

## SYNTHESIS OF POLYCATECHOL WITH ELECTROCHEMICAL ACTIVITY AND ITS PROPERTIES

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**Abstract** The electrochemical polymerization of catechol on platinum has been carried out using repeated potential cycling between  $-0.2$  and  $1.1$  V (versus SCE). The electrolytic solution consisted of  $0.2 \text{ mol dm}^{-3}$  catechol,  $0.5 \text{ mol dm}^{-3}$  NaCl and  $0.1 \text{ mol dm}^{-3}$   $\text{Na}_2\text{HPO}_4$  with pH 8.72. Catechol can not be polymerized at pH  $\geq 10.12$ . Polycatechol has an electrochemical activity at pH  $\leq 4$ . The anodic and cathodic peak potentials of polycatechol shift towards more negative values as the pH of the solution increases from 1 to 4. The electrochemical activity of polycatechol hardly changes in this pH region, but it decreases slowly with time. This is caused by oxygen in air, which leads to an irreversible oxidation of polycatechol. This property is favorable for protecting metals from corrosion. Raman and FTIR spectra of polycatechol and catechol are quite different. AFM images of polycatechol films provide evidence that the image of the oxidized state of polycatechol is markedly different from that of the reduced one. This difference is caused by doping and dedoping of polycatechol.

**Keywords** Catechol, Polycatechol, Electrochemical activity, Raman spectra, FTIR spectra, AFM images

### INTRODUCTION

The anodic oxidation of phenol and phenol derivatives in basic and alcoholic media has been studied extensively by Pham and Lacaze *et al.* using various metals as electrodes<sup>[1, 2]</sup>. It was found that a passivation layer, in fact a polymer layer without electrochemical activity, was formed on the metal surface during the oxidation process, which plays an important role in protecting metals from corrosion<sup>[3–5]</sup>. In general, the polymeric passivation layers were very thin ( $5 \text{ nm}$  to  $15 \text{ }\mu\text{m}$ ). Most polymerizations of phenol and phenol derivatives were carried out at a large scan potential ranging from  $-0.2$  to  $2.0$  V (versus SCE)<sup>[5]</sup> and in a weakly basic solution, such as in  $0.15 \text{ mol dm}^{-3}$  NaOH solution<sup>[3]</sup>,  $0.1 \text{ mol dm}^{-3}$   $\text{Na}_2\text{CO}_3$  solution<sup>[4]</sup> and phosphate buffer with pH 7.4<sup>[5]</sup>. Only a few papers reported that the polymerization of phenol derivatives was performed in acidic solution<sup>[6]</sup>. 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 to the hydroxyl group were occupied<sup>[1]</sup>. This means that the polymerization of phenol and phenol derivatives is mainly carried out via head-to-tail coupling.

However, polymers from catechol derivatives polymerized on carbon substrates were electroactive, and have been used as biosensor materials and a mediator for the redox of  $\text{NAD}^+/\text{NADH}$ <sup>[7–9]</sup>. Davis *et al.* reported the electrochemical polymerization of catechol and its derivatives on a glassy carbon electrode and the effect of ethylene diamine on the polymerization of catechol and the properties of polymers<sup>[10]</sup>. These polymers

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polymerized on the glassy carbon electrode were also electroactive. The above results indicated that whether polycatechol had electroactivity or not was strongly dependent on the electrode material used. Recently, the polymerization of catechol in the presence of silver surface has been reported<sup>[11]</sup>, for which a possible polymerization mechanism was suggested.

We found that phenol in  $3 \text{ mol dm}^{-3}$  NaOH can be polymerized on platinum at the scan potential range of 0 to 0.8 V (versus SCE), and that its film grows quickly with time during the electrolysis process<sup>[12]</sup>. Polyphenol obtained in this condition has a conductivity of  $2.1 \times 10^{-5} \text{ S cm}^{-1}$ , but has no electrochemical activity. This indicates that the polymerization mechanism of phenol and the properties of polyphenol are strongly affected by the electrolytic conditions.

