INTRODUCTION

I. INTRODUCTION

I.1 GENERAL

Amongst the substances with which the chemist and the chemical engineer deal either in the laboratory or in industrial production is a group of materials which, though differing greatly in physical and mechanical behaviour amongst themselves, show certain common characteristics and can be distinguished clearly from other chemical compounds. These substances which can be characterised as rubbers, fibres, resins, plastics, etc., consist of molecules of high molecular weight varying from few thousands to the tens of millions. The overall molecular weight of each of these materials can be expressed only as a statistical average of the total of the molecular species of which it consists. The molecules of each of these high molecular weight substances consist of a sequence of one or more basic units which are linked together in chains or network of primarily covalent bonds. The basic unit or units are called monomers, and the corresponding network or chain of linked monomers is known as a polymer.

Modern technological demands for materials which have desirable chemical, mechanical and electrical characteristics have directed the attention of investigators to polymeric systems which may be strictly organic, inorganic or inorganic-organic in character.

I.2 POLYMER FORMATION

There are three principal types of reactions which lead to the formation of substances of high molecular weight.

(a) CONDENSATION POLYMERIZATION

In condensation polymerization, the monomers interact by an ionic reaction mechanism, involving the elimination of small molecules such as water, alcohol, ammonia, etc., and forming new C-C, C-N, C-O, etc. bonds. The structure of the monomer would be such that the process can repeat itself in building up the polymer molecule. Since small molecules are eliminated in the reaction, the ultimate analysis of the polymer is different from that of the monomers from which it was formed (Fig.I.1(a)).

(b) ADDITION POLYMERIZATION

In addition polymerization, the monomers interact by the free radical or ionic reaction mechanism without eliminating other products and the polymer chains (Fig.I.1(b)) contain only C-C bonds. These are the polymers in which the molecular formula of the repeating unit is identical with that of the monomer.

(c) CO-ORDINATION POLYMERIZATION

In coordination polymerization, ligands are linked to metal atoms by coordinate-covalent bonds (ionic and covalent bonds being their extreme cases). Although they are frequently classified under both condensation and

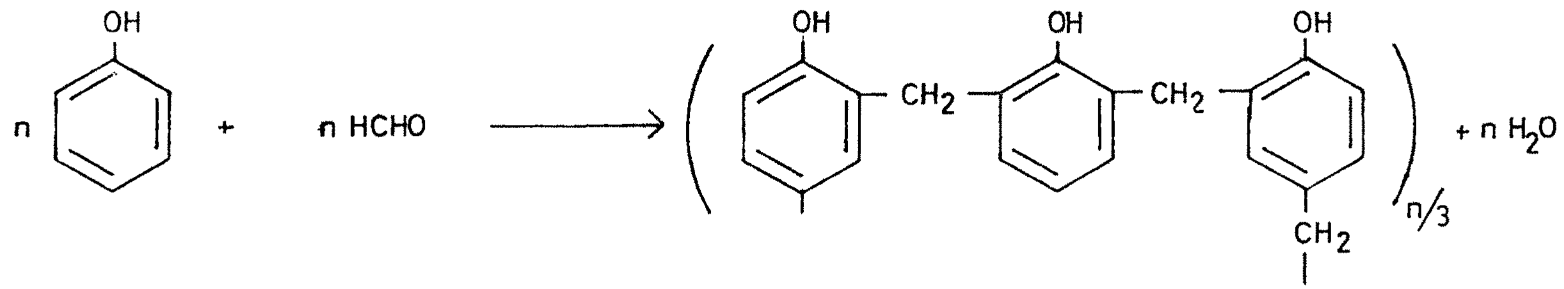


Fig. I .1(a)

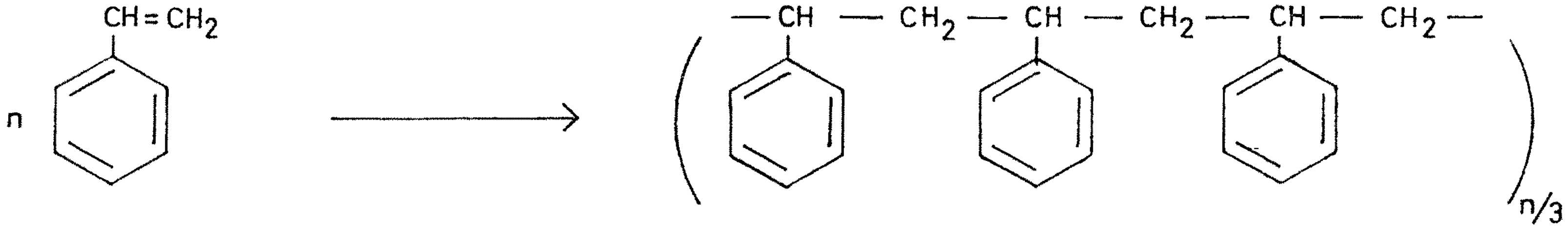


Fig. I .1(b)

addition polymerization reactions, they are sufficiently distinctive to warrant separate consideration.

Reactions leading to the formation of polymers containing coordinated or chelated metal ions can be divided into three general categories:

(a) Metal ligand chain formation:

Polymers may result when suitable metal-ions and ligands combine. The possibility of using reactions of this type depends primarily on the fact that many metal-ions are poly-coordinated in character and can combine with polydentate ligands resulting in chain or cross-linked polymeric structures.

(b) Polymerization of coordination complexes or chelates:

Some polymers are obtained when monomers containing coordinated or chelated metal ions are polymerized through functional groups.

(c) Metal insertion in polymeric ligands:

Some metal-containing polymers are obtained by the combination of metal ions with preformed polymeric ligands having suitable coordination sites.

A brief consideration of these three categories follows.

(a) METAL LIGAND CHAIN FORMATION

In theory, a ligand molecule which contains two pairs of unshared electrons on donor atom(s) can be used to link metal ions. Under certain circumstances, in which the stereo-chemistry of the donor group and of the metal ion are favourable, chelate ring formation occurs. Polymeric compounds are formed

(i) when both pairs of electrons are on the same donor atom in the coordinating group (e.g., Cl and OH),

(ii) when the electron pairs are on atoms linked to each other (e.g., CN), and

(iii) when the donor atoms are widely separated in ligand molecule.

Examples of polymeric complexes formed as indicated by (a-i), (a-ii) and (a-iii) are the metal chlorides, e.g., palladium (II) chloride existing as infinite chain (Fig.I.2(a)) in the solid state, metal cyanides, e.g., silver-cyanide existing as linear polymer (Fig.I.2(b)) and coordination polymers, e.g., copper (II) polychelate of 2,5-dihydroxy-p-benzoquinone (Fig.I.2(c)).

Coordination polymers obtained by reaction (a-iii) are numerous. It has been observed in many cases that chelation with metal ions greatly enhances the thermal stability of organic ligands. Monomeric chelate compounds are obtained with bidentate ligands but polydentate agents can give rise to polymeric compounds. The degree of cross-linking in any polymer of this type is governed by the coordination number of the metal and the number of coordinating centres of the ligand. Combination between a bis(bidentate) ligand and tetra-coordinate metal ion, or between a bis(tridentate) ligand and hexa-coordinate metal ion, will lead to a linear polymer if the two bidentate or tridentate functions of the ligand are unable to coordinate with the same metal ion. A bis(bidentate) ligand and hexa-coordinate metal-ion on the other hand, can give highly cross-linked polymeric product. A hexa-coordinate metal ion can be used with bis(bidentate) ligand to prepare linear polymers by blocking two of the coordination positions with other groups. Tetra-coordinate metal ions when treated with bis(bidentate) ligands yield linear polymers. Cross-linked polymers would be obtained in most of the cases when 6-coordinate M(III) and 8-coordinate M(IV) are used with the above ligands and no coordination positions are blocked by other ligands.

