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In Situ UV–Vis Spectroelectrochemical Studies on the Copolymerization of Diphenylamine and *o*-Phenylenediamine

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Abstract

The *in situ* ultraviolet-visible (UV-Vis) spectroelectrochemical study on the copolymerization of diphenylamine (DPA) and *o*-phenylenediamine (OPD) has been performed at a constant potential of 0.8 V using indium tin oxide (ITO)-coated glass electrodes as working electrode. And also, as a comparison, the electrochemical homopolymerizations of DPA and OPD have been investigated by using the *in situ* spectroelectrochemical technique. The intermediate species generated during the electrochemical homopolymerization of DPA and OPD, and the copolymerization of DPA with OPD have been identified by using the *in situ* spectroelectrochemical procedure. The results reveal the formation of an intermediate in the initial stage of copolymerization through the cross-reaction of the cation radicals of DPA and OPD, and the absorption peak located at 538 nm in the UV–Vis spectra is assigned to this intermediate. To further investigate the copolymerization of DPA with OPD, cyclic voltammetry (CV) has been used to study the electrochemical ho- mopolymerization of DPA and OPD and also the copolymerization of DPA and OPD with different concentration ratios in solution. The different voltammetric characteristics between the homopolymerization and copolymerization processes exhibit the occurrence of the copolymerization, and the difference between the copolymerization of DPA and OPD with different concentration ratios shows the dependence of the copolymerization on the concentrations of DPA and OPD. The copolymer has also been characterized by Fourier transform infrared spectroscopy (FT-IR).

Keywords: *o*-Phenylenediamine, Diphenylamine, Copolymerization, *In Situ* UV-Vis Spectroelectrochemistry

1. Introduction

Electronically conducting polyaniline (PANI) has attracted significant attention owing to its environmental stability and its electrical, optical and electrochemical properties [1-3]. However, the insolubility of PANI in common organic solvents and its limited electrochemical activity in media with pH ≥ 4 make its applications difficult. To extend its application in practice, several studies have been made toward the improvement of solubility and processability of PANI. The typical procedures are as the following: preparation of the substituted PANI through post-treatment of the base form of PANI [4]; electrochemical or chemical homopolymerization of aniline derivatives [5-7]; and the electrochemical or chemical copolymerization of aniline with different kinds of ring or N-alkyl substituted aniline derivatives [8-10]. The improved processability, electrochromism and other properties over PANI have been noticed for the polymers derived from the various benzene ring substituted and N-substituted aniline derivatives. This means that copolymerization can provide an alternative and easy approach to modify the structure of PANI, thus, it becomes possible to tune the electrochemical and electronic properties by altering the conditions of copolymerization.

The N-substituted derivatives exhibit an additional property of the comparable conductivity to that of PANI. In comparison with PANI, the copolymers of aniline with phenyl-substituted or N-substituted aniline derivatives show better solubility, decreased conductivity, disordered structure, and enhanced electrochemical stability [10-13]. The polymer of diphenylamine (DPA), a N-aryl substituted aniline derivative, possesses the properties between PANI and poly (*p*-phenylene). DPA has been polymerized by Comisso *et al.* [14] in a mixture of 4 M H_2SO_4 and ethanol, in which ethanol was used as co-solvent to lead to the dissolution of oligomeric products and to hinder the growth of poly(diphenylamine) (PDPA) on electrode surface. Also, some reports can be available on the polymerization of N-alkyl diphenylamine, 3-methoxy diphenylamine and 3-chlorodiphenylamine [15,16]. The obtained polymers have been found to have the C-C phenyl-phenyl coupling in their backbone. Recently, Wu *et al.* [17] have reported the electrochemical copolymerization of DPA with anthranilic acid and used X-ray photon spectroscopy to confirm the formation of the copolymer. Poly(DPA-*co*-aniline) [18] has been synthesized by pulse potentiostatic technique and a possible growth scheme has been proposed correlating the conditions of copolymerization with the charge associated with film deposition. Santhosh and coworkers [19] have studied the electrochemical copolymerization of DPA with *m*-toluidine (MT), and found that the electronic transitions as noticed from the *in situ* UV-Vis spectra recorded during electropolymerization with different molar feed concentration ratios of DPA depend on molar compositions of DPA and MT units in the co- polymer. Also, the electrochemical copolymerization of DPA with 2,5-diaminobenzene sulphonic acid (DABSA) has been reported, the intermediates formed during the electrochemical copolymerization have been followed through the *in situ* UV–visible studies [20]. And, Wu's research group [21] have reported the formation of the short-lived intermediates, showing the absorption peaks at 310 nm and 500 nm in the UV–Vis regions for their electronic states, during the electrochemical oxidation of DPA in 2 M H_2SO_4 medium by using the *in situ* spectroelectrochemical procedure.

Due to the potential applications of poly (*o*-pheny- lenediamine) (POPD) in the fields of electrochromism [22], sensors [23-25], rechargeable batteries [26] and corrosion protection [27], etc, the copolymers of OPD and other aniline derivatives have been widely studied in order to improve the properties of homopolymers. Recently, Holze *et al.* [28,29] have reported the electrochemical copolymerization of OPD with *o*-toluidine (OT) and MT, respectively, both being substituted anilines, with various concentrations of OPD in the feed. The obtained homo-/co-polymers had been characterized using CV and *in situ* conductivity measurements, and it was found that the copolymers showed an extended electrode potential range of redox activity and good redox responses at higher pH-values in comparison with the homopolymers of POPD, poly(*o*-toluidine) (POT) and poly (*m*-toluidine) (PMT) as well as good electrochemical stability. Also, Holze *et al.* [30] have studied the initial stages of the copolymerization of OPD with MT, monitored with *in situ* UV–vis spectroscopy, using an ITO-coated glass electrode in solutions with a constant concentration of MT and varying OPD concentrations. The formation of aniline type mixed intermediates as a result of the cross-reaction between the cation radicals of OPD and MT was proposed from the presence of the band at 497 nm during the electro-polymerization of OPD and MT.