Considering the fact that catechol can be polymerized, and the polymerization of phenol is strongly affected by the electrolytic conditions, the electrochemical polymerization of catechol in aqueous solution was also attempted using platinum as a working electrode.

## EXPERIMENTAL

The chemicals used were all reagent grade. Doubly distilled 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 were referred to the saturated calomel electrode (SCE).

A Model HPD-1A potentiostat-galvanostat was used for the cyclic voltammetry. The cyclic voltammograms were recorded using a YEW Model 3036 X-Y recorder. FTIR spectra of catechol and polycatechol were measured on KBr pellets using a Nicolet 740 FTIR instrument and Raman spectra of catechol and polycatechol were determined using Lab Ram I spectrometer. The Atomic Force Microscope (AFM) images of the polycatechol films deposited on platinum foils were recorded using a Nanoscope III instrument. All experiments were performed at room temperature.

## RESULTS AND DISCUSSION

### *Effects of Composition and pH Value of the Electrolytic Solution on Polymerization*

Figure 1 shows the cyclic voltammograms for the electrolysis of catechol. The electrolytic solution consisted of  $0.2 \text{ mol dm}^{-3}$  catechol,  $0.5 \text{ mol dm}^{-3}$  NaCl and  $0.1 \text{ mol dm}^{-3}$   $\text{Na}_2\text{HPO}_4$  with pH 8.72. There are two anodic peaks at 0.35 and 0.90 V on curve 1 for the first cycle. The first anodic peak at 0.35 V is attributed to the oxidation of catechol at the bare platinum. When the potential is over 0.5 V, the anodic current increases quickly with further increasing potential. This indicates that the second oxidation peak is caused by the polymerization of catechol. From Fig. 1, we can see that the anodic current decreases with increasing number of potential cycles. Finally, a brown film of polycatechol was formed on the working electrode.

Cyclic voltammetry for the electrolysis of the solution containing  $0.2 \text{ mol dm}^{-3}$  catechol and  $0.5 \text{ mol dm}^{-3}$  NaCl with pH 8.72 was carried out. There are two anodic peaks at 0.09 V and 0.95 V and a cathodic peak at 0.12 V for the first cycle (omitted here), which is different from curve 1 in Fig.1. This indicates that the presence of  $\text{Na}_2\text{HPO}_4$  affects the redox of catechol in the low potential range and the polymerization potential of catechol. After electrolysis, a brown film was also found on the working electrode.

Cyclic voltammetry for the electrolysis of the solution containing  $0.2 \text{ mol dm}^{-3}$  catechol and  $0.1 \text{ mol dm}^{-3}$   $\text{Na}_2\text{HPO}_4$  with pH 8.72 was performed. Its cyclic voltammograms are very similar in shape to those in Fig. 1. Only the oxidation current during electrolysis process is smaller than that in Fig. 1. This is caused by the low conductivity of the solution. Sodium chloride is a supporting electrolyte, which plays an important role in increasing the conductivity of solution. Based on the above results, the polymerization of catechol in the following experiments is carried out in a solution consisting of  $0.2 \text{ mol dm}^{-3}$  catechol,  $0.5 \text{ mol dm}^{-3}$  NaCl and  $0.1 \text{ mol dm}^{-3}$   $\text{Na}_2\text{HPO}_4$ .

