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HEINEMANN

*Polymer* Vol. 36 No. 15, pp. 3013-3018, 1995

0032-3861/95/\$10.00+0.00

# Synthesis of mainly linear poly(dichlorophenylene oxide) based on the electro-oxidation of bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II) complex in dimethylformamide

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*(Received 9 March 1994; revised 17 June 1994)*

Anodic oxidation of bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II) complex leads mainly to linear poly(2,6-dichlorophenylene oxide) under constant-potential electrolysis in the dimethylformamide–tetrabutylammonium tetrafluoroborate solvent–electrolyte couple at room temperature under air or nitrogen. Polymerization conditions were based on the peak potentials measured by cyclic voltammetry. Characterization of the polymer was performed by $^{13}$C and $^{1}$H nuclear magnetic resonance, Fourier-transform infra-red spectroscopy, differential scanning calorimetry, molecular-weight and dipole moment measurements.

**(Keywords: poly(dichlorophenylene oxide); $Py_2Cu(Br\text{-}DCP)_2$ complex; nuclear magnetic resonance)**

## INTRODUCTION

Our previous studies indicate that polymerization of bis(trihalophenoxo)bis(pyridine)copper(II) complex can be achieved by electro-oxidation in diemthylformamide at room temperature, under air or nitrogen[1–5]. During the course of our studies on the synthesis of poly(dihalophenylene oxide)s, the effects of the type and the position of the halogen on the structure of the polymers were investigated. In the present study, mainly linear poly(dichlorophenylene oxide) has been synthesized by electro-oxidation and then characterized. A major aim of this work was to carry out this synthesis with a view to comparing the properties of the polymer obtained from 4-bromo-2,6-dichlorophenol with those of poly(dichlorophenylene oxide)s synthesized with different halogens, mainly chlorine and/or bromine substituted at various positions of the phenol rings with the non-chelating ligand pyridine of copper(II) complex.

## EXPERIMENTAL

### *Materials*

2,6-Dichlorophenol (2,6-DCP) provided by Aldrich Chemical was used to prepare 4-bromo-2,6-dichlorophenol (4-Br-DCP). Bromination was performed using a similar procedure to that described previously[6]. Pyridine (Py), purchased from Merck, was used as neutral ligand. Copper sulfate, $CuSO_4 \cdot 5H_2O$, was commercially available reagent-grade material. $N,N'$-dimethylformamide (DMF) provided by Merck was dried with anhydrous $CuSO_4$ for 48 h and then distilled under 5 mmHg. It was used as solvent for both cyclic voltammetry (c.v.) and electro-initiated polymerization. Tetrabutylammonium tetrafluoroborate (TBAFB) from Merck was used as electrolyte.

### *Synthesis of copper complex*

The copper complex was prepared according to the previously described method[7]. The complex was characterized by elemental analysis using a Hewlett-Packard F and M 185 carbon–hydrogen–nitrogen Analyser, with oxidation furnace at 1000°C, reduction furnace at approximately 500°C, column oven temperature at 80°C and the flow rate of helium gas of 100 cm$^3$ min$^{-1}$. The results of the elemental analysis are: calculated, H 2.0%, N 4.0%, C 37.6%; found, H 2.32%, N 3.95%, C 37.2%. The experimental error limit is ±0.3. The 4-Br-DCP and the complex are also characterized by i.r. measurements.

### *Cyclic voltammetry*

The cyclic voltammetry cell consisted of three electrodes: Pt bead as working electrode, Pt wire as counter-electrode and Luggin capillary containing Ag/$Ag^+$ (0.01 M) as reference electrode, as described elsewhere[8]. The measurements were taken in DMF–TBAFB (0.1 M) as solvent–supporting electrolyte couple at room temperature with a 200 mV s$^{-1}$ scan rate.

The cyclic voltammetry system was composed of a potentiostat (Tacussel, model PRT 30-0.1), a function generator (Tacussel Pilote Servoit), an $X-Y$ recorder (Sefram) and a cyclic voltammetry cell.

