SYNTHESIS, CHARACTERIZATION AND APPLICATION OF NANOPOROUS CYCLODEXTRIN POLYMERS

BY

MOKAE FANUEL BAMBO

Dissertation submitted in fulfilment of the requirement for the degree of Master of Technology in Chemistry in the Faculty of Science, Department of Chemical Technology, of the University of Johannesburg

APRIL 2007
I hereby declare that the work presented in this dissertation, apart from the recognized assistance of my supervisors, is my own work. It is being submitted for the degree of Master of Technology at the University of Johannesburg, Department of Chemical Technology and has not been submitted before for any degree or examination at any other university or college.

_________________________ on this _______ day of _________________
Mr. M. F. Bambo
(Candidate)

_________________________ on this _______ day of _________________
Dr. B. B. Mamba
(Supervisor)

_________________________ on this _______ day of _________________
Dr. R. W. M. Krause
(Co-Supervisor)

_________________________ on this _______ day of _________________
Dr. T. J. Malefetse
(Co-Supervisor)
DEDICATION

This work is dedicated to my late beloved grandparents;

Onicca & Geelbooi “Merekeng” Papo

Ditlou
ACKNOWLEDGEMENT

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Call to me and I will answer you and show you great and mighty things, which you do not know… Jeremiah 33:3
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GLOSSARY OF TERMS

\( \alpha \)-CD  Alpha Cyclodextrin
\( \beta \)-CD  Beta Cyclodextrin
\( \gamma \)-CD  Gamma Cyclodextrin
\( \lambda \)  Wavelength
AC  Activated Carbon
B.E.T  Brunauer, Emmet and Teller
S\( _{N2} \)  Bimolecular Nucleophilic Substitution
CBP’s  Chloro-biphenyls
CD(s)  Cyclodextrin(s)
d  Doublet
dd  Doublet of doublets
DBPs  Disinfection By-Products
DCM  Dichloromethane
DMF  \( N, N \)-Dimethyl formamide
DMSO  Dimethylsulfoxide
D6-DMSO  Deuterated DMSO
EC  European Community
EU  European Union
EtOAc  Ethyl acetate
FT-IR  Fourier transform-Infra red
GAC  Granular Activated Carbon
GC/MS  Gas Chromatography / Mass Spectroscopy
HMDI  Hexamethylene diisocyanate
mp  Melting point
mg/L  milligrams per litre
m  Multiplet
ND  Not Detected
NMR  Nuclear Magnetic Resonance
p-NP  \( p \)-Nitriphenol
PCD  Poly-Cyclodextrin
PAC  Powdered Activated Carbon
KBr  Potassium Bromide
POP  Priority Organic Pollutant
ppb  parts per billion
ppt  parts per trillion
SEM  Scanning Electron Microscopy
s  Singlet
SPE  Solid Phase Extraction
SDVB  Styrene divinylbenzene
t-BuMe₂Si  Tert-butyldimethylsilane
TEMPO  2, 2, 6, 6-tetramethylpiperindinyloxy
TDI  Toluene 2, 6-diisocyanate
TGA  Thermogravimetric Analysis
TLC  Thin Layer Chromatography
THMs  Trihalomethanes
t  Triplet
USEPA  United States Environmental Protection Agency
UV  Ultraviolet
ABSTRACT

The presence of organic contaminants in water has caused great concern over their potential adverse health impact on humans and animals. Organic contaminants found in water are both naturally occurring and synthetic.

Various chemical and physical water treatment processes are being used to remove organic contaminants. Conventional water treatment methods include the utilization of activated carbon for the removal of organic contaminants. It is generally conceded that activated carbon owes its adsorptive properties primarily to its large surface area, as well as to its pore size. Although activated carbon is nonselective against most of the water contaminants, it does not remove the concentration of organic contaminants to acceptable levels i.e. ppb. Moreover, activated carbon also absorbs moisture from the air and as a result loses its absorptive effectiveness. For this reason attention has been being given to alternative methods for water treatment especially for the removal of organic pollutants.

In this study, cyclodextrin polymers that were water insoluble were synthesized and tested for their ability to remove organic species in water.

Cyclodextrins (CDs) and their corresponding derivatives have been used in a wide range of applications including pharmaceutical and pesticide removal and catalysis. Cyclodextrins are cyclic oligosaccharides derived from enzyme degradation of starch. They are known as molecular hosts capable of including of forming inclusion complexes, with a degree of selectivity, with a range of guest molecules via a noncovalent interaction in their hydrophobic cavities. Although the interaction between cyclodextrin and an organic molecule is the basis for absorption or separation of various organic agents, the solubility of cyclodextrin in water and organic solvents impose limitations to the application of cyclodextrins
in water treatment. Therefore, polymerizing a cyclodextrin monomer with an excess of a bifunctional linker produces an insoluble polymer which can form inclusion complexes with guest molecules.

In this project, the synthesis of a number of cyclodextrin polymers was performed by reacting cyclodextrin with bifunctional linkers. Three methods were deployed in this study to achieve this objective as shown in Scheme 1.

Scheme 1: A general synthetic pathway for the polymerization of cyclodextrin and “host guest” phenomenon

The synthesized polymer materials were characterized using NMR and FT-IR spectroscopic techniques to determine their molecular structure. Some characteristic features of the polymers have been highlighted in the study. Further characterizations of the polymer materials were undertaken to elucidate their physical properties. BET analyses gave information with respect to the surface area and pore volume, which the SEM technique gave insight to surface morphology, TGA analysis employed for thermal stability showed that the polymers were stable over a wide temperature range (100-350 °C).
The application of the polymers to test their ability to absorb organic contaminants was demonstrated. Their degree of absorption was measured and quantified using UV-Visible spectroscopy and GC-Mass spectrometry.
CHAPTER ONE
INTRODUCTION AND STUDY PURPOSE

1.1 Background

Water is vital for the survival of all forms of life. Not only does water make up life forms but it is a commodity that is vital for human existence. In fact about 70% of the human body is made up of water.

However, water contamination is inevitable since natural resources; human activities and the advancement in technology tend to contribute towards water contamination. Pollutants compromise the quality of water thereby affecting the quality of available water for general usage.

Currently most water sources contain a large number of organic contaminants. As a result water contaminated by organic materials cannot be used directly for human consumption or industrial use without some form of treatment.

1.2 Organic compounds

Sources of organic contaminants are divided into three categories, namely:

- Naturally occurring organic materials (e.g. humic materials and microorganisms).
- Domestic and commercial compounds and
- Disinfection by-products such as trihalomethanes (THMs) that are produced during water treatment.
Examples of organics found in water supplies include chlorinated solvents such as trichloroethylene and tetrachloroethylene as well as aromatic compounds such as benzene, toluene and phenols.

Some of the organic contaminants are known to be Persistent Organic Pollutants (POP’s). They include a broad range of industrial chemicals that have been discharged to the environment. Petroleum hydrocarbons, volatile organic compounds (VOCs), polychlorinated biphenyls (PCBs), endocrine disrupting chemicals (EDCs), and phenolic compounds are some of the known examples of POPs.\(^{(a)}\) They resist degradation by any process—physical, biological or even chemical. By being persistent, these compounds accumulate in biological systems. Organic contaminants are also known to be present in very low concentration, thus making them difficult to remove by filtration methods.

Sources of organic contaminants include leaking organic waste dumps, leaking gasoline storage tanks, landfills and accidental spills of chemicals on land. Other sources such as household chemicals and cosmetics (e.g. detergents and solvents) as well as pesticides sprayed on land are known.\(^{(b),(c)}\) Unlike inorganic metal ions, organic molecules do not bind to most polymeric resins or solidify into minerals.\(^{2}\)

Toxicological profiles of organic compounds have been established by health officials in order to regulate and provide reasonable guidelines in identifying the effects with respect to each or group of these compounds.\(^{3}\) Some organic contaminants can be extremely toxic and this poses a threat to human beings and the environment in general.

Water treatment technologies for the removal of inorganic compounds have been intensely studied. However, competitive methods for removing organic compounds are not always available. Several water treatment methods such as activated carbon have been widely used to remove organic contaminants from water. The shortcoming of activated carbon is that it cannot remove these contaminants to very low levels (ppb).
Activated carbon also tends to lose its absorbing capacity during the water treatment process. 4

Local authorities have imposed stringent regulations and laws with regard to contamination control and management. These laws put pressure on municipalities to remove organic molecules from water supplies to very low levels (at least ppb). In addition, many industries require ultra-pure water and this entails removing very low concentrations of impurities from their incoming water supply. For example, the semiconductor manufacturing industry recently identified the regeneration and recycling of ultra-pure water as critical to its future. 5 The search for new technologies that can economically ensure high quality water has thus been increased. Cyclodextrins have shown some ability to encapsulate organic molecules and have, as a result, found important applications in the removal of organic molecules from water. 6

Whereas parent cyclodextrins have shown some ability to remove organic molecules from water, they are soluble in water and some organic solvents and these properties restrict their usage. This problem is solved by polymerizing the parent cyclodextrins into water insoluble polymers called nanosponges, using compatible linkers.

The purpose of this study was, therefore, to firstly synthesize polymer materials of cyclodextrins using different linking monomers. Thereafter an investigation into the effect of the linkers on the absorptive capability of the polymer was carried out. This involved testing the ability of the new nanoporous polymers to absorb organic contaminants from water.

1.3 Project objectives

The aim of this project was, to prepare a series of nanoporous cyclodextrin-based polymers using novel linking monomers and study the ability of the newly prepared polymers to remove organic contaminants from water.
The research was carried out with the following specific objectives:

i. Synthesis of nanosponge polymeric materials using the β-cyclodextrin backbone and selected linkers such as diacid chlorides, halogenated hydrocarbons and epoxides. The goal here was to optimize the reaction conditions so as to scale up the synthesis of crosslinked polymers. Novel polymers with an enhanced ability to quench organic contaminants from water were generated,

ii. Characterization of the nanoporous polymers. This was achieved using instrumental techniques such as FT-IR and NMR spectroscopy. Structural morphologies of the polymers were determined using BET and SEM analysis. Also the thermal behaviour of the polymers were studied using TGA technique.

1.4 Outline of the dissertation

The succession of chapters to follow in this dissertation together with their contents is now laid out.

Chapter 2 introduces the cyclodextrin technology. Specifically, the discovery, properties and applications of cyclodextrins will be discussed. Current conventional technologies used for water treatment are also reviewed.

Chapter 3 outlines the methodology employed for the synthesis of the nanoporous cyclodextrin polymers. Analytical techniques used for the characterization of these polymers are also described.

In Chapter 4, detailed analyses of the results obtained as well as challenges encountered in the study are described.
The application of the synthesized cyclodextrin polymers is described in Chapter 5. Conclusions and recommendations are laid out in Chapter 6.
CHAPTER TWO

LITERATURE REVIEW

2.1 Introduction

Supramolecular chemistry has made a dramatic progress over the past years. Unlike molecular chemistry that is more concerned with covalent bonding of molecules, supramolecular chemistry is based on developing highly complex chemical systems from components interacting through noncovalent intermolecular forces. Supramolecular chemistry involves the use of host molecules. Cyclodextrins (CD) have been at the heart of supramolecular chemistry as “host molecules” forming inclusion complexes with a range of molecules. Since their discovery, cyclodextrins have attracted increasing attention in many fields of studies. In this chapter cyclodextrins, cyclodextrin derivatives and some of their properties are reviewed. Their application, particularly in the absorption of organic molecules in water, is discussed. Other available water treatment methods aimed at the removal of organic compounds will also be reviewed.

2.2 The Cyclodextrin Technology

2.2.1 What are Cyclodextrins?

Different names have been used to refer to cyclodextrins. These include Schardinger dextrins, cycloamyloses and cycloglucans; cyclodextrins is the most common name. Cyclodextrins are composed of a number of glucopyranose units attached by α-(1-4)-linkages. The glucopyranose units are designated by Greek letters to denote the number of glucose units; α representing 6 glucose units, β for 7 and γ for 8 glucose units. Cyclodextrins that contain 9 to 100 glucose units are known, however, the most commonly studied cyclodextrins are those of α-, β- and γ-cyclodextrins (Figure 2.1). The
structures of α- and β-CD were unknown until 1942 when they were characterized by X-ray crystallography. The structure of γ-cyclodextrin was elucidated much later in 1948.\textsuperscript{6a}

2.2.2 The discovery and production of Cyclodextrins

Cyclodextrins were first recorded by Villiers\textsuperscript{6a} in 1891. He first named this product "cellulosine", which he isolated from a crystalline substance. Its composition was found to be \((C_6H_{10}O_5)_\gamma \cdot 3H_2O\) because it represented cellulose in its resistance against acidic hydrolysis and it also displayed reducing properties. Even after isolation it was discovered that two distinct cellulose units were formed, which were related to α- and β-CDs.

Later Schardinger\textsuperscript{6b} reported that digestion of starch with a microorganism resulted in the formation of small amounts of two different crystalline products that seemed to be identical to Villiers cellulosine. It is through the work of Schardinger that a detailed description of cyclodextrins preparation and isolation was made.
According to Szejtli\textsuperscript{7} cyclodextrin production consists of two phases, the cyclodextrin-transglycosylase enzyme (CTG-enzyme) is produced by \textit{Bacillus macerans}. The cell-free filtrate of the culture media contains the crude enzyme which has to be concentrated and purified. Treatment of a partially pre-hydrolyzed starch with this enzyme gives a mixture of \(\alpha\)-, \(\beta\)- and \(\gamma\)-cyclodextrin together with a series of linear dextrins. Cyclic and linear products of enzymatic degradation of starch then have to be separated, for this purpose a different procedure is used. Separation of the mixture can be achieved by the addition of an appropriate organic solvent. This process results in the precipitation of the mixed crystalline complexes of the solvent, while linear dextrins remain in the mother liquor. After filtration, the crystalline complexes are decomposed by steam distillation, which removes the included organic solvent. The mixture of cyclodextrins is then fractionated by repeated dissolution and reprecipitation with different complex-forming organic substances, which selectively form crystalline complexes either with \(\alpha\)-, \(\beta\)- and \(\gamma\)-cyclodextrin.

Alternative processes for the isolation of cyclodextrins from the conversion mixture utilize glucoamylases. These enzymes convert linear dextrins to glucose, and cyclodextrins which are then obtained due to their lower solubility by direct crystallization. While such a process avoids the use of organic solvents, it encounters the drawback that only a certain amount of the \(\beta\)-cyclodextrin formed is separated as a crystalline substance, the rest remains in the mother liquor together with the much more soluble \(\alpha\)- and \(\gamma\)-cyclodextrin. Current use of selective amylase produce \(\alpha\)-, \(\beta\)-, or \(\gamma\)-cyclodextrins.

2.2.3 Properties of Cyclodextrins

An important structural feature to notice in these compounds is their toroidal shape with a well defined cylindrical cone defining a cavity of about 8 Å deep and 5-10 Å in diameter, depending on the number of glucose units. The cyclodextrin ring contains primary hydroxyl groups lying on the narrow end of the cone and the secondary
hydroxyls on the wider side making their extension hydrophilic, with cavities that are rather hydrophobic (Figure 2.2).

