II. POLYMER-METAL COMPLEXES: SYNTHETIC, STRUCTURAL AND ANALYTICAL ASPECTS

The study of the polymer-metal complexes has received increased interest recently in various branches of chemistry, chemical technology and biology and the subject has been reviewed periodically\textsuperscript{1-4}. The chelating polymers find application in collecting transition metal ions as well as alkali and alkaline earth metal ion separations\textsuperscript{5,6}, preconcentration and recovery of trace metal ions\textsuperscript{7}, catalysis\textsuperscript{8,9}, organic synthesis\textsuperscript{10,11}, nuclear chemistry\textsuperscript{12}, water- and waste water-treatment\textsuperscript{13,14}, pollution control\textsuperscript{15}, industrial processes\textsuperscript{16}, hydrometallurgy\textsuperscript{17-19} and polymer drug grafts\textsuperscript{20}. In addition polymer-metal complexes are also used as mechanochemical systems\textsuperscript{21} and as models of bioinorganic systems\textsuperscript{22,23}.

A polymer-metal complex is a coordination complex between a ligand function anchored on a polymer matrix and a metal ion in which the metal ion is attached to the polymeric ligand by a coordinate bond. Here a polymeric ligand is considered as a polymeric substance that contains coordinating groups or atoms mainly N, O and S. The polymeric ligand can be obtained by the polymerization of monomers containing coordinating sites.
or by the reaction between a polymer and a low-molecular weight compound having coordinating ability. In a polymer-metal complex, a complex with a specific structure results since the metal ion is surrounded by a structured polymer chain. Polymer-metal complexes show unique properties which are distinctly different from their low-molecular weight analogues. These unique properties originate from the properties of the polymer backbone.

II.A. Formation of Polymer-Metal Complexes

There are different approaches for the preparation of polymer-metal complexes. The methods involve complexation between a ligand function anchored on a polymer matrix and metal ion, reaction of a multifunctional ligand with metal ions, reaction of a metal complex with a neutral polymer and the polymerization of low molecular weight complexes.

II.A.1. Complexation of Polymeric Ligand with Metal Ion

This type of polymer-metal complex is formed by the reaction of a polymer containing coordinating groups with metal ions. Examples of some typical ligands are given in Table II.1. The general
<table>
<thead>
<tr>
<th>Ligand</th>
<th>Active Structure</th>
</tr>
</thead>
</table>
| 1. Iminodiacetic acid  | \[
|                        | \text{CH}_2\text{COOH} \text{CH}_2\text{COOH} \] |
| 2. 8-hydroxy quinoline | \[
|                        | \text{O} \text{H} \] |
| 3. Polyamines          | \[
|                        | \text{H}_2\text{N}\{\text{CH}_2\text{CH}_2\text{NH}\}_x \text{CH}_2\text{CH}_2\text{NH}_2 \] |
| 4. Cyclic Polyamines   | \[
|                        | \text{R} \text{N} \text{N} \text{R} \text{N} \text{N} \text{R} \text{N} \text{N} \text{R} \] |
| 5. Guanidine           | \[
|                        | \text{S} \text{C} \text{NH} \downarrow \downarrow \text{NH}_2 \] |
| 6. Dithiocarbamate     | \[
|                        | \text{N} \text{C} \text{S} \downarrow \downarrow \text{N} \text{H} \] |

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<table>
<thead>
<tr>
<th>Ligand</th>
<th>Active Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mercapto groups</td>
<td><img src="image1" alt="Mercapto group" /></td>
</tr>
<tr>
<td>Hydroxamic acid</td>
<td><img src="image2" alt="Hydroxamic acid" /></td>
</tr>
<tr>
<td>Aminophosphoric acid</td>
<td><img src="image3" alt="Aminophosphoric acid" /></td>
</tr>
<tr>
<td>Crown ether</td>
<td><img src="image4" alt="Crown ether" /></td>
</tr>
<tr>
<td>Schiff base</td>
<td><img src="image5" alt="Schiff base" /></td>
</tr>
<tr>
<td>Alcohol</td>
<td><img src="image6" alt="Alcohol" /></td>
</tr>
</tbody>
</table>
methods of incorporating active functional groups (ligands) have been summarised\textsuperscript{24}. The methods can be mainly classified into four different groups: (i) direct polymerization and/or copolymerization of monomers containing the desired functional groups; (ii) chemical modification of the preformed polymer; (iii) functional monomer inhibition into or grafting onto the prepared polymer, followed by polymerization and (iv) immobilization of hydrophobic chelating extractants during polymerization or post-polymerization (physical impregnation). These methods have been used in one or other form to synthesise majority of chelating resins. The synthesis of a chelating resin involving minimum number of steps is favoured because of the decreased possibility of contamination of the end product with by-products and intermediate products due to their incomplete conversion and the inherent problem of their removal.

Usually the reaction of a polymeric ligand with a metal ion or a stable metal complex in which one coordination site remains vacant results in various coordination structures which can be divided into pendant and inter-and/or intra-molecular bridged complexes.
a. Pendant Complexes

A pendant metal complex is one in which the metal ion is attached to the ligand function which is appended on the polymer chain. Based on the chelating abilities of the ligands, pendant complexes are classified as monodentate and polydentate pendant complexes.

(i) Monodentate Pendant Complexes

A monodentate pendant complex is formed when a metal ion or a stable metal complex in which the central metal ion is already masked with low-molecular weight ligands except for one coordination site that remains vacant. Such complexes have a simple structure of the monodentate type as shown in Scheme II.1. In these complexes, the effects of polymer chains are exhibited clearly and the polymer complex is often soluble since it contains few bridged structures which reduce the solubility.

Even if the metal ion or the metal complex has more than two labile ligands, it is often possible to form a monodentate complex by selecting an appropriate reaction condition. When the reaction between the metal
Scheme II.1. Monodentate Pendent Metal Complexes

Ion or metal complex and the polymeric ligand is carried out with excess of the metal or metal complex, the probability of the substitution of the second labile ligand of the metal ion would be very less, resulting in a predominantly monodentate type structure.

An example of the formation of a pendant monodentate complex is the complexation of cis-
\[ \text{[Co(en)}_2X_2\text{]}X \] with poly(4-vinyl pyridine)^25 (1).

\[ X = \text{Cl, Br, N}_3 \]

\[ \text{en = ethylenediamine} \]
(ii) Polydentate Pendant Complexes

When the polymer backbone contains multidentate ligands the coordination structure of the polymer-metal complex can be represented as in scheme II.2. Polydentate ligands often result in the formation of stable metal complexes with bridged structures. Most of the chelating resins come under this category. Pendant polymer-metal complexes are characterised by their relatively well-defined coordination structure. The effect of the polymer chains is more predominant here.

