CHELATING POLYMERS

I : GENERAL INTRODUCTION

CHELATING POLYMERS

I : GENERAL INTRODUCTION

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

Polymer formation :

There are three principal types of reactions which led to the formation of substances of higher molecular weight.

1. condensation reactions which involve the elimination of simple molecules.
2. Addition reactions in which the monomeric, low molecular weight units are caused to react additively with same or other monomeric units to yield polymeric products.

3. Co-ordination polymerisation reactions in which ligands get co-ordinated or chelated to metal atoms, and which are frequently classified under both condensation and addition polymerisation reactions, but are sufficiently distinctive to warrant separate consideration. They may be strictly inorganic or inorganic-organic in character.

Reactions leading to the formation of polymers containing co-ordinated or chelated metal ions can be divided into three general catagories.

(i) Metal-ligand chain formation :

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

(ii) Polymerisation of co-ordination complexes or chelates :

Some polymers are obtained when monomers containing co-ordinated or chelated metal ions are polymerised through functional groups.

(iii) Metal insertion in polymeric ligands :

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

(i) Metal-ligand chain formation :

In theory, a ligand molecule which contains two pairs of unshared electrons can be used to link metal ions.

Under certain circumstances, when the stereo chemistry of the donor group and the metal ions are favourable, chelate ring formation occurs. Polymeric compounds are formed (a) when both pairs of electrons are on the same atom in the co-ordinating group. (e.g. Cl, OH and NH_2), (b) when the electron pairs are on atoms linked directly to each other (e.g. -CN), or (c) when the donor atoms are widely separated in the ligand molecule.

Examples of polymeric complexes formed as indicated by (i-a) are the metal chlorides. Palladium (II) chloride exists as infinite chains (I-S-1) in the solid state.

Metal cyanides are the familiar examples of polymers formed by reaction (i-b). Thus silver cyanide is a linear polymer (I-S-2); and R_2 AuCN is represented as a cyclic tetramer (I-S-3), if R groups occupy cis position; however, if R groups can be made to occupy trans instead of cis positions, a linear polymer (I-S-4) would result.

Co-ordination polymers obtained by reaction (i-c) are numerous. It has been observed in many cases that chelation with metals ions greatly enhances the thermal stability of organic ligands. Monomeric chelate compounds are obtained with bidentate ligands such as ethylene diamine but polydentate agents can give rise to polymeric compounds. The degree of cross-linking in any polymer of this type is governed by the co-ordination number of the metal and the number of co-ordinating centres of the ligand. Combination

between a bis-(bidentate) ligand and tetra co-ordinate metal ion, or between a bis-(tridentate) ligand and hexa co-ordinate metal ion, will lead to a linear polymer if the two bidentate or tridentate functions of the ligand are unable to co-ordinate with the same metal ion. A bis-(bidentate) ligand and hexa co-ordinate metal ion or a poly functional ligand with tetra co-ordinate metal ion, on the other hand, can give highly cross-linked polymeric products. A hexa co-ordinate metal ion can be used with bis-(bidentate) ligand to prepare linear polymers by blocking two of the co-ordination positions with other groups.

Tetra co-ordinate metal ions such as Cu (II) and Ni (II) when treated with bis-(bidentate) ligands such as 2,5-dihydroxy-p-benzoquinone, bis-(acetylacetone), bis-(salicylaldehyde), bis-(amino acid), bis-(dioxime), etc., yield linear polymers. Cross-linked polymers would be obtained in most of the cases when 6-co-ordinate M(III) and 8-co-ordinate M(IV) are used with the above ligands and no co-ordination positions are blocked by other ligands.

(ii) Polymerisation of monomeric chelate complexes :

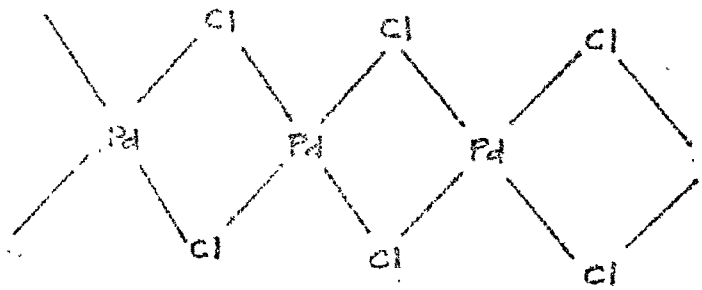
Chelate polymers can be obtained by polymerisation of monomeric chelate complexes. Higher molecular weight compounds can be prepared from chelate complexes when the ligand contains functional groups capable of undergoing conventional addition or condensation reactions. If the ligand contains an ethylenic side-chain, the usual addition polymerisation

