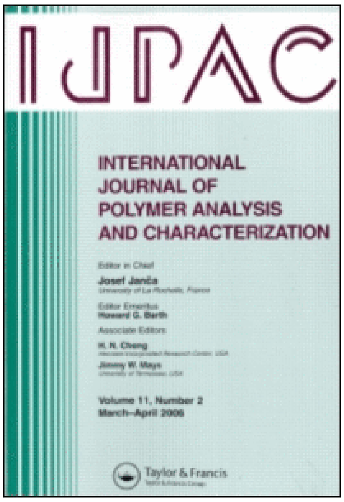

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Electrochemical Synthesis and Characterization of Conducting Poly(diphenylamine-co-2-methoxyaniline)

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Abstract: Electrochemical growth characteristics of copolymer deposition were monitored by performing copolymerization of diphenylamine (DPA) with 2-methoxyaniline (MA) at different molar feed ratios of the comonomers. Cyclic voltammograms of the copolymer films were recorded in the background electrolyte. Reactivity ratios of the two monomers were evaluated through elemental analysis using Fineman-Ross and Kelen-Tudos equations. FT-IR spectroscopy of the copolymer revealed the compositional variations of the comonomer units in the copolymer. Thermogravimetric analysis of the copolymer shows that the thermal stability of the copolymers varies with compositions of two monomers in the copolymers.

Keywords: Electrocopolymerization; Cyclic voltammetry; Reactivity ratios; FT-IR spectroscopy; Thermal analysis

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INTRODUCTION

Polyaniline, PANI, is considered to be the most promising intrinsically conducting polymer due to its important potential applications such as for light-weight batteries, electrochromic display devices, and optoelectronic devices.[1–3] However, the doped form of the conducting polymer is insoluble in common organic solvents and aqueous solutions. Several studies such as (i) post-treatment of parent polyaniline base,[4–6] (ii) homopolymerization of suitable aniline derivatives[7–9], and (iii) copolymerization of aniline with different kinds of ring or N-alkyl substituted derivatives[10–12] have been carried out to improve the solubility. Besides the solubility, depending on the nature of the substituent covalently bonded to polyaniline backbone, changes in electrochemical properties of the polymer are seen.

Poly(2-methoxyaniline), PMA, was prepared by Macinnes and Funt[13] and Gazotti et al.[14] and doped with functionalized acids. Concalves et al. and De Paoli et al.[15,16] studied the electrochromic properties of PMA. High coloumbic efficiency and intense chromic changes were observed for pure films,[15] and an electrochromic window was developed in aqueous, nonaqueous, and polymer electrolyte media using PMA as an optically active electrode.[16]

Diphenylamine, DPA, the N-substituted aniline derivative, has been electro-polymerized by Comisso et al.[17] in a mixture of 4 M H_2SO_4 and ethanol. They could not grow poly(diphenylamine), PDPA, film continuously on the surface of the electrode. The presence of ethanol as co-solvent caused dissolution of oligomeric products and hindered the film growth. Studies on the synthesis of poly(N-alkyl diphenylamine), poly (3-methoxy diphenylamine),[18] and poly(3-chloro diphenylamine)[19] have been reported. These studies revealed that polymer is formed mainly through C-C phenyl-phenyl coupling of DPA monomer.

Copolymerization is a simple way to prepare new polymers with specifically desired properties. It is also well known that studies of copolymerization could lead to knowledge of reactivities of monomers and their relationship to the chemical structure of monomers and, therefore, to a better understanding of the mechanism of polymerization.[20–22] Bagheri et al.[23] reported the electrochemical preparation and characterization of poly(diphenylamine-co-benzidine). The electroactivity of a copolymer has been found to be altered by the variation of comonomer feed ratios. Ram et al.[24] synthesized conducting poly(aniline-co-o-toluidine) and poly(aniline-co-o-anisidine) electrochemically. Copolymers prepared with $-CH_3$ or $-OCH_3$ groups in the phenyl rings of aniline lead to a better solvation effect with faster electrochromic response.[25] Dao and coworkers[26–28] have prepared a series of poly(aniline-co-N-butyl aniline) copolymers by chemical and electrochemical methods. Several copolymers of aniline with phenyl substituted and N-substituted anilines show better solubility, disordered structure, and decreased electrical conductivity.[29–33]

Electrochemical copolymerization of aniline derivatives with p-phenylenediamine in aqueous sulphuric acid medium has been investigated using cyclic voltammetry.[34] Poly(diphenylamine-co-aniline)[35] film has been deposited by the pulse potentiostatic method and a growth equation was deduced correlating the conditions of copolymerization. Also, electrochemical copolymerization of DPA with anthranilic acid[36] was performed using cyclic voltammetry. The copolymer compositions were determined by X-ray photoelectron spectroscopy. However, reports on copolymerization with DPA as one monomer are scarce.

In the present study, electrochemical copolymerization of diphenylamine (DPA) with 2-methoxyaniline (MA) was carried for different feed ratios of comonomers (DPA and MA) to deposit the copolymer film. Cyclic voltammetry was employed to deposit and simultaneously characterize the copolymer films. The copolymers were also characterized by elemental analysis, Fourier transform-infrared (FT-IR) spectroscopy, and thermogravimetric analysis.

