Introduction

INTRODUCTION

In the last decades, polymers and polymeric complexes attracted the attention of several investigators(1). Review of the literature reveals that the reaction of metal ions with polymers containing pendant functional groups produces coordinated systems having enhanced thermal stability and improved chemical resistance(2-4).

Insoluble resins of polymeric ligands have been used for the adsorption of toxic metal ions or trace metals from sea and water to clean-up the environment and to save energy. The selective adsorption of metal ions depends on the kind of polymers, ratio of cross-linking agent and the stability constant of the polymer-metal complex formed.(5)

The properties of polymers can be modified by the attachment of metal ions. So, many researchers (6 - 9) have been devoted their attention to the production of different polymeric metal complexes.One of the very important type is the model for the metalloenzymes which shows an interesting characteristics different from the corresponding ordinary metal complexes of low molecular weight. The production of polymeric metal complexes may enhance their uses as efficient catalysts, new promising semiconductors and immobilized reagents for industrial purposes. Some polymeric metal complexes can also adsorb reversibly gas molecules such as oxygen, carbon monoxide or olefines. Poly-oxime-palladium complex(10) absorbs reversibly carbon monoxide, while the corresponding complex containing cyanogroups(11) adsorbs gaseous olefines such as ethylene, propylene or 1-butene.

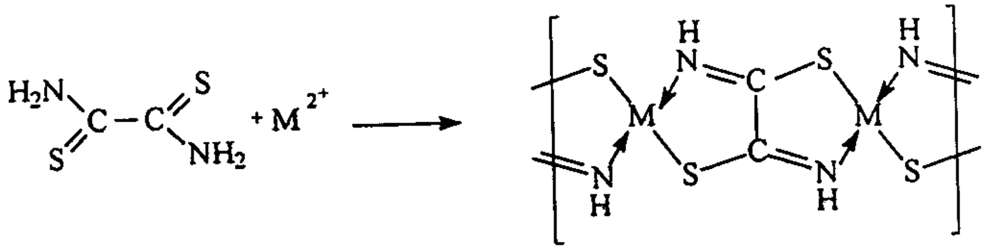
The polymeric metal complexes can be prepared according to the following methods :

1. Direct coordination of polymeric ligand with metal ion :

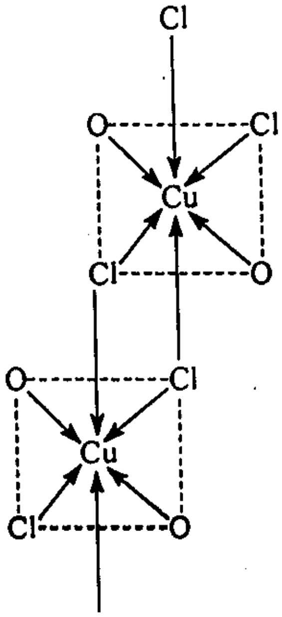
This type of polymeric metal complex formation proceeds easily by the reaction of polymer containing donating groups such as amine, heterocyclic nitrogen, carboxylic acid, ketone, phosphonic acid or thiol , etc.... with metal ion (12).

2- Metal ion bridging method.

This type of preparation obtained when a bifunctional ligand reacts with metal ion to give polymeric complexes with chains linked by metal ion as follow (I & II). (13 , 14)



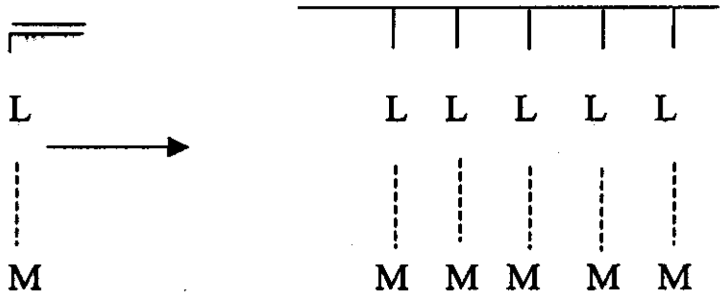
(I)



(II)

3- Polymerization of metel complexes.

This type of preparation obtained when vinyl compounds of the metal complex are polymerized with itself to give polymeric metal complexes (III) (15).



(III)

Three different general methods for obtaining coordination polymers have been described.

