SYNTHESIS AND CHARACTERIZATION OF POLY(DIHALOPHENYLENE OXIDE)S AND ITS DERIVATIVES FROM DIAMMINE BIS(TRIHALOPHENOLATO) Cu(II) COMPLEXES

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Master of Science.

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This is to certify that we have read this thesis and that in our opinion it is fully adequate, in scope and quality, as a thesis for the degree of Master of Science.

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF POLY(DIHALOPHENYLENE OXIDE)S AND ITS DERIVATIVES FROM DIAMMINE BIS(TRIHALOPHENOLATO) Cu(II) COMPLEXES

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In this study, synthesis and characterization of poly(dihalophenylene oxide)s were done by thermal decomposition of diamminebis(trichlorophenolato) copper(II) and diamminebis(tribromophenolato) Cu(II) complexes in solid state. 2,4,6-trichlorophenol (TCP), 2,4,6-tribromophenol (TBP) and ammonia were used as ligands in the complex syntheses. The complexes were characterized by means of X-ray diffraction, FTIR, DSC, mass spectroscopy, magnetic susceptibility and C, H, N elemental analyses.

Synthesized complexes were decomposed thermally in solid state for the production of poly(dihalophenylene oxide)s. Polymerizations were carried out at two different conditions. In the first condition, the decomposition time was kept constant at 3 hours and temperature was varied for each sample to observe the effect of temperature on decomposition. In the second condition, the decomposition temperature was kept constant at maximum conversion temperature and the period of time was varied from 3 hours to 48 hours in order to define the effect of time on the decomposition. Synthesized polymers were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, DSC, SEM, FAAS and viscometric measurements.

At the end of the study, it was observed that, the percent conversion and the structure of the polymeric product depend on polymerization condition and the type of the starting complex.

Keywords: Poly(dihalophenylene oxide), diamminebis(trihalophenolato) complexes, thermal decomposition, solid state polymerization.

ÖZ

POLİ(DİKLOROFENİLEN OKSİT) VE TÜREVLERİNİN Cu(II) KOMPLEKSLERİNDEN SENTEZİ VE KARAKTERİZASYONU

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Bu çalışmada, poly(dihalofenilen oksit)lerin, diaminbis(triklorofenolat) Cu(II) ve diaminbis(tribromofenolat) Cu(II) komplekslerinin ısıl olarak bozunması ile sentezi ve karakterizasyonu yapılmıştır. Bu amaçla, komplekslerin sentezinde 2,4,6-triklorofenol (TCP), 2,4,6-tribromofenol (TBP) ve amonyak ligand olarak kullanılmıştır. Kompleksler X-ışını difraksiyonu, FTIR, DSC, kütle analizi, manyetik duyarlılık ve C, H ve N element analizleri kullanılarak karakterize edilmişlerdir.

Sentezlenen kompleksler, poli(dihalofenilen oksit) elde etmek için ısıl bozunmaya tabii tutulmuştur. Polimerleşme iki farklı koşulda gerçekleştirilmiştir. İlk koşulda, bozunma üzerinde sıcaklığın etkisini tayin etmek için, süre 3 saate sabit tutulup bozunma sıcaklığı değiştirilmiştir. İkinci koşulda, bozunma sıcaklığı en yüksek yüzde dönüşüm veren değerde sabit tutulup, süre 3 saatle 48 saat arasında değiştirilmiştir. Sentezlenen polimerler FTIR, ^{1}H-NMR, ^{13}C-NMR, DSC, SEM, FAAS ve viskometrik ölçümleriyle karakterize edilmiştir.

Çalışmanın sonunda, yüzde dönüşüm ve polimerin yapısının başlangıç kompleksinin türüne ve polimerleşme koşullarına bağlı olduğu gözlenmiştir.

Anahtar Kelimeler: Poli(dihalofenilen oksit), diaminbis(trihalofenolat) komplexleri, ısıl bozunma, katı halde polimerleşme.

To My Family

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ABBREVIATIONS

TCP : 2,4,6-Trichlorophenol
TBP : 2,4,6-Tribromophenol
$Cu(NH_3)_2(TCP)_2$: Diammine bis(2,4,6-trichlorophenolato) Cu(II) complex
$Cu(NH_3)_2(TBP)_2$: Diammine bis(2,4,6-tribromophenolato) Cu(II) complex
FTIR : Fourier Transform Infrared
DSC : Differential Scanning Calorimeter
NMR : Nuclear Magnetic Resonance
SEM : Scanning Electron Microscope
MS : Mass Spectrum
FAAS : Flame Atomic Absorption Spectrophotometer
Tg : Glass Transition Temperature

CHAPTER 1

INTRODUCTION

1.1 Poly(phenylene oxide)s

Poly(phenylene oxide)s are polyethers having aromatic groups connected by an oxygen linkage at the backbone [1]. They had been synthesized in various forms since 1916 because of mechanical, chemical, electrical and thermal properties. These polymers have high Tg values [2]. The largest commercial usage of poly(phenylene oxide)s is in Noryl (General Electric Co.) engineering resin, which are alloys of poly(2,6-dimethyl, 1,4-phenylene ether). Poly(dihalophenylene oxide)s are obtained by attachment of halogen atoms to the phenyl ring. These polymers have flame-retarding property due to the existence of halogens [3].

2,4,6-trihalophenols can be converted to poly(dihalophenylene oxide)s by a reaction that resembles free-radical initiated displacement polymerization. Either a copper or silver complex of phenols are heated to produce a branched product [4]. Poly(diphenylene oxide)s can be linear or branched, amorphous or crystalline and have high or low molecular weight depending on the type and the position of the substituent on the starting phenol [5]. Ether linkage is either at ortho- or para-position or both. When it is at para-position the polymer is called poly(1,4-phenylene oxide) (Figure 1.1a) and when it is at ortho-position it is called poly(1,2-phenylene oxide) (Figure 1.1b) and 1,4 and 1,2 addition may take place at the same monomeric unit (Figure 1.1c).

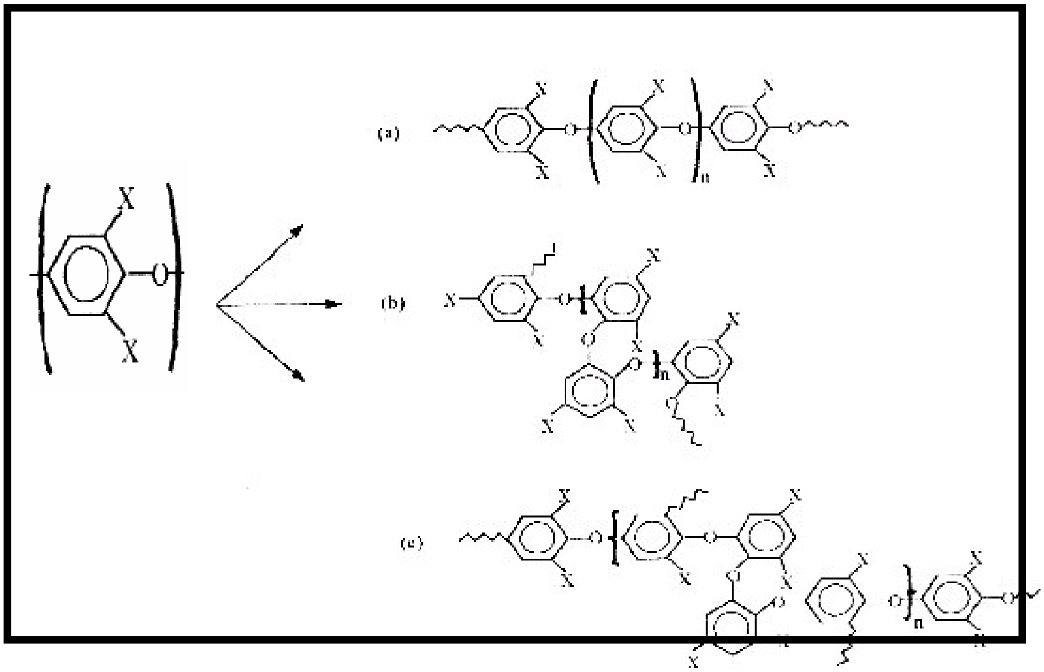


Figure 1.1. Possible structures of poly(halogenated phenylene oxide)s (X: Cl, Br, CH_3) (a) 1,4-addition (b) 1,2-addition (c) both 1,4 and 1,2-additions.

1.2 History of Poly(phenylene oxide)s

Poly(phenylene oxide)s have been synthesized from alkyl substituted or halogenated phenols for many years. Hunter and et. al. synthesized a poly(dihalophenylene oxide) first time in 1916 [6]. The synthesis was achieved from the decomposition of silver salts of trihalogenated phenols in the presence of ethyl iodide in hot benzene, into silver bromine and amorphous polymerized residue as follows;

$$nC_6H_2Br_3OAg \xrightarrow{EtI} nAgBr + (C_6H_2Br_2O)_n$$

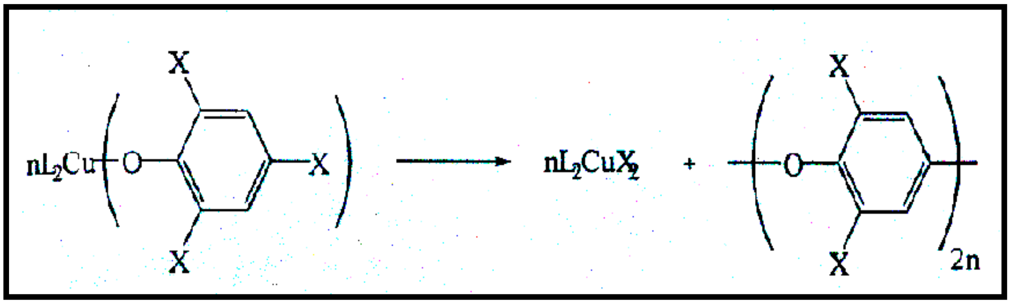
The obtained polymer was white amorphous powder and the estimated molecular weight was about 6000-12000.

In 1917, Hunter and co-workers studied on the polymerization of symmetrically substituted trihalophenols. They reported that iodine was displaced more rapidly than bromine and bromine was displaced more rapidly than chlorine and a para halogen reacted more rapidly than ortho halogen [7].

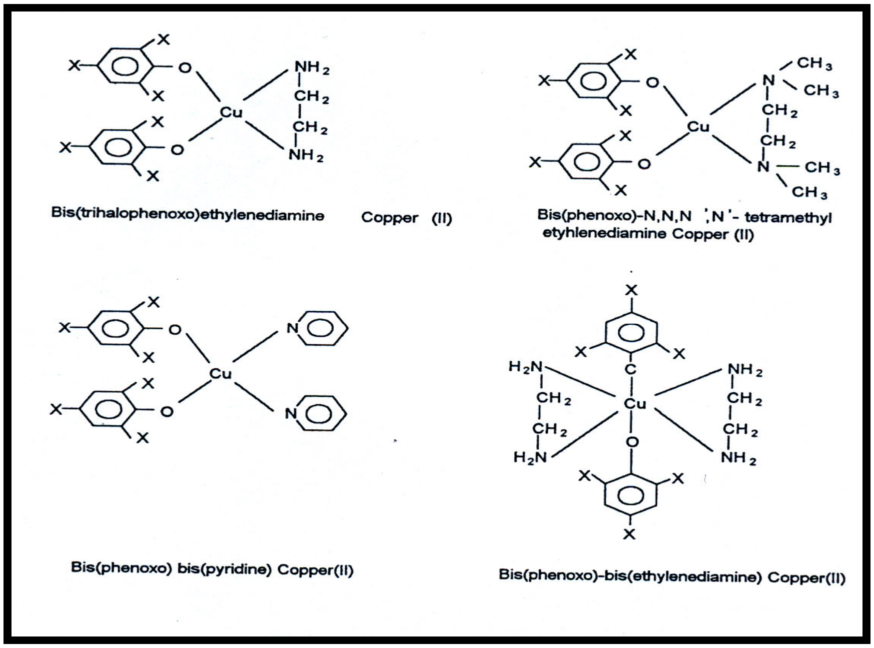
In 1932, Hunter and Whitney continued the study on the decomposition of certain penol metalic salts [8]. In 1959, Staffin and Price have worked the polymerization of 4-bromo-2,6-disubstituted phenol with several oxidizing agents such as ferricyanide, PbO_2, I_2, O_2 and light. They proposed a radicalic mechanism for the polymerization, where the displacement of bromine ion by phenoxy radical is taking place at the propagation step [9].

In 1962, Blanchard et. al. studied on the preparation and the characterization of bis(pyridine) copper(II) complexes. They showed that 4-halo-2,6-dimethyl phenols can be polymerized to high molecular weight of poly(2,6-dimethylphenylene ether)s by the action of cupric ions, providing pyridine is also present [10].

In 1969, J. F. Harrod studied the thermal decomposition of several copper(II) complexes containing various amine ligands [11]. He reported that the thermal stability of the complexes depends on the nature of the ligands. The phenoxo complexes with chelating ligands are highly resistant to thermal decomposition compared to non-chelating ligands. The suggested reaction was as follow;



J. F. Harrod prepared a series of phenoxo complexes of copper(II) containing a variety of halophenolato ligands of amine type ligands. The structures of these complexes are shown in Figure 1. 2. He reported that thermal stability of these complexes was lower with those ligands, which increase the oxidizing power of the copper(II).



Bis(trihalophenoxo)ethylenediamine Copper (II)

Bis(phenoxo)-N,N,N ',N '- tetramethyl etyhlenediamine Copper (II)

Bis(phenoxo) bis(pyridine) Copper(II)

Bis(phenoxo)-bis(ethylenediamine) Copper(II)

Figure 1.2. Structures of trihalophenolato copper complexes with neutral ligands

Since 1980's. Kısakürek and et. al. have been studying the polymerization of halogenated phenols from the decomposition of the transition and inert transition metal complexes with various amine ligands. Different types of decomposition techniques were employed for the decomposition of the complexes. They are electroinitiated in solution [12-26], thermally decomposed in solid state [27-42] and in solution [43-48]. In addition to decomposition method, type of the amine ligand and the type of the halogen substituted on the phenol ring were found to be effective on the structure, molecular weight and the the percent conversion of the polymeric product. The lowest molecular weight polymers are obtained in electroinitiated polymerization, and the highest with thermal decomposition in solution, where the solid state polymerization is close to electroinitiation with slightly higher values. The nature of the neutral amine ligand also affects the thermal decomposition and the structure of the polymer. The phenoxo complexes with chelating ligands were exceptionally resistant to thermal decomposition compared to non-chelating ligands increasing the induction periods of polymer formation [25, 28, 29, 49]. Bromine atom in the para-position of 2,4,6-trihalophenoxides results in polymers with higher linearity [16, 23, 50]. In the case of trichlorophenoxide, 1-2 and 1-4 addition is taking place at equal rates with non-chelating ligand pyridine in thermal polymerization, either in solution or in solid state and in electroinititation with ligands pyridine and ethylenediamine [49, 51, 52]. In addition to these, the effect of the type of the transition metal on the structure, molecular weight and the percent conversion of the polymeric product were also examined. Halogenated phenol complexes of Cu, Co and Ni with pyridine were synthesized and then decomposed. At the and of these studies, it was found that in solid state, Cu complexes[32, 43, 44] decompose much more easily than Co [33, 43, 46] and Ni [47] complexes.

1.3 Solid State Polymerization

1.3.1. History and General Aspects

Special interest sto study solid state polymerization were increased after invention of Ziegler Natta catalyst. In solid state polymerization, polymer obtained was expected to be crystalline and well oriented, due to small molecular movements in the crystall lattice [53]. It was assumed that, in this case, the polymerization propagates along the crystallographic axis of that monomer. However, it was reported that only a few kinds of monomers could yield crystalline polymer by solid state polymerization.