The effect of pH value on the polymerization of catechol is performed in the pH range of 1 to 10. The cyclic voltammograms for the electrolysis of catechol at pH 1.03 show that there are an anodic peak at 0.68 V and a

cathodic peak at 0.28 V on the  $i$ - $E$  curves (omitted here). An anodic peak in the low potential range disappears. This means that catechol at pH 1.03 is directly polymerized without the formation of an intermediate, because of protonation of catechol. Even an anodic peak and a cathodic peak appear on the cyclic voltammogram during the polymerization process in this case, which is different from the electrochemical polymerization of catechol on the glassy carbon electrode in 0.1 mol dm<sup>-3</sup> phosphate buffer of pH 7 as mentioned above<sup>[10]</sup>, in which an anodic peak and a cathodic peak for the first cycle appear at 0.30 and 0.15 V (versus Ag/AgCl), respectively. In order to verify the cause of this difference, the electrochemical polymerization of catechol in the above electrolytic solution with pH 7.0 was carried out using a platinum electrode and a glassy carbon electrode. The results show that a small anodic peak at 0.35 V, a large anodic peak at 1.0 V and a small cathodic peak at 0 V occurred on the first cycle for the glassy carbon electrode; the cyclic voltammogram for the polymerization of catechol at the platinum electrode is similar to that at the glassy carbon electrode, but the second anodic peak at the platinum electrode is at 0.88 V for the first cycle. This indicates that the above difference is caused by the nature of the electrode material, the composition of the electrolytic solution and the pH value. After the electrolysis, a polymer film is also found on the glassy carbon electrode.

The cyclic voltammograms for the electrolysis of catechol at pH 5.78 (omitted here) are similar to those at pH 1.03. A small difference is that a small anodic peak at 0.27 V appears on the cyclic voltammogram, which is caused by the oxidation of catechol to quinone.

Figure 2 shows the cyclic voltammograms for the electrolysis of catechol at pH 10.12. There is only one anodic peak at 0.07 V. After electrolysis, no polymer film is formed. Thus, catechol at pH 10.12 can not be polymerized. Based on the above results, polycatechol used in the following experiments is synthesized in the solution containing 0.2 mol dm<sup>-3</sup> catechol, 0.5 mol dm<sup>-3</sup> NaCl and 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>HPO<sub>4</sub> with pH 8.72.

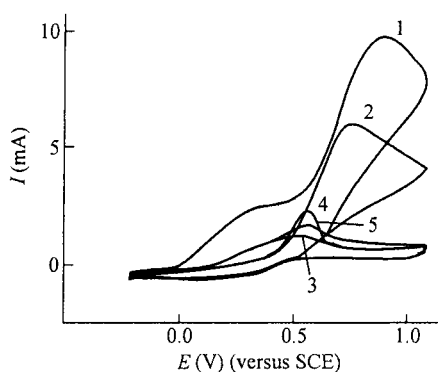


**Fig. 1** Film growth of polycatechol during electrolysis of the solution consisting of 0.2 mol dm<sup>-3</sup> catechol, 0.5 mol dm<sup>-3</sup> NaCl and 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>HPO<sub>4</sub> with pH 8.72

Curves: (1) first cycle, (2) second cycle, (3) twentieth cycle, (4) fiftieth cycle, (5) eightieth cycle

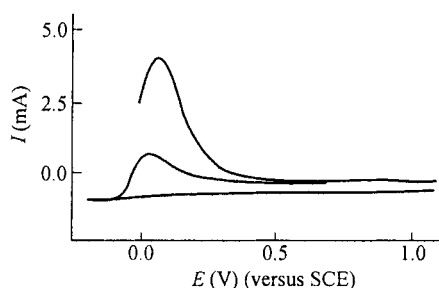


**Fig. 2** Cyclic voltammograms for electrolysis of the solution consisting of 0.2 mol dm<sup>-3</sup> catechol, 0.5 mol dm<sup>-3</sup> NaCl and 0.1 mol dm<sup>-3</sup> Na<sub>2</sub>HPO<sub>4</sub> with pH 10.12

Curves: (1) first cycle, (2) second cycle, (3) tenth cycle, (4) twentieth cycle

The above results show that the electrochemical polymerization behavior of catechol is strongly affected by the composition of the electrolytic solution, pH value and the electrode material. So the polymerization of catechol is rather complicated.

