

THE ELECTROCHEMICAL PREPARATION OF POLYPHENOL WITH
CONDUCTIBILITY*

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Abstract Polyphenol film deposited on platinum foil can continuously grow with time during the electrolysis of a phenol solution consisting of 0.1 mol L^{-1} phenol, 3 mol L^{-1} NaOH and 0.5 mol L^{-1} Na_2SO_4 , as has been proved by the methods of sweep potential, constant potential and constant current, and visible spectra during the electrolysis of phenol. A polyphenol film with thickness of 0.11 mm was obtained by the electrolysis of phenol at a constant potential of 0.70 V (versus Ag/AgCl with saturated KCl solution). Polyphenol film is inactive and stable in 2 mol L^{-1} H_2SO_4 solution, neutral solution and 3 mol L^{-1} NaOH solution and in the potential range between -0.95 and 1.35 V . The usable potential range is dependent on the pH value. Polyphenol has an ESR signal with a g factor of 2.0049 . The conductivity of polyphenol is $1.2 \times 10^{-4} \text{ S cm}^{-1}$. In the solution of polyphenol dissolved in DMSO, the mobility of polyphenol anions is $8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$ at 20°C .

Keywords Phenol, Concentrated alkaline solution, Electrochemical polymerization, Polyphenol, Electrochemical properties, Mobility, Spectra of FTIR and ESR

INTRODUCTION

The anodic oxidation of phenol and phenol derivatives in alkaline and alcoholic media has been studied extensively and intensively by Pham and Lacaze *et al.* using various metals as electrodes^[1–3]. The passivating layer formed on the metal surface during the oxidation process plays an important role in protecting metals from corrosion^[4–6]. In fact, the passivating layers are polymers of insulating nature^[1, 7]. In general, the passivating layers of these polymers are very thin (5 nm to $15 \text{ }\mu\text{m}$)^[1, 5, 8], which depends on the electrolytic conditions. Most polymerizations of phenol derivatives were carried out in weaker alkaline solutions, *e.g.*, 0.15 mol L^{-1} NaOH solution^[7], 0.22 mol L^{-1} KOH solution^[5], 0.1 mol L^{-1} Na_2CO_3 solution^[9] and phosphate buffer (pH 7.4)^[10]. Only a few papers deal with the polymerization of phenol derivatives in acidic solution^[11].

Pham *et al.* found that polymer film was not formed during the electrochemical oxidation of phenol derivatives when the *para* position and one of the *ortho* positions with respect to the hydroxyl group are occupied^[1]. This means that the polymerization of phenol and phenol derivatives is mainly carried out via head-to-tail coupling^[1]. The results obtained from IR spectroscopy and X-ray photoelectron spectroscopy (XPS) of polymers in the basic solutions confirm that the C—O—C bond is present in polymers of phenol and its derivatives^[12, 13]. These results are very helpful in explaining of the polymerization mechanism of phenol and its derivatives and structure of polymers.

Polyphenol and most of polymers prepared using phenol derivatives are insulators. However, the polymers obtained by polymerization of hydroxymethyl phenol derivatives (such as *o*-, *m*-, *p*-hydroxybenzyl alcohol) in the presence of ferrocene^[2] and polymers obtained by the electrochemical oxidation of phenol derivatives substituted by amino or anilino groups (such as polytyramine film after treatment with ferrocene) are electroactive^[3]. Then,

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these films are also very thin, since the film growth is still inhibited during the polymerization process. No conductivities of these polymers were reported.

Wang *et al.* employed the electrochemical quartz crystal microbalance (EQCM) to study the formation of inhibitory polyphenol layers on the surface of gold electrode^[10]. Their results show that the passivation process is dependent on the specific phenolic compound, its concentration and operational conditions^[10]. However, little is known about the effect of the concentrated base solution on the polymerization of phenol. The basic solutions of the low concentration may inhibit film growth of polyphenol.

Recently, Mandal *et al.* reported a new class of single-ion-conducting solid polymer electrolytes, which were synthesized from both monomers of hydroquinone and 4-methoxyphenol using enzymatic polymerization^[14].