EXPERIMENTAL SECTION

Chemicals

Analytical grade DPA (E-Merck), MA (Fluka), and potassium peroxodisulphate (E-Merck) were used as received. All reagents were prepared from doubly distilled water.

Electrochemical Copolymerization/Homopolymerization

Electrochemical copolymerization was performed in a single compartment reaction cell fitted with Pt electrode (area 0.0245 cm^2) as working electrode, a Pt wire as auxiliary electrode, and Ag/AgCl as reference electrode by using EG & G PAR- Model 173, Potentiostat/Galvanostat Versastat^{II}. The copolymer films were deposited electrochemically on the Pt electrode surface from aqueous 4 M H_2SO_4 solution of a mixture of DPA and MA with a fixed feed ratio (0.25) of DPA (represented as mole fraction of DPA in the feed) by reversible cycling of the potential between 0.0 and 1.0 V at a constant scan rate of 50 mV/s. The cyclic voltammograms (CVs) of the growing film of copolymer were recorded continuously and coincidently with synthesis. Similar experiments were conducted using various feed ratios (0.38, 0.50, 0.63, 0.75, and 0.88) of DPA, and CVs of the growing film were recorded for 50 cycles.

Electrochemical homopolymerization of DPA and MA were also performed by cyclic voltammetry in the same potential range.

Electrochemical Characterization of Copolymer Films

The copolymer film coated electrode was repeatedly washed with 4 M H_2SO_4. The electrode was then placed in a monomer-free background electrolyte (4 M H_2SO_4) and equilibrated by repetitive cycling of potential in the range 0.0–1.0 V (versus Ag/AgCl) until a constant CV pattern without any appreciable change in peak current was obtained. The CVs of the stabilized copolymer films were then recorded in the same potential range for various scan rates.

Synthesis of Copolymers

Copolymers were synthesized by chemical oxidative polymerization for various molar feed ratios of DPA and MA by using potassium peroxydisulphate (PDS) as the oxidant. A solution of monomers (40 mM DPA and 40 mM MA) was prepared in 4 M H_2SO_4 and cooled below 273 K using a freezing mixture. A pre-cooled solution of PDS (30 mM) was then added dropwise to the monomer solution with constant stirring over a period of 20 minutes. The solution was further stirred for one hour in the freezing mixture. A bright emerald green precipitate was formed. The precipitate was filtered through a sintered-glass crucible and washed with 4 M H_2SO_4 continuously until the filtrate was colorless. The acid-doped polymer was then dried under vacuum for 48 h at room temperature.

Other Characterization

Elemental analysis FT-IR spectra of copolymers were recorded by using a NEXUS$_{TM}$ 470 FT-IR ESP Nicolet spectrophotometer. Thermal stability of copolymers was studied by thermogravimetric analysis (TGA) in TA Instruments 2050 analyzer, from 50° to 800°C (10°C min^{-1}) under nitrogen atmosphere.

RESULTS AND DISCUSSION

Electrochemical Copolymerization/Homopolymerization

The cyclic voltammograms (CVs) recorded during electrochemical copolymerization with mixed solution containing diphenylamine (DPA) and 2-methoxyaniline (MA) showed strikingly different growth and electrochemical characteristics than those with individual homopolymerization.

Figure 1 presents the CVs recorded for the 50 cycles for copolymerization of DPA with MA using different molar feed ratios of DPA (0.25, 0.38, 0.50, 0.63, 0.75, and 0.88). The anodic upper potential was kept as 1.0 V. Under this potential limit both monomers were found to be simultaneously oxidized to produce their cation radicals.[37]

For all selected ratios of DPA to MA, a peak was observed at 0.65 –0.68 V (versus Ag/AgCl) in the first anodic scan of potential, which corresponds to the oxidation of monomers (DPA and MA). In the reverse scan, two peaks were noticed at around 0.31 to 0.30 V and 0.38 to 0.40 V (versus Ag/AgCl), respectively. These peaks are assigned for the reduction of dimeric or oligomeric products produced from the chemical reactions of the oxidized monomer species, diphenylamine cation radical and 2-methoxyaniline cation radical. The CVs of the subsequent cycles of potential scan during copolymerization reveal few interesting characteristics.

