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### Electroinitiated Polymerization of the Bis(2,6-Dibromo-4-Chlorophenoxy)-N,N,N<sup>1</sup>,N<sup>1</sup>-Tetramethylethylenediamine Copper (II) COMPLEX

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# ELECTROINITIATED POLYMERIZATION OF THE BIS(2,6-DIBROMO-4-CHLOROPHENOXY)-*N,N,N',N'*-TETRAMETHYLETHYLENEDIAMINE COPPER (II) COMPLEX

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## ABSTRACT

Electroinitiated polymerization of the bis(2,6-dibromo-4-chlorophenoxy)-*N,N,N',N'*-tetramethylethylenediamine copper(II) complex was accomplished upon anodic oxidation in acetonitrile. Anodic and cathodic peak potentials of the complex were measured by cyclic voltammetry (CV) in advance. Constant potential electrolyses carried out at peak potentials yielded polymers only in the anolyte. The presence of polymers in the anode compartment and the effect of radical inhibitor indicated a free-radical mechanism. In the absence of current, the complex in acetonitrile did not yield any trace of polymer for 10 days. The electrochemi-

cally produced radicals were very stable. When the polymerization was started by electroinitiation, it continued after discontinuance of the current. In order to follow the rate of monomer consumption, CV was employed. Use of six electrodes, in the specially designed H-type cell, allowed *in situ*, simultaneous monitoring of the monomer concentration. The structure of the polymer was studied by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and FTIR spectral analyses. Molecular weight measurements were carried out by the isopiestic method.

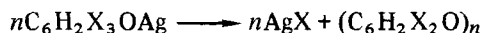
## INTRODUCTION

Electroinitiated polymerizations of various olefins [1-6] and phenol derivatives [7-9] have been reported. However, until recently there were no reports on electroinitiated polymerization of trihalophenoxo copper(II) complexes [10, 11].

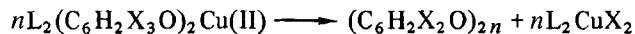
2,6-Dimethylphenol had been polymerized thermally in the presence of  $\text{O}_2$ ,  $\text{CuCl}$ , and pyridine by Blanchard et al. [12]. The authors also reported that *para*-halogenated 2,6-dimethylphenols yield polymers upon thermal decomposition. Silver salts of trihalophenols were reported to decompose thermally and yield poly(dihalophenylene oxides) [12].

Synthesis and thermal polymerization of bis(halophenoxo) copper(II) complexes with various ligands have been reported [13, 14]. Branched polymers were obtained mainly by thermal polymerization of halophenol copper(II) complexes. A free-radical mechanism was suggested for thermal polymerization.

Polymerization was suggested to proceed according to following reaction [12-14]



for silver salts, and



for copper(II) complexes, where L is the ligand and X is the halogen.

Hunter and Joyce [15] synthesized the silver salt of 4-chloro-2,6-dibromophenol and studied the structure of the polymer produced thermally. The authors reported that halogen was removed not only from the *para* position. A bromine atom had been removed from one of the *ortho* positions of the

trihalophenol for each chlorine atom present. The presence of chlorine atoms along with bromine in the final polymer indicated that polymerization had proceeded not only through *para* positions. Electrooxidation of 2,6-dimethylphenol was reported to yield polymers [9]. Dubois et al. [7, 8] also reported that various phenols can be polymerized by electroinitiation upon oxidation.

## EXPERIMENTAL

### Materials

Purification of acetonitrile and synthesis of tetrabutylammonium fluoroborate (TBAFB) have been described previously [16]. The synthesis of 2,6-dibromo-4-chlorophenol was accomplished by bromination of 4-chlorophenol (Aldrich Chemical Co.).

The procedure given by Harrod et al. [17] was followed for the synthesis of bis(2,6-dibromo-4-chlorophenoxy-*N,N,N',N'*-tetramethylethylenediamine copper(II) complex (DB4CP).