The polymerization of solid monomers presents unique problems when compared with polymerizations in liquid states. Since mobility of molecules in solid state is severely restricted, the rate of reaction will be determined by local concentrations of reactants. Moreover, changes in the crystal lattice during course of reaction may influence the rate of polymerization.

The first study about solid state polymerization was done by Schmitz and Lawton in 1951 [54]. They polymerized glycoldimethylacrylate explosively by ionization radiation.

Up to now, high energy radiation, X-rays, γ-rays, UV radiation, electron beam, thermal and chemical activators have been used for solid state polymerization. Adler et al found that acrylamide could be polymerized in solid state by high energy radiation [55]. It was expected that a well-oriented crystalline polymer would be obtained after polymerization due to limited mobility of molecules in solid matrix. However, resulting polymer was amorphous. This drew attention of scientists to study the effect of crystal structure on solid state polymerization. Besides, polymerization continued after removing sample from irradiation source which is called post polymerization. ESR studies showed that in the irradiated mixture of polymer and monomer trapped free radicals were present. When the residual monomer was not seperated precisely from polymer, these radicals lead to post polymerization.

Restaiona et al studied the polymerization of acrylamide and related monomers in 1956 [56]. The molecules of acrylamide in crystal lattice were in suitablelocation to form dimer. However, the addition of a third monomer to dimer molecule required an appreciable rearrangement. So crystal structure of monomer distrupted or polymerization enchainment did not proceed in crystallographic direction. Therefore, polymer obtained was amorphous. Some monomers have been found to polymerize faster in solid state than liquid state. For example, Chapiro showed that 3,3-bis(chloromethyl)cyclooxobutane was polymerized in solid but not in liquid state. This is prbably associated with a favorable steric configuration in solid phase [57].

Morawetz and Rubin observed polymerization of alkali metals of acrylic acid and methacrylic acid [58]. They showed that polymer conversion and polymer molecular weights are dependent on the kinds of alkali metals. Therefore different kinds of alkali metal salts of acrylic acid and methacrylic acid polymerized in different mechanism since they have different crystal structure.

Adler and Reams indicated that polymerization would proceed at the interphase between monomer and polymer of acrylamide after some polymer formed [59] . It was supported by an experiment in which acrylamide single crystal was divided into two parts, one part was wrapped with aluminum foil, other part was exposed to gamma radiation. After some time, the sample photographed under polarized microscope. In the photograph, the side polymerized was black, while other part was bright. Two sides were clearly different from each other. So, Adler believed that the crystal structure of acrylamide molecules exerted to influence on the polymerization because polymerization proceeded at the interphase between monomer and polymer. Adler et al explained that the reason for the formation of amorphous acrylamide polymer, was due to the structure of monomer, the C=C double bond (1.34 Å) opened and transformed to -C-C- single bonds (1.54 Å) during polymerization [60]. However, intermolecular distance between molecules decreased from Van der Walls distance of about 3.75 Å to 1.54 Å, C-C single bond length. When both changes combined, overall volume of the system was decreased about 12 %. That volume reduction created a strain in the crystal lattice. Therefore, the crystal structure broke down and caused the polymer to be amorphous.

The mechanism of polymerization is greatly influenced by monomer crystal geometry in the solid state. The change in the crystal structure most probably orients the molecules ina more favorable arrangements for polymerization of allylthiourea leading to a higher maximum conversion [61]. When IR spectrum of partially polymerized monomer was investigated, it was seen that, although monomer peaks were partially covered by broad amorphous polymer peak, the monomer molecules still retained their crystalline structure at 46 % conversion. The changes in relative intensities of monomer peaks during polymerization were most probably due to distortion of crystal morphology. The polymer was amorphous and isotropic; it always looked dark between crossed polarizers, where the monomer was anisotropic and looked bright except at extinction positions in polarizing microscope. The results proved that polymerization did not proceed by a two phase mechanism like the monomer-polymer interphase polymerization.

The effect of oxygen on the polymerization of allylthiourea was investigated by Usanmaz and Yılmaz [61]. The accelerating effect of oxygen was clear at conversions above 40 %. This suggests that the crystal structure becomes distorted with the formation of polymer to allow easier diffusion of oxygen.

The solid state polymerization of acrylamide showed that an inhibiting effect of oxygen on the polymerization process were observed. The strongly inhibiting effect of oxygen proves that the reaction has free radicalic mechanism [62].

1.3.2. Proposed Mechanism

The proposed mechanism for solid state polymerization is in addition polymerization. It is usually produced by a chain mechanism involving active centers of one short or another. Addition polymerization reaction involves essentially three steps;

i) Initiation
ii) Propagation
iii) Termination

Initiation: The first step is the activation of a monomer molecule to form a free radical.

$$M \xrightarrow{k_i} R^{\bullet}$$

Also if a catalyst, such as peroxides, is present it'll be activated to give radicals.

$$Cat \xrightarrow{k_d} 2R^{\bullet}$$

$$R_i = f\ k_i\ [Cat] \qquad (1)$$

Where f is the efficiency factor and k_i is the initation rate constant.

Propagation: A free radicalic add on to a double bond of a monomer molecule, thereby regenerating another free radical etc.

$$R + M \xrightarrow{\quad} RM^{\bullet}$$

....

....

$$RM_n^{\bullet} + M \xrightarrow{k_p} RM_{n+1}^{\bullet}$$

Where R is a primary radical, M is the monomer and RM_n is a growing polymer chain. The propagation rate equation used in conventional homogeneous polymer kinetics.

$$-d[M]/dt=k_p[M][R] \qquad (2)$$

Where k_p is the propagation rate constant, [M] is the monomer concentration and [R] is the total concentration of radical. Usually a steady state concentration of [R] is assumed at low conversions where [M] is high, that can be considered to be constant and desreases at higher conversions as [M] desreases.

Termination: The termination step involves the mutual annilation of activity of two radicals. This can take place in two ways. The two chains may terminate by combination.

$$RM_n^{\bullet} + RM_n^{\bullet} \xrightarrow{\qquad} P_{n+m}$$

or they may undergo disproportionation with the transfer of a hydrogen atom and the formation of an unsaturated end group.

$$RM_n^{\bullet} + RM_n^{\bullet} \xrightarrow{\qquad} P_n + P_m$$

$$P_n^{'}\text{—}CH_2\text{—}CH_2^{\bullet} + P_m^{'}\text{—}CH_2\text{—}CH_2^{\bullet} \xrightarrow{\qquad} P_n^{'}\text{—}CH_2\text{—}CH_3 + P_m^{'}\text{—}CH{=}CH_2$$

1.4 Complexes of Copper

The copper(II) ion is a typical transition metal ion which forms coordinate covalent complexes, but less typical in its reluctance to take up a regular octahedral or tetrahedral stereochemistry. Cu(II) ion with its d^9 electron configuration provides one of the best opportunities for the observation of Jahn-Teller effect [63]. Most cupric salts dissolve readily in water and form complex, which may be written as $[Cu(H_2O)_6]^{2+}$, keeping in mind that two of the water molecule are further away from the metal atom than the other four. Addition of ligands to such solutions leads to the formation of complexes by successive displacement of water molecules, for example NH_3 molecule displaces with water molecule to form $Cu(NH_3)(H_2O)_4^{+2}$, $Cu(NH_3)_2(H_2O)_4^{+2}$, $Cu(NH_3)_3(H_2O)_3^{+2}$, $Cu(NH_3)_4(H_2O)_2^{+2}$ complexes. The addition of fifth and sixth NH_3 molecules in the complex makes its color dark blue. This is because the amines produce a stronger field than water leading shift in the absorption band. Halide ion complexes are also formed in aqueous solution on addition of HCl, HBr, LiCl, LiBr to the solutions, all having flattened tetrahedral stucture [63].

In 1976, Rosalind and et. al. prepared the single crystal of bis(trichlorophenolato)diimidazole copper(II) monohydrate complex. The X-ray diffraction studies revealed that this complex was in distorted octahedron structure where the axial bond were due to the ortho-chlorine atoms of the trichlorophenols [64].

In 1981, Ainscough and et. al. prepared the bis(tribromophenolato)-diimidazole copper(II) complex. According to the magnetic moment studies of the complex, it was suggested that structure may contain binuclear copper(II) with bridging phenolate rings [65].

1.5 Aim of the Study

Up to now, poly(dihalophenylene oxide)s have been synthesized by different methods. The achieved polymers showed low or high molecular weight and linear or branched chain structures. It is well known that decomposition time and temperature, percent conversion, structure and the intrinsic viscosity of the polymers depend on the starting material. Keeping all these points in mind, the aim of the study can be summarized as;

a) To prepare $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes and characterize them by means of DSC, FTIR, mass spectroscopy, elemental analysis and magnetic susceptibility techniques.
b) To prepare poly(dihalophenylene oxide)s in solid state from $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes and characterize them by ^{1}H-NMR, ^{13}C-NMR, FT-IR, DSC, SEM, FAAS and viscometric measurements.
c) To investigate the effects of type of transition metal complexes and amine ligand on molecular weight, intrinsic viscosity and percent conversion of the polymers.

CHAPTER 2

EXPERIMENTAL

2.1.Reagents

2.1.1. 2,4,6-trichlorophenol (TCP) and 2,4,6-tribromophenol (TBP)

Analytical grade 2,4,6-trichlorophenol and 2,4,6-tribromophenol were purchased from Aldrich Chemical Co. Ltd. and used without further purification.

2.1.2. Ammonia (NH_3) and Copper Sulphate ($CuSO_4.5H_2O$)

Reagent grade ammonia (Aldrich Chemical Co. Ltd.) and copper sulphate (Merck) were used without further purification for preparation of the complexes.

2.1.3. Ethanol (C_2H_6O)

Ethanol (96%) was purchased from Aklar Company and used for precipitation of the polymers.

2.1.4. Toluene (C_7H_8)

It was purchased from Merck and used as a solvent to dissolve the polymer and to measure the intrinsic viscosity of the polymers.

2.1.5. Hydrochloric Acid (HCl)

Hydrochloric acid was used to dissolve the by-products formed during polymerization step of the polymer.

2.1.6. Sodium Hydroxide (NaOH)

Analytical grade sodium hydroxide (NaOH) was purchased from Merck and used without further purification.

2.1.7. Deuterated Chloroform ($CDCl_3$)

$CDCl_3$ was purchased from Merck and used for ^1H and ^{13}C-NMR measurements.

2.1.8. Potassium Bromide (KBr)

Spectroscopic grade KBr was provided from Merck and used to obtain FTIR spectra of the 2,4,6-trichlorophenol, 2,4,6-tribromophenol, synthesized complexes and polymers.

2.2. Apparatus and Instrument

2.2.1. Oven

Stuart Scientific type oven was used for the solid state decomposition of the complexes. The temperature range was between 50 ^oC - 250 ^oC with temperature fluctuation of $\pm1^oC$.

2.2.2. Automatic Viscometer

Schott Gerate AVS 400 model automatic viscometer equipped with Schott CT 1150 model thermostat was used to determine the viscosity of the polymers.

2.2.3. Differential Scanning Calorimeter (DSC)

Thermal Analyst 2000 DSC 910S Differential Scanning Calorimeter (DSC) from Du Pont was used to examine the thermal behaviour of the complexes and the glass transition temperatures (Tg) of the polymers. About 6-7 mg of the complex was insert to the holder and heated with a rate of 5 ^{o}C/min in air to observe the thermal behaviour. To observe Tg of the polymers again 6-7 mg of the polymer samples was used with a heating rate of 5 ^{o}C/min. Heating was continued up to 50 ^{o}C above the expected transition temperature. Then, it was cooled to 50 ^{o}C below the expected transition temperature by a cooling rate of 5^{o}C/min. Treatment of the polymer samples was performed under nitrogen atmosphere.

2.2.4. Nuclear Magnetic resonance Spectrometer (NMR)

^{1}H and ^{13}C-NMR decoupled spectra of samples were taken with BRUCKER Instruments, Avance Series (DPX 400), 400 MHz High Performance Digital FT-NMR Spectrometer by using $CDCl_3$ as a solvent and TMS as an internal reference.

2.2.5. Fourier-Transform Infrared Spectrometer (FTIR)

Nicolet 510 model FTIR spectrometer was used between 4000 and 400 cm^{-1} in order to obtain IR spectra of all trihalophenolato copper complexes and synthesized polymers by dispersing the samples in KBr pellets.

2.2.6.Carbon-Hydrogen-Nitrogen (CHN) Analyzer

The complexes were characterized by Leco 932 CHNSO elemental analyzer. The elemental analysis results have the experimental error ± 0.3.

2.2.7. Magnetic Susceptibility Balance

Sherwood Scientific magnetic suceptibility balance was used to determine the magnetic moment of the complexes. Magnetic susceptibilities of the complexes were measured at room temperature and magnetic moments (μ_{eff}) in a Bohr magneton were calculated.

2.2.8. Mass Spectrometer (MS)

Mass Spectroscopy data of the complexes were obtained at 190 ^{o}C using LC/MS Platform II Micromass UK (Electron Impact) mass spectrometer via personel computer for the control of the MS acquisition and analysis. It was used for characterizing the weight loss during solid state polymerization of the complexes.

2.2.9. Scanning Electron Microscobe (SEM)

Surface morphologies of polymers were inspected by a JEOL JSM – 6400 scanning electron microscobe having attachment Noran Instrument EDS - X-ray microanalysis system

2.2.10. Atomic Absorption Spectrophotometer

Philips 9200X FAAS was used for copper measurements at 324.8 nm resonance line of copper with a band-pass of 0.7 nm. Fuel-rich air-acetylene flame with a 50 mm burner slot was used for the atomization.