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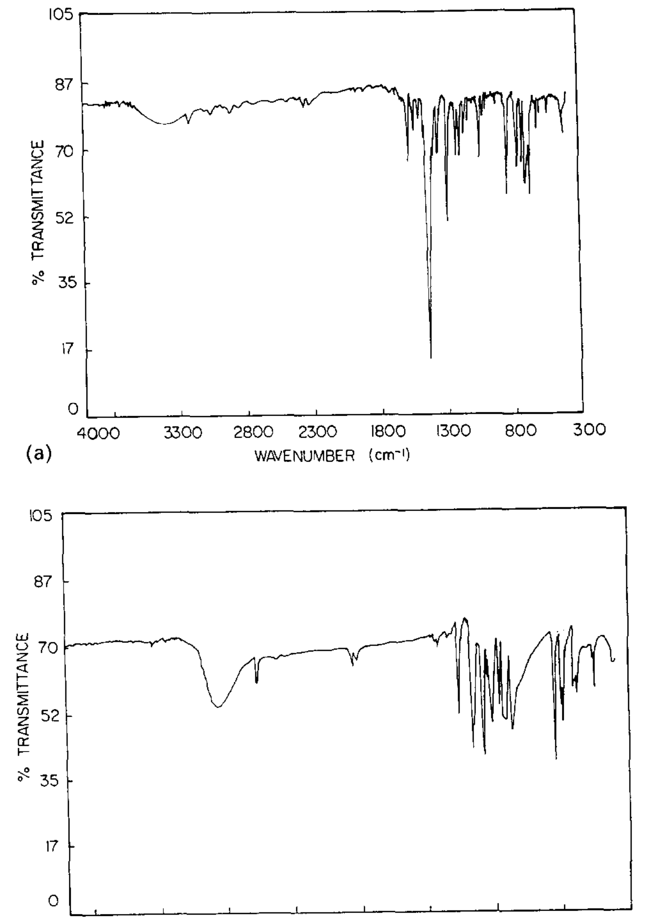

**Figure 1** *FT*i.r. spectra of (a) bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)Cu(II) complex and (b) 4-bromo-2,6-dichlorophenol

**Table 1** Electro-initiated polymerization of bis(4-bromo-2,6-dichlorophenoxo)bis(pyridine)copper(II) complex

| | Yield (%)[b] | |
|---|---|---|
| $E_{pol}$[a] | Under $N_2$ | Under air |
| +0.2 | 14 | – |
| +0.4 | 21 | 26 |
| +0.65 | 27 | 33 |
| +1.1 | 34 | – |
| +1.3 | 37 | – |
| −0.5[c] | – | 4 |
| −1.2[c] | 28 | 29 |
| −2.1[c] | 33 | 36 |

[a] Polymerization potential obtained from c.v. measurements of $\mathrm{Py_2Cu(4\text{-}Br\text{-}DCP)_2}$ complex
[b] Polymer recovered from anolyte at the end of 3 h electrolysis
[c] Polymer obtained only at anode compartment

**Table 2** Oxidation ($E_{p,a}$) and reduction ($E_{p,c}$) peak potentials of various halogenated phenoxocopper(II) complexes in DMF at room temperature at a scan rate of 200 mV s$^{-1}$ with ligand pyridine using the same c.v. system

| Complex | $E_{p,a}$ (V) | $E_{p,c}$ (V) |
|---|---|---|
| $\mathrm{Py_2Cu(TCP)_2}$[a] | +0.3, +0.65, +1.0 | −0.7, −1.6, −2.1 |
| $\mathrm{Py_2Cu(4\text{-}Br\text{-}DClP)_2}$ | +0.2, +0.65, +0.9, +1.3 | −0.5, −1.2, −2.1 |
| $\mathrm{Py_2Cu(TBrP)_2}$[b] | +0.4, +0.65, +1.1 | −0.75, −1.4, −2.2 |
| $\mathrm{Py_2Cu(4\text{-}Cl\text{-}DBrP)_2}$[c] | +0.4, +0.75, +1.1 | −0.65, −1.3, −1.9 |
| $\mathrm{Py_2Cu(2\text{-}Br\text{-}DClP)_2}$[d] | +0.4, +0.7, +1.15 | −0.85, −1.35, −1.7, −2.1 |