### Procedures

The apparatus and procedures of cyclic voltammetry have been described earlier [18]. Polymerizations were carried out in an H-type cell containing six electrodes, shown in Fig. 1. Acetonitrile (55 mL), TBAFB (0.1 mol/L), and DB4CP (7.24 mmol/L) were introduced into the cell. For polymerization,  $W_1$  (graphite),  $C_1$  (stainless steel), and  $R_1$  ( $Ag^0/Ag^+$ ) electrodes were connected to a potentiostat, and the required potential was applied. During electrolysis, cyclic voltammograms of the anolyte were obtained via  $W_2$  (Pt wire),  $C_2$  (Pt wire), and  $R_2$  ( $Ag^0/Ag^+$ ) electrodes at definite time intervals. A Tacussel potentiostat, Type PRT 30-0.1, was used for electrolysis. During polymerization, *in-situ* monitoring of reacted monomer concentration by CV was carried out. For simultaneous CV measurements, a Bank Elektronik LB 75 L potentiostat, a Bank Elektronik Wenking Model VSG 72 function generator, and a Yokogawa Technicorder, Type 3073 XY, recorder were employed. Polymerizations were carried out at room temperature, under a nitrogen atmosphere and in air. The polymers were precipitated in ethanol after 3 h of electrolysis. The precipitated polymers were dried under vacuum at 50°C for 24 h.

The polymers were dissolved in chloroform and reprecipitated in ethanol for spectral analysis and molecular weight measurements.  $^1H$ -NMR and  $^{13}C$ -NMR spectra were obtained in  $CS_2$  and  $CDCl_3$ , respectively, with a Bruker AC-200 FT NMR. IR spectra were obtained in KBr disks with a Perkin-Elmer

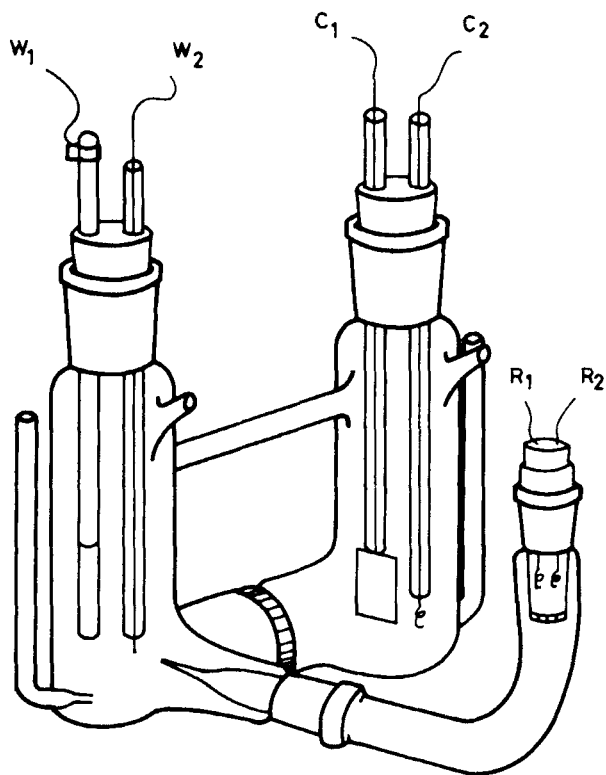


FIG. 1. Electrolysis cell.  $W_1$ ,  $C_1$ , and  $R_1$  are the working, counter, and reference electrodes, respectively, for polymerization.  $W_2$ ,  $C_2$ , and  $R_2$  are the working, counter, and reference electrodes, respectively, for cyclic voltammetry.

Model 1710 FTIR. Molecular weight measurements were made by the isopiestic method with a Perkin-Elmer Coleman 115 molecular weight apparatus. The solvent was chloroform. Benzil was used for calibrations.

