Electroinitiated polymerization of bis(4-bromo-2,6-dichlorophenoxo)*N,N,N′,N′*-tetramethylethylenediamine copper(II) complex

M. Saçak and U. Akbulut*
Chemistry Department, Faculty of Sciences, Ankara University, 06100 Ankara, Turkey

and D. Kısakürek
Chemistry Department, Middle East Technical University, 06531 Ankara, Turkey

and L. Toppare
Department of Science, Middle East Technical University, 06531 Ankara, Turkey
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Electroinitiated polymerization of bis(4-bromo-2,6-dichlorophenoxo)*N,N,N′,N′*-tetramethylethylenediamine copper(II) complex was achieved upon oxidation. Prior to polymerization a cyclic voltammogram (CV) of the complex was obtained. Polymerization potentials were selected as the oxidation and reduction peak potentials of the complex, obtained by CV. Polymers in the form of poly(dihalophenylene oxide), were obtained by constant potential electrolyses carried out at redox peak potentials of the complex. No ligand or copper was found to incorporate into the final polymer product. The mechanism of polymerization was found to be free radicalic. It was also found that post-polymerization proceeds in the absence of current, when current is ceased after approximately 10 minutes of electrolysis. Percent conversions of polymerization had been measured by an electrochemical technique via simultaneous measurement of reacted monomer concentration. In order to follow the reacted monomer concentration by simultaneous CV measurement, a special H-type electrolysis cell with six electrodes was constructed. Polymers were characterized by ^{1}H-n.m.r., ^{13}C-n.m.r. and *FT*i.r. spectroscopy along with molecular weight measurements by the isopiestic method.

(Keywords: electroinitiation; electropolymerization; bis(4-bromo-2,6-dichlorophenoxo)*N,N,N′,N′*-tetramethylethylenediamine copper(II); poly(dihalophenylene oxide))

INTRODUCTION

Electroinitiated polymerization can be carried out via constant current or constant potential electrolysis. The polymerization mechanism depends on the type of electrolysis process. In constant potential electrolysis analysis of the mechanism is simplified, especially in case of direct electron transfer. Electroinitiation by direct electron transfer simply means that electron transfer occurs directly from monomer to anode or from cathode to monomer.

Various olefins have been polymerized cationically by direct electron transfer upon anodic oxidation[1–5]. Ring opening polymerizations via a cationic mechanism by electro-oxiation have also been reported[6–8]. Electrochemical oxidation can initiate free radical polymerization via the Kolbe reaction[9].

Prior to electroinitiated polymerization, the electrochemical behaviour of the monomer must be studied. Cyclic voltammetry (CV) gives information about the potentials at which the monomer is oxidized or reduced. Anodic peak potential ($E_{p,a}$) is the potential at which one or more electrons are transferred from the monomer to the anode. $E_{p,a}$ is related to the highest occupied molecular orbital (HOMO) energy level of the monomer[10]. The solvent and the electrolyte must be selected so that they do not oxidize at potentials near the $E_{p,a}$ of the monomer. Otherwise, the electrolysis products of solvent, electrolyte and monomer can all be responsible for the initiation of polymerization. The mechanism of polymerization in such cases can be very difficult to elucidate. Once $E_{p,a}$ of the monomer is measured, constant potential electrolysis (CPE) can be employed for electroinitiated polymerization. CPE allows the generation of radicals, cations or radical-cations from the monomer only. In such systems electroinitiated polymerization can be accomplished by direct electron transfer. If the polymerization system is suitable for post polymerization, addition of inhibitors after ceasing the current can enlighten the mechanism.