### Electrochemical Properties of Polycatechol

Figure 3 shows the cyclic voltammograms of polycatechol films and a bare platinum electrode in 0.5 mol dm<sup>-3</sup> NaCl solution of pH 1.0. Two pieces of polycatechol films synthesized at pH 8.72 (Curve 1) and pH 2.90 (Curve 2) were used in this experiment. The  $i$ - $E$  curve 1 is similar as curve 2 in shape. The differences between them are that the area under  $i$ - $E$  curve 2 is smaller than that of  $i$ - $E$  curve 1 and the relative intensity of the peak current at 0.33 V to another two anodic peak currents on curve 2 is smaller than that on curve 1. This result is in good

agreement with the above results of polycatechol films synthesized at pH 1.03 and 5.78. The shape of *i*-*E* curve 3 for a bare platinum electrode is much different from those of curves 1 and 2. This proves that polycatechol has electrochemical activity.

Figure 4 shows the pH dependence of cyclic voltammograms of polycatechol prepared at pH 8.72. Curves 1, 2, 3 and 4 show the cyclic voltammograms of polycatechol in 0.5 mol dm<sup>-3</sup> NaCl with pH 1.0, 2.0, 3.0 and 3.5, respectively. Both the anodic peak potential at 0.33 V and the cathodic peak potential at 0.29 V shift towards the negative direction with increasing pH value from pH 1.0 to 3.5. This indicates that the redox of polycatechol is related to the concentration of protons in the solution. This behavior is similar to that of polyaniline<sup>[13]</sup>. However, the anodic peak potential at 0.5 V is almost independent of pH value. The anodic peak current at 0.33 V (on curve 1) decreases and the cathodic peak current increases with increasing pH value, respectively. Even though the peak potentials and peak currents of polycatechol change with pH value, the area under each *i*-*E* curve changes slightly with pH value. In another words, the electrochemical activity of polycatechol in this pH region is almost independent of pH value.

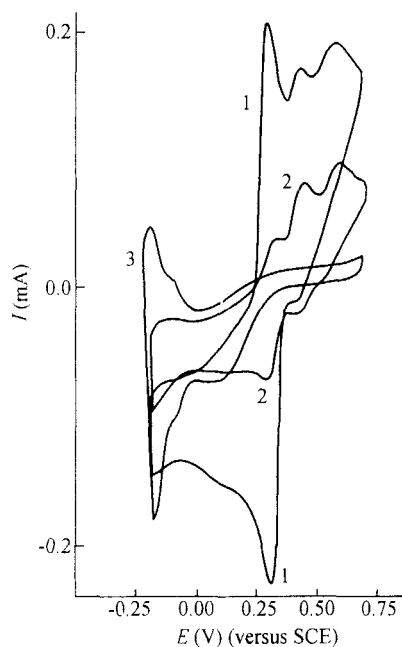


**Fig. 3** Cyclic voltammograms, 0.5 mol dm<sup>-3</sup> NaCl of pH 1.0  
Curves: (1) polycatechol synthesized at pH 8.72, (2) polycatechol synthesized at pH 2.9, (3) bare platinum

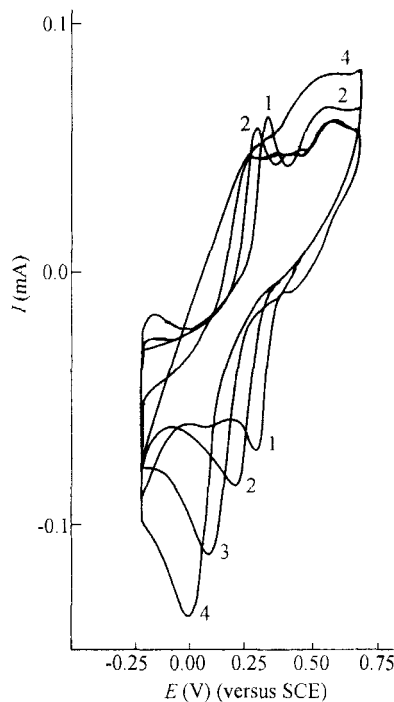


**Fig. 4** Cyclic voltammograms of polycatechol in 0.5 mol dm<sup>-3</sup> NaCl solution at various pH values, polycatechol prepared at pH 8.72  
Curves: (1) pH 1.0, (2) pH 2.0, (3) pH 3.0, pH 3.5