(b) POLYMERIZATION OF MONOMERIC CHELATE COMPLEXES

Chelate polymers can be obtained by polymerization of monomeric chelate complexes. Higher molecular weight compounds can be prepared from chelate complexes when the ligand contains functional groups capable of undergoing conventional addition or condensation reactions. If the ligand contains an ethylenic side chain, the usual addition polymerization may be possible. Vinylferrocene has been shown to undergo homo- and co-polymerization with vinyl-monomers, dienes, etc., and although trans-cinnamoyl ferrocene does not homo-polymerize, a variety of co-polymers has been obtained. On the other hand, polyesterification of a chelate compound having alcoholic functions in the ligand with diacid has produced a low molecular weight polymer (Fig.I.3).

(c) METAL INSERTION IN POLYMERIC LIGANDS

Production of chelate polymers using preformed polymeric ligands has been studied from different angles. An interesting and well-known example of this is the tanning of leather by metal-ions, which involves the cross-linking and stabilising of polypeptide polymers by coordination. Preformed polymers capable of chelation are designated as chelating polymers. Polydentate ligands have been prepared, say, by the reaction of pyridine-2,6-dialdehyde and diamine such as ethylene-diamine, hexamethylene-diamine, benzidine, etc., (Fig.I.4(a)), where X is $-(CH_2)_2$, $-(CH_2)_6$ or $-C_6H_4-C_6H_4$. These products gave chelate polymers of unknown molecular weight when treated with bivalent copper or iron-salts. Similarly, polymeric schiff bases(Fig.I.4(b)) with molecular weight in the region of 10,000 have been prepared and used to get polymetallic chelates with Cu(II), Zn(II), etc.

The chelating polymers may be obtained as linear polymeric chains or as cross-linked polymeric networks depending largely on the functionality of the monomers. These polymers possess ion exchange properties.

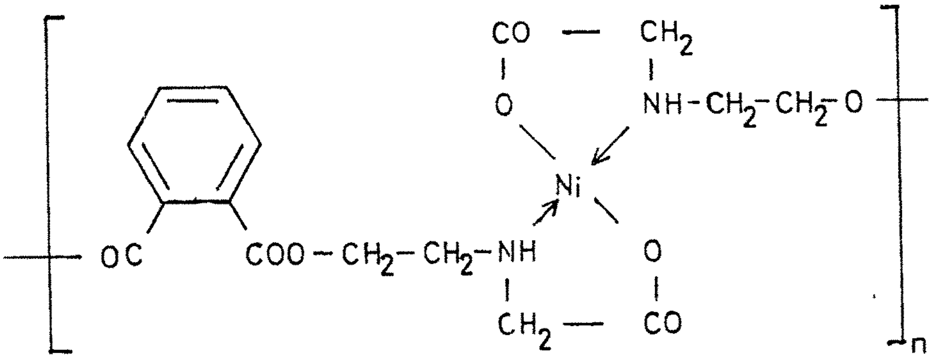


Fig. I . 3

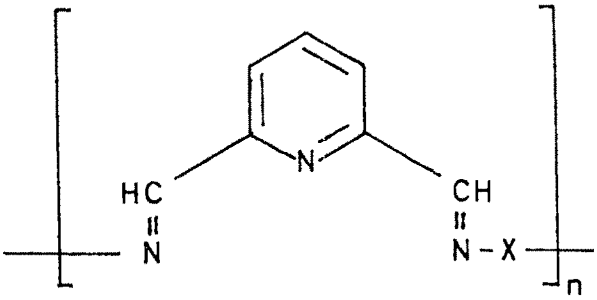


Fig. I . 4(a)

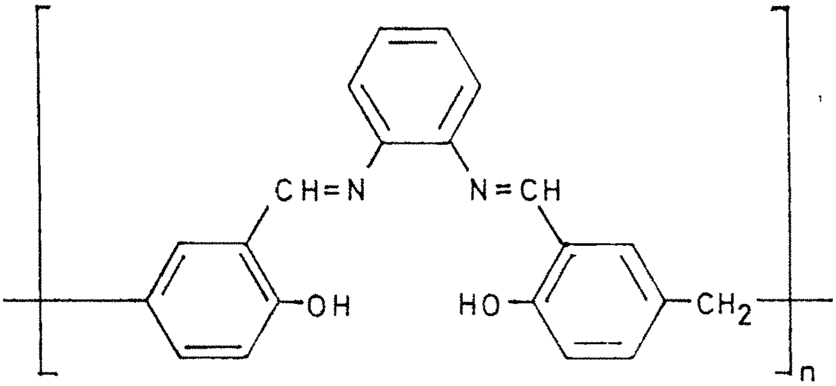


Fig. I . 4(b)

I.3 ION EXCHANGE RESINS

These are synthetic organic ion-exchange materials having appropriate functional groups incorporated into polymeric structures. The structure may be based upon polystyrene and divinyl-benzene, phenol and formaldehyde, or similar stable polymeric chemical structures. To function as a cation exchanger, the resin should contain acidic groups, such as sulphonic, phosphonic, etc. Anion exchangers are obtained by introducing amino groups into a polymeric lattice.

Solid ion-exchangers are suitably insolubilized high molecular weight polyelectrolytes possessing labile or mobile ions capable of exchange for ions of equal charge from the surrounding medium, without altering the general physical nature of the ion-exchanger. These ions are cations in the cation-exchanger and anions in an anion-exchanger.

Viewed in a different light, ion-exchangers can be considered as high molecular weight acids or bases, which can exchange their hydrogen or hydroxyl ions for equally charged ions and thus are converted into high molecular weight salts. The mobile ions bound to the polyelectrolytes can be displaced by other ions of equal charges resulting in ion exchange.

Ion-exchange may be defined as the reversible interchange of ions between ion-exchanger phase (solid or liquid) and a liquid phase, in which there is no permanent change in structure.

Since the ionic functional groups are hydrophilic, these groups attached to the polymeric matrix tend to draw the whole exchanger into solution. To prevent this, the polymer structure in the synthetic resin is held together with cross-linkers forming a three dimensional insolubilized network.

For practical purposes, the desirable characteristics of an ion-exchanger are that it should provide an insoluble, chemically stable stationary phase possessing mechanical strength.

The most important class of ion-exchangers are the organic ion-exchange resins. They are typical gels and their framework consists of irregular, macromolecular, three dimensional network of hydrocarbon chains. Depending on the acidic or basic nature of the functional group attached to the matrix, the ion exchange resins are classified as cation exchange resins (weakly or strongly acidic) (Fig.I.5) and anion exchange resins (weakly or strongly basic), and may often be bifunctional or polyfunctional.