Scheme II.2. Polydentate Pendent Metal Complexes

b. Inter- and/or Intra-Molecularly Bridged Complexes

In the case of the reaction of a polymeric ligand with a metal ion, which has four or six
coordinating bonding hands, the polymer-metal complex formed may be of the intra-polymer chelate type or inter-polymer chelate type (Scheme II.3). The coordination

Scheme II.3. (a) Intra-Polymer Metal Complexes, (b) Inter-Polymer Metal Complexes

structure in this type of polymer-metal complex is not clear and it is often difficult to distinguish between the inter- and intra-molecular bridging. Thus it is not easy to elucidate the polymer effect in studying the characteristics of the polymer-metal complexes. Intra-polymer metal complex is sometimes soluble while inter-polymer complex formation results in precipitation of the linear polymer-metal complexes. A typical example of this type of polymer-metal complex is the poly(vinyl alcohol)-Cu(II) complex(2).
II.A.2. Polymerization of Coordinated Monomers

Metal complexes of low-molecular weight monomers are polymerized to give polymer-metal complexes. There are three basic polymerization techniques for the preparation of polymer metal complexes from the corresponding monomer complexes.

a. Polymerization of Vinyl Compounds Containing Metal Complexes

This type of polymer-metal complex is characterized by a clear coordination structure. The vinyl monomers which can be polymerized are limited and the polymerization depends on the electrostatic interaction between the coordinated monomer and the growing radical. The polymerization occurs by the
radical or ionic initiation to form a polymer of high molecular weight as depicted in scheme II.4.

Scheme II.4. Polymerization of Coordinated Vinyl Monomers

Some transition metal salts and metal complexes act as inhibitors in the polymerization of vinyl monomers. Thus the polymerization of 4-vinyl pyridine is strongly inhibited in the presence of Cu(II) or Fe(III)\(^{27}\). But Zn(II), Co(III) or Cu(I)-4-vinyl pyridine complexes can be polymerized to form the corresponding poly(4-vinyl pyridine)-metal complexes\(^{28}\). Methacrylate coordinated with amine-Co(III) complexes to form methacrylato-pentamine-Co(III) perchlorate(3) and cis-dimethacrylatotetramine-Co(III) perchlorate(4). Homo- and co-polymerization of these complexes with methacrylic acids can be carried out using redox initiators\(^ {29,30}\).
The metal ion in the polymerizable vinyl monomer complexes has a completely filled d-orbital. These complexes are relatively inert to redox reactions with organic radicals and ions. Generally, coordination decreases the electron density of the vinyl group. Hence the metal ion species is selected to avoid redox reaction and to polymerize the vinyl monomer.

b. Polycondensation of Metal Complexes Containing Free Functional Groups

The preparation of polymer-metal complex by condensation is reported by Hartwell and Bailer\textsuperscript{31} (Scheme II. 5). Polyesters and polyamides have been synthesized by interfacial polycondensation with aryl acid chlorides.
c. Ring-Opening Polymerization

This involves the polymerization of a metal complex containing a strained ring which is capable of ring-opening polymerization as shown in scheme II.6. An example of this type of polymer-metal complex formation is the polymerization of beryllium complex of bis-β-carbonyl compound (Scheme II.7). 32

The polymer-metal complexes obtained by polycondensation and ring-opening polymerization are considered as coordination polymers since the polymer chain is composed of coordinate bonds.
Scheme II.6. Ring-Opening Polymerization of Low-
molecular Weight Metal Complexes

Scheme II.7. Ring-Opening Polymerization of Beryllium Complex of bis-β-carbonyl Compound
II.A.3. Reaction of Peripheral Functional Groups in Metal Complexes with Polymers

This type of polymer-metal complex is formed by the chemical reaction of neutral or functional polymers with peripheral functional groups of metal complexes as shown in scheme II.8. These polymer-metal complexes have definite coordination structures.

![Scheme II.8. Formation of Polymer-Metal Complex by Polymer-Analogous Reactions](image)

crosslinked polystyrene and its modified forms and silica are widely used as the insoluble polymer systems here. Some examples are given in scheme II.9.

![Scheme II.9. Formation of Polystyrene- and Silica-Supported Polymer-Metal Complexes by Polymer-analogous Reactions](image)
The immobilization of metal-porphyrins into a polymer-matrix has been achieved by the reaction of peripheral functional groups in the metal-porphyrins with reactive polymers and they have been used as enzyme models. The fixation of Mg(II)-chlorophyll into preformed polymer by chemical modification is shown in scheme II.10.

Scheme II.10. Immobilization of Mg(II)-Chlorophyll on Chloromethyl Polystyrene

II.A.4. Coordination Polymers

A low-molecular weight compound with multidentate ligands on both ends of the molecule grows into a linear network polymer as shown in Table II.2.
Table II.2. Various Types of Coordination Polymers

<table>
<thead>
<tr>
<th>Coord. No. of metal</th>
<th>Ligand</th>
<th>Types of polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>2A–A</td>
<td>--A–A–M–A–A–M--</td>
</tr>
<tr>
<td></td>
<td>3A–A</td>
<td>M–A–M--</td>
</tr>
<tr>
<td>4</td>
<td>4A–A</td>
<td>M–A–A–M–A–A–A–M</td>
</tr>
</tbody>
</table>
The polymer chain is composed of coordinate bonds and the ligand is the bridging unit as shown in scheme II.11. Multidentate ligands capable of forming this type of coordination polymers are classified into (a) linear coordinated polymers and (b) network coordinated polymers.

![Scheme II.11. Formation of Coordination Polymers by Bridging of Ligands by Metal Ions](image)

**a. Linear Coordinated Polymers**

Linear coordinated polymers can be prepared by two methods, from bifunctional ligands and from simple compound or ion as ligands.