In order to test the stability, the cyclic voltammetry of polycatechol film polymerized on platinum was performed in 0.5 mol dm<sup>-1</sup> NaCl solution of pH 1.0. The potential was controlled between -0.2 and 0.6 V. After fifty cycles, a decrease in the anodic and cathodic peak currents was found. This indicates that polycatechol is not too stable.

To confirm further the stability, subsequent experiments were performed using the same solution as shown in Fig. 3. Curves 1, 2 and 3 in Fig. 5 show the cyclic voltammograms of freshly prepared polycatechol, and polycatechol kept in air for 1 and 3 days, respectively. The anodic peak at 0.33 V and the area under each *i*-*E* curve become smaller and smaller with respect to time. So the electrochemical activity of polycatechol decreases with time. The cyclic voltammogram of polycatechol, which has been kept in vacuum for 3 days, indicates that

there are still three anodic peaks. Only the peak at 0.33 V becomes smaller, but the area under the  $i$ - $E$  curve changes a little as compared with that of freshly prepared polycatechol. From the above results, we can conclude that the peak at 0.33 V is a probe of the oxidation of polycatechol. And the instability of polycatechol is caused by oxygen, which leads to an irreversible oxidation of polycatechol.

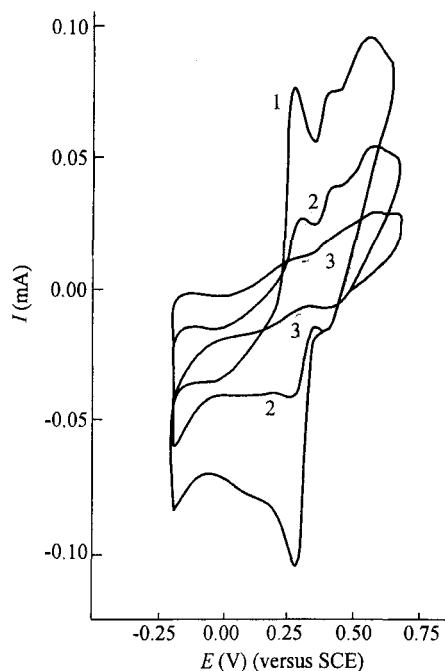


**Fig. 5** The change in the electrochemical activity of polycatechol with storage time  
CV was carried in  $0.5 \text{ mol dm}^{-3}$  NaCl solution of pH 1.0  
Curves: (1) freshly prepared polycatechol, (2) polycatechol stored in air for one day, (3) polycatechol stored in air for three days

### Raman Spectra

Figure 6 shows the Raman spectra of catechol, freshly prepared polycatechol and polycatechol kept in air for 3 days, respectively. There are several sharp peaks on spectrum 1. However, only two broad peaks at  $1375$  and  $1583 \text{ cm}^{-1}$  appear on spectra 2 and 3. This indicates that after polymerization, the vibrational modes are reduced. This is also a characteristic of polymerization for a monomer. In general, *ortho*-substituted aromatic compounds have a peak at  $1037 \text{ cm}^{-1}$ <sup>[14]</sup>. So the peak at  $1038 \text{ cm}^{-1}$  on spectrum 1 is attributed to the vibration of the *ortho*-substituted ring of catechol. However, this peak disappears on spectra 2 and 3. This means that one of the *o*-hydroxyl groups is occupied by the chain of the polymer after polymerization. The peak at  $1583 \text{ cm}^{-1}$  on each spectrum is attributed to the vibrations of phenyl ring deformation<sup>[15]</sup>. Its intensity is obviously enhanced after polymerization. This result is to be expected since the polymer molecules are composed of chains of repeating units of monomers, and they may have higher deformability than the monomers. The peak appearing at  $1375 \text{ cm}^{-1}$  in spectra 2 and 3 is a new peak, which is caused by the polymerization of catechol. This peak may be attributed to multi-ring deformation vibrations. So this peak is a characteristic of polymerization of catechol. The peak at  $1583 \text{ cm}^{-1}$  is also a criterion for the oxidation extent of polycatechol because the relative intensity of the peak at  $1375 \text{ cm}^{-1}$  to the peak at  $1583 \text{ cm}^{-1}$  is decreased with increasing storing time of polycatechol. This result is similar to that of the cyclic voltammogram of polycatechol, in which an anodic peak at 0.33 V is very sensitive to oxygen.

