Chapter 1

Introduction

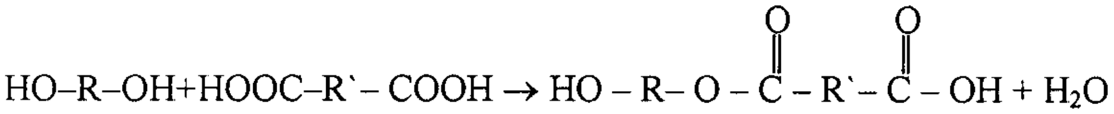
INTRODUCTION

I-A-General Introduction:

The word polymer is of Greek origin and means a molecule that consists of many parts and, the units that built up a polymer are called monomers. Natural polymers such as wood, cotton, wool, silk, rubber and many types of gums have been used in all kinds of particular applications. Synthetic polymers were prepared which have very interesting applications as fibers, plastics, rubbers, coatings or adhesives.

Carothers(1) proposed that polymerizations be classified as addition or condensation reactions depending on whether or not a simple molecule was split out during the polymerization. An example of condensation polymer is the polyester formed from diacid and diol with the elimination of water.

Flory(2) classified polymerization into step-growth and chain-growth reactions depending on the mechanism of the growth reaction. Polyesterification is a classical example of a step-growth polymerization. The first step in polyesterification reaction is the reaction of the diol and the diacid monomers to form dimer as follow:



$$HO{-}R{-}OH + HOOC{-}R'{-}COOH \rightarrow HO - R - O - \overset{\overset{\displaystyle O}{\|}}{C} - R' - \overset{\overset{\displaystyle O}{\|}}{C} - OH + H_2O$$

The dimer then reacts with itself to form tetramer or with unreacted monomer to yield trimer and any two molecular species in the reaction mixture can react. The monomer is almost all incorporated in a chain molecule in the early stages of the reaction and the chain length increase steadily as the reaction proceeds. Hence long reaction times and high conversions are necessary for the production of a high molecular weight polyester.

I-A-1-Methods of preparation polyesters:

A large number of synthetic methods for preparation of polyesters have been studied. Some of these methods are:

1- The stoichiometrically balanced reaction between dibasic acid and a glycol(3). Failure to maintain exact stoichiometry prevents attainment of high molecular weights. This is circumvented by having the glycol present in slight excess which is gradually removed by vacuum(4), by an inert gas sweep or by passing a current of vapor from an inert substance through the molten reaction mixture(5).

2- The transesterification reaction between a glycol, and either the aliphatic diester, half ester, or aryl ester of a dibasic acid(6).

3- The reaction between the silver salt of a dibasic acid and an aliphatic dibromide(3).

4- The self-condensation of a γ-hydroxy acid. This reaction was first described by Carothers and later described by Whin Field(7).

5- The reaction between an acid anhydride and a glycol(8).

6- The reaction between a cyclic glycol and a dibasic acid (9).

7- The reaction of the glycol ester of acetic acid with a dibasic acid(10).

8- The reaction of a diacid chloride with a glycol.

9- The reaction of the diacetate of a diphenol with a dibasic acid(11) or its diester(12). Similarly, the reaction of a diphenol with a dicarboxylic acid in the presence of acetic anhydride(13).

10- Reaction of a diacid chloride with an alkali diphenate in which the alkali diphenate is dissolved in water and the diacid chloride is dissolved in an immiscible organic solvent(14).

11- The reaction between a glycol and a dicarboxylic acid, or its ester in an inert high boiling liquid which is capable of dissolving appreciable amounts of the polymer produced(15).

In spite of the many possible methods of making polyesters the ester-interchange reaction between a glycol and an ester of a diacid has been the one which has found greatest commercial applications.

Polyester resins may be classified into three groups(16), linear, three dimensional, and unsaturated polyesters. The type of polyesters formed in a polyesterification reaction is determined by the functionality of the monomers. Bifunctional monomers give linear polyesters, and polyfunctional monomers, with more than two functional groups per molecule, give branched or cross-linked polyesters. The properties of the linear and cross-linked polyesters differ widely as a result of the difference in the structure of each.

Polymers are divided into three major classes: thermoplastics, thermosets, and elastomers. Thermoplastics (like polyethylene, polymethyl methacrylate and poly styrene), sometimes called engineering plastics, are processed in the molten state, their final shape and internal structure established by cooling, and they can be softened and reshaped by reapplication of heat and pressure. Also, their polymer chains, whether linear or branched, remain discrete after molding.

Thermoset polymers (like the epoxies, the polyesters and fromaldehyde-based resins) usually go through three formative stages. In the A- stage, the resin is still soluble and fusible. In the B-stage, thermosets are nearly insoluble, but are still thermoplastics. They can, however, spend only a relatively short time in the molten state because the temperatures that promote flow also cause the material to crosslink. The cross-linking reaction is accomplished in the final stages of polymerization, the C-stage, during molding of the product under the controlled influence of heat and pressure over time. Thus, thermosets build their final structure during processing, forming a three dimensional internal structural network of highly crosslinked polymer chains. And the final product is insoluble and not thermally reformable. Thermoset matrix systems dominate the composite industry because of their reactive nature. Generally thermosetting has been developed to provide specific cost performance balance(17-24).

Elastomers share characteristics of thermoplastics and thermosets. Elastomers being as thermoplastic polymers with discrete chains that later develop a network of covalent cross-links. However, elastomers are distinguished from thermosets by the fact that the cross-link network is formed in a separate post-polymerization step called vulcanization.

The interest in polymers containing metallochelate units has increased since the decade of the 1960s as they show many potential uses as functional materials with desirable chemical and physical properties. Polymers supported metal complex catalysts, biological agents such as models for various metalloenzymes or biomedical control release agents, solid-state materials such as semiconducting substances, and heat-resistant materials for aerospace requirements were further studied. Sheats presented the history of organometallic polymers have been reported(25). Some extensive reviews have appeared on metal-containing polymers (26-30).

In polymer-metal complexes, the central metal ions are surrounded by polymeric ligands. The polymer-metal complexes can show interesting characteristics, especially with reference to catalytic activities differing from the corresponding ordinary metal complexes of low molecular weight.

I-A-2-Methods of synthesis of polymer complexes:

There are several types of synthesis of polymer complexes as follow:

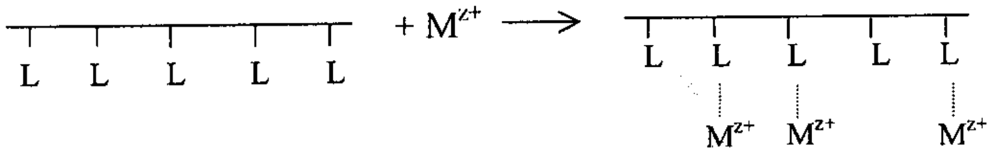
A-Formation through complexation polymeric ligand with metal ion:

This type of polymer-metal complex is synthesized by reaction of a polymer containing donating groups such as amine, heterocyclic nitrogen, carboxylic acid, ketone, phosphonic acid, and thiol. The complex formation is often achieved very easily simply by mixing each of the solutions(26). The reaction of polymer ligand with metal ion or metal complex usually results in various coordination structures, which are divided chiefly into pendant and inter- and /or intramolecular bridged complexes.