The latter features play a role in the trapping of organic molecules (hydrophobic) of different sizes into their cavities and have been exploited for applications such as chemical processing agents, chromatographic separations and the pharmaceutical industry.8
The table below (Table 2.1) summarizes important physical properties of α-, β- and γ-cyclodextrins.

**Table 2.1 Physical properties and molecular dimension of cyclodextrins**

<table>
<thead>
<tr>
<th>Property</th>
<th>α-cyclodextrin</th>
<th>β-cyclodextrin</th>
<th>γ-cyclodextrin</th>
</tr>
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<tr>
<td>Number of glucose units</td>
<td>6</td>
<td>7</td>
<td>8</td>
</tr>
<tr>
<td>Molecular weight (g/mol)</td>
<td>972</td>
<td>1,135</td>
<td>1,297</td>
</tr>
<tr>
<td>Water solubility (g/100 cm³) at 25°C</td>
<td>14.5</td>
<td>1.85</td>
<td>23.2</td>
</tr>
<tr>
<td>Internal diameter (Å)</td>
<td>4.9</td>
<td>6.2</td>
<td>7.9</td>
</tr>
<tr>
<td>External diameter (Å)</td>
<td>14.6</td>
<td>15.4</td>
<td>17.5</td>
</tr>
<tr>
<td>Height cone (Å)</td>
<td>7.9</td>
<td>7.9</td>
<td>7.9</td>
</tr>
<tr>
<td>Cavity volume (Å)</td>
<td>176</td>
<td>346</td>
<td>510</td>
</tr>
</tbody>
</table>

### 2.2.4 Host-Guest interaction of Cyclodextrins

Cyclodextrin can form inclusion compounds in solution as well as crystalline clathrates with a large variety of molecules, and exhibit size specificity in binding organic compounds. They are known as molecular hosts capable of including, with a degree of selectivity, a range of guest molecules via a non-covalent interaction in their hydrophobic cavities. This phenomenon is known as “host-guest” interaction (**Figure 2.3**).
Although the interaction between cyclodextrins and organic molecules has been used as a basis for absorption or separation of various organic agents, the solubility of these cyclodextrins in water and other organic solvents impose limitations to their application in such mediums.

Cyclodextrins can form inclusion complexes with low molecular weight compounds, both organic and inorganic. This has resulted in cyclodextrins being used in complexation with polymers. This type of complex formation was first reported by Harada and Kamachi in the early 1990s. It has since been recorded as a big breakthrough since such types of complexes are used widely in the biomedical field.

Many applications followed suit in exploiting the complexation of cyclodextrin with polymer materials. As a result, highly branched polymers have been used to covalently bind modifiers with cyclodextrins. Zhu et al. investigated crystalline inclusion complexes of cyclodextrins with a polyether. It is from this work that the discovery was made on the covalent intermolecular forces between cyclodextrins and polymers that play a vital role in the formation of complex architectures. Ogoshi and Chujo exploited the host-guest interaction ability of cyclodextrin to synthesize organic-inorganic polymer hybrids. In this work the cyclodextrin was used as a compatibilizer between an organic polymer and silica gel.
A glucoconjugated polymer was prepared with a high degree of control over the arm of the star polymer and introduction of functional groups to the polymer with seven arms via 2,2,6,6-tetramethylpiperindinyloxy (TEMPO) mediated radical polymerization using a multifunctional initiator based on β-cyclodextrin. \(^{13}\) β-Cyclodextrin was a suitable core-molecule since it is known to be a well defined cyclic molecule with multiple hydroxyl groups. Other star polymers having the cyclodextrin core were synthesized through the atom transfer radical polymerization technique.

Polyaniline conducting redox polymers are known for their applications in, amongst others, lithium batteries, electrochromic devices and electrochemical super capacitor material. Highly oxidized conducting polymers are prone to nucleophilic degradation by water and other nucleophiles that readily attack and become incorporated into the oxidized polyaniline. Zheng et al.\(^ {14}\) prepared β-CD modified poly (N-acetylaniline) film electrodes by oxidation of the film in a β-CD solution. β-CD acts as a nucleophile that is attached to the backbone of the film.

### 2.2.5 Cyclodextrin modifications

Several reviews on the chemical modification of cyclodextrin to effect the introduction of functional groups onto the cyclodextrin backbone by different chemical mechanisms have been reported.\(^ {15}\) Modification of cyclodextrins offers both enormous opportunities and challenges for chemists. Considerable efforts have been devoted to the design and synthesis of novel cyclodextrin derivatives with functional substituents that are of scientific and technological importance.\(^ {16}\) Chemically modified cyclodextrin are synthesized for a variety of reasons, depending on the use of the final compound; they can be modified in order to vary their solubility behaviour, to change their complexation properties, or to introduce certain specific functional groups.\(^ {17,18}\)
D’Souza et. al.\textsuperscript{19} suggested methods for modification of cyclodextrin in which they categorized them according to the product of interest. The methods were categorized as follows:

1. The “clever” method: this method uses the chemistry of cyclodextrin to get to the final product by the shortest possible route.

2. The “long” method: here a series of protection and deprotection step take place in order to selectively reach the desired position, which would otherwise not be selectively accessible.

3. The “sledgehammer” method: in this method the cyclodextrin is indiscriminately reacted to give a mixture of products and then the desired product is painstakingly separated out from other products and homologues by chromatographic methods.

Some primary factors need to be taken into consideration in the chemistry of cyclodextrins during their modification; the nucleophilicity of the hydroxyl groups and the ability of cyclodextrins to form complexes with the reagents used. Modifications take place at the hydroxyl groups. Since hydroxyl group are nucleophilic in nature, the initial reaction, which directs the regioselectivity and the extent of modification of all subsequent reactions, is an electrophilic attack on these positions.

Of all the hydroxyl groups of cyclodextrin, those at position-6 are known to be the most basic (most nucleophilic), and those at position-2 are most acidic while those at position-3 are the most inaccessible (see Figure 2.4).
2.2.5.1 Primary alcohol modifications

Among many modifications, Boger et. al.\textsuperscript{20} described two efficient methods for the selective modification of all six primary hydroxyl groups of \(\alpha\)-cyclodextrin. An indirect strategy, which involves protection of all 18 hydroxyl functions as benzoate esters followed by selective deprotection of the six primary alcohol groups, was employed. The other method uses a direct strategy that involves selective activation of the primary hydroxyl groups via a bulky triphenylphosphonium salt, which is then substituted by azide anion as the reaction proceeds.

The efficient synthesis of \(\beta\)-cyclodextrin derivatives that are fully substituted on their primary faces with amino acids L-phenylalanine and L-cysteine have been reported.\textsuperscript{21} Regioselective bifunctionalization on the secondary face of cyclodextrin has been previously proven difficult to accomplish.

2.2.5.2 Secondary alcohol modifications

A convenient method for functionalization of the C-2 position of cyclodextrins involving deprotonation by sodium hydride followed by a nucleophilic attack of the resultant cyclodextrin oxyanion on the desired electrophile, which gives a high yield of the
cyclodextrin derivative, was proposed.\textsuperscript{22} In this way, monosubstituted cyclodextrins (R-CD: R = Me, Et, etc.) have been synthesized.

Preparation of monofunctionalized cyclodextrin continues to be of much interest in several areas of science and technology.\textsuperscript{23} Krois \textit{et. al.}\textsuperscript{24} have successfully monofunctionalized \(\alpha\)-cyclodextrin in the solid state. This was accomplished by the insertion of photochemically generated carbenes, a reaction that takes place chemospecifically at the cyclodextrin’s C3-OH and C2-OH bonds in 39 and 18\% yields, respectively. This model reaction surpasses conventional methods in terms of yield as well as selectivity.

Recently, regiospecific monofunctionalization and polyfunctionalization on the secondary hydroxyl groups of cyclodextrin has been reported.\textsuperscript{25} Tosylation of cyclodextrin compounds has proved to be an important method since it serves as an intermediate for other synthesis of many chemically modified cyclodextrin compounds. Regiospecific mono-tosylation of cyclodextrin has been reported and its mechanism was suggested.\textsuperscript{26} Zhang \textit{et. al.}\textsuperscript{27} achieved the formation of amphiphilic cyclodextrin by hydrophobic esterification at the C2-OH and C3-OH positions of \(\beta\)-cyclodextrin in high overall yield \textit{via} protection by the \(t\)-BuMe\textsubscript{2}Si- group at the C6-OH position and the use of dimethylaminopyridine as an acylation catalyst. These types of molecules are interesting candidates for the trans-membrane transport of biologically active molecules.

\textbf{2.2.5.3 Alcohol multi-modifications}

Selective functionalization of the primary and the secondary hydroxyl groups is complicated by statistical and steric problems. Several strategies have been developed to selectively functionalize either all the primary hydroxyl group or all the secondary groups, but the complexity of the problem is increased if control on the degree of functionalization (mono-, di-, etc) is desired.\textsuperscript{28}
If a highly water soluble cyclodextrin is required for application, then random conversion of hydroxyl groups to sulphate groups can be easily achieved and the product will have the desired solubility. Similarly, if a cyclodextrin with a high solubility in organic solvents is desired, hydroxyl groups are to be converted to silyl ethers in a random fashion.\textsuperscript{19}

Diverse methods for the selective and direct functionalization of the primary and C2-OH secondary hydroxyl groups individually in $\alpha$-, $\beta$- and $\gamma$-cyclodextrin has been explored.\textsuperscript{29} Extensive modifications of cyclodextrins have not only been concerned with influencing their solubilities but also modifying their binding behaviour. Cyclodextrin symmetrically substituted with amino acids have been exploited.\textsuperscript{30}

Other modified cyclodextrins containing nucleophilic or electrophilic substituents alter the behaviour of native cyclodextrin towards the guest molecule. Mono-bis and tris-cyclodextrins with phosphoryl tethers were synthesized and their thermodynamic behaviour was determined.\textsuperscript{31} Many derivatizations of cyclodextrin at the primary and secondary face have been reported.\textsuperscript{22}

2.2.6 Cyclodextrin polymers

When two or more cyclodextrins are covalently linked they are known as polymers. The cyclodextrins fixed into polymeric structures behave differently from their monomeric derivatives. Cyclodextrin polymers can be classified as one of two types; those that are soluble in water and those that are water insoluble. By varying the reaction conditions, either water soluble or insoluble polymers can often be obtained.

A considerable amount of work has been done using cyclodextrins to synthesize polyesters, polyurethanes and various other types of polymeric materials.\textsuperscript{18} Much of this work has been completed in the last 10-20 years with the majority of the work dealing with both native cyclodextrins and their derivatives.
A variety of polymers obtained by more exotic routes than simple polycondensation, radical or even suspension reactions of functionalities attached to cyclodextrin are known.\textsuperscript{13}

Girek \textit{et. al.}\textsuperscript{32} suggested two ways in which cyclodextrins can be polymerized, where one is to attach a cyclodextrin molecule as a pendant group on another polymer chain. Polymers with cyclodextrin pendants are usually prepared by radical polymerization of the functional cyclodextrin monomers such as acryloyl cyclodextrin. These monomers are further copolymerized with other compatible monomers such as acrylamide.

The second type of polymerization is to react cyclodextrin molecules with bifunctional agents. The commonly used agent is epichlorohydrin, which result in both water soluble and water insoluble polymers. Other agents such as dihalogenated hydrocarbons and dicarboxylic derivatives are also used. These nucleophilic substitution reactions with bifunctional agents usually occur under strong alkaline conditions in order to deprotonate the hydroxyl groups of the cyclodextrin.

### 2.2.6.1 Water soluble cyclodextrin polymers

Water soluble polymers have been the subject of many investigations. These polymers have a wide variety of potential applications such as controlling the release of a soluble substance across a membrane and partitioning of organic compounds in an aqueous two-phase system. As with other cyclodextrin-based compounds, the usefulness of these polymers lies mainly in their ability to form inclusion complexes with lipophilic guests. The polymeric form can increase the stability constant of the complexes.\textsuperscript{33}

Renard \textit{et. al.}\textsuperscript{34} have investigated the relationship between preparation conditions and properties of the water soluble cyclodextrin polymers. The polymers obtained were characterized by physicochemical measurements. The preparation was achieved by reacting $\beta$-cyclodextrin with epichlorohydrin in an alkaline medium by a two-step
procedure. Several reaction parameters were considered to develop the conditions of a reproducible synthesis. For example, the size of the reaction vessel, the speed of the stirrer and the volume of the reaction mixture were kept constant. These parameters have a strong influence on the preparation of water soluble β-cyclodextrin-epichlorohydrin polymers. Again, the use of lower mole ratio of epichlorohydrin/β-cyclodextrin gave water soluble polymers even for longer reaction times. It has been observed that at epichlorohydrin/β-cyclodextrin ratios greater than 7, insoluble polymers are usually formed.

Szejtli\textsuperscript{7} also gives conditions by which water soluble polymers are obtained namely short reaction times and lower concentrations of cyclodextrin. Monomeric fraction also has some remarkable solubilizing effect, where the cyclodextrin monomer with low molecular weight is water soluble with respect to higher molecular weight compounds.

It has been observed that some water soluble cyclodextrin polymers have higher solubility in aqueous solutions than their parent cyclodextrins. The main applications of these polymers are related to chromatographic techniques (e.g. thin layer and liquid chromatography).\textsuperscript{34}

2.2.6.2 Water insoluble cyclodextrin polymers

Although water-insoluble polymers have not been extensively investigated, some examples are known. Insoluble products can often be obtained by increasing the ratio of cyclodextrin/crosslinking agent in the polymerization process. These types of polymers usually have a high water sorption capability that tends to make them swell in an aqueous medium. Polymers that are insoluble can either be crosslinked or linear.

One example of this class of polymer is the polyurethanes. Polyurethane resins containing cyclodextrin units as specific sorption sites were prepared by crosslinking β-cyclodextrin with diisocyanates.\textsuperscript{35}
2.2.6.3 Applications of cyclodextrin polymers

Polymers of cyclodextrin have very diverse applications, some of which have been highlighted in the previous sections. Sebille et al.\textsuperscript{36} reported on the properties of chemically modified cationic β-cyclodextrin-epichlorohydrin polymer as a chiral support. The polymer was used in liquid chromatography for enatioselective separations.\textsuperscript{37}

In food, the epichlorohydrin polymer of cyclodextrin plays a major role. Wilson et al.\textsuperscript{38} used β-cyclodextrin-epichlorohydrin polymer to reduce the bitterness components in grape fruit and navel orange juices in a fluidized bed process. These polymers were compared with neutral XAD resins used under similar fluidized bed conditions. It was found that cyclodextrin polymers and XAD resins show effective debittering potential to acceptable levels.\textsuperscript{39}

Baille et al.\textsuperscript{40} prepared what they called poly-(β-cyclodextrin) (PCD) resins by crosslinking β-cyclodextrin with different amounts of epichlorohydrin in which some cyclodextrin hydroxyl groups were functionalized with alkyl quaternary ammonium groups. These polymers were used to bind several bile salts from phosphate buffer solutions. Aminated PCD resins have a higher binding capacity for bile salts. Jiang et al.\textsuperscript{8} prepared a β-cyclodextrin epichlorohydrin polymer functionalized it with 1-(2-pyridylazo)-2-naphthol and used it for the determination of cobalt in foods.

