Polymerization of bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine) copper (II) complex in DMF by electroinitiation

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Polymerization of bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine) copper (II) complex was achieved in dimethylformamide by electrooxidation. A cyclic voltammogram (CV) of the complex was obtained in dimethylformamide in advance. Constant potential yielded polymers in anode compartment only under nitrogen atmosphere and air. In the final polymer product, incorporation of neither the ligand nor the copper was observed and the post-polymerization proceeded in the absence of current. The structural analyses of the polymers were done by ^{13}C n.m.r., ^{1}H n.m.r., *FT*i.r. spectroscopy, differential scanning calorimetry (d.s.c.) and dipole moment measurements. The molecular weight of the polymer was determined by cryoscopic method. The poly(dihalophenylene oxides) obtained at different potentials were found to be similar in structure and both 1,2 and 1,4 catenations took place at roughly equal rates.

(Keywords: electroinitiated polymerizations; bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine) copper (II) complex; poly(dihalophenylene oxide))

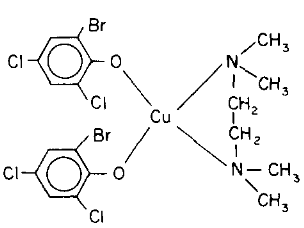
INTRODUCTION

In a series of papers, polymerization of trihalophenols under a variety of conditions has been reported[1–16]. Originally, decompositions of the silver salts of symmetrically substituted halogenated phenols[1] and later, those having the same halogen in the two *ortho* positions and a different one in the *para* positions were studied[2]. Novel synthesis was achieved from the decomposition of bis(trihalophenoxo) copper (II) complexes using various ligands thermally[4–9,13] and electrochemically[10–12,14,15].

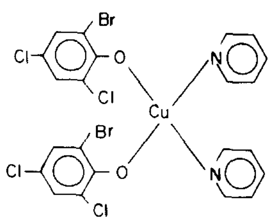
Many variations of bromine and chlorine atoms in 2,4 and 6 positions of the phenol were tried. Polymerization of 4-bromo, 2,6-dichlorophenoxide yielded a polymer with a high proportion of 1,4 catenation units indicating a high selectivity for displacement of bromine rather than chlorine[5,16]. Polymerization of 4-chloro, 2,6-dibromophenoxide yielded a polymer with a high proportion of 1,2 catenate unit in *N*,*N*,*N'*,*N'*-tetramethylethylenediamine[15] (A) and with pyridine ligand an equal amount of 1,2 addition and 1,4 addition units[10,14] by electroinitiation. The intent was to put bromine in the *ortho* position and having chlorine atoms in the *para* and other *ortho* positions to promote 1,2-coupling in thermal decomposition of bis(2-bromo-4,6-dichlorophenoxo)bis (pyridine) copper (II) complex (C)[7,8]. This was not the case, however, from elemental analysis, ^{1}H n.m.r., ^{13}C n.m.r. spectra[7,8,16] and radius of gyration[17] studies. It was reported that somewhere between one half and two thirds of the available bromine was displaced[16] and the branches were monomeric[7].

One of the major problems encountered was the achievement of sufficiently low molecular weight polymer samples for spectral analysis in structural determinations. Lower molecular weight polymers than previously available[7] are usually obtained in electroinitiation polymerization of trihalophenoxo copper (II) complexes[11,12,14,15].

In this study, electroinitiated polymerization of bis(2-bromo-2,6-dichlorophenoxo)bis(pyridine) copper (II) complex was carried out. There are no records in literature about the electroinitiated polymerization of this complex. The control of the polymerization potential also leads to a selective initiation generally, in comparison to other methods. The exact anodic and cathodic peak potentials of the complex were measured simultaneously by cyclic voltammetry (CV) in acetonitrile containing 0.1 M tetrabutylammonium fluoroborate (TBAFB) prior to electroinitiated polymerization.



(a)



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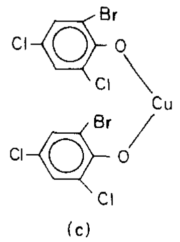

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EXPERIMENTAL

Materials

2,4-Dichlorophenol. Dihalogenated phenol was purchased from Aldrich Chemical Co. Ltd.