1- Pendant complexes:

a- Monodentate pendant complexes:

When a metal ion or a metal complex has only one labile ligand which is easily substituted by a polymeric ligand, and when other coordination sites are substitution inactive, the complex formed has a simple structure of monodentate type.



Even if the metal ion or metal complex has more than two labile ligands, it is often possible to realize a monodentate complex structure by selecting an appropriate reaction condition.

For example, when the reaction between the metal ion or metal complex and the polymeric ligand is carried out with the excess of the metal or metal complex, the probability of the substitution of the second labile ligand of the metal ion would be very low, giving a predominantly monodentate-type structure(26).

Important characteristics of this type of polymer complex are:

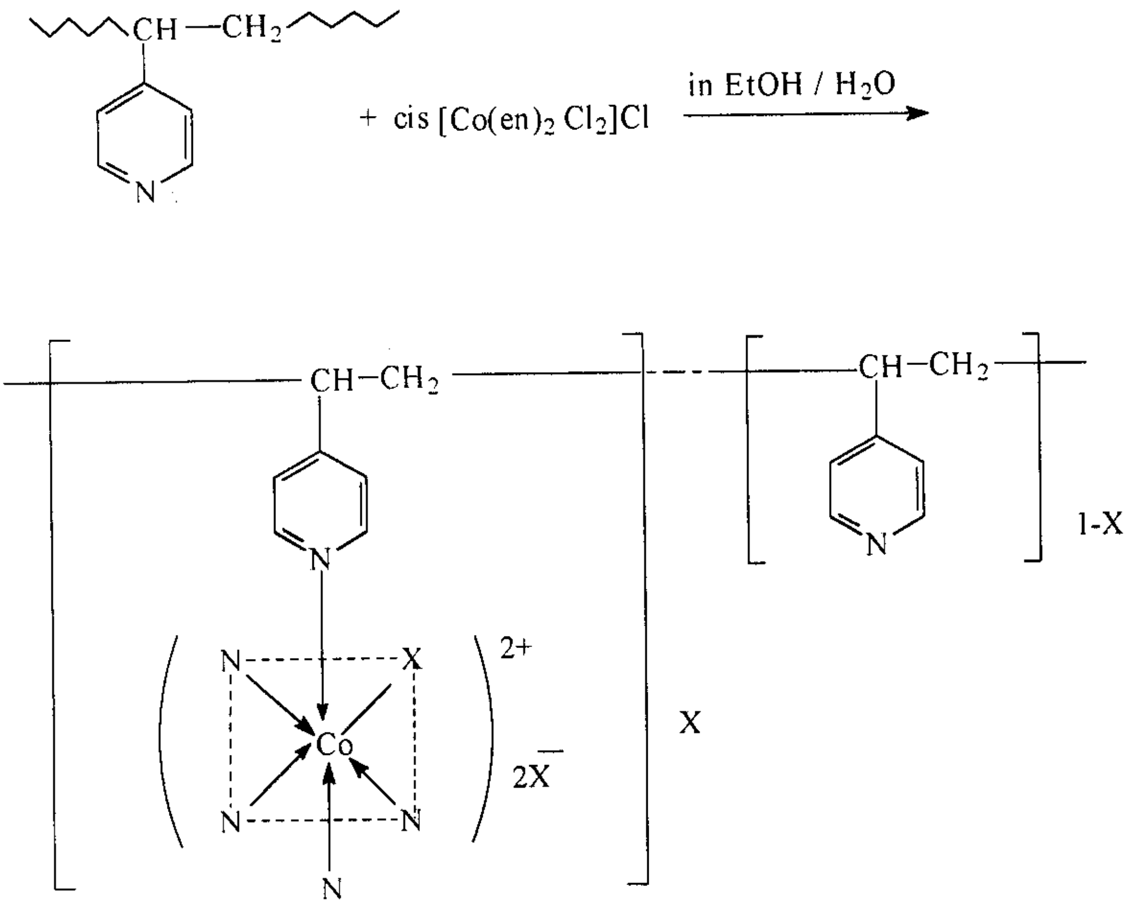
i) The coordination structure is very clear.

ii) The effects of polymer chains are exhibited clearly.

iii) The polymer complex is very often soluble in water or in organic solvents, since it contains few, if any, very few bridged structures which often reduce the solubility(31).

On this point Tsuchida et al.(32) have tried the reaction of poly (4-vinly pyridine) (PVP) with various metal chelates and succeeded in obtaining polymer-metal complexes containing only simple structures of monodentate type.

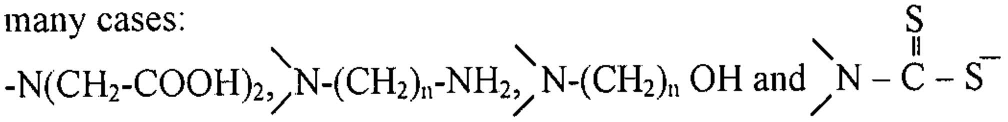
The polymer complex cis $[Co(en)_2 PVP. Cl] Cl_2$ was prepared as follows:



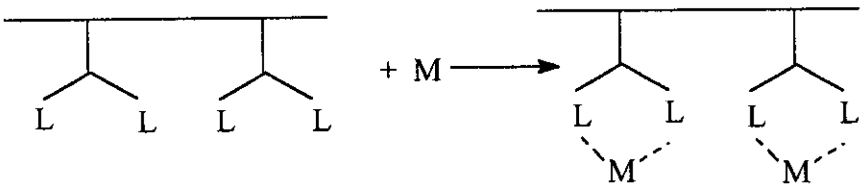
X = Cl, Br, N_3, NN = ethylenediamine

b- Polydentate pendant complexes:

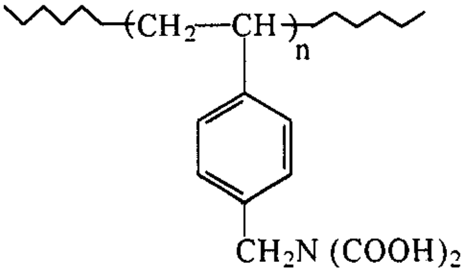
When the polymer-pendant coordinating group has a polydentate structure, the coordination structure of the polymer-metal complex can be occured, and high stability is expected. The chelating ligand groups are in many cases:



$-N(CH_2\text{-}COOH)_2,\ >N\text{-}(CH_2)_n\text{-}NH_2,\ >N\text{-}(CH_2)_n\ OH$ and $>N-\overset{\overset{S}{\|}}{C}-S^-$

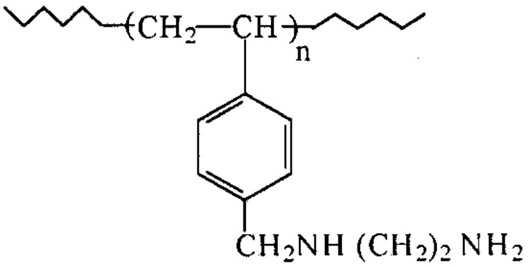


The best known example is the cross-linked polystyrene containing iminoacetic acid-type pendant groups (I).



(I)

Polyamine ligands such as ethylenediamine, diethylenetriamine, or triethylentetramine are excellent chelating agents(33). They were bound to chloromethylated polystyrene resin, and the resulting resin (II) absorbed Cu^{2+} ions effectively.