We found that the electrolytic behavior of phenol in the concentrated solution of NaOH is very different from that of phenol in the basic solutions of low concentrations. The current during the electrolysis of phenol in the concentrated solution of NaOH increases continuously with time. As a result, the polyphenol film continues to grow as the electrolysis proceeds. In this paper, we report the preparation of the thick polyphenol film in the concentrated solution of NaOH, conductivity, the spectra of electron spin resonance (ESR) and FTIR of polyphenol, and mobility of polyphenol anions.

EXPERIMENTAL

Phenol and other chemicals used in this work were reagent grade. Redistilled water was used to prepare solutions. The electrolysis cell consisted of two platinum foils and a reference electrode. The area of the working electrode was $4 \times 4 \text{ mm}^2$. Potentials given here are referred to the Ag/AgCl with saturated KCl solution. The reference electrode was designed especially to avoid the leakage of liquid. All experiments were carried out at 28°C .

A HPD-1A potentiostat-galvanostat was used for the cyclic voltammetry. A PAR Model 173 potentiostat-galvanostat with a Model 179 digital coulometer was used for the electrolysis of phenol at constant potentials. A YEW model 3036 *X-Y* recorder and a YEW Model 3066 pen recorder were used to record the cyclic voltammograms and to plot current versus time and potential versus time, respectively. The measurements of visible spectra during the electrolysis of phenol were carried out using a MPS 2000 spectrophotometer. The working cell contained an ITO (indium-tin oxide) working electrode, a platinum net counter electrode and a Ag/AgCl electrode (with saturated KCl solution) as the reference electrode. The reference cell contained a corresponding electrolytic solution and an ITO electrode. The FTIR and ESR spectra of polyphenol were recorded using a Nicolet 740 FTIR instrument and a JES-FEKG spectrometer, respectively. The conductivity of polyphenol was measured on a pressed pellet using a four-probe technique. The mobility of polyphenol anions in the organic solvent was determined using a transfer tube with an inner diameter of 3.08 mm on a Model 83/2 regulated DC power supply.

RESULTS AND DISCUSSION

Effect of the Concentration of Basic Solution on the Growth of Polyphenol Film

Figure 1 shows the cyclic voltammograms of phenol. The solution for the electrolysis consisted of 0.1 mol L^{-1} phenol, 0.15 mol L^{-1} NaOH and 0.5 mol L^{-1} Na_2SO_4 . From the first cycle (Fig. 1, curve 1), it can be seen that an anodic peak with a large current appears at 0.45 V, and then this peak current decreases quickly with increasing number of potential cycles. After fifty one cycles, a very thin film with yellow color was found on the working electrode, which is identified as polyphenol. This result is very similar to those reported earlier^[1-4]. Except for the first cycle, the oxidation currents for other cycles are very small as shown in Fig. 1. This indicates that the polyphenol formed on the platinum working electrode has a very low conductivity, which passivates the surface of the platinum electrode. As a result, polymer film growth was inhibited.

Figure 2 shows the cyclic voltammograms of polymer film growth during the electrolysis of the solution containing 0.1 mol L^{-1} phenol, 3 mol L^{-1} NaOH and 0.5 mol L^{-1} Na_2SO_4 . An anodic peak with a large current

appears at 0.5 V for the first cycle (curve 1), and then the anodic peak current decreases quickly for the second cycle (curve 2). However, the anodic peak current increases again at the third cycle (curve 3) and remains almost unchanged afterwards. Figure 2 also shows that the anodic peak gradually becomes broader as the potential cycle increases from the eleventh to the fifty first one. This is caused by the low conductivity of polyphenol, since phenol was polymerized on the polymer film in this case. As a result, the anodic peak current changes a little, but the oxidation potential of phenol increases with increasing potential cycles. The above result indicates that the polymer film grows with elapse of time. The cyclic voltammograms in Fig. 2 are quite different from those shown in Fig. 1. This difference is caused by the concentration of NaOH. After electrolysis, a thick film with deep yellow color was found at the working electrode. The thickness of this polymer film is dependent on the time of electrolysis. It is evident that no reduction peak appears in Fig. 2. This is because the polymerization of phenol is irreversible and polyphenol is electrically inactive.