[a] Ref. 1 [b] Ref. 5 [c] Refs. 1,2 [d] Ref. 3

*Constant potential electrolysis system*

The c.p.e. system consisted of a potentiostat, an $X-Y$ recorder and an H-type electrolysis cell containing 5 mm diameter graphite as working electrode, 6 cm$^2$ stainless-steel foil as counter-electrode and Ag/Ag$^+$ (0.01 M) as reference electrode[3].

*Polymer synthesis*

Electro-initiated polymerizations of $\mathrm{Py_2Cu(4\text{-}Br\text{-}DCP)_2}$ complex were carried out by c.p.e. for 3 h electrolysis in DMF under air or $N_2$, at room temperature. Polymerization conditions were based on the peak potentials measured by c.v.

*Polymer characterization*

*Spectral analysis.* A Perkin Elmer 1710 model Fourier-transform infra-red spectrophotometer was used to obtain i.r. spectra of the polymer, complex and 4-Br-DCP on KBr discs.

For structural determination, $^1$H n.m.r. spectra and $^{13}$C n.m.r. spectra were obtained by Bruker AC 80 in $CS_2$ and Bruker AC 200 in deuterated chloroform respectively.

*Molecular-weight determination.* The number-average molecular weight of the polymer was determined by the vapour-pressure method in chloroform with PE Coleman 115 molecular-weight apparatus. The $M_n$ value of the polymer was $4.0 \times 10^3$.

*Capacitance-measuring assembly.* A General Radio Co. Type 1620-A capacitance-measuring assembly was used to measure capacitance at 10 kHz frequency and 30 V. It consisted of a Type 1615-A audio oscillator on a Type 1232-A tuned amplifier and a null detector[3].

**Table 3** Comparison of oxidation peak potentials of various halogenated phenoxocopper complexes measured in DMF at room temperature at a scan rate of 200 mV s$^{-1}$ with non-chelating ligand pyridine (Py) to chelating ligand ethylenediamine (en)

| Trihalophenol | Ligand | $E_{p,a}$ (V) |
|---|---|---|
| TCP[a] | Py | +0.3, +0.65, +1.0 |
| | en | +0.3, +0.7 |
| | Py | +0.2, +0.65, +0.9, +1.3 |
| 4-Br-DCP[a] | en | +0.2, +0.4, +0.9 |
| TBrP[a] | Py | +0.4, +0.65, +1.1 |
| | en | +0.3, +0.4, +1.0 |
| 4-Cl-DBrP[b] | Py | +0.4, +0.75, +1.1 |
| | en | +0.3, +0.7, +1.3 |