(i) Preformed metal complexes polymerized through functional groups, where the actual polymer-forming step can be either a condensation or an addition reaction.

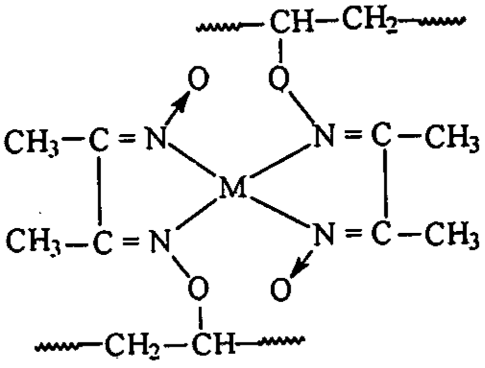
(ii)Coordination of a metal ion by a preformed polymen containing chelating groups.

(iii) Polymer formation through a coordination reaction using a ligand which can attach itself simultaneously to two metal atom or ion (16).

The use of metal chelates with aromatic and heterocyclicamines as a hardeners for polymers based on epoxy oligmers was studied by kurnoskin (17).

Rosthauser et al.(18) reported the synthesis of polymers bearing widely spaced hydroxamic acid (HA) by copolymerization of the N-hydroxysuccinimide ester of N-methacryloyl-β-alanine with acrylamide, followed by treatment with methylhydroxylamine. The hydroxamic acid content was measured spectrophotometrically, using the absorption of the 1 : 1 HA-Fe^{+3} complex of λ_{max} 504 nm. The effect of the HA : Fe ratio and the overall polymer concentration on the intrinsic viscosity was also studied.

Poly-vinyl chloride (PVC) has been reacted with dimethylglyoxime (DMG) to form PVC-DMG ligand, which has been characterized by spectroscopic and elemental analysis. The interaction of PVC-DMG with metal ion such as Co^{2+}, Ni^{2+} and Cu^{2+} gave the PVC-DMG-M^{2+} complexes (IV) with the following general formula(19).



(IV)

The structures of these complexes have been analyzed. The thermal stability of PVC-DMG-M^{+2} increases in the order PVC < PVC-DMG-Cu^{2+} < PVC-DMG-Ni^{+2} < PVC-DMG-Co^{+2} (19).

Reactive macroporous and beaded glycidylmethacrylate-divinylbenzene copolymers of controlled particle size were synthesized. The role of crosslinking density, pore generating solvent type pore volume, concentrations of protective colloids and polymerization initiator were studied(20).

Macroreticular glycidylmethacrylate ethyleneglycol dimethacrylate copolymer of controlled particle size were synthesized by suspension polymerization. The vanadium chelated copolymers were used in combination with cyclohexanone as redox reagent for the free radical polymerization of acrylamide at 30°C(21).

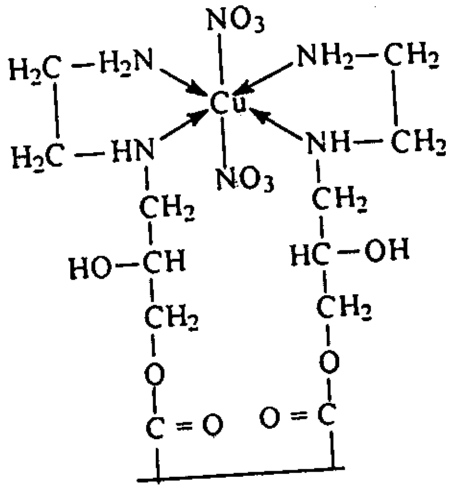
Kalalova, et al.(22) reported the formation of complexes of Cu^{2+} with ethylendiamine ligands bound by chemical bounds to copolymers of glycidylacrylate-ethylendimethacrylate and glycidylacrylate-methylene-bis-acrylamide.

The formation of transition metal complexes on the reactive hydrophilic copolymer glycidylmethacrylate-ethylenedimethacrylate, through the reaction with chemically bonded ethylenediamine molecules had been described. Particular attention has been paid to complexes of Cu^{+}, Cu^{2+}, Co^{2+}, Co^{3+}, Fe^{2+} and Fe^{3+}. The different degrees of oxidation of the central metallic ions lead to the formation of active and inactive compounds against the magnetic measurements. Electronic paramagnetic resonance EPR was chosen as a method for providing a direct proof for chemical bond between the metal and the polymeric chelating sorbent(23).

