DESIGNED FUNCTIONALIZED POLYMERS BY ANIONIC MACROMOLECULAR ENGINEERING FOR MEMBRANE DEVELOPMENT AND FABRICATION

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

INTRODUCTION

In the South African context, industrialization, water pollution, rapid urbanization and the scarcity of good quality water resources make efficient and effective water resources management a high priority. Since the national economy is dependent on the protection and conservation of precious water reserves, well-structured programs in water pollution prevention, production of high purity water for potable use and waste water utilization are essential to produce high quality water for human consumption and industrial and biological use.

Advances in materials technology, specifically in the development of novel polymeric separation membranes, can play an important role in the sustenance of natural water resources and waste water treatment processes in South Africa. Thus, the development of new synthetic methods for the preparation of novel functionalized polymers is needed to meet the increased industry demand for precursor polymeric material for the fabrication of cost-effective membrane systems with improved performance in the purification and treatment of water for potable use, industrial utility and the abatement of environmental pollution.

Polysulfone is an engineering thermoplastic widely used as precursor material for the fabrication of membranes for applications in the area of liquid and gas separations. Commercial applications include carbon dioxide stripping from natural gas streams and the production of high purity nitrogen from air. In addition, polysulfones have been investigated as ion exchange membranes in electro-membrane processes such as electrodialysis, and polymer electrolyte membrane electrolysis. The chemical and physical characteristics of polysulfone such as good thermal and chemical stability, mechanical strength and excellent oxidative resistance makes polysulfone the material of choice for use as membrane substrates. However, the hydrophobic nature of polysulfone makes it susceptible to fouling by various mechanisms that effectively inhibits its application as polymeric substrates in membrane separation technology in food and biological separations as well as the chelation of heavy metals in hydrophilic environments. Thus, the synthesis and applications of new, reactive functionalized polymers have been the focus of industrial and academic research to meet the increased industrial need for hydrophilic polysulfones.

It is well known that the incorporation of bulky pendant polar or non-polar groups onto the polymer backbone effects significant changes to the gas permeability, permselectivity, mechanical and surface properties of polysulfone membranes. Thus, this research project focused on the development of new synthetic strategies for the chemical modification of polysulfone such that the introduction of chemical functionalities onto the polysulfone backbone would lead to improved membrane characteristics without detrimental effect on chemical and thermal stability of the polysulfone derivative.

RESEARCH METHODOLOGY

The main objectives of the project were the design and synthesis of functionalized polysulfones and subsequent evaluation of the membrane matrix characteristics of the functionalized polysulfone derivatives in order to meet the increased industrial need for polysulfone membranes with increased hydrophilicity, high flux and low fouling. The project adopted the following strategy:

The Chemical Modification of Polysulfone

The first approach involves the use of living anionic polymerization methods to prepare novel functionalized polymers and graft copolymers based on commercially available polysulfone using the following method:

- the organic synthesis of mono- and disubstituted 1,1-diphenylethylenes with emphasis on the tertiary amine, the aromatic hydroxyl, primary amine and carboxylic acid groups in the protected or unprotected forms as well as the organic synthesis of vinylidenedipyridine derivatives.
- the lithiation of polysulfone and subsequent reactions with 1,1-diphenylethylene, substituted 1,1-diphenylethylenes and vinylidenedipyridines.
- the polysulfone graft copolymerization using acrylamide, styrene and methylmethacrylate as co-monomers.

The second approach focused on the preparation of functionalized polymers using a controlled free radical process called Atom Transfer Radical Polymerization. However, the success of the synthetic technique centers on the reactivity of the benzyl radical in ATRP reactions. Thus, the reactivity of the benzyl radicals in atom transfer radical polymerization processes with regard to the preparation of the aromatic carboxyl, tertiary amine, primary amine, siloxyl and hydroxyl functionalized polymers as well as polysulfone-g-polystyrene polymers have been investigated by the following general method:

- the synthesis of methyl substituted polysulfone by the reaction of lithiated polysulfone with methyl iodide;
- bromination of methylated polysulfone with N-bromosuccinimide to form the brominated polysulfone macroinitiator;
- the reaction of brominated polysulfone macroinitiator with styrene and the 1,1-diarylethylene derivatives by atom transfer radical polymerization methods to form polysulfone-g-polystyrene and diaryl functionalized polysulfones, respectively.

Membrane Production

- The preparation of asymmetric membranes by casting dilute organic solutions of the polymer matrix on a glass plate followed by immersing in water.
- Evaluation of the membrane characteristics of the virgin functionalized polysulfone matrices by considering the following:
    - membrane morphology
    - thermal characteristics
    - hydrophilicity
    - pure water flux measurements

RESEARCH OUTCOMES

Potential impact of the project is on technological advancement and the development of human resources in synthetic polymer chemistry for utilization in water purification programs in South Africa.

Industry

Current research is centered on the design of new synthetic approaches to develop separation membranes with high chemical resistance, increased hydrophilicity, good permeability, controlled selectivity as well as enhanced chlorine tolerance. The synthesis of functionalized polysulfones with pendant polar functional groups could provide polymer substrates with enhanced membrane characteristics for use as precursors for the fabrication of water and industrial effluent purification and desalination separation membranes.

Human Resources Development and Capacity Building

The current research work:

- Emphasized extensive research and technical skills development in Organic/Polymer synthesis with specialization in the design and synthesis of novel polymers by anionic and radical and mechanisms.
- Facilitated the formal training and upgrading of the technical and research skills of postgraduate students from the disadvantaged community of South Africa, especially women.
- Improved scientific awareness within the disadvantaged communities of South Africa.

- Promoted interaction with academics and centers of expertise, locally and abroad.

SUMMARY OF RESULTS

- The chemical modification of polysulfone was performed by a two-step process which involved the lithiation of polysulfone and subsequent reaction of lithiated polysulfone with stoichiometric amounts of 2,2'-vinylidenedipyridine to afford novel dipyridyl functionalized polysulfone with 45% degree of functionalization.

- Novel dipyridyl functionalized polysulfone with 80% degree of functionalization was prepared by the reaction of lithiated polysulfone with excess of 2,2'-vinylidenedipyridine.

- The dipyridyl functionalized polysulfone with 45% degree of functionalization was evaluated for the chelation of trace heavy metal ions such as copper and nickel in aqueous medium and the results show that dipyridyl functionalized polysulfone shows better complexing affinity for nickel ions at specific concentrations of test solutions.

- Quaternization reactions of dipyridyl functionalized polysulfone with dimethyl sulfate in the presence of perchloric acid quantitatively affords the corresponding polymeric pyridinium perchlorate derivative and provided evidence of the incorporation of the dipyridyl groups pendant to the polysulfone backbone.

- The introduction of pendant dipyridyl groups onto the polymer backbone imparts hydrophilic characteristics to the resulting polymeric membrane and makes such membranes suitable for the preparation of membranes with anti-fouling properties.

- The membrane obtained from polysulfone with the higher degree of dipyridyl substitution exhibits enhanced membrane morphological characteristics, higher water permeate flux and better structural integrity as determined by atomic force microscopy and scanning electron microscopy analysis.

- The dipyridyl functionalized polysulfones are thermally less stable than the parent polysulfone. The glass transition temperatures of the modified polysulfones with the pendant dipyridyl groups decrease with higher substitution because of increased chain mobility.

- Aromatic carboxyl functionalized polystyrenes with well-defined structures were prepared in quantitative yields by atom transfer radical polymerization methods by the α-bromo-p-toluic acid initiated polymerization of styrene in the presence of copper (I) bromide and 2,2'-dipyridyl as catalyst system.

- Tertiary-amine functionalized polystyrene was prepared in quantitative yields by atom transfer radical polymerization methods. In a one-pot synthesis method and by using the adduct of 1-(bromoethyl)benzene with 1-(4-dimethylamino- phenyl)-1-phenylethylene as initiator, the polymerization of styrene in the presence of a copper (I) bromide/2,2'-bipyridyl catalyst system proceeded via a controlled free radical polymerization process to afford the corresponding tertiary amine functionalized polystyrene with well-defined polymer structure. All experimental evidence is consistent with quantitative functionalization via the 1,1-diphenylethylene derivative.

- Primary amine functionalized polystyrenes with good control of polymer parameters such as number average molecular weights, narrow molecular weight distributions and chain functionalities were prepared in quantitative yields by atom transfer radical polymerization. In a one-pot synthesis, the adduct of 1-(bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene was used as initiator for styrene polymerization in the presence of a copper (I) bromide/N, N,N=, N=,N=>-pentamethyldiethylenetriamine catalyst system. Good control of the polymerization process was observed and initiator efficiencies as high as 0.92 were obtained.

- Siloxyl and hydroxyl functionalized polymers with well defined structures were synthesized in quantitative yields by atom transfer radical polymerization using 1,1-diphenylethylene derivatives as initiator precursors. Siloxyl functionalized polystyrenes were prepared by a one pot synthesis method using the adduct of 1-(bromoethyl)- benzene with 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene as initiator for polymerization of styrene in the presence of a copper (I) bromide/2,2'-bipyridyl or copper (I) bromide/ N,N,N=,N=,N@-pentamethyldimethyltriamine (PMDETA) catalyst complexes.

- Acid catalyzed hydrolysis of siloxyl functionalized polystyrene with concentrated hydrochloric acid produced the corresponding hydroxyl functionalized polystyrene.

- The results show that functionalization of polysulfone by the ATRP method is possible using the benzyl brominated polysulfone as macroinitiator and functionalized 1,1-diphenylethylene derivatives as functionalizing agents.

FUTURE RESEARCH

- Results show that the functionalization reaction of lithiated polysulfone with different amounts of 2,2'-vinylidenedipyridine produces the corresponding dipyridyl functionalized polysulfones with a degree of functionalization of 45% and 80%. Thus, it is necessary to focus on new synthetic strategies to improve the functionalization efficiency and the yield of functionalized polymers. Therefore, it is proposed to conduct the synthesis of dipyridyl functionalized polysulfone by condensation polymerization with 3-(2,2-(2,2'-dipyridyl)ethenyl)-4-fluorophenyl-4'-fluorophenylsulfone and bisphenol A as monomers.

- The synthesis of functionalized polysulfone substituted with pendant diaryl groups as well as graft copolymers with polysulfone backbone and polystyrene, polymethylmethacrylate or polyacrylamide grafts by ATRP methods using low molecular mass polymer to effect higher functionalization yields as well as better analytical characterization of products.

- The chemical modification of polysulfone by ATRP methods using the reaction of brominated polysulfone macroinitiator with disubstituted 1,1-diarylethylenes.

- The evaluation of the membrane characteristics of the new functionalized polysulfone derivatives.

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CHAPTER 1

LITERATURE REVIEW

1.1 Introduction

Polysulfone is an engineering thermoplastic widely used as precursor material for the fabrication of membranes for applications in ultrafiltration, reverse osmosis and in the area of liquid and gas separations.[1-17] Commercial applications include carbon dioxide stripping from natural gas streams and the production of high purity nitrogen from air. In particular, polysulfones have been investigated as ion exchange membranes in electro-membrane processes such as electrodialysis, and polymer electrolyte membrane electrolysis.[5-8] The chemical and physical characteristics of polysulfone such as good thermal and chemical stability, mechanical strength and excellent oxidative resistance makes polysulfone the material of choice for use as membrane substrates. However, due to its hydrophobic nature, polysulfone membranes are susceptible to fouling by various mechanism that inhibits its application as polymeric substrates in membrane separation technology in food and biological systems and chelation of heavy metals in hydrophilic environments.[1-17] 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 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.

1.2 Chemical Modification of Polysulfone

Several reviews on the chemical modification of polysulfone to effect the introduction of functional groups onto the polysulfone backbone by different chemical mechanisms have been reported.[1-17]

Anionic polymerization methodology provides the most efficient route to the synthesis of polymers with controlled molecular weight, molecular weight distribution, chain-end and in-chain functionality and morphology.[18-20] The general method for the introduction of functional groups onto the polysulfone backbone by anionic methods involves the formation of the lithiated polysulfone precursor followed by the addition of an appropriate electrophile lead to the introduction of different functional groups such as the carboxyl, primary amine and silyl groups pendant to the polymer backbone.

Guiver and coworkers[1-5,9,10,17] focused on the chemical modification of commercially available polysulfone in its polymer form by using homogenous anionic solution chemistry to introduce functional groups onto the polymer backbone. For example, the quantitative *lithiation* of polysulfone or the corresponding brominated polysulfone precursor and subsequent addition of methyl iodide produced the methyl substituted polysulfone.[1,2] Guiver and coworkers[2] also reported on the formation of carboxylated polysulfone by the direct lithiation of polysulfone followed by quenching the lithiated intermediate with carbon dioxide to afford carboxylated polysulfones in quantitative yields. Recently, a quantitative and regiospecific method for the synthesis of primary amine functionalized polysulfones via novel azide intermediates has been developed. The process involves the regioselective lithiation of polysulfone and the lithiated intermediates converted quantitatively to azides by treatment with tosyl azide.[4,5] The azide functionalized polysulfone was subsequently reduced to the primary amine derivative with sodium borohydride.

Kerres and coworkers[8] reported a new process for the sulfonation of polysulfones by the reaction of lithiated polysulfone with sulfur dioxide followed by oxidation of the resulting polymeric sulfinate intermediate. Membranes prepared from the sulfonated polysulfone show good conductivity, permselectivity and hydrolytic stability in acid and water at elevated temperature.

Functionalized polymers containing metal-ion chelating ligands for the selective and quantitative chelation of heavy metals has been extensively applied in the metallurgy and environmental and water purification fields.[1-16] Kan and coworkers[9] prepared functionalized polysulfone by immobilizing metal-ion chelating ligands such as 8-hydroxyquinoline, 1-(2-pyridylazo)-2-naphthol and 4-(2-pyridylazo)resorcinol onto the polysulfone backbone by diazo coupling with primary amine functionalized polysulfone precursor. The 8-hydroxyquinoline modified polysulfone showed the greatest chelating efficiency to heavy metal ions as well as greater chemical stability to alkaline environments. Also, the polymers functionalized with quaternary ammonium and pyridinium functionalities have been found to be effective as ultrafiltration membrane material for chelating heavy metals as well as for the removal of viruses from water by filtration.[15,16]

Belfort and coworkers[21-26] developed a novel photochemical method for producing hydrophilic poly(aryl sulfones) by chemically modifying polysulfone in the membrane form. The photochemical technique involves the treatment of ultrafiltration membranes with a solution containing the appropriate hydrophilic olefinic monomer in the presence of a chain transfer reagent and followed by UV irradiation to produce short polyolefin grafts from the polysulfone backbone. For example, polysulfone-g-poly(N-vinyl-2-pyrrolidinone) ultrafiltration membranes formed by such photochemical techniques exhibit increased wettability and decreased protein adsorptive fouling, but with slight decrease in permeability when compared to the commercially available polysulfone membranes.

In addition, Belfort and coworkers[27-29] reported the surface modification of poly(ether sulfone) ultrafiltration membranes by using low temperature plasma modification techniques. For example, the low temperature helium plasma treatment of unmodified virgin poly(ether sulfone) membranes followed by the grafting of N-vinyl-2-pyrrolidone from the poly(ether sulfone) backbone produced modified polymer membrane surfaces which are less susceptible to protein fouling and exhibits high flux.

1.3 Chemical Modification of Polysulfone by Living Controlled Free Radical Polymerization Methods

The uses and formulations of low molecular weight functionalized polymers with well defined molecular weight and polymer architecture, especially telechelic polymers, are widely investigated in industry and academia in several areas such as nanotechnology, chain extension reactions, reversible ionic association, reactive processing, catalysis, drug delivery, membrane separation technology and compatibilization of polymer blends.[30-34]

Atom Transfer Radical Polymerization (ATRP) provides an efficient method for the synthesis of styrene, methyl methacrylate and acrylonitrile polymers with controlled molecular weight, molecular weight distribution, chain functionality, polymer architecture and composition.[35-37] The classical ATRP method encompasses the reversible homolytic cleavage of a carbon-halogen bond of an alkyl halide initiator molecule, such as 1-phenylethyl chloride, catalyzed by a transition metal salt such as cuprous chloride, complex with suitable ligands such as 2,2'-bipyridyl, followed by successive monomer insertion into the carbon halogen bond. The structure of the polymer obtained by ATRP contains a halogen at the ω-terminal end group with the initiator fragment at the α-terminus. Thus, the versatility of ATRP technique facilitates the synthesis of telechelic polymers by the utilization of functionalized initiators for the controlled, living polymerization of styrene and methyl methacrylate. A plethora of functionalized initiators was employed in the initiation of styrene polymerizations by ATRP methods to afford polystyrene functionalized with ends groups such as the hydroxyl, epoxy, aryl bromide and primary amino groups.[38-50]

1.3.1 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization: Carboxylation

In the classical ATRP process, the polymerization of carboxylic acid containing monomers as well as the synthesis of carboxyl functionalized polymers by ATRP is not considered synthetically viable, since poisoning of the transition metal-ligand catalyst complex system is observed due to the rapid reversible formation of copper (I) carboxylates.[43-48] In addition, the presence of copper (I) carboxylates and carboxylic acids influences the rate of polymerization of the metal catalyzed controlled radical polymerization of styrene. Haddleton and coworkers[44] reported that the 2-bromoisobutyrate initiated polymerization of methyl methacrylate, catalyzed by the (N-n-butyl-2-pyridylmethanimine) copper (I) bromide system, proceeded with good control of molecular weight and molecular weight distribution. However, upon the addition of stoichiometric amounts of benzoic acid relative to initiator, the rate of polymerization was enhanced with concomitant broadening of the molecular weight distribution, indicating the poisoning of the copper-ligand catalyst system and low initiation efficiency. Also, reports by Percec and coworkers[45] show that the addition of sodium benzoate to the CuCl/bpy catalyzed living radical polymerization initiated by p-methoxybenzene sulfonyl chloride enhances the rate of polymerization of butyl acrylate in diphenyl ether. However, poor control of molecular weight is observed and polymers with broad molecular weight distribution are formed. In addition, Zhang and Matyjaszewski[48] reported that, in the ATRP of styrene by 1-phenylethyl bromide in the presence of benzoic acid, dark blue solutions were observed in the polymerization process, consistent with literature data that carboxylic acids coordinate strongly with copper (II) species and only weakly with copper (I) species.[51] Furthermore, at low concentrations of benzoic acid (0.5 equiv. of benzoic acid to initiator), no significant effect on the polymerization of styrene was observed, and well-defined polymers with low polydispersities were obtained. However, at higher concentrations of benzoic acid, decrease in the polymerization rate and broadening of the molecular weight distribution were observed. Thus, literature results indicate that the carboxylic acid group plays an active role in the metal-catalyzed living radical polymerization of styrene and acrylate monomers, especially at high concentrations. The initial role of the carboxylic acid is to complex with the copper (I) center, displacing the ligand, thereby creating a coordination site on the cuprate intermediate for propagation to occur.[44-48]

Nevertheless, well-defined polystyrene with terminal carboxylic acid groups can be prepared via ATRP methods using initiators with carboxylic acid groups remote to the initiator halogen end. Zhang and Matyjaszewski[48] reported the synthesis of carboxyl functionalized polystyrene with low polydispersity and initiator efficiency of 0.7 using 4-(1-bromoethyl)benzoic acid as initiator in the presence of CuBr and N,N′,N″, N‴-pentamethyldiethylenetriamine as catalyst system.[51] The dark blue polymerization solutions observed in the reaction suggests the occurrence of coordination of carboxylic acid groups to the transition metal catalyst. The straight line semi-logarithmic kinetic plots for styrene conversion versus time obtained indicate that fast initiation and the generation of a constant number of propagating species has occurred. The experimentally observed $M_{n,SEC}$ increased linearly with conversion, but was slightly higher than the theoretical molecular weight, $M_{n,th}$, indicating low initiation efficiency.

1.3.2 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry

The addition reactions of simple and polymeric organolithium compounds to 1,1-diphenylethylene derivatives functionalized with the hydroxyl, carboxyl, amide, primary and tertiary amine groups in the protected or free form to produce functionalized polymers by anionic polymerization methods have been used extensively since (a) these addition reactions are simple and quantitative, and (b) due to steric factors, only monoaddition reactions have been reported, that is, no oligomerization of the 1,1-diphenylethylene unit occurs.[52-57] Although a variety of functionalized initiators have been employed in ATRP processes, to our knowledge, the use of functionalized 1,1-diphenylethylene derivatives as initiator precursors in ATRP reactions has not been exploited.

1.3.2.1 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry: Tertiary Amine Functionalized Polymers

Although Atom Transfer Radical Polymerization (ATRP) is a versatile technique for the synthesis of functionalized polymers, only a few reports on the use of tertiary amine functionalized initiators in the initiation of styrene polymerizations by ATRP methods to prepare tertiary amine functionalized polystyrene have been reported in the literature. Percec and coworkers[50] reported a new procedure for the synthesis of tertiary amine functionalized polymers using functionalized sulfonyl chlorides as initiators for the transition metal-catalyzed controlled radical polymerization of styrene and methacrylates. However, using dansyl chloride as initiator, the polymerization of methyl methacrylate shows slow initiation and polymers with broad polydispersities are formed.[50]

1.3.2.2 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry: Primary Amine Functionalized Polymers

The versatility of ATRP technique facilitates the synthesis of telechelic polymers by the utilization of functionalized initiators for the controlled, living polymerization of styrene and methyl methacrylate. Haddleton and Waterson[58] described a procedure for the synthesis of primary aromatic amine functionalized polymers using a primary amine functionalized phenolic ester derivative as initiator for the transition metal-ligand catalyzed controlled free radical polymerization of methacrylates. The polymerization reaction proceeded with high efficiency to provide polymers with well defined molecular weight and narrow polydispersity and illustrated a method to introduce an aromatic primary amine group into a polymer without the need for protection group chemistry. Also, indirect methods for the introduction of primary amine groups into polymers can be achieved when the ATRP polymers with the halogen end groups are subjected to post polymerization functional group transformation reactions. By converting the halogen groups to azides and subsequently via phosphoboranes intermediates provides a useful method for the introduction of the primary amine group at the ω-terminal end of the polymer chain.[59]

1.3.2.3 Chain-End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry: Siloxyl and Hydroxyl Functionalized Polymers

Different synthetic strategies for the preparation of hydroxyl functionalized polymers by ATRP mechanisms are possible. The controlled living free radical polymerization of monomers such as 2-hydroxyethyl methacrylate affords the corresponding well-defined hydroxyl functionalized polymers with the hydroxyl group pendant to the polymer backbone.[60] In addition, Kops and coworkers[61] reported the preparation of 4-acetoxystyrene polymers by ATRP, which, upon hydrolysis of the pendant ester groups affords the corresponding hydroxyl functionalized polystyrenes. Also, hydroxyl functionalized polymers can be prepared by chemical modification reactions of the halogen end group to the hydroxyl group by standard organic chemistry procedures using 2-aminoethanol as reagent.[62] Furthermore, since allyl alcohol does not polymerize via ATRP methods, ω-terminal hydroxyl functionalized polymers can be prepared via ATRP mechanisms by the chain end termination reactions with allyl alcohol.[63]

In addition to functional groups pendant to the polymer backbone, the structure of the polymer obtained by ATRP methods contains a halogen at the ω-terminal end group with the initiator fragment at the α-terminus. Thus, the versatility of the ATRP technique facilitates the synthesis of telechelic polymers by the utilization of functionalized initiators in the controlled, living polymerization of styrene and methyl methacrylate.

Although functionalized initiators were employed in the initiation of styrene polymerizations by ATRP methods to prepare polystyrene functionalized with end groups such as the aromatic carboxyl, epoxy, aryl bromide, tertiary amine and primary amine groups,[35-50] the literature reports on the use of hydroxyl functionalized initiators in ATRP reactions are limited to the use of activated sulfonyl halides and alkyl halides activated by the ester group. Haddleton and coworkers[40] utilized 2-hydroxyethyl-2-bromoisobutyrate as functionalized initiator for methylmethacrylate polymerization to form α-hydroxy functionalized polymethylmethacrylate. Matyjazsewski and Coessens[64] reported the synthesis of hydroxyl functionalized polymethylacrylate by ATRP using 2-hydroxyethyl-2-bromopropionate as functionalized initiator in the presence of CuBr/4,4'-di(nonan-5-yl)/2,2-bipyridyl metal ligand catalyst complex. Pan and coworkers[65] outlined the use of 2-hydroxylethyl-2'-bromobutyrate in combination with CuBr/2,2-bipyridine for ATRP of styrene to form polystyrene with hydroxyl and bromine groups at each end of the polymer chain. Percec and coworkers[66] reported the synthesis of hydroxyl functionalized polymers using hydroxyl functionalized aromatic sulfonyl chlorides as initiators for the transition metal-catalyzed controlled radical polymerization of styrene and methacrylates. Pionteck and coworkers[67] described the preparation of well-defined hydroxy functionalized polymers using N-(2-hydroxyethyl)-4-(1-bromoethyl)benzoic acid amide as initiator for the ATRP of styrene.