## RESULTS AND DISCUSSION

CV of the complex DB4CP in acetonitrile was obtained prior to electrolysis to obtain anodic ( $E_{p,a}$ ) and cathodic ( $E_{p,c}$ ) peak potentials. As seen in CV of

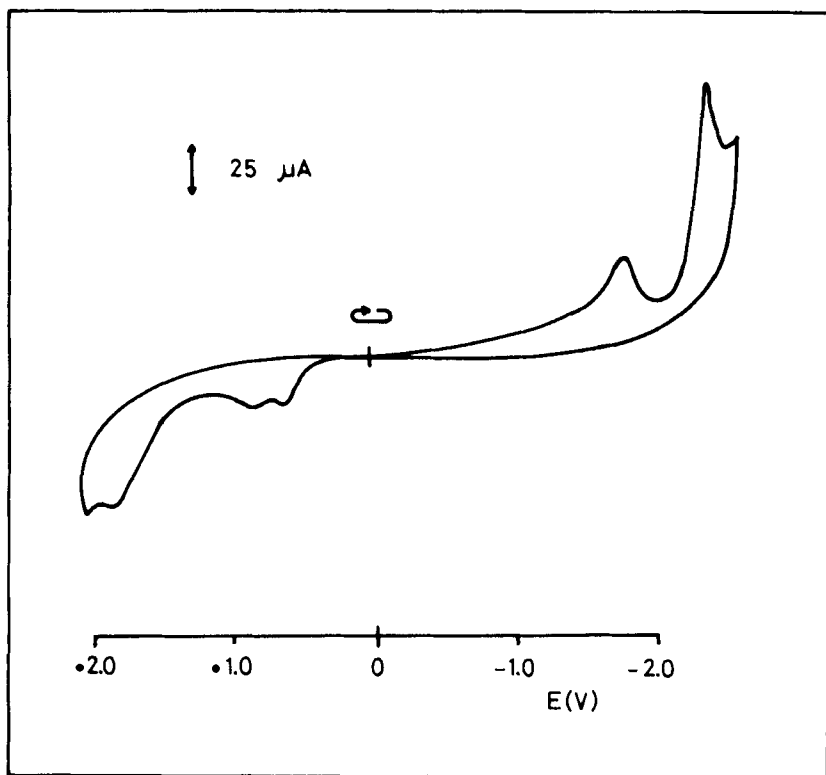


FIG. 2. The cyclic voltammogram of DB4CP recorded in acetonitrile-tetrabutylammonium fluoroborate at 20°C. Voltage scan rate: 200 mV/s.

the complex (Fig. 2), there are three  $E_{p,a}$  peaks, at +0.60, +0.80, and +1.70 V vs  $\text{Ag}^0/\text{Ag}^+$ .  $E_{p,c}$  peaks are observed at -1.80 and -2.40 V vs  $\text{Ag}^0/\text{Ag}^+$ .

The electroinitiated polymerization of DB4CP was carried out at each  $E_{p,a}$  of the complex. The complex does not polymerize in acetonitrile in the absence of current. No polymer was formed in the cathode compartment during electrolysis. Formation of polymers only in the anolyte indicated that electroinitiated polymerization proceeds only upon oxidation and on the anode. For this complex it was impossible to measure the concentration of unreacted monomer during electrolysis by the cyclic voltammetric anodic peak heights. The anodic peak height was found to grow as polymerization proceeded.

This unusual behavior was found to be due to formation of  $L_2CuX_2$ . The anodic peaks of  $L_2CuX_2$  were found to be in the same region as the  $E_{p,a}$  peaks of DB4CP. Therefore, as polymerization proceeded, formation of  $L_2CuX_2$  caused irregularities in the anodic peak heights of the complex. To overcome this difficulty,  $L_2CuX_2$  was synthesized in acetonitrile, and its CV was obtained in a separate experiment. It was found that blue-colored  $L_2CuX_2$  had an  $E_{p,c}$  at  $-1.10$  V that did not exist in the original complex. A calibration curve was obtained by plotting the cathodic peak height of  $L_2CuX_2$  at  $-1.10$  V vs the concentration of  $L_2CuX_2$ . During polymerization, cathodic peak heights (at  $-1.10$  V) of the polymerization solution (anolyte) were measured by CV.

It was found that, as polymerization proceeded, the cathodic peak (at  $-1.10$  V) began to form and to grow gradually in height. From the cathodic peak height, the reacted monomer concentration was calculated from the calibration curve.

