SYNTHESIS AND CHARACTERIZATION OF POLY(DIHALOPHENYLENE OXIDES) FROM THE DECOMPOSITION OF BIS(PYRIDINE)BIS(TRIHALO PHENOXO) COPPER(II) COMPLEXES

A Ph.D.THESIS

in Chemistry

Middle East Technical University

By

Şadi ŞEN

December, 1989

TO MY FAMILY

Approval of the Graduate School of Natural and Applied Sciences

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I certify that this thesis satisfies all the requirements as a thesis for the degree of Doctor of Philosophy in Chemistry.

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We 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 Doctor of Philosophy in Chemistry.

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ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF POLY(DIHALOPHENYLENE OXIDES) FROM THE DECOMPOSITION OF BIS(PYRIDINE)BIS(TRIHALOPHENOXO) COPPER(II) COMPLEXES

ŞEN, ŞADİ

Faculty of Arts and Sciences, Department of Chemistry

Ph. D. Thesis

Supervisor: Prof. Dr. Duygu Kısakürek

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In this study, bis(pyridine)bis(trihalophenoxo)copper(II) complexes have been polymerized with electrochemical way under constant potential electrolysis. The oxidation and reduction peak potentials of several halophenols and complexes were determined by cyclic voltammetry in suitable solvent-electrolyte couple. Polymerization was carried out by constant potential electrolysis at each anodic and cathodic potential of the complex. Electrolysis of complexes yielded polymers in anode compartment only. The unreacted monomer concentration was simultaneously followed by cyclic voltammetry in the same special electrolysis cell. The mechanism of polymerization was found to be radicalic along with postpolymerization of complexes. Structures of polymers were studied by ^{1}H-NMR, ^{13}C-NMR and FTIR spectral analysis. Molecular weight measurements were carried out by isopiestic and cryoscopic methods. Molecular weights of polymers were found to be lower than ten thousands. Tg values of polymers were found to be high in between 180-300°C depending on the structure of the polymer. Dipole moment and dielectric constant measurements indicating structural conformation were done for some polymers.

Key Words: Electroinitiated polymerization, electrolysis, phenols, cyclicvoltammetry, poly(halophenyleneoxides), bis(pyridine)bis(trihalophenoxo)copper(II) complex.

Science Code: 405.04.02

ÖZET

BİS(PİRİDİN)BİS(TRİHALOFENOXO)BAKIR(II) KOMPLEKSLERİNİN BOZUNMASINDAN OLUŞAN POLİ(DİHALOFENİLEN OKSİTLERİN) ELDESİ VE KARAKTERİZASYONU

ŞEN, ŞADİ

Fen ve Edebiyat Fakültesi

Kimya Bölümü, Doktora Tezi

Tez Yöneticisi: Prof. Dr. Duygu Kısakürek

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Bu çalışmada, sabit gerilim altında, bis(piridin)bis(trihalofenoxo) bakır(II) kompleksleri, elektrokimyasal yöntemlerle polimerleştirildi. Çeşitli halofenol ve komplekslerin indirgenme ve yükseltgenme tepe gerilim değerleri, uygun çözücü-elektrolit sisteminde dönüşümlü voltametri vasıtası ile tayin edildi. Komplekslerin elektrolizi sonunda, sadece anot bölümünde polimer meydana geldiği görüldü. Reaksiyona girmeyen monomer derişimi, aynı elektroliz hücresinde, dönüşümlü voltametri ile aynı anda takip edildi. Polimerleşme mekanizmasının radikalik olduğu tespit edildi. Elde edilen polimerlerin yapıları, ^{1}H-NMR, ^{13}C-NMR ve FTIR spektral analiz yöntemleri ile incelendi. İzopiestik ve kriyoskopik yöntemlerle molekül ağırlıkları tayin edildi. Camsı geçiş sıcaklıklarının, polimerin yapısına bağlı olarak, 180°ile 300°C

arasında olduğu gözlendi. Dipol moment ve dielektrik sabit değerleri, bazı polimerler için bulundu.

Anahtar Kelimeler: Elektrokimyasal başlatıcılı polimerleşme, elektroliz, fenoller, dönüşümlü voltametri, polihalofenilenoksit, bis(piridin)bis(trihalofenokso)bakır(II)kompleks.

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Py: Pyridine

ED: Ethylene diamine

TCP: 2,4,6-trichlorophenol

TBrP: 2,4,6-tribromophenol

4-Cl-DBrP: 4-chloro-2,6-dibromophenol

4-Br-DCP: 4-bromo-2,6-dichlorophenol

2-Br-DCP: 2-bromo-4,6-dichlorophenol

TIP: 2,4,6-triiodophenol

4-CP: 4-chlorophenol

2,6-DCP: 2,6-dichlorophenol

2,4-DCP: 2,4-dichlorophenol

DMF: N,N'-Dimethyl formamide

DMSO: Dimethyl sulfoxide

T_g: Glass transition temperature

V: Volt

$\bar{M}_n$: Number average molecular weight

DSC: Differential scanning calorimeter

CHN: Carbon-hydrogen-nitrogen

TBAFB: Tetrabutylammonium fluoroborate

FTIR: Fourier transform infrared

NMR: Nuclear magnetic resonance

$E_{p,a}$: Oxidation peak potential

$E_{p,c}$: Reduction peak potential

LUMO: Lowest unoccupied molecular orbital

HOMO: Highest occupied molecular orbital

HMO: Huckel molecular orbital

$Py_2Cu(TCP)_2$: bis(pyridine)bis(2,4,6-trichlorophenoxo) copper(II) complex

$Py_2Cu(TBrP)_2$: bis(pyridine)bis(2,4,6-tribromophenoxo) copper(II) complex

$Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$:bis(pyridine)bis(4-chloro-2,6-dibromo phenoxo)copper(II) complex

$Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$:bis(pyridine)bis(4-bromo-2,6-dichloro phenoxo)copper(II) complex

$Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$:bis(pyridine)bis(2-bromo-4,6-dichloro phenoxo)copper(II) complex

TMED : N,N,N',N'-Tetramethylethylene diamine

1. INTRODUCTION

1.1.PHENOLS

It has been well known for a very long time that phenols are readily oxidized by many different reagents. The products are mostly complicated mixtures of compounds, dimeric, polymeric and quinonoid in nature. In general, the dimeric and polymeric products can be formulated by abstracting one hydrogen atom from the starting phenol and coupling together these intermediates by C-C and C-O bonds, exclusively at ortho and para positions to the hydroxyl groups.

Oxidation of phenols covers an extensive field.The importance of phenol oxidation is in the biosynthesis of natural products, alkaloid field, aphid pigments, lignin, lignans and cyclolignans.

Natural products found in higher plants and in microorganisms can be derived formally from oxidative coupling of phenolic compounds involving carbon-carbon and carbon-oxygen linkages. Natural products obtained from the oxidation of several phenolic type substances are

pummerer's ketone [1], usnic acid [2], tannis [3], bisnaphtols [4], bisantraquinones [5], hypericin[6], bisterpenoids [7], thyroxine [8], depsidones [9], xanthones [10], grisans [11], geodin and erdin [12]. The alkaloids have proved to be a particularly valuable group of compounds for the study of biosynthesis in which phenol oxidation is an important step. There are more than 2000 alkaloids, which can be accommodated within the framework of oxidative coupling of phenols [13, 14]. The enzymic oxidation and coupling of phenols are subjects of great importance in biochemistry [15, 16, 17].

Lignin which is a natural polymeric product of phenol oxidation is well known to the botanist and organic chemist as a hydrolysis-resistant amorphous methoxylated phenolic polymer that makes up about 20 to 30 % of dry weight of the woody tissues of plants.

The general term lignan covers a group of naturally occuring phenols made up of two C_6C_3.(phenyl propane) units linked by the central carbon of the side chain. Their biosynthesis involves the oxidative coupling of two phenyl propane units.

Several oxidizing agents had been employed for

different substituted phenols [18].

General coupling mechanism has been suggested as follows

$$ArO. + ArO. \longrightarrow DiO. \longrightarrow Di$$

$$Ar\overset{\cdot}{\overset{+}{O}}H + ArO. \longrightarrow Di + H^{+}$$

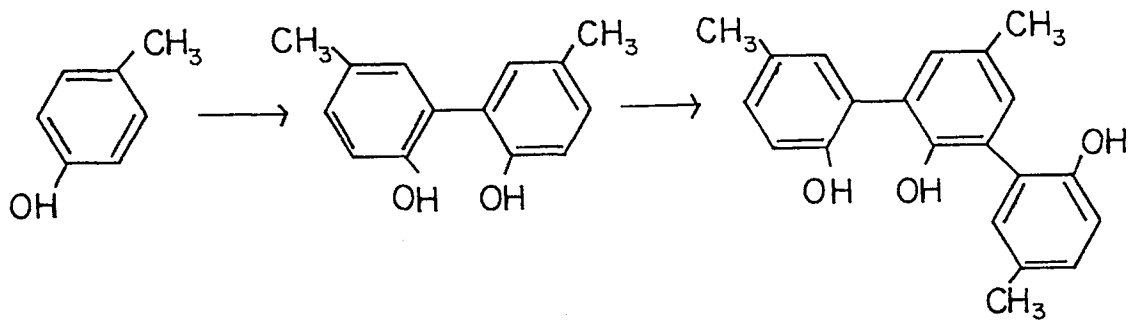
$$Ar\overset{\cdot}{\overset{+}{O}}H + Ar\overset{\cdot}{\overset{+}{O}}H \longrightarrow Di + 2H^{+}$$

$$ArOH + ArO^{+} \longrightarrow Di + H^{+}$$

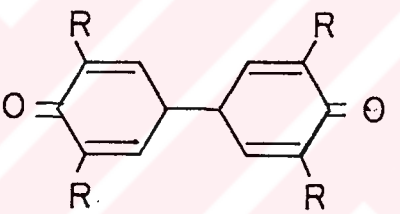
$$ArO^{-} + ArO^{+} \longrightarrow Di$$

The phenolate radical ($ArO^{\cdot}$) is formed from a phenolate anion (ArO^{-})by removal of one electron or alternatively, from a phenol by loss of proton as well as removal of one electron . It is generally considered that such phenolate radicals give stable molecular products by coupling in pairs . In principle, we may consider the above reactions for joining together the two phenolate residues (Di = dimer) .

As an example, p-cresol is oxidized with potassium ferricyanide [1] in aqueous alkaline solution and also under many other conditions such as in the presence of H_2O_2 and enzymes [19] to the o-dimer, the trimer,pummerer's ketone and polymers.



When two of the three coupling positions are blocked by substituents such as alkyl, halogen or methoxyl, the dimeric o,o- or o,p- products can be isolated in high yields. With strong oxidizing agents, diphenoquinones are the final products resulting from further oxidation of the dimer

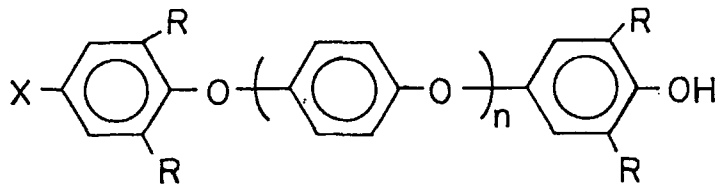


Some oxidizing agents are as follows [18]:

$FeCl_3$; $O_2/h\nu$; HNO_3,fuming ; $Fe(NH_4)_2(SO_4)_2$; $K_2S_2O_8/AgNO_3$; Air/NaOH ; $ZnCl_2$/air ; CrO_3,HOAc ; $NaNO_2$/HOAc ; Air/NH_3,C_2H_5OH ; CH_2N_2 ;$K_3Fe(CN)_6/OH^-$ etc.

Oxidizing agents are employed for desired products forming either C-O bond or C-C bond under special conditions. Polymers containing C-O bonds are often found

as undesired byproducts. High yields of polymeric ethers can be isolated under special conditions.



e.g.MnO_2 [20, 21], silver oxide in benzene [22] or copper salts and air in nitrobenzene-pyridine [23, 24] or o-halogenophenols leads via a radical chain process to ethers with a molecular weight in the range of 2000 to 10000 [24-30].

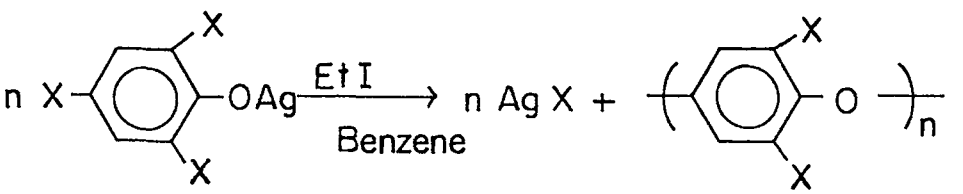
1.2. POLY(DIHALOPHENYLENE OXIDES)

1.2.1. CHEMICAL STUDIES

Poly(dihalophenylene oxides) have the potential for important mechanical, chemical, electrical and thermal properties. Such polymers have also been found to be extremely fire resistant, due to the existence of halogens attached to phenyl ring.

Poly(dihalophenylene oxide) was first synthesized by Hunter et al. in 1916 [31]. The synthesis was achieved from the decomposition of the silver salts of trihalogenated phenols in the presence of ethyl iodide in

hot benzene. It was noticed that silver salts of trihalogenated phenols decomposed to form a metal halide and a polymeric product called as dihalophenylene oxide. Proposed mechanism was given as follows :



where x represents the halogen.

The same effect is produced by heating silver salt to temperatures slightly above 100°C.

Later, Hunter and Joyce [32] noticed that iodine was displaced somewhat more readily than chlorine, and p-halogen reacted more readily than ortho.

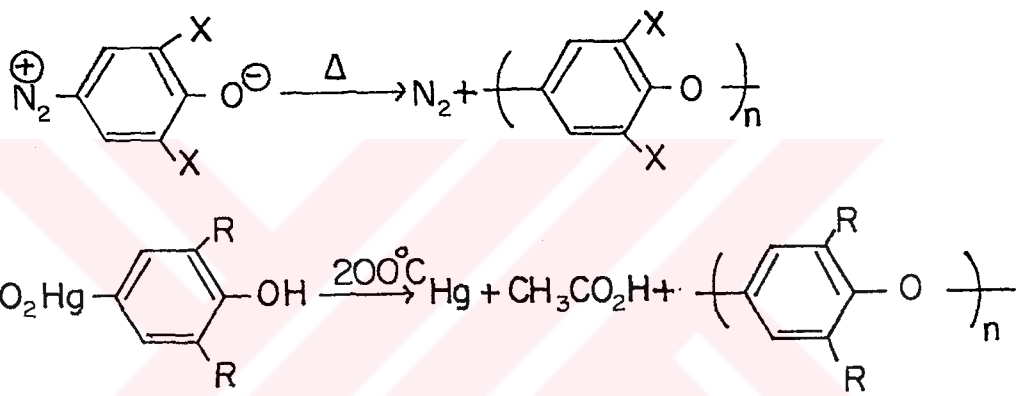
In 1932 Hunter and Whitney [33] have continued the study on the decomposition of certain phenol silver salts.

In 1958 Dewar and James [34] in an extension of earlier work reported by Sus and coworkers [35] attempted the synthesis of poly-2,6-disubstituted-1,4-phenylene ethers by the thermal decomposition of substituted benzene-1,4-diazooxides but only with limited success.

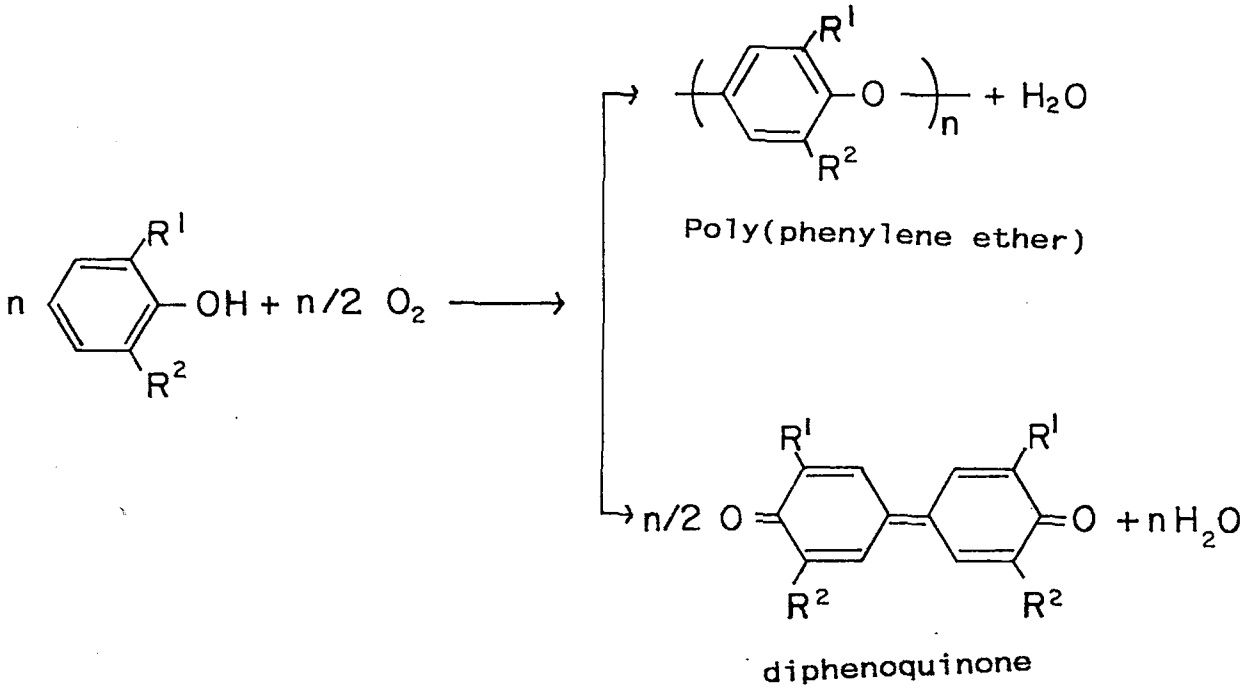
In 1960 Staffin and Price [36] examined the reaction of 4-bromo-2,6-dimethylphenolate ion with a number of

oxidizing agents such as ferricyanide ion, lead dioxide, iodine, oxygen and light to be ready conversion to polymer at room temperature.

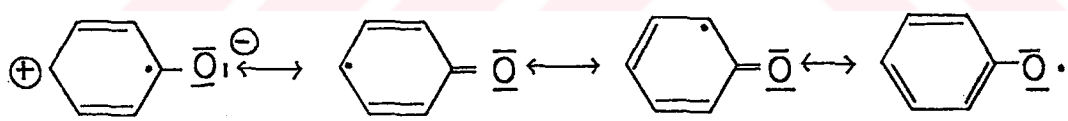
Dewar [34] has reported that poly(phenylene oxide) structures could be prepared by pyrolysis of diazooxides. It occured that a somewhat similar process might occur on the pyrolysis of phenol mercuryacetates.



The improvements on the polymerization of substituted phenols proceeded by Hay and his group [24]. They described catalytic oxidation of 2,6-disubstituted phenols to give high molecular weight poly(phenylene ethers) or diphenoquinones in the presence of oxygen.



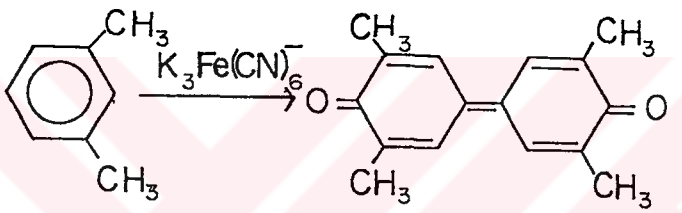
Phenols are very similar in reactivity to aromatic amines and the first step in the oxidation of a phenol is generally considered to be formation of aryloxy radical. The phenoxy radical is a resonance hybrid of the following structures :



Carbon-carbon coupling of radicals as well as carbon-oxygen coupling can occur at the ortho and para positions. When 2,6-dimethyl phenol was oxidized in pyridine solution in the presence of copper(I)chloride, high molecular weight polyphenylene of about 150000 was

obtained. The polymer was soluble in chlorinated hydrocarbons such as chloroform and 5-tetrachloroethane and aromatic solvents such as nitrobenzene and toluene, and evaporation of these solvents from the polymer solutions-left transparent, tough, flexible film.

Waters [1] in England had described the oxidation of 2,6-dimethyl phenol with potassium ferricyanide. The products were principally the diphenoquinone and some uncharacterized low molecular weight polymeric materials.



The oxidation of highly hindered phenols to yield diphenoquinones had been also reported by a number of workers [37].

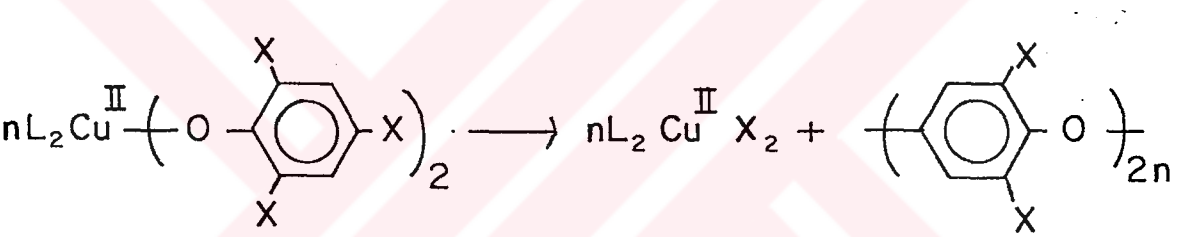
Brackman and Havinga [38] had described an unusual copper-catalyzed oxidation of phenol with oxygen to a 3,4-diamino ortho-benzoquinone in the presence of secondary amine, morpholine.

In 1962 Blanchard et al [27] reported the oxidation of 4-halo-2,6-dimethyl phenol to a high molecular weight poly(aryl ether) or to a tetramethyl diphenoquinone in the

presence of cupric ions and pyridine by passing oxygen through the solution. This reaction requires a stoichiometric amount of cupric ions and probably proceeds through complexed phenoxy radicals. Although the polymerization can not be initiated by catalytic quantities of cupric ions, the same cupric salts which are active in the stoichiometric reaction will initiate the polymerization of the 4-halo-2,6-dimethyl phenols in basic solution. Here the products are high molecular weight poly(aryl ethers) and this reaction involves the displacement of halide ions by phenoxy radicals. In addition to this study, di-(2,4,6-trihalophenoxo)-bis(pyridine)-copper(II) complexes were prepared and characterized. These complexes were decomposed under a variety of conditions, yielding poly(halophenylene ethers),which are highly branched as evidenced by their low intrinsic viscosities. Similiarly, the polyhalophenylene ethers prepared by decomposition of the silver salts are also branched. In this connection, however, silver-4-chloro- and silver-4-bromo-2,6-dimethyl phenolates were prepared and decomposed to a poly-2,6-dimethylphenylene ether of molecular weight of

1800-2200 possessing one halogen and one hydroxy per polymer chain.

Harrod has [39] made several studies on phenoxo copper complexes to polymerize them. He prepared a series of several halophenoxo copper(II) complexes containing a variety of amine ligands. It has been noticed that thermal stability of any complex was lower with these ligands which increase the oxidizing power of copper(II). All of the trichlorophenoxo complexes prepared were to decompose according to following reaction :



where L is a ligand and X is a halogen

The ease of decomposition was found qualitatively to vary to a considerable degree, depending on the neutral ligand (L) such as biquinolyl, triphenyl phosphine, 2,6-dimethylpyridine, ammonia, ethylamine, pyridine and etc.

It has been proposed [27] that the initiation step in thermal decomposition reaction is a ligand-to-metal

electron transfer. After a thorough study of the effect of amine ligands on the redox potential of the Cu(II)/Cu(I) system, James and Williams [40] concluded that the order for stabilization of Cu(II) was ethylenediamine >> 2,2'-bipyridyl > 1,10-phenanthroline > pyridine ≅ ammonia >> 2,2'-biquinolyl.

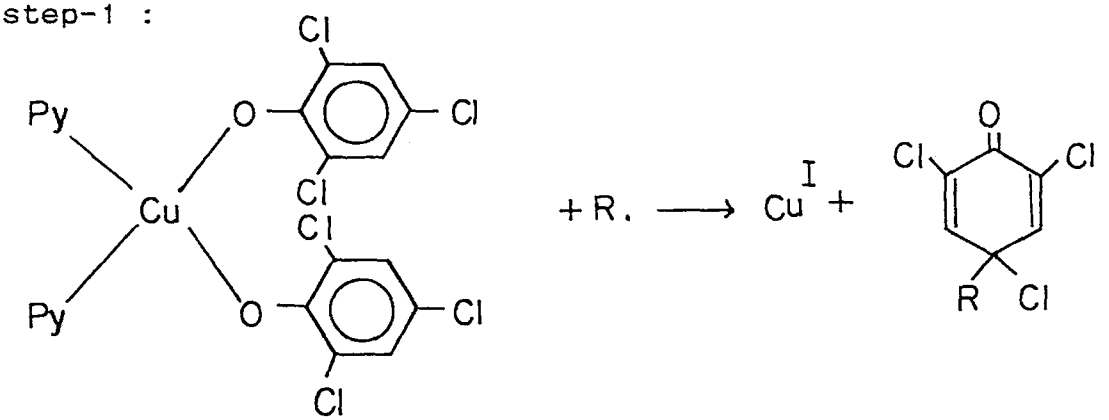
Harrod et al [41] obtained poly(phenylene oxides) by thermal decomposition of trichlorophenoxo copper(II) complexes with different ligands such as pyridine and N,N,N',N', tetramethylethylene diamine. They have examined the effect of i-) concentration of complex ii-) concentration of free trichlorophenol iii-) changing solvent from cumene to toluene, to benzene on the molecular weights of poly(phenylene oxides). Maximum $\bar{M}_n$ obtained by decomposition of bis(pyridine)bis(2,4,6-trichlorophenoxo)copper(II) was 80000. These polymers were branched. Decomposition of bis(2,4,6-trichlorophenoxo) bis(N,N,N',N'-tetramethylethylene diamine) copper(II) gave the polymers of molecular weight of about 150000.

It was shown that the thermal decomposition of bis(pyridine)bis(2,4,6-trichlorophenoxo)copper(II) in solution did not occur spontaneously, but could be induced

by oxygen or free-radical initiator. Induction period was diminished by free-radical initiators.

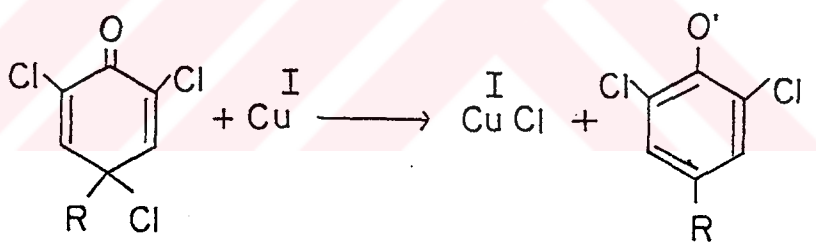
The reaction mechanism suggested was as follows :

step-1 :



In the first step the complex was induced by a radical to give Cu^{I} complex and 2,4,6-trichlorocyclohexadienone.

step-2 :

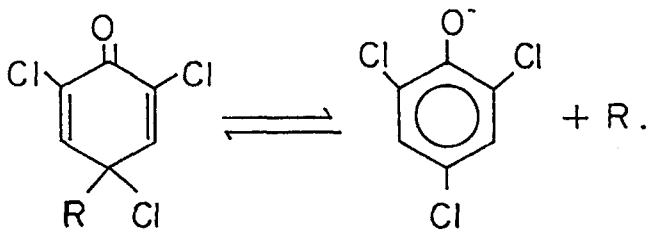


There is a slow dissociation of 2,4,6-cyclohexadienone into a radical initiator and a 2,4,6-trichlorophenoxy radical (chain branching).

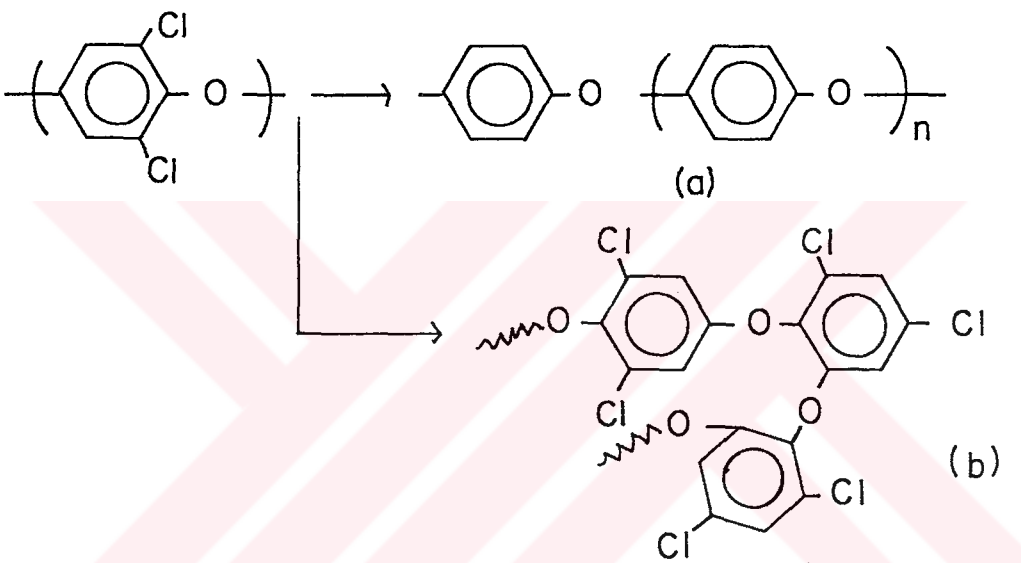
step-3 :

There is an abstraction of a chlorine atom from 2,4,6-cyclohexadienone by Cu(I) to give $Cu^{II}Cl$ and a

substituted phenoxy radical.



The phenoxy radical can complete the chain growth and propagate the polymerization as linear(a) or branched(b).



In 1981 poly(dihalophenylene oxides) were obtained in acetonitrile from decomposition of copper(II) trihalophenoxides by Kısakürek and Harrod [42]. The structure of such low molecular weight polymers have been examined by using ^{1}H-NMR and ^{13}C-NMR spectroscopy. It was concluded that when the monomer contained bromine in the 4-position, 1,4-catenation was favored over ortho

substitution and lead to a more linear structure.

In 1987 Kisakurek et al [43] studied on solution properties of several different halophenylene oxide polymers from the thermal decomposition of $Py_2Cu(trihalophenoxo)_2$ by using light scattering. For such polymers of molecular weight around $5*10^4$, those obtained from 4-bromo-2,6-dichlorophenoxide, 2-chloro-4,6-dibromophenoxide and 2,4,6-tribromophenoxide appear to be relatively linear with higher values of $\langle s^2 \rangle^{1/2}$ whereas those obtained from 2,4,6-trichlorophenoxide and 2-bromo-4,6-dichlorophenoxide appear to have branched or condensed structures with lower values of $\langle s^2 \rangle^{1/2}$.

In 1988 Kısakürek et al [44] achieved thermal polymerization of bis(trihalophenoxo)bis(ethylenediamine) copper(II) complex and bis(trihalophenoxo)bis (N,N,N',N'-tetramethylethylene diamine) copper(II) complex. The effect of ligand was examined. It has been found that, the ligand was effective on the molecular weight of the polymers. The polymers prepared with (TMED) ligand have higher molecular weight compared to those obtained with ethylene diamine(e.d) when tribromophenol(TBrP) was used as a monomer. It has also

been observed that the ligand used was effective on the structures of polymers. When TMED-Cu-$(TBrP)_2$ complex was used, 1,4-catenation was favoured to 1,2-catenation, but with e.d-Cu-$(TBrP)_2$ complex, 1,2 and 1,4 catenation took place at equal rates. It has been found that the polymers obtained by using both ligands had high glass transition temperatures (T_g) above 200^{o}C.

1.2.2. ELECTROCHEMICAL STUDIES

The importance of phenols in biological systems provides a link between biochemistry and electrochemistry. Oxidation of phenols has major importance in organic electrochemistry in preparation of some substances.

From the series of papers concerning the preparation of poly(phenylene oxides) either by chemically oxidative or electrooxidative ways of phenolic compounds, it has been realized that there is no essential difference on mechanism of each way. The difference is only initiation step. For the chemical oxidative polymerization, initiator is needed. But for the electrochemical polymerization, additional initiator is not employed. In electrochemical

polymerization, the initiation occurs at the electrode surface with either monomer itself or by any other species like supporting electrolyte or additives present in the system. The species activated at the electrode surface initiate the polymerization in the bulk of the solution either by free radicalic, anionic or cationic mechanism.

