



Electrochemical copolymerization study of *o*-toluidine and *o*-aminophenol by the simultaneous EQCM and in situ FTIR spectroelectrochemistry

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ABSTRACT

The electrochemical synthesis and characterization of a copolymer, poly(*o*-toluidine-co-*o*-aminophenol), were conducted using in situ piezoelectric FTIR spectroelectrochemistry. The monomer feed ratio strongly affects the copolymerization rate and the properties of the copolymer during the electrosynthesis in 0.5 M H₂SO₄ aqueous solution. The effects of scan rate and pH value on the electrochemical activity of the obtained copolymer were also studied. The copolymer synthesized in higher molar ratio of *o*-toluidine/*o*-aminophenol exhibited good electrical activity and stability in a broad pH range. The copolymerization mechanisms of *o*-toluidine and *o*-aminophenol were deduced. The copolymer formed through the head-to-tail coupling of the two monomers via –NH– groups was a new polymer rather than a mixture of poly(*o*-toluidine) and poly(*o*-aminophenol).

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1. Introduction

A great amount of attention has been paid to the development of conducting polymers such as polyaniline, polypyrrole, polythiophene, polyphenylene, poly(benzoxazole), due to their useful electronic properties in batteries, electronic devices, functional electrodes, electrochromic devices, optical switching devices, sensors and so on [1–8]. Among conducting polymers, polyaniline (PANI) has received special attention owing to its good environmental stability and easily synthesized by chemical or electrochemical oxidation of aniline in acidic media [9]. PANI and the ring-substituted PANI derivatives are known to have three oxidation states: fully reduced, leucoemeraldine (LE); intermediately oxidized, emeraldine (E); and fully oxidized, permigraniline (PN). The last form is unstable in aqueous media and the polymer easily degrades to benzoquinone and oligomers [10]. Furthermore, each structure of these states is not only affected by electrochemical oxidation and reduction but also by possible

concomitant protonation–deprotonation of the nitrogen atom in polymer backbone, especially in an aqueous medium [11]. And the electrochemical and optical properties are also strongly dependent on the nature of surface morphology and molecular organization of the polymeric film [12,13]. It should be noticed that poly(*o*-toluidine) (POT) has been found to have an additional advantage over polyaniline due to its fast switching time between the oxidized and reduced states [14]. And the switching behavior of insulator/conductor of POT films synthesized by the electrochemical method has been extensively studied [15].

As the synthesized copolymers show quite different electrochemical characteristics from those of the homopolymers [16], copolymerization is considered to be an important method to develop new conductive materials and improve the properties of homopolymers. With regard to the polyaniline type copolymers, a pioneering work has been done by Wei et al. [17,18]. They reported that aniline could be copolymerized with *o*-toluidine (OT) to control conductivity in a broad range. Yang [9] has reported that the toluidines are more reactive than aniline in the copolymerization. Borole et al. [19] have also studied the copolymerization of aniline with toluidine and found that many physical characteristics of copolymer lie in between their individual homopolymers. Successful copolymerizations of *o*-toluidine with nitroaniline [20], phenylenediamine [21] and naphthylamine [22] have also been reported. The copolymer of aniline-*o*-anisidine-*o*-toluidine [23] has

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been used to construct biosensors. All these reports show that the electrochemical generation of copolymers is a convenient method to prepare new materials with the desired properties which are different from individual homopolymers. In order to investigate the electrochemical characteristic of toluidines and their copolymers more adequately, we studied the homo- and copolymerization processes of the OT and *o*-aminophenol (OAP) by in situ piezoelectric FTIR spectroelectrochemistry, which is a combination of the electrochemical quartz crystal microbalance (EQCM) technique and in situ FTIR spectroelectrochemistry.

In situ piezoelectric FTIR spectroelectrochemical combination method has been described in detail in our previous paper [24]. The electrical information such as potential, current, electric charge, resistance is obtained by traditional electrochemistry method through an electrochemical workstation. The piezoelectric information, such as resonance frequency and resistance, is obtained from EQCM. The distinguishing feature of EQCM technique is that the nanogram mass change at the electrode surface can be monitored dynamically without disturbing the electrochemical reaction. This technique has been widely used to study the electrochemical process, such as, electrocatalytic problems [25], deposition of polymers [26]. The frequency–mass relationship for loading or removal of a rigid and thin film depends on the Sauerbrey's equation [27]. For a 9 MHz (f_0) crystal used in this work, the mass changed about $\pm 5.5 \text{ ng cm}^{-2}$ when the frequency changes of $\pm 1 \text{ Hz}$ (minus/plus sign for mass increase/decrease, respectively). A net viscosidity effect on the loading of a Newtonian liquid can be characterized by [28,29] the slope value of Δf_{0L} versus ΔR_{1L} and for a net density/viscous effect on the 9 MHz PQC resonance is $\sim -10 \text{ Hz } \Omega^{-1}$, which is, in fact, characteristic of a net liquid-loading effect. It is expected that the larger the absolute value of $\Delta f_0/\Delta R_1$ the weaker the density/viscous effect and the stronger the mass effect reflected [29].

In situ FTIR spectroscopic method [30], which can also be called Fourier transform infrared reflection–absorption spectroscopy (FTIR-RAS), is powerful to identify the species concerned with the electrochemical redox process and has been widely used to study

the electrochemical mechanisms of different materials, such as aminophenol [31]. The combination of EQCM and in situ FTIR spectroscopic method could provide more complete information about electrode reaction, such as mass change and structure change of the species adhered on electrode surface, which is helpful to understand electrochemical processes at modified electrode [32,24]. In our lab, in situ piezoelectric FTIR spectroelectrochemistry (carried out with simultaneous QCM measurement and in situ FTIR spectroelectrochemistry) has been further developed and successfully used to study the polymerization and characterization of poly(aniline-co-*o*-aminophenol) [24]. In this paper, the copolymerization of the OT and OAP, and the properties of the homopolymer and copolymer were studied by in situ FTIR piezoelectric spectroelectrochemistry method.

2. Experimental

o-Toluidine (reagent grade, Shanghai, China) was distilled and stored under nitrogen. *o*-Aminophenol was from Merck (analytical grade, Germany). All of the solutions were used as received (analytical grade, Shanghai, China) and prepared by distilled water.

