Polymerization of bis(trichlorophenoxo) ethylenediamine copper (II) complex by electro-oxidation

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Electroinitiated polymerization of bis(trichlorophenoxo) ethylenediamine copper (II) complex was carried out in dimethyl-formamide at various anodic peak potentials of the complex. The oxidation and reduction peak potentials were determined by cyclic voltammetry. These potentials were measured in tetrabutylammonium fluoroborate-dimethylformamide supporting electrolyte–solvent couple at room temperature. Polymerization reactions were carried out under air and nitrogen atmospheres using a constant potential approach at room temperature. The kinetics of the polymerization were followed by cyclic voltammetry. The polymers obtained were characterized by ^{1}H n.m.r., ^{13}C n.m.r. and FTi.r. spectroscopy and differential scanning calorimetry. Vapour pressure (isopiestic) was used for the molecular weight determinations. The polymers obtained at different potentials were found to be similar in structure.

(Keywords: electroinitiated polymerization; bis(trichlorophenoxo) ethylenediamine copper (II) complex; polymerization kinetics)

INTRODUCTION

Poly(dihalophenylene oxides) have been prepared from trihalogenated phenols for many years. Their original syntheses were made by Hunter *et al.* in 1916[1]. Between 1916 and 1933, Hunter and colleagues did extensive work on the thermal decomposition of silver phenolates in solution[1–3]. They studied the decomposition of the silver salts of trihalophenols into silver halide and an amorphous polymer residue, later named as poly(phenylene oxide), by refluxing the salt in an organic solvent.

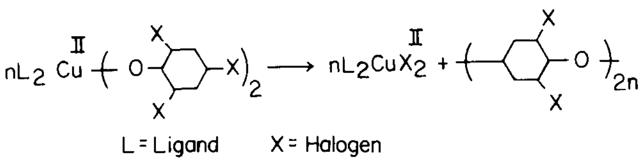
The suggested chemical reaction is:

$$nC_6H_2X_3OAg \rightarrow nAgX + (C_6H_2X_2O)n$$

where X represents the halogens. It was also suggested that the *para* position was preferred over the *ortho* position and that the halogens selectively displaced the phenols in the order F > Br > Cl. The reported molecular weight of the polymers was around 2.0×10^3. Staffin *et al.*[4] have extended the earlier work by using 4-bromodimethyl phenolates. Hay and his group[5] used Cu(I) instead of silver for the polymerization of the phenols for the first time.

Later, a synthesis of poly(phenylene oxides) by thermal decomposition of bis(halophenoxo) bis(pyridine) copper(II) was described by Blanchard *et al.*[6] under a wide variety of reaction conditions. In addition, very low intrinsic viscosities led the authors to conclude that the polymers were all significantly branched. Harrod *et al.*[7–11] and Kısakürek *et al.*[10–14] made progress in understanding the mechanism of the reaction.

The general chemical reaction for the preparation of these polymers from the thermal decomposition of the halophenoxo–copper(II) complex in solution was suggested to be



The ease of decomposition was found to vary to a considerable degree depending on the nature of the neutral ligand which strongly influences the thermal stability of the starting complex. Hence, the phenoxo complexes with ethylenediamine were found to be exceptionally resistant to thermal decomposition compared to non-chelating ligands[15].

Recently, thermal decomposition of bis(trichlorophenoxo) ethylenediamine copper (II) in toluene, at 70°C was carried out[10]. It was reported that mostly 1,2-addition polymerization was favoured and the yield was up to approximately 60% after 48 h. Also, there was an induction period of 56 min.

Electrochemistry as a method of initiation of polymerization has been widely used for many years. The control of the polymerization potential generally leads to a selective initiation in comparison to other methods.

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However, the exact peak potentials of the monomers must be measured. Cyclic voltammetry is a way of rapidly determining the anodic and cathodic peak potentials simultaneously.

