INTRODUCTION

PYROLYSIS OF POLYCHELATES

I INTRODUCTION

I.1 Pyrolysis of Polymers:

Thermal decomposition is the oldest characterization technique still used by the chemist. Williams (1) isolated the basic isoprene unit by pyrolyzing natural rubber in 1860. And various investigations employing thermal decomposition technique have demonstrated that pyrolytic fragmentation and identification of the fragments can serve as an effective means of determining the nature and structure of polymers.

The thermal decomposition is quick and easy to perform and provides a good guide to the identity of the polymer. From the days of the alchemist to the present time, the testing of a material in a flame is often the first step to quickly identify a substance.

Pyrolysis is also applicable for specific type of synthesis. In this method two or more fragments obtained on pyrolysis in absence of air react to give final compounds. In the same way pyrolysis is also used to get new fragments from specific compounds. Pyrolysis of high molecular weight compounds and cracking of heavy petroleum fractions under pressure were studied by Ipät'ev (2). Methanol and acetone are obtained by pyrolysis of wood in absence of air. Poly-p-xylylenes have been prepared by the pyrolysis of p-xylene by Szwarc and co-workers (3,4,5).

The pathways of the pyrolytic decomposition of organic polymers are so varied and complex as to render generalizations practically useless. In the polymer field, the random scission versus zip-down depolymerization has received some attention with the conclusion that, if there are possibilities for a resonance stabilization of the intermediate fission product, chain depolymerization will be likely. Extensive studies by Madorsky (6) Jellinek (7) and Grassie (8) have led to the interesting conclusions concerning the decomposition of rubber, halogen-containing polymers, crosslinked polymers and polyamides that, isolated allylic groups, branch points and halogenated or oxygenated hydrocarbons break down more easily than aromatic substituted hydrocarbons. Sensitivity to hydrogen abstraction, because of electronegativity of neighbouring atoms or groups, or resonance stabilization by neighbouring group, also destabilizes a polymer.

Substitution of labile hydrogen by more stable groups such as fluorine, methyl, phenyl, etc. offers an excellent way to improve pyrolytic stability. Mechanisms which lead to the formation of conjugated double bonds along the chain e.g., the condensation of cyano groups in polyacrylonitrile or the fission of halogen acids from halo polymer, also enhances stability. Polymeric material however may decompose by loss of side groups, or to less stable structures than the starting material.

According to Winslow and co-workers (9) polymer pyrolysis consists of two competitive processes, scission reaction to form low molecular weight fragment and gases and recombination reactions resulting in the formation of polymeric carbon. While the first reaction occurs at low temperature, very little is yet known about the very complicated mechanism for the recombination reactions, yielding polymeric carbon and graphite-like structures.

According to Grassie (8) three different mechanisms of the depolymerization reaction of vinyl polymers, namely I - random degradation, where chain scission occurs at random points along the chain leaving relatively large fragments, II - stepwise depolymerization where an unzipping reaction starts from the chain end, producing exclusively monomer, and III - reverse polymerization reaction where chain scission at random points or at weak links yield free radicals which rapidly lose monomer until they are degraded completely. After scission at weak link, occurs, the reverse polymerisation process in reality is identical to the stepwise depolymerization. Many of the addition polymers, such as vinyl polymers, seem to decompose according to reverse polymerization mechanism involving initiation, propagation, transfer and termination. Transfer is much more important in decomposition reactions than in polymerization reaction as higher temperatures involved favourtransfer. Because transfer reactions provide opportunities to form non-monomeric material, they tend to reduce monomer yields (10,11). Complete analysis of the degradation mechanism would involve determination of degradation products, rate of volatilization versus time and conversion, molecular weight and molecular weight distribution, dilution of the polymer in a relatively inert substance, and rates and activation energies of the degradation processes.

The molecular weight drops rapidly as random degradation proceeds, but changes gradually in chain depolymerization as polymer molecules yield volatile monomeric products that escape from the residual sample. The ultimate product of random degradation is likely to be a disperse mixture of fragments of widely varying molecular weight. The depolymerization kinetics and products of degradation of polymers for a variety of polymers have been studied by Madorsky (6), Grassie (8), Jellinek (7) and Wall and Florin (11). These investigators found that the types and relative amounts of the pyrolysis products are functions of the molecular structure and the kind and frequency of side groups. Thus thermal stability and degradation products can be related to the strengths of the C-C bonds in the polymer chain i.e., secondary $>$ tertiary $>$ quaternary.