There are various reports of electroinitiated polymerization of some phenols[11,12]. However, there are no records in the literature of electroinitiated polymerization of halophenol copper complexes. Thermal polymerization of various halophenol copper complexes have been reported[13–15]. Thermal decomposition of bis(halophenoxo)bis(pyridine) copper(II) was reported to yield

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* To whom correspondence should be addressed

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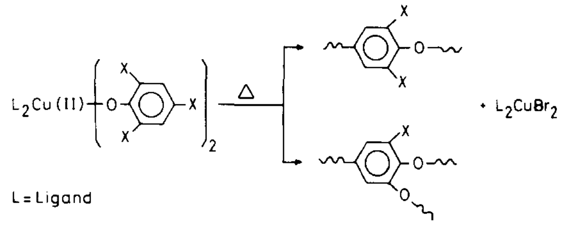
poly(phenylene oxides)[13]. Thermal polymerization of bis(trichlorophenoxo)ethylenediamine copper(II) in toluene was reported to yield highly branched polymers[14]. An induction period of 56 minutes for thermal polymerization was observed. It was also reported that at the end of 48 h of polymerization, the yield was approximately 60%. Molecular weights of thermally obtained polymers were reported to be very high (*c.* 2×10^5) (ref. 16).

The following mechanism has been proposed for thermal polymerization of trihalophenol copper(II) complexes[16]. Polymers produced by 1,4 addition have a linear structure. Branched polymers are the products of 1,2 additions along with 1,4 catenation.



Copper(II) complexes of 4-bromo-2,6-dichlorophenols have been polymerized thermally[15–17]. Electroinitiated polymerization of bis(4-bromo-2,6-dichlorophenoxo)-*N*,*N*,*N*′,*N*′-tetramethylethylenediamine copper(II) complex (4-BDCP) has not yet been reported. In the present study 4-BDCP was selected for electroinitiated polymerization, in order to investigate the possibility of obtaining linear polymers. Since bromine in the *para* position is a better leaving group than chlorine in the *ortho* position, 1,4 addition is expected to be the major product. Moreover, lower molecular weight polymers are usually obtained in electroinitiated polymerization. Therefore, linear polymers of 4-BDCP with low molecular weights, should permit a better spectral analysis of the structure of the polymer.

EXPERIMENTAL

Materials

Acetonitrile was dried over CaH_2 for 24 h then fresh CaH_2 was added. The acetonitrile was fractionally distilled under nitrogen, and stored over molecular sieves (4A) until use. Tetrabutylammonium fluoroborate was synthesized as described previously[1]. Silver fluoroborate (Aldrich Chemical Co.) and tetramethylethylenediamine (Sigma Chemical Co.) were used without further purification.

4-bromo-2,6-dichlorophenol was synthesized by dropwise addition of a 150 ml solution of KBr (21.3 g) and Br_2 (16.0 g) into an ethanol solution containing 2.6 g of 2,6-dichlorophenol. The mixture was stirred for 2 h and then cooled to 0°C. The precipitated product was filtered, dried and recrystallized from n-hexane.

4-BDCP was synthesized from 4-bromo-2,6-dichlorophenol. $CuSO_4 \cdot 5\ H_2O$ (0.02 mole) and 0.02 mole of tetramethylethylenediamine were dissolved in 50 ml water (solution A). 4-bromo-2,6-dichlorophenol (0.04 mole) and 0.04 mole of NaOH were dissolved in water (solution B). Solution B was added to solution A while being stirred. The product (4-BDCP) was filtered, washed several times with water and dried.

