

## TABLE OF CONTENTS

|                         |      |
|-------------------------|------|
| EXECUTIVE SUMMARY ..... | ii   |
| ACKNOWLEDGEMENTS .....  | viii |
| TABLE OF CONTENTS ..... | x    |
| LIST OF FIGURES .....   | xvi  |
| LIST OF TABLES .....    | xix  |

## CHAPTER 1

### LITERATURE REVIEW

|   |   |
|---|---|
| 1.1 Introduction .....  | 1 |
| 1.2 Chemical Modification of Polysulfone .....  | 1 |
| 1.3 Chemical Modification of Polysulfone by Living Controlled Free Radical Polymerization Methods .....   | 3 |
| 1.3.1 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization : Carboxylation .....   | 3 |
| 1.3.2 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry .....  | 4 |
| 1.3.2.1 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry : Tertiary Amine Functionalized Polymers .....       | 5 |
| 1.3.2.2 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry : Primary Amine Functionalized Polymers .....        | 5 |
| 1.3.2.3 Chain End Functionalized Polymers by Atom Transfer Radical Polymerization using 1,1-Diphenylethylene Chemistry : Siloxyl and Hydroxyl Functionalized Polymers ..... | 6 |
| 1.3.3 Synthesis of Polysulfone-g-polystyrene by Atom Transfer Radical Polymerization .....  | 7 |

## CHAPTER 2

### CHEMICAL MODIFICATION OF POLYSULFONE : ANIONIC SYNTHESIS OF DIPYRIDYL FUNCTIONALIZED POLYSULFONE

|   |    |
|---|----|
| 2.1 Abstract .....  | 8  |
| 2.2 Introduction .....  | 8  |
| 2.3 Synthesis of 2,2'-vinylidenedipyridine (2) .....  | 8  |
| 2.4 Functionalization of Polysulfone with 2,2'-Vinylidenedipyridine –<br>Synthesis of Dipyrindyl Functionalized Polysulfone .....             | 9  |
| 2.5 Quaternization of dipyrindyl functionalized polysulfone (3) : Synthesis<br>of pyridinium perchlorate functionalized polysulfone (4) ..... | 11 |
| 2.6 Chelation of heavy metals by polysulfone (1) and dipyrindyl<br>functionalized polysulfone (3) .....                                       | 11 |
| 2.7 Conclusions .....   | 12 |

## CHAPTER 3

### FUNCTIONALIZED POLYSULFONE BY LIVING ANIONIC POLYMERIZATION : DIPYRIDYL FUNCTIONALIZED POLYSULFONES FOR MEMBRANE PRODUCTION

|  |    |
|--|----|
| 3.1 Abstract .....   | 14 |
| 3.2 Introduction .....   | 14 |
| 3.3 Synthesis of 2,2'-vinylidenedipyridine (2) .....   | 15 |
| 3.4 Functionalization of Polysulfone with 2,2'-Vinylidenedipyridine :<br>Synthesis of Dipyrindyl Functionalized Polysulfone, PFPS-80 ..... | 15 |
| 3.5 Atomic Force Microscopy (AFM) .....  | 17 |
| 3.6 Flux Measurements .....  | 20 |
| 3.7 Membrane Morphology .....  | 21 |
| 3.8 Contact Angle Tests .....  | 25 |
| 3.9 Thermal Analysis .....   | 25 |
| 3.10 Electrochemistry .....  | 27 |

|                        |    |
|------------------------|----|
| 3.11 Conclusions ..... | 28 |
|------------------------|----|

## 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 .....  | 29 |
| 4.2 Introduction .....  | 29 |
| 4.3 Atom Transfer Radical Polymerization of Styrene Initiated by $\alpha$ -Bromo- $p$ -toluic acid in Diphenyl ether : Synthesis of Carboxyl Functionalized Polystyrene ..... | 30 |
| 4.4 Polymerization Kinetics : Atom Transfer Radical Polymerization of Styrene initiated by $\alpha$ -Bromo- $p$ -toluic acid .....  | 33 |
| 4.5 Conclusions .....   | 37 |

## CHAPTER 5

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

|  |    |
|--|----|
| 5.1 Abstract .....   | 38 |
| 5.2 Introduction .....   | 38 |
| 5.3 The Synthesis of Tertiary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization .....                           | 39 |
| 5.4 Polymerization Kinetics : The Synthesis of Tertiary Amine Functionalized Polystyrene by Atom Transfer Radical Polymerization ..... | 43 |
| 5.5 Conclusions .....  | 46 |