1.3.3 Synthesis of Polysulfone-g-polystyrene by Atom Transfer radical Polymerization

The controlled free radical graft copolymerization of vinyl monomers such as styrene, methyl methacrylate and acrylamide from polymeric macroinitiator has been reported in the literature. Yan and coworkers[68] reported that novel graft copolymers such as poly(aryl ether sulfone)-graft-polystyrene and poly(aryl ether sulfone)-graft-[polystyrene-block-poly)methyl methacrylate)] were successfully synthesized by ATRP methods catalyzed by $FeCl_2$/isophthalic acid in DMF. Hedrick and coworkers[69] used (2-bromo-2-methyl propionyl)-ε-caprolactone as an initiator for the controlled free radical polymerization of methyl methacrylate to synthesize poly(ε-caprolactone-graft-poly(methyl methacrylate). Also, syndiotactic polystyrene graft copolymers were synthesized by ATRP methods using brominated syndiotactic polystyrene as the initiator and CuBr and pentamethyldiethylenetriamine as the catalyst.[70]

The project objective was extended to include the synthesis of diaryl functionalized polysulfone as well as polysulfone-g-polystyrene by the following synthetic route:

(i) the synthesis of methyl substituted polysulfone by the reaction of lithiated polysulfone with methyl iodide;

(ii) bromination of methylated polysulfone with N-bromosuccinimide to form the brominated polysulfone macroinitiator;

(iii) the synthesis of diaryl functionalized polysulfone and polysulfone-g-polystyrene by atom transfer radical polymerization methods using the brominated polysulfone as macroinitiator.

CHAPTER 2

CHEMICAL MODIFICATION OF POLYSULFONE: ANIONIC SYNTHESIS OF DIPYRIDYL FUNCTIONALIZED POLYSULFONE

2.1 Abstract

The synthesis of a new functionalized polysulfone with pendant dipyridyl groups is described.[71] The functionalization process involves the formation of lithiated polysulfone from polysulfone and subsequent reaction with stoichiometric amounts of 2,2'-vinylidenedipyridine in tetrahydrofuran at -78 °C under argon atmosphere. The dipyridyl functionalized polysulfone was evaluated for the chelation of trace heavy metal ions such as copper and nickel in aqueous medium. The dipyridyl functionalized polysulfone shows better complexing affinity for nickel ions at specific concentrations of test solutions. Quaternization reactions of dipyridyl functionalized polysulfone with dimethyl sulfate in the presence of perchloric acid quantitatively affords the corresponding polymeric pyridinium perchlorate derivative.

2.2 Introduction

To our knowledge, the synthesis of dipyridyl functionalized polysulfone has not been reported in the literature. In this study, the novel synthesis of dipyridyl functionalized polysulfone was prepared by a two-step process which involves the quantitative lithiation of polysulfone (**1**) followed by the reaction with stoichiometric amounts of 2,2'-vinylidenedipyridine. In order to determine the extent of incorporation of the functional groups pendant to the polysulfone backbone, the dipyridyl functionalized polymer has been evaluated for its efficiency in chelation of trace amounts of heavy metal ions from aqueous solution. Furthermore, post-functionalization quaternization reactions were conducted by using the dipyridyl functionalized polysulfone as precursor to form the corresponding dipyridinium perchlorate polysulfone derivative to determine the presence of the dipyridyl groups on the polysulfone backbone.

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

The reaction of lithiated polysulfone with stoichiometric amounts of 2,2'-vinylidenedipyridine was utilized to effect the incorporation of dipyridyl units onto the polysulfone backbone. A 41% yield of 2,2'-vinylidenedipyridine was obtained by the classical Wittig reaction of di-2-pyridyl ketone with the ylide, an intermediate which was generated from the reaction of sodium hydride and methyltriphenylphosphonium bromide in dimethyl sulfoxide.[71,72] The ^{1}H NMR spectrum of 2,2'-vinylidenedipyridine shows a singlet at $\delta = 6.05$ which is attributed to the resonance of alkene protons, as well as a multiplet between $\delta = 6.97 - 8.60$ due to the chemical shifts of the aromatic protons of the pyridyl rings. The structure of the 2,2'-vinylidenedipyridine was also confirmed by IR spectral data with the presence of a strong C=N absorption frequency of the pyridyl groups at 1634 cm^{-1}.

2.4 Functionalization of Polysulfone with 2,2'-Vinylidenedipyridine. Synthesis of Dipyridyl Functionalized Polysulfone

The reaction of living polymeric carbanions with 2,2'-vinylidenedipyridine provides an efficient functionalization method for the synthesis of pyridyl functionalized polymers. The functionalization of polysulfone (**1**) with (**2**) involves two steps: (a) the regiospecific lithiation of polysulfone with n-butyl lithium at low temperatures, and (b) the reaction of lithiated polysulfone with (**2**) at low temperature. Initial results of the reaction of lithiated polysulfone with stoichiometric amounts of (**2**) in dry THF at 0 °C produced low yields of functionalized polysulfone, with concomitant formation of crosslinked material. At 0 °C, precipitation of the lithiated polysulfone is observed, possibly due to aggregation of lithiated species and intermolecular rearrangement reactions. The most efficient functionalization reaction was effected by the treatment of lithiated polysulfone with stoichiometric amounts of (**2**) in THF at -78 °C to afford the corresponding dipyridyl functionalized polysulfone (**3**) with degree of functionalization of 45%, as determined by nuclear magnetic resonance spectroscopy (**Figure 2.1**). The presence of the lithiated polysulfone carbanions were manifested by the initial formation of a green-brown colour and then formation of a red-brown homogenous, viscous solution. Upon the addition of (**2**), the colour of the reaction mixture immediately changed to brown orange. Upon quenching the reaction mixture with methanol, the functionalized polysulfone was precipitated in methanol, filtered off and vacuum dried.

The ^1H NMR spectrum (**Figure 2.2**) for dipyridyl functionalized polysulfone (**3**) exhibits resonances at δ = 3.78 and δ = 4.65 due to the presence of CH_2 and CH proton resonances of the functionalizing agent, respectively, indicating the incorporation of the functionalizing agent onto the polysufone backbone. Furthermore, the resonances between δ = 6.3 -6.7 and 7.4-7.8 and 8.1-8.4 are attributed to the aromatic proton resonances of the pyridyl groups. These resonances are absent in the proton NMR spectrum of unfunctionalized polysulfone (**1**).

FTIR analysis shows the presence of an absorption band at 1634 cm^{-1}, which is characteristic of the C=N stretching mode of the pyridine group. This absorption band is absent in the FTIR spectrum of unfunctionalized polysulfone (**1**).

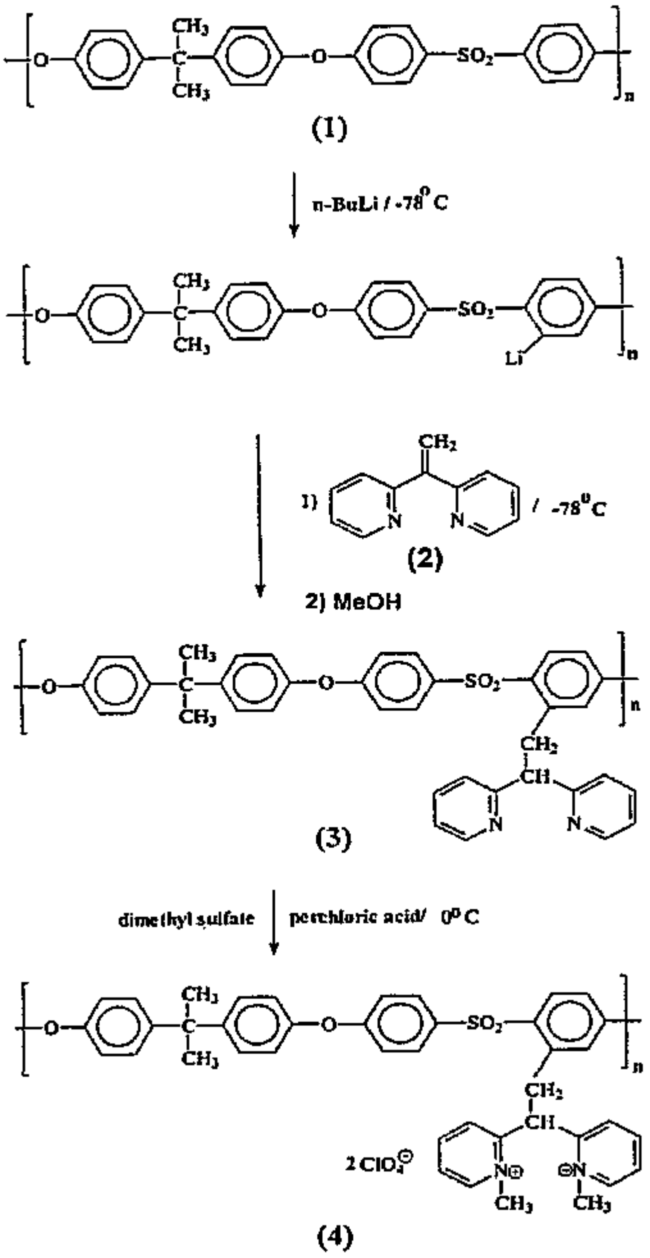

Figure 2.1 Synthesis of dipyridyl functionalized polysulfone and pyridinium perchlorate functionalized polysulfone

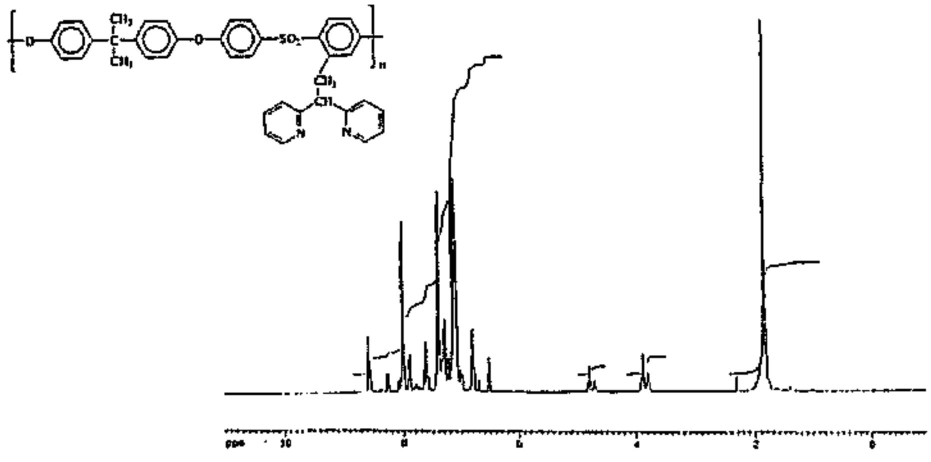

Figure 2.2 ^{1}H NMR ($CDCl_3$) spectrum of dipyridyl functionalized polysulfone

2.5 Quaternization of dipyridyl functionalized polysulfone (3): Synthesis of pyridinium perchlorate functionalized polysulfone (4)

The dipyridyl functionalized polysulfone (3) was subjected to the process of quaternization by the reaction with dimethyl sulfate in the presence of perchloric acid to form the corresponding pyridinium perchlorate functionalized polysulfone (4)
(Figure 2.1).

The ^{1}H NMR (d_6-DMSO) spectrum of (4) exhibits a strong, broad resonance at $\delta = 4.15$, which corresponds to the presence of the N-methyl protons of the N-methyl pyridinium groups (**Figure 2.3**). The success of the quaternization reaction confirms the presence of the dipyridyl groups on the polysulfone backbone.

2.6 Chelation of heavy metals by polysulfone (1) and dipyridyl functionalized polysulfone (3)

Finely ground powders of polysulfone (1) and dipyridyl functionalized polysulfone (3) were packed into columns and analysed for their ability to complex with heavy metal ions. The concentration of separate copper and nickel ion solutions ranged between
5 - 20 mmol in distilled water. In the analysis using unfunctionalized polysulfone (1) as substrate, complete recovery of the metal ions, after passage through the column, was observed. With the functionalized polysulfone (3) as substrate, the heavy metal ions were retained due to complexing with the pendant dipyridyl groups on the polysulfone backbone. The metal ions were flushed from the column by an acidic solution and subjected to Atomic Absorption Spectroscopic measurements.

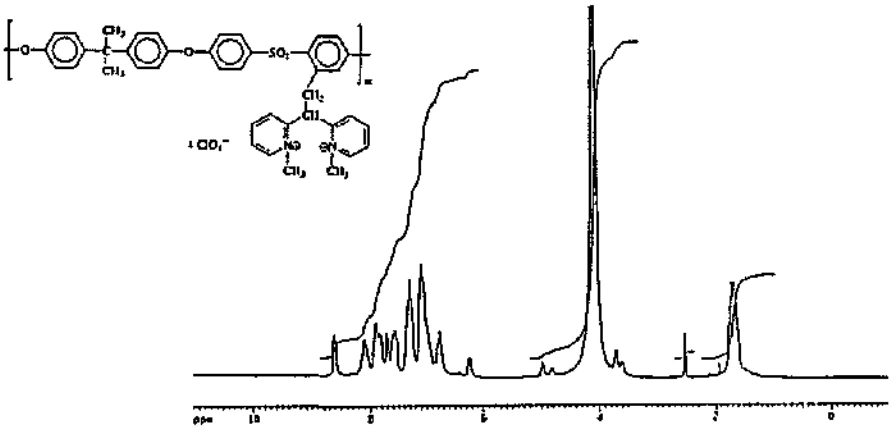

Figure 2.3 ^1H NMR (DMSO) spectrum of pyridinium perchlorate functionalized polysulfone

Figure 2.4 shows the chelating behaviour of dipyridyl functionalized polysulfone (**3**) when treated with different standard concentrations of solutions of copper and nickel ions, respectively. Results show that the uptake of heavy metal ions increases with an increase in the concentration of the standard solutions. In addition, the dipyridyl functionalized polysulfone (**3**) shows better complexing affinity for nickel ions at low concentrations of test solutions. However, higher chelation efficiency for copper ions is observed at higher concentrations.

2.7 Conclusions

The functionalization reaction of lithiated polysulfone with stoichiometric amounts of 2,2'-vinylidenedipyridine produces the corresponding dipyridyl functionalized polysulfone, with the degree of functionalization of 45%. The dipyridyl functionalized polysulfone powder shows good chelating efficiency to heavy metal ions such as copper and nickel. The quantitative quaternization reaction was carried out by the addition of dimethyl sulfate to dipyridyl functionalized polysulfone precursor in the presence of perchloric acid to afford the corresponding polymeric pyridinium salt derivative.

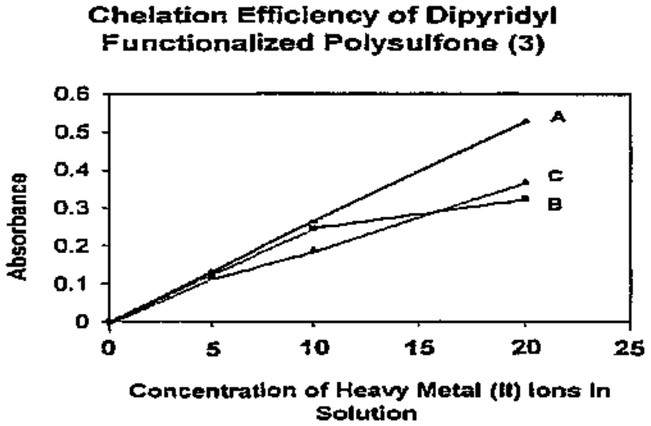

Figure 2.4 Plots of absorbance vs concentration (mmol) for the trace metal analysis of heavy metals(II) ions in aqueous solution for:

A : unfunctionalized polysulfone
B : Chelation of copper (II) ions by dipyridyl functionalized polysulfone
C: Chelation of nickel (II) ions by dipyridyl functionalized polysulfone

CHAPTER 3

FUNCTIONALIZED POLYSULFONE BY LIVING ANIONIC POLYMERIZATION:

DIPYRIDYL FUNCTIONALIZED POLYSULFONES FOR MEMBRANE PRODUCTION

3.1 Abstract

The synthesis of dipyridyl functionalized polysulfone with high degree of substitution, improved hydrophilicity and enhanced membrane morphological characteristics is described.[73] The polymer functionalization process involves the formation of lithiated polysulfone from polysulfone and subsequent reaction with excess of 2,2'-vinylidene-dipyridine in tetrahydrofuran at -78 °C under argon atmosphere to afford the corresponding dipyridyl functionalized polysulfone with a degree of functionalization of 80%. The functionalized polymers were characterized by size exclusion chromatography, 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, electrochemical and contact angle measurements.

3.2 Introduction

A generic chemical route to introduce bulky 1,1-diarylethylene functional groups onto the polysulfone backbone by anionic methods has been developed in our laboratories.[71] This technique involves the formation of a lithiated polysulfone precursor from polysulfone followed by the addition of an appropriate 1,1-diarylethylene derivative to afford the corresponding functionalized polysulfone derivative. The quantitative lithiation of polysulfone and subsequent addition of stoichiometric amounts of 2,2-vinylidene- dipyridine produced the corresponding dipyridyl functionalized polysulfone with a degree of functionalization of only 45% as described in the literature.[71]

Hereby, a more efficient synthetic route for the preparation of both the functionalizing agent, 2,2'-vinylidenedipyridine[71,72] and the subsequent dipyridyl functionalized polysulfones is described.[73] The quantitative lithiation of polysulfone followed by the reaction with excess 2,2'-vinylidenedipyridine produces dipyridyl functionalized polysulfone with an 80% degree of functionalization. Dipyridyl functionalized polysulfones with varying degrees of functionalization as well as polymer blends of the virgin polysulfone and dipyridyl functionalized polysulfone were evaluated for their potential as membrane substrates by considering membrane morphology, thermal characteristics, hydrophilicity and pure water flux measurements. The properties of the dipyridyl functionalized polysulfones were compared with unfunctionalized polysulfone.

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

The reaction of lithiated polysulfone with the 2,2'-vinylidenedipyridine was utilized to effect the incorporation of dipyridyl units onto the polysulfone backbone. A 80% yield of 2,2'-vinylidenedipyridine was obtained by the classical Wittig reaction[74] of di-2-pyridyl ketone with the ylide, an intermediate which was generated from the reaction of potassium t-butoxide and methyltriphenylphosphonium bromide in THF. The characterization data is consistent with spectral and chromatographic data reported in the literature.[71,72]

3.4 Functionalization of Polysulfone with 2,2'-Vinylidenedipyridine: Synthesis of Dipyridyl Functionalized Polysulfone, PFPS-80

The reaction of living polymeric carbanions with 2,2'-vinylidenedipyridine provides an efficient functionalization method for the synthesis of dipyridyl functionalized polymers. The functionalization of polysulfone (**1**) with (**2**) involves two steps: (a) the regiospecific lithiation of polysulfone with n-butyl lithium at low temperatures, and (b) the reaction of lithiated polysulfone with (**2**) at low temperature. Formation of a homogenous red-brown viscous solution, which indicates the formation of lithiated polysulfone carbanions, was observed at low temperatures and precipitation of the lithiated polysulfone was only observed room temperature. A higher yield functionalization reaction was effected by the treatment of lithiated polysulfone with excess of (2) in THF at -78 ^{0}C to afford the corresponding dipyridyl functionalized polysulfone (3) with 80% degree of functionalization, as determined by nuclear magnetic resonance spectroscopy **(Figure 3.1)**. The ^{1}H NMR spectrum **(Figure 3.2)** for dipyridyl functionalized polysulfone (3) exhibits resonances at δ = 3.78 and δ = 4.65 due to the presence of CH_2 and CH proton resonances of the functionalizing agent, respectively, indicating the incorporation of the functionalizing agent onto the polysufone backbone. Furthermore, the resonances between δ = 6.3 -6.7 and 7.4-7.8 and 8.1-8.4 are attributed to the aromatic proton resonances of the pyridyl groups. These resonances are absent in the proton NMR spectrum of unfunctionalized polysulfone (**1**). FTIR analysis 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. This absorption band is absent in the FTIR spectrum of unfunctionalized polysulfone (1).

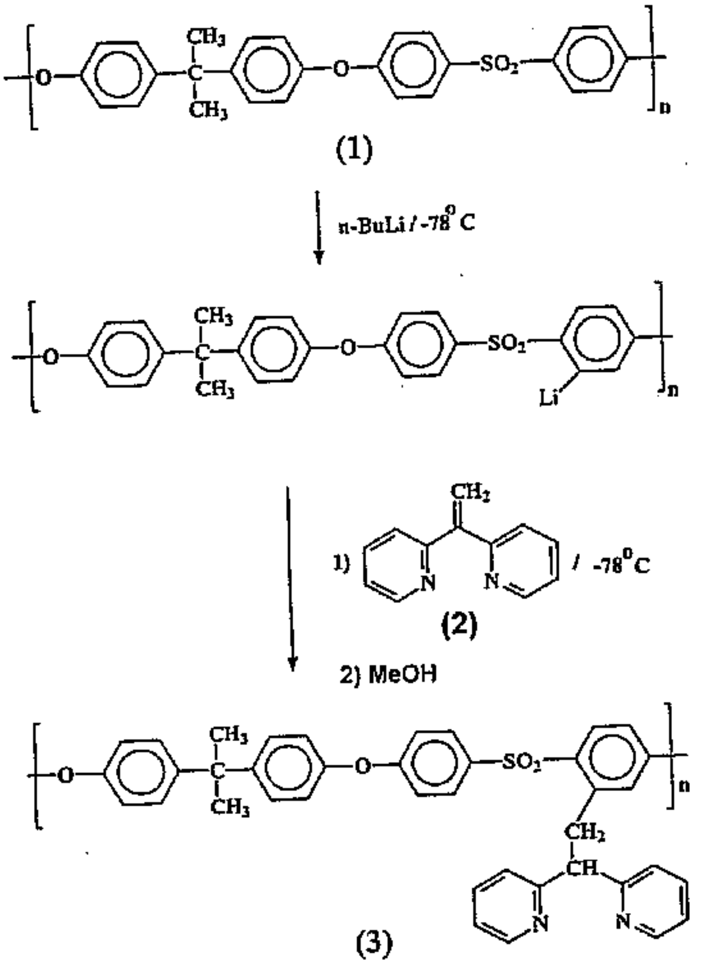

Figure 3.1 Synthesis of Dipyridyl Functionalized Polysulfone, PFPS-80

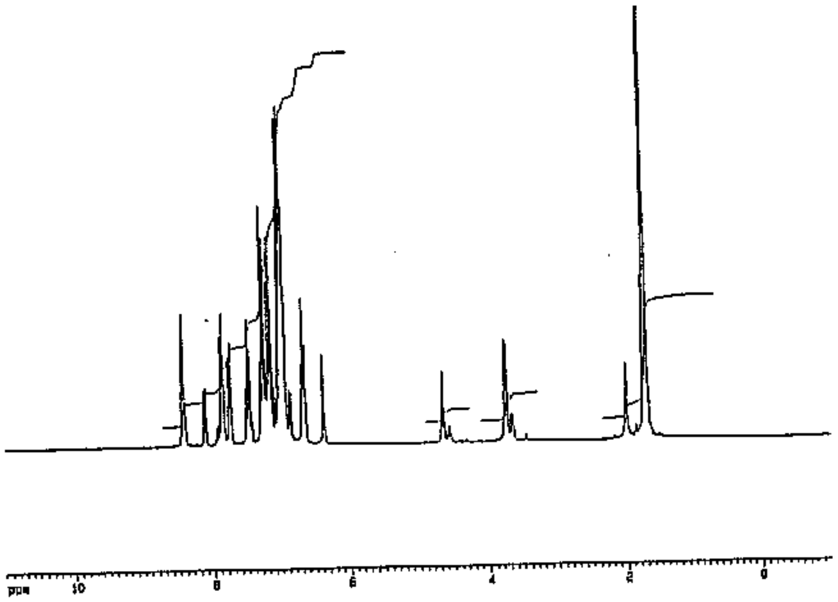

Figure 3.2 ^{1}H NMR ($CDCl_3$) spectrum of Dipyridyl Functionalized Polysulfone, PFPS-80

3.5 Atomic Force Microscopy (AFM)

Membranes were prepared by casting 15% (w/w) polymer solutions in N-methyl-2-pyrrolidone onto a glass plate followed by immersing into water to form asymmetric membranes of 150 micrometers in thickness.

AFM images of unmodified (PS) and dipyridyl functionalized polymers (PFPS-45 and PFPS-80) were obtained with the 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:

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

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

The three dimensional images for the different polysulfone membranes, PS, PFPS-45 and PFPS-80 are displayed in **Figure 3.3.** The topography 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 modules than the bottom, indicated by the higher roughness values obtained. The diameters of the modules range from 1.02 to 1.26 μm, with module diameter sizes on the bottom side ranging from 0.35 to 0.42 μm. The diameters of the pores on the bottom side of the PS membrane vary between 0.13 and 0.21 μm compared to the pore size diameters on the top of the membrane of 0.24 to 0.42 μm.

For sample PFPS-45, the roughness values of 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 has more densely packed modules than the bottom. Modules in the membrane skin surface range from 0.83 to 1.39 μm and from 0.24 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 module sizes of the PS sample seem to be larger than the PFPS-45 sample, which has a larger range of module 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 and167 nm in diameter. Thus, the pore sizes of PFPS-45 are significantly smaller than those in the PS membrane.

