dried at 120 ^{o}C for 24 hours prior to use and all reactions were carried out under a dry argon or nitrogen atmosphere, where applicable.

3.2 Characterization

Nuclear Magnetic Resonance Spectrometry (NMR)

^{1}H NMR spectra were recorded on a Varian Gemini 300 MHz spectrometer with $CDCl_3$ solvent at ambient temperature. Polymers were dissolved in an appropriate deuterated solvent to give a viscous polymer solution in an NMR tube.

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}. Polymer samples were placed over the ATR crystal and maximum pressure applied using the slip-clutch mechanism.

Size Exclusion Chromatography (SEC)

Molecular weights and molecular weight distributions of polymers were measured by size exclusion chromatography (SEC) on a Waters Alliance SEC autosampler equipped with a Phenogel guard column and a Phenogel column (5 µ, 500 Å pore size, 1K-15K MW range, 300 mm x 7.8 mm) in series with refractive index and dual angle laser light scattering detectors. THF was used as an eluent at a flow rate of 1 mL/min at 30 ^{o}C. The lazer light scattering detector of the SEC system was calibrated with monodisperse polystyrene and poly(methyl methacrylate) standards (Aldrich Chemical Company). Polymers were dissolved in THF (4 mg/1.5 mL) before characterization by size exclusion chromatography.

Gas Chromatography (GC)

The monomer conversion was determined by gas chromatography using a Shimadzu Gas Chromatograph 17Å equipped with PB-5 M column (30 m x 0.32 mm; 0.25 µm film) at a constant flow rate of 1.7 mL/min. The initial column temperature was set at 90 ^oC with a hold time of 3 minutes, followed by an increase in temperature to 280 ^oC at a heating rate of 10 ^oC /min. Tetrahydrofuran (THF) was used as the internal standard for the analysis. An aliquot of 1 µL of the test sample was injected *via* a syringe into the injection port for the GC analysis.

Thermogravimetric Analysis (TGA)

Thermogravimetrical curves were generated on a TA instrument Auto Hi-Res Q500 Thermogravimetrical Analyzer at a heating rate of 10 ^oC /min under nitrogen atmosphere. Approximately 600 mg of the polymer sample was placed on a preweighed TGA pan for analysis.

Differential Scanning Calorimetry (DSC)

Glass transition temperatures of polymeric samples were determined on a TA Instruments Auto MDSC Q100 Differential Scanning Calorimeter by heating the polymers from 10 ^oC to 700 ^oC. Polymer sample sizes with masses ranging from 5-10 mg were measured into a DSC sample pan for analysis.

Thin Layer Chromatography (TLC)

Thin layer chromatographic analyses of all the products were performed on Silica gel plates (Merck, Silica Gel 60 F_{254}). Samples were dissolved in suitable solvents. Solutions containing the sample were then spotted on the TLC plates, about one centimeter from the base and developed in a standard chromatography chamber.

Melting point determination

The melting points of the different samples are uncorrected. The melting points of samples were recorded on a Stuart Melting Point Analyser (Barloworld Scientific Limited) with a measuring range of 25 – 400 ^{o}C, accuracy of ± 0.3 ^{o}C (25 – 200 ^{o}C) and ± 0.5 ^{o}C (200 – 400 ^{o}C) and reproducibility of ± 0.2 ^{o}C. The dried samples were loaded into capillary tubes, with sample height between 2.0 mm and 3.0 mm and placed in the melting point apparatus.

Non-Aqueous Titrations

The number average molecular weights of the primary and tertiary amine functionalized polymers were determined by non-aqueous titrations of amine groups[186-191]. The concentrations of primary and tertiary amine end groups in the functionalized polymers were determined by separate non-aqueous titrations of 0.1 g polymer samples in a 1/1 (v/v) mixture of chloroform and glacial acetic acid with standardized perchloric acid (0.01 M) in glacial acetic acid using methyl violet as an indicator.

Contact Angle Tests

Contact angle data was obtained at the University of Stellenbosch with an ERMA G-1 contact angle meter at 20 ^{o}C using pure water as probe liquid.

Water Permeability Tests

Water permeability tests were carried out at 25 ^{o}C at transmembrane pressures ranging between 20 and 100 kPa and membrane surface of 0.0050731 m^2 using pure water obtained by ion exchange and reverse osmosis treatment.

Flux Data

Flux data were obtained by passing pure water under pressure through the flat sheet membranes and collecting permeate on a Mettler balance to determine the water permeability of the membranes.

Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) images of unmodified and dipyridyl functionalized polysulfone membranes were obtained at the University of Stellenbosch with an Explorer TMX 2000 AFM from Topometrix operated in the low amplitude non-contact mode. The resonance frequency of the low frequency non-contact silicon cantilevers (Nanosensors GmbH) was 35-65 N/m. The low resonance cantilever was 220 µm long and 40 µm wide. The average roughness of the membrane surface, R_a was determined using the following equation:

$$R_a = \left(\frac{1}{N}\right)\sum_{i=0}^{N}\left|Z_i - \overline{Z}\right|$$

where N is the total number of points in the image matrix and Z_i is the height of the *i*th point of reference value. AFM analyses were performed at different scan ranges for each polysulfone sample at different places on the sample. At least three interpore regions of each membrane were analyzed to obtain average R_a values.

Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) photographs were obtained at the University of Pretoria with a JEOL 6000F in-lens field emission SEM and a

JEOL 840 scanning electron microscope as follows:

(a) Freeze drying

To prevent the collapse of the polysulfone membrane pores, the membranes were kept in distilled water. The wet membranes were cut into 0.4 cm^2 (0.4 cm x 1 cm) samples and freeze-dried in liquid propane at -180 ^oC with a Riechert KF 80 freeze plunger. The frozen samples were transferred under liquid nitrogen into slots in a copper block (63 mm x 63 mm x 15 mm). The copper block was kept completely immersed in liquid nitrogen in a plastic container, thus keeping the material under nitrogen atmosphere and preventing the condensation of moisture onto the sample. The copper block was thereafter transferred to a Fisons high vacuum unit where the evacuation started immediately. The temperature of the copper block was below -130 ^oC when the vacuum reached 1.33 Pa (1×10^{-2} Torr). Freeze-drying was carried out over 2 days, during which the temperature steadily increased back to room temperature.

(b) Sample preparation

Samples of the membrane were cut and placed flat and upright onto the polished side of graphite stubs to view the surface and cross-section, respectively of the membrane. The stubs were made from spectrographic rods turned down to a diameter of 5 mm with a lathe. Disks of 1 mm thickness were cut from the rod and subsequently polished. Double-sided carbon tape was used to secure the samples onto the stub. Furthermore, carbon dag (Leit C, Neubauer Chemikalien) was applied to the edges of the sample for additional support and to reduce the charging of the specimen surface.

(c) Coating and sample viewing

Samples were coated with chromium (ca. 3-4 nm) in a Gatan Ion beam coater, model 681. The samples were viewed at a minimum magnification of 5000x. To obtain lower magnification photos the samples were gold spurred in a Polaron E5200 sputter coater for viewing.

3.3 Anionic Synthesis of Functionalized Polysulfone

3.3.1 Purification of Polysulfone, (1)

Commercially available polysulfone, (**1**) (Ultrason S, BASF, $M_n = 47 \times 10^3$ g/mol, $M_w/M_n = 1.05$) was dissolved in THF and precipitated in methanol, filtered and vacuum dried at 120 ^{o}C prior to the chemical modification reactions.

3.3.2 The synthesis of 2,2'-vinylidenedipyridine, (2)

The synthesis of 2,2'-vinylidenedipyridine, (**2**) according to the procedures outlined by Eckard and Summers[192] and Summers and coworkers[193] afforded the desired product in low yields. Thus, a new method to synthesize 2,2'-vinylidenedipyridine, (**2**) was developed using the synthetic route outlined by Subramanyam[194], with modifications.

Under an argon atmosphere, potassium tert-butoxide (27.51 mL of a 1.0 M solution, 0.027 mol) was added to methyltriphenylphosphonium bromide (9.7 g, 0.027 mol) in freshly distilled anhydrous THF (200 mL) at 0 ^{o}C and the reaction stirred for 1.5 hours. After complete reaction, di-2-pyridylketone (5.0 g, 0.027 mol) in dry THF (100 mL) was added to the freshly prepared phosphorous ylide at 0 ^{o}C. The resultant dark orange solution was stirred for 12 hours at room temperature to achieve complete reaction. The colour of the reaction mixture

changed from dark-orange to orange-green to brown. The reaction was quenched by the addition of methanol (2 mL). The triphenylphosphine oxide salt which precipitated from the solution was removed by vacuum filtration. The filtrate was concentrated on a rotary evaporator and the resultant brown oil purified by silica gel chromatography using toluene as eluent to give 4.21g (92%) of pure 2,2'-vinylidenedipyridine as a light brown oil: ^{1}H NMR ($CDCl_3$): • 6.05 ppm [s, 2H, C$\underline{H}_2$], 6.97-7.70 ppm [m, 6H, aromatic H], 8.50-8.60 ppm [d, 2H, aromatic H]; FTIR (oil): 1634 cm^{-1} (C=N); TLC (Silica Gel 60F_{254}, Merck),
R_f (acetonitrile) = 0.35.

3.3.3 Synthesis of Dipyridyl Functionalized Polysulfone, (3)

The synthesis of dipyridyl functionalized polysulfone with 45% degree of functionalization (PFPS-45) was conducted according to the procedure of Summers and coworkers[39,193]. To improve the degree of functionalization, the preparation of dipyridyl functionalized polysulfone with 80% (PFPS-80) and 95% (PFPS-95) degree of functionalization were effected using 10% and 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) respectively. In a typical procedure, for the preparation of dipyridyl functionalized polysulfone, PFPS-80, dry, unmodified polysulfone, (**1**) (1.0 g, 0.0023 mol, $M_n = 47 \times 10^3$ g/mol; $M_w/M_n = 1.05$) was transferred into a clean, dry 250 mL round bottomed flask under an argon atmosphere. Freshly distilled, dry THF (40 mL) was added to dissolve the polymer. The reaction mixture was cooled to -78 ^{o}C using a dry ice/isopropanol bath. *n*-Butyllithium (2.2 mL of a 1.6 M solution in hexane, 0.0035 mol) was added to the reaction mixture. The reaction mixture was stirred for 2 hours at -78 ^{o}C to effect complete metalation. Freshly prepared 2,2'-vinylidenedipyridine, (**2**) (1.03 g, 0.0057 mol) in THF (20 mL) was then added to the viscous deep-red lithiated polymer *via* a cannula, whereupon the reaction mixture turned to a deep orange colour. The reaction mixture was allowed to stir at -78 ^{o}C for 4 hours. The colour and the viscosity of the reaction mixture remained unchanged. Upon quenching the reaction mixture with methanol (2 mL), a homogenous orange solution was obtained. The mixture was concentrated on a rotary evaporator and the functionalized polysulfone was precipitated in excess methanol, filtered off and dried at 120 °C to afford 1.35 g (96% yield) of dipyridyl functionalized polysulfone, (**3**), PFPS-80, as a white solid: ^{1}H NMR ($CDCl_3$): • 3.78-3.91 ppm [broad m, 2H, $C\underline{H}_2$], 4.68-4.85 ppm [broad m, 1H, H,$C\underline{H}$], 6.43-8.62 ppm [m, aromatic H]; FTIR (film): 1634 cm^{-1} (C=N); SEC: M_n = 56.87 x 10^3 g/mol, M_w/M_n = 1.22.

The preparation of dipyridyl functionalized polysulfone, (**3**), PFPS-95 was conducted *via* a similar procedure by adding 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the corresponding lithiated polysulfone derivative.

3.3.4 Membrane Preparation

Membranes were prepared from 15% (w/w) polymer (PS, PFPS-45, PFPS-80 and PS-1-80) solutions in N-methyl-2-pyrrolidone. Sample PS-1-80 is a blend of 1% PFPS-80 in PS. Solutions were cast at 25 °C on a glass plate to form thin films with thickness of 150 µm. After exposure to air for 15 seconds at 20 °C and 60% relative humidity, the thin films were immersed in water at 15 °C. After an immersion period of 5 minutes in distilled water, the membranes detached from plate and were leached for an additional 3 hours under running water before use.

3.4 Atom Transfer Radical Polymerization: Synthesis of Amine Chain End Functionalized Polymers

3.4.1 Primary Amine Functionalized Initiator Precursor: Synthesis of 1-(4-Aminophenyl)-1-phenylethylene, (4)

Freshly distilled tetrahydrofuran (100 mL) was added to a three necked round bottom flask containing methyltriphenylphosphonium bromide (10.81 g; 0.0303 mol). The mixture was purged with argon for 15 minutes. Methyllithium (18.91 mL of a 1.6 M solution in diethyl ether, 0.0303 mol) was added dropwise to the reaction flask *via* a syringe at 0 ^{o}C to form a ylide. The mixture turned yellow upon addition of methyllithium. After stirring for 4 hours at room temperature, the resultant phosphorous ylide was transferred via a cannula into the solution of 4-aminobenzophenone (5.0 g, 0.0254 mol) and dry THF (100 mL) at 0 ^{o}C with stirring. The reaction mixture immediately turned orange in colour. After stirring the reaction mixture at room temperature for 12 hours, methanol (2 mL) was added to quench the reaction. The triphenylphosphine oxide salt, which precipitated from solution, was removed by vacuum filtration. The filtrate was concentrated and the crude product was purified by column chromatography using toluene as eluent. After removing the solvent *via* a rotary evaporator, yellow-white crystals were formed. Recrystallization of the product from 80% aqueous ethanol gave 4.47 g (90%) of 1-(4-aminophenyl)-1-phenylethylene, (**4**) as light yellow crystals: mp = 81.2-82.6 ^{o}C (lit. mp^{51} = 80-81 ^{o}C); ^{1}H NMR ($CDCl_3$): • = 3.67 ppm [broad s, 2H, NH_2], 5.19 ppm [s, 2H, $C\underline{H_2}$], 6.62 and 7.18 ppm [m, 6H and 5H respectively, aromatic H]; FTIR (solid): 3468 cm^{-1} (N-H); TLC: R_f (toluene) = 0.44.

3.4.2 Synthesis of • -Aminophenyl Functionalized Polystyrene, (6)

All polymerization reactions were performed in Schlenk flasks and under dry argon atmosphere.

In a typical procedure, copper (I) bromide (0.0735 g, 0.5122 x 10^{-3} mol) and 2,2'-bipyridyl (0.2401 g, 1.5366 x 10^{-3} mol) were added to a Schlenk flask, followed by the successive addition of (1-bromoethyl)benzene (0.095 g, 0.07 mL, 0.5122 x 10^{-3} mol), 1-(4-aminophenyl)-1-phenylethylene, (**4**) (0.1 g, 0.5122 x 10^{-3} mol) and diphenyl ether (1.7 mL). The reaction mixture was stirred at room temperature for 5 minutes. The heterogenous mixture was degassed by three freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 110 ^{o}C for 60 minutes with stirring. The disappearance of 1-(4-aminophenyl)-1-

phenylethylene, (**4**) was monitored by TLC analysis. Freshly distilled styrene (1.86 mL, 1.6903 g, 0.0162 mol) was added to the resultant green reaction mixture *via* a stainless steel syringe at room temperature and the reaction mixture was heated at 110 ^{o}C for 12 hours. Upon cooling and addition of tetrahydrofuran (10 mL), the resultant green solution was purified by passage through a short silica gel column to remove copper and ligand impurities. The polymer solution was concentrated on a rotary evaporator and precipitated from THF solution into excess methanol to afford 1.94 g of the corresponding •-aminophenyl functionalized polystyrene, (**6**) as a white solid: ^{1}H NMR: • = 1.20 – 2.39 ppm [m, polystyrene CH_2 and CH], 3.69 ppm [broad s, 2H, NH_2], 6.26 - 7.41 ppm [aromatic H]; FTIR (solid): 3469 cm^{-1} (N-H); $M_{n,\ theory} = 3.30 \times 10^3$ g/mol; SEC: $M_n = 3.10 \times 10^3$ g/mol, $M_w/M_n = 1.08$; $M_{n,\ titration} = 3.35 \times 10^3$ g/mol.

3.4.3 Primary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis(4-aminophenyl)ethylene, (7)

Under an argon atmosphere, freshly distilled tetrahydrofuran (100 mL) was added to a dry three necked round bottom flask containing methyltriphenyl-phosphonium bromide (10.05 g; 0.0281 mol). The mixture was degassed with argon for 15 minutes. Methyllithium (17.60 mL of a 1.6 M solution in diethyl ether, 0.0281 mol) was added dropwise to the reaction flask *via* a syringe at 0 ^{o}C. The mixture turned yellow upon addition of methyllithium. After stirring for 4 hours at room temperature, the resulting ylide was transferred *via* a cannula into a solution of 4,4'-diaminobenzophenone (5.0 g; 0.0236 mol) in dry THF (100 mL) at 0 ^{o}C, with stirring. The reaction mixture was heated to reflux for 12 hours. Methanol (2 mL) was then added to quench the reaction. The triphenylphosphine oxide salt, which precipitated from solution, was removed by vacuum filtration. The filtrate was concentrated and the crude product was purified by column chromatography using hexane/ethyl acetate (*v/v*, 20/80) to give a dark brown solid. Recrystallization of the solid from 80% aqueous ethanol solution gave

3.98 g (80%) of pure 1,1-bis(4-aminophenyl)ethylene, (**7**) as pale yellow crystals: mp = 160.5 - 162.0 ^oC (lit. mp[194,195] = 159-160 ^oC); ^1H NMR ($CDCl_3$): • = 3.69 ppm [broad s, 4H, 2 x NH_2], 5.21 ppm [s, 2H, =C$\underline{H}_2$], 6.63 and 7.20 ppm [d x d, 8H, aromatic H]; FTIR (solid): 3443 cm^{-1} (N-H); TLC: R_f (hexane/ethyl acetate, v/v, 20/80) = 0.71.