Gao and Zhao\textsuperscript{42} synthesized a polymer by the supramolecular reaction of β-cyclodextrin crosslinking polymer with 1-(2-pyridylazo)-2-naphthol (PAN). The polymer was used to prepare electrorheological materials of an inclusive complex, named β-cyclodextrin-PAN polymer.

A porous tubular ceramic membrane impregnated with a β-cyclodextrin polymer used to obtain a chiral-selective membrane, was prepared by Krieg et al.\textsuperscript{41} This membrane was
evaluated in terms of the effectiveness of impregnation as well as the ability to separate the enantiomers of the racemic pharmaceutical chlorthalidone (Figure 2.5).

![Figure 2.5 Chlorthalidone structure](image)

Amiel and Sebille\textsuperscript{43} proposed a new class of heteropolymers, where the principle is to add a water soluble \(\beta\)-cyclodextrin polymer to an aqueous solution of an amphiphilic polymer. The added cyclodextrin polymer promotes the association between the amphiphilic polymers by forming inclusion complexes between the hydrophobic moieties and \(\beta\)-cyclodextrin cavities.

\subsection{2.2.6.4 Other cyclodextrin supramolecular architectures}

Attempts to design and synthesize molecular-level machines using cyclodextrins as a cyclic component have been described.\textsuperscript{44} Rotaxanes, catenanes and knot compounds are some prototypes used in this new synthetic methodology which might eventually be used to attain nanometer-scale structures. Rotaxanes are considered to be a typical prototype of molecular machines, because they have rotor and an axle in the molecule. \(\alpha\)-Cyclodextrin was first used as a rotor of rotaxane by Ogino and Ohta in 1978.\textsuperscript{45}

Armspach et. al.\textsuperscript{46} prepared catenanes containing cyclodextrin where one or two cyclodextrin are incorporated in a catenane structure. Mechanically interlocked
molecules are suitable candidates for the construction of molecular motors and machines.

2.3 Water treatment

The processes and technologies used to remove contaminants from water and to improve and protect water quality varies. The choice of which treatment method to use from the variety of available processes depends on the characteristics of the water, the types of water quality problems likely to be presented, and the cost of the different treatment techniques.

The most widely applied water treatment technologies can be a combination of some or most of the processes. Recent years have experienced a steady growth in the need for water purification methods. A broad range of applications and requirements for water quality has stimulated researchers to improve existing methods by investigating and developing new water purification technologies. Rapid interest in new water treatment methods is not only caused by advancements in technology, but also a need to protect the ecosystems.

2.3.1 Currently used technologies for the removal of organic pollutants

2.3.1.1 Activated Carbon (AC)

Several methods have been used with varying degrees of success to control contamination of water by organic compounds. However, the use of activated carbon is perhaps the best well known broad-spectrum technology available at present. As a consequence, the use of activated carbon in water treatment has increased throughout the world. It is generally conceded that activated carbon owes its adsorptive properties primarily to its very developed surface area, and its pore size. Its stability and ability to
withstand thermal regeneration and resistance to attrition losses during transport and handling are added benefits.\textsuperscript{50, 51}

The use of activated carbon for the treatment of municipal and industrial waters has developed rapidly in the last three decades. Activated carbon filtration is most effective in removing organic contaminants from water. Activated carbon is recognized by most water quality authorities as an acceptable method to maintain organic pollutants within required limits.\textsuperscript{1b} Different types of activated carbon (AC) are available for use in water treatment, namely powdered activated carbon (PAC) and granular activated carbon (GAC). The use of PAC in most modern water treatment plants processing surface water is a routine practice. The use of PAC in water treatment is more adaptable to applications where relatively low contaminant levels require less carbon. However, when continuous application of AC is required or in situations where the contaminants have low absorbability, the powder form may be more costly and may generate sludge disposal problems. The use of GAC absorption and filtration is recommended as the best available technology for removing a broad spectrum of organic contaminants from water.\textsuperscript{52}

In most water applications, the original cost of activated carbon adsorbents precludes usually its use on a throw-away basis. Thus, thermal reactivation of hard-coal-based carbon has been proven to be most efficient. Chemical regeneration is generally limited to applications where partial recovery of capacity is acceptable and regenerant disposal is not a problem.

Although activated carbon is nonselective against most of the water contaminants, it does not remove the concentration of organic contaminants to very low levels i.e. ppb levels.\textsuperscript{4} Also, it absorbs moisture from air and as a result loses its absorptive effectiveness.
2.3.1.2 Synthetic Ionic Resins

The potential use of wide range of synthetic adsorbents as alternative to activated carbon for removing organic contaminants from water has received considerable attention in recent years.

Synthetic ion exchange resins, for example, are termed macro-porous due to the large pore size distribution of between 25,000-250,000 Å, with a mean pore size of approximately 70,000 Å. The principles of removal of organic contaminants when using ionic functionality are similar to the adsorption techniques employed by activated carbon. This is mainly due to the similarities in pore structure and available surface area. The difference between the two media is that the ion exchange resin has some degree of ionic functionality. Many types of synthetic resins that differ both in the matrix that supports the functional groups themselves have been used for the removal of organic compounds. A few resins, called adsorbent resins, such as the styrene divinylbenzene (SDVB) resin and the phenol-formaldehyde have functional groups that make it possible for substances to be taken up by ion-exchange or by specific interaction with a specific functional group. In addition, the cross linking between the polymers that constitute the matrix can be varied and thus resins with different pore size distribution can be prepared.

The regeneration of the resins can easily be accomplished with acids, bases and organic solvents as well as hot gases or steam. Besides regenerability, synthetic polymer resins may have a number of other advantages such as selectivity, wide surface functionality, and physical and chemical stability.

Resins are therefore generally not used as adsorbents for water treatment. While they are more selective than activated carbon, they do not meet quality as adsorbents to be able to remove a wide variety of compounds. They may be applied in specific situations...
that require only a particular type of contaminant to be removed. However, they would fail to remove organic contaminants to ppb levels.

2.3.1.3 Zeolites and Molecular sieves

Zeolites are another type of adsorbent materials used for adsorbing organic pollutants. Zeolite can be called an archetype nanostructure (Figure 2.6). Consider a crystalline object offering high regular, ordered cages and channels of nanometer scale, with choice of one dimensional, two dimensional intersecting pores, and finally three-dimensional connected networks, similar to the architectures found in large buildings.

More than 90 different framework topologies and many more compositions are known, with pore sizes ranging from about 0.3-3 nm (3-30 Å), resulting in a vast range of different sorption properties, and internal surface properties ranging from hydrophilic to hydrophobic and from basic to acidic. Their micro-pore structures mimic the molecular size opening of protein folding, enzyme activity and molecular sieving. They have high surface area and well-defined porosity, but show little affinity for organic compounds.
Zeolites also absorb moisture from air and this decreases their absorptive effectiveness.4

Molecular sieves contain a network of uniform pores and empty cavities. They are non-toxic and insoluble in water and most organic solvents. Most often they are used as selective absorbents for both organic and inorganic materials. 55 Like activated carbon and zeolites, molecular sieves tend to absorb moisture and thus lose effectiveness in removing organic compounds to parts-per-billion levels.

2.3.1.4 Reverse Osmosis (RO)

Reverse osmosis appears to be the most common type of membrane filtration technology and is best known for its use in desalination of sea water (i.e. turning seawater into drinking water). It is also becoming a common home treatment method for contaminated drinking water; it can reduce the amount of both organics and inorganic compounds, bacteria and particulates that can be found in contaminated drinking water.

Just as with most water treatment technologies, reverse osmosis does not solve all water purification problems. First and foremost, RO requires high pressure to overcome hydrophobic resistance produced by the dense membrane. The process consumes a lot of energy in achieving separation efficiency; also, only 5-10% of the water entering the system is recovered and it does not remove small organic molecules from water. A low concentration of small molecules normally leaks into the permeate side because the membrane is not perfectly semipermeable.4 Therefore, the cost and inefficiency associated with this technology makes it an ineffective decontamination technique.
2.3.1.5 Ozonation

Powerful oxidants like ozone (O$_3$) are continuously used in municipal water treatment and disinfection of water supplies. Other advanced oxidation technologies have emerged as some of the main environmentally friendly technologies in the remediation of wastewater and for the general treatment of water.$^{57}$ The combined use of UV, ozone and hydrogen peroxide to facilitate the complete degradation of contaminants is also receiving increasing interest.

Although ozonation is effective in the rapid decomposition of phenolic compounds in aqueous media, decomposition of halogenated organic compounds is more rapid in organic solvents.$^{58,59}$ Ozonation is an effective process for the reduction of by-products of chlorobiphenyls (CBP’s).

Ozonation is less versatile than AC and can produce by-products that are less desirable; some of the by-products are biodegradable which can be removed by biological processes. A major limitation of the ozonation process is the relatively high cost of ozone generation process coupled with very short half-life period of ozone.$^{60}$

2.3.1.6 Dendrimers

Arkas et. al.$^{61}$ reported the development of a water purification technology that employs long chain-alkylated dendrimers. Several toxic polycyclic aromatic compounds dissolved in water were investigated and removed pollutants to ppb levels. However, no comparative studies were made by the authors with respect to the cost of this technology.
CHAPTER THREE

EXPERIMENTAL

3.1 Introduction

This chapter gives a detailed account of procedures (namely, Methods A, B, and C) employed to synthesize a series of novel nanoporous cyclodextrin polymers. Characterizations of the polymers using various analytical techniques are also outlined.

The first method (Method A) involves the use of NaH for the deprotonation of hydroxyl groups of the cyclodextrin molecule. The resulting cyclodextrin oxyanion is then reacted with a series of bifunctional linkers to access the desired polymers. Catalytic polymerization under acidic conditions (H₂SO₄) is an alternative method (Method B) for making these novel polymers. The third and simpler method (Method C) involves a direct reaction between the parent CD and a bifunctional linker such as diacid chloride or diisocyanate to form the desired polymeric material.

3.2 General experimental procedures

3.2.1 Reagents and solvents

β-CD [(C₆H₁₀O₅)₇·3H₂O] was purchased from Wacker Chemie and was used as received unless otherwise indicated. N,N-Dimethylformamide (DMF) 99% (Merck) was predried on molecular sieves (4Å) and thereafter distilled under reduced pressure over CaH₂ as reported by Armarego and Perrin. Sodium hydride (NaH) 60-75% (Merck) suspended in oil was used for the deprotonation of cyclodextrin where necessary. Acetone AR 99.5% was obtained from ACE.
The following linkers were used for the polymerization of the cyclodextrin: adipoyl chloride 98% (Riedel-de Haën); epichlorohydrin 99% (Acros Organics); bromoacetyl bromide 98+ % (Aldrich); succinic acid 99% (Acros Organics); 1,6 dibromohexane 97 %, dimethyldichlorosiloxane 99%, sebacoyl chloride 97%, terephthaloyl chloride 99%, glutaryl chloride 97% and glutaric anhydride were purchased from Fluka Chemie; maleic anhydride, phthalic anhydride were obtained from Aldrich. Unless otherwise stated, these linkers were used without any pretreatment. All the gases (N₂ and Ar) were of high purity (UHP or HP) and were obtained from AFROX South Africa.

3.2.2 Spectroscopic Techniques

- **Nuclear Magnetic Resonance (NMR)** - all NMR spectra were recorded on a Bruker Avance 300 unless stated otherwise. Chemical shifts (δ) were recorded in parts-per-million (ppm) referenced against the deuterated solvent used. The operating frequency for proton analysis was 300 MHz. These analyses were performed at the University of Witwatersrand, Johannesburg.

- **Fourier Transform-Infrared (FT-IR)** - spectra were measured using the Midac FT-IR 5000 Spectrophotometer. IR data were recorded with characteristic peaks in wave numbers (cm⁻¹).

3.2.3 Surface Analysis

- **Brunauer, Emmet and Teller (BET)** - measurements of gas adsorption isotherm are widely used for determining the surface area and pore size distribution of various solid materials. BET is usually the method of choice. Nitrogen was used as the adsorbent in the determination of surface area.

In this work, the surface area measurements were done on a Quantachrome NOVA instrument. Approximately 0.5 g of the sample was subjected to classical
N₂ adsorption surface area measurement at liquid nitrogen temperatures. The BET surface area, pore volume and average pore size were determined at the University of Pretoria.

- **Scanning Electron Microscopy (SEM)** - SEM JEOL 5600 instrument was used for visual characterization to obtain information of the surface characteristics of the nanoporous cyclodextrin polymer material. Samples used in this study were used in the granular and powdery forms and coated with gold to improve visibility. All samples were subjected to beam energy of 15 kV.

### 3.2.4 Thermal Analysis

- **Melting Point Determinations** - melting points of the polymer materials were determined using an Electrothermal Digital melting point apparatus and are reported as uncorrected values.

- **Thermogravimetric Analysis (TGA)** - by arbitrarily defining the thermal behaviour of polymers as a function of the amount of weight loss and the temperature specifying a particular environment it is possible to establish a stability criterion. However, such a criterion is only valid for a comparison of materials under the predefined particular set of conditions. Experimentally such a method can be important for screening many polymer materials.