Electrochemical synthesis and characterization were carried out in a three-electrode cell using a CHI 660A electrochemical workstation (CH Instruments Co., USA) and a research quartz crystal microbalance (RQCM, Maxtek Inc., USA) on which the QCM frequency and resistance were recorded. At-cut 9 MHz piezoelectric quartz crystals (PQCs) gold plated on both sides (diameter: 12.5 mm-quartz; 6 mm-gold) were adapted. One side of PQC electrode in contact with a solution served as work electrode (WE) while the other side was located in the waterproof air compartment. A Pt foil and a saturated Ag/AgCl KCl electrode served as the counter electrode (CE) and reference electrode (RE) respectively. All potentials reported in the paper are according to this reference electrode. POT, POAP and poly(OT-co-OAP) films were deposited on the pretreated gold PQC electrodes by repeated potential cycling between -0.1 and 0.9 V in the polymerization bath

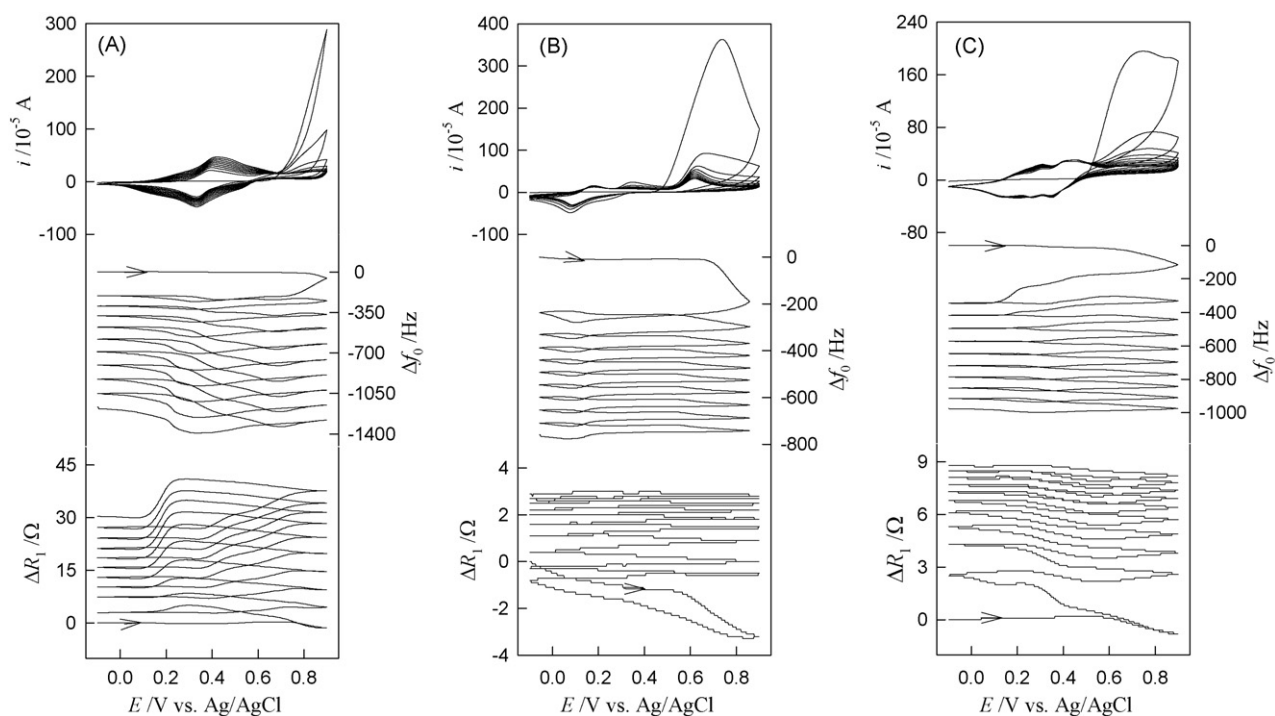


Fig. 1. Cyclic voltammograms and simultaneous Δf_0 and ΔR_1 responses during the electropolymerization of OT (A); OAP (B) and OT-co-OAP (C) in 0.2 M monomer and 0.5 M H_2SO_4 . Scan rate: 50 mV s^{-1} .

which contains 0.2 M monomer and 0.5 M H_2SO_4 at a scan rate of 50 mV s^{-1} .

A Nicolet Nexus 670 FTIR spectrometer (Nicolet Instrument Co., Madison, WI) equipped with an external reflection unit and a liquid nitrogen-cooled MCT detector was employed for the in situ piezoelectric FTIR measurements. The thin layer spectroelectrochemical cell with a prismatic CaF_2 window was made of PVC and was kept beveled at 60° . The PQC electrode mechanically polished to a mirror-like surface was pushed against the CaF_2 window and kept vertical to the plane of IR incidence light to form a thin electrolyte layer. And the thickness of the thin layer can be calculated from the oxidation/reduction of $\text{Fe}(\text{CN})_6^{3-}/\text{Fe}(\text{CN})_6^{4-}$ [24], giving the value of $\sim 10 \mu\text{m}$. The resolution of spectra was 8 cm^{-1} and the signal was presented as $\Delta R/R$.

3. Results and discussion

3.1. Electrosynthesis of POT, POAP and poly(OT-co-OAP)

3.1.1. Piezoelectrochemistry results during the electropolymerization

In order to confirm the deposition of polymer on the electrode surface, the electrochemical quartz crystal microbalance (EQCM) was used to monitor the process of electropolymerization of monomers. Fig. 1 shows the cyclic voltammograms (CVs) recorded during the electrosynthesis of POT, POAP and poly(OT-co-OAP) films in a solution of 0.5 M H_2SO_4 solution containing 0.2 M monomer or 0.2 M mixture, respectively. In the case of OT (Fig. 1A), an irreversible oxidation peak appeared at 0.8 V in the first cycle, indicating that the monomer was oxidized at the surface of the electrode. In the second and subsequent scans, the redox peak is observed at around 0.39/0.42 V, which is either due to the dimer soluble products [33] or to quinone/hydroquinone loosely surface bound hydrolysis products [34]. These products were grown into polymer during electrochemical deposition, which can be seen from the obvious frequency decrease in this potential region. Upon

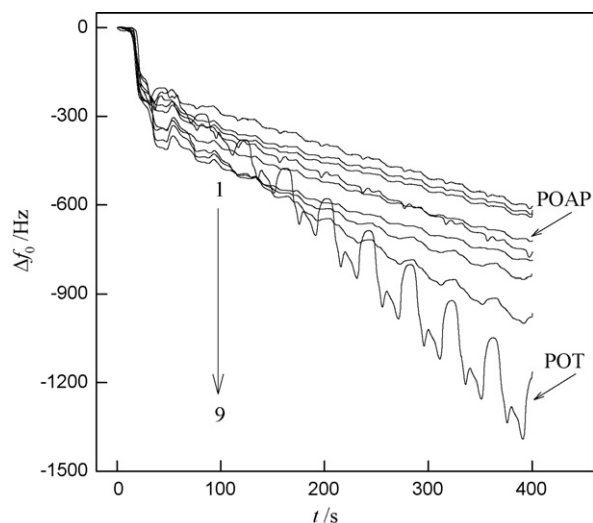


Fig. 2. Real time responses of frequency shift in the copolymerization solution with the different molar ratios of monomer during the copolymerization of OT-co-OAP. Scan rate: 50 mV s^{-1} . The numbers 1–9 represent the concentration ratios of OT:OAP = 0.1:0.1, 0.12:0.08, 0.15:0.05, 0.2:0.2, 0.14:0.06, 0.16:0.04, 0.18:0.02, 0.19:0.01 and 0.2:0 respectively. Total molarities: 0.2 M.

increasing the number of scan cycles, the peak currents and the polymerization rate ($\Delta f/\Delta t$) increase rapidly. This experimental phenomenon may be caused by the quick growth of POT film, which is due to the autocatalytic polymerization of OT [35]. After several potential cycles, green film was formed on PQC Au electrode surface.