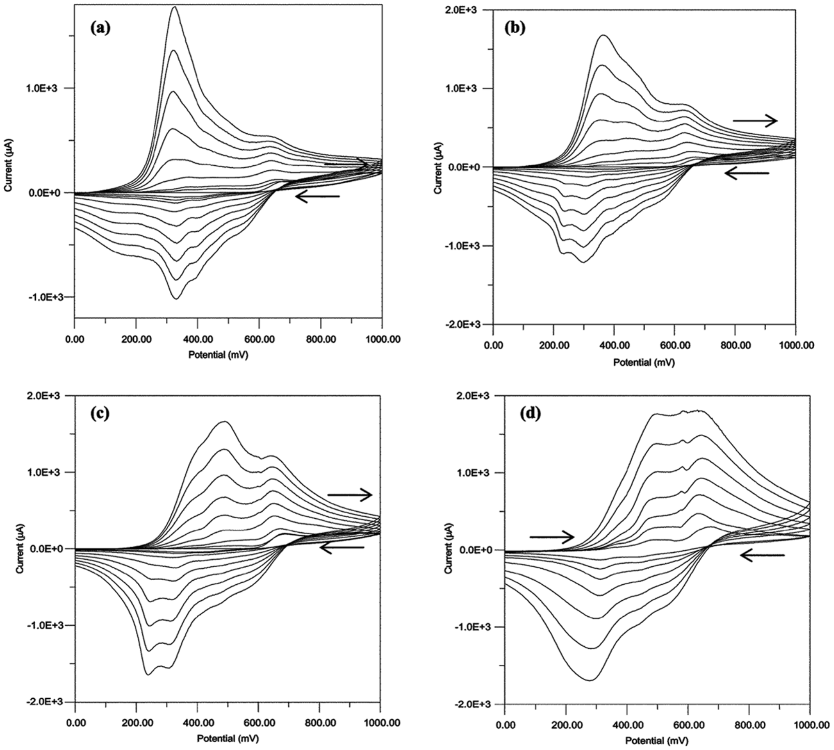


Figure 1. CVs recorded during the electrochemical copolymerization of DPA with MA using different feed ratios of DPA: 0.25 (a), 0.38 (b), 0.50 (c), 0.63 (d), 0.75 (e), and 0.88 (f). [DPA] and [MA] = 40 mM and electropolymerization of DPA (g) [DPA] = 20 mM. CVs of every five cycles are presented.

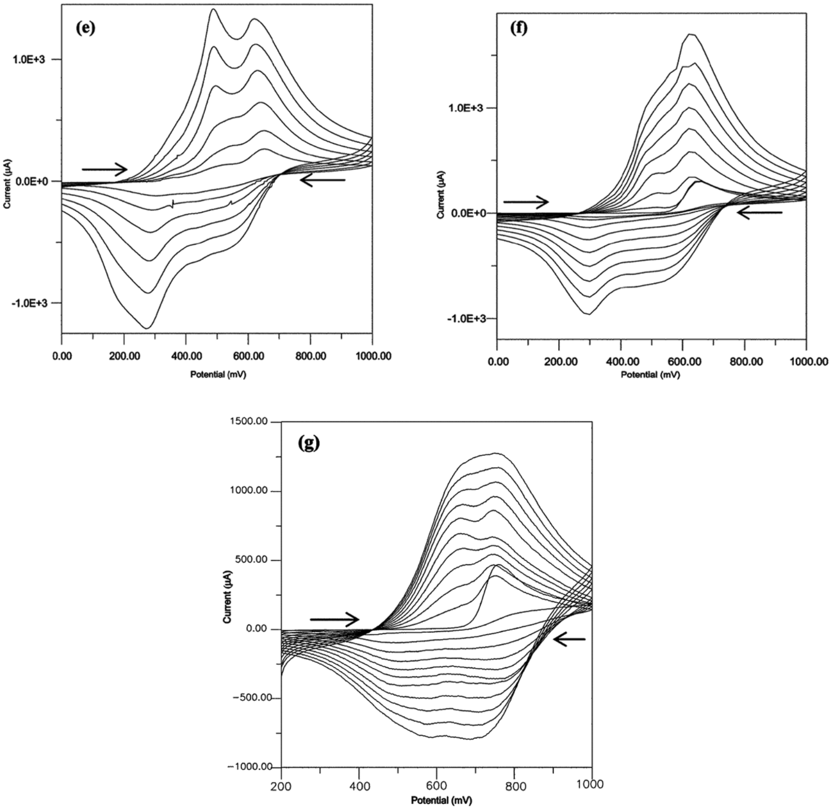
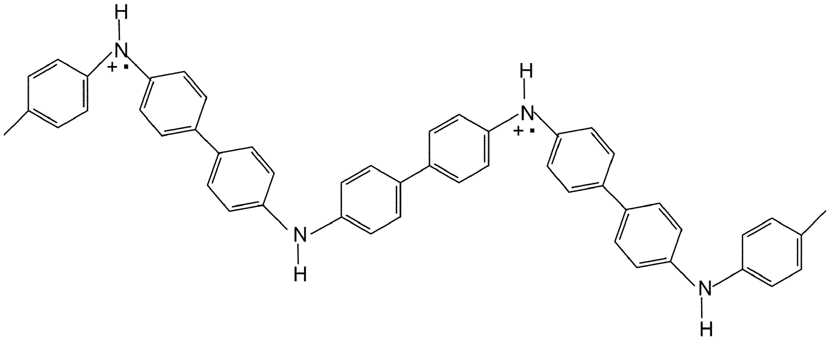


Figure 1. Continued.