Perkin Elmer Pyris 1 TGA instrument was used for thermal analyses of the polymer materials. The weight loss was measured on 10-20 mg of the polymer using linear temperature programming (10°C/min) under an inert atmosphere (N₂ gas) and this enabled the determination of the stability of polymers at high temperatures. Polymers usually require some form of thermal stabilization for
3.3 Synthesis of nanoporous Cyclodextrin polymers

3.3.1 Method A: Polymerization of CD via the oxyanion

Typically β-CD (1.1350 g, 10.0 mmol) was placed in a previously flame-dried 250 ml round bottomed flask containing magnetic stirring bar and dry DMF (25 ml). To the stirred solution was added slowly and under N₂ an oil-suspended NaH (0.2800 g, 80.0 mmol, 8.0 equiv.). Stirring was continued at room temperature for a further 24 hrs. At this point the cyclodextrin oxyanion had formed. The bifunctional linker (8.0 equiv.) was added dropwise under inert conditions to the stirred oxyanion solution. After stirring at elevated temperatures and under inert conditions for a further 16-24 hours, the solvent was removed using a rotary evaporator. The resulting solid was washed with copious amounts of acetone (typically 3 × 100ml) to remove residual DMF. Drying of the product under vacuum led to the isolation of the solid. This reaction is depicted in Scheme 3.1.
Scheme 3.1 Synthetic pathway for the polymerization of cyclodextrins with diacid chloride using Method A
### Table 3.1 Summary table of the reaction conditions and polymer characteristics (Method A)

<table>
<thead>
<tr>
<th>Bifunctional Linker</th>
<th>Temp (°C)</th>
<th>Time (hours)</th>
<th>Yield (%)</th>
<th>m.p (°C)</th>
<th>Colour</th>
<th>Solubility</th>
<th>H¹ NMR (ppm)</th>
<th>IR (cm⁻¹)</th>
<th>Polymer Name</th>
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<tbody>
<tr>
<td>Glutaryl chloride</td>
<td>60</td>
<td>16</td>
<td>60</td>
<td>150-156</td>
<td>White (granules)</td>
<td>soluble</td>
<td>1.89 (β-CH₂, d)</td>
<td>3359 (O-H)</td>
<td>CD-GC</td>
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<td>3.65-3.53 (H-4, H-5, m)</td>
<td>1691 (C=O)</td>
<td></td>
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<td>3.93-3.77 (H-2, H-3, H-6, m)</td>
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<td>1012 (C-O)</td>
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<tr>
<td>Adipoyl chloride</td>
<td>100</td>
<td>16</td>
<td>80</td>
<td>201</td>
<td>Brown (flakes)</td>
<td>insoluble</td>
<td>3.38-3.29 (H-4, H-5, m)</td>
<td>3368 (O-H)</td>
<td>CD-AC</td>
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<td></td>
<td>3.67-3.55 (H-2, H-3, H-6, m)</td>
<td>2937 (C-H)</td>
<td></td>
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<td></td>
<td>4.45 (OH-6, s)</td>
<td>1732 (C=O)</td>
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<td></td>
<td></td>
<td>4.83 (H-1, s)</td>
<td>1680 (ArC=Ar)</td>
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<td></td>
<td></td>
<td>5.71 (OH-2, OH-3, s)</td>
<td>1284 (C-O)</td>
<td></td>
</tr>
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<td></td>
<td></td>
<td>8.01 (ArH, s)</td>
<td>1027 (C-O)</td>
<td></td>
</tr>
<tr>
<td>Sebacoyl chloride</td>
<td>100</td>
<td>16</td>
<td>61</td>
<td>137-140</td>
<td>White (powder)</td>
<td>soluble</td>
<td>1.40-1.20 (β-CH₂, m)</td>
<td>3336 (O-H)</td>
<td>CD-SC A</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>1.60 (α-CH₂, m)</td>
<td>2934 (C-H)</td>
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<td></td>
<td>2.40-2.22 (H-4, H-5, H-2, H-3, H-6, m)</td>
<td>1707 (C-O)</td>
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<td></td>
<td></td>
<td></td>
<td>4.84 (H-1, s)</td>
<td>1161 (C-O)</td>
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<td></td>
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<td>3.38-3.29 (H-4, H-5, m)</td>
<td>1006 (C-O)</td>
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<tr>
<td>Terephthaloyl chloride</td>
<td>100</td>
<td>24</td>
<td>92</td>
<td>181-185</td>
<td>White (flakes)</td>
<td>soluble</td>
<td>3.38-3.29 (H-4, H-5, m)</td>
<td>3368 (O-H)</td>
<td>CD-TC</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>3.67-3.55 (H-2, H-3, H-6, m)</td>
<td>2937 (C-H)</td>
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<td></td>
<td>4.45 (OH-6, s)</td>
<td>1732 (C=O)</td>
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<td></td>
<td></td>
<td>4.83 (H-1, s)</td>
<td>1680 (ArC=Ar)</td>
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<td></td>
<td></td>
<td></td>
<td>5.71 (OH-2, OH-3, s)</td>
<td>1284 (C-O)</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>8.01 (ArH, s)</td>
<td>1027 (C-O)</td>
<td></td>
</tr>
<tr>
<td>Bifunctional Linker</td>
<td>Temp</td>
<td>Time</td>
<td>Yield (%)</td>
<td>m.p</td>
<td>Colour</td>
<td>Solubility</td>
<td>H¹ NMR (ppm)</td>
<td>IR (cm⁻¹)</td>
<td>Polymer Name</td>
</tr>
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<td></td>
<td>(°C)</td>
<td>(hours)</td>
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<td>(°C)</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>Glutaric anhydride</td>
<td>60</td>
<td>24</td>
<td>75</td>
<td>350-356</td>
<td>White (powder)</td>
<td>soluble</td>
<td>2.08 (β-CH₂, d)</td>
<td>3351 (O-H)</td>
<td>CD-GA</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>2.27 (α-CH₂, d)</td>
<td>2924 (C-H)</td>
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<td></td>
<td></td>
<td>4.00-3.11 (H-4,H-5, H-2, H-3,H-6, m)</td>
<td>1745 (C=O)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>4.34 (OH-6, s)</td>
<td>1238 (C-O)</td>
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<td></td>
<td></td>
<td>4.79 (H-1, s)</td>
<td>1145 (C-O)</td>
<td></td>
</tr>
<tr>
<td>Maleic anhydride</td>
<td>120-130</td>
<td>24</td>
<td>60</td>
<td>132-135</td>
<td>Dark brown (fine solid)</td>
<td>soluble</td>
<td>3.62-3.69 (H-4,H-5)</td>
<td>3490 (=C-H)</td>
<td>CD-MA</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.97-3.91 (H-2, H-3, OH-)</td>
<td>3346 (O-H)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>5.01 (H-1, s)</td>
<td>2908 (C-H)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>6.62 (=CH, s)</td>
<td>1568 (C=O)</td>
<td>and (C=O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.67 (=CH, s)</td>
<td>1089 (C-O)</td>
<td></td>
</tr>
<tr>
<td>Phthalic anhydride</td>
<td>120</td>
<td>24</td>
<td>90</td>
<td>270-275</td>
<td>Brown (powder)</td>
<td>soluble</td>
<td>3.55-3.45 (H-4, H-5, m)</td>
<td>3359 (O-H)</td>
<td>CD-PA</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>3.81-3.62 (H-2, H-3,H-6, m)</td>
<td>2930 (=CH)</td>
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<td></td>
<td></td>
<td></td>
<td>4.95 (H-1, s)</td>
<td>1659</td>
<td>(ArC=O)</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.84 (ArH, s)</td>
<td>1291 (C-O)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>8.34 (ArH, s)</td>
<td>1033 (C-O)</td>
<td></td>
</tr>
<tr>
<td>Epichlorohydrin</td>
<td>60</td>
<td>16</td>
<td>60</td>
<td>230 (dec)</td>
<td>Brown (granules)</td>
<td>insoluble</td>
<td></td>
<td>3392 (O-H)</td>
<td>CD-ECH</td>
</tr>
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<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>2908 (C-H)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>1021 (C-O)</td>
<td></td>
</tr>
<tr>
<td>Bifunctional Linker</td>
<td>Temp (°C)</td>
<td>Time (hours)</td>
<td>*Yield (%)</td>
<td>m.p (°C)</td>
<td>Colour</td>
<td>Solubility (water)</td>
<td>H\textsuperscript{1} NMR (ppm)</td>
<td>IR (cm\textsuperscript{-1})</td>
<td>Polymer Name</td>
</tr>
<tr>
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</tr>
<tr>
<td>1,6-Dibromohexane</td>
<td>100</td>
<td>16</td>
<td>96</td>
<td>170-178</td>
<td>White</td>
<td>soluble</td>
<td>1.25 (γ-CH\textsubscript{2}, m)</td>
<td>3377 (O-H)</td>
<td>CD-DBH</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.38 (β-CH\textsubscript{2}, m)</td>
<td>2908 (C-H)</td>
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<td></td>
<td></td>
<td></td>
<td>3.36 (α-CH\textsubscript{2}, m)</td>
<td>1594 (CH\textsubscript{2}, bands)</td>
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<td></td>
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<td></td>
<td></td>
<td>3.61-3.33 (H-4,H-5, H-2,H-3, H-6, m)</td>
<td>1037 (C-O)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>4.07 (OH-6, s)</td>
<td>730 (CH\textsubscript{2})</td>
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<td></td>
<td></td>
<td></td>
<td>4.80 (H-1, s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dichlorodimethylsiloxane</td>
<td>60</td>
<td>16</td>
<td>75</td>
<td>160-165</td>
<td>Yellow (flakes)</td>
<td>soluble</td>
<td>1.00 (CH\textsubscript{3}, s)</td>
<td>3377 (O-H)</td>
<td>CD-DDS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.08 (CH\textsubscript{2}, d)</td>
<td>2908 (C-H)</td>
<td></td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2.27 (CH\textsubscript{2}, d)</td>
<td>1393 [Si(CH\textsubscript{3})\textsubscript{2}O]</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>3.52-3.40 (H-4,H-5, m)</td>
<td>1035 (Si=O)</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.83-3.69 (H-2, H-3, H-6, m)</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>4.90 (H-1, s)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Percentage yield of the polymers was determined using the following equation: \( \% \text{ Yield} = \frac{\text{Feed}}{\text{Polymer}} \times 100\% \) where Feed representing the reactant used and Polymer representing the resulting polymer material.
3.3.2 Method B: Reaction of CD with dicarboxylic acids in the presence of catalytic H₂SO₄

To a stirred solution of β-CD (1.1350 g, 10.0 mmol) dissolved in H₂O (50 ml) was added succinic acid (0.8267 g, 80.0 mmol) and catalytic amounts of H₂SO₄ (98 %, 3 drops). The temperature was increased to 100 °C and stirred for a further 40 hrs. At this point a precipitate had formed. Evaporation of the solvent generated a solid, which was washed with copious amounts of acetone (typically 3 × 100 ml). A water-soluble product was isolated as white powder after drying under vacuum. The reaction is depicted in Scheme 3.2 below.

A similar procedure was adopted with slight modification for the reaction of 2, 3-naphthalene dicarboxylic acid linker. As before, the reagents were allowed to react for 40 hours at 100 °C. However, a white precipitate only formed after the solution was cooled to room temperature and acetone added to it. The solvent was then decanted. The resulting solid was further washed with acetone (3 x 100 ml) and ethanol (100 ml) to remove unreacted diacid residue. White water-soluble granules were isolated after drying under vacuum.

Scheme 3.2 A general scheme of the reaction of CD with a dicarboxylic acid using method B
<table>
<thead>
<tr>
<th>Bifunctional Linker</th>
<th>Temp (°C)</th>
<th>Time (hours)</th>
<th>Yield (%)</th>
<th>m.p (°C)</th>
<th>Colour</th>
<th>Solubility</th>
<th>H¹ NMR (ppm)</th>
<th>IR (cm⁻¹)</th>
<th>Polymer Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Succinic acid</td>
<td>100</td>
<td>40</td>
<td>98</td>
<td>262-265 (dec)</td>
<td>White (powder)</td>
<td>soluble</td>
<td>2.67 (CH₂, s)</td>
<td>2492 (C-H)</td>
<td>CD-SA</td>
</tr>
<tr>
<td>2, 3-Naphthalene dicarboxylic acid</td>
<td>100</td>
<td>40</td>
<td>45</td>
<td>222-230 (dec)</td>
<td>White (granules)</td>
<td>soluble</td>
<td>3.47-3.37 (H-4, H-5, m)</td>
<td>3354 (=C-H and O-H)</td>
<td>CD-NDA</td>
</tr>
</tbody>
</table>
3.3.3 Method C: Typical direct reaction method

3.3.3.1 Direct reaction of CD with diacid chloride

Trimethylamine (2.4 ml, 17 mmol) was added dropwise to a stirred solution of β-CD (1.1350 g, 10.0 mmol). Upon dropwise addition of a solution of sebacoyl chloride (1.5 ml, 80.0 mmol) dissolved in THF (10 ml), instant formation of a precipitate was observed. The solution was stirred for a further 16 hrs and a white solid was isolated after removal of the H₂O and THF. The solid was washed with H₂O (250 ml) and ethanol (2 x 100 ml) to remove water soluble materials and unreacted diacid, respectively. The resulting solid was dried under vacuum. The reaction scheme is depicted below (Scheme 3.3).

![Scheme 3.3 An illustration of the reaction between CD and sebacoyl chloride](image-url)
3.3.3.2 Direct reaction of CD with diisocyanates

A β-CD dissolved in DMF was reacted with a diisocyanate linker (1:8 molar ratio). The solution flask was heated to 75°C in an oil bath and stirred for 24 hours under inert conditions. The resulting clear solution was allowed to cool to room temperature. Upon addition of acetone to this solution a precipitate was formed. Filtration of the precipitate followed by continuous washing resulted with an insoluble solid material. The solid was then dried under *vacuo* overnight to produce the polymer of interest.

![Scheme 3.4 Typical reaction of CD with diisocyanate linkers](image-url)
Table 3.3 Summary of the reaction conditions and properties of the polymer (Method C)

<table>
<thead>
<tr>
<th>Bifunctional Linker</th>
<th>Temp (°C)</th>
<th>Time (hours)</th>
<th>Yield (%)</th>
<th>m.p (°C)</th>
<th>Colour</th>
<th>Solubility</th>
<th>NMR (ppm)</th>
<th>IR (cm⁻¹)</th>
<th>Polymer Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sebacoyl chloride</td>
<td>30</td>
<td>16</td>
<td>11</td>
<td>105-105</td>
<td>White</td>
<td>soluble</td>
<td>1.38 (CH₂, m)</td>
<td>3341 (O-H) 2966 (C-H) 1725 (C=O) 1163 (C-O) 1021 (C-O)</td>
<td>CD-SC B</td>
</tr>
<tr>
<td>Hexamethylene diisocyanate</td>
<td>80</td>
<td>24</td>
<td>100</td>
<td>243-250</td>
<td>White</td>
<td>insoluble</td>
<td>3392 (N-H) 2916 (C-H) 1727 (C=O) 1521 (NH-CO)</td>
<td>CD-HMDI</td>
<td></td>
</tr>
<tr>
<td>Isophorone diisocyanate</td>
<td>75</td>
<td>16</td>
<td>85-90</td>
<td>247-249 (dec)</td>
<td>White</td>
<td>insoluble</td>
<td>3388 (N-H) 2927 (C-H) 1730 (C=O) 1527 (NH-CO)</td>
<td>CD-IDI</td>
<td></td>
</tr>
<tr>
<td>Toluene diisocyanate</td>
<td>80</td>
<td>24</td>
<td>98</td>
<td>261-266</td>
<td>White</td>
<td>insoluble</td>
<td>3390 (N-H) 2922 (C-H) 1724 (C=O) 1527 (NH-CO)</td>
<td>CD-TDI</td>
<td></td>
</tr>
<tr>
<td>Polydiisocyanate</td>
<td>75</td>
<td>16</td>
<td>60</td>
<td>230 (dec)</td>
<td>Brown</td>
<td>insoluble</td>
<td>3396 (N-H) 2941 (=C-H) 1769 (C=O)</td>
<td>CD-Poly(DI)</td>
<td></td>
</tr>
</tbody>
</table>
3.4 The conversion of CD maleic anhydride (CDMA) polymer into a water-insoluble material

The polymer was synthesized by dissolving β-CDMA polymer (0.1000 g) in DMF (25 ml), to the solution was added poly (hexamethylene diisocyanate) (2 ml) while stirring. The solution was heated to about 80°C and then allowed to stir for further 16 hrs.