**(i) Bifunctional Ligands**

Here the polymer chain is composed of bifunctional ligands and metal ions. A typical example for the coordination complex formed between a bifunctional ligand and metal ion is the complex between dithiooxamide and metal ions (Scheme II.12)\(^{36}\).
Scheme II.12. Formation of Network-Coordinated Polymer-Metal Complex of Dithiooxamide

(ii) Simple Compound or Ion as Ligands

A simple compound or ion can function as a bridging ligand giving rise to a polymeric structure. Cupric chloride forms an associated structure in which the chloride occupying as bridging ligands on both the axial and equatorial coordination sites of Cu(II) (5).
b. Network-Coordinated Polymers

This type of polymer-metal complex is formed by a "template reaction" between two functional groups of the ligands induced by their coordination to metal ions resulting in a chelate type metal complex as depicted in scheme II.13. Poly-(metal phthalocyanine) is an example for this type of network-coordinated polymers. It is formed by the reaction of tetracyanobenzene with metal halides (Scheme II.14).38.
II.B. Analysis and Characterization of Polymer-Metal Complexes

Usual chemical methods of analysis applied to low-molecular weight species have been found to be satisfactory with linear polymers. But with crosslinked polymers such methods which require solubilization of the samples cannot be applied. The detection and estimation of the elements present in the polymer-complexes are carried out by elemental analysis. The different functional groups (ligands) are detected qualitatively by the general chemical tests and from their typical IR absorptions. If the ligand functions supported on the polymer are acidic or basic, a quantitative estimation of the groups can be done by titrimetric method, provided, the support material allows penetration of the aqueous reagents. In the case of reagents where the penetration of the aqueous reagents is difficult, it is better to react the supported group with excess of acid or base, allowing the reaction for a sufficiently long period and then to carry out back titration. The complexed metal ions are estimated by volumetric, spectrophotometric or gravimetric methods. The metal ion intake is usually expressed as milligram of metal ion complexed by one gram of the resin.
The coordination of a polymeric ligand to metal ion and the structures of the resulting polymer metal complexes are studied spectroscopically and by measuring the magnetic properties. Infrared (IR), visible, electron spin resonance (ESR), NMR, Scanning electron microscopy (SEM), X-ray, optical rotatory dispersion (ORD) and circular dichroism (CD) can be made use of for the structure elucidation of polymer-metal complexes. Thermal studies (TGA/DTA) have also been used to explore composition, structure and thermal stabilities of polymeric ligands and their metal complexes. Applications of these methods are illustrated in the respective sections dealing with individual chelating polymers and their metal complexes. Increasing importance is not attached to the use of these methods as various physical measurements can help in adequate characterisation of crosslinked chelating resins to indicate the chemical environment of the attached chelating group.

II.B.1. Spectral Characterization of Polymer-Metal Complexes

a. Formation of Polymer-Metal Complexes

The formation of polymer-metal complexes can be followed from their characteristic absorption
bands in visible, infra-red and far infra-red spectra and by comparing them with the corresponding low-molecular weight complexes. The IR absorptions by a ligand are usually shifted by complex formation with metal ions. The coordination structures of the Co(III)-complex of poly(4-vinyl pyridine) and the corresponding low molecular weight complex are studied by spectroscopy. The visible spectra of cis-[Co(en)$_2$(PVP)Cl]Cl$_2$ are similar to the pyridine complex, cis-[Co(en)$_2$(Py)Cl]Cl$_2$, which has the cis configuration. The IR absorption at 1600 cm$^{-1}$, which is the stretching band of the pyridine ring, shifts by 20 cm$^{-1}$ to a higher wavenumber, corresponding to the coordination of the pyridine unit of poly(4-vinyl pyridine) to the Co(III) chelate. The absorption at 1600 cm$^{-1}$ is also observed in the poly(4-vinyl pyridine) complexes, indicating that the uncoordinated repeating unit of poly(4-vinyl pyridine) remains in the PVP-Co(III) complexes. Attempts have also been made to study the metal-ligand vibrations in the far-infrared region. The far-infrared absorption bands characteristic of the bonding between Co and N of the polymeric ligands are shifted by about 3 - 8 cm$^{-1}$ to a lower wavenumber in the PVP-Co(III) complexes. It is presumed that the coordinate bond between Co and pyridine unit in PVP is weaker than the bond of the monomeric pyridine. There is a close relation between
the macromolecular complex stability and C-C stretching frequency of the chelate ring similar to that observed in low-molecular weight complexes. When a polymer ligand has more than two kinds of ligands capable of coordination, it is possible to decide from IR absorptions, which group participate in the coordination. In the case of the Cu(II) complexes of vinylamine-vinylalcohol copolymer, the relative absorbances of the IR spectra indicate that the Cu(II) ion is coordinated exclusively with nitrogen atoms of the copolymer. Fourier-transform infrared spectroscopy has also been used to investigate crosslinked polymers and their metal complexes.

Proton magnetic resonance has not been widely used for the structural analysis of crosslinked polymer-metal complexes due to their insolubility and the broadening of the spectrum on complexation of the polymeric ligand. However, $^{13}$C-NMR spectroscopy can be used for the analysis of the organic structure of highly swollen, lightly crosslinked polymers and magic-angle spinning methods can be used to extend this to more rigid materials. $^{13}$C and $^1$H NMR with the multivalent metal atoms have been used to determine the sites of metal coordination on the polymer. Generally complex formation with metal ion leads to shifts, splitting, or
broadening of the peaks arising from the ligand molecule. In the absence of anion effect, a downfield shift is observable due to the increased electronegativity of the donor atoms of the ligand$^{50}$. The complex of poly(ethylene glycol) and its dimethyl ether with alkali and alkaline-earth metal ions was studied by NMR spectroscopy$^{51}$. The ethylene proton signal of octaethylene glycol in methanol-d$_4$ was split into three lines by the addition of the alkaline-earth metal ions. The latter two cations also caused large downfield shifts. These splittings can be ascribed to strong complexation with the metal ions.

b. Coordination Structure of Polymer-Metal Complexes

Electron spin resonance (ESR) has been used for the structure elucidation of polymer-metal complexes. The ESR spectrum of polymer-metal complex reflects its coordination structure. The interaction between the spin of the metal ion and the coordinated ligand and its "g" value dictates the ESR spectrum in such cases. The ESR spectral curves of poly(4-vinylpyridine)-Cu(II) complex which is partially quaternized with ethyl bromide (6) are given in Fig. II.1$^{52}$. The spectral curves 2 - 5 in Fig. II.1. correspond to the Cu(II) complexes of the partially quaternized and
crosslinked poly(4-vinyl pyridine) by 1,4-dibromobutane (7). The spectral curves 1 - 3 are typical patterns for the square planar Cu(II) complex and the corresponding parameters are $g_{||} = 2.3$, $g_{\perp} = 2.1$ and $A_{||} = 150 \pm 10$ G.

Fig. II.1. ESR Spectra of Cu(II) Complex of Partially Quarternized PVP (a) Linear (b) 4\% Crosslinked (c) 12\% Crosslinked (d) 31\% Crosslinked (e)
These values are in agreement with those of the monomeric Cu(pyridine)$_4$ complex. In the highly crosslinked complexes which correspond to curves 4 and 5, the signal due to the parallel orientation is shifted to higher magnetic field. This indicates the decrease of anisotropy which originates from a square-planar structure, and the approach to a distorted tetrahedral structure. In the highly crosslinked polymer ligands, the ligand chain is considered to be unable to form a stable square-planar Cu(II) complex because of the strong hindrance of the tetramethylene bridges. Moreover the conformation of the ligand chain cannot easily be mobilized due to the number of crosslinking points.