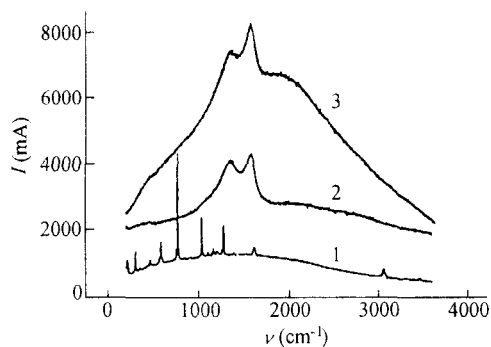


**Fig. 6** Raman spectra

Curves: (1) catechol, (2) freshly prepared polycatechol, (3) polycatechol was kept in air for three days

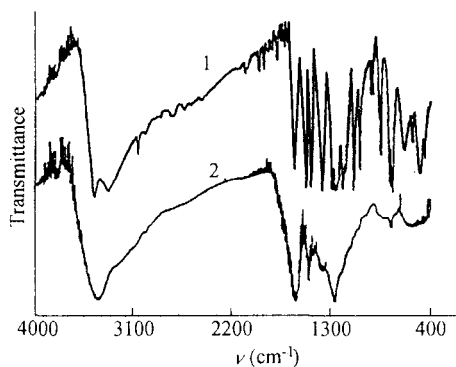


**Fig. 7** FTIR Spectra

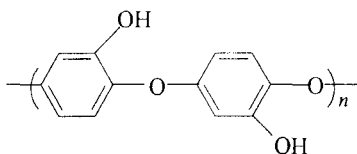
Curves: (1) catechol, (2) polycatechol

### FTIR Spectra

Figure 7 shows the FTIR spectra of catechol and polycatechol, respectively. Many peaks appear in spectrum 1, especially in the wavenumber range of 1360 to 500  $\text{cm}^{-1}$ . So the IR spectrum of catechol is very complicated. We will briefly assign some main peaks in spectrum 1. The peaks between 1700 and 1900  $\text{cm}^{-1}$  are caused by the oxidation of O—H groups in catechol. This is indicative of the presence of C=O groups, *i.e.*, catechol is partly oxidized to quinone.

A comparison between spectrum 1 and spectrum 2 shows that the number of absorption peaks of polycatechol is much less than that of catechol. This is a general feature for polymerization of a monomer. The  $\nu_{\text{OH}}$  peak at 3328  $\text{cm}^{-1}$  in spectrum 1 disappears in spectrum 2. This indicates that the polymerization of catechol may be carried out by eliminating one of the two O—H bonds in catechol and retaining the another one in polycatechol. A strong peak at 1260  $\text{cm}^{-1}$  may be attributed to the asymmetrical stretching vibration of C—O—C<sub>arom</sub> (1245  $\text{cm}^{-1}$ )<sup>[16]</sup> or =C—O—C (1250  $\text{cm}^{-1}$ )<sup>[17]</sup>. This indicates that a C—O—C bond is contained in the polymer. Spectrum 2 shows that the peak at 1260  $\text{cm}^{-1}$  is rather broad, extending between 1115 and 1320  $\text{cm}^{-1}$ , so the two peaks at 1040 and 1283  $\text{cm}^{-1}$  in spectrum 1 attributable to the stretching and bending vibrations of C—O bond<sup>[18]</sup> are overlapped by the 1260  $\text{cm}^{-1}$  peak in spectrum 2. In fact, the wavenumber range of the peak concentrated at 1612  $\text{cm}^{-1}$  is rather wide. The formation of this peak begins at about 1854  $\text{cm}^{-1}$ . This means that a carbonyl bond is present in the polymer, because of oxidation.