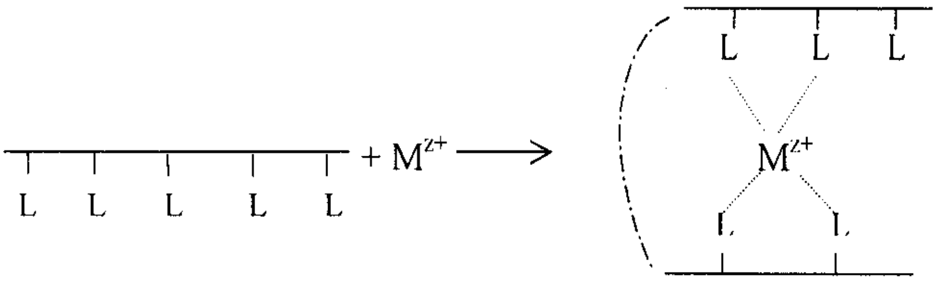


(II)

Bipyridine, also being an excellent chelating ligand, was bound to polystyrene beads, and its complexes with $Cr(NO_3)_3$, $Mn I_2$, $Ru Cl_3$, or $CuBr_2$ was isolated(34).

2- Inter-and / or Intramolecular bridging:

The reaction of polymer ligand with metal ions very often results in inter-and /or intramolecular bridging.



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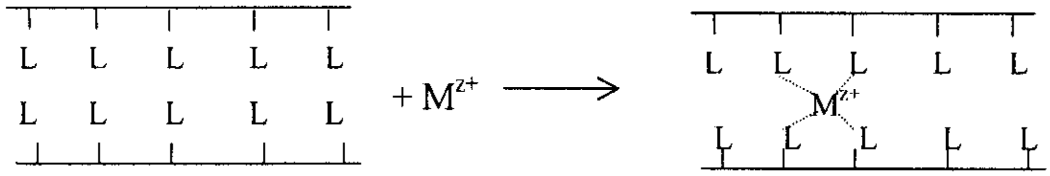
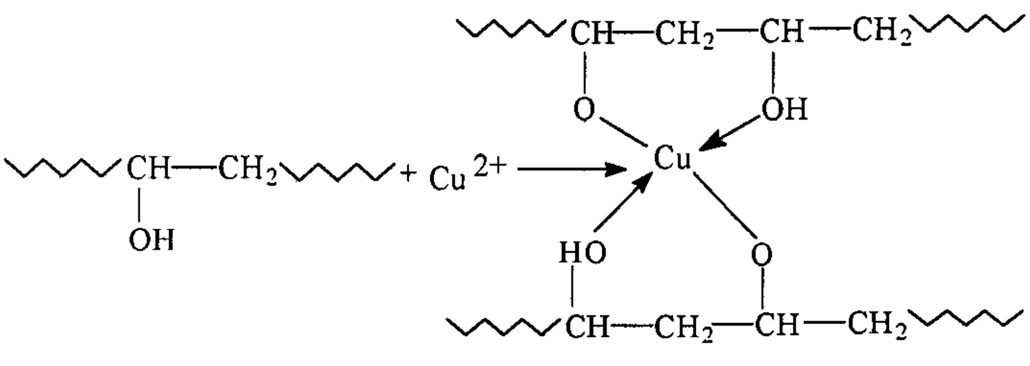


Intermolecular Bridging

The coordination structure of the resulting polymer-metal complex is not clear in this case, and the polymer complex is sometimes insoluble in water or in organic solvents. Moreover, it is usually difficult to distinguish between the inter-and the intramolecular bridging. Because of these facts, it is often not easy to elucidate the polymer effect in studying the characteristics of the polymer complex.

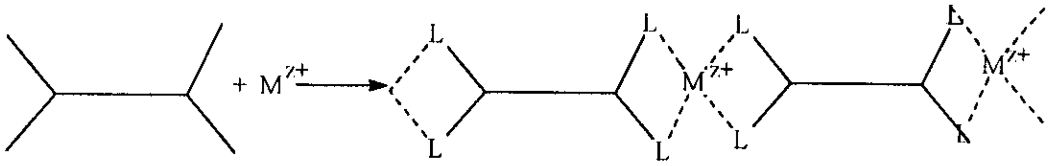
A typical and the simplest example of this type of polymer complex is the poly (vinyl alcohol) (PVA)-Cu(II) complex$^{(35)}$, the formation reaction of which is illustrated in following equation:



Molecular weight dependencies of the inter-and intramolecular complex formations of PVA with Cu^{2+} were studied spectrophotometrically by Morishima et al.(36). Polymers with a degree of polymerization larger than 260 form a stable complex with coordination of four hydroxy groups of the same PVA molecule sharing a constant λ_{max} value of 690 n. Polymers with a degree of polymerization smaller than 160 form an intermolecular complex resulting in precipitation by cross-liking.

B- The chain linked through complexation of bifunctional ligand with metal ion:

When bifunctional ligands form a complex with metal ions having more than two labile ligands which are easy to be substituted, a polymer complex is formed through metal ion bridging.



This type of polymer-metal complex has been synthesized since 1950 for the purpose of obtaining semicoducting organic materials, heat-resistant organic polymers or polymer Catalysts(37). Bridged ligands capable of forming polymer-metal complexes of this type are classified as follows:

i) Compounds having more than two coordinating groups.

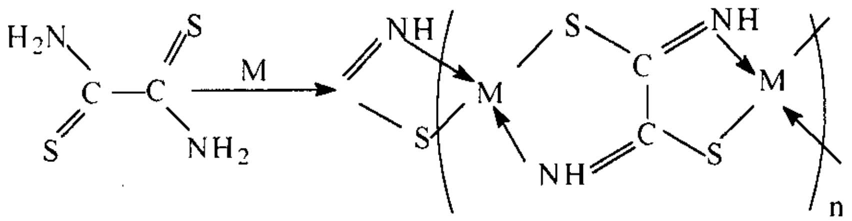
ii) Simple compounds having more than two coordinating atoms, or simple ion which is able to function as bridged ligand.

When the complex formation of ligands having four coordinating groups induced chemical reaction between the ligands, the resulting polymer complex sometimes has a network structure (template reaction).

1-Linear coordinated polymers:

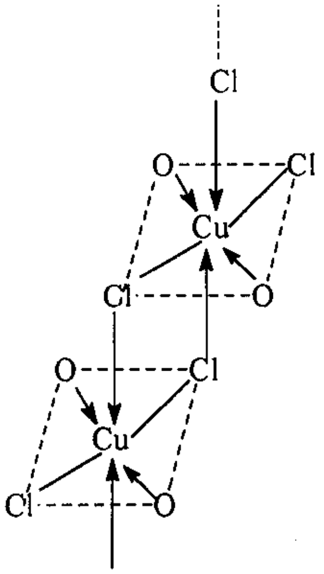
a) Linked by bifunctional ligand:

Dithiooxamide (rubeanic acid) is a typical bifunctional ligand which forms a linear-type polymer-metal complex with metal ions(38).



