

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Preparation of functionalized polymers

Polymers which the desired chemically functional groups attached to the structure are called functionalized polymer. They posse the potential advantages of small molecules with the same functional groups. Their application is related both to the functional groups and to their polymeric nature³.

The selection of the polymeric matrix, both synthetic aliphatic and aromatic polymers, is an important factor for successful application. In addition, a wide range of natural polymers have also been functionalized and used as reactive materials.

However, the first step in the preparation of a functionalized polymer is the introduction of functional groups to a polymer. The functional groups may be a part of the polymer backbone or attached to a side chain as a pendant group either directly or through a spacer group. An introduction of required functional group onto a polymeric support can be done by

- (a) Polymerization (both homopolymerization and copolymerization) of desired functional monomers
- (b) Chemical modification of a suitably non-functionalized polymer
- (c) A combination of (a) and (b)

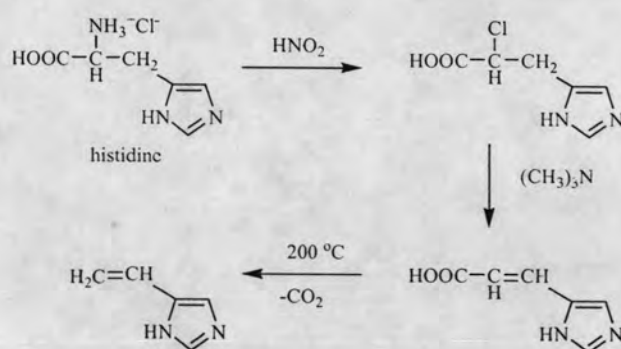
Each of the approach has its own advantages and disadvantages. One of them may be suited for the preparation of a particular functional polymer when the other would be totally impractical. The selection between the two ways to the synthesis of functionalized polymers depends mainly on the required chemical and physical properties of the support for a specific application.

2.1.1 Polymerization

The aim of this technique is to obtain the specific structures and properties of functional polymer. The modification by this method can be divided into a homopolymerization and copolymerization. The resulting polymer, either a

homopolymer or a copolymer, can be used in the desired application immediately as it is or after further modification. The key to the utility of this approach is whether the required functional group can be incorporated into a monomer that undergoes polymerization.

The example of homopolymerization can be illustrated for the preparation of poly[4(5)-vinylimidazole] catalyst. Synthesis involves the sequence of reactions starting from histidine to yield 4(5)-vinylimidazole, which is subsequently polymerized by radical initiation as shown in Scheme 2.1.



Scheme 2.1 Preparation of 4(5)-vinylimidazole monomer.

Morris, L. R. and co-workers⁴ prepared vinyl-substituted amino acids as intermediates in the synthesis of chelating polymers. Most of the syntheses started with vinylbenzyl chloride and its derivatives. These products retained the polymerizability of styrene as well as the capacity to chelate metal ions. The resulting polymers, both soluble and crosslinked, have been prepared and show interesting properties as chelating resins.

In order to obtain a product with a particular combination of desirable properties, the chemical structure of a polymer can be varied over a wide range by means of copolymerization. Copolymerization is the reaction that merges two or more monomer units to give polymer that contains more than one type of structural units in the chain with only a fraction of the segments carrying the required group on the molar ratio of monomers employed. This method is used to change polymer properties and to allow the synthesis of an almost unlimited number of different products by variations in the nature and relative amounts of the monomers unit in the copolymer product. In addition, the main advantages of copolymerization lie in the

modified properties of the obtained polymers, e.g. a change in solubility or a crosslinked structure. The required physical form of crosslinked polymers containing the functional groups can be achieved during the polymerization process itself by copolymerization process itself by copolymerizing monomer with divinyl compounds. For example, Feng and his co-workers⁵ synthesized the chelating resin by copolymerization of 1-(β -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 towards Fe(III).

In addition, the main advantages and disadvantage of polymerization technique are shown in Table 2.1.

Table 2.1 Advantages and disadvantages of polymerization technique

Advantages	Disadvantages
<ul style="list-style-type: none"> • Polymer is homogeneous with more uniform of functionalization • Structure of required functional group can be determined by analysis of monomers prior to polymerization • Possible to control the loading and distribution of functional groups 	<ul style="list-style-type: none"> • Introduction of a functional group during polymerization requires an appropriately substituted monomer • Some monomers lose stability and exhibit incompatibility during polymerization. • In some cases, copolymerization is the great difficulty • Optimum molecular weight, desirable distribution and compositional homogeneity can be accomplished sometimes with difficulty • Monomers must be highly pure

2.1.2 Chemical functionalization of polymers

This is an important technique in the preparation of functional polymers. It has been used extensively both in industry to modify the properties of polymers for various technological applications and in the polymer-supported chemistry to prepare chemically reactive polymers. Chemical modification makes the possibility to create new types of functionalized polymers which cannot be prepared by direct polymerization of the monomers due to their instability or unreactivity and to modify the structure and physical properties of other polymers to make them suitable for specific applications. For example, attempts to prepare linear poly(*N*-alkylethylenimines) directly by ring-opening polymerization of *N*-alkylethylenimines were unsuccessful but these products could be successfully prepared by the chemical modification of poly(*N*-alkylethylenimines)⁶ as shown in Figure 2.1.

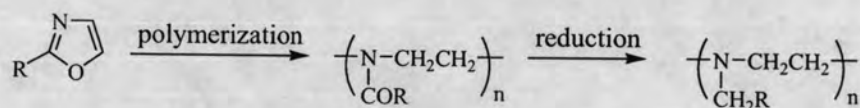


Figure 2.1 Preparation of linear poly(*N*-alkylethylenimines).

Generally, chemical reactions of polymers can be divided into two types.

1. Reactions at the main chain of polymer, include the degradation which are accompanied by a decrease in molecular weight or intermolecular reactions which results in three-dimensional structures (increase of molecular weight), and the synthesis of a graft or block copolymer.

2. Reactions at the side chain which result in a change in composition of the polymer without alternating the molecular weight. Starting from an already polymeric matrix with reactive groups and then replacing them with the desirable functional groups via chemical reaction. This is the simplest and more frequently used technique for the preparation of high molecular weight polymers with functional groups.

In this way, high quality commercially polymers are normally used and the desired functional groups are introduced by using standard organic synthesis procedures. The ease of chemical modification and the level of success in its

subsequent application can depend substantially on the physical properties of the resin.

2.1.3 Polystyrene functionalization

Polystyrene is the most widely used as a support material. It has hydrophobic surface. Most recent works on the chemical modification of polymers have been focused on the introduction and modification of various functionality groups on polystyrene. The uses of other polymers have met with limited success for reasons such as lack of reactivity, degradation of the polymer chain, or other unsuitable physical properties of the finished polymer. In principle, polystyrene fulfils the major requirements for a solid support because it has many advantages over other resins.