2.3. Syntheses of the complexes and the polymers

2.3.1. Synthesis of diamminebis(2,4,6-trichlorophenolato) copper(II) complex

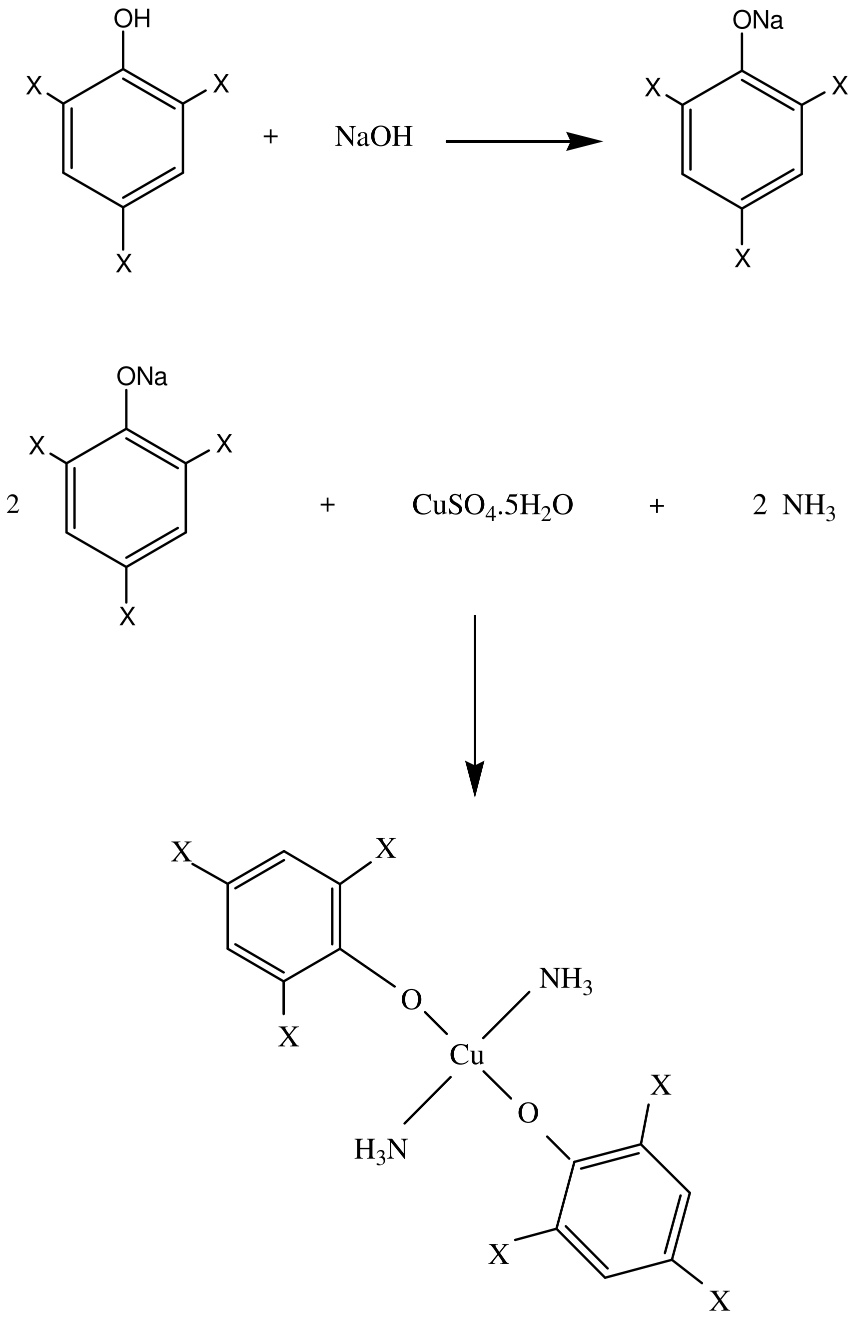
An aqueous solution (42 ml) of sodium 2,4,6-trichlorophenolate (0.805 g, 0.00408 mol), which was prepared by adding excess concentrated NaOH (0.428 g, 0.01205 mol) to 2,4,6-trichlorophenol in water, was added dropwise to a concentrated aqueous solution (10 ml) of $CuSO_4$ (0.325g, 0.00204 mol) with stirring. Immediate formation of a dark brown precipitate was observed. This dark brown precipitate turned light blue after after addition of the sodium 2,4,6-trichlorophenolate solution was complete. Concentrated ammonia (0.1338 mol, 10 ml) solution was added to this mixture until the light-blue precipitate dissolved to give a clear dark-blue solution. Upon leaving this solution on the bench for dseveral days, dark-brown crystals were formed. These crystals were collected, washed with a small amount of cold water and dried in a vacuum overnight.

2.3.2. Synthesis of diamminebis(2,4,6-tribromophenolato) copper(II) complex

An aqueous solution (25 ml) of sodium 2,4,6-tribromophenolate was prepared by mixing excess NaOH (0.21500 g, 0.00537 mol) dissolved in water (10 ml) with 2,4,6-tribromophenolate in water (15ml). This solution was added dropwise to a concentrated aqueous solution (5ml) of $CuSO_4$ (0.21073 g, 0.00132 mol) with stirring. Initially, the formation of a light-brown precipitate was observed. The precipitate color then turned to light blue after addition of all of the 2,4,6-tribromophenolate solution. Concentrated ammonia (5.2 ml, 0.06947 mol) and water (60 ml) were added to this mixture until the light-blue precipitate dissolved to give a clear dark-blue solution. Upon leaving this solution on the bench for several days, dark brown preicipitates were formed. These crystals were collected, washed with a small amount of cold water and dried in a vacuum overnight.

General reaction for the complex formation was;

(X: Cl and Br)



2.3.3. Characterization of Complexes

All of the complexes were characterized by FTIR, DSC, elemental analysis, mass spectroscopy and magnetic susceptibility. FTIR samples were prepared by dispersing the sample in KBr pellets. C, H and N contents were investigated by elemental analysis. DSC measurements and mass spectroscopy were also applied to determine the behaviour on heating and to characterize the decomposition products. Magnetic susceptibility measurements were also performed to find the number of unpaired electrons on metal ion in the prepared complexes.

2.3.4. Polymer Synthesis Through the Decomposition of the Complexes

For solid state polymerization, about 3 g of complex in a glass sample holder (3.5 cm in height and 3 cm in diameter) was inserted to another iron sample holder. It was allowed to stand in the oven at a given temperature for a given time under oxygen atmosphere. The color of the polymers obtained from this procedure was light brown, instead of white. Decomposed product was allowed to cool to room temperature and weighed to determine the weight loss during thermal decomposition. The decomposed complex was dissolved in minimum amount of toluene and filtered into large amount of ethyl alcohol containing a few drops of concentrated hydrochloric acid. After the seperation of undissolved estimated by product ($Cu(NH_3)_2X_2$) by filtration, precipitated polymer was filtered, washed with ethanol and dried until constant weight under vacuum. Two different types of decomposition sets were applied. In the first set, the decomposition time was kept constant at 3 hours and the temperature was varied for each sample to observe the effect of temperature on decomposition (Table 2.1.). In the second set, decomposition temperature was kept constant at the maximum conversion temperature and the time period was varied from 3 hours to 48 hours. By this way, the effect of time on the decomposition was investigated.

Table 2.1. Decomposition conditions for the complexes

Complex	Decomposition temperatures for 3 hours			State after decomposition
	Lowest	Max. Conv.	Highest	
$Cu(NH_3)_2(TCP)_2$	110 ^oC	190 ^oC	210 ^oC	powder and melt
$Cu(NH_3)_2(TBP)_2$	130 ^oC	190 ^oC	250 ^oC	powder and melt

2.3.5. Characterization of the Polymers

Polymers were characterized by FTIR, ^{1}H-NMR, ^{13}C-NMR, DSC and viscometric measurements. FTIR spectra were taken by preparing KBr pellets of the polymers and NMR spectra were taken in deuterated chloroform solution. Intrinsic viscosity values (g/dL) of polymer samples were determined in toluene at 30^{o}C. Glass transition temperatures were examined by using differential scanning calorimeter (DSC) under nitrogen atmosphere.

CHAPTER 3

RESULTS AND DISCUSSION

This section consists of two parts. The first part includes the characterization of the $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes. The second part includes the synthesis and characterization of the poly(dichlorophenylene oxide)s and poly(dibromophenylene oxide)s.

3.1. Characterization of the complexes

The synthesis of single crystals of $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes are given in experimental section. These prepared complexes were characterized by X-ray diffraction, elemental analysis, FTIR, magnetic susceptibility, DSC and mass spectroscopy.

3.1.1. Crystal structure

The crystal structure of these complexes have been determined by X-ray diffraction. Both of the Cu(II) complexes crystalize in the monoclinic system and form *trans*-planar CuO_2N_2 coordination sphere, with the fifth and sixth coordination sites occupied by Cl and Br atoms from the phenoxide ions for $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$, respectively, (Figure 3.1.a and b), (Figure 3.2.a and b) and Table 3.1 [66,67]. It was found that both of the Cu(II) complexes have a tetragonally elongated octahedral structure and some of the geometrical parameters such as Cu─O , Cu─N and Cu─Halogen distances are given in Table 3.2.a and b [66,67].

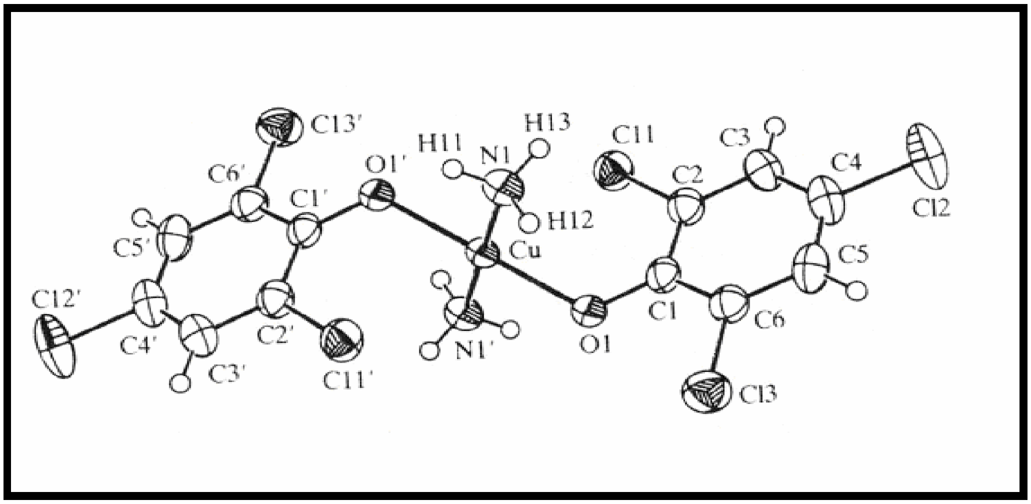


Figure 3.1a. *ORTEP-3* (Farrugia, 1997) drawing of Cu$(NH_3)_2$(TCP)$_2$ with the atom-numbering scheme. Displacement ellipsoid are drawn at the 50 % probability level and H atoms are shown as small circles with arbitrary radii.

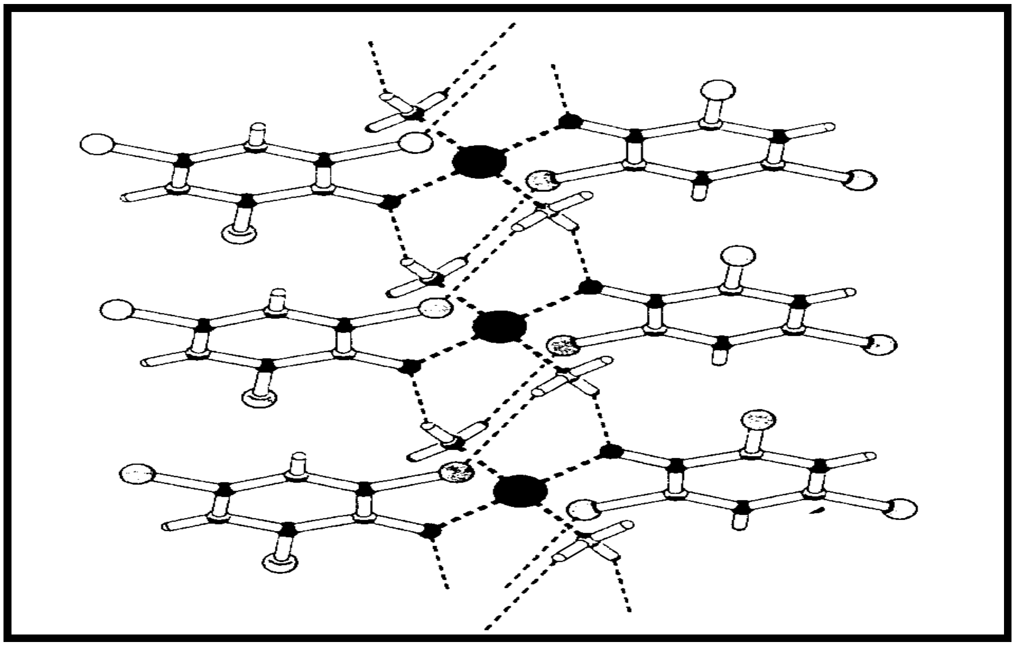


Figure 3.1b. *PLATON* (Spek, 1990) drawing illustrating the hydrogen bonding for Cu$(NH_3)_2$(TCP)$_2$.

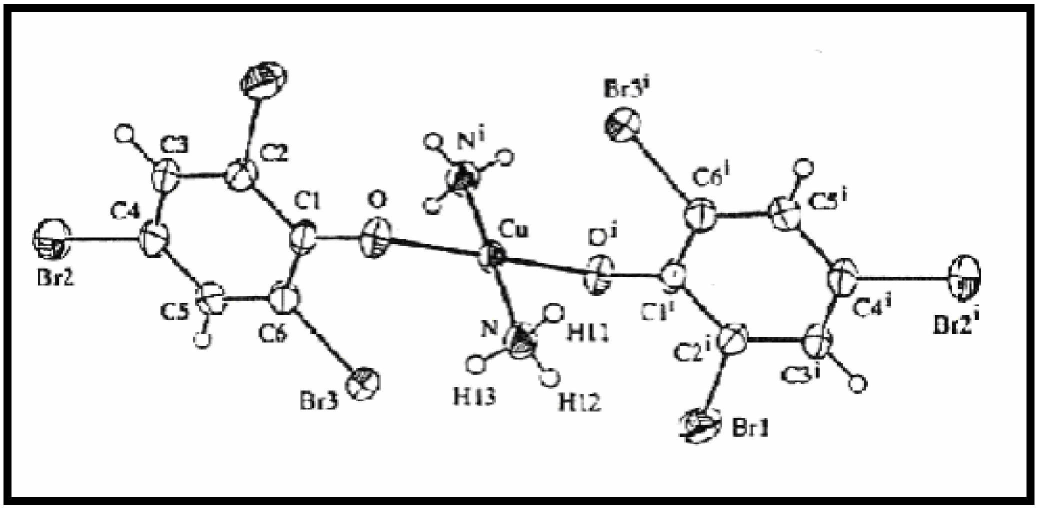


Figure 3. 2a. *ORTEP-3 for Windows* (Farrugia, 1997) drawing of $Cu(NH_3)_2(TBP)_2$ with the atom-numbering scheme. Displacement ellipsoid are drawn at the 50 % probability level and H atoms are shown as small circles of arbitrary radii.

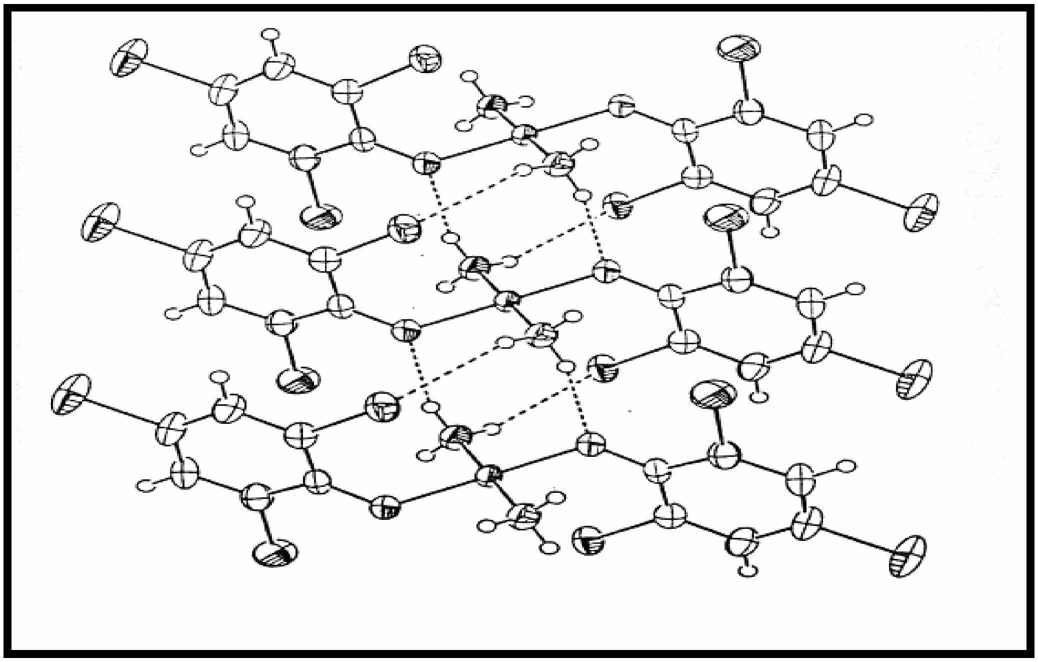


Figure 3. 2b. PLATON 99 (Spek, 1990) drawing illustrating the hydrogen bonding for $Cu(NH_3)_2(TBP)_2$ complex.