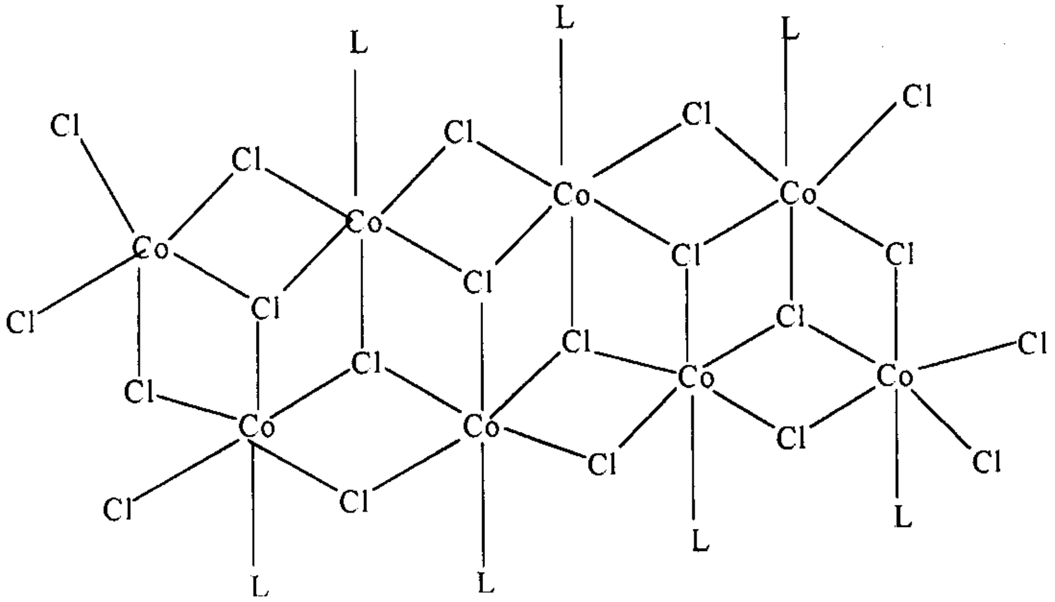
b) Linked by simple compound or ion:

A simple ion or compound can work as a bridging ligand giving a polymeric structure. A metal salt such as cupric chloride forms an associated structure in a very concentrated aqueous solution of hydrogen chloride(39). The chlorides occupying as bridging ligands both the axial and equatorial coordination sites of Cu^{2+}



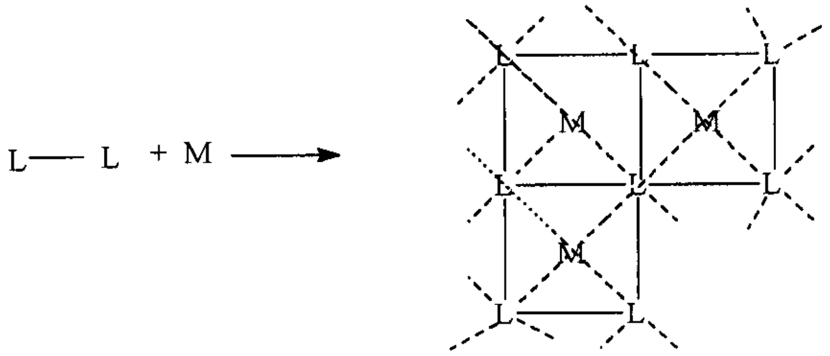
A similar structure similar to that of $CuCl_2.2H_2O$ was established by x-ray analysis.

Polymeric Co(II) complex of 3-or 4- benzoylpyridine (BzPy), $[CoCl_2(BzPy)_2]_n$ was prepared in ethyl alcohol by Cabral et al.,$^{(40)}$ on heating this compound at 160°C for 4 days, one of the BzPy ligand is eliminated, giving a polymeric structure in which a chlorine atom is bonded to three cobalt atoms.

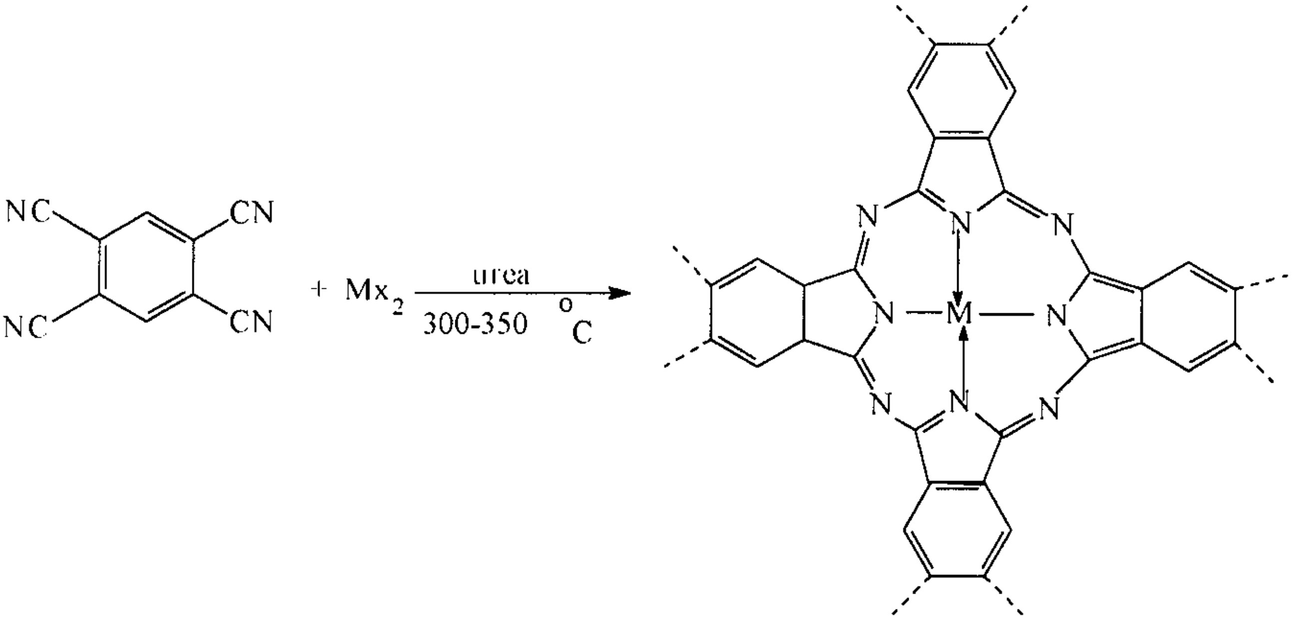


2-Network-coordinated polymers:

The most usual method to prepare this type of polymer complex is to make use of a "template reaction". This is a reaction between two functional groups of the ligand induced by their coordination to metal ions, resulting in a chelated-type metal complex.

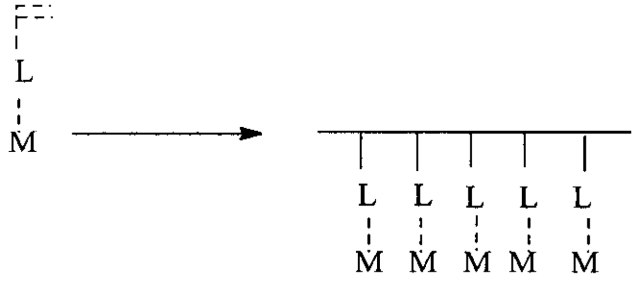


A typical example is poly (metal phthal phthalocyanine) which is formed by the reaction of tetracyanobenzene with metal halide catalyzed by urea(41).