Chelate and non-chelate complexes of organo mercury with poly-methylenediamines were investigated by means of elemental analysis, proton magnetic resonance and potentiometric titration. The data obtained suggesting the molar ratio is (1 : 1) and (2 : 1) (metal : ligand) complexes. The stability constant of the chelate with the ratio (1 : 1) decreased in the order,

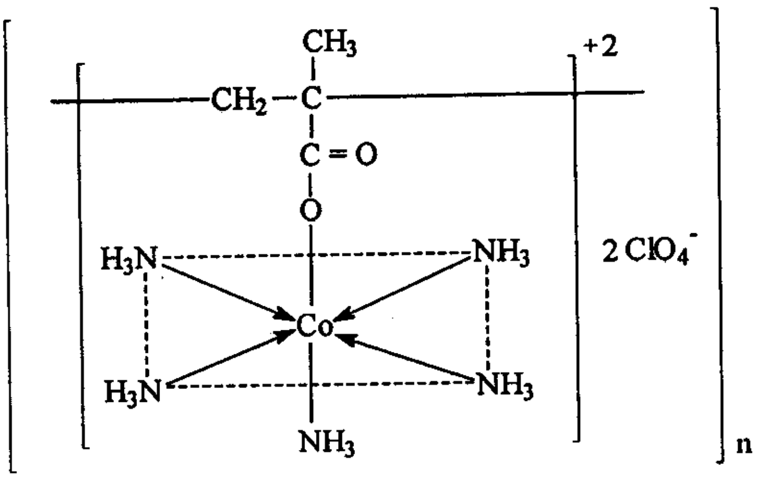
complexes. The stability constant of the chelate with the ratio (1 : 1) decreased in the order,
[EDTA > ethylenediamine > trimethylenediamine.] (24)

Polymers containing ethylenediamine groups bound to copolymers of glycidylacrylate-ethylenedimethacrylate and of glycidylacrylate-methylene-bis-acrylamide were prepared .
The structure with Cu^{2+} complex (V) was obtaind from the study of its monomeric analog.(25)



(V)

Methacrylate monomer coordinated to Co^{3+} amine complex. e.g. methacrylatopentaamine cobalt(III) perchlorate was radically polymerized giving the following polymer (VI).(26, 27)

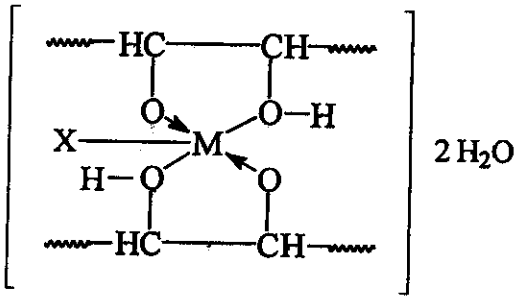


(VI)

Poly-Vinyl chloride anchored dimethylglyoxime complexes of Co^{2+}, Ni^{2+} and Cu^{2+}, initiate the solution polymerization of N-vinylcarbazole by a conventional cationic mechanism.(28)

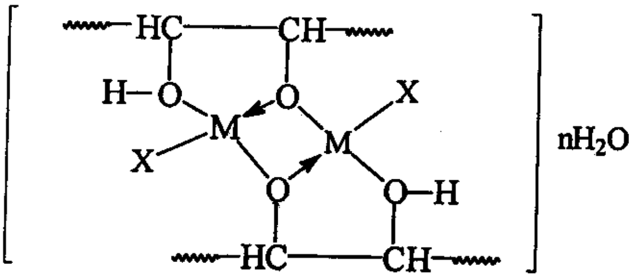
Diab, etal. (29) studied the rates of polymerization of methylmethacrylate in the absence and presence of metal chlorides. The activation energies of the prepared polymeric complexes were calculated.

Complexes of poly(ethyleneglycol) (PEG) with Cu^{2+}, Co^{2+}, Ni^{2+} and Cd^{2+} chloride have been prepared (VII & VIII) and characterized. The thermal stabilities of the polymeric complexes have been studied. The activation energies of the degradation of the polymeric complexes were also determined(30).