A yellow sticky paste substance was observed. This was washed with acetone (3 x 100 ml) several times, and then dried under vacuum. The yellow granules (2.436 g) were isolated and collected.

Table 3.4 Summary of polymer results and properties

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Time (hours)</th>
<th>m.p (°C)</th>
<th>Colour</th>
<th>Solubility (water)</th>
<th>IR (cm⁻¹)</th>
<th>Polymer Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>80</td>
<td>16</td>
<td>239-241</td>
<td>Yellow</td>
<td>insoluble</td>
<td>3373 (=C-H and O-H)</td>
<td>CDMA-Poly(HMDI)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(granules) (dec)</td>
<td></td>
<td></td>
<td>2932 (C-H)</td>
<td>1688 (C=O)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1629 (C=C)</td>
<td>1469 (C=C)</td>
</tr>
</tbody>
</table>
CHAPTER FOUR

RESULTS AND DISCUSSIONS

4.1 Introduction

Nuclear magnetic resonance (NMR) spectroscopy is a very useful tool for the characterization of cyclodextrins and their derivatives. For example, direct comparison of proton NMR spectra of both modified and unmodified β-cyclodextrin enables one to establish whether a specific substituent has been attached to the parental CD skeleton. Solubility of the CD polymer permitting, the incorporation of the bifunctional linker onto the polymeric backbone can also be established through proton NMR analysis.

The secondary hydroxyl groups (C3-OH and C2-OH) of the unmodified β-CD are located at the greater rim of the CD. Because of their close proximity, these secondary hydroxyl groups form intramolecular bonds with each other; the OH-3 group of the one glucose unit interacts with the C2-OH group of the neighbouring glucose unit (Figure 4.1). These interactions lead to a belt of hydrogen bonds around the secondary hydroxyls thereby giving the whole molecular structure a rather rigid configuration.

The primary hydroxyl groups placed at the smaller rim do not contribute to the intramolecular hydrogen bonding. This obviously suggests that the primary hydroxyls are less restricted in terms of movement. However, their ability to rotate leads to a partial blockage of the hydrophobic CD cavity.
Protons involved in the hydrogen bonding are much more deshielded than the free-rotating protons, and therefore appear in different regions of the proton NMR spectrum. As shown in Figure 4.2, peaks associated with C3-OH and C2-OH protons appear at 5.67 ppm and 5.72 ppm, respectively.

The free-rotating protons are clearly separated from the protons associated with the C6-OH groups. The triplet of the C2-OH proton is less deshielded and was hence observed at 4.46 ppm. All the other protons (C2-H-C6-H), except the doublet of the anomeric protons (C1-H) appearing at 4.81 ppm, are found in the region 3.25-3.67 ppm. The anomeric protons are more deshielded because they are attached to carbon atoms that are bonded to two highly electronegative (oxygen) atoms. The C3-H and C5-H protons are located within the cavity of the CD and are thus, as shown in the spectrum, more deshielded than the C2-H and C4-H, which are located on the exterior of the cavity.
Figure 4.2 $^1$H NMR spectrum of unsubstituted $\beta$-cyclodextrin in DMSO-$d_6$

$^{13}$C NMR chemical shifts of CDs (Figure 4.3) extend over a larger range than proton shifts and are especially suitable and useful for identifying these starch-based compounds and their derivatives. The anomeric C-1 carbon is more highly deshielded (102 ppm) than the rest of the carbon atoms; as mentioned previously, the deshielding effect emanates from the two oxygen atoms that are bonded to the C-1 atom. The most highly shielded carbon (C-6) appears low field at 59.9 ppm. Carbons C-2 and C-3 as well as C-5, which experience an almost similar electronic environment, are located closely together in the region 72 - 73 ppm. Lastly, C-4 is clearly separated from these carbon atoms and was observed at 82 ppm.
IR spectroscopy is another tool that is useful for the characterization of CDs and their derivatives. Typically, a broad and intense absorption band associated with the hydroxyl groups is observed at about 3370 cm$^{-1}$. This technique is particularly useful for the confirmation of the structure of the CD polymer where NMR is not always possible (e.g. in insoluble polymers). The broad hydroxyl group band is less intense in the IR spectrum of the CD polymer. Therefore, the decrease in the intensity of OH peak serves to confirm that the polymerization has occurred. Furthermore, the polymerization step (in essence the degree of polymerization) can be easily monitored using the IR spectroscopy.

The aim of this project was primarily to synthesize and characterize nanoporous cyclodextrin based polymers. Polymerization of the β-cyclodextrin was achieved by the reaction of the hydroxyl groups of the cyclodextrin moiety with a series of
bifunctional linkers. A very simple method of accessing the CD polymers was employed in this study. This method involves the direct reaction of well studied bifunctional linkers such as hexamethylene diisocyanate (HMDI) and toluene-2,6-diisocyanate (TDI) with $\beta$-CD. In addition, other complex methods that utilize more exotic and novel linkers were investigated. The findings of this work are reported in detail in the sections that follow.

### 4.2 Synthesis of Cyclodextrin polymers

There are two ways of making cyclodextrin polymers (Scheme 4.1). The cyclodextrin can be attached as a pendant to an already existing polymer backbone (Route 1, Scheme 4.1). Alternatively, the cyclodextrin is reacted with a bifunctionalized linker to generate a polymer in which the cyclodextrin forms part of the polymer skeleton (Route 2, Scheme 4.1). Route 2, which is referred to as the bifunctionalized linker route, has been successfully applied in our laboratories and was, as a result, adopted for this study.

![Scheme 4.1 Synthetic routes for the polymerization of cyclodextrin molecule](image_url)
For simplicity, we chose to further divide the bifunctionalized linker route (i.e. Route 2) into three smaller sub-routes, namely Method A, B and C. The different reaction conditions that were employed for the three sub-routes allowed easy access to novel and variously linked CD polymers. While an oxyanion was used to effect the polymerization in Method A, the polymerization reaction was performed under acidic conditions in Method B. As for Method C, the polymerization was carried out using a direct reaction of a CD with the linker. The three sub-routes (Methods A, B and C) are discussed individually in the next section.

4.2.1 Preparation of β-CD polymers using Method A

In this method, an oxyanion is formed prior to the reaction with the bifunctionalized linker. The protons of C2-OH hydroxyl group are known to be more acidic than those at C6-OH. In this method, this feature is exploited by using a strong base (NaH) for the deprotonation of the hydroxyl groups at position-2 prior to the formation of the polymer (Scheme 4.2). The reaction was carried out under anhydrous conditions so as to avoid the reprotonation of the resulting CD oxyanion back to the starting material (i.e. the monomeric CD. Therefore, it was necessary to use dry solvent (DMF). Additionally, the reaction was performed in a previously flame-dried reaction flask and under an inert atmosphere (N2 or Ar). On the basis of evidence from the literature, this reaction was assumed to be complete after 16-24 hours, depending on the type of linker used.
Scheme 4.2 Synthetic route for the formation of the β-CD oxyanion
**Reaction of β-CD oxyanion with diacetyl chlorides**

Reaction of the highly reactive oxyanion with a DMF solution of a series of diacid chlorides (glutaryl, adipoyl, sebacoyl and terephthaloyl chlorides) yielded in satisfactory yields (60-92%) the desired polymers (Scheme 4.3).

![Scheme 4.3 Synthesis of polymers using diacid chlorides as linkers](image)

Evidence for the incorporation of the dicarbonyl linkers was provided by IR spectroscopy. Typically, these polymers displayed C=O band at 1691-1732 cm\(^{-1}\) in their IR spectra. Bands associated with the C-O and O-H stretches were also detected at around 1129 cm\(^{-1}\) and 3363 cm\(^{-1}\), respectively. In addition to these bands, for the CD-TC polymer, additional aromatic C-H and C=C bands were observed at 2937 cm\(^{-1}\) and 1284 cm\(^{-1}\).

NMR spectroscopy provided more evidence for the incorporation of the linkers; new peaks associated with both the α-CH\(_2\) and β-CH\(_2\) protons were detected in the NMR spectra of polymers prepared from glutaryl and sebacoyl chloride. Due
to the anisotropic effects associated with the carbonyl groups, the α-CH$_2$ protons of both the CD-GC and CD-SC A polymers are more deshielded and thus appear at 2.20 ppm (CD-GC) and 1.60 ppm (CD-SC A). However, the splitting pattern of the α-CH$_2$ protons of CD-GC polymer was unexpected; doublets instead a triplet was observed, whereas the CD-SC A polymer exhibited a multiplet. The β-CH$_2$ protons, which are an extra carbon away from carbonyl group, expectedly appear at a lower chemical shift (2.08 ppm for glutaryl; 1.40-1.20 ppm for sebacoyl). Because of the insolubility of the CD-AC polymer in common NMR solvents, it was not possible to obtain an NMR spectrum for this polymer. It is quite clear from the proton NMR spectrum of the CD-TC polymer that the aromatic protons are under the same environment; a singlet was spotted at 8.01 ppm.
**Reaction of β-CD oxyanion with cyclic acid anhydrides**

The cyclic acid anhydrides (glutaric, maleic and phthalic anhydrides) were reacted with an oxyanion (2) to form the desired polymer; yields of 60-90% were achieved (Scheme 4.4).

![Scheme 4.4 General synthetic route for the synthesis of polymers using cyclic acid anhydrides as linkers](image)

The desired polymers were characterized by FT-IR and proton NMR techniques; this also served to confirm for the incorporation of the linker into the cyclodextrin polymer. Typically, peaks representing the C=O and C-O functionalities were observed in IR spectra of these polymers. These appear at around 1700 cm$^{-1}$ and 1230 cm$^{-1}$, respectively. Additional bands representing the linker can be clearly identified. For the polymer prepared with the glutaric linker, only a C-H band was observed at 2924 cm$^{-1}$.

Bands associated with C-H (3490 cm$^{-1}$) and C=C (1568 cm$^{-1}$) stretches of the C=C-H moiety provided evidence for the incorporation of the maleic anhydride
linker into the polymer backbone. Phthalic anhydride (PA) is an aromatic derivative of maleic anhydride (MA); new peaks associated with the hydrophobic phenyl ring were thus observed at 2930 cm\(^{-1}\) (ArC-H) and 1659 cm\(^{-1}\) (ArC=C).

\(^1\text{H}\) NMR spectroscopy was also used to provide more evidence for the incorporation of the anhydride linkers to the cyclodextrin. While the \(\alpha\)-CH\(_2\) protons were observed at 2.27 ppm, the \(\beta\)-CH\(_2\) multiplet appeared slightly downfield at 2.08 ppm (i.e. for the CD-GA polymer). The protons of the maleic anhydride linker (-CH=CH-) are clearly visible at 6.62 ppm and 6.67 ppm. The NMR spectrum of CD-PA polymer showed in the aromatic region the characteristic aromatic protons at 7.84 ppm and 8.34 appearing as singlets.
• Reaction of β-CD oxyanion with epichlorohydrin (ECH)

The synthesis of CD-ECH polymer is illustrated in **Scheme 4.5**. This involves the reaction of a previously synthesized oxyanion (2) with epichlorohydrin under anhydrous condition. The desired product was isolated by washing the crude product with acetone and ethanol before drying under vacuum. As with previous syntheses of the polymer washing with the two solvents is important as acetone precipitate the product and ethanol removes any unreacted epichlorohydrin. The polymer, which was isolated in a yield of 60%, is insoluble in water and common organic solvents.

![Chemical structure of CD-ECH polymer](image)

**Scheme 4.5 Synthesis of CD-ECH polymer**

The polymer structure was determined by FT-IR. The FT-IR spectrum of the polymer confirmed the disappearance of the CH$_2$-Cl (stretching vibration) at 672 cm$^{-1}$ and C-O-C (bending vibration) bands of the epoxy group at 1196 cm$^{-1}$, which are the major functional groups of epichlorohydrin monomer. The identifiable absorption band found at 1021 cm$^{-1}$, which is associated with the C-O bands formed as a result of the reaction between the epichlorohydrin and the cyclodextrin. The insolubility of the polymer material precluded the use of proton NMR.
• Reaction of β-CD oxyanion with a dibromohexane (DBH)

The dihalogenated alkane (1, 6-dibromohexane) was reacted with an oxyanion according to the reaction shown in Scheme 4.6. The reaction was performed under inert conditions at 100 °C for a period of 16 hours. This resulted in a white flaky product (96% yield) after washing with acetone and dried under vacuum.

\[
\begin{align*}
2 \quad \text{Br} & \quad \text{Br} \\
100 \, ^{\circ} \text{C}, 16 \, \text{Hrs}, \text{N}_2 \\
\end{align*}
\]

Scheme 4.6 Synthesis polymers using 1, 6 dibromohexane (DBH) as a linker

FT-IR and proton NMR were employed in the characterization of the synthesized CD-DBH polymer. The IR spectrum exhibit absorption bands associated with CH\(_2\) and C-O at 1594 and 1037 cm\(^{-1}\), respectively. Further characteristic absorption was observed at 730 cm\(^{-1}\) that is associated with CH\(_2\) rocking absorption. A slightly weakened O-H band could still be observed at 3377 cm\(^{-1}\), this indicated that not all hydroxyl groups in the cyclodextrin participate in the polymerization process. New methylene peaks were also observed at 1.38 and 1.25 ppm in the NMR spectrum of the polymer.
• Reaction of β-CD oxyanion with a dichlorodimethylsiloxane (DDS)

The dichlorodimethylsilane derived polymer was accessed via **Scheme 4.7**. Specifically, this was achieved by a dropwise addition of dichlorodimethylsilane onto a DMF solution of the oxyanion (2). The product was washed with copious amount of acetone and isolated as white flakes (75 %) after drying under vacuum.

![Scheme 4.7 Synthesis of CD-DDS polymer](image)

The IR spectrum exhibited characteristic peaks at 1393 cm⁻¹ and 1035 cm⁻¹, which are associated with Si-C and Si-O absorption bands. This functionality is the core characteristic of the dichlorodimethylsiloxane linker. NMR analysis revealed the presence of multiplets at 1.00 ppm than the expected high intensity singlet. Other multiplets were also observed at 1.12 ppm, which cannot be assigned to known protons in the expected structure of the polymer.
4.2.2 Preparation of cyclodextrin polymers using Method B

The reaction of the cyclodextrin with a free dicarboxylic acid linker (succinic acid and 2,3-naphthalene dicarboxylic acid) was carried out. This type of reaction was induced by the addition of catalytic amounts of sulphuric acid. Stirring of the reaction mixture at 100°C for a period of 40 hours led to the isolation of the desired polymers after work-up. The reaction is summarized by Scheme 4.8 below.

Scheme 4.8 General synthetic route for the synthesis of polymer using dicarboxylic acid as linker

While the succinic acid-linked polymer was isolated as a white powder, the 2,3 naphthalene dicarboxylic acid-linked polymer gave white granules. The yield of the CD-NDA polymer was less satisfactory (45%) than that of the succinic acid-linked polymer (98%). Both the dicarboxylic acid-linked polymers were found to be soluble in both water and common organic solvents. It was also observed that the solubility of the polymeric materials is more pronounced than the parent cyclodextrin monomer. The linker has somehow contributed to the increased solubility of the cyclodextrin.