In this study, electroinitiated polymerization of bis(trichlorophenoxo) ethylenediamine copper (II) was achieved for the first time under constant potential conditions. Several peak potentials were measured by cyclic voltammetry in acetonitrile containing 0.1 M tetrabutylammonium fluoroborate (TBAFB) which is a sufficiently electroinert solvent–electrolyte couple at room temperature. Because the complex polymerizes immediately in acetonitrile, this solvent could not be used although it has a larger range. Instead dimethylformamide was preferred as a solvent.

EXPERIMENTAL

Materials

2,4,6-Trichlorophenol was purchased from Aldrich Chemical Co. Ltd (analytical grade). Ethylenediamine (Fluka AG; reagent grade) was used as a ligand. Commercially available reagent grade copper sulphate was used. Dimethylformamide (DMF) and ethanol were purified by standard techniques when required as solvents.

Preparation of the copper complex. Bis(trichlorophenoxo) ethylenediamine copper (II) was prepared by mixing the following two solutions and stirring vigorously. Solution I contained 0.04 mol NaOH and 0.04 mol trichlorophenol in 100 ml distilled water. It was slowly added to solution II which contained 0.02 mol $CuSO_4 \cdot 5H_2O$ and 0.02 mol ethylenediamine in 100 ml distilled water. The dark brown complex was filtered and dried in vacuum oven. The complex was characterized by elemental and spectral analysis carried out using a Hewlett-Packard F and M 185 Carbon–Hydrogen–Nitrogen analyser with a flow rate of 100 cc/min, oxidation furnace of 1050°C, reduction furnace of 500°C and column oven temperature of 80°C. The complex was found to contain: C, 31.91%; H, 2.27%; N, 5.16%. The expected values based on calculations were: C, 32.52%; H, 2.32%; N, 5.42%.

Spectral analyses were done by FTi.r. (in KBr). In addition to the peaks present in the i.r. spectrum of the polymer, the bands due to N–H ($3335\,cm^{-1}$) and N–C ($1065\,cm^{-1}$) absorptions were noted in the complex.

Cyclic voltammetry

The cyclic voltammetry system contained three electrodes: working, counter and reference[16]. The working and counter electrodes consisted of a platinum bead and wire, respectively. The reference electrode was a luggin capillary containing Ag/Ag^+ (0.01 M). Cyclic voltammetry measurements were made in dimethylformamide at room temperature.

POLYMER SYNTHESIS

Poly(dichlorophenylene oxides) were synthesized by electroinitiation in DMF for 3 h under different atmospheres at room temperature. The H-type polymerization cell contained graphite as the anode rod (5 mm diameter), and a stainless steel ($2.54\,cm^2$) as the counter electrode. The reference arm of the cell contained $Ag^+/AgBF_4$ (0.01 M). The electrolyses were achieved mainly at the two anodic peak potentials: +0.3 V and +0.7 V of the complex (0.022 M), each under air and nitrogen atmospheres. However, when cathodic peak potentials were applied, polymers were obtained only at the anode compartment. At the end of the electrolyses both cell compartments were poured into ethanol containing a few drops of HCl.

The kinetics of the polymerization were studied by cyclic voltammetry (c.v.), using two potentiostats at the same time. An electrolysis system (Potentiostat-G. Bank. Elektronik) and a c.v. system (Potentiostat Tacussel PRT 30–0.1 Function Generator, Tacussel Pilote type Servovit) were employed. Each cell contained six electrodes (*Figure 1*).

The working and the counter electrodes were graphite and steel for electrolysis and platinum bead and platinum wire for c.v. Ag^0/Ag^+ reference electrodes were used for both systems. At regular intervals during electrolysis cyclic voltammograms were taken at a 200 mV/s scan rate without stopping the electrolysis. The peak at +0.3 V *versus* Ag^0/Ag^+ reference electrode was followed. The reacted monomer concentration was calculated from the peak heights. Kinetic experiments were carried out with 10^{-2} M and 5×10^{-3} M complex concentrations because higher concentrations were not found suitable for c.v. purposes.

Post polymerization studies with 10^{-2} M complex concentration were also carried out. At a given time, the electrolysis was stopped and the unreacted monomer concentrations were determined by cyclic voltammetry via anodic peak potential at +0.3 V.