[a] Ref. 10 [b] Ref. 11

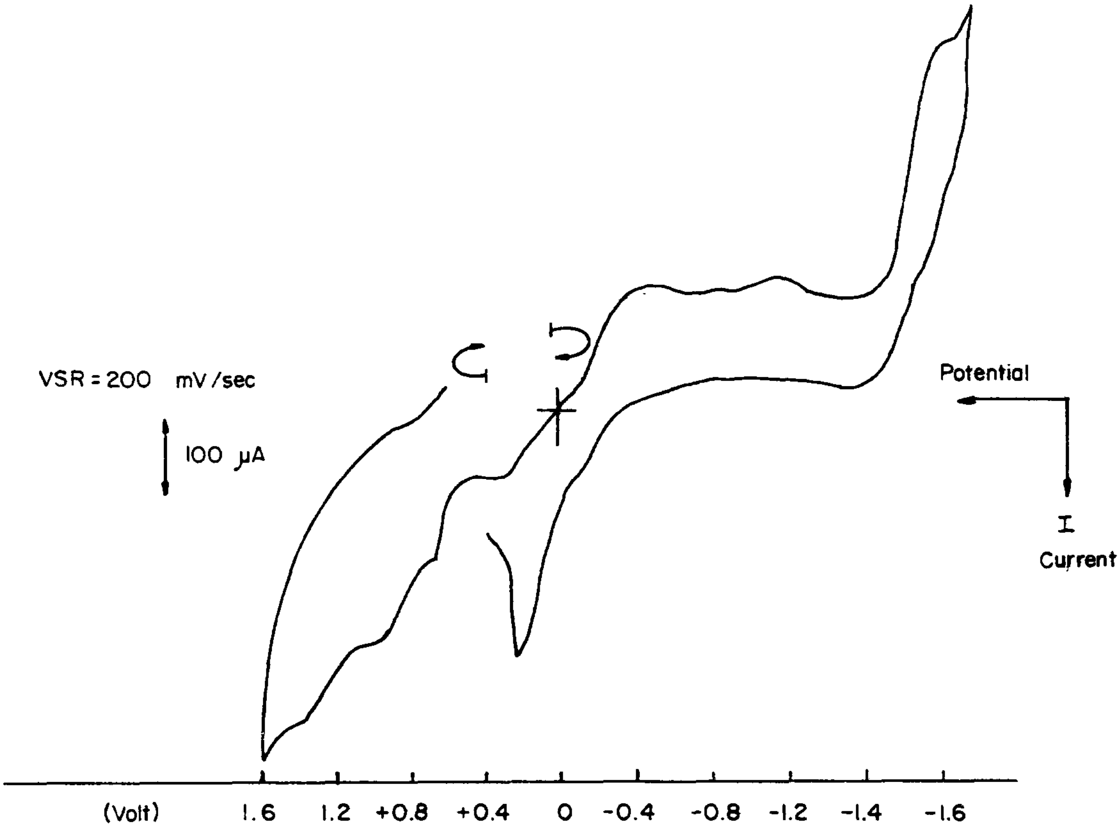

**Figure 2** Cyclic voltammogram of $Py_2Cu(4\text{-}Br\text{-}DCP)_2$

**Table 4** Temperature dependence of dielectric constants and mean-squared dipole moments per repeat unit (D = Debye) for $Py_2Cu(4\text{-}Br\text{-}DCP$

| $T$ (°C) | $\epsilon_{polymer}$ | $(\langle\mu^2\rangle/x)_{polymer}$ ($D^2$) |
|---|---|---|
| 25 | 0.144 | 2.1300 |
| 40 | 0.111 | 2.7623 |
| 45 | 0.127 | 3.4824 |
| 60 | 0.085 | 3.2216 |
| 70 | 0.114 | 4.9944 |

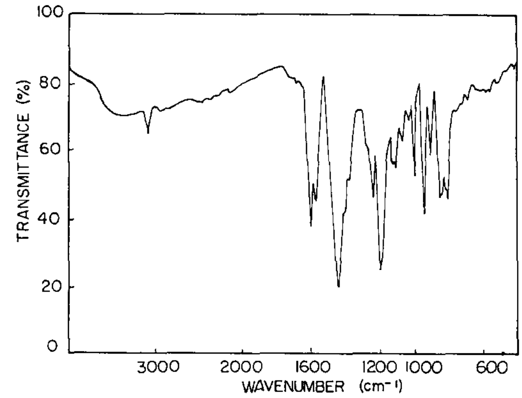

**Figure 3** *FT*i.r. spectrum of poly(dichlorophenylene oxide) obtained by electro-oxidation of $Py_2Cu(4\text{-}Br\text{-}DCP)_2$ complex in DMF

*Refractive-index increments.* These (d$n$/d$c$) were obtained with a standard Brice-Phoenix differential refractometer model BP-2000.