In 1964 Vermillion and Pearl [45] studied with some techniques on the oxidation of phenolic compounds. Phenoxy radicals produced at electrode surface proceed the reaction by coupling mechanism .

In 1968, the electrolytic polymerization of phenol with simultaneous deposition on the electrodes was studied by Grace [46]. An aqueous solution of caustic soda and phenol were placed in the anode compartment of an electrolytic cell. The surface of iron anode was coated with poly(phenylene oxides).

In 1968 Borman [47] studied on the polymerization of phenols using copper salts to produce poly(phenylene oxides). He reported the polymerization of various substituted phenols using copper salts as catalysts with ammonia or amines as complexing agents in aqueous solution.

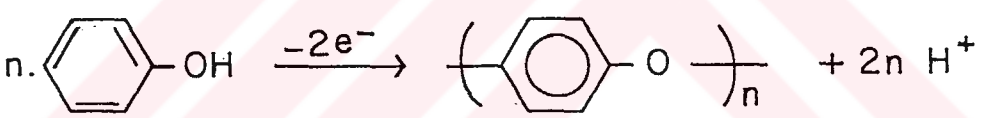
In 1971, Kifkstra and Jonge [48] reported the polymerization of various substituted phenols by electrochemical oxidation in nonaqueous solvents.

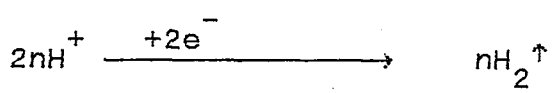
In some cases, the resulting polymers deposited on electrode surface and "thin-film-coated electrodes" could be obtained from phenols [49]. Some interesting functions such as pH sensor [50], protection of metal corrosion [51], and permselectivity [52] have been reported for the film-coated-electrodes prepared by electropolymerization of several phenolic compounds. Bruno et al [53] have characterized chemical and physical properties of poly(phenylene oxide) films. Glarum and Marshall [54] reported the studies on the electric properties of electrodes coated with poly(phenylene oxide) films in aqueous electrolytes. Polymers of 2,6-dimethyl phenol have been examined and the ortho positions were blocked in 2,6-dimethyl phenol and coupling should take place at the para position, leading to "linear polymer".

Ohnuki et al[52] prepared poly(2,6-dimethyl-1,4-phenylene oxide) films from electro-polymerization of 2,6-dimethyl phenol in different electrolytic solutions to have different permselectivities. Also, Ohsaka et al [55]

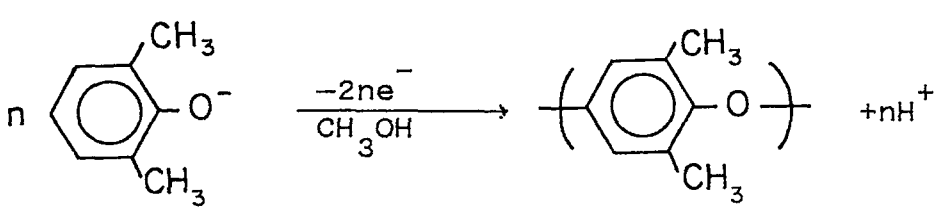
have examined the selective ion permeabilities of poly(phenylene oxide) films prepared from different electrolytic solutions.

Tscuchida et al [56,57] reported that substituted phenols were electrooxidatively polymerized to produce poly(phenylene oxides). They have pointed out that polymerization occured at anode. Anodic oxidation of 2,6-disubstituted phenols gave poly(phenylene oxide) by using dichloromethane and tetraethylammonium bromide as the solvent and supporting electrolyte respectively. Reported molecular weight of poly(phenylene oxide) was about 1200~2500. The mechanism was reported as :





Yamamoto et al [58] studied on the electro-oxidatively polymerization of 2,6-dimethylphenol in the presence of methanol as suggested :



Recently, various reports were published on the conducting polymers of phenols. It was found that poly(phenylene oxides) are insulators.

Kumar et.al. [59] obtained films of the copolymer of phenylene oxide-pyrrole. Copolymer was found to be flexible and did not show any thermal degradations up to $100^{o}C$.

Up to 1988, there was no work on the electroinitiated polymerizations of the copper complexes of trisubstituted halophenols in the presence of neutral ligands as mentioned except the electrolysis of silver salts of trihalogenated phenols in pyridine at anode compartment [60].

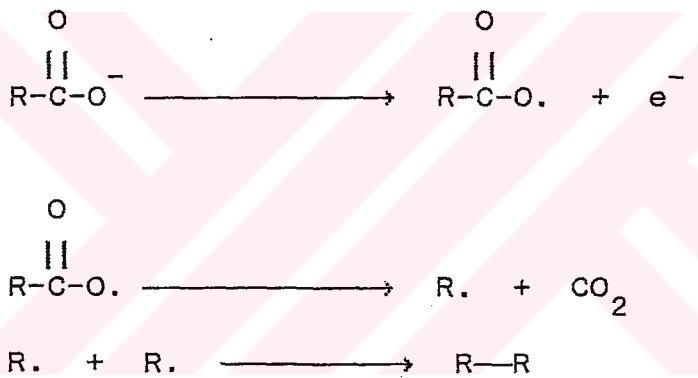
In 1988, electroinitiated polymerization of bis(trichlorophenoxo)ethylenediamine copper(II) complex was carried out in dimethyl formamide at various anodic peak potentials of the complex by S.Yigit [61] et al. Sacak et al. [62] studied with a similiar complex by changing ligand as N,N,N',N'-Tetramethylethylene diamine [TMED]. These two ligands are chelating ones. The polymers obtained were characterized by ^{1}H-NMR, ^{13}C-NMR and FTIR spectroscopy. In literature, there is no work on the

electroinitiated polymerizations of the copper complexes of trisubstituted halophenols with non-chelating ligands such as pyridine except these studies [78,79].

1.3. ELECTROCHEMICAL INITIATION

1.3.1..FREE-RADICAL INITIATION

Electrochemical oxidation of salts of carboxylic acids produce free radicals at anode compartment. The reaction is known as "Kolbe reaction".



These acyl radicals can initiate polymerization in the presence of olefinic compounds such as methyl methacrylate. Electrochemical oxidation of acetate yields methyl radical and in aqueous solution this methyl radical can initiate the polymerization of methyl methacrylate.

Potassium acetate had been used to initiate the polymerization of styrene and acrylonitrile

electrochemically.

1.3.2.. ANIONIC INITIATION

Anionic initiation may take place in two ways as indirect and direct initiations.

1.3.2.1.. Indirect Anionic Initiation

When an electroactive salt is used as electrolyte in electrochemical polymerization, the metal ion of the salt can initiate the polymerization. It has been shown by Yamozaki that sodium ion is easily reduced in comparison to many monomers.

$$Na^+ + e^- \longrightarrow Na.$$

$$Na. + H_2C{=}CHR \longrightarrow H_2\dot{C}\cdot\text{-}\bar{C}HR + Na^+$$

$$2H_2\dot{C}\text{—}\ \bar{C}HR \longrightarrow R\bar{C}H\text{—}\ CH_2\text{—}\ CH_2\text{—}\ \bar{C}HR$$

The radical anion or dianion can propagate the polymerization.

1.3.2.2.. Direct Anionic Initiation

If an electroinert electrolyte such as tetraalkylammonium salts is utilized, the polymerization reaction may be initiated directly. If the reduction peak potential of monomer is less cathodic than tetraalkylammonium salt, the monomer will be more easily reduced and thus initiate the polymerization

$$R\text{-}CH{=}CH_2 + e^- \longrightarrow R\text{-}\bar{C}H\text{-}CH_2\cdot$$

$$2R\text{-}\bar{C}H\text{-}CH_2\cdot \longrightarrow R\text{-}\bar{C}H\text{-}CH_2\text{-}CH_2\text{-}\bar{C}H\text{-}R$$

An electron is transfered directly from cathode to lowest unoccupied molecular orbital(LUMO) of the monomer to yield a radical anion. Radical anion or dianion can propagate the electrochemical polymerization.

1.3.3.. CATIONIC INITIATION

1.3.3.1.. Indirect Cationic Initiation

In 1960 and 1962 Breitenbach reported the electroinitiated cationic polymerizations of methyl methacrylate , isobutylvinyl ether and styrene. Tetrabutyl ammonium perchlorate or tetrabutyl ammonium fluoroborate

was used as electrolyte and polymers were obtained at anode compartment. The mechanism for the initiation of these polymerization reaction are

$$ClO_4^- \longrightarrow ClO_4^{\cdot} + e^-$$

$$ClO_4^{\cdot} + RCH{=}CH_2 \longrightarrow R\overset{+}{C}H{-}CH_2^{\cdot} + ClO_4^{\cdot}$$

$$2R\overset{+}{C}H{-}CH_2^{\cdot} \longrightarrow {}^{+}RCH{-}CH_2{-}CH_2{-}CHR^{+}$$

The radical cations or dications can propagate the cationic polymerization. For these mechanisms, monomers should have higher oxidation potentials with respect to the electrolytes.

1.3.3.2.. Direct Cationic Initiation

In this mechanism the initiation step is the formation of cations or radical cations of the monomer. These are generated by an electron transfer directly from the highest occupied molecular orbital (HOMO) of monomer to anode that can be shown as

$$RCH{=}CH_2 \longrightarrow {}^{+}RCH_2{-}\dot{C}H_2 + e^-$$

$${}^{+}RCH_2{-}CH_2^{\cdot} \longrightarrow {}^{+}RCH{-}CH_2{-}CH_2{-}CHR^{+}$$

These radical cations or dications can propagate the cationic polymerization reaction.

1.4.. ELECTROCHEMICAL TECHNIQUES

Electrosynthesis usually involves electrolysis at a constant current or at a controlled potential.

1.4.1.. CONSTANT CURRENT ELECTROLYSIS

The current is held constant at a set of value and electrode potential is allowed to vary. To achieve such an electrolysis, the equipment used is a cell of two electrodes. A major disadvantage of this method is that the products may be further oxidized or reduced.

1.4.2.. CONSTANT POTENTIAL ELEECTROLYSIS

This is the best way to carry out an electrolysis. It is product-selective and the reaction can be followed indirectly by monitoring the current. A voltage is applied between a working electrode and a counter electrode. This is called as cell voltage. The potential of the working electrode with respect to the reference electrode may be measured by connecting these two electrodes to a high

resistance voltmeter. The three electrode system provides greater flexibility in the location of the reference and the working electrodes and minimizes the effect of potential(iR) drop. It has also the advantage that no current passes through the reference electrode. Potential control is maintained between the working and the reference electrode by a potentiostat, but the cell current passes between the working and the counter electrodes.

1.5.DIELECTRIC PROPERTIES OF MATTERS

The investigation of dielectric properties provides an important approach to an understanding of the structure of the matter. Dielectric properties have also great importance in the determination of physicochemical properties of polymers. The theoretical and experimental investigation of the dipole moment of macromolecules have important fields not only in basic science, but also in technology. In fact, many technical applications of solid polymeric materials are determined by their dielectric properties. Study of dielectric constant gives information

about molecular conformation and thus can be very useful in the characterization of the macromolecule structure.

1.5.1. POLARIZABILITY

Polarizability is characterized by a definite type of displacement of the charges of the particles of the dielectric under the electrostatic field. All types of polarizability can be generally reduced to two main types :

a-) Elastic displacement of charges in the atoms and molecules under the action of electric field.

b-) Orientation of the permenant dipoles in the direction of the applied field.

1.5.1.1. Electronic Polarization (P_e)

This type of polarization arises from the elastic displacement of the electron charge cloud relative to the nuclei when the atom or molecule is acted upon by an electric field. The electronic polarizability formulated as below exists in all atoms and molecules of both polar and non-polar dielectrics.

$Pe = 4/3 * \pi * N * \alpha_e$

where α_e : electronic polarizability

1.5.1.2. Atomic Polarization (Pa)

In an electric field, the actual nuclei of the atoms forming molecule are affected. The atomic polarization is comparatively small, being considerably less than the electronic polarization.

1.5.1.3. Orientation Polarization (P_o)

The behavior in an electric field of a polar dielectric, the molecules of which possess a permenant dipole moment, μ_o, differs from the behaviour of a non-polar dielectric. While the deformation polarizability is only the effect of the applied field for non-polar molecules but in the case of polar molecules, in addition to the deformation polarizability , there is another form of polarizability caused by the orientation of the permenant dipoles in the electric field. This form of polarizability is called orientation polarizability, α_o. In the absence of

the electric field, a free molecule with moment, μ_o, possesses not only translational but also rotational and vibrational motions. Since rotational movement of the molecules is a function of temperature, the P_o must depend on the temperature and is smaller, the higher the temperature.

1.5.2. DEBYE EQUATION

It was pointed out by Faraday that the particles of dielectric behave like a series of small, insulated conductors, each consisting of a single molecule, which can be polarized as a whole [63]. When such polarization occurs, one side of the molecules behaves as a positive charge and opposite side of the molecules behaves as a negative charge of the same magnitude, so that the molecules as a whole remains neutral. The magnitude of dipole can be expressed by its moment through the distance between them. Two charges with magnitudes of $e=4.8*10^{-10}$ e.s.u separated by a distance $1A^{o}$ would have a dipole moment of $4.8*10^{-18}$ e.s.u.cm. The unit $1*10^{-18}$ e.s.u.cm is called 'Debye'(D) [64].

Debye equation has been derived step by step in the thesis of Ihsan Kocak [65].

The static dielectric constant(ϵ) is easily expressed in terms of the capacitance in vacuum and while it is filled with dielectric.

$\epsilon = \frac{C}{C_o}$ where C is the capacitance of dielectric and C_o is the capacitance of vacuum.

The mean-squared dipole moments were calculated by Guggenheim-Smith equation as follows :

$$\frac{\langle \mu^2 \rangle}{x} = A \left[\frac{d\epsilon/c}{(\epsilon_1+2)^2} - \frac{2n_1(dn/dc)}{(n_1^2+2)^2} \right]$$

where,

$A = \frac{27kTM_o}{4\pi N_A}$ x=number of repeating units

M_o = molecular weight of the repeating unit

N_A = Avogadro's number

k = Boltzmann's constant

T = Absolute temperature

ϵ = static dielectric constant

n = refractive index

c = concentration (n grams polymer per 100 grams of solvent)

$d\epsilon = \epsilon_2 - \epsilon_1$

subscript 1 refers to values for pure solvent (toluene)

subscript 2 refers to values for solution.

2. EXPERIMENTAL

2.1. CHEMICALS

2.1.1. HALOPHENOLS

Analytical grade halophenols were provided from Aldrich chemical Co.ltd. They were used without further purifications. Halophenols used in this experiment are :

a-) 2,4,6-trichlorophenol (TCP)

b-) 2,4,6-tribromophenol (TBrP)

c-) 2,6-dichlorophenol (2,6-DCP)

d-) 4-chlorophenol (4-CP)

e-) 2,4-dichlorophenol (2,4-DCP)

2.1.2. PYRIDINE (Py)

Pyridine was a reagent grade material provided from Merck. Pyridine, considered to be a nonchelating neutral ligand, was used without further purification.

2.1.3. N,N'-DIMETHYL FORMAMIDE (DMF)

It was purchased from Merck. N,N'-dimethyl formamide was stirred with anhydrous copper sulphate for 48 hours. and distilled at 5 mm Hg (boiling point was 38^{o}C at that pressure). DMF was used as a solvent for cyclic voltammetry and electrolysis.

2.1.4. COPPER SULPHATE ($CuSO_4.5H_2O$)

Copper sulphate was commercially available reagent grade material. It was used for the preparation of phenol complexes

2.1.5. ETHANOL

Ethanol, used as a precipitating reagent, was fractionally distilled under atmospheric pressure at b.p.75^{o}C.

2.1.6. HYDROCHLORIC ACID

Reagent grade concentrated hydrochloric acid was provided from Merck and used to dissolve the by-product salts formed during polymerization in precipitation procedure of the polymer.

2.1.7. TETRABUTYLAMMONIUM FLUOROBORATE (TBAFB)

TBAFB salt was obtained by titrating 40 % tetrabutylammonium hydroxide with fluoroboric acid until the solution was slightly acidic. It was filtered and then recrystallized twice by using 1:3 ethanol-water mixture. Then it was dried under vacuum at 50^{o}C.It was also donated by U.Akbulut and Merck Co.

2.1.8. CHLOROFORM

Reagent grade chloroform was provided from Riedel-De Haen AG. and was used without any purification. It was used as a solvent for determining the molecular weight of polymers.

chloroform (merck) was used.

2.1.9. CARBON DISULPHIDE (CS_2)

Analytical grade carbon disulphide was purchased from Merck. It was used without further purification for ^{1}H-NMR spectra.

2.1.10. SILVER FLUOROBORATE

Silver fluoroborate was prepared by titration of 10 % fluoroboric acid with 5 % silver oxide solution. The salt was recovered by evaporating the solution and then recrystallized several times from water. The salt obtained was dried under vacuum at 40^{o}C for 24 hours donated by U. Akbulut [67]. Decomposition temperature was 200^{o}C .

2.1.11. ACETONITRILE

Acetonitrile provided from merck was dried over CaH_2 for 24 h, then refluxed over fresh CaH_2 under nitrogen for 10 h, then fractionally distilled and stored over

molecular sieves. It was used to take the cyclic voltammograms of various phenols.

2.2. APPARATUS

The apparatus and instruments used in this work are listed below with their details.

2.2.1. POTENTIOSTAT

A Tacussel electronique potentiostat model PRT 30-0.1 was used in this work for polymerizations. The kinetics of the polymerizations were followed by cyclic voltammetry technique using two potentiostats at the same time. The potentiostat is a device which was capable of giving a cell voltage of 30 V and a maximum current of 0.1 ampere. The potentiostat compensates for the IR voltage drop in the solution and maintains the working electrode-reference electrode voltage difference at a desired value. Potential remains constant despite the changes in the current passing through the electrolysis cell. The potentiostat continuously compares the potential of the working

electrode measured against the reference electrode with the programmed voltage and instantly changes the potential difference between auxiliary electrode and working electrode to compensate for any changes in potential of working electrode.

2.2.2. FUNCTION GENERATOR

In cyclic voltammetry the potential of the working electrode is changed on a desired rate and reversed after a suitable potential is reached. Such a function is carried out by function generator that can reduce triangular and sinusoidal potential excitations which was connected to the potentiostat. In cyclic voltammetry, initial and final potential limits are achieved by function generator.

2.2.3. RECORDER

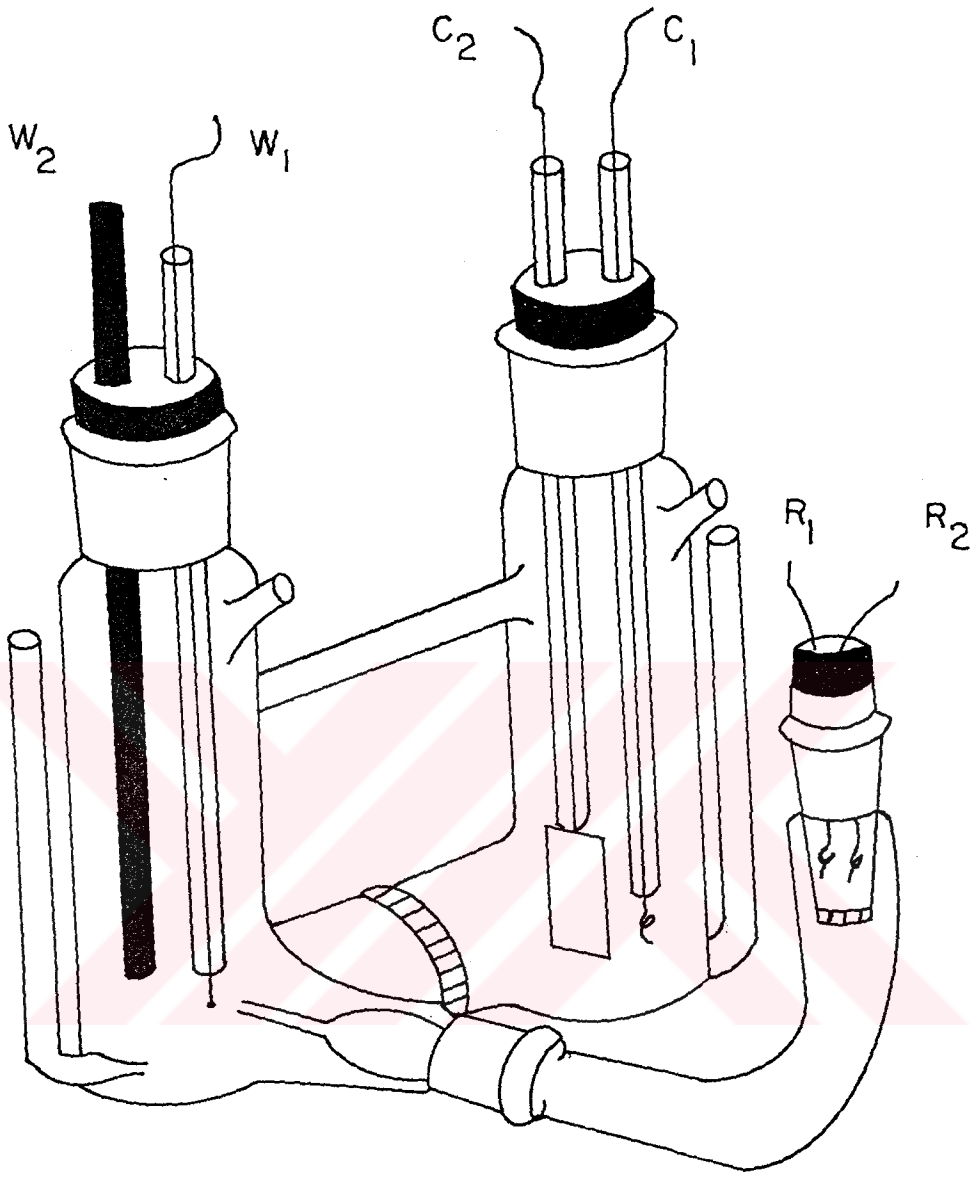
XY recorder was manufactured by **Sefram** to plot the current-potential curves.

2.2.4. ELECTROLYSIS CELL

The electrolysis cell was an H-type cell containing three electrodes as working , counter (or auxiliary) and reference electrodes. The graphite electrode with a diameter of 5mm. was the anode. A stainless steel employed as cathode, has the area of 1 in^2 . Reference electrode was $Ag/AgBF_4$(0.01 M). The total volume of electrolysis cell was about 50 ml and working and counter compartments were separated by a sintered disk. Kinetic studies of polymerizations were made in the same cell containing 6 electrodes (Fig.1).

2.2.5. CYCLIC VOLTAMMETRY CELL

The cell was consisted of three electrodes. They are namely working, counter and reference electrodes. The working and reference electrodes were platinum bead and platinum(Pt) wire respectively. Pt wire was 3 cm. in length. The reference electrode was a luggin capillary containing $Ag^{o}/AgBF_4$(0.01 M) as shown in Fig.2 . Cyclic



W:working electrode C:counter electrode R:reference electrode

subscript 1 refers to cyclic voltammetry system

subscript 2 refers to electrolysis system

Figure.1. Electrolysis cell

voltammetry measurements of complexes were done in dimethyl formamide(DMF)-tetrabutylammonium fluoroborate(TBAFB) as solvent-electrolyte couple at 20^{o}C in cyclic voltammetry cell (Fig.3) For cyclic voltammetry measurements of phenols, acetonitrile was used instead of DMF as a solvent.

2.2.6. CYCLIC VOLTAMMETRY SYSTEM

The system was composed of a potentiostat, a function generator, an XY recorder and a cyclic voltammetry. The cyclic voltammetry system has been discussed in a previous publication [67] .

2.2.7. CONSTANT POTENTIAL ELECTROLYSIS SYSTEM

Polymerizations were done under constant potential electrolysis system that was composed of a potentiostat, an XY recorder and electrolysis cell (Fig.4). Such a system has been already discussed (67) .

Figure.2. Reference electrode

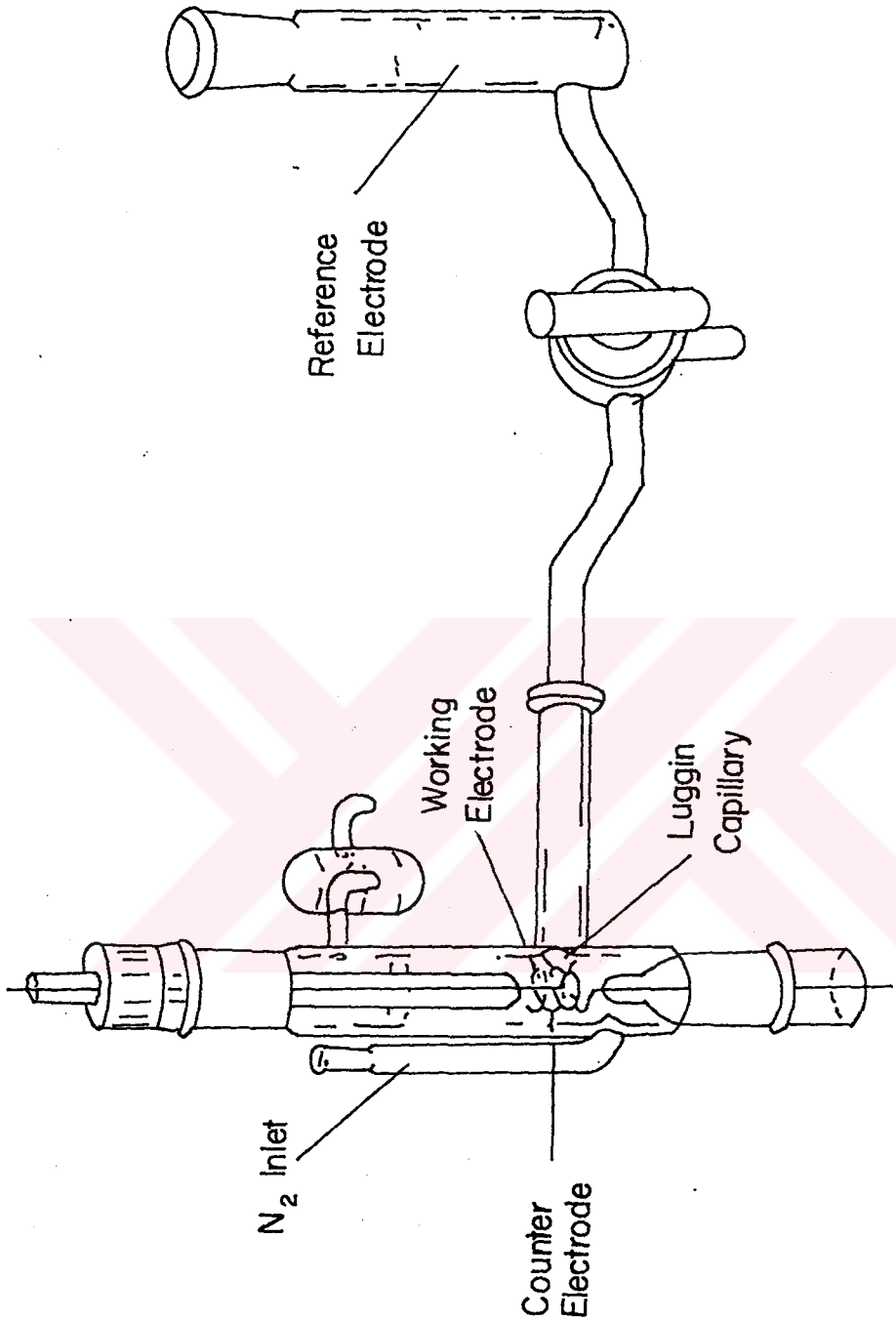
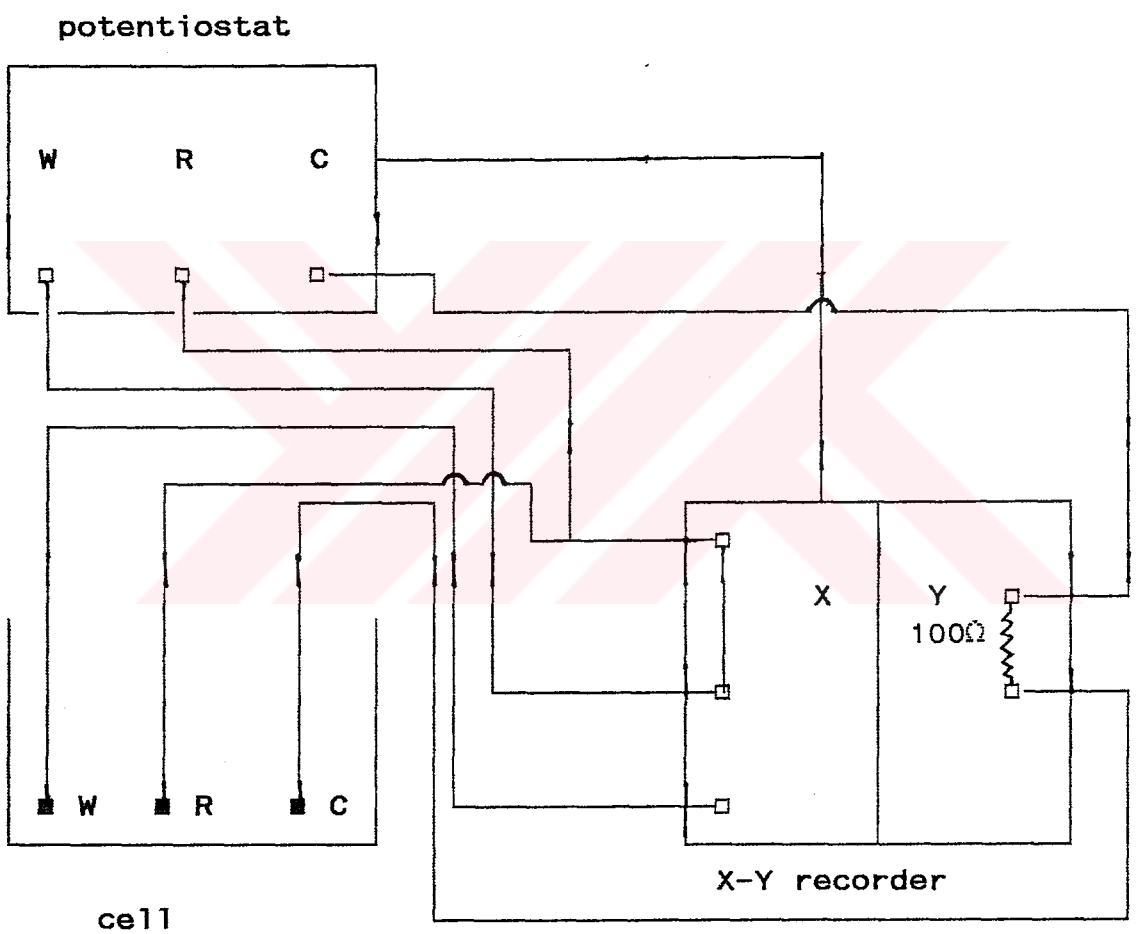


Figure.3. Cyclic voltammetry cell

2.2.8.FOURIER-TRANSFORM INFRA-RED SPECTROPHOTOMETER (FTIR)

A Perkin Elmer 1710 model FTIR was used to obtain IR of polymers dispersed in KBr disc.Computer library output suggests poly(oxy-dihalo-phenylene) spectra for the polymers synthesized electrochemically.



W:counter electrode W:working electrode R:reference electrode

Figure.4. Constant potential electrolysis system

2.2.9. MOLECULAR WEIGHT APPARATUS

Molecular weight of polymers were measured by vapor pressure (isopiestic) method by a Perkin Elmer Coleman 115 Molecular Weight apparatus. The solvent was chloroform. Suboven and main oven temperatures were 24°C and 32°C respectively. The calibration curves were obtained by chloroform-benzyl couple as a solvent and a standard respectively.Cryoscopic method was also used to determine $\bar{M}_n$ of some polymers. This method is based on the principle at which the addition of substance decreases the freezing point of solvent. By regarding the following formula $\bar{M}_n$ can be found.

$$T_2-T_1=K_f*G_1/G_2*1000/\bar{M}_n$$

where T_1 =freezing point of pure solvent (camphor)
T_2 =freezing point of polymer solution
G_1 = wt.of polymer G_2 = wt.of camphor

for camphor K_f=freezing point depression constant=-39.7. Beckman thermometer was used as a sensitive thermometer.