In recent years, pyrolytic methods in conjunction with others instrumental techniques have gained increased attention. Davison et al (12) first suggested this approach in 1954. The pyrolysis gas chromatographic techniques have been given by Levy (13).

The mechanism of pyrolytic reactions is rarely predictable and the quantitative composition of the pyrolyzate may exhibit excessive sensitivity to variations of the pyrolysis conditions bound to occur in different laboratories.

The nature of relative amounts of pyrolysis products often vary widely with the type of pyrolysis unit used as well as with the experimental conditions such as column packings and column temperatures employed.

The pyrolysis unit should be so designed that primary pyrolysis products can escape rapidly from the high temperature zone. The primary pyrolysis products formed in the vicinity of the source of heat should rapidly enter the low temperature zone and be frozen. Thus, the probability of secondary or undesirable side reactions and recombinations drop sharply to zero.

For quantitative studies of the mechanism and kinetics of polymer degradation where accurate analysis of the volatile and non-volatile reaction products obtained at a certain accurately controlled temperature and closely controlled conditions is required, it is preferable to employ continued heating system. For a simple systematic scheme of polymer identification, the pyrolysis technique should be rapid, simple to perform, and suitable for direct application to polymer-containing samples of any form.

Pyrolysis Gas Chromatographic technique (PGC) is best known now-a-days. This technique can be used for the qualitative determination of resin components in adhesives (14 a,b), characterization of anion and cation exchange resins (15), identification of polymers in paper (16) and qualitative analysis of phenol and cresol-formaldehyde resins (17).

Using higher pyrolysis temperature, Merrit and Robertson (18) analysed a group of 17 aminoacids and 10 peptides by a combined PGC mass spectrometer system that provides for decomposition of the sample, separation of degradation products, and qualitative identification of these products by means of a single integrated operation. PGC has also been applied to life detection and chemotaxonomy (19).

Other characteristics useful for identifying polymers may be obtained on controlled pyrolysis occuring in I - an oxidising or reducing atmosphere, II - the presence of depolymerization catalysts, III - the presence of non- volatile acids or bases,IV - the presence of hydrolytic agents and V - the presence of ionizing radiations from various sources like radioactive substances, lasers and high-intensity UV emitters.

Laser-induced polymer decompositions have not been studied in detail. Recently a pyrolysis apparatus using a pulsed ruby laser has been described (20).

Mercury-sensitized decomposition by means of high intensity UV radiation appears promising (21). Advantages of this technique include the relative ease with which reproducible results may be obtained and the simplicity of the apparatus.

For closest control of degradation conditions and accurate measurement of temperature, the sample can be pyrolyzed in vacuum or closely controlled atmosphere using the apparatus of Barlow et al (22), Sonntag (23), Cramers and Keulemans (24), Farre-Rius and Guiochon (25), and Garn and Anthony (26), that are particularly suited to study the kinetics and thermodynamic aspects of the pyrolysis of volatile organic substances.

One of the earliest attempts to estimate the kinetic parameters for pyrolysis such as frequency factor, reaction order, and activation energy, was made by van krevelen et al. (27) who studied the pyrolysis of materials such as coal and polystyrene. In 1958, Freeman and Carroll (28) developed a method for the study of reaction kinetics using the thermo-balance. The value of these parameters can be of major importance in the elucidation of mechanisms involved in polymer degradation (29,30) and in the estimation of thermal stability (31).

It has been suggested (32) that the polymeric compound may retain its usefulness when it retains 50% of its strength after one hour of exposure to a specific temperature and the limit is reached after a 90% weight loss has occurred.

Pyrolysis studies of some polymers are presented below: Jeffrey (33) suggested that the thermal stability of the phenolic resin in air decreases with increasing molecular weight of the meta-substituted phenol i.e. the stability decreases in the order, phenol > m-cresol > m-isopropylphenol > cardenol > m-tertbutylphenol.

