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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

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### Polymerization of Bis(Pyridine)bis-(2,4,6-tribromophenoxy)copper(II) Complex (Py<sub>2</sub>Cu(TBrP)<sub>2</sub>) by Electrooxidation and Structural Characterization by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FTIR Spectroscopies

Sadi Sen<sup>a</sup>; Duygu Kisakurek<sup>a</sup>; Levent Toppare<sup>b</sup>

<sup>a</sup> Department of Chemistry, Middle East Technical University, Ankara, Turkey <sup>b</sup> Department of Sciences, Middle East Technical University, Ankara, Turkey

**To cite this Article** Sen, Sadi , Kisakurek, Duygu and Toppare, Levent(1993) 'Polymerization of Bis(Pyridine)bis-(2,4,6-tribromophenoxy)copper(II) Complex (Py<sub>2</sub>Cu(TBrP)<sub>2</sub>) by Electrooxidation and Structural Characterization by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FTIR Spectroscopies', Journal of Macromolecular Science, Part A, 30: 6, 481 – 492

**To link to this Article:** DOI: 10.1080/10601329308009424

**URL:** <http://dx.doi.org/10.1080/10601329308009424>

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# **POLYMERIZATION OF BIS(PYRIDINE)BIS-(2,4,6-TRIBROMOPHENOXO)COPPER(II) COMPLEX (Py<sub>2</sub>Cu(TBrP)<sub>2</sub>) BY ELECTROOXIDATION AND STRUCTURAL CHARACTERIZATION BY <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, AND FTIR SPECTROSCOPIES**

SADI SEN and DUYGU KISAKUREK

Department of Chemistry

LEVENT TOPPARE

Department of Sciences

Middle East Technical University  
06531 Ankara, Turkey

**Key Words:** Electroinitiated polymerization of tribromohalophenoxy copper complex; Constant potential electrolysis; Poly(dibromophenylene oxide); <sup>1</sup>H-NMR spectroscopy; <sup>13</sup>C-NMR spectroscopy

## **ABSTRACT**

Electroinitiated polymerization of bis(2,4,6-tribromophenoxy)-bis(pyridine)copper(II) complex was achieved in dimethylformamide-tetrabutylammonium tetrafluoroborate solvent–electrolyte couple under air or nitrogen at room temperature by constant potential electrolysis. Polymerization conditions were based on the peak potentials measured by cyclic voltammetry. The structural analyses of the polymers were done by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and FTIR spectral analyses along with molecular weight measurements by cryoscopy. The poly(dibromophenylene oxide)s obtained only at oxidation potentials in either atmosphere

were found to be highly linear, indicating mainly 1,4-catenation was taking place.

## INTRODUCTION

It is well known that several substituted phenols are readily oxidized by many different reagents [1] such as  $\text{FeCl}_3$ ;  $\text{O}_2/h\nu$ ;  $\text{HNO}_3$ , fuming;  $\text{ZnCl}_2/\text{air}$ ;  $\text{CH}_2\text{N}_2$ ; air/ $\text{NaOH}$ , etc. Thermal decomposition of silver salts of trihalogenated phenols [2] was the first successful study of the polymerization of substituted phenols reported [2-7]. Harrod made several studies on the polymerization of phenoxo copper complexes [8-10]. Further success was achieved in the polymerization of trihalophenoxo copper complexes thermally or electrochemically in solution or in the solid state by Kisakurek et al. [11-27]. The oxidation of phenols is of major importance in organic electrochemistry for the preparation of some substances. From a series of papers concerning the preparation of poly(phenylene oxides) either by chemically oxidative or electrooxidative methods from phenolic compounds, it has been realized that there is no essential difference in the mechanism of each route; the difference is only in the initiation step. In electrochemical polymerization, the initiation occurs at the electrode surface either through the monomer itself or via any other species, such as 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 radical, anionic, or cationic mechanisms.

Many scientists have studied the oxidation of phenolic compounds [28-34] either in solution or on an electrode surface by several electrochemical methods. There was no work on the electroinitiated polymerization of copper complexes of trihalophenols with neutral ligands reported up to 1988. In 1988, electroinitiated polymerizations of bis(trihalophenoxo)copper(II) complexes with different ligands were carried out at various anodic peak potentials of these complexes [16-25].