Reacted monomer concentration vs time plots for polymerizations carried out at each  $E_{p,a}$  are given in Fig. 3. Because the calibration curve was linear up to  $2.4$  mmol/L DB4CP concentration, this concentration was used for all the kinetic studies in Fig. 3. As seen in Fig. 3, as the polymerization potential increases, the rate of polymerization increases. In order to check the possibility of postpolymerization, the electrolysis was stopped at  $\sim 10\%$  conversion. As seen in Fig. 3, polymerization still continues after the current was stopped.

In order to check the possibility of a free radical mechanism, hydroquinone was used as inhibitor. As seen in Fig. 3, when hydroquinone was added after stopping the current after 15 min of electrolysis, polymerization stopped. Hydroquinone was not added during electrolysis to eliminate the possible electrolytic decomposition of the inhibitor. Postpolymerization proceeded in the absence of a free radical inhibitor but stopped in its presence. Thus, the inhibition effect proved that electrolysis had initiated polymerization by a free-radical mechanism.

Electroinitiated polymerization was also attempted at the cathodic peak potentials of DB4CP. However, no polymer formed cathodically, instead polymerization took place in the anode compartment. Therefore, it is concluded that DB4CP can only be polymerized via a free-radical mechanism by oxidation in the case of electroinitiation. As seen in Table 1, polymerization can proceed in air or under nitrogen in the anode compartment.

The polymers produced were insoluble in acetonitrile, and a small amount of coating of electrode was also observed. Dimethylformamide (DMF) dissolves the polymer; however, polymerization in DMF was unsuccessful due

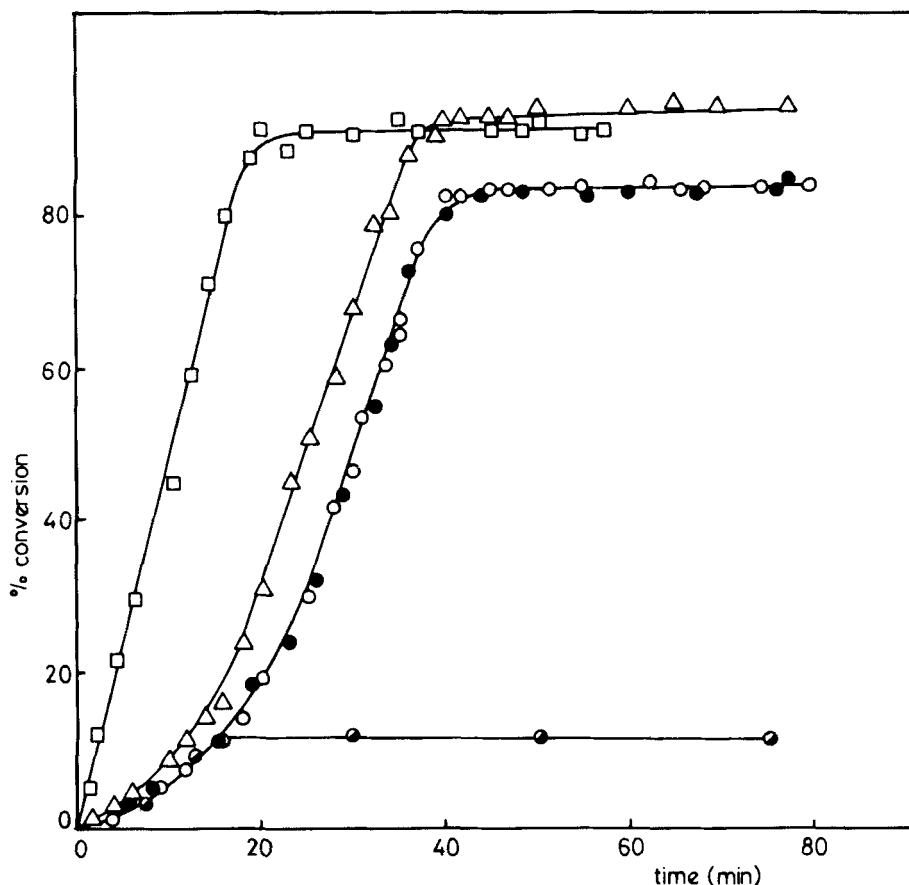


FIG. 3. Electroinitiated polymerization of DB4CP in acetonitrile at various polymerization potentials. (○) +0.60 V, (△) +0.80, (□) +1.70 V, (●) post-polymerization at +0.60 V, and (○) polymerization initiated at +0.60 V and inhibited after 15 min of electrolysis by hydroquinone.