POLYMER CHARACTERIZATIONS

Molecular weight measurements

The number-average molecular weights of the polymers were determined by the vapour pressure

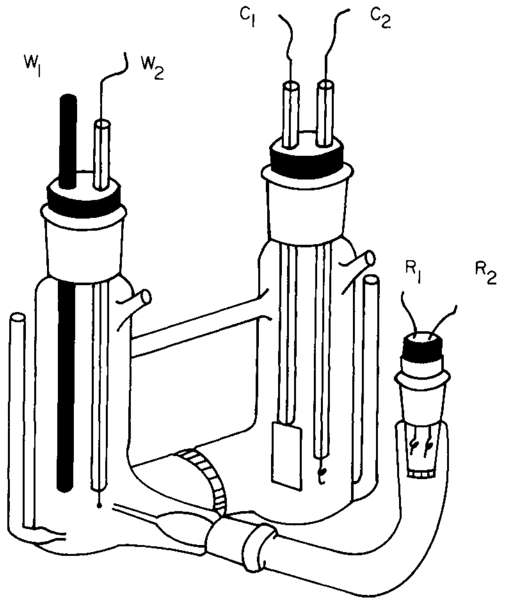

Figure 1 The CV-electrolysis cell utilizing six electrodes: subscript 1 indicates electrodes for electrolysis; subscript 2 indicates electrodes for cyclic voltammetry. Working (W), counter (C) and reference (R) electrodes

(isopiestic) method. Measurements were made in chloroform with benzil as a standard by using Perkin Elmer Model Coleman 115 molecular weight apparatus. The main oven and sub oven temperatures were 43°C and 36°C, respectively.

Spectral analysis

^{1}H n.m.r. spectra were carried out with a Bruker n.m.r. Spectrophotometer type AC 80 using CS_2 as the solvent and TMS as an internal reference.

^{13}C n.m.r. spectra were obtained by Bruker AC 200 n.m.r. spectrophotometer. The polymers were dissolved in deuterated chloroform-carbondisulphide ($CDCl_3$–CS_2) mixture. The solvent used provided a deuterium signal for field and frequency stabilization.

FTi.r. spectra were measured with the polymers dispersed in KBr discs. A Perkin Elmer 1710 Model FTi.r. combined with a PE 7500 Data Station was used.

Differential scanning calorimeter

A Perkin Elmer DSC system 4 apparatus was used for d.s.c. measurement. High pressure cups sealed with o-rings were used to eliminate leakage of poly(dichlorophenylene oxides). The scanning speed was 20°C/min and the weights of the samples were around 10–20 mg.

RESULTS AND DISCUSSION

Bis(trichlorophenoxo) ethylenediamine copper (II) was polymerized electrochemically via direct electron transfer at different potentials in DMF–TBAFB solvent–electrolyte couple. The potentials applied to polymerize the complex were determined by cyclic voltammetry. The cyclic voltammogram of the complex was determined in DMF–TBAFB solvent–electrolyte system at room temperature. The voltammogram of the complex is given in *Figure 2*. As seen in *Figure 2*, the complex has two oxidation and three reduction peak potentials at +0.3, +0.7, −0.7, −0.9, −1.1 volts. The chosen solvent–electrolyte couple was inert in between −2.5 and +1.5 V at room temperature. Scanning in either direction did not change the number and the shapes of oxidation and the reduction peaks.

The complex was electrolysed at these potentials by constant potential electrolysis. Polymers were only obtained from the anode compartment. Therefore, it can be concluded that polymerization was initiated by direct electron transfer from the complex to the anode. The polymers were obtained at the anode compartment of the electrolysis cell even when the electrolyses were carried out at −0.7 and −0.9 V. The structures of the polymers obtained by electrolysis at oxidation or at reduction peak potentials under N_2 or at air atmospheres were the same. The polymers have rather high T_g values (185°C) with a molecular weight of ≈6800.

