



## CHAPTER I

### INTRODUCTION

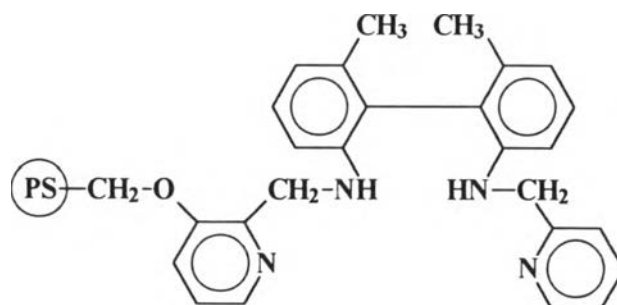
During recent years chelating polymers have been gained numerous attention from research scientists in the fields of polymer chemistry, analytical, inorganic and organic chemistry. The interest originates from their possible applications in metal processing, waste water treatment and in solving problems in environmental chemistry. In the last decade several reviews [1] have been published describing the applications of commercially available chelating resins. Properties of the resins including high capacity, high selectivity and fast kinetics of chelation are primarily concerned in order to meet users' requirements. Therefore the trends for development of resins have been improved directly to such the properties.

#### **Chelating Polymers [2]**

Chelating polymers have received considerable attention owing to their inherent advantages over simple ion exchange resins in their high selectivity of metal ions in sorption processes [3]. They have been used for water treatment, pollution control, and recovery of metals or in analytical chemistry. The selective adsorption depends on a stability constant of a complex occurring between a particular polymer ligand with a particular metal ion at a definite pH. The higher value of the constant is, the more stability of the complex obtains. However, the selectivity of most ligands with metal ions resides predominantly in their ability to form complexes, which rely on many factors.

In general, the selectivity coefficient of chelating polymers for specific separation is influenced by (a) the nature and type of ions to be separated, (b) the nature and structure of the chelating group, (c) the molecular structure surrounding the chelating group, (d) the degree of metal ion adsorption, (e) stability of the resulting metal complex, (f) solvent and pH used, and (g) temperature of separation.

Polymers containing coordination groups (ligands) have been used for a selective separation of metal ions depending on the coordination number and the geometry of the ions. Polymer ligand (1) with a maximum of four N-donor atoms restricts to a tetrahedral arrangement of the complex that was found to favour chelation of ions such as  $\text{Cu}^{2-}$  over  $\text{Fe}^{3+}$ . 1 have higher ability to form complex with  $\text{Cu}^{2-}$  [2].



PS = Polystyrene

1

Bond length and angles between the chelated central metal ion and the ligands are dependent upon types of metal ions and ligands. When a coordinated stereostructure of a polymer-metal complex is fixed, then the central metal ions are removed, while the stereostructure is maintained fixed. The remaining polymer ligand will have pockets especially fitted for the same

metal ion. The coordinated stereostructure of a polymer-metal complex chain has been made by crosslinking the complex. The metal was removed by deformation of the polymer-metal complex. The crosslinking procedure corresponds to a kind of template formation. For example, when a metal complex of polyvinylpyridine is crosslinked with dilute acid, the remains metal-free resin shows selectivity to adsorb the same type of metal ions that were removed [4,5].

Polymers attached to macrocyclic ethers have been shown to complex metal ions. Recently, three different types of polymeric ethers, crown ethers, cryptands and podands have been introduced as a new class of neutral ligands to replace the conventional ion exchangers [6]. The ion-chelating properties of these neutral ligands have led to their selective applications in extraction or separation of trace metals or isotopes and organic solutes. Their selectivity depends on the ring member as well as on the diameter and steric factors of the ring [7]. A number of neutral ligands with considerable enhanced selectivity to bind metal ions have therefore been developed over recent years.

The chelating resins are usually regenerated for reuse by eluting or extracting the sorbed metal from the resins. Mineral acids such as HCl, H<sub>2</sub>SO<sub>4</sub> or HNO<sub>3</sub> have been used to regenerate loaded chelating resin.

Feng and his co-workers [8] synthesized the chelating resin by copolymerization of 1-( $\beta$ -acrylamidoethyl)-3-hydroxy-2-methyl-4(1H) pyridinone (AHMP) and N,N'-dimethylacrylamide (DMMA) in the presence of N,N'-ethylene-bis-acrylamide (EBAA) as a crosslinking agent. The resins showed high selectivity for iron (III) and the iron (III) chelating capacity was

146  $\mu\text{mol/g}$  in the batch process. While that using the column process was 144  $\mu\text{mol/g}$ .