The C=O and C-O bands were observed at 1724 cm\(^{-1}\) and 1196 cm\(^{-1}\) respectively, in the IR spectra of the polymers. Aromatic =C-H and C=C bands of
the incorporated naphthalene dicarboxylic acid moiety were also detected at 3354 cm$^{-1}$ and 1634 cm$^{-1}$, respectively.

The polymer structure was further characterized with proton NMR. The peak associated with the two -CH$_2$- groups, which are sandwiched between the carbonyl groups, in the succinic acid linker was observed as a singlet at 2.67 ppm. The aromatic protons closest to the carbonyl group in the 2,3-naphthalene dicarboxylic acid linker appear as a multiplet at 8.80 ppm. The rest of the aromatic protons were observed as a multiplet as well at a lower chemical shift of 7.60 ppm. Analysis of both the IR and NMR data suggests the incorporation of the linkers onto the cyclodextrin.

However, the integration of the signals of the primary OH groups of the CD-NDA polymer seems to suggest poor linker incorporation. This phenomenon is also supported by the poor yield of the desired polymer. Poor incorporation of the acid could be attributed to the sensitivity of cyclodextrin towards the acid, leading to hydrolysis and not the envisaged the esterification. The 1,2-disubstitution pattern of the acid is also suspected of impeding the polymerization process. Another reason that may be responsible for poor linker incorporation is steric hindrance associated with the 2,3-naphthalene dicarboxylic acid linker.

### 4.2.3 Preparation of the cyclodextrin polymers using Method C

Unlike Method A, which involves a reaction of the oxyanion with a series of bifunctional linkers, Method C involves a direct reaction of the unmodified cyclodextrin with more reactive bifunctional linkers such as diacid chlorides and diisocyanates. Reactions involving these linkers are discussed individually in the following section.
• Direct reaction of the cyclodextrin with a diacid chloride linker

Although esterification of the cyclodextrin to the corresponding polymer using a dicarboxylic acid chloride (sebacoyl chloride) was successful, the polymer was generated in very low yields (11%). The triethylamine was used to trap the hydrochloric acid produced as a side product during the reaction. This is important as the highly reactive HCl would usually be involved in an unwanted side reaction with the monomeric cyclodextrin. The reaction was carried out at room temperature. The ester-linked polymeric material was found to be insoluble in water but sparingly soluble in organic solvents such as DMF and DMSO.

Scheme 4.9 General synthetic route for the synthesis of polymer using sebacoyl chloride as linker

As expected the IR spectrum of the polymer shows characteristic peaks at 1707 cm\(^{-1}\) and 1161 cm\(^{-1}\) due to C=O and C-O of the ester group of the linker. It was also observed that the intensity of the band at 3336 cm\(^{-1}\) a characteristic peak of the OH group of the cyclodextrin molecule does not disappear completely but is significantly weakened due to partial reaction with diacid chloride.

The proton NMR spectrum of the CD-SC B polymer is shown below (Figure 4.4). The signals marked (a) and (b) in the spectrum represent the secondary OH groups found in the cyclodextrin monomer. Two things can be said about the
signals of the OH groups in Figure 4.4. Firstly, the intensity of the signals has decreased significantly and secondly the signals have broadened.

![Figure 4.4 1H NMR of CD-SC B polymer dissolved in DMSO-d_6 solvent](image)

The decrease in the intensity and the broadening of the signal brings us to the conclusion that the reaction between the cyclodextrin monomer and sebacoyl chloride linker has occurred. The new proton signals observed at 1.25 ppm, 1.48 ppm, 2.08 ppm and 2.59 ppm (Figure 4.4) represent the methylene protons of sebacoyl group in the polymer.

- **Direct reaction of the cyclodextrin with a dicarboxylic acid chloride linker**

The use of diisocyanate as a linker is a conventional direct reaction method used for the synthesis of amide linked cyclodextrin polymers. Unlike Method A, which requires the deprotonation of cyclodextrin molecule prior to polymerization with linker and pre-drying of the solvents, this method involves a direct reaction of the
cyclodextrin with a diisocyanate linker (Scheme 4.10). The reaction takes place without the use of any catalysts or initiators and was monitored with IR spectroscopy over a period of 16 to 24 hours. This reaction is very popular with chemists working in this field; the simplicity and high yields associated with this method makes it very attractive.

Li and Min4 reported quantitative yields when hexamethylene diisocyanate (HDI) and toluene diisocyanate (TDI) were used as linkers. The reactions were carried out at about 80°C for a period of 24 hours. Similar yields were also achieved when the isophorone diisocyanate (IDI) linker was used under similar reaction conditions.

The reactions were monitored by IR and all of them were complete after a period of 16 hours. As the reaction progresses, the isocyanate peak at around 2271 cm$^{-1}$ gradually disappeared from the spectrum. The newly formed polymeric material (CD-IDI) exhibited peaks at around 2930 cm$^{-1}$ corresponding to the

Scheme 4.10 General synthetic route for the synthesis of cyclodextrin polymers using the diisocyanate linker
aliphatic –CH group of the new linker. The carbonyl vibration peak of the newly formed amide could also be observed at 1700 cm$^{-1}$. The initial diisocyanate peak was no longer observed spectroscopically (IR) in the crude product mixture of the reactions. Interestingly, the diisocyanate derived cyclodextrin polymers are resistant to many solvents that will normally dissolve cyclodextrin. This is true both at ambient and elevated temperatures.

4.3 Surface and Thermal analyses of the Cyclodextrin polymers

4.3.1 Surface analysis

A comprehensive analysis of the cyclodextrin and the polymer materials was carried out to establish its surface characteristics. The analyses included important parameters such as pore size, pore volume and surface morphology. These parameters play a significant role in the use of the polymers during the separation and absorption processes. The analysis was achieved by using two techniques, namely Brunauer-Emmett-Teller (BET) and Scanning Electron Microscopy (SEM).

4.3.1.1 Brunauer-Emmett-Teller (BET) Analysis

The Brunauer-Emmett-Teller (BET) method$^{63}$ is now generally accepted as a standard procedure for evaluating the porosities of a variety of adsorbents such as activated carbon, zeolites, silica gel and polymeric materials. It has been argued, however, that BET surface area values are overestimates compared to the true values.$^{64}$ The accuracy of any BET surface area estimation is unknown since a standard adsorbent possessing a truly well-defined surface area is unavailable. Despite this inaccuracy the relative comparison is useful. BET surface area analysis results for the polymers are summarized in Table 4.1 where surface area, pore volume and radius are given.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area (m²/g)</th>
<th>Pore Volume (cc/g)</th>
<th>Pore Radius (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) CD-IDI&lt;sup&gt;a&lt;/sup&gt;</td>
<td>50.74</td>
<td>1.99 x 10⁻²</td>
<td>8.8</td>
</tr>
<tr>
<td>(ii) CD-NDA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>19.89</td>
<td>8.03 x 10⁻³</td>
<td>8.8</td>
</tr>
<tr>
<td>(iii) CD-GC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>18.86</td>
<td>7.70 x 10⁻³</td>
<td>8.8</td>
</tr>
<tr>
<td>(iv) CD-SA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>9.82</td>
<td>3.65 x 10⁻³</td>
<td>8.8</td>
</tr>
<tr>
<td>(v) CD-DBH&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.86</td>
<td>3.55 x 10⁻³</td>
<td>8.8</td>
</tr>
<tr>
<td>(vi) CD-SC&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7.66</td>
<td>3.11 x 10⁻³</td>
<td>8.8</td>
</tr>
<tr>
<td>(vii) CD-TC&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.60</td>
<td>2.98 x 10⁻⁴</td>
<td>8.9</td>
</tr>
<tr>
<td>(viii) CD-MA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.49</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(ix) CD-GA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(x) CD-PA&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(xi) CD-Poly(HMDI)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(xii) CDMA-Poly(HMDI)&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&lt; 0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(xiii) CD-DDS&lt;sup&gt;b&lt;/sup&gt;</td>
<td>&lt; 0.01</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(xiv) β-CD&lt;sup&gt;a&lt;/sup&gt;</td>
<td>&lt; 0.01</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

<sup>a</sup>Water insoluble, <sup>b</sup>Water soluble

Needless to say, the specific surface area of sorbents plays an important role in adsorption. Generally speaking, the larger the specific surface area of the sorbent is, the greater the amount of adsorbates adsorbed is. Li and Min<sup>4</sup> studied the surface area and pore radius of activated carbon as compared to the β-CD-TDI polymer. Surface area of both the polymer and activated carbon were found to be 1-7-1.9 and 750 m²/g and pore radius 7-9 and 20-1000 Å, respectively. From our results, CD-IDI polymer demonstrate some increased surface area of about 50.74 m²/g as compared to that of β-CD-TDI polymer and the pore radius remaining unchanged. Five other polymers exhibited higher surface area as compared to that of the authors. The pore radius of most of the polymers remained constant. It has been also observed that an increase in the surface area results in an increase in pore volume. The effect of the linker can be clearly observed since the surface areas of the polymers have been enhanced than that of the parent cyclodextrin monomer. Increased surface area promised higher absorption efficiency.
4.3.1.2 Scanning Electron Microscopy (SEM) Analysis

In support of the BET analysis, the morphological studies were conducted by SEM to further confirm the surface porosity of the polymers. Porous materials have been used in various areas including gas separation, catalysis and water purification. The cyclodextrin polymers that were synthesized possess randomly interconnected meso- and micropores.

- Polymers from Method A, B and C

Figure 4.5a shows the crystalline structure of the cyclodextrin monomer. A non-smooth surface with cracks, which can be attributed to the crystallinity of the cyclodextrin, is clearly visible.

Figures 4.5b-c shows SEM micrographs of the CD-AC and CD-ECH polymers. It can be seen that the polymer particles are packed into a network. There are many mesopores and macropores within the network structure. The size and the shape of individual polymer nanoparticles observed in the different samples are different from the parent cyclodextrin. The packing pattern tends to vary according to the linker employed.

The surface structure of the CD-AC polymer (Figure 4.5b) is totally different from that of parent cyclodextrin monomer; it has no crystalline structure. The surface is also not aligned and there are no openings or cracks; the particles appear to be clinging together. The SEM micrograph of the CD-ECH polymer (Figure 4.5c) shows a cluster of separate particles. Although there are bigger cracks, the surface of the single particle is closely packed with minor openings. The polymers demonstrate enhanced surface characteristics. According to the SEM micrographs the CD-ECH polymer as compared to CD-AC polymer will have higher absorption capacity due to its pore structure. No BET data available for these polymers to support SEM micrograph results.
The surface of CD-TC polymer (Figure 4.6a) shows not so closely packed material and has very minor cracks. There are some loosely held particles on the surface. Some spaces on the surface of the polymer are exposed by a crack. The CD-TC polymer show opening that can play a role in adsorption studies. The SEM of CD-GC polymer (Figure 4.6b) shows a very smooth surface with particles that are closely packed. There are no visible openings. The SEM micrograph (Figure 4.6c) shows almost similar structure as the previous one (Figure 4.6b), smooth surface with no openings in between the surface. According to the BET results, CD-GC demonstrates higher surface area and pore volume (18.86 m²/g and 7.70 x 10⁻³ cc/g) as compared to CD-GA surface area (0.33 m²/g, pore volume results not available for the polymer).
Figure 4.6 SEM micrographs of: (a) CD-TC; (b) CD-GC and, (c) CD-GA polymers

Figure 4.7a (CD-PA polymer) shows a closely packed surface with lump-like features appearing on the surface. The SEM of the CD-MA polymer (Figure 4.7b) shows a unique flower-like structure that appears to be crystalline. The CD-DDS polymer (Figure 4.7c) shows very large visible pore openings. The SEM results of the CD-DDS do not agree with that of the BET analysis. The BET result shows no pore volume results. This polymer will demonstrate higher absorption based on its pore structure.

Figure 4.7 SEM micrograph of: (a) CD-PA; (b) CD-MA and (c) CD-DDS polymers
The polymers, CD-NDA and CD-SA (Figure 4.8) exhibit a very smooth surface but CD-NDA polymer shows some minor openings. The BET results of the two polymers (CD-NDA and CD-SA) demonstrated pore volume of this magnitude $8.03 \times 10^{-3}$ and $3.65 \times 10^{-3}$ cc/g, respectively.

From the figure below (Figure 4.9), SEM analysis show that the polymer materials are rather amorphous as compared to the parent cyclodextrin, and hence show some or no crystalline properties. The CD-SC B shows some pore opening in its surface structure. The CD-ID1, which has demonstrated higher surface area and pore volume in the BET analysis, in SEM it shows smooth surface with smaller cracks.
It can be observed from the SEM analysis (Figure 4.5 to Figure 4.9) that introduction of the linker to the cyclodextrin introduces some changes in the surface characteristics of the resulting polymer.

4.3.2 Thermal analysis

There is a general need for materials that can function at both room temperature and very high temperature for extended periods of time without significant compromise in their physical properties. Stability changes of the polymer may be due to a number of complex, interrelated phenomena ranging from the structure of the substance itself to changes in the crystallinity of the bulk phase.

Although some changes in morphology cannot be directly traceable to physical or chemical changes occurring within the polymer, they can have a profound effect on the ability of the polymer to undergo chemical changes. Because of this factor it is far more reasonable to approach the stability of polymers from the opposite extreme, that is, the degradation of polymers. Therefore, the thermal stabilities of the cyclodextrin polymers were investigated by doing thermogravimetric (TGA) analysis. TGA is a very reliable and fast method for studying the thermal stability of CD polymers. It allows for the determination of mass and heat flow changes
simultaneously with the structural identification of sample and/or decomposition products.

4.3.2.1 Thermogravimetric Analysis (TGA)

The thermal stability of the newly-synthesized cyclodextrin polymers was investigated using dynamic thermogravimetric analysis from 50°C to 550°C under inert environment at the heating rate of 10°C/min. This was done to show the thermal behavior of the polymers in relation to cyclodextrin and how each linker affects the overall thermal behaviour of the polymer.

Thermal profiles associated with cyclodextrin polymers generally show a similar pattern. Small differences relating to the volatile constituent content, onset temperatures and mass loss values at given temperatures are usually detected. The profiles are divided into four different regions and consist of three distinctive steps in which appreciable weight losses were detected. These steps are summarized as follows:

(i) The first step, which occurred from ambient temperature to about 250°C, can be interpreted as loss of volatile substances.
(ii) The second and third weight loss steps account for most of the weight loss and are associated with the formation of a residue of the polymer.
(iii) The fourth step, which occurred at temperatures over 500°C, can be related to a relatively slow degradation of the remaining residue.

• Polymers from Method A, B and C

The thermal analyses data of the preliminary test of cyclodextrin and cyclodextrin polymers are summarized in Table 4.3. The TGA scan of the parent cyclodextrin shows a two stage weight loss (Figure 4.10). The first weight loss of 2.44% at around 100°C can be associated with loss of volatile substances and the second
weight loss of 84.14% at 350°C can be interpreted as decomposition of glucose in cyclodextrin. The remaining black brittle char is stable above 350°C.