Copper sulphate ($CuSO_4 \cdot 5H_2O$). This was commercially available reagent grade material.

Pyridine. Reagent grade pyridine from Fluka A6 was used as a neutral ligand without further purification.

N,N′-*Dimethylformamide* (*DMF*). DMF was provided from Fisher Scientific Co. and Merck. It was stirred for 24 h with anhydrous $CuSO_4$, filtered and distilled at 5 mmHg (b.p. 39°C).

Tetrabutylammonium fluoroborate (*TBAFB*). The electrolyte was prepared by titrating 40% tetrabutylammonium hydroxide with concentrated fluoroboric acid until the solution was slightly acidic. It was filtered by suction and recrystallized twice by using 1:3 ethanol–water mixture. It was dried for 24 h under vacuum at 50°C.

Bromination of 4,6-dichlorophenol

Deionized aqueous solution (150 cm^3) of 0.10 M bromine containing 0.15 M KBr was added dropwise to the required amount of 4,6-dichlorophenol dissolved in a minimum amount of ethanol with constant stirring for a given period of time. The precipitated product was cooled on ice for a short time, then filtered, washed and dried in a vacuum oven.

Preparation of the complex

The standard procedure was used as described in literature[18]. In the synthesis of copper complex, pyridine was used as a neutral ligand and 2-bromo-4,6-dichlorophenol (2Br–DCP) as trihalogenated phenol. A solution of 0.02 mol $CuSO_4 \cdot 5H_2O$ and 0.04 mol pyridine dissolved in 50 cm^3 distilled water was added slowly to the solution of 0.04 mol 2Br–DCP and 0.04 mol NaOH in 50 cm^3 distilled water with vigorous stirring. The resulting dark brown precipitate was filtered, washed with distilled water thoroughly and dried in a vacuum. The complex was characterized by elemental analysis using a Hewlett-Packard F and M 185 carbon–hydrogen–nitrogen analyser with a flow rate of 100 $cm^3 min^{-1}$, an oxidation furnace of 1050°C, a reduction furnace of 500°C and column oven temperature of 80°C. The complex was found to contain: C: 35.2%; H: 1.8%; N: 4.2%. The expected values based on calculations were: C: 37.6%; H: 2.0%; N: 4.0%.

Cyclic voltammetry

The system consists of function generator (Tacussel Pilote Servovit; Tacussel, PRT 30-0.1) potentiostat and recorder (Sefram X–Y). The cell used was a three-electrode system, i.e. the working electrode, (1 cm long platinum bead), the counter electrode (3 cm platinum spiral) and the reference electrode (a Luggin capillary containing Ag/Ag^+ (0.01 M)). The measurements were carried out in DMF at room temperature.

Procedure for polymer synthesis

Electrochemical polymerization was carried out in a special electrolysis cell holding about 55 cm^3 of solution accommodated with working and counter electrodes. The cell consisted of anode and cathode compartments divided by 2 cm diameter sintered glass as described previously[12,15]. Graphite rod (5 mm diameter) and 1 cm^2 stainless steel were employed as working and counter electrodes, respectively where the side of the cell connected to the Luggin capillary of reference electrode with an opening. The cell was designed also to be capable of passing nitrogen through or above the solution by inlets. The DMF, equal amounts of TBAFB electrolyte and the complex (10^{-2} M) were placed in both cell compartments. Electrolysis was carried out by adjusting the working electrodes (+0.4, +0.7 and +1.15 V) under nitrogen atmosphere and in air, always at room temperature. At the end of electrolysis the contents of both cell compartments were poured into ethanol containing a few drops of HCl to precipitate the polymers. The precipitated polymers were filtered and dried under vacuum. The percent yield of the polymer was calculated with respect to initial complex concentration as listed in *Table 1*.

