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## Synthesis of Ollgo (Phenyleneoxide) by Electro-Oxidative Polymerization

E. Tsuchida, H. Nishide, and T. Maekawa

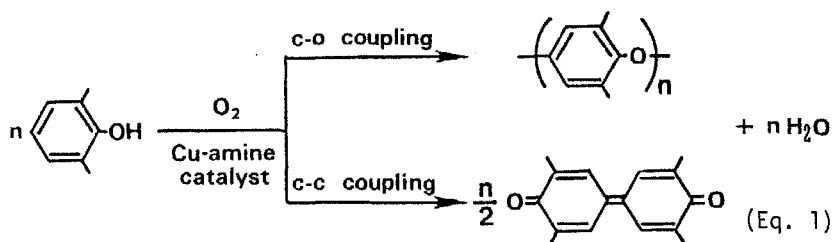
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### ABSTRACT

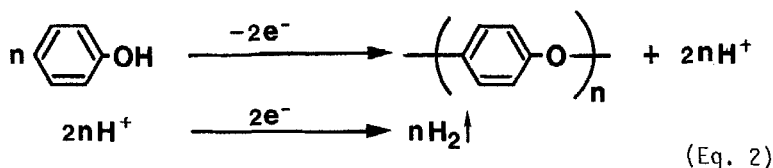
Anodic oxidation of 2,6-disubstituted phenols gave poly(2,6-disubstituted-1,4-phenyleneoxide)s quantitatively by using dichloromethane and tetraethyl ammonium bromide as the solvent and the supporting electrolyte respectively. Phenol was also electro-oxidatively polymerized to yield oligo(1,4-phenyleneoxide) with molecular weight of 1200~2500. The 2-step polymerization and the polymerization in the presence of bisphenol were carried out to increase the molecular weight of the oligo(phenyleneoxide). The mechanism of the electro-oxidative polymerization was discussed by electrochemical and ESR measurements.

### INTRODUCTION

It is well known that 2,6-dimethylphenol is oxidatively polymerized to poly(2,6-dimethylphenyleneoxide) with a copper-amine complex as catalyst in the presence of oxygen at room temperature. This polymerization can also proceed by anodic oxidation accompanying equivalent hydrogen evolution (Eq. 1).



Recently much research has been made to coat electrode with thin polymer film by electro-oxidative polymerization of phenols [1]; the formed thin and uniform poly(phenyleneoxide) films on electrode are interesting because of their electric properties. However the formation of thin polymer film on electrode, i.e. passivation of the electrode, resulted in cessation of the polymerization. The electro-oxidative polymerization as a producing method of poly(phenyleneoxide) had not been reported except in one patent [2], in which a copper-amine complex was added as an electron-mediator during the electrolysis. The author recently found that 2,6-disubstituted phenols are electro-oxidatively polymerized to yield poly(2,6-disubstituted-1,4-phenyleneoxide)s quantitatively under mild conditions and that the electro-oxidation of simple phenol also gives oligo(1,4-phenyleneoxide) (Eq. 2). The present paper reports the electro-oxidative oligomerization of phenol, its mechanism, and properties of the oligomer.



## EXPERIMENTAL

### Materials

Phenol, *o*-cresol, and *p*-bromophenol were purified by distillation. 2,6-Dimethylphenol was recrystallized from petroleum ether. 2,6-Dichloro-, 2,6-dimethoxy- and 2,6-di-*t*-butylphenol of special grade were used without further purification. 2,6-Diphenylphenol was gifted from Akzo Co.

2,2-Bis(3,5-dimethyl-4-hydroxyphenyl)propane (bisphenol) was prepared by the reaction of 2,6-dimethylphenol with acetone in the presence of 3-mercaptopropionic acid. Yield 60%, m.p. 165-168°C.

Tetraethylammonium bromide and chlororide of special grade were used. Tetraethylammonium perchlorate and tetrafluoborate were prepared by anion-exchange of tetraethylammonium bromide with perchloric acid or fluoboric acid and recrystallized from water.

Lead dioxide of special grade was used. Copper(I) chloride was prepared by reduction of copper(II) chloride with ascorbic acid.

Benzene, dichloromethane, methanol, pyridine and acetonitrile were distilled before use.