M = Cu^{2+}, X = H_2O
M = Ni^{2+}, X = Zero

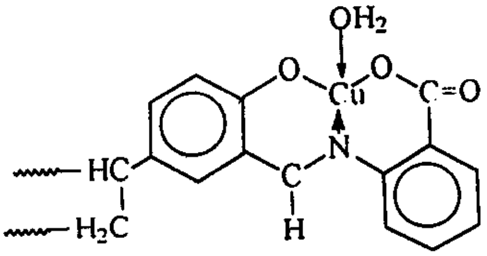
(VII)



M = Co^{2+}, n = 3
M = Cd^{2+}, n = 6

(VIII)

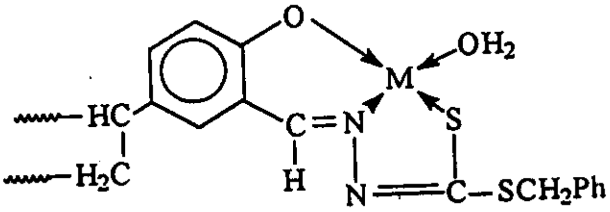
Poly-5-vinyl-salicylidene-anthranilicacid homopolymer and its polymeric complexes (IX) with some transition metal salts have been prepared and characterized. The thermal stability of the homopolymer and the polymeric complexes were studied. The activation energies of the degradation of the samples were calculated(31).



(IX)

Polymeric complexes of 5-vinylsalicylideneaniline with some transition metals were also prepared and characterized. Thermal stabilities of the polymeric complexes were compared with poly-5-vinyl-salicylideneaniline homopolymer and the order of the stability of the complexes was also given. (32)

Complexes (X) derived from polymeric 5-vinyl salicylidene hydrazine-S-benzyl dithiocarbazate (VSH) with $CuCl_2$, $CoCl_2$, $NiCl_2$, $CdCl_2$ and uranyl acetate were prepared and characterized. The stereo chemistry of the polymeric complexes have also been studied(33).



(X)

Pyromellitic dianhydride and dipyridyl/dipyridylamine have been polycondensed in the presence of anhydrous $ZnCl_2$ under selective conditions. Fe^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} complexes of the poly-condensates have been prepared. Tentative structures for PMDAspecific sorption towards to the Cu^{2+} ion in the presence of other metal ions.(38)

Poly-ethyleneasparatate (PEA) was synthesized by the condensation of D.L. aspartic acid and ethylene glycol. PEA containing pendant groups used as ligand for complexation with transition metal ions Co^{2+}, Ni^{2+}, Cu^{2+}, Mn^{2+}, Zn^{2+}, Cd^{2+}, Ca^{2+}, Pb^{2+} and Hg^{2+}. The resulting polyester metal complexes have been characterized. The thermal stabilities of the polyester metal complexes were investigated.(39)

Partially chloromethylated Polystyrene-divinyl benzene (PS-DVB) has been modified by anchoring dipyridyl amine (DPA) followed by subsequent complexation with Fe^{3+}, Co^{2+} and Cu^{2+}. Analytical and spectroscopic evidences have been presented to confirm the attachment of the metal-dipyridyl complex on the PS-DVB matrix. All the metal loaded polymers exhibit appreciable improvement in thermal stability.(40)

A new homopolymer drived from cinnamaldehyde and 2-substituted aniline was prepared and characterized. The metal complexes with Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+} and Hg^{2+} complexes has been synthesized and investigated. The corrosion inhibition of aluminum in HCl using PCA was studied. The antimicrobial activity of all the metal complexes had also been demonstrated.(41)

Polymer complexes of 2-dimethylaminoethylacrylate (DAEA) with Ni^{2+}, Cu^{2+}, Fe^{3+} and Co^{2+} chloride were prepared and characterized. The thermal stability of the homopolymer was compared with those of polymeric complexes and the order of stability was also given. (42)

Polymeric complexes of homopolymer 2-acrylamido-1-phenyl-2-amino-thiourea (APATH) with rodium and ruthenium have been prepared and characterized. Different types of coordination behaviour were reported. Monomeric distorted octahedral or trimeric chloride-bridged structures are proposed. TGA studies indicate that the complexes undergo decomposition to form stable metal oxides.(43)

A novel series of transition metal complexes derived from poly-(5-vinyl-salicylidine)-1,2-diaminobenzene in the presence of pyridine had been prepared. The polychelates had been characterized by chemical analysis. Thermal stability of the homopolymer and the polymeric complexes were studied. The activation energies of their degradations were calculated.(44)

Poly (4-vinyl pyridine homopolymer and polymeric complexes of 4-vinylpyridine with $CuCl_2$ and $NiCl_2$ have been prepared and characterized by Khairou.(45) The thermal behavioar and stabilities of the homopolymer and the polymeric complexes were also studied.