The ion exchange behaviour of the resin is chiefly determined by the nature and number of the fixed ionic

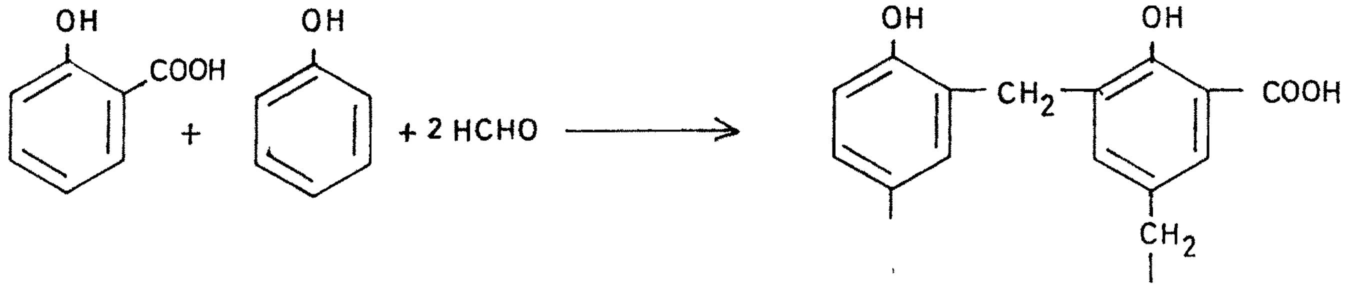


Fig. I . 5(a)

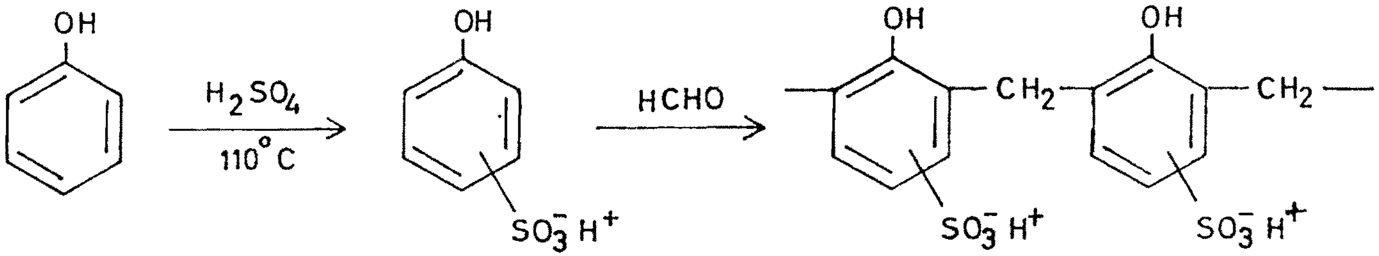


Fig. I . 5(b)

groups. The number of groups determines the ion-exchange capacity. The capacity of the weakly acidic exchanger is a function of pH and the titration curve, i.e., the curve of ion exchange against pH has the form shown in (Fig.I.6). On the other hand, the capacity of the strongly acidic exchanger is substantially independent of pH as shown in (Fig.I.7).

Amphoteric ion exchangers contain both acidic and basic groups and may exhibit chelation.

Condensation products of amines and phenols contain phenolic -OH groups of very low acid strength in addition to the amino groups. The resins with iminodiacetic acid groups, contain weak base groups in addition to carboxylic acid groups.

Amphoteric resins with strong acid groups have been prepared (1,2). More recently amphoteric resins with amino-alkyl-phosphonic and carboxylic acid groups have been synthesized (3,4).

The resins with strongly basic and strongly acidic groups have been prepared (5), for example, by copolymerization of styrene, vinylchloride and a cross-linking agent, followed by quaternization and sulfonation of the product (Fig.I.8).

An important class of amphoteric resins is the so called "snake cage polyelectrolytes." These resins are