3.4.4 Synthesis of • -Bis(aminophenyl) Functionalized Polystyrene, (9)

In a typical experiment, under argon atmosphere, copper (I) bromide (0.0493 g, 0.3433 x 10^{-3} mol), 2,2'-bipyridyl (0.1609 g, 1.030 x 10^{-3} mol), (1-bromoethyl)benzene (0.0640 g, 0.047 mL, 0.3433 x 10^{-3} mol), 1,1-bis(4-aminophenyl)ethylene, (**7**) (0.072 g, 0.3433 x 10^{-3} mol) and diphenyl ether (1.70 mL) were added to the Schlenk tube. The tube was tightly sealed with a rubber septum and degassed by three freeze-pump-thaw cycles. The Schlenk tube was then immersed in an oil bath, preset at 110 ^oC, for an hour. The disappearance of 1,1-bis(4-aminophenyl)ethylene, (**7**) was monitored by TLC. Subsequently, freshly distilled styrene (1.70 mL, 1.545 g, 0.0135 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was heated at 110 ^oC for 12 hours. The tube was withdrawn from the oil bath and THF (10 mL) was added to the reaction flask. The reaction mixture was then passed through an silica gel column to remove the metal/ligand impurities. The polymer product was isolated by precipitation from a THF solution into excess methanol and dried under vacuum at 60 ^oC to give 1.89 g of • -bis(aminophenyl) functionalized polystyrene, (**9**) as a white solid: ^1H NMR: • = 1.22 – 2.45 ppm [m, polystyrene CH_2 and CH], 3.62 ppm [broad s, 4H, 2 x NH_2], 6.28 - 7.45 ppm [aromatic H]; FTIR (solid): 3412 cm^{-1} (N-H); $M_{n,theory}$ = 4.5 x 10^3 g/mol; SEC: M_n = 4.10 x 10^3 g/mol, M_w/M_n = 1.11; $M_{n,\ titration}$ = 4.35 x 10^3 g/mol.

3.4.5 Synthesis of •-Bis(aminophenyl) Functionalized Poly(methyl methacrylate), (10)

In a typical experiment, under argon atmosphere, copper (I) bromide (0.0504 g, 0.3510 x 10^{-3} mol), 2,2'-bipyridyl (0.1645 g, 1.0530 x 10^{-3} mol), (1-bromoethyl)-benzene (0.0650 g, 0.048 mL, 0.3510 x 10^{-3} mol), 1,1-bis(4-aminophenyl)-ethylene, (**7**) (0.074 g, 0.3510 x 10^{-3} mol) and diphenyl ether (1.0 mL) were added to a Schlenk tube. The tube was tightly sealed with a rubber septum and degassed by three freeze-pump-thaw cycles. The Schlenk tube was then immersed in an oil bath, preset at 90 ^{o}C. After 1 hour, freshly distilled methyl methacrylate (1.50 mL, 1.404 g, 0.0140 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe and the reaction mixture was heated at 90 ^{o}C for 12 hours. The tube was then withdrawn from the oil bath and THF (10 mL) was added to the reaction flask. The reaction mixture was passed through a silica gel column to remove the metal/ligand impurities. The polymeric product was isolated by precipitation from THF solution into excess methanol. The polymer product was filtered and dried under vacuum at 60 ^{o}C to give 1.76 g of •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) as a white solid: ^{1}H NMR: • = 3.69 ppm [broad s, 4H, 2 x NH_2], 6.50 - 7.22 ppm [aromatic H]; FTIR (solid): 3469 cm^{-1} (N-H); $M_{n,\ theory}$ = 4.0 x 10^{3} g/mol; SEC: M_n = 3.60 x 10^{3} g/mol, M_w/M_n = 1.18;
$M_{n,\ titration}$ = 3.85 x 10^{3} g/mol.

3.4.6 Synthesis of •,• -Tetrakis(aminophenyl) Functionalized Polystyrene, (11)

A Schlenk tube was charged with copper (I) bromide (0.0525 g, 0.3660 x 10^{-3} mol), 2,2'-bipyridyl (0.1715 g, 1.098 x 10^{-3} mol), (1-bromoethyl)benzene (0.068 g, 0.050 mL, 0.3660 x 10^{-3} mol), 1,1-bis(4-aminophenyl)ethylene, (**7**) (0.80 g, 0.3660 x 10^{-3} mol) and diphenyl ether (1.7 mL). The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove

oxygen. Under argon atmosphere, the Schlenk tube was then immersed in a thermostatically controlled oil bath at 110 ^oC. After 60 minutes, freshly distilled styrene (1.7 mL, 1.537 g, 0.0148 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was heated at 110 ^oC for 24 hours. An aliquot of the reaction mixture was removed and subjected to GC analysis to determine the presence of styrene in the reaction mixture. After complete consumption of styrene, as evidenced by GC analysis, 1,1-bis(4-aminophenyl)ethylene, (**7**) (0.1 g, 0.4756 x 10^{-3} mol) was added to the reaction mixture in the solid form at room temperature. The resultant reaction mixture was heated at 110 ^oC for 2 hours. The tube was then withdrawn from the oil bath, 10 mL THF was added to dissolve the reaction mixture and passed through a silica gel column to remove the catalyst and ligand impurities. The polymer product was isolated by precipitation from THF solution into excess methanol, filtered and dried under vacuum at 60 ^oC to give 1.90 g of •,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) as a white solid: ^1H NMR: • = 1.23 – 2.46 ppm [m, polystyrene CH_2 and CH], 3.65 ppm [broad s, 8H, 4 x NH_2], 6.24 - 7.44 ppm [aromatic H]; FTIR (solid): 3469 cm^{-1} (N-H); $M_{n, theory}$ = 4.20 x 10^3 g/mol;
SEC: M_n = 3.80 x 10^3 g/mol, M_w/M_n = 1.13; $M_{n, titration}$ = 4.17 x 10^3 g/mol.

3.4.7 Tertiary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis[(4-dimethylamino)phenyl]ethylene, (12)

4,4'-Bis(dimethylamino)benzophenone (98%) was purified by recrystallization from absolute ethanol. In a dry three-necked round bottom flask, methyltriphenylphosphonium bromide (5.25 g; 0.0147 mol) in freshly distilled, dry THF (100 mL) was degassed with argon for 15 minutes. Methyllithium (10.5 mL of a 1.4M solution in diethyl ether, 0.0147 mol) was added dropwise to the reaction flask *via* a syringe at 0 ^oC to form the corresponding phosphorous ylide. After stirring for 4 hours at room temperature, the resulting ylide was transferred *via* a cannula into a solution of 4,4'-bis(dimethylamino)benzophenone (3.30 g; 0.0123 mol) in dry

THF (100 mL) at 0 °C, with stirring. The reaction mixture immediately turned orange in colour. After stirring the reaction at room temperature for 12 hours, methanol (2 mL) was added to quench the reaction. Using hexane/ethyl acetate (*v/v,* 20/80) mixture as eluent, the product was purified by column chromatography. Recrystallization of the resultant orange solid from absolute ethanol gave 2.92 g (89%) of pure 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) as light green crystals: mp = 126.8 - 127.9 °C (lit. mp[196] = 120-121 °C);
^{1}H NMR ($CDCl_3$): • = 2.96 ppm [s, 12H, 2 x $N(C\underline{H}_3)_2$], 5.20 ppm [s, 2H, $=CH_2$], 6.71 and 7.29 ppm [d x d, 8H, aromatic H]; FTIR (solid): 1334 cm^{-1} (N-C);
TLC: R_f (hexane/ethyl acetate, v/v, 20/80) = 0.88.

3.4.8 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Polystyrene, (14)

A Schlenk tube was charged with copper (I) bromide (0.0449 g, 0.3128 x 10^{-3} mol), 2,2'-bipyridyl (0.1466 g, 0.9384 x 10^{-3} mol), (1-bromoethyl)benzene (0.05790 g, 0.043 mL, 0.3128 x 10^{-3} mol), 1,1-bis[(4-dimethylamino)phenyl]-ethylene, (**12**) (0.083 g, 0.3128 x 10^{-3} mol) and diphenyl ether (1.7 mL). The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. Under argon atmosphere, the flask was then immersed in a thermostated oil bath at 110 °C. The consumption of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was monitored by TLC analysis. After 60 minutes, freshly distilled styrene (1.90 mL, 1.6893 g, 0.0162 mol) was introduced to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was then heated at 110 °C for 12 hours. The tube was withdrawn from the oil bath, followed by the addition of THF (10 mL) to the reaction mixture. The reaction mixture was then passed through a silica gel column to remove copper-catalyst impurities. The polymer product was purified by precipitation from THF solution into excess methanol, filtered and dried under vacuum at 60 °C to give 2.03 g of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) as a white solid:

^{1}H NMR: • = 1.22 – 2.46 ppm [m, polystyrene CH$_2$ and CH], 3.02 ppm [2 x s, 12H, 2 x N(CH$_{3)2}$], 6.28 - 7.79 ppm [aromatic H]; FTIR (solid): 1350 cm^{-1} (N-C); M$_{n,\ theory}$ = 5.40 x 10^3 g/mol; SEC: M$_n$ = 5.10 x 10^3 g/mol, M$_w$/M$_n$ = 1.14;
M$_{n,\ titration}$ = 5.21 x 10^3 g/mol.

3.4.9 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Poly-(methyl methacrylate), (15)

A Schlenk flask was charged with copper (I) bromide (0.0397 g, 0.2730 x 10^{-3} mol), 2,2'-bipyridyl (0.1280 g, 0.8190 x 10^{-3} mol), (1-bromoethyl)benzene (0.0506 g, 0.038 mL, 0.2730 x 10^{-3} mol), 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) (0.73 g, 0.2730 x 10^{-3} mol) and diphenyl ether (1.0 mL). The Schlenk tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. Under argon atmosphere, the Schlenk tube was then immersed in a thermostated oil bath at 110 ^{o}C. The disappearance of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was monitored by TLC. After 1 hour, freshly distilled methyl methacrylate (1.60 mL, 1.5016 g, 0.0150 mol) was added to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature and the reaction mixture was then heated at 90 ^{o}C for 12 hours. The tube was withdrawn from the oil bath and THF (10 mL) was added to the reaction mixture. The reaction mixture was passed through a silica gel column to remove the copper/ligand impurities. The functionalized polymer product was isolated by precipitation from the THF solution into excess methanol. The polymer was filtered, dried under vacuum at 60 ^{o}C to give 1.80 g of •-bis(4-dimethylamino-phenyl) functionalized poly(methyl methacrylate), (**15**) as a white solid: ^{1}H NMR: • = 3.01 ppm [broad s, 12H, 2 x N(CH$_3$)$_2$], 6.26 - 7.41 ppm [aromatic H];
FTIR (solid): 1349 cm^{-1} (N-C); M$_{n,\ theory}$ = 5.50 x 10^3 g/mol; SEC:
M$_n$ = 5.23 x 10^3 g/mol, M$_w$/M$_n$ = 1.03; M$_{n,\ titration}$ = 5.35 x 10^3 g/mol.

3.4.10 Synthesis of •,• -Tetrakis(4-dimethylaminophenyl) Functionalized Polystyrene, (16)

A Schlenk tube was charged with copper (I) bromide (0.0429 g, 0.2956 x 10^{-3} mol), 2,2'-bipyridyl (0.1385 g, 0.8868 x 10^{-3} mol), (1-bromoethyl)benzene (0.0547 g, 0.041 mL, 0.2956 x 10^{-3} mol), 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) (0.079 g, 0.2956 x 10^{-3} mol) and diphenyl ether (1.7 mL). The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. Under argon atmosphere, the Schlenk tube was then immersed in a thermostated oil bath at 110 ^{o}C. After 1 hour, freshly distilled styrene (1.7 mL, 1.537 g, 0.0148 mol) was added to the resultant green reaction mixture using a degassed stainless steel syringe. The reaction mixture was heated at 110 ^{o}C for 24 hours. An aliquot of the reaction mixture was removed and subjected to GC analysis to determine the presence of styrene in the reaction mixture. After complete consumption of styrene, as evidenced by GC analysis, the reaction tube was cooled to room temperature and 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) (0.1 g, 0.3754 x 10^{-3} mol), in its solid form, was added to the reaction mixture. The Schlenk tube was then heated at 110 ^{o}C for 2 hours, with stirring. The Schlenk tube was withdrawn from the oil bath and THF (10 mL) was added to the reaction mixture. The resultant reaction mixture was then passed through a silica gel column to remove copper-catalyst impurities. The polymer product was isolated by precipitation from the THF phase into excess methanol. The tetrafunctional polymer product was filtered, vacuum dried at 60 ^{o}C to give 1.84 g of •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) as a white solid: ^{1}H NMR: • = 1.20 – 2.42 ppm [m, polystyrene CH_2 and CH], 3.16 ppm [broad s, 24H, 4 x $N(CH_3)_2$], 6.38 - 7.27 ppm [aromatic H]; FTIR (solid): 1349 cm^{-1} (N-C); $M_{n,\ theory}$ = 5.20 x 10^{3} g/mol; SEC: M_n = 4.93 x 10^{3} g/mol, M_w/M_n = 1.16; $M_{n,\ titration}$ = 5.13 x 10^{3} g/mol.

3.5 A New Supported Catalyst System for the Atom Transfer Radical Polymerization of Styrene

Dipyridyl functionalized polysulfone, (**3**), (PFPS-95), which was used as the polymeric ligand in the reaction, was prepared by the addition of 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the lithiated polysulfone according to the procedure outlined in Section 3.3.3 of the experimental work. In a typical ATRP experiment for the polymerization of styrene in the presence of the new supported catalyst system, a Schlenk flask was charged with PFPS-95 (0.2 g, 0.3343 mmol), CuBr (0.0240 g, 0.1672 mmol) and diphenyl ether (1.0 mL) to give a yellow-green solution. On addition of (1-bromoethyl)benzene (0.0309 g, 0.023 mL, 0.1672×10^{-3} mol) to the reaction mixture, the mixture turned green. The tube was tightly sealed with a rubber septum and subjected to several freeze-pump-thaw cycles to remove oxygen. The Schlenk flask was then immersed in an oil bath at 110 ^{o}C for 5 minutes. Upon cooling the reaction mixture to room temperature, freshly distilled styrene (1.5 mL, 1.3635 g, 0.0131 mol) was then added to the resultant green reaction mixture by using a degassed stainless steel syringe. The reaction mixture was subsequently heated at 110 ^{o}C for 12 hours. Upon cooling, THF (10 mL) was added to the reaction mixture to dissolve the polystyrene product. The resultant mixture was added to toluene (500 mL) to remove the PFPS-95 catalyst support, which precipitated from toluene solution. The polysulfone derivative, PFPS-95 was filtered and the toluene filtrate was passed through a short silica gel column. The toluene was removed in vacuo and the polymer product was precipitated into excess methanol, filtered, dried under vacuum at 60 ^{o}C to give 1.2 g of pure polystyrene, (**17**) as the final product: ^{1}H NMR: • = 1.10 – 2.22 ppm [m, polystyrene CH_2 and CH], 6.46 - 7.49 ppm [aromatic H]; $M_{n,\ theory} = 8.15 \times 10^{3}$ g/mol; SEC: $M_n = 8.13 \times 10^{3}$ g/mol,
$M_w/M_n = 1.14$.

3.6 Amine Functionalized Polymers by Atom Transfer Radical Polymerization: Polymerization Kinetics Studies

A series of polymerization kinetics experiments were conducted using each amine functionalized initiator system with monomer: initiator ratios of 50:1, 100:1 and 200:1 for each reaction sequence. Polymerization kinetics experiments for the following three systems were performed:

(a) Synthesis of • -aminophenyl functionalized polystyrene, (**6**) by ATRP
(b) Synthesis of • -bis(aminophenyl) functionalized polystyrene, (**9**) by ATRP
(c) Synthesis of • -bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) by ATRP

In a typical experiment, the procedure for the synthesis of • -aminophenyl functionalized polystyrene, (**6**) by ATRP methods is outlined as follows:

A Schlenk flask was charged with copper (I) bromide (0.1488 g, 1.0244 x 10^{-3} mol), 2,2'-bipyridyl (0.44 g, 3.0732 x 10^{-3} mol), (1-bromoethyl)benzene (0.1896 g, 0.14 mL, 1.0244 x 10^{-3} mol), 1-(4-aminophenyl)-1-phenylethylene (0.2 g, 1.0244 x 10^{-3} mol) and diphenyl ether (5 mL). The mixture was degassed by three freeze-pump-thaw cycles to remove the oxygen and then purged with argon for 15 minutes. The reaction mixture was stirred at room temperature for 5 minutes. The flask was immersed in an oil bath thermostated at 110 ^{o}C for 60 minutes, with stirring. Upon cooling the reaction mixture, freshly distilled and degassed styrene (5.86 mL, 5.3344 g, 51.218 x 10^{-3} mol) was added to the resultant green reaction mixture *via* a degassed stainless steel syringe at room temperature. An aliquot (1 mL) of the sample was withdrawn from the reaction mixture, diluted with THF (9 mL) and subjected to gas chromatography analysis to determine the amount of styrene in the sample at t = 0. Under an argon atmosphere, the mixture was then heated to 110 ^{o}C. At different time intervals, aliquots of 1 mL sample were withdrawn from the reaction flask under argon and diluted with a known amount of THF (9 mL). The residual styrene content was determined by gas chromatographic analysis. At the completion of the analysis, the polymer samples were purified by passage through a short silica gel column to remove catalyst impurities and then precipitated from THF solution into excess methanol. The different •-aminophenyl functionalized polystyrene, (**6**) samples were precipitated several times from THF solution into methanol, filtered off and vacuum dried in preparation for size exclusion chromatography analyses to determine the number average molecular weights and molecular weight distributions of the polymers.