Table 1 Electroinitiated polymerization of bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine) copper (II) after 3 h electrolysis

E_{001}	% Yield[a]	
	N_2	Air
+0.400	32	24
+0.700	38	31
+1.150	23	28
−1.314	–	13
−1.670	–	
+0.705	–	21[b]
+0.400[c]	58.4[c]	–

[a] Calculations based on initial complex concentrations for the polymers recovered from analyte only

[b] Polymer recovered at the end of 18 h electrolysis

[c] Polymer yielded after 30 min application of voltage and then left for post-polymerization overnight

POLYMER CHARACTERIZATION

Spectral analysis

^1H n.m.r. spectral analysis was carried out with a Bruker n.m.r. spectrophotometer type AC 80 using CS_2 as the solvent and TMS as an external reference.

^{13}C n.m.r. coupled and decoupled spectra were obtained using a Bruker AC 200 n.m.r. spectrophotometer. The polymer was dissolved in $CDCl_3$ which provided a deuterium signal for field and frequency stabilization.

The i.r. spectrum of the polymer dispersed in KBr disc was measured using a Perkin-Elmer 1710 model *FT*i.r. spectrophotometer coupled with a PE 7500 data station.

Glass transition temperature (T_g)

A Mettler differential scanning calorimeter, d.s.c. TA-3000 system apparatus was used for T_g measurements of the polymer, in the range 20–500°C. The scanning speed was 10 K min^{-1} and the weight of the polymer was around 3–4 mg.

Molecular weight (M_n) *measurements*

Measurements were made using camphor as a solvent. This solvent has a melting point of 175°C and K_f about

-39.7 obtained using a cryoscopic method. The number average molecular weight of polymer was 2.5×10^3.

Dipole moment measurements

A General Radio Company Type 1620-A capacitance measuring assembly was used to measure capacitances at the 10 kHz frequency. The solutions were confined in a Balsbaugh Laboratories model 350-G three-terminal cell of two coaxial cylinders which requires about 50 ml of solution. Three-terminal cell was mounted into a plastic vessel and immersed in a thermostat. Solvent evaporation was completely eliminated and the temperature of the cell was controlled to ±0.1°C. Solutions were prepared by weighting both components and the thermal expansion of all solutions was assumed to be the same as that of the pure solvent.

Refractive index increments were obtained with standard Brice-Phoenix equipment.

RESULTS AND DISCUSSION

The cyclic voltammogram (CV) of the bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine) copper (II) was obtained in dimethylformamide prior to electrolysis in order to determine anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) peak potentials. As seen from the CV in *Figure 1*, the complex has three oxidation and five reduction peak potentials at +0.4, +0.7, +1.15, −0.5, −0.85, −1.35, −1.7 and −2.1 V, respectively. The chosen solvent–electrolyte couple, DMF–TBAFB, was inert between −2.5 and +1.5 V at room temperature.

The complex does not polymerize in DMF in the absence of current. The polymerization of the complex was carried out at each $E_{p,a}$ of the complex because no polymer was obtained at cathode compartment under nitrogen or air (*Table 1*).

When constant potential electrolyses were carried out at −1.7 and −1.3 V, polymer was obtained only in the anode compartment, indicating that electroinitiated polymerization of the complex proceeds only upon oxidation on the anode via a free radical mechanism[15]. Post-polymerization studies revealed that once the critical radical concentration is reached, the reaction follows the same sequence (*Table 1*).

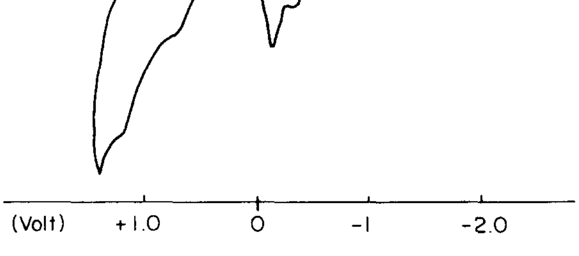

Figure 1 Cyclic voltammogram of the complex recorded in dimethylformamide–tetrabutylammonium fluoroborate *versus* Ag°/Ag$^+$ reference electrode