ESR absorptions can be used to derive information about the bonding between metal ion and ligand. Covalent character of a bond becomes more pronounced when the parameters $g_\parallel$ and $g_\perp$ decrease and when $A_{\parallel}$ and $A_{\perp}$ increase. Since the most selective of these parameters is $g_\parallel$, the variation in $g_\parallel$ is the best indication of the covalent character. Information about the movements of the polymer ligands surrounding the central metal ion in an aqueous solution can also be obtained from ESR spectra. The symmetrical ESR spectrum of poly(1-vinyl imidazole)-Cu(II) complex at 293 K indicates that molecular motion of the polymer ligand is
depressed, causing no averaging out of the anisotropy due to the molecular motion of the low-molecular ligand\textsuperscript{54}. The diffused-reflectance electronic spectra provide an accurate and simple method for the determination of the geometry of transition metal ions in the complexes of chelating resins\textsuperscript{55-58}.

c. X-ray Analysis of Polymer-Metal Complexes

Due to the amorphous nature of the polymer-metal complexes the application of X-ray analysis for the structure elucidation of polymer-metal complexes is limited. The Cu(II) complex of poly(o-isophthaloyl-isophthalamide oxime) was studied by X-ray diffraction. It shows sharp diffraction patterns which do not differ much from that of the polymer ligand\textsuperscript{59}. This suggests that the polymer ligand and the complexed polymer have similar structures. Thus, the complexation with Cu(II) ions seems to compete with hydrogen bonding between the polymer chains. The interplanar distances increase somewhat upon reaction with Cu(II) ions which need a greater volume than the hydrogen bonds.

Due to the noncrystallizing nature of the polymer-metal complexes it is difficult to study its coordination structure by X-ray methods. However,
recently it has been demonstrated that extended X-ray absorption fine structure (EXAFS) can be used to determine interatomic distances and coordination in polymer-metal complexes. The EXAFS analysis of 2% DVB-crosslinked polystyrene-bound bromotris(triphenylphosphine)-rhodium(I) complex indicated two phosphorous atoms at 2.49 Å as nearest neighbour to the rhodium atom, which is consistent with a dimeric structure\textsuperscript{60,61}. On the other hand, the 20% DVB-crosslinked polymer bound catalyst was found to have three phosphorous atoms, one at 2.14 Å and two at 2.26 Å and one bromine atom at 2.50 Å from the rhodium atom. It was concluded that the 2% crosslinked polymer is not rigid enough to prevent dimerization of the attached rhodium complex. But the 20% crosslinked polymer has less mobility, preventing the dimerization of the attached rhodium complex.

**d) Microenvironment Around Metal Ions**

The microenvironment around the polymer ligand is altered by complexation with metal ions. This change in the helical structure of the polymer ligand has been studied by optical rotatory dispersion (ORD) and circular dichroism (CD)\textsuperscript{62}. The coordination of metal ions to poly(amino acid)s or to polynucleotides sometimes induces and disrupts helical structure of the polymer.
ligand. ORD and CD spectra of the Ag(I) complex of single and multistranded polynucleotides revealed that Ag(I) binds to the heterocyclic bases of the polynucleotides and not to the phosphate groups. The CD spectra, visible and UV absorption and potentiometric studies of the cupric complexes of poly(L-amino acids) have lead to the conclusion that the so-called type-II complexes of Cu(II) involve amide nitrogen in the coordination sphere of Cu(II). The structure of such complexes is not compatible with the a-helical conformation of the peptide backbone.

The study of the static as well as the dynamic changes around a central metal ion in a polymer-metal complex will provide information about the characteristics and reactions of polymer-metal complexes. Laser scattering or broad-band NMR spectroscopy can be made use for this purpose.

II.B.2. Stability Constants of Polymer-Metal Complexes

The stability constants of the metal complexes of polymeric ligands reflect the properties of the polymer backbone. The polymer-metal complexes are characterised by their increased stability compared to the corresponding monomeric analogues. Fully
coordinated metal complex is often formed at the first stage of the complexation reaction due to the high local concentration of the ligands in the polymer chain. Stepwise formation of multidentate complex is not observed. When stepwise formation of a multidentate complex is observed, the stepwise stability constants usually increase with the degree of coordination, which is contrary to the behaviour of the monomeric ligand and a distortion of the polymer chains in some cases reduces the stability of its metal complex. Thus stability can strongly depend on the backbone configuration.

The stability of a polymer-metal complex is often determined by the modified Bjerrum method\textsuperscript{67,68}. When a metal ion (M) forms a complex with N ligands (L), the successive stability constant ($k_i$) and the overall stability constant ($K_j$) are given by

$$ ML_{i-1} + L \rightleftharpoons ML_i , \quad i = 1 \sim N $$

$$ k_i = \frac{[ML_i]}{[M_{i-1}][L]} $$

$$ K_j = \prod_{i=1}^{j} k_i $$

The formation function ($\bar{n}$), which represents the average number of ligands bound to the metal ion is given by
The plots of $\bar{n}$ vs. $P[L]$ ie. $[\log(L)]$ are called "formation curves."\textsuperscript{69}

The complexation of polymeric ligands is influenced by the charges on the polymer chain. In the case of $\text{LH} + M^+ \rightarrow LM + H^+$ there is a net change of the charges of the ligands. The equilibrium constant could be expected to be effectively constant for both monomeric and polymeric ligands. The successive stability constant ($b_i$) and the overall stability constant ($B_j$) are then expressed as

$$b_i = \frac{[ML_i][H^+]}{[ML_{i-1}][LH]} = k_a k_i$$

where $k_a$ is the dissociation constant of $\text{LH}$ defined as $[L][H^+]/[LH]$

$$B_j = \prod_{i=1}^{j} b_i$$

The formation function can be represented by

$$\bar{n} = \frac{\sum_{j=1}^{N} jB_j([LH]/[H^+])^j}{1 + \sum_{j=1}^{N} B_j([LH]/[H^+])}$$
The formation curve is then obtained from the plot of \( \bar{n} \) vs. \( p \frac{[LH]}{[H^+]} \). In the formation of the Cu(II) complexes of poly(vinyl alcohol) the dissociation of alcohols takes place as shown in scheme II.15.

\[
\text{OH} \quad \text{OH} \leftrightarrow \quad \text{OH} \quad \text{O}^+ + H^+
\]

Scheme II.15. Complexation of PVA with Cu(II) Ions

For this complexation the modified Bjerrum plots in which the ratio of Cu(II) and hydroxyl group \( \frac{T \text{Cu(II)}}{T \text{HL}} \) varied from 0.025 - 0.200. The saturated \( \bar{n} \) value of 2 shows the average coordination number of 4. If intermolecular PVA-Cu(II) complexation dominates the polymer chain must be considerably bent for such complexes to be formed. The coordination of Cu(II) ions to the ligand would cause the bending of polymer chain and therefore it is necessary to alter its conformation more favourably for further complex formation. The distortion of the polymer chain reduces the stability of the polymer-metal complex. The stability in this case is strongly dependent on the configurational structure of the polymer backbone. The situation would become more favourable over the ratio described above. Thermodynamic parameters indicate that entropic factor is important in the chelate
formation of polymeric ligands. The large change in entropy observed for polymer chelation is associated with the effect of a polymer ligand and the high local concentration of ligands.