Experimental data for the different polymerization kinetics experiments for [M]/[I] ratio of 50:1, 100:1 and 200:1 is given below:

Synthesis of • -aminophenyl functionalized polystyrene, (6)

[M]/[I]	**(4)**	Styrene	(1-bromo-ethyl)-benzene	Copper (I) Bromide	2,2'-Bipyridyl	DPE (mL)
50:1	0.2 g; 1.0244 mmol	5.33 g; 5.87 mL; 0.0512 mol	0.1896 g; 0.1404 mL; 1.0244 mmol	0.1488 g; 1.0244 mmol	0.480 g; 3.0732 mmol	5.0
100:1	0.15 g; 0.7683 mmol	8.0 g; 8.8 mL; 0.0768 mol	0.1422 g; 0.1053 mL; 0.7683 mmol	0.1102 g; 0.7683 mmol	0.360 g; 2.3049 mmol	7.0
200:1	0.1 g; 0.5122 mmol	10.67 g; 11.7mL; 0.1024 mol	0.0948 g; 0.0702 mL; 0.5122 mmol	0.0735 g; 0.5122 mmol	0.240 g; 1.5366 mmol	8.0

Synthesis of • -bis(aminophenyl) functionalized polystyrene, (9)

[M]/[I]	**(7)**	Styrene	(1-bromoethyl)-benzene	Copper (I) Bromide	2,2'-Bipyridyl	DPE (mL)
50:1	0.20 g; 0.9512 mmol;	4.95 g; 5.5 mL; 0.0476 mol	0.1760 g; 0.1304 mL; 0.9512 mmol	0.1365 g; 0.9512 mmol	0.4457 g; 2.8278 mmol	3.0
100:1	0.16 g; 0.7610 mmol	7.93 g; 8.7 mL; 0.0761 mol	0.1408 g; 0.1043 mL; 0.7610 mmol	0.1092 g; 0.7610 mmol	0.3566 g; 2.283 mmol	7.0
200:1	0.11 g; 0.5232 mmol	10.90 g; 12.0 mL; 0.1046 mol	0.0968 g; 0.0717 mL; 0.5232 mmol	0.0751 g; 0.5232 mmol	0.2452 g; 1.5696 mmol	8.0

Synthesis of • -bis(4-dimethylaminophenyl) functionalized polystyrene, (14)

[M]/[I]	**(12)**	Styrene	(1-bromoethyl)-benzene	Copper (I) Bromide	2,2'-Bipyridyl	DPE (mL)
50:1	0.26 g; 0.9761 mmol	5.08 g; 5.6 mL; 0.0488 mol	0.1806 g; 0.1338 mL; 0.9761 mmol	0.140 g; 0.9761 mmol	0.4574 g; 2.9283 mmol	3.0
100:1	0.20 g; 0.7509 mmol	7.82 g; 8.6 mL; 0.0751 mol	0.1390 g; 0.1030 mL; 0.7509 mmol	0.1077 g; 0.7509 mmol	0.3518 g; 2.2527 mmol	7.0
200:1	0.15 g; 0.5631 mmol	11.73 g; 13.0 mL; 0.1126 mol	0.1050 g; 0.0778 mL; 0.5631 mmol	0.0808 g; 0.5631 mmol	0.2638 g; 1.6893 mmol	8.0

3.7 Synthesis of Polystyrene, (17) using Dipyridyl Functionalized Polysulfone, (3) as Ligand: Polymerization Kinetics Studies

In a typical experiment, a Schlenk flask was charged with dipyridyl functionalized polysulfone, (**3**) (PFPS-95, 0.4088 g, 0.6555 mmol), CuBr (0.0313 g, 0.2185 mmol) and diphenyl ether (5 mL) to give a yellow-green solution. On addition of (1-bromoethyl)benzene (0. 0313 g, 0.0232 mL, 0.2185 x 10^{-3} mol) to the reaction mixture, the mixture turned green. The flask was then degassed by three freeze-pump-thaw cycles to remove the oxygen. After purging with argon for 15 minutes, freshly distilled styrene (5.0 mL, 4.545 g, 0.0437 mol) was introduced by syringe and stirred for 5 minutes to ensure dispersion of the PFPS-95 support. The polymerization was monitored by gravimetric analysis. At different intervals, 1 mL aliquot was withdrawn from the solution and diluted with a known amount of THF (2 mL). The product was then precipitated into excess toluene to remove the PFPS-95/CuBr catalyst complex. The toluene filtrate was passed through a silica gel column, transferred into a flask and concentrated on the rotary evaporator. The polystyrene was precipitated into excess methanol, filtered and vacuum dried to constant mass. Each polystyrene sample was subjected to size exclusion chromatography analysis to determine its number average molecular weight and molecular weight distribution.

CHAPTER 4

RESULTS AND DISCUSSION

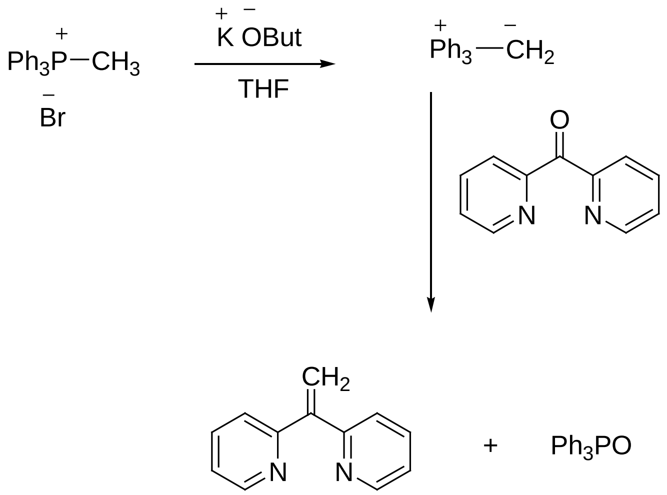
4.1 Chemical Modification of Polysulfone by Anionic Methods

Several reviews on the chemical modification of polysulfone by different chemical methods to effect the introduction of functional groups onto the polysulfone backbone have been reported in the literature. The most efficient method, which has been developed by Guiver and coworkers[35], involves the treatment of unmodified polysulfone with an organolithium compound and the subsequent reaction of lithiated polysulfone with different electrophiles which introduced different functional groups onto the polymer backbone. For example, for the preparation of amine functionalized polysulfones, Guiver and coworkers[35] reported an efficient methodology for quantitatively introducing amine groups onto commercially available Udel P3500 polysulfone and Radel R5000 poly(aryl sulfone) by the azidation of lithiated polysulfone followed by sodium borohydride reduction of the azide derivative. The process provided amine functionalized polysulfone having a high degree of functionality with site specificity to either the sulfone aromatic ring or the bisphenol ring.

The present study focused on the development of a new synthetic method for the preparation of novel dipyridyl functionalized polysulfones[39]. The anionic functionalization process involves the formation of lithiated polysulfone from unmodified polysulfone, (**1**) and subsequent reaction with 2,2'-vinylidenedipyridine, (**2**) in THF at -78 ^{o}C under argon atmosphere to afford the corresponding dipyridyl functionalized polysulfone, (**3**). In addition, the unmodified polysulfone, (**1**) as well as the different dipyridyl functionalized polysulfone, (**3**) samples were used as membrane substrates for membrane formation to determine the membrane characteristics of each sample by standard membrane characterization methods.

4.1.1 Synthesis of 2,2'-vinylidenedipyridine, (2)

The method for the synthesis of 2,2'-vinylidenedipyridine, (**2**) outlined by Eckard and Summers[192] and Summers and coworkers[193] afforded the desired product in low yields. Thus, a new synthetic strategy[39], using the experimental design of Subramanyam[194] was adopted, with modifications, for the preparation of 2,2'-vinylidenedipyridine, (**2**). 2,2'-Vinylidenedipyridine, (**2**) was obtained as a light brown oil in 80% yield by the classical Wittig reaction of di-2-pyridylketone with the phosphorous ylide, an intermediate which was generated from the reaction of potassium tert-butoxide and methyltriphenylphosphonium bromide in THF:



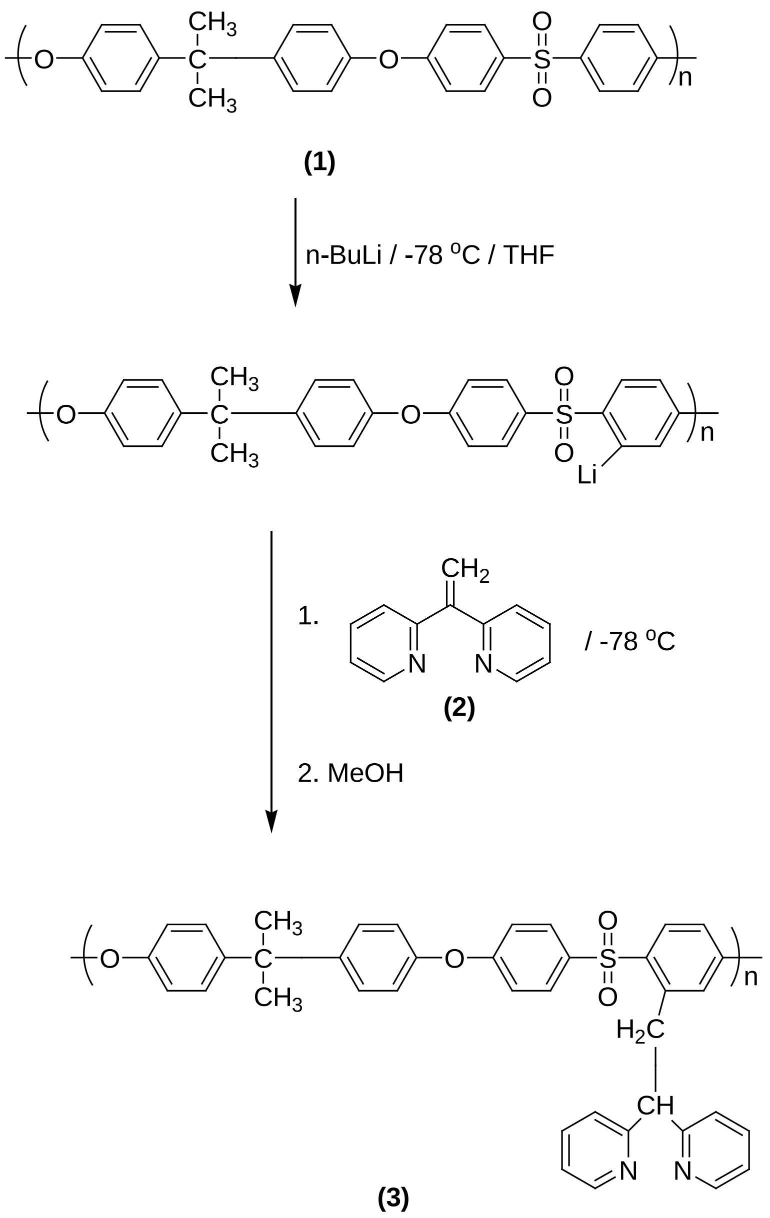
(2)

The ^1H NMR spectrum **(**Figure 1**)** of 2,2'-vinylidenedipyridine, (**2**) exhibits a singlet at • = 6.05 ppm, due to the resonances of equivalent alkene protons and a multiplet between • = 6.97 – 8.61 ppm, attributed to the resonances of the aromatic protons of the pyridyl groups. The FTIR spectrum (Figure 2) of 2,2'-vinylidenedipyridine, (**2**) shows a strong C=N absorption frequency at 1634 cm^{-1}, typical of the presence of pyridyl groups[192,197].

4.1.2 Synthesis of Dipyridyl Functionalized Polysulfone, (3)

The reactions of lithiated polysulfone with different electrophiles provide efficient synthetic routes for the preparation of polysulfones with different functional groups pendant to the polysulfone backbone[14-17,35-38]. Such synthetic procedures were adopted for the preparation of polysulfone derivatives substituted with pyridyl groups. The reaction of living polymeric carbanions with 2,2'-vinylidene-dipyridine, (**2**) provides a novel method for the synthesis of dipyridyl functionalized polysulfone, (**3**). The functionalization of polysulfone, (**1**) with 2,2'-vinylidenedipyridine, (**2**) involves two steps: (a) the regiospecific lithiation of polysulfone, (**1**) with *n*-butyllithium at low temperature, and (b) the reaction of lithiated polysulfone with 2,2'-vinylidenedipyridine, (**2**) at low temperature.

Upon lithiation of unmodified polysulfone, (**1**) with *n*-butyllithium, formation of a homogenous red-brown viscous solution, which indicates the formation of the lithiated polysulfone, was observed at low temperature. However, precipitation of the lithiated species occured at room temperature[14,15]. The stoichiometry of the reaction affects the degree of pyridyl substitution of the product. When equimolar amounts of lithiated polysulfone and 2,2'-vinylidenedipyridine, (**2**) were employed in the reaction, dipyridyl functionalized polysulfone, (**3**) PFPS-45, with degree of functionalization as high as 45% was obtained. However, higher degrees of functionalization were effected by the treatment of lithiated polysulfone with excess of 2,2'-vinylidenedipyridine, (**2**) in THF at -78 ^oC to afford the corresponding dipyridyl functionalized polysulfones, (**3**). With the addition of 10% and 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the corresponding lithiated polysulfone, the corresponding dipyridyl functionalized polysulfones, (**3**) PFPS-80 and PFPS-95, with degrees of functionalization of 80% and 95%, respectively, were obtained according to the following synthetic pathway:



The different dipyridyl functionalized polysulfones, (**3**) were characterized by ^{1}H NMR, FTIR, DSC and thermogravimetric analysis. Using sample PFPS-80, the spectroscopic characterization data for dipyridyl functionalized polysulfone, (**3**) is provided to confirm the structure of the functionalized polysulfones. The ^{1}H NMR spectrum (Figure 3) of dipyridyl functionalized polysulfone, (**3**) (PFPS-80) exhibits signals at • = 3.78 and • = 4.65 ppm, due to the resonances of CH_2 and CH protons, respectively, indicating the incorporation of the functionalizing agent onto the polysulfone backbone. Furthermore, the signals between • = 6.3 – 6.7

ppm, 7.4 – 7.8 ppm and 8.1 – 8.4 ppm are attributed to the resonances of the aromatic protons of the pyridine groups[194]. The resonances for pyridine protons are absent in the proton NMR spectrum of unfunctionalized polysulfone. The FTIR spectrum (Figure 4) of dipyridyl functionalized polysulfone (**3**), (PFPS-80) shows the presence of a strong absorption band at 1634 cm^{-1}, which is characteristic of the C=N stretching mode of the pyridine group of dipyridyl derivatives such as 2,2'-vinylidenedipyridine[192,197].

The thermal stabilities of the unfunctionalized polysulfone and the different dipyridyl functionalized polysulfones, (**3**) were determined by thermogravimetric analysis (TGA). The TGA thermograms (Figure 5) show that the PFPS-45 and PFPS-80 samples are thermally less stable than the parent unfunctionalized polysulfone, most probably due to the introduction of the bulky groups along the polymer backbone. With the onset of weight loss at 250 ^{o}C, PFPS-45 exhibits a two phase degradation pattern with a distinct weight loss of 8% observed at 350 ^{o}C, with a total weight of 56% at 534 ^{o}C. The initial weight loss in PFPS-45 is believed to be due to the loss of pyridine functional groups as well as the removal of water which is associated with the dipyridine groups. In contrast, the PFPS-80 is thermally more stable with the degradation pattern showing the onset of weight loss at 307 ^{o}C, with 25% weight loss at 404 ^{o}C, followed by the major weight loss of 38% at 537 ^{o}C. The presence of more polar dipyridyl pendant groups on the PFPS-80 polysulfone sample accounts for its higher thermal stability as compared to the PFPS-45 sample.

The glass transition temperatures of each polysulfone sample were obtained from differential scanning calorimetry and the data is listed below:

Sample	T_g (^{o}C)
PS	189
PFPS-45	185
PFPS-80	161

For the PFPS-45 and PFPS-80 derivatives with pendant dipyridyl substituents, a decrease in the glass transition temperature is observed when compared to the parent polysulfone sample. However, the largest decrease in the glass transition temperature was observed for the PFPS-80 sample. The introduction of more pendant dipyridyl groups along the polymer backbone increases polymer mobility which ultimately lowers the glass transition temperature value.

Membranes obtained from unmodified as well as the dipyridyl functionalized polysulfones, (**3**) were characterized by atomic force microscopy, scanning electron microscopy, pure water permeation measurements and contact angle analysis.

The three dimensional AFM images for the different polysulfone membranes, PS, PFPS-45 and PFPS-80 are displayed in Figure 6. The topographic images of PS show a distinct difference between the top and bottom surfaces of the membrane. The top or skin side of the membrane has larger nodules than the bottom, indicated by the higher roughness values obtained. The diameters of the nodules range from 1.02 to 1.26 µm, with nodule diameter sizes on the bottom side ranging from 0.35 to 0.42 µm. The diameter of the pores on the bottom side of the PS membrane vary between 0.13 to 0.21 µm compared to the pore size diameters on the top of the membrane of 0.24 – 0.42 µm.

For sample PFPS-45, the roughness values for the skin surface were much larger than that of the PS membrane, while the bottom surface of PFPS-45 was much smoother than that of the PS membrane. The top of the PFPS-45 membrane was much smoother than that of the PS membrane. The top of the PFPS-45 has more densely packed nodules than the bottom. Nodules in the membrane skin surface range from 0.83 µm to 1.39 µm and 0.24 µm to 1.13 µm in the bottom surface. The bottom surface has rod-like structures that are 2.97 µm long and 1.37 µm wide. Thus, the nodule size of the PS sample seems to be larger than the PFPS-45 sample, which has a larger range of nodule size diameters. The diameter of the pores on the bottom of the PFPS-45 sample varies between 0.51 and 1.31 µm. The pore sizes on the top were between 166 and 167 nm in diameter. Thus, the pore sizes of PFPS-45 are significantly smaller than those in the PS membrane.

Similarly, for example PFPS-80, the surface roughness was significantly greater than the unmodified polysulfone sample. Cross-section profiles show that average nodule size of PFPS-80 is 347 nm, which is slightly larger than the nodules present in the PS sample. Also, the average pore size of the PFPS-80 sample was 390 nm, whereas, the average pore size of the PS sample was 254 nm. Analysis shows that pore size distribution of the PFPS-80 sample is larger than that of the PS sample.