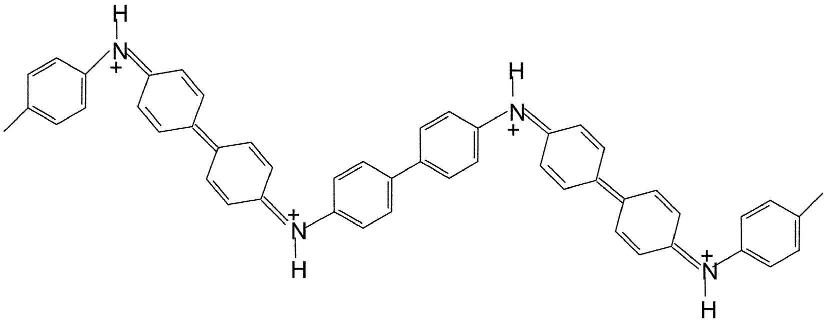
CVs of the continuous cycle of potentials show redox couples corresponding to the copolymer deposition on the surface of the working electrode. The CV pattern showed striking variations upon changing the molar feed ratios of two monomers (DPA and MA) during copolymerization. We envisage that this type of changing trend in the CV pattern would arise from the changes in the composition of the copolymer deposited during copolymerization. Since both DPA and MA would generate electroactive sites in the copolymer, the electroactitvity of the deposited copolymer is expected to show variations with composition of the comonomer in the copolymer. This supposition is confirmed through a careful analysis of peak potentials, peak current, and charge associated with the copolymer deposition and further supported with the determination of copolymer compositions and reactivity ratios through elemental analysis.

Two redox couples are easily observable for the copolymerization with molar feed ratios of DPA as 0.88 and 0.75. The anodic peaks were observed at 0.60 V and 0.70 V (versus Ag/AgCl) with complementary cathodic peaks at 0.58 V and 0.60 V (versus Ag/AgCl), respectively (Figure 1(f) and (e)). The peak potentials noticed are totally different from those of homopolymerization of DPA alone (Figure 1(g)). For the polymerization of DPA, the anodic process occurs at 0.57 V and 0.74 V (versus Ag/AgCl), with cathodic counterparts at 0.42 V and 0.65 V (versus Ag/AgCl) respectively.[35,36] The two anodic peaks observed during polymerization of DPA are assigned for the generation of N, N′-diphenylbenzidine type radical (DPB$^{+\cdot}$, polaronic form of PDPA structure) and N, N′-diphenylbenzidine dication (DPB^{2+}, bipolaronic form of PDPA) respectively (Scheme 1).

Variations in the peak positions for the oxidation and reduction process for the copolymerization in comparison with homopolymerization are seen for the different conditions of electropolymerization. The presence of MA units in the deposited poly(DPA-co-MA) makes the redox process of DPA units occur in different potential ranges.



Polaronic forms of PDPA structure



Bipolaronic forms of PDPA structure

Scheme 1.

It is known from earlier reports that electropolymerization of aniline in the presence of aniline derivatives resulted in the incorporation of units of aniline derivatives in the PANI structure.[23,32,33] The DPA units present in the copolymer are expected to be oxidized to diphenosemiquinoaminimine ($DPB^{+\cdot}$) and diphenoquinonediimine (DPB^{2+}) in the two anodic peaks.[36] The corresponding two-step reduction occurs at 0.63 V (versus Ag/AgCl) (DPB^{2+} to $DPB^{+\cdot}$) and 0.53 V (versus Ag/AgCl) (DPB^{+} to DPB type) respectively (Scheme 1). The peak current values for all these peaks were found to increase progressively with number of cycles (Figure 2). This type of increasing peak current value with cycle number has been observed for electropolymerization of aniline and substituted anilines[35,36] and attributed to the continuous buildup of electroactive polymer film on the surface of the working electrode during electropolymerization. In fact, a green-colored deposit could be seen on the surface of the working electrode in the present study.

For copolymerization with a molar feed ratio of DPA of 0.25, four redox processes become identifiable in the CVs (Figure 1(a)) in contrast to the two redox processes noticed for the copolymerization with DPA

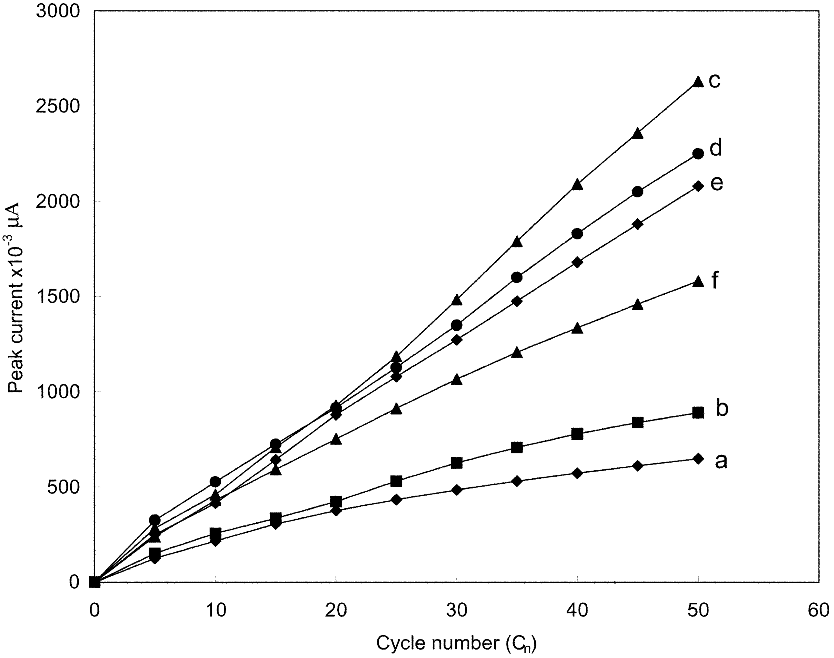


Figure 2. Effect of cycle number on peak current values for copolymer deposition with various molar feed ratios of DPA: 0.25 (a), 0.38 (b), 0.50 (c), 0.63 (d), 0.75 (e), and 0.88 (f).