Latha *et.al.* [9] reported the preparation and application of the chelating resin based on the hydrophilic polyacrylamide using N,N'-methylene-bis-acrylamide as the crosslinking agent. The resins could be used to adsorb  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cu}^{2+}$  at the capacity of 3.62, 4.22, 1.48 and 1.67 meqv/g, respectively.

Table 1.1 lists some of the chelating polymers that have been used in selective separation of metal ions.

Table 1.1 Chelating polymers.


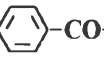
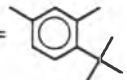
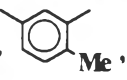
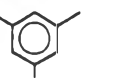
Chelating polymer	Application	Reference
$\left( \begin{array}{c} \text{N}-(\text{CH}_2)_2-\text{NH}-(\text{CH}_2)_2 \\   \\ \ominus \text{S}-\text{C}=\text{S} \end{array} \right)_n$	adsorption of various metal ions	[10,11]
$\left( \text{NH}-\text{R}'-\text{NH}-\overset{\text{S}}{\parallel}{\text{C}}-\text{R}-\overset{\text{S}}{\parallel}{\text{C}} \right)_n$	adsorption of various metal ions	[12]
$\left[ \begin{array}{c} \text{CH}-\text{R}-\text{CH} \\ \diagup \quad \diagdown \\ \text{S}-\text{R}'-\text{S} \\ \text{S}-\text{R}'-\text{S} \end{array} \right]_n$ <p> <math>= -(\text{CH}_2)_3-</math> ; <math>\text{R}' = -(\text{CH}_2)_4-</math>  <math>\text{R} = </math>  ; <math>\text{R}' = -\text{CO}-</math>  <math>-\text{CO}-</math> </p>	selective separation of $\text{Hg}^{2+}$	[13,14]
$\left( \text{S}-\underset{\text{R}}{\text{CH}}-\text{CH}_2 \right)_n$ <p> <math>\text{R} = \text{Me}, \text{CH}_2-\underset{\text{Me}}{\text{N}}-\underset{\text{Me}}{\text{C}}\text{HR}'</math> ; <math>\text{R}' = \text{Et}</math> </p>	adsorption of $\text{Cu}^{2+}$	[15]
$\left[ \text{NH}-\text{R}-\text{NH}-\begin{array}{c} \text{N}-\text{N} \\ \diagdown \quad \diagup \\ \text{S}-\text{Cu}-\text{S} \\ \diagup \quad \diagdown \\ \text{N}-\text{N} \end{array} \right]_n$ <p> <math>\text{R} = </math>  ,  ,  </p>	selective separation of $\text{Cu}^{2+}$	[16]

Table 1.1 (continued).

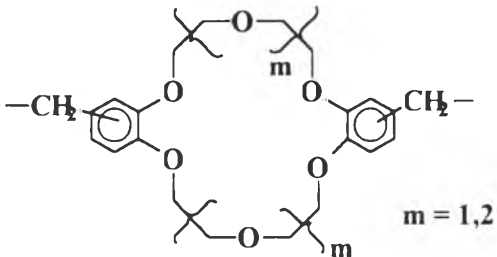
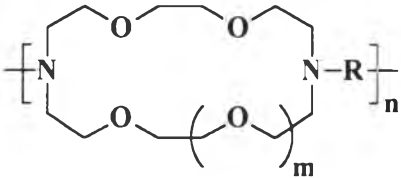
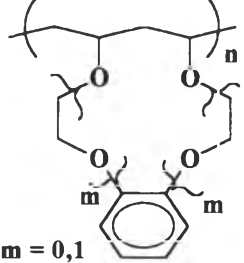
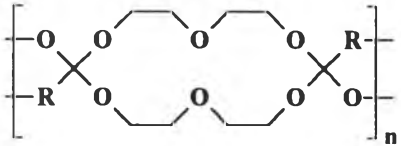
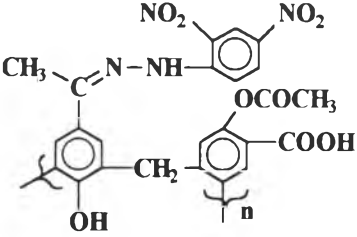
Chelating polymer	Application	Reference
 <p style="text-align: right;"><math>m = 1,2</math></p>	selective separation of $K^+$ , $Pb^{2-}$ and $Cs^+$	[17]
	binding of alkali metal ions	[18-20]
 <p style="text-align: center;"><math>m = 0,1</math></p>	extraction of $UO_2^{2+}$ from seawater	[21]
	binding of various metal ions	[22]



Table 1.1 (continued).