Since the intermediates formed during the polymerizetion of aniline and other aniline derivatives are short-lived, it is difficult to detect these intermediates by using electrochemical techniques only. While, as an effective and useful tool for following the short-lived intermediates generated during the early stages of the electrooxidation of aniline and its derivatives, the *in situ* UV-Vis spectroscopy has been widely used to study the homopolymerization of aniline and its derivatives, and the copolymerization of aniline with its derivative. For example, Gopalan *et al.* [17,31-34] have used CV and *in situ* UV-Vis spectroscopy to study the copolymerization of DPA with some aniline derivatives and explained the copolymer formation through a plausible mechanism. And, the electrochemical copolymerization of DPA with OT in 4 M H_2SO_4 medium has also been studied by Santhosh *et al.* using electrochemical and spectroelectrochemical methods [35]. The composition of the two monomers in the obtained copolymer and the reactivity ratios of DPA and OT had been determined, and a possible copolymer model for explaining the changes in electrochemical and spectroelectrochemical characteristics was proposed. Recently, Zhang *et al.* [36] have studied the homopolymerization of *o*-toluidine (OT) and *p*-phenylenediamine (PPDA) and also the electrocopolymerization of OT with PPDA on an ITO conductive glass electrode at 0.7 V, 0.8 V, and 0.9 V using *in situ* UV–vis spectrometry in 0.5 mol/L sulfuric acid media. The spectral results indicated that the electrocopolymerization of OT and PPDA did happen. Also, Zhang *et al.* [37] have reported the electrochemical copolymerization of MT with PPDA using *in situ* UV–vis spectrometry procedure, and indicated that PPDA might react with MT to yield some more active intermediates, which can promote the electropolymerization.

In this study, the electrochemical copolymerization of DPA with OPD in 4 M H_2SO_4 medium has been investigated using the techniques of cyclic voltammetry and *in situ* UV-Vis spectroscopy. The course of electropolymerization has been followed by *in situ* UV-Vis spectroscopy to provide an insight about the intermediates formed during copolymerization and the mechanism of copolymer formation. The obtained copolymer has also been characterized by FT-IR spectroscopy.

2. Experimental

2.1. Reagents and Solutions

DPA (Sigma) and OPD (Sigma) were used without any further purification. Other chemicals were used as received. All reagents were prepared with ultrapure water, and freshly prepared solutions were used throughout the experiment. All chemicals were of analytical grade.

2.2. Apparatus and Procedures

2.2.1. Electrochemical Homo-/Co-Polymerization

Electrochemical synthesis and cyclic voltammetric studies were performed using a CHI 660B electrochemical workstation (CH instruments, USA). Ultrapure water was used for the preparation of electrolyte solutions containing 4.0 M H_2SO_4. A three-electrode cell was used with a platinum foil (1×1 cm^2) as working electrode, an Ag/AgCl electrode as reference, and a platinum wire serving as counter electrode. Electrochemical copolymerization of DPA with OPD was carried out by potential scanning between –0.2 - 1.2 V at 100 mV/s. Electrochemical homopolymerizations of DPA and OPD had also been performed using the same procedure as that of the copolymerization.

2.2.2. *In Situ* Spectroelectrochemistry

The *in situ* UV–Vis spectra were recorded by using a UV-1800 UV-Vis spectrophotometer (Shimadzu). Electrochemical copolymerization was carried out by applying a constant potential of 0.8 V for the binary mixture of DPA and OPD with different feed ratios. The homopolymerizations of DPA and OPD were also performed using the same procedure as that of the above copolymerization. The UV–Vis spectra were collected simultaneously while potentiostatic electrolysis was performed. Spectroelectrochemical experiments were made in a quartz curvet of 1 cm path length by placing an in- dium-doped tin oxide (ITO) coated glass electrode (with a specific surface resistance of 10 Ω/cm^2) installed perpendicular to the light path. A platinum wire was used as counter electrode and Ag/AgCl was used as reference electrode. For each experiment, a fresh ITO-coated glass electrode was used, which had been degreased with acetone and rinsed with plenty of ultrapure water. In the reference channel of spectrometer, a quartz curvet containing 4.0 M H_2SO_4 aqueous solution was inserted. All the spectra recorded are background-corrected.