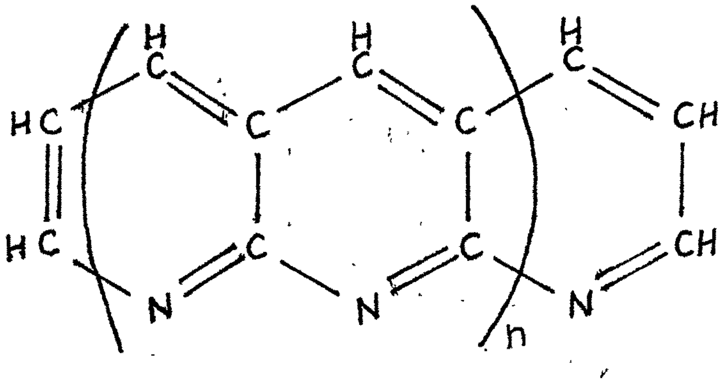
Anderson and Freeman(34) found three stages in the thermal decomposition of high-pressure polyethylene(DYNH) in vacuum. Igarashi and Kambe(35) also studied the thermal decomposition of polyethylene using DTA and TGA techniques.

Madorsky (36) found that in the degradation of polyethylene, a whole spectrum of chain fragments was obtained, each containing from one to fifty or more carbons depending on the pyrolysis temperature.

Igarashi and co-workers (37) studied the thermal degradation of polyoxymethylene(POM) in vacuum, in air and in nitrogen atmosphere by TGA and isothermal techniques and by IR spectroscopy. They also studied the acetylated derivative (POMAC) and commercial Delrin (5000 X). From IR spectroscopy, they found that the carbonyl content increased as weight loss increased in the decomposition of POM in air, in nitrogen and in vacuum.

Anderson and Freeman (38) studied the thermal degradation of styrenated polyster. TGA, DTA, IR and MS techniques were used for the study of the thermal degradation of this polymer in both air and argon.

Igarashi and Kambe (39) studied, by TGA method, the effect of molecular weight and composition, on the thermal stability of a styrene - acrylonitrile copolymer. The thermal degradation of polyacrylonitrile may be attributed to intramolecular cyclisation of CN group (40,41). When polyacrylonitrile was pyrolyzed under a controlled oxygen atmosphere at a temperature of 160-300°C, a product with the following cyclic structure (A) was obtained (42,43,44,45). Similarly when the pyrolysis of poly-methyl-acrylonitrile was carried out at a lower temperature (140°C) an analogous product was obtained(41).



(A)

Bremmer (46) reported on various factors, which affect the heat stability of brominated epoxy resins in presence of air. The thermal degradation behaviour of conventional bisphenol-A based epoxy resin (Epon 820) was compared with fluorinated epoxy resin derivative for both the cured and uncured systems (47). Anderson (48) studied the heat stability of resorcinol based epoxy resins.

Lee (49) carried out TGA, DTA, chromatographic, and MS experiments in order to study the thermal degradation of cured and uncured bisphenol-A and novolac-based resins. Oüchi and Honda (50) pyrolyzed several types of phenol-formaldehyde (PF) resins in vacuum and found that the volatiles formed consisted of methane, carbon monoxide, hydrogen, and water.

Anderson (51) studied the pyrolysis of Teflon in vacuum by means of TGA techniques, over the temperature range of 450 to 550°C.

Backus and co-workers (52) investigated the thermal degradation in air of rigid urethane foams, by means of TGA, DTA, IR and other techniques.

Gillham and Schwenker (53) studied the degradation of poly-caprolactam (Nylon 6) in nitrogen by means of DTA, TGA and other techniques. They proposed a primary degradation reaction in which there was homolytic scission of -NH-CH_2-groups in the polymer chain.

The thermal stability of the fully aromatic poly-benzothiazoles was measured by Levine (54) and Iwakura (55,56) in air by thermogravimetric analysis. These compounds have excellent oxidative stability upto the temperature of 600°C in air. The thermal stability of poly-4-phenyl-1,2,4-triazoles was demonstrated by DTA and TGA under nitrogen atmosphere (57).