2.2.10. NMR-SPECTROPHOTOMETER

^{1}H-NMR spectra were carried out with a Bruker AC 80 NMR spectrophotometer by using CS_2 as solvent and TMS as internal reference. ^{13}C-NMR spectra were obtained by Bruker AC 200 NMR spectrophotometer by using deuterated

chloroform as solvent.

2.2.11. DIFFERENTIAL SCANNING CALORIMETER (DSC)

Mettler DSC TA-3000 system apparatus was used to obtain the glass transition temperatures (Tg) of polymers. Scanning rate was 10 ^{o}K/min and the weights of the samples were around 3-4 mg.

2.2.12. CARBON-HYDROGEN-NITROGEN (CHN) ANALYZER

Hewlet Packard 185 CHN Analyzer was used to identify copper complexes. The temperature of the oxidation furnace was 1000^{o}C, and the temperature of reduction furnace was approximately 500^{o}C and a column oven temperature of 80^{o}C. The flow rate of Helium gas was 100 cc/min.

2.2.13. CAPACITANCE MEASURING ASSEMBLY

For capacitance measurements a General Radio Company Type-1620-A Capacitance Measuring Assembly was used. It consists of a Type 1615-A Capacitance bridge with a Type 1311-A Audio oscillator and a Type 1232-A Tuned amplifier and a Null detector. All capacitance values were taken at 10 kC frequency and 30 volts.

2.3. PROCEDURE

2.3.1. BROMINATION OF 2,6-DICHLOROPHENOL, 4-CHLOROPHENOL and 2,4-DICHLOROPHENOL

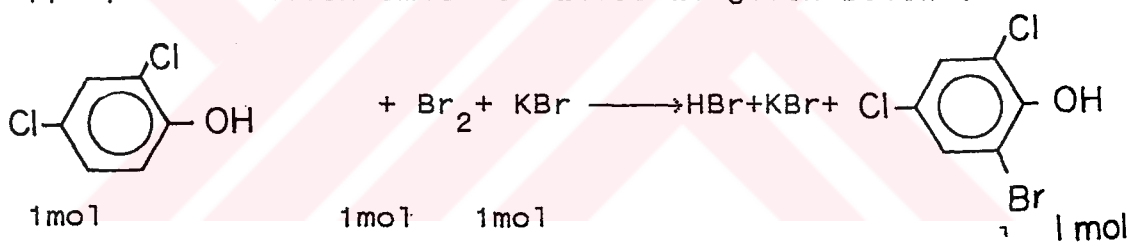
Halophenols mentioned above were brominated to produce trihalogenated phenols. 4-chlorophenol(4-CP) , 2,6-dichlorophenol(2,6-DCP) and 2,4-dichlorophenol (2,4-DCP) were subjected to bromination to synthesize :

i-) 2-bromoo-4,6-dichlorphenol from 2,4-DCP

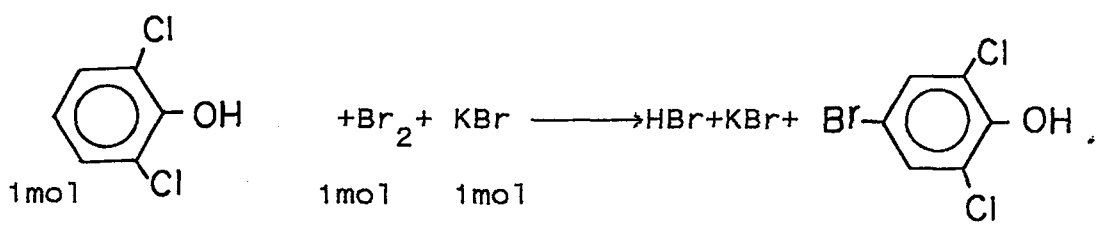
ii-) 4-bromo-2,6-dichlorophenol from 2,6-DCP

iii-) 4-chloro-2,6-dibromophenol from 4-CP

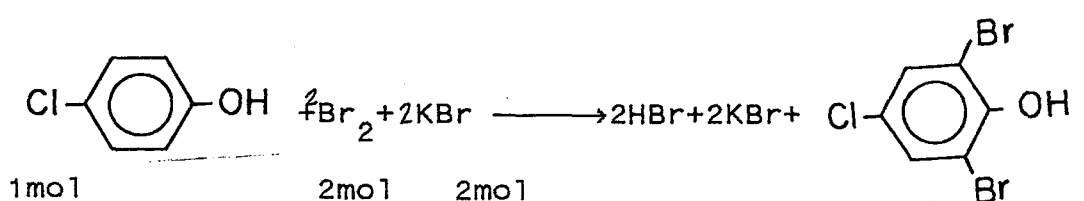
in appropriate stoichiometric ratios as given below :



1mol 1mol 1mol 1 mol



1mol 1mol 1mol 1mol 1 mol



1mol 2mol 2mol 1 mol

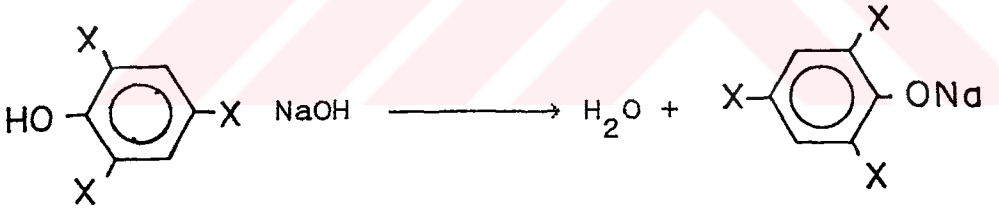
The dichlorophenols were brominated by mixing two different solutions. Solution(I) was prepared by dissolving o.1M bromine with 0.15M KBr in 150ml. of water. Solution(II) was made by dissolving the required amount of dichlorophenol in a minimum amount of ethanol . Then, solution(I) was added to solution(II) dropwise with constant stirring for a given period of time . The precipitated product was cooled on ice for a short time, filtered and dried. For chlorophenol, similar procedure has been followed except that stoichiometric ratios of Br_2 and phenol have been changed.

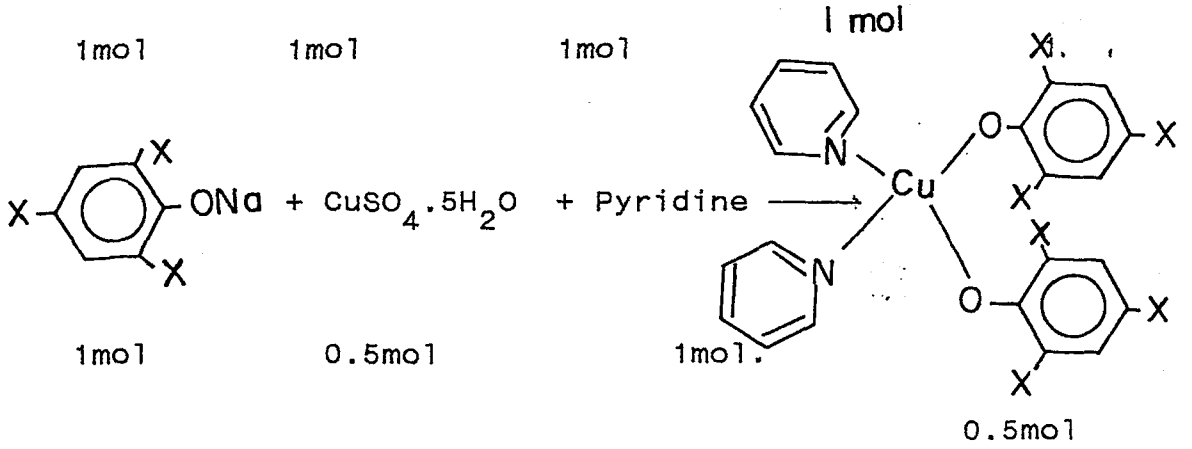
2.3.2. PREPARATION OF BIS(PYRIDINE)BIS (TRIHALOPHENOXO) COPPER(II) COMPLEXES

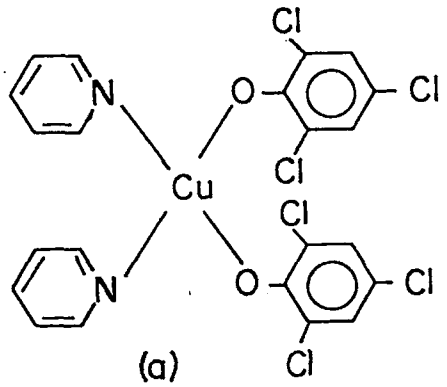
Complexes derived from trihalogenated phenols were prepared easily and in high yield from aqueous solutions of reagents[66]. In the preparation of copper complexes with pyridine, 2,4,6-tribromophenol(TBrP), 2,4,6-trichlorophenol (TCP), 4-chloro-2,4,-dibromophenol (4-Cl-2,6-DBrP), 2-bromo-4,6-dichlorophenol(2Br-4,6-DCP), 4-bromo-2,6-dichlorophenol(4-Br-2,6-DCP), were used as

halophenols. Bis(pyridine)bis(trihalophenoxo)copper(II) complexes were prepared by mixing the following two solutions:

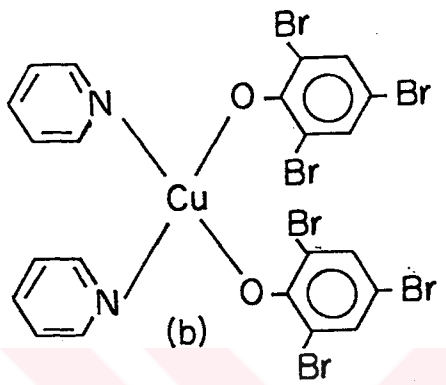
Solution(I) containing 0.04 mol NaOH and 0.04 mol halophenol in 100 ml distilled water was slowly added to solution(II) containing 0.02 mol $CuSO_4.5H_2O$ and 0.04 mol of pyridine in 100 ml distilled water with vigorous stirring. In each case, the precipitated brown complexes were filtered, washed with distilled water and dried in vacuum oven. The complexes (Fig.5) were characterized by taking IR spectra (Fig.6-10) and elemental analysis. It is possible to obtain required amount of complex regarding the following stoichiometric ratios :



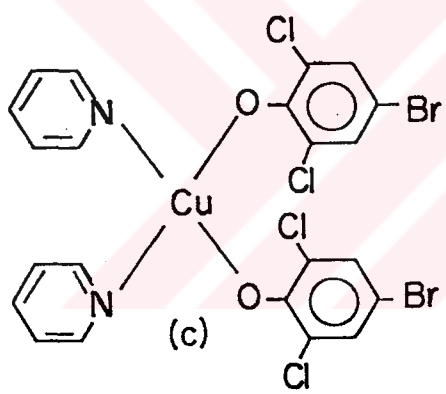




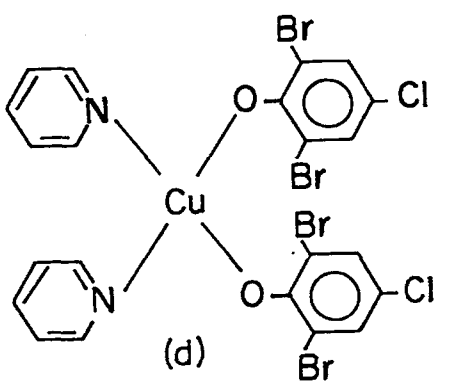
$Py_2Cu(TCP)_2$



$Py_2Cu(TBrP)_2$

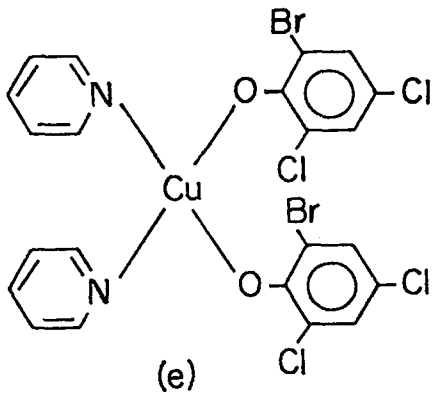


$Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$



$Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$

Figure.5. Structures of various complexes



(e)

$Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$

2.3.3. CYCLIC VOLTAMMETRY

The oxidation and reduction peak potentials of the complexes were determined by cyclic voltammetry. These potentials were measured in TBAFB-DMF as supporting electrolyte-solvent couple at room temperature under nitrogen atmosphere. The working and counter electrodes were platinum bead and platinum wire respectively. The reference electrode was $Ag^{o}/AgBF_4$(0.01M).

The concentrations of monomers were in the order of 10^{-3}M. First of all, the solution was deaerated with nitrogen, then voltage was scanned from zero to anodic (or cathodic) direction until it became reversed by handing and stopped at zero again. Before the addition of monomer, always a background voltammogram was taken to check the presence of impurity.

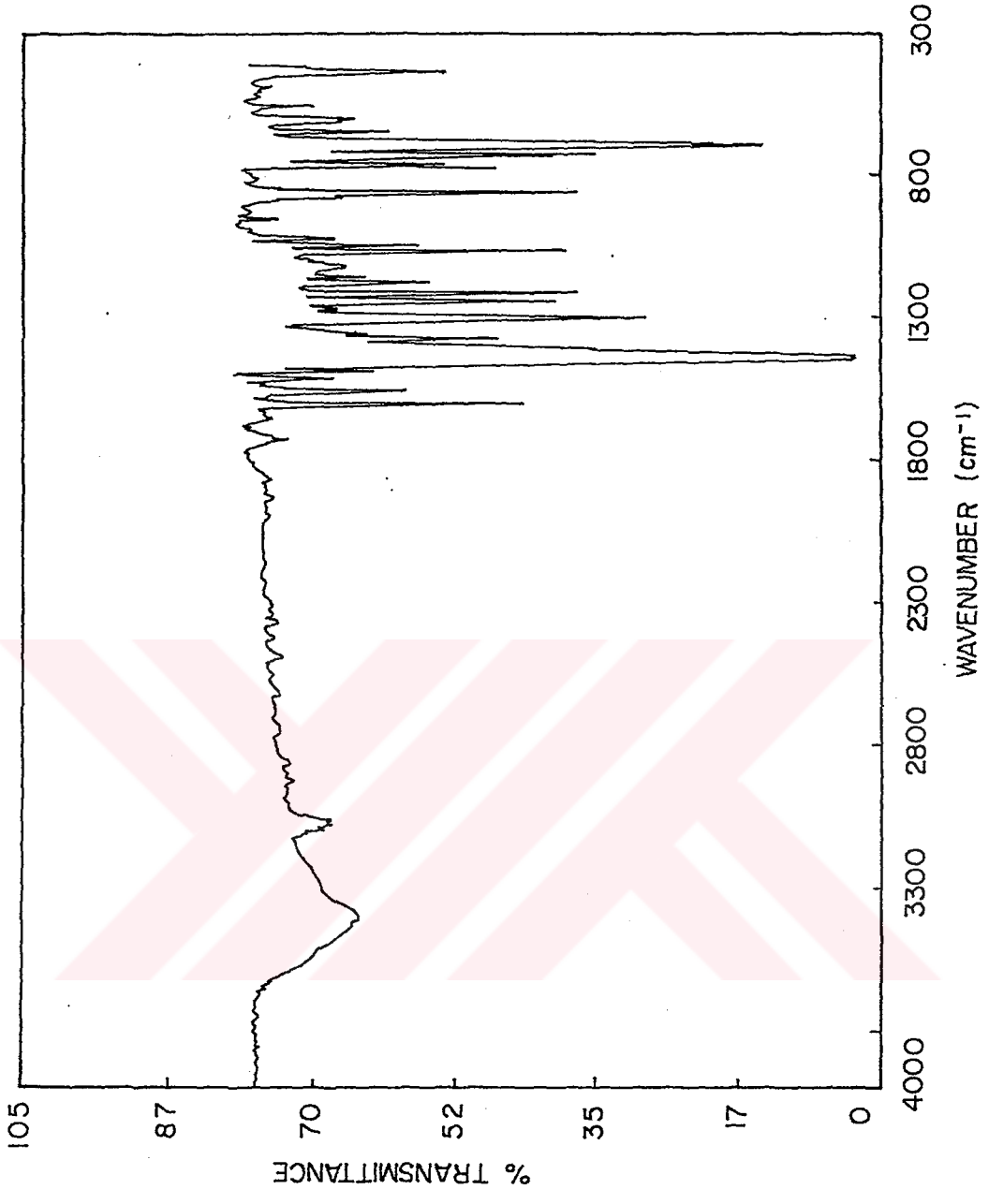


Figure.6. FTIR spectrum of $Py_2Cu(TBrP)_2$ complex

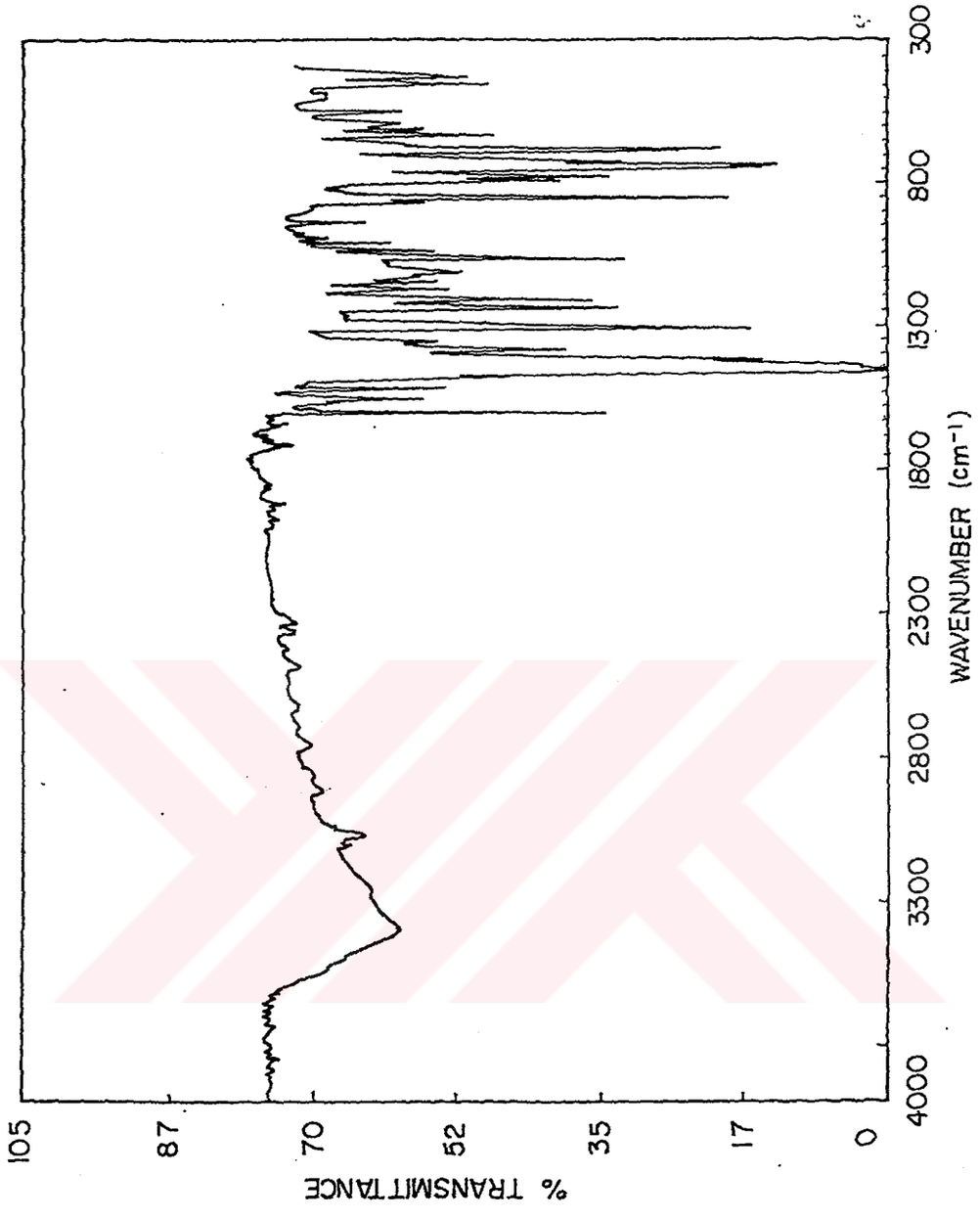


Figure.7. FTIR spectrum of $Py_2Cu(TCP)_2$ complex

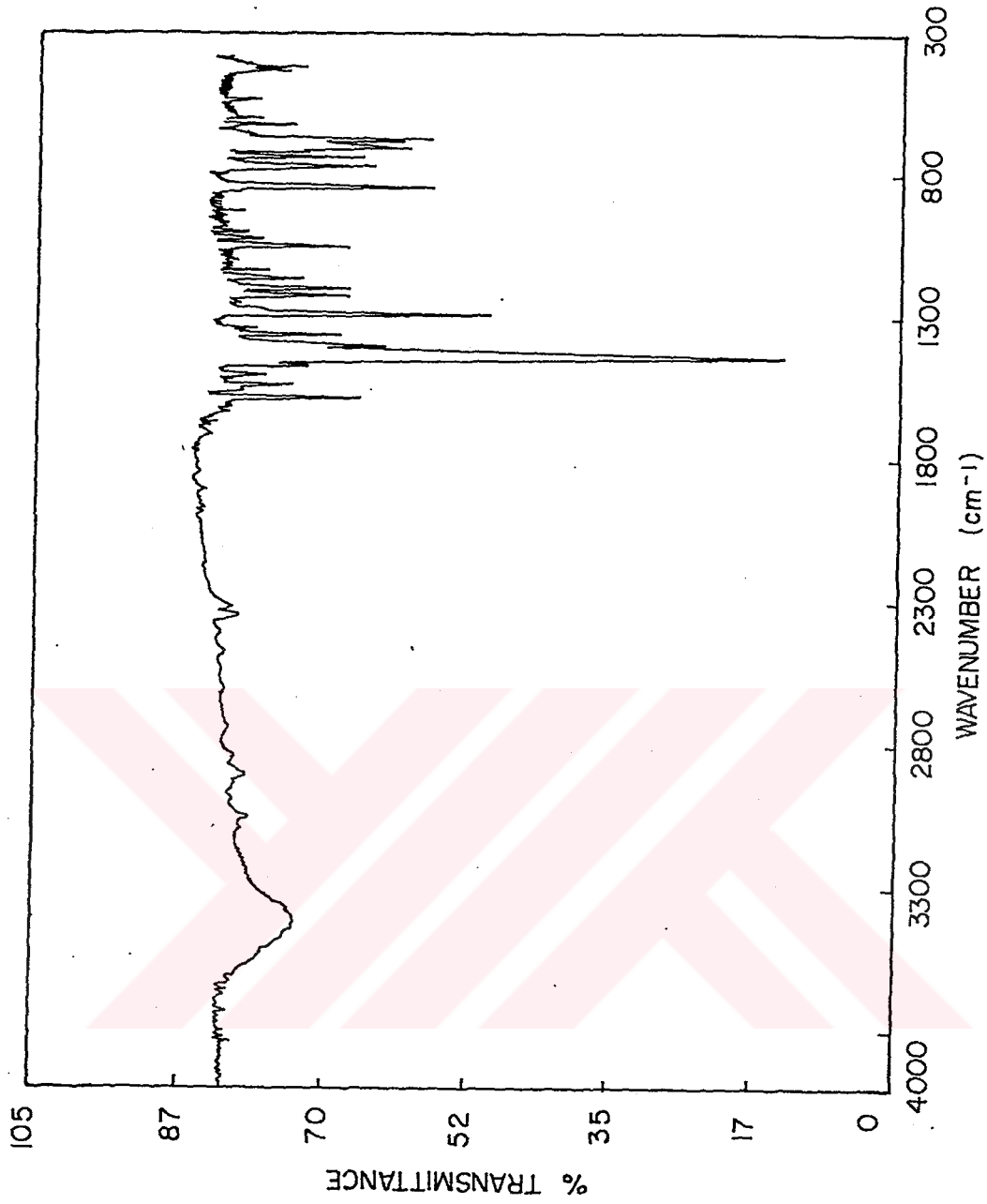


Figure.8. FTIR spectrum of $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$

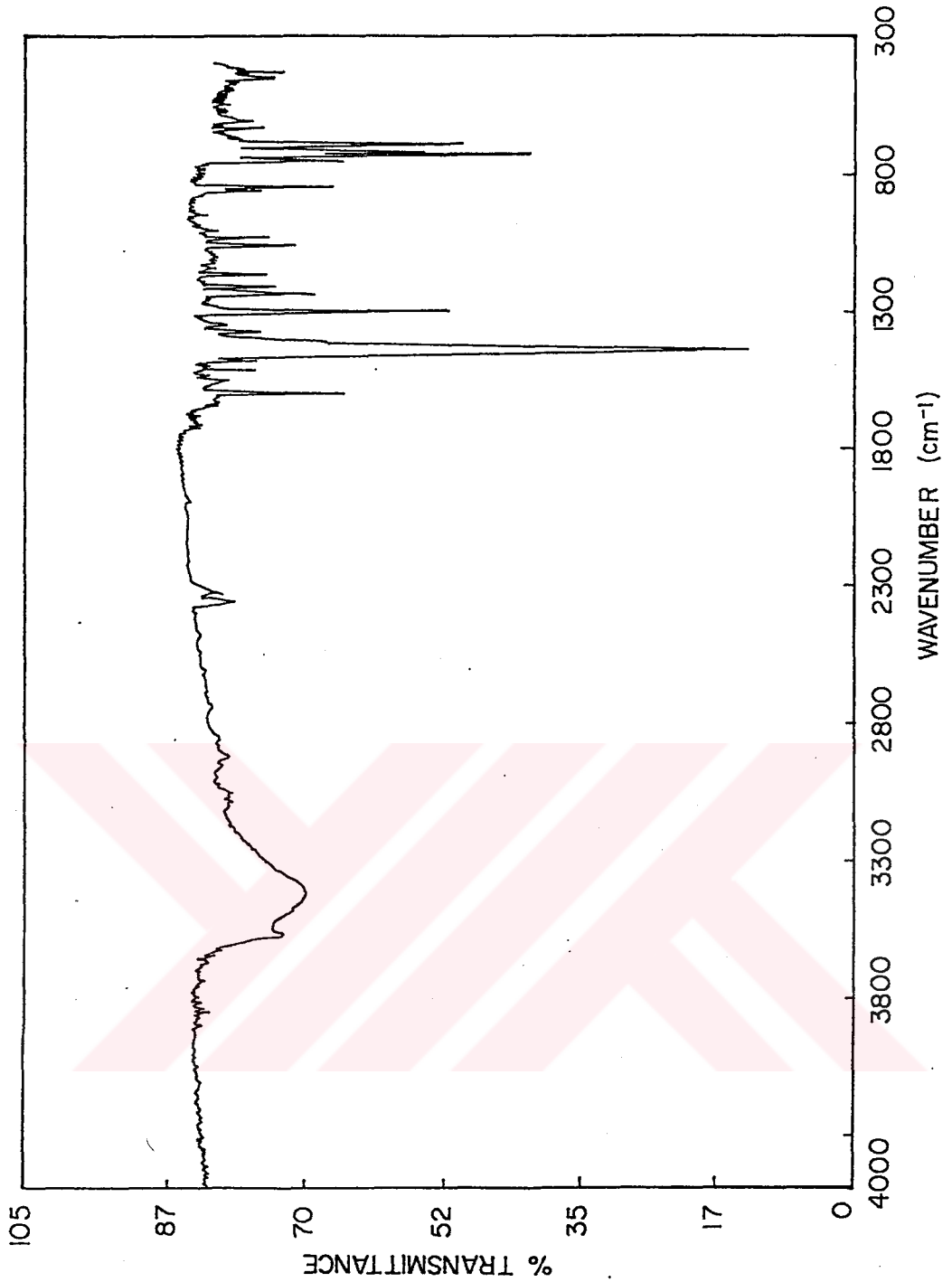


Figure.9. FTIR spectrum of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$

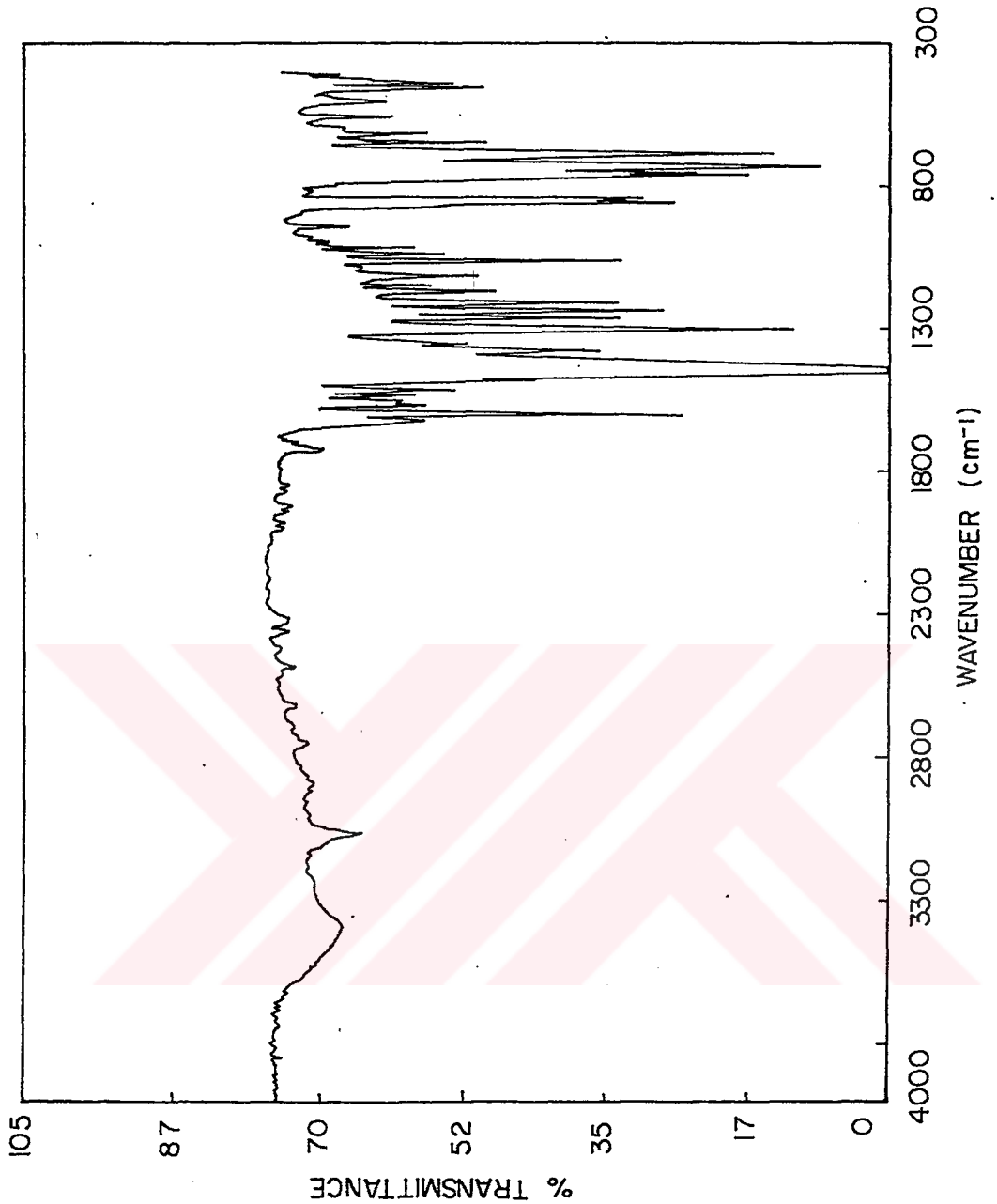


Figure.10. FTIR spectrum of $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$