The synthesis and application of poly(dibromophenylene oxide) prepared by electroinitiated polymerization of bis(2,4,6-tribromophenoxo)copper(II) complexes using  $N,N,N',N'$ -tetramethylethylenediamine and ethylenediamine as the chelating ligand have previously been investigated [22,23]. In the present investigation, the electroinitiated polymerization of the bis(2,4,6-tribromophenoxo)copper(II) complex with pyridine as a nonchelating ligand has been studied to provide additional information on this system.

## EXPERIMENTAL

### Materials

2,4,6-Tribromophenol (TBrP). Analytical grade 2,4,6-tribromophenol (from Aldrich Chemical Co.) was used without further purification.

Pyridine (Py). Reagent grade pyridine (Merck) was used without further purification.

*N,N*-Dimethylformamide (DMF). (Merck) was stirred with anhydrous copper sulfate for 48 hours and distilled at 5 mmHg pressure (bp 38°C).

Copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ). Reagent grade copper sulfate was used for the preparation of the phenol complex.

Ethanol. Ethanol was used as a precipitating reagent. It was fractionally distilled under atmospheric pressure at 75°C.

Tetrabutylammonium fluoroborate (TBAFB). TBAFB was obtained by titrating 40% tetrabutylammonium hydroxide with fluoroboric acid until the solution was slightly acidic. It was filtered and recrystallized twice from a 1:3 ethanol-water mixture. Then it was dried under vacuum at 50°C.

Silver fluoroborate ( $\text{AgBF}_4$ ).  $\text{AgBF}_4$  was prepared by the titration of 10% fluoroboric acid with a 5% silver oxide solution [35].

Deuterated chloroform ( $\text{CDCl}_3$ ).  $\text{CDCl}_3$  was obtained from Merck Co.

Carbon disulfide ( $\text{CS}_2$ ). Analytical grade  $\text{CS}_2$  (Merck) was used without further purification for recording the  $^1\text{H-NMR}$  spectra.

Bis(pyridine)bis(2,4,6-tribromophenoxy)copper(II) complex ( $\text{Py}_2\text{Cu}(\text{TBrP})_2$ ).  $\text{Py}_2\text{Cu}(\text{TBrP})_2$  was prepared by mixing the following two solutions. Solution I containing 0.04 mol NaOH and 0.04 mol 2,4,6-tribromophenol in 100 mL distilled water was slowly added to Solution II containing 0.02 mol  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  and 0.04 mol pyridine in 100 mL distilled water with vigorous stirring. The brown precipitate was filtered, washed with distilled water, and dried in vacuum. The complex was characterized by elemental analysis.

### Polymerization Apparatus

Potentiostat. A Tacussel potentiostat model PRT 30-0.1 was used in this work for polymerizations. It was capable of giving a voltage of 30 V and a maximum current of 0.1 A.

Recorder. A Sefram XY recorder was used to plot the current-potential curves.

Electrolysis Cell. The electrolysis cell was an H-type cell containing three electrodes operating as the working, counter, and reference electrodes. A graphite anode with a diameter of 5 mm and a stainless steel cathode with an area of  $6.5 \text{ cm}^2$  were employed. The reference electrode was  $\text{Ag}/\text{AgBF}_4(0.01 \text{ M})$ , as reported in the literature [23].

Cyclic Voltammetry System. This consisted of three electrodes: working, counter, and reference. The working and counter electrodes were platinum bead and platinum wire, respectively. The Pt wire was 3 cm in length. The reference electrode was a Luggin capillary (Fig. 1). Cyclic voltammetry measurements of the complex were done in DMF-TBAFB as the solvent-electrolyte couple at 20°C in a cyclic voltammetry cell.

The cyclic voltammetry system was composed of a potentiostat, a function generator, an XY recorder, and a cyclic voltammetry cell, discussed previously [35].

Constant Potential Electrolysis System. This was composed of a potentiostat, an XY recorder, and an electrolysis cell employed for polymerizations [35].