Similarly, for sample PFPS-80, the surface roughness was significantly greater than the unmodified polysulfone sample. Cross section profiles show that average module size of PFPS-80 is 347 nm, which is slightly larger than the modules 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 the literature.[75,76,77]

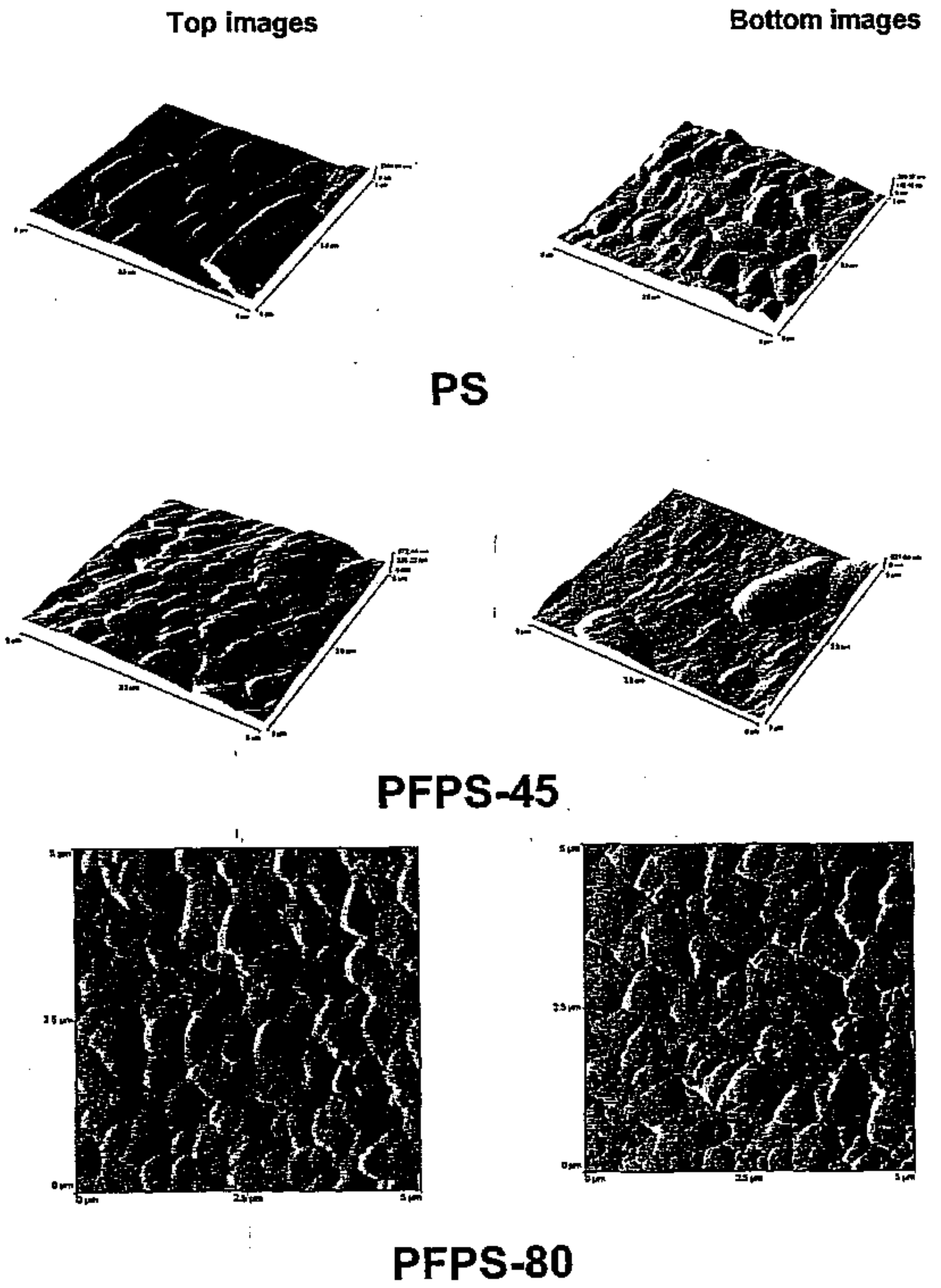

Figure 3.3 AFM micrographs of polysulfone membranes, PS, PFPS-45 and PFPS-80

3.6 Flux Measurements

Water permeability tests were carried out at 25 ^{o}C at transmembrane pressures ranging between 20 kPa and 100 kPa and membrane surface of 0.0051731 m^2 using pure water obtained by deionization resin and reverse osmosis treatment. Flux data were obtained passing pure water under pressure through the flat sheet membranes and collecting the permeate on a Mettler balance to determine the water permeability of the membranes.

Figure 3.4 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 the permeate production increases linearly with pressure. The unmodified polysulfone, PS, exhibits low 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 plateaux is observed at higher pressures, probably due to membrane compaction. 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, shows larger pure water flux values as compared to the unfunctionalized polysulfone at a given pressure, but smaller values than the PFPS-80 sample, indicating that the introduction of polar groups such as the dipyridyl group onto the polysulfone backbone does improve membrane permeability data.

In general, 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 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.

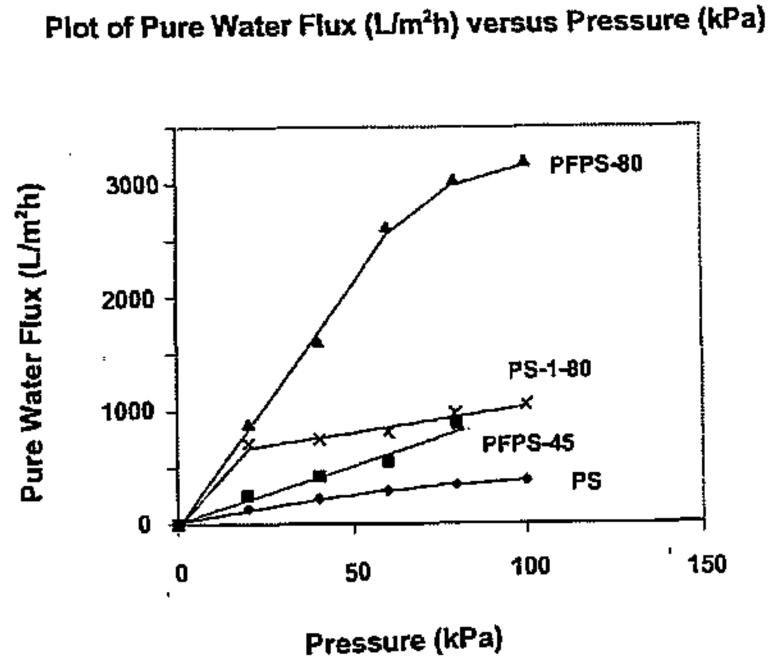

Figure 3.4 Plot of Pure Water Flux (L/m^{2}h) versus Pressure (kPa)

3.7 Membrane Morphology

SEM photographs reveal distinctly different morphological patterns for each of the membranes produced. **Figure 3.5** 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 PFPS-45 was more brittle and the PFPS-80 sample was thicker and more dense on the top.

Figure 3.6 shows the SEM analysis of the top view of the 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.

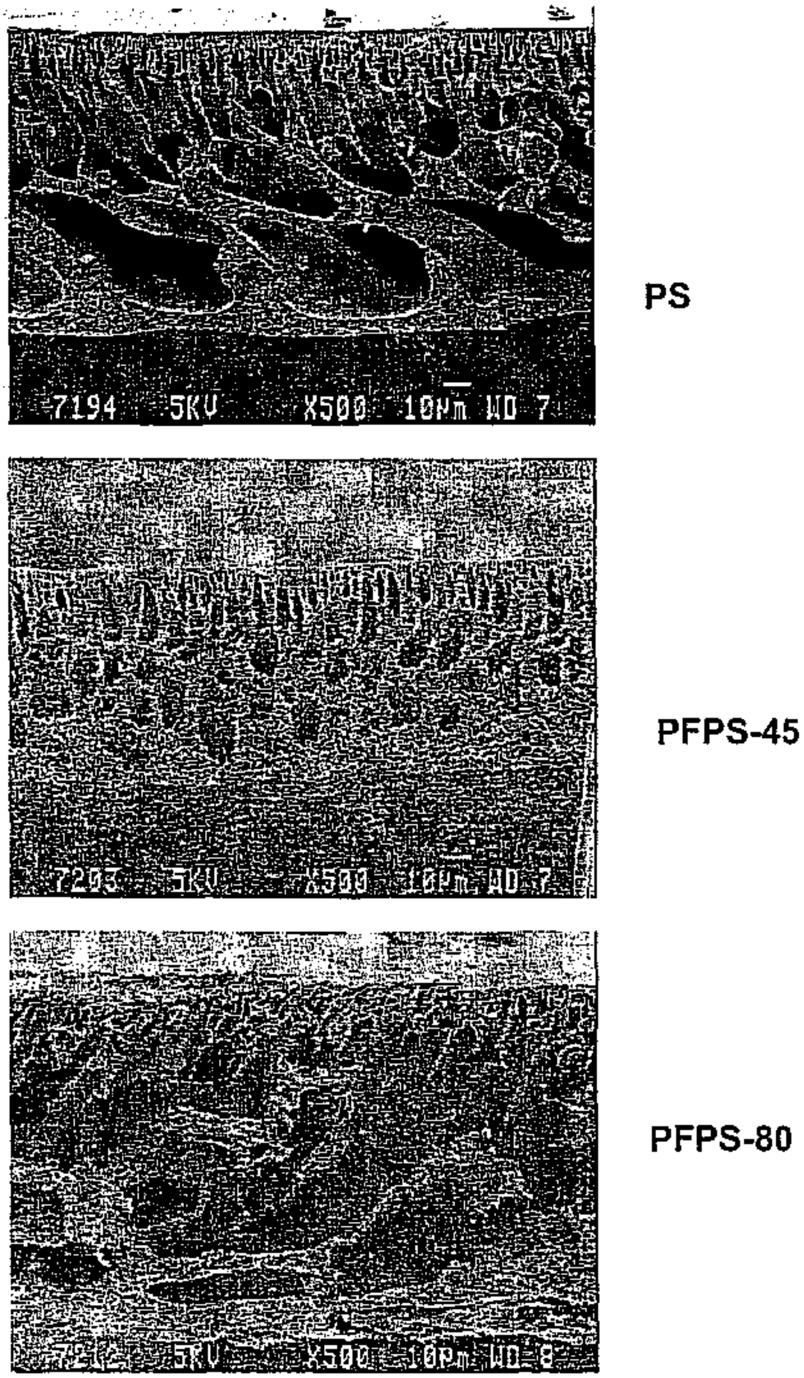

Figure 3.5 SEM micrographs of the cross-sections of the polysulfone membranes, PS, PFPS-45 and PFPS-80

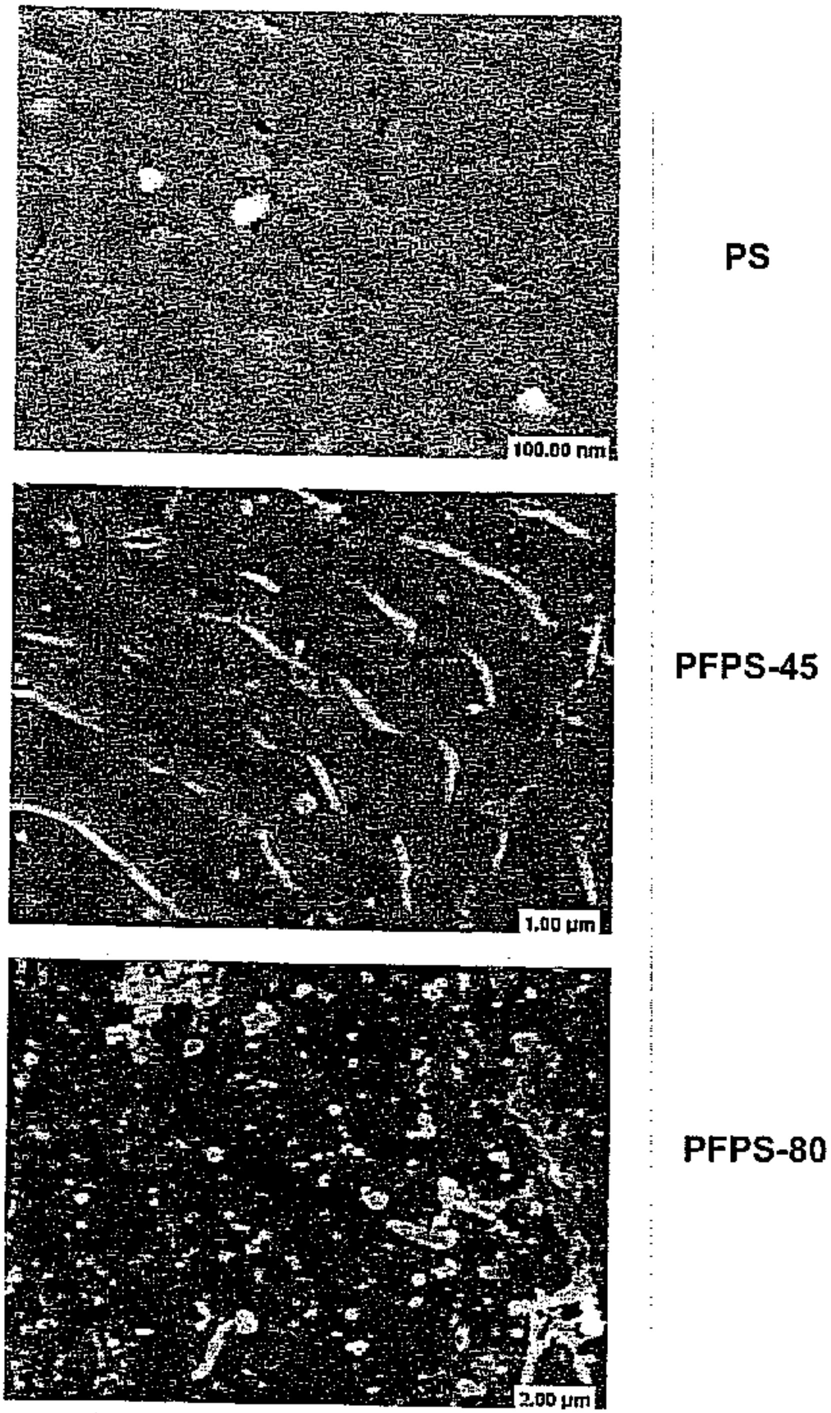

Figure 3.6 SEM micrographs of the top view of the polysulfone membranes, PS, PFPS-45 and PFPS-80

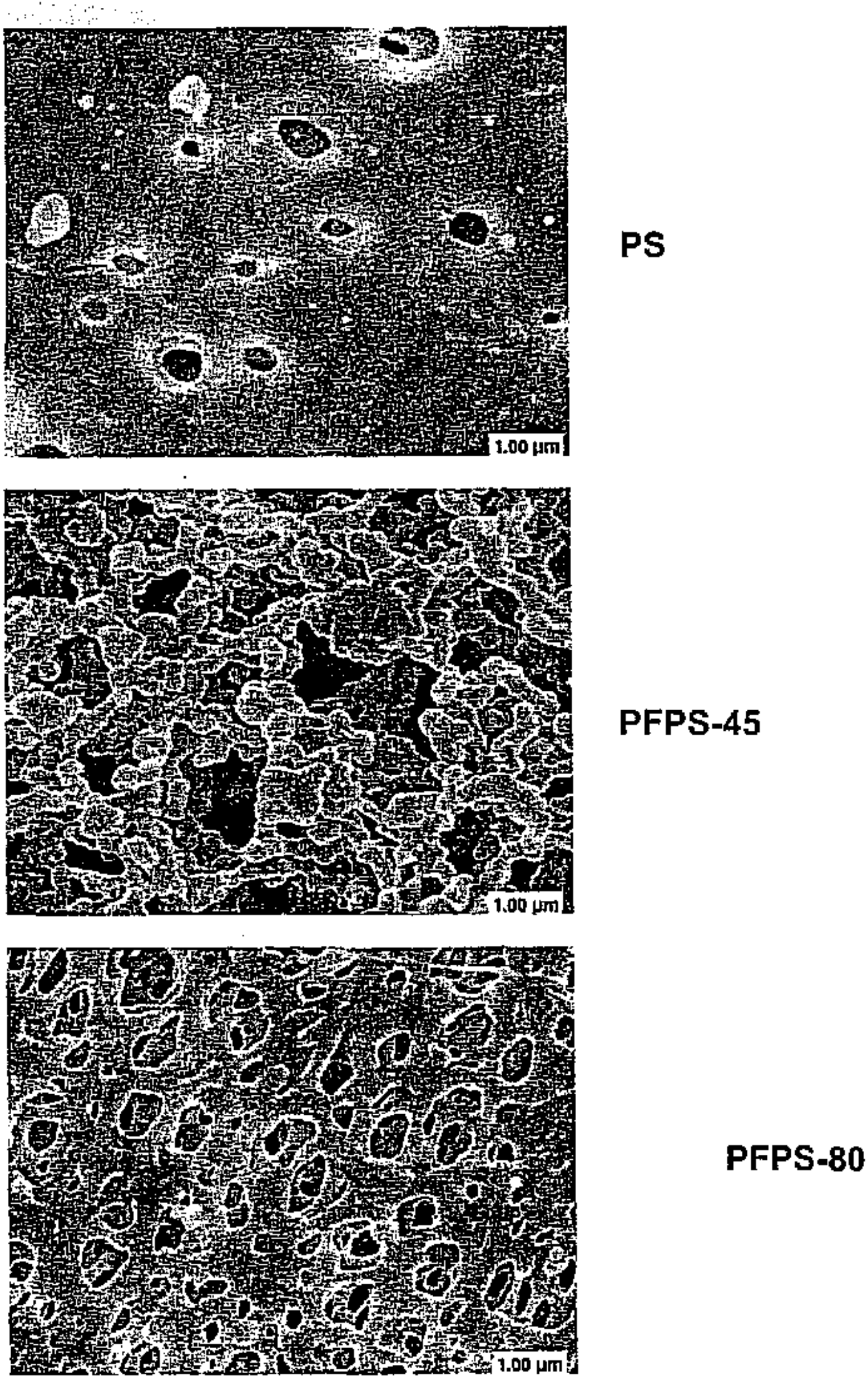

Figure 3.7 SEM micrographs of the bottom view of the polysulfone membranes, PS, PFPS-45 and PFPS-80

Figure 3.7 shows the SEM analysis of the bottom view of the different 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 PFPS-80, 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 disc fragments of different sizes and shapes as well as variable pore sizes between the polymer fragments.

3.8 Contact Angle Tests

Contact angle data were obtained at 20 °C with an ERMA G-1 contact angle meter using pure water as probe liquid. The flat sheet asymmetric membranes as well as dense films were prepared and characterized through contact angle measurements to evaluate the hydrophilic character of each membrane. The contact angle data for PS and PFPS-80 in Table 3.1:

Table 3.1: Contact angle measurement for different membranes

Sample:	**Asymetric membrane**	**Dense Film**
PS:	78 °	74 °
PFPS-80	87 °	84 °

Results show that the dipyridyl functionalized polysulfone samples 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 hydrophilic groups on the surface as well as the surface roughness and porosity of the asymmetric membranes and dense films.

3.9 Thermal Analysis

The thermal stabilities of the unfunctionalized polysulfone and the dipyridyl functionalized polysulfones were determined by TGA (**Figure 3.8**). The TGA thermograms 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 pendant groups along the polymer backbone. With the onset of weight loss at 250 °C, PFPS-45 exhibits a two-phase degradation pattern with a distinct weight loss of 8% observed at 350 °C, with a total weight loss of 56% at 534 °C. The initial weight loss in PFPS-45 is believed to be due to the brittleness of the membrane and the loss of pyridyl functional groups as well as the desorption of water which is associated with the dipyridyl groups. In contrast, the PFPS-80 is thermally more stable with the degradation pattern showing the onset of weight loss at 307 °C, with 25% weight loss at 404 °C, followed by the major weight loss of 38% at 537

°C. The presence of more polar dipyridyl pendant groups on the PFPS-80 polysulfone sample accounts for its higher thermal stability as compare to the PFPS-45 sample.

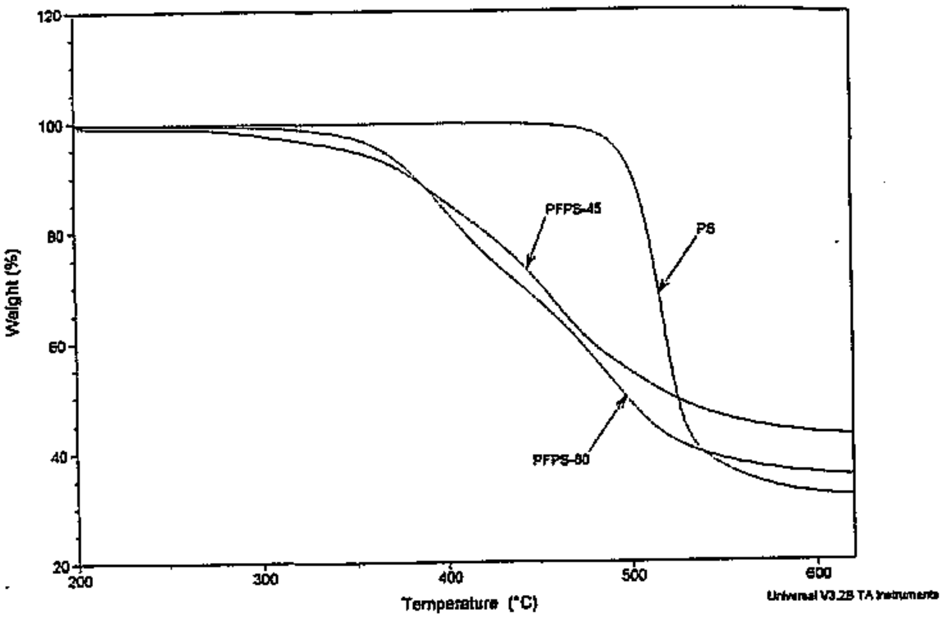

Figure 3.8 TGA thermograms of different polysulfone samples, PS, PFPS-45 and PFPS -80

The glass transition temperature of each sample was obtained from differential scanning calorimetry and outlined in Table 3.2:

Table 3.2: Glass transition temperature for the different polysulfone samples

Sample	T_g
PS	**189 °C**
PFPS-45	**185 °C**
PFPS-80	**161 °C**

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.

3.10 Electrochemistry

The development of functionalized polysulfones as well as the polymer-metal complexes for use as polymer substrates in the electroanalytical and photocatalytic removal of organic impurities is considered new technology for the purification and treatment of water for potable use, the recovery of water from waste in the industrial environment and the abatement of environmental pollution. In particular, polymer-metal complexes of ruthenium (II) with pyridine derivatives have attracted much attention in the solar conversion industry and as photocatalysts for water cleavage as well as the electrocatalysts for the removal of organic impurities, such as phenol, from water.

The new dipyridyl functionalized polysulfones and associated pyridine-metal derivatives were evaluated for their electrochemical behaviour to determine their potential use as polymeric substrates in electrochemical reactors necessary for the direct electrochemical oxidation of organics in waste water streams.

In cyclovoltammetric analysis, no oxidation or reduction peaks were observed for the unfunctionalized polysulfone sample coated on a glassy carbon electrode, indicating that the polysulfone is not electroactive in the potential range scanned.

The cyclovoltammogram of the dipyridyl functionalized polysulfone complexed with $RuCl_4$ shows a peak for the oxidation of Ru^{2+} to Ru^{3+} for both the forward and reverse scans, which clearly indicates that the polymer-ruthenium complex is electrochemically active. The redox behaviour of ruthenium at the unmodified glassy electrode shows electrochemical response at the same potentials as peaks observed at the modified electrode, confirming that the peaks in the cyclovoltammogram are indeed due to the redox behaviour of ruthenium. However, a leaching effect associated with ruthenium was observed, as evidenced by the decrease in peak height with time.

The electrochemical oxidation of phenol using the dipyridyl functionalized polysulfone-ruthenium complexes as well as complexes of other platinum group metals were determined to evaluate the catalytic capacity of the polymeric films to remove organic pollutants from waste water. Electrochemical oxidation of phenol by the polysulfone-ruthenium complex does occur, but to a lesser extent when compared to the oxidation by platinum.

3.11 Conclusions

Polysulfone and dipyridyl functionalized polysulfones were prepared to investigate the effect of increasing the degree of substitution of the dipyridyl groups on membrane morphology, water permeability, hydrophilicity and other properties of the polymer. The modified polymers were prepared by a general two-step process, which involves the functionalization reaction of lithiated polysulfone with different concentrations of 2,2'-vinylidenedipyridine to produce the corresponding dipyridyl functionalized polysulfone, with degrees of functionalization of 45% and 80%. Detailed NMR data and IR analysis support the chemical structures of the dipyridyl functionalized polymers. The dipyridyl modified polysulfones were thermally less stable than the parent polysulfone. The glass transition temperatures of modified polymers with the pendant dipyridyl groups decreased with higher degree of substitution because of increased polymer chain mobility.

The introduction of pendant dipyridyl groups onto the polymer backbone imparts hydrophilic characteristics to the resulting polymeric membrane and makes it suitable for the preparation of membranes with anti-fouling properties. The membrane obtained from polysulfone with the higher degree of substitution, PFPS-80, exhibits higher permeate flux with better structural integrity of the membrane as determined by SEM and atomic force microscopy analysis. Cyclovoltammetric analysis show that the dipyridyl functionalized polysulfone-ruthenium complex is electroactive and shows low levels of electrochemical oxidation of phenol.

CHAPTER 4

FUNCTIONALIZED POLYSULFONE BY CONTROLLED LIVING FREE RADICAL POLYMERIZATION FOR MEMBRANE PRODUCTION: THE SYNTHESIS OF AROMATIC CARBOXYL FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION

4.1 Abstract

The α-bromo-p-toluic acid initiated polymerization of styrene in the presence of copper (I) bromide and 2,2'-bipyridyl affords quantitative yields of the corresponding aromatic carboxyl functionalized polystyrene.[78] The polymerization proceeded via a controlled free radical polymerization process to afford quantitative yields of the corresponding aromatic carboxyl functionalized polymers with predictable molecular weights (M_n = 1 600 -25 900), narrow molecular weight distribution (M_w/M_n= 1.1-1.40) and an initiator efficiency above 0.87. The polymerization process was monitored by gas chromatographic analysis. The functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, spectroscopy, potentiometry and elemental analysis.