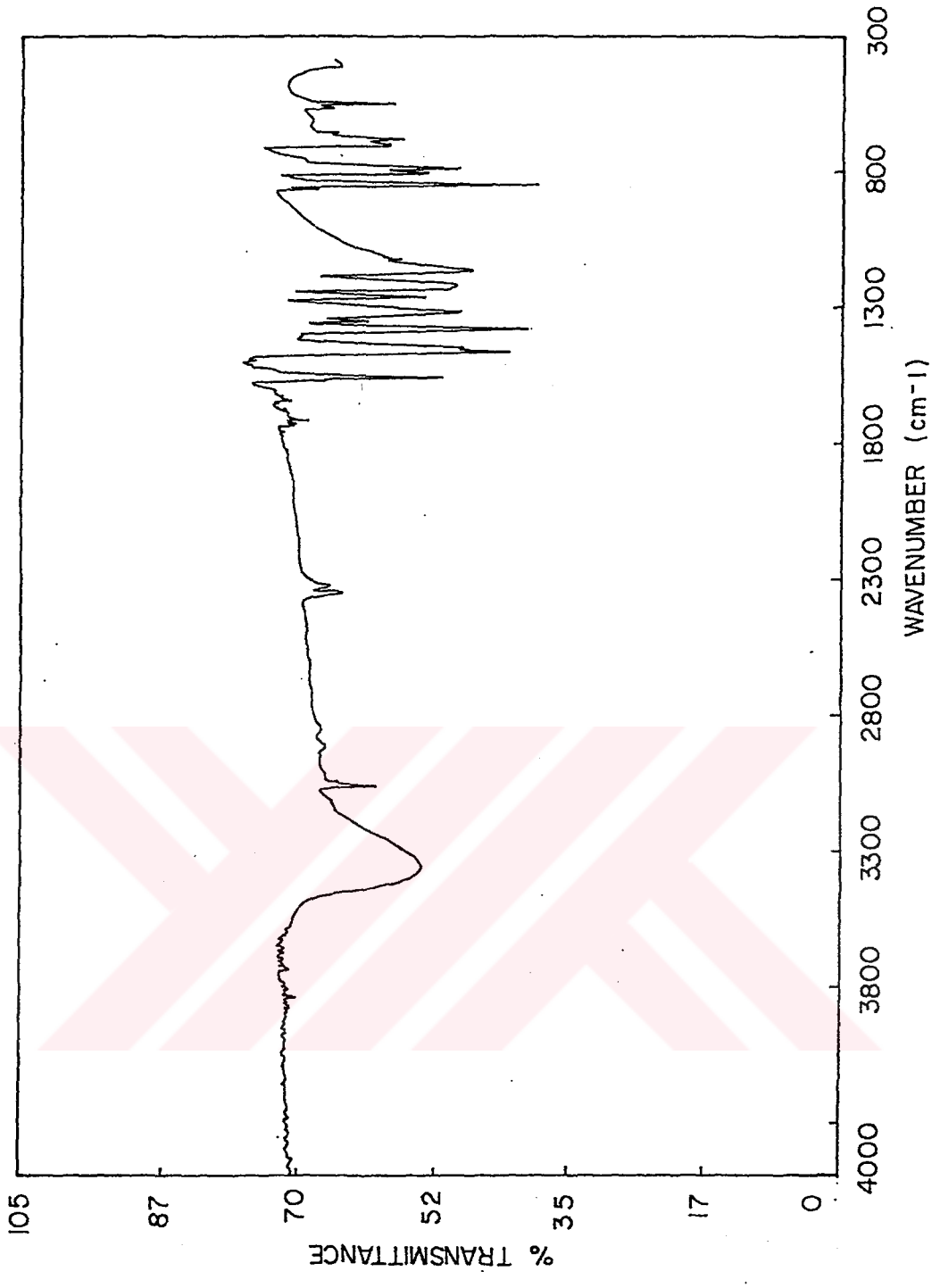


Figure.11. FTIR spectrum of 4-Br-2,6-DCP

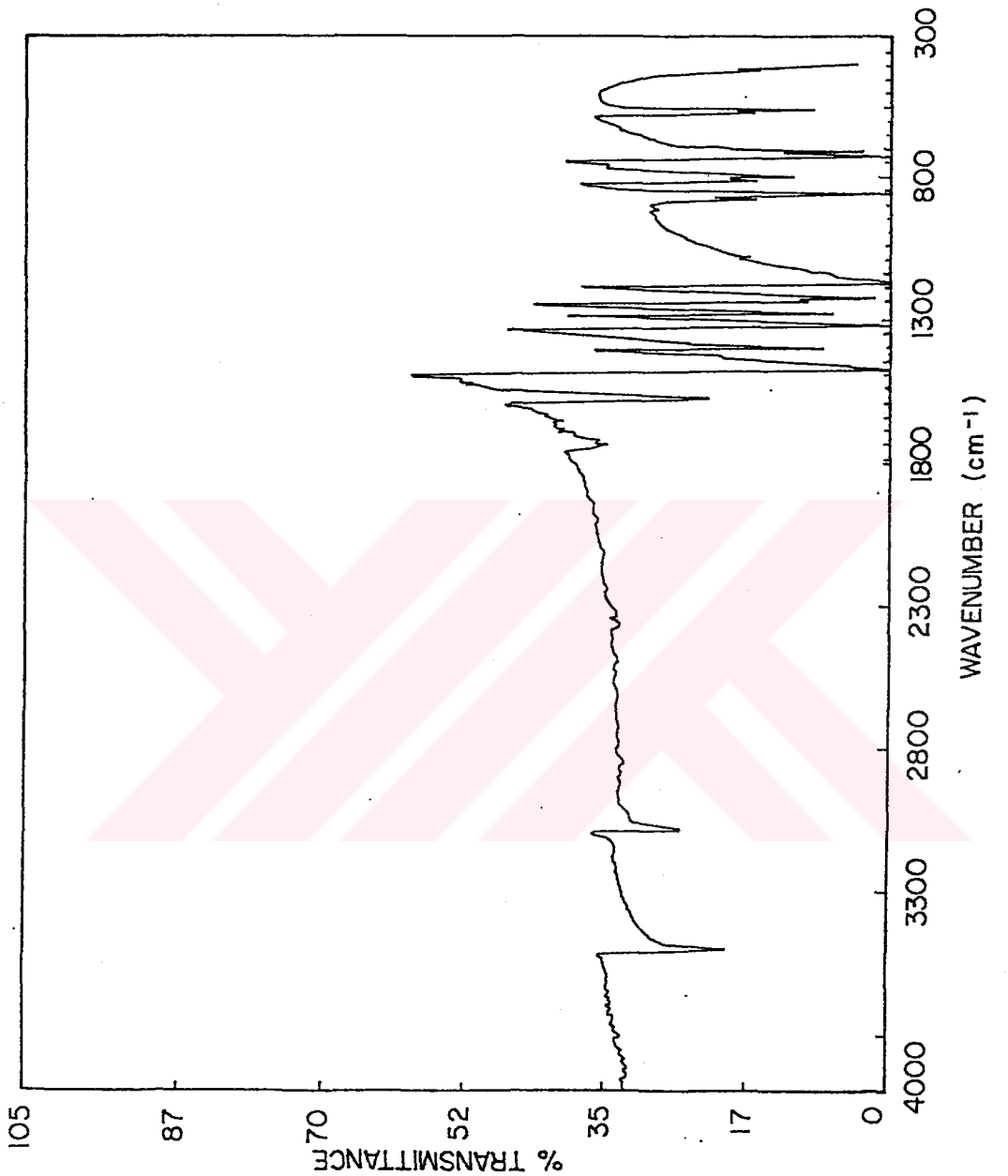


Figure.12. FTIR spectrum of TCP

2.3.4. POLYMER SYNTHESIS

Poly(dihalophenylene oxides) were synthesized by electroinitiation in DMF for 3 h under different atmospheres, at room temperature. Electrolysis system was described earlier in section 2.2.4 and 2.2.7. H-type polymerization cell contains a graphite as the anode with a diameter of 5mm. and a stainless steel ($1in^2$) as the counter electrode. The reference electrode containing Ag^{o}/Ag^{+}(0.01M) was placed in the reference arm of the cell. TBAFB was dissolved in a cell containing ca.50 ml of DMF. Then, suitable amounts of comlex were dissolved in this cell.Electrolysis were achieved at nitrogen and air atmospheres. When the electrolysis were carried out under nitrogen atmospheres, dry nitrogen gas was passed through the solution. After the solutions in each compartment of the cell were equilibrated, nitrogen gas was allowed to flow only through the counter electrode part of the cell to avoid convection. The electrodes were attached to the potentiostat and XY recorder. Potentiostat was adjusted to desired potential and electrolysis was started by switching on the potentiostat. The electrolysis were

carried out only at the anodic peak potentials of the monomers. When the cathodic potentials were applied, it was observed that polymers were obtained only at anode compartments. All polymerizations were achieved at room temperature.After 3 h, electrolysis was ceased by switching off the potentiostat. The polymers were precipitated by transfering the anolyte and catholyte separately into 200 ml ethanol containing few drops of conc.HCl. The isolated product was filtered, washed and dried under vacuum and characterized.

2.3.5. KINETICS of POLYMERIZATION

The kinetics of the polymerization were followed by cyclic voltammetry technique, using two potentiostats at the same time. An electrolysis system and a CV system together were employed. The kinetic studies of the polymerizations were made in the same cell containing 6 electrodes being 3 electrodes for electrolysis and 3 electrodes for CV measurements (Fig.1) . The working and the counter electrodes for electrolysis were graphite and steel, whereas in cyclic voltammetry measurements, they

were platinum bead and platinum wire respectively. $Ag^{o}/AgBF_4$(0.01M) reference electrode was used for both systems. During electrolysis at certain time intervals, the cyclic voltammograms were taken at 200 mV/s scan rate without stopping the electrolysis. The peaks at certain potentials were followed for all polymers. The reacted complex concentrations were calculated from the peak heights. Kinetic experiments were carried out with 10^{-2}M complex concentrations.

2.3.6. POSTPOLYMERIZATION

Postpolymerization studies were carried out. After certain time interval, electrolysis was stopped and polymerization was observed to continue.

3. RESULT AND DISCUSSION

In the present work, electroinitiated polymerization of bis(trihalophenoxo)bis(pyridine)copper(II) complexes was achieved for the first time under constant potential conditions. In the early stage of this study , peak potentials of several halophenols were determined. In the second stage, trihalophenoxo copper complexes were prepared and characterized. In the third stage, polymerization peak potentials of all complexes were measured by using cyclic voltammetry technique. In the fourth stage, poly(dihalophenylene oxides) were obtained at measured polymerization potentials under air and nitrogen atmospheres. Finally, polymers obtained at several potentials were characterized by ^{1}H-NMR , ^{13}C-NMR , FTIR , DSC , in addition to the kinetic study of the polymerization.

3.1. CHARACTERIZATION OF COMPLEXES

It has been clearly demonstrated that Cu(II) can form

stable complexes with a variety of substituted phenols with pyridine completing the coordination sphere of the complex [27]. All the complexes obtained (Fig.5) were characterized by IR spectra and CHN elemental analysis. IR spectra of all complexes are given in Fig.6-10 . Characteristic C-N stretching was observed at about 1065 cm^{-1} . As can be seen from spectrum of trichlorophenol (Fig.12), phenolic O-H peak that was appeared at about 3500 cm^{-1} disappeared mostly in the IR spectrum of bis(trichlorophenoxo)bis(pyridine)copper(II) complex (Fig.7) .This case is also valid for 4-Br-2,6-DCP and $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ (Fig.8 and Fig.11).

The results of CHN elemental analysis of complexes were listed in Table.1 . It was found that experimental results are in agreement with calculated ones in nitrogen,where the experimental error limit is between the range of about ±0.2 .The two seperate analysis for the same complexes were not in agreement in hydrogen and carbon which can be only due to the instrumental errors [a and b]. The repetation of the analysis from some samples indicated that experimental values were in agreement with the theoretical values as has been reported

for the preparation of complexes since 1962 [27,66]. IR and elemental analysis of the complexes prove the structure to be square planar as previously reported in literature [66].

Table-1 : Elemental analysis results of complexes

COMPLEX	(calculated) C %	H %	N %	(found) C %	H %	N %
$Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$	33.3	1.76	3.53	29.2	1.43	3.58b
				35.1	2.57	3.73a
$Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$	37.6	2.0	4.0	35.2	1.76	- b
				39.3	2.71	4.17a
$Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$	37.6	2.0	4.0	—	1.85	3.97b
				37.1	2.97	3.93a
				37.2	2.32	3.95c
$Py_2Cu(TCP)_2$	43.1	2.3	4.6	40.9	2.32	4.48b
				45.4	3.01	4.61a
				43.2	2.7	4.54c
$Py_2Cu(TBrP)_2$	30.0	1.7	3.2	27.6	1.58	3.09b
				33.0	2.5	3.1 a
				30.3	1.94	3.0 c

a ;METU results [3-12-1987]

b:CUKUROVA university results [4-2-1988]

c:METU results [30-10-1989]

3.2 CYCLIC VOLTAMMETRY

Electrochemical technique as a method of initiation in polymerization was widely used . The control of the polymerization potential generally leads to a selective initiation as compared to that of other methods . Hence, the exact peak potentials of the monomers must be measured, using cyclic voltammetry technique which is a rapid way of obtaining the anodic and cathodic peak potentials simultaneously. The cyclic voltammetry system has been discussed in a previous publication [67] .

Oxidation and reduction peak potentials of various halophenols were measured on a Pt^{o} electrode versus Ag^{o}/Ag^{+} in acetonitrile-TBAFB system as solvent-electrolyte couple. This coupled system was electroinert in the high potential range of between -2,6 and +2.8 volt . Anodic(Ep_a) and cathodic(Ep_c) peak potentials of solvent-electrolyte system together with cyclic voltammogram of various halophenols are seen in Fig.13-14 .

Turker et.al [78] have reported that lowest unoccupied molecular orbital (LUMO) energies of the monomers were calculated by Huckel molecular orbital

theory (HMO) . The experimental Ep_c values were correlated to theoretical LUMO energies and electron densities using a multivariable linear regression model by Turker . To visualize the effects which cause variations

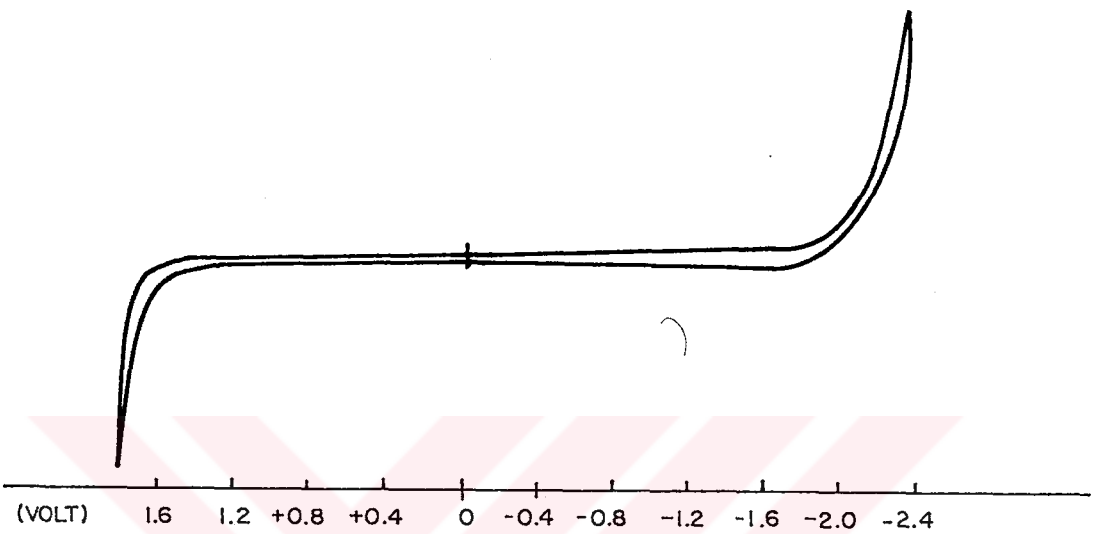


Figure.13. Cyclic voltammogram of DMF-TBAFB as solvent-electrolyte system.

in Ep_c , HMO calculations were carried out [68,69] . Heteroatom parameters (h_p and $k_{\mu p}$) used in the calculations were taken from literature [69] . The HMO calculations, adapted to the present study, reveal that for various halophenols the largest LUMO coefficients (

$C_{p,lumo}$) lie on the ring carbons, which implies that the molecule should approach the electrode surface parallel to the nodal plane of its π-skeleton.

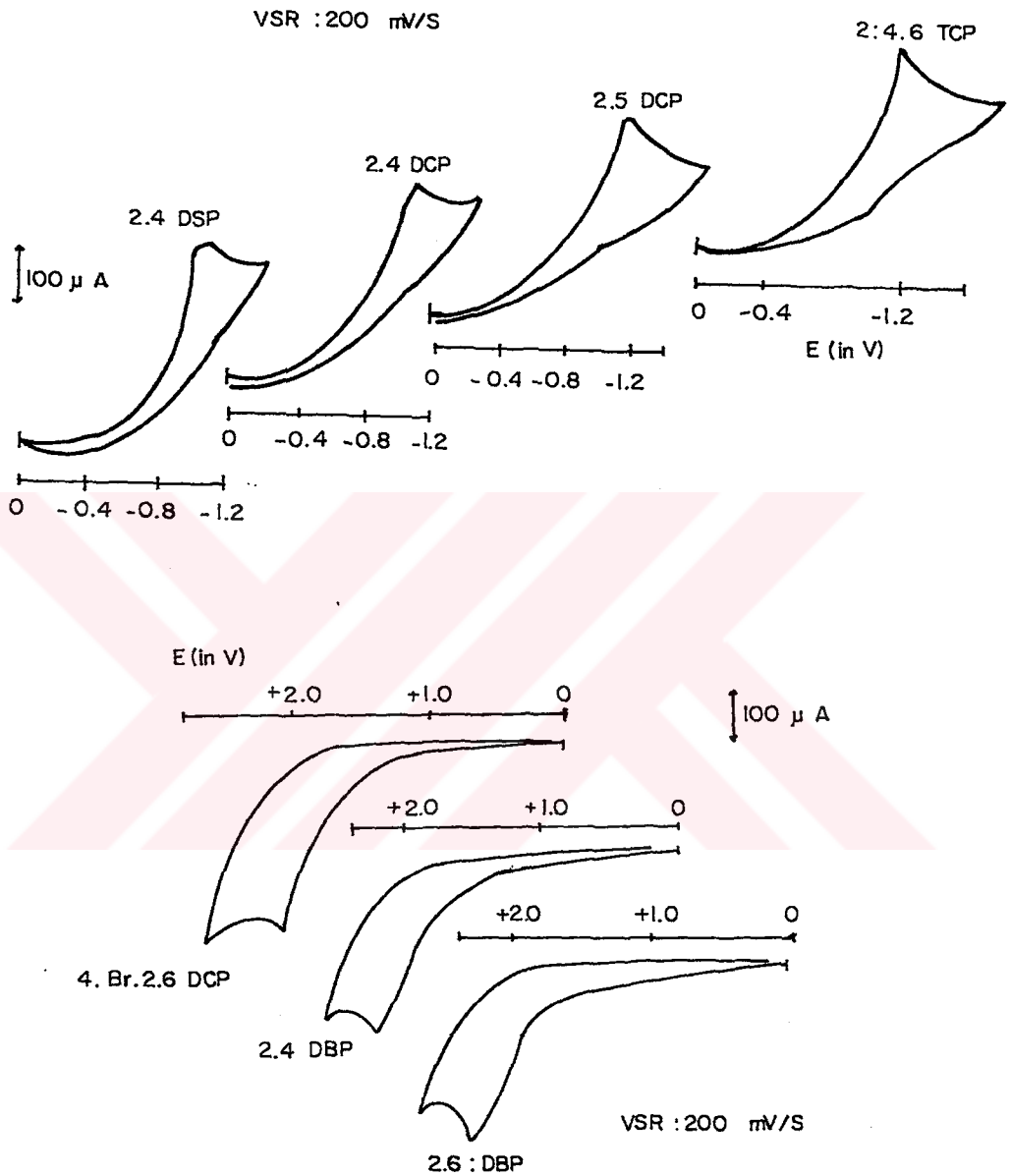


Figure.14. Cyclic voltammogram of various halophenols

$$\epsilon_{LUMO}(F) = A\epsilon^{o}_{LUMO} + \sum_{k}\sum_{\rho} B_k \, C\rho_{LUMO} + G \qquad \text{Eq.1}$$

where F is electric field

index k is for the same kind of atoms

G is for the residues

Then Eq.1 can be approximated as

$$Ep_c = b_o + b_1\epsilon_{LUMO} + b_2\sum_{c} C^2_{i,LUMO} \qquad \text{Eq.2}$$

where the summation is over all the ring carbons. Table-2 tabulates ϵ^{o} and $\sum_{c} C^2_{LUMO}$ values of various halophenols.

The regression of the multivariable Eq.2 yields

$$Ep_c = 37.4813062\ \epsilon^{o}_{LUMO} - 93.31543247\ \sum_{c} C^2_{i,LUMO} + 129.760179 \qquad \text{Eq.3}$$

with a coefficient of determination $R^2 = 0.99$. It should be noted that there exists a colinearity between ϵ_{LUMO} and $\sum_{c} C^2_{i,LUMO}$.

Table-2 : Measured reduction peak potential relations with molecular orbital properties

COMPOUND	Ep_c [a]	$\in_{LUMO}$ (β units) [b]	$\sum_c C_\rho^2$ [b]
TCP	-1.21	-1.0267	0.99113
2,4-DCP	-1.11	-1.0127	0.99571
2,5-DCP	-1.18	-1.0226	0.99245
2,4-DCP	-1.04	-1.0087	0.99652
TBrP	-1.03	-1.01803	0.99269
2,6-DCP	-1.03	-1.01803	0.99269
4-Cl-2,6-DCP	-1.03	-1.01803	0.99269

a : First reduction peak potential measured experimentally

b : Theoretically calculated values taken from literature

Highest occupied molecular orbital (HOMO) energies of the monomers have been calculated by Huckel molecular orbital considerations. Measured Ep_a values were correlated to theoretical HOMO energies using a linear regression model by Turker et.al.[79], who has reported the relation between measured Ep_a values and HOMO

energies. He pointed out that theoretically halogens fall into -E-type substituents which are isoconjugate with odd alternant hydrocarbon anions, and attached to the parent molecule, through active atoms [70,71]. Halogens have opposing Π-inductive and electrometric effects [77]. They inductively should lower the energies of HOMO and LUMO, and mesomerically raise up the energies of these frontier orbitals . Table-3 indicates Ep_a values and HOMO energies of various halophenols by using linear regression model .

Because it has the largest range in terms of electroactivity, acetonitrile was preferred over other solvents in measurements of the halophenols.

Table-3. $E_{p,a}$ values and HOMO energies of various halophenols

Compound	(c) $E_{p,a}$ (volt)	(d) $\in_m$ (β units)
2,6-DBrP	2.10	0.79603
TCP	2.10	0.76152
4-Br-2,6-DCP	2.10	0.76333
TBrP	2.10	0.76487
2-Br-4,6-DCP	2.10	0.76231

4-Cl-2,6-DBrP	2.10	0.76310
2,6-DCP	2.30	0.79481
2,4-DBrP	2.20	0.77626

(c) : Measured peak potential of various halophenols

(d) : Calculated HOMO energies taken from literature

The oxidation and reduction peak potentials of each complex were measured in DMF-TBAFB solvent-electrolyte couple at room temperature. The solvent-electrolyte couple was electroinert in the potential range of between -2.5 V and +1.5 V where the solvent discharge occurs at above these potentials. The anodic and cathodic peak potential of solvent-electrolyte system was given in Fig.13 .

The anodic and cathodic peak potentials of $Py_2Cu(TCP)_2$ $Py_2Cu(TBrP)_2$,$Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$,$Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ and $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ were measured versus Ag^{o}/Ag^{+}reference electrode at room temperature. The voltage scan rate was 200 mv/s .Cyclic voltammograms of all complexes are to be shown in Figures 15,16,17,18,19..Anodic and cathodic peak potentials of related complexes are listed in Table-4 .

Table-4. Oxidation ($E_{p,a}$) and Reduction ($E_{p,c}$) peak potentials of complexes specified

Complex	Anodic peak potentials($E_{p,a}$) (in volt)	Cathodic peak potentials($E_{p,c}$) (in volt)
$Py_2Cu(TCP)_2$	+0.3	-0.7
	+0.65	-1.6
	+1.0	-2.05
$Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$	+0.2	-0.5
	+0.65	-1.20
	+0.9	-2.1
	+1.3	
$Py_2Cu(TBrP)_2$	+0.4	-0.75
	+0.65	-1.4
	+1.1	-2.2
$Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$	+0.42	-0.65
	+0.75	-1.3
	+1.1	-1.9

		-2.1
$Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$	+0.4	-0.85
	+0.7	-1.35
	+1.15	-1.7
		-2.1

Figure.15. Cyclic voltammogram of $Py_2Cu(TBrP)_2$

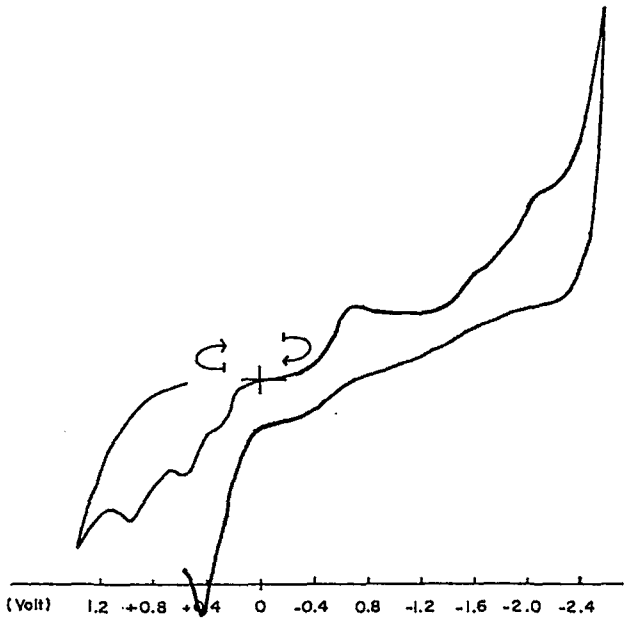


Figure.16. Cyclic voltammogram of $Py_2Cu(TCP)_2$

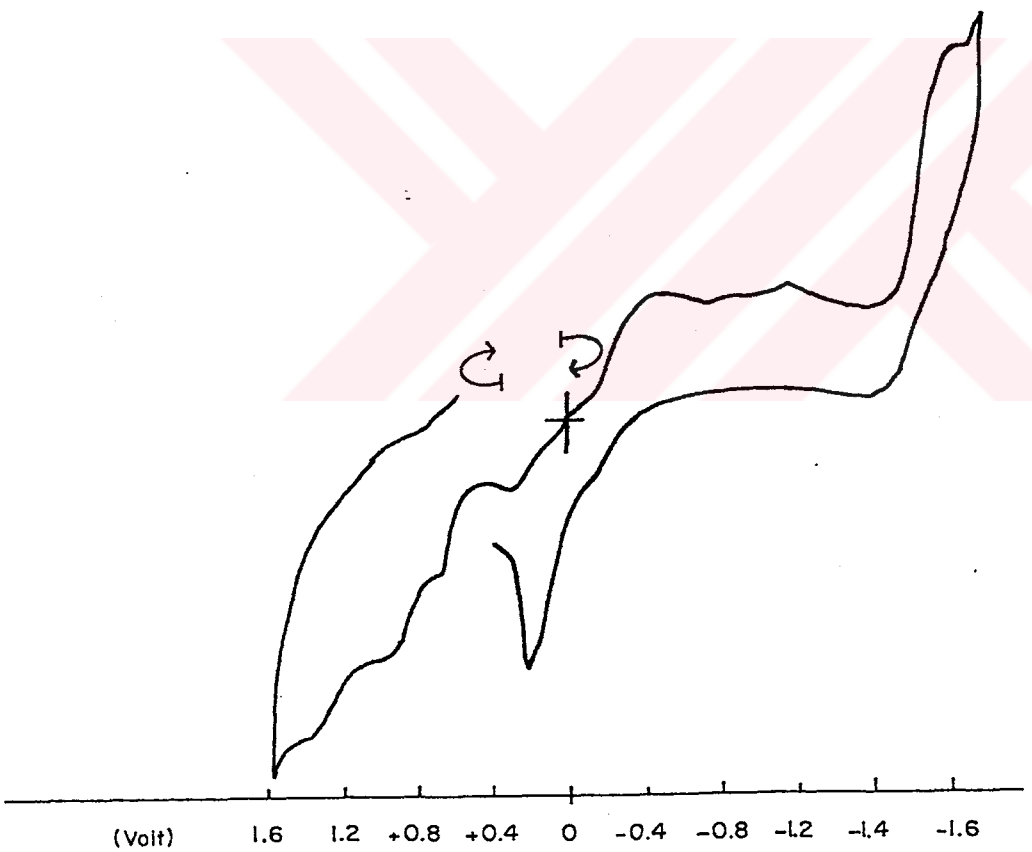


Figure.17. Cyclic voltammogram of $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$

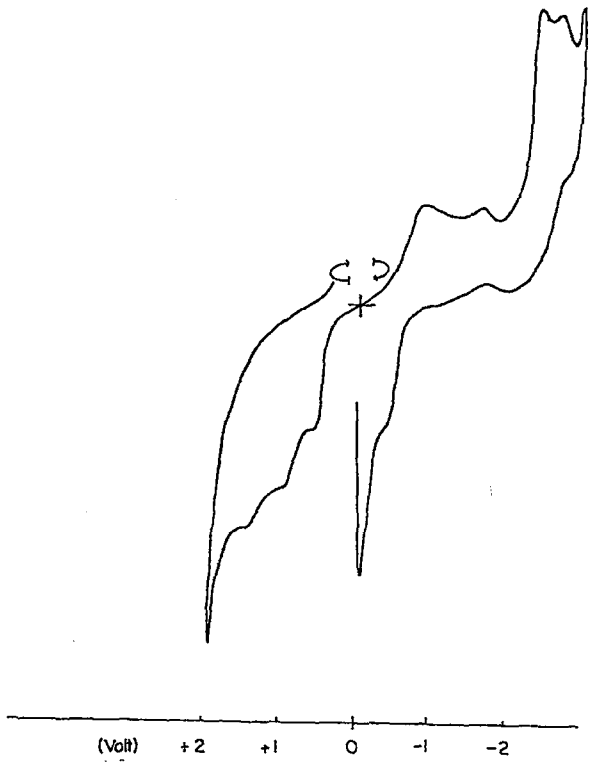


Figure.18. Cyclic voltammogram of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$

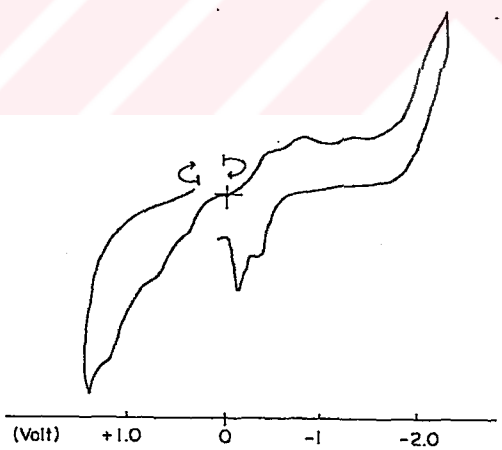


Figure.19. Cyclic voltammogram of $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$

3.3. ELECTROINITIATED POLYMERIZATION

Electroinitiated polymerization of $Py_2Cu(TCP)_2$ $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCPO)_2$, $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$, $Py_2Cu(TBrP)$, $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ were carried out in the presence of TBAFB-DMF as supporting electrolyte-solvent couple at room temperature. All the polymerizations were achieved at the redox potentials of the complexes under nitrogen and air atmospheres. Reference electrode was Ag^{o}/Ag^{+} (0.01 M) in each case. Although electrolysis were carried out both at cathodic and anodic peak potentials, polymers were recovered only from anode compartments of the electrolysis cell. There was no polymer in cathode compartment during electrolysis . Formation of polymers in anolyte only, indicated that electroinitiated polymerization proceeds only upon oxidation on the anode. Although acetonitrile has a larger potential range when compared with that of dimethyl formamide(DMF), DMF was used as a solvent during all polymerizations, because, all these complexes have high tendency to be polymerized immediately in acetonitrile without passing current.

$Py_2Cu(TCP)_2$ complex was electrolyzed at different

anodic and cathodic peak potentials under nitrogen and air atmospheres. The polymer was obtained at anode compartment of the electrolysis cell with formation of salt at the bottom of the anode compartment, when the electrolysis were achieved at redox potentials as given in Table-4 . At the beginning of the electrolysis, the color of the solution is dark brown which is the characteristic color of the complex. The color of the solution in working electrode compartment,where oxidation takes place, turned to green as polymerization proceeds in time. At the end of the electrolysis, working electrode compartment was completely green while counter electrode compartment was still dark brown. Blue precipitate was observed at the bottom of the anode compartment.