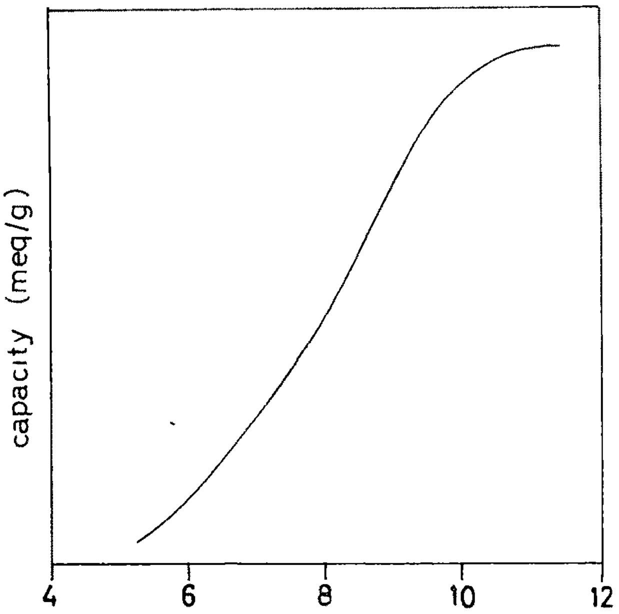


Fig.I.6 **Titration** Curve of a typical unifunctional weakly acidic resin

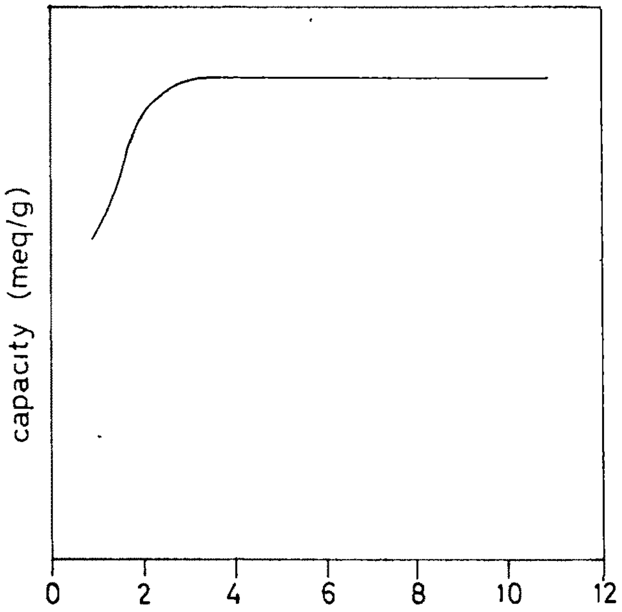


Fig I.7 Titration Curve of a typical unifuntional strongly acidic resin

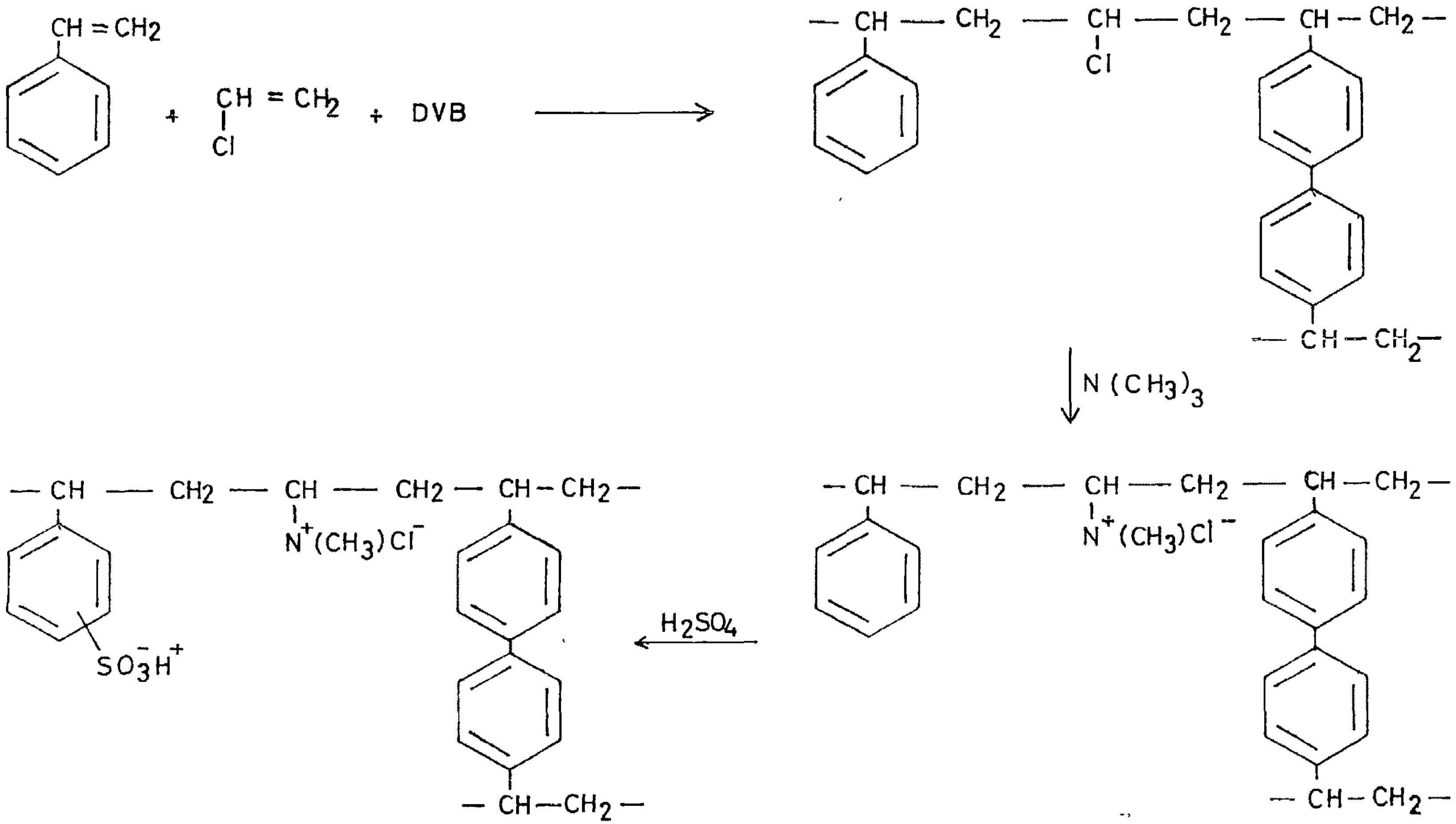

CH = CH2
CH = CH2
Cl
DVB
— CH — CH2 — CH — CH2 — CH — CH2 —
Cl
— CH — CH2 —
N (CH3)3
— CH — CH2 — CH — CH2 — CH — CH2 —
N+(CH3)Cl−
— CH — CH2 —
H2SO4
— CH — CH2 — CH — CH2 — CH — CH2 —
N+(CH3)Cl−
SO3−H+
— CH — CH2 —

Fig. I . 8

excellent reversible sorbents for electrolytes and are used for separation by "ion retardation."

I.4 CHELATING ION EXCHANGE RESINS

In analytical as well as in preparative inorganic chemistry, there exists a need for chelating polymers that combine the ease of operation of conventional ion exchangers and the selectivity of organic analytical reagents.

The selectivity of most organic reagents for metals resides predominantly in their ability to form chelates with certain cations. Therefore, organic polymers have been synthesized that contain chelate forming groups (frequently derivatives of iminodiacetic acid) as exchanging functions. The selective behaviour of these resins is based on the different stabilities of the metal complexes on the resin at appropriate pH values.

The resin should have good selectivity and sufficient mechanical and chemical stability, especially towards acids and bases which are used for the regeneration of the resin. The amount of resin required should be as small as possible, and it should have an effective exchange capacity. Furthermore, it is necessary that the rate of the complexation reaction be relatively high.

According to Gregor and coworkers (6), the following properties are required for a chelating agent that is to be incorporated as a functional agent into an ion-exchange resin:

(i) The chelating agent should yield a resin gel of sufficient stability or should be capable of being incorporated by substitution into a polymer matrix.

(ii) The chelating molecule must possess sufficient chemical stability, so that during the synthesis of the resin the functional structure is not changed by polymerization or any other reaction.

(iii) The steric structure of the chelating molecule should be compact so that the formation of the chelate rings will not be hindered by the matrix.

(iv) Because the agents forming relatively stable complexes are at least tridentate, it is necessary that the functional groups of the chelating molecule be situated appropriately so that the specific arrangement of the ligands will be preserved in the resin.

I.5 LINEAR CHELATING POLYMERS

5(a) Natural Chelating Polymers:

Alginic acid is a polyuronide found in brown seaweeds whose chemical formula is suggested as (Fig.I.9). The alginate in seaweed behaves as a base exchange material and is present as a mixed salt of cations, mostly calcium, able to render it insoluble. The amount of divalent ions necessary

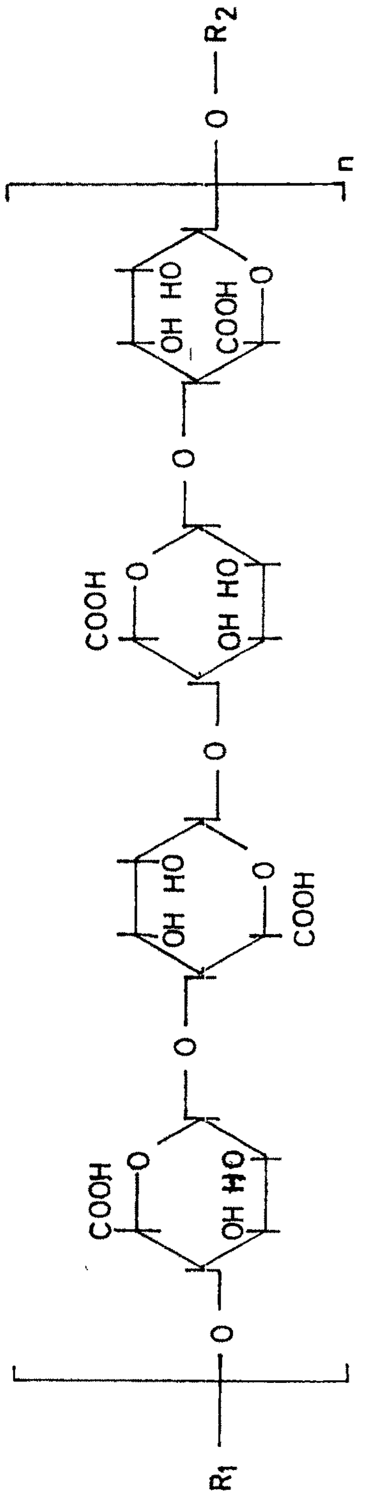


Fig. I. 9

to obtain precipitation of alginates increases in the order Pb, Cu < Ca < Co, Ni, Zn < Mn (7). Through divalent ions alginic acid may also be combined to other substances (8,9). As alginate was found to be a very effective agent for inhibiting intestinal strontium uptake, without interfering appreciably with the metabolism of calcium and alkali metal ions, it was proposed for prevention and therapy of strontium radio-contamination (10). Chromatography of metal ions and organic substances on alginic acid has been studied by Cozzi and coworkers (11,12,13).