In general, the rough surface structures observed for the dipyridyl functionalized polysulfones should produce a looser surface fouling layer in applications of the membrane substrate in separation technologies, consistent with data reported in literature[14-17,35-38,198,199].

SEM photographs reveal distinctly different morphological patterns for each of the membranes. Figure 7 shows the cross-section photographs of the PS, PFPS-45 and PFPS-80 membrane samples and indicates that each polymer membrane structure is composed of a thin, dense layer at the top of the membrane, with a porous sublayer in the middle and porous architecture at the bottom. However, the membrane prepared from the PFPS-45 sample was more brittle and the PFPS-80 sample was thicker and denser on the top.

Figure 8 shows the SEM analysis of the top view of different membranes. The PS sample reveals a smooth human skin-like upper layer with tiny pores on the surface. However, the top view of PFPS-45 shows an irregular wave-like orientation of polymer rods with the pores oriented on the side of the polymer rod. The topology of PFPS-80 exhibits an irregular, fibrous orientation of polymer material on the surface.

Figure 9 shows the SEM analysis of the bottom view of the different polysulfone membranes. The photograph for the unmodified polysulfone membrane shows Swiss-cheese like structures with well defined smooth areas between pore openings as well as pores of different sizes. In the PFPS-80 sample, the Swiss-cheese morphology is more pronounced with smooth areas between pore openings, but with more pores of different sizes and shapes. In contrast, a bottom view of the PFPS-45 sample shows more particulate structures with jig-saw-like aggregates or discs fragments of different sizes and shapes as well as variable pore sizes between the polymer fragments.

Figure 10 shows the plot of pure water flux as a function of pressure at 25 ^{o}C for the different polysulfone membranes. For all membrane substrates, the rate of permeate production increases linearly with pressure. The unmodified polysulfones exhibits a lower pure-water flux at a given pressure as compared to the dipyridyl functionalized polysulfones, PFPS-45 and PFPS-80 and the polysulfone blend. Both PS and PFPS-45 produce linear flux-pressure plots, with relatively small amount of permeate flux at a given pressure. In contrast, the PFPS-80 sample exhibits a linear flux-pressure plot, but a non-linear flux-pressure plateau is observed at higher pressures, probably due to membrane compaction. Furthermore, the variations in permeate flux data could be attributed to the degree of functionalization, surface roughness, pore sizes and pore size distribution. Thus, for the dipyridyl functionalized polysulfone with higher degree of functionalization, PFPS-80, the pure water flux is the highest, most probably as a result of increased hydrophilicity and larger pore sizes and pore density which makes the PFPS-80 sample the most suitable precursor to prepare membranes with anti-fouling properties and improved permeability.

Nevertheless, the PFPS-80 sample exhibits greater permeation rates at a given pressure value, even though it is more expensive to prepare as evidenced by the methods of synthesis. More significantly, the PS-1-80 sample, the blend of 1% PFPS-80 in a polysulfone matrix, show larger pure water flux values as compared to the unfunctionalized polysulfone at a given pressure, but smaller values than the PFPS-80 sample, which indicates that the introduction of polar groups such as the dipyridyl group onto the polysulfone backbone does improve membrane permeability properties.

The flat sheet asymmetric membranes as well as dense films were prepared and characterized by contact angle measurements to evaluate the hydrophilic character of each membrane. Contact angle data was obtained at 20 ^{o}C with an ERMA G-1 contact angle meter using pure water as probe liquid. The contact angle data for PS and PFPS-80 is given below:

Sample	Asymmetric membrane (^{o})	Dense film (^{o})
PS	78	74
PFPS-80	87	84

Results show that the dipyridyl functionalized polysulfone sample PFPS-80 is more hydrophilic than the unmodified polysulfone sample. The increased contact angle value for PFPS-80 is most probably influenced by the introduction of the hydrophilic dipyridyl groups on the surface as well as the surface roughness and porosity of the asymmetric membranes and dense films.

The detailed spectroscopic, chromatographic, thermal and microscopic data and contact angle measurements provide evidence for the synthesis of well defined dipyridyl functionalized polysulfones, (**3**) with improved hydrophilicity and excellent thermal and membrane properties.

4.2 Atom Transfer Radical Polymerization: Synthesis of Chain End Functionalized Polymers

The process of Atom Transfer Radical Polymerization (ATRP), which was developed by Matyjaszewski in 1995, provides the most versatile method for the synthesis of well defined polymers with high regiospecificity with respect to chain end functionality. One of the best synthetic strategies for the introduction of a functional group at the •-terminus of the polymer chain is *via* the use of functionalized initiators during the ATRP polymerization process. However, limited work on the ATRP preparation of polymers with the amine group at the •-terminus of the polymer using functional initiators has been documented[159-166]. Since the ligands used in ATRP systems are mostly bidentate and multidentate amine molecules, appropriately designed functionalized initiators are required for the successful ATRP reactions whereby the interaction between the amine functionality of the functionalized initiator and the catalyst/ligand system is reduced.

The current research focuses on the synthesis of well defined primary and tertiary amine functionalized polymers based on a general, quantitative ATRP chain end functionalization method using different functionalized unimolecular initiator systems[53]. The study outlines the synthetic pathways for different amine functionalized 1,1-diphenylethylene compounds and the determination of their utility as amine functionalized initiator precursor compounds in ATRP reactions. The *in situ* formation of the specific unimolecular functionalized initiator adduct is based on a simple reaction of alkyl halides with functionalized amine or diamine 1,1-diphenylethylene derivatives substituted with the primary and tertiary amine groups. Different •-amine and •-bis(amine) functionalized polymers can be prepared using the specific amine or diamine functionalized initiator adducts as initiators for the ATRP of styrene and methyl methacrylate.

The synthesis of different amine chain end functionalized polymers by ATRP methods were conducted by using the following methods:

a) the synthesis of 1-(4-aminophenyl)-1-phenylethylene, (**4**) and its use as a primary amine functionalized initiator precursor for the preparation of •-aminophenyl functionalized polystyrene, (**6**) by ATRP methods. The use of a new primary amine initiator adduct, (**5**), generated *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene, (**4**), as the initiator for the ATRP of styrene provides a new method for the synthesis of the corresponding •-aminophenyl functionalized polystyrene, (**6**).

b) the preparation of 1,1-bis(4-aminophenyl)ethylene, (**7**) and its utility as a primary diamine functionalized initiator precursor for the synthesis of •-bis(aminophenyl) functionalized polymers by ATRP methods. The utilization of a new primary diamine functionalized initiator adduct, (**8**), obtained *in situ* by the reaction of (1-bromoethyl)benzene with 1,1-bis (4-aminophenyl)ethylene, (**7**), as the initiator for the styrene and methyl methacrylate polymerization by ATRP methods provides a unique synthetic route for the preparation of the corresponding •-bis(aminophenyl) functionalized polystyrene, (**9**) and •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**), respectively.

c) the synthesis of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**), and its use as a tertiary diamine functionalized initiator precursor for the preparation of •-bis(4-dimethylaminophenyl) functionalized polymers. The use of a new tertiary diamine functionalized initiator adduct, (**13**), prepared *in situ* by the reaction of (1-bromoethyl)benzene with 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) in the presence of copper (I) bromide/2,2'-bipyridyl as the catalyst system, for the styrene and methyl methacrylate polymerization by ATRP methods affords a new method for the preparation of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) and •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**), respectively.

The current study investigates the controlled/living nature of each ATRP reaction leading to the preparation of the different amine chain end functionalized polymers by evaluating the polymerization kinetics data for each polymerization reaction.

The preparation of •,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) and •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) can be prepared by post ATRP chain end modification reactions according to the following synthesis strategy:

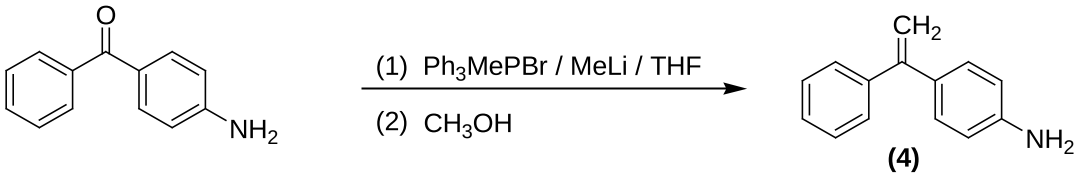
a) the atom transfer radical polymerization of styrene initiated by the appropriate new diamine functionalized initiator adduct, derived from the specific diamine functionalized 1,1-diphenylethylene derivative.
b) the addition of the appropriate diamine functionalized 1,1-diphenylethylene compound to the • -terminus of the specific •-bis(amine) functionalized polystyrene after the completion of the polymerization process.

4.3 Synthesis of Primary Amine Functionalized Polymers by Atom Transfer Radical Polymerization

In general, direct and indirect methods, which involve unimolecular organohalide compounds with free and protected primary amine groups, respectively, have been employed as initiators for the polymerization of different styrenic and acrylate monomers in the ATRP reactions to produce •-primary amine functionalized polymers[147]. To reduce the possible interaction between the primary amine functional group and the amine-ligand catalyst system used in the ATRP reactions, the careful selection of the amine substituted initiator molecule or initiator system is essential for a well controlled ATRP functionalization reaction. The present work describes the preparation of primary amine and diamine functionalized 1,1-diphenylethylene derivatives and the determination of their utility as unimolecular, primary amine functionalized initiator precursor compounds for the ATRP of styrene and methyl methacrylate in ATRP functionalization reactions to form •-primary amine and •-primary diamine functionalized polymers.

4.3.1 Primary Amine Functionalized Initiator Precursor: Synthesis of 1-(4-Aminophenyl)-1-phenylethylene, (4)

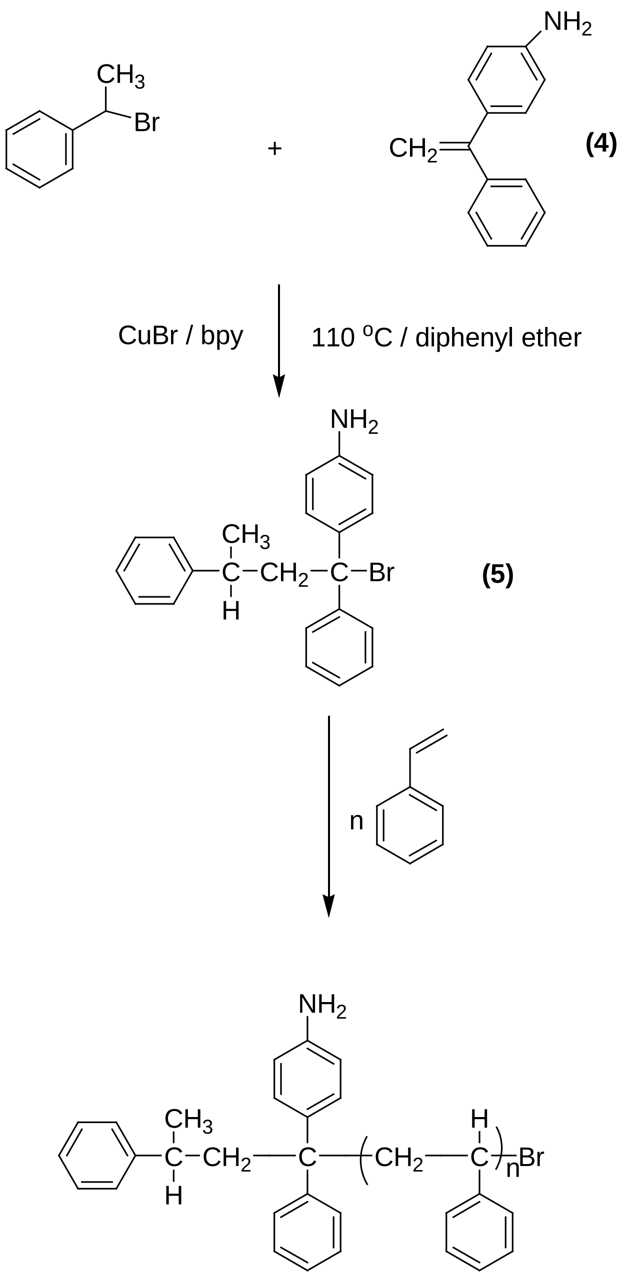
The synthesis of 1-(4-aminophenyl)-1-phenylethylene was performed according to the methodology outlined by Quirk and Lynch[51]. The preparation sequence for 1-(4-aminophenyl)-1-phenylethylene, (**4**) involved the classical Wittig reaction of 4-aminobenzophenone with a ylide, generated *in situ* from the reaction of methyllithium and methyltriphenylphosphonium bromide in freshly distilled tetrahydrofuran (THF) at room temperature. The following pathway outlines the synthesis route for the preparation of 1-(4-aminophenyl)-1-phenylethylene, (**4**):



Purification of the final product was achieved by column chromatography on silica gel using toluene as an eluent. Recrystallization of the product from 80% aqueous ethanol afforded 4.47 g (90%) of 1-(4-aminophenyl)-1-phenylethylene, (**4**) as light yellow crystals with a melting point of 81.2-82.6 ^{o}C. The ^{1}H NMR (Figure 11) of 1-(4-aminophenyl)-1-phenylethylene, (**4**) exhibits a singlet at • = 5.19 ppm, which is attributed to the resonance of equivalent vinyl protons (=CH_2) and a singlet at • = 3.67 ppm, due to the resonance of the NH_2 protons. Figure 12 depicts the FTIR spectrum of 1-(4-aminophenyl)-1-phenylethylene, (**4**) and shows the structurally significant absorption bands at 3468 cm^{-1}, which corresponds to the N-H stretching vibrations of the primary amine groups.

4.3.2 Synthesis of • -Aminophenyl Functionalized Polystyrene, (6)

The general synthetic pathway for the preparation of •-aminophenyl functionalized polystyrene, (**6**) by the ATRP method employs a new primary amine functionalized initiator adduct, (**5**) as unimolecular, primary amine functionalized initiator for the polymerization of styrene. Prior to the addition of styrene, the primary amine functionalized initiator adduct, (**5**) was prepared *in situ* by reacting stoichiometric amounts of 1-(4-aminophenyl)-1-phenylethylene, (**4**) with (1-bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3. The completion of the reaction was determined by TLC analysis by monitoring the disappearance of 1-(4-aminophenyl)-1-phenylethylene, (**4**) [R_f = 0.44, toluene]. The rapid initiation of styrene polymerization occurred after the addition of styrene monomer as evidenced by the rapid increase in the viscosity of the reaction medium, which indicates that the free radical generated from the adduct was reactive enough to initiate the polymerization of styrene. The polymerization proceeded *via* a controlled free radical polymerization process to afford quantitative yields of the corresponding •-aminophenyl functionalized polystyrene, (**6**) according to the following reaction pathway:



(4)

(5)

(6)

After polymer purification, TLC analysis of •-aminophenyl functionalized polystyrene, (**6**) [R_f = 0.89, toluene] shows only one spot on the chromatogram, consistent with the formation of the primary amine functionalized polymer in quantitative yields and the absence of any unfunctionalized polystyrene.

The size exclusion chromatogram (Figure 13) of •-aminophenyl functionalized polystyrene, (**6**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 3.10 x 10^3 g/mol and M_w/M_n = 1.08. The SEC value compares favourably with a theoretical $M_{n,theory}$ value of 3.30 x 10^3 g/mol and corresponds to 94% monomer conversion during the polymerization reaction.

The ^{1}H NMR spectrum (Figure 14) of •-aminophenyl functionalized polystyrene, (**6**) exhibits a broad peak in the region of • = 3.7 ppm, due to the resonance of amine protons[51] as well as a broad resonance at • = 4.3 ppm, due to the resonance of the terminal –CHPhBr proton[76]. The amine group functionality value for •-aminophenyl functionalized polystyrene, (**6**) was 0.99, as determined by end-group titration[54,200] and corresponds to a number average molecular weight value of 3.10 x 10^3 g/ mol.

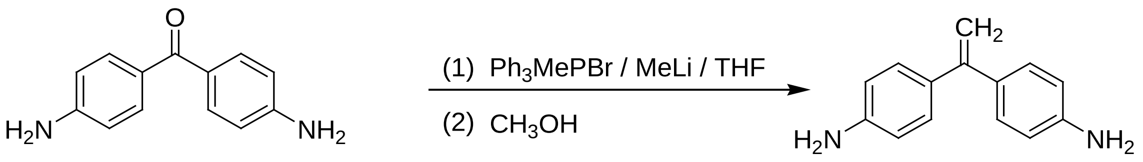
The FTIR spectrum (Figure 15) of •-aminophenyl functionalized polystyrene, (**6**) shows an absorption band at 3469 cm^{-1}, characteristic of the N-H stretching vibration of the NH_2 group. A sharp absorption band at 696 cm^{-1} is due to the stretching vibrations of the C-Br bond at the omega terminus of the polymer chain.

Initiation of the atom transfer radical polymerization of styrene by a new primary amine functionalized initiator adduct, (**5**), obtained *in situ* by the reaction of (1-bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene, (**4**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system afforded quantitative yields of •-aminophenyl functionalized polystyrene, (**6**). All polymer characterization data is consistent with the incorporation of the aminophenyl group of the initiator molecule at the •-terminus of the polymer chain[51,91].

4.3.3 Primary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis(4-aminophenyl)ethylene, (7)

Different synthetic strategies for the preparation of symmetrical diamine 1,1-diphenylethylene derivatives were reported in the literature[52,194]. Bencze[201] outlined the synthesis method for 1,1-bis(4-aminophenyl)ethylene, (**7**) by the reaction of 3,3-di(4-aminophenyl)-2-butanone with polyphosphoric acid. In addition, Sudalai and coworkers[195] prepared 1**,**1-bis(4-aminophenyl)ethylene, (**7**) in excellent yields by treatment of 1,1,1-trichloroethane with the appropriate aromatic substrate under Friedel-Craft reaction conditions.