1. The functionalization undergoes through the aromatic ring by electrophilic substitution reaction.

2. Styrenic polymers are compatible with most organic solvents. Thus, the functional groups are easily accessible to the reagents and the solvents.

3. The aliphatic hydrocarbon backbone is chemically stable to the attraction by most reagents. The polymer chains are not susceptible to degradative scission by most chemical reagent under ordinary conditions.

4. Styrenic polymers are mechanically stable to the physical handling required in sequential synthesis.

5. The degree of crosslinking in the polymer influences its swelling nature and the pore dimension. The type and degree of crosslinking can easily be controlled during manufacture by regulating the concentration of divinylbenzene.

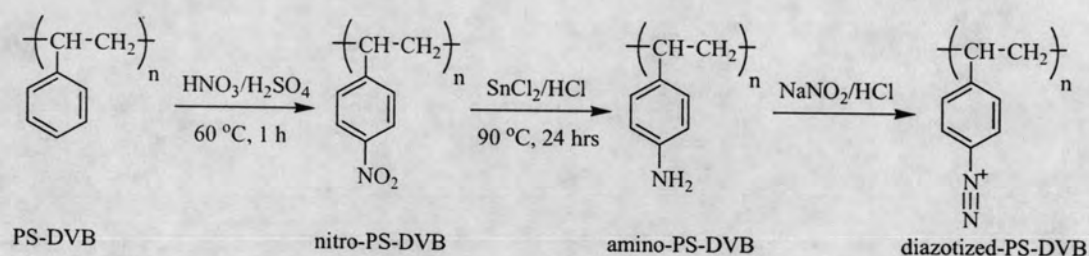
6. Polystyrene is readily available commercially. Amberlite XAD-1, XAD-2, XAD-4 and XAD-16 are commercially polystyrene-divinylbenzene (PS-DVB) resins with a high hydrophobic character and no ion-exchange capacity.

Polystyrene, chloromethylated polystyrene and ring-lithiated polystyrene are often used in the chemical modification of styrene resins for the preparation of new functionalized polymers because they have a wide variety method of attaching of functional group, both electrophilic and nucleophilic species.

There are many ways in preliminary in chemical modification of polystyrene. After that, the desired chemical group can be introduced later. An example of preliminary method can be done as the following:

2.1.3.1 Nitration

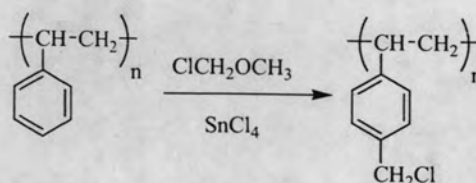
PS-DVB reacts with a mixture of hot, concentrated nitric acid and sulfuric acid to give nitro group at benzene ring. Sulfuric acid is a catalyst, allowing nitration to take place more rapidly, safer and at lower temperatures than use only concentrated nitric acid. Nitro group of benzene can be reduced with SnCl_2 in HCl to give amino group and this group can change to diazonium group by diazotization of an amine. Diazonium group can be reacted with various ligands. This method is often used in modification of PS-DVB. Nitration and related reactions of PS-DVB were shown in Scheme 2.2.



Scheme 2.2 Nitration and related reactions of PS-DVB.

2.1.3.2 Chloromethylation

Chloromethyl group can be introduced to styrene-divinylbenzene copolymer by treatment of copolymer with chloromethyl methyl ether in presence of a Friedel-Crafts catalyst⁷ as shown in Scheme 2.3. This functionalized resin was used in solid-phase peptide synthesis, ion-exchange resin with reacted with tertiary amine⁸, and solid phase extraction etc.



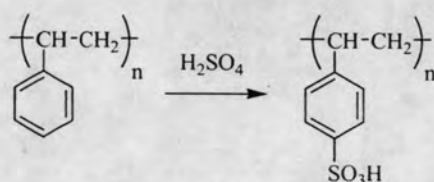
Scheme 2.3 Chloromethylation of PS-DVB.

2.1.3.3 Acylation

Acylation allows a variety of functionalization to be achieved; these transformations are normally carried out easily from an acylating agent by means of the Friedel–Crafts reaction⁹, using, for example, carbon disulfide or nitrobenzene¹⁰ as the solvent and catalyst such as aluminium chloride or aluminium chloride. Such reaction can made many derivative of PS-DVB such as hydroxymethyl derivative¹¹, benzoyl derivative¹², *o*-carboxybenzoyl derivative¹³, 2,4-dicarboxybenzoyl derivative¹⁴ and Tetrakis (*p*-carboxyphenyl)porphyrin derivative¹⁵.

2.1.3.4 Sulfonation

Sulfonation is carried out by reaction of the resin with sulfuric acid¹⁶ as was shown in Scheme 2.4. These derivatives of PS-DVB are frequently used as ion exchangers in chromatography technique and preparative analysis. They are commercially available under different names and characteristics such as Hamilton PRP-X200, Amberlite IRA-200, Dowex DR-2030, Sep IC-H (Lida) or NovoClean IC-H (Alltech).



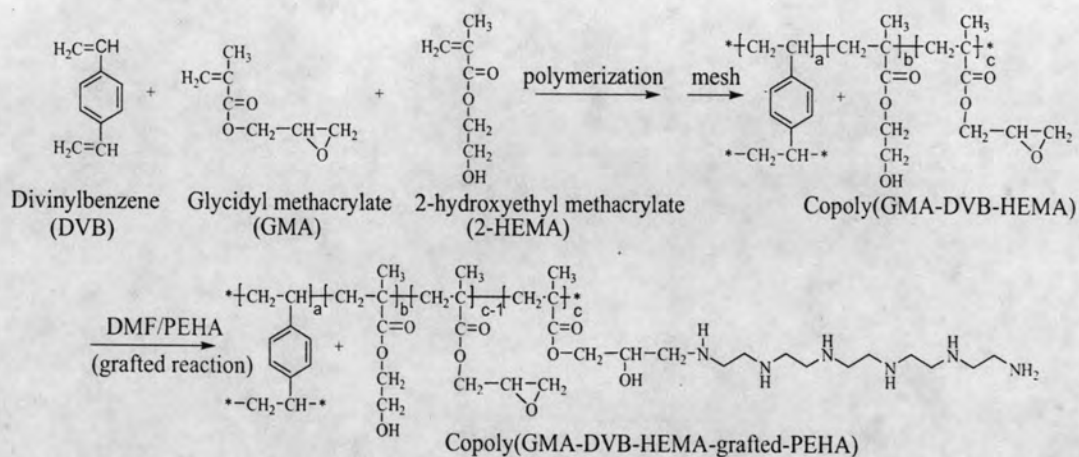
Scheme 2.4 Sulfonation of PS-DVB.