Poly-methacryloylphenylhydrazine and polymethacryloyl-2-benzo thiazol and their complexes with some transition metal chlorides were prepared and characterized by elemental analysis IR, U.V. and magnetic measurements. The thermal stability was also investigated. The polymeric metal complexes are more stable than their corresponding polymeric ligand. (46)

El-Sonbati et al.(47) prepared and characterized a number of transition metal polymeric complexes by thermal and spectral analysis. The magnetic measurement were also carried.

Mononuclear and hetero, bi and trinuclear polymeric complexes of Ni^{2+}, Cu^{2+} and oxovanadium (IV) chloride with 2-acrylamido-1-phenyl-2-amino-thiourea (APATH) monomer derived from amidation of acryloyl chloride with 2-amino-1-phenylthiourea have been prepared. The polymeric complexes obtained have been characterized on the basis of their elemental analysis, magnetic susceptibility, electronic and IR spectral measurements, EPR and thermal analysis.(48)

2-hydroxy-4-acryloyloxy acetophenone formaldehyde (HAAF) macromonomer containing polymerizable vinyl group was prepared. Elemental analysis of the polychelates indicates a metal ligand ratio of (1 : 2). IR, diffuse reflectance spectra, magnetic moments of polychelates and x-ray diffraction were studied. The viscosity and the thermal properties of both polymer and its metal complexes were discussed.(49)

2-hydroxy-4-acryloyloxy benzaldehyde (2H4ABA) prepared from acryloyl chloride and 2,4 dihydroxy-benzaldehyde was polymerized. The thermal properties of polymeric metal complexes and their catalytic activity were discussed. Catalytically active polymeric metal complexes containing Mn^{2+} moieties were synthesized and used in the selective epoxidation of olefins.(50)

N-methylacryloyloxy-tetrabromophtalimide (NMTP) monomer was prepared and studied by elemental analysis, IR, NMR and U.V. spectroscopy. Complexes of (NMTP) with Cu^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} and Fe^{3+} chlorides have been studied. The equilibrium constants of some metal ions, molar extinction coefficients, ionization potential, the stoichiometry and foreign ions are determined. The solid complexes have been prepared and investigated by elemental analysis, IR, U.V. and ESR spectroscopy to elucidate the structural configuration.(51)

Polymeric metal complexes of Cu^{2+}, Ni^{2+}, Co^{2+} and Zn^{2+} with poly 1-acrylamido -2 (2-pyridyl)ethane had been prepared and characterized by chemical, spectral and thermal methods.. The crystal field parameters for Co^{2+} and Ni^{2+} polymeric complexes were calculated.(52)

4Acetyl-3-hydroxyphenylacrylate was synthesized and polymerized Poly-(4-acetyl-3-hydroxyphenylacrylate) was characterized by IR and nuclear magnetic resonance techniques. The molecular weight of the polymer was determined. Cu^{2+} and Ni^{2+} chelates of (PAHAH) were synthesized and investigated. (53)

Solid-state characterization of poly (L-histadine) was obtained via differential scanning calorimetry (DSC), TGA, optical microscopy and infrared spectroscopy. The glass transition temperature of poly L-histadine increases when the complexes are produced with the divalent transition metal chloride of Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}.(54)

The thermal behaviour of poly (N-acryloyl, N`-cyano-acetohydrazide) (PACAH) and its copper and Nickel complexes was investigated using (TGA) and DTA techniques. The data obtained showed that the thermal behaviour of PACAH- metal complexes is significantly different from that of PACAH it self, spectral analysis (IR) was used to follow the structural changes accompanying the thermal degradation process. A mechanism for the degradation reaction of PACAH has been proposed (55).