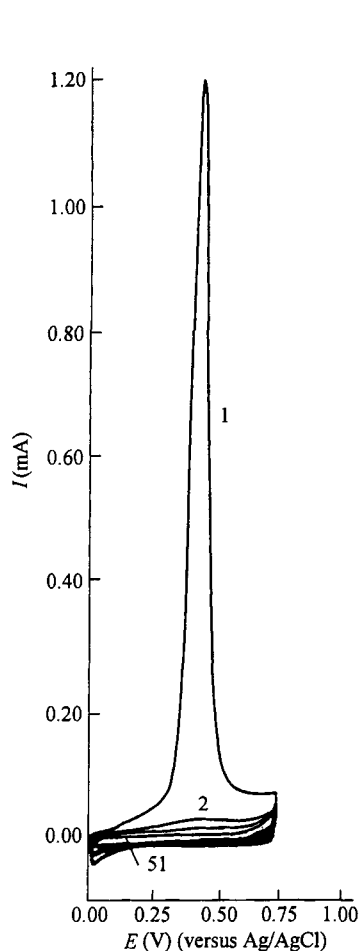


Fig. 1 The cyclic voltammograms of phenol, the solution consisting of 0.1 mol L^{-1} phenol, 0.15 mol L^{-1} NaOH and 0.5 mol L^{-1} Na_2SO_4 . The numbers on the curves in the plot correspond to the number of the cycle.

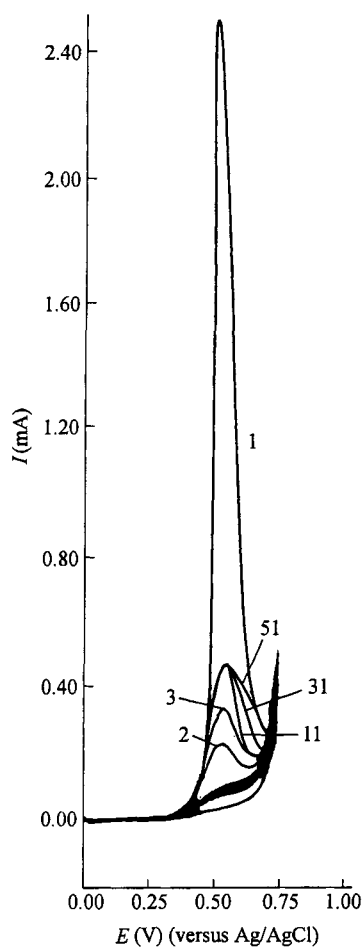


Fig. 2 Cyclic voltammograms of polyphenol film growth from the solution containing 0.1 mol L^{-1} phenol, 3 mol L^{-1} NaOH, and 0.5 mol L^{-1} Na_2SO_4 . The numbers on the curves in the plot correspond to the number of the cycle.

Preparation of Polyphenol at Constant Potentials

In view of the results shown in Fig. 2, the electrolysis of phenol was carried out at 0.65, 0.70 and 0.75 V. The electrolytic solution consisted of 0.1 mol L^{-1} phenol, 3 mol L^{-1} NaOH and 0.5 mol L^{-1} Na_2SO_4 . The solution was

stirred at about 300 r/min. Figure 3 shows the change of current with respect to time during the electrolysis of phenol. The oxidation current of phenol at each potential increases slowly as the electrolysis proceeds. This result confirms that polyphenol film in 3 mol L⁻¹ NaOH can grow continuously with elapse of time. The increase of the oxidation current with time in Fig. 2 and Fig. 3 may be caused by polyphenol itself, which catalyzes the electrochemical polymerization of phenol similar to the electrochemical polymerization of aniline^[15-17].

After electrolysis for 7 h at 0.70 V, a polyphenol film of 0.11 mm thickness was obtained. The cumulative charge passed during the period of the electrolysis process was 16.26 C. After electrolysis, the colorless electrolytic solution turned yellow, indicating a part of the polyphenol deposited on platinum foil was dissolved into the solution.