### Electrolysis

3 Pairs of platinum plate (2 x 5 cm) were set in a cell with 1 mm spacing as the working and the auxiliary electrode. Reference electrode was  $\text{Ag}^+/\text{AgCl}$  one. The dichloromethane solution (50 ml) of phenol (0.47 g) and tetraethylammonium bromide (2.10 g) was kept under nitrogen atmosphere in the cell. The electrolysis was carried

out with constant current density ( $10 \text{ mA/cm}^2$ ) which was supplied by a galvanostat. During the electrolysis hydrogen gas was evolved from the cathode. After the electrolysis, the reaction mixture was washed with water to extract the supporting electrolyte. The concentrated organic layer was slowly poured into methanol. White or pale brown powder was collected by filtration, washed with methanol, and dried in vacuo.

#### Polymerization of Phenols by Other Methods

The oxidative polymerization of phenols was carried out as in lit.[3]. The pyridine solution (20 ml) of copper(I) chloride (0.1 g) was stirred under oxygen to oxidize Cu(I)-ion to Cu(II). The benzene solution (100 ml) of the phenol (0.01 mol) was added to the catalytic solution and the mixture was stirred for 0.5 hr under oxygen atmosphere at  $30^\circ\text{C}$ . Then the reaction mixture was slowly poured into methanol containing hydrochloric acid. The white powder was filtered and washed with methanol and dried in vacuo.

The polymerization of phenols with lead dioxide was carried out according to lit.[4]. Lead dioxide (4 g) was added to the benzene solution (50 ml) containing the phenol (0.002 mol) and triethylamine (1 ml), and the mixture was stirred for 5 hrs at  $30^\circ\text{C}$ . The polymer was obtained in the similar manner described above.

Oligo(*p*-phenyleneoxide) was synthesized by Ullmann reaction according to lit.[5]; sodium *p*-bromophenoxide was condensed in hydroquinonedimethylether for 3 hrs at  $200^\circ\text{C}$ , resulting tan-colored powder in 15% yield.

Identification of the polymers

The NMR signals of the polymerization product agreed with those assigned to the poly(phenyleneoxide) structures shown in Eq. 1. The IR spectrum of the polymerization product showed that the absorption at  $3400\text{ cm}^{-1}$ , corresponding to the hydroxyl group, has disappeared, and new absorption assigned to an ether bond was observed as follows.

Poly(2,6-dimethyl-1,4-phenyleneoxide):  $^1\text{H NMR}(\text{CDCl}_3)$   $\delta = 2.10(\text{CH}_3)$   $6.90(\text{phenyl})$ , IR  $1180\text{ cm}^{-1}(\nu_{\text{C-O-C}})$ , poly(2,6-diphenyl-1,4-phenyleneoxide);  $^1\text{H NMR}$   $\delta = 6.70, 7.65(\text{phenyl})$ , IR  $1170\text{ cm}^{-1}(\nu_{\text{C-O-C}})$ , poly(2,6-dichloro-1,4-phenyleneoxide):  $^1\text{H NMR}$   $\delta = 7.3(\text{phenyl})$  IR  $1180\text{ cm}^{-1}(\nu_{\text{C-O-C}})$ , poly(2,6-dimethoxy-1,4-phenyleneoxide);  $^1\text{H NMR}$   $\delta = 6.27(\text{OCH}_3)$ ,  $7.10(\text{phenyl})$  IR  $1210\text{ cm}^{-1}$ ,  $1195\text{ cm}^{-1}(\nu_{\text{C-O-C}})$ , poly(2-methyl-1,4-phenyleneoxide):  $^1\text{H NMR}$   $\delta = 2.18(\text{CH}_3)$ ,  $6.60, 7.00, 7.20(\text{phenyl})$ , IR  $1200\text{ cm}^{-1}(\nu_{\text{C-O-C}})$ , poly(1,4-phenyleneoxide):  $^1\text{H NMR}$   $\delta = 7.2(\text{phenyl})$ , IR  $1190\text{ cm}^{-1}(\nu_{\text{C-O-C}})$ , co-oligomer of phenol and bisphenol:  $^1\text{H NMR}$   $\delta = 7.10(\text{phenyl})$ ,  $2.30(\text{CH}_3)$ ,  $1.80(\text{C}(\text{CH}_3)_2)$ , IR  $1190\text{ cm}^{-1}(\nu_{\text{C-O-C}})$ ,  $1359, 1378\text{ cm}^{-1}(\text{geminal dimethyl } \delta_{\text{C-H}})$ .