2.1.3.5 Copolymerization

Copolymerization is the useful method in order to change the chemical structure and properties of polystyrene by choosing the appropriated and the relative amount of monomers. By mean of this method, the synthesis of an unlimited different product can be done.

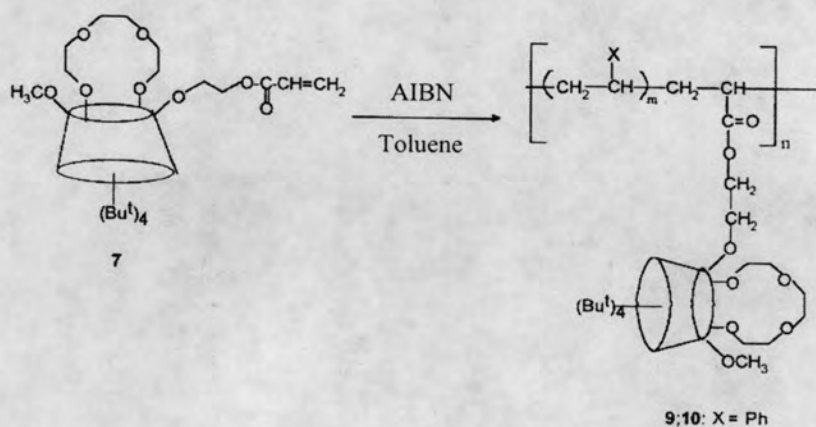
For example, Wang, C.C. and Wang, C.C.¹⁷ prepared copoly(GMA-DVB-HEMA) from glycidyl methacrylate (GMA), divinylbenzene (DVB) and 2-hydroxyl

ethyl methacrylate (2-HEMA) via suspension polymerization (Scheme 2.5). Then, pentaethylenehexamine was grafted onto copolymer obtain chelating copolymer. The chelating copolymer exhibits a chelating ability that allow them to compete with Cu(II)-EDTA complex for cupric ion in waste-water.



Scheme 2.5 The preparation of copoly(GMA-DVB-HEMA-grafted-PEHA).

Memon, S. Uysal, G. and Yilmaz, M.¹⁸ synthesized new polymers containing pendant calix[4]crown-4 units via radical initiated reactions involving a copolymerization of vinylic monomer (5,7,11,23-tetra-tert-butyl-25-[2-(Acryloxy)ethoxy]-27-methoxycalix[4]arene-crown-4) (Scheme 2.6) and with styrene monomer at different molar. The modified resins were tested for metal ion adsorption with Li⁺, Cs⁺, Hg²⁺, Cu²⁺ and Cd²⁺.



Scheme 2.6 Copolymerization of calix monomer(7) with styrene monomer.

2.1.4 Chelating agents^{19,20}

The chelating agent is a molecule that fulfills at least two conditions. First, it must possess at least two appropriate functional groups, the donor atoms of which are capable of bonding to the same metal atom by donating a pair of electrons. Elements that act as donors are the more electronegative ones on the right-hand side of the periodic table. They are primarily found in Group V (nitrogen, phosphorus, arsenic, and antimony) and in Group VI (oxygen, sulphur, selenium, and tellurium). Donor atoms may be part of a basic or an acidic functional group. A basic group is one that contains an atom carrying a lone pair of electrons which may interact with a metal ion (or a proton). An acidic group loses a proton and coordinates with a metal atom. Some examples of these are shown in Table 2.2.

Table 2.2 Some examples of basic and acid group of chelating agent

Basic groups		Acid groups	
-NH ₂	(amino)	-CO ₂ H	(carboxylic)
-NH	(imino)	-SO ₃ H	(sulphonic)
-N=	(tertiary acyclic or heterocyclic nitrogen)	-SH	(thioenolic and thiophenolic)
=O	(carbonyl)	-PO(OH) ₂	(phosphoric)
-O-	(ether, ester)	-OH	(enolic and phenolic)
=N-OH	(oxime)	=N-OH	(oxime)
OH	(alcohol)		
-S-	(thioether)		
-PR ₂	(substituted phosphine)		
-AsR ₂	(substituted arsine)		

Second, these functional groups must be so located in the molecule that they permit the formation of a chelating ring with a metal atom as the closing member is sterically possible. The process of forming a chelate is chelation. For example, in ethylenediamine the two amino groups are separated by two linked carbon atoms and this carbon bridge confers some degree of flexibility on the molecule so that it easily adopts conformations in which the nitrogen atoms occupy adjacent positions in the coordination shell of a metal ion without much departure from the 'natural' tetrahedral bond angles of four-covalent carbon. Thus chelation of ethylenediamine imposes relatively little strain on the ligand molecule. The chelating properties of propylenediamine (1,3-diaminopropane) and longer-chain aliphatic diamines are similar to those of ethylenediamine because the flexibility of the carbon chain permits chelation to occur easily.

Chelating agents can be classified according to:

(a) The number of donor atoms capable of combining with a metal atom present. A chelating agent that has two donor atoms is called bidentate; one that has three, tridentate; and so on.

(b) Based on the particular types of functional groups which are described as basic (or coordinating e.g. NH_2) and acidic

This provides a basis for consideration of the properties of ligands that are of major significance in chelation. The nature of the functional group will give an idea of the selectivity of the ligand towards trace elements.

In practice, inorganic cations (metal ion) may be divided into 3 groups²¹:

group I-'hard' cations: these preferentially react via electrostatic interactions (due to a gain in entropy caused by changes in orientation of hydration water molecules); this group includes alkaline and alkaline-earth metals (Ca^{2+} , Mg^{2+} , Na^+) that form rather weak outer-sphere complexes with only hard oxygen ligands.

group II-'borderline' cations: these have an intermediate character; this group contains Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+} , Mn^{2+} . They possess affinity for both hard and soft ligands.

group III-'soft' cations: these ions tend to form covalent bonds, such as Ag^{2+} , Cd^{2+} , Pd^{2+} , Pt^{2+} and Hg^{2+} . Hence, Ag^{2+} , Cd^{2+} possess strong affinity for intermediate (N) and soft (S) ligands.

For soft metals, the following order of donor atom affinity is observed: $\text{O} < \text{N} < \text{S}$. A reversed order is observed for hard cations. For a bidentate ligand, affinity for

a soft metal increases with the overall softness of the donor atoms: (O, O) < (O, N) < (N, N) < (N, S). The order is reversed for hard metals. In general, the competition for a given ligand essentially involves Group I and Group II metals for O sites, and metals of Group II and Group III for N and S sites. The competition between metals of Group I and Group III is weak.

2.2 Characterization of functionalized polymers

There are several techniques used to characterize functionalized polymer. Most of them involve spectroscopy technique, such as:

2.2.1 Infrared spectroscopy

Infrared spectroscopy is one of the most commonly used in spectroscopy techniques that engage with the infrared region of the electromagnetic spectrum²².

It is widely used for analysis, both organic and inorganic, of sample types such as gases, liquids and solid by using various sampling accessories.