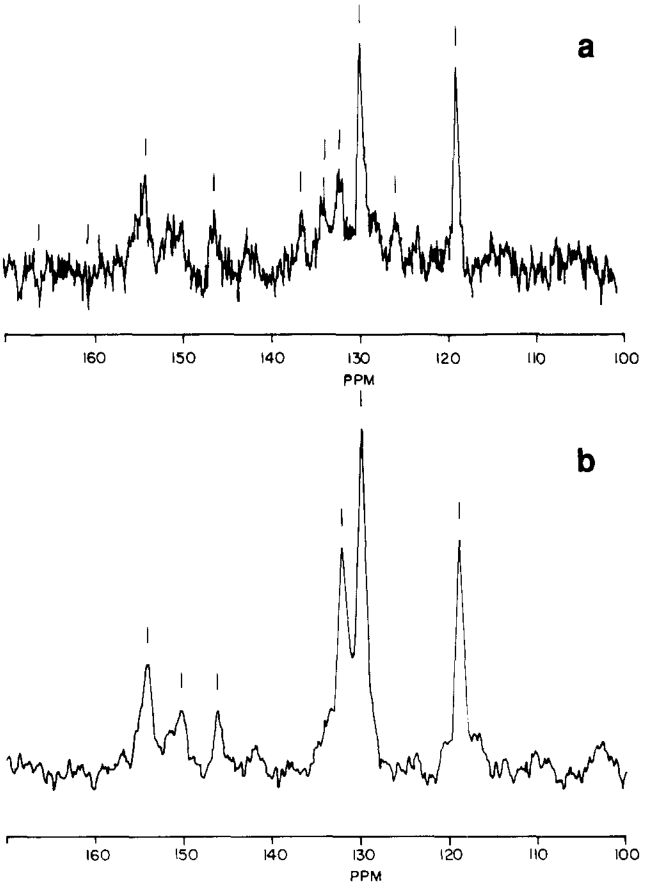

Figure 2 ^{13}C n.m.r. spectra of the polymer (a) proton-coupled and (b) decoupled

The structure of the polymer was analysed by various spectroscopic methods. The polymer gave reasonable spectra with a small number of scans in both the proton coupled and decoupled modes.

Figure 2 shows ^{13}C n.m.r. proton-coupled and decoupled spectra of the polymer dissolved in $CDCl_3$. The theoretical ^{13}C chemical shift data for the possible six catenation products of the monomer were calculated by using the correlation tables[19–21].

Figure 3 displays the observed and the calculated ^{13}C n.m.r. data. By inspection of *Figures 2* and *3*, one can conclude that the 1,2-catenation process (structures B, C and F) implied by the presence of 119.06 Hz and 146.38 Hz lines, should have formed together with 1,4- and mixed type catenation processes.

The ^{1}H n.m.r. spectrum (*Figure 4*) of the polymer recorded in CS_2, was characterized by three broad peaks located at 6.33, 6.93 and 7.41 respectively. In the structures of polymers of 2-bromo-4,6-dichlorophenol, indicated by units A, B and C (*Figure 3*), there should exist three different chemically and magnetically inequivalent protons. These are the protons flanked by Cl, Br, O, Br, Cl–Cl and Cl, O pairs. The presence of three broad peaks and the integration ratios clearly indicate that the catenation process was not solely 1,4-, but overwhelmingly 1,2- type.

Figure 5 displays the *FT*i.r. spectrum of the polymer studied. The bonds which absorb at 1380, 1400, 1440, 1470, 1550 and 1600 cm^{-1} are the C=C ring stretchings.