2.2.3. Fourier Transform Infrared Spectroscopy

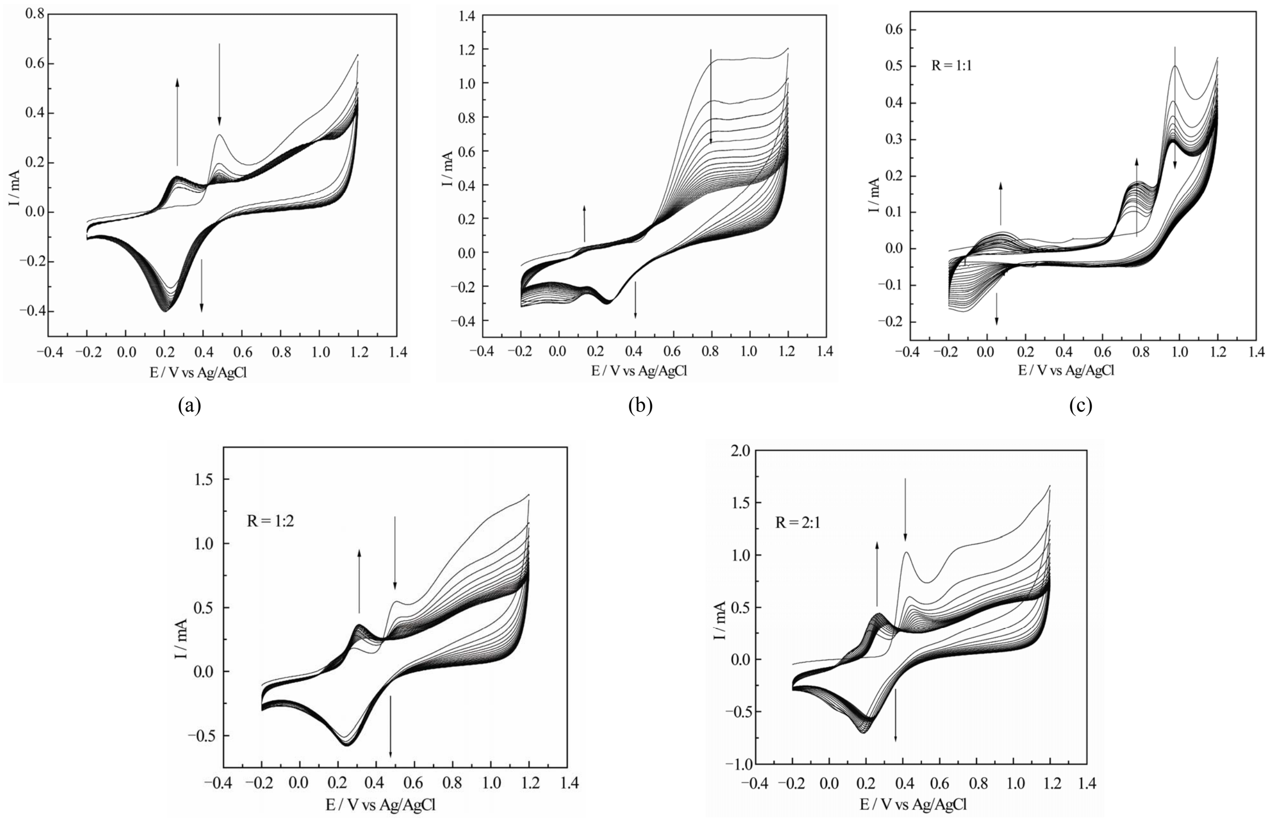
FT-IR spectra were recorded on a KBr disk containing about 1% sample by weight using a Nicolet Avatar 370 DTGS (USA) spectrophotometer. For each sample, a total of 120 scans at a resolution of 4 cm^{-1} was used.

3. Results and Discussion

3.1. Electrochemical Homo-/Co-Polymerization

To investigate the electrochemical behaviors of the homo-/co-polymerization of DPA and OPD, the cyclic voltammograms (CVs) have been recorded during the electrochemical homopolymerization of DPA and OPD, and the copolymerization of DPA with OPD with different concentration ratios (R = 1:1, 1:2, and 2:1) in 4.0 M H_2SO_4 by scanning the potentials in the limits -0.2-1.2 V for 20 cycles (**Figure 1**). **Figure 1(a)** shows the CVs recorded for the homopolymerization of DPA. As can be seen, in the first cycle, an irreversible oxidation peak is observed at 0.49 V, which could be assigned to the electrooxidation of DPA to generate the diphenylamine cation radicals (DPACRs), and after the first potential scanning, another anodic peak was observed at 0.27 V. This peak is caused by the products that could be identified as the DPA dimer, which is shown to be able to grow into the final polymer during electrochemical de position [38]. On the other hand, one can note that the peak current for the oxidation peak located at 0.27 V increased gradually with the continuous potential scanning, while, for the wave at 0.49 V, the peak current decreased gradually with the continuous potential scanning. This is because that, after the formation of the DPACRs, they will react each other or with the DPA monomers in solution to generate the DPA dimer, thus, with the continuous formation of the DPA dimer, the amount of DPACRs in solution will decrease gradually, and the amount of DPA dimer will show a corresponding increase. This will, thus, lead to the decrease for the oxidation current of the peak at 0.49 V and the increase for the peak current of the oxidation wave at 0.27 V. And, for the reduction wave at 0.21 V, the peak current increases gradually with the con- tinuous electrolysis. These electrochemical behaviors are the typical characteristics for the polymerization of compound. Finally, a dark green PDPA film was deposited on the electrode surface. **Figure 1(b)** shows the CVs obtained during the electro-oxidation of OPD from a solution containing 0.002 M OPD. As can be seen, in the first anodic sweep, the oxidation peak, corresponding to the oxidation of OPD at 0.80 V, indicates formation of the OPD cation radicals (OPDCRs) from the reduced leucoemeraldine. And, during the subsequent potential cycling, another anodic peak at 0.13 V can be noticed. This peak can be assigned to the further oxidation reaction of OPDCRs to dications. The anodic peak at 0.80 V shows a decrease in peak current with increase in the number of cycles, while the current response for the oxidation peak at 0.13 V increases gradually with continuous potential cycling. This is due to the conversion of OPDCRs into their dications. As for the reduction wave at 0.02 V and 0.26 V, the peak current increase gradually with the continuous electrolysis. These electrochemical properties indicate the polymerization of OPD on electrode surface. A bronze-brown film was finally obtained on the working electrode.