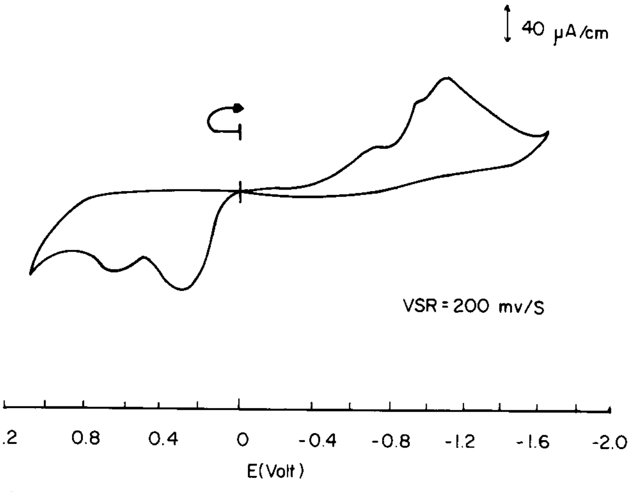

Figure 2 Cyclic voltammogram of bis(trichlorophenoxo)ethylenediamine copper (II)

Table 1 Electroinitiated polymerization of bis(trichlorophenoxo) ethylenediamine copper (II)[a]

E_{pol}[b]	(% Yield anode)[c]
+0.3	69.0
+0.7	80.0
−0.7	57.0
−0.9	78.0

[a] Open to air during 3 h of electrolysis
[b] Polymerization potential as measured by cyclic voltammetry vs. Ag^0/Ag^+ reference electrode
[c] Calculated from precipitating polymer

When the total molecular weight of the complex is taken, the results can be misleadingly low because the ligand and the copper does not incorporate in the polymer. Only the phenol moieties are considered in the calculation of initial amount of the monomer. As it can be seen from *Table 1*, the per cent yield of the polymers increases with increasing potentials of the electrolysis. In this case the applied potential is found to be effective in terms of the polymer yield only. Structurally the polymers are all alike.

The peak at +0.3 V decreases with time regularly up to about 20% conversion. Thereafter the decrease is enhanced until about 85% conversion. At 90% conversion the monomer consumption reached a plateau and remained constant (*Figure 3*). The rate is also affected by the initial monomer concentration. The rate is found to be faster at a higher monomer concentration. Previously it was reported that there was a 56 min induction period in the thermal polymerization of this monomer. Post polymerization studies reveal that once

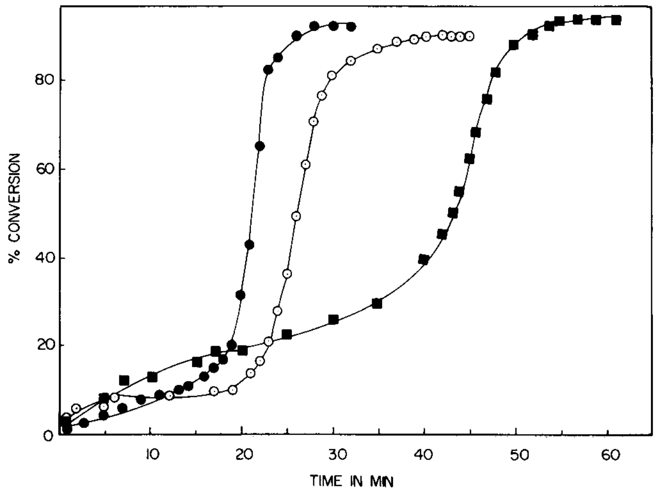

Figure 3 Kinetic curve followed by taking successive voltammograms during electrolysis: ●, polymerization with 10^{-2} M complex concentration; ○, polymerization with 10^{-2} M complex concentration with current stopped at 20 min; ■, polymerization with 5×10^{-3} M complex concentration