Measurements

Molecular weight of the polymer was measured with gel permeation chromatography standardized by poly(styrene). Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out under nitrogen atmosphere (heating rate  $5^\circ\text{C}/\text{min}$ , from room temperature to  $400^\circ\text{C}$ ). ESR measurement was carried out with a ESR

spectrometer (JEOL FE-3X) at room temperature. Cyclic voltammogram was recorded with a potentiostat and a frequency generator. Platinum disk, platinum wire, and  $\text{Ag}^+/\text{AgCl}$  were used as the working, the auxiliary, and the reference electrode.

### RESULTS AND DISCUSSION

Fig. 1 shows the reaction curve of the electro-oxidative polymerization, using the example for 2,6-dimethylphenol. The remained amount of the phenol monomer decreased and the yield of the polymer increased with the supplied current amount. The side-reaction to form diphenoquinone (3,3',5,5'-tetramethyl-4,4'-diphenoquinone) was

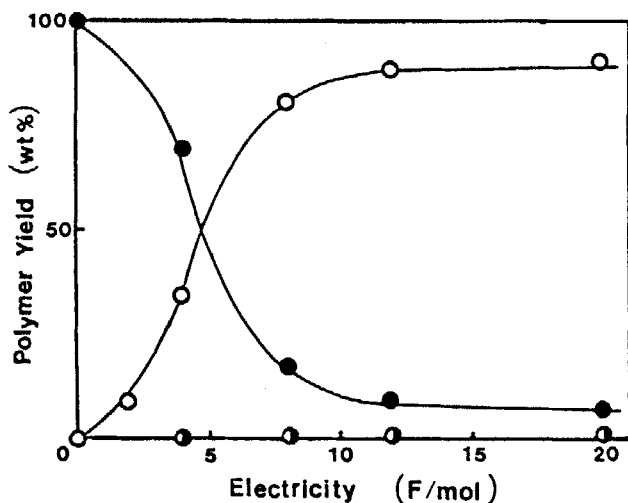


FIGURE 1. Electro-oxidative Polymerization of 2,6-Dimethylphenol. ●: yield of poly(2,6-dimethylphenyleneoxide), ○: yield of 3,3',5,5'-tetramethyl-4,4'-diphenoquinone, ●: remained amount of 2,6-dimethylphenol,  $[\text{dimethylphenol}] = 0.1 \text{ mol/l}$ ,  $[(\text{C}_2\text{H}_5)_4\text{NBr}] = 0.2 \text{ mol/l}$ , in  $\text{CH}_2\text{Cl}_2$ -20% $\text{CH}_3\text{OH}$ ,  $10 \text{ mA/cm}^2$ .

suppressed under this electrolysis condition. The polymer yield reached to ca. 90% with 20 F/mol: The reaction efficiency was sufficiently high, although the overall current efficiency resulted in ca. 10%.

Electro-oxidative polymerization of 2,6-disubstituted phenols is listed in Table 1 with the polymerizations catalyzed by the copper-pyridine complex and oxidized by lead dioxide. 2,6-Dimethylphenol was electro-oxidatively polymerized to yield poly(2,6-dimethyl-1,4-phenyleneoxide) with molecular weight  $1\text{--}1.5 \times 10^4$  as was by the other polymerization methods. The  $^1\text{H}$  NMR and IR spectra were in complete agreement with those obtained by the other methods

TABLE 1

## Electro-oxidative Polymerization of 2,6-Disubstituted Phenols

2,6-Disubstituents of Phenol	Polymer Yield (%) <sup>a)</sup>		
	Electrolysis <sup>b)</sup>	Catalysis with Cu-Pyridine <sup>c)</sup>	Oxidation with PbO <sub>2</sub> <sup>d)</sup>
CH <sub>3</sub> -	83	85	54
C <sub>6</sub> H <sub>5</sub> -	38	46	86
CH <sub>3</sub> O-	23	0	32
Cl-	98	0	0
CH <sub>3</sub> (H)-	39	46	38
H-	78	0 <sup>e)</sup>	0

a) at room temperature, b) [phenol] = 0.1 mol/l, [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr]/[phenol] = 2 in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>OH (4/1), 8 F/mol, 10 mA/cm<sup>2</sup>, c) [Cu-pyridine complex]/[phenol] = 0.01 in benzene, d) [PbO<sub>2</sub>]/[phenol] = 2.5 in benzene, e) also at 60°C



(see Experimental Part). The electro-oxidation was also effective for 2,6-diphenyl-, 2,6-dichloro-, 2,6-dimethoxy-, and 2-methylphenol to produce the corresponding polymers. Poly(2,6-dimethoxyphenyleneoxide) was formed by the electro-oxidation as well as by the oxidation with lead dioxide, while 2,6-dimethoxyphenol with the copper-pyridine catalyst gave only diphenoquinone (3,3',5,5'-tetramethoxy-4,4'-diphenoquinone) through C-C coupling reaction. For 2,6-dichlorophenol the polymer was produced in high yield by the electro-oxidation. On the other hand, the phenol reacted very slowly with the copper-pyridine catalyst and lead dioxide even at 60°C and did not at room temperature. 2,6-Di-*t*-butylphenol having bulky substituent groups gave only its diphenoquinone by every methods due to the steric hindrance of the substituents.