Chitin is a polysaccharide constituted of β-(1→4)2-acetamido-2-deoxy-D-glucose units, some of them being deacetylated. This natural polymer that can be called poly-N-acetyl-D-glucosamine, can be formally considered a derivative of cellulose where the C-2 hydroxyl groups have been completely replaced by acetamido groups. It is represented in (Fig.I.10). It occurs widely in lower animals, fungi, etc. The exoskeletons of crabs, lobsters, etc. are good sources of chitin (14). Metal concentration factors in zooplankton support Boweni statement that among cations the increasing order of affinity for living matter is; tetravalent elements < trivalent elements < divalent transition elements < divalent group IIA elements < group IA elements (15).

Chitosan is deacetylated chitin, and is conceived as a clarification aid and viscosity builder in solutions.

for rapid settling of suspended solids (16). It can also be obtained as a chelating membrane. Chitosan membranes generally show lower capacity than chitosan powder (17). It is possible to use chitosan as a polymer for collection of trace metals by chelation accompanied by coprecipitation (18).

Many polysaccharide derivatives have been studied as natural chelating polymers (19). The polyanions are polyguluronate, polymannuronate, pectate, hyauronate, etc. Polysaccharides are present in soil humus also (20). Ligand groups in soil organic matter may be found in arrays sterically favourable for the chelation of particular metal ions (21,22).

Metal coordination/complex formation in cartilage, elastin, etc. is important in primary calcification process (23). Wool is a complex protein containing hydroxyl, amino, amido, carboxyl, sulphuryl and disulphide groups. Wool protein has been investigated (24) for thin layer chromatography. Nucleic acids also are known to interact with various metal ions (25-28).

5(b) Synthetic Chelating Polymers:

Linear polymers containing chelating sites can be obtained by addition polymerization and condensation polymerization.

(i) Addition Polymers

Linear addition polymers containing chelating groups would have vinyl backbone. Styrene may be copolymerized with maleic anhydride to produce (Fig.I.11). Polystyrene may be chloromethylated and then treated with a suitable chelating diamine to yield (Fig.I.12(a)) or with iminodiacetate (IDA) to yield (Fig.I.12(b)). Dowex A-1 chelating resin has the polymer backbone structure shown in Fig.I.12(b) and has metal chlating properties similar to IDA itself (29). Amino acid chelating resin structures have been prepared containing aminodipropionate (30), glycine (31), anthranilic acid (6), pyridine dicarboxylic acid (32), hydroxamic acid (33), etc.

(ii) Condensation Polymers

Linear condensation polymers containing complexing sites are obtained by condensing bifunctional complexing ligand with an appropriate bifunctional reagent. Some of these products are shown as-

(Fig.I.4(a)) (34), (Fig.I.4(b)) (35,36),
(Fig.I.13) (37,38), (Fig.I.14) (39),
(Fig.I.15) (40), (Fig.I.16) (41),
(Fig.I.17) (42), (Fig.I.18) & (Fig.I.19) (43)

I.6 CROSS-LINKED POLYMERIC NETWORKS

There has been considerable activity in the field of chelating ion-exchange polymers in recent years. Studies

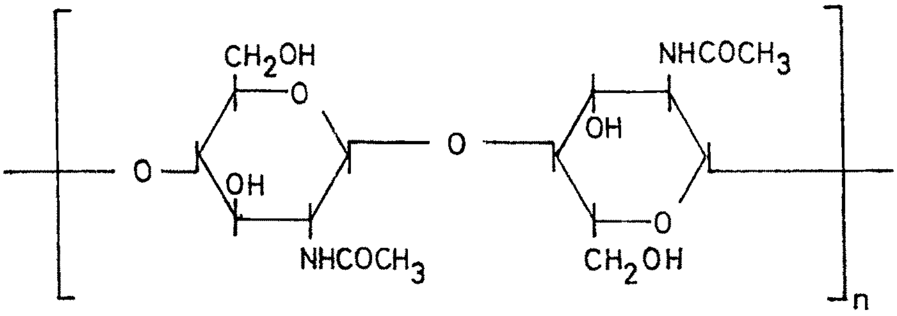


Fig. I . 10

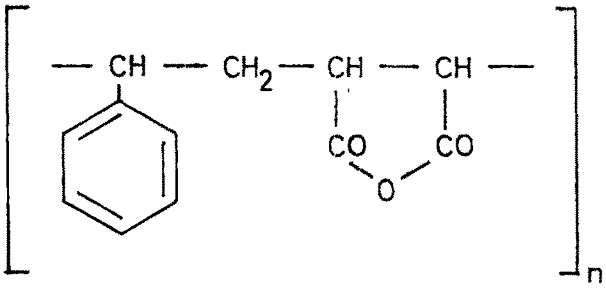


Fig. I . 11

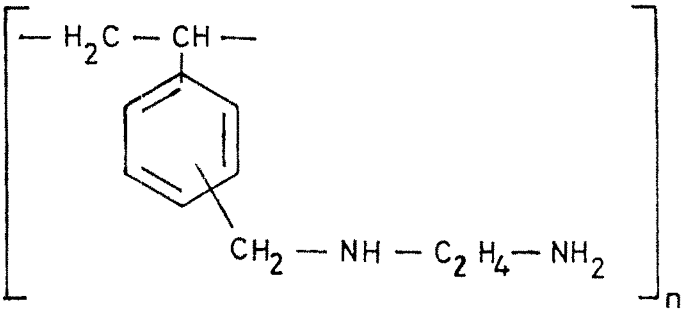


Fig. I . 12(a)

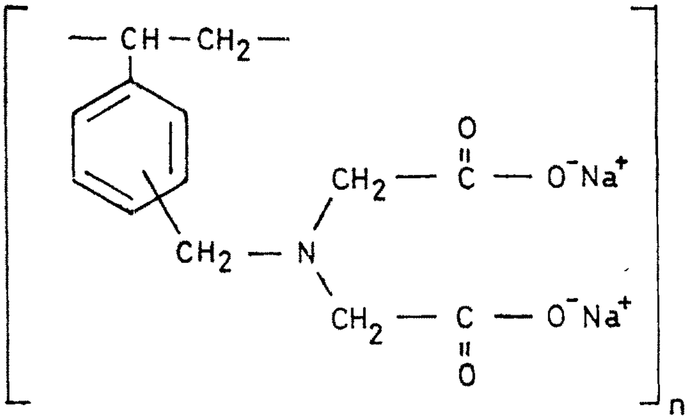


Fig. I .12(b)