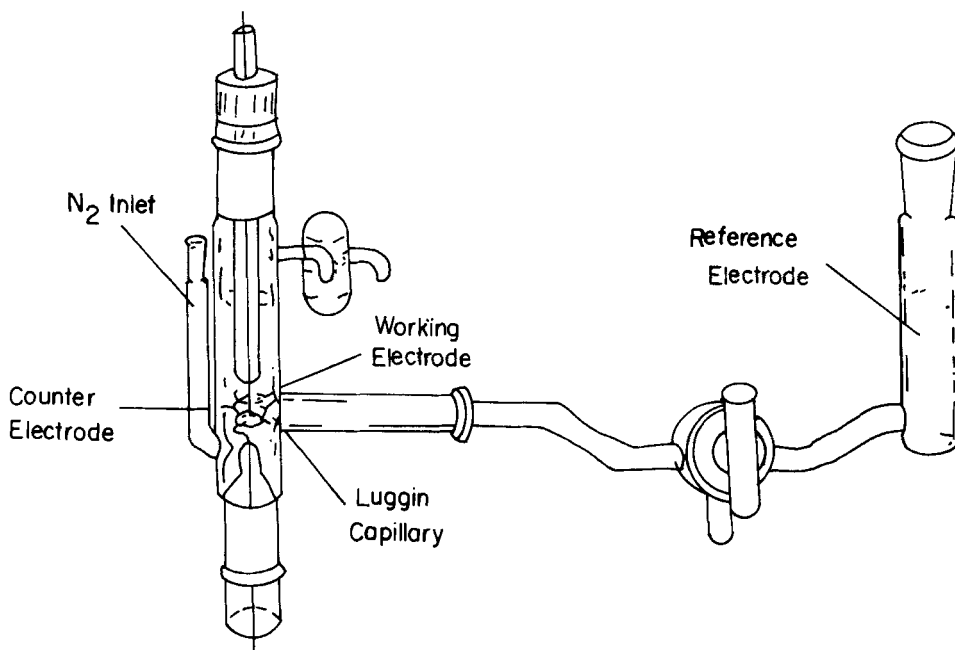


FIG. 1. Cyclic voltammetry cell.

**Molecular Weight Determination.** Molecular weight measurements were made by the cryoscopic method, using camphor as the solvent.

**NMR Spectrometer.**  $^1\text{H}$ -NMR spectra were carried out on a Bruker AC 80 NMR spectrometer using  $\text{CS}_2$  as the solvent and TMS as the internal reference.  $^{13}\text{C}$ -NMR spectra were run on a Bruker AC 200 NMR spectrometer, using deuterated chloroform as the solvent.

**Carbon-Hydrogen-Nitrogen (CHN) Analyzer.** A Hewlett-Packard 185 CHN Analyzer was used to identify the monomer complex. The temperature of the oxidation furnace was  $1000^\circ\text{C}$  and the temperature of the reduction furnace was approximately  $500^\circ\text{C}$ , with a column oven temperature of  $80^\circ\text{C}$ . The flow rate of helium was  $100\text{ mL/min}$ .

**Fourier-Transform Infrared (FTIR) Spectrometer.** A Nicolet 510 FTIR Spectrometer was used.

TABLE 1. Elemental Analysis Result of Complex  $\text{Py}_2\text{Cu}(\text{TBrP})_2$