## CHAPTER 6

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

|   |    |
|---|----|
| 6.1 Abstract .....  | 47 |
| 6.2 Introduction .....  | 47 |
| 6.3 The Synthesis of Primary Amine Functionalized Polystyrene by<br>Atom Transfer Radical Polymerization .....                              | 48 |
| 6.4 Polymerization Kinetics : The Synthesis of Primary Amine<br>Functionalized Polystyrene by Atom Transfer Radical<br>Polymerization ..... | 51 |
| 6.5 Conclusions .....   | 54 |

## CHAPTER 7

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

|  |    |
|--|----|
| 7.1 Abstract .....   | 55 |
| 7.2 Introduction .....   | 55 |
| 7.3 The Synthesis of Siloxyl and Hydroxyl Functionalized Polystyrene<br>by Atom Transfer Radical Polymerization .....                              | 56 |
| 7.4 Hydrolysis of Siloxyl Functionalized Polystyrene : Preparation of<br>Hydroxyl Functionalized Polystyrene .....                                 | 58 |
| 7.5 Polymerization Kinetics : The Synthesis of Siloxyl and Hydroxyl<br>Functionalized Polystyrene by Atom Transfer Radical<br>Polymerization ..... | 59 |
| 7.5.1 Atom Transfer Radical Polymerization of Styrene in the presence<br>of CuBr/bpy catalyst .....  | 59 |
| 7.5.2 Atom Transfer Radical Polymerization of Styrene in the presence of<br>CuBr/PMDETA catalyst .....   | 62 |
| 7.6 Conclusions .....  | 62 |

## CHAPTER 8

### EXPERIMENTAL

|   |    |
|---|----|
| 8.1 General .....   | 67 |
| 8.1.1 Materials .....   | 67 |
| 8.1.2 Materials Characterization .....  | 67 |
| 8.2 Experimental Procedures .....   | 68 |
| 8.2.1 The Synthesis of 2,2'-Vinylidenedipyridine : Method 1 .....   | 68 |
| 8.2.2 The Synthesis of 2,2'-Vinylidenedipyridine : Method 2 .....   | 69 |
| 8.2.3 The Synthesis of Dipyridyl Functionalized Polysulfone [PFPS-45] .   | 69 |
| 8.2.4 The Synthesis of Dipyridyl Functionalized Polysulfones [PFPS-80].   | 70 |
| 8.2.5 Quaternization of Dipyridyl Functionalized Polysulfone .....  | 70 |
| 8.2.6 Evaluation of Chelation Efficiency of Dipyridyl Functionalized<br>Polysulfone : Adsorption of Metal Ions to Polymers .....                  | 71 |
| 8.2.7 Atom Transfer Radical Polymerization of Styrene Initiated by<br>$\alpha$ -Bromo- $p$ -toluic acid .....                                     | 71 |
| 8.2.8 Polymerization Kinetics : Atom Transfer Radical Polymerization of<br>Styrene Initiated by $\alpha$ -Bromo- $p$ -toluic acid .....           | 71 |
| 8.2.9 Synthesis of Tertiary Amine Functionalized Polystyrene by Atom<br>Transfer Radical Polymerization .....                                     | 72 |
| 8.2.10 Polymerization Kinetics : Synthesis of Tertiary Amine Functionalized<br>Polystyrene by Atom Transfer Radical Polymerization .....          | 72 |
| 8.2.11 Synthesis of Primary Amine Functionalized Polystyrene by Atom<br>Transfer Radical Polymerization .....                                     | 73 |
| 8.2.12 Polymerization Kinetics : Synthesis of Primary Amine Functionalized<br>Polystyrene by Atom Transfer Radical Polymerization .....           | 73 |
| 8.2.13 Synthesis of Siloxyl and Hydroxyl Functionalized Polystyrene by<br>Atom Transfer Radical Polymerization .....                              | 74 |
| 8.2.14 Polymerization Kinetics : Synthesis of Siloxyl and Hydroxyl<br>Functionalized Polystyrene by Atom Transfer Radical<br>Polymerization ..... | 74 |

|                                     |    |
|-------------------------------------|----|
| 8.3 Membrane Preparation .....      | 75 |
| 8.4 Membrane Characterization ..... | 75 |