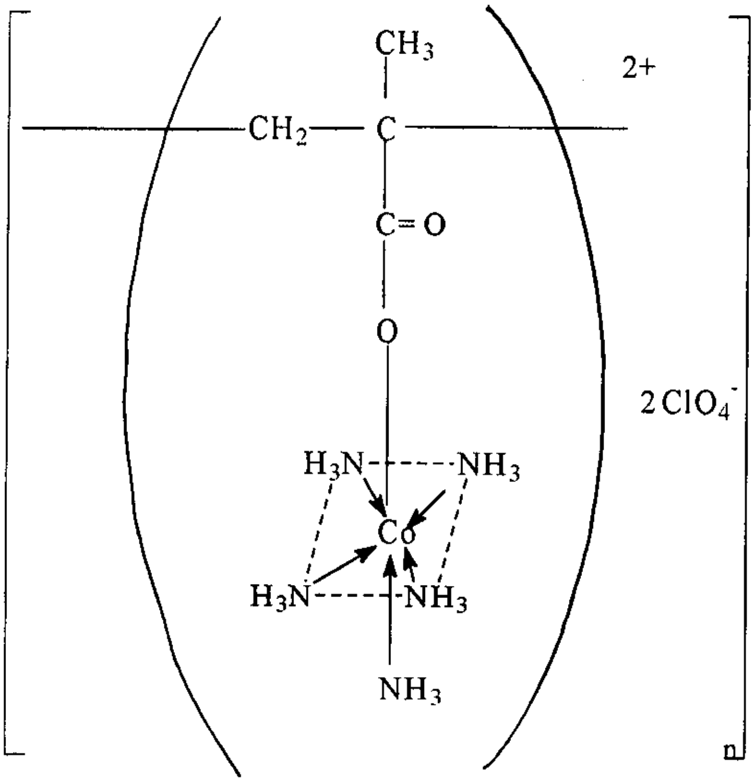
C- Formation through polymerization of metal complexes:

Vinyl compounds of metal complex are polymerized giving polymer-metal complexes



This type of polymer complex is characterized by its clear coordination structure. There are disadvantages, however, that the vinyl compounds which can be polymerized are limited, and that the metal complex itself sometimes hinders the vinyl polymerization.

Methacrylate monomer coordinated to Co(III) complex, e.g. methacrylatopentaamine cobalt(III) parchlorate(42), was radically polymerized giving polymer metal complex (III).



(III)

The copolymerizability of this monomer with methacrylic acid was studied at pH 3 and 7, and was related to the electrostatic interactions between the reaction species, i.e., between the monomer and the growing radical(43).

D- Cluster complexes:

Cluster complex is designated as the complex containing two or more metal ions bonded to each other. Metal ions are sometimes bridged by ligands, such as sulphur, alkylthiolate, carbon monoxide, nitriles, halogen ions, etc.

Iron-sulphur cluster have received much attention as ferredoxin models. The first model complex $[Fe_4\ S_4\ (SR)_4]^{2-}$ was synthesised according to the following equation:

$$4\ FeCl_3 + 12\ NaSR \longrightarrow (4/n\ [Fe(SR)_3]_n \xrightarrow{4\ NaHS\ +\ 4\ Na\ OMe}$$
$$Na_2\ [Fe_4S_4\ (SR)_4] + RSSR + 6\ NaSR \xrightarrow{R_4N^+} (R_4N)_2\ [Fe_4S_4(SR)_4]$$

This tetramer complex was known to have a cubic-type crystalline structure(44).

Cluster complexes containing metal-metal bonding are considered to serve as valid models in the study of catalysis by heterogeneous metal surfaces, since these complexes are often soluble in solvents and act as a homogeneous catalyst(36).

I-A-3-Characterization of polymer-metal complexes:

The complexing ability of polyesters has been of particular interest as they bound in polar groups and are able to coordinate and / or associate with metal ions. The coordination reaction of a polymer ligand to metal ions or to metal complexes and the structure of the resulting polymer-metal complex can be studied spectrophotometry by means of IR, nuclear magnetic resonance (NMR), electron spin resonance (ESR), X-ray, optical rotatory dispersion (ORD), or circular dichroism (CD) analysis. Absorption spectra of polymer ligand or metal ion are changed, sometimes drastically, by complex formation. Since in a polymer-metal complex a huge macromolecular chain is a adjacent to the coordinating groups, not only the kind of the coordinating groups but also the environment around the metal complex are strongly influenced by the polymer-chain.

The characteristics of a polymer-metal complex in a solution as well as in solid state are dependent on such a microenvironment given by the polymer chain. The microenvironment around the metal ion can also be studied spectrophotometrically by ORD and CD.

Solid state chemistry studies are performed in organic and inorganic complexes to explain the rates of solid reactions and the changes occurring in physical properties (especially the electrical conduction properties) of the organic compounds forming the complexes.

I-A-4-Electrical properties of polymer-metal complexes:

In the last few years, organic and inorganic complexes with semi conducting properties attracted attention because of the fact that semiconductor equipment is being increasingly applied in various fields of science and engineering(45).

The electrical conductivity of solid complexes and their dependence on temperature and composition provided the first main challenge to theories of the solid state, and they continue to be among the central concerns of a wide range of scientists concerned with solids and their electronic applications.

It is well known that the electrical conductivity in solids is a very important property to differentiate between various types of solids. Now, there are many theories and mechanisms used to explain the electrical conduction in the solids(46).

As a general rule the electrical conductivity of metals was found to decrease with increasing the temperature, while the conductivity of semiconductors and insulators show a reverse temperature effect with the respect to the nature and behaviour of charge carriers in these materials.

In metals, electrons are the main charge carriers and move freely, they are localized or bound to atomic sites. So there is no activation energy required for the conduction process.

The number of the mobile electrons are large and essentially constant, but there mobility gradually decreases with rising temperature due to the electron-phonon collisions. Consequently conductivity gradually drops with rising temperature.

In semiconductors, the number of mobile electrons is usually small, this number may be increased in one of two ways, either by rising the temperature so as to promote more electrons from the valance band to the conduction band, or by doping with impurities that provide either electrons donor atoms or acceptor atoms.

In insulators, however, electrons are not free to move throughout the bulk of materials but are bound to atomic sites. They differ from semiconductors only in the magnitude of their conductivity, which are usually several orders of magnitude lower. The conductivity of insulators is sensitive to both temperature and defects(47).

However, a complete characterization of the electrical conductivity in solids such as polymers requires that the charge, concentration and mobility of each charge carrier be determined as a function of the perminent parameters (e.g. temperature, composition, atmosphere, pressure, ……). In general, these quantities can not be determined directly by experiments. Usually the results from several different experimental measurements may be used in combination with the theoretical interpretation in order to provide this information.

I-B-Literature Survey

A few research groups have been actively engaged in the synthesis and study of metal -containing polyesters(48-51). Polymers having the amino acid moiety in the main chain or in the side chain find a variety of useful applications, such as chelating agents for metal ions, ion-exchange resins, polymer catalysts with enzyme like behavior, and promoieties for preparing polymeric prodrugs(26, 52-57).

Polyesters with pendant amino groups and carbonyl oxygen of the ester group as donor sites per unit may yield metal coordinated polymers with interesting properties. However, few investigations have been reported on the synthesis of polyesters having amino acid moieties in the main chain(58).

The synthesis and characterization of poly (ethylene asparate)-metal complexes which were found to be thermally more stable than the polyester itself were reported(59). It was found that, the nature of the metal ion influences the thermal degradation behavior of the polyester metal complexes(60).