The electroinitiated polymerization of Py_2Cu(2-Br-4,6-DCP) was achieved at specified potentials as indicated in Table-4 under air and nitrogen atmospheres at room temperature. As in the previous case,polymerizations were carried out always in anode compartment even if reduction potentials were applied. At the end of the electrolysis, color of the solution at anode compartment was green-yellow, while the color of the

solution at cathode compartment was still dark brown. There was no polymer in the cathode compartment as expected.

$Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ was polymerized with specified redox potentials as indicated in Table-4. Polymer was obtained from anolyte only again. Appearance of color change of solution resembles to that of two previous cases. Polymer was found to be soluble as in the previous cases.

The electroinitiated polymerization of $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ was carried out with given oxidation and reduction potentials at room temperature as usual. Polymer was recovered from anolyte only. During the electrolysis, polymer was not found only in soluble case, but colloidal solution was also observed. Some sections of the surface of working electrode compartment has been coated with salt,which was not soluble in solution. Again counter electrode compartment remained unchanged.

$Py_2Cu(TBrP)_2$ was electrolyzed at different specified potentials as given in Table-4. Polymerization was just similar to that of $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$.

It is a general way for all electrolysis that the

content of both anode and cathode compartments were transferred with syringes and poured into two different ethanol solution containing few drops of conc.HCl. The polymers were obtained by precipitation in ethanol and washed and dried under vacuum.

Since all polymers were only obtained at the anode compartment of the cell, this could be due to the fact that polymerization was initiated by a direct electron transfer from complex to the anode as in the proposed mechanism (Fig.20). Once the phenoxy radical was produced, it propagated the polymerization reaction in the bulk of the solution. The percent yields were calculated by considering complex quantities below:

$$\%Yield = \frac{\text{weight of the polymeric product}}{\text{initial weight of the complex}} * 100$$

Tables 5-9 indicate the yields of the polymers obtained by the electrolysis of $Py_2Cu(TCP)_2$, $Py_2Cu(TBrP)_2$ $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$,$Py_2Cu(4\text{-}CL\text{-}2.6\text{-}DBrP)_2$, $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ under nitrogen and air atmospheres.

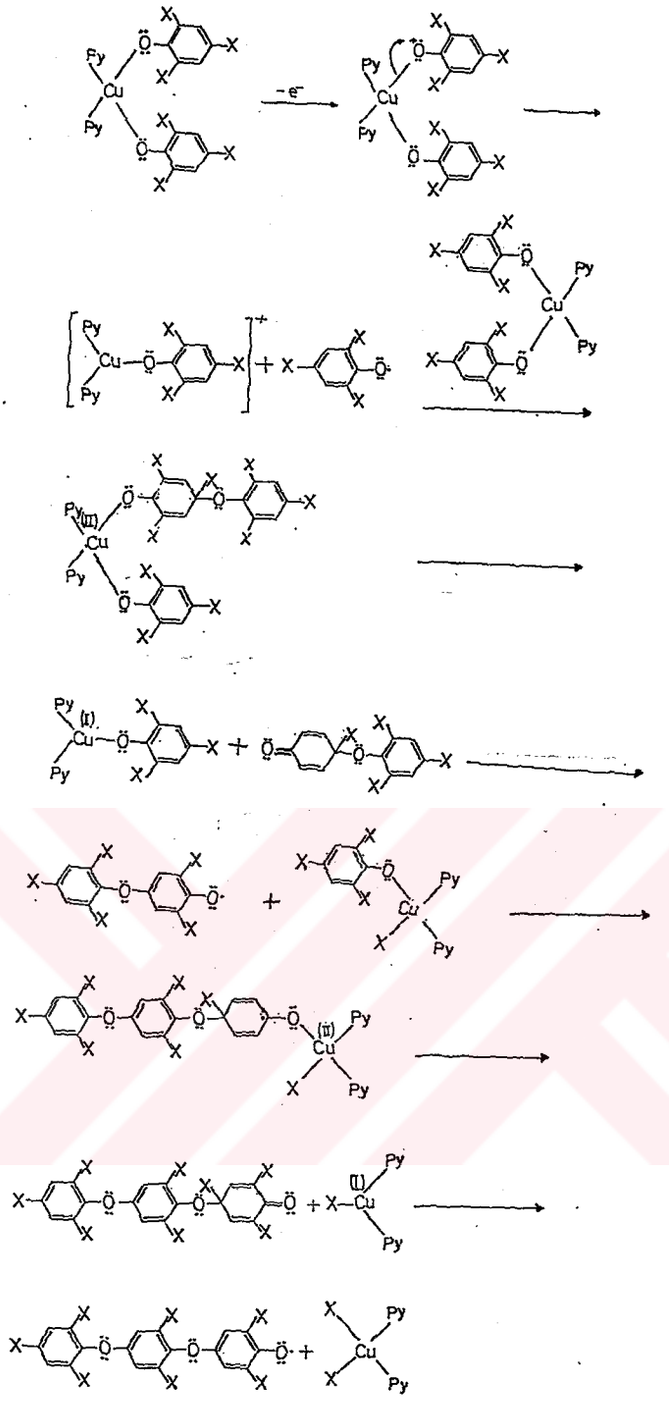


Figure.20. Proposed mechanism of the reaction

(Above mechanism was originally proposed by S.Yigit[76] for ED ligand)

Table-5. Percent yield from the polymerization of bis(2,4,6-tribromophenoxo)bis(pyridine)copper(II)complex

E_{pol}[a] (in volt)	% yield[b] under N_2	% yield[b] under air
+0.66	39	46
+1.1	39	46
-0.70[c]	-	12
-1.4[c]	28	30
-2.2[c]	30	31

a: Measured peak potentials as polymerization potentials

b : Polymer yield recovered from anolyte at the end of the electrolysis

c : Polymer was obtained in anode compartment (at counter electrode part)

Table-6. Percent yield from the polymerization of bis(2,4,6-trichlorophenoxo)bis(pyridine)copper(II) complex

E_{pol}[a] (in volt)	% yield[b] under N_2	% yield[b] under air
+0.65	40	39
+1.1	49	38
-0.7[c]	-	7.0
-0.9[c]	29	28
-1.6[c]	29	30
-2.04[c]	33	31

a. Measured peak potentials employed as polymerization potentials

b.: Polymer recovered from anolyte at the end of the electrolysis

c.: Polymer was obtained only at anode compartment

E_{pol}.: Polymerization potential

Table-7. Percent yield from the polymerization of bis(4-Br-2,6-dichlorophenoxo)bis(pyridine)copper(II) complex

E_{pol}[a] (in volt)	% yield[b] under N_2	% yield[b] under air
+0.65	36	38
+1.3	37	40
-0.5[c]	-	4
-1.2[c]	28	29
-2.1[c]	33	36

a,b, c and E_{pol} have been specified in Table-6

Table-8. Percent yield from the polymerization of bis(4-Chloro-2,6-dibromophenoxo)bis(pyridine)copper(II) complex

E_{pol}[a] (in volt)	% yield under N_2	% yield under air
+0.76	36	35
+1.1	40	41
-0.7[c]	-	10
-1.3[c]	39	40
-1.9[c]	32	38
-2.1[c]	38	38

a, b, c and E_{pol} have been specified in table-6

Table-9. Percent yield from the polymerization of bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine)copper(II) complex

E_{pol}[a] (in volt)	% yield under N_2	% yield under air
+0.7	38	31
+1.15	23	28
-0.75[c]	-	21
-1.314[c]	-	13
-1.670[c]		
+0.4[d]	54	

a, b, c and E_{pol} have already been explained in Table-6

d.: Polymer yielded after 10 minutes application of voltage and then left for post polymerization for overnight.

As can be seen from Tables, the percent yields of the

polymers increase with increasing polymerization potential slightly.Usually the polymerizations achieved under nitrogen atmosphere have almost the same percent yields compared to that of under air. It means that oxygen does not affect the polymerizations.

The mechanism of polymerization was found to be free radicalic which was checked by addition of hydroquinone. Hydroquinone was added to polymerization solution at ca.12% conversion and it was observed that polymerization of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ stopped completely. It was also found that post-polymerization proceeded in the absence of current after approximately 5 minutes of electrolysis of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$. It was also observed that the other complexes with different ligands obeyed this behaviour of polymerization mechanism [76].

3.4. KINETICS OF POLYMERIZATION

Kinetics of polymerization reactions can be followed by gas chromatography, precipitation and other spectroscopic methods. In the present work, a new technique was applied. This technique enables us to follow

the rate of the reaction without removing samples from the reaction medium during the electrolysis. According to the Randles and Sevcik [72] equation, peak current(i_p) is directly proportional to the concentration of the monomer in the cyclic voltammetry.

$$i_p = 2.687*10^5.n^{3/2}.A.D^{1/2}.C.V^{1/2}$$

i_p = peak current

A = electrode area

D = diffusion constant of the substrate

C = concentration of the substrate

V = voltage scan rate

n = number of electrons transferred

Therefore, as the reaction proceeds, concentration of monomer decreases, causing the peak height to decrease. The advantage of this method over other techniques is that, the kinetic study of the reactions can be followed without disturbing the system during the course of the reaction by using two potentiostats simultaneously. The first one was used for the electrolysis whereas other one was employed to follow the decrease in height at the oxidation potential of the complex. The cyclic voltammogram were

taken at certain time intervals with the scan rate of 200 mV/s without stopping the electrolysis. For each complex, the lowest oxidation potentials were employed for that purpose. The first initial oxidation peak is taken before electrolysis proceeds, the peak heights are followed in time by cyclic voltammetry. The unreacted monomer concentration is calculated from the peak heights by using the following equation :

$$\% \text{ conversion} = \frac{[H]_o - [H]_t}{[H]_o}$$

where

$[H]_o$: initial peak height of the complex

$[H]_t$: peak height of the complex at any time (t) of electrolysis

Kinetic experiments were carried out at 10^{-2} M complex concentrations. The data for some complexes are related with percent conversions which were given in Tables-10,11,12.. Previously it was reported that there was an induction period in the thermal polymerization of these complexes[80] .However, there was no induction period in the electroinitiated polymerizations of these complexes and the polymerization reaction immediately

started with electrolysis at room temperature.

Table-10. Conversion-time values calculated from cyclic voltammograms of $Py_2Cu(TCP)_2$ during polymerization at 0.757V (at 13.5^{0}C).

Time (min)	Peak[a] height	Conversion	Time	Peak[a] height	Conversion
5	14	0.0	82	10.7	23.6
10	14	0.0	85	9.9	29.3
15	14	0.0	88	8.9	36.4
20	14	0.0	90	8.3	40.7
25	14	0.0	92	7.7	45
30	14	0.0	95	7.5	46.4
35	14	0.0	98	7.3	47.9
40	14	0.0	101	7.1	49.3
45	14	0.0	103	7.0	50.0
50	14	0.0			
55	13.7	2.1			
60	13.7	2.1			
62	13.7	2.1			
67	13.4	4.2			
75	13.0	7.1			
80	11.3	19.3			

a : Peak heights are found from voltammograms in cm.

Table-11. Conversion-time values calculated from cyclic voltammograms of $Py_2Cu(TCP)_2$ during electrolysis at 0.701 V (at room temperature).

Time (minute)	Peak[a] height	Conversion	Time	Peak height	Conversion
0	4.5	0.0	68	3.9	13.3
4	4.4	2.2	72	3.9	13.3
8	4.4	2.2	76	3.9	13.3
12	4.3	4.4	80	3.8	13.3
16	4.3	4.4	84	3.7	17.8
20	4.2	6.7	88	3.5	22.2
24	4.2	6.7	92	3	33.3
28	4.2	6.7	96	3	33.3
32	4.2	6.7	100	1.4	68.9
36	4.2	6.7	104	1	77.8
40	4.1	8.9	108	0.9	80.0
44	4	11.1	112	0.8	82.2
48	4	11.1	116	0.8	82.2
52	4	11.1	120	0.7	84.4
56	4	11.1	124	0.7	84.4

60	4	11.1	128	0.7	84.4
64	3.9	13.3			

a. has been specified in Table-11.

Table-12. Conversion-time values calculated from cyclic voltammogram of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ during electrolysis

Time (min)	Peak[a] height	Conversion %
0	7.5	0
2	7.5	0
6	4.5	0
8	7.4	1.3
10	7.4	1.3
12	7.4	1.3
14	7.4	1.3
20	7.4	1.3
22	7.4	1.3
24	7.4	1.3
26	7.4	1.3
28 [b]		

a has already been specified in Table-10.

b: formation of a new peak

The data related to percent conversion for $1*10^{-2}$M concentration of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ were given in Table-12. As can be seen from this table, the peak at +0.25 V decreases up to about 1.3% conversion value smoothly.However, a new peak formation took place at the end of 28.minute which showed that it is not possible to continue the kinetic studies. The working potential was 0.260 volt during electrolysis.

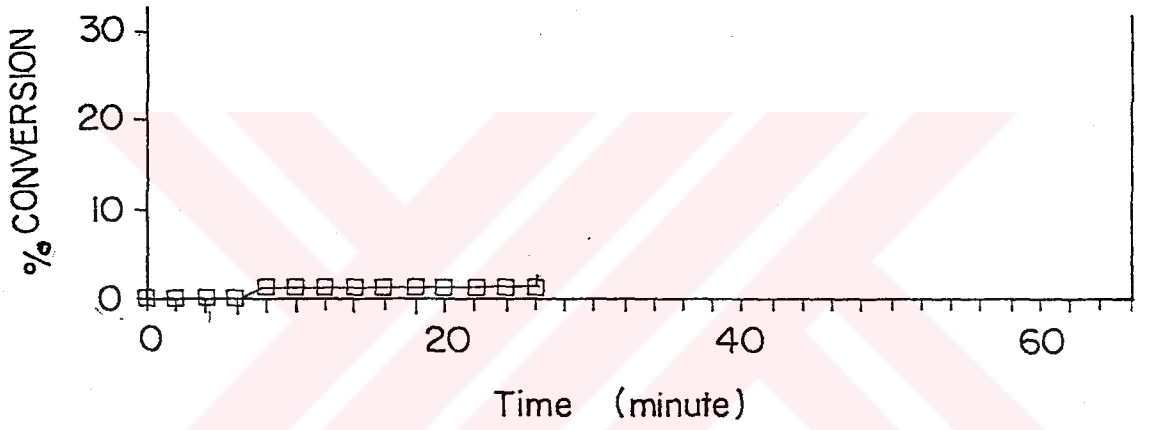


Figure.21. Conversion-time relation in the polymerization of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ at 0.260 volt.

With another study, the peak at +1.15 V was followed for the kinetic study of $Py_2Cu(TCP)_2$ complex at 10^{-2} M concentration and at 13.5^{0}C. The data related with the percent conversion-time plot were listed in Table-10. In that case, after a certain time, polymerization starts and

conversion increases slowly with time up to 7.1 % and then sharp increase up to 45 % as shown in Fig.22. Polymerization potential was +0.757 V during electrolysis under nitrogen atmosphere.

It was studied at +0.701 volt(V) during electrolysis and +0.25-V peak was followed for $Py_2Cu(TCP)_2$ complex at room temperature. The data related with percent conversion-time were given in **Table-11** .Rate was slower up to almost 20 % conversion in 90 minutes. Then, conversion increases sharply up to 84.4 % and it remains constant as seen in **Figure-23** . Kinetic studies for $Py_2Cu(TCP)_2$ at two different temperatures indicated that initial rate is very slow at low temperatures. This kinetic study was done one time.

For the kinetic study of $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$, +0.25 V and +0.65 V peaks on the cyclic voltammograms were followed with certain time intervals as seen in Fig.24. It did not indicate the same trend as in the case of $Py_2Cu(TCP)_2$. As the peak at +0.65 V disappeared, the new peak is formed at +0.10 V in 30 minutes as in the case of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ .On the other hand, within this

period,color of the solution turned to green indicating complete polymerization.+0.25V-peak remained unchanged in

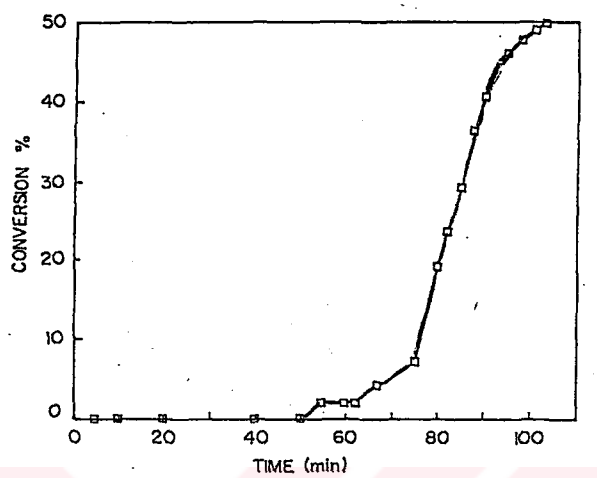


Figure.22. Conversion-time relation in the polymerization of $Py_2Cu(TCP)_2$ at 0.757 V.(at 13.5^{0}C)

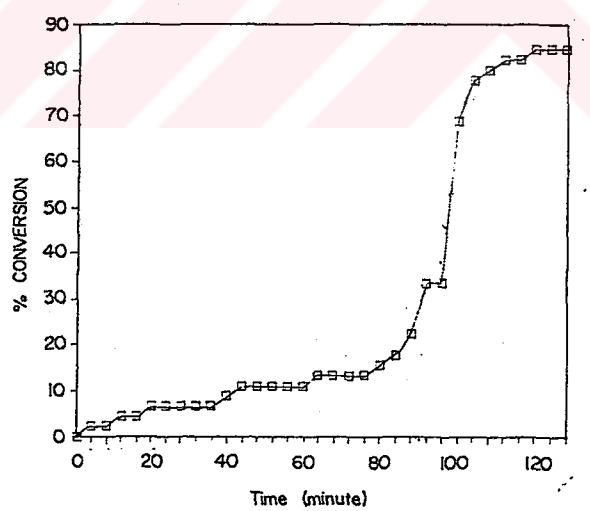


Figure.23. Conversion-time relation in the polymerization of $Py_2Cu(TCP)_2$ at 0.701 volt (room temp.).

height,up to the end of the electrolysis.The new peak is due to the formation of product, which gives the same peak throughout the electrolysis.

It is known that polymerization depends on some factors such as the type of ligand and halogens. Hence, it should not be expected for all complexes to follow the same path. For example, in the kinetic study of $TMEDCu(TBrP)_2$ complex by M.Sacak [62], a reduction peak has been followed. This study revealed that as the polymerization proceeded, the growth amount of $TMEDCuBr_2$ salt formed has been followed by cyclic voltammogram via its reduction peak potential. Kinetic study of this complex could not be achieved by following any oxidation peak regularly.

In this present study, it was intended to follow a reduction peak. But, as seen from the cyclic voltammogram of $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$, there are three reduction peak potentials on it. This makes diffucult to follow any reduction peak among three over plateau. For that reason, this possibility is not valid for such complexes. The most suitable way for those is to follow any oxidation peak in this study.

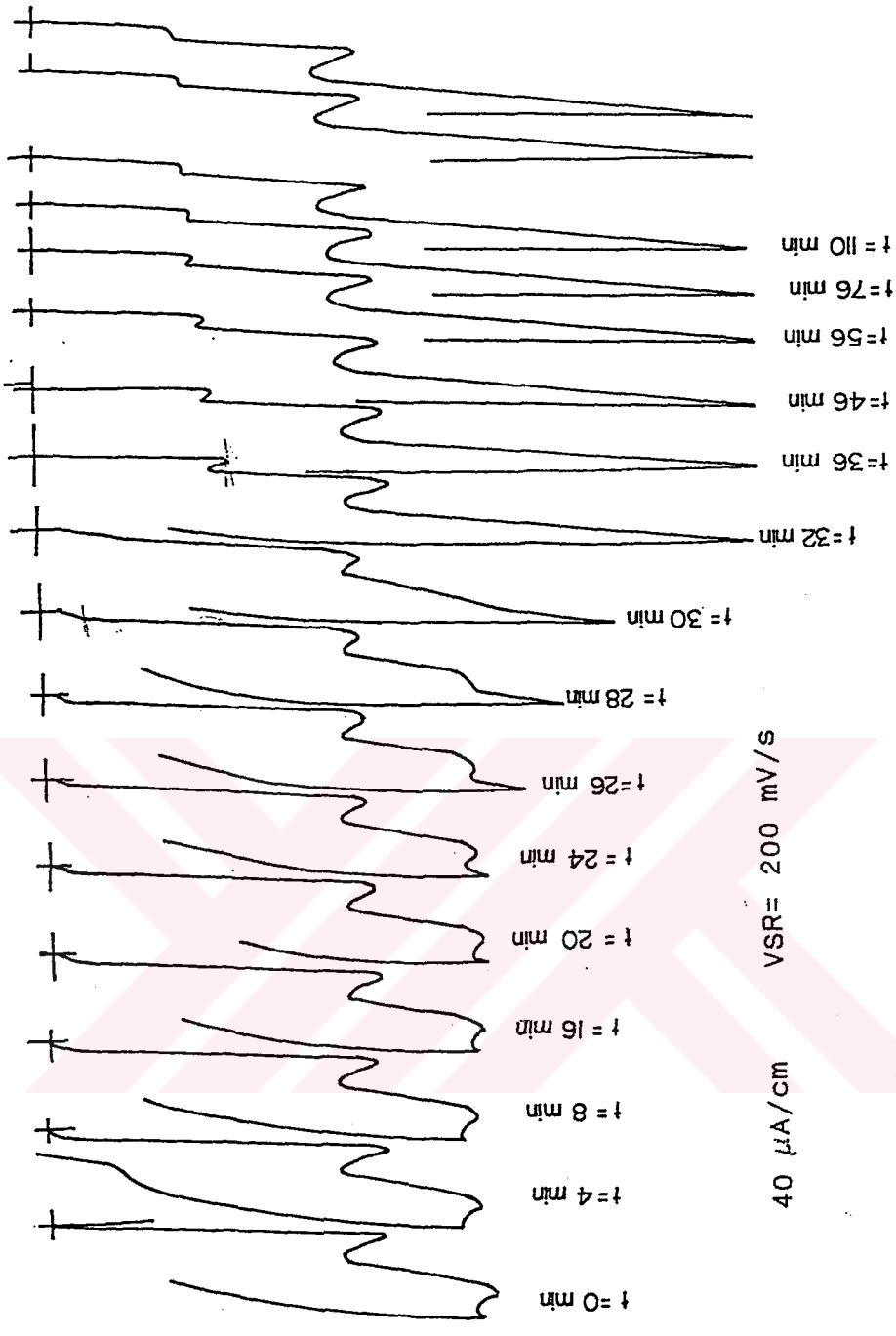


Figure.24. Cyclic voltammogram of $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ taken during the course of electrolysis.

Kinetic study of $Py_2Cu(TBrP)_2$ gave similar trend as in the case of $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$. In the study of $Py_2Cu(TBrP)_2$, at the end of 30 minutes, the new peak at +0.10 V was observed and it remained unchanged during the electrolysis. This is in contrast to the cyclic voltammogram of $Py_2Cu(TCP)_2$ taken during the course of electryolysis at +0.701 V and +0.757 V (Fig.25).

In the case of $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$, there was no any discrete peak followed as seen in cases of $Py_2Cu(TBrP)_2$, $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ and $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ .This fact is attributed to the presence of bromine atom attached to the phenyl ring.

3.5. MOLECULAR WEIGHT DETERMINATIONS

The number average molecular weights ($\bar{M}_n$) of some polymers obtained by electroinitiated polymerization of the complexes were measured by using vapour pressure (Isopiestic) method and Freezing point depression (Cryoscopic) method. $\bar{M}_n$ values of the polymers synthesized from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ and $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ are

about 4000 and 4500 respectively measured by Isopiestic method. $\bar{M}_n$ values of polymers synthesized from $Py_2Cu(TCP)_2$, $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ and $Py_2Cu(TBrP)_2$ were found to be 2250 , 2450 and 3400 respectively by using Cryoscopic method.

As a result , it was conluded that molecular weight of polymers are low, which is an advantage to investigate the structure of the polymer better spectroscopically.Since molecular weights are too low ,such polymers does not bear industrial importance.

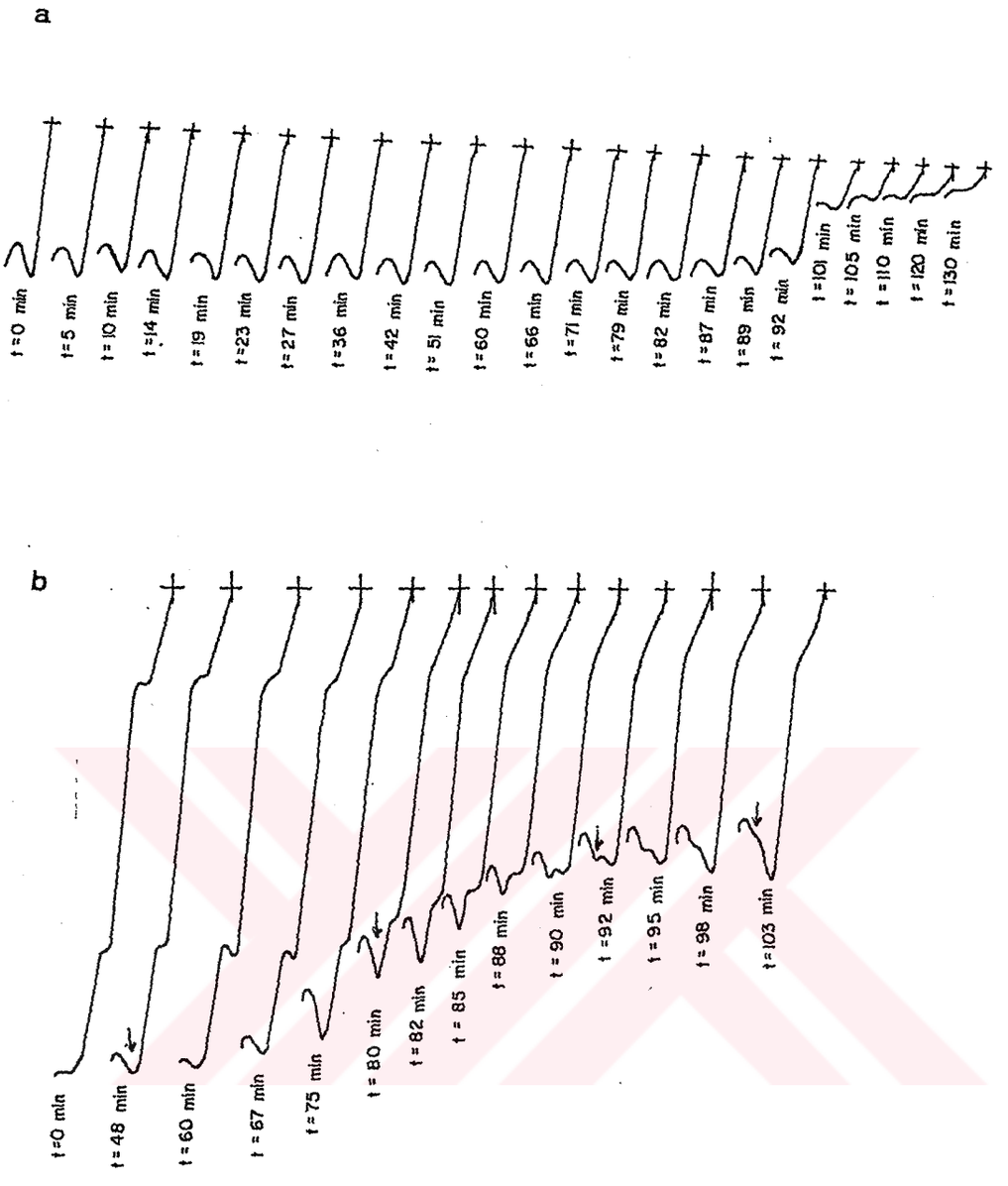


Figure.25. Cyclic voltammogram of $Py_2Cu(TCP)_2$ taken during the course of electrolysis (a: at + 0.701 volt in which+0.25 volt-peak is followed b: at + 0.757 volt in which +1.25 volt-peak is followed).

3.6. GLASS TRANSITION TEMPERATURES (T_g)

The glass transition temperatures (T_g) of various polymers were listed in Table-13. All of them have high T_g values indicating that they are very rigid polymers. From the results as seen in Table-13, it has been concluded that T_g's of the branched-type structure of $Py_2Cu(TCP)_2$ was lower than that of the linear-type structure of $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$. Polymers obtained from $Py_2Cu(TCP)_2$ at both reduction and oxidation potentials as given in Table-13 showed different T_g values although their similar structures were confirmed. T_g of the poly(dichlorophenylene oxide) obtained at a reduction potential is greater than that of polymer as in the case of the oxidation potential. This may be attributed to the uncontrolled high oxidation potential created at anodic part.

For polymers obtained from $Py_2Cu(TCP)_2$, $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ and $Py_2Cu(TBrp)_2$, there is one T_g value for each polymer.

For polymers obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ and

$Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$, however, there are three transitions, which could be due to the highly branched structures of the polymers.

Table-13. T_g values of polymers obtained from all complexes used.

Complexes	structural type	T_g(°C)	M_n
$Py_2Cu(TCP)_2$ [a]	branched	207	
$Py_2Cu(TCP)_2$ [b]	branched	173	2250
$Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$	linear	278	$4*10^3$
$Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$	highly	172	
	branched	185	2450
		199	
$Py_2Cu(TBrP)_2$	linear	284	3400
$Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$	highly	291	
	branched	299	4500
		309	

a : polymer obtained at cathodic potential

b: polymer obtained at anodic potential

3.7. INFRARED SPECTRAL ANALYSIS OF POLYMERS

Fig.26. displays fourier transform infrared (FTIR) spectrum of the polymer obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ .The bands which absorb at 1380, 1400, 1440, 1470, 1550 and 1600 cm^{-1} are C=C ring stretchings. The spectrum displays C-O absorbtions at 1105, 1115, 1180, 1200 and 1240 cm^{-1} . In addition to these, C-O-C bonds (940, 1000 and 1030 cm^{-1}), C-H bonds (840 and 860 cm^{-1}), C-Cl and C-Br bonds (700 and 770 cm^{-1}) exist.

FTIR spectrum of the polymeric product obtained from $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ is shown in Fig.27. The absorbtion bands at 1375, 1450, 1470, 1550, 1560 and 1590 cm^{-1} are the characteristic C=C stretchings . The spectrum displays C-O stretchings (1130, 1180, 1210, 1240 cm^{-1}), symmetric C-O-C stretchings (930, 1000, 1100 cm^{-1}), C-H out of plane bendings (810, 880 cm^{-1}), and C-Cl and C-Br absorbtions (750, 770 cm^{-1}).