to decomposition of the monomer in DMF. Therefore, all polymerizations were carried out in acetonitrile in spite of the poor solubility of the polymer. The heterogeneity of the electrolysis solution was a handicap which affected the rate and possibly the molecular weight.

During polymerization, the brown color of the anolyte turned to blue.



TABLE 1. Electroinitiated Polymerization of Bis(2,6-dibromo-4-chloro-phenoxo)-tetramethylethylenediamine Copper(II)

$E_{\text{pol}}^{\text{a}}$	%Yield <sup>b</sup>	
	N <sub>2</sub>	Air
+0.60	94.5	82.3
+0.80	92.0	83.5
+1.70	98.2	85.3
-1.80	—	70.9
-2.40	—	78.3

<sup>a</sup>Measured peak potentials of DB4CP are used as polymerization potentials.

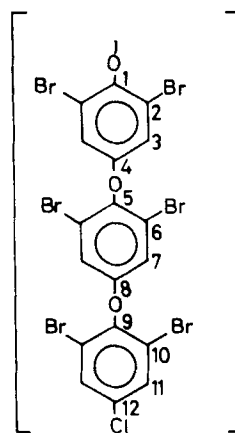
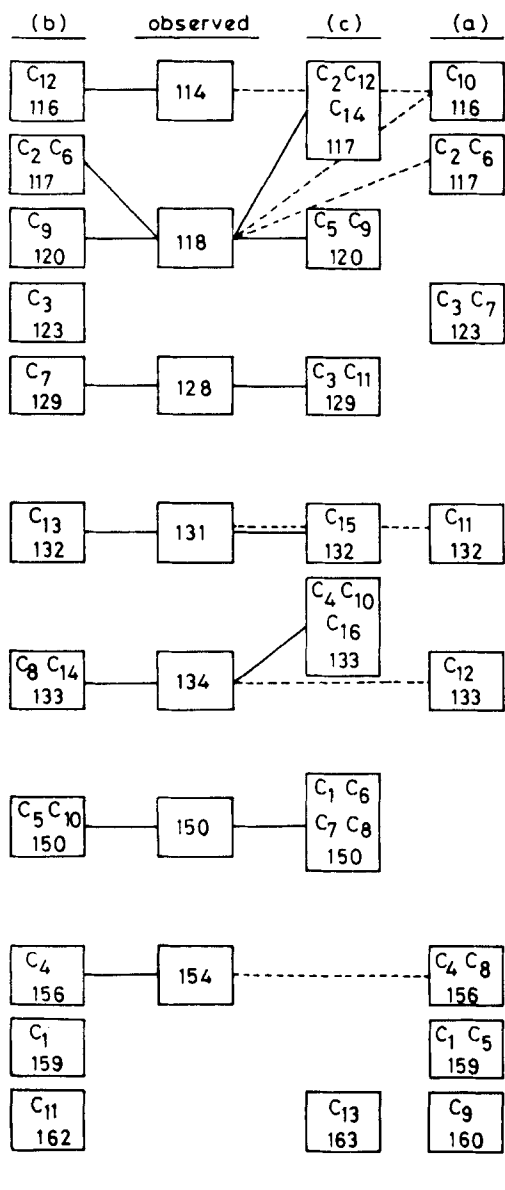
<sup>b</sup>Polymer recovered from anolyte at the end of 3 h of electrolysis. DB4CP concentration: 7.24 mmol/L.

This blue color was found to be due to formation of  $L_2CuX_2$ . As seen in Table 1 and Fig. 3, the yields obtained by gravimetric measurements are in good agreement with the conversions obtained by CV measurement.