Calculated, %			Found, %		
C	H	N	C	H	N
30.0	1.7	3.2	30.3	1.94	3.0

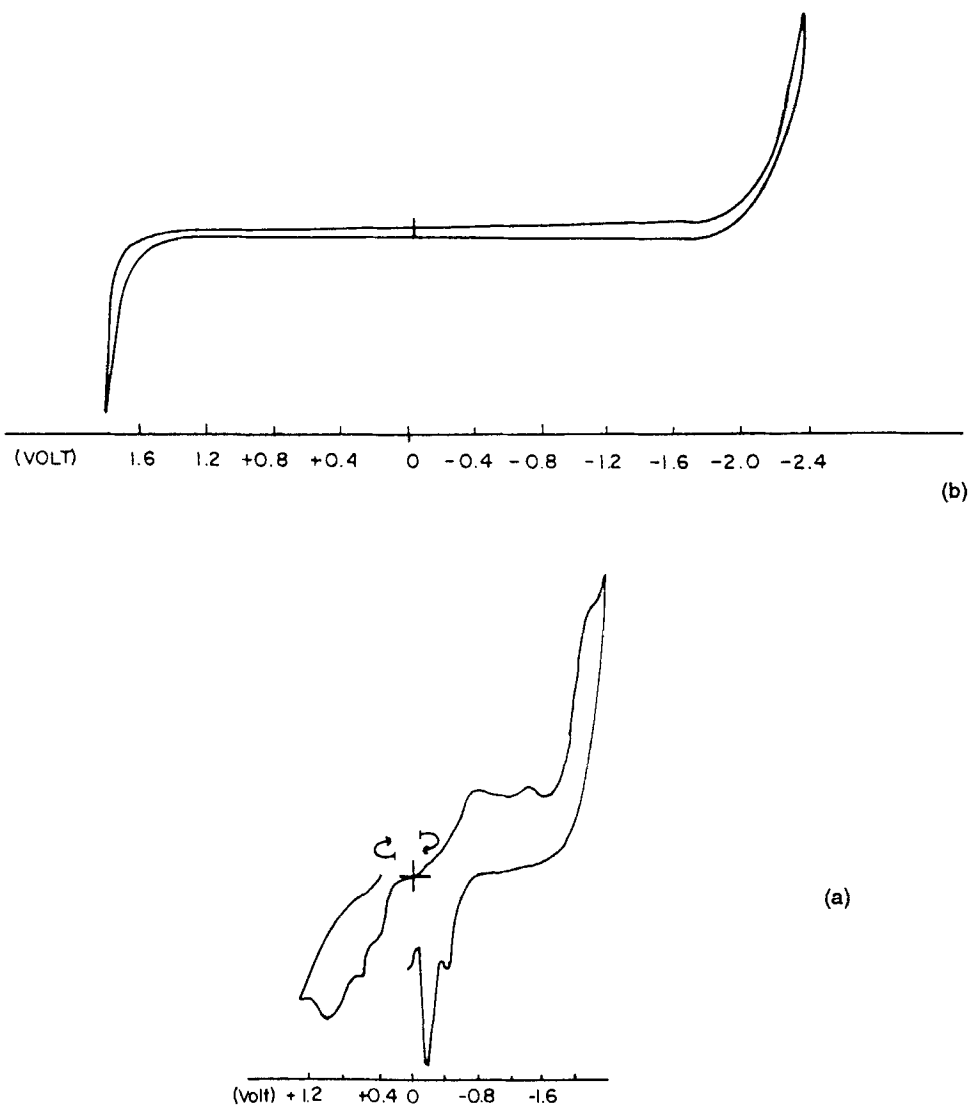
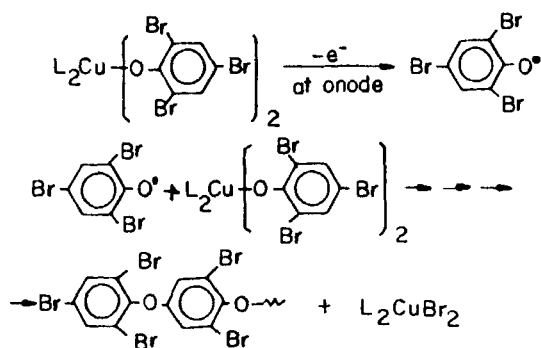


FIG. 2. (a) Cyclic voltammogram of  $\text{Py}_2\text{Cu}(\text{TBrP})_2$  with a scan rate of 200 mV/s. (b) Cyclic voltammogram of TBAFB-DMF as the solvent-electrolyte system.

TABLE 2. Oxidation ( $E_{p,a}$ ) and Reduction ( $E_{p,c}$ ) Peak Potentials of the Complex

Complex	Anodic peak potential ( $E_{p,a}$ ), in volts	Cathodic peak potential ( $E_{p,c}$ ) in volts
$\text{Py}_2\text{Cu}(\text{TBrP})_2$	+0.4	-0.75
	+0.66	-1.4
	+1.1	-2.2



SCHEME 1.

## RESULTS AND DISCUSSION

The result of CHN elemental analysis of the complex is listed in Table 1. The experimental results are in agreement with the calculated ones to about  $\pm 0.3$ . IR and elemental analysis of the complex were as expected from the literature [8].

**Cyclic Voltammetry Measurements.** The oxidation and reduction peak potentials of the complex TBrP were determined prior to electrolysis in TBAFB-DMF at room temperature under  $\text{N}_2$  by cyclic voltammetry. As seen in the CV of the complex (Fig. 2a), there are three anodic ( $E_{p,a}$ ) and cathodic ( $E_{p,c}$ ) potentials as listed in Table 2. Prior to addition of monomer, the background voltammogram indicated the absence of any impurities (Fig. 2b).

**Polymer Synthesis.** Electrolysis were carried out anodically. When cathodic potentials were applied, it was observed that polymer was formed only at the anode compartment. Polymerization was continued for 3 hours. Polymerization was clearly initiated by a direct electron transfer from complex to anode as in the proposed mechanism [36] of Scheme 1.