Iwakura and co-workers (58) and Ehlers (59) reported that poly phenylene-1,3,4-oxadiazoles, which showed no loss in weight up to 450°C in air or nitrogen retained over 50% of the original weight upto 700°C.

Iwakura (58) also reported that the film of poly-p-phenylene-1,2,4-oxadiazole on heating at 450°C for 2 hours in air, turned black and brittle but the IR spectrum remained unchanged.

Vogel and Marvel (60) and Gray and co-workers (61) carried out thermal degradation studies of polybenzimidazoles by measuring the rate of weight loss in nitrogen atmosphere at 400, 450, 500, 550 and 600°C.

The thermal stability of poly (quinazolinediones) and poly (benzoxazinones), has been demonstrated by their behaviour in TGA studies (62,63).

The aromatic polyimides have been extensively studied, with particular emphasis, on thermal behaviour (64 to 71). Thermal stability of films, as indicated by TGA, showed that polypyromellitimide films derived from aromatic diimines had very little weight loss up to 500°C in vacuo or inert atmosphere (64,65,66). For polypyromellitimides in which the diamine component was p-phenylenediamine, benzidine etc, there was a sharp increase in weight loss above this temperature.

Heacock and Berr (71) have described the principal gaseous products of decomposition of polypyromellitimide derived from bis (4-aminophenyl) ether, in a closed system or in vacuo at 540°C, as carbon dioxide and carbon monoxide.

It was observed that fully aromatic heterocyclic polymers have thermal stabilities comparable to that of aromatic polyimides, polybenzimidazoles, and poly benzoxazoles.

Golden (72) and Wright and co-workers (73) studied the thermal stability in vacuum of some representative polyphenylene oxides using a quartz spring, to determine weight loss of samples at a series of elevated temperatures. The order of stability was found as polyphenylene oxide > poly 2,6-dichlorophenylene oxide > poly-2,6-dibromophenylene oxide > poly tetrachlorophenylene oxide. Increase in substitution of the benzene nucleus led to a decrease in thermal stability due to the fact that the C-Cl and C-Br bonds were weaker in the system and provided sites for initiation of degradation. The pyrolysis IR-technique of Mackillop (74) appears to be the method of choice for the rapid routine analysis of elastomers in vulcanized rubber compounds.

I-2 Pyrolysis of chelates and coordination complexes:

Over the last two decades, intensive research into coordination compounds has revealed an enormous range of products and much effort has been expended on structure determinations and other properties. Many workers have used pyrolytic techniques for these investigations.

Allen et al (75,76) have elegantly demonstrated the use of DTA in the observation of phase transitions in square planer complexes of palladium and platinum with phosphine ligands.

Tetahata et al (77) studied the effect of temperature upon the solid state racemization of phenanthroline or dipyridyl iron (II) and nickel (II) perchlorates. They showed that racemization of these complexes occurred after the dehydration process.

An example of the combined use of TGA and DTA was given by Amigo (78) in the study on thermal behaviour of $[CoCO_3(NH_3)_4]_2 SO_4 3H_2O$. The final product obtained at 800°C was shown by X-ray diffraction to be Co_3O_4. Further studies on cobalt amine complexes were reported by Halmos and Wendlandt (79).

Savant and Patel (80) studied the pyrolysis of some diphenyl sulphoxide (DPSO) complexes of thorium (IV). $ThCl_4(DPSO)_4$, $Th Br_4 (DPSO)_4$ and $Th (NO_3)_4 (DPSO)_3$ decomposed endothermically both in air and nitrogen, whereas $Th (DPSO)_6 (ClO_4)_4$ and $Th (NCS)_4 (DPSO)_4$ decomposed exothermically. Carbon was formed during decomposition of all of these complexes. Steger (81) studied the influence of atmospheric parameters on the decomposition of Fe(II), Co(II), Cu(II) and Zn(II) complexes of 1,5 bis (2 mercaptoethylthio) pentane.

Using the isothermal method, Dhar and Basole (82) studied the thermal decomposition of Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes of 2,2'-bipyridine $M(bipy)_3 Br_2$ under vacuum using thermobalance.