molar feed ratio of 0.88 (Figure 1(f)). The four anodic waves were observed around 0.65 V (I), 0.43 V (II), 0.31 V (III), and 0.14 V (IV) (versus Ag/AgCl) respectively. The first two redox processes are attributed to the generation of DPB^{2+} and $DPB^{+\cdot}$ type structures in the copolymer (Scheme 1). The two new redox peaks with midpoint potentials of 0.15 V and 0.32 V (versus Ag/AgCl) are assigned for the formation of polaronic and bipolaronic forms of MA units in the copolymer.[38] The peak current values of these peaks increase with cycle number (Figure 2). It is pertinent to note that the CV pattern as observed for copolymerization is not a simple superposition of two CV patterns of homopolymerization. It is interesting to note that the ratio of peak currents for the fourth to first anodic peak (i_p^a (IV)/i_p^a (I)) increases progressively with increasing cycle number. It is therefore envisaged that under these conditions the copolymer deposited would have more MA units than DPA units; this aspect is discussed below.

For the feed ratios of DPA between 0.88 and 0.25 (i.e., 0.75, 0.63, 0.50, and 0.38), the four redox pairs were seen in the CVs (Figure 1) with differences in peak potentials. The peak current values increase steadily with number of cycles, indicating continuous binding up of electroactive polymer on the surface of the working electrode in all these cases. Few interesting observations could be made in comparing the CVs of the copolymerization performed with these feed ratios of DPA and MA. When the feed ratio of DPA was increased from 0.25 to 0.38, the third and fourth anodic peaks merged into a single peak and were observed at a potential higher than the third anodic peak for the copolymerization with feed ratio of DPA of 0.25. The second peak moved to a more positive potential. The first anodic peak did not show any change in position. On continuous cycling of potential, while the peak positions remain unchanged, the increase in peak current of the second peak was more dominant than the peak current of the fourth peak. Merging of the third and fourth peaks and shifting of the second anodic peak to more positive values were also seen for the copolymerization with feed ratios of DPA of 0.38 and 0.50. However, the increase in peak current of the second peak was not significant as seen for the copolymerization with molar feed ratio of DPA of 0.25.

CVs recorded during copolymerization with DPA feed ratios of 0.63 and 0.75 predominantly had first and second oxidation peaks. The second oxidation peak was found to be positively shifted from 0.47 to 0.49 V (versus Ag/AgCl) when the feed ratio of DPA was increased from 0.63 to 0.75. Hence, a change in the electrochemical behavior of copolymer deposited was seen when the feed ratio of the DPA was above 0.50.

Stillwell and Park[39] correlated the growth rate of conducting polyaniline deposition with experimental conditions. In the present work, the cathodic charge associated with copolymer deposition was calculated for different cycles (>5) through graphical integration of CV curves in

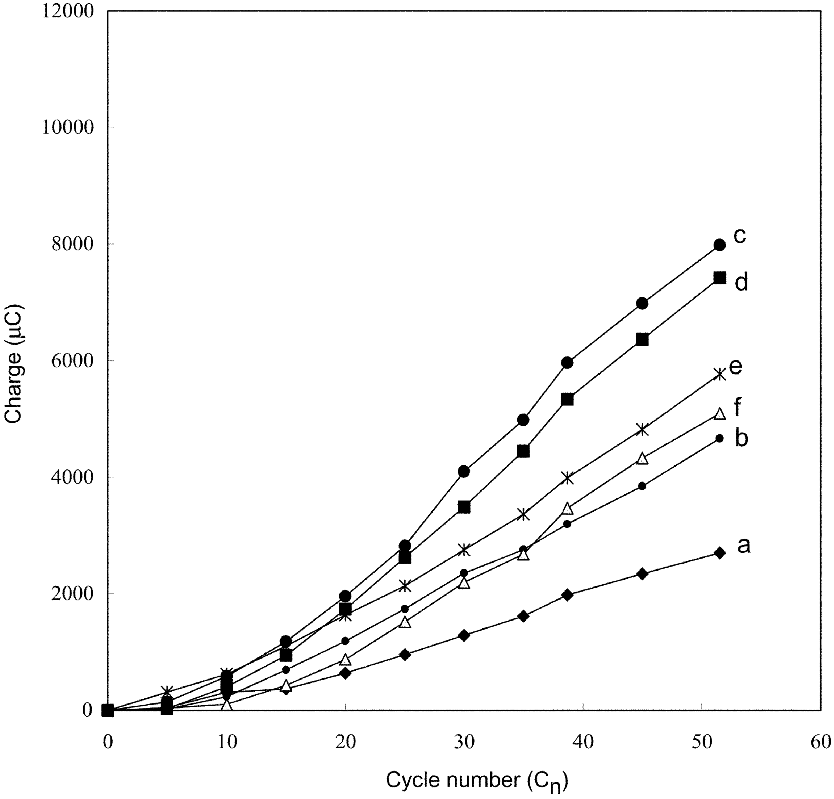


Figure 3. Effect of cycle number on charge for copolymer deposition for various feed ratios of DPA: 0.25 (a), 0.38 (b), 0.50 (c), 0.63 (d), 0.75 (e), and 0.88 (f).