4.2 Introduction

The chemical modification of polysulfone by the reactions of lithiated polysulfone with diarylethylene derivatives was conducted in our laboratories.[71,73] However, low yields of the corresponding functionalized polysulfone were obtained. In order to obtain greater functionalization efficiency in the preparation of functionalized polysulfone, Atom Transfer Radical Polymerization (ATRP) can be utilized for the chemical modification of polysulfone.[35-37] For example, by ATRP, the initiation of styrene and methyl methacrylate polymerization with functionalized initiators in the presence of copper (I) bromide and 2,2'-bipyridyl as catalytic system proceeded via a living fashion affords quantitative yields of the corresponding functionalized polymers with predictable molecular weights, narrow molecular weight distributions and well-defined chain functionality.[35-37]

The project objective was extended to include the synthesis of diaryl functionalized polysulfone as well as polysulfone-g-polystyrene by the following synthetic route:

(i) the synthesis of methyl substituted polysulfone by the reaction of lithiated polysulfone with methyl iodide;

(ii) bromination of methylated polysulfone with N-bromosuccinimide to form the brominated polysulfone macroinitiator;

(iii) the synthesis of diaryl functionalized polysulfone and polysulfone-g-polystyrene by atom transfer radical polymerization methods using the brominated polysulfone as macroinitiator.

The success of the synthetic technique centers on the reactivity of the benzyl radical in ATRP reactions. Thus, the synthesis of aromatic carboxyl functionalized polymers by the atom transfer radical initiated polymerization of styrene with α-bromo-p-toluic acid, as functionalized initiator, in the presence of copper (I) bromide and 2,2'-bipyridyl, as catalyst system, was explored to determine reactivity of the benzyl radical as initiator in the ATRP reactions of styrene.

4.3 Atom Transfer Radical Polymerization of Styrene Initiated by α-Bromo-p-toluic acid in Diphenyl ether: Synthesis of Carboxyl Functionalized Polystyrene

Figure 4.1 illustrates the general synthetic pathway for the α-bromo-p-toluic acid (**1**) initiated polymerization of styrene in diphenyl ether solution in the presence of copper (I) bromide catalyst and 2,2'-bipyridyl as ligand. The polymerization proceeded via a controlled free radical polymerization process to afford quantitative yields of the corresponding aromatic carboxyl functionalized polystyrenes with predictable molecular weights (M_n = 1 600 -25 900) and narrow molecular weight distribution (M_w/M_n= 1.1-1.40). To illustrate the synthetic utility of aromatic carboxyl functionalized initiators in ATRP, α-bromo-p-toluic acid (1) was employed as functionalized initiator in the polymerization of styrene in solution in the presence of copper (I) bromide and 2,2'-bipyridyl in the molar ratio of $[CuBr]_0 : [\mathbf{1}]_0 : [2,2'\text{-bipyridyl}]_0 = 1:1:3$. No dark blue coloration of the reaction mixture was observed upon the addition of the initiator (**1**), suggesting that no coordination of the carboxylic acid groups and the transition metal catalyst has occurred during the polymerization process. However, as evidenced by FTIR analysis, the functionalized polymer was initially isolated as the copper carboxylate salt and, upon acidification with 1% aqueous hydrochloric acid, produced the aromatic carboxyl functionalized polystyrene derivative (**2**).

TLC analysis of the aromatic carboxyl functionalized polystyrene (**2**), [R_f = 0, toluene] shows only one spot on the chromatogram, which corresponds to the formation of aromatic carboxyl functionalized polymer in quantitative yields. The size exclusion chromatographic analysis of the aromatic carboxyl functionalized polystyrene (**2**) shows a monomodal molecular weight distribution (**Figure 4.2**) with M_w/M_n = 1.22 and M_n = 3 040 g/mol. The results obtained from SEC analysis are consistent with the theoretical $M_{n,th}$ value of 2 917 g/mol for 85% monomer conversion as calculated according to equation 1, where $[M]_0$ and

$[R\text{-}X]_0$ represent the initial concentration of the monomer and the initial concentration of initiator, respectively, with $(MW)_0$ and MW_{init} representing the molecular weight of the monomer and initiator, respectively.

$$M_{n,th} = ([M]_0/[R\text{-}X]_0) \times (MW)_0 \times \%Conversion/100 + MW_{init} \quad (1)$$

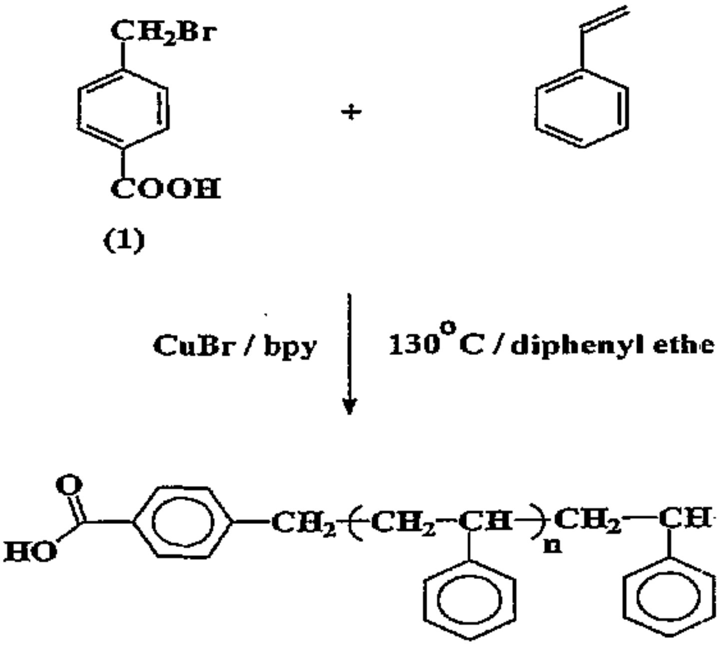

Figure 4.1 Synthetic pathway for the α-bromo-p-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenyl ether.

The FTIR spectrum of the carboxylated polystyrene, **(2)** obtained after acidification of the copper carboxylate derivative, exhibits a carbonyl group absorption band at 1689 cm^{-1}, consistent with the incorporation of the initiator fragment into the functionalized polymer.

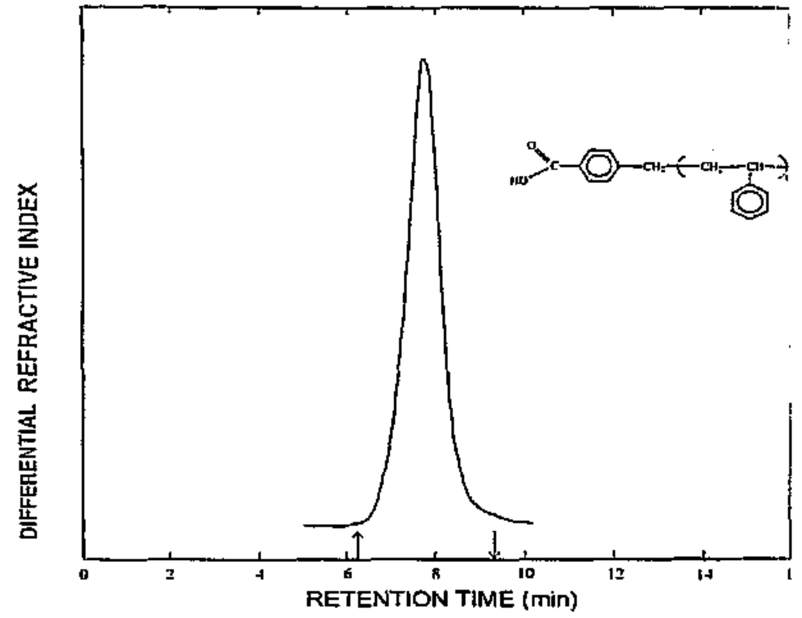

Figure 4.2 Size exclusion chromatogram of aromatic carboxyl functionalized polystyrene

The ^{13}C NMR spectrum of the carboxylated polystyrene **(Figure 4.3)** shows a resonance at 171.6 ppm, which indicates the incorporation of the aromatic carboxyl functional group into the polymer chain. Potentiometric titration measurements[79] of the carboxyl functionalized polymer with standardized sodium hydroxide indicate the quantitative incorporation of the carboxylic acid group into the polymer chain end and the value of M_n = 3 317 g/mol obtained is in good agreement with the size exclusion measurements (M_n = 3 040 g/mol) and elemental analysis data (M_n = 3 022 g/mol).

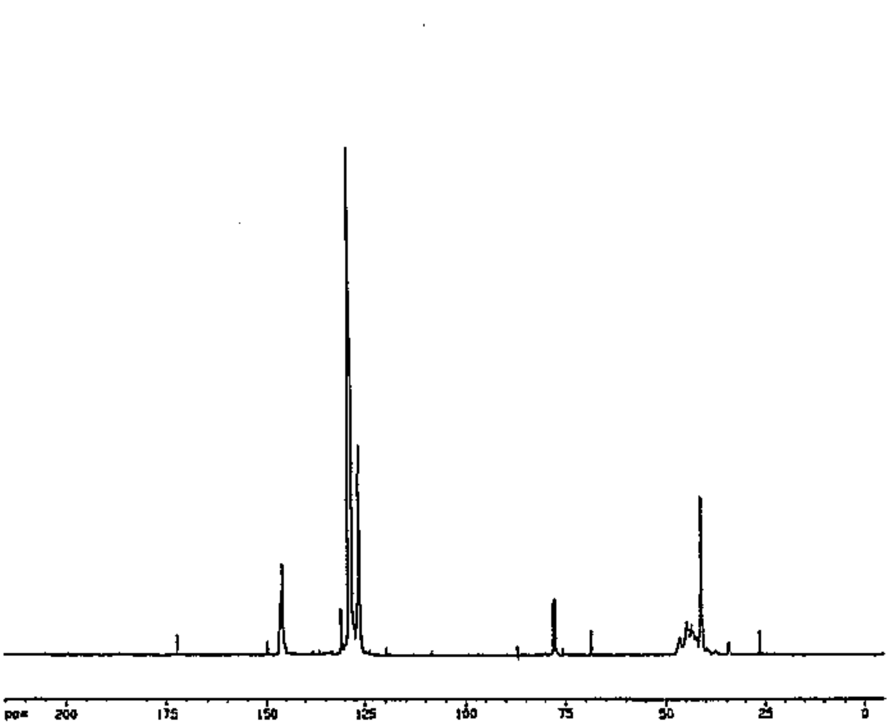

Figure 4.3 ^{13}C NMR spectrum of aromatic carboxyl functionalized polystyrene

α-Bromo-p-toluic acid is an effective initiator for the ATRP of styrene. The acid functionality does not totally deactivate the catalyst. However, the acid functionality does cause a slight increase in the observed number average molecular weight, which indicates a decrease in initiator efficiency ($I_{eff} = M_{n,th}/M_{n,SEC} = 0.95$). The decrease in initiator efficiency can be ascribed to the partial complexation of (**1**) with copper, thereby reducing the concentration of active initiator present.

4.4 Polymerization Kinetics: Atom Transfer Radical Polymerization of Styrene Initiated by α-Bromo-p-toluic acid

The solution atom transfer radical polymerization of styrene was initiated with three different concentrations of α-bromo-p-toluic acid (**1**) relative to styrene in the presence CuBr/bpy catalyst in diphenyl ether at 130 °C and the reaction proceeded under heterogeneous conditions. The ratio of the concentration of monomer to initiator affects the rate of polymerization of styrene. At lower $[M]_0/[\mathbf{1}]_0$ ratios, the reaction was the fastest and 95% monomer conversion was reached in 4 hours (**Figure 4.4**). When the $[M]_0/[\mathbf{1}]_0$ ratio is increased to 100, monomer conversion with time decreases dramatically and a retardation in the reaction is observed at higher $[M]_0/[\mathbf{1}]_0$ ratios.

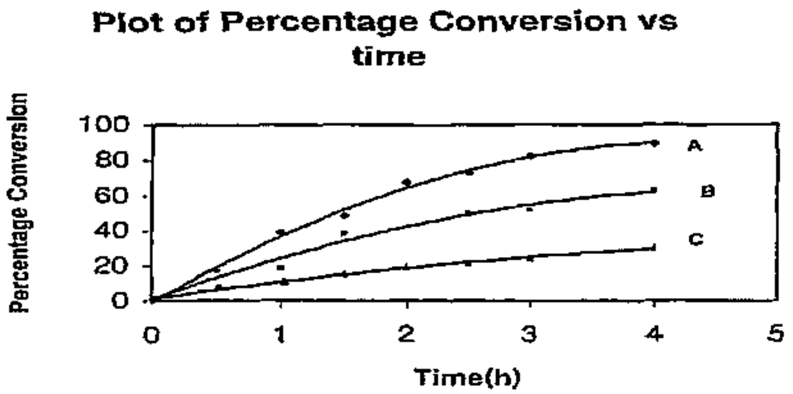

Figure 4.4 Plot of percentage monomer conversion versus time for the α-bromo-p-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 130°C:

A: $[\text{Styrene}]_0 = 4.37\ \text{mol}^{-1}$, $[1]_0 = [\text{CuBr}]_0 = 0.085\ \text{mol}^{-1}$, $[\text{bpy}]_0 = 0.175\ \text{mol}^{-1}$
B: $[\text{Styrene}]_0 = 4.37\ \text{mol}^{-1}$, $[1]_0 = [\text{CuBr}]_0 = 0.045\ \text{mol}^{-1}$, $[\text{bpy}]_0 = 0.085\ \text{mol}^{-1}$
C: $[\text{Styrene}]_0 = 4.37\ \text{mol}^{-1}$, $[1]_0 = [\text{CuBr}]_0 = 0.020\ \text{mol}^{-1}$, $[\text{bpy}]_0 = 0.045\ \text{mol}^{-1}$

The number average molecular weight increases with percentage monomer conversion, which suggests that no significant termination reactions are present once the initiation step is complete **(Figure 4.5)**. Functionalized polymers with polydispersities ranging from 1.1-1.23 were obtained, indicating a fast initiation process which involves the rapid equilibrium exchange between active and dormant species during polymerization. However, the observed number average molecular weight was consistently lower than the theoretical number average molecular weight values throughout the polymerization.

The first order kinetic plots of ln ($[M_0]/[M]$ vs time for the atom transfer radical polymerization of styrene initiated by (**1**) are shown in **Figure 4.6**. The linear kinetic plots of polymerization obtained indicate that fast initiation has occurred and that a constant number of propagating species was generated throughout the polymerization. At the lower $[M]_0/[1]_0$ ratios, the reaction rate is the fastest and the reaction rate drops significantly with increasing monomer concentration for the reaction [CuBr]:[1] = 1. However, when $[M]_0/[1]_0 = 100$ with the addition of 2 mole equivalents of CuBr relative to initiator (polymerization D), no significant effect on the rate of polymerization of styrene is observed when compared to polymerization B where equimolar amounts of CuBr and (**1**) were used. Moreover, the addition of 3 mole equivalents of CuBr relative to initiator (polymerization E) led to a dramatic retardation effect in the polymerization rate (relative to polymerization B) with the formation of somewhat higher polydispersity polymers in the range 1.16-1.23, suggesting complexation of the copper (I) bromide with the acid functionality of (1), that is, a decrease in initiator efficiency.

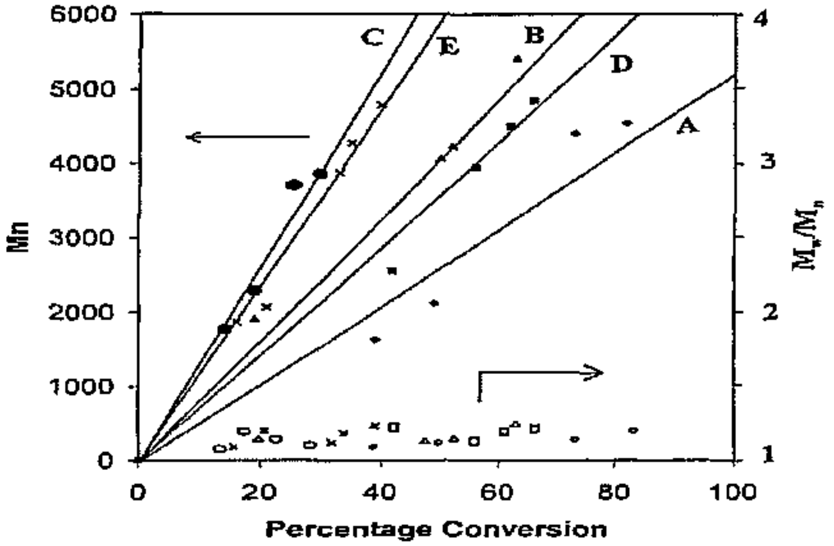

Figure 4.5 M_n versus percentage monomer conversion data (filled shapes and crosses) and M_w/M_n versus percentage conversion data (corresponding open shapes and crosses) for the α-bromo-p-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 130°C:

A: $[\text{Styrene}]_0 = 4.37$ mol^{-1}, $[1]_0 = [\text{CuBr}]_0 = 0.085$ mol^{-1},$[\text{bpy}]_0 = 0.175$ mol^{-1}
B: $[\text{Styrene}]_0 = 4.37$ mol^{-1}, $[1]_0 = [\text{CuBr}]_0 = 0.045$ mol^{-1},$[\text{bpy}]_0 = 0.085$ mol^{-1}
C: $[\text{Styrene}]_0 = 4.37$ mol^{-1}, $[1]_0 = [\text{CuBr}]_0 = 0.020$ mol^{-1} ,$[\text{bpy}]_0 = 0.045$ mol^{-1}
D: $[\text{Styrene}]_0 = 4.37$ mol^{-1}, $[1]_0 = 0.045$ mol^{-1} , $[\text{CuBr}]_0 =[\text{bpy}]_0 = 0.085$ mol^{-1};
E: $[\text{Styrene}]_0 = 4.37$ mol^{-1}, $[1]_0 = 0.045$ mol^{-1}, $[\text{CuBr}]_0 = 0.130$ mol^{-1},
$[\text{bpy}]_0 = 0.085$ mol^{-1}

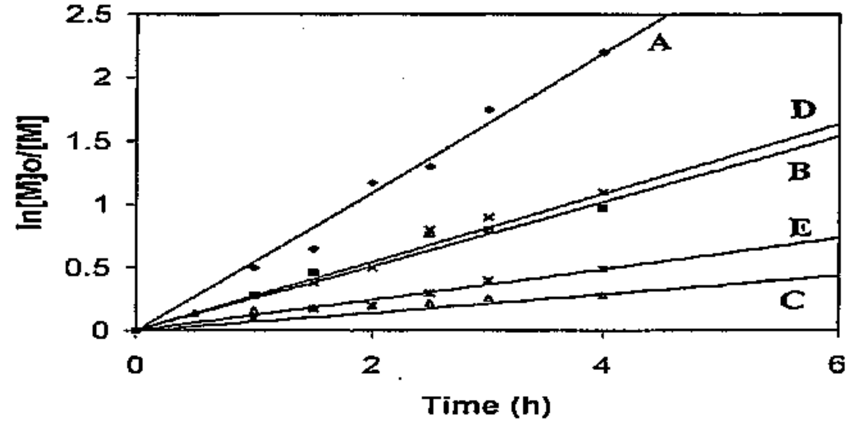

Figure 4.6 First-order kinetic plots for the α-bromo-p-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 130°C

A: $[\text{Styrene}]_o = 4.37\ \text{mol}^{-1}$, $[1]_o = [\text{CuBr}]_0 = 0.085\ \text{mol}^{-1}$,$[\text{bpy}]_o = 0.175\ \text{mol}^{-1}$
B: $[\text{Styrene}]_o = 4.37\ \text{mol}^{-1}$, $[1]_o = [\text{CuBr}]_0 = 0.045\ \text{mol}^{-1}$,$[\text{bpy}]_o = 0.085\ \text{mol}^{-1}$
C: $[\text{Styrene}]_o = 4.37\ \text{mol}^{-1}$, $[1]_o = [\text{CuBr}]_0 = 0.020\ \text{mol}^{-1}$,$[\text{bpy}]_o = 0.045\ \text{mol}^{-1}$
D: $[\text{Styrene}]_o = 4.37\ \text{mol}^{-1}$, $[1]_o = 0.045\ \text{mol}^{-1}$, $[\text{CuBr}]_0 =[\text{bpy}]_o = 0.085\ \text{mol}^{-1}$
E: $[\text{Styrene}]_o = 4.37\ \text{mol}^{-1}$, $[1]_o = 0.045\ \text{mol}^{-1}$, $[\text{CuBr}]_0 = 0.130\ \text{mol}^{-1}$,
$[\text{bpy}]_o = 0.085\ \text{mol}^{-1}$

Experimental results indicate that **(1)** is a good initiator for the solution ATRP of styrene and initiator efficiencies greater than 0.94 are obtained for most polymerization reactions. The slightly reduced initiator efficiency suggests that complexation of the acid functionality of the functionalized initiator with copper (I) bromide occurs, even at low concentrations, rendering the copper salt-ligand catalyst complex inefficient. The quantitative incorporation of initiator fragment into the polymer chain end in the ATRP of styrene and the control of major polymer properties of number average molecular weight and polydispersity are attributed to the more efficient and rapid reaction of the benzyl bromide derivative with copper bromide-dipyridyl complex to facilitate rapid initiation of polymerization. However, complexation does occur between the copper ions and the α-bromo-p-toluic acid initiator fragment of the functionalized polymer chain to form copper carboxylates, since the functionalized polymer was isolated as the copper carboxylate salt, which upon acidification produced the aromatic carboxyl polystyrene derivative.

4.5 Conclusions

The α-bromo-p-toluic acid initiated polymerization of styrene in the presence of copper (I) bromide and 2,2'-bipyridyl produces quantitative yields of the corresponding aromatic carboxyl functionalized polystyrene. The polymerization is complete within several hours and proceeds via a living, controlled fashion to afford quantitative yields of the corresponding aromatic carboxyl functionalized polymers with predictable molecular weights (M_n = 1 600-25 900), narrow molecular weight distribution (M_w/M_n= 1.1-1.40) and initiator efficiency above 0.94. The polymerization process was monitored by gas chromatographic analysis. The functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, spectroscopy, potentiometry and elemental analysis. All polymer characterization data are consistent with the quantitative incorporation of the aromatic carboxyl group into the polymer chain end.

CHAPTER 5

FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION USING 1,1-DIPHENYLETHYLENE METHODOLOGY: TERTIARY AMINE FUNCTIONALIZED POLYMERS

Details of the work are described in the publication entitled "Tertiary Amine functionalized Polymers by Atom Transfer radical Polymerization" in the J. Polym. Sci.Polym. Chem. ED., 39, 2058-2067 (2000)

5.1 Abstract

Tertiary amine functionalized polystyrene was prepared by using the adduct, formed by the reaction of 1-(bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenyl- ethylene, as initiator in the atom transfer radical polymerization of styrene in the presence of a copper (I) bromide/2,2'-bipyridyl catalyst system.[80] The polymerization proceeds via a controlled free radical polymerization process to afford quantitative yields of the corresponding tertiary amine functionalized polystyrene with predictable molecular weights (M_n = 1 600 to 4 400) and narrow molecular weight distribution (M_w/M_n= 1.09-1.31) and an initiator efficiency of 0.95. The polymerization process was monitored by gas chromatographic analysis. The tertiary amine functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, potentiometry and spectroscopy. All experimental evidence is consistent with quantitative functionalization via the 1,1-diphenylethylene derivative. Polymerization kinetic measurements show that the polymerization reaction follows first order rate kinetics with respect to monomer consumption and the number average molecular weight increasing linearly with monomer conversion.

5.2 Introduction

In principle, the anionic reactions of lithiated polysulfone with functionalized 1,1-diphenylethylenes should produce quantitative yields of the corresponding functionalized polysulfone with the 1,1-diphenylethylene unit pendant to the polysulfone backbone. However, low yields of the functionalized polysulfone were obtained in such reactions. Thus, new methods to introduce pendant functional groups onto the polysulfone backbone had to be developed and the synthetic approach was to employ Atom Transfer Radical Polymerization methods.[35-37]

By ATRP, the initiation of styrene and methyl methacrylate polymerization with functionalized initiators in the presence of catalysts systems such as copper (I) bromide and 2,2'-bipyridyl proceeded via a living fashion and affords quantitative yields of the corresponding functionalized polymers with predictable molecular weights, narrow molecular weight distributions and well-defined chain functionality.

The project objective was extended to the synthesis of functionalized polysulfone derivatives with pendant diphenylethylene functionalities on the polysulfone backbone using substituted 1,1-diphenylethylene derivatives as initiator precursors in atom transfer radical polymerization methodology.

Herein, the first experimental results for the preparation of functionalized polymers by utilizing the methodology of 1,1-diphenylethylene chemistry in atom transfer radical polymerization processes are reported. To illustrate the process, the synthesis of tertiary amine functionalized polymers was effected using an initiator adduct, formed quantitatively in situ by the stoichiometric addition reaction of 1-(bromoethyl)benzene, with 1-(4-dimethylaminophenyl)-1-phenylethylene as initiator, in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system for the polymerization of styrene.[80]

5.3 The Synthesis of Tertiary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

Figure 5.1 illustrates the general synthetic pathway for the preparation of tertiary-amine functionalized polystyrene by the atom transfer radical polymerization of styrene using the adduct (**1**) as functionalized initiator. The adduct (**1**) was quantitatively prepared in situ by reacting stoichiometric amounts of 1-(4-dimethylaminophenyl)-1-phenylethylene with 1-(bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system in diphenylether at 130 °C in the molar ratio of $[\mathrm{CuBr}]_0$: $[1\text{-(bromoethyl)benzene}]_0$: $[2,2'\text{-bipyridyl}]_0$ = 1:1:3, prior to the addition of the styrene monomer. The quantitative formation of adduct (**1**) was determined by TLC analysis by monitoring the disappearance of 1-(4-dimethylaminophenyl)-1-phenylethylene [R_f = 0.56, toluene] with concomitant appearance of the adduct (**1**) [R_f = 0.63, toluene]. Rapid initiation of styrene polymerization occurred after the subsequent addition of styrene monomer indicating that the free radical species generated from adduct (**1**) 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 tertiary amine functionalized polystyrenes with predictable molecular weights (M_n = 1 600 to 4 400 g/mol) and narrow molecular weight distributions (M_w/M_n= 1.09 - 1.31).