Each of functional groups has its own absorbance characteristic frequencies of IR radiation. Thus, the spectra of IR spectroscopic analysis provide the present of chemical functional groups in the matrix. This can give the information about its molecular structure and chemical nature.

The characteristic frequencies of functional group can be divided into the region such as: 4000-2500 cm^{-1} as single bond stretch, 2500-2000 cm^{-1} as triple bond, 2000-1500 cm^{-1} as double bond and fingerprint region around 1500-500 cm^{-1} .

Polymers in solid form have to be grind with KBr or dissolved in a suitable solvent, while in sheet or film form can be directly analyzed by mounting with appropriate sample holder and in liquid form can be analyzed using neat technique prior to analysis. The water should be removed from sample if possible because it will disturb the analysis.

2.2.1.1 Fourier transform infrared spectroscopy

All frequencies are examined simultaneously in Fourier transform infrared (FT-IR) spectroscopy. Fourier transform spectrometer is the most commonly used

infrared instrument for most applications due to their superior speed, sensitivity and better resolution. They have greatly extended the capabilities of infrared spectroscopy and have been applied to many research areas. For example, the FT-IR is used to study the suitable preparation for quantitative analysis, study of effect of phase separation and the prediction of the blending composition between styrene acrylonitrile copolymer and poly(methyl methacrylate)²³.

2.2.1.2 Attenuated total reflection fourier transform infrared spectroscopy

Attenuated total reflection (ATR) is one of analytical techniques in infrared spectroscopy which enables samples to be directly determined in the solid or liquid form without sample preparation. So, it is suitable for characterization of materials which are either too thick or too strong absorbing to be analyzed by transmission spectroscopy. This technique provides the functional group on the surface of polymer. For example, ATR is used to detect the changing of chemical structure of polyethylene film surface due to hydroxylation²⁴.

2.2.2 Fourier transform raman spectroscopy

Raman spectroscopy is about the inelastic scattering of photons. Unlike the infrared spectroscopy, it rather implicates intermediate virtual states and does not directly engage the absorption or emission from energy levels²⁵.

This characterization technique gives similar information as infrared spectroscopy. However, it has an advantage over the infrared spectroscopy such as the water will not interfere the characterization (because there is no spectrum of water), the scattering peaks in raman spectrum are more narrow than infrared spectrum and peaks in overtone region has a weak intensity so the spectrum is less complicate²⁶.

2.2.3 Thermogravimetry

Thermogravimetry is the method that measures the weight change in materials as a function of temperature and/or time in air or nitrogen atmosphere. This technique is usually used to determine the thermal stability and composition of both organic and

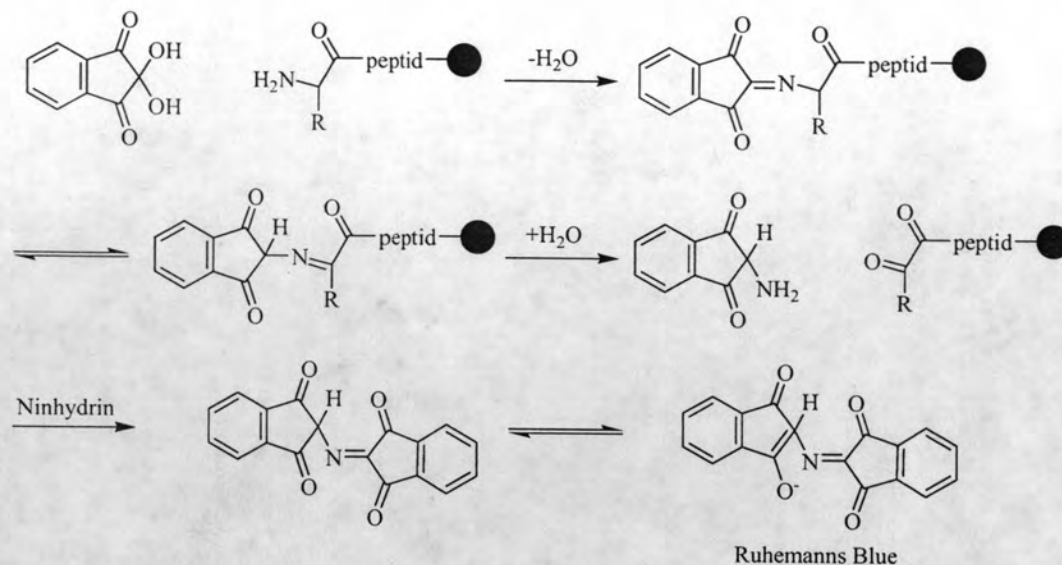
inorganic material, especially in polymer²⁷. Its application provides many information such as: moisture and volatile contents, composition, thermal stability, oxidative stability, shelf-life studies using kinetic analysis, decomposition kinetics and effect of reactive atmospheres etc. In determination of polymer, TGA commonly provides the information about degradation temperatures, residual solvent levels, absorbed moisture content, and the amount of inorganic (noncombustible) filler in polymer or composite material compositions.

2.2.4 Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance spectroscopy provides the information of nuclei, such as ^1H , ^{13}C , ^{29}Si , etc. This technique is highly sensitive to small variations in chemical structure. Polymer in form of liquid or soluble polymer can directly be analyzed by dissolving in proper solvent. In case of insoluble polymer, solid state nuclear magnetic resonance is used to characterize sample. Bruch, M. D. used such technique in order to analyze the surface of modified silica gel²⁸.

2.2.5 Ninhydrin test

Ninhydrin test is the rapid, simple and sensitive method for the determination both qualitative and quantitative of free terminal amino groups. This technique was used to monitor the completeness of amino acid coupling in Solid Phase Peptide Synthesis (SPPS) and Solid Phase Organic Synthesis (SPOS) and to determine amino acid. Ninhydrin test was applied to detect the free primary amine, unreacted terminal amine group of the chelating ligands in the preparation of chelating polymers. The reaction is based upon the development of color between a free amino group and ninhydrin reagent as illustrated in Scheme 2.7. When free primary amine is present, the resin beads and the solution turn dark blue. In contrast, the resin beads remain their color and the solution stayed yellow when free primary amine is not present.



Scheme 2.7 Reaction scheme of the ninhydrin reaction.

2.3 Application of functionalized polymers in separation

One of the applications of functionalized polymers is separation. It is used to selectively bind to one or more species in a complex mixture.

Generally, the functionalized polymer used in the separation must fulfill certain criteria. The bonding between functional group in polymer and species to be separated must be stable under the conditions of separation and not interfere with the polymer backbone. Moreover, the functional group-substrate bond must be reversible and specific. After separation of the desired species with the functional group of the polymer from the other components of the mixture, the separated species is recovered by a release from the polymer by simple means such as altering the pH. The simple process of separation of functionalized polymer can be illustrated in Figure 2.2.