Preparation of Polyphenol at Constant Currents

To prove further whether the electrochemical polymerization of phenol is a catalytic reaction or not, the best approach is to perform electrolysis at constant current. The solution used for the electrolysis in this case is the same for as the experiment at constant potential. The solution was also stirred. The current was controlled at 0.30 (curve 1 in Fig. 4) and 0.45 mA (curve 2 in Fig. 4), and the area of the working electrode was also 4 × 4 mm². Figure 4 shows the change in the potential of the working electrode with time. After the onset of the electrolysis, the potentials on both curve 1 and curve 2 increase first, and then decrease at different rates with respect to time. The potential decreases more quickly at 0.3 mA (curve 1) than at 0.45 mA (curve 2). This is due to the fact that the electrode was polarized more easily at higher current density. The decrease of potential during the electrolysis at constant current is strong evidence for electrocatalysis. Therefore, the electrochemical polymerization of phenol in 3 mol L⁻¹ NaOH solution is a autocatalytic reaction. The catalyst is polyphenol itself.



This is why polyphenol film can grow continuously with time, but this catalytic effect is much weaker than that of polymerization of aniline in the acidic solution^[16].

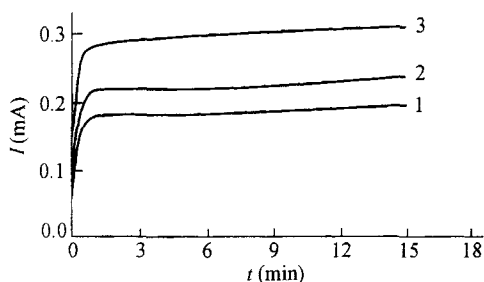


Fig. 3 Relationship between the current and time during the electrolysis of phenol solution at different potentials, the solution consisting of 0.1 mol L⁻¹ phenol, 3 mol L⁻¹ NaOH and 0.5 mol L⁻¹ Na₂SO₄. Curves: (1) 0.65, (2) 0.70, (3) 0.75 V (versus Ag/AgCl with saturated KCl solution).

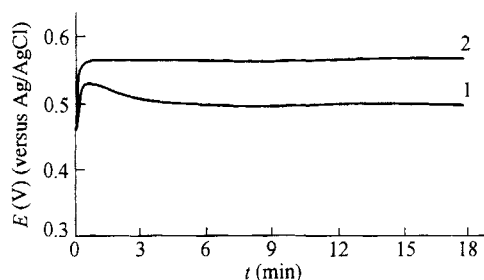


Fig. 4 Relationship between the potential and time during the electrolysis of phenol solution at different current densities, the solution consisting of 0.1 mol L⁻¹ phenol, 3 mol L⁻¹ NaOH and 0.5 mol L⁻¹ Na₂SO₄. Curves: (1) 0.3 mA, (2) 0.45 mA, the area of the working electrode is 4 × 4 mm².

The results in Fig. 4 bring about another valuable information on the polymerization potential of phenol. From Fig. 4, we can see that the polymerization potential of phenol in 3 mol L⁻¹ NaOH solution is 0.50 (curve 1) and 0.57 V (curve 2), respectively, *i.e.*, depending on the current density. In general, the passivating layers of polyphenol were formed in the potential region of 0.9 to 2.0 V (versus SCE)^[5, 9, 12], which is much higher than those values shown in Figs. 2, 3, and 4. This difference is caused by the alkaline concentration. At such low potentials, the electrode in this case can not be passivated. This is reason why the polyphenol film grows continuously during the electrochemical polymerization of phenol in a concentrated solution of NaOH.

Visible Spectra during Polymerization of Phenol

The electrolysis was carried out at 0.75 V and the measurements of visible spectra were carried out at an interval of 3 min between two measurements. Figure 5 shows the visible spectra during the polymerization of phenol. The peak at 390 nm grows with time. This peak is attributed to polyphenol deposited on the ITO working electrode.