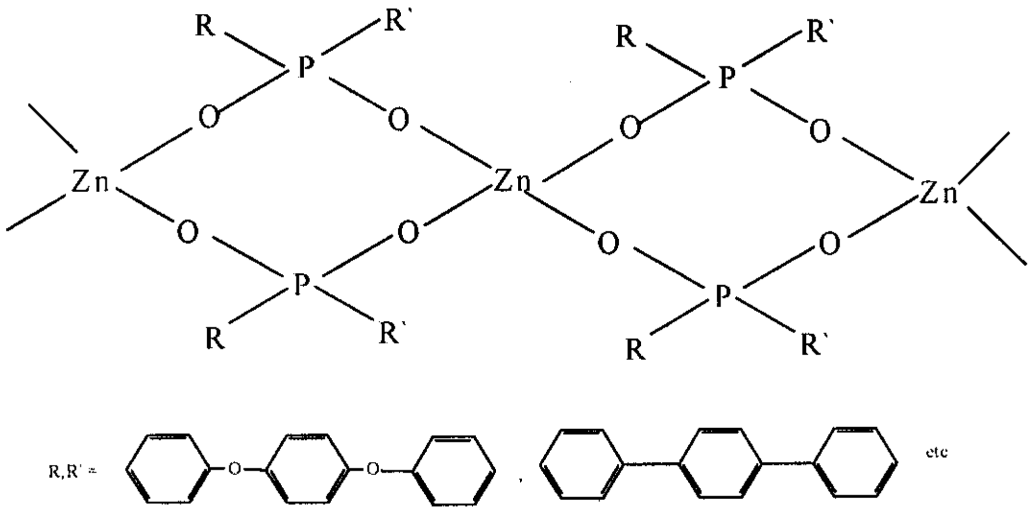
Only decades ago polychelates derived from polymeric ligands and transition metal ions attracted the attention of many investigators(61). Review of the literature reveals that the reaction of metal ions with polymers containing pendant functional groups produce coordinated systems possibly having enhanced thermal stability (62-64).

Oligomeric polyester, namely, poly (tetramethylene asparate) (PTMA), was synthesized from D, L-aspartic acid and 1,4 butanediol by a metl-condensation technique. Polyester-metal complexes were synthesized by the reaction of PTMA with hydrated acetates of Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II), Mg(II), Ca(II), Pb(II), and Ce(IV) in DMSO. The polyester-metal complexes were characterized by elemental analysis, IR spectral studies, magnetic susceptibility measurements, and thermogravimetry. The metal ions were found to be six-coordinated with two water molecules as additional ligands besides oxygen and nitrogen atoms of polyester repeating units. Thermogravimetric analysis showed that coordination polymers are thermally more stable than is polyester(59).

Complexes of ethylene glycol-resacetophenone copolymer with Cu(II), Ni(II), Zn(II) and Co(II) were prepared(65). It was found that, electronic spectra in conjunction with magnetic moments were in accord with an octahedral environment around the central metal ion in all polymeric chelates except Cu(II) and Zn(II) polymeric chelates which possessed square planer and tetrahedral geometries, respectively, also IR spectral studies further suggested that the metal ions are coordinated through the oxygens of the carbonyl and the phenolic hydroxyl groups. All the chelates were paramagnetic except Zn(II), which was diamagnetic.

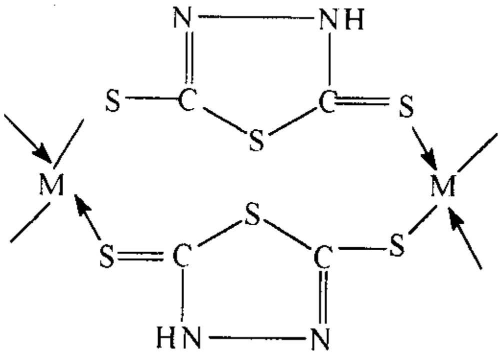
Two novel Schiff base ligands containing oxyethylene glycol chains, N-(4-pentaoxy ethylene glycol chains, N-(4-pentaoxyethyleneglycolphenyl) salicylaldimine, and N-(4-nona-oxyethyleneglycol phenyl) salicylaldimine, were synthesized by reacting salicylaldehyde with 4-aminophenylnonaoxyethylene glycol or 4-aminopheylnonaoxyethylene glycol, respectively(66). Their Ni(II), Cu(II) and Co(II) complexes were synthesized. The novel schiff base ligands and their complexes were characterized by elemental analysis, ^{1}HNMR, IR and UV-visible spectra. The analytical data show that the metal to ligand ratio in the complexes is 1:2.

Poly(metal phosphinates) are the examples of thermally stable polymer complexes, which are prepared by Nannelli et al.(67) from phosphinic acid and metal ion such as Zn or Cr hving the structure (IV):



(IV)

Bifunctional ligands such as 2,5-dimercapto-1,3,4-thiadiazole(68), cyclophosphazene derivatives(69), 2,5-dihydroxy-p-benzoquinone(70), bissalicylaldehyde(71), and alkylenediamine(72) formed polymer complexes having the following structures as shown in (V-IX), respectively:



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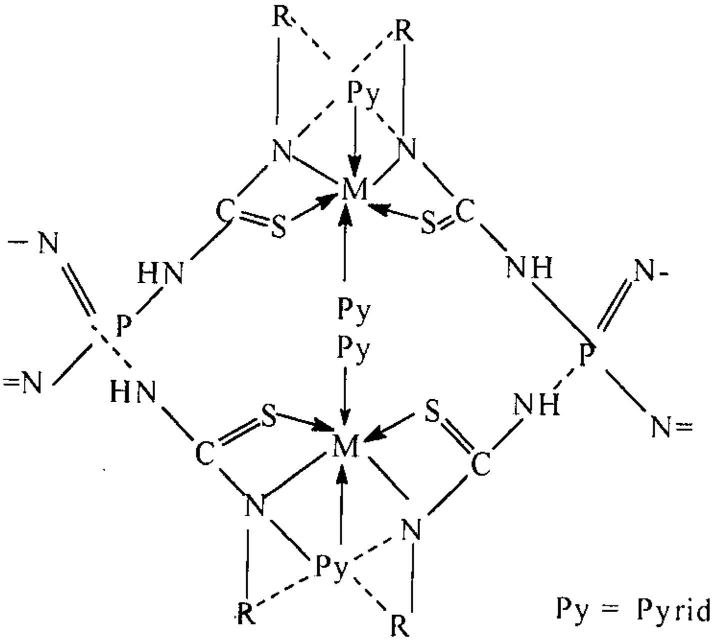
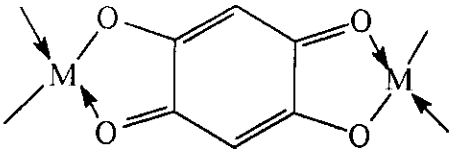


Py = Pyridine

(IV)



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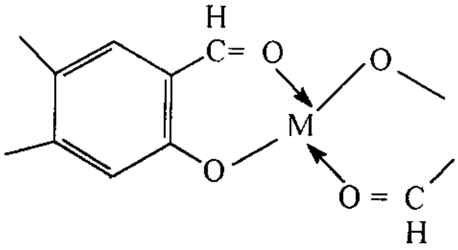
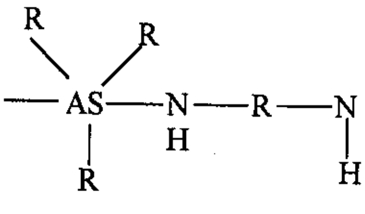