Based on the FTIR spectra shown in Fig. 7, we infer that the electrochemical polymerization of catechol proceeds via head-to-tail coupling similar to the electrochemical polymerization of phenol and phenol derivatives as mentioned above<sup>[1]</sup>. The structure of polycatechol is suggested as follows:

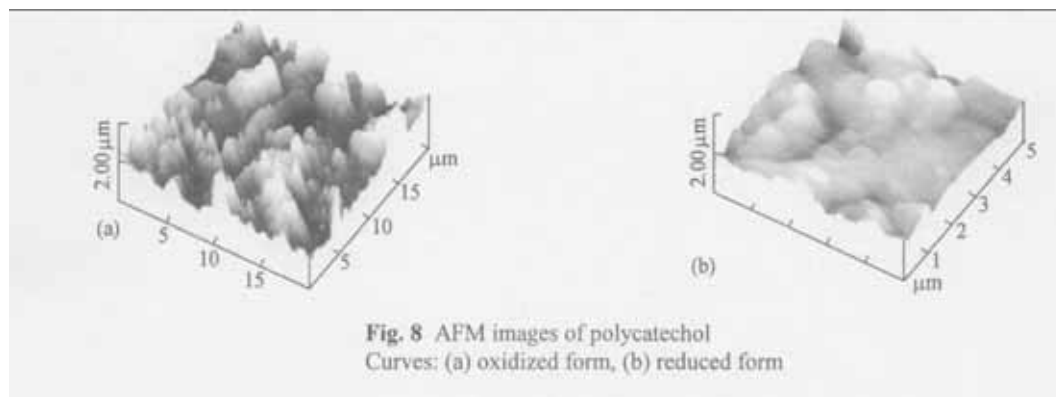


### AFM Image of Polycatechol

Figure 8(a) shows the AFM image of a freshly prepared polycatechol film, which is prepared using repeated potential cycling. Before stopping the electrolysis of catechol, the potential is kept at 1.1 V for 5 min. So this polymer film is in its oxidized state. From the photograph, we can see that the film surface consists of cylinders with a diameter of 1–5  $\mu\text{m}$ .

Figure 8(b) shows the image of the reduced polycatechol film, which is obtained by the reduction of

polycatechol film in  $0.5 \text{ mol dm}^{-3}$  NaCl of pH 1.0 at  $-0.20 \text{ V}$  for 5 min. Its image is also in cylindrical form. The difference between them is that almost all cylinders in (b) are planar. This may be caused by dedoping because the anions in the reduced polycatechol film have been mostly removed by the reduction. The feature that the images of both films have in common is that they contain certain cross-linked chains in the polymer.



## CONCLUSION

The electrochemical polymerization of catechol on platinum is carried out at the pH range of 1.03 and 10.12. Catechol can be polymerized between pH 1.03 and 8.72, but can not be polymerized at  $\text{pH} \geq 10.12$ . This is different from the result reported by Davis *et al.*<sup>[10]</sup>, in which catechol on the glassy carbon electrode can be polymerized in NaOH solution of pH 13. Polycatechol polymerized on platinum has electrochemical activity at  $\text{pH} \leq 4$ , but is not too stable in air. This is caused by oxygen, which leads an irreversible oxidation of polycatechol. Polycatechol may be oxidized to a certain extent to the quinone form. This property is favorable for protecting metals from corrosion.

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