Figure 6 shows the relationship between absorbance of polyphenol film at 390 nm and time. It is clear that the absorbance first increases linearly with time. This indicates that the thickness of polyphenol film grows with time. This result is in good agreement with that in Fig. 3, in which the oxidation current increases with time.

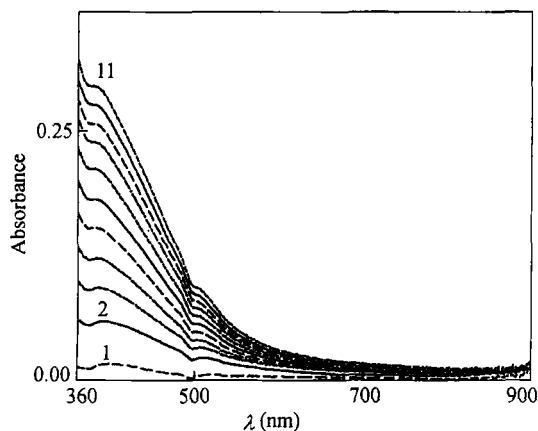


Fig. 5 Visible spectra during polymerization of phenol, at 0.75 V, the solution consisting of 0.1 mol L⁻¹ phenol, 3 mol L⁻¹ NaOH and 0.5 mol L⁻¹ Na₂SO₄. Curves: (1) first scan, (2) second scan, (11) eleventh scan

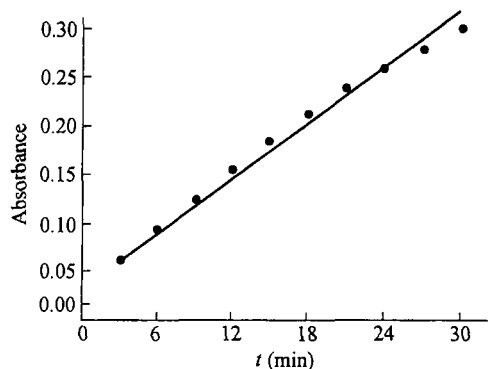


Fig. 6 Relationship between absorbance of polyphenol film at 390 nm and time during the electrolysis, based on the results in Fig. 5

Electrochemical Study of Polyphenol using Cyclic Voltammetry

The electrochemical property of polyphenol was examined using cyclic voltammetry. The experiments were carried out in 0.5 mol L⁻¹ Na₂SO₄ solutions with pH values ranging from 1.0 to 13.0. The scan potential was controlled between -0.20 and 1.20 V for pH 1.0 to 4.0, and -0.70 and 0.85 V for pH 5.0 to 13. The scan potential was set between -0.10 and 1.35 V in 2 mol L⁻¹ H₂SO₄ solution, and between -0.95 and 0.45 V in 3 mol L⁻¹ NaOH solution. The results show that polyphenol was neither oxidized nor reduced, and the film was undestroyed in these solutions within the potential ranges. This means that polyphenol is very inactive in the acidic and basic solutions within a wide potential region. Polyhydroquinone and poly(4-methoxyphenol) are the single-ion-conducting solid polymer electrolytes. So polyphenol synthesized in this manner may be a solid polymer electrolyte.

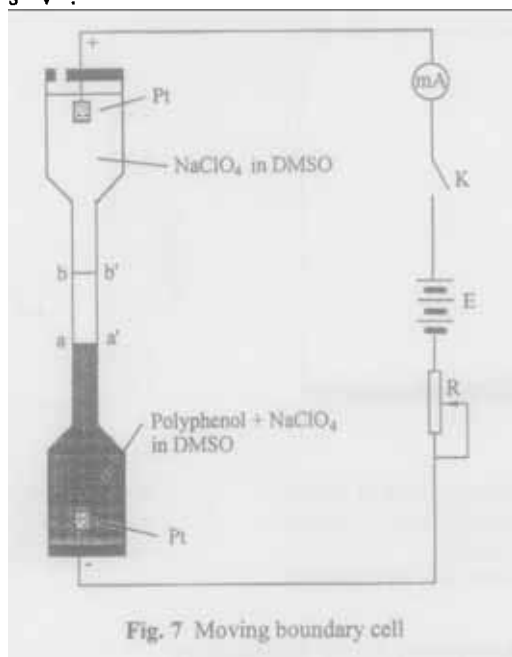
ESR Spectrum and Conductivity of Polyphenol