Table 4.2  TGA results of cyclodextrin molecule, CD-AC and CD-ECH polymers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Onset temperature of decomposition (°C)</th>
<th>1st Weight loss step (%m/m)</th>
<th>2nd Weight loss step (%m/m)</th>
<th>3rd Weight loss step (%m/m)</th>
<th>Residue at 500°C (%m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclodextrin</td>
<td>334.26</td>
<td>2.44</td>
<td>84.14</td>
<td>-</td>
<td>9.479</td>
</tr>
<tr>
<td>CD-AC</td>
<td>191.56</td>
<td>4.50</td>
<td>22.31</td>
<td>33.16</td>
<td>36.92</td>
</tr>
<tr>
<td>CD-ECH</td>
<td>276.17</td>
<td>3.655</td>
<td>32.17</td>
<td>38.02</td>
<td>23.77</td>
</tr>
</tbody>
</table>

CD-AC polymer shows higher residue (~37%). The polymers, CD-AC and CD-ECH show that the decomposition occurs in several steps as compared to the cyclodextrin, decomposition starting as early as ~ 100°C. The observed weight loss can be associated with the moisture present in the polymer and other volatile low molecular weight materials formed during polymerization, which were still present in the polymer since it was not purified. Thermal decomposition of CD-AC polymer was observed at ~ 190°C. The higher thermal stability of the polymers can be attributed to the degree of crosslinking formed by the interaction of the linker with the cyclodextrin moiety.
Similar TGA profiles of the polymers were observed. Table 4.3 as shown below, represents the onset and weight loss percentage profiles of the synthesized polymers. The onset temperatures of these materials are around 100-230°C and are accompanied by a 1st weight loss percentage of about ~10% with higher weight loss seen at the 2nd weight and 3rd loss steps. The remaining residue was not quantified since most analyses were cut off at 550°C. The TGA curves of other polymers are outlined in Appendix B.
Table 4.3  Summary of the TGA analysis of cyclodextrin polymers showing weight loss steps.

<table>
<thead>
<tr>
<th>Polymers</th>
<th>Onset temperature of decomposition (°C)</th>
<th>1st Weight loss (%m/m)</th>
<th>2nd Weight loss (%m/m)</th>
<th>3rd Weight loss (%m/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CD-GA</td>
<td>175</td>
<td>10</td>
<td>39</td>
<td>23</td>
</tr>
<tr>
<td>CD-DBH</td>
<td>160</td>
<td>7</td>
<td>28</td>
<td>24</td>
</tr>
<tr>
<td>CD-TC</td>
<td>174</td>
<td>6</td>
<td>22</td>
<td>45</td>
</tr>
<tr>
<td>CD-PA</td>
<td>230</td>
<td>15</td>
<td>36</td>
<td>14</td>
</tr>
<tr>
<td>CD-DDS</td>
<td>153</td>
<td>6</td>
<td>68</td>
<td>22</td>
</tr>
<tr>
<td>CD-MA</td>
<td>100</td>
<td>7</td>
<td>18</td>
<td>40</td>
</tr>
<tr>
<td>CD-NDA</td>
<td>180</td>
<td>11</td>
<td>25</td>
<td>23</td>
</tr>
<tr>
<td>CD-IDI</td>
<td>208</td>
<td>16</td>
<td>44</td>
<td>20</td>
</tr>
<tr>
<td>CD-Poly(HMDI)</td>
<td>200</td>
<td>10</td>
<td>51</td>
<td>18</td>
</tr>
</tbody>
</table>
For some polymers, most of their fractions were decomposed during the 2\textsuperscript{nd} step, while for other polymers (e.g. CD-TC and CD-MA polymers) resulted in higher fraction being decomposed in the 3\textsuperscript{rd} step. Other polymers maintained approximately equal fractions at both stages. Most polymers showed thermal stability below 250 °C and were charred at temperatures above 350 °C, resulting in the formation of the residue.

The polymers demonstrate that they can withstand high thermal conditions (up to 350°C) if they were to be applied in high temperature water treatment processes.


CHAPTER FIVE

PRELIMINARY STUDIES ON APPLICATION OF CYCLODEXTRIN POLYMERS

5.1 Introduction

In analytical chemistry, cyclodextrins are mainly used in gas chromatography, high-performance liquid chromatography and capillary zone electrophoresis in order to separate molecules, especially chiral isomers. The mechanism for the separation is based on the different binding constants of the isomers with cyclodextrins. A general review on some cyclodextrin polymer applications has been made in Chapter 2. However, the aim of this chapter is to outline the ability of cyclodextrin polymers at removing phenolic compounds from water.

Phenolic compounds are an important group of compounds, which are of interests because of their toxicity to the environment. They are found in the environment as a result of their many industrial applications. These compounds are generated in the production of plastics and other industrial chemicals. Nitrophenols, which are derivatives of phenolic compounds, are formed photochemically in the atmosphere from vehicle exhausts. Because of their toxicity, their determination and effective means of removal from the environment is receiving increasing attention. Phenols have been included in the US Environmental Protection Agency (USEPA) (Methods 604, 625 and 804) list of priority pollutants (Table 1). Also, the European Union (EU) has classified several phenols as priority contaminants and the 80/778/EC directive states a maximum concentration of 0.5 µg/L for total phenols in drinking water.
<table>
<thead>
<tr>
<th>US-EPA list of priority pollutants (EPA 804)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenol</td>
</tr>
<tr>
<td>2-Methylphenol</td>
</tr>
<tr>
<td>4-Methylphenol</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
</tr>
<tr>
<td>2,6-Dichlorophenol</td>
</tr>
<tr>
<td>2,4,5-Trichlorophenol</td>
</tr>
<tr>
<td>2,3,4,6-Tetrachlorophenol</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
</tr>
<tr>
<td>4-Nitrophenol</td>
</tr>
<tr>
<td>Dinoseb (DNMP)</td>
</tr>
<tr>
<td>4,6-Dinitro-2-methylphenol</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Commission of the European Communities Directive 76/464/EC</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Amino-4-chlorophenol</td>
</tr>
<tr>
<td>4-Chloro-3-methylphenol</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
</tr>
<tr>
<td>3-Chlorophenol</td>
</tr>
<tr>
<td>4-Chlorophenol</td>
</tr>
<tr>
<td>Pentachlorophenol</td>
</tr>
<tr>
<td>Trichlorophenols</td>
</tr>
</tbody>
</table>

Known analytical techniques for the determination of phenols include high-performance liquid chromatography and capillary electrophoresis in combination with various detectors. Gas chromatography is a common tool for the analysis of phenols, more especially derivatised phenols.

The removal of these compounds has been the subject of research in the industrial and academic fields. Conventional techniques mentioned in the previous chapters are known to have a number of constraints.
5.1.1 The use of Solid Phase Extraction (SPE)

Solid-phase extraction (SPE) is a simple sample extraction technique, where a liquid sample is passed through a sorbent. Both the analytes to be determined and the interferences of the sample are retained on the sorbent by different mechanisms.

The analytes are eluted in a small volume of a solvent thus effectively concentrating the analytes. The function of the SPE is also to clean the sample. The first application (concentration of samples) is used mainly for liquid samples. The second application (cleaning samples), which is usually employed after another sample-treatment technique, is used for solids, gases or liquids. For this reasons, SPE is extremely versatile in the sense that it can be used for a wide range of samples.\textsuperscript{68,70}

The effectiveness of the SPE to retain the analytes is very dependent on the sorbent material used. Several kinds of sorbent materials are known, they can be either cartridges or discs although cartridges are commonly used because only a few sorbents are commercially available in discs. The main advantage of membrane discs is the considerable reduction in the extraction, which means fewer clogging problems for the sorbent.

Various types of sorbent materials with selective sorption properties are being utilized to a large extent in the SPE. Besides natural sorbents, much attention is given to tailored sorbents, which allow the optimal solution of a particular separation problem. Carbonaceous sorbents, the matrix of which mainly consists of carbon, belong to the group of materials of interest.

Nowadays the well known C\textsubscript{18} and C\textsubscript{8} bonded silica, carbon black and polymeric resins are the most commonly used sorbent materials. Non-polar reversed-phase sorbents with silica base were the first materials to be tested in SPE of phenols in
water, of which, C18 is the popular. Retention of phenols from water samples by a C18 sorbent is the result of a reversed-phase mechanism (apolar van der Waals interactions between analytes and sorbent). While apolar compounds can be easily preconcentrated with a C18 or C8 sorbent, most polar compounds, for which polymeric or carbon sorbent are recommended, can be a problem because of their low breakthrough volumes.67

Several attempts have been made to develop new materials for polar compounds mainly using highly crosslinked copolymers or by using chemically modified polymeric resins.71,72

As already mentioned, the main use of SPE is to retain analytes from the sample. This is achieved by the use of appropriate sorbent material to retain specific analytes from the sample. In this part of the project, common and novel cyclodextrin polymers are being used as sorbent material to absorb phenolic compounds from water. This was to evidently prove the ability of these polymer materials to remove organic compounds from water, which forms part of the objectives of this project.

5.2 Experimental procedure

This section explains the analytical methods and experimental procedures that were carried out in order to achieve the objectives of the study. It explains the processes used to carry out laboratory assessment experiments of CD polymers. The preparation of samples, pre-concentration and quantification procedures are also outlined. The techniques used were selected on their merits to fulfill the requirements of this study.
5.2.1 Reagents and solvents

All chemicals used here are from commercial sources and of highest available purity and they were used without further purification. para-Nitrophenol (98 %) was purchased from Aldrich Chemical.

Deionised water (Milli-Q) was used for the preparation of the standards. Dichloromethane was used as GC/MS solvent and for eluting the SPE cartridges together with methanol and ethyl acetate.

5.2.2 Instrumentation

The analytical techniques used to determine absorbing ability of the polymers were Ultra Violet-Visible Spectroscopy (UV-Vis Spectroscopy) and Gas Chromatography-Mass Spectrometry (GC/MS). UV-Vis Spectroscopy was used because of its ability to detect components based on their chromophore characteristics. The UV-Vis spectroscopy measurements were carried out with a CARY 50 UV Spectroscopy using both the “scan” (to determine the maximum absorbance) and the wavelength and “simple read” modes. For the external calibration, at least five standards were used to prepare the calibration curve. The 10 mm quartz cuvette cells were used as sample holders for analysis.

GC/MS was used to determine the concentration at ppb levels, which UV-Vis spectroscopy could not detect. Gas chromatography-mass spectrometry (GC-MS) is by far the most frequent analysis tool for identifying phenols. Important advantages of the GC-MS based methods are: (i) the high amount of structural information yielded and the possibility of using commercial libraries, which make the identification of unknown phenols feasible; (ii) the ruggedness and reliability of the GC-MS interface; and (iii) the high sensitivity and separation efficiency, which avoid the overlapping of compounds with similar structures.73
5.2.3 Absorbent

The use of absorbents in water treatment has been the subject of many investigations. These absorbents are widely used in filtrations (ultrafiltration, micro/macro-filtration) and even in separation (osmosis). The cyclodextrin polymers themselves have also been used in some of these techniques. Some of their many applications have been highlighted in the previous chapters. It is in this part of our work that the synthesized cyclodextrin polymers were tested for their effectiveness in the removal of organic compounds from water. Five water insoluble cyclodextrin polymers: **Polymer 1 (CD-IDI)**, **Polymer 2 (CD-ECH)**, **Polymer 3 (CD-AC)**, **Polymer 4 (CD-Poly (HMDI))** and **Polymer 5 (CDMA-Poly (HMDI))** were selected and used for decontamination of water studies.

5.3 Methodology

5.3.1 UV-Visible analysis

In the following experiments, the stock solution of $p$-Np was prepared by dissolving the solid $p$-Np (35.3 mg) in small volume of warm deionised water (10 ml) then transferred into a 250 ml volumetric flask before filling to the mark with deionised water. From the stock solution five standards (1.0, 1.5, 1.7, 2.0 and 2.5 mg/L) were prepared by drawing a measured aliquot with calibrated pipette into a volumetric flask (100 ml).

The standards were run on the UV-Vis in order to prepare the calibration curve, which was used to determine the concentrations of the samples during the analysis.
5.3.2 Absorption procedure

The cyclodextrin polymers were used without any pretreatment. The 2.0 mg/L \( p \)-Np solution (20 ml) was transferred into five 100 ml conical flasks and to flask 1 was added \textbf{CD-IDi} (0.2008 g), to flask 2 was added \textbf{CD-Ech} (0.2013 g), flask 3 \textbf{CD-AC} (0.2032 g), flask 4 \textbf{CD-Poly(HMDI)} (0.2012 g) and flask 5 \textbf{CDMA-Poly(HMDI)} (0.2003 g), respectively. Once the addition was complete, the polymer in each flask was allowed to stand for noted periods (30 minutes, 2 hrs and 72 hrs) at room temperature. After each period an aliquot was drawn from the solution and run on the UV-Vis instrument to determine the absorbance.

5.3.3 GC-MS analysis

GC/MS analysis was performed using a Varian 3800 capillary gas chromatograph coupled with a Saturn 2000 mass spectrometer. The instrument was equipped with a capillary column (Chrompack CP Sil 8 CB, 30m 0.25mm ID, and 0.25\( \mu \)m), an injector (1\( \mu \)l splitless) at 300\( ^\circ \)C temperature and a mass spectrometer selective detector (Ion trap). The mass spectrometer was operated in the full scan (FS) mode. The temperature of the GC/MS transfer line was 290\( ^\circ \)C; the temperature program was as follows: 35\( ^\circ \)C hold for 2 min to 260\( ^\circ \)C, at 20\( ^\circ \)C/min to 330\( ^\circ \)C and at 6\( ^\circ \)C/min hold for 1 min. The carrier was gas helium at constant flow rate of 1.16 ml/min.

5.3.4 Solid Phase Extraction (SPE) method

A previously weighed polymeric material was placed in a laboratory-made SPE apparatus. This method was adopted and used in our laboratory.\textsuperscript{74} This was achieved by the use of a cartridge, Buchner flask and tap connected to a vacuum manifold. Owing to dealing in very low concentration, it is vital to preconcentrate the solution before any further analysis can be carried out.
The method, as shown in (Table 5.2), includes some steps to ensure complete preconcentration of the solution from conditioning of the sorbent to the elution of the analyte by appropriate solvents.