Table 3. 1. Crystal data of $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$.

	$Cu(NH_3)_2(TCP)_2$	**$Cu(NH_3)_2(TBP)_2$**
Crystal System	Monoclinic	Monoclinic
Space Group	$P2_1/n$	$P2_1/n$
a (Å)	4.7711 (7)	4.8249 (5)
b (Å)	12.4592 (10)	13.0267 (16)
c (Å)	14.9907 (13)	15.5518 (11)
β (°)	94.3700 (1)	90.7660 (7)

Table 3. 2. a) Selected bond lengths and bond angles of $Cu(NH_3)_2(TCP)_2$

Cu-O1	1.946 (2)	Cl2-C4	1.747 (3)
Cu-N1	1.984 (2)	Cl3-C6	1.738 (3)
Cu-Cl1	2.982 (1)	O1-C1	1.312 (3)
Cl1-C2	1.742 (3)		
O1-Cu-N1	90.66 (9)	Cl1-C2-C3	118.4 (2)
Cl1-Cu-Cl1^{i}	179.99 (1)	Cl2-C4-C3	119.2 (2)
Cu-O1-C1	123.7 (2)	Cl2-C4-C5	119.3 (2)
O1-C1-C2	123.9 (3)	Cl3-C6-C1	118.0 (2)
O1-C1-C6	122.0 (3)	Cl3-C6-C5	118.4 (2)
Cl1-C2-C1	117.9 (2)		

Table 3. 2. b) Selected bond lengths and bond angles of $Cu(NH_3)_2(TBP)_2$

Cu-O	1.943 (5)	Br2-C4	1.903 (8)
Cu-N	1.977 (6)	Br3-C6	1.909 (7)
Cu-Br3	3.129 (1)	O-C1	1.322 (8)
Br1-C2	1.888 (8)		
N-Cu-O	89.1 (2)	Br1-C2-C1	118.5 (5)
N-Cu-O^i	90.9 (2)	Br1-C2-C3	117.9 (6)
Br3-Cu-N	87.1 (2)	Br2-C4-C3	118.9 (6)
Br3-Cu-O	70.9 (2)	Br2-C4-C5	119.5 (7)
Cu-O-C1	123.7 (4)	Br3-C6-C1	118.4 (5)
O-C1-C2	122.1 (7)	Br3-C6-C5	117.5 (6)
O-C1-C6	123.8 (6)		

Intermolecular hydrogen bonds hold the complex molecules together in a one-dimensional chain. The hydrogen bonds are formed between H atoms of ammonia and the halogen of one 2,4,6-trihalophenol ligand and the oxygen of the second 2,4,6-trihalophenol ligand, which are in trans position (Fig 3.1.b and Fig 3.2.b.)

3.1.2. Elemental Analysis

The theoretical and experimental analysis results of C, H and N elements of $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes are given in Table 3. The theoretical and the experimental results are in good agreement within the experimental error range [± 0.3]

Table 3. 3. Elemental analysis results of $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$

Complexes	% C Theo & Exp*	% H Theo & Exp	% N Theo & Exp
$Cu(NH_3)_2(C_6H_2Cl_3O)_2$	29.383 & 29.500	2.059 & 2.160	5.713 & 5.680
$Cu(NH_3)_2(C_6H_2Br_3O)_2$	19.030 & 19.270	1.334 & 1.366	3.700 & 3.555

* Theo & Exp = Theoretical and experimental elemental analysis values.

3.1.3. FTIR

FTIR spectra of the $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes are given in Figure 3.3 a and b, respectively. The FTIR pattern of both complexes are very similar to each other except 630-832 cm^{-1} region. In this region, it is possible to observe C-Cl and C-Br stretching frequencies. The characteristic bands of the prepared complexes are given in Table 3. 4.

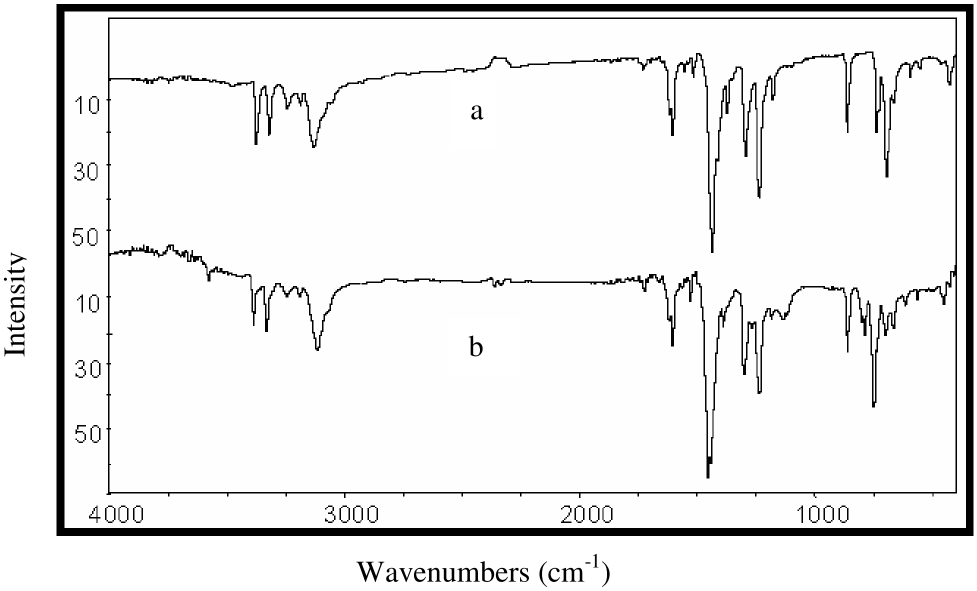


Figure 3. 3. FTIR spectrum of **a)** $Cu(NH_3)_2(TCP)_2$, **b)** $Cu(NH_3)_2(TBP)_2$

Table 3.4. The characteristic bands of the complexes

	Cu $(NH_3)_2(TCP)_2$	Cu $(NH_3)_2(TBP)_2$
ν (N-H) and ν (C-H) aromatic	3420-3000	3420-3000
ν (aromatic rings)	1605	1605
ν (C=C) ring stretchings	1510-1270	1490-1260
ν (C-O)	1237	1239
ν (C-H) bending	860	862
ν (C-Cl)	832-630	___
ν (C-Br)	___	760-630
ν (C=C) bending	454	431

3.1.4. Magnetic Susceptibility

Magnetic susceptibility measurements was performed at the room temperature using a Sherwood magnetic susceptibility balance. The magnetic moment values of $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes were found 1.84 and 1.81 μB, respectively. Calculated spin-only magnetic moments (μ/μB) for a single unpaired electron complexes is 1.73 μB. The slight increase in spin-only magnetic moment values may raise from the mixing of an orbitally degenerate excited state into ground state via spin-orbit coupling [68]. Consequently, the observed magnetic moments for the prepared complexes are consistent with a single unpaired electron. As stated before, the prepared Cu(II) complexes, which has nine d electrons, form six coordinated complexes with a tetragonally elongated octahedral structure. The distortion from perfect octahedral structure causes splitting of t_{2g} (d_{zx}, d_{yz}, d_{xy}) and e_g (d_{x2-y2}, d_{z2}) degenerate energy levels which is known as Jahn-Teller effect. Therefore, the position for a single unpaired electron in the ground state electron configuration of the prepared Cu(II) complexes can be written as $(d_{x2-y2})^1$. Magnetic susceptibility result showed that the oxidation state of copper in the prepared complexes is +2.

3.1.5. DSC

Thermal behavior of the complexes was studied by DSC measurements. DSC thermograms were taken with a heating rate of 1 ^{o}C/min under atmospheric condition for both complexes. DSC thermograms of $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes are shown in Figure 3. 4.(a and b) respectively. A sharp and broad exothermic peaks were observed at 165.82 ^{o}C and 187.46 ^{o}C for $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$, respectively. These exothermic peaks can be attributed to the new bond formation during polymerization.

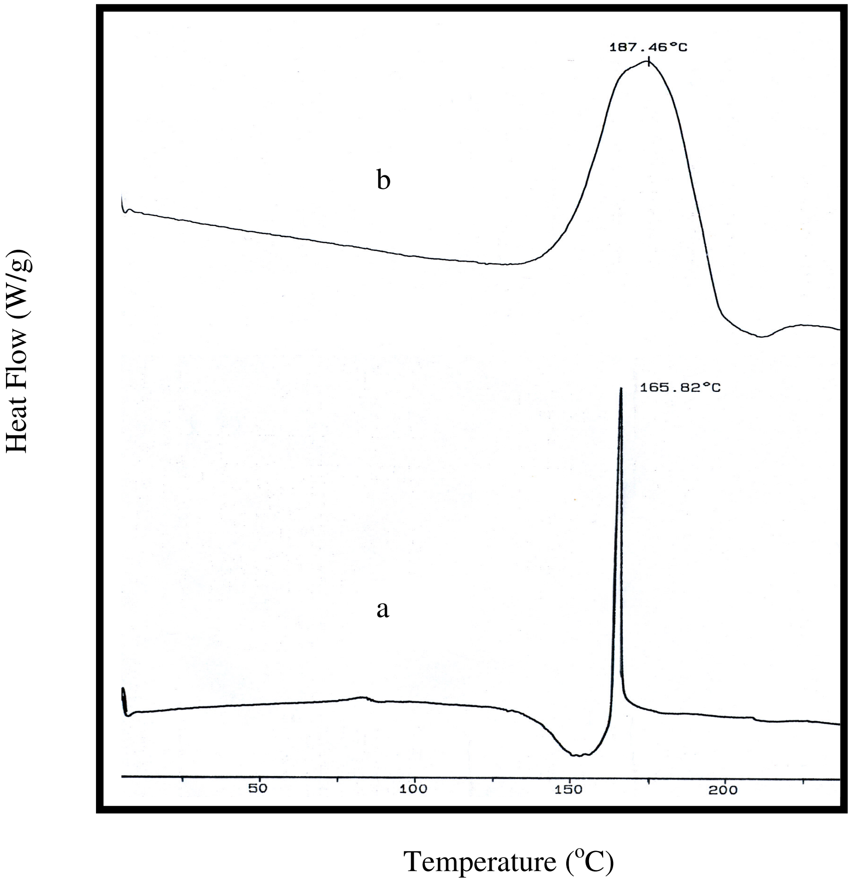


Figure 3. 4. (a) DSC thermogram of $Cu(NH_3)_2(TCP)_2$
(b) DSC thermogram of $Cu(NH_3)_2(TBP)_2$

3.1.6. Mass Spectroscopy

Synthesis of the polymers through the thermal decomposition of the complexes results in a weight loss of the initial complex due to the formation of gaseous products during the polymerization. $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ were subject to the mass spectroscopy to understand the origin of the gaseous product. The main peaks of interests, their assignments and originating ligands were given in Table 3.5, 3.6, 3.7. Results of the mass spectroscopy imply that the gaseous products originate from the loss of mainly neutral amine ligands and to some extend from the loss of phenol. All these result explain the nature of the weight loss in the initial complex during the polymerization process. The acceptable error limit in data evaluation is ± 2 units.

Table 3. 5. Possible origin of the peaks detected by MS. (mass / charge)

Peaks from TCP	Peaks from TBP	Peaks from Ammonia
$C_6H_2Cl_3O$ (197)	$C_6H_2Br_3O$ (330)	NH_3 (18)
$C_6H_2Cl_2O$ (160)	$C_6H_2Br_2O$ (248)	
C_6H_2ClO (125)	C_6H_2BrO (170)	
C_6H_2O (90)	C_6H_2O (90)	
$C_5H_2Cl_3$ (168)	$C_5H_2Br_3$ (302)	
$C_5H_2Cl_2$ (133)	$C_5H_2Br_2$ (222)	
C_5H_2Cl (98)	C_5H_2Br (142)	
C_5HCl_2 (132)	C_3HBr_2 (197)	
Cl (36)	C_3HBr (117)	
C_6H_3Cl (111)	Br (80)	
C_6Cl_4 (214)	C_3HBr_2O (213)	
C_2H_2Cl (62)	Br_2 (160)	
	CH_2BrO (110)	
	C_5H_5 (65)	
	C_3H_2OBr (134)	
	C_6Br_4O (406)	

Table 3.6. MS data for $Cu(NH_3)_2(TCP)_2$

Relative Intensity (%)	**M / Z**	**Possible origin of the peak**
22.74	196	TCP
16.29	18	Ammonia
16.03	36	TCP
10.65	97	TCP
9.49	112	TCP
9.13	132	TCP
6.45	213	TCP
5.01	160	TCP
4.21	62	TCP

Table 3.7. MS data for $Cu(NH_3)_2(TBP)_2$

Relative Intensity (%)	**M / Z**	**Possible origin of the peak**
29.26	110	TBP
27.26	18	Ammonia
9.93	82	TBP
9.42	160	TBP
9.03	213	TBP
3.32	135	TBP
3.07	405	TBP
2.96	228	TBP
2.89	330	TBP
2.16	65	TBP

3.2. Polymer Synthesis

Solid state thermal polymerization of $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ were performed at two different conditions. In the first condition, the time was kept constant at 3 hours and temperature was varied. In the second condition, temperature was kept constant at the maximum conversion temperature and time was varied from 3 hours to 48 hours.