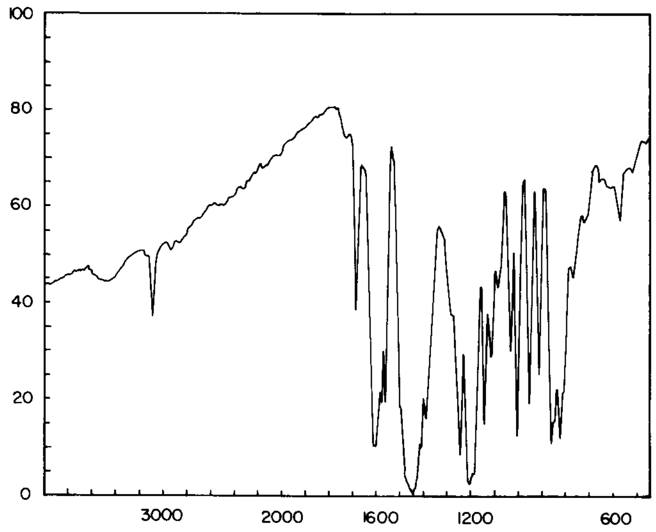

Figure 4 FTi.r. spectrum of poly(dichlorophenylene oxide)

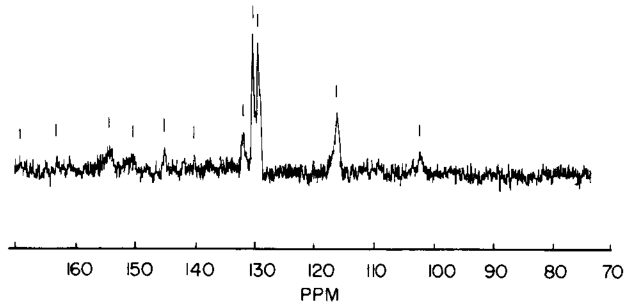

Figure 5 ^{13}C n.m.r. spectrum of the polymer

the critical radical concentration is reached, the reaction follows the same sequence, though more slowly, as the polymerization at applied potential of +0.3 V.

The FTi.r. spectrum of the product, shown in *Figure 4* is characterized by 1380, 1440, 1560, 1580 and 1600 cm^{-1} C=C ring stretchings, 1140, 1200, 1240 cm^{-1} symmetric C–O–C stretchings and 810, 850 cm^{-1} out of plane C–H bendings. Computer library output is in

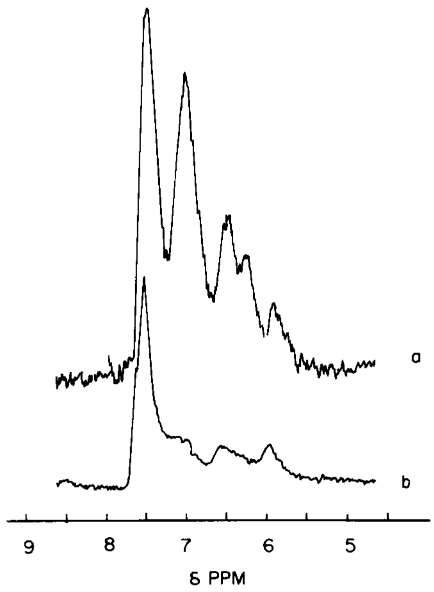

Figure 7 ^{1}H n.m.r. spectra of the polymer synthesized (a) electrochemically and (b) thermally[13]