A new synthetic method is used for the preparation of 1,1-bis(4-aminophenyl)-ethylene, (**7**), *via* the classical Wittig reaction, which involves the treatment of 4,4'-diaminobenzophenone with a phosphorous ylide, generated *in situ* from the reaction of methyllithium and methyltriphenylphosphonium bromide in freshly distilled tetrahydrofuran at room temperature according to the following reaction:



(7)

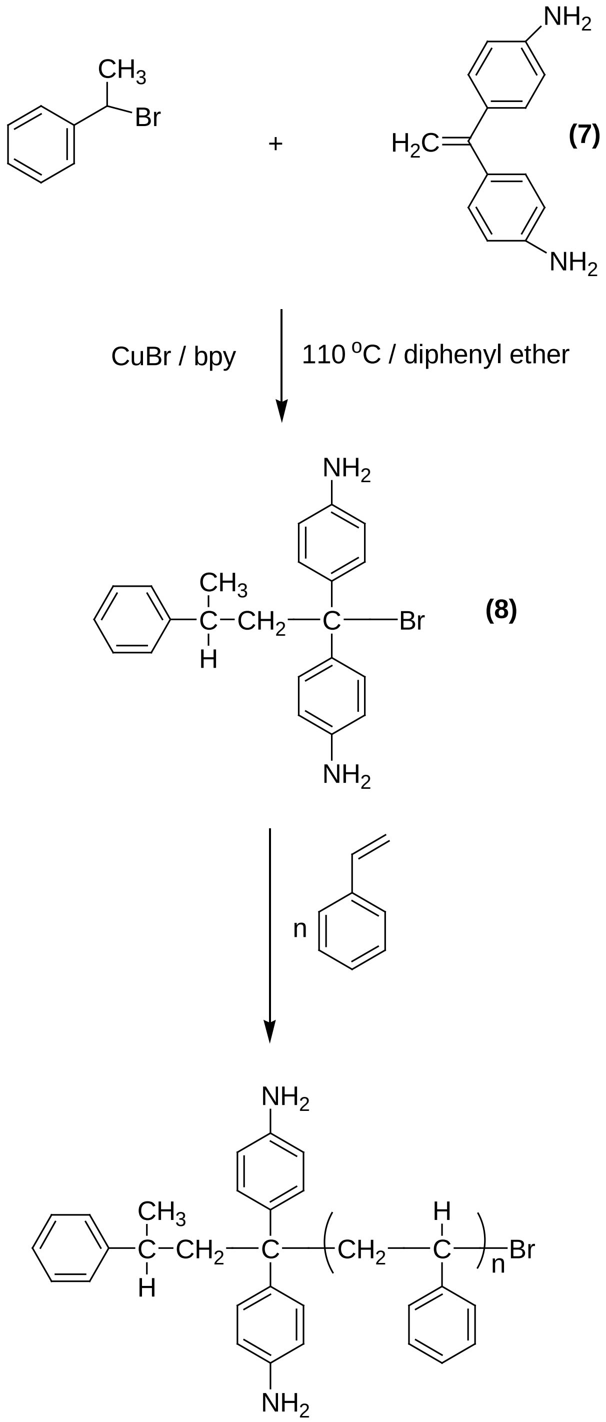
Purification of the crude product by column chromatography on silica gel using a hexane/ethyl acetate (*v/v*, 20/80) mixture as eluent and subsequent recrystallization from 80% aqueous ethanol solution gave 3.98 g (80.21%) of pure 1,1-bis(4-aminophenyl)ethylene, (**7**) as pale yellow crystals with a melting point of 160.5-162.0 °C.

The ^{1}H NMR spectrum (Figure 16) of 1,1-bis(4-aminophenyl)ethylene, (**7**) shows a singlet at • = 5.21 ppm, which is attributed to the resonance of the equivalent methylene protons $[=C\underline{H}_2]$. In addition, the broad peak at • = 3.69 ppm corresponds to the resonance of primary amine protons of the NH_2 groups.

The FTIR spectrum (Figure 17) of 1,1-bis(4-aminophenyl)ethylene, (**7**) shows the absorption band of C=C stretching vibrations at 1605 cm^{-1}, due to the presence of the $C=CH_2$ group. In addition, the strong absorption band at 3402 cm^{-1} is attributed to the N-H stretching vibrations of NH_2 groups. The absence of the strong C=O absorption band at 1669 cm^{-1} implies the quantitative conversion of the precursor benzophenone derivative to the olefin compound, which is consistent with the data of pure 1,1-bis(4-aminophenyl)ethylene, (**7**).

4.3.4 Synthesis of • -Bis(aminophenyl) Functionalized Polystyrene, (9)

The preparation of • -bis(aminophenyl) functionalized polystyrene, (**9**) by ATRP methods was conducted by using a new primary diamine functionalized initiator adduct, (**8**) for styrene polymerization. Quantitative yields of • -bis(aminophenyl) functionalized polystyrene, (**9**) was obtained according to the following reaction pathway:



(9)

The primary diamine functionalized initiator adduct, (**8**) was prepared *in situ* by the reaction of stoichiometric amounts of 1,1-bis(4-aminophenyl)ethylene, (**7**) with (1-bromoethyl)benzene in the presence of copper(I) bromide complexed with 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of

$[CuBr]_0$: [(1-bromoethyl)benzene]$_0$: $[bpy]_0$ = 1:1:3. Rapid initiation of styrene polymerization occurred after the addition of styrene monomer, as observed by the increase in the viscosity of the reaction medium. The polymerization proceeded *via* a controlled free radical polymerization process which indicates that the free radical generated from the primary diamine functionalized initiator adduct, (**8**) was reactive enough to initiate polymerization of styrene.

Thin layer chromatography was utilized to monitor the polymerization reaction and to determine the presence of functionalized and unfunctionalized polymer as well as unreacted initiator precursor in the polymerization reaction. Only one spot [R_f = 0.78, toluene], corresponding to •-bis(aminophenyl) functionalized polystyrene, (**9**), was observed on the thin layer chromatogram at the completion of the polymerization reaction.

The size exclusion chromatogram (Figure 18) of •-bis(aminophenyl) functionalized polystyrene, (**9**) shows a monomodal molecular weight distribution curve corresponding to the M_n value of 4.10 x 10^3 g/mol and M_w/M_n = 1.11. By comparison with the theoretical $M_{n,theory}$ value of 4.5 x 10^3 g/mol, the extent of polymerization corresponds to 91% monomer conversion during the polymerization reaction. The $M_{n,\ titration}$ value of 4.35 x 10^3 g/mol obtained from non-aqueous titration of the primary amine end groups of •-bis(aminophenyl) functionalized polystyrene, (**9**) shows a good comparison with M_n (SEC) and $M_{n,theory}$ values and indicates the quantitative incorporation of the bis(aminophenyl) group at the •-terminus of the polymer chain.

The chemical structure of •-bis(aminophenyl) functionalized polystyrene, (**9**) was determined by proton nuclear magnetic resonance spectrometry. The ^{1}H NMR spectrum (Figure 19) of •-bis(aminophenyl) functionalized polystyrene, (**9**) shows a broad peak at • = 3.65 ppm, due to the resonance of the amine protons of two NH_2 groups[51], as well as a broad peak at • = 4.5 ppm, due to the resonance of the terminal –CHPhBr proton[76].

FTIR spectroscopy was used to determine the presence of the amine functionality in the functionalized polystyrene sample. The FTIR spectrum (Figure 20) of •-bis(aminophenyl) functionalized polystyrene, (**9**) exhibits an absorption band at 3412 cm^{-1}, characteristic of the N-H stretching vibrations of the NH$_2$ groups.

Well defined •-bis(aminophenyl) functionalized polystyrene, (**9**) with good control of major polymer characteristics was prepared by ATRP methods using a new primary diamine functionalized initiator adduct, (**8**) as an initiator for styrene polymerization in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system.

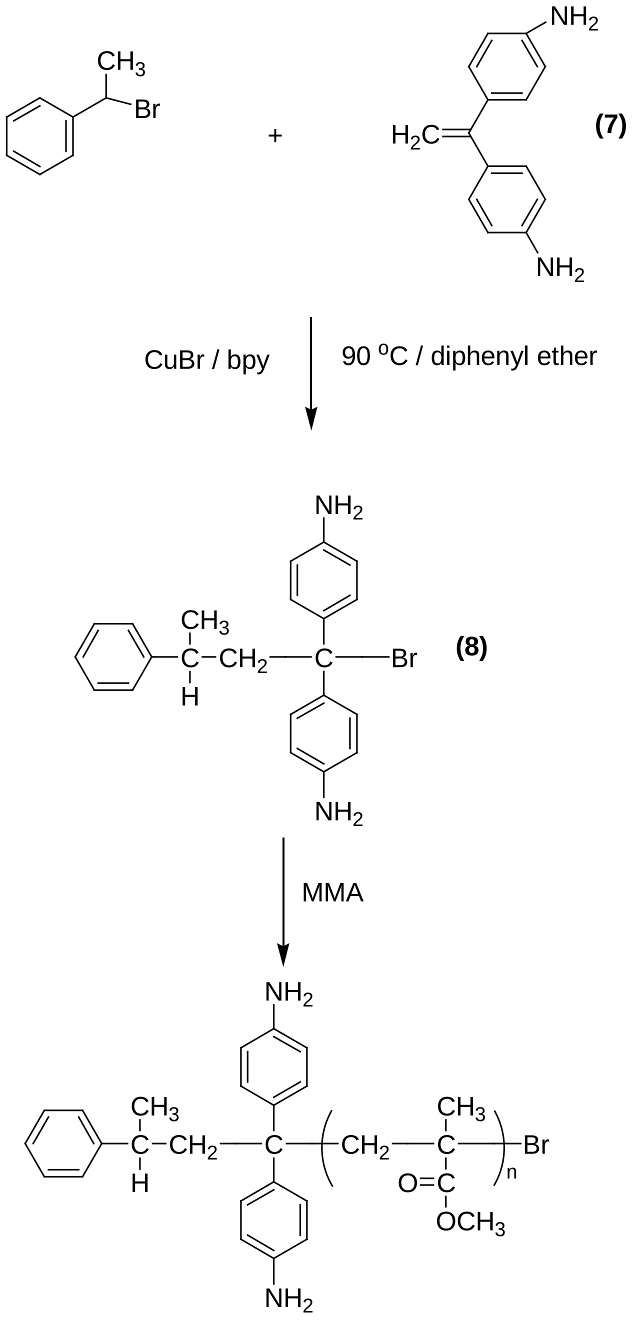
4.3.5 Synthesis of •-Bis(aminophenyl) Functionalized Poly(methyl methacrylate), (10)

•-Bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) was prepared by the ATRP of methyl methacrylate using a primary diamine functionalized initiator adduct, (**8**) as initiator. The new primary diamine functionalized initiator adduct, (**8**) was prepared *in situ* by the reaction of 1,1-bis(4-aminophenyl)ethylene, (**7**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 90 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3.

The size exclusion chromatogram (Figure 21) of •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) shows a monomodal molecular weight distribution curve, which corresponds with the number average molecular weight of $M_n = 3.6 \times 10^3$ g/mol and narrow molecular weight distribution of $M_w/M_n = 1.18$. By comparison to the theoretical M_n value of 4.0×10^3 g/mol, the SEC analysis indicates that although polymerization only proceeded to 90% monomer conversion, good chain length control and essentially controlled initiation and polymerization process was observed, especially for the formation of low molecular weight functionalized polymers.

The ^{1}H NMR spectrum (Figure 22) of •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**) shows a broad peak at • = 3.8 ppm, corresponding to the resonance of the protons of the NH_2 groups. The presence of multiplets between • = 6.50-7.22 ppm, attributed to aromatic proton resonances, confirms the incorporation of the bis(aminophenyl) moiety of the initiator fragment at the •-terminus of the poly(methyl methacrylate) chain.

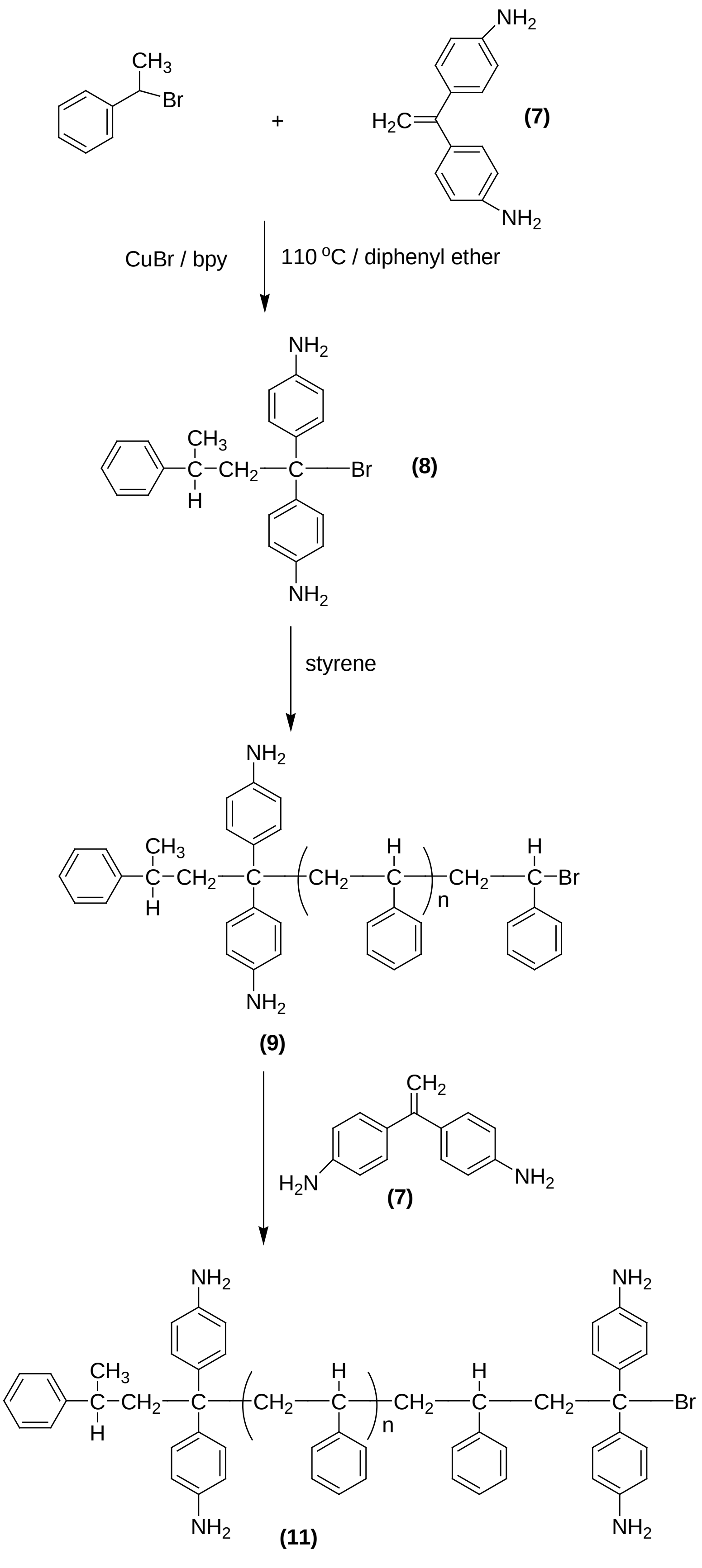
The extent of incorporation of •-bis(aminophenyl) groups at the •-terminus of the poly(methyl methacrylate) chain was determined by non-aqueous titrations of the primary diamine groups. The M_n value of 3.85 x 10^3 g/mol obtained by non-aqueous titration measurements is consistent with the M_n values obtained by SEC data. The detailed spectroscopic, chromatographic and non-aqueous titration data provide evidence for the quantitative incorporation of the bis(aminophenyl) group at the •-terminus of the polymer chain according to the following synthetic pathway:


CH3
Br
+
NH2
H2C
(7)
NH2
CuBr / bpy
90 oC / diphenyl ether
NH2
CH3
C
CH2
C
Br
H
(8)
NH2
MMA
NH2
CH3
C
CH2
C
CH2
CH3
C
Br
n
H
O=C
OCH3
NH2

(10)

4.3.6 Synthesis of • ,• -Tetrakis(aminophenyl) Functionalized Polystyrene, (11)

The preparation of • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) was performed *via* a post ATRP chain end functionalization reaction using a primary diamine functionalized initiator adduct, (**8**) as functionalized initiator for the ATRP of styrene followed by the chain end functionalization reaction by the addition of 1,1-bis(4-aminophenyl)ethylene, (**7**) at the end of the polymerization reaction. Under argon atmosphere, the primary diamine functionalized initiator adduct, (**8**) was prepared by the reaction of stoichiometric amounts of 1,1-bis(4-aminophenyl)ethylene, (**7**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3. Since styrene undergoes copolymerization reactions with 1,1-diphenylethylene derivatives, the success of the chain end functionalized reaction is dependant on the completion of the polymerization reaction prior to the addition of 1,1-bis(4-aminophenyl)ethylene, (**7**). The completion of the polymerization process was determined by the absence of styrene in the reaction mixture as evidenced by GC analysis. After 24 hours, 1,1-bis(4-aminophenyl)ethylene, (**7**) was added to the reaction mixture which contains the • -bis(aminophenyl) functionalized polystyrene precursor, (**9**) to form • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) according to the following synthetic pathway:



CH3
Br
+
NH2
H2C
(7)
NH2
CuBr / bpy
110 oC / diphenyl ether
NH2
CH3
C
CH2
C
Br
H
(8)
NH2
styrene
NH2
CH3
C
CH2
C
CH2
H
C
n
CH2
H
C
Br
H
NH2
(9)
CH2
H2N
(7)
NH2
NH2
CH3
C
CH2
C
CH2
H
C
n
CH2
H
C
CH2
C
Br
H
NH2
NH2
(11)
NH2

The size exclusion chromatogram (Figure 23) of • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 3.80 x 10^3 g/mol and M_w/M_n = 1.13. The SEC analysis also shows that no side reactions such as polymeric dimer or trimer formation occurred during the ATRP chain end functionalization reaction. The M_n values obtained by SEC analysis compares favourably with the theoretical M_n value of 4.20 x 10^3 g/mol for 100% monomer conversion during the polymerization process. The SEC analysis indicates that the polymerization proceeded *via* a controlled free radical polymerization process and that the subsequent chain end functionalization reaction affords quantitative yields of the corresponding • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**).