For all synthesis, percent conversion and weight loss were calculated as follows;

$$\% \text{ Conversion} = \frac{\text{Weight of the polymeric product}}{\text{Initial weight of the complex}} \text{ x } 100$$

$$\% \text{ Weight loss} = \frac{\text{Weight loss}}{\text{Initial weight of the complex}} \text{ x } 100$$

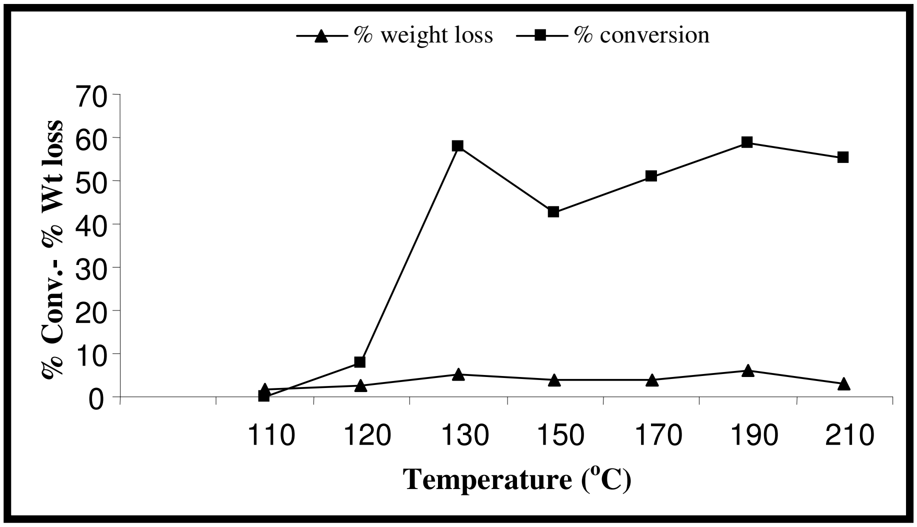
Weight loss = Initial wt of complex – Wt of complexes after decomposition

$Cu(NH_3)_2(TCP)_2$

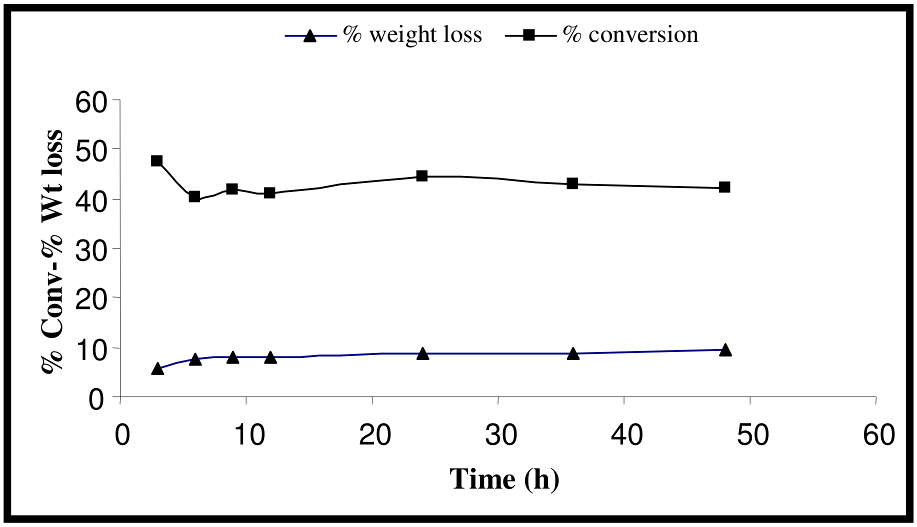
The polymerization of 3 gram of $Cu(NH_3)_2(TCP)_2$ complex was studied within a temperature range of 110 ^oC – 210 ^oC for about 3 hours. Percent conversions and percent weight losses were calculated according to the given formula above and tabulated values are given in Table 3. 8. Two maximum percent conversions (58.0 and 58.5) % and % weight losses (5.1 and 6.0) were observed at 130 ºC and 190 ºC, respectively. MS studies revealed that the weight loss mainly originated from phenol, which results from the reduction of the phenol content. DSC thermogram of the $Cu(NH_3)_2(TCP)_2$ complex indicated a single sharp exothermic peak at 165.82 ºC and broad endothermic peak at about 150 ºC, could be due to melting of the by-product. % conversion slightly increase to 8.0 % at 120 ^oC and followed by a sharp increase up to 58.0 % at 130 ^oC. Then % conversion was slightly changed with temperature between 190 °C (42.7) – 210 °C (58.5). The % weight loss slightly increased as the temperature increased. When the temperature was kept constant at maximum conversion temperature of 190 °C and the time was varied from 3 hours to 48 hours for 2 g complex, the % weight loss and % conversion were slightly affected.

Table 3.8. % Conversion and % Weight loss data for $[Cu(TCP)_2(NH_3)_2]$

T (°C)	Time (h)	% Weight loss	% Conversion
110	3	1.6	0.1
120	3	2.8	8.0
130	3	5.1	58.0
150	3	4.0	42.7
170	3	3.9	50.9
190	3	6.0	58.5
210	3	2.8	55.3
190	3	6.0	47.6
190	6	7.7	40.3
190	9	7.9	41.7
190	12	8.1	40.9
190	24	8.6	44.4
190	36	8.9	42.9
190	48	9.6	42.2



(a)



(b)

Figure 3.5.(a) % Conversion vs. Temperature and % Weight loss vs. Temperature graph of $Cu(NH_3)_2(TCP)_2$ complex at constant decomposition time (3 hours)

(b) % Conversion vs. Time and % Weight loss vs. Time graph of $Cu(NH_3)_2(TCP)_2$ complex at constant decomposition temperature (190 °C)

Cu $(NH_3)_2(TBP)_2$

Similar to the polymerization of $Cu(NH_3)_2(TCP)_2$, $Cu(NH_3)_2(TBP)_2$ was also polymerized within a temperature range of 130 °C – 250 °C for 3 hours. The percent conversions and percent weight losses were again calculated according to the previously given formula and the values were tabulated in Table 3. 9. Maximum conversion value of 59.3 % was achieved at 190 °C. DSC thermogram of $Cu(NH_3)_2(TBP)_2$ showed a broad exothermic peak at 187.46 °C, which could be related to the significant increase in the percent conversion values between 170 – 190 °C. % conversion and % weight losses sharply increases to 59.3 %, 4.9 % at 190 °C and slightly decreases to 44.2 %, 2.9 % at 250 °C, respectively. When the temperature was kept constant at maximum conversion temperature of 190 °C, % weight loss highly increases at longer time durations whereas % conversion was not affected by the higher % weight loss.

Table 3.9. % Conversion and & weight loss data of $Cu(NH_3)_2(TBP)_2$ complex

T (°C)	Time (h)	% Weight loss	% Conversion
130	3	0.5	8.8
150	3	1.0	34.4
170	3	3.3	54.7
190	3	4.9	59.3
210	3	6.5	52.0
230	3	4.6	50.3
250	3	2.9	44.2
190	3	4.9	59.3
190	6	7.5	47.8
190	9	10.5	52.4
190	12	11.3	49.9
190	24	12.8	50.6
190	36	14.6	51.5
190	48	16.0	50.8

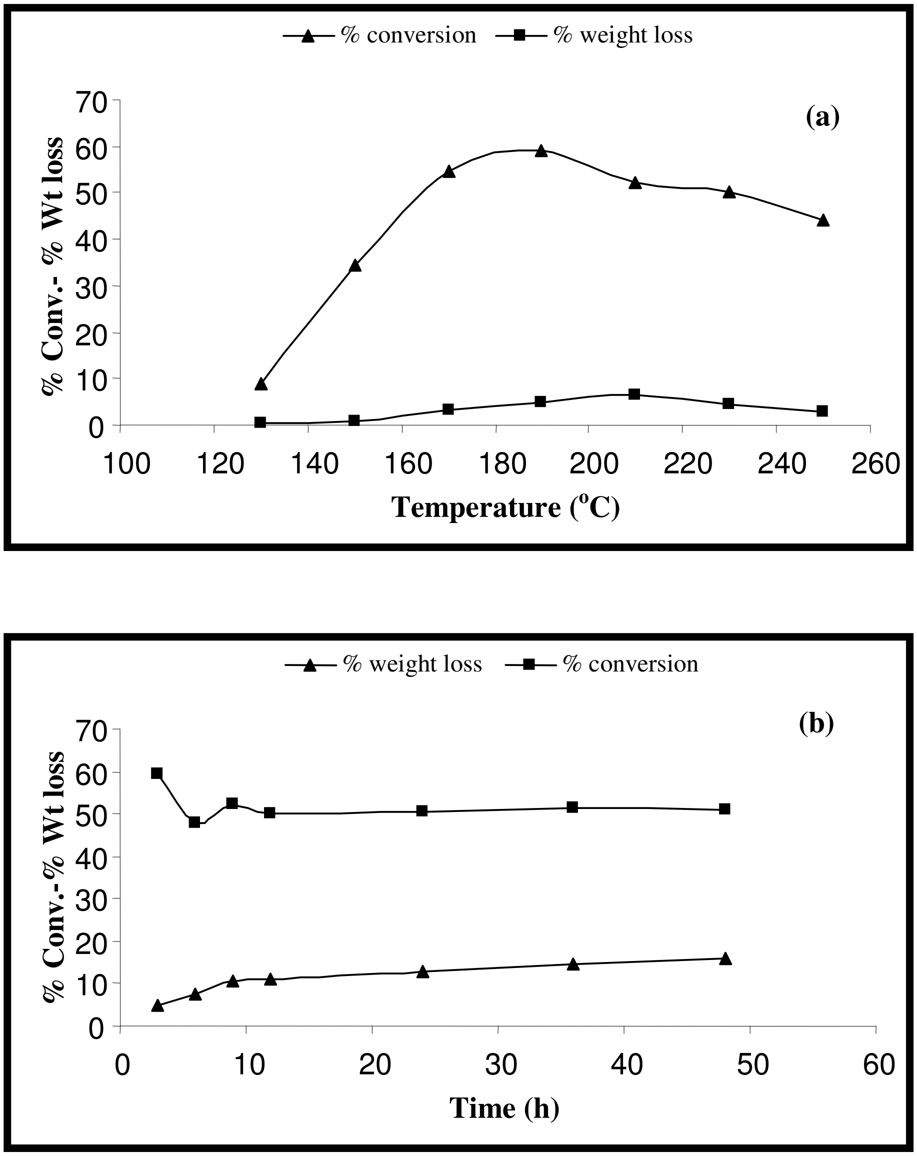
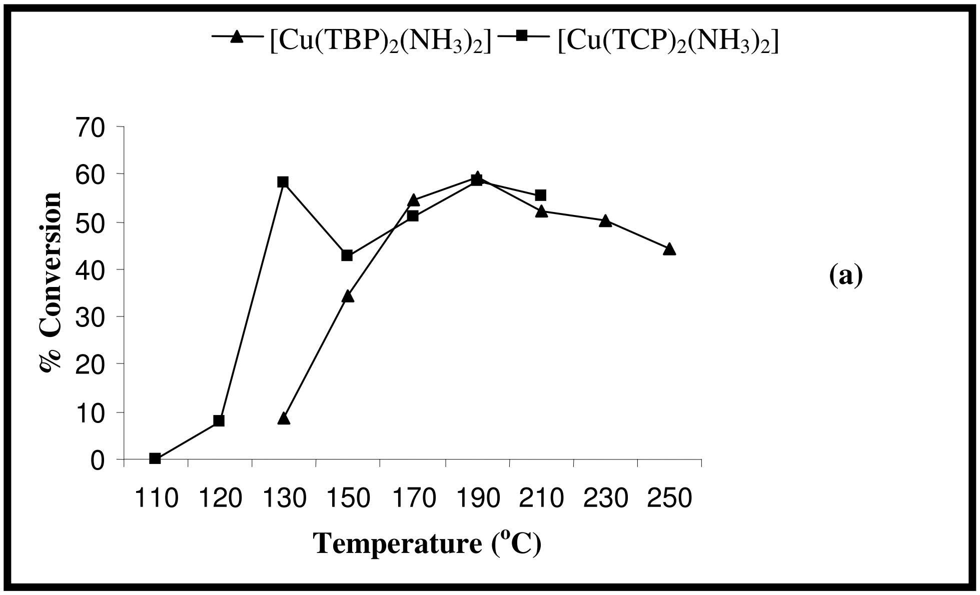


Figure 3.6.(a) % Conversion vs. Temperature and % Weight loss vs. Temperature graph of $Cu(NH_3)_2(TBP)_2$ complex at constant decomposition time (3 hours)
(b) % Conversion vs. Time and % Weight loss vs. Time graph of $Cu(NH_3)_2(TBP)_2$ complex at constant decomposition temperature (190 °C)

The comparison of percent conversion versus time, Figure 3.7.a and percent conversion versus temperature, Figure 3.7.b for $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ indicated similar trend for both complexes except at 130 ºC for

$Cu(NH_3)_2(TCP)_2$ complex. These similar observations might be due to the same crystal structure for both Cu(II) complexes



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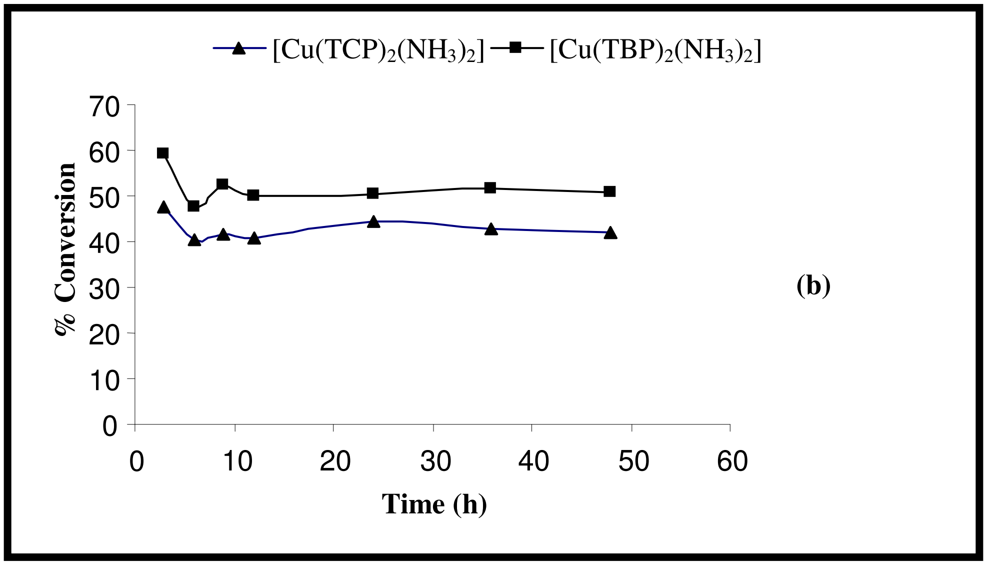


Figure 3.7.(a) Dependence of the polymerization yield of the $[Cu(TBP)_2(NH_3)_2]$ and $[Cu(TCP)_2(NH_3)_2]$ complexes on decomposition temperature (decomposition time = 3 h). **(b)** Dependence of the polymerization yield of the $[Cu(TBP)_2(NH_3)_2]$ and $[Cu(TCP)_2(NH_3)_2]$ complexes on decomposition time (Decomp. Temp. = 190 °C).

3.3 Characterization of the polymers

3. 3. 1. NMR

***^{1}H*-NMR**

^{1}H-NMR spectra of the polymers obtained from decomposition of the complexes were shown in Figure 3.8. and 3.9. ^{1}H-NMR spectrum of the polymer obtained from $Cu(NH_3)_2(TCP)_2$ complex was characterized by the peak at 7.63 ppm due to the 1-2 addition and by the peak at 7.00 ppm due to the 1-4 addition (Figure 3.8.). The broader peaks at the higher field indicate the presence of both the 1-2 and 1-4 addition at the same monomeric unit. As a result, it is clear that 1-2 addition is predominant than 1-4 addition for this polymeric product.

Polymer obtained from $Cu(NH_3)_2(TBP)_2$ complex was also characterized by ^{1}H-NMR spectra. The peaks at nearly 7.63 ppm and 7.00 ppm indicate mainly 1-2 addition and slightly 1-4 addition, respectively. Both 1-2 and 1-4 addition were again observed as broader peaks at the higher field at the same monomeric unit (Figure 3.9.). In this spectra 1-2 addition highly predominant than 1-4 addition.

***^{13}C*-NMR**

^{13}C - {^{1}H} - NMR spectra of the polymers obtained from the starting Cu(II) complexes are given in Figure 3.10. and 3.11. Theoretical ^{13}C-NMR chemical shift data for the main three possible 1-2 , 1-4 or both 1-2 and 1-4 addition products were calculated using appropriate correlation tables [69] and binary relations between the observed and the calculated data for both polymers are listed in Figure 3.12 and Figure 3.13.

Within the three possible structures of synthesized poly(dichlorophenylene oxide), ^{13}C-NMR shift data show that all possible structures a, b and c seem to be the possible structure leading to a 1-2 addition as confirmed by ^{1}H-NMR (Figure 3. 12).

For the poly(dibromophenylene oxide), again a, b and c structure seem to be possible structures according to ^{13}C-NMR shift data calculations (Figure 3.13). But ^{1}H-NMR confirm that 1-2 addition is more predominant.