TABLE 3. Polymer Yield under Air and  $\text{N}_2$  at Various Peak Potentials after 3 hours of Electrolysis in DMF of  $\text{Py}_2\text{Cu}(\text{TBrP})_2$

$E_p$ , <sup>a</sup> V	% Yield	
	Under nitrogen	Under air
+0.4	30	33
+0.66	39	46
+1.1	39	46
-0.70 <sup>b</sup>	—	12
-1.4 <sup>b</sup>	28	30
-2.2 <sup>b</sup>	30	31

<sup>a</sup>Peak potentials as polymerization potentials.

<sup>b</sup>Polymer recovered from anolyte.

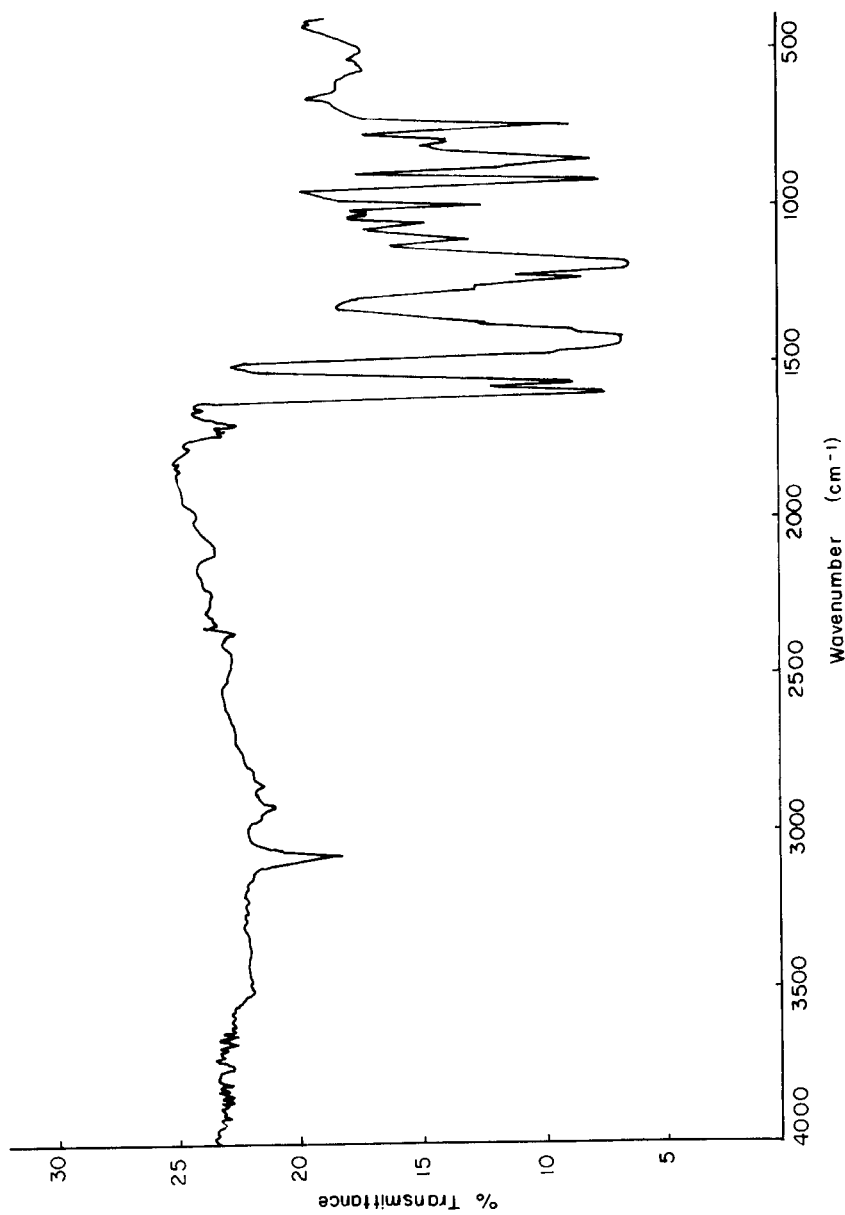


FIG. 3. FTIR spectrum of poly(dibromophenylene oxide) obtained by electroinitiation at +0.66 V.