Non-aqueous titration data with standardized perchloric acid indicate the quantitative incorporation of the bis(aminophenyl) groups at both ends of the polystyrene chain. The value of the number average molecular weight, $M_{n,\ titration}$ = 4.17 x 10^3 g/mol, calculated from titration measurements, assuming the presence of four amine groups per polymer chain, is in good agreement with the M_n value obtained from SEC data.

The ^{1}H NMR spectrum (Figure 24) of • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) exhibits a broad peak in the region • = 3.65 ppm, due to the resonance of amine protons of four primary amine groups[68].

By post ATRP chain end modification reactions, well defined • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) was prepared in quantitative yields and high chain end functionality by ATRP methods. Using a primary diamine functionalized initiator adduct, (**8**) in the presence of CuBr/2,2'-bipyridyl catalyst system for styrene polymerization and the subsequent addition of 1,1-bis(4-aminophenyl)ethylene, (**7**) at the end the polymerization reaction gave • ,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**) in an efficient chain end functionalization reaction.

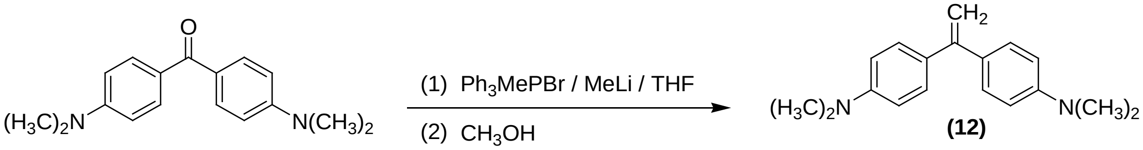
4.4 Synthesis of Tertiary Amine Functionalized Polymers by Atom Transfer Radical Polymerization

In the general ATRP process, the reversible homolytic cleavage of a carbon halogen bond of an alkyl halide initiator derivative by a redox reaction with a transition metal/amine ligand complex is essential to effect the rapid, efficient initiation of the polymerization of vinyl monomers. One of the most efficient methods for the preparation of chain end functionalized polymers by the ATRP methods is by the utilization of functionalized alkyl halide compounds as initiators for the polymerization of styrene and acrylates. Limited reports on the preparation of tertiary amine functionalized polymers by the ATRP methods using functionalized initiators bearing the tertiary amine group have been reported in the literature. Percec[173] and Yagci[155] reported the preparation of well-defined amine functionalized polymers with narrow molecular weight distributions and the incorporation of the tertiary amine group at the • -terminus of the polymer chain. In addition, tertiary amine functionalized polymers were prepared in quantitative yields by ATRP methods using an adduct of (1-bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene as an initiator for styrene polymerization in the presence of copper (I) bromide/2,2'-dipyridyl catalyst system[53]. All the polymerization reactions proceeded in a controlled manner without evidence of interaction between the tertiary amine functional group of the initiator molecule and the amine-ligand catalyst system used in ATRP reactions.

The present work describes the preparation of a tertiary diamine functionalized 1,1-diphenylethylene derivative and the determination of its utility as a unimolecular, tertiary diamine functionalized initiator precursor compound for the ATRP of styrene and methyl methacrylate as well as a functionalizing agent in post ATRP functionalization reactions to form different tertiary amine functionalized polymers.

4.4.1 Tertiary Diamine Functionalized Initiator Precursor: Synthesis of 1,1-Bis[(4-dimethylamino)phenyl]ethylene, (12)

In general, the synthetic route for the preparation of symmetrical disubstituted 1,1-diphenylethylene derivatives involves the conversion of the appropriate benzophenone derivative to the corresponding carbinol, followed by the spontaneous thermal or acid catalyzed dehydration of the intermediate carbinol[196,202,203]. Another method for the direct conversion of disubstituted benzophenones to the corresponding disubstituted 1,1-diphenylethylene derivatives is *via* the classical Wittig reaction with phosphoryl ylides or the Tebbe reagent[52]. The synthetic sequence for the preparation of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) *via* the Wittig reaction, involved the treatment of 4,4'-bis(dimethylamino)benzophenone with a phosphorous ylide, generated *in situ* from the reaction of methyllithium and methyltriphenylphosphonium bromide in freshly distilled tetrahydrofuran at room temperature:



The target molecule, 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was purified by silica gel column chromatography using hexane/ethyl acetate (*v/v*, 20/80) mixture as the eluent. Recrystallization of the product from 80% aqueous ethanol solution gave 2.92 g (89.1%) of pure 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) as light green crystals with a melting point of 126.8 - 127.9 ^{o}C.

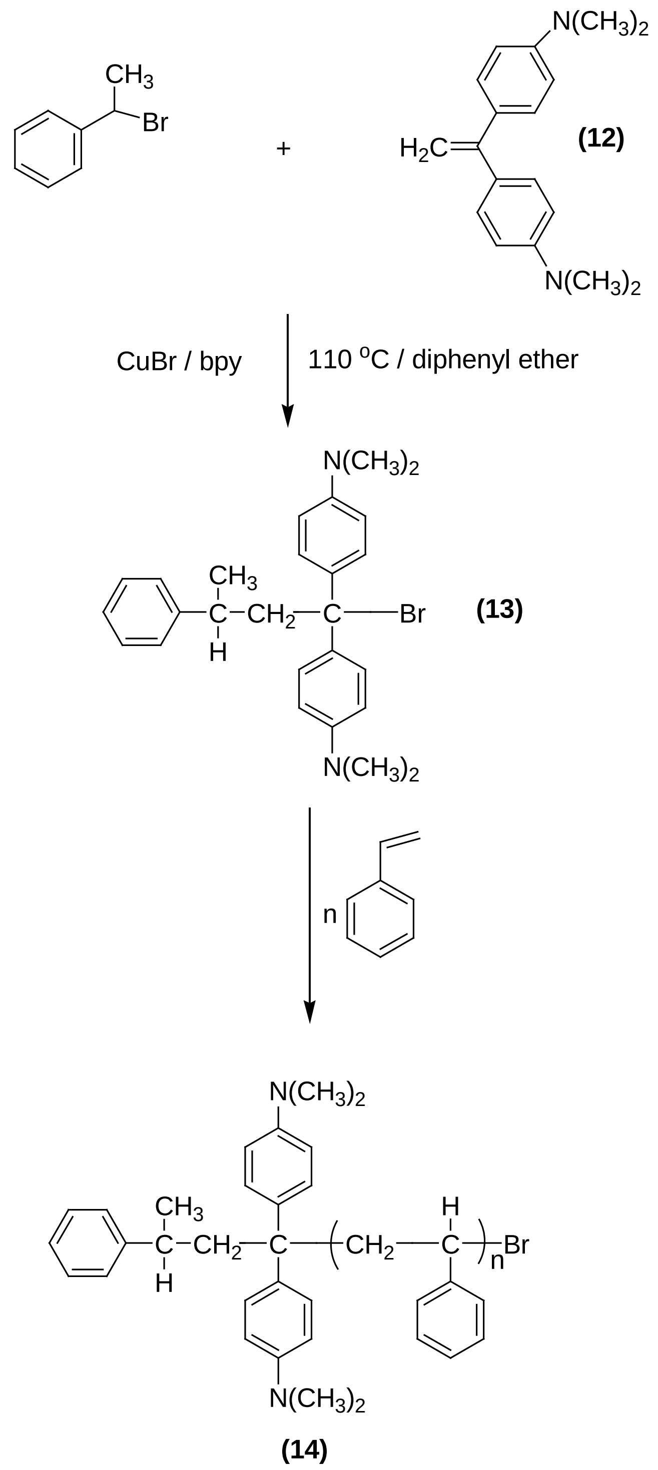
The ^{1}H NMR spectrum (Figure 25) of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) shows a singlet at • = 5.20 ppm, attributed to the resonance of equivalent methylene protons [$=C\underline{H}_2$] and a singlet at • = 2.96 ppm, attributed to the resonance of twelve hydrogens of the dimethylamino groups [2 x $-N(C\underline{H}_{3})_{2}$]. The doublet of doublets at • = 6.71 - 7.29 ppm, corresponding to the resonance of the protons of the phenyl rings, is characteristic of p-substituted benzene rings.

The FTIR spectrum (Figure 26) of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) shows an absorption band at 1605 cm^{-1}, due to the C=C stretching vibrations of the C=CH$_2$ group and an absorption band at 1334 cm^{-1}, due to the N-C stretching vibrations of the N(CH$_3$)$_2$ groups.

The spectroscopic data provides evidence of the synthesis of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) by the classical Wittig reaction using 4,4'-bis(dimethylamino)benzophenone as precursor.

4.4.2 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Polystyrene, (14)

The atom transfer radical polymerization of styrene, initiated by a new tertiary diamine functionalized initiator adduct, (**13**) afforded •-bis(4-dimethylamino-phenyl) functionalized polystyrene, (**14**) in quantitative yields. The tertiary diamine functionalized initiator adduct, (**13**) was prepared *in situ* by the reaction of stoichiometric amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of [CuBr]$_0$: [(1-bromoethyl)benzene]$_0$: [bpy]$_0$ = 1:1:3. After 12 hours, the polymer product was isolated by precipitation from THF solution into excess methanol, filtered and vacuum dried to give •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) in quantitative yields according to the following synthetic pathway:



Thin layer chromatography analysis of the purified polymer product shows only one spot on the chromatogram [R_f = 0.79, toluene] which corresponds to the formation of • -bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) in quantitative yields.

The size exclusion chromatogram (Figure 27) of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 5.10 x 10^3 g/mol and M_w/M_n = 1.09, compared with the $M_{n,theory}$ value of 5.40 x 10^3 g/mol at 94% monomer conversion. The $M_{n,\ titration}$ value of 5.21 x 10^3 g/mol obtained from non-aqueous titration of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) corresponds with the number average molecular weight data of M_n = 5.10 x 10^3 obtained from SEC analysis and is consistent with the incorporation of two dimethylamino groups per polymer chain.

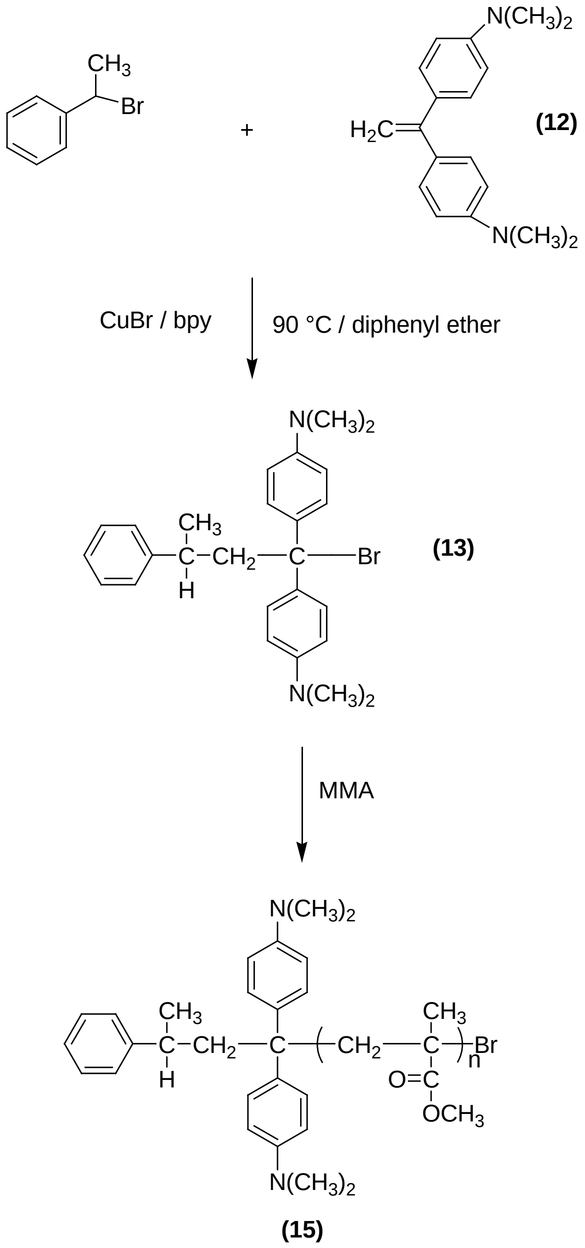
The ^{1}H NMR spectrum (Figure 28) of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) shows a signal at • = 3.02 ppm, due to the resonance of the protons of the tertiary amine groups[53,155] of the functionalized initiator fragment. The peak at • = 4.5 ppm corresponds to the proton resonance of the CHPhBr end group at the • -terminus of the polymer chain[76].

The FTIR spectrum (Figure 29) of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) shows a strong absorption band at 1350 cm^{-1}, characteristic of the N-C stretching vibrations of the $N(CH_3)_2$ groups. A sharp absorption band at 697 cm^{-1} is due to the C-Br bond vibrations at the • -terminus of the polymer chain.

The atom transfer radical polymerization of styrene, initiated by a new tertiary diamine functionalized initiator adduct, (**13**) afforded quantitative yields of well defined •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**). The spectroscopic and end group analysis data provide detailed evidence for the incorporation of the bis(4-dimethylaminophenyl) group at the •-terminus of the polymer chain[52,53,105,173,174].

4.4.3 Synthesis of •-Bis(4-dimethylaminophenyl) Functionalized Poly(methyl methacrylate), (15)

The preparation of •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) by ATRP methods was effected by the initiation of methyl methacrylate polymerization using a new tertiary diamine functionalized initiator adduct, (**13**) as outlined in the following synthetic pathway:



The tertiary diamine functionalized initiator adduct, (**13**) was prepared *in situ* by treatment of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) with (1-bromoethyl)-benzene in the presence of copper(I) bromide/ 2,2'-bipyridyl catalyst system in diphenyl ether at 90 ^{o}C, in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})\text{benzene}]_0$: $[\text{bpy}]_0$ = 1:1:3. The polymer product was purified by precipitation from THF solution into excess methanol, filtered and vacuum dried to give • -bis(4-dimethyl-aminophenyl) functionalized poly(methyl methacrylate), (**15**) as a white solid.

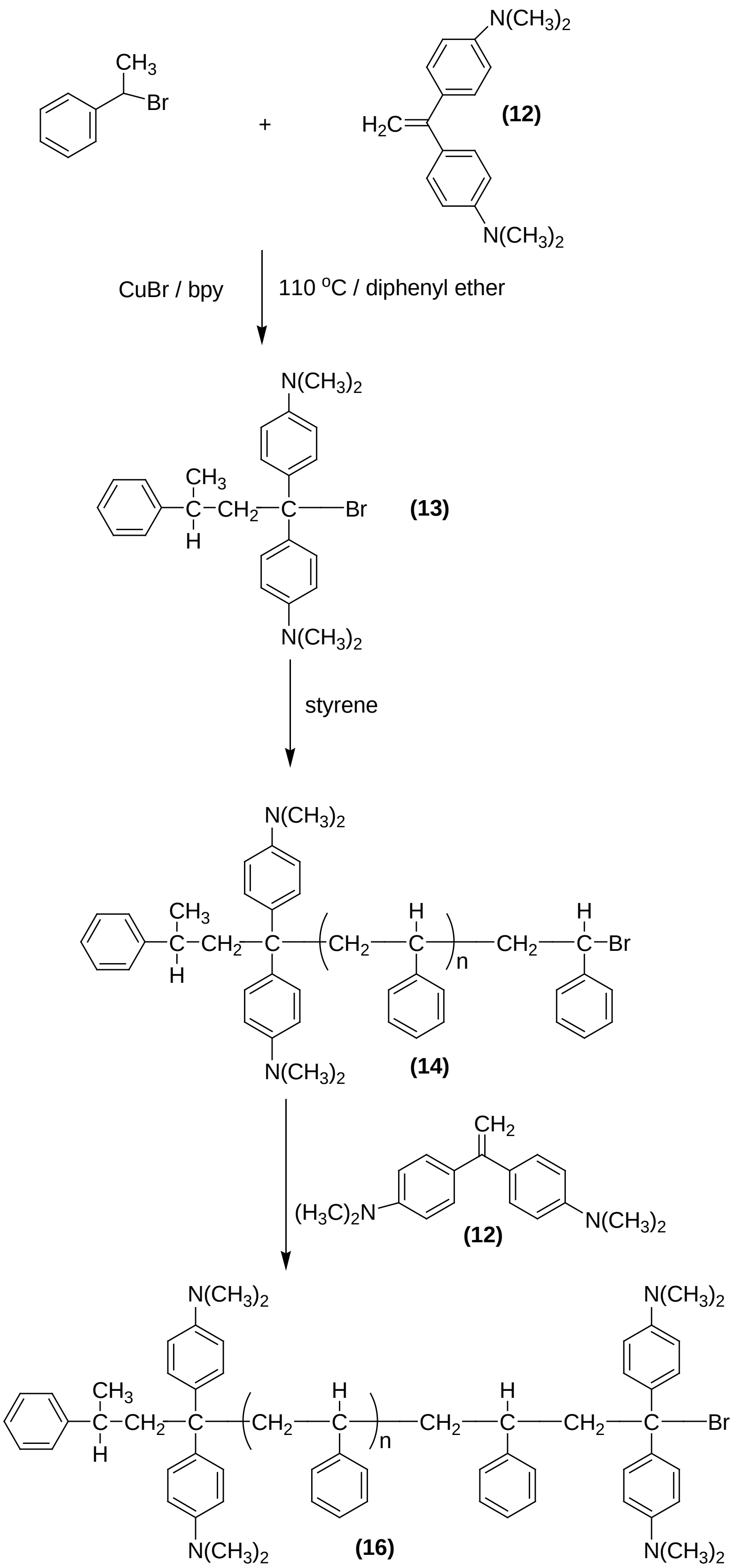
The size exclusion chromatogram (Figure 30) of • -bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) shows a monomodal molecular weight distribution curve, with the number average molecular weight of M_n = 5.23 x 10 ^{3} g/mol and narrow molecular weight distribution of M_w/M_n = 1.03. The M_n value obtained from SEC analysis compared favourably with the $M_{n,\text{theory}}$ = 5.50 x 10^3 g/mol obtained from the stoichiometry of the reaction for 95% monomer conversion during the polymerization process. The M_n value of 5.35 x 10^3 g/mol, obtained from the non-aqueous titration of • -bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) is in agreement with the number average molecular weight data of M_n = 5.23 x 10^3 g/mol obtained from SEC analysis for a polymer chain with two dimethylamino groups per chain.