FTIR of polymer obtained from $Py_2Cu(TBrP)_2$ is shown in Fig.28. It is characterized by 860, 855 cm^{-1} out of plane C-H bendings; 920, 1000, 1030, 1060, 1090 cm^{-1}

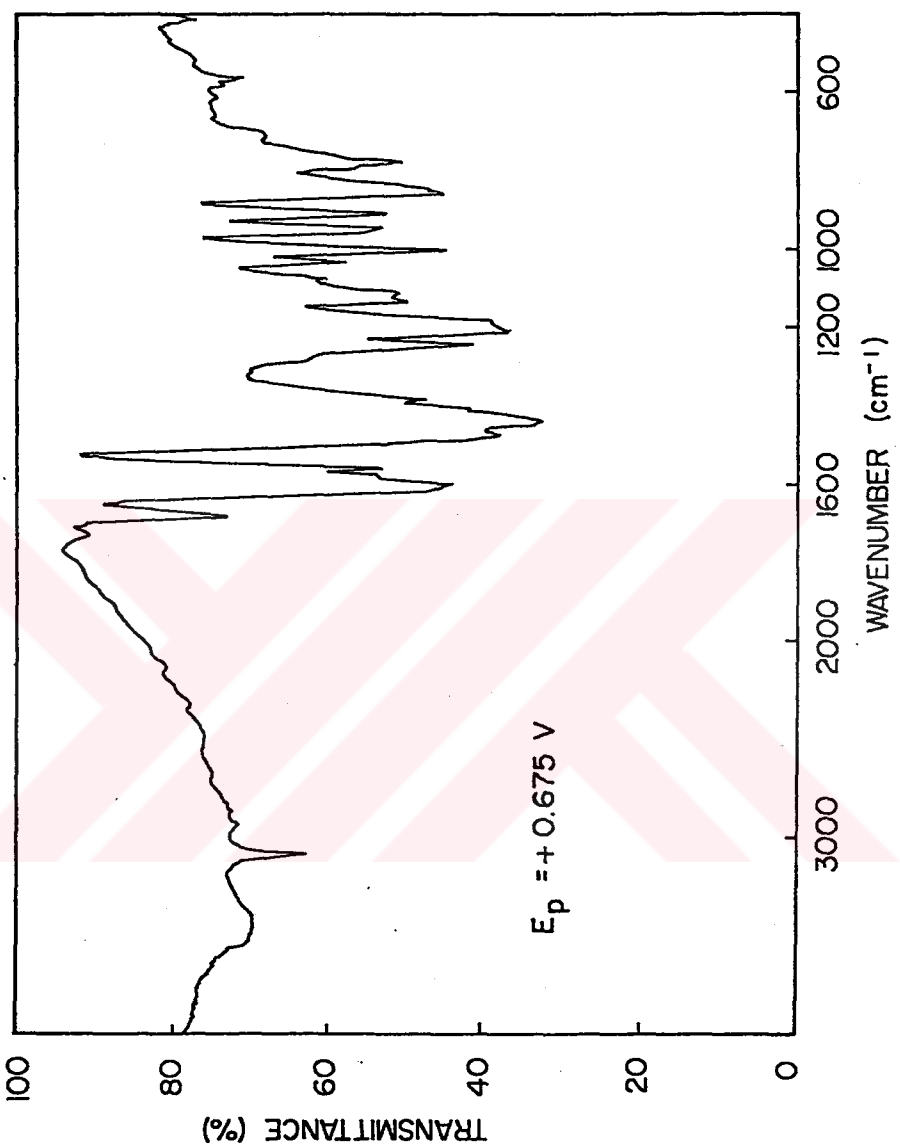


Figure.26. FTIR of polymer obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$.

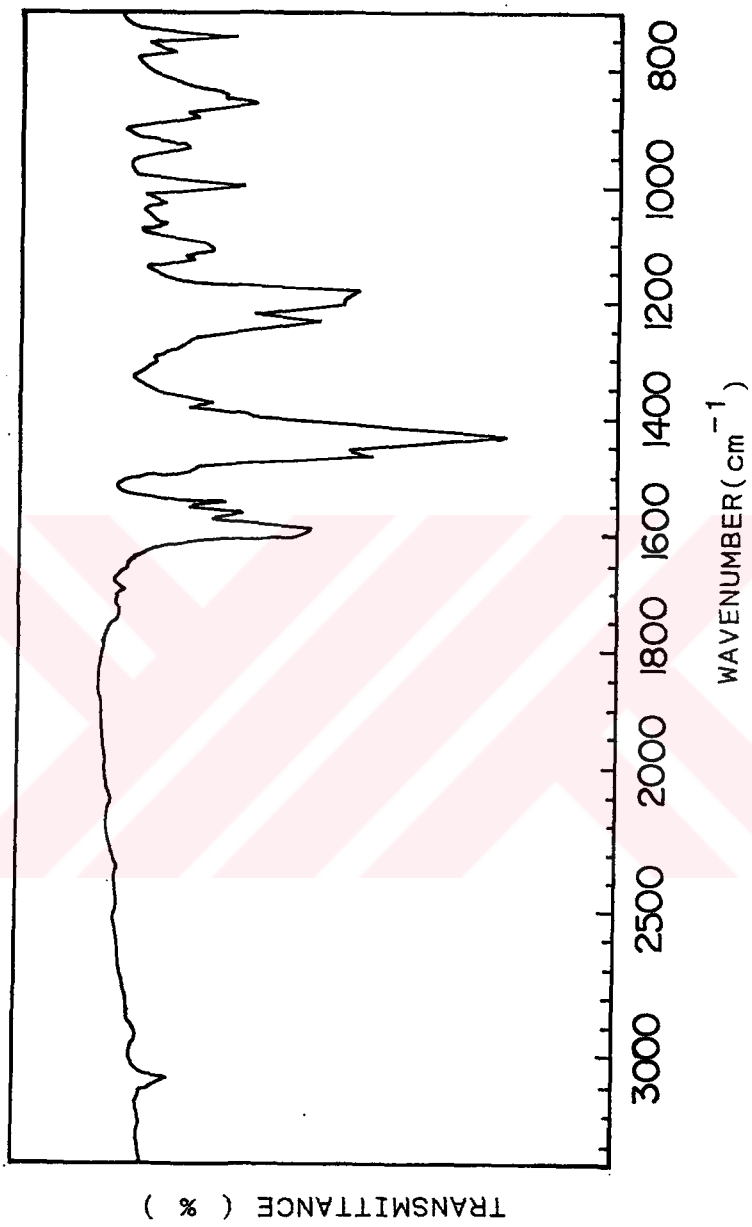


Figure.27. FTIR of polymer obtained from $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$.

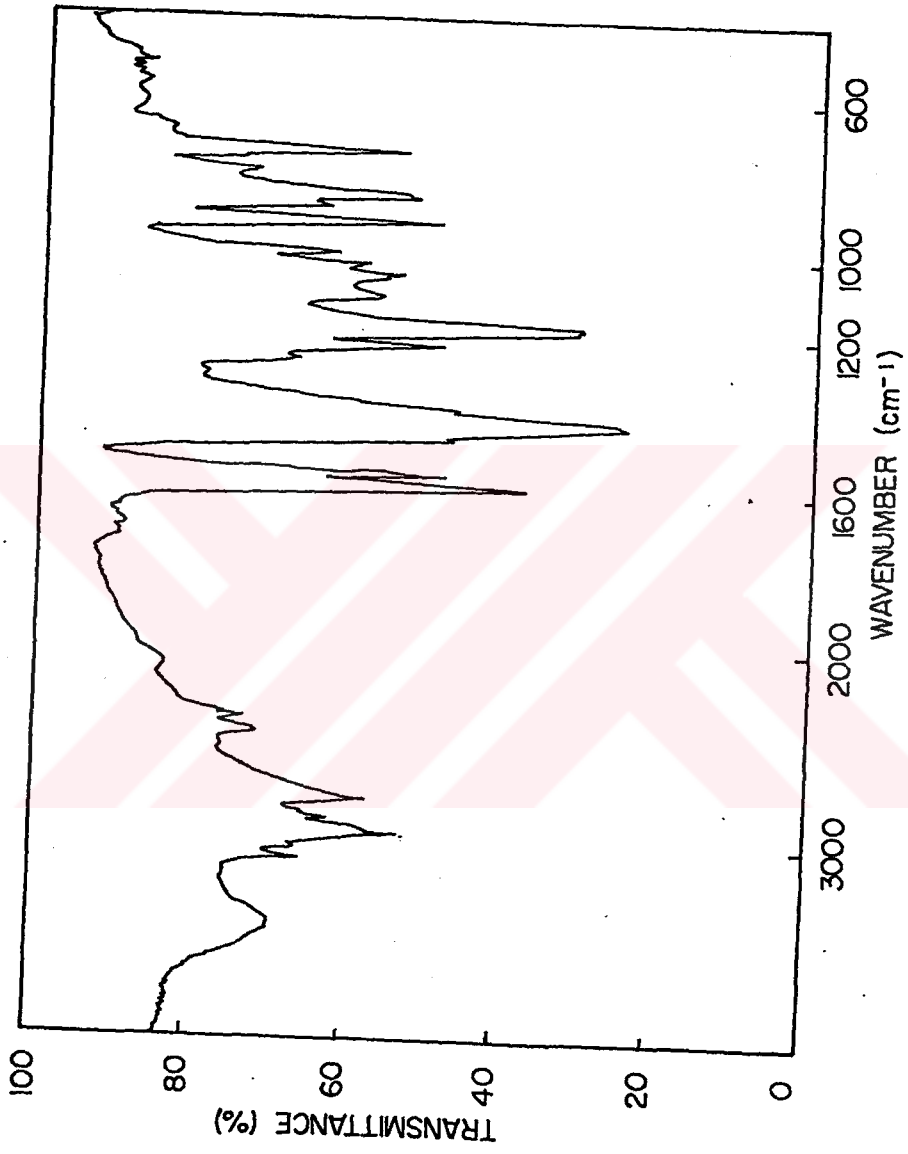


Figure.28. FTIR of polymer obtained from $Py_2Cu(TBrP)_2$

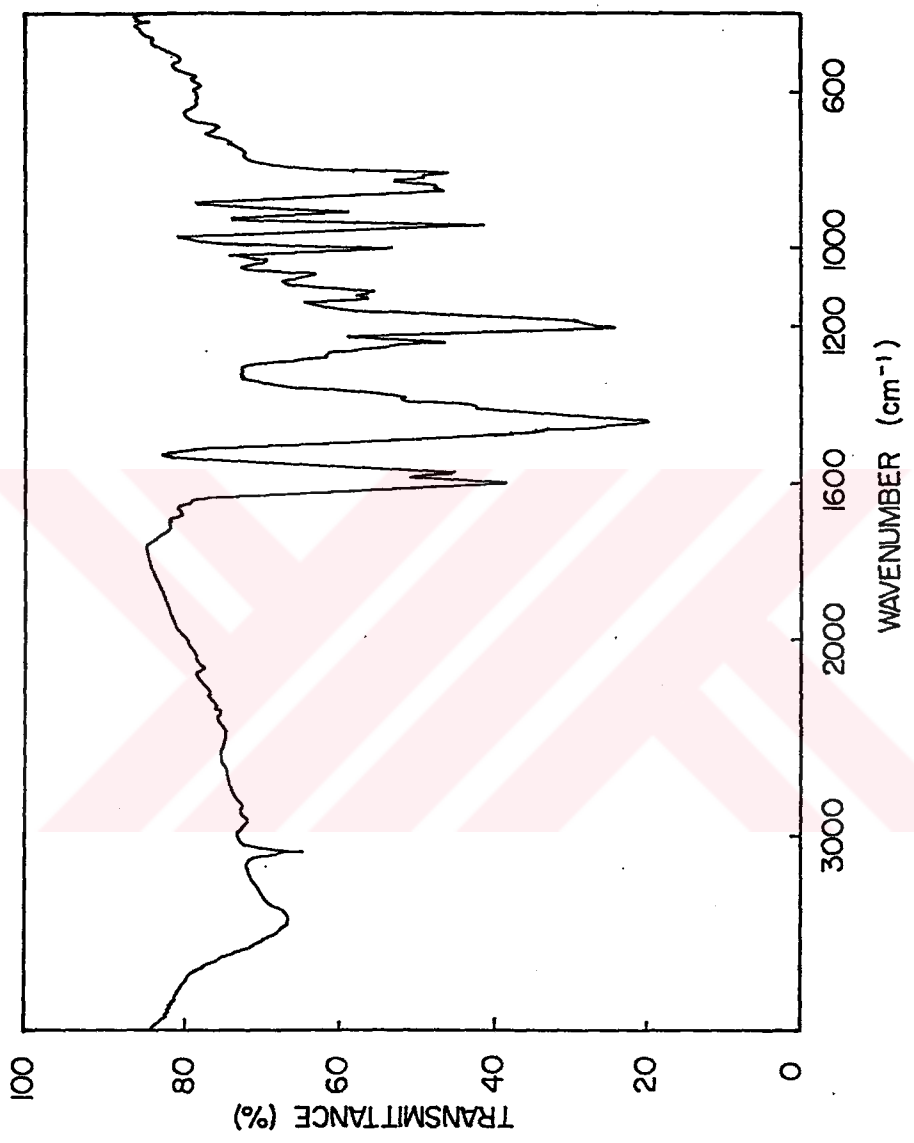


Figure.29. FTIR of polymer obtained from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$.

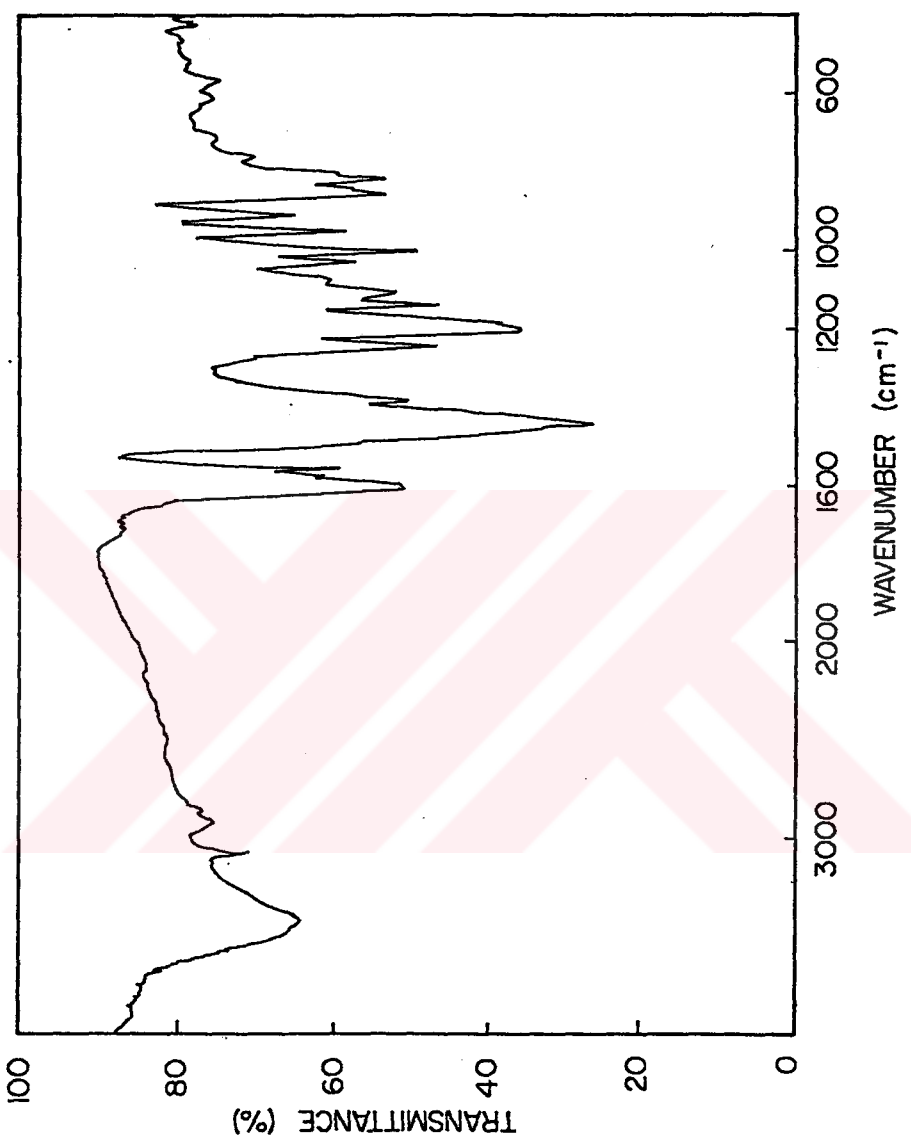


Figure.30. FTIR of polymer obtained from $Py_2Cu(TCP)_2$

symmetric C-O-C stretchings; 1200, 1230 and 1270 cm^{-1} C-O stretchings; and 1370, 1410, 1550, 1600 cm^{-1} C=C ring stretchings.

FTIR spectrum of the polymer obtained from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ is given in Fig.29. From the figure the polymer is characterized by 820 and 550 cm^{-1} out of plane C-H bendings; 910, 940, 1000, 1030, 1060, 1100 cm^{-1} C-O-C stretchings; 1200 and 1240 C-O stretchings and 1400, 1570 and 1600 cm^{-1} C=C ring stretchings.

FTIR spectrum of the product obtained from $Py_2Cu(TCP)_2$ is shown in Fig.30. It is characterized by 1380, 1400, 1560 and 1600 cm^{-1} (C=C stretchings); 960, 1000, 1030 cm^{-1} (symmetric C-O-C stretchings); 1100, 1140, 1200 and 1240 cm^{-1} (C-O stretchings); 810, 850 cm^{-1} (out of plane C-H bendings). FTIR spectrum of the product fits very well to infrared spectrum of the polymer given in the literature [73].

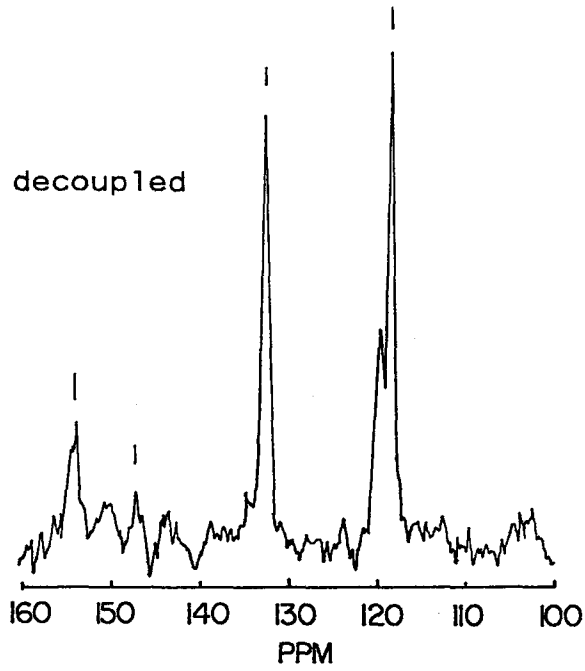
3.8. NUCLEAR MAGNETIC RESONANCE(NMR) CHARACTERIZATION

The structures of polymers were examined by ^{1}H-NMR and ^{13}C-NMR spectroscopy.

3.8.1. ^{13}C-NMR

Theoretical ^{13}C-NMR chemical shift data for the main three possible 1,4- or 1,2- catenation products of TCP, TBrP, 4-Br-2,6-DCP, 2-Br-4,6-DCP, 4-Cl-2,6-DBrP were calculated by using appropriate correlation tables [74]. ^{13}C-NMR coupled and decoupled spectra for all the polymers were given in Figures 31-35. Binary relations between the observed and calculated data are presented in Figures.36-40.

Figure 32 shows schematic representation of ^{13}C-NMR for 4-Cl-2,6-DBrP .The presence of 148 Hz. peak in the observed spectrum is characteristic. It indicates that some 1,2- catenation processes (structure a and b) occur at the expense of the linear polymer formation. In fact, this is the theoretically expected situation [75]. It also suggests that the observed data is more or less a superimposed spectra of structures a and c. Theoretically structure b has a missing line at line 154 ppm. On the other hand, it could be predicted that a polymer chain of 4-Cl-2,6-DBrP having high degree of stereoregularity (



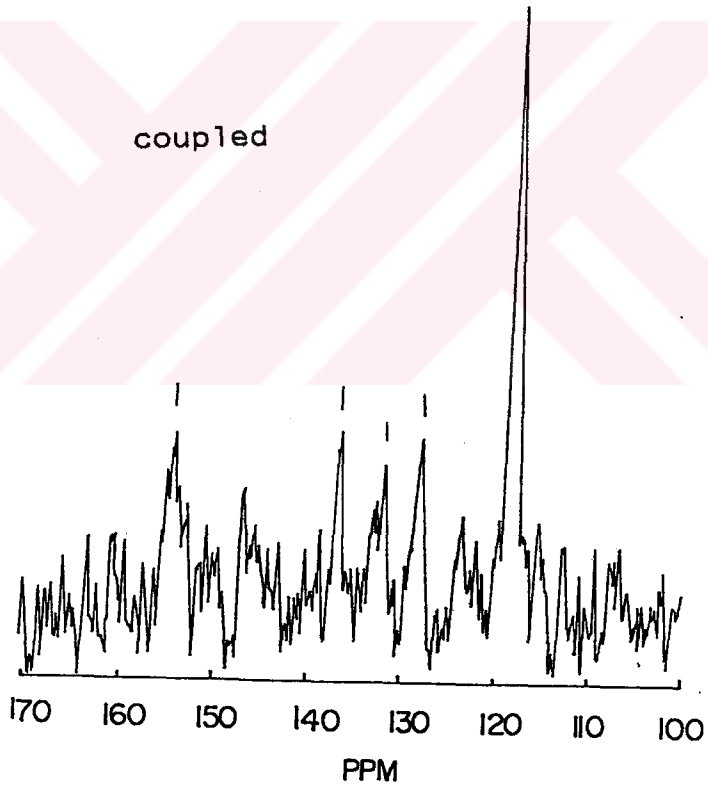


Figure.31. ^{13}C-NMR decoupled and coupled spectra for polymer obtained from 4-Cl-2,6-DBrP

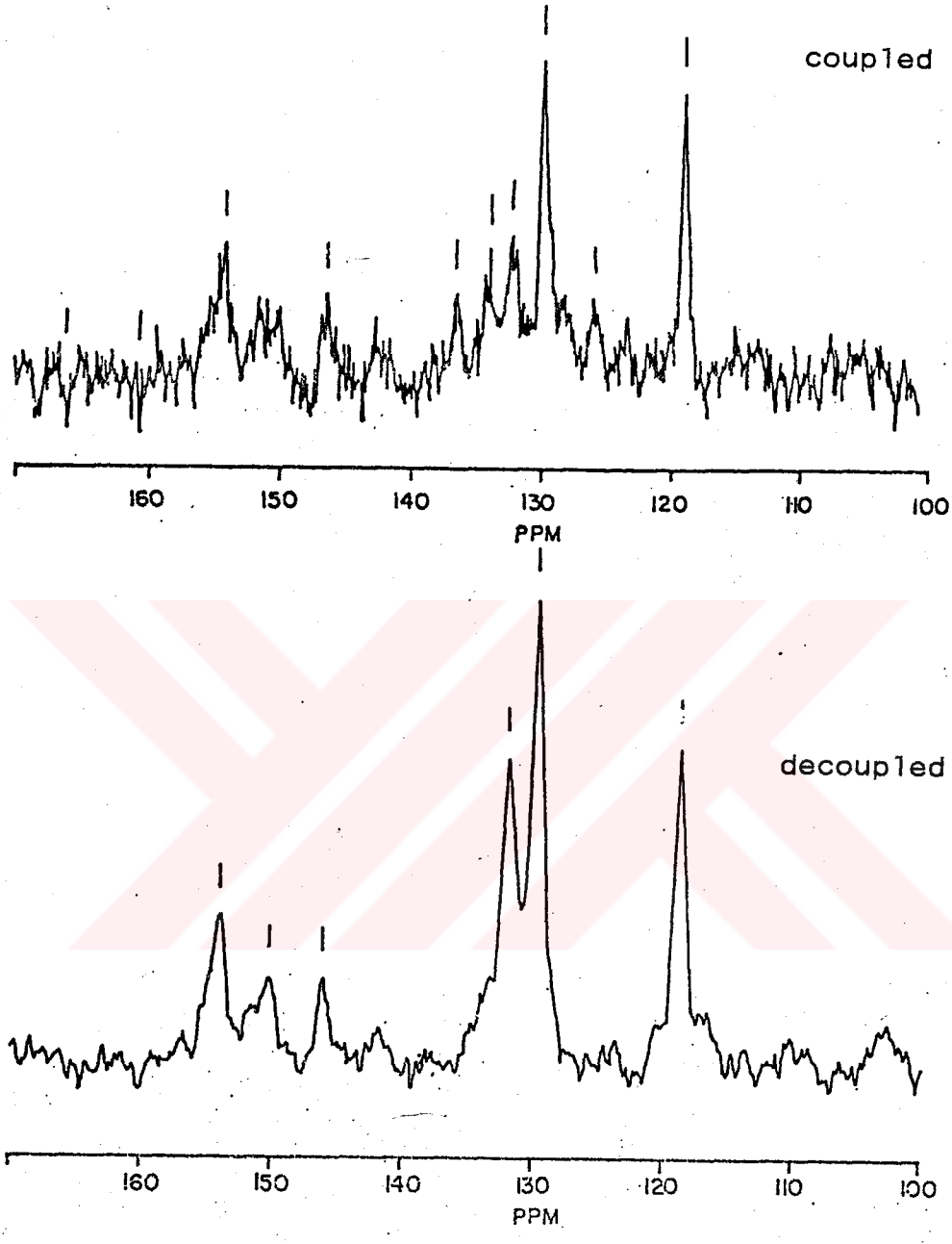


Figure.32. ^{13}C-NMR decoupled and coupled spectra for polymer obtained from 2-Br-4,6-DCP .

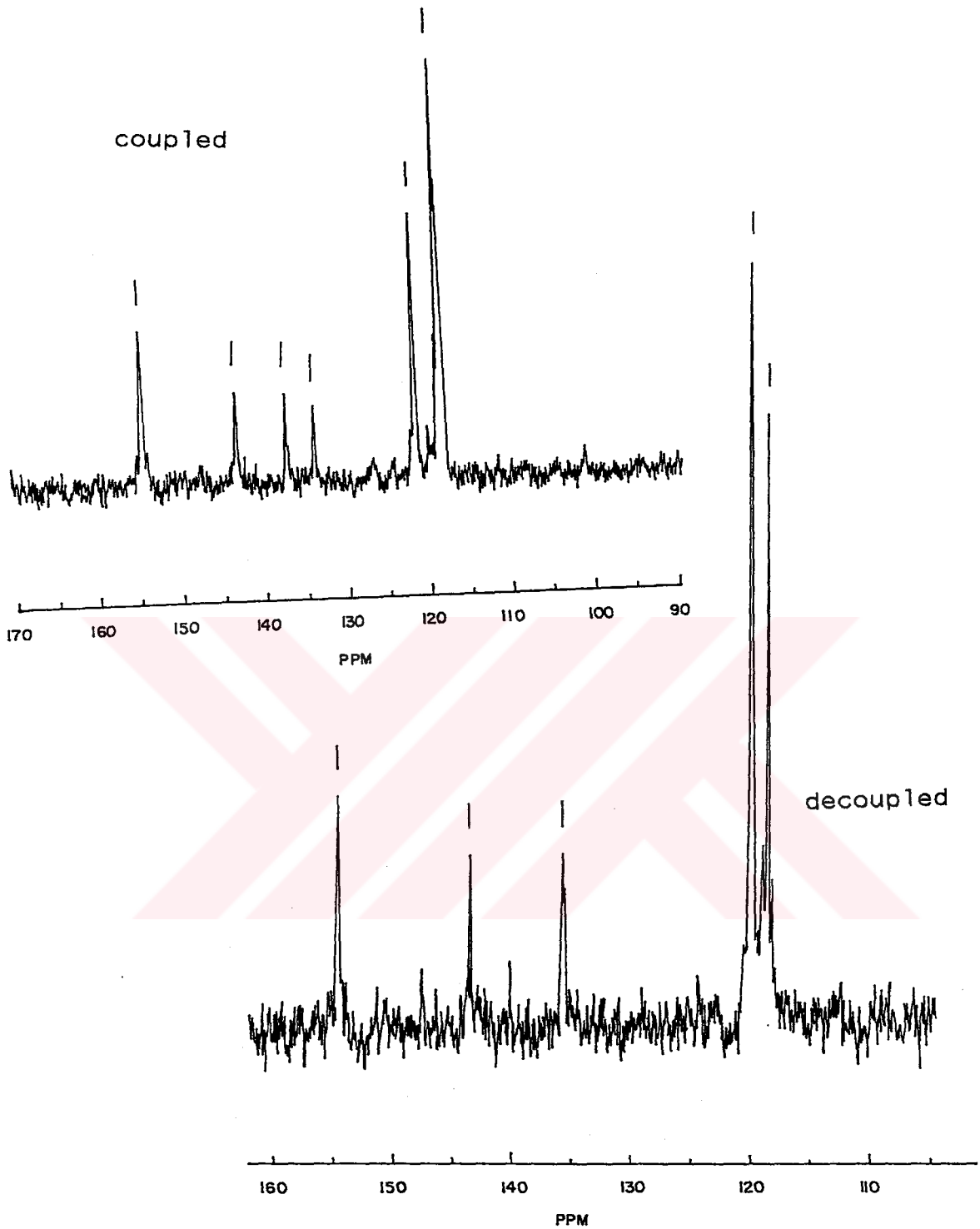


Figure.33. ^{13}C-NMR decoupled and coupled spectra for polymer obtained from TBrP .

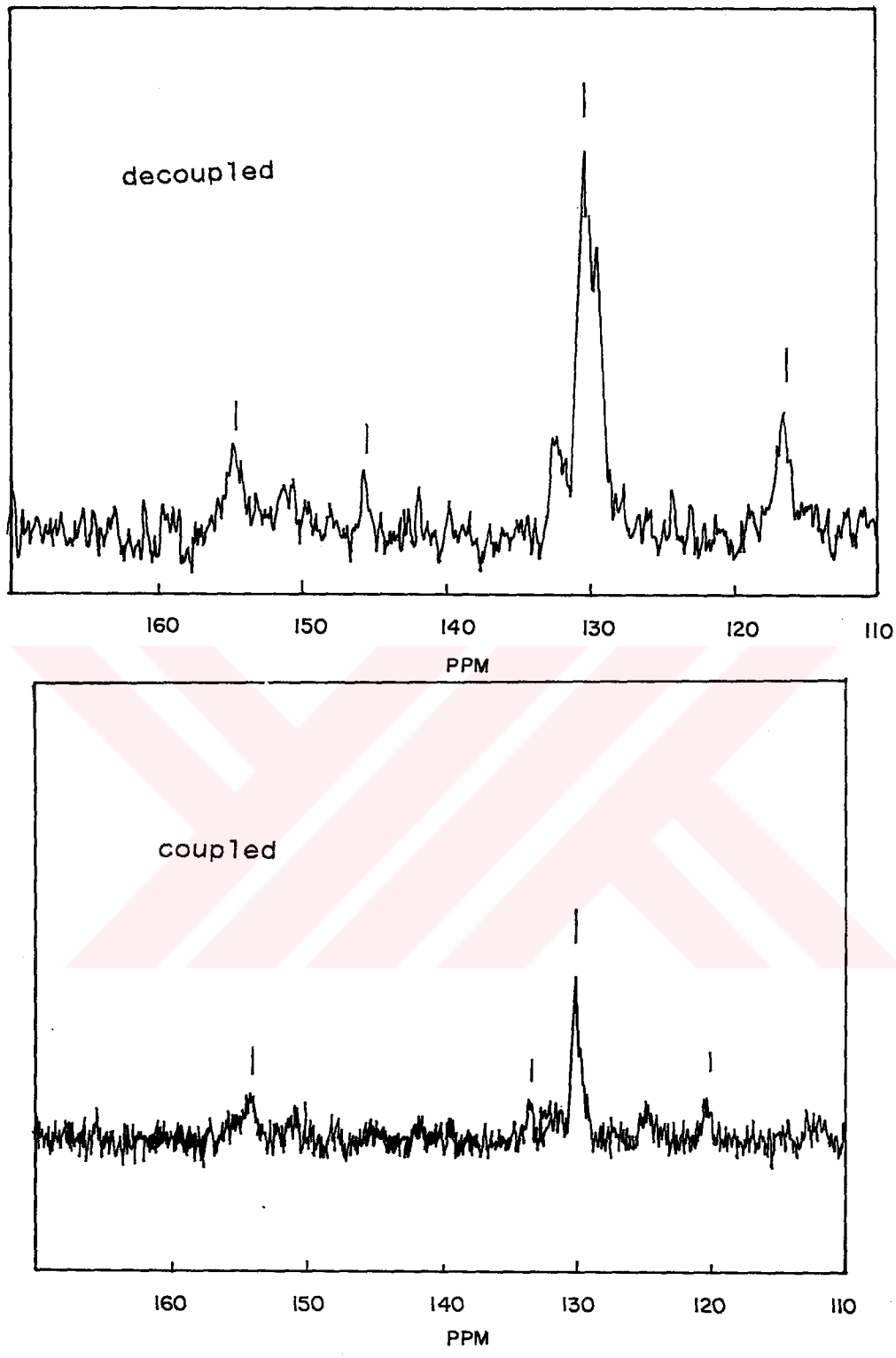
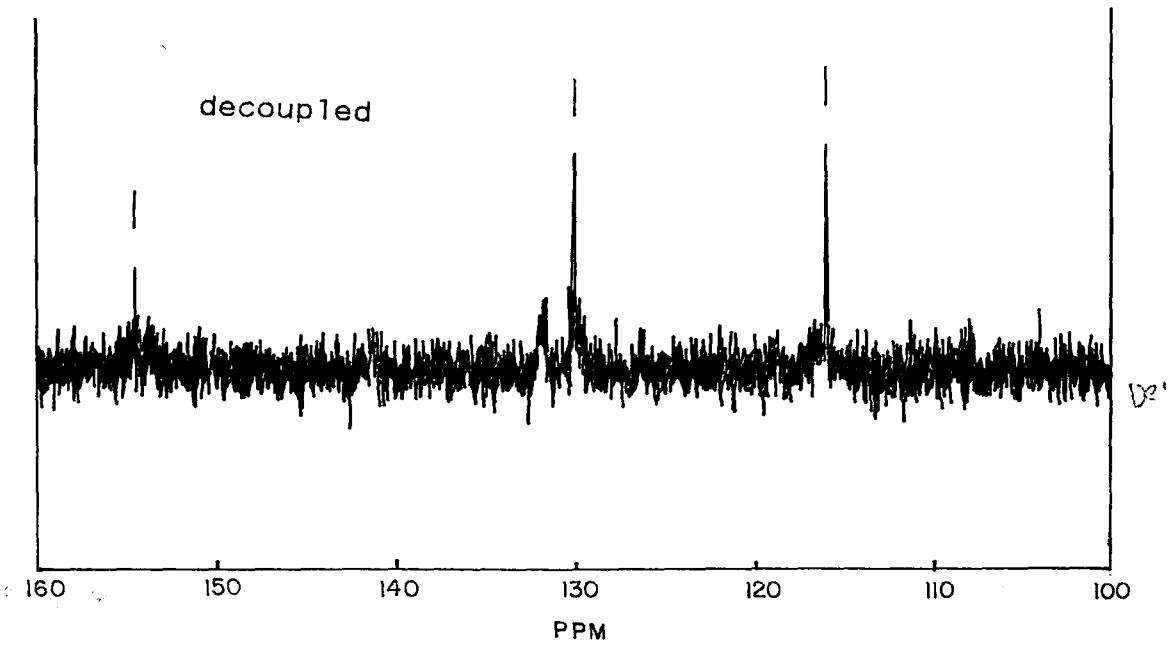


Figure.34. ^{13}C-NMR decoupled and coupled spectra for polymer obtained from TCP .