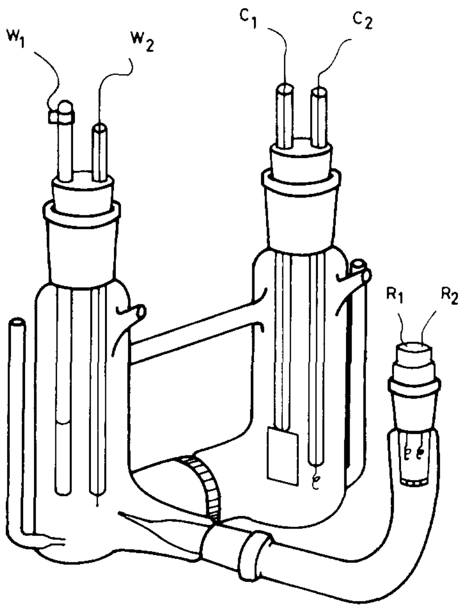


Figure 1 Electrolysis cell. W_1 (graphite), C_1 (stainless steel) and R_1 (Ag^0/Ag^+) are working, counter and reference electrodes, respectively, for polymerization. W_2 (Pt wire), C_2 (Pt wire) and R_2 (Ag^0/Ag^+) are working, counter and reference electrodes, respectively, for cyclic voltammetry

Procedures

Cyclic voltammetry measurements were carried out in acetonitrile as described previously[3]. Polymerizations were carried out in a specially designed cell shown in *Figure 1*. Three electrodes W_1, C_1 and R_1 were employed for electrolysis. For simultaneous cyclic voltammetry measurements another set of three electrodes (W_2, C_2, R_2) were used. For the solvent 55 ml acetonitrile was used. Electrolyte (10^{-1} M) and 4-BDCP were added into the cell. The cell content was then equally divided into both compartments. Cyclic voltammograms were obtained before and during electrolysis, to determine the amount of reacted monomer concentration. Electrolyses were carried out by adjusting the potential of the working electrodes (+0.65, +0.95, +1.40 and −1.80 V) at room temperature in air, and under a nitrogen atmosphere. At the end of electrolysis the cell content was poured into 600 ml of ethanol containing few drops of concentrated HCl, to precipitate the polymer. Polymers were filtered and dried under reduced pressure at 50°C. A Tacussel Potentiostat type PRT 30-0.1 was employed for electrolysis. For CV measurements, a Bank Elektronik LB 75 L potentiostat, a Bank Elektronik VS 72 function generator and a Yokogawa 3073 X–Y recorder were used.

Polymers were dissolved in chloroform and reprecipitated in ethanol for spectral analyses and molecular weight determinations. ^{13}C-n.m.r. and ^{1}H-n.m.r. spectra were obtained in $CDCl_3$ on a Bruker AC-200 FT-n.m.r. spectrometer. An i.r. spectrum was obtained in a KBr disc on a Perkin Elmer Model 1710 *FT*i.r. spectrophotometer.

The molecular weight of the polymer was obtained by a Perkin Elmer Coleman 115 molecular weight apparatus, in chloroform. Benzil was used for the calibration curve. Sub oven and main oven temperatures were 25 and 32°C, respectively.

RESULTS AND DISCUSSION

The structure of the synthesized compounds was verified by spectral and elemental analysis. CV measurements showed that 4-BDCP has three anodic peaks ($E_{p,a}$) at +0.65, +0.95 and +1.40 V and one reduction peak ($E_{p,c}$) at −1.80 V *versus* the Ag^0/Ag^+ (0.01 M) reference electrode in acetonitrile (*Figure 2*).

4-BDCP in acetonitrile in the absence of current was found to give no polymer. When 0.1 g of 4-BDCP was electrolysed in acetonitrile by adjusting the potential of working electrode (W_1) to any one of the $E_{p,a}$ values polymers formed in anode compartment only. The brown colour of anolyte turned to blue-green at the end of electrolysis. The CV of the blue-green coloured anolyte had a cathodic peak at −1.10 V *versus* Ag^0/Ag^+ which does not exist in CV of the complex before electrolysis, as seen in *Figure 2*. CV of the anolyte was obtained during electrolysis at definite time intervals. It was found that the height of the reduction peak at −1.10 V grew as electrolysis continued. This observation indicated the production of a side product such as L_2CuBr_2 as polymerization proceeded (L_2 = tetramethylethylenediamine). The polymer was analysed and it was found that no ligand or Cu had been incorporated into the polymer. Therefore formation of L_2CuBr_2 during polymerization seemed feasible. In a separate experiment L_2CuBr_2 was synthesized in acetonitrile. The solution was also blue-green in colour. The CV of the synthesized L_2CuBr_2 has a reduction peak at −1.10 V *versus* Ag^0/Ag^+ as expected. It has been reported that thermal polymerization of trihalophenol copper(II) complexes similar to 4-BDCP also yields L_2CuBr_2[17].