In Table 1, one notices also that phenol is electro-oxidatively polymerized although it can not be by the other methods. The yield increased with the supplied current amount and reached to ca. 100% with 10F/mol (overall current efficiency for the reaction: ca. 20%). Molecular weight 1200-2500,  $^1\text{H}$  NMR and IR (see Experimental Part). It has been reported by the study on oligo(phenyleneoxide) prepared by Ullmann reaction that oligo(1,2-phenyleneoxide) showed the IR absorption at 970 and 1025  $\text{cm}^{-1}$  but the linear oligo(1,4-phenyleneoxide) did not this absorption (Eq. 3)[5]. The IR spectrum of oligo(phenyleneoxide) prepared by the electro-oxidation showed no



absorption signal at both 970 and 1025  $\text{cm}^{-1}$ : The linear 1,4-phenylene structure was estimated.

The first requisite to proceed the polymerization is the electrolysis solvent. Table 2 shows the electro-oxidative polymerization of phenol and 2,6-dimethylphenol in various solvents. The polymer was deposited on the electrode, i.e. passivation of the electrode was occurred in poor solvents of the polymer such as methanol and acetonitrile. Dichloromethane and its mixture were selected as the solvent because the polymer and a supporting electrolyte well dissolved in them and they were relatively stable under electrolysis conditions.

The second requisite is the supporting electrolyte. The oligo(phenyleneoxide) yields obtained by using various electrolytes are shown in Table 3. Tetraalkyl ammonium halides, e.g. tetraethyl ammonium bromide, were good electrolytes to produce the polymer.

TABLE 2

Electro-oxidative Polymerization of 2,6-Dimethylphenol and Phenol in Various Solvents

Solvents	Polymer Yield (%) <sup>a)</sup>	
	Poly(2,6-dimethylphenyleneoxide)	Poly(phenyleneoxide)
$\text{CH}_2\text{Cl}_2$	22	28
20% $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$	83	78
20% $\text{CH}_3\text{CN}-\text{CH}_2\text{Cl}_2$	trace	passivation
$\text{CH}_3\text{OH}$ , $\text{CH}_3\text{CH}$ or $\text{C}_6\text{H}_6$	passivation	passivation

a)  $[\text{phenol}] = 0.1 \text{ mol/l}$ ,  $[(\text{C}_2\text{H}_5)_4\text{NBr}]/[\text{phenol}] = 2, 8 \text{ F/mol}$ ,  $10 \text{ mA/cm}^2$ , at room temperature.

TABLE 3

Electro-oxidative Polymerization of Phenol with Various Supporting Electrolytes

Supporting Electrolyte	Polymer Yield (%)
$\text{Et}_4\text{NCl}$	5
$\text{Et}_4\text{NBr}$	28
$\text{Et}_4\text{NI}$	35
$\text{Et}_4\text{NClO}_4$ or $\text{Et}_4\text{NBF}_4$	passivation

Et: ethyl, [phenol] = 0.1 mol/l, [electrolyte] = 0.2 mol/l, in  $\text{CH}_2\text{Cl}_2$ , 8 F/mol, 10 mA/cm<sup>2</sup>.

The following questions remain to discuss the polymerization mechanism. (i) Phenol was smoothly polymerized which could not be by the oxidation with the copper catalyst or lead dioxide. (ii) Phenol was preferentially reacted in the *p*-position and to form the 1,4-phenyleneoxide structure.