By non-isothermal method, decomposition reactions of 8-quinolinol chelates of uranium and thorium (83) complex sulfate, arsenate, and phosphate of chromium (84), EDTA complexes (85), divalent metal chelates (86), $[Cr(en)_3]X_3$ complexes (87) and $[Co(NH_3)_4(H_2O)_2]X_3$ complexes (88) have been studied.

The pyrolysis of coordination complexes $[Co(NH_3)_5H_2O]X_3$ (x = Cl, Br) (89), $[Cu(en)(H_2O)_2]SO_4$ (90), $CoBr_2 \cdot (H_2O)_6$ (91) and $Co(Py)_2Cl_2$ (92) has also been investigated.

The bi/poly dentate ligands attached to central metal ions and forming chelates are more stable to heat than simple coordination complexes. The pyrolyzates were studied employing DTA, TGA, X-ray, IR and hot stage microscopy techniques. The thermogravimetry of Cd(II), Cu(II), Co(II) and Ni(II) metal chelates of

2-(o-hydroxyphenyl) benzoxazole (HPB) was studied by Wendlandt (93) in which all metal chelates decomposed to yield the metal oxide in the temperature range from 500-600°C. Chelates of salicylaldoxime - with Zinc(II) were studied by Rynasiewicz and Flagg (94) and de Clerq and Duval (95).

The cupferron and neocupferron metal chelates of trivalent rare-earth elements were studied by thermogravimetry by Wendlandt (96,97) and Wendlandt and Bryant (98) in which they found that the heavier rare-earth metal cupferrates were less stable thermally than the corresponding lighter rare-earth complexes, and the neocupferrates of lighter rare-earth metal ions were less stable than the corresponding Fe(III) and Cu(II) chelates. The pyrolysis of several hydrated and anhydrous metal chelates was studied by Wendlandt and Horton (99) and Charles (100). They found that the thermal stability for hydrated metal chelates decreased in order Co(II)=Al $>$ Ni(II) $>$ Co(III) $>$ Mn $>$ Cd=Bi $>$ Zn $>$ Pb $>$ Cu and for anhydrous metal chelates (100) the order was Ca $>$ Mg $>$ Sr $>$ Cd $>$ Mn $>$ Ba $>$ Co $>$ Ni $>$ Zn $>$ Pb $>$ Cu. The stability of metal chelates of Cu(II), Al(III) and Th(IV) with various substituted 8-quinolinols was also studied, and it was observed that for copper and aluminium chelates, the order of decreasing thermal stability was 5,7-dichloro-> unsubstituted> 5-iodo-7-chloro-> 5,7 dibromo-> 5,7-di iodo-> 5-iodo-> 2 methyl- . In conjuction with DTA and MS studies, Wendlandt et al (101) studied the pyrolysis of some metal chelates of cupferron, salicylaldehyde, salicylaldimine, etc. The studies indicated the presence of ammonia, water, nitrogen(II) oxide, nitrogen, nitrogen(I) oxide, and higher mass number hydrocarbon entity in decomposition products. For copper(II) cupferrate chelate, the decomposition gases NO and N_2 were detectable at 250°C.

1. 3 Pyrolysis of Polychelates

The polychelates may be formed as follows:-

(a) linking of polydentate ligands by metal ions,

(b) formation of polymer with simultaneous incorporation of metal ions,

(c) incorporation of metal ions into existing polymers and

(d) formation of polymer by reaction with chelate containing functional groups.

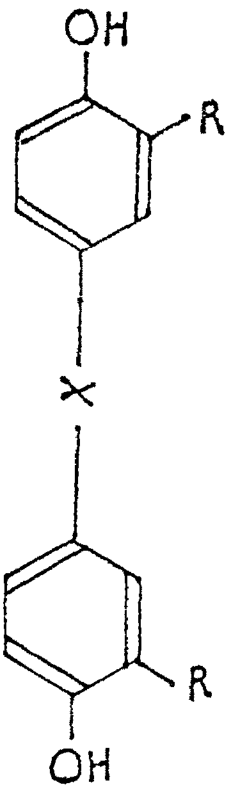
The thermal studies of polychelates are reviewed in this order.