*Differential scanning calorimeter.* A DSC 910 S differential calorimeter equipped with TA Instruments Thermal Analyst 2000 System was used to measure glass transition temperature ($T_g$) of poly(dichlorophenylene oxide).

## RESULTS AND DISCUSSION

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[7]. Bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II) complex was characterized by *FT*i.r. spectroscopy (*Figure 1*). Characteristic C–N stretching was observed at about 1065 cm$^{-1}$, and the characteristic OH peak at 3500 cm$^{-1}$ in *Figure 1b* disappeared.

The oxidation and reduction peak potentials of the complex were determined prior to electrolysis in TBAFB–DMF under $N_2$ by cyclic voltammetry. Four distinct main oxidation peak potentials $E_{p,a}$ (+0.2, +0.65, +0.9 and +1.3 V) and three reduction peak potentials $E_{p,c}$ (−0.5, −1.2 and −2.1 V) were observed in the cyclic voltammogram of the complex (*Figure 2*). Successive scans gave the same peak potential values when scans were reversed for both cathodic and anodic regions.

Although electrolyses were carried out at both cathodic and anodic peak potentials, polymers were recovered only from the anode compartment, indicating that electro-initiated polymerization proceeds only upon oxidation on the anode. The possibility of thermal

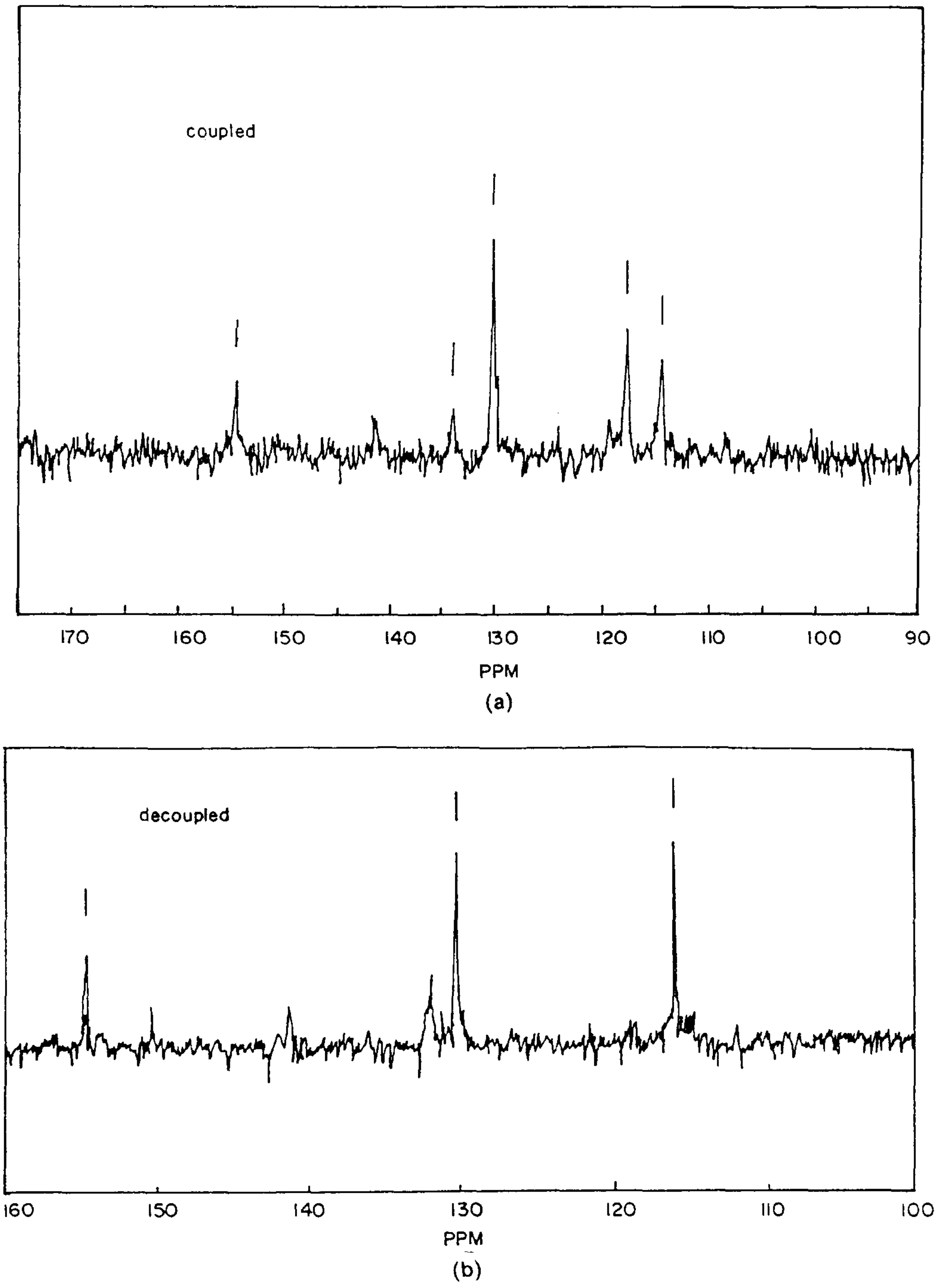

**Figure 4** $^{13}C$ n.m.r. coupled (a) and decoupled (b) spectra

polymerization under the experimental conditions is ruled out as there was no reaction in the absence of applied constant potential[9].