Fig. 1B presents the responses obtained during the electropolymerization of OAP. An oxidation peak at ca. 0.7 V without a cathodic counterpart was observed and the frequency decreased during the first potential scan of OAP, which is consistent with the previous research [36,37]. During the subsequent cycling, the monomer oxidation peak at 0.7 V decreased and a new redox couple at 0.3/0.4 V

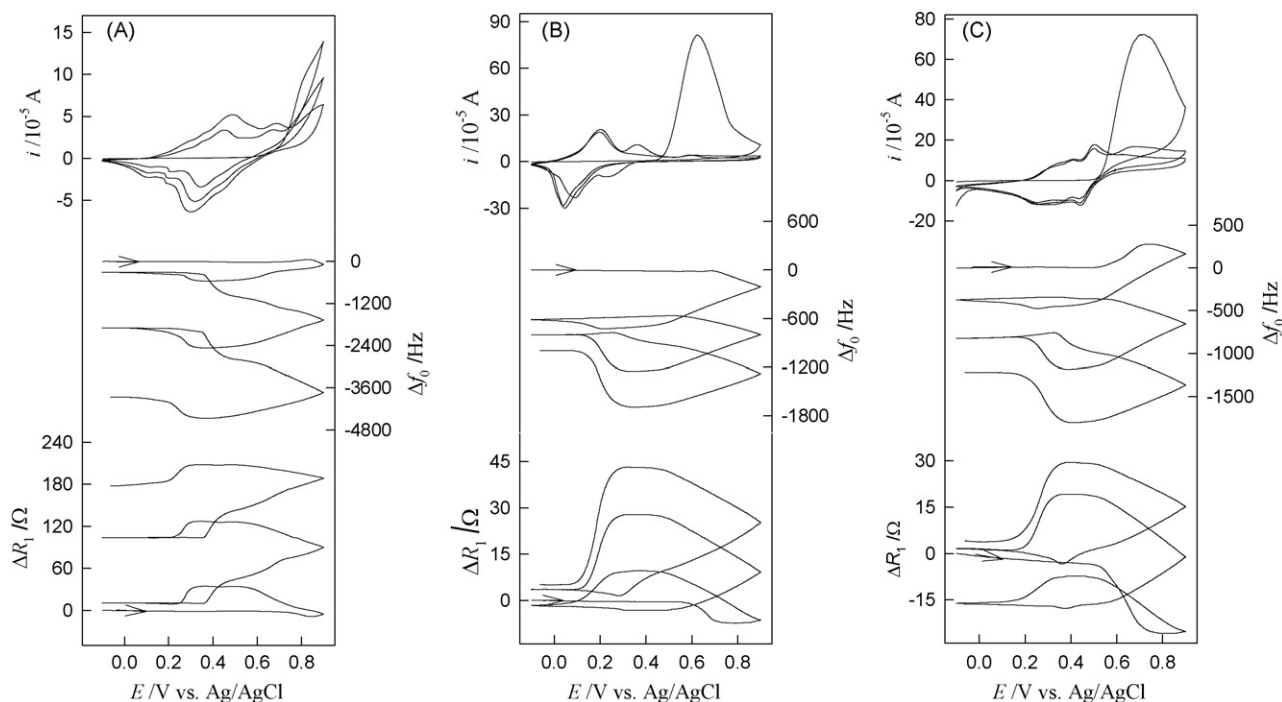


Fig. 3. Cyclic voltammograms curve and simultaneous of Δf_0 and ΔR_1 responses during potential cycling in polymerization solution containing 0.5 M H_2SO_4 and 0.2 M OT (A); 0.2 M OAP (B) or 0.2 M OT-co-OAP (C) in the thin layer cell. Scan rate: 5 mV s^{-1} . The OT-co-OAP solution was a mixture of 0.19 M OT and 0.01 M OAP in 0.5 M H_2SO_4 solution.