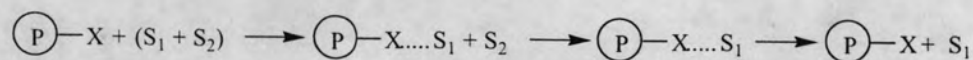


Figure 2.2 Separation by functionalized polymer.

(P = polymeric support, X = functional group, S₁ = separated species and S₂ = other species)

Polymeric materials have been used widely in solid phase separation such as chromatographic column stationary phases and have proved useful in both gas and liquid phase separations.

2.3.1 Solid-phase extraction²⁹

Solid-phase extraction (SPE) is a method of sample preparation that concentrates and purifies analytes from solution. The basic approach involves passing the liquid sample through a column, a cartridge, a tube or a disk containing an adsorbent that retains the analytes. After the entire sample has been passed through the sorbent, retained analytes are subsequently recovered upon elution with an appropriate solvent.

The principle of SPE is similar to that of liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix) and a solid (sorbent) phase.

To understand any of solid-phase extraction techniques, it is first necessary to understand the physical-chemical processes of sorption. Schwarzenbach *et al.*³⁰ make the distinction between *absorption* meaning into a three-dimension matrix, like water uptake in a sponge, and *adsorption* as meaning onto a two-dimensional surface. Absorption, also referred to as a *partitioning*, occurs when analytes pass into the bulk of the extracting phase and are retained. Adsorption is the attraction of an analyte to a solid that results in accumulation of the analyte's concentration at porous surfaces of the solid. Absorption results from weaker interactive forces than adsorption. Because adsorption and/or absorption processes are sometimes difficult to distinguish experimentally and often occur simultaneously, the general term *sorption* will be used here when referring to these processes. The term *sorbent* will refer to the solid extracting phase, including certain solid-supported liquid phases. To predict and optimize extraction, it is important for the analyst to be aware of the nature of the sorbent used.

Although different processes may dominate in different situations, it can be assumed that multiple steps occur during sorption of an organic compound from

liquids “into” or “onto” a solid phase. Any of the steps may become a rate-limiting process in controlling sorption of an analyte. The analyte may interact with a solid-phase sorbent in at least four ways:

1. Through absorption, the analyte may interact with the sorbent by penetrating its three-dimensional structure; similar to water being absorbed by a sponge. Three-dimensional penetration into the sorbent is a particularly dominating process for solid-supported liquid phases. In the absorption process, analytes do not compete for sites; therefore, absorbents can have a high capacity for the analyte.

2. The analyte may interact two-dimensionally with the sorbent surface through adsorption due to the intermolecular forces such as van der Waals or dipole-dipole interactions. Surface interactions may result in displacement of water or other solvent molecules by the analyte. In the adsorption process, analytes may compete for sites; therefore, adsorbents have limited capacity. Three steps occur during the adsorption process on porous sorbents: *film diffusion* (when the analyte passes through a surface film to the solid-phase surface), *pore diffusion* (when the analyte passes through pores of the solid-phase), and *adsorptive reaction* (when the analyte *binds, associates* or *interacts* with the sorbent surface).

3. If the compound is ionogenic (or ionizable) in aqueous solution, there may be an electrostatic attraction between the analyte and charge sites on the sorbent surface. Sorbents specifically designed to exploit these types of ionic interactions are referred to as *ion-exchange* (either anion or cation-exchange) *sorbents*.

4. Finally, it is possible that the analyte and the sorbent may be chemically reactive toward each other such that the analyte becomes covalently bonded to the solid-phase sorbent. This type of sorption is generally detrimental to analytical recovery and may lead to slow or reduced recovery, also termed *biphasic desorption*. All of these interactions have the potential of operating simultaneously during sorption.

2.3.2 Metal ion separations

Adsorption of trace elements on the solid sorbent is required for preconcentration. The mechanism of retention depends on the nature of the sorbent, and may include simple adsorption, chelation or ion-exchange. Also, for trace elements, ion-pair solid phase extraction may be used.

Adsorption: Trace elements are usually adsorbed on solid phases through van der Waals forces or hydrophobic interaction. Hydrophobic interaction occurs when the solid sorbent is highly non-polar (reversed phase). The most common sorbent of this type is octadecyl-bonded silica (C_{18} -silica). More recently, reversed polymeric phases have appeared, especially the styrene-divinylbenzene copolymer that provides additional π - π interaction when π -electrons are present in the analyte. However, because most trace element species are ionic, they will not be retained by such sorbents.

Chelation: Several functional group atoms are capable of chelating trace elements. The atoms most frequently used are nitrogen (e.g. N present in amines, azo groups, amides, nitriles), oxygen (e.g. O present in carboxylic, hydroxyl, phenolic, ether, carbonyl, phosphoryl groups) and sulfur (e.g. S present in thiols, thiocarbamates, thioethers).

Ion-pairing: When a non-polar sorbent is used, an ion-pair reagent (IP) can be added to the sorbent³¹. Such reagents contain a nonpolar portion (such as a long aliphatic hydrocarbonated chain) and a polar portion (such as an acid or a base). Typical ion-pair reagents are quaternary ammonium salts and sodium dodecylsulfate (SDS). The non-polar portion interacts with the reversed-phase non-polar sorbent, while the polar portion forms an ion-pair with the ionic species present in the matrix (that could be either free metallic species in solution or complexes).

Ion exchange: Ion-exchange sorbents usually contain cationic or anionic functional groups that can exchange the associated counter-ion. Strong and weak sites refer to the fact that strong sites are always present as ion-exchange sites at any pH, while weak sites are only ion-exchange sites at pH values greater or less than the pK_a . Strong sites are sulfonic acid groups (cation-exchange) and quaternary amines (anion-exchange), while weak sites consist of carboxylic acid groups (cation-exchange) or primary, secondary and tertiary amines (anion-exchange). These groups can be chemically bound to silica gel or polymers (usually a styrene-divinylbenzene copolymer), the latter allowing a wider pH range.

An ion-exchanger may be characterized by its capacity, resulting from the effective number of functional active groups per unit of mass of the material. The theoretical value depends upon the nature of the material and the form of the resin. However, in the column operation mode, the operational capacity is usually lower

than the theoretical one, as it depends on several experimental factors, such as flow-rate, temperature, particle size and concentration of the feed solution. As a matter of fact, retention on ion-exchangers depends on the distribution ratio of the ion on the resin, the stability constants of the complexes in solution, the exchange kinetics and the presence of other competing ions. Even though ion-exchangers recover hydrated ions, charged complexes and ions complexed by labile ligands, they are of limited use in practice for preconcentration of trace elements due to their lack of selectivity and their retention of major ions.

A chelating polymer essentially consists of two components: the chelate agent and the polymeric support matrix (or sorbent). The properties of both components determine the features and the applications of the respective material.