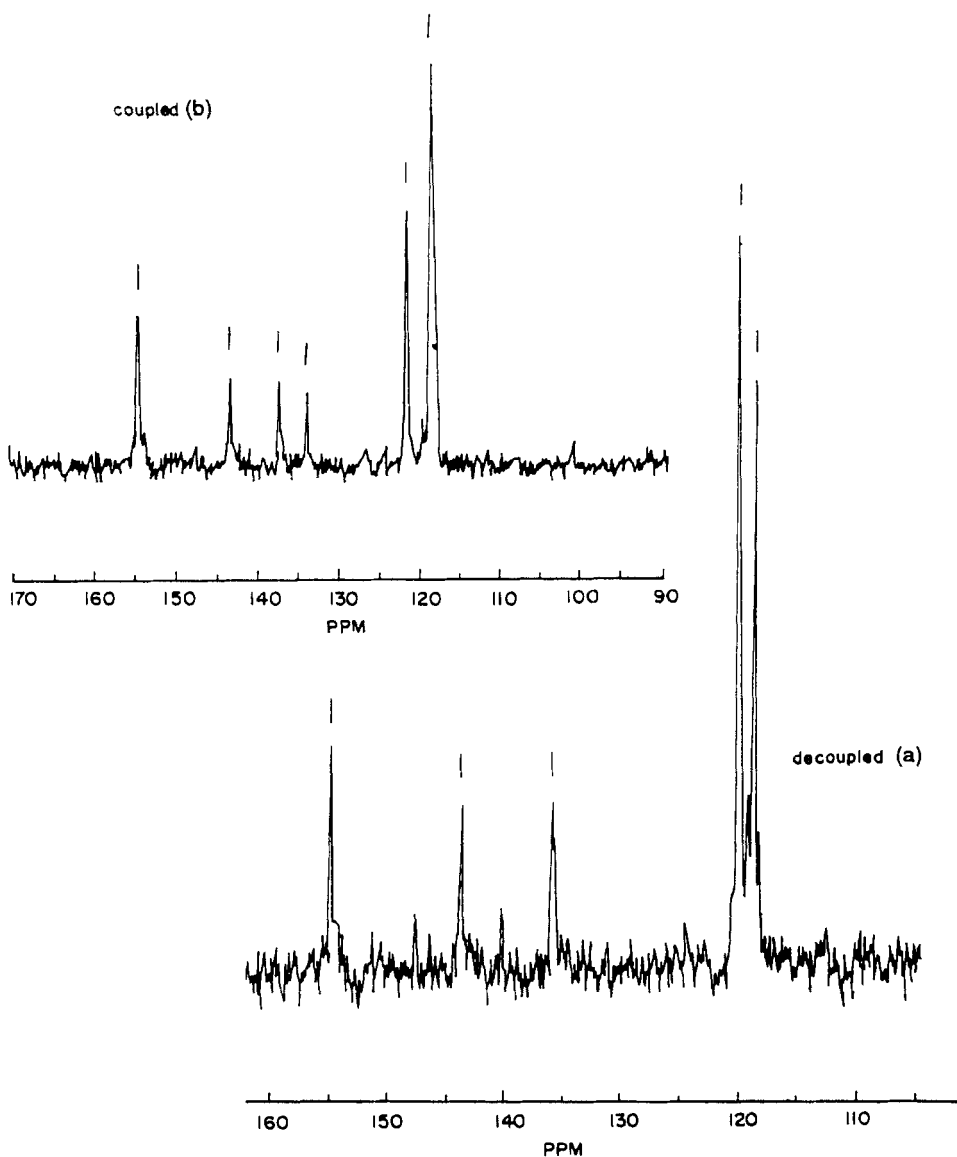


FIG. 4.  $^{13}\text{C}$ -NMR decoupled (a) and coupled (b) spectra for polymer obtained at +0.66 V.

Percent yields based on the initial weight of the complexes (ligand and copper do not incorporate into the polymer) are given in Table 3.

The concentration of the complex was of the order of  $10^{-2}$  M. The polymer obtained at the anolyte had a molecular weight of  $3.5 \times 10^3$  ( $\overline{M}_n$ ).

The structure of the polymer was characterized by FTIR,  $^1\text{H}$ -NMR, and  $^{13}\text{C}$ -NMR spectroscopy.