Heterogeneous polymerization was employed to prepare macroporous copolymers from glycidylmethacrylate with ethylendimethacrylate. Conditions of the formation of the macroporous structure were defined and the properties of the prepared copolymers were studied. The resulting polymers find wide applications.(56)

A series of macroporous beads were synthesized by suspension copolymerization of glycidylmethacrylate (GMA) with divinyl-benzen (DVB) in presence of various diluents to act as precipitants, the effect of diluents on the surface appearance and the pore structure of copolymer beads was studied. The macroporous copolymer beads which have large specific surface area and pore volume could be prepared.(57)

Reactive glycidylmethacrylate (GMA) divinyl-benzene (DVB) copolymers of widely varying crosslink densities were synthesized in bead form. Porosity surface area and pore size were found to increase with concomitant increase in cross-linking monomer and volume of porogen. It was possible to control the pore volume in the range 0.0 to 2.06 ml/g.(58)

Resin containing phosphonium groups were prepared by reaction of chlorohydroxylated glycidylmethacrylate divinylbenzene macroreticulare resins with three trialkylphosphines, Adsorption and elution behavior of sodium benzene sulfonate (SBS) and sodium dodecyl benzene sulfonate (SDBS) on the resins were studied. Adsorption of (SBS and SDBS) increased with increasing the alkyl chain length of phosphonium groups in the resins. The adsorption of SBS decreased with increasing the ionic strength of the solution, while the adsorption of SDBS increased with increasing the ionic strength of the solution.(59)

Six chelating hollow fiber membranes were prepared by radiation induced grafting of glycidyl methacrylate on a polyethylene hollow fiber membrance and subsequent amination. The adsorption characteristic of Pb^{2+} and Pd^{2+} for chelating hollow fiber membranes were presented when the solution of Pb^{2+} and Pd^{2+} permeates across the chelating membrane respectively. The degree of grafting for glycidylmethacrylate increases with the increase of monomer concentrations. The chelating hollow fiber membrance modified with iminodiacetic acid adsorbes Pb^{2+} ions much more than Pd^{2+}. (60)

Some insoluble resins have been used for adosrption of metal ions. Removal of toxic metal ions from water or collection of trace metals from the sea-water is strongly desired from the social stand point of clean up of the environment and of energy saving. Selective adsorption of metal ions is especially important and which is realized only by using polymeric ligands. The selectivity depends upon the stability of the metal complex, structure of the ligand and on the kind of metal ions. A small difference of the stability constant of the complex between polymeric ligand and metal ion enables the selective adsorption of metal ion by the polymer. Adsorption of metal ions by resin has been studied well and described in many books and articles.(5) The study showed that the selective adsorption of some metal ion can be accomplished by operating the adsorption at a definite pH. Polystyrene pendant polyamine (L) adsorbed metal ions selectively in the following order at pH = 6, $Hg^{2+} > Cu^{2+} > Cd^{2+} > Ca^{2+}$. (61-63)

The synthesis and characterization of a number of chelating resins having multiple functional groups cabable of coordination to several metal ions is reported. The resins were synthesized by condensing schiff bases dreived from 4,4-diaminodiphenyl-sulphone and hydroxy benzaldehydes with formaldehyde and furfuraldehyde. The resins formed a number of polychelates with metal ions like Cu^{+2} and Ni^{+2}. The schiff bases, resins and the polychelates were characterized by IR, uv-vis., HNMR spectra and TGA. From the spectral data the possible coordination sites of the resins towards the metal ions were determend. The intrinsic viscosity of the resins was determined by viscometry in DMSO. The adsorption characteristic of the resins towerds metal ions in dilute a queous solutions were measured. The structure and the molecular geometry of the resins was observed to strongly influence the metal uptake behaviour, in addition to the influence of pH, temperature, partical size and metal ion concentration. Metallization of the resins significantly affected the thermal stability, the polychelates were found to be less stable than the resines.(64)

Poly-Amine ligands such as ethylendiamine, diethylenetriamine, triethylene-tetraamine or any excellent chelating agents were bound to chloromethylated polystyrene resins (XI) and the resulting polyamine resins adsorbed Cu^{2+} ion effectively(65).