(a) Linking of Polychelate Ligands with Ions:

The thermal stability of bis (acetylacetonates)of various metal ions has been the subject of investigation of various workers (102, 103, 104). Kluiber and Lewis (105) showed that beryllium chelate was thermally degraded at 150-200°C in vacuo to give cyclic monomer or alternatively dimer.

Thermal stability of iron, cobalt, nickel and copper polychelates of (B-i) has been studied by Terent'ev and co-workers (106, 107) and Marvel and Tarkoy (108). Thermal stability of Co, Ni and Cu polychelates of (B-ii) has been investigated by Kapadia (109). Charles (110, 111) investigated the thermal stability and decomposition temperatures of cobalt, nickel, copper, zinc, cadmium and magnesium polychelates of tetra-acetyl ethane. Korshak and co-workers (112, 113) investigated thermomechanical behaviour of cobalt, nickel, copper, zinc, cadmium, manganese and beryllium polychelates of bis (beta-diketones).

Thermal stability of iron, cobalt, nickel, copper and zinc polychelates of 2,5-dihydroxy p-benzoquinone, naphthazarin, quinizarin and anthrarufin has been investigated by Bottei and co-workers (114, 115),



(B)

X =	R =
(i) $-CH_2-$	CHO , CH=NY, CH=N-NHY , $CH=NY_{0.5}$
(ii) $-N_2C_6H_4C_6H_4N_2-$	CHO
(iii) $-SO_2-$	CHO

Mistry (116), Inoue and co-workers (117). Talati and co-workers (118) studied the thermolysis and electrical conductivity of copper polychelate of 2,5-dihydroxy p-benzoquinone. Korshak and co-workers (119, 120, 121) studied the thermomechanical behaviour of the homopolychelates of quinizarin and copolychelates of quinizarin and bis (beta-diketone).

The chelate polymers of different chelating agents showed marked decomposition at temperatures of 330-350°C from TGA studies (122 to 125).

The metal chelates obtained by heating in vacuo equimolar quantities of 4,4'-bis (alpha-thiopicolinamido) diphenyl and metal acetylacetonate were stable thermally in air upto 380-390°C and decomposed over 400°C (126).

(b) Polymer Formation in the Presence of Metal Ions:

Polymeric metal phthalocyanines (127, 128) withstood heating in air upto 350°C and decomposed at temperatures in excess of 400°C. Similarly the polychelates prepared by the reaction of tetracyanoethylene with metal or metal-containing compounds withstood prolonged heating at 500°C.

(c) Incorporation of Metal Ions in Preformed Polymers:

Metal chelate polymers prepared from the reaction of 8-hydroxyquinoline-formaldehyde polymers and metal ions such as zinc, nickel, aluminium and iron decomposed between 300 and 450°C (129).

Zinc, nickel, silver, lead, mercuric, copper and cadmium metal chelates of aromatic polyhydrazides (130) and copper, cadmium and magnesium metal chelates of poly (aminoquinones) (131) were also studied.

(d) Polymer Formation by Reaction with Chelates Containing Functional Groups:

Polymers obtained from compounds containing difunctional unsaturated acids, did not lose volatile materials at temperatures as high as 400°C, but disproportionated even at room temperature (132).

Some metal thiopicolinamides stable at 400°C, and polymers from bis-thiopicolinamide, stable at 350°C have been prepared (133).

I.4 Pyrosynthesis

Pyrosynthesis suggested earlier is considered further. Poly (p-xylylene) was first obtained by conversion of p-xylylene by vacuum pyrolysis at 900-950°C The intermediate, on condensation, spontaneously polymerises (134). The commercial synthesis of poly (p-xylylene) is accomplished by vacuum pyrolysis of di-p-xylylene to p-xylylene which spontaneously polymerises on cooling. Di-p-xylylene was prepared by pyrolyzing p-xylene in steam at 250°C and is collected in 15% yield (135).

The pyrolysis of organic polymers yields a variety of polymer carbons (136). Thus, on heating p-vinylidene chloride, hydrochloric acid is evolved producing a tough polymer with remarkably uniform pores (137). Polyvinylenes have been prepared by removal of hydrobromic acid from poly vinylidene bromide.