As seen in *Figure 3* electroinitiated polymerization of 4-BDCP had been carried out at each $E_{p,a}$ of the complex. An attempt to determine the amount of unreacted monomer concentration by CV from the heights of anodic peak potentials was made. Because L_2CuBr_2 formed as polymerization proceeded, the anodic peaks of this side product masked the anodic peaks of the unreacted 4-BDCP. Therefore, anodic peak heights could not be used to follow the rate of polymerization. The reduction peak of L_2CuBr_2, however, was found to be suitable for the determination of the amount of reacted monomer concentration during electrolysis.

CV measurements during electrolysis allowed *in situ* simultaneous monitoring of the reacted monomer concentration. Calibration curves were obtained in advance from CV measurements of synthesized L_2CuBr_2 solutions with various concentrations. Gravimetric measurements of polymers produced were in good agreement with conversions determined by CV.

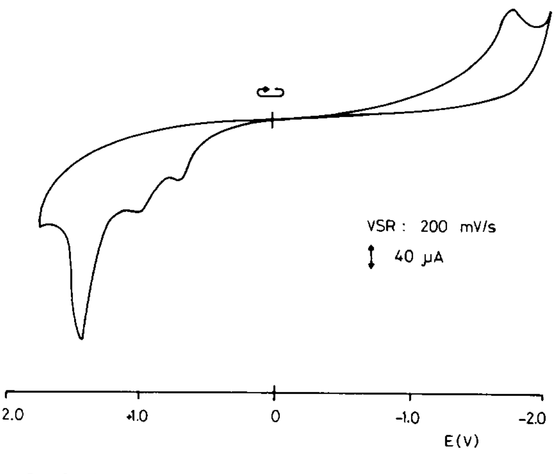


Figure 2 Cyclic voltammogram of 4-BDCP obtained in acetonitrile. VSR is the voltage scan rate

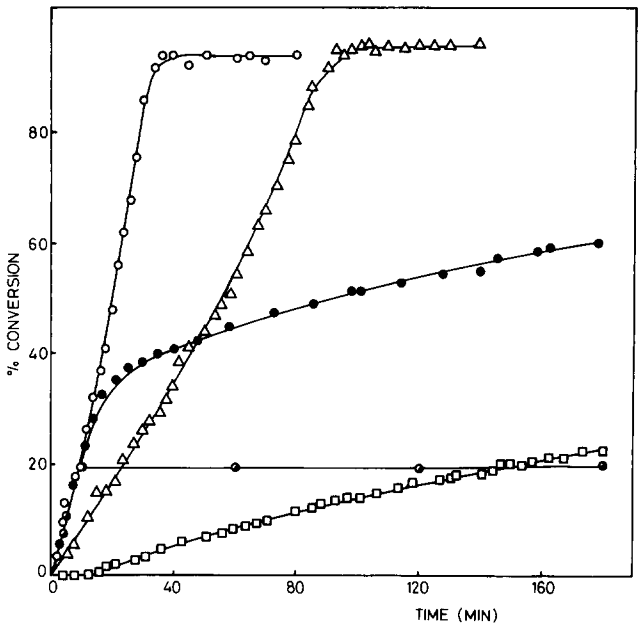
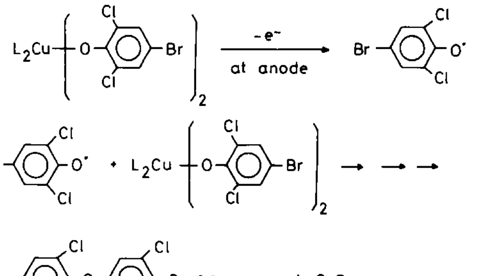