Calculations of the yields for the polymerization based on the initial weight of the complex appear to be low due to the ligand pyridine and Cu, which do not incorporate into the polymer. After 3 h electrolysis, the percentage yields increase with increasing oxidation potential under $N_2$ but a higher yield is observed under air (*Table 1*). The values of $E_{p,a}$ and $E_{p,c}$ obtained from c.v. measurements are almost the same for different halogenated related bis(pyridine)bis(trihalophenoxo)copper(II) complexes (*Table 2*). One can see from *Table 3* that when a non-chelating ligand like pyridine is changed to a chelating ligand, ethylenediamine, the oxidation peak potentials are almost identical.

The *FT*i.r. spectrum of poly(dichlorophenylene oxide) obtained by electro-oxidation of $Py_2Cu(4\text{-}Br\text{-}DCP)_2$ in DMF is shown in *Figure 3*. It is characterized by bands at 820 and 850 $cm^{-1}$ (out-of-plane C–H bending), at 910, 940, 1000, 1030, 1060 and 1100 $cm^{-1}$ (asymmetric C–O–C stretching), at 1200 and 1240 $cm^{-1}$ (C–O stretching) and at 1570 and 1600 $cm^{-1}$ (C=C ring stretching)[12].

The polymers synthesized at various potentials were characterized by using $^{13}C$ n.m.r. and $^{1}H$ n.m.r. Three basic structures were drawn for the polymer. The theoretical $^{13}C$ n.m.r. chemical-shift data for the three possible addition products of 4-Br-DCP were calculated