between the potential limits. For all feed ratios of DPA, charge (Q_G^c) was found to increase with increase in cycle number (Figure 3), which indicates the increasing amount of copolymer on the surface of the working electrode with increase in cycle number. Q_G^c was found to increase with feed ratio of DPA up to a value of 0.50 and thereafter showed a decreasing trend. The growth rate of copolymer deposition showed an initial increasing trend with molar feed ratio of DPA followed by a decreasing trend at higher feed ratios of DPA (>0.50).

Electrochemical Behavior of Copolymer Films

Figure 4 represents the CVs of the copolymer films recorded in monomer-free background electrolyte. The copolymer films were deposited with different molar feed ratios of DPA during copolymerization. The CV patterns of the stabilized copolymer films are similar to the CV pattern

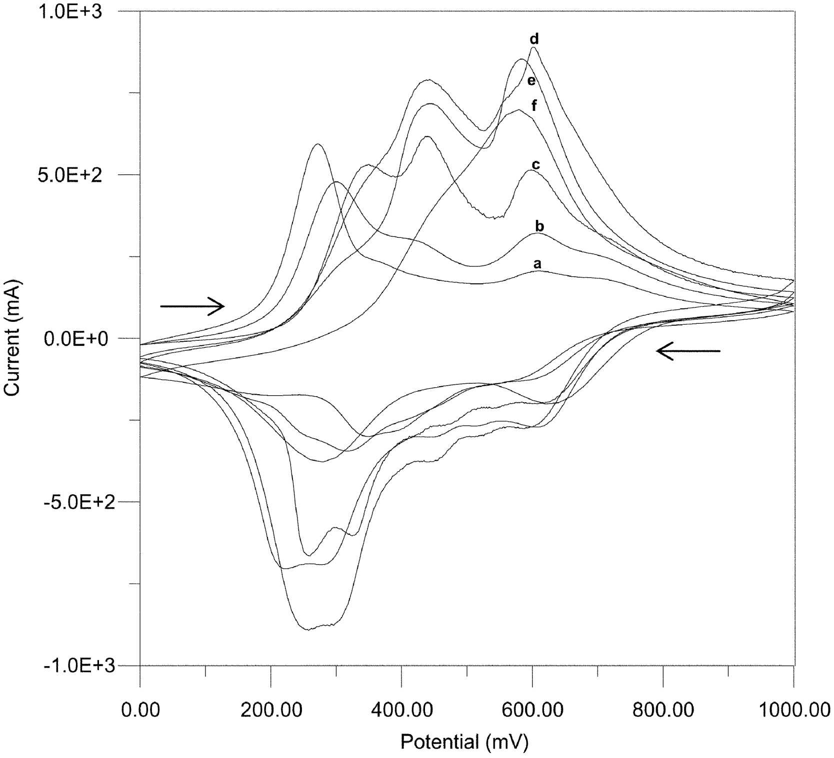


Figure 4. CVs of the films of poly(DPA-co-MA) in 4 M sulphuric acid. The copolymer films were deposited using different feed ratios of DPA: 0.25 (a), 0.38 (b), 0.50 (c), 0.63 (d), 0.75 (e), and 0.88 (f).

recorded during copolymerization. A slight difference in peak size and peak potential could be seen which is attributed to the changes in the number of charge sites available for this film and the absence of electrochemical reactions involving monomer. More than 95% of the charge utilized for deposition of the copolymer was retained in the copolymer film. This indicates the absence of co-deposition of oligomers and the stable nature of copolymer film on the surface of the working electrode.

The dependence of peak current on sweep rate was monitored for the copolymer films (figure not shown). A linear relationship could be seen between peak current (fourth anodic peak) and sweep rate, indicating surface-bound redox characteristics of the copolymeric films.

Synthesis and Characterization

For characterization purposes, the copolymers were prepared with various feed ratios of DPA and MA using potentiostatic as well as chemical oxidative polymerization. The chemically synthesized copolymers were cast as films on the platinum working electrode using a suspension of the sample in acetone. The copolymer-coated electrode was then placed in monomer-free background electrolyte and the potential was cycled between 0.0 and 1.0 V at a scan rate of 50 mV/s until a stable CV pattern was reached (without change in peak positions and peak current values on further cycling).