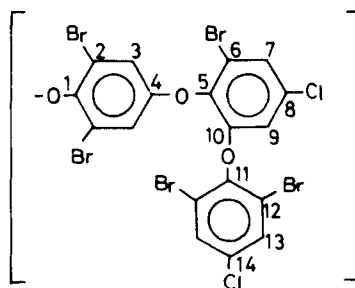
Constant-potential electrolysis was carried out at each anodic peak potential of the complex as measured by CV. However, it is difficult to estimate to which specific reactions the oxidation peaks at +0.60, +0.80, and +1.70 V correspond, due to the fast rate of polymerization. It can be said that those potentials represent removal of electrons from oxygen atoms of the phenol moiety and/or from nitrogen atoms of the ligand. As a result of removal of the electron(s), radical cations form, and they initiate the polymerization.

The molecular weight of the polymer produced by electroinitiation at +0.60 V was found to be 4100.

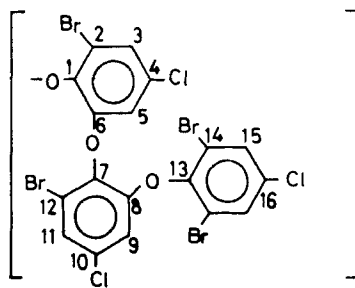
The structure of the polymer was analyzed by <sup>13</sup>C-NMR spectroscopy. There are three main 1,4 and 1,2 unit structures which can represent the polymer. Theoretical <sup>13</sup>C-NMR chemical shift data for three possible structures were calculated from the relevant correlation tables [19]. Binary relations between the observed and the calculated data are shown in Fig. 4. The <sup>13</sup>C-NMR proton-coupled spectrum of the polymer is given in Fig. 5. From Fig. 4 it can be concluded that the polymer obtained at +0.60 V by electroinitiation of DB4CP is mainly a mixture of 1,4 and 1,2 units. Bromine atoms in *ortho*-positions seem to be involved in polymerization as well as chlorine atoms in *para*-positions. Linear polymers with high molecular weight can be



(a)



(b)



(c)

FIG. 4. Possible relations between observed and calculated  $^{13}\text{C}$ -NMR chemical shifts.

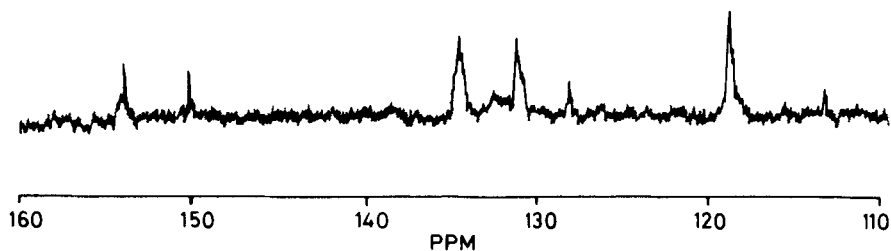


FIG. 5.  $^{13}\text{C}$ -NMR proton-coupled spectrum of polymer obtained from DB4CP by electroinitiation.

expected to be produced by 1,4-addition. Since 1,2-addition also took place in this case, along with 1,4-addition, the molecular weight is as low as 4100.

As the polymerization potential increases, the current intensity increases, which can cause a decrease in molecular weight. However, since the molecular

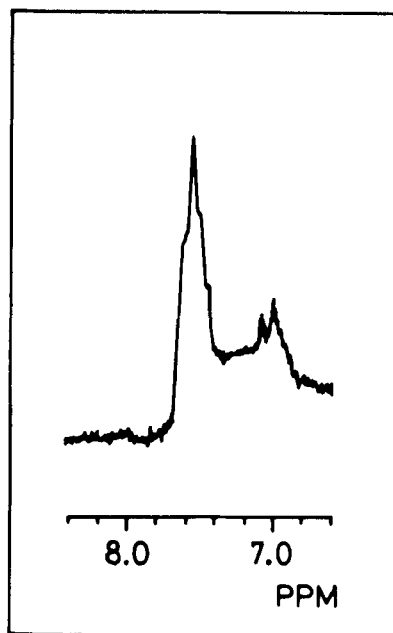


FIG. 6.  $^1\text{H}$ -NMR spectrum of polymer obtained at +0.60 V.

weight observed was very low, no significant effect on molecular weight was observed. Possibly the amounts of oligomer were higher at high polymerization potentials than at low polymerization potentials. Since the oligomers are not precipitated by ethanol, there was no significant difference in the molecular weight of the precipitated polymers obtained at +0.60, +0.80, and +1.70 V.