Pyrolysis of polyacrylonitrile yields semiconducting polymers (138). Saturating the polymer with metal salts, before pyrolysis, increases the conductivity of the resulting polymer considerably. Pyrolyzed polyacrylonitrile catalyses the decomposition of hydrogen peroxide (139) and the dehydration of formic acid at 240-300°C (140).

Polymer carbon formed by heat treatment of naphthalene formaldehyde resins at 560°C is believed to possess a condensed ring system (141). Nickel salt of carboxylic ion exchanger resin may be oxidised and then pyrolyzed to yield highly conducting polymer containing upto 12 atom % of Nickel (142).

Poly phenylacetylenes result from the thermal polymerisation of phenylacetylenes (143). Paramagnetic properties of polymers obtained by heat treatment of phenyl acetylenes are reported (144).

Poly-p-phenylenes are formed by decomposing bis-diazotised benzidines in presence of cuprous salts. The products have partial inclusion of azo group (143,145).

Poly pyrroles have been made by pyrolyzing tetra-iodo pyroles at 150-500°C (146,147,148). Pyrolysis of pyridine in presence of chlorine at 800°C yields poly-pyridine possessing electron-donor properties (148).

Infusible, insoluble polymer is obtained by heating copper acetylacetonate with TCNE at 180-300°C in vacuo (145).

Acrylic fibres shrink on pyrolysis to carbon fibres; shrinkage is reduced by pyrolyzing the fibres under tension (149).

Silyl metal carbonyls on pyrolyzing at 773° K have yielded metal silicides (M = Co, Fe, Mn) (150).

Pyrophoric metals (iron, cobalt, bismuth, zinc, magnesium, lead, rare earths, etc.) and alloys are obtained by pyrolyzing metal alkyls and suitable metal salts of organic acids (151).

I.5 Present Work

In the intensive research initiated in the past two decades in an attempt to synthesize polymer systems of desired properties, capable of withstanding prolonged exposure to elevated temperatures, the effort has been three pronged:

i) improve existing polymers by introducing structural modifications,

ii) devise new organic systems tailored to meet the requirements,

iii) synthesize new class of inorganic or inorganic-organic (semi-organic) polymers.

In the first approach, conventional organic polymers consisting of inherently flexible chains were modified such that use temperature was raised or intractable inherently inflexible polymers were modified to yield more tractable systems.

In the second method of attack, a new generation of carbon-based polymers with inherently rigid chains tailored as required, has been developed.

The third line of attack was promoted by the unusual success of silicones developed in forties and the observation that many bond types are stronger than the carbon-carbon bond. Considerable effort has also been expended on the synthesis of metal chelate polymers.

Pyrolysis has supplemented the three-pronged attack. The polymers not degrading into low molecular weight.

products on pyrolysis will undergo transformation into products capable of withstanding elevated temperatures. Such products, depending on the original and modified structural characteristics, will have variations in their mechanical, optical, electrical and magnetic properties.

As presented earlier, few studies have been made on the pyrolysis of the polychelates and the study of the residual products of pyrolysis. Considerable work has been carried out in our laboratories on the polychelates (109,116). Since polychelates having through-conjugation have interesting electrical and magnetic properties (152), their products of pyrolysis can have unusual electrical and magnetic properties. The unpaired spins of the transition metal ion clusters can reorient parallel or anti-parallel with associated exchange interactions. The organic part may get transformed into free radical or biradical which may get stabilized. Further, the metallic centres may become centres of modified activity and may alter the mechanical strength of the material.

Keeping the above considerations in view, the work was planned as follows;

i) Preparation of bis-bidentate or polydentate ligands of different characteristics and having different functional groups;

ii) Preparation of the polychelates of the above ligands with transition element ions in general;

iii) Study of the electrical and magnetic properties of the above polychelates;

iv) Study of their thermal behaviour using DTA and TGA techniques; (heating rate 20°C per minute)

v) Pyrolysis of the polychelates under controlled conditions, and

vi) Study of the residual products of pyrolysis for their spectral, magnetic and electrical properties as possible.

Investigations carried out with the above points in view, the results obtained and the discussion of the results are presented in the following pages.