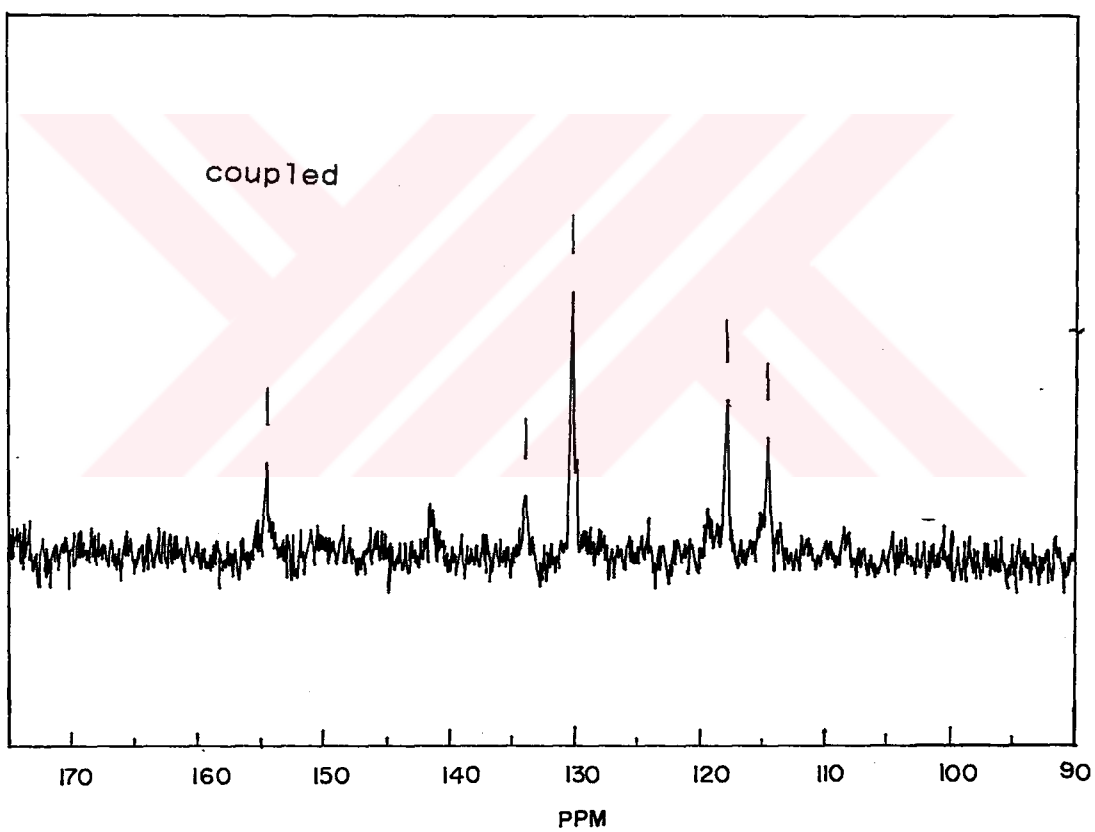


Figure.35. ^{13}C-NMR decoupled and coupled spectra for polymer obtained from 4-Br-2,6-DCP .

structure c),in this figure, should exhibit a fairly single ^{13}C-NMR spectrum in contrast to structures b and a .

Theoretical ^{13}C-NMR chemical shift data for the three probable modes of ternary catenation products of TCP were calculated by using the appropriate correlation tables. The observed and the calculated values are shown in Fig.39. By the inspection of the shielding of carbon atoms, it is reasonable to comment on the characterization of a variety of polymeric structures. It could be predicted that a polymer chain of TCP having high degree of stereoregularity (structure c in Fig.39.) should exhibit a fairly simple ^{13}C-NMR spectrum, i.e. that of the simple repeating unit , depending, of course, on the complexity of the monomer. On the other hand, structures a and b should display fairly complex spectra. The observed and calculated ^{13}C-NMR spectra show a much better agreement for 1,2- catenation process as compared to the others.

Theoretical ^{13}C-NMR chemical shift data for the main three possible 1,4- or 1,2- catenation products of tribromophenol(TBrP) were calculated by using the

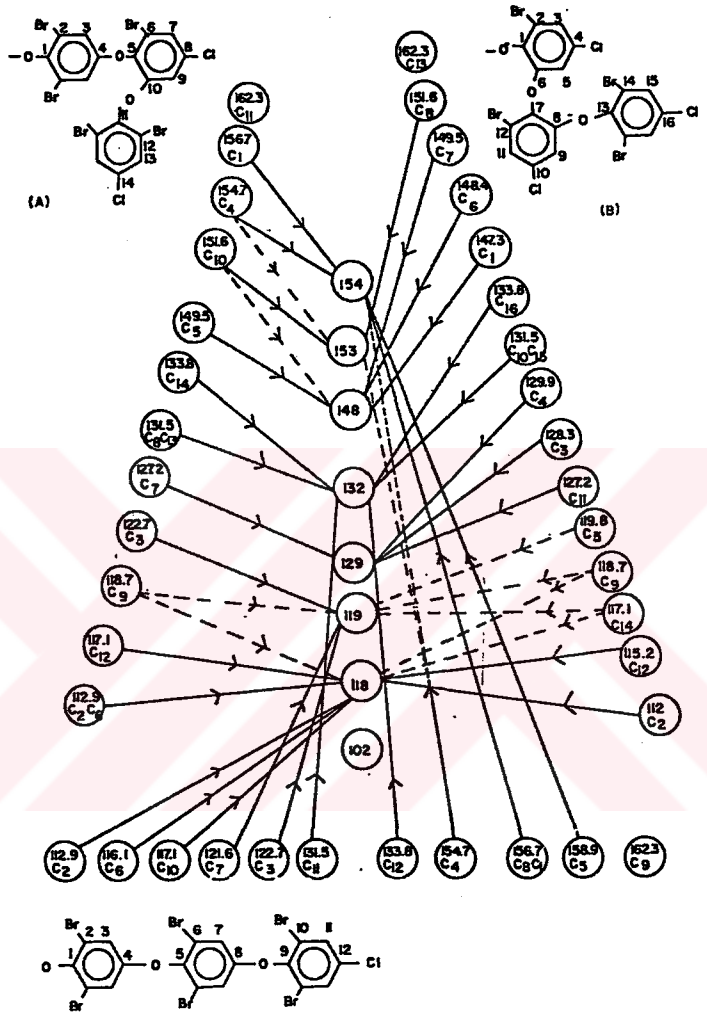


Figure.36. Schematic representation of ^{13}C-NMR data for various forms of polymer obtained from $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$.

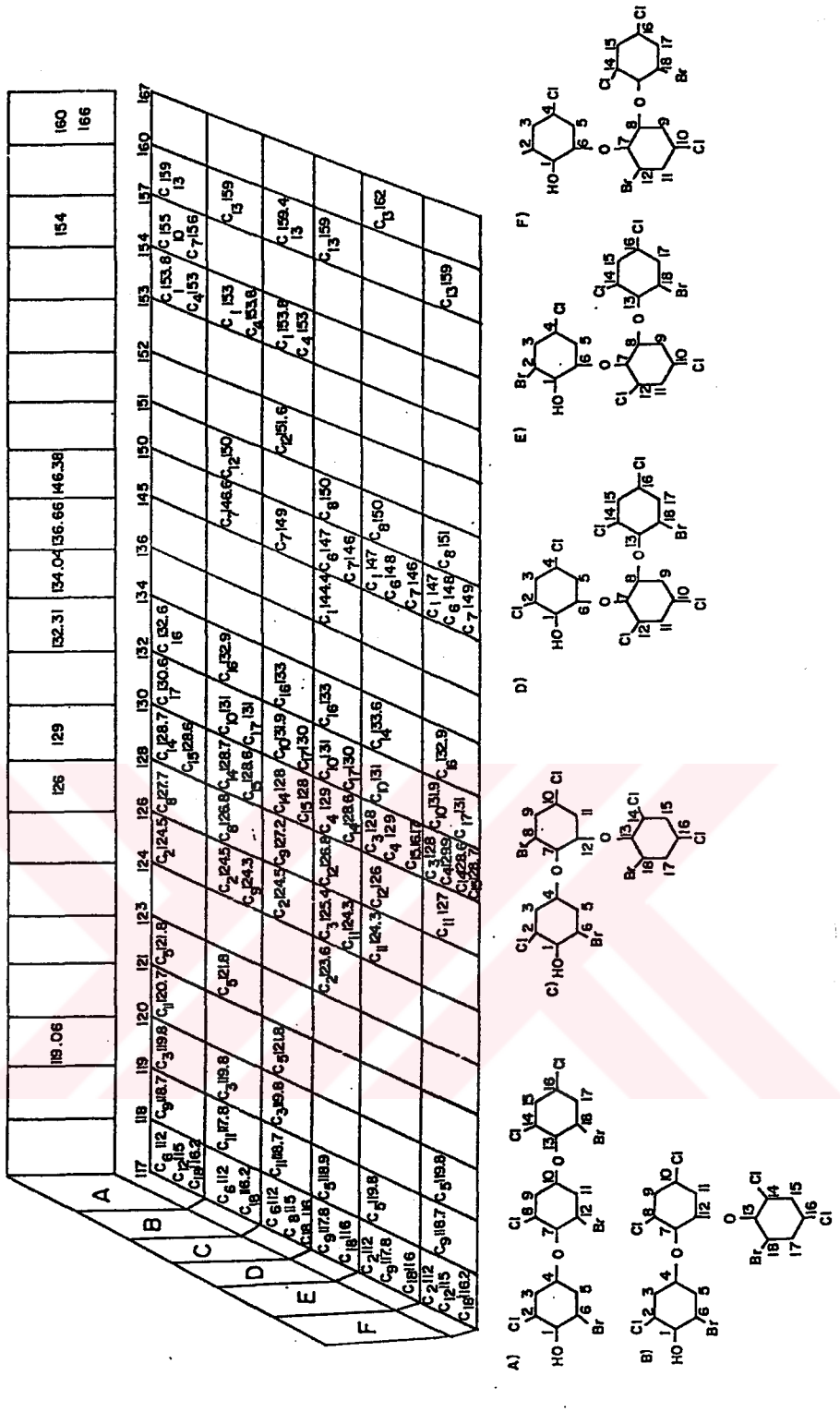


Figure.37. Schematic representation of ^{13}C-NMR data for various forms of polymer obtained from $Py_2Cu(2\text{-Br-}4,6\text{-DCP})_2$.

appropriate correlation tables [78]. Binary relations between the observed and calculated data are presented in Fig.38. It suggests that the observed data is more or less a superimposed spectra of structures a and c . Theoretically, structure b has a missing line at 163.2 ppm. On the other hand, it could be predicted that a polymer chain of TBrP having high degree of stereoregularity (structure c) in this Fig.38 should exhibit a fairly single ^{13}C-NMR spectrum in contrast to structures a and b . The spectrum of the poly(dibromophenylene oxide) given in this figure derived from TBrP shows similarity to the polymer derived from thermal decomposition of bis(tribromophenoxo)bis(pyridine) copper(II) complex in literature [42,82].

Fig.37 shows ^{13}C-NMR coupled and decoupled spectra of the polymer dissolved in $CDCl_3$. The theoretical ^{13}C-NMR chemical shift data for the possible six catenation products of the monomer were calculated by using correlation tables [74].

Three basic structures can be drawn for the polymer obtained from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$. The theoretical ^{13}C-NMR chemical shift data for the three possible

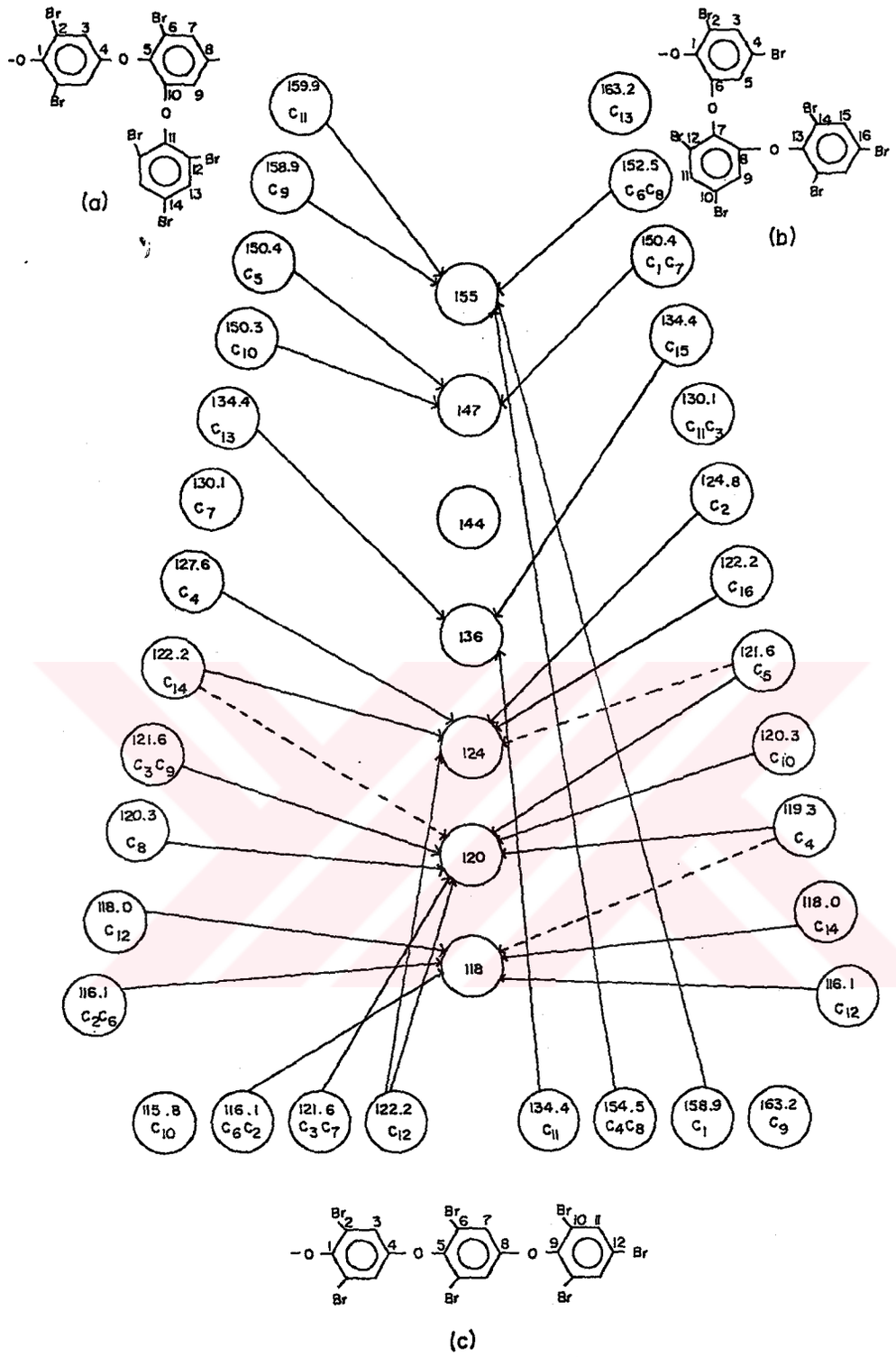


Figure.38. Schematic representation of ^{13}C-NMR data for various forms of polymer obtained from $Py_2Cu(TBrP)_2$

addition products of 4-Br-2,6-DCP were calculated from the related correlation tables. Observed resonating frequencies are compared with the calculated values for the three possible structures as shown in Fig.40.which seems to have a better correlation with the observed data. The ^{1}H-NMR spectrum, however, clearly reveals that the polymer has mainly a linear structure.

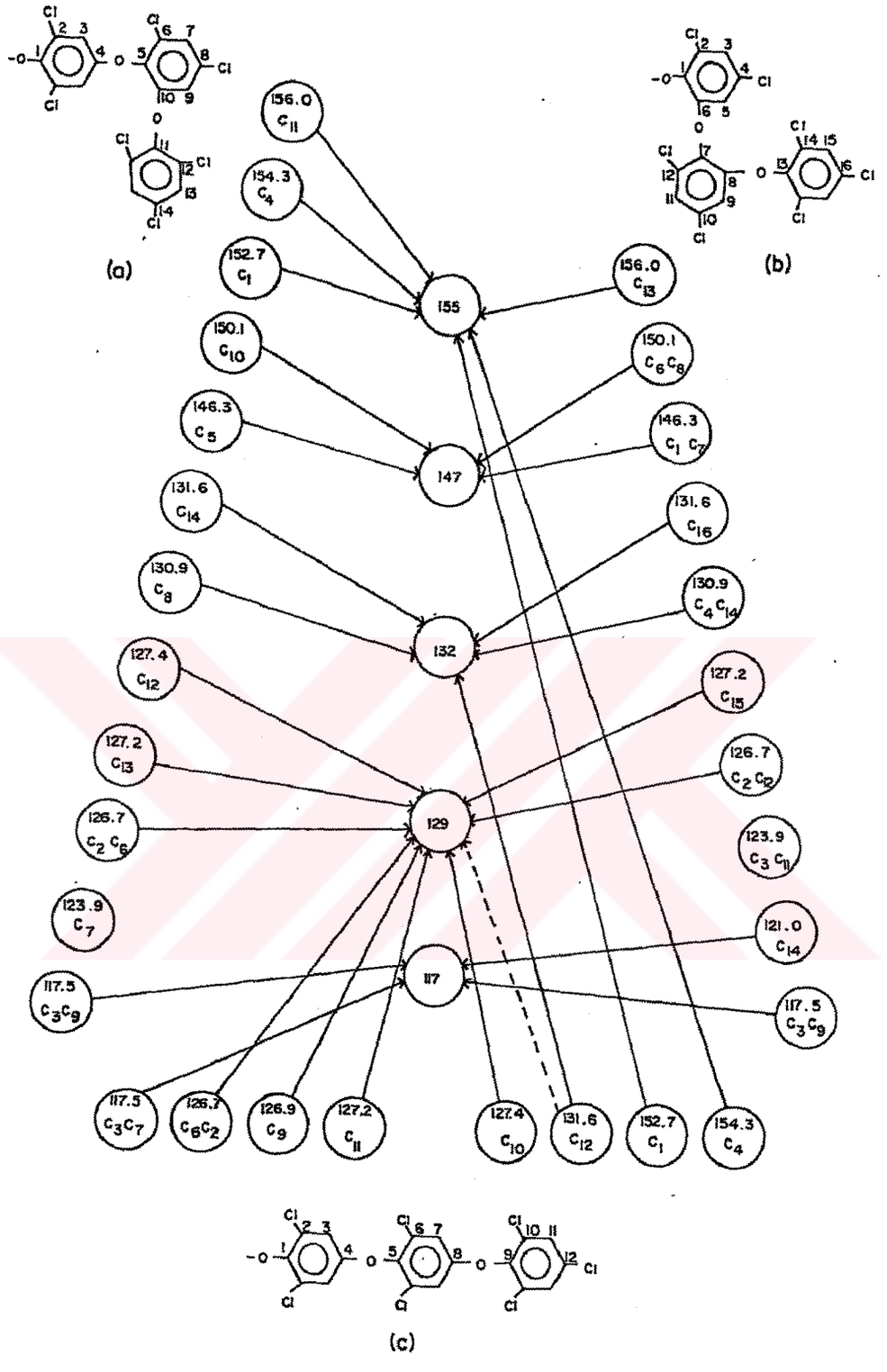


Figure.39. Schematic representation of ^{13}C-NMR data for various forms of polymer obtained from $Py_2Cu(TCP)_2$

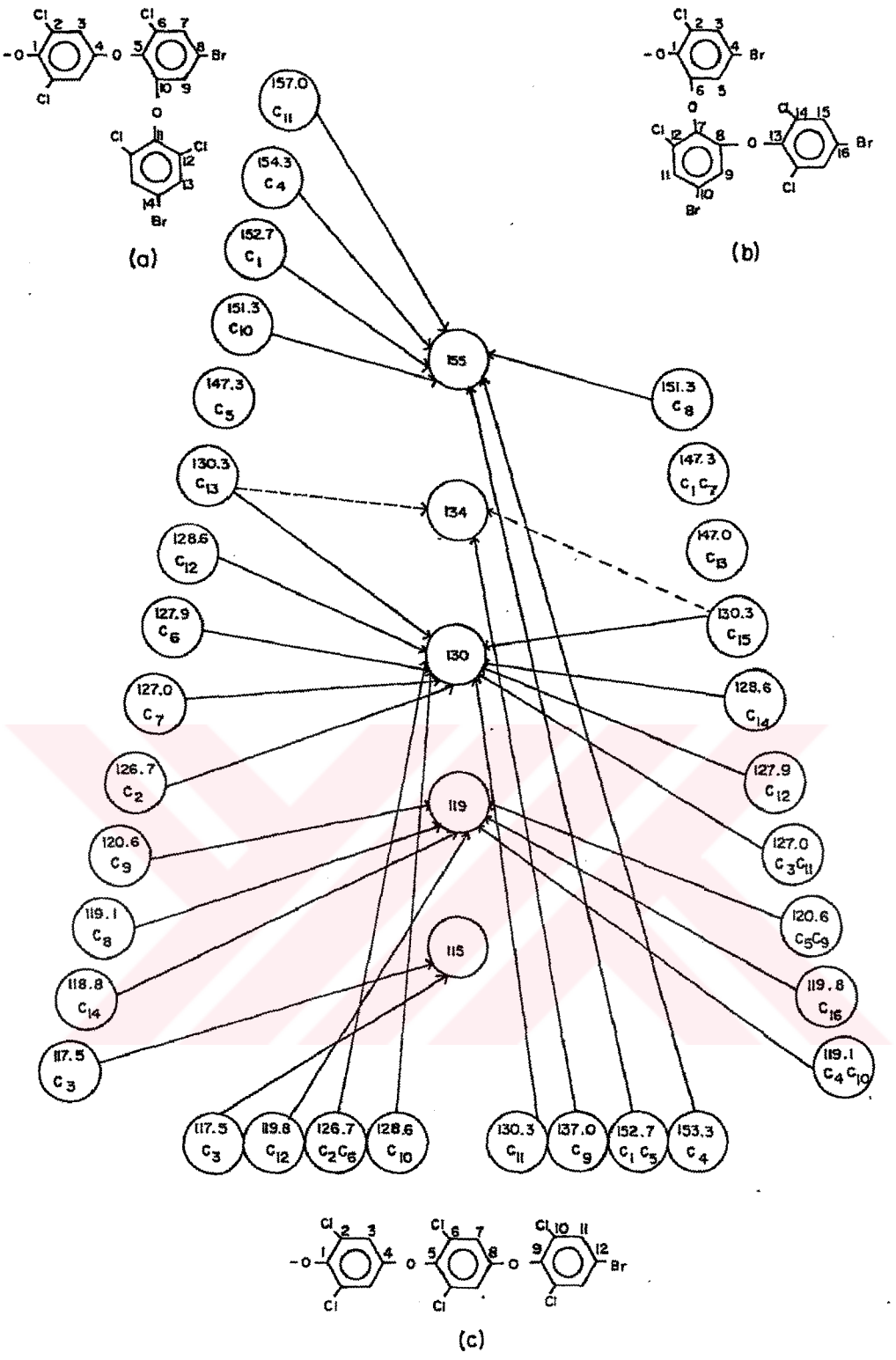
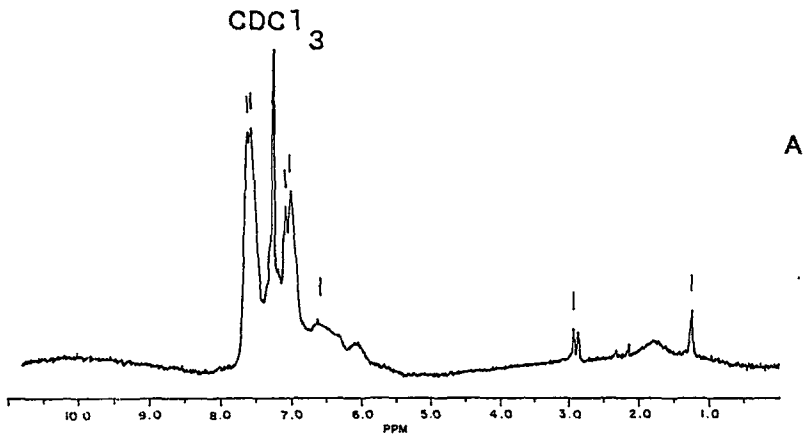


Figure.40. Schematic representation of ^{13}C-NMR data for various forms of polymer obtained from $Py_2Cu(4\text{-Br-}2,6\text{-DCP})_2$.

3.8.2. ^{1}H-NMR

As it is seen from ^{13}C-NMR spectra of all polymers, although the observed ^{13}C-NMR spectrum for each polymer is rather simple, the data may be in agreement equally well with the calculated spectra of the three possible modes of ternary catenation products. In that sence, ^{1}H-NMR is more informative.

The ^{1}H-NMR spectra of the polymers revealed a highly branched structure in Fig.41, which provides evidence that both 1,2- and 1,4- addition reactions play important roles in the polymerization of bis(pyridine)bis(4-Cl-2,6-DBrP) copper(II) complex. In the spectra, there are two lines. The one at δ=7 ppm may be reasonably assigned to the protons of 2,6-dibromo-1,4-phenylene oxide units. The lower field at δ=7.5 ppm is assigned to the 5-proton of 4-chloro-2-bromo-1,6-phenylene oxide units. It can easily be observed that 1,2- 1,4 additions take place at about equal rates against the high selectivity for displacement of bromine rather than chlorine and the easier access to the 4 position relative to the 2 position. Also, the structure of the polymer is found to be the same as the potential is varied as seen in Fig.41. and Fig.42.



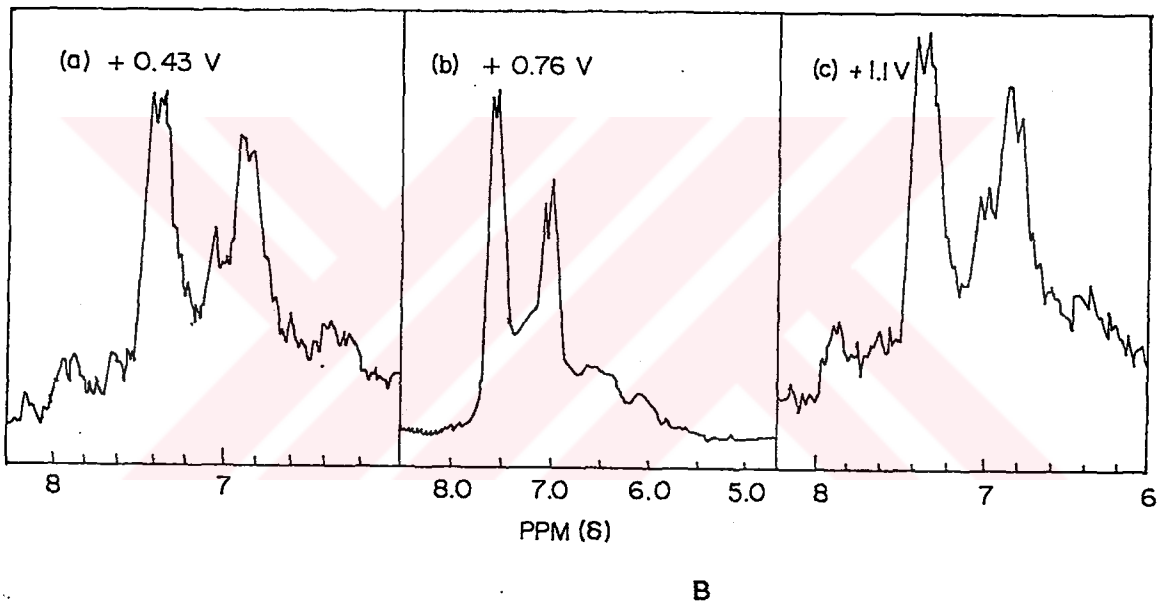


Figure.41. ^{1}H-NMR spectra of polymer obtained from $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ at anodic potentials(A:complete region of ^{1}H-NMR spectra , B: main region of ^{1}H-NMR spectra for structural determination).

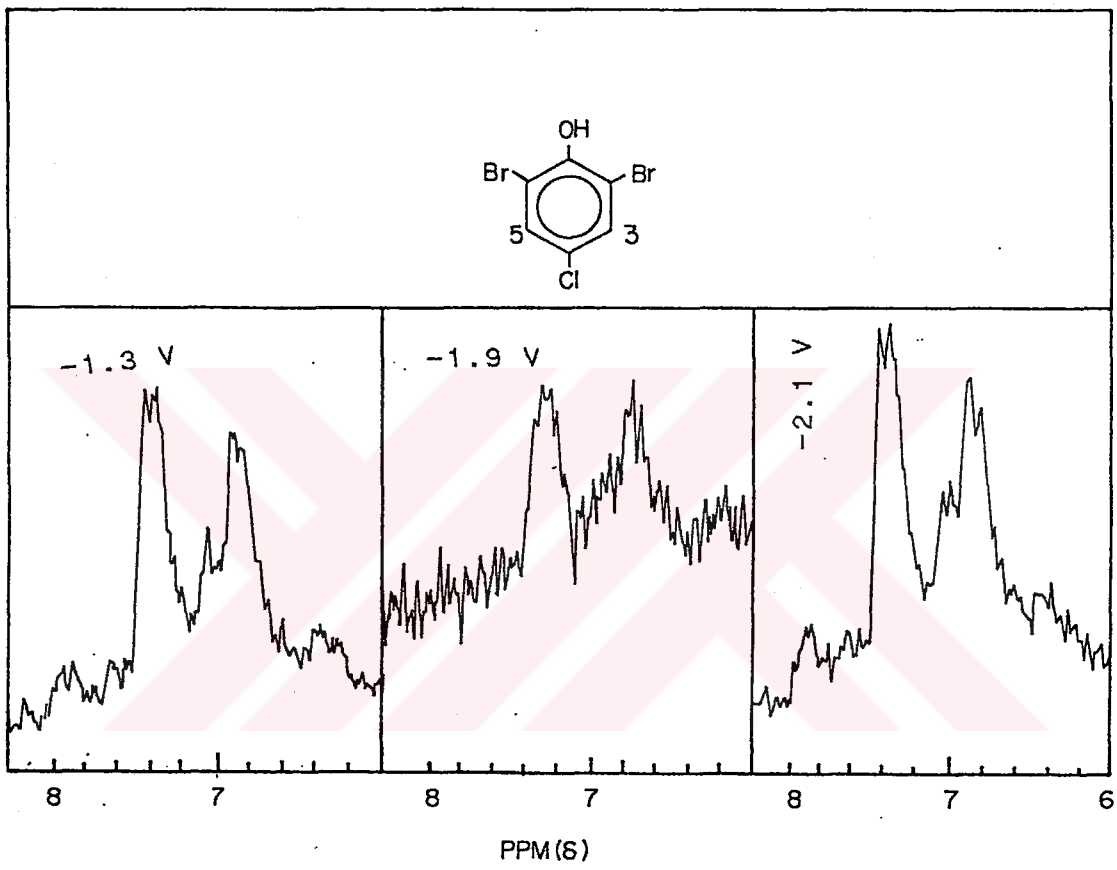
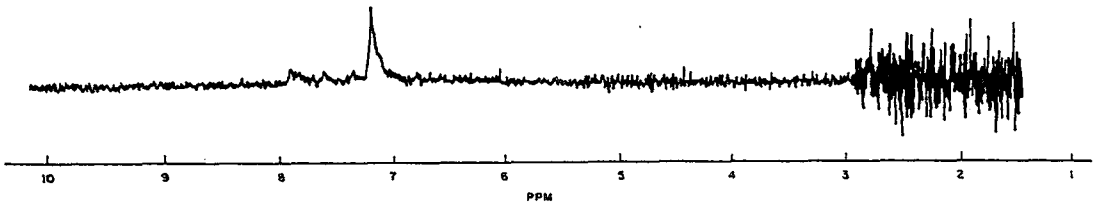


Figure.42. ^{1}H-NMR spectra of polymer obtained from $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ at cathodic potentials.