Figure 1(c-e) show the CVs for the electrochemical copolymerization of DPA and OPD with different concentration ratios (c: R = 1:1; d: R = 1:2; e: R = 2:1). Firstly, it can be seen that the electrochemical behaviors of the copolymerization of DPA with OPD are apparently different from that of the homopolymerizations of DPA (**Figure 1(a)**) and OPD (**Figure 1(b)**). This demonstrates that the copolymerization of DPA and OPD do occur during the electrolysis of their binary mixture. Secondly, the different growth characteristics can be observed for the copolymers synthesized with different concentration ratios of DPA and OPD. It can be seen from **Figure 1(c)** (R = 1:1) that, during the first anodic scan of potential on the copolymerization of DPA with OPD, an anodic peak is observed at 0.98 V, which could be due to the formation of the electroactive species generated from the oxidation of both DPA and OPD that can ultimately result in the oligomer/polymer formation [35]. This is justifiable by the fact that when the anodic potential is beyond 0.70 V, both DPA and OPD could be simultaneously oxidized to generate their cation radicals, diphenylamine cation radical (DPACR) and *o*-phenylenediamine cation radical (OPDCR) [35, 39]. And after the first cycle of potential scanning, three anodic peaks were observed in the CVs at 0.07 V, 0.78 V, and 0.98 V, respectively, which distinctly differs from the CVs with the two anodic peaks during the copolymerization of DPA and OPD with the concentration ratios of 1:2 and 2:1. The peaks located at 0.07 V and 0.78 V could be assigned to the oligomers/ polymers generated by the cross-reaction between the intermediate species of DPACR and OPDCR. Thirdly, apart from the different anodic and cathodic peak potentials shown in **Figures 1(c), 1(d)** and **1(e)**, the peak currents for the copoly- merization of DPA and OPD with R = 1:2 and R = 2:1 (**Figures 1(d)** and **1(e)**) are higher than those shown in **Figure 1(c)** for the copolymerization of DPA and OPD



(a) (b) (c)

(d) (e)

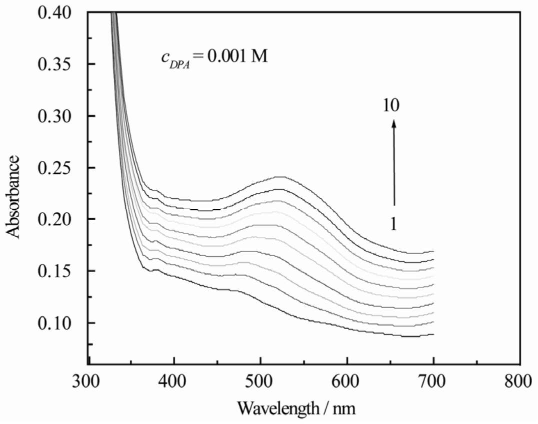
Figure 1. (a): CVs of the electrochemical polymerization of 0.001 M DPA in 4 M H_2SO_4; (b): CVs of the electrochemical polymerization of 0.002 M OPD in 4 M H_2SO_4; (c-e): CVs recorded during the electrochemical copolymerization of DPA with OPD (c: R = 1:1; d: R = 1:2; e: R = 2:1) in 4 M H_2SO_4. Scan rate = 100 mV/s.

with concentration ratio of 1:1. This may be because that the surface bound polymer film deposited on electrode surface exhibits different redox characteristics as a result of the incorporation of DPA or OPD in different extent. Finally, a dark golden-brown film can be observed on electrode surface. These results not only show that the copolymerization of DPA and OPD do happen using the proposed electrochemical procedure, but also indicate that the copolymerization process is related to the concentration ratio of DPA and OPD in the feed.

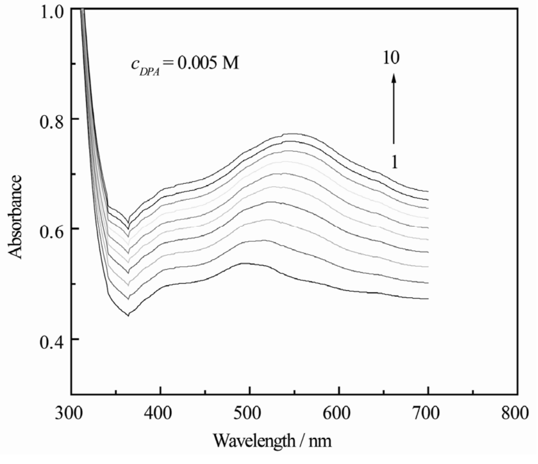
3.2. In-Situ Spectroelectrochemistry

3.2.1. In-Situ Spectroelectrochemistry of the Homopolymerization of DPA

Figures 2(a) and **2(b)** show the *in situ* UV–Vis spectra for the homopolymerization of DPA with different concentrations (0.001 M and 0.005 M) in 4.0 M H_2SO_4 aqueous solution at a potential of 0.80 V. Typically, three absorption bands at around 380 - 410 nm, 500 nm and > 600 nm are noticed during the homopolymerization of DPA. And, the absorption peaks at about 430 nm, 500 nm and > 600 nm have also been reported for the homopolymerization of DPA by earlier workers [34,40]. Based on the literature [34], the band at 380 - 410 nm is assigned to the aniline type cation radical and/or oxidized benzidine type dimer generated in the backbone. The other two bands at 500 nm and >600 nm are assigned to the generation of diphenyl benzidine type oligomer cation radical (DPB^+) and N', N-diphenyl benzidine type dication radical (DPB^{2+}) of the oligomer (**Scheme 1**), respectively. Both of the peaks grow in intensity gradually during the electrooxidation of DPA with the time going on. This is because that with the continuous electrolysis, more and more intermediates are formed.