## CHAPTER 9

### CONCLUSIONS

|  |           |
|--|-----------|
| 9.1 Introduction .....                             | 77        |
| 9.2 Summary of results .....                       | 77        |
| 9.3 Research Outputs and Technology Transfer ..... | 79        |
| 9.3.1 Patents .....                                | 79        |
| 9.3.2 Publications in peer reviewed journals ..... | 79        |
| 9.3.3 Publications in preparation .....            | 80        |
| 9.3.4 Peer reviewed conference proceedings .....   | 80        |
| 9.3.5 Graduate Student Training .....              | 82        |
| <b>REFERENCES .....</b>                            | <b>83</b> |

## LIST OF FIGURES

- Figure 2.1** Synthesis of dipyridyl functionalized polysulfone (3) and pyridinium perchlorate functionalized polysulfone (4)
- Figure 2.2**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of dipyridyl functionalized polysulfone (3)
- Figure 2.3**  $^1\text{H}$  NMR (DMSO) spectrum of pyridinium perchlorate functionalized polysulfone (4)
- Figure 2.4** Plot of absorbance vs concentration for the trace metal analysis of heavy metals (II) ions in aqueous solution
- Figure 3.1** Synthesis of dipyridyl functionalized polysulfone PFPS-80
- Figure 3.2**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) spectrum of dipyridyl functionalized polysulfone, PFPS-80
- Figure 3.3** AFM micrographs of polysulfone membranes, PS, PFPS-45 and PFPS-80
- Figure 3.4** Plot of Pure Water Flux ( $\text{L}/\text{m}^2\text{h}$ ) versus Pressure (kPa)
- 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 3.8** TGA thermograms of different polysulfone samples, PS, PFPS-45 and PFPS -80
- Figure 4.1** Synthetic pathway for the  $\alpha$ -bromo-p-toluic acid initiated polymerization of styrene in the presence of  $\text{CuBr}/\text{bpy}$  catalyst in diphenyl ether.
- Figure 4.2** Size exclusion chromatogram of aromatic carboxyl functionalized polystyrene

- Figure 4.3**  $^{13}\text{C}$  NMR spectrum of aromatic carboxyl functionalized polystyrene
- Figure 4.4** Plot of percentage monomer conversion versus time for the  $\alpha$ -bromo-p-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 130°C
- 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  $\alpha$ -bromo-p-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 130°C
- Figure 4.6** First-order kinetic plots for the  $\alpha$ -bromo-p-toluic acid initiated polymerization of styrene in the presence of CuBr/bpy catalyst in diphenylether at 130°C
- Figure 5.1** Synthetic pathway for the preparation of tertiary amine functionalized polymers
- Figure 5.2** Size exclusion chromatograph of tertiary amine functionalized polymer
- Figure 5.3**  $^1\text{H}$  NMR spectrum of tertiary amine functionalized polymer
- Figure 5.4** Plot of the percentage monomer conversion versus time data for the preparation of tertiary amine functionalized polymers at 130°C
- 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
- Figure 5.6** First-order kinetic plots for the preparation of tertiary amine functionalized polymers at 130°C
- Figure 6.1** Synthetic pathway for the preparation of primary amine functionalized polystyrene
- Figure 6.2** Size exclusion chromatogram of primary amine functionalized polystyrene
- Figure 6.3**  $^1\text{H}$  NMR spectrum of primary amine functionalized polystyrene

- Figure 6.4** Plot of percentage monomer conversion versus time for the preparation of primary amine functionalized polystyrene in diphenylether at 130°C
- Figure 6.5**  $M_n$  vs percentage monomer conversion and  $M_w/M_n$  vs percentage monomer conversion data for the preparation of primary amine functionalized polymers at 130°C
- Figure 6.6** First-order kinetic plots for the preparation of primary amine functionalized polymers at 130°C
- Figure 7.1** Synthetic pathway for the preparation of siloxyl and hydroxyl functionalized polystyrene
- 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
- 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
- Figure 7.4**  $M_n$  and  $M_w/M_n$  versus percentage monomer 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
- 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
- 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
- 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

## **LIST OF TABLES**

**Table 3.1** Contact angle measurement for different membranes

**Table 3.2** Glass transition temperature for the different polysulfone samples