Chelating polymers have received considerable attention owing to their inherent advantages over simple ion exchange resin, e.g. their greater selectivity to bind metal ion. The selectivity adsorption of metal ions depends on a difference in the stability constant of the complex between a polymer ligand (chelating agent) and a metal ion and can be accomplished by operating the adsorption at a definite pH. However, the selectivity of most chelating groups for metal resides predominantly in their ability to form chelates with cations.

Chelating agents may be directly added to the sample for chelating trace elements, the chelates being further retained on an appropriate sorbent. An alternative is to introduce the functional chelating group into the sorbent. For that purpose, three different means are available:

- (1) The synthesis of new sorbents containing such groups (*new sorbents*)
- (2) The chemical bonding of such groups on existing sorbents (*functionalized sorbents*)
- (3) The physical binding of the groups on the sorbent by impregnating the solid matrix with a solution containing the chelating ligand (*impregnated, coated or loaded sorbents*).

The latter remains the most simple to be used in practice. Its main drawback is the possible flush of the chelating agent out of the solid sorbent during sample percolation or elution that reduces the lifetime of the impregnated sorbent.

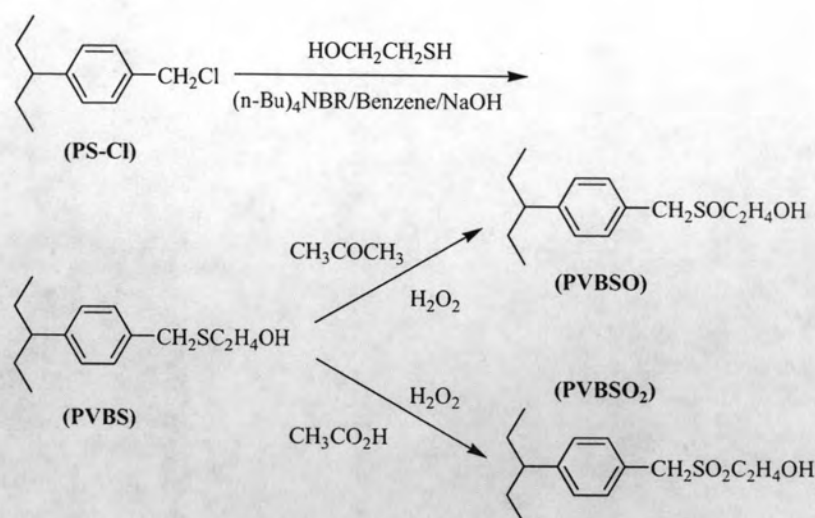
In general, the binding of metal ions to the chelate functionality is dependent on several factors such as

- (a) The nature, charge and size of the metal ion
- (b) The nature of the donor atoms in the ligand and structure of the chelating group
- (c) Buffering conditions which favor certain metal extraction and binding to active donor or groups
- (d) Stability of the resulting metal complex and
- (e) The nature of the solid support (e.g. degree of cross-linkage for a polymer)

In some cases, the behavior of immobilized chelating sorbents towards metal preconcentration may be predicted using the known values of the formation constants of the metals with the investigated chelating agent³³. However, the presence of the solid sorbent may also have an effect and lead to the formation of a complex with a different stoichiometry than the one observed in a homogeneous reaction³⁴. In fact, several characteristics of the sorbent should be taken into account, namely the number of active groups available in the resin phase³⁵, the length of the spacer arm between the resin and the bound ligand³⁶, and the pore dimensions of the resin³⁷.

There are many reports on the functionalization of polystyrene-divinylbenzene for metal separation using chemical modification.

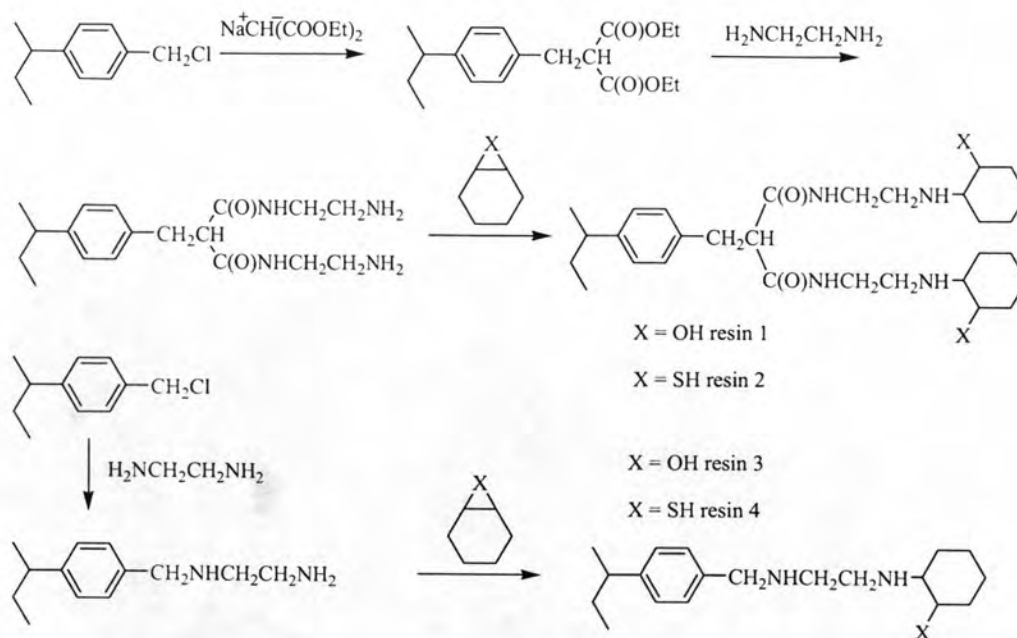
In 2005, Qu, R. *et al.*³⁸ synthesized poly[4-vinylbenzyl-(2-hydroxyethyl)] sulfoxide (PVBSO) and poly[4-vinylbenzyl-(2-hydroxyethyl)] sulfone (PVBSO₂) using poly[4-vinylbenzyl-(2-hydroxyethyl)] sulfide (PVBS), which was prepared by the reaction of chloromethylated polystyrene with 2-mercapto ethanol under phase transfer catalyzed condition. Then PVBS reacted with acetone or acetic acid to yield PVBSO or PVBSO₂, respectively, as shown in Scheme 2.8.



Scheme 2.8 Synthetic route of PVBS, PVBSO and PVBSO₂.

Experimental results showed that PVBSO had good adsorption and selectivity for Au^{3+} , Pd^{2+} and Cu^{2+} when the coexisting ion was Pt^{4+} , Ni^{2+} , Pb^{2+} or Cd^{2+} . In the aqueous system containing Cu^{2+} and Pb^{2+} or Cu^{2+} and Cd^{2+} , PVBSO₂ only adsorbed Cu^{2+} .