Another important characteristic of polymer-metal complex is its relative value of the stepwise formation constant when stepwise coordination reactions are observed. In some cases the stability of a polymer-metal complex is lower than the corresponding low molecular weight analogue. In the visible and ESR spectra of poly(4-vinyl pyridine) and pyridine the stepwise blue shifts of the molar ratio \( \text{Py}/(\text{Cu(II)}) \) indicate the stepwise formation of the complexes \( \text{Cu(Py)} \), \( \text{Cu(Py)}_2 \), \( \text{Cu(Py)}_3 \) and \( \text{Cu(Py)}_4 \). The maximum absorption of the PVP-Cu(II) complex, however, does not shift; it is at a lower wavelength indicating that the complex formation is not stepwise.

The stability of polymer-metal complex depends to some extent on the polymer backbone since the large polymer backbone sterically influences the coordination. When the coordinating groups on the side chain rotate free from the rigid polymer backbone, the coordination of metal ion occurs without much strain. A case in point is the biuret reaction of polypeptides with \( \alpha \)-helical
structure where violet Cu(II) chelates are not formed due to steric hindrance\textsuperscript{73}

The configuration of polymer ligands also influence complex formation. Dependence on polymer microstructure may be regarded as an indication of the so-called configuration effect. In complex formation reactions of isotactic (8) and syndiotactic (9) isomers

![Chemical Structures](attachment:image.png)

of polyacrylic and polymethacrylic acids the isotactic acid exhibits higher reactivity compared to its syndiotactic isomer because of the formation of a more stable Cu(II) complex\textsuperscript{74}. The rate of the complex formation in the case of the isotactic isomer is 1.5 times higher than the syndiotactic isomer.
II.C. Specific Applications of Polymer-Metal Complexes

Polymer-metal complexes are marked by their use as immobilized reagents which are useful for industrial purposes. They are widely used as immobilized catalysts, in which a specific catalytic behaviour was induced by the polymer-matrix\textsuperscript{75}. In addition to this catalytic activity, polymer-metal complexes have immense application in various areas like conductivity\textsuperscript{76}, modification of material surfaces by binding of metal complexes\textsuperscript{77}, separation of metal ions\textsuperscript{17-19} and in the model investigation of the metal complexes of bioinorganic systems\textsuperscript{22,23}. In each case, the polymer matrix imparts certain selectivity and specificity for that particular reaction. The giant polymer ligand causes steric, cooperative, electrostatic, configurational and hydrophobic effects on the reactivities of the polymer-metal complexes\textsuperscript{80}.

An important advantage of polymer-metal complexes is their easy separation from the reaction mixture by simple filtration for the crosslinked polymers and ultra-filtration or selective precipitation for soluble polymers. The polymer-metal complexes can be regenerated and reused.
II.C.1. Catalytic Activities of the Polymer-Metal Complexes

The catalytic activities of metal complexes bound on polymer matrices are entirely different from the corresponding monomeric analogue due to the specificities induced by the macromolecular ligands. In a polymer-metal complex the insoluble polymer support provides a specific catalytic site and acts as an effective matrix for the formation of active centres. The catalytic cycle of a metal complex-catalyzed reaction is illustrated below:

\[
\begin{align*}
MLn^+ + S & \rightleftharpoons Ln^{-1} M-S \\
\uparrow & \\
M'L + S^* & \rightleftharpoons Ln^{-1} M'S^*
\end{align*}
\]

M = metal ion, L = ligand, S = substrate

In the first step a substrate coordinates to a metal catalyst and forms an intermediate mixed complex. The substrate is then activated by metal ion and dissociates from the catalyst. The complex catalyst having accomplished its function is regenerated to the original complex. The catalytic action of a metal ion depends
substantially on the nature of the ligands in the intermediate mixed complex. Certain ligands induce an increase in catalytic activity while multidentate ligands like ethylenediamine tetraacetic acid (EDTA) often lowers the activity of metal ions. Thus, if a polymer-metal complex is used as catalyst its properties may affect the catalytic action of metal ion, since one component in the metal complex is the macromolecular chain. The activities of the polymer-metal complexes are generally lower than the corresponding monomeric analogue due to steric effects. However the activities can sometimes be higher than the monomer complexes due to the unsaturated coordination structure or the formation of inactive dimeric complex by steric effect.

The use of polymer-metal complexes as catalyst reduces the possibility of catalyst poisoning since the catalytic site is somehow protected by the polymer matrix. In low-molecular weight complexes, the catalytic efficiency decreases due to aggregation and insolubilisation. In a polymer-metal complex aggregation is physically prevented by the rigidity of the polymer matrix and the polymer-supported catalyst has the advantage of maintaining its catalytic activity over a wide range of concentration. In polymer-metal complexes the selectivity arises from the steric hindrance and/or
chemical environment of the polymer matrix. The characterization of metal complexes bound on polymer matrices by usual physicochemical methods is generally difficult and therefore no thorough quantitative studies have been made on the catalytic activities of polymer-metal complexes. The catalytic activities of polymer-metal complexes in oxidation, hydrogenation, hydrolysis, hydroformylation, decomposition of hydrogen peroxide, initiation of radical polymerization, asymmetric synthesis and optical resolution are reported.

II.C.2. Mechanochemical Systems

A mechanochemical system is one which can convert chemical energy into mechanical change which results in the deformation of the materials. A polyelectrolyte or a polymer-metal complex acts as a sensor in a mechanochemical system. The addition of Cu(II) ions to the filaments of poly(vinyl alcohol) dipped in an aqueous solution caused a shrinkage of filaments. The film is extended by about 20% on the reduction of Cu(II) to Cu(I) and shrinks back to its original state on the oxidation of Cu(I) to Cu(II). The poly(vinyl alcohol) chain is densely crosslinked by the extremely stable Cu(II) chelate but is loosened when
Cu(II) forms the unstable Cu(I) chelate. This change is reversible as shown in Fig. II.2. The mechanochemical system consisting of a polymer-metal complex is more effective than those without metal ion because it makes use of the conformational changes of the polymer ligands induced by the complexation with metal ions. The conformational change of polymer ligand induced by complex formation is much greater than that of the usual polyelectrolytes.