Fig. 2 shows typical cyclic voltammogram for the oxidation of phenol at a platinum electrode in methanol or dichloromethane solution containing tetrabutylammonium perchlorate. A rapid decrease in current with successive cycles of potential sweep for the oxidation in methanol indicated that the electro-oxidative polymerization of phenol produced an insulating film which adhesively coated the electrode surface. On the other hand, only a slow decrease in current was observed for the oxidation in dichloromethane: The polymer formation in dichloromethane did not significantly insulate the platinum electrode. From Fig. 2 the oxidation poten-

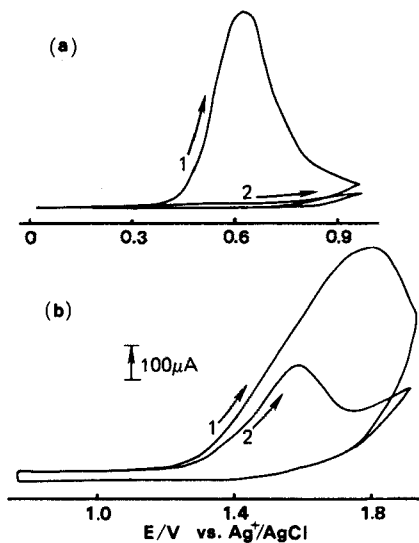
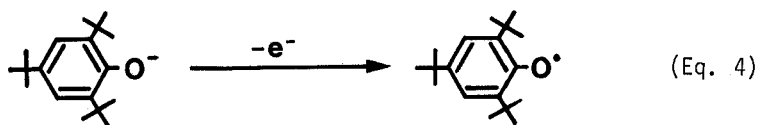


FIGURE 2. Cyclic Voltammogram for the Oxidation of Phenol in Methanol (a) and Dichloromethane (b). [phenol] = 10 mmol/l,  $[(n-C_4H_9)_4NClO_4] = 0.2$  mol/l, scan rate 100 mV/s.

tial of phenol was estimated to be 1.8 V, which agrees with the value in lit.[6] and is relatively high among phenol derivatives. During the polymerization the electrolysis potential was remained ca. 2.0 V, which was higher than the oxidation peak potential.

Fig. 3 shows the ESR spectrum of phenoxy radical formed by the electrolysis of tri-*t*-butylphenol (Eq. 4). The  $g$  value (= 2.006) and the hyperfine structure of the signal coincided with one produced



by the oxidation with lead dioxide. This radical was accumulated

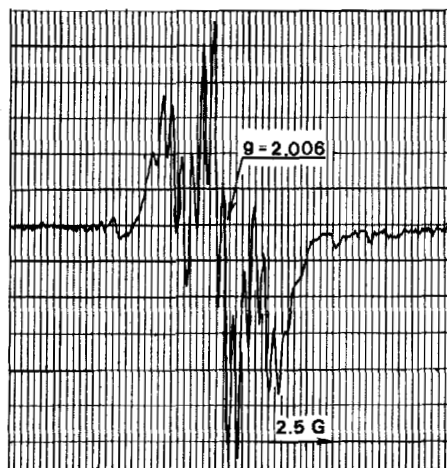


FIGURE 3. ESR Spectrum of Tri-*t*-butylphenoxy Radical Formed by Electrolysis. [phenol] = 0.1 mol/l, [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>NBr] = 0.2 mol/l, in CH<sub>2</sub>Cl<sub>2</sub>, at room temperature.

in the solution with supplied current amount, as shown in Fig. 4. The profile of the reaction curve in Fig. 4 was similar to that in Fig. 1, taking into account for the differences that the calculated current amount for the radical formation and the polymerization were 1 and 2 F/mol respectively and that the current efficiency was not same for them. This suggests that the electro-oxidative polymerization proceeds through a phenoxy radical formation. The weak signal of the phenoxy radical with the same ESR absorption was observed for the electrolysis solution of phenol. This also suggests that the active species of the reaction is the phenoxy radical.

Fig. 5 shows effect of the current density on the poly-(phenyleneoxide) yield at the constant electricity. The yield increased with the current density, although the molecular weight of

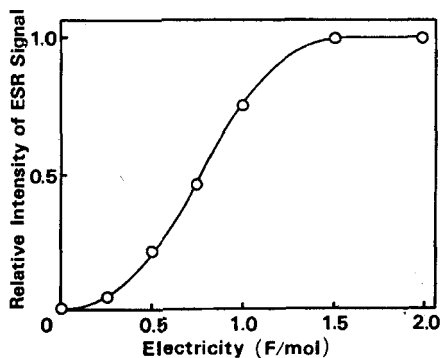


FIGURE 4. Intensity of ESR Signal of Tri-*t*-butylphenoxy Radical During the Electrolysis. [phenol] = 0.1 mol/l,  $[(C_2H_5)_4NBr]$  = 0.2 mol/l, in  $CH_2Cl_2$ , at room temperature.