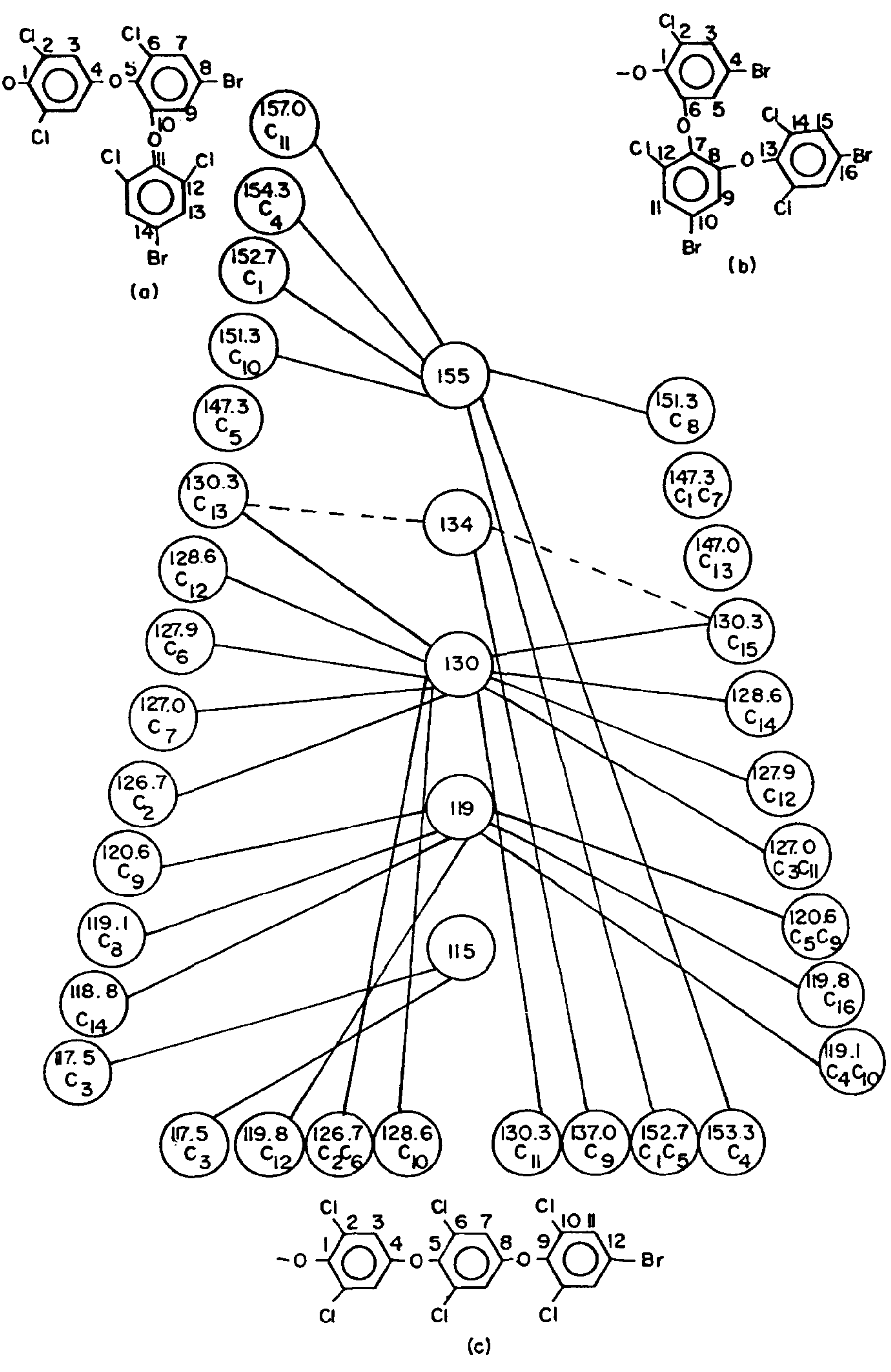

**Figure 5** Schematic representation of $^{13}$C n.m.r. data. The correlation of observed and calculated chemical-shift data

from the related correlation tables given in the literature[13]. $^{13}$C n.m.r. coupled and decoupled spectra are given in *Figure 4*. Observed resonance frequencies are compared with the calculated values for the three possible structures in *Figure 5*. There is no significant difference between the calculated and the experimental data. This observation reveals that the polymer mainly consists of 1,4-addition (*Figure 5c*), together with some branched products (*Figure 5b,c*) at the same time. The $^{1}$H n.m.r. spectrum in *Figure 6* clearly reveals that the polymer has a mainly linear structure, exhibiting a sharp singlet peak at $\delta = 6.8$ ppm due to 1,4-addition and a minor peak at $\delta = 7.4$ ppm due to 1,2-addition. All the polymers were found to be structurally the same irrespective of the applied potential.