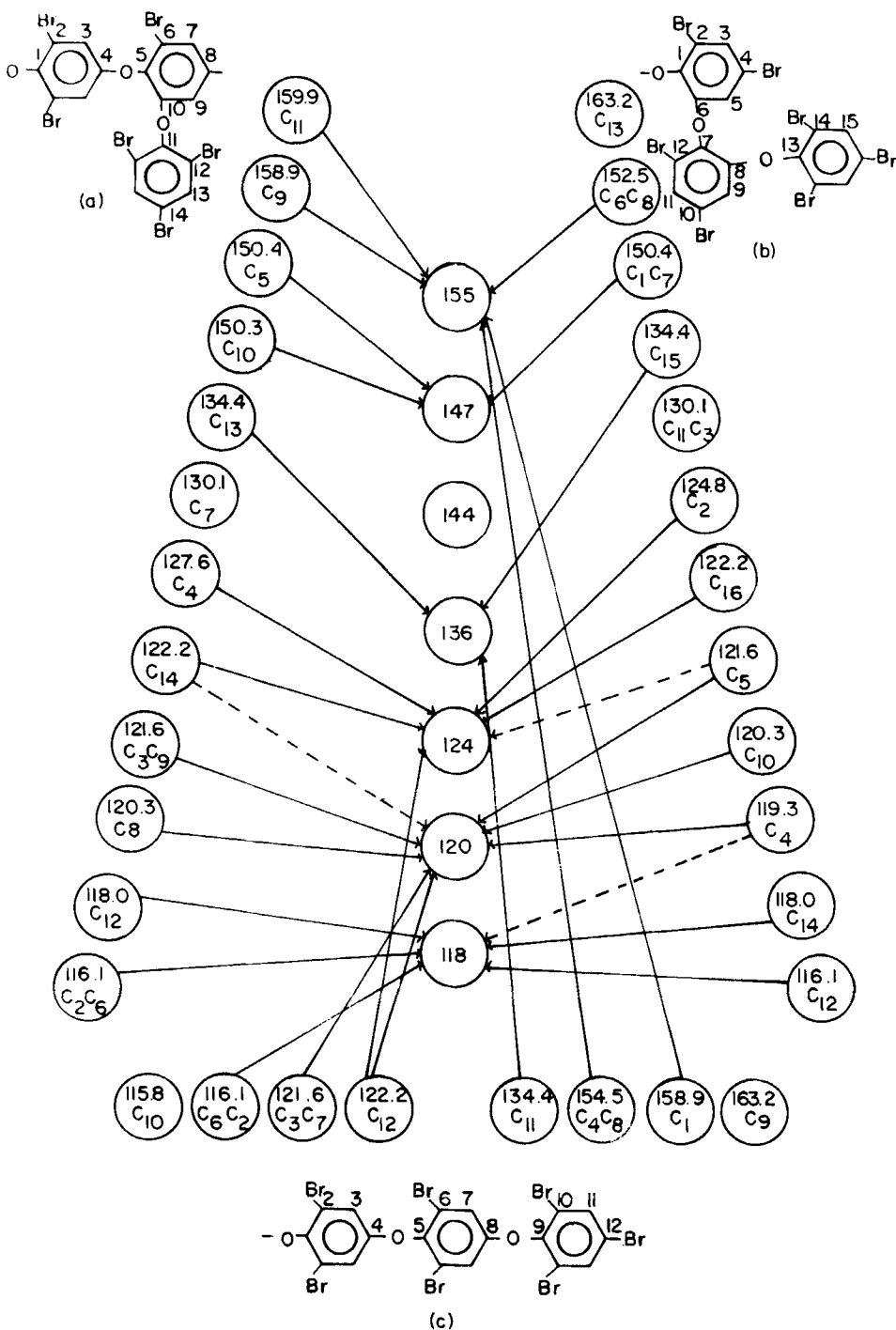


FIG. 5. Schematic representation of  $^{13}\text{C}$ -NMR chemical shift data for the polymer.