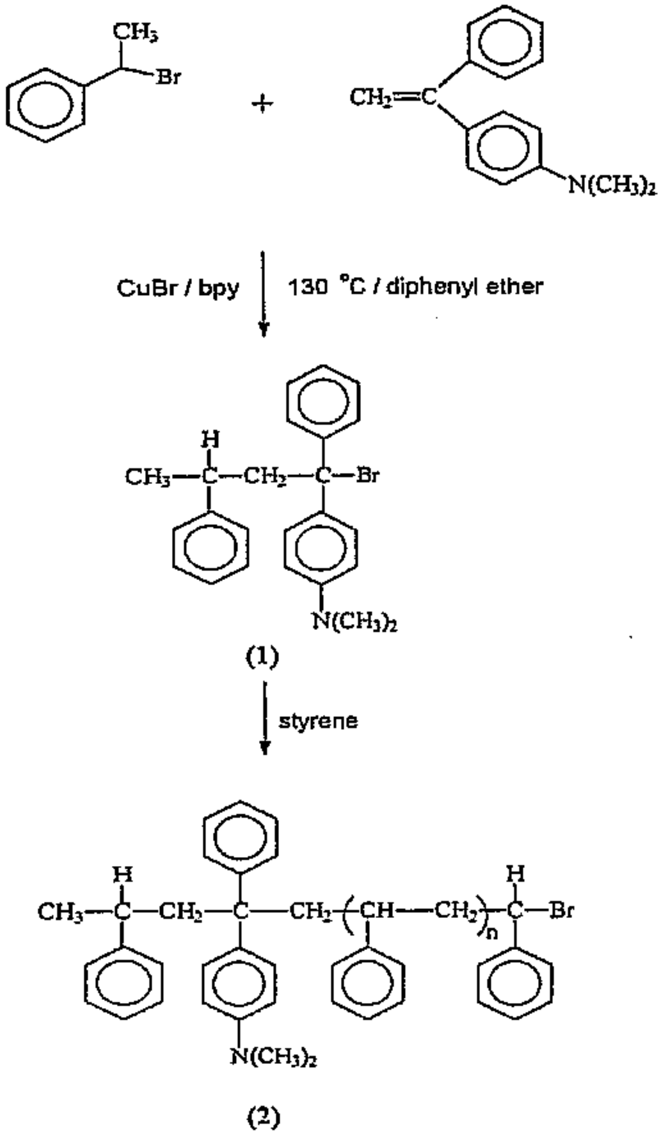

Figure 5.1 Synthetic pathway for the preparation of tertiary amine functionalized polymers

TLC analysis of the tertiary amine functionalized polystyrene (**2**), [$R_f = 0$, toluene] shows only one spot on the TLC chromatogram, consistent with formation of the tertiary amine functionalized polymer in quantitative yields. The size exclusion chromatographic analysis of the tertiary amine functionalized polystyrene (**2**) shows a monomodal molecular weight distribution (**Figure 5.2**) with M_n (GPC) = 3 368 g/mol and $M_w/M_n = 1.11$. The theoretical $M_{n,th}$ value of 3 184 g/mol for 92% conversion is calculated according to equation 5.1, where $[M]_O$, $[R\text{-}X]_O$ and $(MW)_O$ represent the concentration of the monomer consumed, the initial concentration of initiator and the molecular weight of the monomer, respectively.

$$M_n = ([M]_O/[R\text{-}X]_O) \text{ X } (MW)_O \text{ X } \%\text{Conversion}/100 + MW_{init} \qquad (5.1)$$

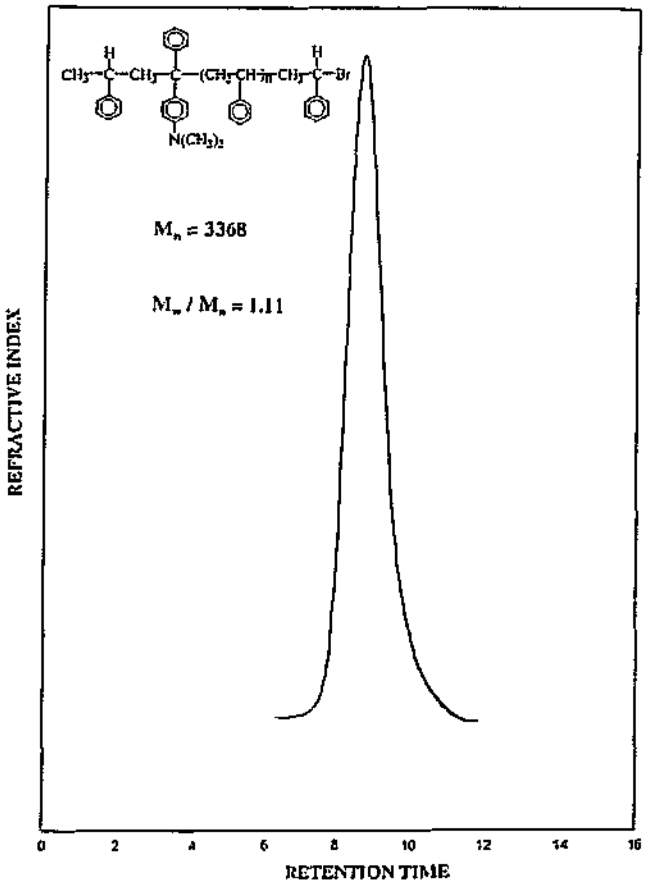

Figure 5.2 Size exclusion chromatograph of tertiary amine functionalized polymer

The FTIR spectrum of the tertiary amine functionalized polystyrene (2) exhibits an absorption band at 1364 cm^{-1}, characteristic of the N-C stretching vibration of the -N(CH$_3$)$_2$ and a sharp peak at 600 cm^{-1}, due to the C-Br bond at the terminating end of the polymer chain, results consistent with the incorporation of the initiator fragment into the functionalized polymer.

The ^{1}H NMR spectrum **(Figure 5.3)** of tertiary amine functionalized polystyrene (2) exhibits a multiplet of peaks in the region δ = 2.84-2.90 due to the resonances of the diastereoisomeric -N(C$\underline{H}_3$)$_2$ group as well as a multiplet at δ =1.0 ppm, due to the CH$_3$ group of the initiator fragment.

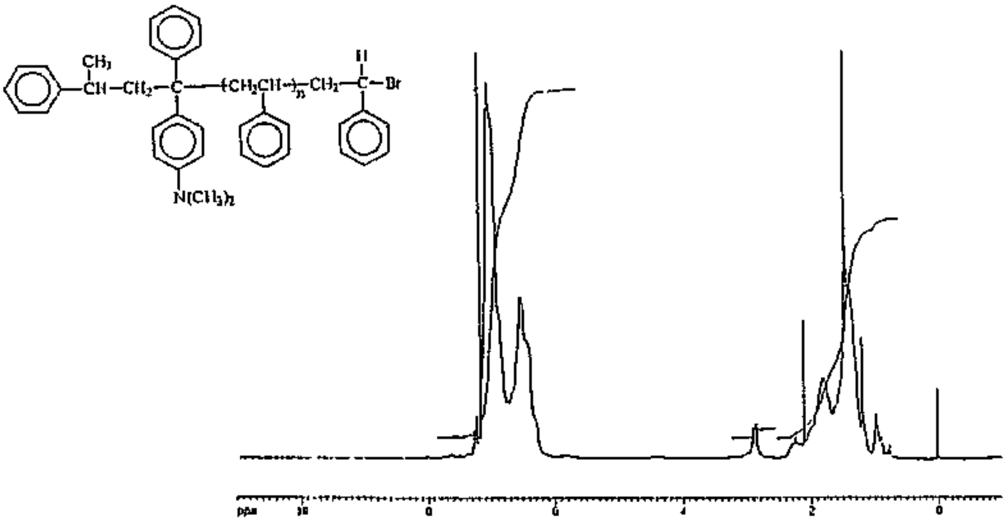

Figure 5.3 ^{1}H NMR spectrum of tertiary amine functionalized polymer

The ^{13}C NMR spectrum of the tertiary amine functionalized polystyrene shows a resonance at δ = 41 ppm, due to the -N($\underline{C}$H$_3$)$_2$ carbon atoms which indicates the incorporation of the tertiary amine functional group into the polymer chain.[52] The amine group functionality of the tertiary amine functionalized polystyrene (2) was 0.99, as determined by end group titration, consistent with a number average molecular weight of M_n = 3 125 g/mol.

5.4 Polymerization Kinetics: The Synthesis of Tertiary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

In a typical procedure, tertiary amine functionalized polymers were prepared using the adduct of 1-(4-dimethylaminophenyl)-1-phenylethylene with 1-(bromoethyl)benzene as initiator in the solution atom transfer radical polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 130 °C at different monomer to initiator concentration ratios. The reactions proceeded under heterogeneous conditions. Results indicate that at lower $[M]_0/[\mathbf{1}]_0$ ratio, the reaction was the fastest and 92% monomer conversion was reached in 4 hours (**Figure 5.4**). When the $[M]_0/[\mathbf{1}]_0$ ratio is increased to 100, monomer conversion with time decreases dramatically and a retardation in the reaction is observed at higher $[M]_0/[1]_0$ ratios.

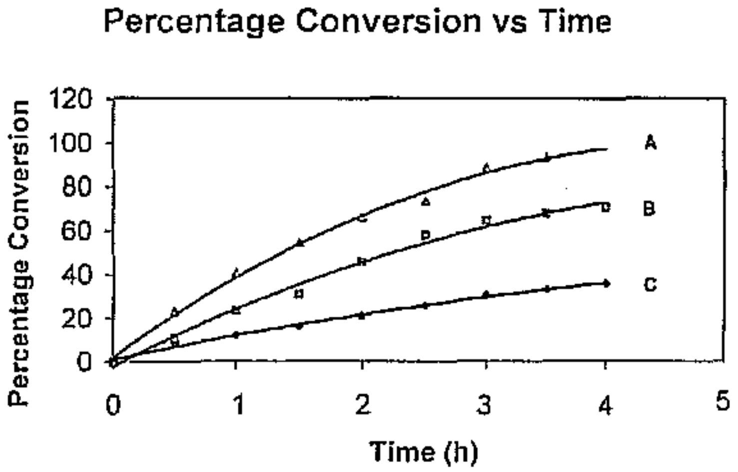

Figure 5.4 Plot of the percentage monomer conversion versus time data for the preparation of tertiary amine functionalized polymers at 130°C

A: $[\mathrm{Styrene}]_0$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_0$ = $[\mathrm{CuBr}]_0$ = 0.0872 mol/L,$[\mathrm{bpy}]_0$ = 0.262 mol/L

B: $\mathrm{Styrene}]_0$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_0$ = $[\mathrm{CuBr}]_0$ = 0.0436 mol/L,$[\mathrm{bpy}]_0$ = 0.131 mol/L

C: $\mathrm{Styrene}]_0$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_0$ = $[\mathrm{CuBr}]_0$ = 0.0218 mol/L,$[\mathrm{bpy}]_0$ = 0.131 mol/L;

In addition, the number average molecular weight increases linearly with conversion, consistent with the theoretical values, and narrow molecular weight polymers were obtained (**Figure 5.5**). Experimental results suggest that rapid exchange between the active and dormant species occurs, that is, fast initiation. However, at lower $[M]_0/[1]_0$ ratio, linearity in the Mn vs conversion plot was only observed after 5% conversion, which suggests that the equilibrium between the dormant and active chain end is obtained after an initial induction period. The linear increase of number average molecular weight with conversion suggested that no significant chain transfer or termination reactions are present once the initiation step is complete. Functionalized polymers with polydispersities ranging from 1.09-1.31 were obtained, indicating a fast initiation process which involves the rapid equilibrium exchange between active and dormant species during polymerization.

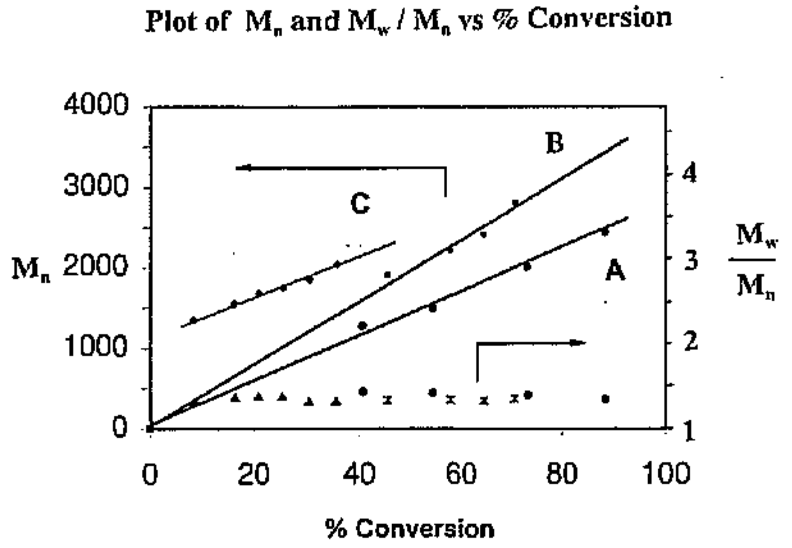

Figure 5.5 M_n vs percentage monomer conversion and M_w/M_n vs percentage monomer conversion for the preparation of tertiary amine functionalized polymers at 130°C

A: $[\text{Styrene}]_o$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_o$ = $[\text{CuBr}]_0$ = 0.0872 mol/L,$[\text{bpy}]_o$ = 0.262 mol/L

B: $\text{Styrene}]_o$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_o$ = $[\text{CuBr}]_0$ = 0.0436 mol/L,$[\text{bpy}]_o$ = 0.131 mol/L

C: $\text{Styrene}]_o$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_o$ = $[\text{CuBr}]_0$ = 0.0218 mol/L,$[\text{bpy}]_o$ = 0.131 mol/L;

Figure 5.6 shows a semilogarithmic plot for the heterogenous ATRP synthesis of tertiary amine functionalized polystyrene using adduct (**1**) as the functionalized initiator system. The kinetic plots of $\ln[M]_O/[M]$ as a function of polymerization time at different $[M]_O/[\mathbf{1}]_O$ ratios shows that the ratio of the concentration of monomer to initiator affects the rate of polymerization. The plots of $\ln [M]_O/[M]$ vs time are linear indicating that fast initiation has occurred and a constant number of propagating species was generated throughout the polymerization. The linearity of the semilogarithmic plots of $\ln [M]_O/[M]$ vs time indicates that the polymerizations were first order with respect to monomer consumption. At the lower $[M]_0/[1]_0$ ratio, the reaction rate is the fastest and the reaction rate drops significantly with increasing monomer concentration.

Experimental results indicate that the stoichiometric addition reaction of 1-(bromoethyl)-benzene to 1-(4-dimethylaminophenyl)-1-phenylethylene to generate the adduct (1), in situ, followed by the addition of styrene is a good method for the solution ATRP of styrene to produce tertiary amine functionalized polystyrene with good control of molecular weight and polydispersities and initiator efficiencies as high as 0.95. The quantitative incorporation of functionalized 1,1-diphenylethylene fragment into the polymer chain end in the ATRP of styrene and the control of major polymer properties such as number average molecular weight, polydispersity and degree of functionalization is attributed to (a) the quantitative formation of (1) in situ, and (b) the subsequent efficient and rapid reaction of the diphenylethylene radical chain end with the styrene monomer.

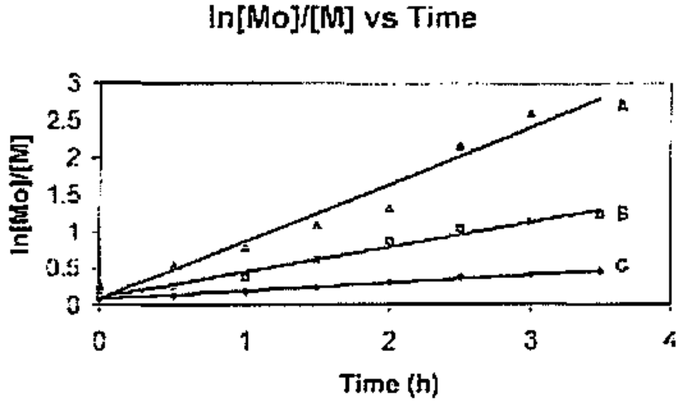

Figure 5.6 First-order kinetic plots for the preparation of tertiary amine functionalized polymers at 130°C

A: $[\text{Styrene}]_0$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0872 mol/L,$[\text{bpy}]_0$ = 0.262 mol/L

B: $\text{Styrene}]_0$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0436 mol/L,$[\text{bpy}]_0$ = 0.131 mol/L

C: $\text{Styrene}]_0$ = 4.364 mol/L, $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0218 mol/L,$[\text{bpy}]_0$ = 0.131 mol/L;

5.5 Conclusions

Tertiary amine functionalized polystyrene was prepared in quantitative yields using the adduct (1), prepared in situ by the reaction of 1-(bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene in the presence of copper (I) bromide and 2,2'-bipyridyl, for the ATRP of styrene. The quantitative formation of the adduct (1) is complete within one hour, as evidenced by TLC analysis, and then rapidly initiates styrene polymerization via a controlled atom transfer radical polymerization process to afford quantitative yields of the corresponding tertiary amine functionalized polymers with predictable molecular weights (M_n = 1 600 - 4 400 g/mol) and narrow molecular weight distribution (M_w/M_n= 1.09 -1.31). The polymerization process was monitored by gas chromatographic analysis. The functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, potentiometry and spectroscopy. All polymer characterization data are consistent with the quantitative incorporation of the tertiary amine group into the polymer chain end.

CHAPTER 6

FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION USING 1,1-DIPHENYLETHYLENE METHODOLOGY: PRIMARY AMINE FUNCTIONALIZED POLYMERS

6.1 Abstract

Primary amine functionalized polystyrenes were prepared in quantitative yields by atom transfer radical polymerization (ATRP) using the adduct of 1-(bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene as initiator for styrene polymerization in the presence of a copper (I) bromide/N,N,N=,N=,N=>-pentamethyl-diethylenetriamine (PMDETA) catalyst system.[81] The polymerizations proceeded via a controlled free radical polymerization process to afford quantitative yields of the corresponding primary amine functionalized polystyrenes with predictable molecular weights ($M_n = 2 \times 10^3$ to 10×10^3 g/mol), relatively narrow molecular weight distributions (M_w/M_n= 1.03 -1.49), well defined chain end functionalities and initiator efficiencies as high as 0.92. The polymerization process was monitored by gas chromatographic analysis. The primary amine functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, potentiometry and spectroscopy. Experimental results are consistent with quantitative functionalization via the 1,1-diphenylethylene derivative. Polymerization kinetic measurements show that the polymerization reaction follows first order rate kinetics with respect to monomer consumption and the number average molecular weight increasing linearly with monomer conversion.

6.2 Introduction

A general quantitative ATRP chain end functionalization method for the preparation of tertiary amine functionalized polymers, which is based on the addition reactions of simple organohalogen compounds to tertiary amine functionalized 1,1-diphenylethylene and catalyzed by a transition metal-ligand complex, was reported in our laboratories.[80] By utilizing the methodology of 1,1-diphenylethylene chemistry in atom transfer radical polymerization processes, the process is extended to the preparation of primary amine functionalized polystyrene. By using an adduct, formed quantitatively in situ by the stoichiometric addition reaction of 1-(bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene, as initiator, for styrene polymerization in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system, primary amine functionalized polystyrene is produced, which illustrates a general, controlled ATRP functionalization reaction, independent of the specific functional group. Such reactions are highly efficient for the synthesis of functionalized polymers because (a) these addition reactions are simple and quantitative, and (b) due to steric factors, only monoaddition reactions occur, that is, no oligomerization of the 1,1-diphenylethylene unit occurs.

6.3 The Synthesis of Primary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

Figure 6.1 illustrates the general synthetic pathway for the preparation of primary-amine functionalized polystyrene by the atom transfer radical polymerization of styrene using the adduct (**1**) as functionalized initiator. Prior to the addition of styrene, the adduct (**1**) was quantitatively prepared in situ by reacting stoichiometric amounts of 1-(4-aminophenyl)-1-phenylethylene with 1-(bromoethyl)benzene in the presence of copper (I) bromide and N,N,N=,N=,N=>-pentamethyldiethylenetriamine as catalyst system in diphenylether at 130 ^{o}C in the molar ratio of $[CuBr]_o$: [1-(bromoethyl)benzene]$_o$: $[PMDETA]_o$ = 1:1:3. The quantitative formation of adduct (**1**) was determined by TLC analysis by monitoring the disappearance of 1-(4-aminophenyl)-1-phenylethylene [R_f = 0.44, toluene] with concomitant appearance of the adduct (**1**) [R_f = 0.92, toluene]. Rapid initiation of styrene polymerization occurred after the subsequent addition of styrene monomer indicating that the free radical generated from adduct (**1**) 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 primary amine functionalized polystyrene.

TLC analysis of the primary amine functionalized polystyrene (**2**), [R_f = 0.89, toluene] shows only one spot on the TLC chromatogram, consistent with formation of primary amine functionalized polymer in quantitative yields. A typical size exclusion chromatogram of the primary amine functionalized polystyrene (**2**) shows a monomodal molecular weight distribution (**Figure 6.2**) with M_n (GPC) = 3.3×10^3 g/mol and M_w/M_n = 1.08 when compared to the theoretical $M_{n,th}$ value of 3.1×10^3 g/mol which corresponds to 92% conversion of reaction. The reaction was carried out with an equimolar ratio of monomer to initiator, targeting a final degree of polymerization of 25, giving a theoretical molecular weight of 3368 g/mol at 100% conversion.

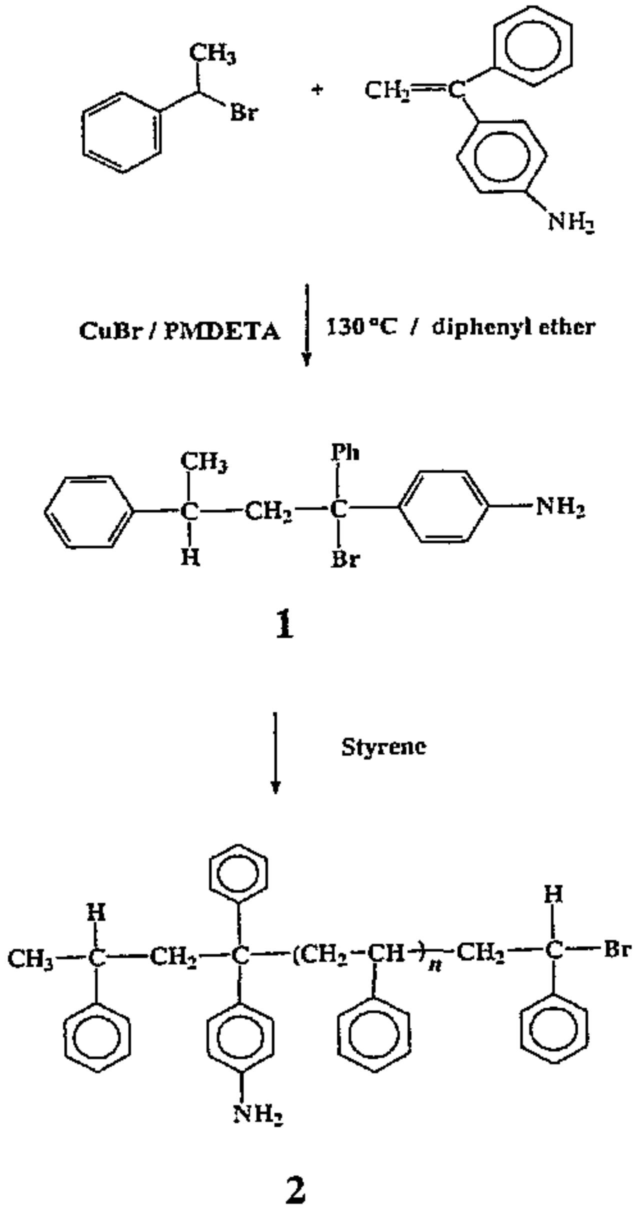

Figure 6.1 Synthetic pathway for the preparation of primary amine functionalized polystyrene

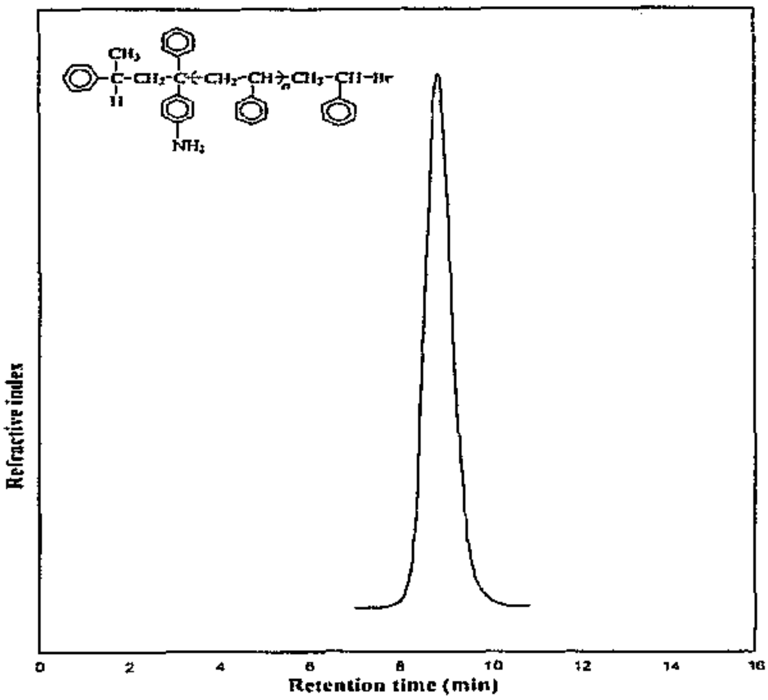

Figure 6.2 Size-exclusion chromatogram of primary amine functionalized polystyrene

The FTIR spectrum of the primary amine functionalized polystyrene (2) exhibits an absorption band at 3469 cm^{-1}, characteristic of the N-H stretching vibration of the -NH_2 group and a sharp peak at 600 cm^{-1}, due to the C-Br bond at the terminating end of the polymer chain. The results obtained from FTIR analysis are consistent with the incorporation of the initiator fragment into the functionalized polymer.[52] The ^{1}H NMR spectrum (**Figure 6.3**) of primary amine functionalized polystyrene (2) exhibits a broad peak in the region δ = 3.7 ppm due to the resonances of the amine protons[35-37] as well as a broad resonance at δ = 4.3 ppm due to the terminal -CHPhBr proton.[7] The amine group functionality of the primary amine functionalized polystyrene (2) was 0.99, as determined by end group titration,[79] consistent with a molecular weight of M_n = 3.3 x 10^3 g/mol.