Chelating polymer	Application	Reference
$\left[ \text{CH}_2 - \underset{\text{C}(\text{OH})=\text{CH}-\text{CO}-\text{CH}_3}{\text{CH}} \right]_n$	adsorption bivalent transition metal ions	[23]
	adsorption of bivalent metal ions	[24-26]

### Objectives and Scope of the Research

8-Hydroxyquinoline is known to form complexes with various metal ions, such as  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Pb}^{2+}$  etc. [27]. When 8-hydroxyquinoline is incorporated into phenol-formaldehyde resin, the resulting polymer shows selectivity in metal separation [2].

Therefore, 2,4-diamino-6-hydroxypyrimidine (**3**) was chosen as a chelating ligand and **3** can be incorporate into the polymer backbone by crosslinking reaction of **3** with Bisphenol-A epoxy resin (**2**).

It is because the excellent properties of polyethers, such as good chemical resistance and flexibility. Besides, the addition of chelating groups on the polymer chain can be performed easily. Therefore, polyether was chosen as the backbone of chelating polymers. The introduction of chelating groups into the polyether matrix can be achieved using crosslinking reaction.

### **Objectives**

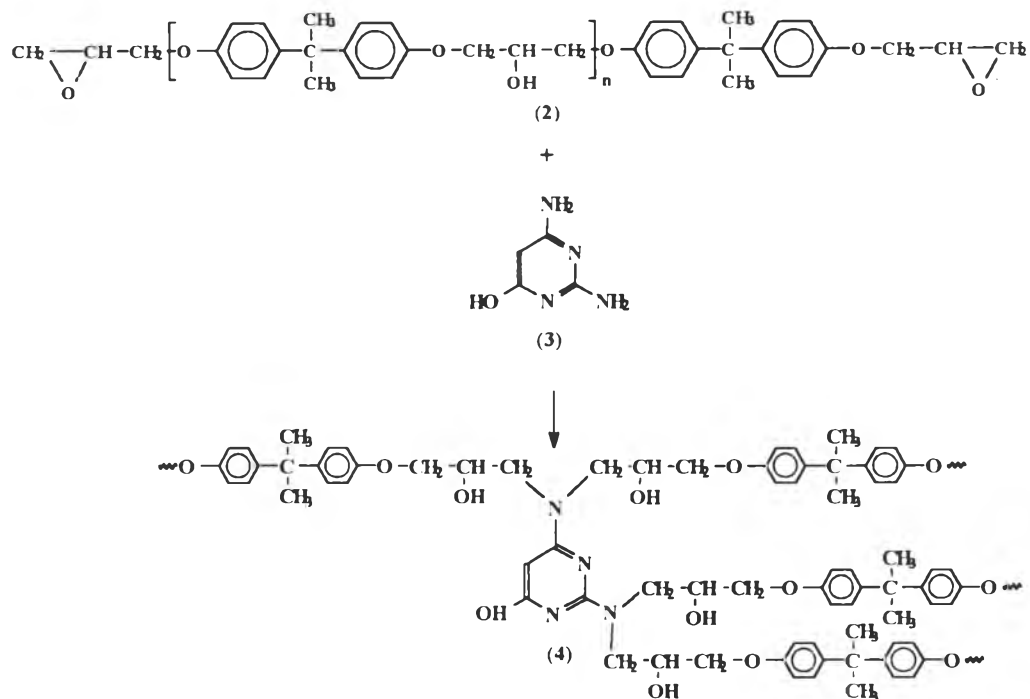
The principle objective of this study was to prepare chelating polyethers containing diamino ligand and to investigate their chelating ability with metal ions.

### **Scope of the Research**

#### **1. Synthesis of the Chelating Polyether**

Bisphenol-A epoxy resin (2) could undergo a crosslinking reaction with 2,4-Diamino-6-hydroxypyrimidine (3) to yield the crosslinked chelating polyether resin (4) containing aromatic diamine ligands. The proposed crosslinking reaction and structure of the crosslinked resin are shown in Scheme 1.1.





Crosslinked chelating polyether having aromatic diamine ligands (4).

Scheme 1.1

## 2. Characterization and Analysis of the Chelating Polyethers

Characterization of the obtained crosslinked resin (4) were carried out using thermal and spectroscopic methods. Complexing ability of the resin (4) with various metal ions were investigated. The chelating capacity and selectivity of the metal-resin complex were determined. Reusable ability of the resin (4) was investigated.