Figure 3 Electroinitiated polymerization of 0.10 g of 4-BDCP in 55 ml acetonitrile, at polymerization potentials of ○, +1.40 V; △, +0.95 V; □, +0.65 V; and ●, post-polymerization at +1.40 V; ◑, polymerization initiated at +1.40 V and inhibited after 10 minutes of electrolysis by hydroquinone

Figure 3 shows that polymerization carried out at the highest $E_{p,a}$ (+1.40 V) has the highest rate of polymerization. In *c*. 40 min, polymerization reaches above 90% conversion. The rate of polymerization decreases as the polymerization potential is reduced. *Figure 3* also shows that polymerization proceeds with a lower rate when the electrolysis is stopped at *c*. 20% conversion (post-polymerization).

Polymers were isolated only from the anode compartment at each polymerization potential. No trace of polymer was found in the cathode compartment. It was found that polymerization proceeds via a free radical mechanism. As seen in *Figure 3*, when hydroquinone was added to polymerization solution at *c*. 20% conversion and current was cut off, polymerization stopped completely.

Because polymerization takes place upon oxidation and proceeds via free radicals, the following mechanism can be proposed.



where L_2 is tetramethylethylenediamine.

Table 1 Electroinitiated polymerization of bis(4-bromo-2,6-dichlorophenoxo)*N*,*N*,*N*′,*N*′-tetramethylethylenediamine copper(II)

E_{pol}[a]	% Yield[b]	
	N_2	Air
+0.65	26.5	17.8
+0.95	96.2	85.4
+1.40	93.6	76.5
−1.80[c]	89.8	83.2

[a] Measured peak potentials are used as polymerization potentials
[b] Polymer recovered from anolyte at the end of 3 h of electrolysis
[c] Polymer was obtained in anode compartment (counter electrode) only

Polymerization of 0.10 g of 4-BDCP initiated by anodic oxidation at potentials equal to each $E_{p,a}$ of the monomer are also given in *Figure 3*. Calibration curves obtained by plotting reduction peak heights at −1.10 V *versus* concentration were linear for solutions corresponding to 0.10 g of 4-BDCP in 55 ml. In order to increase the amount of precipitated polymer, electrolysis of 0.30 g of monomer were also conducted. CV measurements during electrolysis were not conducted in those cases. When 0.30 g of monomer was electrolysed at each $E_{p,a}$ of monomer, electrolyses were continued for 3 h. Polymers were isolated by precipitation and used for spectral analyses and molecular weight measurements. *Table 1* gives percent yields (gravimetric) of electrolyses carried out at each $E_{p,a}$ and $E_{p,c}$ in air and under a nitrogen atmosphere.

Even in cases of electrolysis carried out at −1.80 V ($E_{p,c}$ of 4-BDCP) polymer was formed only in the anode compartment. No trace of polymer was observed in cathode compartment. This behaviour indicated that polymerization can proceed only upon oxidation via the same mechanism suggested for positive potential electrolysis. Since the monomer was placed equally to both compartments as reduction takes place on cathode, the monomer is oxidized on the anode which initiated polymerization. Therefore, in all electrolysis, polymerization is initiated via oxidation of the monomer. In the case of positive potential electrolysis, the polymer was formed in the working electrode compartment. In the case of negative potential electrolysis (−1.80 V), the polymer was formed in the counter electrode compartment. However, in each case polymer formation took place in the anode compartment. Molecular weight measurements, ^{1}H-n.m.r., ^{13}C-n.m.r. and *FT*i.r. spectral analyses were obtained for polymers produced at +0.95 V under nitrogen atmosphere, under conditions in *Table 1*. The molecular weight of the polymer was found to be 4.1×10^3 by the isopiestic method.