![Mechanism of Mechanochemical change of PVA Filament Induced by Redox Reaction of Cu(II) Ion](image)

Fig. II.2 Mechanism of Mechanochemical change of PVA Filament Induced by Redox Reaction of Cu(II) Ion

The viscosity of an aqueous solution of poly(vinyl amine) in the presence of Cu(II), Ni(II) or Zn(II) ions was sharply changed by changing the pH of the solution due to the conformational change of the polymer. The mechanochemical behaviour caused by pH
change is less than the change caused by the redox reaction of the complexed metal ions.  

II.C.3. Biologically Important Polymer-Metal Complexes  

Metal ions have an important role in the activity of bioinorganic materials in which metal ions are bound to proteins, nucleic acids and related ligands. Here the metal ions are bound to huge polymeric ligands and give rise to characteristic properties which are different from those of the corresponding low-molecular weight analogues.  

a. Complex Formation of Metal Ions with Biopolymers  

(i) Metal Complexes of Polypeptides  

Metalloenzymes are generally formed between a polypeptide and metal ion. The coordination structure of the complex, the conformation of the polypeptide which is dependent on the sequence of the amino acids in the polypeptide, stiffness of the backbone and the interaction between the pendent groups cause specificities in metalloenzymes. The onset of coordination in polypeptides is generally by the presence of sulphur, nitrogen and oxygen in various functional groups. The
coordination structures of the Cu(II) complexes of synthetic poly(amino acid)s are generally dependent on the pH of the solution. Mainly these complexes are planar or distorted planar. The coordination of poly(L-histidine) with Cu(II) ions gave a square-planar structure at pH 5. This square-planar complex is formed by the coordination of three imidazolyl groups of histidine and one peptide nitrogen on the main chain. At pH 14, a distorted square-planar structure is formed by the coordination of four neighbouring peptide nitrogens with one imidazolyl group coordinated at an apical position.

(ii) Metal Complexes of Nucleic Acids and Related Compounds

Due to the presence of negatively charged phosphate groups in RNA and DNA, their structure can be stabilized only in the presence of positive charges like metal ions or organic cations. The role of metal ions is to maintain higher structure or to participate in the replication, transcription or translation of DNA. Metal ions cause the denaturation of DNA or RNA by binding to it.
(iii) Mixed Ligand Complexes

The microenvironment around the central metal ion in vivo is different from that in vitro. The presence of many kinds of biological substances having coordinating ability around the metal ion and the occurrence of the reactions by metalloenzymes via the mixed complex with the substrate requires the study of the fundamental coordination chemistry of mixed ligand complexes in order to elucidate the behaviour of metal ions in vivo. In order to elucidate the coordination behaviour of blood plasma, the complex formation of Mg(II), Cu(II), Mn(II), Fe(III), Co(II), Zn(II) and Pb(II) ions with amino acids and other organic acids are simulated\textsuperscript{101}.

The apoenzyme of a metalloenzyme consists of a protein which is composed of a definite sequence of amino acids. The specific sequence of amino acids decides the activity of the central metal complex working as a prosthetic group. The characteristics arising from the large protein molecule profoundly affect the enzymatic action. In metalloenzymes, the large protein ligand decides the character and the activity of the central metal ions by providing a selective binding site for the substrate. This selectivity was generated by the
long chain of apoprotein. A distorted coordination structure was developed for the complex by the hydrophobic environment created by the protein molecule surrounding the central metal ion.

In blue-copper-proteins the coordination geometry of the central copper ion is not square-planar but shows a distorted tetrahedral structure which is caused by steric strain of the peptide chain. The coordination structures of its oxidised and reduced states are very similar due to the rigid stereostructure around the Cu(II) ion. Such a rigid structure is retained by a specific configuration of the polypeptide chain. The Cu(II) ion itself is surrounded by hydrophobic groups. Such a distorted structure and a hydrophobic environment caused by the polypeptide chain are largely responsible for the anomalous characteristics of blue-copper-proteins.

II.C.4. Polymeric Ligands in Metal Ion Separations

An important application of polymer-supported ligands is in the selective separation of metal ions and efforts in the recovery of metal ions from aqueous solutions using polymeric chelating agents are steadily increasing. Separation of metal ions is
realised only by using polymeric ligands and by making use of the dependencies of the stability of the metal complex upon the structure of the ligands and the kind of metal ions. Although it is possible to separate some definite metal ion from a mixture of metal ions, it has not yet been possible to adsorb or complex any desired metal ion selectively from a mixture of metal ions.

The attempts to separate metal ions selectively using polymeric ligands involve (i) the chemistry of a given ion under special conditions, including the interaction of the ion $M^{n+}$ with other metallic ions, ligand exchange and redox reactions, (ii) the chemistry of the ligand in the solid phase, (iii) the swelling behaviour of the polymer network under the separation conditions, (iv) good chemical and thermal stabilities of ligands and polymer-supports, (v) reversible complexation/elution steps, (vi) kinetic phenomena in the solution and polymer phases, (vii) pH of the separation conditions and (viii) stability constant of the complexation. A successful separation system must accommodate all these factors. But most polymeric materials only partially fulfill these demands. The chemical stability depends much on polymerization method, polymer tacticity, ligand distribution and mode of attachment of ligands to the polymer.
Fundamentally, two types of polymeric matrices are considered - inorganic and organic. Silica is the most extensively used inorganic support. The organic matrices used as supports include naturally occurring polymers or synthetic polymers. Among naturally occurring polymers cellulose, starch, lignin and chitin derived chelating resins have been widely used. Of the synthetic matrices, the most widely used supports are crosslinked polystyrenes and acrylates. Higher chemical stability is shown by aromatic polymers and chemical modification methods are also of importance. Multi-step functionalizations lead to structurally ill-defined polymers, while single-step modification generally leads to more defined polymer structures.