Polyphenol was stored for 20 days at room temperature before the ESR experiment. The ESR spectrum shows a single line, and its signal is asymmetric. The calculated *g* factor is 2.0049, which is close to the free electron value. It is clear that polyphenol possesses unpaired electrons. The peak-to-peak line width ΔH_{p-p} is about 0.5 mT, which is much larger than 0.2 mT for polyaniline.

The conductivity of polyphenol was found to be 1.2×10^{-4} S cm⁻¹ at 10°C, which is much lower than those of polyaniline and polypyrrole.

The solubility of polyphenol in *N*-dimethylformamide (DMF), chloroform and dimethyl sulfoxide (DMSO) was determined at 20°C to be 6, 15 and 30 mg in 10 mL of each solvent, respectively. To prove whether polyphenol radicals carry positive or negative charges, the DMSO solution of polyphenol was studied by the moving boundary method. Figure 7 shows schematically the diagram of the moving boundary cell. The polyphenol solution containing 0.01 mol L⁻¹ NaClO₄ was introduced into the bottom of the transfer tube. A

solution of $0.01 \text{ mol L}^{-1} \text{ NaClO}_4$ in DMSO was placed above the layer of the solution to be studied. A sharp boundary was established between the two solutions, the upper layer was colorless and the lower layer was brown. Two platinum foils were used as a cathode and an anode, respectively. When a current was applied to the cell, the brown boundary moved upwards toward the anode. During electrolysis, the boundary always remained sharp. The above result indicates that polyphenol in the solution is negatively charge. Based on the distance of the boundary movement, the transfer time, the electric field of unit strength, the mobility of polyphenol anions was calculated to be $8 \times 10^{-9} \text{ m}^2 \text{ s}^{-1} \text{ V}^{-1}$.



The results from the ESR of polyphenol and the moving boundary method of polyphenol in DMSO give strong evidence that polyphenol is a polymer with anion radicals.

FTIR Spectrum of Polyphenol

Figure 8 is the FTIR spectrum of polyphenol showing main peaks at 3377, 1586, 1488, 1454, 1384 (small shoulder), 1209, 1162 (small peak), 892, 818, 745 and 687 cm^{-1} , respectively.

In order to assign the IR peaks of polyphenol, the IR spectrum of phenol monomer is used^[18]. Its IR peaks appear at 3340, 1590, 1500, 1470, 1360, 1230 with a small shoulder at 1208, 1070, 1025, 1000, 880, 810, 740 and 685 cm^{-1} , respectively.

The main difference between IR spectra of polyphenol and phenol monomer is as follows: a prominent peak (1360 cm^{-1}) with very small shoulders appears in the IR spectrum of phenol, which is attributed to O—H in-plane bending vibration — this peak disappears in Fig. 8, where only a very small peak at 1384 cm^{-1} occurs instead; a strong broad peak at 1230 cm^{-1} with a small shoulder at 1208 cm^{-1} in the spectrum of phenol is attributed to C—O asymmetric stretching vibrations^[19] — only a strong, sharp peak at 1208 cm^{-1} occurs in Fig. 8. This strong peak also occurs in the IR spectrum of polyphenol synthesized in the acidic solution^[20]. The peak at 1188 cm^{-1} is assigned to the C—O—C stretch in the IR spectrum of poly(2-6 dimethyl phenol) synthesized in alkaline methanolic solution^[13], and the strong, broad and resolved band at $900\text{--}1150 \text{ cm}^{-1}$ in the IR spectrum of polyphenol synthesized in aqueous carbonate solutions^[9], can be associated with ether C—O symmetric and asymmetric stretching vibration ($=\text{C}-\text{O}-\text{C}=\text{ring}$)^[9, 21]. Hence the peak at 1208 cm^{-1} in Fig. 8 can be attributed to C—O—C stretching vibrations. Two weak peaks at 1070 and 1025 cm^{-1} occur in the IR spectrum of phenol, which also are attributed to the C—O stretching vibrations^[18], however, they disappear in Fig. 8. A weak peak at 1000 cm^{-1} attributable to the C—H in-plane bending vibration occurs in the IR spectrum of phenol, but