Figure 4 gives the ^{13}C-n.m.r. spectra of the polymer obtained by electro-oxidation of 4-BDCP. Three basic structures can be drawn for this polymer. The theoretical ^{13}C-n.m.r. chemical shift data for the three possible addition products of 4-BDCP were calculated from the related correlation tables[18]. Observed resonating frequencies are compared with the calculated values for the three possible structures, as shown in *Figure 5*. Structure (a) in *Figure 5* seems to have a better correlation with the observed data. The ^{1}H-n.m.r. spectrum, however, clearly reveals that the polymer has a mainly linear structure, as seen in *Figure 6*.

The linear polymer, poly(2,6-dichloro-1,4-phenylene-oxide), should exhibit a sharp singlet in the ^{1}H-n.m.r. spectrum. The polymer obtained from 4-BDCP by electroinitiation indeed has a sharp singlet at $\delta = 6.8$ ppm with a minor peak at $\delta = 7.5$ ppm (1,2-addition) as seen in *Figure 6*. The spectrum suggests that the polymer is a 1,4-catenation product containing a small amount of

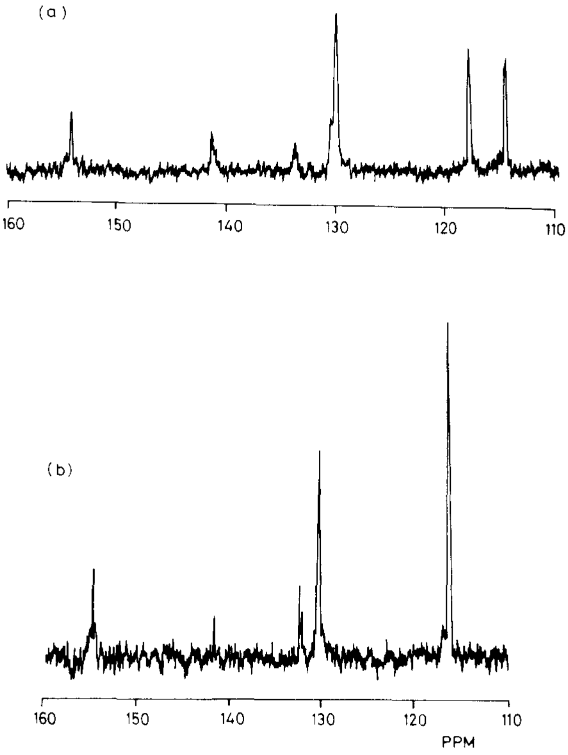


Figure 4 Proton-coupled (a) and -decoupled (b) spectra of polymer obtained from 4-BDCP by electroinitiation at +0.95 V