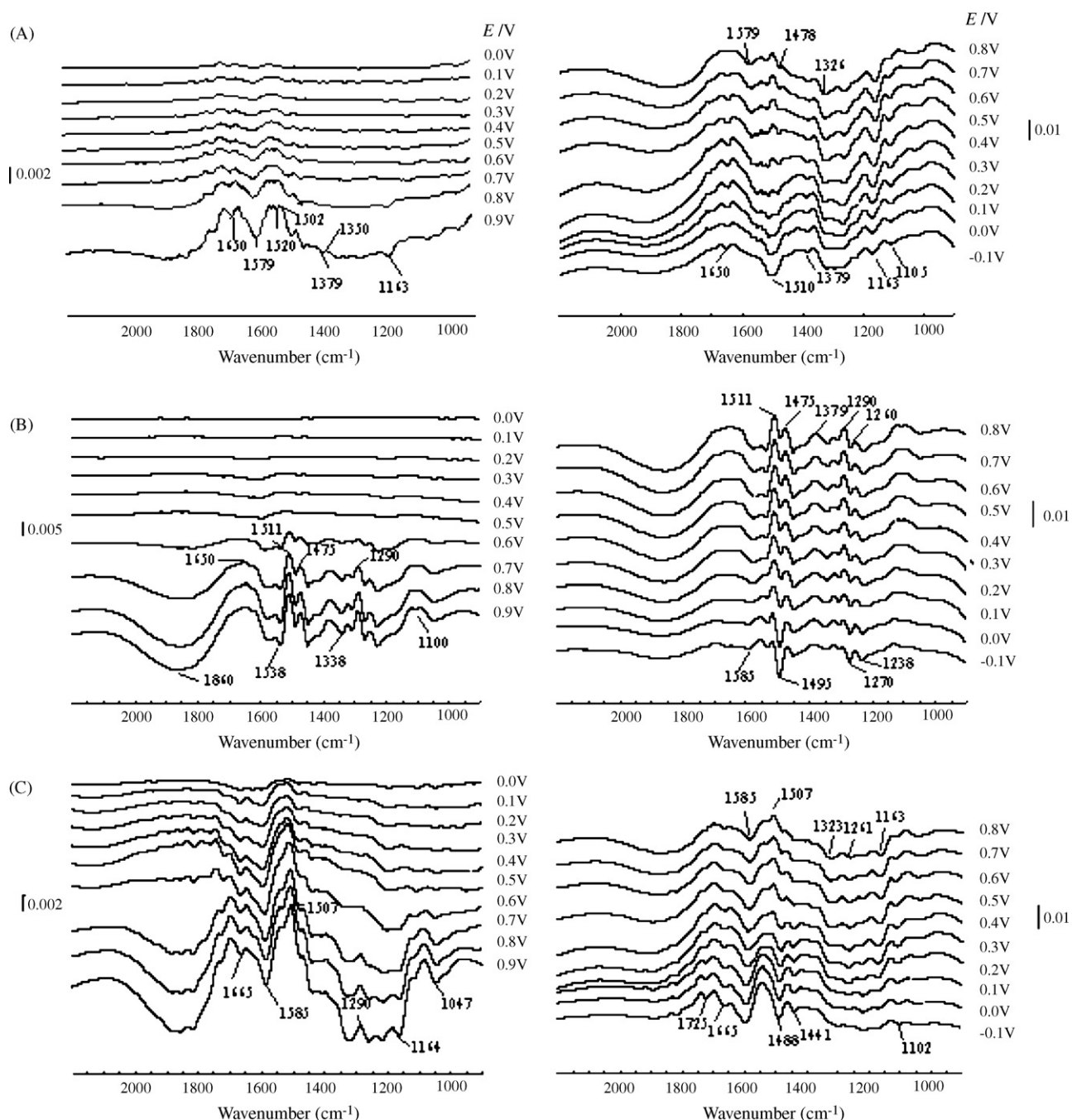


Fig. 4. In situ FTIR spectra of 0.2 M OT (A); 0.2 M OAP (B) and 0.2 M OT-co-OAP (C) electropolymerization during the first potential cycling between -0.1 and 0.9 V in 0.5 M H₂SO₄ in the thin layer cell. $E_r = -0.1$ V.

appeared, indicating that the gold surface was partially blocked by oxidation products deposited on electrode surface. And the peak at 0.3/0.4 V may be due to the oxidation of dimer (3-aminophenoxazone) and/or the electroactive polymer (POAP) [31]. The current and $\Delta f/\Delta t$ decreased with the increase of potential cycles. After 10 potential cycles, a goldish film was found on the working electrode.

Fig. 1C shows the responses in the electrochemical copolymerization of 0.19 M OT and 0.01 M OAP. The copolymerization behavior is different from that of homopolymerization. There are two anodic peaks in the first cycle. An anodic peak appearing at 0.7 V is mainly attributed to the oxidation of hydroxyl group in phenyl ring of OAP which occurs at lower potentials [36,37].

Another anodic peak at 0.87 V is caused by the oxidation of amino groups from both monomers. The frequency decreased slightly at 0.5 V and the change became more notably at about 0.7 V during the first positive potential scanning. This phenomenon also indicated that the formation of the new polymer was different from the two homopolymers. After the first potential cycle, two new pairs of redox peaks arose from the redox of the poly(OT-co-OAP) copolymer itself [36]. A light brown yellow film formed on the working electrode in the electro-synthesis process. The film color was different from that of each individual polymer, which shows that the copolymer was of different property from homopolymers. After scanning 10 cycles, the Δf_0 of POT, POAP and poly(OT-co-OAP) modified PQC electrode were -1190,

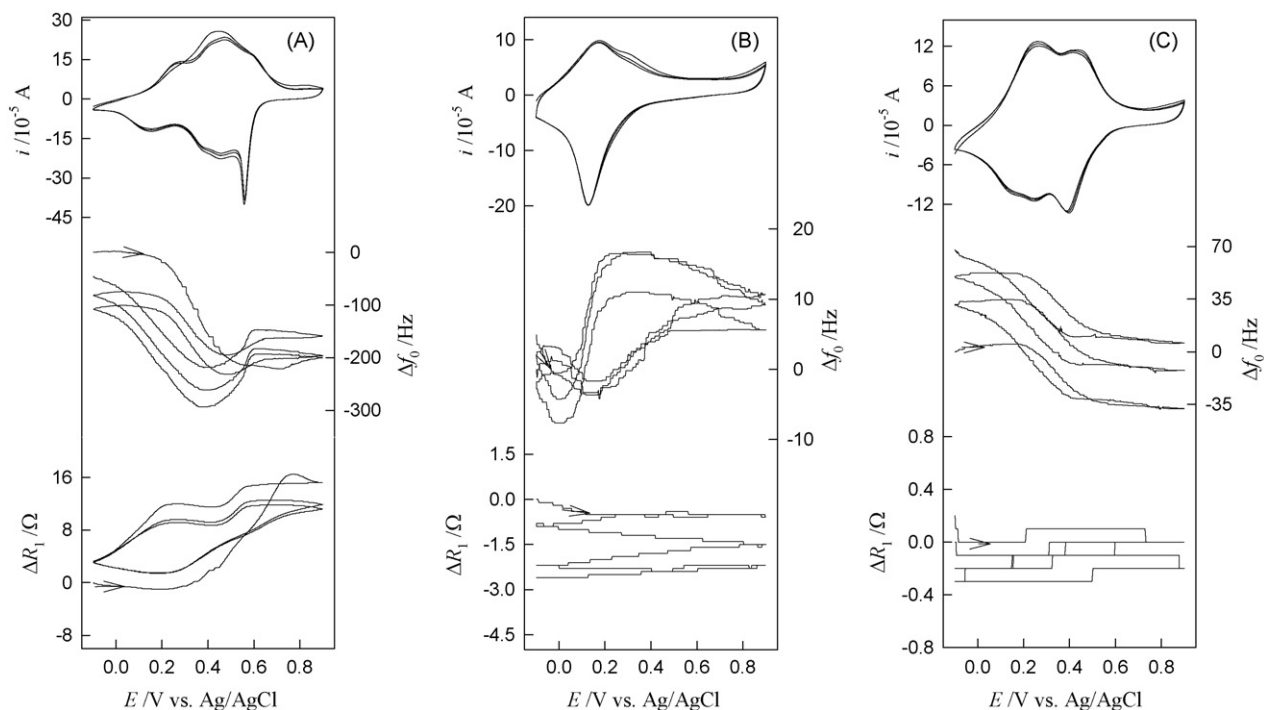


Fig. 5. Cyclic voltammograms and simultaneous Δf_0 and ΔR_1 responses of POT (A); POAP (B) and poly(OT-co-OAP) (C) films in 0.5 M H_2SO_4 . Scan rate: 50 mV s^{-1} . Poly(OT-co-OAP) was obtained in 0.5 M H_2SO_4 solution containing 0.19 M OT and 0.01 M OAP.

–788, –986 Hz, respectively. The polymerization rate ($\Delta f/\Delta t$) of copolymer lied between the rates of the individual homopolymers.