The ^{1}H NMR spectrum (Figure 31) of • -bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) shows a signal between 2.85 ppm and 2.96 ppm**,** corresponding to the proton resonance of the $N(CH_3)_2$ groups. The presence of peaks at • = 6.58-7.24 ppm, due to aromatic proton resonances, confirms the incorporation of the • -bis(4-dimethylaminophenyl) moiety at the end of the poly(methyl methacrylate) chain.

The chromatographic, spectroscopic and non-aqueous titration analysis data indicate that the polymerization of methyl methacrylate, initiated by a tertiary diamine functionalized initiator adduct, (**13**), proceeded *via* a controlled atom transfer radical polymerization process with the quantitative incorporation of the bis(4-dimethylaminophenyl) group at the •-terminus of the •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**) chain.

4.4.4 Synthesis of •,•-Tetrakis(4-dimethylaminophenyl) Functionalized Polystyrene, (16)

The preparation of •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) was conducted by the ATRP of styrene initiated by a tertiary diamine functionalized initiator adduct, (**13**), followed by the post ATRP chain end modification reaction by the addition of 1,1-bis[(4-dimethylamino)phenyl]-ethylene, (**12**) to the polymer chain end of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) at the completion of the polymerization process. Under argon atmosphere, the tertiary diamine functionalized initiator adduct, (**13**) was prepared by the reaction of stoichiometric amounts of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) with (1-bromoethyl)benzene in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C in the molar ratio of $[CuBr]_0$: $[(1\text{-bromoethyl})\text{benzene}]_0$: $[bpy]_0$ = 1:1:3. The styrene polymerization proceeded for 24 hours to ensure complete monomer consumption during the polymerization process, as evidenced by GC analysis. To effect the chain end functionalization reaction, 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) was added to the reaction mixture in the solid form after completion of the polymerization process. After passage of the crude product through a silica gel column to remove catalyst impurities, the polymer product was isolated by precipitation from THF solution into excess methanol, filtered and vacuum dried to afford •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) as a white powder. The synthesis pathway for the preparation of •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) is outlined as follows:


CH3
Br
+
N(CH3)2
H2C
(12)
N(CH3)2
CuBr / bpy
110 °C / diphenyl ether
(13)
styrene
(14)
(H3C)2N
(12)
(16)

The size exclusion chromatogram (Figure 32) of •,• -tetrakis(4-dimethylamino-phenyl) functionalized polystyrene, (**16**) shows a monomodal molecular weight distribution curve with M_n (SEC) = 4.93 x 10^3 g/mol and M_w/M_n = 1.16, consistent with the theoretical $M_{n,theory}$ value of 5.20 x 10^3 g/mol for 100% monomer conversion during the styrene polymerization process. The M_n value of 5.13 x 10^3 g/mol obtained from non-aqueous titration analysis of •,• -tetrakis(4-dimethyl-aminophenyl) functionalized polystyrene, (**16**) for the incorporation of four dimethylamino groups per polymer chain is consistent with the number average molecular weight data of M_n (SEC) = 4.93 x 10^3 g/mol obtained from SEC analysis.

The ^{1}H NMR spectrum (Figure 33**)** of •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) exhibits a signal at • = 3.16 ppm, due to the resonance of protons of the four dimethylamino groups at the polymer chain ends[52,53]. The absence of a broad peak at • = 4.4 – 4.6 ppm, which is due to the resonance of the proton of the CHPhBr end group[76] of the precursor polymer molecule, indicates the complete addition of the 1,1-diphenylethylene unit during the chain end modification reaction. In addition, the quantitative incorporation of four dimethylamino groups at the end of the polymer chain provides evidence that no styrene was present to undergo copolymerization reactions with 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) during the ATRP chain end functionalization reaction.

The ATRP method allows the preparation of well-defined polymers with high end group functionality. By post ATRP chain end modification reactions, well defined •,• -tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) was prepared in quantitative yields and high chain end functionality by the addition of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) to the polymer chain end of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**).

4.5 Synthesis of Amine Chain End Functionalized Polymers by Atom Transfer Radical Polymerization: Polymerization Kinetics Studies

For an effective and well controlled ATRP reaction, three primary experimental features must be established, namely, (i) the first order rate plot of $\ln[M]_o/[M]$ versus time should be linear, indicating that the concentration of active radical species is constant throughout the reaction; (ii) the molecular weight distributions of polymers should be below 1.5; and (iii) the increase in the number average molecular weight of the polymers with respect to percentage monomer conversion should be linear, indicating that all chains are growing concomitantly with consumption of monomer and the absence of any chain transfer and termination reactions[126].

4.5.1 Syntheses of • -Aminophenyl Functionalized Polystyrenes, (6)

A series of • -aminophenyl functionalized polystyrenes, (**6**) were prepared by ATRP methods using the primary amine functionalized initiator adduct, (**5**), formed by the reaction of 1-(4-aminophenyl)-1-phenylethylene, (**4**) with (1-bromoethyl)benzene, as the initiator in the solution polymerization of styrene. Experiments were performed in the presence of copper (I) bromide/2,2'-bipyridyl with ratios of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3 in diphenyl ether at 110 ^oC at different monomer to initiator concentration ratios. The ATRP reactions proceeded under heterogeneous conditions in high initiator efficiency reactions.

Figure 34 shows the plots of percentage monomer conversion versus time for each polymerization reaction. Results indicate that at the lower $[M]_0/[I]_0$ ratio, the reaction was the fastest and 98% monomer conversion was reached in 4.5 hours. When the $[M]_0/[I]_0$ ratio is increased to 100, the percentage monomer conversion with time decreases slightly to 83% after 5 hours of polymerization time. A retardation in the reaction is observed at the higher $[M]_0/[I]_0$ ratio = 200, whereby only 10% monomer consumption occurs after one hour of reaction time and a percentage monomer conversion value of 61% was recorded after 5.5 hours of reaction.

Figure 35 shows the semilogarithmic kinetic plots of $\ln[M]_0/[M]$ as a function of polymerization time at different $[M]_0/[I]_0$ ratios for the heterogenous synthesis of •-aminophenyl functionalized polystyrene, (**6**) using the primary amine functionalized initiator adduct, (**5**) as the initiator system for styrene polymerization by ATRP methods. The kinetic plots show that the ratio of the concentration of monomer to initiator affects the rate of polymerization. Linear relationships were obtained for the kinetic plots of $\ln[M]_0/[M]$ versus polymerization time, indicating that fast initiation has occurred and that the radical concentration remains constant throughout the polymerization process. The linearity of the semilogarithmic plots of $\ln[M]_0/[I]$ versus time indicates that the polymerizations were first order with respect to monomer consumption. At the lower $[M]_0/[I]_0$ ratio, the reaction rate is the fastest and the reaction rate drops significantly with decreasing initiator concentration. The linear behaviour of the kinetic plots is further confirmed by the observed linear regression coefficient values of 0.97 or greater:

$[M]_0/[I]_0$	Linear Regression Coefficient R^2	Slope
50 : 1	0.9962	0.01374
100 : 1	0.9721	0.00711
200 : 1	0.9778	0.00189

Figure 36 shows the plots of the experimental number average molecular weights and molecular weight distributions with percentage monomer conversion for the different ATRP reactions for the preparation of •-aminophenyl functionalized polystyrenes, (**6**). The number average molecular weights of •-aminophenyl functionalized polystyrenes, (**6**) increase linearly with percentage monomer conversion and are consistent with the theoretical values. Polymers with narrow molecular weight distributions were obtained. The linear increase of number average molecular weight with percentage monomer conversion suggests that no significant chain transfer or termination reactions occurred once the initiation step is complete. Primary amine chain end functionalized polymers with predictable number average molecular weights (M_n = 1.89 x 10^3 g/mol to 13.43 x 10^3 g/mol) and molecular weight distributions ranging from 1.03 to 1.25 were obtained, indicating the occurrence of a fast initiation process which involves the rapid equilibrium exchange between active and dormant species during the polymerization reaction.

Experimental results show that good control of the number average molecular weight, molecular weight distributions and high initiator efficiency reactions in the solution ATRP synthesis of • -aminophenyl functionalized polystyrenes, (**6**) was observed using the primary amine functionalized initiator adduct, (**5**) as initiator for styrene polymerization. The quantitative incorporation of the functionalized 1,1-diphenylethylene fragment at the polymer chain end in the ATRP of styrene and the control of major polymer properties, such as the number average molecular weight, molecular weight distribution and degree of functionalization is attributed to the *in situ* formation of the amine functionalized initiator adduct, (**5**) by the stoichiometric addition reaction of (1-bromoethyl)benzene to 1-(4-aminophenyl)-1-phenylethylene, (**4**) and the subsequent efficient and rapid reaction with the styrene to initiate styrene polymerization by ATRP methods.

4.5.2 Syntheses of • -Bis(aminophenyl) Functionalized Polystyrenes, (9)

A series of • -bis(aminophenyl) functionalized polystyrenes, (**9**) were prepared by the ATRP of styrene using a new primary diamine functionalized initiator system. The primary diamine functionalized initiator adduct, (**8**) was prepared by the reaction of 1,1-bis(4-aminophenyl)ethylene, (**7**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C with the stoichiometry of $[CuBr]_0$: $[(1\text{-bromoethyl})benzene]_0$: $[bpy]_0$ = 1:1:3. In a typical experiment, starting at t = 0, aliquots of 1 mL were removed at

30 minute intervals, diluted with THF (9 mL) and subjected to gas chromatographic analysis to determine the percentage monomer conversion of styrene with time.

Figure 37 shows the plots of percentage monomer conversion with polymerization time for the ATRP of styrene, initiated by the adduct of 1-bis(4-aminophenyl)ethylene, (**7**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C. The syntheses of • -bis(aminophenyl) functionalized polystyrenes, (**9**) were carried out under different molar ratios of monomer to initiator. The conversion of monomer during the polymerization process increased as the molar ratios of monomer to initiator decreased. At the lower $[M]_0/[I]_0$ ratio = 50, the reaction was the fastest and 89% monomer conversion was reached in 4 hours. When the $[M]_0/[I]_0$ ratio is increased to 100, the extent of monomer conversion reduced slightly to 76% within 4 hours. At monomer to initiator ratio of 200, a lower percentage monomer conversion value to 61% was recorded after 4 hours.

Figure 38 shows the first order kinetic plots of $\ln[M]_0/[M]$ as a function of polymerization time for the ATRP of styrene using the primary diamine functionalized initiator adduct, (**8**) as initiator for styrene polymerization. In all plots, linear relationships between $\ln[M]_0/[M]$ versus time are observed, indicating that the radical concentration stays constant throughout the course of the polymerization reaction and that rapid exchange between the active and dormant species occurs, i.e. fast initiation of styrene polymerization. Furthermore, considering the slope of the plots, the reaction is the fastest for the lower $M]_0/[I]_0$ ratio = 50 and the polymerization time decreases as the $M]_0/[I]_0$ ratio increases. The observed linear regression coefficients of the reactions are close to or greater than 0.98, which indicates the linearity of the first order kinetic plots:

$[M]_0/[I]_0$	Linear Regression Coefficient R^2	Slope
50 : 1	0.9890	0.01434
100 : 1	0.9994	0.00764
200 : 1	0.9827	0.00357

Figure 39 shows the plots of the number average molecular weights and molecular weight distributions as a function of percentage monomer conversion for the different ATRP reactions. The solution atom transfer radical polymerization of styrene was initiated by the primary diamine functionalized initiator adduct, (**8**) in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C. The M_n values increases linearly with percentage monomer conversion, which suggests that no significant chain transfer or termination reactions occured once the initiation step is complete. For the $[M]_0/[I]_0$ ratio of 200, polymers with number average molecular weights up to 13.42 x 10^3 g/mol are obtained, whereas low molecular weight polymers ranging from 1.1 x 10^3 to 4.2 x 10^3 g/mol are obtained when the $[M]_0/[I]_0$ ratio = 50. Furthermore, the molecular weight distributions of the resultant •-bis(aminophenyl) functionalized polystyrenes, (**9**) are relatively narrow, ranging from 1.03 to 1.25.

The polymerization kinetics data shows that a series of different •-bis(aminophenyl) functionalized polystyrenes, (**9**) 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 styrene using a primary diamine functionalized initiator adduct, (**8**) as initiator for the styrene polymerization. The primary diamine functionalized initiator adduct, (**8**), prepared *in situ* from the reaction of 1,1-bis(4-aminophenyl)ethylene, (**7**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 ^{o}C, is a good primary diamine functionalized initiator for the ATRP of styrene and affords •-bis(aminophenyl) functionalized polystyrenes, (**9**) in quantitative yields.

4.5.3 Syntheses of •-Bis(4-dimethylaminophenyl) Functionalized Polystyrenes, (14)

The copper-mediated ATRP of styrene, initiated by the tertiary diamine functionalized initiator adduct, (**13**) produces •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) in quantitative yields. Styrene polymerization was initiated by the tertiary diamine functionalized initiator adduct, (**13**), prepared *in situ* by the stoichiometric reaction of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst in diphenyl ether at 110 ^{o}C. Different experiments were conducted by varying the monomer to initiator concentration ratios from 50:1, 100:1 to 200:1 for the different experiments. Starting at t = 0, aliquots of 1 mL were removed at 30 minute intervals, diluted with THF (9 mL) and subjected to gas chromatographic analysis to determine the percentage monomer conversion of styrene as a function of polymerization time.

Figure 40 shows the plots of percentage monomer conversion versus polymerization time for the synthesis of the different •-bis(4-dimethylamino-phenyl) functionalized polystyrene, (**14**) derivatives. When the $[M]_0/[I]_0$ ratio = 50, the polymerization reaction was the fastest and a monomer conversion of 94% was reached within 4 hours. The percentage monomer conversion decreased considerably on increasing the monomer to initiator ratio from 100 to 200, where the respective percentage monomer conversions values of 80% and 63% were obtained within the same polymerization time.

Figure 41 shows a linear relationship between $\ln[M]_0/[M]$ and time for the different experiments where the $[M]_0/[I]_0$ ratios range from 50 to 200. Styrene polymerization was initiated by the tertiary diamine functionalized initiator adduct, (**13**), derived from the reaction of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst in diphenyl ether at 110 ^{o}C. The experimental data shows that the polymerization kinetics for each reaction was first order with respect to monomer consumption and that the concentration of the propagating radicals in each reaction remains constant throughout the polymerization process. The linear behaviour of each reaction kinetics plot is further confirmed by the observed linear regression coefficients values of 0.98 for each polymerization process:

$[M]_0/[I]_0$	Linear Regression Coefficient R^2	Slope
50 : 1	0.9896	0.01088
100 : 1	0.9783	0.00632
200 : 1	0.9773	0.00366

Figure 42 shows the plots of the experimental number average molecular weight and molecular weight distribution with percentage monomer conversion for the different ATRP reactions for the preparation of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**). The number average molecular weights of the different •-bis(4-dimethylaminophenyl) functionalized polystyrenes, (**14**), obtained by SEC, increases linearly with the percentage monomer conversion. The linearity of the plots indicates the polymerization proceeded by normal ATRP mechanisms which involves a fast exchange between active and dormant species, that is, fast initiation of styrene polymerization and no measurable 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. Also, polymers with narrow molecular weight distributions were obtained, indicating that the rate of initiation was at least equal to or greater than the rate of propagation for each reaction. The molecular weight distribution values of the •-bis (4-dimethylaminophenyl) functionalized polystyrenes, (**14**) ranged from 1.03 to 1.44.

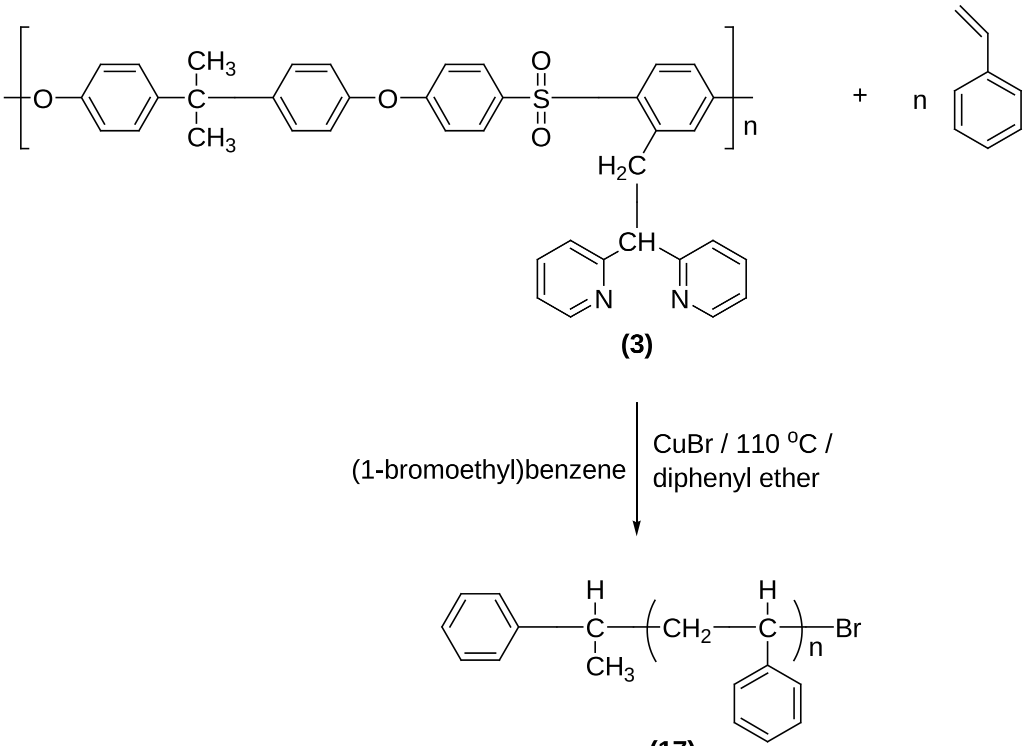
The polymerization kinetics data shows that a series of different •-bis(4-dimthylaminophenyl) functionalized polystyrenes, (**14**) with good control of polymer characteristics such as the number average molecular weight, molecular weight distribution and chain end functionality are obtained by the ATRP of styrene using a tertiary diamine functionalized initiator adduct, (**13**) as initiator for the styrene polymerization. The tertiary diamine functionalized initiator adduct, (**13**), prepared *in situ* from the reaction of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) and (1-bromoethyl)benzene in the presence of copper (I) bromide/2,2'-bipyridyl catalyst system in diphenyl ether at 110 °C, is a good tertiary diamine functionalized initiator for the ATRP of styrene and affords •-bis(4-dimethylaminophenyl) functionalized polystyrenes, (**14**) in quantitative yields.