may be possible. Vinyl ferrocene has been shown to undergo homo and co-polymerisation with vinyl monomers and dienes and although trans cinnamoyl ferrocene does not homo-polymerise, a variety of co-polymers has been obtained. On the other hand, polyesterification of chelate compounds having alcoholic functions in the ligand with diacid gave low molecular weight polymer (I-S-5).

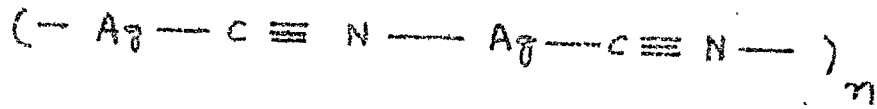
(iii) Metal inseration in polymeric ligands :

Production of chelate polymers using preformed polymeric ligands is still being studied from different angles. An interesting and well known example of this is the tanning of leather by metal ions, which involves the cross-linking and stabilising of polypeptide polymers by co-ordination. Preformed polymers capable of chelation are designated as chelating polymers. Polydentate ligands have been prepared by the reaction of pyridine-2-6-dialdehyde and diamines such as ethylenediamine, hexamethylenediamine and benzidine. The chelating polymers considered to have the following structure : (I-S-6), where X is $-(CH_2)_2-$, $-(CH_2)_6$ or $-C_6H_4-C_6H_4$, gave chelate polymers of unknown molecular weight when treated with bivalent copper or iron salts. Similarly polymeric schiff bases (I-S-7) with molecular weight in the region of 10000 have been prepared and used to get polymetallic chelates with Cu (II), Zn (II), etc.

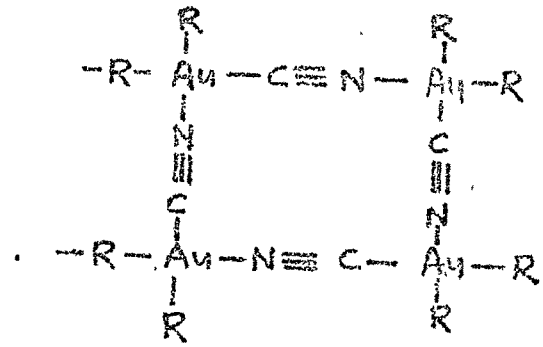
The chelating polymers may be obtained as linear polymeric chains or as cross-linked polymeric networks depending largely on the functionality of the monomers. In the following pages are discussed (1) the preparation of linear condensation polymers as chelating polymers and their tendency towards chelation with some transition metal ions in presence of different anions and (2) the preparation of cross-linked condensation polymers as chelating polymers and the study of their ion exchange behaviour towards acid, alkali and copper ion.



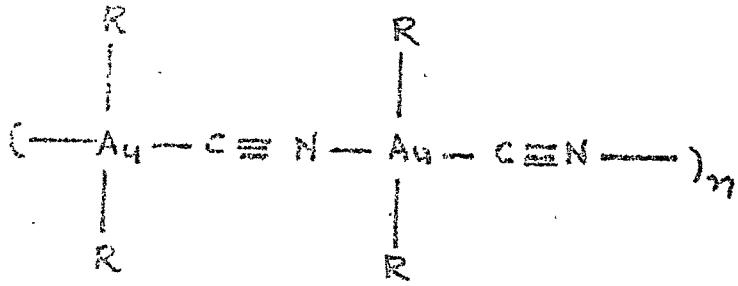
(I-S-1)