(a)



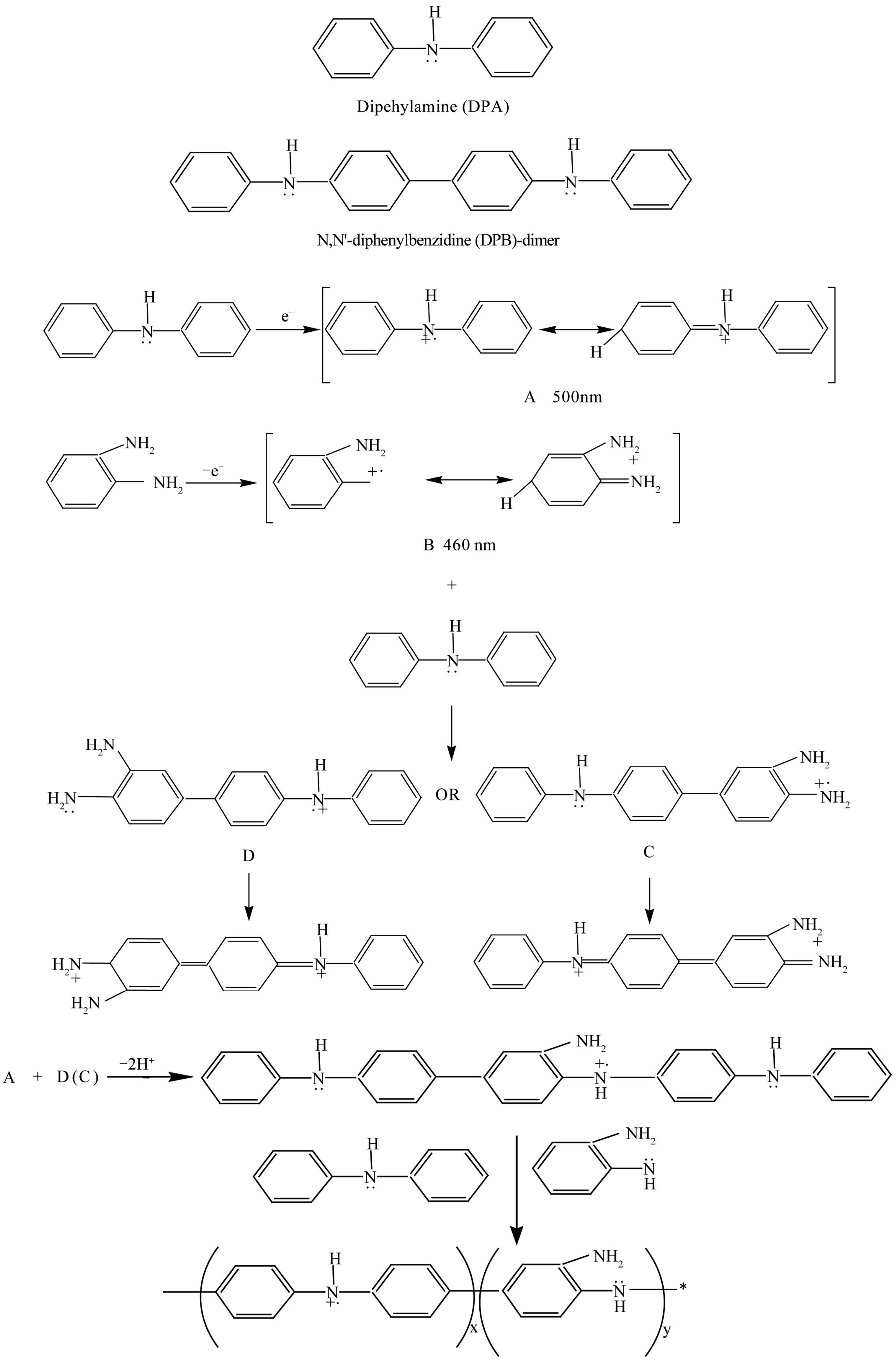
(b)

Figure 2. (a and b): UV–Vis spectra obtained at different time intervals (in minutes) after applying a potential of 0.80 V in solutions containing different concentrations of DPA (a: 0.001 M; b: 0.005 M).

The assignment of these peaks to the intermediates could be supported by the results of the spectral studies after switching off the applied potential. **Figure 3** illustrates the UV–Vis spectra obtained at different time intervals (1 - 6 min) after interruption of 10 min electrolysis of 0.005 M DPA. As can be seen, the intensity of the absorption bands at about 500 nm and > 600 nm show a significant decrease with the time going on, and the intensity of the absorption band at > 600 nm decreases more quickly than that of the absorption peak at 500 nm. This is because that, after interruption of electrolysis, the intermediates of DPB^+ and DPB^{2+} of the oligomers would not be generated any more. While, although the potential electrolysis is ended, the DPB^{2+} intermediates would keep reacting each other as before. Thus, the content of DPB^{2+} intermediates in solution becomes less and less, which would lead to the significant decrease of the absorption intensity. On the other hand, one can note that, with the time going on, the absorption peak at about 500 nm shifts negatively gradually. This may be attributed to the transformation of intermediates into the end product.

3.2.2. *In Situ* Spectroelectrochemistry of the Homopolymerization of OPD

Figure 4 displays the UV–vis spectra recorded at various time intervals for initial stages of the polymerization of OPD (0.002 M) in 4.0 M H_2SO_4 aqueous solution at an applied potential of 0.8 V versus Ag/AgCl. As can be seen, two absorption bands located at λ = 460 nm and λ = 490 nm can be firstly found in the UV–Vis spectra. However, with the time increasing, another weak absotption peak at 550 nm can be observed. It has been reported that there are three absorptive bands located at 420 nm, 462 nm and 492 nm, respectively, in its UV-Vis spectrum [30]. This difference may be resulted from the different medium used. It has been known that there are two



Scheme 1. Copolymerization of DPA and OPD.

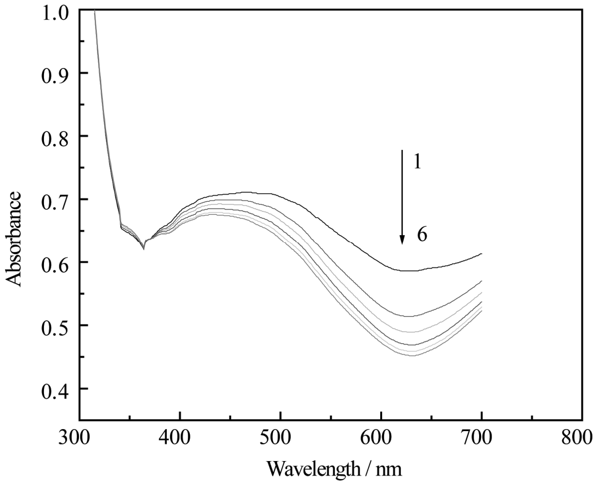


Figure 3. UV–Vis spectra obtained at different time intervals (1-6 minutes) after interruption of the electrolysis of 0.005 M DPA performed for 10 min.