A number of chelating resins containing ligands such as iminodiacetic acid, amidoxime, aminophosphoric acid, oxine, thiol, dithiocarbamate, pyridine, amine and isothiouronium are widely used for the separation of metal ions. The complexation/adsorption of polymeric ligands is influenced by a number of factors characteristic of the polymer matrix.
II.D. Macromolecular Effects on Complexation

The complexation behaviour of ligand functions supported on polymers is generally different from the corresponding low-molecular weight analogues. This variation is connected with the polymer matrix to which the ligand function is attached. Complexing groups in a macromolecular ligand may exist in conformations different from that required by the preferred stereochemistry of a given metal ion. Functional groups are statistically distributed over a macromolecule so that both the more favourable conformations and the less favourable conformations will occur. Hence the formation of a given spatial structure required by the electronic configuration of an ion $M^{n+}$, is followed by a conformational change in the ligand so that it may assume an appropriate orientation. This change is associated with a greater energy loss, the more the chain conformation differs from ideal and the less flexible is the macromolecule. These limitations result in a decreasing coordination saturation of the central metal ion and may give rise to stereochemical distortion of the coordination centers and also to a lowering of the stability of the macromolecular complex. Since the coordination bond energy remains constant for a given metal-ligand pair, the stability of the polymeric complexes is proportional to the flexibility...
of a macromolecule and to the set of conformations it can generate.

The characteristics of the polymer matrix like the matrix structure, matrix configuration, matrix nature, spacer between the crosslinked matrix and the ligand function and the extent of crosslinking has a significant effect on complexation. The polymer chain causes steric, electrostatic and configurational effects on complexation.

II.D.1. Matrix Structure

In the development of chelating resins for metal ion separations, the variation in matrix structure significantly affects ion diffusion rates and ion selectivities. Recently, the variation in reaction conditions and the influence in resin performance have gained much attention\textsuperscript{113-115}. In the suspension polymerization of acrylonitrile and divinylbenzene and subsequent aminolysis of the polymer with hydroxylamine to yield the amidoxime resin, the parameters of the polymer matrix like apparent density, pore volume, surface area and average radius change with the polarity of solvent used for polymerization\textsuperscript{116}. It is easier to obtain consistent control over pore structure by choosing a slightly polar aromatic
solvent toluene and varying the concentration of this solvent in the reaction mixture and the other variable is the crosslinking agent, divinylbenzene. Optimum polymeric resins should have large surface area and average pore radius. Matrix structure has significant influence on diffusion properties within polymers. Fig.II.3 shows the dependence of the adsorption rate of uranium to an amidoxime resin on the content of divinylbenzene crosslinking.\(^{117}\)

![Graph showing the dependence of the adsorption rate of uranium to an amidoxime resin on the content of divinylbenzene crosslinking.](image)

Fig. II.3. Rate of Adsorption of Uranium on Amidoxime Resins of 2.6-21% DVB-Crosslinking

In the extraction of uranium from sea water using amidoxime resins with divinylbenzene or oligo-ethyleneglycol diacrylate crosslinking or the simultaneous
use of the two types of crosslinking agents resulted in polymers with various matrix structures\textsuperscript{118-122}. The pore size and surface area of the different polymers varied with the nature and the extent of the crosslinking agent.

II.D.2. Matrix Nature

The ability of the polymer-supported ligands to form complexes depends on a certain degree on the nature of the main chain whether it is a polymeric alkane or polyaromatic compound obtained by the polymerization of corresponding monomer or otherwise contains heteroatoms representing the polycondensation polymers\textsuperscript{123}.

![Chemical structures]

Polymeric iminoacetic acid, with functional groups in different polymeric matrices like polyethylene iminodiacetic acid (10) and polystyrene iminodiacetic acid (12)
(11), is an example of the matrix nature effect. The matrix effect on ion binding is clearly exhibited when molecular ligands and their polymeric analogues are compared in the case of iminodiacetic acid ligands supported on polystyrene (11) and polyacrylamide (12).

Similar observations on the variation in complexation by ligands anchored on various supports are reported. The metal intake by polymeric ligands is varied by the incorporation of crosslinking agents which differ in their polarity and flexibility.

II.D.3. Matrix Configuration

The bond length and the bond angle between the central metal ion and the coordinated ligands in a metal complex are determined by the kind of metal ion and the ligand. When the coordination stereostructure of a polymer-metal complex is fixed and then the central metal ions are removed while maintaining the fixed stereostructure, the remaining polymeric ligand may have "pockets" especially fitted for that particular metal ion which is removed from the polymer matrix. Such a selective adsorption of metal ion is realized by fixing a stereostructure of the polymer chain by crosslinking its metal complex as depicted in scheme II.16. This procedure
corresponds to a kind of template formation. When a metal complex of poly(4-vinyl pyridine) is crosslinked with \(\alpha,\omega\)-dibromobutane and then the metal ions are removed by washing with dilute acid, the resulting metal free resin shows selectivity to adsorb the metal ion which was

**Table III.3. Adsorption of Metal Ions by Crosslinked Template Resins Prepared from Its Cu(II), Co(II) and Zn(II) Complexes**

<table>
<thead>
<tr>
<th>Template-forming Metal Ion</th>
<th>Rate of Metal Ion Adsorption(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu(II)</td>
</tr>
<tr>
<td>None</td>
<td>15</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>52</td>
</tr>
<tr>
<td>Co(II)</td>
<td>16</td>
</tr>
<tr>
<td>Zn(II)</td>
<td>1.2</td>
</tr>
</tbody>
</table>
initially present. The crosslinked template resin prepared from its Cu(II), Co(II), Zn(II) and Fe(III) complexes adsorbs the corresponding metal ions selectively (Table II.3).

II.D.4. Effect of Spacer Grouping

The complexing power of macromolecular ligands also depends upon the arrangement of functional groups relative to the main chain. The shorter the distance between them, the lower the efficiency of complex formation because of steric hindrance.

The role of the spacer in binding the metal coordination of pyridine has been investigated by introducing pyridine group far away from the rigid polystyrene backbone through a spacer (13) or graft chain (14). Oligo(ethylene oxide) and the copolymers of 1-vinyl pyrrolidone were selected as the spacer group and as the graft chain for use in water. It has been observed that the magnitude of the rate of metal ion complexation is higher than the ligand where the pyridine group is located at the near end of the spacer. The stability constants for polymers with larger spacers are three orders of magnitude higher than those for poly(4-vinyl pyridine) but there is only a small difference between the pyridine and
bipyridine ligands\textsuperscript{130}. This confirms the increased availability of the spacer group and the formation of intrapolymer complexes with cooperative interaction of several pyridine groups in metal complex formation.

\begin{equation}
\text{[13]}
\end{equation}

\begin{equation}
\text{[14]}
\end{equation}

The ESR spectra of these complexes also reveal the effect of the long spacer group and the graft chain\textsuperscript{131}. The ESR parameters ($g_{//} = 2.070$, $g_{\perp} = 2.242$, $A_{//} = 150$ G) showed that the coordination structure of the Cu(II) complexes is square-planar based on the pyridine beads. The ESR signals were clearly split for the Cu(II) complexes of the spacer and graft-modified pyridines since they can complete the complexation with Cu(II) while the pyridines directly attached to polymer matrix do not coordinate with Cu(II).
II.D.5. Effect of the Extent of Crosslinking