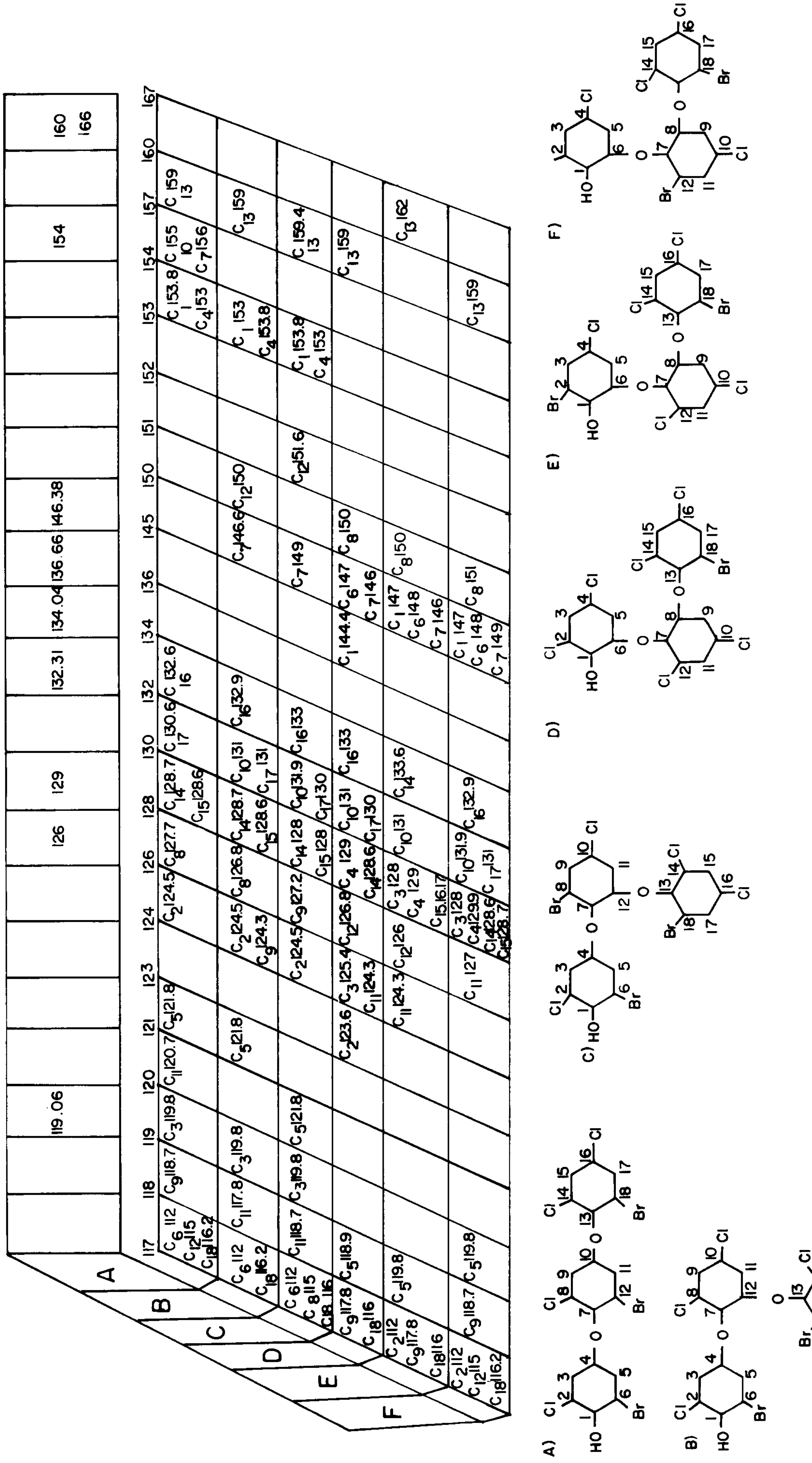

Figure 3 Schematic representation of the observed and the calculated ^{13}C n.m.r. spectra