In 2001, Trochimczuk, A.W. *et al.*³⁹ prepared two types of polymeric resins through a ring opening reaction with either cyclohexene oxide or cyclohexene sulphide (Scheme 2.9). Both resins contained amino groups, one being obtained by reacting the vinylbenzyl chloride/divinylbenzene (VBC/DVB) copolymer with ethylenediamine, the second by reacting the VBC/DVB copolymer with diethyl malonate followed by aminolysis with ethylenediamine. These resins are highly selective towards Cu^{2+} in acetate buffered solutions. The selectivity of the modified resins decreases in the order, $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$. The highest affinity towards Cu^{2+} ions has been found for the resin modified with cyclohexene oxide, for which $\log K_d$ was 4.91 at pH 5.6.



Scheme 2.9 Schematic diagram of the investigated resins syntheses.

In 2002, Jain, V. K. *et al.*⁴⁰ prepared calix[4]arene-semicarbazone derivative and then covalently linked with commercially available Merrifield's peptide resin at the "lower-rim" to obtain polymeric chelating resin (Figure 2.3). The resins were used for separation La(III), Ce(III), Th(IV) and U(VI) from aqueous solution.

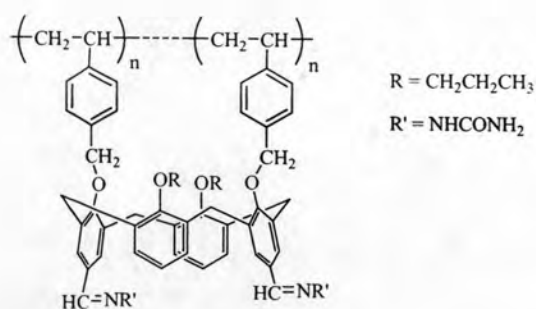
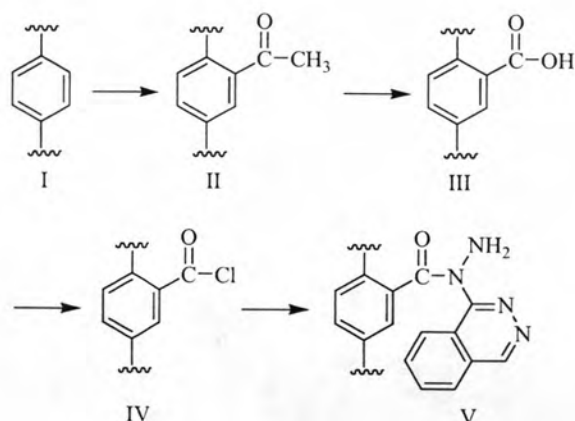


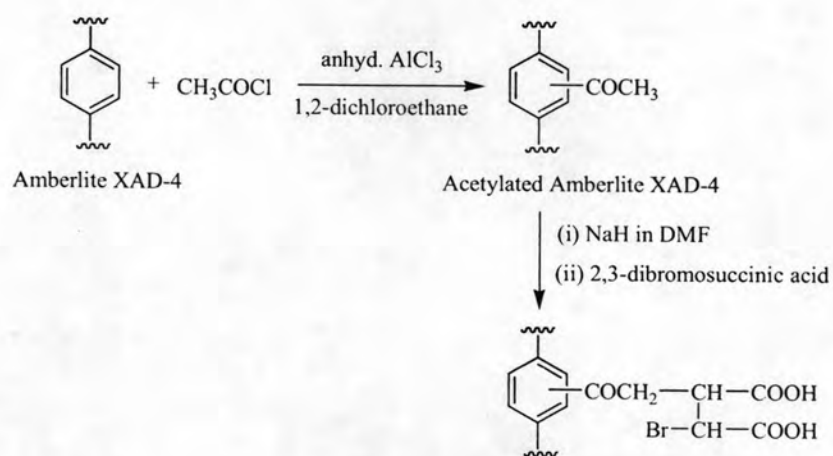
Figure 2.3 Calix[4]arene-semicarbazone derivative loaded on PS-DVB.

Acetylated PS-DVB can be coupled with selected ligand. In 1997, Pathak, R. and Rao, G.N.⁴¹ used 1-hydrazinophthalazine to coupling with acetylated PS-DVB (Scheme 2.10). The modified resin was used to extract Cu(II), Ni(II), Co(II), Zn(II), Cd(II), Pb(II), Fe(III) and Cr(III) but was found to be selective for Fe(III).



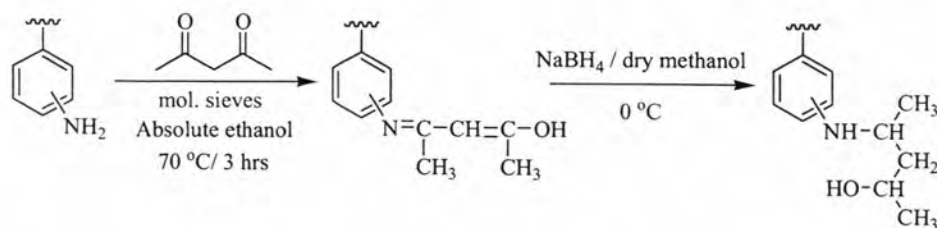
Scheme 2.10 Functionalization of PS-DVB with 1-hydrazinophthalazine.

In 2005, Metilda, P. *et al.*⁴² functionalized Amberlite XAD-4 resin (Scheme 2.11) by coupling it with dibromosuccinic acid after acetylation. The resulting resin has been used for preconcentrative separation of uranium(VI) from host of other inorganic species prior to its determination by spectrophotometry.



Scheme 2.11 Synthesis of succinic acid functionalized Amberlite XAD-4.

In 2003, Prabhakaran, D. and Subramanian, M.S.⁴³ prepared new chelating polymeric sorbent via condensation of amino-Amberlite XAD-16 with acetyl acetone and further reduction and were shown in Scheme 2.12.



Scheme 2.12 Functionalizing Amberlite XAD-16 with 1,3-dimethyl-3-aminopropan-1-ol.

The newly developed chelating matrix offered a high resin capacity and faster sorption kinetics for the metal ions such as Mn(II), Pb(II), Ni(II), Co(II), Cu(II), Cd(II) and Zn(II).

The chelating polymers were also prepared by coupling with various chelating ligand through an azo spacer of PS-DVB such as:

In 2005, Venkatesh, G. and Singh, A.K.⁴⁴ synthesized 2-[[1-(3,4-dihydroxyphenyl)methylidene]amino] benzoic acid (DMABA) loaded Amberlite XAD-16 via azo linker and was shown in Figure 2.4.

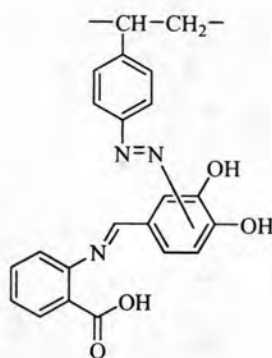


Figure 2.4 Structure of DMABA-PS-DVB.