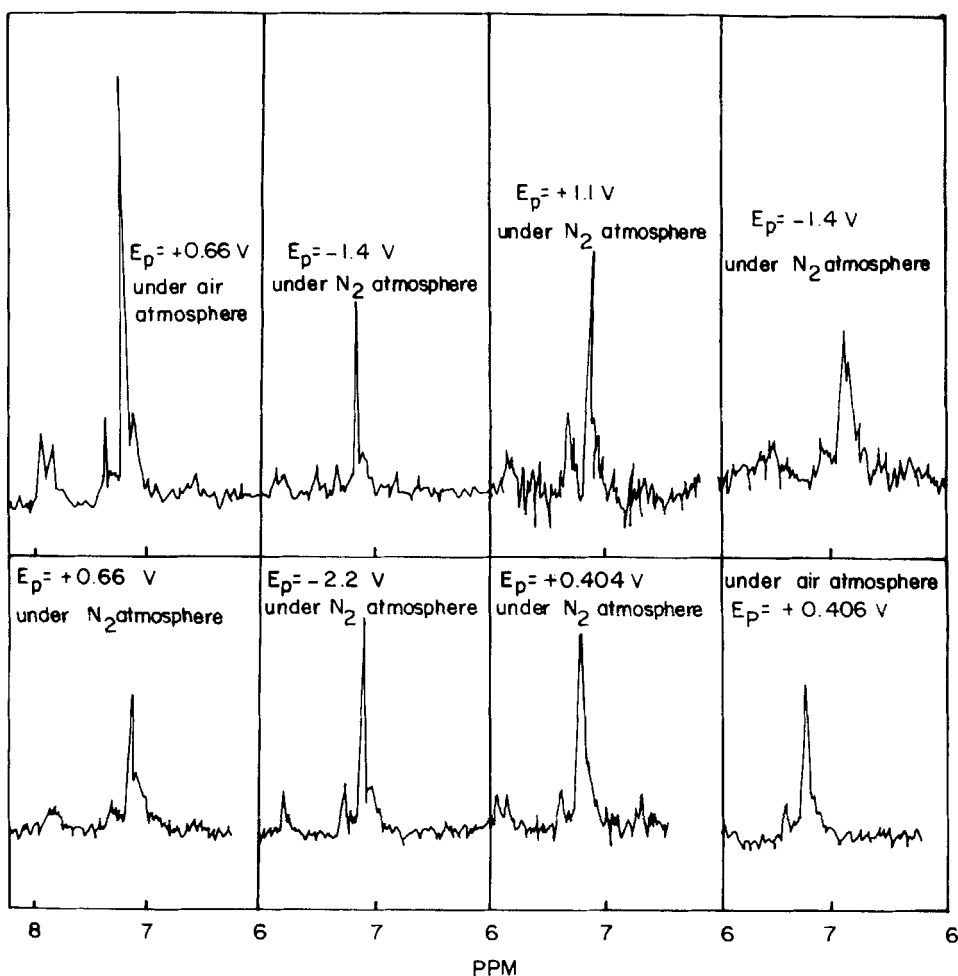


FIG. 6.  $^1\text{H}$ -NMR spectra of poly(dibromophenylene oxide) at different peak potentials under air and  $\text{N}_2$  atmospheres.

The Fourier-transform infrared (FTIR) spectrum of the polymer is shown in Fig. 3. It is characterized by 860, 855 (out-of-plane C—H bendings); 920, 1000, 1030, 1060, 1090 (symmetric C—O—C stretchings); 1200, 1230, 1270 (C—O stretchings); and 1370, 1490, 1550, 1600  $\text{cm}^{-1}$  (C=C stretchings) as given in the literature [37]. The peak at 3100  $\text{cm}^{-1}$  is due to aromatic C—H stretchings.

Theoretical  $^{13}\text{C}$ -NMR chemical shift data for the main three possible 1,4- or 1,2-catenation products of TBrP were calculated by using the appropriate correlation tables [38].  $^{13}\text{C}$ -NMR coupled and decoupled spectra for the polymer are given in Fig. 4. It suggests that the observed data are more or less a superimposed spectra of Structures a and c (Fig. 5). The polymers synthesized at various potentials and atmospheres were characterized by using  $^1\text{H}$ -NMR (Fig. 6). A very simple spectrum having a rather sharp peak at about  $\delta$  7.2 ppm is displayed in Fig. 6, and it indicates that the polymer is mainly linear, i.e., the 1,4-catenation product of tribromophenol

with some monomeric ortho branches is observed at about  $\delta$  7.5 ppm. Interaction energy calculations also revealed that ortho and para positions have almost equal susceptibilities toward dimer formation. However, both the dimeric radicals should attract the para position of the phenolate ion much faster than the ortho position. Hence, selectivity toward 1,4-catenation is favored over 1,2-catenation [13]. All the polymers were found to be structurally the same, irrespective of the applied potential and the nature of the atmosphere (Fig. 6).

## CONCLUSION

The present study has proved that the bis(2,4,6-tribromophenoxy)copper(II) complex having a nonchelating ligand such as pyridine can be polymerized by electrooxidation. Although the ease with which the decomposition of such complexes occurs is profoundly affected by the nature of the neutral ligands on the copper, low molecular weight linear poly(dibromophenylene oxides) were obtained irrespective of the applied potential and the nature of the atmosphere.

## ACKNOWLEDGMENT

We are grateful to the METU Research Fund (AFD) for partial support of this work.

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Received September 18, 1992

Revision received December 5, 1992