(XI)

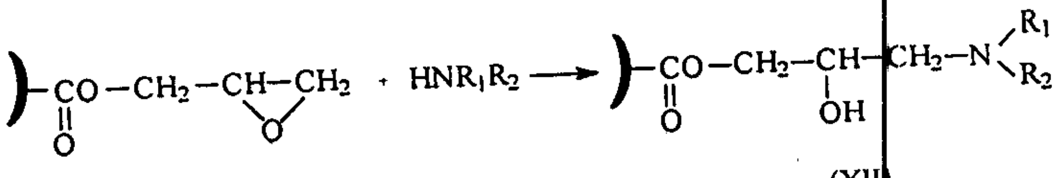
Krystyna (66) reported the possibility of using bromopyrogallol-red, chromotropic acid and alizarin red-S as complexing agent for the separation of metal ions on strongly basic anion exchangers.

Cu^{2+} and Ag^{+} or Ni^{2+} are selectively removed from acidic aqueous solutions of transition metal ions mixtures by polymers containing chelating ligands based on the derivatives of N, N bis (2-pyridyl methyl) 2, 2` diamino biphenyl and N (2-pyridyl methyl) 2, 2` diamino biphenyl. The chelated ions are recovered by stripping with 6N mineral acid. Polymer chelating capacities depend on the ligand structure and range up to 1.7 mmol of metal ion per gram of polymer.(67)

The complexing properties of the copolymer of glycidylmethacrylate-ethylenedimethacrylate (GMA-EDMA) with attached ethylendiamine (en) as a ligand were previously studied(68-69). Three types of complexing polymers were allowed to react with bivalent ions of Cu^{2+}, Zn^{2+}, Fe^{2+}, Co^{2+} and Ni^{2+} their sorption ability and selectivity towards individual ions were investigated.(56)

Two chelating resins beaded on poly (glycidylmethacrylate co-ethyleneglycoldimethacrylate) and two based on poly (styrene co-divinyl benzene) have been used in small scale column extractions of Cu^{2+} from sulphate solutions containing 1.0 mg/L of metal ions at pH = 5(70). The selective properties of the two efficient resins in extraction of Cu^{2+} ions from solution containing a large excess of Zn^{2+} ions were also investigated. The effect of a 250 fold excess of Zn^{2+} proved negligible in both cases and Cu^{2+} was rapidly and selectivity extracted.(70)

Reaction of the glycidylmethacrylate-ethylene dimethacrylate with ethylamine, diethylamine, and 2-hydroxyethylamine were employed to prepare new types of macroporous resins (XII). Reactions of macroporous copolymer(71) with Cu^{2+}, Zn^{2+}, Fe^{2+}, Ni^{2+} and Co^{2+} ions was studied. The amount of the metal ion sorbed as well as the selectivity coefficient for the reactions with Cu^{2+} and Co^{+2} ions were established. Different complexes were formed utilizing further-OH groups or H_2O molecules contained in the resin. The extistance of the complexes were also demonstrated.(71)


(XII)

The ligand-8-hydroxyquinoline-5-sulfonic acid forms anionic complex with Co^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}. Each resulting complex showing a high affinity for anion-exchange resins. All four metals are quantitatively retained by the column elution method. Distribution coefficients for the metal complexes and their ligand/metal ratios were determined using the batch methods that may also serve as the isolation procedure.(72)

Poly-Vinylbenzoylacetone (VBA) was prepared by a condensation of p-vinylacetophenone and ethylacetate. This monomer was homopolymerized and copolymerized with acrylamide or malic anhydride to produce polymers the polymeric complexes of this polymer with Cu^{2+}, Ni^{2+}, Co^{2+}, Eu^{3+} and VO^{2+} was obtained .In the case of Cu^{2+} and Ni^{2+} complexes the metal ion could be eluted. The resulting eluted products have porous structure because they are capable of rechelating this ions from water solutions.(73)

A new chelate-forming resin bearing mercapto and azo groups was prepared from a common anion-exchange resin by treatment with azothiopyrine disulphonic acid (ATPS). (ATPS) resin was very stable and highly effective for the collection of Hg^{2+} by the batch and column methods. The adsorbed Hg^{2+} could be eluted with thiourea solution and the resin could be used repeatedly(74).

Different series of new liquid crystalline homopolymers containing paramagnitic units of copper (II) salicyaldiminates have been synthesized. Interfacial polycondensation of hydroxy-functionalized copper (II) complexes is shown to be the most suitable way of obtaining these polymers. Ingeneral, the polymers, exhibit good thermal stability. (16)

Reactions of the copolymer glycidylmethacrylate-ethylenedimethacrylate with ethylamine, diethylamine and 2-hydroxy ethylamine were employed to prepare a new type of macroporous complexing resins (75).