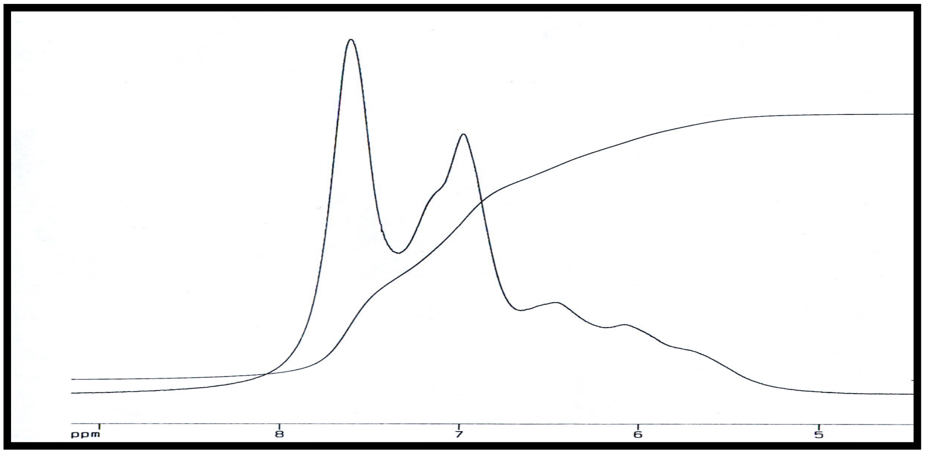


Figure 3. 8. ^{1}H-NMR Spectrum of the polymer obtained from $Cu(NH_3)_2(TCP)_2$ complex

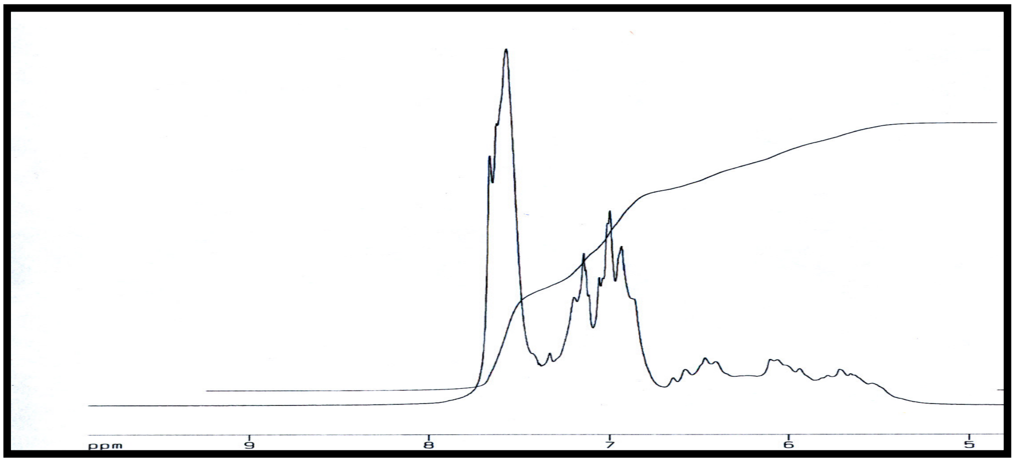


Figure 3. 9. ^{1}H-NMR Spectrum of the polymer obtained from $Cu(NH_3)_2(TBP)_2$ complex

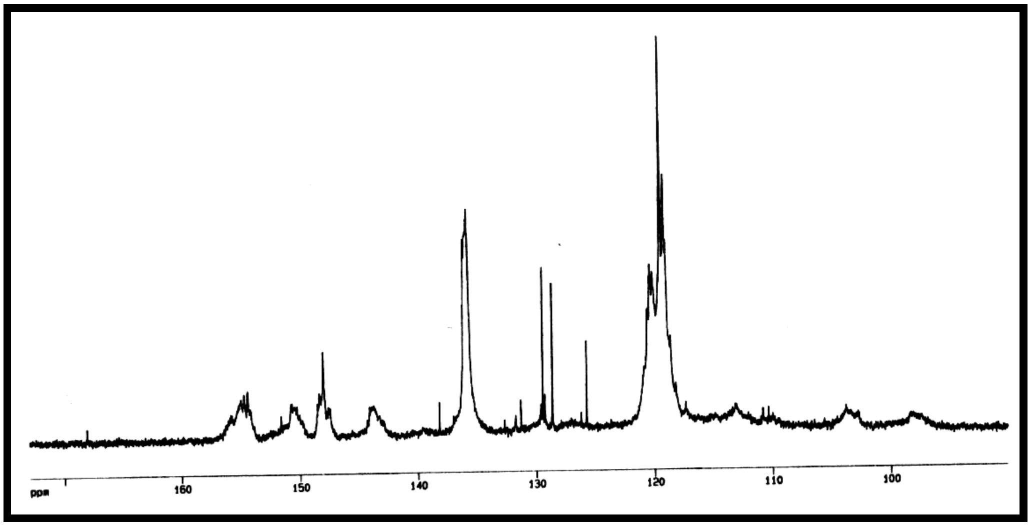


Figure 3. 10. ^{13}C-NMR Spectrum of the polymer obtained from $Cu(NH_3)_2(TCP)_2$ complex

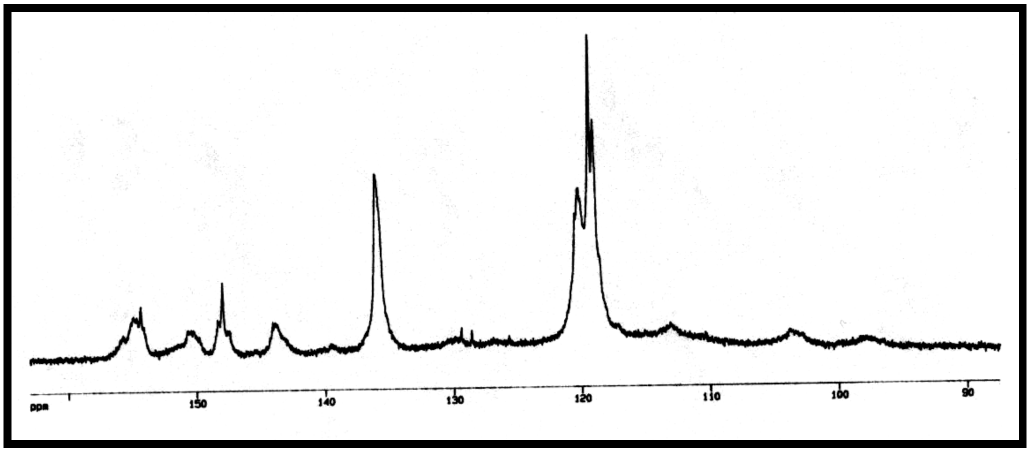


Figure 3. 11. ^{13}C-NMR Spectrum of the polymer obtained from $Cu(NH_3)_2(TBP)_2$ complex

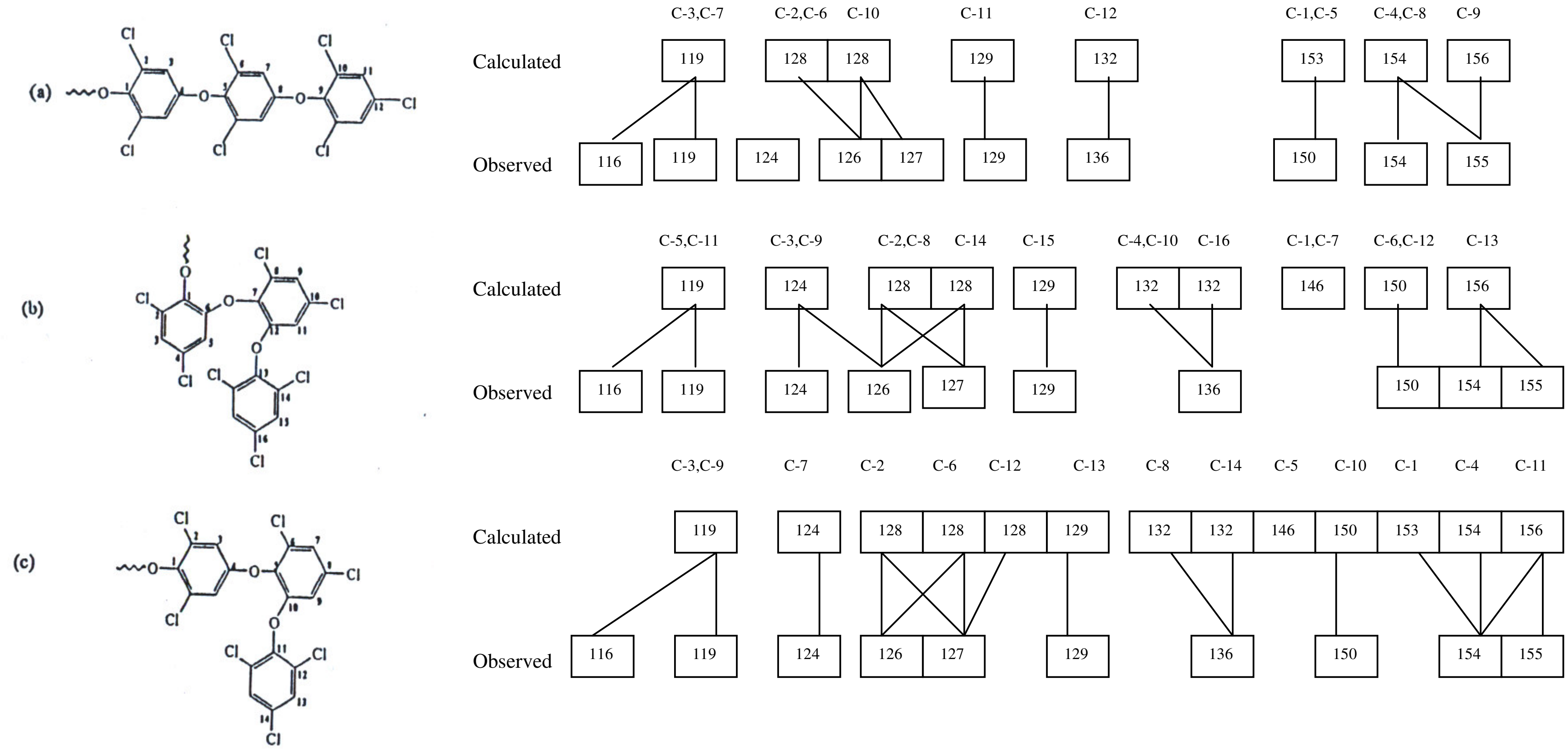


Figure 3.12. ^{13}C NMR shift data of the polymer obtained from $Cu(NH_3)_2(TCP)_2$

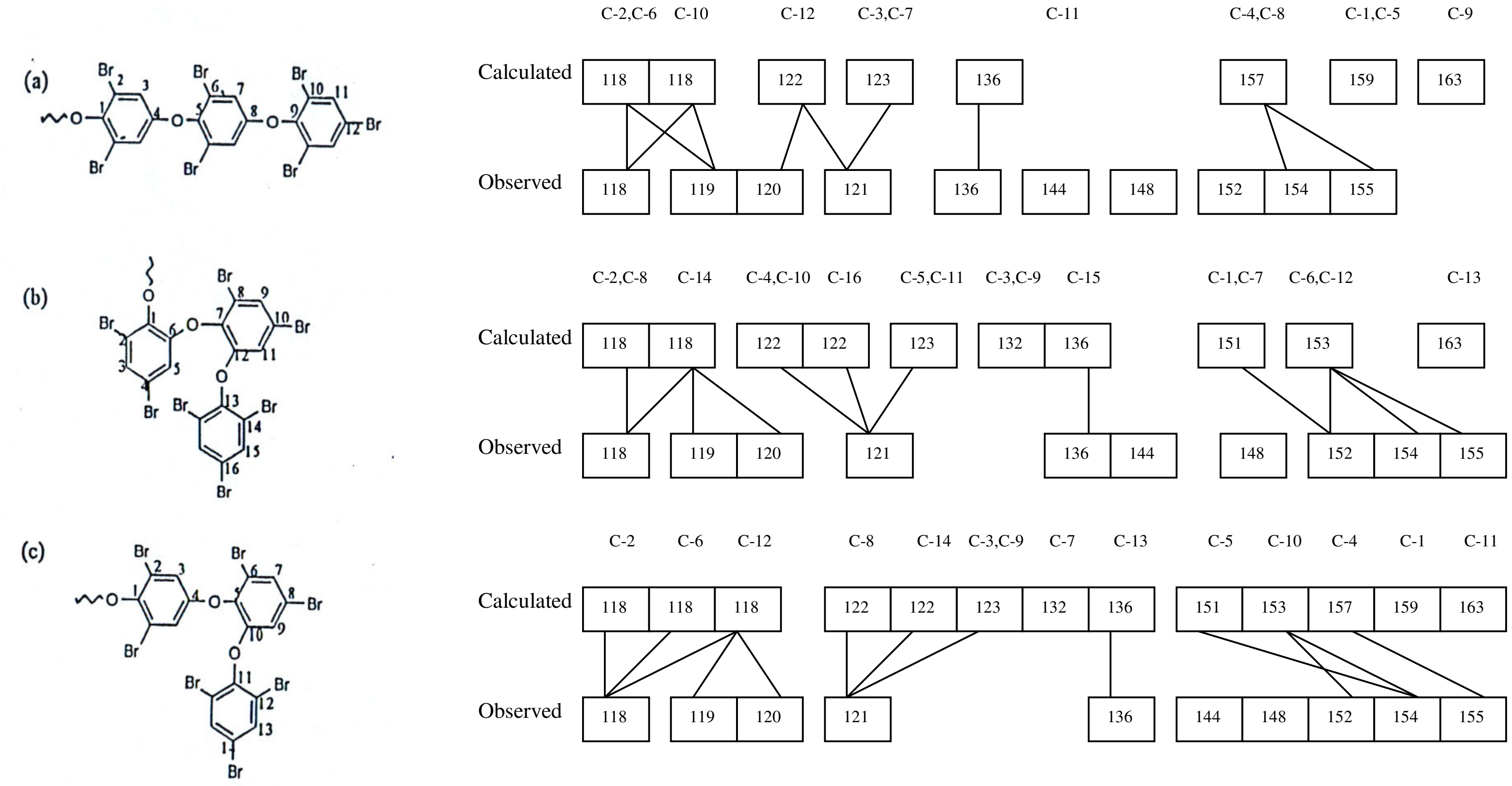


Figure 3.13. ^{13}C-NMR shift data of the polymer obtained from $Cu(NH_3)_2(TBP)_2$

3. 3. 2. Intrinsic Viscosity

Intrinsic viscosity of the poly(dichlorophenylene oxide)s and poly(dibromophenylene oxide)s were measured in toluene at 30 ^oC and their values are given in Table 3.10 and Table 3.11, respectively.

Since K (1.5 x 10^{-3}) and a (0.327) values are only known for poly(dichlorophenylene oxide), the molecular weight of the polymer obtained from TCP complexes was calculated using Mark Hauwink equation [33].

$Cu(NH_3)_2(TCP)_2$

The intrinsic viscosity values of polymers obtained from $Cu(NH_3)_2(TCP)_2$ complex at different time and temperatures are tabulated in Table 3. 9. At 150 ^oC, minimum intrinsic viscosity value was observed, then an increase was observed as the decomposition temperature increased (Figure 3.14.a). When the temperature was kept constant at maximum conversion temperature of 190 ^oC and the time was varied from 3 hours to 48 hours, random intrinsic viscosity values were observed (Figure 3.14.b) which could be due to presence of the copper complexes attached to the polymer.