**Table 5.2 SPE process**

<table>
<thead>
<tr>
<th>Loading procedure</th>
<th>Flow rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1: Process one sample using the following procedure</td>
<td>Condition Flow: 10 ml/min</td>
</tr>
<tr>
<td>Step 2: Wash syringe with 2ml of MeOH</td>
<td>Load Flow: 10ml/min</td>
</tr>
<tr>
<td>Step 3: Rinse column with 5ml of EtOAc into solvent waste</td>
<td>Rinse flow: 10 ml/min</td>
</tr>
<tr>
<td>Step 4: Rinse column with 5 ml of DCM into solvent waste</td>
<td>Elute Flow: 5 ml/min</td>
</tr>
<tr>
<td>Step 5: Condition column with 10ml of MeOH into solvent waste</td>
<td>Condition air push : 10 ml/min</td>
</tr>
<tr>
<td>Step 6: Condition column with 10ml of deionized water into aqueous waste</td>
<td></td>
</tr>
<tr>
<td>Step 7: Load 500 mL of sample onto column</td>
<td></td>
</tr>
<tr>
<td>Step 8: Dry column with gas for 15 minutes</td>
<td></td>
</tr>
<tr>
<td><strong>Eluting Procedure</strong></td>
<td></td>
</tr>
<tr>
<td>Step 1: Soak and collect 3 ml fraction using EtOAc</td>
<td></td>
</tr>
<tr>
<td>Step 2: Collect 2ml fraction into sample tube using EtOAc</td>
<td></td>
</tr>
<tr>
<td>Step 3: Soak and collect 3ml fraction using DCM</td>
<td></td>
</tr>
<tr>
<td>Step 4: Collect 2ml fraction into sample tube using DCM</td>
<td></td>
</tr>
<tr>
<td>Step 5 END</td>
<td></td>
</tr>
</tbody>
</table>

**5.3.5 EPA Method 8270**

EPA method 8270 was adopted in our group as a method for analyzing the samples on the GC/MS instrument. This method is used by the EPA to analyze semi-volatile organic components in water. It can also be used to analyze the phenols and their substituted derivatives.
5.3.6 Standard solution

The Megamix standard (100 µg/L), which comprises a number of common water contaminants, was used for quantification of the samples. A volume of 1 µL of this standard was injected into the GC/MS.

5.3.7 Recyclability of the cyclodextrin polymers

The study of the recyclability of the produced cyclodextrin polymers was carried out using the manual SPE method. The cartridge used was prepared by loading the polymer (CD-ECH, 0.2003 g) into the cartridge. About 500 ml $p$-Np standard solution (10 ppb) prepared in a 4000 ml flask was allowed to pass through the polymer cartridge at a flow rate of 10 ml/min. The collected filtrates were then passed through a $C_{18}$ cartridge. The $C_{18}$ cartridge was then flushed with ethyl acetate (10 ml) followed by dichloromethane (10 ml). The filtrates were then collected and injected into the GC/MS. The passing of the $p$-Np solution through both the polymer and $C_{18}$ cartridge and the flushing thereafter was repeated 15 times. The 16th cycle was unsuccessful due to the slurring of the polymer, which started to block the cartridge opening.
5.4 RESULTS AND DISCUSSIONS

5.4.1 UV-Visible spectroscopy results

The absorption capacity was investigated using para-nitrophenol (p-Np) as the model guest molecule. Besides being available in our laboratories, p-Np is included in the priority list of pollutants as a dangerous substance. This pollutant is also found in many river waters in some parts of South Africa. Organic molecule, para-Nitrophenol, was also selected because of its colour, which makes it possible to visualize when it is absorbed by the polymer. Additionally, it absorbs in the UV-Visible domain thus making it possible to detect its presence by UV-Vis spectroscopy. The calibration curve below shows the absorbances of the standards (Figure 5.1)

![Absorbance against Concentration Curve](chart.png)

Figure 5.1: Calibration curve for p-Np standards

The calibration curve was plotted and used to determine the residual filtrate concentration of each sample from which the amount of the p-Np absorbed by the polymer was determined. The absorption efficiency was determined using the
equation: \( \frac{C_0 - C}{C_0} \times 100\% \) where \( C_0 \) and \( C \) refers to the initial feed (i.e. before absorption) and final (i.e. after absorption) concentrations, respectively.

**Figure 5.2**, shown below, represents the overall absorption capacity of \( p \)-Np on the synthesized cyclodextrin polymers. CD-IDI displays the highest absorption capacity. **CD-AC** and **CD-Poly (HMDI)** display similar absorption maxima with **CDMA-Poly (HMDI)** showing the lowest absorption capacity of about 20%.

**Figure 5.2** Overall absorption capacity of \( p \)-Np on cyclodextrin polymers

**Figure 5.3** display the absorption capacity of the cyclodextrin polymers after 72 hours. It can be noted that at this time, some polymer have reached their maximum absorption capacity and others show low absorption capacity. CD-ECH and CD-AC display the lowest absorption capacity at the noted time 10% and 12%, respectively. It was realized that after this period, polymers (CD-ECH, CD-AC and CDMA-Poly (HMDI)) has reached saturation and therefore started to release the pollutant and thus decreasing their absorption capacity, while again increasing the pollutant concentration in solution. The polymer that demonstrated higher absorption capacity was found to be CD-IDI.
Figure 5.3 Absorption capacity of $p$-Np on cyclodextrin polymers at 72 hours

Figure 5.4 (a and b) shows the absorption capacity of cyclodextrin polymers towards $p$-Np over few hundred hours. This was done to determine the breakthrough point of the polymer. The maximum absorption was obtained after 2 hours by CD-ECH (Figure 5.4b). The highest absorption capacity was obtained after 35 hours by CD-IDI (92%). Leaching behaviour of these polymers, CD-ECH, CD-AC and CD-Poly(HMDI), was observed at different times. CD-ECH and CD-AC start to show the leaching behaviour earlier as compared to other polymers.
Figure 5.4a Kinetics of absorption capacity (in %) of p-Np by cyclodextrin polymers

Figure 5.4b Kinetics of absorption capacity (in %) of p-Np by cyclodextrin polymers
5.4.2 GC/Mass Spectrometry

5.4.2.1 Introduction

The ability of the synthesized cyclodextrin polymers to absorb low concentrations of the $p$-Np (10 ug/L) was demonstrated by passing spiked deionised water with known concentration of $p$-Np and analyzed using GC/MS technique. Since trace analysis was involved, pre-concentration of the sample is very crucial, SPE was employed to achieve this task. Pre-concentration procedure is best achieved by these four sequential steps: washing, conditioning, loading (sample) and elution.

5.4.2.2 Absorption studies

Figure 5.5 shows the standard chromatogram with numerous organic compounds. Each of the compounds in the spectrum can be identified using their mass ratio ions (m/z) from the mass spectra together with a library match of the spectrum.
Figure 5.5  Megamix standard chromatogram showing the peak intensities and retention times of some of the compounds in the standard mixture

In order to study the recoveries for the p-Np compound, a sample volume (500 ml) of the analyte studied was preconcentrated on the C$_{18}$ sorbent. The chromatogram obtained when 500 ml of p-Np solution were preconcentrated by using the C$_{18}$ cartridges is shown in Figure 5.6.
Figure 5.6  The spectrum of C$_{18}$ absorbent after passing the p-Np solution through the cartridge

The p-Np compound retained in the cartridges was eluted with a mixture of ethyl acetate and dichloromethane (1:1). It can be seen from the chromatogram that the p-Np peak appears. The C$_{18}$ was unable to retain all of the p-Np from the solution.
The above procedure was repeated with a cyclodextrin polymer in the laboratory made cartridge. Figure 5.7 shows the GC/MS spectrum of CD-ECH cartridge after 500 ml of p-Np was passed through.

Figure 5.7 The chromatogram of CD-ECH polymer after 500 ml of p-Np solution was passed through the polymer cartridge

From the chromatogram (Figure 5.7), it is clear that the > 99% p-Np was retained by the polymer. This was observed with other polymer materials. Based on the results obtained in this work, GC/MS allows the quantification of nitrophenol in the µg/L range in water by solid phase extraction from sample volumes of 500 ml.
Table 5.4  The retention times of $p$-Np from the Megamix standard chromatogram, C$_{18}$ sorbent and CD-ECH (from Figures 5.5-5.7)

<table>
<thead>
<tr>
<th>Sorbent material</th>
<th>Retention time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{18}$ Megamix</td>
<td>10.799</td>
</tr>
<tr>
<td>C$_{18}$ $p$-Np</td>
<td>10.773</td>
</tr>
<tr>
<td>CD-ECH $p$-Np</td>
<td>ND</td>
</tr>
</tbody>
</table>

*ND: not detected, m/z ($p$-Np)= 139 , Rt ($p$-Np)=10.799 min

5.4.3  The recycleability study of the polymers

A study on the regenerability of the CD polymers was performed using cartridges. Studies were performed using the adipoyl linked polymer. The aim was to observe how effective the polymers would be in removing the organic contaminants after a number of cycles of use. Repetitive absorption experiments were carried out using the same polymer. Studies were initially performed by flushing 500mL of 10 µg/L of standard $p$-Np water sample through a cartridge packed with polymer. Experiments were performed to the fifteenth cycle. Figure 5.8 shows a graphical representation of the results obtained.
The polymer was recycled several times and relatively consistent absorption efficiency was observed up to the last cycle. The polymer was washed with 10 mL of ethanol to remove the absorbed organic contaminants from the polymer cavities. It was then dried before the next experiment was conducted. In the first experiment conducted about 100% of 10 µg/L concentration was absorbed. Better absorptions were also observed in subsequent experiments. The fifteenth experiment also showed absorption capacities of > 99%.

It can be concluded that cyclodextrin polymer has shown some ability to absorb > 99% of the \( p \)-Np from the solution. Even though the breakthrough point of the polymer material was not reached the polymer nevertheless was able to retain > 99% of the \( p \)-Np. The polymer started to disintegrate into finer particles in the sixteenth cycle resulting in clogged cartridge opening. This disadvantaged further cycle to be performed. In another study\(^7\) the recycleability was performed and twenty cycles were achieved with the \( \beta \)-CDHDI polymer. The polymer also demonstrated maximum absorption efficiency of greater than 99.9%.

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**Figure 5.8** The amount of organic pollutant removed after treating 10 µg/L sample with CD-AC polymer
polymer used was powdery material and swells without showing any sign of disintegration in water.
CHAPTER SIX

CONCLUSIONS AND RECOMMENDATIONS

The main aim of this study was to prepare and characterize a series of cyclodextrin polymers and test their ability to remove organic pollutants from water. It can be concluded that these aims were successfully achieved. This section summarizes the results that were obtained in this study and concludes with recommendations.

6.1 Conclusions

♦ The synthesis of nanoporous cyclodextrin polymers was demonstrated. There were three synthetic methods (Method A, B and C) that were adopted in this study towards the preparation of the polymers. Both water soluble and insoluble polymers were produced and characterized. Satisfactory yields of the polymers were generally obtained with the exception of few polymers, the lowest being 20%.

♦ The reaction parameters (temperature, mole ratio and time) for the polymerization were also investigated and reported. Some reactions when operated at high temperature, produced gelatinous substances.

♦ Molecular structures of the polymers were determined using FT-IR and proton NMR. Through both techniques, the identity of the polymers was elucidated.

♦ Thermal analysis revealed the stability of the cyclodextrin polymers over a wide temperature range (100-350°C). Further characterization of surface area and morphology of the polymers was achieved using BET and SEM analyses.
To test the absorption ability of cyclodextrin polymers to remove organic contaminants in water, water was spiked with 10 µg/L and 10 mg/L concentration and preconcentrated using SPE and analyzed using GC-MS and UV-Visible spectroscopy. The polymer (CD-IDI) showed higher absorption efficiency of about 92% with higher concentration (10 mg/L). At lower concentration (10 µg/L) more than 99% was absorbed by the CD-AC polymer.

When higher concentration (10 mg/L) was used some polymers tend to lose their absorption effectiveness and showed some leaching behaviour. This behaviour confirms the assertion observed that the cyclodextrin polymers are more suitable for the removal of micro-organic pollutants at low concentrations (ppb).

The recyclability studies demonstrated that the polymer still maintains high absorption efficiency after a number of cycles.

6.2 Recommendations

Although most cyclodextrin polymers have been synthesized and characterized, further characterization of the materials is still necessary especially with the use of solid state NMR spectroscopy for both proton and carbon analyses.

Since the use of synthetic polymers has surpassed that of natural polymers, further polymerization methods of cyclodextrin need to be explored (e.g. attaching cyclodextrin as pendant to other polymers). Combination of cyclodextrin polymers with other novel materials (e.g.
carbon nanotubes) may further enhance the strength of polymers and improve their absorption capacity.


APPENDIX A

SELECTED $^1$H NMR SPECTRA OF CYCLODEXTRIN POLYMERS
Figure A1: $^1$H NMR spectrum of CD-NDA polymer
Figure A2: $^1$H NMR spectrum of CD-PA polymer
Figure A3: $^1$H NMR spectrum of CD-SC A polymer
Figure A4: $^1$H NMR spectrum of CD-SC B polymer
Figure A5: $^1$H NMR spectrum of CD-TC polymer
Figure A6: $^1$H NMR spectrum of CD-MA polymer
Figure A7: $^1$H NMR spectrum of CD-DDS polymer
APPENDIX B

THERMOGRAVIMETRIC ANALYSIS OF CYCLODEXTRIN POLYMERS
Figure B1: TGA thermogram of CD-AC polymer

Figure B2: TGA thermogram of CD-MA polymer
Figure B3: TGA thermogram of CD-PA polymer

Figure B4: TGA thermogram of CD-SC B polymer
Figure B5: TGA thermogram of CD-DBH polymer

Figure B6: TGA thermogram of CD-GC polymer
Figure B7: TGA thermogram of CD-GA polymer

Figure B8: TGA thermogram of CD-TC polymer
Figure B9: TGA thermogram of CD-DDS polymer

Figure B10: TGA thermogram of CD-NDA polymer
Figure B11: TGA thermogram of CDMA-Poly(HMDI) polymer

Figure B12: TGA thermogram of CD-Poly (HMDI) polymer
Appendix C

Absorbance and Concentration results of the $p$-Np standard

Table C1: Absorbance of the $p$-Np standards

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<th>Concentration (mg/L)</th>
<th>Absorbance</th>
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<tbody>
<tr>
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<tr>
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<td>1.4473</td>
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<td>1.7</td>
<td>1.6642</td>
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<td>1.9801</td>
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<tr>
<td>2.5</td>
<td>2.4098</td>
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APPENDIX D

CHROMATOGRAPHIC DATA OF \( p \)-NITROPHENOL

Selected chromatographs and mass spectra of the investigated organic contaminants are shown below (Figure D1-D7). Each figure shows the characteristic peak together with the ion fragments from the mass spectra.
Figure D1: Absorption of \( p \)-Np by \( C_{18} \) adsorbent polymer
Figure D2: Absorption of $p$-Np by CD-ECH polymer
Figure D3: Absorption of \( \rho \)-Np by CD-AC polymer
Figure D4: Absorption of p-Np by CD-IDI polymer
Figure D5: Absorption of $\rho$-Np by CD-Poly(HMDI) polymer
Figure D6: Absorption of \( p \)-Np by CDMA-Poly(HMDI) polymer
Figure D7: Absorption of ρ-Np by CD-TDI polymer
APPENDIX E

RECYCLEABILITY OF CYCLODEXTRIN POLYMERS CHROMATOGRAPH
Figure E1: Absorption of $\rho$-Np by CD-AC polymer (Run 1)
Figure E2: Absorption of $p$-Np by CD-AC polymer (Run 5)
Figure E3: Absorption of $\rho$-Np by CD-AC polymer (Run 15)