The CV obtained for the electrode coated with chemically synthesized copolymers was found to have a CV pattern similar to electrochemically deposited ones. This obviously means that the samples of copolymers prepared with definite molar ratios of DPA and MA by oxidative polymerization or electrochemical deposition are one and the same material.

Copolymer Composition and Reactivity Ratios

The compositions of DPA and MA units in the copolymers were determined through elemental analysis and further used to find the reactivity ratios of DPA and MA. Proper polymerization time was given to ensure the percentage formation of polymer as less than 10%. A simple copolymerization model involving four possible reactions between oligomeric radicals with terminal units as DPA (M_1^*) or MA (M_2^*) and neutral monomers DPA or MA is envisaged as:

$$M_1^* + M_1 \rightarrow M_1^* \quad \text{Rate} = k_{11}[M_1^*][M_1]$$

$$M_1^* + M_2 \rightarrow M_2^* \quad \text{Rate} = k_{12}[M_1^*][M_2]$$

$$M_2^* + M_2 \rightarrow M_2^* \quad \text{Rate} = k_{22}[M_2^*][M_2]$$

$$M_2^* + M_1 \rightarrow M_1^* \quad \text{Rate} = k_{21}[M_2^*][M_1]$$

where M_1^* and M_2^* represent the radical form of oligomer chain with DPA and MA units respectively, and k_{11}, k_{12}, k_{21}, k_{22} are the propagation rate constants. Using the ratios of propagation rate constants, the reactivity ratios of DPA and MA are defined as

$$r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21}$$

On rearranging the differential form of the copolymer composition equation that relates the composition of two monomer units in the copolymer and feed composition of the two monomers to the Fineman-Ross form,[40]

$$G = r_1F - r_2 \tag{1}$$

where $G = x(y - 1)/y$ and $F = x^2/y$.

In the above equation x and y are molar concentration ratios of comonomers in the feed and copolymer respectively. Further linearization through introduction of an arbitrary constant α(which makes the spread of data points even) results in the Kelen and Tudos[41] equation:

$$\eta = [r_1 + r_2/\alpha]\varepsilon - r_2/\alpha \tag{2}$$

$$\eta = G/(\alpha + F), \quad \varepsilon = F/(\alpha + F) \quad \text{and} \quad \alpha = (F_m \cdot F_M)^{1/2} \tag{3}$$

where F_m and F_M are maximum and minimum values of F respectively.

Both the Fineman-Ross and Kelen-Tudos (Equation (2)) equations were used to find reactivity ratios of DPA and MA. The plot of G versus F (Figure 5(a)) gives r_1 and r_2 as 0.237 and 0.232. A plot of η versus ξ (Figure 5(b)) gives r_1 and r_2 as 0.241 and 0.241 respectively. The values of r_1 and r_2 determined through the Fineman-Ross and Kelen-Tudos equations (Equation (2)) closely agree with each other. It is interesting to note that reactivity ratios of DPA and MA are close to each other. Hence, both DPA and MA are equally reactive towards reactive sites M_2^* and M_1^* to generate the copolymer. Since r_1 and r_2 values are less than unity, an azeotropic composition is expected. The plot of F_{MA} versus f_{MA} (Figure 6) (F_{MA} = molar concentration of MA in the copolymer and f_{MA} = molar concentration of MA in the feed) gives an azeotropic composition as ≈ 0.5. A crossover of composition of DPA in the copolymer from the ideal line beyond the feed ratio of DPA of 0.5 can now be ascribed as the reason for the changes in CV characteristics (peak position and charge, Figures 1 and 3).

Conductivity Measurements

The conductivity of chemically synthesized copolymer was determined using the four-point probe technique. At room temperature, the output voltage was measured for various current values ranging from 1.0 to 10 mA. Using the measured values, the conductivity of the copolymer, σ, at room temperature was determined as $1.25 \times 10^{-2}\,\mathrm{S\,cm}^2$.

FT-IR Spectroscopy

FT-IR spectra of copolymers are presented in Figure 7. The absorption bands around 3390 cm^{-1} and 1316 cm^{-1} correspond to N-H stretching mode of secondary amine. The absorption band around 1500 cm^{-1} is characteristic of C-C multiple bond stretching modes of benzene ring.[8] The strong absorption band at 1596 cm^{-1} is assigned for the bending mode of aromatic secondary amine.[9] The bands around 1170 cm^{-1} and