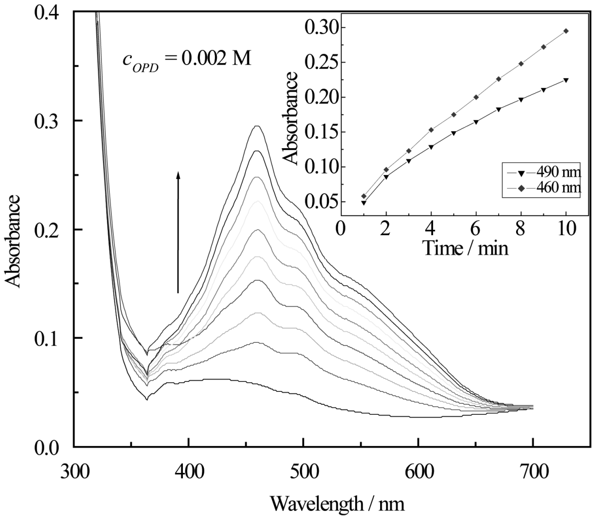
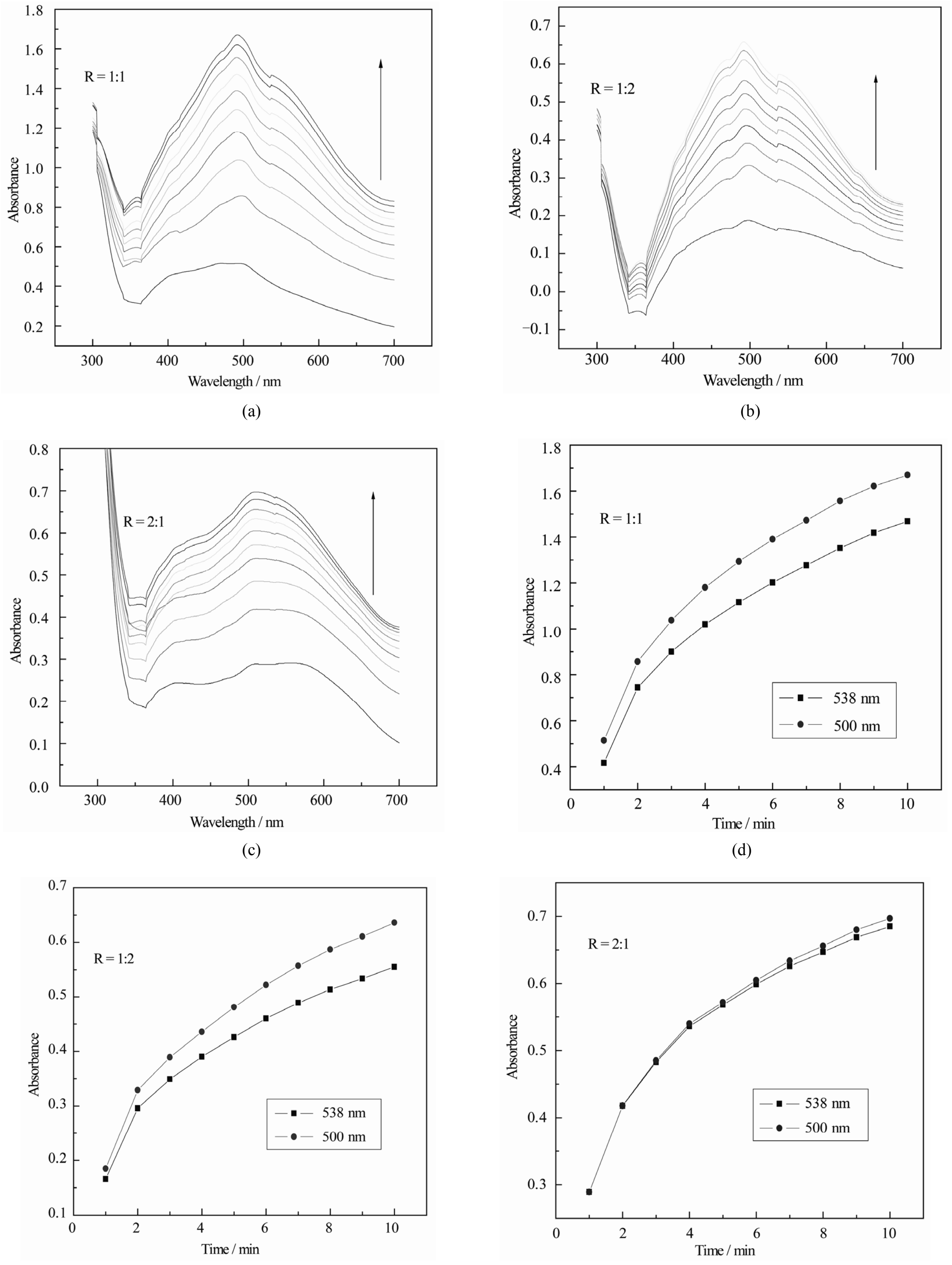


Figure 4. UV–Vis spectra obtained at different time intervals (in minutes) after applying a potential of 0.80 V in solutions containing 0.002 M OPD. Inset: plots of the intensities of the absorptive peaks at 460 nm (red line) and 490 nm (black line) with time.