3.1.2. Effect of the molar ratios on the copolymerization

In order to study the effect of the molar ratios of OAP in monomer solution on the copolymerization process, the copolymers were prepared in various concentrations of monomer. Fig. 2 shows the responses of frequency shift against time in different co-monomer molar ratios of OAP in 0.2 M monomer solution during the copolymerization. As shown in Fig. 2, with the increase in concentration of OAP, the frequency shift became smaller and the deposition speed ($\Delta f/\Delta t$) became slower. It indicates that the polymerization speed was largely affected by the molar ratio of monomer. Lower OAP concentration can result in

higher polymerization speed and larger deposition mass. Therefore, in the next study the molar ratio of 0.19–0.01 was chosen for the mixture of OT and OAP to synthesize the copolymer film.

3.1.3. Simultaneous FTIR piezo spectroelectrochemistry results

In order to study the polymer formation and further infer the structure of the polymer, the electropolymerizations of OT, OAP and OT-co-OAP were studied by *in situ* piezoelectric FTIR spectroelectrochemistry. The results are shown in Figs. 3 and 4. Fig. 3 represents the CVs and simultaneous Δf_0 and ΔR_1 responses during potential cycles in 0.5 M H_2SO_4 containing 0.2 M monomer in the thin layer spectroelectrochemical cell. The peak potential of CVs obtained in the thin layer cell is similar to that obtained in the conventional cell, but smaller peak currents were observed in the first potential cycle.

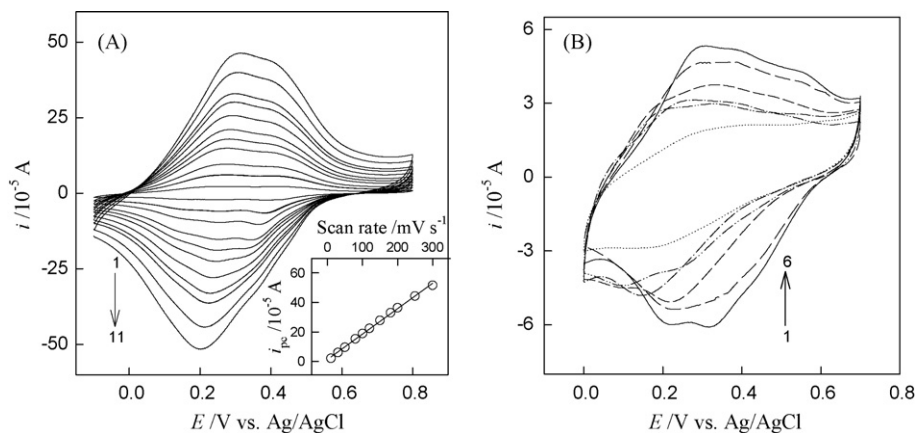


Fig. 6. (A) Cyclic voltammograms of 1400-Hz copolymer film on PQC Au electrode at different scan rates in 0.5 M H_2SO_4 . The 1–11 represent the scan rate: 10, 30, 50, 80, 100, 120, 150, 180, 200, 250 and 300 mV s^{-1} , respectively. Inset: dependence of the cathodic peak current on scan rate. Poly(OT-co-OAP) was obtained in 0.5 M H_2SO_4 solution containing 0.19 M OT and 0.01 M OAP. (B) Cyclic voltammograms of a 2000-Hz copolymer film coated on PQC gold electrode in a $\text{H}_2\text{SO}_4 + 0.2 \text{ M Na}_2\text{SO}_4$ solution with different pH values. Scan rate: 50 mV s^{-1} , pH from 1 to 6 were 1.0, 2.0, 3.0, 5.0, 7.0, 9.0, respectively.

With the same monomer concentration, the frequency changes are obviously larger for all the three cases in the thin layer cell comparing with those in the corresponding conventional cell. The difference may be due to the fact that the diffusion of oligomer intermediates around electrode surface to bulk solution is very difficult in the thin layer cell. The oligomer intermediates are profitably to form polymer on electrode surface or dissolve in thin layer solution, which leads to the decrease in frequency or increase viscosity in the thin layer solution. After 3 potential cycles, the frequency shifts resulting from the polymerization of POT, POAP and copolymer are 3843, 1098 and 1400 Hz, respectively. The copolymerization speed is still between the polymerization speeds of POT and POAP. The difference of the resistance change between the two different electrochemical cells was also presented. For POAP and copolymer, the resistance change was relatively small with the increasing of the cycling number. The $|\Delta f_0/\Delta R_1|$ values generally used to evaluate the viscous effect on PQC surface, are 22, 207 and 280 $\text{Hz } \Omega^{-1}$ for the depositions of POT, POAP and poly(OT-co-OAP) in the thin layer cell respectively, but 38, 774 and 102 $\text{Hz } \Omega^{-1}$ in the conventional cell (3 cycles). It indicates that the viscous effect is more notable in the thin layer cell than that in the conventional electrochemical cell in cases of POT and POAP. The $|\Delta f_0/\Delta R_1|$ values of POAP and copolymer modified PQC electrode are far larger than $10 \text{ Hz } \Omega^{-1}$, which indicates that the frequency shift of the PQC should be mainly attributed to the deposited film on the electrode and the density/viscosity effect can be ignored [29]. For POT, the $|\Delta f_0/\Delta R_1|$ values are close to $10 \text{ Hz } \Omega^{-1}$ in both cells, thus the density/viscosity effect may result in an extra frequency shift of the PQC. The different changes of the Δf_0 and ΔR_1 of homo- and copolymers suggest that their properties may be different and their structure may be changed.

In situ FTIR spectra collected simultaneously during the first cycle of potential scan for a PQC Au electrode are shown in Fig. 4. The reference potential was set at $-0.1 \text{ V vs Ag/AgCl}$. The downward peaks indicate the formation of species and the upward peaks indicate the consumption at the collected potential (E_s) as compared with the reference potential (E_r). Several downward peaks and upward peaks appeared in the redox process of the

OT (A), OAP (B) and OT-co-OAP (C) in the wave number region of $2200\text{--}900 \text{ cm}^{-1}$.

Fig. 4A shows the in situ FTIR spectra of the electropolymerization of OT. There are several negative bands at 1650 , 1579 , 1520 , 1478 , 1379 , and 1163 cm^{-1} appearing around 0.8 V during the positive scan. The band at 1650 cm^{-1} is ascribed to the deformation vibration of $-\text{NH}_2$ [38]. The band at 1579 cm^{-1} is assigned to a quinoid ring or C=N stretching vibration in the phenoxazine units [38]. This indicates that the imine group is formed during the oxidation of OT. And the bands around 1500 cm^{-1} (1520 , 1510 , and 1478 cm^{-1}) correspond to aromatic C=C stretching vibration and the ring C=C vibration of meta-disubstituted benzenes [39], which imply the formation of dimmer or POT. Other downward peak at 1379 cm^{-1} is also clearly seen at 0.9 V and it could be also assigned to C-N stretching of quinonoid rings containing C=N and C-N groups [40]. The band intensity decreased in the case of negative scan, which indicates that OT monomer was oxidized and the polymer was formed at the same time. The changes in the characteristic absorbance of $-\text{NH}_2$ and phenyl ring indicates that $-\text{NH}_2$ group oxidized during the electrochemical process. Besides, the peaks at 1105 and 1050 cm^{-1} are ascribed to the absorbance of SO_4^{2-} vibration and symmetric stretching vibration of HSO_4^- [41], respectively. During the cyclic scanning, the intensity of these two bands changes indicate that the polymer films have properties for anion doping and dedoping. When SO_4^{2-} and HSO_4^- doped in the polymer film, the concentration of ion in the thin layer decreased, which led to a decrease in the intensity of IR absorbance.