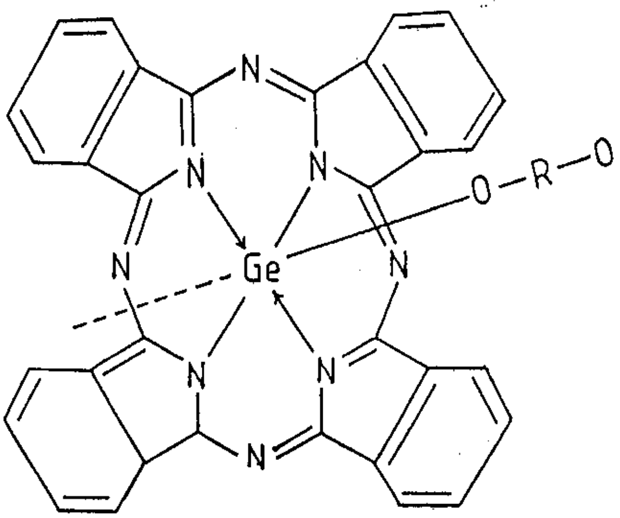
(VIII)



(IX)

Carbonyl group of amide can also coordinate to metal ions giving polymeric complex, e.g. bis (1- asparaginato) Cu(II)(73).

New polymer complexes having an interesting structure were prepared by Hartmann et al.(74). Metal complexes containing macrocyclic ligands were linked at axial positions giving a linear polymeric structure. Dihydroxy (phthalocyanino) germanium reacts with divalent alcohol to afford the polymer complex (X):



(X)

A series of metal-containing polyurethanes with ionic links in the main chain were synthesized by poly addition of diisocyanates and divalent metal (Zn^{2+}, Cd^{2+}, and Hg^{2+}) salts of mono (hydroxyethyl) phthalate(75). The polymers obtained were generally yellow-to brown-colored powders or solids, the polymers synthesized were characterized by viscometry, spectral studies (IR, UV, and NMR) and X-ray diffraction.

Polyesters and polyamides derived from 4,4`-azobis (4-cyanopentanoic acid) were prepared by direct poly condensation using 1-methyl-2-chloropyridinoium iodide as a condensation reagent at room temperature(76). These polyesters and polyamides containing azo groups could be used as effective initiators of radical polymerization of some vinyl monomers.

Polymers containing dithiocarbamate(77) or thio carbonyl group have been used as metal-chelating agents, but their coordination structure was not studied.

By poly condensation of epichlorohydrin with ethylene diamine 1,2-Diaminoethane units in the resulting cross-linked polymer provide high chelating ability for transition metal ions, such as Cu(II), Ni(II), Co(II), Cd(II), Fe(III) and Cr(III)(78). Having all-amine ligating groups, the polymer represents unique properties and can sorb not only metal cations but also their concentrations, such as chloride, sulphate, nitrate and acetate. The cross-linked polymer is stable hydrolyrically and regenerable by acid without losing its activity. It can be recycled and offers a means of simultaneous removal of cations and anions from aqueous solutions.

Dynamic thermogravimetry (with linear temperature increase) is widely used as a tool to study the degradation of different polymeric materials, to elucidate, the decomposition product, the thermal stability, the order of reaction and also to estimate the kinetic parameters(79). The thermal stability of polymer and the activation energy of degradation process depends to a large extent on the given polymeric material. The differences depend on several factors:

(1) Preparation method of the polymer, i.e. anionic, thermal or other type of polymer preparation and lattice defects, weak links and impurities(80).

(2) Molecular weight of the polymer(81-85).

(3) Experimental technique and operating conditions (81-86).

Although unified by direct concern with the effects produced by electric fields, the subject of the electrical properties of polymers covers a diverse range of molecular phenomena. By comparison with metals, where the electrical response is over whelmingly one of electronic conduction, polymers display a much less striking response. This absence of any overriding conduction does allow, however a whole set of more subtle electrical effects to be observed more easily. For instance, polarization resulting from distortion and alignment of molecules under the influence of the applied field becomes apparent(87).

Electrical conductivity of materials is a property, which spans a very wide range. Organic polymers have conductivities eighteen orders of magnitude smaller than those of metals. Polyethylene, polytetrafluoroethylene and polystyrene are the best insulators known(87). On the other hand in most conjugated polymers the conductivity is little better than that in ordinary polymers(88).

Poly (acene quinone radical) (PAQR) polymers and in the order of 500 nm in length, have been made and found to have high conductivity in the range $1\text{-}10^{-2}$ $ohm^{-1}m^{-1}$(89).

Graphitik-like structures are readily formed by pyrolysis of many organic polymers, such as pyrolysis of polyacrylonitrile to give conducting filaments called black Orlon(87).

Discovery of the compound 7, 7, 8, 8- tetracyanoquinodimethane (TCNQ)(90) consider as a central to the development of highly conductive materials. With some cations TCNQ will form both simple and complex salts. These salts have higher conductivity values $\simeq 10^{2} - 10^{-3}$ ohm^{-1}m^{-1}.

Organometallic groups in polymers may work in several different ways to improve electronic conductivity. The metal d-orbitals may overlap with Π-orbitals of the organic structure and there by extend electron delocalization along a molecule. Being rather diffuse, the d-orbitals may also serve to bridge molecules in adjacent layers of a crystal. Thus the high conductivity ($10^{-3} - 10^{-2}$ Ohm^{-1}m^{-1}) found in the polymeric square –planar Cu(II)-complex of 1,5-diformyl-2,6-dihydroxynaphthalene dioxime(91). Superconducting polymers have been also prepared(87).

I-D-Theoretical Review and Methods of Calculations

Solids can be classified into many types depending on their electrical conductivity values (σ):

Insulators $\sigma < 10^{-21}$ Ohm^{-1}. cm^{-1}, Semiconductors $\sigma = 10^{-12}$-10^{2} Ohm^{-1}. cm^{-1}, Metallic $\sigma = 10^{2} - 10^{6}$ Ohm^{-1}. cm^{-1} and superconducting materials where the resistance of the sample go to zero value.

Semiconductors may be classified into two types:

1- Intrinsic semiconductors,: in which the charge carriers originate from the pure materials by a thermal excitation process.

2- Extrinsic semiconductors, in which the carriers are present in constant temperature independent concentration (either at trace concentrations doped in to the crystal lattice, or in stoichiometric concentration at high concentration, in mixed valance compounds).

The band theory is one of the most important theory used to explain the electrical conduction is solids. According to this theory(37,92) the number of charge carriers per unit volume present in conduction band, n, is given by:

$$n = 2\,(2\,\pi\, m^*\, KT/h^2)^{3/2}\, e^{-Ea/KT} \longrightarrow (1)$$

Where m* is the effective mass of charge carriers (assumed to be equal of the rest mass of the electron), E_a is the activation energy required for migration of charge carriers, K is Boltzman constant, h is Blank constant, and T is the absolute temperature.