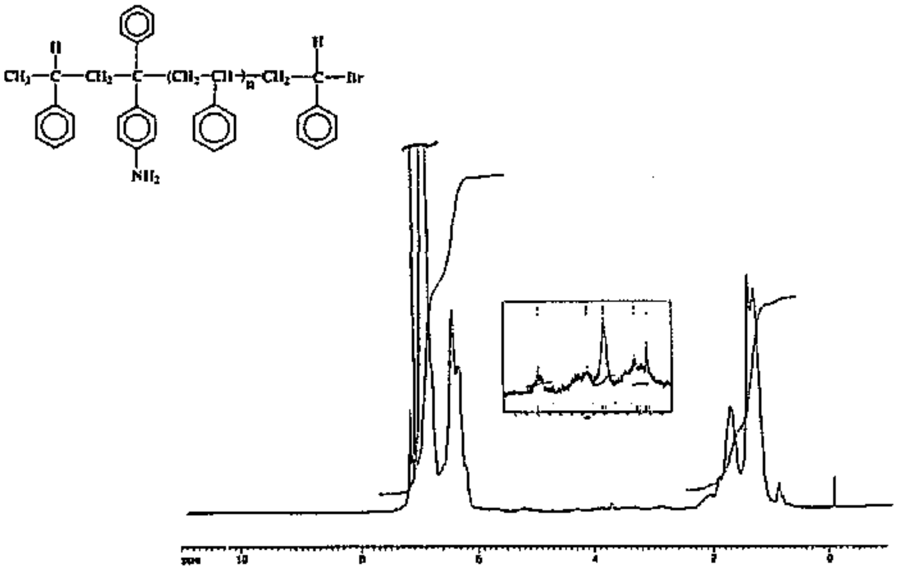

Figure 6.3 ^{1}H NMR spectrum of primary amine functionalized polystyrene

6.4 Polymerization Kinetics: The Synthesis of Primary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

In a typical procedure, primary amine functionalized polymers were prepared using the adduct of 1-(4-aminophenyl)-1-phenylethylene with 1-(bromoethyl)-benzene as initiator in the solution atom transfer radical polymerization of styrene in the presence of CuBr/N,N,N=,N=,N=>-pentamethyldiethylenetriamine catalyst in diphenylether at 130 °C at different monomer to initiator concentration ratios. The reactions proceeded under heterogeneous conditions and with high initiator efficiencies in the atom transfer radical polymerization process. Results indicate that at lower $[M]_0/[1]_0$ ratio, the reaction was the fastest and 98% monomer conversion was reached in 4 hours (**Figure 6.4**). When the $[M]_0/[1]_0$ ratio is increased to 100, monomer conversion with time decreases dramatically and a retardation in the reaction is observed at higher $[M]_0/[1]_0$ ratios. In addition, the number average molecular weight increases linearly with conversion, consistent with the theoretical values and narrow molecular weight polymers were obtained (**Figure 6.5**). Experimental results suggest that rapid exchange between the active and dormant species occurs, that is, fast initiation. The linear increase of number average molecular weight with conversion suggested that no significant chain transfer or termination reactions are present once the initiation step is complete. Functionalized polymers with predictable molecular weights ($M_n = 2 \times 10^3$ to 10×10^3 g/mol) and polydispersities ranging from 1.03 -1.49 were obtained, indicating a fast initiation process which involves the rapid equilibrium exchange between active and dormant species during polymerization.

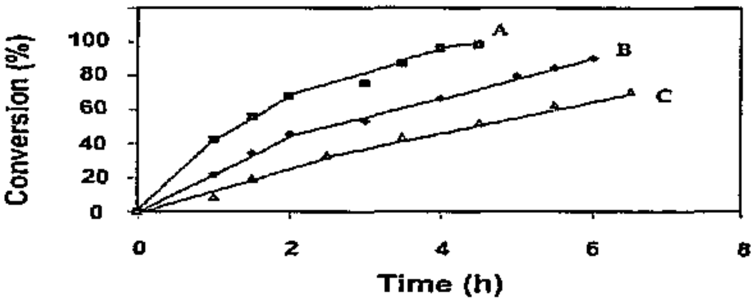

Figure 6.4 Plot of percentage monomer conversion versus time for the preparation of primary amine functionalized polystyrene in diphenylether at 130°C:

A: $[\text{Styrene}]_0$ = 4.7129 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0943 mol/L; $[\text{PMDETA}]_0$ = 0.2829 mol/L

B: $[\text{Styrene}]_0$ = 4.7129 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0472 mol/L; $[\text{PMDETA}]_0$ = 0.1415 mol/L

C: $[\text{Styrene}]_0$ = 4.7129 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0236 mol/L; $[\text{PMDETA}]_0$ = 0.0707 mol/L

Figure 6.6 shows semilogarithmic kinetic plots of $\ln[M]_0/[M]$ as a function of polymerization time at different $[M]_0/[1]_0$ ratios for the heterogenous ATRP synthesis of primary amine functionalized polystyrene using adduct (1) as the functionalized initiator system. 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 $\ln [M]_0/[M]$ vs 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 $\ln [M]_0/[M]$ vs time indicates that the polymerizations were first order with respect to monomer consumption. At the lower $[M]_0/[1]_0$ ratio, the reaction rate is the fastest and the reaction rate drops significantly with increasing monomer concentration.

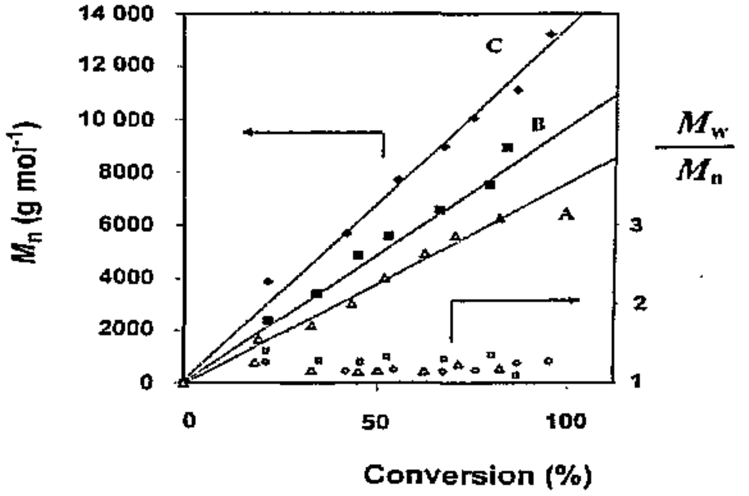

Figure 6.5 M_n vs percentage monomer conversion and M_w/M_n vs monomer conversion data for the preparation of primary amine functionalized polymers at 130°C

A: [Styrene]$_0$ = 4.7129 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.0943 mol/L; [PMDETA]$_0$ = 0.2829 mol/L

B: [Styrene]$_0$ = 4.7129 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.0472 mol/L; [PMDETA]$_0$ = 0.1415 mol/L

C: [Styrene]$_0$ = 4.7129 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.0236 mol/L; [PMDETA]$_0$ = 0.0707 mol/L

Experimental results show that good control of molecular weight, polydispersities and high initiator efficiencies in the solution ATRP synthesis of primary amine functionalized polystyrene can be obtained using the initiator adduct (**1**), generated by the stoichiometric addition reaction of 1-(bromoethyl)benzene to 1-(4-aminophenyl)-1-phenylethylene. The quantitative incorporation of the functionalized 1,1-diphenylethylene fragment into the polymer chain end in the ATRP of styrene and the control of major polymer properties such as number average molecular weight, polydispersity and degree of functionalization is attributed to (a) the quantitative formation of (**1**) in situ, and (b) the subsequent efficient and rapid reaction of the diphenylethylene radical chain end with the styrene monomer.

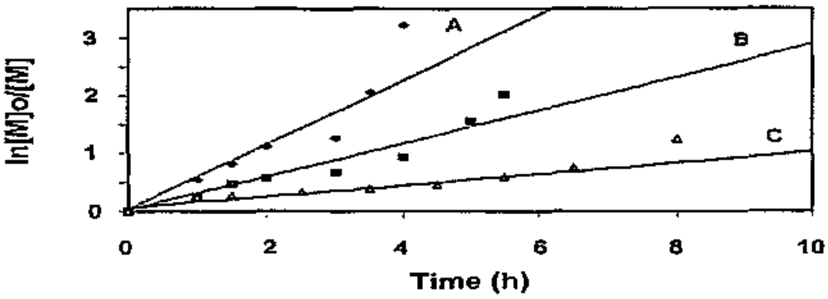

Figure 6.6 First-order kinetic plots for the preparation of primary amine functionalized polymers at 130°C

A: $[\text{Styrene}]_0$ = 4.7129 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0943 mol/L; $[\text{PMDETA}]_0$ = 0.2829 mol/L

B: $[\text{Styrene}]_0$ = 4.7129 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0472 mol/L; $[\text{PMDETA}]_0$ = 0.1415 mol/L

C: $[\text{Styrene}]_0$ = 4.7129 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.0236 mol/L; $[\text{PMDETA}]_0$ = 0.0707 mol/L

6.5 Conclusions

The addition reaction of 1-(bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene in the presence of copper (I) bromide and CuBr/N,N,N=,N=,N=>-pentamethyldiethylenetriamine produces an efficient initiating system for the in situ ATRP of styrene and affords primary amine functionalized polystyrene in quantitative yields. The formation of the adduct (**1**) is complete within one hour, as evidenced by TLC analysis, and then rapidly initiates styrene polymerization via a controlled atom transfer radical polymerization process to afford the corresponding primary amine functionalized polymers with predictable molecular weights (M_n = 2 x 10^3 - 10 x 10^3 g/mol) and relatively narrow molecular weight distribution (M_w/M_n= 1.03 -1.49). The polymerization process was monitored by gas chromatographic analysis. The functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, potentiometry and spectroscopy. All polymer characterization data are consistent with the quantitative incorporation of the primary amine group into the polymer chain end.

CHAPTER 7

FUNCTIONALIZED POLYMERS BY ATOM TRANSFER RADICAL POLYMERIZATION USING 1,1-DIPHENYLETHYLENE METHODOLOGY: SILOXYL AND HYDROXYL FUNCTIONALIZED POLYMERS

7.1 Abstract

Siloxyl and hydroxyl functionalized polymers were synthesized in quantitative yields by atom transfer radical polymerization.[82] Siloxyl functionalized polystyrenes were prepared by a one pot synthesis method using the adduct of 1-(bromoethyl)benzene with 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene as initiator system in the atom transfer radical polymerization of styrene in the presence of a copper (I) bromide/2,2'-bipyridyl or copper (I) bromide/N,N,N=,N=,N@-pentamethyldimethyltriamine (PMDETA) catalyst complexes. Acid catalyzed hydrolysis of siloxyl functionalized polystyrene with concentrated hydrochloric acid produced the corresponding hydroxyl functionalized polystyrene. Quantitative yields of the corresponding precursor siloxyl functionalized polystyrene with predictable molecular weights (M_n = 1 900 to 7000 g/mol) and narrow molecular weight distributions (M_w/M_n= 1.03 -1.34) and an initiator efficiencies as high as 0.67 were obtained, consistent with a controlled free radical polymerization process. The polymerization process was monitored by gas chromatographic analysis. The siloxyl and hydroxyl functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, potentiometry and spectroscopy. All experimental evidence is consistent with quantitative functionalization via the 1,1-diphenylethylene derivative. Polymerization kinetic measurements show that the polymerization reaction follows first order rate kinetics with respect to monomer consumption and the number average molecular weight increasing linearly with monomer conversion.

7.2 Introduction

The use of functionalized 1,1-diphenylethylene derivatives as initiator precursors for the preparation of functionalized polymers by the atom transfer radical polymerization methods have been described in our laboratories.[80, 81] For example, by utilizing the methodology of 1,1-diphenylethylene chemistry in atom transfer radical polymerization processes, the quantitative synthesis of tertiary amine functionalized polymers was effected by the polymerization of styrene using a functionalized initiator adduct, formed quantitatively in situ by the stoichiometric addition reaction of 1-(bromoethyl)benzene with 1-(4-dimethylaminophenyl)-1-phenylethylene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system. Hereby, the ATRP functionalization process has been extended to the use of siloxyl substituted 1,1-diphenylethylene as initiator precursor for the preparation of siloxyl and hydroxyl functionalized polymers.

7.3 The Synthesis of Siloxyl and Hydroxyl Functionalized Polystyrene by Atom Transfer Radical Polymerization

The general synthetic pathway for the one-pot preparation of siloxyl and the corresponding hydroxyl functionalized polystyrene by the atom transfer radical polymerization of styrene using the adduct (**1**) as functionalized initiator is outlined in **Figure 7.1**. In a typical reaction, the adduct (1) was quantitatively prepared in situ by reacting stoichiometric amounts of 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene with 1-(bromoethyl)benzene in the presence of copper (I) bromide and 2,2'-bipyridyl as catalyst system in diphenylether at 110 °C in the molar ratio of $[CuBr]_0$:[1-(bromoethyl)benzene]$_0$: [2,2'-bipyridyl]$_0$ = 1:1:3, prior to the addition of the styrene monomer. After one hour of reaction time, rapid initiation of styrene polymerization occurred after the subsequent addition of styrene monomer indicating that the free radical generated from adduct (**1**) 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 siloxyl functionalized polystyrenes with predictable molecular weights (M_n = 1 900 to 7 000 g/mol) and narrow molecular weight distributions (M_w/M_n= 1.03 - 1.34).

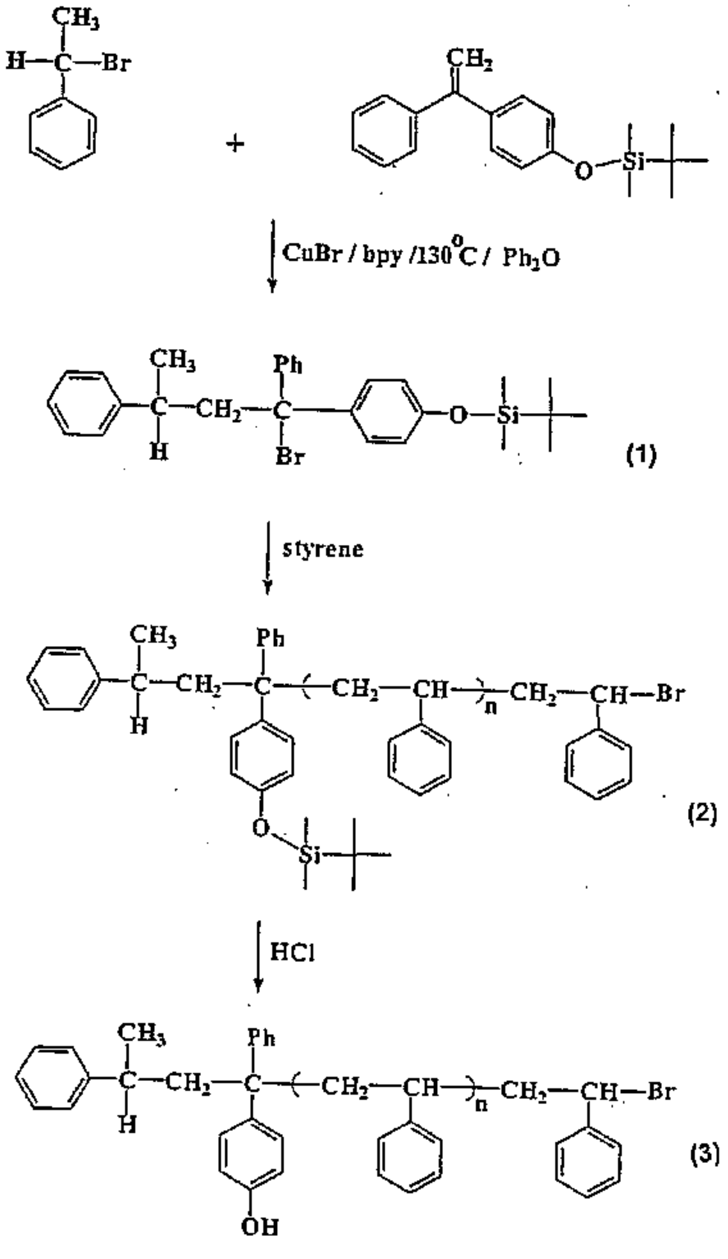

Figure 7.1 Synthetic pathway for the preparation of siloxyl and hydroxyl functionalized polystyrene

TLC analysis of the siloxyl functionalized polystyrene (2), [R_f = 0.8, toluene] shows only one spot on the TLC chromatogram, consistent with formation of siloxyl functionalized polystyrene in quantitative yields and the absence of polystyrene which was initiated by 1-(bromoethyl)benzene only. The size exclusion chromatographic analysis of the siloxyl functionalized polystyrene (2) shows a monomodal molecular weight distribution with M_n (GPC) = 5067 g/mol and M_w/M_n = 1.09 at 89% conversion in comparison with the theoretical $M_{n,th}$ value of 4758 g/mol which indicates that some side reactions such as radical termination and radical coupling are observed during the in situ formation of the functionalized initiator system (1), but that no chain transfer reactions occur once the initiation is complete.

The FTIR spectrum of the siloxyl functionalized polystyrene (2) exhibits an absorption band at 1261 cm^{-1}, characteristic of the $Si-CH_3$ stretching vibrations of the functionalized initiator and a sharp peak at 600 cm^{-1}, due to the C-Br bond at the terminating end of the polymer chain, results are consistent with the incorporation of the initiator fragment into the functionalized polymer. The ^1H NMR spectrum of siloxyl functionalized polystyrene (2) exhibits a multiplet at δ = 0.1 ppm, due to the resonances of the diasteroisomeric $Si-(CH_3)_2$ groups as well as a multiplet at
δ =0.9 ppm, due to the $Si-C-(CH_3)_3$ groups of the functionalized initiator fragment.

7.4 Hydrolysis of Siloxyl Functionalized Polystyrene: Preparation of Hydroxyl Functionalized Polystyrene

Acid catalyzed hydrolysis of α-siloxyl functionalized polystyrene (2) produced the corresponding α-hydroxyl functionalized polystyrene (3) in 90% yield with the quantitative conversion of the siloxyl group to the hydroxyl group. The extent of hydrolysis for the conversion of (2) (R_f = 0.80) to the hydroxyl functionalized polystyrene (3) (R_f = 0) was monitored by TLC analysis. The ^1H NMR spectrum of hydroxyl functionalized polystyrene (3) exhibits a broad resonance at δ = 2.9 ppm, due to the resonance of the hydroxyl group proton, with total disappearance of the resonances which are attributed to the $Si-(CH_3)_2$ and $Si-C-(CH_3)_3$ groups.

Potentiometric titration measurements[79] of functionalized polymer (3) with perchloric acid in glacial acetic acid indicated the quantitative incorporation of the hydroxyl group in polymer (3) and the value of Mn = 5.1 x 10^3 g/mol obtained. From size exclusion chromatography measurements, the number average molecular weight value of the precursor siloxyl functionalized polystyrene is Mn = 4.9 x 10^3 g/mol.

7.5 Polymerization Kinetics: The Synthesis of Siloxyl and Hydroxyl Functionalized Polystyrene by Atom Transfer Radical Polymerization

7.5.1 Atom Transfer Radical Polymerization of Styrene in the presence of CuBr/bpy catalyst

In a typical procedure, siloxyl functionalized polymers were prepared using the initiator adduct of 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene with 1-(bromoethyl -benzene in the solution atom transfer radical polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 110 °C at different monomer to initiator concentration ratios. The reactions proceeded under heterogeneous conditions. Results indicate that at the lower $[M]_0/[I]_0$ ratio of 50:1, the reaction was the fastest and 65% monomer conversion was reached in 8 hours **(Figure 7.2)**. When the $[M]_0/[I]_0$ ratio is increased to 100, monomer conversion with time decreases slightly due to lower initiator concentration. The polymerizations are relatively fast at the early stage, with conversion of 10% after 2 hours, but for the reaction where the $[M]_0/[I]_0$ ratio of 200:1, the polymerization rate slows down later with only 28% monomer conversion obtained after 6 hours.

Figure 7.3 shows the semilogarithmic kinetic plots for the heterogenous ATRP synthesis of siloxyl functionalized polystyrene using adduct (**1**) as the functionalized initiator system. The kinetic plots of logarithmic monomer concentration, $\ln[M]_0/[M]$ as a function of polymerization time at different $[M]_0/[I]_0$ ratios show that the ratio of the concentration of monomer to initiator affects the rate of polymerization. The plots of $\ln [M]_0/[M]$ vs time are linear indicating that once initiation has occurred, no termination reactions are observed and concentration of active propagating radicals was constant throughout the polymerization. The linearity of the semilogarithmic plots of $\ln [M]_0/[M]$ vs 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 increasing monomer concentration and decreasing initiator concentration.

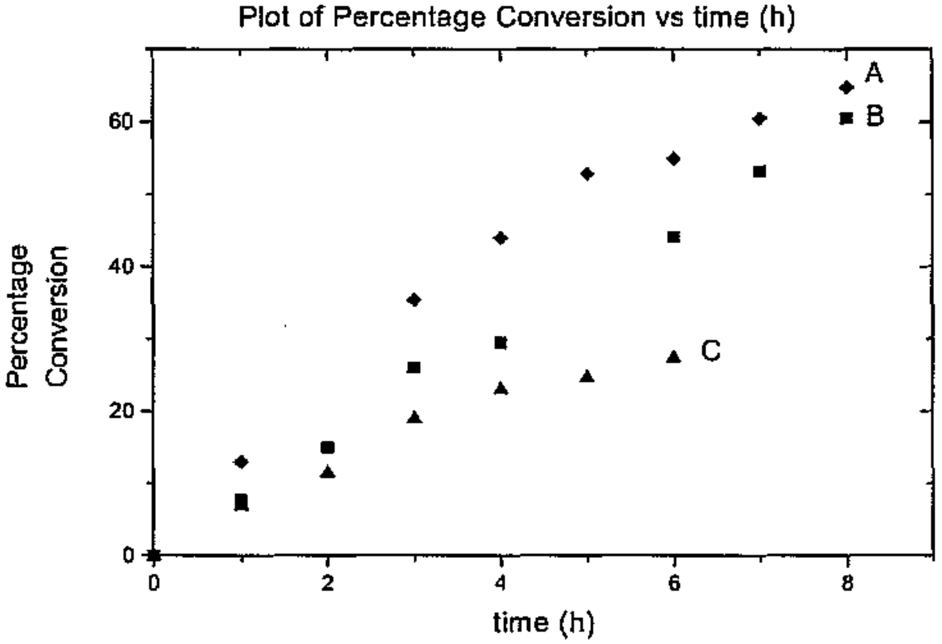

Figure 7.2 Plot of percentage monomer conversion versus time data for the polymerization of styrene initiated by adduct **(1)** in the presence of CuBr/bpy catalyst systems in diphenyl ether at 110 °C

A: [Styrene]$_0$ = 8.728 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.175 mol/L; [bpy]$_0$ = 0.524 mol/L
B: [Styrene]$_0$ = 8.728 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.088 mol/L; [bpy]$_0$ = 0.262 mol/L
C: [Styrene]$_0$ = 8.728 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.044 mol/L; [bpy]$_0$ = 0.131 mol/L

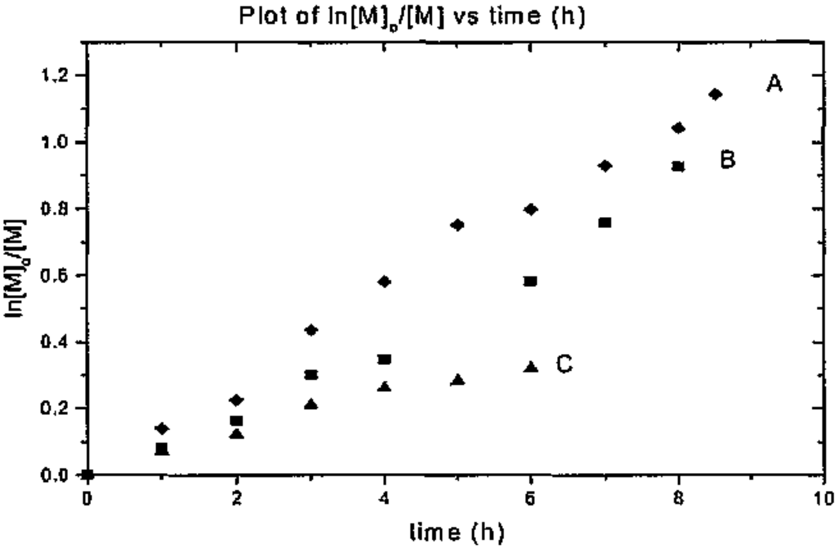

Figure 7.3 First-order kinetic plots for the polymerization of styrene initiated by adduct (**1**) in the presence of CuBr/bpy catalyst system in diphenyl ether at 110 °C:

A: [Styrene]$_0$ = 8.728 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.175 mol/L; [bpy]$_0$ = 0.524 mol/L
B: [Styrene]$_0$ = 8.728 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.088 mol/L; [bpy]$_0$ = 0.262 mol/L
C: [Styrene]$_0$ = 8.728 mol/L; [1-(Bromoethyl)benzene]$_0$ = [CuBr]$_0$ = 0.044 mol/L; [bpy]$_0$ = 0.131 mol/L

The number average degree of polymerization increases linearly with monomer conversion, but with higher values than the theoretical values calculated from the stoichiometry of the reaction (**Figure 7.4**). Results show that negligible contribution from chain transfer or other side reactions occur once initiation is complete. Experimental results suggest that a constant number of chains are generated throughout the polymerization and that rapid exchange between the active and dormant species occurs, that is, fast initiation as compared to propagation with the absence of radical termination and chain transfer reactions once the initiation step is complete. Functionalized polymers with polydispersities ranging from 1.03-1.34 were obtained, indicating that the rate of initiation is at least comparable with the rate of propagation and the rapid equilibrium exchange between active and dormant species occurs during polymerization. Initiator efficiencies as high as 0.67 for the preparation of the functionalized polymers were obtained, which might indicate that side reactions occur during the initiation process.