For OAP (Fig. 4B), the positive bands near 1500 cm^{-1} (1511 , 1495 and 1475 cm^{-1}), which can be ascribed to the aromatic C=C stretching vibration or ring C=C vibration of meta-disubstituted benzenes [39], indicates that the oxidation of OAP. During OAP oxidation the band at 1338 cm^{-1} accompanying with the positive band at 1379 cm^{-1} appeared at 0.7 V is assigned to C=N or C-N stretching of quinoid rings [31,40]. These band intensities decrease during negative potential scan, suggesting that the imine group turns to the amino group. The upward peaks at 1290 and 1260 cm^{-1} are ascribed to O-H deformation vibration and C-O stretching vibra-

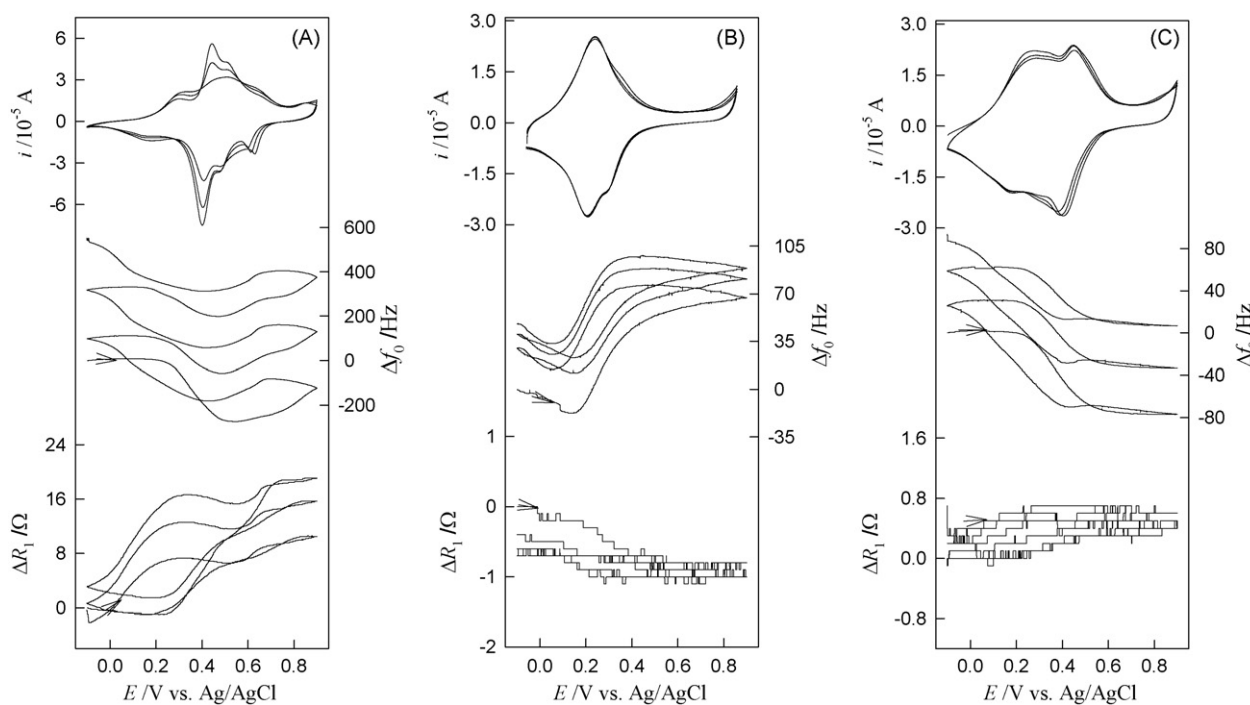


Fig. 7. Real time response of current, Δf_0 and ΔR_1 of OT (A); POAP (B) and poly(OT-co-OAP) (C) films during CV in $0.5 \text{ M H}_2\text{SO}_4$ in thin layer cell. Scan rate: 5 mV s^{-1} . Poly(OT-co-OAP) was obtained in $0.5 \text{ M H}_2\text{SO}_4$ solution containing 0.19 M OT and 0.01 M OAP .

tion of phenols [31,38]. The band intensity decreased during the negative scan, which means that the –OH groups reduced. And the spectra are different from the original IR spectra when potential turns back to the initial value, which indicates the formation of the POAP. There is no characteristic band around the 1680 cm^{-1} of C=O stretching vibration [31,38] in IR spectra, suggesting that POAP may be formed through the –NH₂ groups rather than the –OH groups.

Fig. 4C shows the in situ FTIR spectra of OT-co-OAP electropolymerization during the first potential cycle between –0.1 and 0.9 V in 0.5 M H₂SO₄ in the thin layer cell. Many different bands around 1500 cm^{-1} from those of individual homopolymers were observed. The positive bands near 1500 cm^{-1} (1507 and 1486 cm^{-1}) can be ascribed to the aromatic C=C stretching vibration or ring C=C vibration of meta-disubstituted benzenes [39]. There is a band at 1323 cm^{-1} that could be assigned to C–N vibration in the spectrum. But no band at 1379 cm^{-1} resulting from C=N stretching of quinoid rings [31,40] appears in the spectrum. No upward peaks at 1290 and 1260 cm^{-1} ascribed to O–H deformation vibration and C–O stretching vibration of phenols [31,38], and no characteristic band around 1680 cm^{-1} of C=O stretching vibration [31,38] appeared in IR spectra. The in situ FTIR spectra of the copolymer indicates that the copolymer was a new polymer formed through the head-to-tail coupling of two monomers through –NH– groups rather than a mixture of POT and POAP, and the oxidation–reduction process of the copolymer was different from those of individual homopolymers.

3.2. The film characteristics

3.2.1. Characterization of the polymers

Fig. 5 shows the CV curves of a POT, POAP, poly(OT-co-OAP)-modified electrode in monomer-free electrolyte solution. The same frequency shift (ca.1400-Hz), that is to say, the same thickness of the film was obtained for studying. It is clear that the CVs of the copolymer, POT and POAP are different in shape and peak potential. In case of POT, the oxidation peaks occur at 0.32, 0.46 and 0.55 V, and reduction peaks occur at 0.20, 0.48 and 0.58 V. For the copolymer, the oxidation potentials are 0.26 and 0.45 V, respectively, which are different from the homopolymer. Among the three curves, the peak current of copolymer decreased to some degree compared with POT film, but became larger than POAP. The results demonstrated that the polymer growing in the copolymerization bath is different from those of homopolymer, which suggests that the copolymer was formed.