The resulting resin AXAD-16-DMABA explored for enrichment of Zn(II), Mn(II), Ni(II), Pb(II), Cd(II), Cu(II), Fe(III) and Co(II).

In 2005, Kim, Y.S. *et al.*⁴⁵ reported the preparation of the XAD-4 bound salen[*N,N'*-bis(salicylidene)ethylenediamine] (Schiff base ligand) by diazonium coupling reaction (Figure 2.5). XAD-4-salen chelating resin had been studied for the separative concentration of Cu(II), Pb(II) and Bi(III) from an aqueous solution.

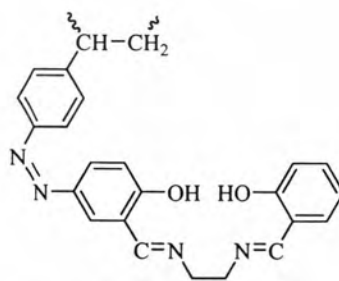


Figure 2.5 Structure of XAD-4-salen.

In 2003, Lemos, V.A. *et al.*⁴⁶ synthesized Amberlite XAD-2 functionalized with Nitroso R salt (disodium 1-nitroso-2-hydroxynaphthalene-3,6-disulfonate). Its application was an online system for preconcentration of Co(II). The structure of NRS-XAD was shown in Figure 2.6.

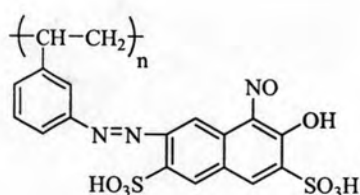


Figure 2.6 Structure of NRS-XAD.

In 2003, Lemos, V.A. *et al.*⁴⁷ prepared Amberlite XAD-2 functionalized with 3,4-dihydroxybenzoic acid (DHB) (Figure 2.7) and used in online preconcentration of Cu(II).

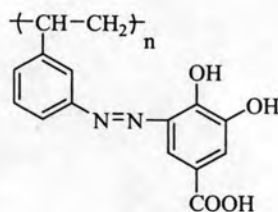


Figure 2.7 Structure of DHB-XAD-2.

In 2001, Tewari, P.K. and Singh, A.K prepared XAD-2 loaded with pyrocatechol⁴⁸ for preconcentration Cd(II), Co(II), Cu(II), Fe(III), Ni(II) and Zn(II). In addition, in 2002, they⁴⁹ reported the functionalization of XAD-2 with chromotropic acid (XAD-2-CA) and thiosalicylic acid (XAD-2-TSA) for preconcentration of Pb(II). The structures of those resins were shown in Figure 2.8.

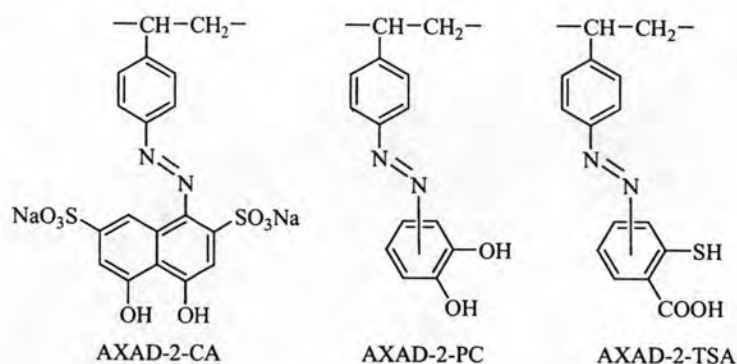


Figure 2.8 Structures of XAD-2-CA, XAD-2-PC and XAD-2-TSA.

By the way, coupling of ligand with resin through azo linkage may be lower in selectivity. This may be from the residue of unreacted amine group in synthesis pathway.

2.3.3 Organic molecule separations

Chemically modified resins have been developed and used in the SPE of polar compound mainly from aqueous samples. Among the polar compounds, phenolics are a most significant group which are the environmental interest⁵⁰.

Retention of polar phenols on PS-DVB sorbents can be improved by the introduction of polar groups into the polymeric support. Most common groups used to modify polymeric sorbents e.g. acetyl, hydroxymethyl, benzoyl, *o*-carboxybenzoyl, and carboxylic.

Yu, J.C. *et al*⁵¹ prepared β -cyclodextrin (β -CD) epichlorohydrin (ECH) copolymer (β -CDEP). The β -CDEP was used in solid-phase extraction (SPE) procedure for 12 aromatic compounds in water samples.

2.5 Heavy metals in the environment and their determination

Metals are described as “heavy metals” when they, in their standard state, have a specific gravity (density) of more than 5 g cm^{-3} . Some of them, such as copper, nickel, chromium and iron, are essential in very low concentrations for the survival of all forms of life. These are described as essential trace elements. Only when they are present in greater quantities, can these, like the heavy metal lead, cadmium and mercury which are already toxic in very low concentrations, cause metabolic anomalies. Here, the boundary between the essential and the toxic effect is somewhat problematic. In addition to its natural occurrence, heavy metals are normally brought into the environment by human activities, which has dramatically influenced and modified natural cycles. The major activities include mining and ore processing, coal and fuel combustion, industrial processing, agricultural, domestic, transportation and nuclear activities.

Heavy metals show a great tendency to form complexes, especially with nitrogen, sulfur and oxygen containing ligands of the biological milieu. Chronic toxicity, caused by repeated exposure over long periods of time, is much more relevant. Beside the fact that mercury, cadmium and arsenic are highly toxic, some other heavy metals such as iron, copper, zinc, manganese, cobalt, nickel, tin and selenium are essential to many organisms. An undersupply of these, so called trace metals, leads to deficiency, while an oversupply results in toxic effects.

Selection of determinative technique is often dictated by equipment and concentration level of metal in samples. Ease of operation, number of analyses, and familiarity of personnel with technique are also influential factors. Spectrometric techniques commonly used include flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS) or electro thermal vaporization atomic absorption spectrometry (ETAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and X-ray fluorescence spectrometry (XRF).

FAAS is often used to determine many elements in samples because of the ease and affordability. However, detection limits of FAAS are relatively high for some element. GFAAS is the method of choice when sensitivity is the major concern. Nevertheless, this technique is very sensitive to variations in the composition of

matrix. Therefore, removal of the matrix components and preconcentration of the analyte are often necessary.

ICP-AES has also been used for routine elemental analysis. Sequential or simultaneous mode ICP-AES allows rapid analysis, dramatically improving throughput. Detection limit in ICP-AES are generally slightly better than FAAS.

ICP-MS has been used for the determination of metals. Its most effective and very fast response time, exceptional detection limit: 0.1-10 ppt, high resolution and high sensitivity have made this technique ideal but the cost of require instrumentation may be prohibitive to many laboratories.