Low-molecular-weight ($M_n = 4.0 \times 10^3$), mainly linear, rigid ($T_g = 215°C$) poly(dichlorophenylene oxide) is also characterized by dipole moment measurements.

### *Dipole moment measurements*

Dipole moment and dielectric constants of polymer are presented in *Table 4*. The mean-squared dipole moments per repeat unit of the polymer chain were

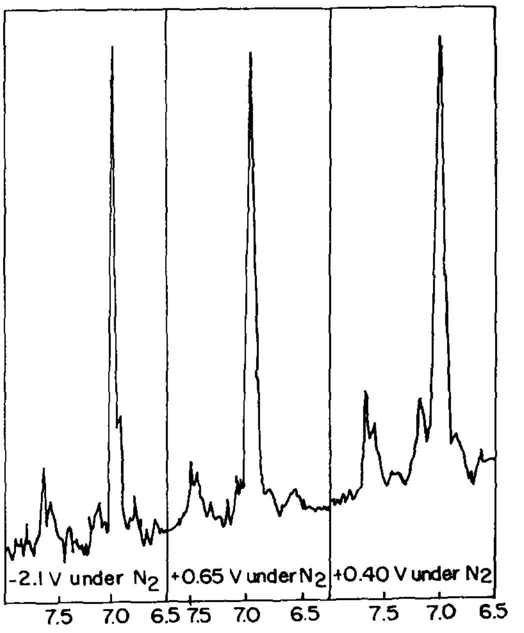

**Figure 6** $^1$H n.m.r. spectra of the polymer obtained at various oxidation and reduction potentials under $N_2$

calculated using the Guggenheim–Smith equation[14]:

$$\frac{\langle\mu^2\rangle}{x} = \frac{27kTM_0}{4\pi N_A}\left(\frac{d\epsilon/dc}{(\epsilon_1+2)^2} - \frac{2n_1(dn/dc)}{(n_1+2)^2}\right)$$

where $M_0$ is the molecular weight of the repeat unit, $N_A$ is Avogadro's number, $k$ is Boltzmann's constant, $\epsilon$ is the static dielectric constant, $n$ is refractive index and $c$ is concentration of polymer in grams of polymer/100 g solvent. Subscript 1 refers to values for pure solvent (toluene). Refractive index increment d$n$/d$c$ was determined at 30°C and 436 nm wavelength with a Brice-Phoenix differential refractometer model BP-2000. This value was taken constant as 0.118 ml g$^{-1}$ for all the temperatures[16].

The mean-squared dipole moments per unit of the polymer chain are given in *Table 4*. When compared with the same values of the polymer obtained from bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine) copper(II) complex[3], approximately 10-fold lower $\langle\mu^2\rangle/x$ values are observed. This fact may suggest that poly (dichlorophenylene oxide) chains are less rigid than poly (dihalophenylene oxide) synthesized from bis(pyridine)bis (2-bromo-4,6-dichlorophenoxo)copper(II) complex[3], and some branching may exist in the chains. It is also well known that low-molecular-weight poly (dichlorophenylene oxide) consists of linear chains[16,17]. Small increases in $\langle\mu^2\rangle/x$ values with temperature are due to the change in chain conformation with increasing temperature.

## CONCLUSION

The present work shows that electro-oxidation of bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II) complex can be achieved in DMF at room temperature under $N_2$ or air. Low-molecular-weight, mainly linear, poly(dichlorophenylene oxide)s were obtained irrespective of the applied potential and the nature of the atmosphere. Comparatively low dipole moment values support the other data to explain the chain structure of the polymer obtained from bis(pyridine)bis(4-bromo-2,6-dichlorophenoxo)copper(II) complex in DMF.

## ACKNOWLEDGEMENT

This work is supported partially by Middle East Technical University Research Fund, which is gratefully acknowledged.

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