In order to gain a further insight into the electrochemical activity of poly(OT-co-OAP), the CVs of copolymer were not only obtained under different potential scan rates, but also in aqueous solution containing 0.2 M Na₂SO₄ with different pH values.

3.2.2. Effects of scan rate on the electrochemical properties of the copolymer

Fig. 6A shows the CVs of the copolymer film on a gold PQC electrode at various scan rates in H₂SO₄ solution. The peak current (*i_p*)

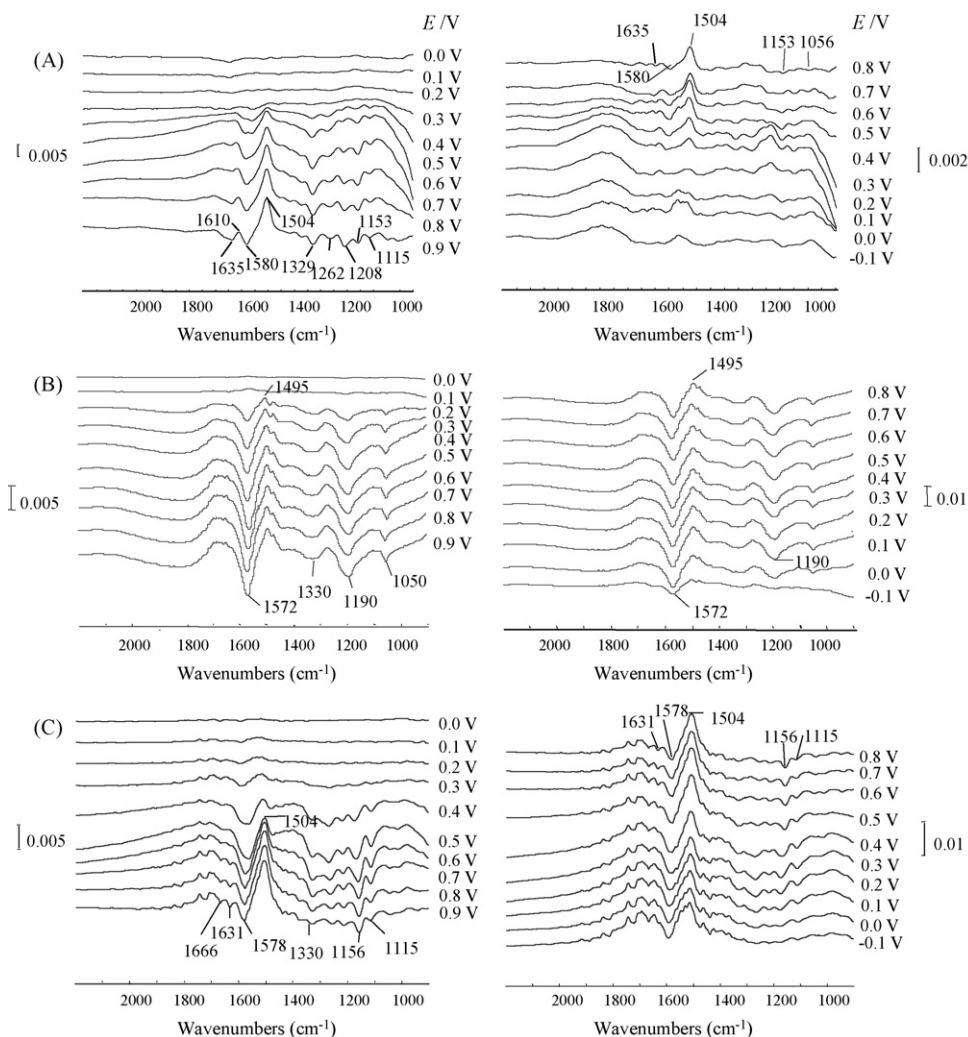


Fig. 8. In situ FTIR spectra of OT (A); POAP (B) and poly(OT-co-OAP) (C) films during the first potential cycling between –0.1 and 0.9 V in 0.5 M H₂SO₄ in the thin layer cell. *E_r* = –0.1 V. Poly(OT-co-OAP) was obtained in 0.5 M H₂SO₄ solution containing 0.19 M OT and 0.01 M OAP.

and the peak–peak potential (ΔE_p) increase with the increasing of scan rate. The linear relationship of the cathodic peak current to the scan rate (Fig. 6A, inset) depicts a surface-controlled electrode process, and the surface-confined copolymer groups could undergo rapid electron transfer reactions with the electrode [42,43].

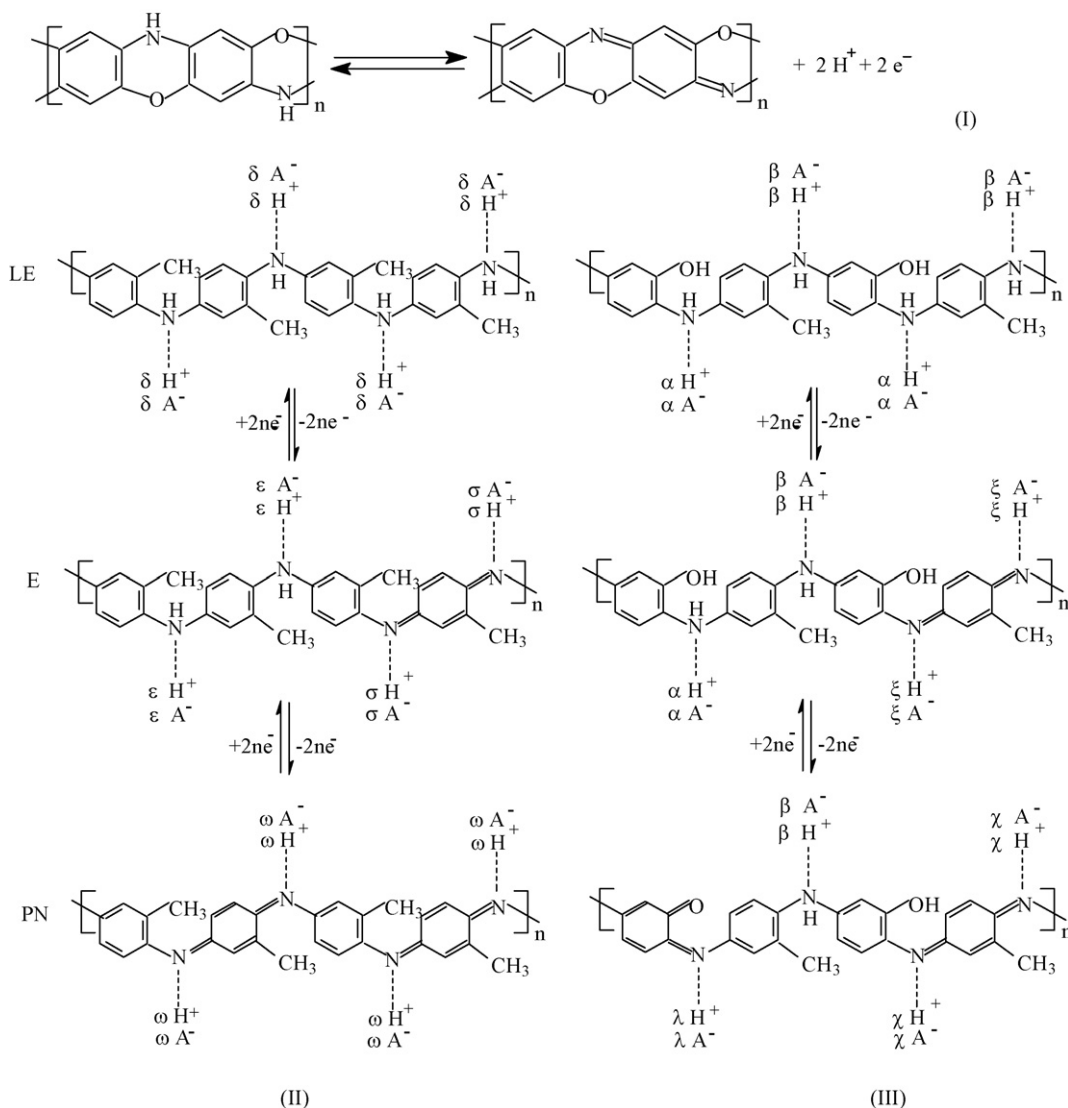
3.2.3. Effects of pH value on the electrochemical properties of the copolymer