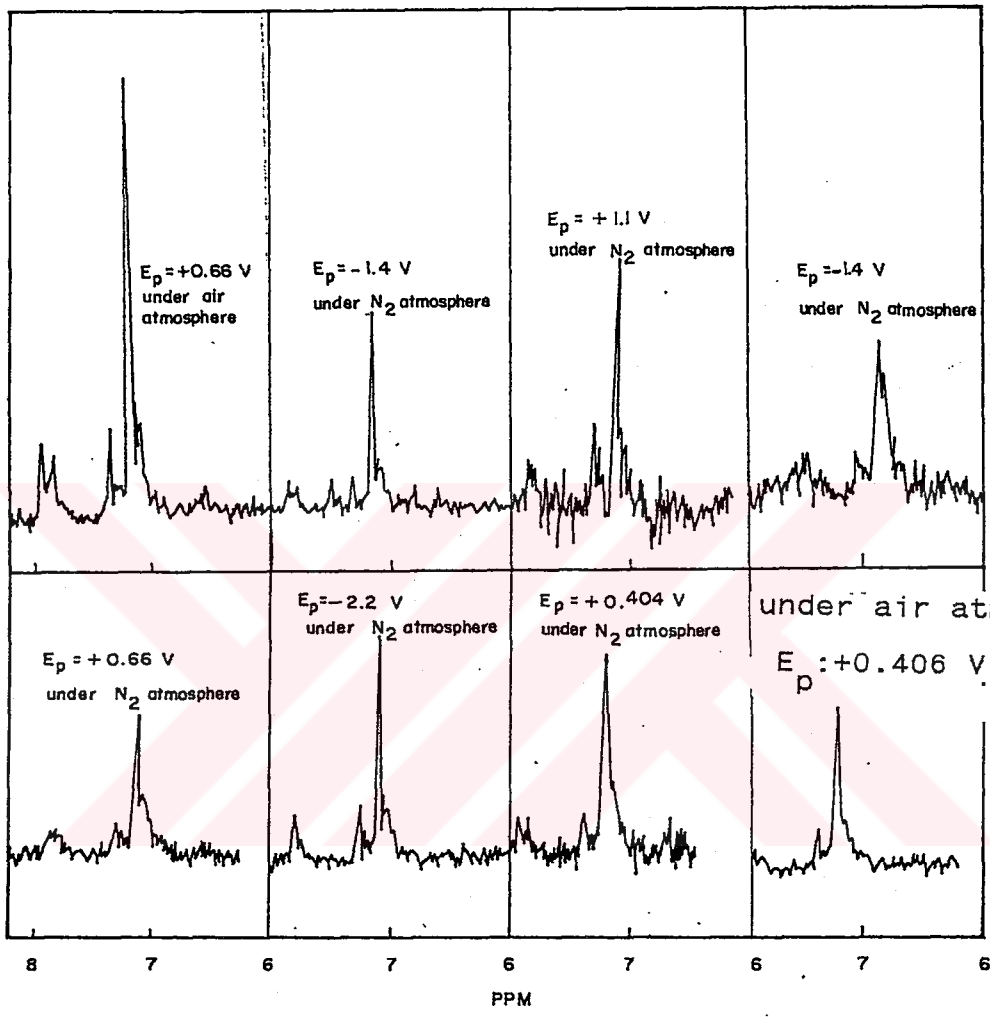
^{1}H-NMR spectra of poly(dibromophenylene oxide) obtained from $Py_2Cu(TBrP)_2$ in the present study is shown in Fig.43. As it is seen, a very simple spectrum having a

rather sharp peak at about δ=7.2 ppm. is displayed. ^{1}H-NMR spectrum of the polymer implies that the polymer is mainly linear i.e. 1-4- catenation product of tribromophenol with some monomeric ortho branches as observed at about δ=7.5 ppm. It was also reported that interaction energy calculations revealed ortho and para positions having almost equal susceptibilities towards dimer formation. Both the dimeric radicals, however, should attract the para position of the phenolate ion much faster than the ortho position. Hence, selectivity towards 1,4- catenation is favored over 1,2- catenation [81]

Fig.44. gives ^{1}H-NMR spectra of polymer obtained by electro-oxidation of $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ at different potentials. ^{1}H-NMR spectrum for each polymer clearly reveals that the polymer has a mainly linear structure. The linear polymer, poly(2,6-dichloro-1,4-phenylene oxide) spectrum exhibits a sharp singlet at δ=6.8 ppm with a minor peak at δ=7.4 ppm as seen in Fig.39. δ=7.4 ppm is due to the 1,2- addition.



A



B

Figure.43. ^{1}H-NMR spectra of polymer obtained from $Py_2Cu(TBrP)_2$ at different potentials under nitrogen and air atmospheres(A: complete region of ^{1}H-NMR spectra for polymer obtained at 0.404 volt under N_2 atmosphere , B: main region for structural determination).

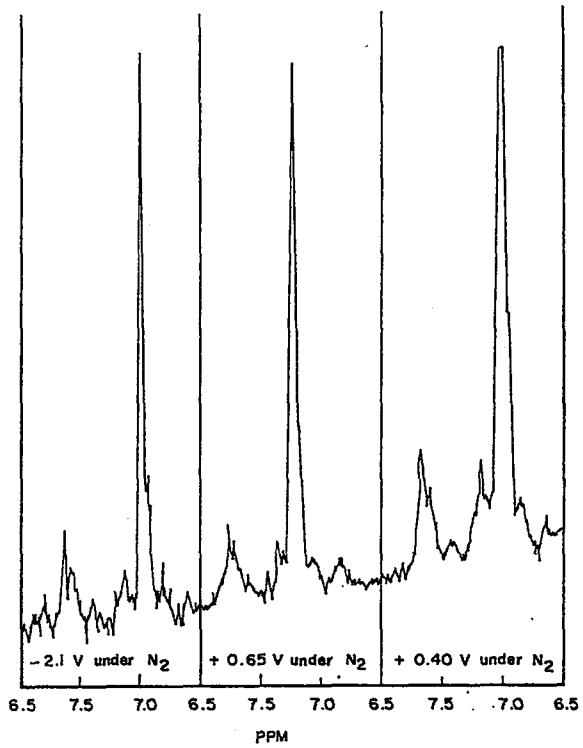


Figure.44. ^{1}H-NMR spectra of polymer obtained from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$.

^{1}H-NMR spectrum of polymer obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ revealed a highly branched structure as seen in Fig.45. In this spectrum, there are two lines. The one at δ=6.8 ppm may be assigned to the 1,4-addition. The lower field at δ=7.4 ppm may be assigned to 1,2-additions. As it is seen in this figure, 1,2- addition is favored over 1,4- addition owing to high selectivity for displacement of bromine rather than chlorine. Broader higher field lines (δ<6.8 ppm) could be due to the polymerization through 2,4- and 2,4,6- positions on the same unit.

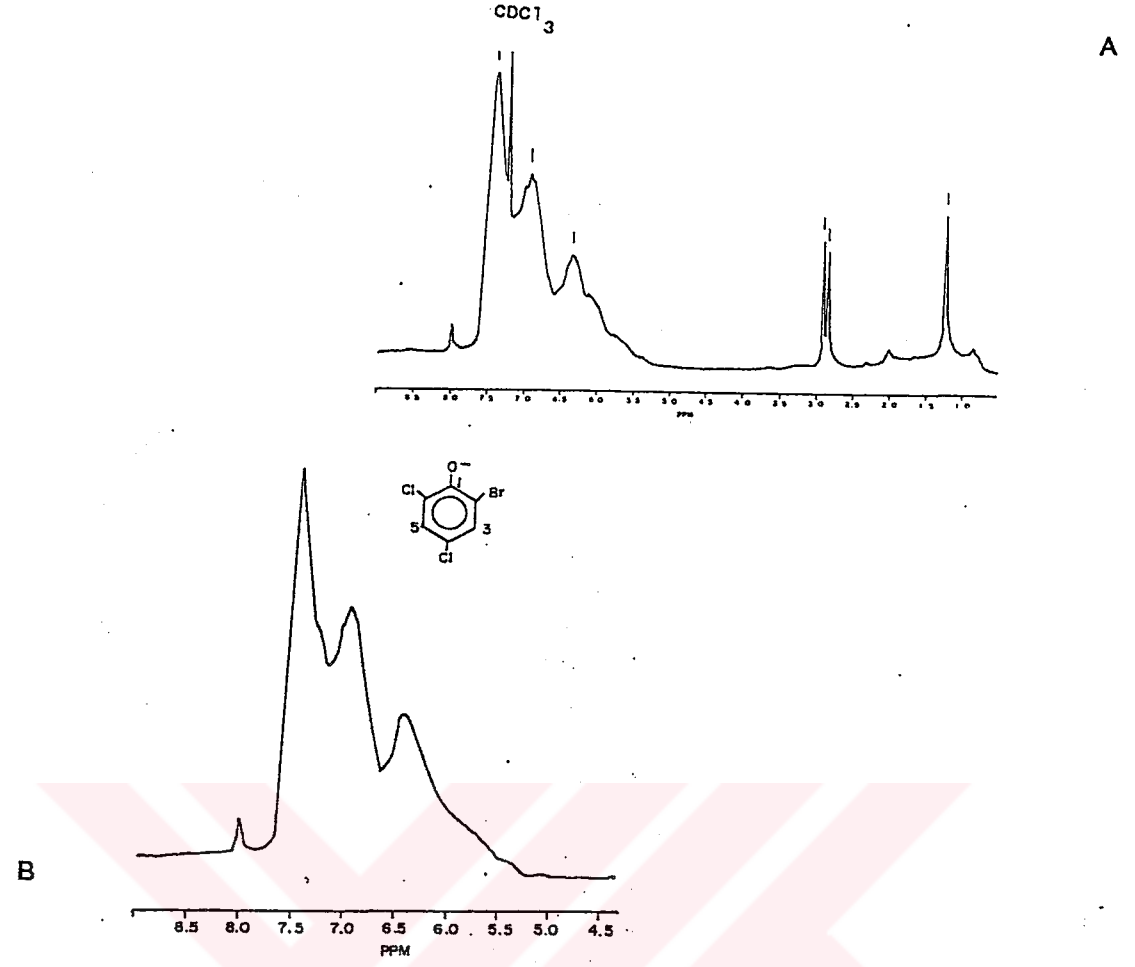


Figure.45. ^{1}H-NMR spectra of polymer obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$.(A: complete region , B: main region for structural determination)

^{1}H-NMR spectrum of polymer obtained from $Py_2Cu(TCP)_2$ resembles to that of $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ except the absence of broader higher field lines . Also, 1,2-addition is favored over 1,4- addition . Peaks are observed at δ=7.2 ppm and δ=6.8 ppm in Fig.46. Again δ=7.2 ppm is assigned to the 1,2- addition and δ=6.8 ppm is assigned to 1,4- addition. The observation reveals that

polymer consists of branched structure together with some monomeric linear products.

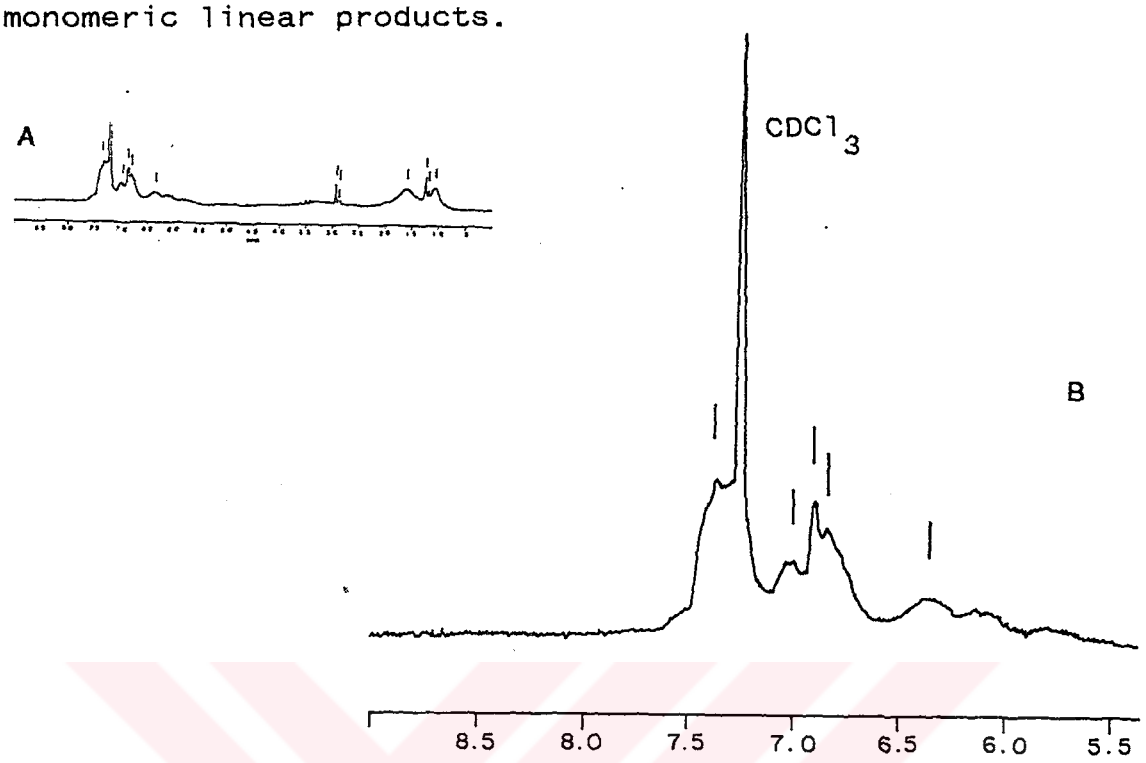


Figure.46. ^{1}H-NMR spectra of polymer obtained from $Py_2Cu(TCP)_2$.(A: complete region B: main region for structural determination)

It was concluded that the polymers obtained from $Py_2Cu(TBrP)_2$ and $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ are linear-like structures with some monomeric branched units, whereas the products obtained from $Py_2Cu(TCP)_2$, $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ and $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ showed highly branched structures.

Structures of polymers, which were obtained at different oxidation or reduction potentials as well as

under air or nitrogen atmospheres were just similar to each other whenever potentials or polymerization atmospheres were varied. This case was seen clearly in **Fig.43.** Here it was observed that structures of the polymers obtained from $Py_2Cu(TBrP)_2$ were the same even with varying conditions.The peaks at high field strength in ^1H-NMR spectra i.e. around 3.0 ppm and 1.5 ppm are due to the solvent impurities.The elemental analysis results indicated for the polymers synthesized from $Py_2Cu(TBrP)_2$, $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$, $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ that there is no nitrogen in the structure of the polymers [carbon and hydrogen results found from elemental analysis :(TBrP): C=33.4, H=2.24 % ; (4-Br-2,6-DCP) : C=40.6 , H=1.84 % ; (2-Br-4,6-DCP) : C=41.3 , H=1.65 %].

3.9. RESULTS OF CAPACITANCE MEASUREMENTS

Dipole moment is a quantity, directly related to the conformation of the polymer chains. Dielectric constant is also related with conformation. The dielectric constants and dipole moments of several polymers and halophenols were determined at several temperatures. The results are given in **Tables :14,15,16,17**. As seen from tables, the dielectric constants of various halophenols and polymers and as a result, the $\langle \underline{\mu}^2_x \rangle$ values for the polymer increase with increasing temperature. The data on dipole moment measurements are indicative of polar groups.Hence,the repetative studies did not give identical results as expected from such highly polar molecules.Dipole moments of branched structures are higher than that of linear structures. This case was observed and compared for polymers obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ as branched and $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP$ as linear. dn/dc values were determined at 30^o and 436 nm wavelength with a Brice -Phoenix differantial refractometer model BP-2000. This value was taken as 0.118.ml/g, constant for all the temperatures.

Table-14. Dipole moments and dielectric constants of polymer obtained from $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ and dielectric constant of 4-Cl-2,6-DBrP itself .

	for polymer		for phenol
T(^oC)	$\epsilon_{polymer}$	$\frac{\langle\mu^2\rangle * 10^{36}}{x}$	ϵ_{phenol}
25	0.189	2.84	0.046
30	0.165	2.96	0.0620
35	0.123	2.61	0.051
40	0.108	2.62	0 .118
45	0.128	3.52	0.143
50	0.119	3.65	0.125
55	0.134	3.90	0.092
60	0.149	5.63	0.088
65	0.100	4.02	0.044
70	0.170	7.59	0.046
75	0.182	8.80	0.065

Table-15. Dipole moments and dielectric constants of polymer obtained from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ at several temperatures.

	for polymer		for toluene
T(^oC)	$\epsilon_{polymer}$	$\frac{\langle\mu^2\rangle * 10^{36}}{x}$	$\epsilon_{toluene}$

25	0.144	2.13	2.3907
30	0.023	0.3206	2.3862
40	0.111	2.7623	2.3715
45	0.127	3.4824	2.3623
50	0.059	1.7960	2.3514
60	0.085	3.2216	2.3379
65	0.164	7.9169	2.3227
70	0.114	4.9944	2.3209
75	0.255	12.4279	2.3025

Table-16. Temperature dependence of dielectric constants of 2-Br-4,6-DCP itself and its polymer with its dipole moment

	for polymer		for phenol
T(^{o}C)	$\epsilon_{polymer}$	$\frac{\langle\mu\rangle^2 * 10^{36}}{x}$	ϵ_{phenol}
25	0.209	12.84	0.085
30	0.184	13.36	0.102
35	0.164	14.32	0.113
40	0.200	20.08	0.232
45	0.216	24.66	0.178
50	0.259	32.996	0.351
55	0.160	22.54	0.360
65	0.318	53.69	0.493
70	0.311	56.97	0.504
75	0.325	64.32	0.351

where x is the number of repeating units of polymer

Table-17. Temperature dependence of dielectric constants of $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ complex.

$T(^oC)$	$\epsilon_{complex}$
25	0.129
30	0.0707
35	-
40	0.0645
45	0.111
50	0.0768
55	0.132
60	0.190
65	0.258
70	0.146
75	0.366

4.CONCLUSION

There exists a number of polymerization examples for the thermal decomposition of bis(pyridine)bis(trihalophenoxo) copper(II) complexes to obtain poly(dihalophenylene oxides). In this study, electroinitiated method was applied to complexes mentioned to polymerize them under constant potential electrolysis system, which is favored over constant current electrolysis. With this system, polymerization proceeds only through the monomer at its oxidation and reduction potentials irrespective of the presence of other constituents such as solvent and electrolyte in the solution.

In this study, reduction and oxidation peak potentials of various halophenols and bis(pyridine)bis(trihalophenoxo) copper(II) complexes were measured. Halophenols itself could not give polymer under its reduction and oxidation potentials in suitable solvent-electrolyte couple such as acetonitrile-TBAFB respectively. But, complexes at certain oxidation and

reduction peak potentials were polymerized in suitable solvent-electrolyte system such as DMF-TBAFB respectively at room temperature under both nitrogen and air atmospheres without adding any catalyst or additives.

The relationship between polymerization potential and yield were estimated for all complexes studied. It was observed that oxidation potentials did not cause a discrete change in yield at that polymerization time of three hours. Also,the effect of polymerization atmosphere on the yield was not observed.

The complexes studied can only be polymerized electrochemically upon oxidation. Even if reduction potentials are applied, polymerization occured at the compartment where oxidation exists.

The structures of polymers obtained from different complexes under varying potentials and atmospheres were examined by spectroscopic techniques such as ^{1}H-NMR, ^{13}C-NMR. It was noticed that polymers obtained from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ and $Py_2Cu(TBrP)_2$ are linear-like structures, but, others are branched structures. It indicates that, whenever bromine atom occupies para position, linear polymers are formed.

The structures of polymers never changed with varying

potentials and atmospheres.

The molecular weights of polymers are very low. This property is an advantage to obtain a better quality ^{1}H-NMR and ^{13}C-NMR spectra.

They are very rigid polymers owing to having high T_g values.

Dipole moment and dielectric constant measurements were done. It indicates that branched polymers have high dipole moments as expected.

As a result, this study can be summarized as follows :

1-).Bis(pyridine)bis(trihalophenoxo)copper(II) complexes were polymerized by means of electroinitiation method at polymerization potentials determined by cyclic voltammetry technique.

2-).The polymerization potential did not affect the percent yield discretely in three hours as polymerization time over +0.65 V.

3-).Atmosphere as nitrogen or air did not affect the percent yield.

4-).Existence of postpolymerization was observed.

5-).Polymerization was proved to be radicalic.

6-).Depending on the type of halogen-substituted

phenol linear or branched poly(dihalophenylene oxides) are obtained

7-).Molecular weights of polymers are very low. This property is an advantage to obtain a better quality ^{1}H-NMR and ^{13}C-NMR spectra than previously available high molecular weight ones

8-).Highly branched polymers have three T_g values, because of three transitions, i.e. polymers obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ and $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$.

9-).The polymers obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$, $Py_2Cu(4\text{-}Cl\text{-}2,6\text{-}DBrP)_2$ and $Py_2Cu(TCP)_2$ are branched-type structures, whereas polymers obtained from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$ and $Py_2Cu(TBrP)_2$ are linear-like structures.

10-).Highly branched polymer obtained from $Py_2Cu(2\text{-}Br\text{-}4,6\text{-}DCP)_2$ has higher dipole moment than that of linear polymer from $Py_2Cu(4\text{-}Br\text{-}2,6\text{-}DCP)_2$.

11-).Cyclic voltammetry proves to be practical and rapid way for determining the rate of reactions in electroinitiated polymerizaton.But this thecnique is not sufficiently suitable for these complexes.

REFERENCES

1. Haynes,C.G., Turner, A.H., and Waters, W.A., J.Chem.Soc.,2823,1956.
2. Barton, D.H.R., Deflorin, A.M., and Edwards, O.E., J.Chem.Soc., 530, 1956.
3. Humphries, S.G., in Biogenesis of Natural Products (p.Bernfeld, ed.), Macmillian, New york, p.617, 1963.
4. Allport, D.C., and Bu'Lock,J.D., J.Chem.Soc., 654, 1960.
5. Gatenbeck, S.,Svensk-Kem. Tidskr., 72, 188, 1960.
6. Brackmann, H., Fortschr. Chem. Org. Naturstoffe, 14, 141,1957. And references cited.
7. Edwards, J.D., and Cashaw, J.L., J.Am.Chem.Soc., 79, 2283, 1957.
8. Matsuura, T., and Cahnmann, H.J., J.Am.Chem.Soc., 82, 2055, 1960.
9. Aghoramurthy, K., Sarma, K.G., and Seshadri, T.R., Tetrahedron, 12, 173, 1961.
10. Lewis, J.R., J.Chem.Soc., 5074, 1964.
11. Rhodes, A., Somerfield, G.A., and Mc Gonagle, M.P., Biochem.J., 88, 349, 1963.

12. Barton, D.H.R., and Sott, A.I., J.Chem.Soc., 1767, 1958.

13. Barton, D.H.R., and Cohen, T., Festschr.Arthur Stoll, 117, 1957.

14. Barton, D.H.R., The Chemistry of Natural Products (3rd International Symposium, Kyoto, Japan), Butterworth, London, p.35, 1964.

15. Swain, T., in The Chemistry of the Flavonoid Compounds (T.A. Geissmann, ed.), Pergamon, New York, p.529, 1962.

16. Roberts, E.A.H., in The Chemistry of the Flavonoid Compounds (T.A.Geissmann, ed.), Pergamon, New York, p.468, 1962.

17. Herrmann, K., Mitt.Gabrete Lebensm Hyg., 50, 121, 1959.

18. Taylor, W.I., and Battersby A.R., Oxidative Coupling of Phenols , 1967.

19. Westerfield, W.W., and Lowe, C., J.Biol.Chem., 145, 463, 1942.

20. Bacon, R.G.R., and Izzat, A.R., J.Chem.Soc., 791, 1966.

21. Mc Neils, E., J.Org.Chem., 31, 1255, 1966.

22. Lindgren, B.O., Acta.Chem.Scand., 14, 2089, 1960.

23. Hay, A.S., Blanchard, H.S., Endres, G.F., and Eustrance, J.W., J.Am.Chem.Soc., 81, 6335, 1959.

24. Hay, A.S., J.Polymer Sci., 58, 581, 1962.

25. Endres, G.F., Hay, A.S., and Eustance, J.W., J.Org.Chem., 28, 1300, 1963.

26. Finkbeiner, H., Hay, A.S., Blanchard, H.S., and Endres, G.F., J.Org.Chem., 31, 549, 1966.

27. Blanchard, H.S., Finkbeiner, H,C., and Russel, G.A., J.Polymer.Sci., 58, 469, 1962.

28. Staffin, G.D., and Price, C.C., J.Am.Chem.Soc., 82, 3632, 1960.

29. Muller, E., Rieker, A., and Beckert, W., Z. Naturforsch., 17b, 567, 1962.

30. Punmerer, R., Schmidutz, G., and Seifert, H., Ber., 85, 535, 1952.

31. Hunter, W.H., Olsan, A.O., and Danields, E.A., J.Am.Chem.Soc.,38, 1761, 1916.

32. Hunter, W.H., and Joyce, F.E., J.Am.Chem.Soc., 39, 2640, 1917.

33. Hunter, W.H., and Whitney, R.B., J.Am.Chem.Soc., 54, 1167, 1932.

34. Dewar, M.J.S., and James, A.N., J.Chem.Soc., 917, 55, 1958.

35. Sus, O., Moller, K., and Heiss, H., Ann., 598, 123, 1956.

36. Staffin, G.D.,and Price, C.C., J.Am.Chem.Soc., 82, 3632, 1960.

37. Musso, H., in Oxidative Coupling of Phenols , Marcel Dekker, Inc., New York, 1967.

38. Brackman, W., and Havinga, E., Rec.Trav.Chim., 74, 1021, 1955.

39. Harrod, J.F., Canadian Journal of Chem., 47, 637,1969.

40. James, B.R.,and Williams, R.J.P., J.Chem.Soc., 2007,1961.

41. Carr, B.G., Harrod, J.F., and van Gheluwe, P., J.Am.Chem.Soc., 95, 5707, 1973.

42. Harrod, J.F., Gheluwe, P.van., Kisakurek, D., Shaver, A., Macromolecules, 14, 565, 1981.

43. Kisakurek, D., Binboga, N., Harrod, J.F., Polymer, 8 28, 1767, 1987.

44. Unal, H.I., Sanli, O., and Kisakurek, D., Polymer, 30 344, 1989.

45. Vermillion, F.J.,and Pearl,I.A.,J.Electrochem.Soc., 111, 1392, 1964.

46. Grace, W.R., and Co., Br.Patent 1, 156,309, 1968.

47. Borman, W.F., Can.Patent 800, 592, 1968.

48. Kijkstra, R., and Jonge, J.De., Extended Abstract,IUPAC, Boston, 1971.

49. Mc Kinney, D.S., and Fugassi, J.P., U.S.Pat. 2, 1961,384, 1960.

50. Cheek, G., Wales, C.P., Nowak, R., J.Anal.Chem., 55,380, 1983.

51. Pham, M.C., Lacaze, P.C., Dubois, J., J.Electroanal.Chem., 86,147, 1978.

52. Ohnuki, Y., Ohsoka, T., Matsuda, H., Oyama, N., J. Electroanal.Chem., 158, 55, 1983.

53. Bruno, F., Pham, M.C., and Dubois, J.E., Electrochim.Acta, 22,451, 1977.

54. Glarum, S.H., and Marshall, J.H., J.Electrochem.Soc., 132(12), 2939, 1985.

55. Ohsaka, T., Hirokowa, T., Miyamoto, H., and Oyama, N., Anal.Chem., 59, 1758,1987.

56. Tsuchida, E., Nishide, H., and Maekawa, T., J.Macromol Sci.-chem., 21, 1081, 1984.

57. Tsuchida, E., Nishide, H., Mackawa, T., ACS Symp.. Ser:282, 175, 1985.

58. Yamamoto, K., Nishide, H., Tsuchida, E., Makromol.Chem., Rapid Commun., 8, 11, 1987.

59. Kumar, N., Malhotra, B.D., Chandra, S., J.Polym.Sci. Polym.Lett.Edit., 23,57, 1985.

60. Hunter, W.H., and Whitney, R.B., J.Am.Chem.Soc.,54, 1167, 1932.

61. Yigit, S., Kisakurek, D., Turker, L., Toppare, L., Akbulut, U., Polymer, 30, 348, 1989.

62. Sacak, M., Akbulut, U., and Kisakurek, D., J.Polym. Sci.Chem.Ed., 27,1599, 1989.

63. Smith, J.W., Electric Dipoles Moments, 1955.

64. Debye, P., Polar Molecules, Dower Publications U.S.A. p.11. 1929.

65. Kocak, I., M.Sc.Thesis, METU, 1988.

66. Harrod, J.F., Can.J.Chem., 47, 637, 1969.

67. Akbulut, U., Fernandez,J.F., and Birke, R.L., J.Poly.Sci.Polym.Chem.Ed., 13,133, 1975.

68. Heilbromer, E., and Bock, H., The HMO-Model and Its Application, John Wiley & Sons, London, 1976.

69. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemists, John Wiley & Sons, New York, 1966.

70. Dewar, M.J.S., Molecular Orbital Theory of Organic Chemistry, Mc Graw-Hill, New York, 1969.

71. Dewar, M.J.S.,and Doupherty, R.C., The PMO Theory of Organic Chemistry. Plenum-Rosetta, New York, 1975.

72. Sevcik, A., Coll.Czech.Chem.Commun., 13, 346, 1948.

73. Tsuruya, S., Kawamura, T., Tsitsuya, S.,and Yanezawa T.Polym.Lett., 7, 709, 1969.

74. Boschke, F.L., Fresenius,W., Huber, J.F.K., Pungor,E., Rechnitzs, G.A., Simon, W., West,Th.S., Tables of Spectral DAta for Structural Determination, Springer-Verlag, Heidelberg, New York, Tokyo, 1968.

75. Turker, L., Kisakurek,D., British Polym.J., 20, 131,1988.

76. Yigit, S., M.Sc.Thesis, METU, 1988.

77. Fukui, K., and Fujimoto, H., Bull-Chem.Soc. Japan, 42,3399, 1969.

78. Turker, L., Kisakurek, D., Akbulut, U., Toppare,L.,Sen, S., J.Polymer.Science. Part.B: Polymer Physics, 26, 2485, 1988.

79. Sen, S., Kisakurek, D., Turker, L., Toppare,L., and Akbulut,U., New Polymeric Mater.,1, No:3. p. in press),1989.

80. Carr, B.G., Harrod, J.F., and van Gheluwe, P., Macromolecules, 6, 498, July-Aug. 1973.

81. Kisakurek, D., and Turker,L., British Polymer Journal,21,1989(in press).

82. Harrod, J.F., and Shaver, A., J.Am.Chem.Soc., 15, 676, 1982.