4.6 A New Supported Catalyst System for the Atom Transfer Radical Polymerization of Styrene

The ATRP process is a powerful technique for the laboratory synthesis of well-defined polymers. However, the purification steps involved after the polymerization process have prevented the extensive application of the ATRP method for polymer production at the industrial scale. Thus, the current industrial research work is centered on the development of new synthetic procedures to make the ATRP technique more amenable to commercialization processes. To overcome the industrial limitations of polymer purification during the ATRP process, three approaches[55] to the reduction of residual catalyst in the final polymer product have been used, namely, (a) the development of a more active catalyst system for catalyst reduction and elimination of the purification step; (b) the utilization of catalyst supports to facilitate catalyst recovery and recycling; and (c) more facile and effective polymer purification methods. Although all these approaches have shown successes, only the first two have been accepted by industry, since the methods allow a reduction in the raw catalyst cost while minimizing the need for post polymerization purification work. Thus, a new polymeric supported catalyst system, based on dipyridyl functionalized polysulfones, was developed for the ATRP of styrene.

4.6.1 Synthesis of Polystyrene, (17) using Dipyridyl Functionalized Polysulfone, (3) as Ligand

A new polymer supported catalyst system, prepared *in situ* by the complexation of dipyridyl functionalized polysulfone, (**3**) (PFPS-95) as ligand with CuBr, was evaluated as a polymeric supported catalyst system for the ATRP of styrene according to the following synthetic pathway.



(17)

The polymerization of styrene was initiated by (1-bromoethyl)benzene in the presence of the PFPS-95/CuBr supported catalyst complex in diphenyl ether at 110 ^{o}C with a mole ratio of $[\text{CuBr}]_0$: $[(\text{1-bromoethyl})\text{benzene}]_0$: $[\text{dipyridyl functionalized polysulfone}]_0$ = 1:1:3. Upon the addition of CuBr to dipyridyl functionalized polysulfone, (**3**) a yellow-green reaction mixture was formed and the CuBr/PFPS-95 complex was soluble in diphenyl ether. At the beginning of the reaction, the observed instantaneous green colouration of the mixture indicates the formation of standard ATRP reaction conditions and the strong anchoring of the transition-metal catalyst on the ligand to form a stable complex. After completion of the polymerization process, the crude polymer mixture was concentrated and precipitated into toluene to remove the polymeric ligand/copper (I) bromide system. The dipyridyl functionalized polysulfone, (**3**), which precipitated in toluene, was filtered and vacuum dried. The ^{1}H NMR spectrum (Figure 43) of dipyridyl functionalized polysulfone, (**3**) shows signals at • = 3.78 and • = 4.65 ppm, due to the proton resonances of CH_2 and CH groups, respectively. Furthermore, the multiplets between • = 6.3 – 6.7 ppm, 7.4 – 7.8 ppm and 8.1 – 8.4 ppm are attributed to the aromatic proton resonances of the pyridyl groups[194], indicating the complete recovery of the polymeric ligand from the ATRP reaction.

The toluene filtrate, which contained polystyrene, (**17**) was passed through a short silica gel column to remove additional copper catalyst/ligand impurities. The toluene phase was concentrated in vacuo and the polymer product was added to excess methanol. The white polymer solid which precipitated was filtered and vacuum dried to give well defined polystyrene, (**17**). The size exclusion chromatogram (Figure 44) of polystyrene, (**17**) shows a monomodal molecular weight distribution curve with $M_n = 8.13 \times 10^3$ g/mol and $M_w/M_n = 1.14$, consistent with the theoretical value of $M_n = 8.15 \times 10^3$ g/mol. The ^{1}H NMR spectrum (Figure 45) of polystyrene, (**17**) shows the classical peaks between • = 1.10 - 2.22 ppm, due to the resonances of the protons of the CH and CH_2 groups of the polystyrene backbone and the peaks at • = 6.46 -7.49 ppm which corresponds to the aromatic proton resonances of the pendant phenyl groups of the polystyrene chain.

Experimental results show that a new polymer supported catalyst system, PFPS-95/CuBr was efficient in promoting the controlled atom transfer radical polymerization of styrene using (1-bromoethyl)benzene as the initiator in diphenyl ether at 110 ^{o}C. Polystyrene, (**17**) with good control of the number average molecular weight and molecular weight distribution was obtained.

4.6.2 Synthesis of Polystyrene, (17) using Dipyridyl Functionalized Polysulfone, (3) as Ligand: Polymerization Kinetics Studies

The polymerization kinetics studies of the atom transfer polymerization of styrene, initiated by (1-bromoethyl)benzene in the presence of a new polymer supported catalyst system of CuBr complexed with dipyridyl functionalized polysulfone, (**3**), (PFPS-95) were performed in diphenyl ether at 110 °C. The stoichiometry of the reaction was initiator: catalyst: ligand = [(1-bromoethyl)benzene]$_0$: [CuBr] : [PFPS-95] = 1: 1: 3 and the monomer: initiator ratio of $[M]_0/[I]_0 = 200$. The dipyridyl functionalized polysulfone/CuBr complex was completely soluble in the reaction mixture. Upon the addition of CuBr to dipyridyl functionalized polysulfone, (**3**), (PFPS-95) in diphenyl ether, a yellow-green reaction mixture was formed. With the addition of the initiator, the homogenous reaction mixture turned green. After the addition of the styrene monomer, starting at t = 0, aliquots of 1 mL were removed at 30 minute intervals, followed by the addition of THF (2 mL). The aliquots were subjected to gravimetric analysis to determine the percentage monomer conversion of styrene with time by evaluating the mass of each polymer sample as a function of time.

Figure 46 shows the plot of percentage monomer conversion versus polymerization time for the ATRP of styrene in the presence of the CuBr/PFPS-95 supported catalyst system in diphenyl ether at 110 °C. The polymerization proceeded slowly and only reached 54% conversion after 3 hours.

Figure 47 shows the semilogarithmic plot of $\ln[M]_0/[M]$ versus time for the ATRP of styrene in the presence of the CuBr/PFPS-95 supported catalyst system. The first order kinetic plot is linear with a slope of 0.00598 and a linear regression coefficient of $R^2 = 0.9896$, suggesting constant radical concentration throughout the polymerization process.

Figure 48 shows the plot of the experimental number average molecular weights and molecular weight distributions with percentage monomer conversion for the ATRP synthesis of polystyrene in the presence of CuBr/PFPS-95 supported catalyst system. The number average molecular weights of the polystyrene samples increased linearly with percentage monomer conversion and are close to the theoretical values. The molecular weight distributions are less than 1.2, which is comparable to values obtained in the presence of CuBr/bpy catalyst system[55,147].

Polymerization kinetics data shows that first order rate kinetics was observed during the ATRP of styrene in the presence of a new polymer supported catalyst system derived from PFPS-95 and CuBr. The number average molecular weights of styrene, (**17**), increase linearly with percentage monomer conversion and polymers with narrow molecular weight distributions were obtained. Experimental data demonstrates that the new PFPS-95/CuBr catalyst complex is an efficient catalytic system for the ATRP of styrene.

CHAPTER 5

CONCLUSION

5.1 Chemical Modification of Polysulfone by Anionic Methods

Dipyridyl functionalized polysulfones, (**3**) with improved hydrophilicity, enhanced membrane morphological properties and excellent ATRP polymeric ligand properties were prepared by the chemical modification of polysulfone by anionic methods. Modification of aromatic polysulfone was achieved by the direct lithiation of the unmodified polysulfone, (**1**), followed by the addition of 2,2'-vinylidenedipyridine, (**2**) to give the corresponding dipyridyl functionalized polysulfones, (**3**) with different degrees of substitution, depending on the stoichiometry of the reactions. A reduced temperature was necessary during the lithiation step to prevent polymer cross-linking. When equimolar amounts of 2,2'-vinylidenedipyridine, (**2**) are added to the lithiated polysulfone, the degree of functionalization obtained was 45%. However, the addition of 10% and 20% molar excess of 2,2'-vinylidenedipyridine, (**2**) to the corresponding lithiated polysulfone, produce dipyridyl functionalized polysulfones, (**3**) with degrees of functionalization of 80% and 95%, respectively.

Detailed spectroscopic analyses of dipyridyl functionalized polysulfone, (**3**) indicated that the reaction was regiospecific in that functionalization occurred solely on the aromatic rings ortho to the sulfone linkage. The dipyridyl functionalized polysulfones, (**3**) are thermally less stable than the parent polysulfone. The glass transition temperature of the modified polysulfones decreased with higher degree of substitution because of increased chain mobility. Furthermore, the dipyridyl modified polysulfones exhibit improved hydrophilic characteristics with excellent membrane properties and therefore can be considered as suitable polymeric substrate precursors for the preparation of membranes with anti-fouling properties. The membrane obtained from dipyridyl functionalized polysulfone, (**3**) with the higher degree of substitution (PFPS-80) exhibits higher water permeate flux with better structural integrity of the membrane as determined by scanning electron microscopy and atomic force microscopic analysis.

5.2 Atom Transfer Radical Polymerization: Synthesis of Amine Chain End Functionalized Polymers

Amine chain end functionalized polymers with controlled number average molecular weights and narrow molecular weight distributions were prepared by ATRP methods using amine or diamine functionalized unimolecular initiator adducts as initiators for styrene and methyl methacrylate polymerization. The preparation of the specific amine or diamine functionalized initiator adduct was based on the reaction of the appropriate amine or diamine functionalized 1,1-diphenylethylene derivative with (1-bromoethyl)benzene in the presence of CuBr/2,2-bipyridyl catalyst. In addition, telechelic amine functionalized polymers were prepared by a facile post ATRP chain end modification reaction which involve the addition of the specific diamine functionalized 1,1-diphenylethylene derivative to the • -bis(amine) functionalized polymer precursor at the completion of the ATRP process.

A general one-pot atom transfer radical polymerization method was adopted for the synthesis of • -aminophenyl functionalized polystyrene, (**6**) according to the following synthesis pathway:

(a) the preparation of 1-(4-aminophenyl)-1-phenylethylene, (**4**) using 4-aminobenzophenone as a starting material.
(b) the *in situ* synthesis of a new primary amine functionalized initiator adduct, (**5**), obtained from the reaction of (1-bromoethyl)benzene with 1-(4-

aminophenyl)-1-phenylethylene, (**4**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C.

(c) the use of the new primary amine functionalized initiator adduct, (**5**) as initiator for the ATRP of styrene afforded the corresponding •-aminophenyl functionalized polystyrene, (**6**) with predictable number average molecular weights (M_n = 1.62 x 10^3 g/mol to 13.21 x 10^3 g/mol) and narrow molecular weight distributions (M_w/M_n = 1.09 – 1.26) in high initiator efficiency reactions.

A series of well defined •-bis(aminophenyl) and •,• -tetrakis(aminophenyl) functionalized polymers were prepared using the following synthesis strategy:

(a) the synthesis of 1,1-bis(4-aminophenyl)ethylene, (**7**) using 4,4'-diamino-benzophenone as precursor.

(b) the *in situ* synthesis of a new primary diamine functionalized initiator adduct, (**8**), generated by the stoichiometric reaction of (1-bromoethyl)benzene with 1,1-bis(4-aminophenyl)ethylene, (**7**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 ^{o}C.

(c) the utilization of the new primary diamine functionalized initiator adduct, (**8**) as initiator for the ATRP of styrene and methyl methacrylate in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system afforded quantitative yields of •-bis(aminophenyl) functionalized polystyrene, (**9**) and •-bis(aminophenyl) functionalized poly(methyl methacrylate), (**10**), respectively.

(d) •-bis(aminophenyl) functionalized polymers with number average molecular weights of M_n = 1.09 x 10^3 g/mol to 15.32 x 10^3 g/mol and narrow molecular weight distributions (M_w/M_n = 1.01 – 1.42) were obtained.

(e) •,• -tetrakis(aminophenyl) functionalized polystyrene, (**11**), with M_n = 3.80 x 10^3 g/mol and M_w/M_n = 1.13 and high chain end functionality was prepared in quantitative yields by the post ATRP chain end modification reaction of •-bis(aminophenyl) functionalized polystyrene, (**9**) with excess 1,1-bis(4-aminophenyl)ethylene, (**7**) in a one-pot chain end functionalization reaction.

Similarly, well defined •-bis(4-dimethylaminophenyl) and •,•-tetrakis(4-dimethylaminophenyl) functionalized polymers were prepared according to the following synthesis strategy:

(a) the preparation of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) using 4,4'-bis(dimethylamino)benzophenone as starting material.

(b) the *in situ* preparation of a new tertiary diamine functionalized initiator adduct, (**13**) by the reaction of (1-bromoethyl)benzene and 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) in the presence of copper(I) bromide and 2,2'-bipyridyl as catalyst system in diphenyl ether at 110 °C.

(c) the use of the new tertiary diamine functionalized initiator adduct, (**13**) as initiator for styrene and methyl methacrylate polymerization by ATRP methods gave quantitative yields of the corresponding •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) and •-bis(4-dimethylaminophenyl) functionalized poly(methyl methacrylate), (**15**), respectively.

(d) •-bis(4-dimethylaminophenyl) functionalized polymers with number average molecular weights of $M_n = 1.23 \times 10^3$ g/mol to 16.78×10^3 g/mol and narrow molecular weight distributions ($M_w/M_n = 1.05 – 1.23$) were obtained.

(e) •,•-tetrakis(4-dimethylaminophenyl) functionalized polystyrene, (**16**) with $M_n = 4.93 \times 10^3$ g/mol and $M_w/M_n = 1.16$ was prepared in quantitative yields and with high chain end functionality by the post ATRP chain end modification reaction of •-bis(4-dimethylaminophenyl) functionalized polystyrene, (**14**) and excess of 1,1-bis[(4-dimethylamino)phenyl]ethylene, (**12**) in a one-pot chain end functionalization reaction.

The polymerization processes were monitored by gas chromatographic analyses. For all polymerization reactions, polymerization kinetics data shows that the polymerization process for each reaction follows first order rate kinetics with respect to monomer consumption. In addition, polymerization reactions leading to the formation of tertiary amine chain end functionalized polymers proceeded at a faster rate when compared to similar reactions for the preparation of primary amine functionalized polymers. The number average molecular weights of the polymers (M_n = 1.3 x 10^3 – 16.4 x10^3 g/mol) increased linearly with percentage monomer conversion and polymers with narrow molecular weight distributions (M_w/M_n = 1.03 – 1.29) were obtained.

The organic compounds, amine and diamine substituted 1,1-diphenylethylene initiator precursor derivatives and the functionalized polymers were characterized by nuclear magnetic resonance spectrometry, fourier transform infrared spectroscopy, size exclusion chromatography and non-aqueous titration analysis.

Experimental results show that good control of the number average molecular weight, molecular weight distributions in high initiator efficiency reactions in the solution ATRP syntheses of •-aminophenyl, •-bis(aminophenyl) and •-bis(4-dimethylaminophenyl) functionalized polymers can be obtained using the respective amine functionalized initiator adducts as initiators. The quantitative incorporation of the functionalized 1,1-diphenylethylene fragment into the polymer chain end in the ATRP of styrene and methyl methacrylate and the control of major polymer properties, such as the number average molecular weight, molecular weight distribution and degree of functionalization, is attributed to the formation of the appropriate amine functionalized initiator adduct *in situ* from the specific amine substituted 1,1-diphenylethylene precursor and the subsequent efficient and rapid initiation of styrene and methyl methacrylate to afford the corresponding amine chain end functionalized polymers.

5.3 A New Supported Catalyst System for the Atom Transfer Radical Polymerization of Styrene

One of the limitations of the ATRP process for industrial development is the presence of residual metal catalyst in the final polymer which is detrimental to the quality of the polymer product as well as the environment. A potential way to overcome the drawback of contamination, cost and recovery of the catalyst, is to immobilize the metal catalyst onto a solid carrier, which could be readily removed from the final product and reused for further ATRP reactions.

Well defined polystyrene, (**17**) with predictable number average molecular weight and narrow molecular weight distribution was prepared by ATRP methods using a new polymer supported catalyst system according to the following synthesis process:

(a) the novel synthesis of a new polymeric ligand, dipyridyl functionalized polysulfone, (**3**) by the reaction of lithiated polysulfone with 20% excess of 2,2'-vinylidenedipyridine, (**2**) in THF at -78 ^oC.
(b) the *in situ* formation of the CuBr/dipyridyl functionalized polysulfone supported catalyst system in diphenyl ether at 110 ^oC.
(c) the ATRP of styrene in the presence of the CuBr/dipyridyl functionalized polysulfone supported catalyst gave well defined polystyrene, (**17**) with number average molecular weight of 8.13 x 10^3 g/mol and molecular weight distribution of $M_w/M_n = 1.14$.

The polymerization kinetics data for the styrene polymerization reaction shows first order rate kinetics with respect to monomer consumption and a linear increase in the number average molecular weight as a function of percentage monomer conversion (M_n = 5.1 x 10^3 to 11.3 x 10^3 g/mol). Polymers with narrow molecular weight distributions (M_w/M_n = 1.25 to 1.31) were obtained.

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APPENDIX