this peak does not appear in Fig. 8. Four peaks in the region of $650\text{--}900\text{ cm}^{-1}$ occur in Fig. 8 as well as in phenol monomer. They can be assigned to the aromatic C—H out-of-plane bending vibrations. This indicates that the IR spectrum of polyphenol in this region is in correspondence with that of phenol monomer.

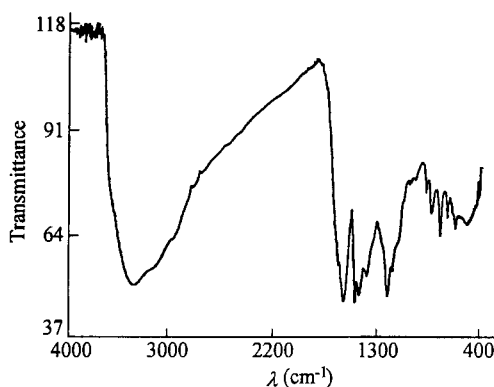


Fig. 8 FTIR spectrum of polyphenol

According to the above results, we can conclude that the difference between the IR spectra of polyphenol and phenol monomer mainly occur in the region of $900\text{--}1360\text{ cm}^{-1}$. After polymerization, the number of peaks in this region was reduced. This is to be expected since the polymerization of the monomer took place. And the wavenumbers of FTIR peaks of polyphenol below 1208 cm^{-1} are higher than the corresponding ones of phenol.

The IR spectrum of polyphenol depends on the conditions of polymerization of phenol. For example, the feature of the IR of polyphenol obtained by the electropolymerization of phenol in carbonate medium is that the intensity of the band at 3300 cm^{-1} decreased markedly with respect to the phenol monomer spectrum, two strong sharp peaks occurred in the region of $2800\text{--}3000\text{ cm}^{-1}$ and a very strong, broad band occurred at about 980 cm^{-1} ^[9]. It is clear that this IR spectrum is much different from that in Fig. 8. However, the IR spectrum in Fig. 8 is similar to that of polyphenol obtained by the electrochemical polymerization of phenol in the acidic solution^[19], but in the latter a sharp peak appeared in the region of $2800\text{--}3000\text{ cm}^{-1}$, and this peak does not occur in Fig. 8. The above results indicate that the structure of polyphenol was strongly affected by the medium used for the electrolysis of phenol, which may be caused by the different polymerization mechanisms.

The polymerization mechanisms of phenol and its derivatives in various media have been presented^[1, 10, 11]. As mentioned above, the polymerization of phenol was mainly carried out via head-to-tail coupling^[1]. In the basic solution, the polymerization of phenol or its derivatives is performed via the phenate radicals^[1, 12]. In this work, the polymerization of phenol was carried out in the concentrated solution of NaOH, so its polymerization mechanism may be similar to those of polyphenol obtained in the basic media^[1], *i.e.*, the polymerization of phenol in our case is also mainly carried out via head-to-tail coupling. The results from the spectra of ESR and FTIR (Fig. 8), and the moving boundary experiment indicate that polyphenol synthesized in the concentrated solution of NaOH is a polymer containing O—H group and C—O—C bond with anion radicals. Its structure is rather complicated. The polyphenol anion radical like polyaniline cation radical^[20] is very stable in air, since it was stored for a long time before the measurement of ESR.

The formation of polyphenol passivating layer in the basic medium was accounted for by the coupling between radicals, and the reaction center remaining continually in the vicinity of the electrode^[1]. In our case, polyphenol anion radicals are very stable, which is very favorable for chain propagation during the polymerization of phenol. It results in continuous growth of polyphenol film. So a very thick polyphenol film can be easily synthesized.