The CVs of poly(OT-co-OAP) films were obtained in aqueous 0.2 M Na₂SO₄ solutions with different pH values (Fig. 6B). Though the electroactivity decreased in some degree and the redox peaks shifted slowly to the negative direction with the increasing of pH values, the effect of the pH values on the electrochemical behavior or conductivity was still smaller compared with the homopolymers. It is reported that the POT have a little electrochemical activity at pH > 3 [21] and the POAP exhibits relatively low values of electrical conductivity [43,44] in aqueous solutions. But for poly(OT-co-OAP), the redox peaks can be observed in the wide pH range from 1 to 9. This suggests that the copolymer had better stability or better redox activity within a boarder pH range in aqueous solutions as compared with the homopolymers.

3.2.4. In situ FTIR piezospectroelectrochemical results

2000-Hz polymer modified PQC electrode was studied in the thin layer spectroelectrochemical cell and the results are shown in Fig. 7. The CVs and Δf_0 curves of the three polymers in the thin layer cell are also similar to those in the conventional cell. But for all polymers, the change in frequency and resistance is different. The increase/decrease of frequency in the process of polymer oxidation/reduction suggested that the doping/dedoping of anions took place. The Δf_0 curves of the three polymers are different from one another, which might come from the different amounts of anions doped into the polymers.

We also collected the in situ FTIR spectra in the CV process. In Fig. 8A, the negative bands appeared at 1635, 1329, and 1153 cm⁻¹, which should be due to the vibration modes of the oxidized POT [15]. The band at 1580 cm⁻¹ should be due to the C=N stretching absorption in E and PN forms when an anion interacts strongly with the C–NH⁺=C group [15]. These band intensity increased notably when the polymer was oxidized from LE to E and PN forms, and decreased from PN to E. In the case of POAP (Fig. 8B), the positive peak at 1497 cm⁻¹ ascribes to the ring C=C stretching vibration of benzenes. And the negative peaks at 1572 and 1330 cm⁻¹ are also due to quinonoid ring or C=N stretching vibration in the phe-



Scheme 1. The pathway for the redox processes of poly(*o*-aminophenol) (I), poly(*o*-toluidine) (II) and of copolymer (III). Here the protonation at all nitrogen atoms is considered, and α , β , δ , λ , ϵ , σ and ω represent the extent of protonation of different nitrogen atoms. And A⁻ represents an anion doped in the copolymer.

noxazine units produced upon the complete oxidation of polymer [15]. The increase or decrease of the characteristic peak intensities of SO_4^{2-} and HSO_4^- indicates the doping or dedoping of SO_4^{2-} into the polymer.

For copolymer (Fig. 8C), the bands at 1666, 1631 and 1130 cm^{-1} could be attributed to the C–N stretching vibrations of quinoid ring and N–H vibration [38]. The peak intensity increased with the potential during the positive scan, and decreased during the negative scan, indicating that the redox reaction occurred through N–H and C–N groups. The band at 1380 cm^{-1} indicates the C–O–H deformation vibration of phenols [42]. Therefore, it is a strong evidence for the presence of OAP unit in the copolymer. The increase of peak value at 1666 cm^{-1} (C=O stretching) and 1330 cm^{-1} (C=N stretching) suggested that the polymerization was formed through $-\text{NH}_2$ and not $-\text{OH}$ of the *o*-aminophenol [31]. In addition, accorded with the EQCM data, the bands at 1190, 1110 and 1050 cm^{-1} are caused by SO_4^{2-} and HSO_4^- which are doped into the copolymer [36].

Based on the fact that the electrochemical polymerization of OT-co-OAP is different from that of monomer and the properties of the poly(OT-co-OAP) are also different from the homopolymers of OT and OAP, the in situ FTIR spectra of poly(OT-co-OAP) indicates that the copolymer redox reaction exists in the copolymer chain according to the general formula of OT and OAP units [45,46]. Therefore, the mechanism could be proposed as shown in Scheme 1. The copolymer has two oxidation steps and two reduction steps. And different nitrogen atoms have different protonation extents in the polymers and the numbers of doped ions are thus different.

4. Conclusions

The electrosynthesis of POT, POAP and poly(OT-co-OAP) and their properties were investigated by the combination technique of in situ FTIR with EQCM in 0.5 M H_2SO_4 media. The electropolymerization rates were affected by the co-monomer feed ratio in the polymerization system. The copolymer obtained in the condition of OT:OAP = 19:1 shows its better stability and electroactivity than homopolymers in aqueous solutions with different pH values. In situ FTIR spectra of the copolymer indicate that the copolymer was a new chain type polymer formed through $-\text{NH}-$ groups of the two monomers rather than a mixture of POT and POAP. The different redox process of poly(OT-co-OAP) shown by EQCM and FTIR results suggested that the property of copolymer is different from that of POT or POAP. Therefore, in situ piezoelectric FTIR spectro-electrochemistry can be used to in situ monitor the polymerization and characterization processes, and it is believed to be a universal method to investigate the formation mechanism of new polymer or copolymer.

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