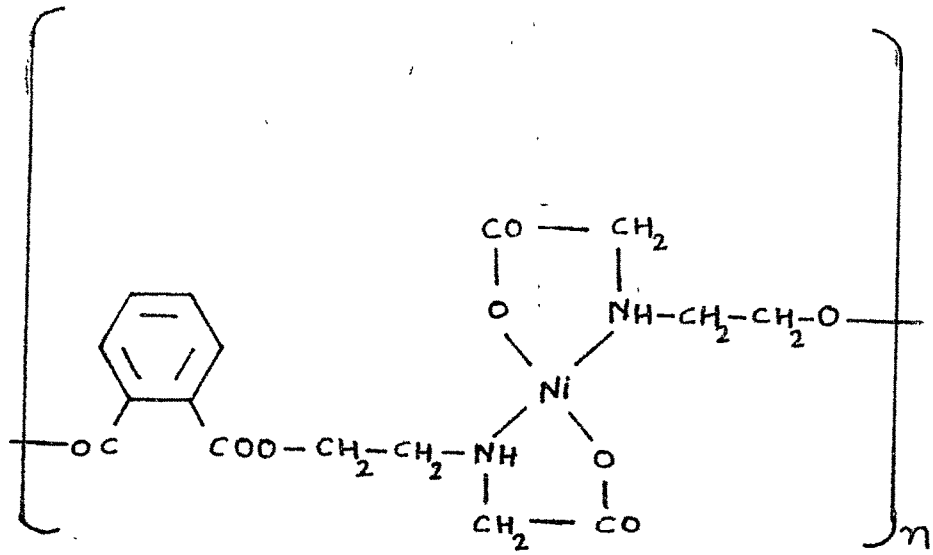
(I-S-2)



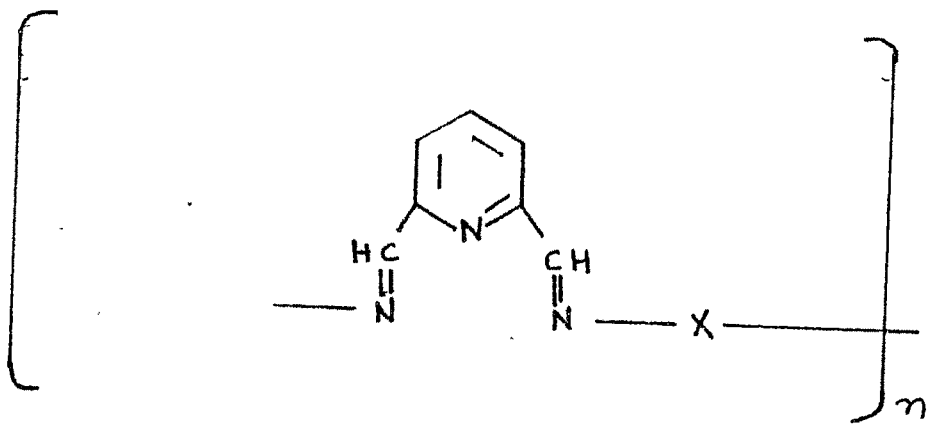
(I-S-3)



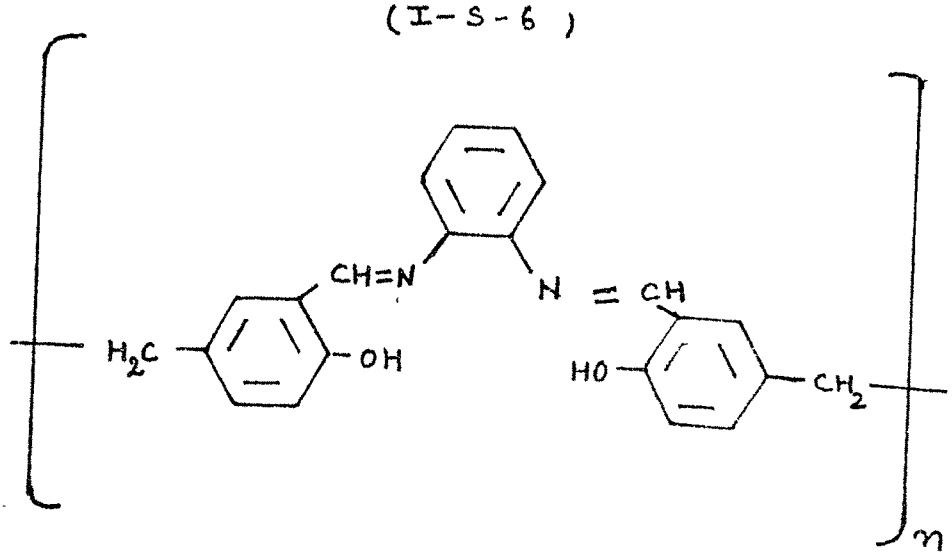
(I-S-4)



(I-S-5)



(I-S-6)



(I-S-7)