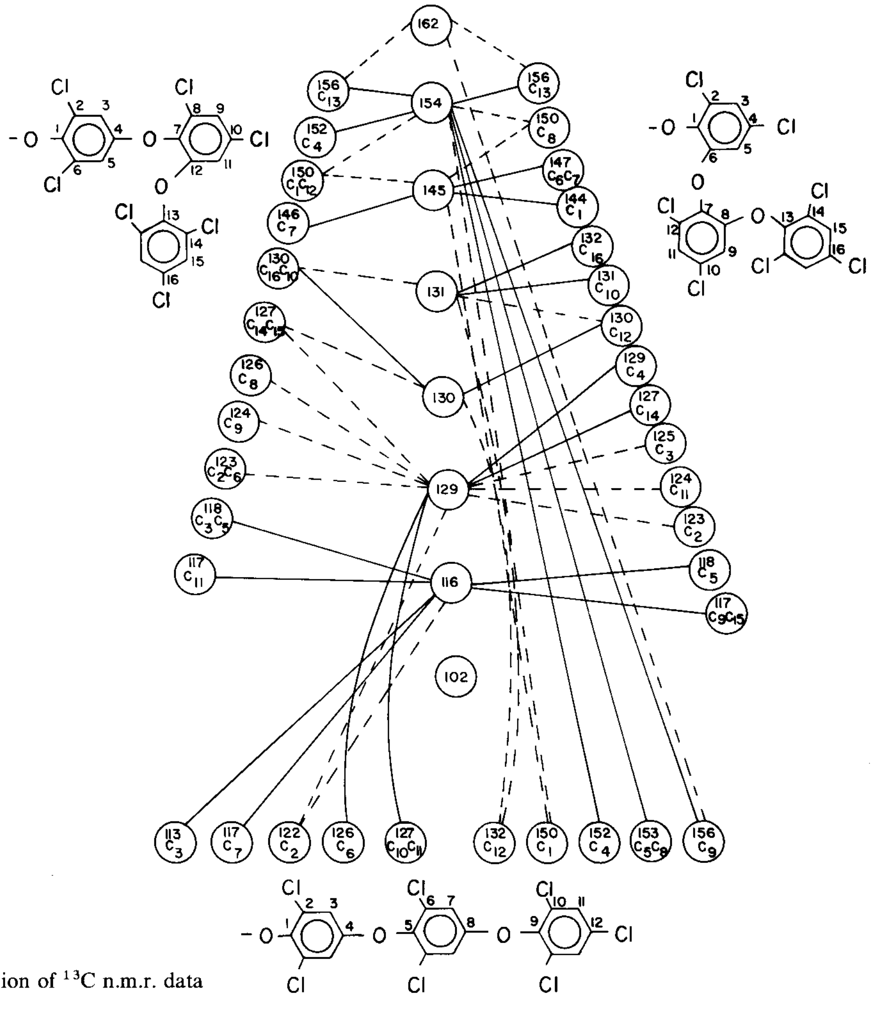

Figure 6 Schematic representation of ^{13}C n.m.r. data

favour of polymeric dichlorophenylene oxide. On the other hand there is no polymerization, if no current is applied initially.

In *Figure 5* the ^{13}C n.m.r. spectrum is shown. Theoretical ^{13}C n.m.r. chemical shift data for the three probable modes of ternary catenation products of TCP were calculated by using the appropriate correlation tables given in the literature[17,18]. The observed and calculated resonating frequencies are shown in *Figure 6*. Although the observed ^{13}C spectrum is rather simple, the data may be correlated equally well to the calculated spectra of the three possible modes of ternary catenation products. In that sense, the ^{1}H n.m.r. spectrum is more informative. As it is seen in *Figure 7a* there are many proton resonance frequencies lying between 5.5 and 8.0 ppm. These have two strong peaks at 6.8 and 7.3 ppm, which implies the existence of a mixture of catenation products of TCP.

Hence, the ^{1}H n.m.r. spectrum reveals that 1,2- and 1,4-addition are taking place at about equal rates. The peak at 6.8 ppm may be assigned to the protons of 2,6-dichloro-1,4-phenylene oxide units whereas the peak at 7.3 ppm may be assigned to the 5-proton of 4,6-dichloro-1,2-phenylene oxide units. A second doublet due to the 3-proton may be obscured. The higher field broad lines can be assigned to branch units of 1,2- and 1,4-additions or 1,2-, 1,4- and 1,6-catenations taking place on the same phenol molecule.

In this study it was shown that induction period can be eliminated via electrochemical methods although 1,2- and 1,4-addition take place simultaneously.

Previously, the polymers obtained were 1,2- and 1,4-catenation products in the thermal polymerization of trichlorophenols (with several ligands like pyridine, tetramethylethylene diamine, or without any ligand). In the case of ethylenediamine ligand, the polymer yielded a rather linear structure favouring 1,2-addition (*Figure 7b*)[13]. It was previously reported that bis(trichlorophenoxo) tetramethylethylenediamine was electrochemically polymerized into a linear polymer[14]. However, in this study the electrochemical initiation yielded 1,2- and 1,4-reaction products. Ligand effect, if any, will be the subject of a future study.

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