7.5.2 Atom Transfer Radical Polymerization of Styrene in the presence of CuBr/PMDETA catalyst

Similar experimental features and trends are observed in the solution atom transfer radical polymerization of styrene using the initiator adduct of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene with 1-(bromoethyl)benzene in the presence of CuBr/PMDETA catalyst in diphenylether at 110 °C at different monomer to initiator concentration ratios. However, when using the CuBr/PMDETA catalyst system instead of the CuBr/bpy system, the reactions are faster with less control of the polymer properties. Higher degrees of monomer conversion, close to quantitative yields of the functionalized polymer products, and polymers with higher number average molecular weights are obtained after 8 hours at $[M]_0/[I]_0$ ratios of 100:1 **(Figure 7.5)** as compared to 60% monomer conversion obtained in the presence of the CuBr/bpy catalyst system. The plot of $\ln[M]_0/[M]$ is linear indicating first order rate kinetics and consistent with a controlled free radical polymerization free of chain transfer and termination reactions once initiation is complete **(Figure 7.6)**. The number average molecular weight increases linearly with conversion and the polydispersity values of the functionalized polymers vary between 1.02 and 1.1 **(Figure 7.7)**.

Experimental results indicate that the one-pot, stoichiometric addition reaction of 1-(bromoethyl)benzene to 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene to generate the adduct (1), in situ, followed by the addition of styrene is a good method for the solution ATRP of styrene to produce siloxyl functionalized polystyrene with good control of molecular weight and polydispersities and initiator efficiencies as high as 0.67. The quantitative incorporation of functionalized 1,1-diphenylethylene fragment into the polymer chain end in the ATRP of styrene and the control of major polymer properties such as number average molecular weight, polydispersity and degree of functionalization is attributed to (a) the formation of (1) in situ, and (b) the subsequent efficient and rapid reaction of the diphenylethylene radical chain end with the styrene monomer.

7.6 Conclusions

Siloxyl and hydroxyl functionalized polystyrenes were prepared in quantitative yields in the ATRP of styrene using the adduct (1), prepared in situ by the reaction of 1-(bromoethyl)benzene with 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene in the presence of copper (I) bromide/2,2'-bipyridyl or copper (I) bromide/PMDETA catalysts systems. After one hour of reaction, the initiator adduct (1) rapidly initiates styrene polymerization via a controlled atom transfer radical polymerization process to afford quantitative yields of the corresponding siloxyl functionalized polymers with predictable molecular weights (M_n = 1 900 - 7000) and narrow molecular weight distributions (M_w/M_n=

1.03-1.34) and initiator efficiencies as high as 0.67. Acid catalyzed hydrolysis of siloxyl functionalized polystyrene (**2**) with concentrated hydrochloric acid produced the corresponding hydroxyl functionalized polystyrene (**3**).

The polymerization process was monitored by gas chromatographic analysis. The functionalized polymers were characterized by thin layer chromatography, size exclusion chromatography, potentiometry and spectroscopy. All polymer characterization data are consistent with the quantitative incorporation of the siloxyl and hydroxyl groups into the polymer chain end.

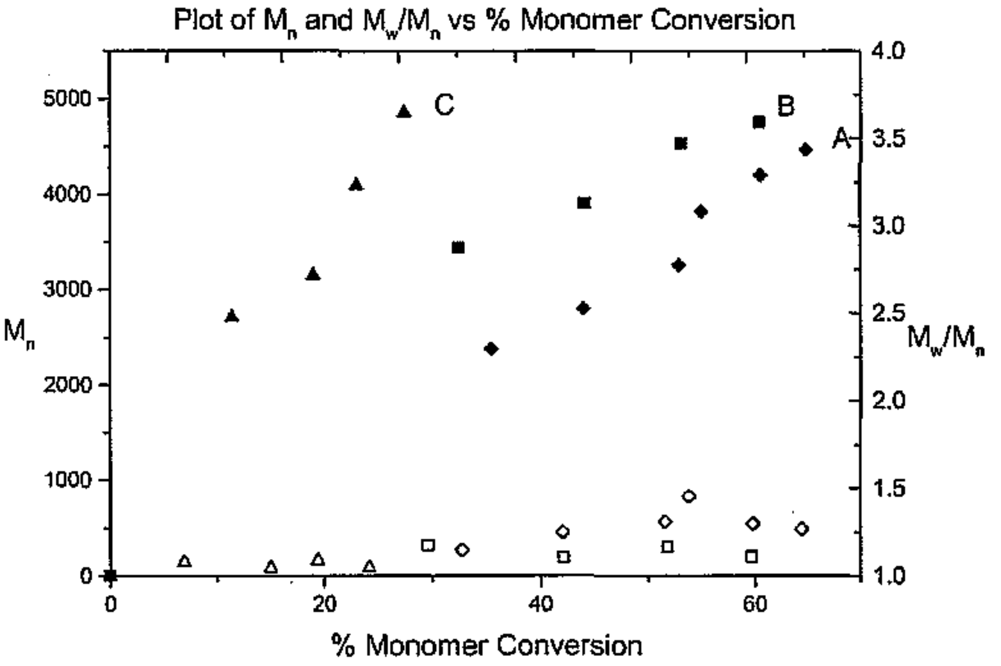

Figure 7.4 M_n and M_w/M_n versus percentage conversion data for the polymerization of styrene initiated by adduct (**1**) in the presence of CuBr/bpy catalyst systems in diphenyl ether at 110 °C:

A: $[\text{Styrene}]_0$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_0 = [\text{CuBr}]_0$ = 0.175 mol/L; $[\text{bpy}]_0$ = 0.524 mol/L; I_{eff} = 0.68

B: $[\text{Styrene}]_0$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_0 = [\text{CuBr}]_0$ = 0.088 mol/L; $[\text{bpy}]_0$ = 0.262 mol/L; I_{eff} = 0.65

C: $[\text{Styrene}]_0$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_0 = [\text{CuBr}]_0$ = 0.044 mol/L; $[\text{bpy}]_0$ = 0.131 mol/L; I_{eff} = 0.64

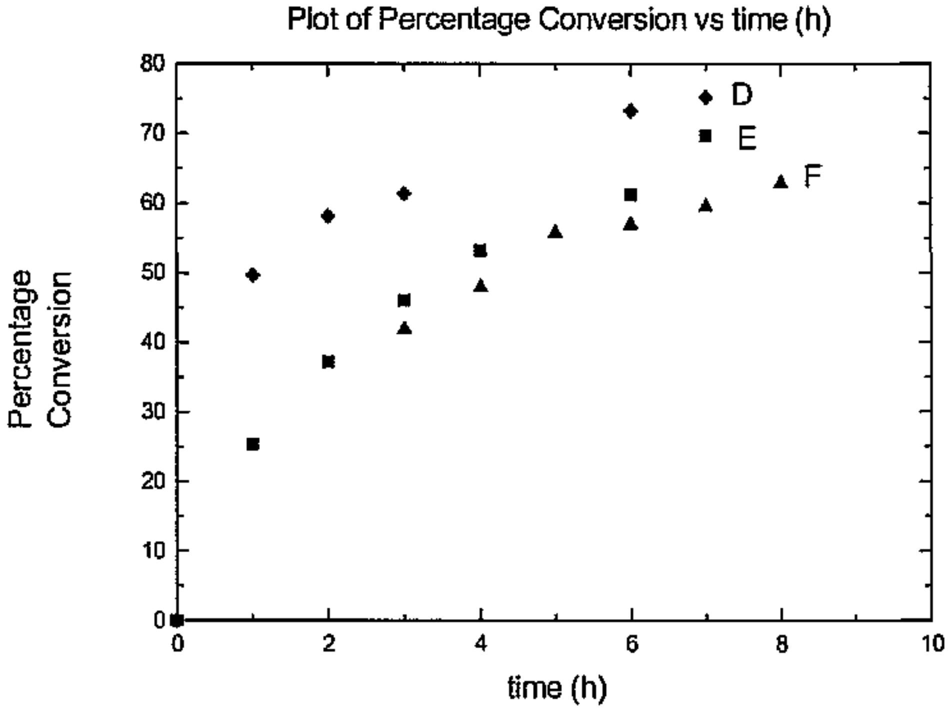

Figure 7.5 Plot of percentage monomer conversion versus time data for the polymerization of styrene initiated by adduct (**1**) in the presence of CuBr/PMDETA catalyst systems in diphenyl ether at 110 °C

D: $[\text{Styrene}]_o$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_o$ = $[\text{CuBr}]_o$ = 0.175 mol/L; $[\text{PMDETA}]_o$ = 0.524 mol/L

E: $[\text{Styrene}]_o$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_o$ = $[\text{CuBr}]_o$ = 0.088 mol/L; $[\text{PMDETA}]_o$ = 0.262 mol/L

F: $[\text{Styrene}]_o$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_o$ = $[\text{CuBr}]_o$ = 0.044 mol/L; $[\text{PMDETA}]_o$ = 0.131 mol/L

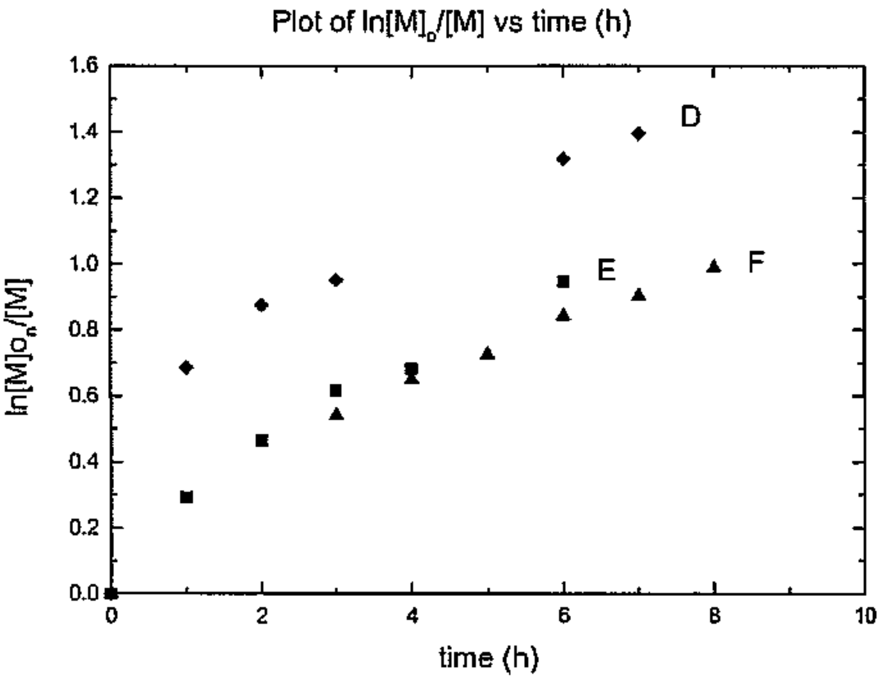

Figure 7.6 First-order kinetics plots for polymerization of styrene initiated by adduct **(1)** in the presence of CuBr/PMDETA catalyst system in diphenyl ether at 110 °C

D: $[\text{Styrene}]_0 = 8.728$ mol/L; $[\text{1-(Bromoethyl)benzene}]_0 = [\text{CuBr}]_0 = 0.175$ mol/L; $[\text{PMDETA}]_0 = 0.524$ mol/L

E: $[\text{Styrene}]_0 = 8.728$ mol/L; $[\text{1-(Bromoethyl)benzene}]_0 = [\text{CuBr}]_0 = 0.088$ mol/L; $[\text{PMDETA}]_0 = 0.262$ mol/L

F: $[\text{Styrene}]_0 = 8.728$ mol/L; $[\text{1-(Bromoethyl)benzene}]_0 = [\text{CuBr}]_0 = 0.044$ mol/L; $[\text{PMDETA}]_0 = 0.131$ mol/L

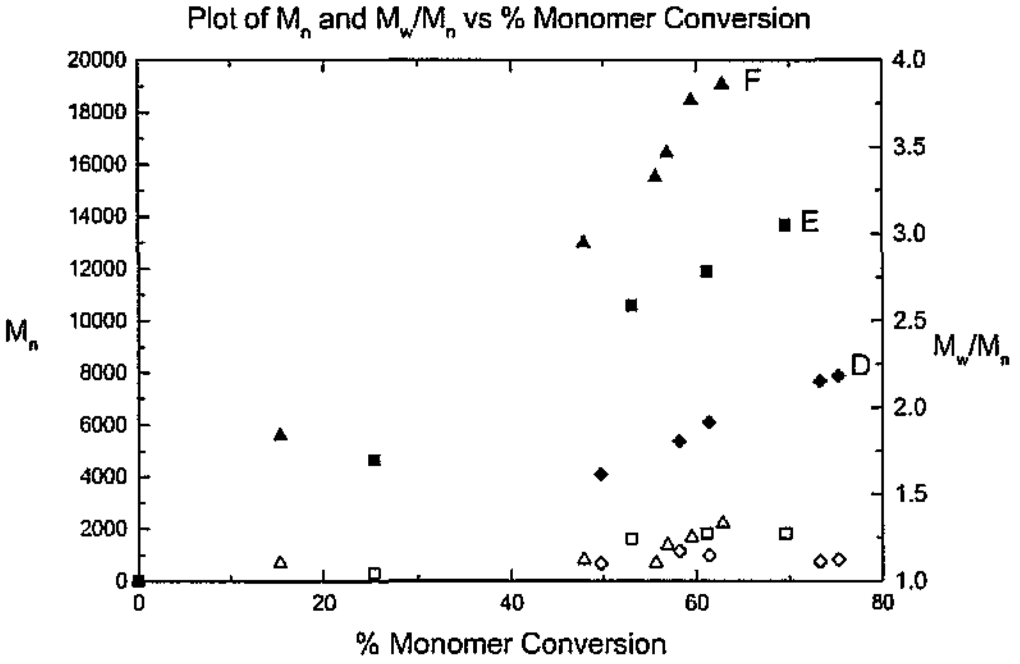

Figure 7.7 M_n and M_w/M_n versus percentage conversion data for the polymerization of styrene initiated by adduct (**1**) in the presence of CuBr/PMDETA catalyst systems in diphenyl ether at 110 °C:

D: $[\text{Styrene}]_0$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.175 mol/L; $[\text{PMDETA}]_0$ = 0.524 mol/L
E: $[\text{Styrene}]_0$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.088 mol/L; $[\text{PMDETA}]_0$ = 0.262 mol/L
F: $[\text{Styrene}]_0$ = 8.728 mol/L; $[\text{1-(Bromoethyl)benzene}]_0$ = $[\text{CuBr}]_0$ = 0.044 mol/L; $[\text{PMDETA}]_0$ = 0.131 mol/L

CHAPTER 8

EXPERIMENTAL

8.1 General

8.1.1 Materials

Tetrahydrofuran (THF) (Aldrich Chemical Company) was carefully purified as described by Quirk and Summers.[56,57]

n-Butyl lithium (1.6 M n-BuLi in hexanes, Aldrich Chemical Company) was used as received.

Commercially available polysulfone (Ultrason S, BASF, Mn = 47 x 10^3 g/mol, Mw/Mn = 1.05) was dissolved in THF and precipitated into methanol, filtered and vacuum dried at 120°C prior to the chemical modification reaction.

Also, polysulfone (1), Mn = 47 x 10^3 g/mol, was synthesized by the condensation polymerization of bisphenol A and bis(4-fluorophenyl)sulfone according to the procedure of Matyjaszewski and coworkers,[83] with modifications.

Methyl triphenylphosphonium bromide (Aldrich Chemical Company), potassium tert-butoxide (Aldrich Chemical Company) and di-2-pyridylketone (Aldrich Chemical Company) were used as received.

8.1.2 Materials Characterization

Size exclusion chromatography was utilized to determine of the molecular weight and molecular weight distributions of polymers and was performed at a flow rate of 1 mL/min in THF at 30°C using a Waters Alliance SEC autosampler equipped with a Phenogel guard column and a Phenogel column (5µ, 500 A pore size, 1K-15K MW range, 300 x 7.8 mm) in series with Refractive Index and Dual Angle Laser Light Scattering Detectors, after calibration with standard polystyrene and poly(methyl methacrylate) samples (Aldrich Chemical Company), where applicable.

^1H NMR ($CDCl_3$ or d_6-DMSO) spectra were recorded on a Varian 300 MHz spectrometer.

Thin layer chromatographic analyses were performed on silica gel plate (Merck, Silica Gel 60 F 254).

Infrared spectra were recorded on a Perkin Elmer 883 Infrared Spectrophotometer.

Thermogravimetrical curves were generated on a TA Instruments Auto Hi-Res Q500 Thermogravimetrical Analyzer by heating the polymer samples at a rate of 10 ^{o}C/min under nitrogen.

Glass transition temperatures were determined on a TA Instruments Auto MDSC Q100 Differential Scanning Calorimeter by heating the polymers from 10 ^{o}C to 700 ^{o}C.

Elemental analyses were performed at the University of Cape Town, Cape Town.

Concentrations of carboxylic acid chain ends were determined by potentiometric titration of 0,1 g polymer sample in toluene with standardized methanolic sodium hydroxide using phenolphthalein as indicator.[79]

Concentrations of tertiary amine, primary amine and hydroxyl end groups were determined by potentiometric titration of 0.1 g polymer sample in a 1/1 (v/v) mixture of chloroform and glacial acetic acid with perchloric acid (0.1 M) in glacial acetic acid using methyl violet as indicator.[79]

8.2 Experimental Procedures

8.2.1 The Synthesis of 2,2'-Vinylidenedipyridine: Method 1

2,2'-Vinylidenedipyridine[71] was synthesized according to the procedure outlined by Eckhard and Summers,[72] with modifications. Dimethyl sulfoxide (Aldrich Chemical Company) was purified under an argon atmosphere by distillation from calcium hydride. Under an argon atmosphere, sodium hydride (1.3 g, 0.054 mol, Aldrich Chemical Company) was added to freshly distilled dimethyl sulfoxide (50 mL). The reaction was heated to 65-70 ^{o}C. A yellow green colour was observed with the evolution of gases (hydrogen gas). The reaction mixture was allowed to stir for 90 minutes at 68 ^{o}C. The reaction flask was cooled in an ice bath, followed by the addition of methyltriphenyl-phosphonium bromide (19.3 g, 0,054 mol, Aldrich Chemical Company) in dimethyl sulfoxide (100 mL). Immediately after the addition, a green-yellow colour was observed in the reaction flask. The reaction mixture allowed to stir at 25 ^{o}C for 25 minutes. Upon the addition of di-2-pyridyl ketone (10 g, 0.054 mol, Aldrich Chemical Company) in dimethyl sulfoxide (100 mL), the reaction mixture immediately turned dark red and eventually brown-red in colour with an increase in temperature to 45 ^{o}C. The brown-red mixture was allowed to stir at 60 ^{o}C for 45 minutes. Excess dimethyl sulfoxide was removed by vacuum distillation at 98 ^{o}C. The residue was dissolved in 10% hydrochloric acid and repeatedly extracted with chloroform to remove triphenylphosphine oxide. The aqueous layer was made alkaline and then extracted with chloroform. The red-brown chloroform solution was washed with water and dried with magnesium sulfate. The chloroform solution was concentrated on a rotary evaporator to afford a brown oil. The brown oil was purified by silica gel column chromatography with acetonitrile as mobile phase to afford 4.26 g (41%) of pure 2,2'-vinylidenedipyridine. ^{1}H NMR ($CDCl_3$): δ 6.05 [s, 2H, C$\underline{H_2}$]; 6.97-7.70 [m, 6H, aromatic H]; 8.50-8.60 ppm [d, 2H, aromatic H]. TLC (Silica Gel $60F_{254}$, Merck): R_f (acetonitrile) = 0.35. IR (oil): 1634 cm^{-1} (C=N).

8.2.2 The Synthesis of 2,2'-Vinylidenedipyridine: Method 2

The synthesis of 2,2'-vinylidenedipyridine according to the procedure outlined by Eckhard and Summers[72] and Summers, Ndawuni and Summers[71] afforded the desired product in low yields. Thus, a new method to synthesize 2,2'-vinylidenedipyridine was developed using the synthetic route outlined in the literature,[73,74] with modifications. Under an argon atmosphere, a ylide was formed by treatment of methyltriphenyl-phosphonium bromide (9.7 g, 0.027 mol) with potassium tert-butoxide (27.51 mL of 1.0 M solution, 0.027 mol) in freshly distilled anhydrous THF (200 mL) at 0 °C for 1.5 hr. Upon the addition of di-2-pyridylketone (5.0 g, 0.027 mol) in dry THF (100 mL) to the freshly prepared ylide at 0 °C, the resultant dark orange solution was stirred for 12 hrs at room temperature to achieve complete reaction. The colour of the reaction mixture changed with time from dark-orange to orange-green to brown. The reaction was quenched by the addition of methanol (2 mL). The triphenylphosphine oxide which precipitated from 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 4.21 (92%) of pure 2,2'-vinylidene-dipyridine. ^{1}H NMR ($CDCl_3$): δ 6.05 [s, 2H, C$\underline{H_2}$]; 6.97-7.70 [m, 6H, aromatic H]; 8.50-8.60 ppm [d, 2H, aromatic H]. TLC (Silica Gel $60F_{254}$, Merck): R_f (acetonitrile) = 0.35. IR (oil): 1634 cm^{-1} (C=N).

8.2.3 The Synthesis of Dipyridyl Functionalized Polysulfone [PFPS-45]

In a typical procedure,[71] under an argon atmosphere, polysulfone (1g, 0.0023 mol, M_n = 4.1 x 10^3 g/mol; M_w/M_n = 1.52) was transferred into a clean, dry 250 mL round bottomed flask. Freshly distilled THF (40 mL) was added to the flask to dissolve the polymer. The reaction mixture was cooled to -78 °C using an acetone-liquid nitrogen bath. Lithiation of polysulfone was effected by the addition of n-butyllithium (2.2 mL of 1.6 M solution in hexane, Aldrich Chemical Company) to the reaction mixture. The reaction mixture was stirred for 2 hours at -78 °C to effect complete metalation.
2,2'-Vinylidenedipyridine (1.03 g, 0.0023 mol) in THF (20 mL) was then added to the viscous deep red lithiated polymer via a cannula, whereupon the reaction mixture turned a deep orange-brown colour. The reaction mixture was allowed to stir at -78 °C for 4 hours. The colour and the viscosity of the reaction mixture remained unchanged. Upon quenching the reaction mixture with methanol, 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 vacuum dried at 120 °C. ^{1}H NMR ($CDCl_3$): δ 3.78-3.91 [broad m, 2H, C$\underline{H_2}$]; 4.68 - 4.85 [broad m, 1H, C$\underline{H}$]; 6.43 -8.62 ppm [m, aromatic H's]. IR (film): 1634 cm^{-1} (C=N).

8.2.4 The Synthesis of Dipyridyl Functionalized Polysulfones [PFPS-80]

The preparation of dipyridyl functionalized polysulfone with 80% degree of functionalization (PFPS-80) was effected according to the following procedure, using excess of 2,2'-vinylidenedipyridine.[73]

In a typical procedure, under an argon atmosphere, polysulfone, PS, (1g, 0.0023 mol, M_n = 47 x 10^3 g/mol; M_w/M_n = 1.05) was transferred into a clean, dry 250 mL round bottomed flask. Freshly distilled THF (40 mL) was added to the flask to dissolve the polymer. The reaction mixture was cooled to -78 ^oC using an acetone-liquid nitrogen bath. Lithiation of polysulfone was effected by the addition of n-butyllithium (2.2 mL of 1.6 M solution in hexane, 0.0035 mol) to the reaction mixture. The reaction mixture was stirred for 2 hrs at -78 ^oC to effect complete metalation. 2,2'-Vinylidenedipyridine
(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 a deep orange-brown 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, 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 vacuum dried at 120 ^oC. ^{1}H NMR ($CDCl_3$): δ 3.78-3.91 [broad m, 2H, $C\underline{H}_2$]; 4.68 - 4.85 [broad m, 1H, $C\underline{H}$]; 6.43 -8.62 ppm [m, aromatic H's]. IR (film): 1634 cm $^{-1}$ (C=N).