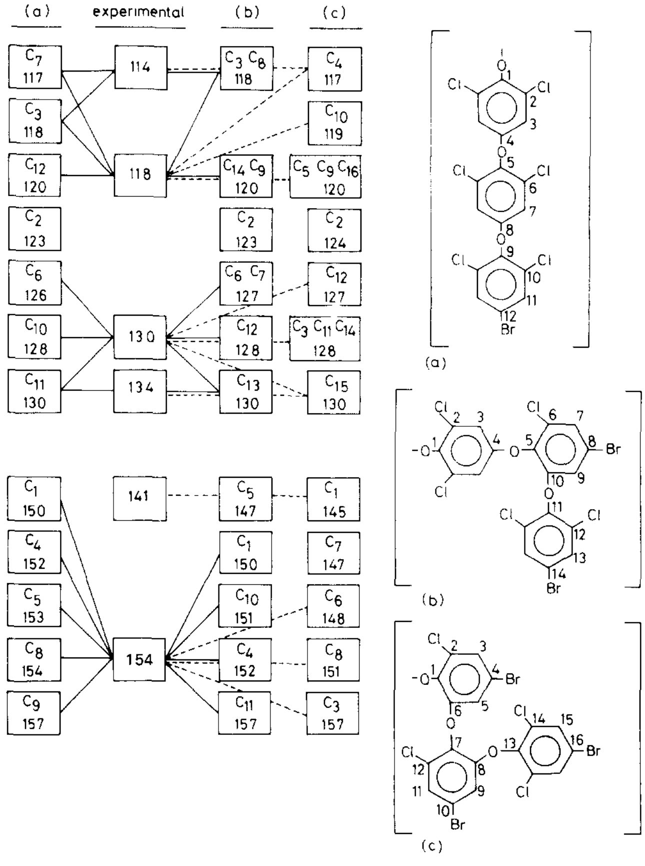


Figure 5 Schematic representation of ^{13}C-n.m.r. chemical shift data

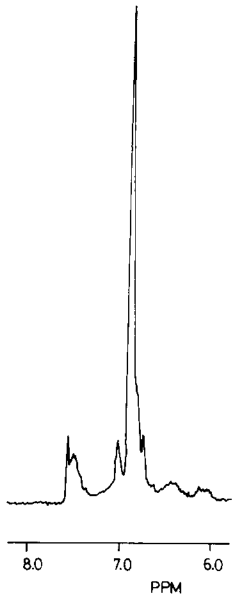


Figure 6 ^{1}H-n.m.r. spectrum of polymer obtained from 4-BDCP by electroinitiation at +0.95 V

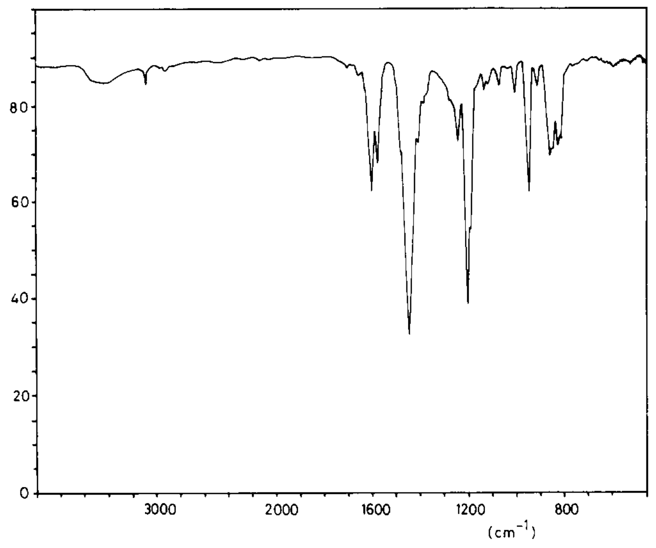


Figure 7 *FT*i.r. spectrum of polymer (in KBr) obtained from 4-BDCP by electroinitiation at +0.95 V

monomeric branches. Bromine in the *para* position is a better leaving group than chlorines in *ortho* positions, and thus a linear polymer was obtained as expected.

The *FT*i.r. spectrum of the polymer is given in *Figure 7*. As seen in the figure the polymer is characterized by 820 and 550 cm^{-1} out of phase C–H bendings, 910, 940, 1000 and 1070 cm^{-1} symmetric C–O–C stretchings, 1200 and 1240, 1570 and 1600 cm^{-1} C=C ring stretchings. The computer library output suggests polymeric dichlorophenylene oxide for the polymer.

CONCLUSIONS

We have shown that the 4-BDCP complex can be polymerized by electroinitiation only in anolyte. The mechanism of polymerization is free radicalic. Linear polymers via 1,4 addition can be obtained as major product by electro-oxidation of 4-BDCP. Electroinitiation yields low molecular weight poly(2,6-dichloro-1,4-phenyleneoxide) and thus spectral analysis is simplified. Moreover, the electroinitiated polymerization rate of 4-BDCP is shown to be much higher than thermal[16] polymerization.

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