different kinds of structure for poly(*o*-phenylenediamine) (POPD), they are the phenazine-type structure [26,41] and the PANI-like backbone structure [22,42], respecttively. The absorbance transient located at 460 nm is assigned to the intermediate of the phenazine-type dimmer/oligomer or the OPD cation radicals. The dimer and oligomer containing the phenazine-type have been reported to give the absorption bands at 420 nm and 451 nm, respectively [43,44]. The transients at 490 nm and 550 nm can be ascribed to the PANI-like dimer and oligomer intermediates, as shown in **Scheme 1**. The absorption intensity of these two bands increase with continuous electro-oxidation of OPD, but the intensity of the absorption at 460 nm grows more quickly than that of the other absorption band at 490 nm (**Figure 4**, inset) and gradually becomes predominant in the later stages of polymerization. This is because that the generation rate of the intermediate of phenazine type dimmer/oligomer or OPD cation radicals is significantly quicker than that of the PANI-like dimer intermediates in 4 M H_2SO_4 aqueous solution at the potential of 0.8 V.

3.2.3. *In Situ* Spectroelectrochemistry of the Copolymerization of DPA with OPD

The UV–Vis spectra recorded during constant potential copolymerization at 0.8 V of DPA and OPD with different concentration ratios (R = 1:1, 1:2, and 2:1) are shown in **Figure 5**. It can be seen from **Figure 5** that there is great difference between the absorption bands for the copolymerization of DPA with OPD and those for the homopolymerization of DPA and OPD. On the one hand, in **Figure 5(a)**, there are three bands, which are located at 400 nm, 493 - 500 nm, and 538 nm, respectively; and in **Figures 5(b)** and **5(c)**, the absorption bands are located at 400 nm, 493 nm and 538 nm, and 400 nm, 507-514 nm and 538 nm, respectively. Compare to the spectra obtained during the homopolymerization of DPA or OPD alone, a new band appeared at 538 nm in the UV-Vis spectra for the copolymerization of DPA and OPD. Under the applied potential of 0.80 V, DPA and OPD can be oxidized to get their corresponding cation radicals (DPACR and OPDCR), which undergo cross-reaction to result in the dimers/oligomers (**Scheme 1**). The existence of the absorption peak at 538 nm in the UV-Vis spectra for the copolymerization is attributed to the formation of these intermediates (dimers/oligomers) as a result of the cross-reaction between DPACR and OPDCR (**Scheme 1**). Besides, one can also notice from **Figure 5** that the intensity ratio for these absorption peaks is different when the concentration ratio of DPA to OPD in the feed is altered. On the other hand, for the copolymerization of DPA and OPD, the bands at around 490-510 nm which correspond to the generation of diphenyl benzidine type oligomer cation radical (DPB^+) and the PANI-like dimer intermediates show shifts while changing the concentration ratio of DPA and OPD in the feed. This demonstrates that the concentration changes of DPA and OPD in the solution produce copolymers with different amounts of DPA or OPD in it. And, the absorption peak assigned for the aniline type cation radical, observed at around 380 - 410 nm in the case of DPA polymerization, appeared at 400 nm for the copolymerization of DPA and OPD. Obviously, the incorporation of OPD units in the backbone of copolymer does happen when electrolysis is performed in the mixture of DPA



(a) (b)

(c) (d)

(e) (f)

Figure 5. (a→c): UV–Vis spectra obtained at different time intervals (in minutes) after applying a potential of 0.80 V in solutions containing DPA and OPD with different molar ratios (a: R = 1:1; b: R = 1:2; c: R = 2:1). (d→f): the time dependence of the absorbance at 500 nm and 538 nm, respectively (d: R = 1:1; e: R = 1:2; f: R = 2:1).

and OPD.

To further investigate the spectroelectrochemical behaviors of these absorption bands at different time intervals, the growth of absorbance of these bands in solutions containing different concentration ratios of DPA and OPD are illustrated in **Figure 5(d)** (R = 1:1), **5(e)** (R = 1:2), and **5(f)** (R = 2:1), respectively. As can be seen, the absorption intensity of these three bands all increase with continuous electro-oxidation in various concentration ratios, but the intensity of the absorption at 500 nm grow more quickly than that of the absorption at 538 nm. This accounts for the high activity of the DPA cation radical, it can react with other cation radicals or/and OPD monomers in solution.

To investigate the different characteristics of the various intermediates generated during the copolymerization of DPA and OPD, the UV–Vis spectra recorded at different time intervals after interruption of 10 min electrolysis of the mixed solution (R = 1:2) is illustrated in **Figure 6**. As can be seen, the absorption bands at 500 nm and 538 nm decrease in intensity with prolonged time. The absorbance value of the band at 538 nm, assigned to the dimers/oligomers resulting from the cross reaction of DPACR and OPDCR, shows less decrease in absorbance in comparison with the neighboring band at 500 nm. This is because that the intermediates continue to react each other and form the end product after interruption of electrolysis, which leads to the continuous decrease of the amount of the intermediates.