The  $^1\text{H-NMR}$  spectrum (Fig. 6) of the polymer supports the suggested structure as a mixture of 1,4 and 1,2 chain units. If the polymer were linear, only a singlet should appear at  $\delta \cong 7.00$  ppm. The presence of other peaks at  $\delta = 7-8$  ppm reveals that the product is a mixture of 1,4 and 1,2 units as shown in Fig. 4.

As seen in the FTIR spectrum in Fig. 7, the polymer can be characterized by 840 and 860  $\text{cm}^{-1}$  out-of-plane C-H bending; 940, 1000, 1030, 1060, and

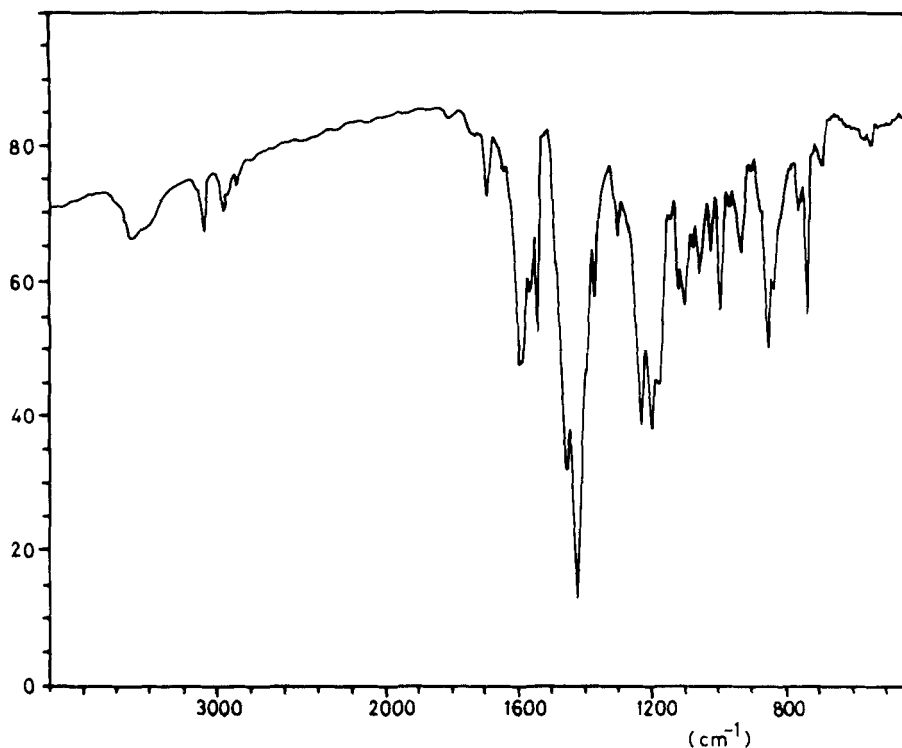


FIG. 7. FTIR spectrum of polymer obtained from DB4CP electrochemically at +0.60 V.

1100  $\text{cm}^{-1}$  symmetric C–O–C stretching; 1200 and 1240  $\text{cm}^{-1}$  C–O stretching; and 1370, 1430, 1460, 1540, and 1600  $\text{cm}^{-1}$  C=C ring stretching bands.

### CONCLUSIONS

In this work we have shown that DB4CP can be polymerized by electroinitiation upon oxidation. The polymerization proceeds by a free-radical mechanism. The rate of polymerization, followed electrochemically by CV, increases as the polymerization potential is increased. There is no induction period. The polymer obtained by electrolysis is a mixture of 1,2 and 1,4 chain units.

### ACKNOWLEDGMENTS

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