

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-butyl dimethylsiloxyphenyl)-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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