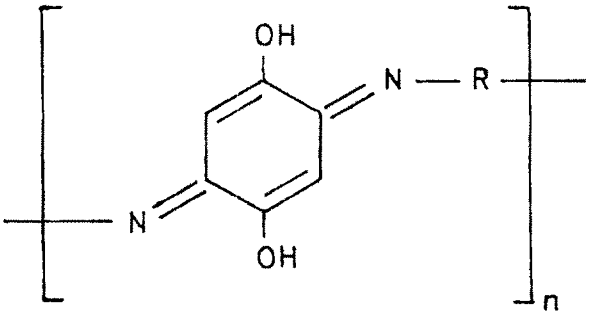


Fig. I .13

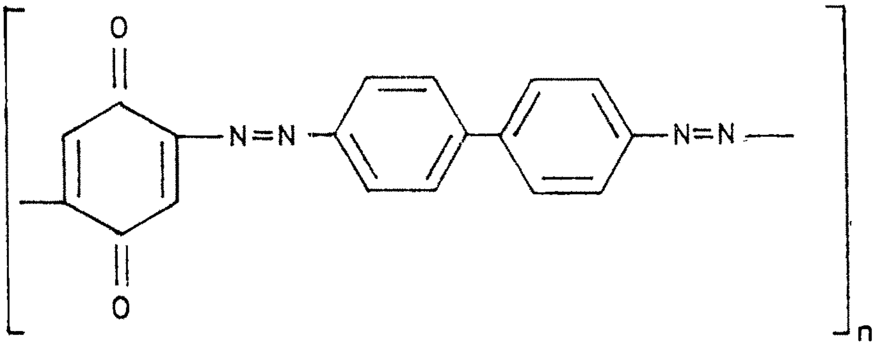
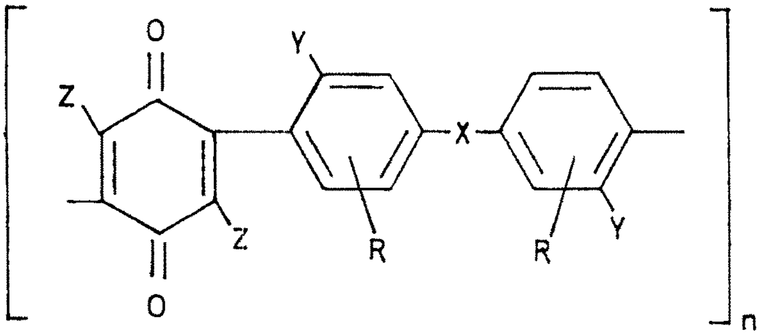


Fig. I.14



X = —CH = CH— or absent

Fig. I.15

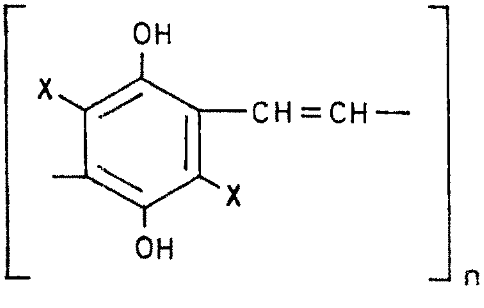


Fig. I.16

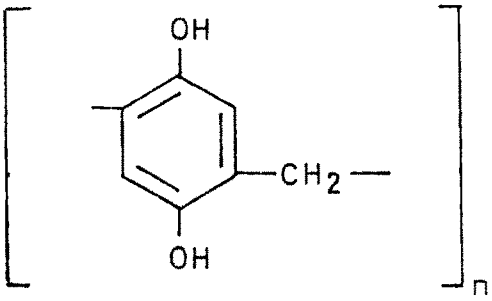


Fig. I.17

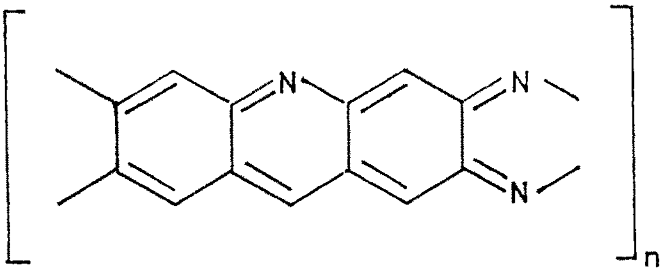


Fig. I.18

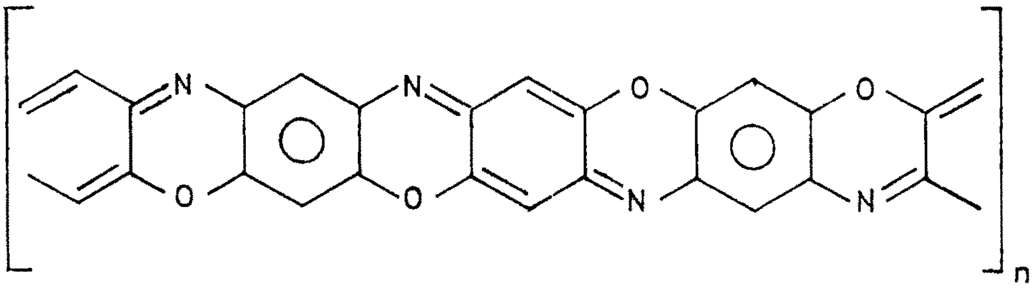


Fig. I.19

on ion-exchangers and organic or inorganic ligands led scientists to develop ion exchange polymers possessing chelating properties. The research schools which contributed considerably towards the preparation and understanding of the nature and behaviour of such chelating polymers are those of Bayer (44-47), Blasius (48), Gregor (49), Hering (50-57), Kennedy (58-62), Manecke (63-64), Schmuckler (65), De Geiso (66), etc. Such polymers can find use in column chromatography, membrane-formation, desalination, waste-water treatment, etc.

Ion-exchangers may be specific in terms of functional groups introduced in them through specific ligands. Because of its specificity, an ion-exchanger can sorb (exchange) one ionic species to the exclusion of others under broad range of conditions. This is exemplified below:-

Skogseid (67) obtained an ion exchanger having structure (Fig.I.20(a)). Dipicrylamine (Fig.I.20(b)) is a specific precipitating agent of potassium, and the above ion exchanger shows an excellent specific uptake of potassium ions.

Specific ion-exchangers include the entire group of chelating resins whose specificity is based on the chelate or complex forming functional groups. The best known commercial type (Fig.I.12(b)) is the iminodiacetate ion exchanger (Dowex A-1), in which iminodiacetate groups are attached to the styrene matrix, and which can fix polyvalent ions with a high affinity by the formation of heterocyclic metal chelate complexes (Fig.I.21).

Many compounds which form chelates with metal cations have been incorporated into resin structure by poly condensation of phenol and amine derivatives with aldehydes.

Salicylic acid-formaldehyde condensation resins have been reported by Topp (68), De Geiso, et al (66), Komiya, et al (69), Rabeck, et al (70) and Davies, et al (71). Anthranilic acid-formaldehyde condensation resin has been studied by Gregor (6,72) and gallic acid-formaldehyde resin by Hojo (73). Resins from naphthoquinone/anthraquinone derivatives and formaldehyde have been studied by Soloway (74), Manecke (75), Izoret (76), etc. Chelating resins based on 8-hydroxyquinoline-resorcinol-formaldehyde have been reported by Von Lillin (77), Parrish (78) and Tolmacher, et al (79). o-Aminophenol-formaldehyde chelating resins have been reported by Gregor, et al (6) and Pennington (80). Pennington, et al (80) reported chelating resins based on resorcinol-formaldehyde, β-resorcylic acid-formaldehyde and resacetophenone-formaldehyde. A chelating resin based on anthranilic acid diacetic acid, m-phenylene diglycine has been reported by Gregor, et al (6). Gregor (81) prepared a chelating resin containing poly(N-vinyltriazole), which forms chelates with Cu(I) and Ag(I) (Fig.I.22).