A resin for the collection of selenium (IV) has been prepared simply by the conversion of a common ion exchange resin with bismuthiol. The binding ratio of selenium (IV) to bismuthiol on the resin was confirmed to be 1:4. Satisfactory results were obtained when this resin was applied to the determination of selenium (IV) in river, esturine or sea water samples.(76)

A sulfonated dithizone, disodium dithiazene-disulfonate (D_2Z) were synthesized and immobilized on an ion exchange resin. The (D_2Z) loaded resin was confirmed to be a chelate forming resin and to be useful for the collection of Hg^{2+}, Me-Hg, Ag^+, Cd^{2+}, Zn^{2+} at pH range between 1.0-7.0. The capacity increased with the amount of (D_2Z) immobilized on the anion-exchange resin.(77)

Two chelating resins beased on poly (glycidylmethacrylate-co-ethyleneglycol dimethacrylate) and two based on poly (styrene co-divinyl benzene) have been used in small scale column extractions of Cu^{2+} from sulphate solutions. Two of the resins bearing 2-aminomethylpyridine residues with saturation capacities up to 15g Cu^{2+}/L resin.(78)

Agricultural waste from apple-juice processing and cider production was used to remove heavy metal cations from solutions. The removal recovery of copper, zinc and nickel ions in packed beds was studied. The apple waste showed most affinity for copper ions and the efficiency of the heavy metal removal was greatly increased after the apple waste had been treated with phosphorus (V) oxychloride. After exhaustion of the waste, the metals were eluted and after subsequent washing the waste was ready for re-use.(89)

A number of lightly cross-linked poly(acrylonitrile-co-divinyl benzene) beads having highly porous-structure had synthesized. The chelating resins containing amidoxime as functional group had been prepared by reaction of the co-polymer beads with hydroxylamine. A set of experiments have been performed to ascertain the potential of the resins for the adsorption of uranium from sea water. Because of their modified pore structures, the chelating resins exhibited a marked adsorption rate for uranuim in sea water as a high as 23 mμg of U/cm^3 of resin/day without alkaline treatment.(80)

Lightly cross-linked poly (acrylonitrile-co-divinyl benzene) beads having highly porous structures. The chelating resins containing amidoxime groups have been prepared by the reaction of copolymer beads with NH_2OH. The resulting chelating resins have been used in the batchwise adsorption of UO_2^{2+} from nitrate solutions. The extraction of UO_2^{2+} was monitored with time and some adsorption profiles were obtained. An increase in porogen content resulted in a marked increase in the batchwise adesorption of UO_2^{2+}. Alkaline treatment allowed a high swelling and hence rapid accessibility of UO_2^{2+} to the ligands. Even after 30 min, the alkali-treated resins were 50% loaded.(81)

Porous chelating resins have been prepared from acrylonitrile-ethylacrylate divinylbenzene terpolymer by suspension polymerization and by reaction of the resins with NH_2OH. The pourous structure was characterized. The metal binding properties of the chelating resins containing amidoxime and hydroxamic acid ligands were also studied. This type of chelating resin has some advantages, e.g. the ease of preparation and particular selectivity for metal ion.(82)

Complex formation of vinylamine-acrylonitrile copolymer with Cu^{2+} ion in equeous solution was examined. The structures of the complexes changed with pH of solution.(83)

Phosphoric acid resins with large cation exchange capacities were prepared.The effects of porosity and crosslinking of the precursor poly (glycidylmethacrylate-co-divinylbenzene) beads on their function were also studied. Two series of precursor copolymers were prepared. It was clarified that the porosity plays an important role in the function of highly porous precursors. The selectivity study has revealed that the precursors exhibit characteristic selectivity among common divalent metal ions. In addition, the resin exhibits highest selectivity towards lead ion.(84)

Recently, laboratories demonstrated that it is possible to use proteins as efficient selective agents for heavy metal removal and recovery. The ability of immobilized transferrin to produce clean water was demonstrated and the mechanism of copper release was studied. It was shown that release was dependent on pH and the chelating ability of the stripping agent. Metal release occurred slowly at pH > 7. However at low pH in the presence of a chelating, agent (ligand) metal removal occurred much more efficiently. The binding constant of copper to immobilized transferrin was determined as function of pH. (81)