In general, cation radicals are rather stable under strongly acidic conditions, and the anion radicals formed in the charge transfer step may be long-lived in aprotic media^[22]. Polyphenol anion radicals formed in the concentrated solution of NaOH are also very stable in our case. This gives us a clue that the strongly basic

solution is of advantage for the formation of anion radicals.

CONCLUSION

The polymerization of phenol was carried out at lower potentials and in concentrated basic solution, and polymer film grows with time as the electrolysis proceeds. The results differ considerably from those of electrochemical polymerization of phenol in basic solutions of low concentration, in which the polymerization was carried out at higher potentials, and the polymerization rate decreases continuously with time very quickly. Therefore, the electrochemical polymerization of phenol is markedly affected by the alkaline concentration. The presence of Na_2SO_4 in the electrolytic solution is favorable for the polymerization rate of phenol. Polyphenol obtained here is an inactive polymer in the wide pH range and potential regions, but has a certain conductivity. The polymerization mechanism of phenol in the concentrated solution of NaOH and the structure of polyphenol are very complicated. Thus, further study is necessary on the polymerization mechanism and the structure of polyphenol.

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REFERENCES

- 1 Bruno, F., Pham, M.C. and Dubois, J.E., *Electrochim. Acta.*, 1977, 22: 451
- 2 Pham, M.C., Dubois, J.E. and Lacaze, P.C., *J. Electroanal. Chem.*, 1979, 99: 331
- 3 Dubois, J.E., Lacaze, P.C. and Pham, M.C., *J. Electroanal. Chem.*, 1981, 117: 233
- 4 Mengoli, G., Daolio, S., Giulio, U. and Folonari, C., *J. Appl. Electrochem.*, 1979, 9: 483
- 5 Mengoli, G., Musiani, M.M. and Furlanetto, F., *J. Electrochem. Soc.*, 1990, 137: 162
- 6 Mengoli, G. and Musiani, M.M., *J. Electrochem. Soc.*, 1992, 139: 2736
- 7 Glarum, S.H. and Marshall, J.H., *J. Electrochem. Soc.*, 1985, 132: 2939
- 8 Santlebury, J.D., Ashworth, V. and Yap, B., *J. Oil Color Chem. Ass.*, 1978, 61: 335
- 9 Lapuente, R., Cases, F., Garcés, P., Morallón, E. and Vázquez, J.L., *J. Electroanal. Chem.*, 1998, 451: 163
- 10 Wang, J., Jiang, M. and Lu, F., *J. Electroanal. Chem.*, 1998, 444: 127
- 11 Gattrell, M. and Kird, D.W., *J. Electrochem. Soc.*, 1993, 140: 903
- 12 Pham, M.C., Lacaze, P.C. and Dubois, J.E., *J. Electrochem. Soc.*, 1984, 131: 777
- 13 Pham, M.C., Adami, F. and Dubois, J.E., *J. Electrochem. Soc.*, 1987, 134: 2166
- 14 Mandal, B.K., Walsh, C.J., Sooksimuang, T. and Behrooz, S.J., *Chem. Mater.*, 2000, 12: 6
- 15 Stilwell, D.E. and Park, S.M., *J. Electrochem. Soc.*, 1988, 135: 2254
- 16 Mu, S.L. and Kan, J.Q., *Electrochim. Acta.*, 1996, 41: 1593
- 17 Kan, J.Q. and Mu S.L., *Acta Polymerica Sinica* (in Chinese), 1989, (4): 466
- 18 "Standard Infrared Grating Spectra", Sadtler Research Laboratories, Inc., Philadelphia, 1980, Vol.1-2, spectrum165k
- 19 Morrison, R.T. and Boyd, R.N., "Organic Chemistry", Second Edition, Allyn and Bacon, Inc., Boston, 1972, p.691
- 20 Mengoli, G. and Musiani, M.M., *J. Electrochem. Soc.*, 1987, 134: 634
- 21 Socrates, G., "Infrared Characteristic Group Frequencies", John Wiley and Sons, New York, 1994
- 22 Baizer, M.M. and Lund, H., "Organic Electrochemistry", Marcel Dekker, Inc., New York, 1983, p.194