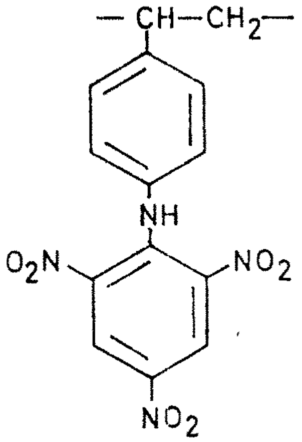


Fig. I.20(a)

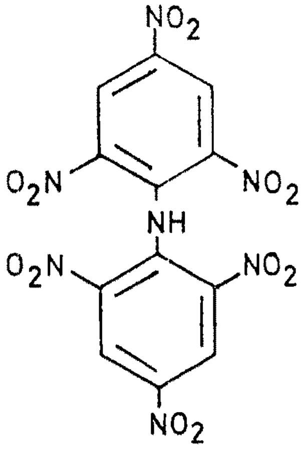


Fig. I.20(b)

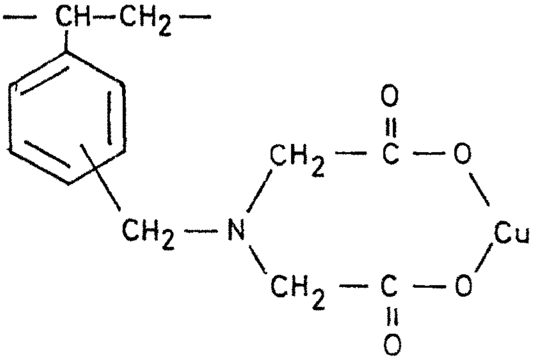


Fig. I.21

Szczepaniak (82) reported a resin specific for Hg(II); it contains diphenylcarbazone.

Blasius and Olbrich (83) prepared a condensation resin from resorcinol, (m-phenylenedinitrilo) tetra-acetic acid and formaldehyde, a resin which allows the chromatographic separation of Co(II) from Ni(II).

Hering (50-57) prepared and studied iminodiacetic acid, sarcosine and (methylamino) propionic acid resins.

Blasius and Bock (48) synthesized several polyiminopolyacetic acid resins by the reaction of chloromethylated polystyrene with various aliphatic amines and subsequent reaction with chloro-acetic acid (Fig.I.23). The resins are very useful for separating transition elements from alkaline earths.

Manecke and Heller (64) copolymerized 2-(1-aziridinyl)-ethylphosphonic acid diesters-ethyl-1-aziridine-acetate and methyl-1-aziridine-propionate together with a novel cross-linking compound 2,2'-bis [2-(1-aziridinyl)ethyl] benzene to obtain chelating resins after partial saponification. Resin shows amphoteric behaviour.

Iron(III) specific hydroxamic acid resins (33,84-87) have been prepared from acrylic acid polymers.

Parrish (78,88) reported the formation of chelating resin by introducing chelating agent 8-hydroxyquinoline in diazotized resins (Fig.I.24).

Sykora and Dubsky (89) described the condensation product from resorcylidene anthranilic acid and formaldehyde, which can be used for chromatographic separations of Cu(II)-Zn(II), Cu(II)-Fe(II) and Cu(II)-Ni(II).

Lautsh and coworkers (90-92) have described a resin with polyaziridine matrix containing chlorophyll or hemin entities as functional groups (Fig.I.25).

Bayer (44-47) reported the chelating resin based on triaminophenol and glyoxal (Fig.I.26). The resin obtained was used to recover Cu(II) and uranyl ions from sea-water.

Bayer and coworkers (47) reported the chelating resin based on aminobenzenethiol-glyoxal. This resin is selective for gold(III), mercury(II) and silver(I) and can be employed for the extraction of gold from sea-water.

Starting with pyrocatechol, Blasius and Kynast (93) prepared a chelating resin containing the oxygen ligand atom in the form of ether linkages and carboxylic acid groups (Fig.I.27). The resin is specific for Zr(IV) separation from Ti(IV), Fe(III), etc.

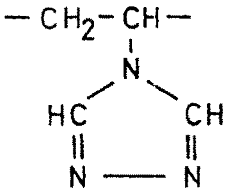


Fig. I. 22

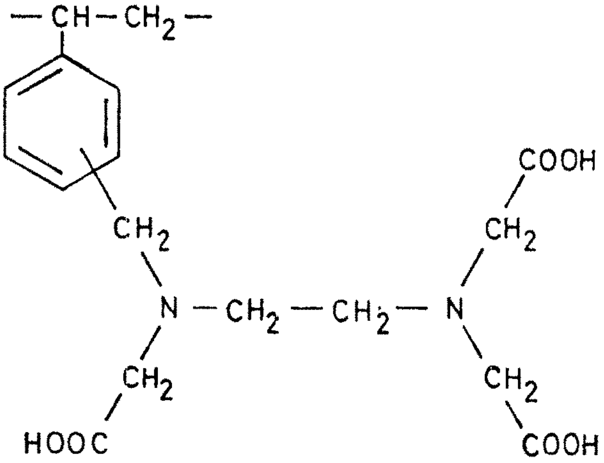


Fig. I. 23

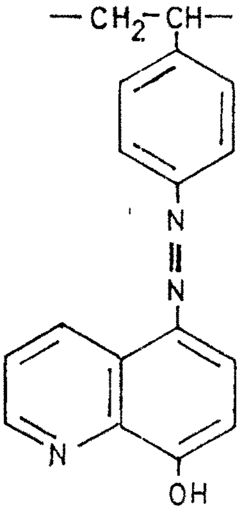


Fig. I 24

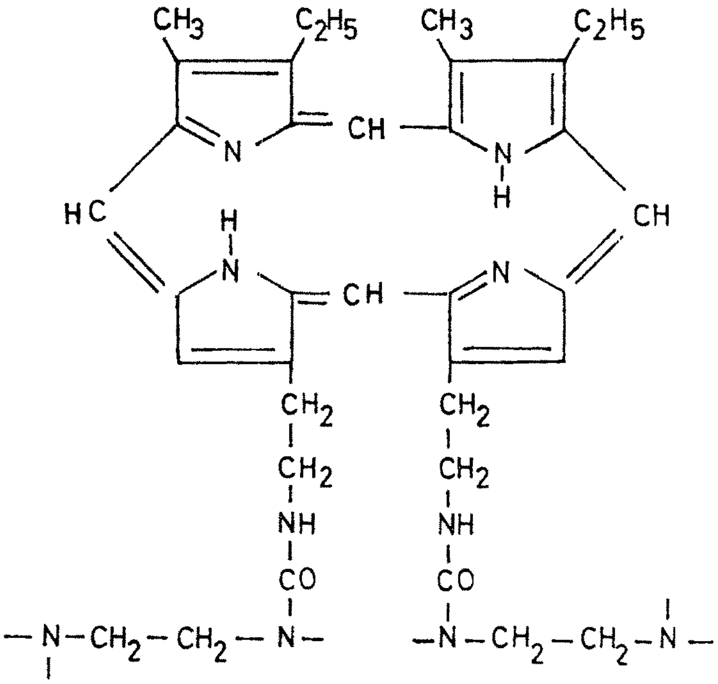


Fig. I.25

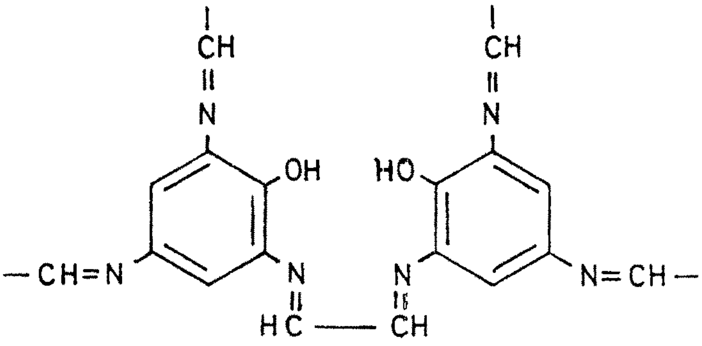


Fig. I.26

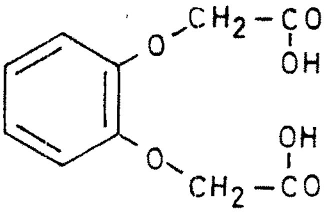


Fig I.27

De Geiso, et al (94) synthesized a copolymer of 5-methyl-5-hexene-2,4-dione and styrene; it has affinity for iron(III).