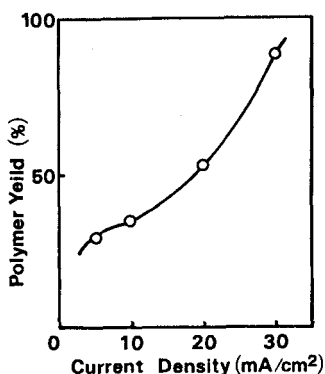
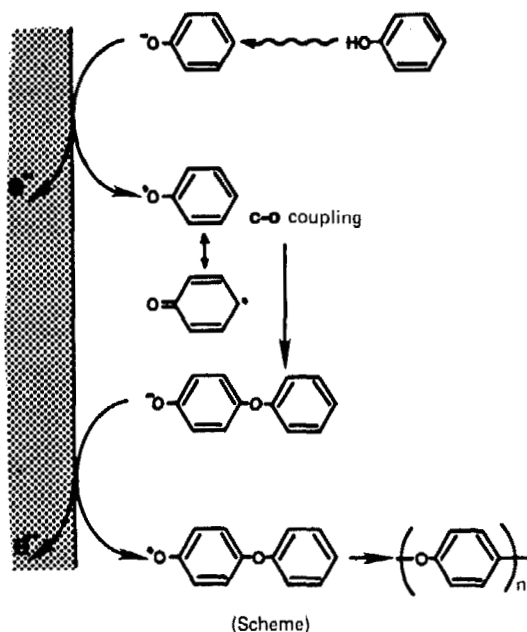


FIGURE 5. Effect of Current Density on the Polymer Yield. [dimethylphenol] = 0.1 mol/l,  $[(C_2H_5)_4NBr]$  = 0.2 mol/l, in  $CH_2Cl_2$ -20% $CH_3OH$ , 4 F/mol.

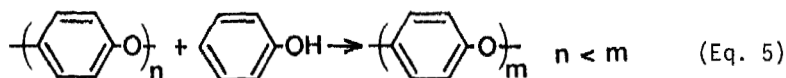
the obtained polymer remained constant. The polymerization rate was related to the current density on the electrode, i.e. the concentration of the activated phenoxy radical.

From these results, the polymerization mechanism of phenol may be illustrated as in Scheme 1. Phenoxy anion is one-electron oxidized to the phenoxy radical upon the surface of electrode, and

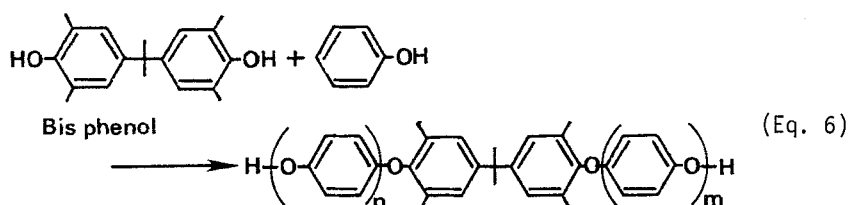


thus formed phenoxy radical is accumulated within the diffusion layer. The concentrated phenoxy radical is coupled with each other at *p*-position to form the dimer, and the dimer repeats the electro-oxidation and coupling. The authors assumed that the phenoxy radical is adsorbed or orientated upon the electrode surface thus resulted in the selective coupling reaction.

To increase the molecular weight of the oligo(phenyleneoxide), two-step reaction was applied (Eq. 5). The electro-oxidation of the mixture of the oligomer and phenol increased the molecular weight to  $M_n 2.8 \times 10^3$ ,  $M_w 7.1 \times 10^3$ .



Eq. 6 shows the procedure to obtain terminally hydroxylated oligo(phenyleneoxide): the electro-oxidative polymerization in the presence of bisphenol. Although the molecular weight was low and ca. 700, the oligomer contained ca. two hydroxy groups per one molecule. The reaction of phenol and bisphenol with the copper-pyridine complex did not give the product.



Thermal stability of the oligomers was shown in Table 4. Decomposition temperature of the oligo(phenyleneoxide) was much higher than that of oligo(2,6-dimethylphenyleneoxide) with the same molecular weight. The poly(1,4-phenyleneoxide) structure is expected to show an interesting property.

TABLE 4

## Thermal Analysis of Oligo(phenyleneoxide)

Polymer	$\bar{M}_n$	Softening Point (°C)	Decomposition Point (°C)
Oligo(2,6-dimethyl-phenyleneoxide)	1500	135	232
Oligo(2-methyl-phenyleneoxide)	1600	175	182
Oligo(phenylene-oxide)	1200 1800	157 170	360 344



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