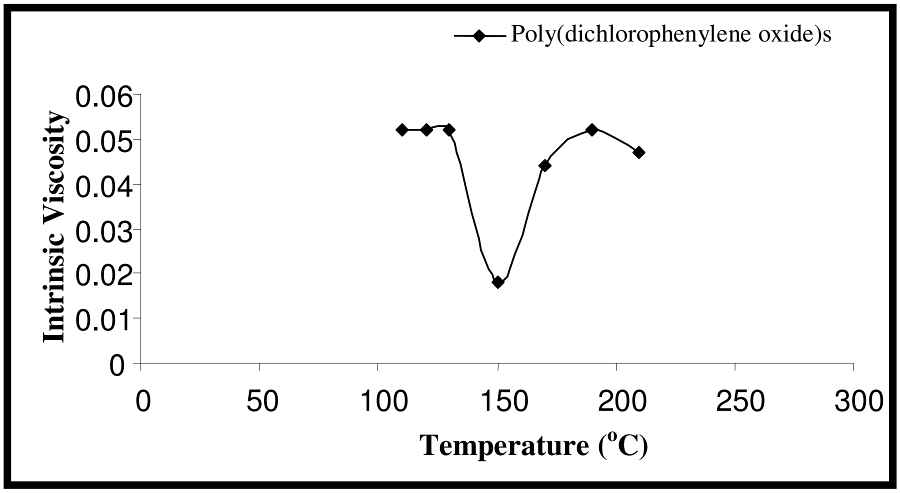
$Cu(NH_3)_2(TBP)_2$

As reflected from Table 3.10 and Figure 3.15.a, intrinsic viscosity values of the polymer obtained from the $Cu(NH_3)_2(TBP)_2$ complex have irregularity because of the copper complexes attached to the polymer as the decomposition temperature increased. It was interesting that minimum intrinsic viscosity value was observed at the maximum decomposition temperature. When the time was varied from 3 hours to 48 hours at 190 ^oC, intrinsic viscosity values showed randomness (Figure 3.15.b).

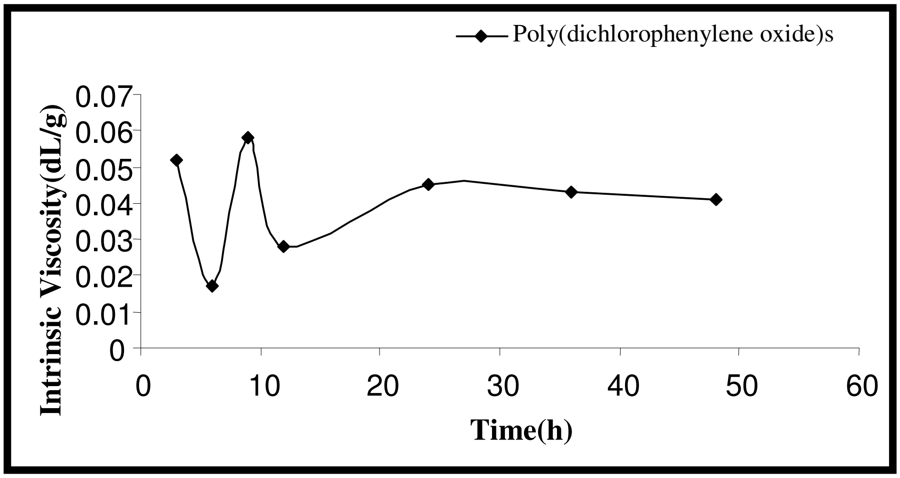
When compared on the basis of intrinsic viscosity, the polymers obtained from $Cu(NH_3)_2(TCP)_2$ have higher intrinsic viscosity values than the polymer obtained from $Cu(TBP)_2(NH_3)_2$ (Figure 3. 16. a and b).

Table 3.10. Intrinsic viscosity values of the polymer obtained from $Cu(NH_3)_2(TCP)_2$ complex at different time and temperatures

T(°C)	Time(h)	Intrinsic Viscosity(dl/g)	MW x10^{-3}
110-130	3	0.052	50.3
150	3	0.018	2.0
170	3	0.044	30.9
190	3	0.052	51.8
210	3	0.047	37.1
190	3	0.052	51.8
190	6	0.017	1.7
190	9	0.058	71.5
190	12	0.028	7.7
190	24	0.045	33.1
190	36	0.043	28.6
190	48	0.041	24.7



(a)



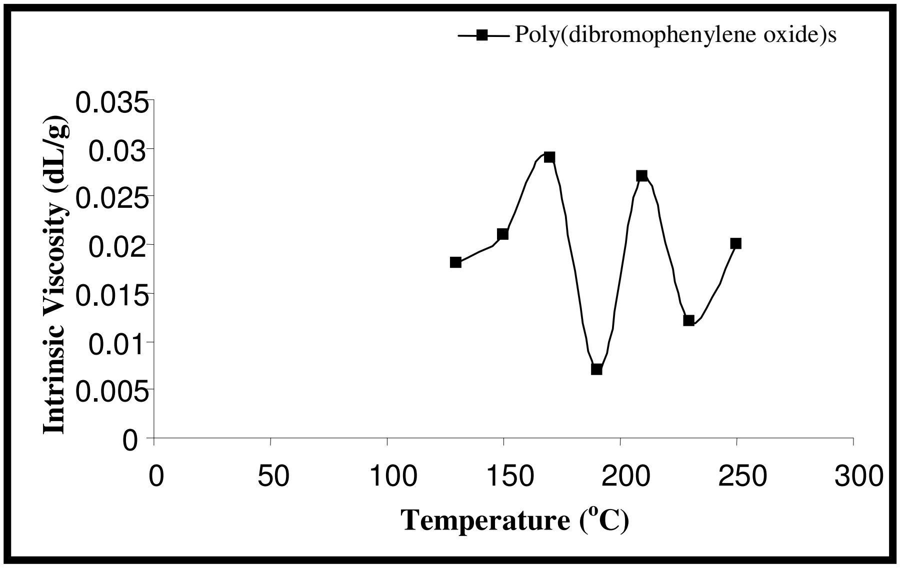
(b)

Figure 3.14.a) [η] vs temperature graph of polymer obtained from $Cu(NH_3)_2(TCP)_2$ complex at constant decomposition time (3 hours)

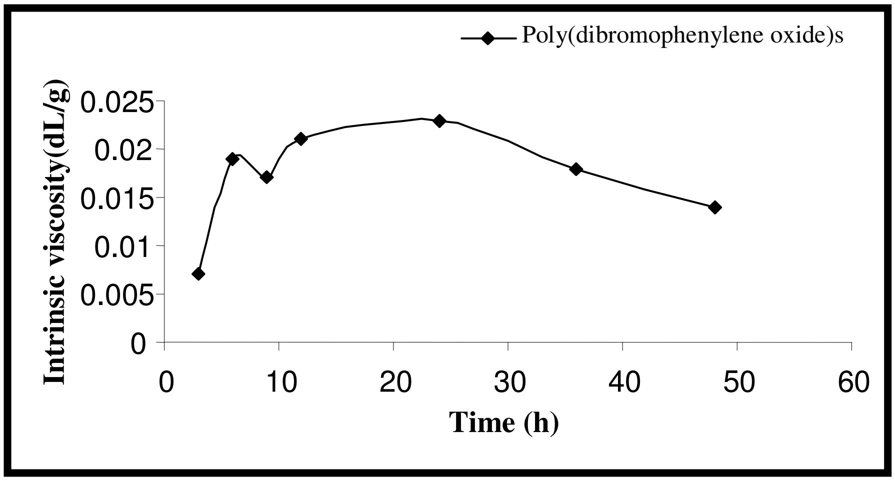
b) [η] vs time graph of the polymer obtained from $Cu(NH_3)_2(TCP)_2$ complex at constant temperature (190 °C)

Table 3. 11. Intrinsic viscosity values of polymers obtained from $Cu(NH_3)_2(TBP)_2$ complex at different time and temperatures

T(^oC)	Time(h)	Intrinsic Viscosity(dl/g)
130	3	0.018
150	3	0.021
170	3	0.029
190	3	0.007
210	3	0.027
230	3	0.012
250	3	0.020
190	3	0.007
190	6	0.019
190	9	0.017
190	12	0.021
190	24	0.023
190	36	0.018
190	48	0.014



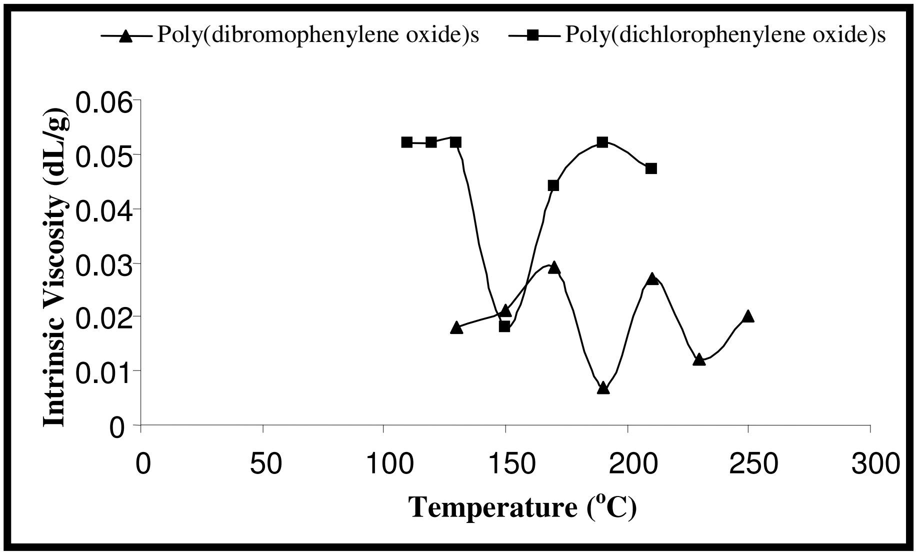
(a)



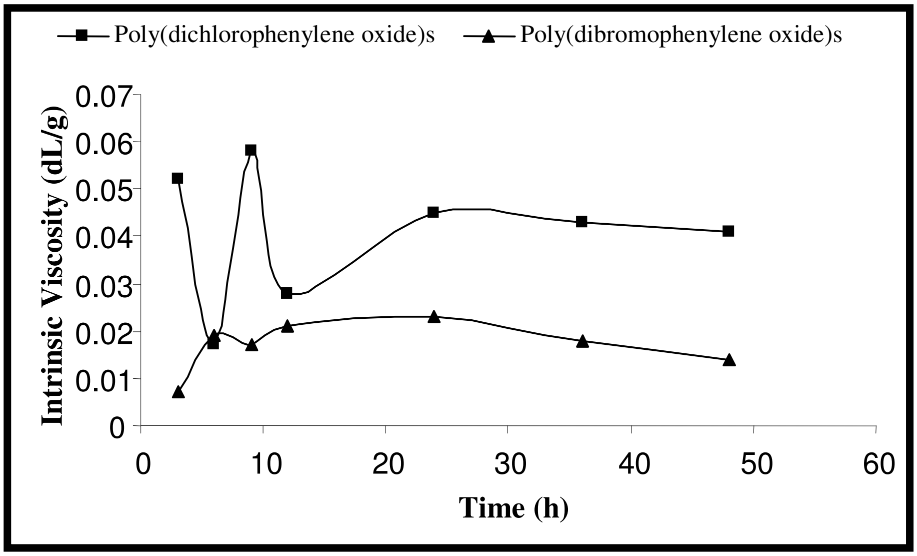
(b)

Figure 3.15.a) [η] vs temperature graph of polymer obtained from $Cu(NH_3)_2(TBP)_2$ complex at constant decomposition time (3 hours)

b) [η] vs time graph of polymer obtained from $Cu(NH_3)_2(TBP)_2$ complex at constant temperature (190 °C)



(a)



(b)

Figure 3.16. **(a)** Intrinsic viscosity vs. Temperature graph of the polymers obtained from $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ at constant time (3 hours)
(b) Intrinsic viscosity vs. Time graph of the polymers obtained from $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ at constant temperature (190 °C)

3.3.3. FTIR

Figure 3.17. displays FTIR spectra of the polymers obtained from $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ complexes. Polymer formation was followed by two regions. The first region is in between 1220 - 880 cm^{-1} and the second region is between 835 - 400 cm^{-1}. In the first region the etheric bond formation is observed at 1000 - 1035 cm^{-1} during polymerization. In the second region, C-Cl and C-Br characteristic bands are observed. The change in the peak pattern in this region might be due to change in the C-Cl and C-Br bands arrangements during the polymer formation. The polymer were also characterized by C=C stretchings (1400 - 1610 cm^{-1}), C-O stretchings (1237 cm^{-1}) and out of plane C-H bending (~860 cm^{-1}). The peak around 2800 cm^{-1} belongs to C-H stretching of benzene ring of phenol and the one around 3300 cm^{-1} is attributed to the phenolic end groups.

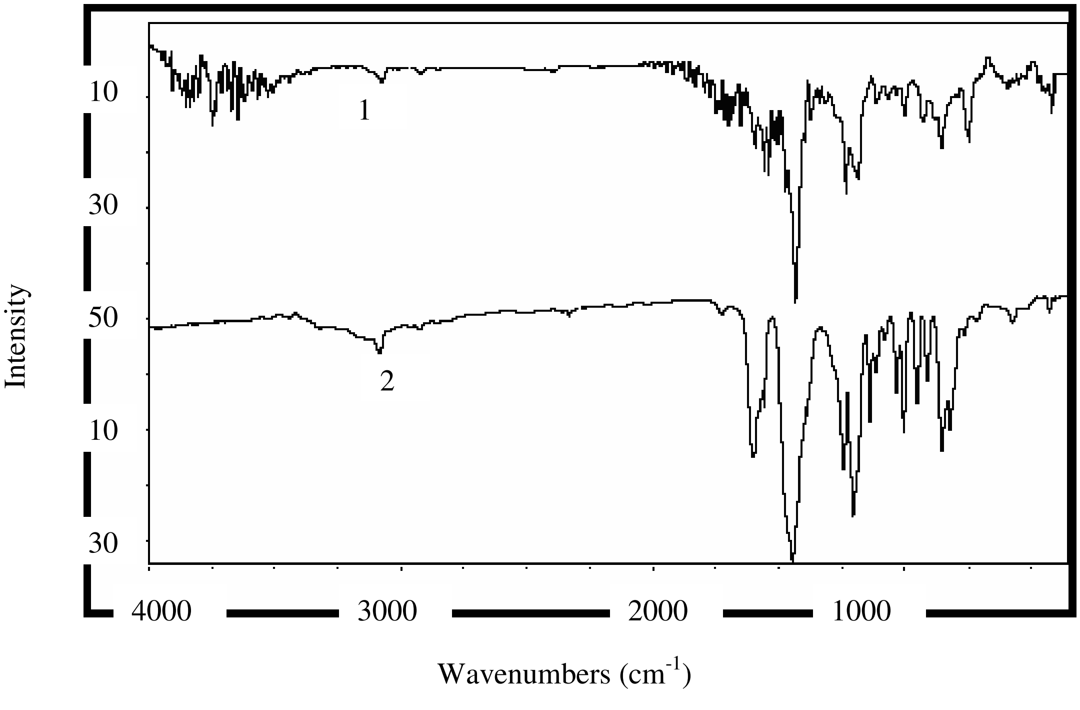
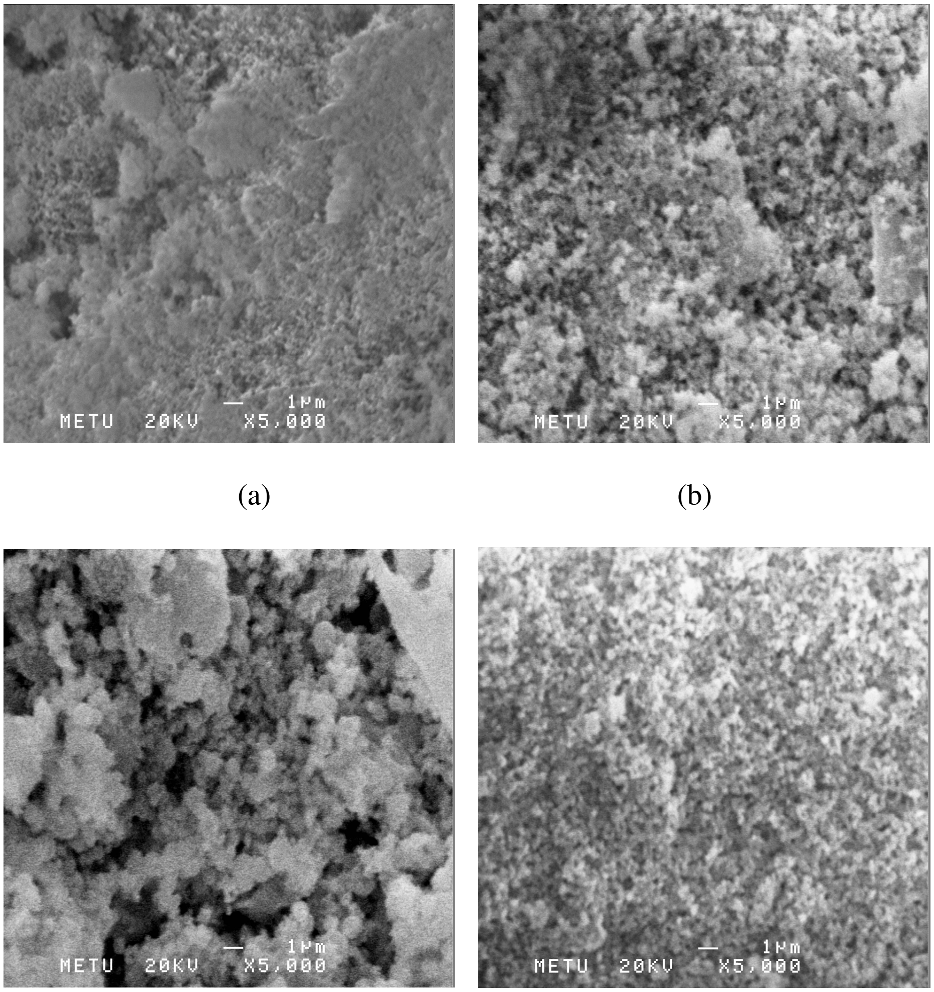