Kennedy and coworkers (58-62) prepared several resins by phosphorylation of chloromethylated polystyrene. Esters of allylphosphonic acid can be polymerized and then hydrolyzed to give a chelating resin (58).

Parrish (88) obtained a resin containing arsonic acid groups from poly(aminostyrene). Lastovskii and coworkers (95) reported chelating resins based on resorcinol and substituted benzene-arsonic acid. Gregor, et al (96) reported the resin containing mercapto group, which is specific for Hg(II).

A promising resin found by Gregor, Taifer and Backer (97) was prepared from m-phenylene diglycine, o-amino-phenol and formaldehyde. The resin showed selectivities for transition elements. A resin exhibiting a very high selectivity for copper has been synthesized by Mc Burney (98).

Chelating ion exchange resins are found to remove phytotoxic and human-toxic metal ions from soil. Thus, grass planted in the soil containing 200 ppm Pb, 69 ppm Cu and 76 ppm Zn showed normal root development when a chelating resin (iminodiacetate on styrene matrix) was added at 1250 g/m^3; no root formation occured in the absence of the resin (99).

A chelating agent loaded resin consisting of 8-quinolinol-5-sulfonic acid and an anion exchange resin has been studied for the selective removal of trace amounts of chalcophile elements in natural water samples prior to neutron activation analysis (100).

Polyesters from 4-hydroxy benzoic acid and its derivatives or compositions containing an ion-exchange or chelating groups have been studied by Yoshisawa (101).

Vernon (102) reported the separations of Fe(III) from various salts on a new hydroxamic acid ion exchanger. Quantitative separation of Cu from Fe, Co, and Ni is possible. Recoveries and separation of Fe and U from simulated seawater samples are demonstrated.

Polyamines and chelating polyamine-carboxylic acids are adsorbed by active carbon and heated to give chelating ion-exchanger (103).

King and Fritz (104) synthesized a chelating resin in which an o-hydroxypropiophenone oxime group is attached to the benzene ring of a divinyl benzene/styrene resin. This resin selectively absorbed Cu(II) and Mo(IV).

Oxine-based chelating resins were prepared by cross-linking metal oxinates with furfural and resorcinol (105).

De Geiso et al (106) reported a chelating resin based on 8-hydroxyquinoline-formaldehyde and measured the chelating activity of polymer in terms of distribution ratios of metal ions between their aqueous solution and the solid, showing that it could separate UO_2^{2+} from Cr^{3+}, Co^{2+} and Al^{3+} at pH 3, UO_2^{2+} from Zn^{2+} at pH 2, V and W from Mo at pH 10.8.

Condensation polymers from 8-hydroxyquinoline and formaldehyde were prepared and used as chelating agents for Mn^{2+}, Cu^{2+} or Co^{2+} (107).

A lightly crosslinked, macroporous, polystyrene-azo-oxine resin showed properties superior to other oxine containing resins produced by polycondensation, and was found to have probable practical applications. Column separations were possible; Hg was isolated from an industrial effluent and a specific method of uranium isolation was indicated (108).

Metal-complexing membranes were prepared by grafting 8-hydroxyquinoline-phenol-formaldehyde copolymer on partly hydrolyzed cellulose acetate. The membranes sorbed Cu^{2+}, Zn^{2+} and Ni^{2+} at pH 9 (109).

The extent of uptake of M^{2+} ions (M = Hg, Ca, Cd, Cu, Mg, Ni, Pb) by 8 new phenolic, thioester and urethane polymers, e.g., formaldehyde-8-hydroxyquinoline polymer, 1,6-di-isocyanatohexane-thioglycerol polymer and isophorone di-isocyanate-thio-glycerol polymer has been studied (110).

Tungsten is adsorbed from alkaline solution such as brines by (8-hydroxyquinoline-resorcinol-formaldehyde) resin in bead form (111).

Phenol-acetaldehyde polymeric chelating resins were prepared by gel technique. The ligands included salicylic acid, pyrocatechol, 8-hydroxyquinoline and 3-hydroxy-2-naphthoic acid. The capacity, moisture content and specificity of the resin towards Ca, Mg, Co, Ni, Zn and Cu at pH 2-8 were determined (112).

A mixture consisting of 8-hydroxy-quinoline, oleophilic phenol derivative, aldehyde and solvents was reacted under pressure to form the metal chelating resin beads (113).

Thermosetting chelating compounds contain a hydroxyquinoline type chelating agent, phenol-formaldehyde type condensed resin, and water soluble swelling agent compatible with the chelating resin. Fe and Cu were removed by the resin from waste-water (114).

Groups such as amide (115, 116), arsonic acid (117), dithiocarbamate (118), thioglycolate (119), oxime (104,120), etc. have been attached to macroporous crosslinked polystyrene; the products exhibit selectivities expected from those of the parent substances in solution. Oxime and thioglycolate resins, for example, are selective for mercury and copper. A cellulose based exchanger carrying salicylic acid absorbs iron (III) and uranium (VI) and one with hydroxyphenyl-azo-2-naphthol absorbs uranium (VI) very strongly (121).

A mercapto azo-benzene-sulfonate loaded on an anion exchange resin absorbs mercury (II) (122), and anion-exchanger loaded with substituted 8-hydroxyquinoline sulfonate absorbs many metal ions (123). The chelating agent may also be placed in mobile phase, using a non-ionic reverse phase support, which essentially becomes a cation exchanger (124).

I.7 PRESENT WORK

Considerable work has been carried out in our laboratories on different aspects of poly chelates, chelating polymers, ion exchange and redox polymers, e.g. on (i) semiconductivity of chelate polymers (125), (ii) pyrolyzed poly chelates (126), (iii) ion exchange resins (127), (iv) redox polymers (128), (v) chelating polymers (129), etc. Literature survey showed that poly vinyl alcohol forms hemiacetals, and acetals (both intramolecular and intermolecular) and though many acetals are useful for various purposes, acetals containing suitable functional groups have not been studied as chelating agents mainly because of the relative unstability of acetal bond (130). Hence it was planned.

(i) to prepare formals, chlorals, etc of poly vinyl alcohol and to study their general, sorption and solubility behaviour,

(ii) to condense ethyl aceto acetate, salicyl aldehyde, etc with poly vinyl alcohol and to study the general, sorption and solubility behaviour of the products,

(iii) to condense formals of poly vinyl alcohol with 8-hydroxy quinoline, salicyl aldehyde, etc and to study their general, sorption and solubility behaviour,

(iv) to condense bisphenol-A, etc with formaldehyde and chelating agents and to study their general and sorption properties,

(v) to modify some of the products by multiple condensation, etc and to study their general and sorption properties and

(vi) to prepare membranes based on the preparatory methods of some of these products and to study their general and ion-exchange properties.

The work carried out and the results obtained are presented and discussed in the following pages.