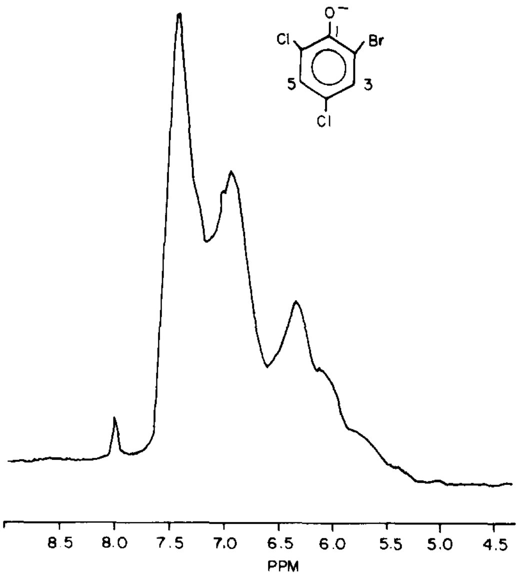

Figure 4 ^{1}H n.m.r. spectrum of the polymer

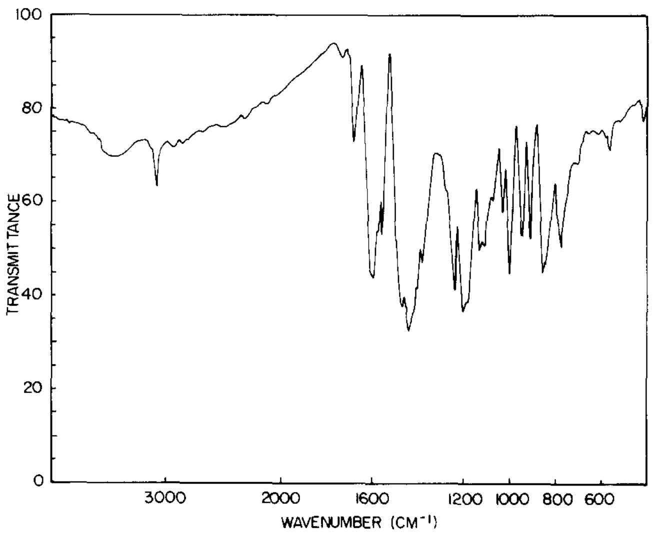

Figure 5 *FT*i.r. spectrum of the polymer at +0.70 V *versus* Ag/Ag$^+$ reference electrode

Table 2 Temperature dependence of dielectric constants of 2Br-DCP and the polymer with its dipole moments (D = Debye)

T (°C)	ε Phenol	ε Polymer	$(\langle\mu^2\rangle/x)D^2$ Polymer
30	0.102	0.184	13.360
40	0.232	0.200	20.08
50	0.351	0.259	32.996
70	0.504	0.311	56.97

The spectrum displays C–O absorptions 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. Computer library output suggests a poly(oxy) structure.

Copper (II) 2-bromo-4,6-dichlorophenoxide complex undergoes polymerization under the influence of opposing kinetic and thermodynamic factors[8]. The former should dictate 1,2- and 1,4-catenation, whereas the latter is exclusively in favour of the 1,2-addition process. The thermally obtained polymer was found to be a mixture of linear and branched 2-bromo-4,6-dichlorophenylene oxide units, whereas the electrochemically obtained polymer, as proved spectroscopically above, suggests a 1,2-catenation product.

The mean squared dipole moments per repeat unit of the polymer chain were calculated using the Guggenheim–Smith equations[22].

$$\frac{\langle\mu^2\rangle}{x}=\frac{27kTM_0}{4\pi N_A}\left(\frac{d\varepsilon/dc}{(\varepsilon_1+2)^2}-\frac{2n_1(dn/dc)}{(n_1^2+2)^2}\right)$$

where M_0 is the molecular weight of the repeat unit; N_A is Avogadro's number; k is the Boltzmann constant; T is the absolute temperature; ε is the static dielectric constant; n is the refractive index and c is the concentration in g polymer/100 g solvent.

The subscript 1 refers to values for pure solvent (toluene). Refractive index increment, dn/dc values were determined at 30°C and 436 nm wavelength with a Brice-Phoenix differential refractometer model BP-2000. This value was taken as 0.118 ml g^{-1}, constant for all the temperatures[17].

Dipole moment is a quantity directly related to the conformation of the polymer chains. In the literature there are only values for polyphenylenesiloxanes[23]. For these reasons the dielectric constants of 2-bromo-4,6-dichlorophenol, poly(dihalophenylene oxide) and the dipole moments of poly(dihalophenylene oxide) were determined at several temperatures. The results are given in *Table 2*. As seen from the table, the dielectric constants of the phenol and the polymer and as a result the μ^2/x values for the polymer increase with increasing temperature.

The glass transition temperatures were found to be 172, 185 and 199°C, indicating the high rigidity and some branching in the polymer.

CONCLUSIONS

The bis(2-bromo-4,6-dichlorophenoxo)bis(pyridine) copper (II) complex can be polymerized by electrooxidation. The polymer obtained by electrolysis is a mixture of 1,2- and 1,4-addition products, but mostly in favour of 1,2-catenation units. This method yields the lowest molecular weight and highly rigid polymers.

ACKNOWLEDGEMENTS

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