8.2.5 Quaternization of Dipyridyl Functionalized Polysulfone

In a typical procedure,[71] dimethyl sulphate (5 mL) was added to a solution of dipyridyl functionalized polysulfone (0.15 g) in THF (1.5 mL). The reaction mixture turned from light brown to a yellow-white cloudy mixture. The reaction mixture was stirred at room temperature for 5 minutes. Upon the addition of concentrated perchloric acid (5 mL), a white solid was formed. The mixture was added into excess ethyl acetate and the precipitate was filtered off and vacuum dried at 120 ^oC to form the corresponding dipyridinium perchlorate functionalized polysulfone.
^{1}H NMR ($CDCl_3$): δ 3.60 -3.81 [broad m, 2H, $C\underline{H}_2$]; 4.15 [s, 6H, 2 x $C\underline{H}_3$]; 4.78 - 5.10 [broad m, 1H, $C\underline{H}$]; 6.19 - 8.79 ppm [m, aromatic H=s].

8.2.6 Evaluation of Chelation Efficiency of Dipyridyl Functionalized Polysulfone: Adsorption of Metal Ions to Polymers

In a typical procedure,[71] copper (II) ion solutions in water with concentrations ranging between 5-20 mmol at room temperature were prepared. A column (Tygon tubing; 4mm i.d.; 50mm in length) packed with finely ground dipyridyl functionalized polysulfone (100 mg) was prepared and coupled to a peristaltic pump (Gilson Minipulse 2). An aliquot of the Cu (II) solution (30 mL) was passed through the column at a flow rate of 0.2 mL per minute and the column effluent was collected to measure the non-retained fraction. After each aliquot of the test solution was passed through the column, the column was flushed at a flow rate of 0.2 mL per minute successively with distilled water (30 mL), 1% hydrochloric acid (30 mL) and deionized distilled water. Atomic absorption spectroscopic measurements were performed to determine the concentration of heavy metal ions in the non-retained effluent as well as the acid eluent and compared to the concentration of metal ions in the feed. Similar reactions were conducted for the analysis of nickel (II) ions.

8.2.7 Atom Transfer Radical Polymerization of Styrene Initiated by α-Bromo-p-toluic acid

The atom transfer radical polymerization of styrene polymerization in solution was carried out in Schlenk flasks under dry argon. In a typical procedure, copper (I) bromide (0.3260 g, 0.0023 mol), 2,2-bipyridyl (1.06 g, 0.0068 mol) and dry diphenyl ether (5 mL) were added to a Schlenk flask. The reaction mixture was stirred for 5 minutes. Freshly distilled styrene (8 mL) followed by α-bromo-p-toluic acid (0.4951 g, 0.0023 mol) were added and the heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 130 °C for 12 hours, with stirring. Upon cooling and addition of tetrahydrofuran (10 mL), the green solution was purified by passage through a short silica gel column to remove copper and ligand impurities. The polymer solution was concentrated in vacuo and precipitated into methanol to afford the functionalized polymer in the carboxylate form. The aromatic carboxyl functionalized polymer was isolated by precipitation several times from THF solution into methanol containing 1% aqueous hydrochloric acid, filtered off and vacuum dried.

Elemental analysis:
$HOOC\ (C_6H_4)\ CH_2\ [CH_2\ CH\ (C_6H_5)]_{26}\ CH_2\ CH\ (C_6H_5)\ Br$
Calc: C 88.86%, H 7.47%; Found: C 89.31%, 7.79%.

8.2.8 Polymerization Kinetics: Atom Transfer Radical Polymerization of Styrene Initiated by α-Bromo-p-toluic acid

The polymerization kinetics of styrene polymerizations was conducted in the bulk and in solution with diphenyl ether as solvent. In a typical procedure,[78] copper (I) bromide (0.0626 g, 0.0004 mol), 2,2-bipyridyl (0.1363 g, 0.0009 mol) and dry diphenyl ether (10 mL) were added to a Schlenk flask. The reaction mixture was stirred for 5 minutes. Freshly distilled styrene (10 mL, 0.0873 mol) followed by α-bromo-p-toluic acid (0.4951 g, 0.0023 mol) were added and the heterogenous mixture degassed three times by freeze-pump-thaw cycles. An aliquot (1 mL) of the sample was withdrawn from the reaction mixture using a stainless steel syringe, dissolved in THF (9 mL) and subjected to gas chromatographic analysis to determine the amount of styrene in the sample at time, t=0. Under argon atmosphere, the mixture was heated to 130 °C. At different time intervals, 1 mL aliquots of samples were withdrawn from the flasks under argon atmosphere, diluted with a known volume 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 followed by precipitation from THF solution into methanol. The functionalized polymers were re-precipitated several times from THF solution into methanol, filtered off and vacuum dried.

8.2.9 Synthesis of Tertiary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

The styrene polymerizations[80] in solution were carried out in Schlenk flasks under dry argon. In a typical procedure, copper (I) bromide (0.0640 g, 0.4478 mmol), 2,2'-bipyridyl (0.21 g, 1.344 mmol) were added to a Schlenk flask, followed by the successive addition of 1-(4-dimethylaminophenyl)-1-phenylethylene (0.1 g, 0.4478 mmol), 1-(bromoethyl)benzene (0.083 g, 0.4478 mmol) and diphenylether (1.5 mL). The reaction mixture was stirred for 5 minutes. The heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 130 °C for 60 minutes, with stirring. Freshly distilled styrene (1.5 mL) was added to the resultant green reaction mixture via a stainless steel syringe and the reaction was heated to 130 °C for 12 hours. Upon cooling and addition of tetrahydrofuran (10 mL), the resultant green solution was purified by passage through a short alumina column to remove copper and ligand impurities. The polymer solution was concentrated in vacuo and precipitated into methanol to afford the tertiary amine functionalized polymer.

8.2.10 Polymerization Kinetics: Synthesis of Tertiary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

The polymerization kinetics of styrene polymerizations were conducted in solution, with diphenylether as solvent. In a typical procedure,[80] under argon atmosphere, copper (I) bromide (0.128 g, 0.8956 mol) and 2,2'-bipyridyl (0.4198 g, 2.687 mmol) were added to a Schlenk flask, followed by the successive addition of 1-(4-dimethylaminophenyl)-1-phenylethylene (0.2 g, 0.8956 mmol), 1-(bromoethyl)benzene (0.1658 g, 0.8956 mmol) and diphenylether (5 mL). The reaction mixture was stirred for 5 minutes. The heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 130 °C for 60 minutes, with stirring. Upon cooling the reaction mixture to room temperature, freshly distilled styrene (5 mL, 4.545 g, 43.639 mmol) was added, with stirring. An aliquot (1 mL) of the sample was withdrawn from the reaction mixture using a stainless steel syringe, dissolved in THF (9 mL) and subjected to gas chromatographic analysis to determine the amount of styrene in the sample at time, t=0. Under argon atmosphere, the mixture was heated to 130 °C. At different time intervals, 1 mL aliquots of samples were withdrawn from the flasks under argon atmosphere, diluted with a known volume 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 alumina column to remove catalyst impurities followed by precipitation from THF solution into methanol. The tertiary amine functionalized polymers were re-precipitated several times from THF solution into methanol, filtered off and vacuum dried.

8.2.11 Synthesis of Primary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

The styrene polymerizations in solution were carried out in Schlenk flasks under dry argon. In a typical procedure,[81] copper (I) bromide (0.0735 g, 0.5122 mmol), N,N,N=,N=,N=>-pentamethyldiethylenetriamine (0.266 g, 1.537 mmol) were added to a Schlenk flask, followed by the successive addition of 1-(4-aminophenyl)-1-phenyl-ethylene (0.1 g, 0.5122 mmol), 1-(bromoethyl)benzene (0.095 g, 0.5122 mmol) and diphenylether (1.7 mL). The reaction mixture was stirred for 5 minutes. The heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 130 °C for 60 minutes, with stirring. Freshly distilled styrene (1.7 mL, 1.536 g, 0.5122 mol) was added to the resultant green reaction mixture via a stainless steel syringe and the reaction was heated to 130 °C for 12 hours. Upon cooling and addition of tetrahydrofuran (10 mL), the resultant green solution was purified by passage through a short alumina column to remove copper and ligand impurities. The polymer solution was concentrated in vacuo and precipitated into methanol to afford the primary amine functionalized polymer.

8.2.12 Polymerization Kinetics: Synthesis of Primary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization

The polymerization kinetics of styrene polymerizations were conducted in solution, with diphenylether as solvent. In a typical procedure,[81] under argon atmosphere, copper (I) bromide (0.1488 g, 1.0244 mol) and N,N,N=,N=,N=>-pentamethyldiethylenetriamine (0.5326 g, 3.0730 mmol) were added to a Schlenk flask, followed by the successive addition of 1-(4-aminophenyl)-1-phenylethylene (0.2 g, 1.0244 mmol), 1-(bromoethyl)-benzene (0.1896 g, 0.14 mL, 1.0244 mmol) and diphenylether (5 mL). The reaction mixture was stirred for 5 minutes. The heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 130 °C for 60 minutes, with stirring. Upon cooling the reaction mixture to room temperature, freshly distilled styrene (5.86 mL, 5.3344 g, 51.218 mmol) was added, with stirring. An aliquot (1 mL) of the sample was withdrawn from the reaction mixture using a stainless steel syringe, dissolved in THF (9 mL) and subjected to gas chromatographic analysis to determine the amount of styrene in the sample at time, t=0. Under argon atmosphere, the mixture was heated to 130 °C. At different time intervals, 1 mL aliquots of samples were withdrawn from the flasks under argon atmosphere, diluted with a known volume 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 alumina column to remove catalyst impurities followed by precipitation from THF solution into methanol. The primary amine functionalized polymers were re-precipitated several times from THF solution into methanol, filtered off and vacuum dried.

8.2.13 Synthesis of Siloxyl and Hydroxyl Functionalized Polystyrene by Atom Transfer Radical Polymerization

The styrene polymerizations in solution were carried out in Schlenk flasks under dry argon. In a typical procedure,[82] copper (I) bromide (0.0462 g, 0.3221 mmol), 2,2'-bipyridyl (0.151 g, 0,3221 mmol) were added to a Schlenk flask, followed by the successive addition of 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene (0.1 g, 0.3221 mmol), 1-(bromoethyl)benzene (0.0596 g, 0.3221 mmol) and diphenylether (1.5 mL). The reaction mixture was stirred for 5 minutes. The heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 110 °C for 60 minutes, with stirring. Freshly distilled styrene (2.0mL, 1.818 g, 0.3221 mol) was added to the resultant green reaction mixture via a stainless steel syringe and the reaction was heated to 110 °C for 12 hours. Upon cooling and addition of tetrahydrofuran (10 mL), the resultant green solution was purified by passage through a short alumina column to remove copper and ligand impurities. The polymer solution was concentrated in vacuo and precipitated into methanol to afford the siloxyl functionalized polymer.

The reaction of a siloxyl functionalized polystyrene sample (1.0 g, Mn = 4.9×10^3 g/mol) in THF (10 mL) with concentrated hydrochloric acid (2 mL) under reflux for 12 hours afforded 0.9 g (90%) of the corresponding hydroxyl functionalized polystyrene.

8.2.14 Polymerization Kinetics: Synthesis of Siloxyl and Hydroxyl Functionalized Polystyrene by Atom Transfer Radical Polymerization

In a typical procedure, the polymerization kinetics of styrene polymerizations were conducted in solution, with diphenyl ether as solvent.[82] Under argon atmosphere, copper (I) bromide (0.250 g, 1.7456 mmol) and PMDETA (0.9075 g, 5.2368 mmol) were added to a Schlenk flask, followed by the successive addition of 1-(4-t-butyl-dimethylsiloxyphenyl)-1-phenylethylene (0.5420 g, 1.7456 mmol), 1-(bromoethyl)-benzene (0.3231 g, 1.7456 mmol) and diphenyl ether (9 mL). The reaction mixture was stirred for 5 minutes. The heterogenous mixture was degassed three times by freeze-pump-thaw cycles. Under an argon atmosphere, the reaction mixture was heated to 110 °C for 60 minutes, with stirring. Upon cooling the reaction mixture to room temperature, freshly distilled styrene (10 mL, 9.09 g, 87.28 mmol) was added, with stirring. An aliquot (1 mL) of the sample was withdrawn from the reaction mixture using a stainless steel syringe, dissolved in THF (9 mL) and subjected to gas chromatographic analysis to determine the amount of styrene in the sample at time, t=0. Under argon atmosphere, the mixture was heated to 110 °C. At different time intervals, 1 mL aliquots of samples were withdrawn from the flasks under argon atmosphere, diluted with a known volume 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 alumina column to remove catalyst impurities followed by precipitation from THF solution into methanol. The siloxyl functionalized polymers were re-precipitated several times from THF solution into methanol, filtered off and vacuum dried.

8.3 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 (Aldrich Chemical Company). 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 of 150μm. After exposure to air for 15 s at 20 °C and 60% relative humidity, the thin films were immersed in water at 15 °C. After an immersion period of 5 min in distilled water, the membranes detached from the plate and were leached for an additional 3 hrs under running water before use.

8.4 Membrane Characterization

Atomic Force Microscopy (AFM) images of unmodified and dipyridyl functionalized polymers were obtained 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:

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

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

Contact angle data were obtained at 20 °C with an ERMA G-1 contact angle meter using pure water as probe liquid.

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

Scanning Electron Microscopy (SEM) photographs were obtained 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 B 180°C with a Reichert KF 80 freeze plunger. The frozen samples were transferred under liquid nitrogen into slots in a copper block (63 x 63 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 B130°C 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 x5000. To obtain lower magnification photos the samples were gold sputtered in a Polaron E5200 sputter coater for viewing.

CHAPTER 9

CONCLUSIONS

9.1 Introduction

The main objectives of the project were to design and synthesize functionalized polystyrenes and polysulfones and to evaluate the membrane matrix characteristics of the new functionalized polymeric materials. Living Anionic and Atom Transfer Radical Polymerization methods were successfully employed in the synthesis of the new polymeric materials. Results of pure water flux measurements, hydrophilicity tests, membrane morphology and thermal studies conducted on the new membranes indicates the potential use of functionalized polysulfones in membrane separation processes in high flux and low fouling applications.

9.2 Summary of results

The specific results of the synthesis, modification and membrane studies of the functionalized polystyrenes and polysulfones were as follows:

- The chemical modification of polysulfone was performed by a two-step process which involved the lithiation of polysulfone and subsequent reaction of lithiated polysulfone with stoichiometric amounts of 2,2'-vinylidenedipyridine to afford novel dipyridyl functionalized polysulfone with 45% degree of functionalization.

- Novel dipyridyl functionalized polysulfone with 80% degree of functionalization was prepared by the reaction of lithiated polysulfone with excess of 2,2'-vinylidenedipyridine.

- The dipyridyl functionalized polysulfone with 45% degree of functionalization was evaluated for the chelation of trace heavy metal ions such as copper and nickel in aqueous medium and the results show that dipyridyl functionalized polysulfone shows better complexing affinity for nickel ions at specific concentrations of test solutions.

- Quaternization reactions of dipyridyl functionalized polysulfone with dimethyl sulfate in the presence of perchloric acid quantitatively affords the corresponding polymeric pyridinium perchlorate derivative and provided evidence of the incorporation of the dipyridyl groups pendant to the polysulfone backbone.

- The introduction of pendant dipyridyl groups onto the polymer backbone imparts hydrophilic characteristics to the resulting polymeric membrane and makes such membranes suitable for the preparation of membranes with anti-fouling properties.

- The membrane obtained from dipyridyl functionalized polysulfone with the higher degree of substitution exhibits enhanced membrane morphological characteristics, higher water permeate flux and better structural integrity as determined by atomic force microscopy and scanning electron microscopy analysis.
- The dipyridyl functionalized polysulfones are thermally less stable than the parent polysulfone. The glass transition temperatures of the modified polysulfones with the pendant dipyridyl groups decrease with higher substitution because of increased chain mobility.
- Aromatic carboxyl functionalized polystyrenes with well-defined structures were prepared in quantitative yields by atom transfer radical polymerization methods by the α-bromo-p-toluic acid initiated polymerization of styrene in the presence of copper (I) bromide and 2,2'-dipyridyl as catalyst system.
- Tertiary-amine functionalized polystyrene was prepared in quantitative yields by atom transfer radical polymerization methods. In a one-pot synthesis method and by using the adduct of 1-(bromoethyl)benzene with 1-(4-dimethylamino- phenyl)-1-phenylethylene as initiator, the polymerization of styrene in the presence of a copper (I) bromide/2,2'-bipyridyl catalyst system proceeded via a controlled free radical polymerization process to afford the corresponding tertiary amine functionalized polystyrene with well-defined polymer structure. All experimental evidence is consistent with quantitative functionalization via the 1,1-diphenylethylene derivative.
- Primary amine functionalized polystyrenes with good control of polymer parameters such as number average molecular weights, narrow molecular weight distributions and chain functionalities were prepared in quantitative yields by atom transfer radical polymerization. In a one-pot synthesis, the adduct of 1-(bromoethyl)benzene with 1-(4-aminophenyl)-1-phenylethylene was used as initiator for styrene polymerization in the presence of a copper (I) bromide/N, N,N=, N=,N=>-pentamethyldiethylenetriamine catalyst system with good control of the polymerization process and initiator efficiencies as high as 0.92.
- Siloxyl and hydroxyl functionalized polymers were synthesized in quantitative yields by atom transfer radical polymerization using 1,1-diphenylethylene derivatives as initiator precursors. Siloxyl functionalized polystyrenes were prepared by a one pot synthesis method using the adduct of 1-(bromoethyl)- benzene with 1-(4-t-butyldimethylsiloxyphenyl)-1-phenylethylene as initiator system for polymerization of styrene in the presence of a copper (I) bromide/2,2'-bipyridyl or copper (I) bromide/ N,N,N=,N=,N@-pentamethyldimethyltriamine (PMDETA) catalyst complexes.

- Acid catalyzed hydrolysis of siloxyl functionalized polystyrene with concentrated hydrochloric acid produced the corresponding hydroxyl functionalized polystyrene.

- The results show that functionalization of polysulfone by ATRP methods is possible using the benzyl brominated polysulfone as macroinitiator and functionalized 1,1-diphenylethylene derivatives as functionalizing agents.

9.3 Research Outputs and Technology Transfer

9.3.1 Patents

APreparation of Functionalized Polysulfones@, G.J. Summers, RSA Patent 98/8525, 30 June 1999

9.3.2 Publications in peer reviewed journals

- ASynthesis of Aromatic Carboxyl Functionalized Polymers by Atom Transfer Radical Polymerization@, Summers, G.J., Beebeejaun, M.P. and Summers, C.A., Polymer Intl, 49, 1722, (2000),

- AChemical Modification of Polysulfone: Anionic Synthesis of Dipyridyl Functionalized Polysulfone@, Summers, G.J., Ndawuni, M.P. and Summers, C.A., Polymer, 42, 397, (2001).

- ATertiary Amine Functionalized Polymers by Atom Transfer Radical Polymerization@, Summers, G.J., Ndawuni, M.P. and Summers, C.A., J. Polym. Sci. Polym. Chem. Ed., 39, 2058, (2001).

- APrimary Amine Functionalized Polymers by Atom Transfer Radical Polymerization@, Summers, G.J., Ndawuni, M.P. and Summers, C.A., Polym. Intl., 52, 158 (2003).

- AHydroxyl and Siloxyl Functionalized Polymers by Atom Transfer Radical Polymerization@, Summers, G.J., Mputumana, N.A, and Summers, C.A., J. Polym. Sci. Polym. Chem. Ed., 00, 0000, (2003) in press.

- ADipyridyl Functionalized Polymers for Membrane Production@, Summers, G.J., M.P. Ndawuni, Summers, C.A., J. Membrane Sci., 226, Issue 1-2, 21-33 (2003).

9.3.3 Publications in preparation

- AAromatic Oxazoline Functionalized Polymers by Atom Transfer Radical Polymerization@, Summers, G.J., Beebeejaun, M.P. and Summers, C.A., Polymer Intl, (2003).

- ADiamine Functionalized Polymers by Atom Transfer Radical Polymerization@, Summers, G.J., Ndawuni, M.P. and Summers, C.A., Polymer, (2003).

- ADihydroxyl and Disiloxyl Functionalized Polymers by Atom Transfer Radical Polymerization@, Summers, G.J., Mputumana, N.A, and Summers, C.A., J. Polym. Sci. Polym. Chem. Ed., (2003).

9.3.4 Peer reviewed conference proceedings

- **ARecent Advances in the Synthesis of Functionalized Polymers by Atom Transfer Radical Polymerization@**, European Polymer Federation, Europolymer Congress, EPF03, Stockholm, Sweden, 23-27 June 2003.

- **ADipyridyl Functionalized Polymers for Membrane Production@**, IUPAC World Polymer Congress,39th International Symposium on Macromolecules, Beijing, China, 7-14 July 2002.

- **ADisiloxyl and Dihydroxyl Functionalized Polymers by Atom Transfer Radical Polymerization@**, IUPAC World Polymer Congress,39th International Symposium on Macromolecules, Beijing, China, 7-14 July 2002.

- **Primary Diamine Functionalized Polymers by Atom Transfer Radical Polymerization@**, IUPAC World Polymer Congress,39th International Symposium on Macromolecules, Beijing, China, 7-14 July 2002.

- **AFunctionalized Polymers by Atom Transfer Radical Polymerization@** 4th IUPAC Conference on Macromolecules and Material Science, University of Stellenbosch, South Africa, 9-11 April 2001.

- **ASiloxyl and Hydroxyl Functionalized Polymers by Atom Transfer Radical Polymerization@**, SACI 2000, 35th Convention of the South African Chemical Institute, Potchefstroom, RSA, September 2000.

- **AFunctionalized Polymers by Atom Transfer Radical Polymerization@**, SACI 2000, 35th Convention of the South African Chemical Institute, Potchefstroom, S.A., September 2000.

- **"Siloxyl and Hydroxyl Functionalized Polymers by Atom Transfer Radical Polymerization"**, World Polymer Congress, IUPAC 38th International Symposium on Macromolecules, Warsaw, Poland July 2000.
- **"Aromatic Carboxyl Functionalized Polymers by Atom Transfer Radical Polymerization"**, 7th Frank Warren Conference on Organic Chemistry, Aventura Spa, Warmbaths, 16-19 January 2000.
- **"Tertiary Amine Functionalized Polymers by Atom Transfer Radical Polymerization"**, 7th Frank Warren Conference on Organic Chemistry, Aventura Spa, Warmbaths, 16-19 January 2000.
- **"Macromolecular Engineering by Anionic and Controlled Radical Polymerization"**, NRF-CNRS Workshop, Centre National de la Recherche Scientifique, Strasbourg, France, 14-20 November 1999.
- **"Aromatic Carboxyl Functionalized Polymers by Atom Transfer Radical Polymerization"**, World Polymer Congress, IUPAC 37th International Symposium on Macromolecules, Gold Coast, Australia, 12-17 July 1998.
- **"Macromonomer Synthesis by Atom Transfer Radical Polymerization"**, World Polymer Congress, IUPAC 37th *International Symposium on* Macromolecules, Gold Coast, Australia, 12-17 July 1998.
- **"Functionalized Polymers by Atom Transfer Radical Polymerization"**, 34th Convention of the South African Chemical Institute and the 7th International Chemistry Conference in Africa, University of Natal, Durban, 7-10 July 1998.
- **"Chemical Modification of Polysulphone: The introduction of Functionalized Diaryl Pendant Groups onto Polysulphone"**, IP '97, IUPAC International Symposium on Ionic Polymerization, Universite Pierre et Marie Curie, Paris, France, 7-11 July 1997.
- **"Chemical Modification of Polysulphone: The introduction of Diaryl Pendant Groups onto Polysulphone"**, APolymers: Europe@, ACS Gordon Conference, Chantilly, France, 29 June-4 July 1997.

"Synthesis, Characterization, Gas and Liquid Separation Properties of Pyridine Functionalized Polysulphone Membranes", SACI, 6th Frank Warren Conference on Organic Chemistry, Mtunzini Chalets and Conference Center, KwaZulu-Natal, 29 June-3 July 1997.

"Synthesis, Characterization, Gas and Liquid Separation Properties of Diaryl Functionalized Polysulphone Membranes", Euromembrane 97, AProgress in Membrane Science and Technology@, Third International Symposium, University of Twente, The Netherlands, 23-27 June 1997.

- **"Designed Functionalized Polymers by Anionic Macromolecular Engineering for Membrane Production"**, Polycondensation '96, International Symposium on Polycondensation, Related Processes and Materials, Paris, France, 23-26 September 1996.
- **"Functionalization of Polysulphone by lithiation reactions with substituted 1,1-diphenylethylenes"**, MacroSeoul, IUPAC 36th International Symposium on Macromolecules, Seoul, Korea, 4-9 August 1996
- **"Designed Functionalized Polymers by Anionic Macromolecular Engineering"**, 33rd Convention of the South African Chemical Institute, University of Cape Town, Cape Town, 28 January-2 February 1996.

9.3.5 Graduate Student Training

Research and human resources development activities centred on post-graduate student training in Chemistry at the University of South Africa, with the area of specialization in polymer chemistry. The following students were associated with the Water Research Commission Project K5/723

Thesis

- **"Amine Functionalized Polymers by Anionic and Controlled Radical Polymerization Methods@**, M. Patrick Ndawuni, graduated with the MSc degree, cum laude, May 2000.
- **"Aromatic Carboxyl Functionalized Polymers by Atom Transfer Radical Polymerization@**, BM Parveen Beebeejaun, graduated with the MSc degree, cum laude, May 2000.
- **ASiloxy and Hydroxyl Functionalized Polymers by Atom Transfer Radical Polymerization@**, Nomfusi A Mputumana, MSc, December 2003.
- **AFunctionalized Polymers by Atom Transfer Radical Polymerization@**, M Patrick Ndawuni, PhD, June 2000-June 2004.

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