3.3. FT-IR Spectroscopy

To confirm the formation of the copolymer of DPA and OPD, the FT-IR spectrum of the copolymer (R = 1:1) is presented in **Figure 7(a)**. As a comparison, the FT-IR spectra of PDPA and POPD have also been shown in **Figures 7(b)** and **7(c)**, respectively. It can be seen from **Figure 7(a)** that, the absorption bands at 3500 cm^{-1} corresponds to the N-H stretching vibration. The absorption

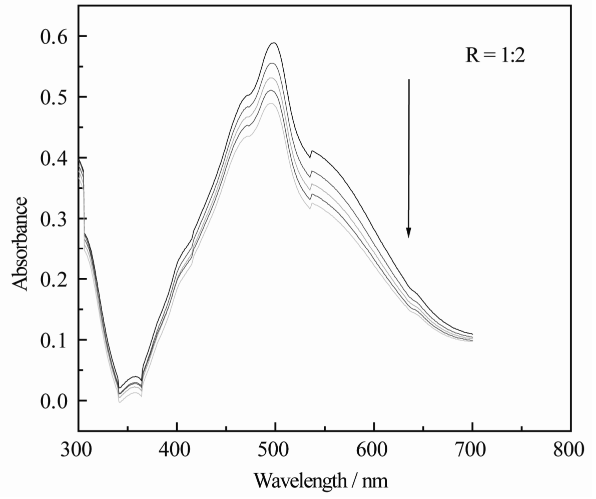
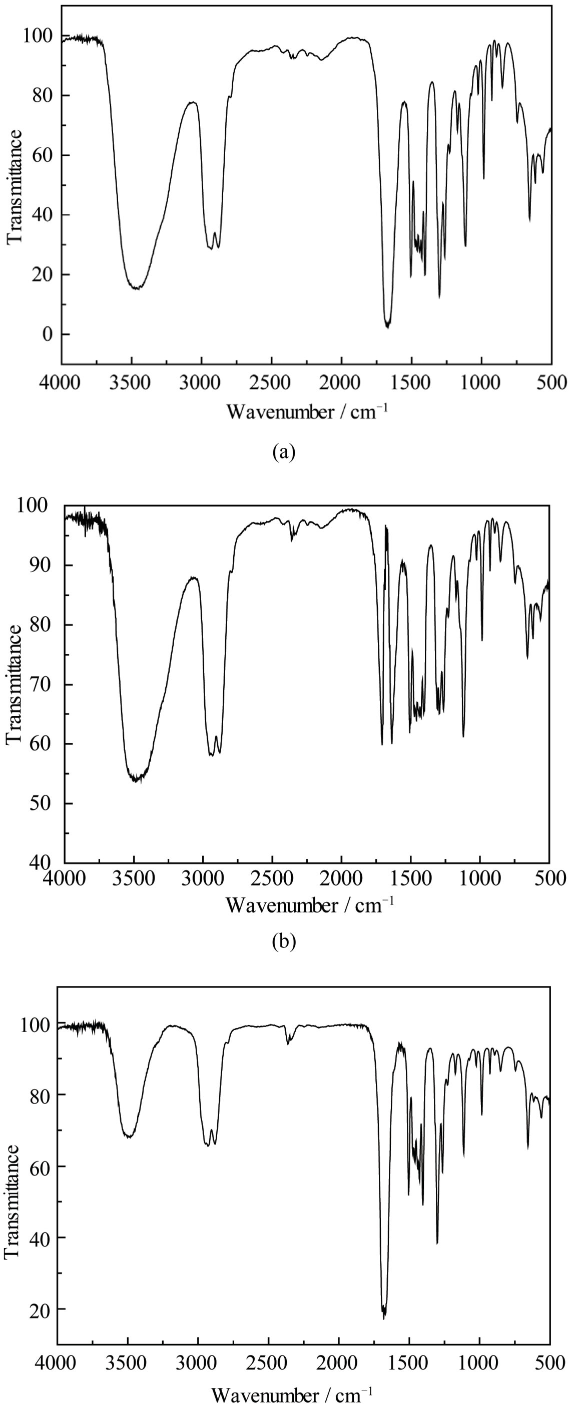


Figure 6. UV–Vis spectra at different time intervals (in minutes) after interruption of the electrolysis in the mixed solution (R = 1:2) performed for 10 min.



(a)

(b)

(c)

Figure 7. FT-IR spectra of the copolymer of DPA with OPD (a), PDPA (b), and POPD (c).

band at 1509 cm^{-1} is the characteristic of C–C multiple bond stretching modes of benzene ring [6]. The strong absorption band at 1670 cm^{-1} is assigned to the bending mode of aromatic secondary amine [7]. And, the band at 1310 cm^{-1} is assigned to the stretching vibration of C-N groups with partially double bonds characteristics. In the lower frequency region, the peak at 1123 cm^{-1} is due to the C-H in-plane deformation, which is used to evaluate the electron delocalization in polymers [45]. Therefore, the enhanced IR absorption at this location indicates that the copolymers have good conductivity, this agrees well with the strong absorption by free electrons in the region 4000 - 2000 cm^{-1}. While, the bands at 1068-1064, 885 and 850 cm^{-1} suggests the presence of phenazine structures in the copolymer backbone [46]. These structures could be due to the presence of the OPD units, which also appears in the spectrum of POPD. The bands at 1249 and 1117 cm^{-1} indicate the presence of the –C–NH–C– units as a consequence of the linking of NH_2 group of OPD with the phenyl carbon atom of DPA [9], which does not appear in the spectrum of PDPA. Thus, the FT-IR spectrum of the copolymer reveals the presence of both OPD and DPA monomer units in the copolymer backbone, as well as the structural differences between the homo- and co- polymers.

4. Conclusions

The electrochemical copolymerization of DPA and OPD has been investigated by using electrochemical and *in situ* spectroelectrochemical techniques. Compare to the CVs for electrochemical homopolymerization of DPA and OPD, the different characteristics in the CVs for the electrooxidation of the mixture of DPA and OPD indicate the occurrence of the copolymerization of DPA with OPD. And, the *in situ* UV–Vis spectroelectrochemical studies on the copolymerization of DPA with OPD demonstrate that the spectral characteristics for the copolymerization are different from those of the polymerization of DPA and OPD alone. The new absorption peak observed at 538 nm in the spectrum reveals the formation of the dimers/oligomers intermediates as a result of the cross- reaction between DPACRs and OPDCRs. FT-IR spectrum of the copolymer reveals the presence of both monomer units in the copolymer backbone, as well as the structural differences between homopolymers and copolymer.

5. Acknowledgements

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6. References

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