The complexation characteristics of insoluble macromolecules are strongly influenced by the extent of crosslinking in the ligand. A crosslinked polymeric ligand often forms a stable metal complex than a linear polymer and it shows some selectivities for metal ions due to the rigid structure. A higher degree of crosslinking results in a lower degree of metal ion intake and a lower stability of the resulting metal complex by making the polymer chain more rigid. This is evidenced from the ESR spectral studies. The colour of copper complexes of poly(4-vinyl pyridine)s changed from blue to green when the extent of divinylbenzene crosslinking increased from 4 - 16 mole%. With increasing divinylbenzene content, a conversion of planar coordination centers to tetrahedral ones occurs. This change in stereostructure results from an increase in steric hindrance to complex formation with a macromolecule, which is also known with low molecular weight coordination compounds. Similar change in coordination structure with the extent of crosslinking is observed in dibromobutane-crosslinked poly(4-vinyl pyridine).

The formation constants for the complexation of poly(methacrylic acid) crosslinked with divinylbenzene
decreased from $K_1$ to $K_4$, which is the opposite of the noncrosslinked system.$^{135}$ The efficiency of crosslinking differs among metal ion species and it is possible by changing the nature and extent of crosslinking to produce resins which selectively bind a specific metal ion. The dependence of the extent of crosslinking on complexation was studied for various systems.$^{136-138}$ The metal ion intake varied with the extent of crosslinking and it depends to a greater extent on the nature of the crosslinking agent.

II.D.6. Steric Effects

Steric effects are clearly exhibited in the complex formation of partially quaternized poly(4-vinyl pyridine)(QPVP) with trans-[Co(en)$_2$Cl$_2$] Cl (Scheme II.16)$^{139}$. When $R = H$, the initial rate of complexation

\[
\text{QPVP} + [\text{Co}(\text{en})_2\text{Cl}_2] \text{Cl} \longrightarrow \text{ClCHCH}_2\text{ClCHCH}_2\text{Cl} + 2\text{Cl}^-
\]

\[R = \text{H, CH}_3, \text{CH}_2\text{C}_6\text{H}_5\]

**Scheme II.16. Steric Effects in the Complexation of Partially Quaternized PVP with trans-[Co(en)$_2$Cl$_2$]Cl**
is independent of the quaternization (Q) percentage. This result suggests that the electrostatic field brought by the quaternized ammononium cation does not affect the complex formation under the applied conditions. With increase of the bulkiness of the quaternizing agent, rate of complexation decreases and the order is \( R = H > CH_3 > CH_2C_6H_5 \). The bulky quaternizing agent sterically hinders the approach of the metal complex to the nonquaternized pyridine groups. Similarly in this case, the degree of coordination was found to be 0.65. When the bulky Co(III) chelate coordinated to the polymer ligand forming the most close packing, one of the four pyridine units must remain uncoordinated for steric reasons (Fig.II.4).

---

Fig. II.4. Conformational Profile of Co(PVP) (acac)$_2$NO$_2$
Although the increase of the degree of coordination brings about distortion of the polymer complex due to the steric hindrance as in the above case, the dissociation temperature of the coordination bond between Co(III) and PVP increased with increasing degree of coordination in the cis-[Co(en)$_2$PVPCl]Cl$_2$ complex. Since the complex, probably has a rod-like rigid structure due to the steric bulkiness of the Co(III) chelates, more energy would be required to break the coordination between Co(III)ion and PVP, causing an increase of the dissociation temperature with the degree of coordination.

II.D.7. Intramolecular Chelation

Complexation of a polymeric ligand with metal ions usually results in an intramolecular chelation which makes the geometrical form of the polymer chain in solution more compact. Such a behaviour is observed in its viscosity, which is reduced when the polymer chain in the solution becomes compact. Such a contraction of the conformation of a polymer chain in solution induced by complex formation often makes further complexation much easier (Scheme II.17).

A synthetic polymer shows a kind of allosteric behaviour which is characteristic of biological
systems\textsuperscript{141}. A similar situation of intramolecular chelation and the concentration of ligand groups on the polymer chain increase the successive stability constants of the polymer-metal complex with an increase in the coordination number. The successive stability constants of the monomeric pyridine-Cu(II) complex decrease with the increase of the coordination number\textsuperscript{142}. Such a behaviour of polymer-metal complex rationalises the one-step formation of the four coordinated PVP-Cu(II) complex.

\textbf{II.D.8. Electrostatic Effect}

Electrostatic effect on the complex formation is distinctly observed when ionic groups are present in the polymer chain. Since electrostatic action is affected by ionic strength (\(\mu\)) of the solution, the dependency of the complex formation on \(\mu\) reveals the
degree of electrostatic effect\textsuperscript{143}. The dependence of the logarithm of the rate constant ($k_{\text{obs}}$) on $\mu$ in the case of the PEI-Cu(II) complex formation is essentially linear and its slope represents the degree of electrostatic interaction between the ions. In the trien-Cu(II) complex, although it shows a linear relationship, a deviation from linearity is observed in the PEI-Cu(II), indicating a stronger electrostatic effect in the PEI-Cu(II) complex than in trien-Cu(II). This result is on the basis of the configuration of the polymer chain. In the low value of $\mu$, the protonated imino groups of PEI bring about electrostatic repulsion of the chain, which lowers the rate of complex formation, since the polymer chain must be contracted in order to form a multidentate complex. However, when the value of it is higher, the electrostatic effect of polymer chain is reduced by the high concentration of the added salt which surrounds the polymer chain making the conformation of the polymer chain compact. Such a contraction of polymer chain would cause the rate of complex formation of multidentate type to increase more than that expected from the value of $\mu$.

The foregoing account summarises the progress made in the chemistry of polymeric ligands with particular reference to their design, synthesis, characterization and applications. The complete understanding of the
complexation reaction, the coordination structure, the conformational state and the effects of the three-dimensional structure of the polymer ligand remain unsolved. In order to get a clear insight on these aspects investigations on the macromolecular structural parameters of the polymer matrix and their effect on complexation are necessary. Such studies are significant in: (i) development of new catalysts with high and specific activities comparable to enzymes based on the specificities brought about by the polymer ligand; (ii) design of tailor-made polymeric ligands specific for a particular metal ion and (iii) detailed understanding of the structure-reactivity correlation in the polymer-metal complexes.