Equation 1 can be written as :

$$n = 4.818 \times 10^{21}\, T^{3/2}\, e^{-Ea/KT} \longrightarrow \qquad (2)$$

I-D-1-Electrical Conduction in Solids

I-D-1-a- DC-Conductivity:

Generally, the transport of charge carriers occurs through different conduction mechanisms(46). The most important of them are:

a- Band mechanism: as mentioned previously.

b- Hopping mechanism: in which the current passes by means of activated jumps of the carries from one site to adjacent sites, or one can say that the charge carriers are assumed to "hop" over a fixed distance, i.e. the distance between nearest neighboring carrier sites.

Also in the light of the band theory, the temperature dependence of conductivity is attributed to the variation of charge carrier concentration with temperature Eqs. (1-2). But, in the hopping theory the variation of charge carrier mobility with temperature is due to the jumping from one molecule to the other(93).

The resistance R of material in Ohmic region is defined by Ohm's law:

$$I = \frac{V}{R}$$

where I is the current and V is the applied potential difference. For a uniform current, the DC-conductivity (σ_{DC}) for the material is defined by:

$$\sigma_{DC} = \frac{L}{S} \cdot \frac{1}{R_{DC}} \qquad (3)$$

where L is the length of the measured sample and S its cross-sectional area.

The electrical conductivity of material is generally attributed to the drift of charge carriers electrons and holes and is given by:

$$\sigma = \sum_i \sigma_i = \sum_i (n_i\ q_i\ \mu_i) \qquad (4)$$

$$\sigma = \sum_i \sigma_i = \sum_i n_i\ q_i\ (\mu_{ei} + \mu_{hi}) \qquad (5)$$

where n_i is the concentration of electrons and or holes; μ_{ei} and μ_{hi} are their respective mobilities.

The temperature dependence of conductivity is usually given by the Arrhenius equation:

$$\sigma = \sigma_o\, e^{-E_a/K_bT} \qquad (7)$$

where E_a is the activation energy required for migration of charge carriers, K_b is Boltzman constant and T is the absolute temperature. Graphs of lnσ against T^{-1} should give straight lines of slope ($-E_a/K_bT$) from which one can calculate the activation energy. The transport number t_i for each type of charge carrier (e.g electron or ion) is defined as the fraction of the total current carried,

i.e.
$$t_i = \frac{n_i\ q_i\ \mu_i}{\sum_i n_i\ q_i\ \mu_i} \qquad (6)$$

I-D-1-b- AC-conductivity:

The conductivity of organic and inorganic semiconductors under AC fields may be higher by several orders of magnitude than that under DC fields(94). This phenomenon may be associated with the polarization occuring in the molecules or in crystal lattices. In general, the conductivity decreases with increasing frequency in the case of band conduction process, while it increases with increasing frequency in the case of hopping conduction process(95).

The frequency dependence of AC-conductivity can be expressed by empirical relation(96):

$$\sigma_{AC}(\omega) \propto \omega^{S'} \qquad (8)$$

where S' is not a constant for all substances, but is a function of temperature, approaching unity at low temperatures and decreasing to 0.5 or less at high temperatures.

I-D-1-c- Dielectric properties of solids:

Dielectric or electrical insulating materials are understood as the materials at which electrostatic field persists for along time. These materials offer a very high resistance to the passage of electric current under the action of the applied direct-voltage and therefor sharply differ in their basic electrical properties from conductors.

Electrical insulating materials should not carry current under the action of direct-current voltage, i.e. they should be non conductive. In other words, the resistivity (specific resistance) of electrical insulating materials should be infinitely high. However, all electrical insulating materials employed in practice do carry a certain, usually very week current (leakage current) when a direct voltage is applied. Thus the resistivity of electrical insulating materials has a finite, although extremely high value; the higher the resistivity of an electrical insulating material the better is quality as insulator.

The most important properties of dielectrics are:

1- They should posses high electric strength, i.e. they should be able to withstand high voltages without undergoing degradation and becoming electrically conducting.

2- They should have low electric loss, i.e. in Ac field the loss of electrical energy, which appears as heat, should be minimized.

3- Application of a potential difference across a dielectric does lead to a polarization of charge within the material although long-range motion of ions or electrons should not occur.

All dielectrics can be divided into two classes:

a- Polar dielectrics (dipole).

b- Non polar dielectrics (neutral).

It is known that "the algebraic sum of all the charges in molecule of any substance is equal to zero" since substance in a sufficiently large volume does not display an electric charge (only if it is not electrified by the action of some outward cause). But the spatial arrangement of charges in a molecule may be different in various substances. If all positive and negative charges of a molecule are replaced by one positive and one negative charge mutually equal in absolute magnitude and located at the centers of gravity of separate positive and correspondingly separate negative charges, these summary charges may either coincide or not coincide in space.

In the first case we have a non-polar molecule, and the matter composed of such molecules is also called non-polar. In the second case the molecule is an electric dipole, even in the absence of external electric field. The most important property of dielectric materials is their ability to be polarized under the action of an external electric field. Under the action of applied alternating voltage any dielectric will pass alternating capacitive current (displacement current). The state of a dielectric acted upon by an electric field can be described by two vector quantities: intensity of an electric field, E and polarization P.

The application of an harmonically varying electric field to a dielectric medium produces time-dependent polarization P(t), which is related to that of the polarizing field $\epsilon(\omega)$ by :

$$P(\omega) = \epsilon_o \, \chi \, (\omega) \epsilon(\omega)$$

Where ϵ_o is the permittivity of free space, and the dielectric susceptibility $\chi(\omega)$ is in general complex and related to dielectric constant ϵ^*, ϵ'' and is given by :

$$\epsilon^* = \epsilon` - i\epsilon''$$

where $\epsilon`$ is the real part of dielectric constant and ϵ'' is the imaginary part. The real part of dielectric constant ϵ' for independent dipoles with the same relaxation time, τ, is given by:

$$\epsilon' = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)}{1 + \omega^2\tau^2} \tag{9}$$

and the imaginary part is given by:

$$\epsilon'' = \epsilon_\infty + \frac{(\epsilon_s - \epsilon_\infty)\omega\tau}{1 + \omega^2\tau^2} \tag{10}$$

where ϵ_s is the static dielectric constant at angular frequency $\omega = o$ and ϵ_∞ is the dielectric constant at very high angular frequency $\omega = \infty$. According to Eq. (10), the position of the peak maximum of $\epsilon''(\omega)$ versus the frequency lying at $\omega\tau = 1$, Eq. 9 and 10 are the Debye equations, which are reasonably applicable to most dispersions at electrical frequencies. The most important parameter of them is the loss factor tan δ

$$\tan\delta = \frac{\epsilon''}{\epsilon'}$$

$$\tan\delta = \frac{(\epsilon_s - \epsilon_\infty)\,\omega\tau}{\epsilon_s + \epsilon_\infty\,\omega^2\tau} \tag{11}$$

The value of tan δ (loss tangent) as well as the other parameters of dielectrics for given specimens of material are not strictly constant and depend on various external factors such as temperature and the applied voltage.

The absorption current in dielectric materials can be attributed to several causes:

1- In polar dielectric due to the orientation of dipole molecules.

2- In non polar dielectric due to the inhomogenity in the electrical properties of a dielectric, the formation of space charges in dielectric under the action of an external electric filed and also due to initiating the processes of redistribution of charges with time in the volume of dielectric.

The condition of the maximum of dielectric losses in a polar dielectric at a given temperature is:

$$\omega_{max} \tau = 1 \qquad (12)$$