Figure 3.17. FTIR spectrum of the polymer obtained from $Cu(NH_3)_2(TCP)_2$ (1) and $Cu(NH_3)_2(TBP)_2$ (2)

3.3.4. SEM

Scanning electron micrograph of poly(dibromophenylene oxide)s and poly(dichlorophenylene oxide)s at different temperature preparations are given in Figure 3.19.

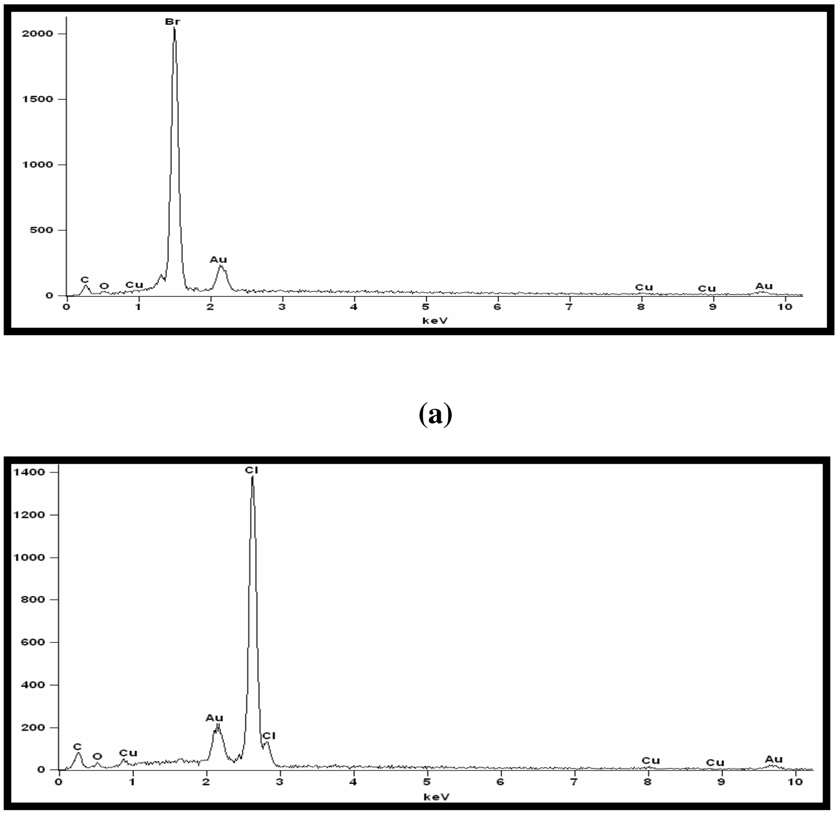


(a) (b)

(c) (d)

Figure 3.18. Scanning electron micrograph of poly(dibromophenylene oxide)s powder at 190 °C, brown (a), at 150 °C, light brown (b); poly(dichlorophenylene oxide)s powder at 190 °C, brown (c), at 170 °C, light brown (d).

When the unwashed polymers (Figure 3. 18. a and c) were washed, homogeneous surphace morphologies with fine granule appearance were observed (Figure 3. 18. b and d). It was not possible to determine the exact amount of Cu in the polymers by EDAX analysis, however it indicated the presence of Cu in all polymers (Figure 3. 19. a and b). The exact amount of Cu was determined by FAAS measurements which is given in the next section.



(a)

(b)

Figure 19. a) Elemental Analysis of poly(dichlorophenylene oxide)
b) Elemental Analysis of poly(dibromophenylene oxide)

3.3.5. FAAS

To determine the amount of copper in the polymers, Flame Atomic Absorption Spectrophotometer was used. Firstly 0.1 g of polymers obtained from $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ and 0.3 g $LiBO_2$ were mixed with each other and heated to 1000 ^{o}C. The molten mixture was digested with 10 % HCl and this sample was analyzed by FAAS. The results are given below. It is clearly seen that all polymers have copper.

Table 3.12. FAAS results of the poly(dichlorophenylene oxide)s and poly(dibromophenylene oxide)s

Polymer	Copper % (W)
Poly(dichlorophenylene oxide) 190 ^{o}C - 48 h	0.0913
Poly(dichlorophenylene oxide) 130 ^{o}C - 3 h	0.1359
Poly(dibromophenylene oxide) 190 ^{o}C - 48 h	0.0357

CHAPTER 4

CONCLUSION

Poly(dichlorophenylene)oxide and poly(dibromophenylene)oxide were synthesized by using $Cu(NH_3)_2(TCP)_2$ and $Cu(NH_3)_2(TBP)_2$ having helical strucural for the first time in this study.

Mass spectroscopy results show that phenol and ammonia leave from the complex during decomposition. This explains weight loss of the complex.

The maximum polymer yield was obtained at 130 ^oC (58.0 %) and 190 ^oC (58.5 %) for poly(dichlorophenylene oxide)s and the maximum polymerization yield of the poly(dibromophenylene oxide)s was obtained at 190 ^oC (59.3 %).

^1H-NMR and ^{13}C-NMR results suggest that the polymeric product obtained from TCP and TBP complexes proceed through mainly 1-2 addition.

Maximum intrinsic viscosity values were observed at 130 ^oC (3 h), 190 ^oC (3 h) and 190 ^oC (9 h) for poly(dichlorophenylene oxide)s. For this polymer, maximum molecular weight was found to be 7.15×10^4 at 190 ^oC (9 h).

For poly(dibromophenylene oxide)s, maximum intrinsic viscosity was observed at 170 ^oC (3h) and 190 ^oC (24 h).

SEM, FAAS and elemental analysis results of the polymers show the existence of the copper due to the chain structure of the complexes which hold them togther with hydrogen bonding.

It was observed that intrinsic viscosity values for poly(dichlorophenylene)oxide higher than poly(dibromophenylene)oxide.

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APPENDIX A

The calculated effective magnetic moments (μ_{eff}) of the prepared complexes are calculated in Bohr magnetons. μ_{eff} was calculated by using the formula;

$\mu_{eff} = 2.828\ [\ X_M .\ T(K)\ ]^{1/2}$ where;

T = absolute temperature
X_M = molar susceptibility = X_g . Mwt
X_g = mass susceptibility
Mwt = molecular weight of the complex

X_g was calculated by using the formula;

$X_g = [\ C_{bal} \times L \times (R - R_0)\ ] / [10^9 \times (W - W_0)]$ where;

C_{bal} = balance calibration constant for $HgCo(SCN)_4$
L = lenght of the sample
W = weight of the sample tube
W_0 = weight of the empty tube
R = reading of the sample tube
R_0 = reading of the empty tube

APPENDIX B

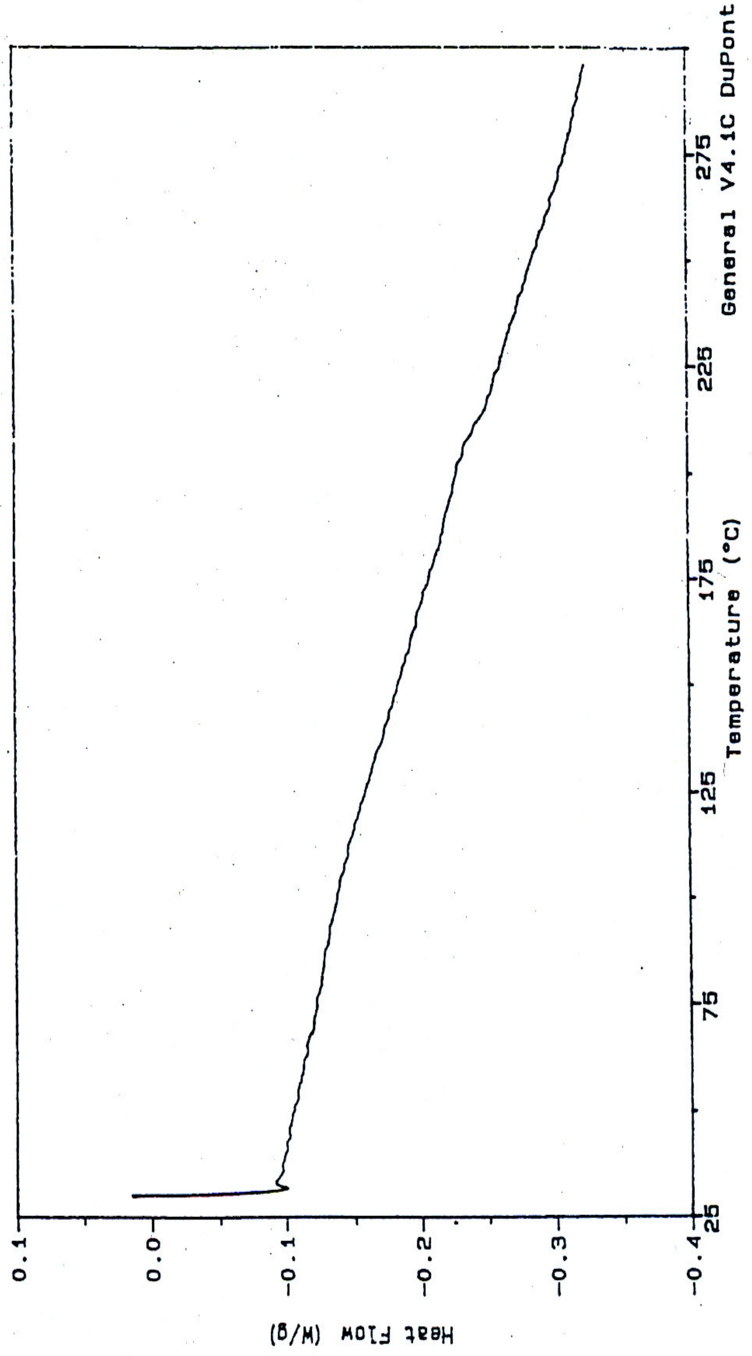

Figure. B.1. DSC thermogram of the polymer obtained from $Cu(NH_3)_2(TCP)_2$

APPENDIX B

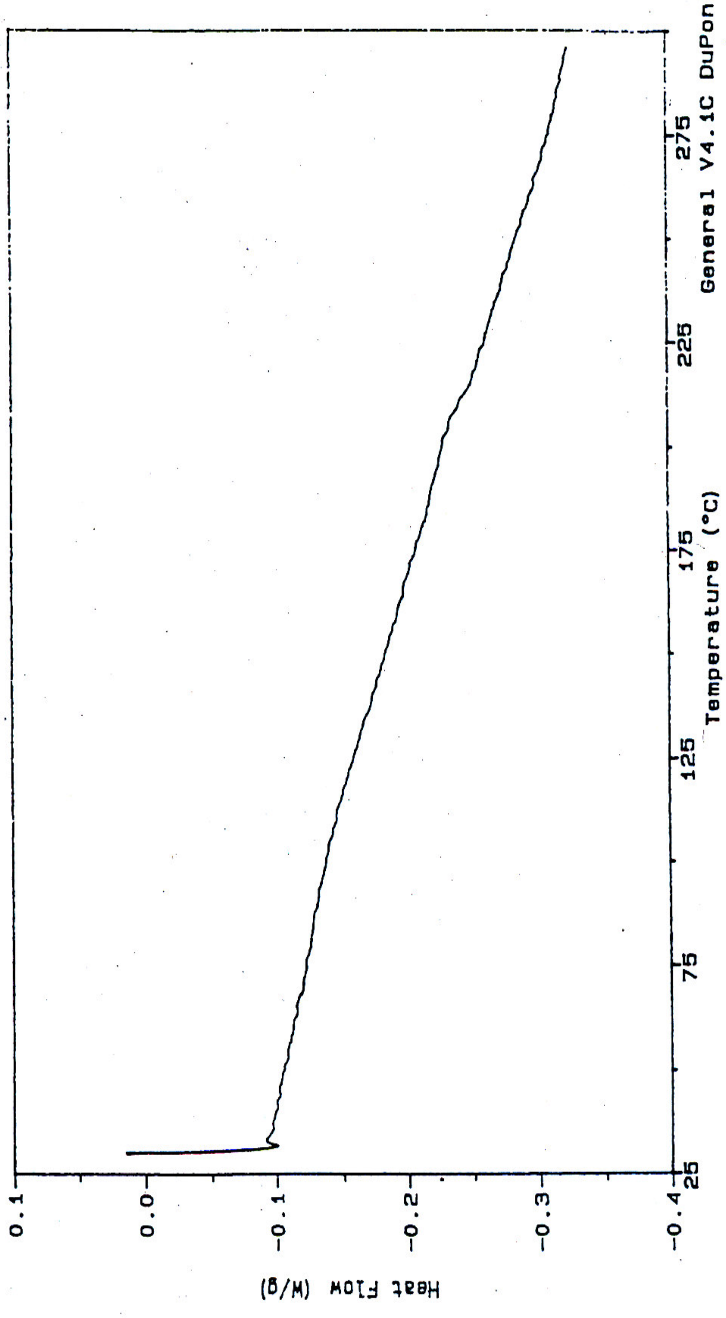

Figure. B.1. DSC thermogram of the polymer obtained from $Cu(NH_3)_2(TCP)_2$