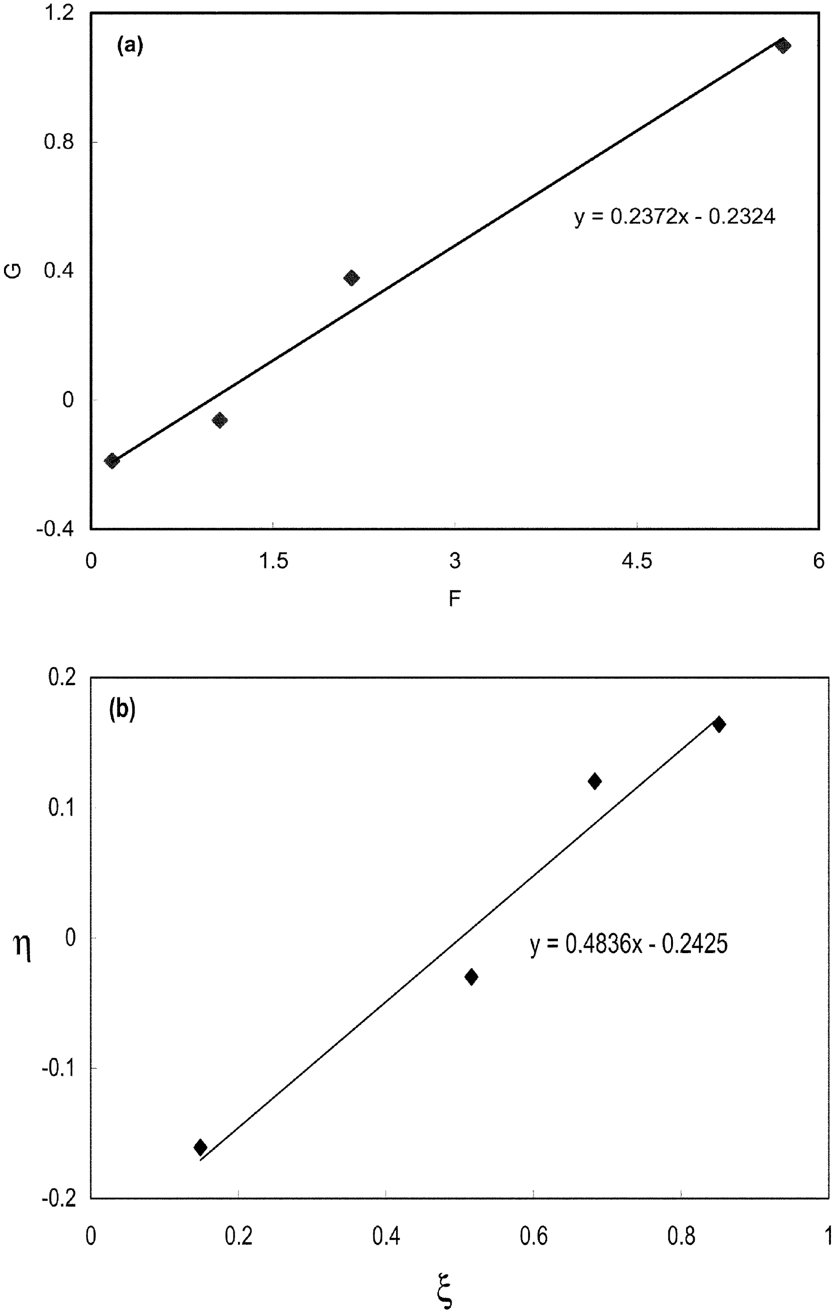


Figure 5. (a) Ross-Fineman and (b) Kelen-Tudos plots for poly(DPA-co-MA) of MA.

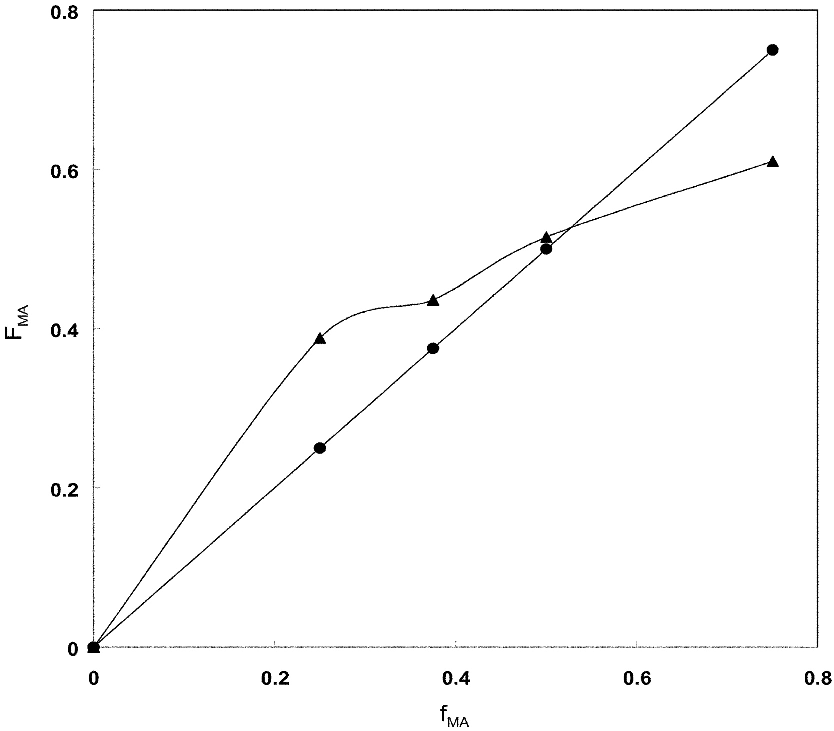


Figure 6. Plot of copolymer composition vs. feed composition of MA.

1140 cm^{-1} are attributed to the presence of diphenoquinone type units and represent the DPA units in the copolymer. The bands around 1236 cm^{-1} and 1112 cm^{-1} indicate the presence of –C–NH–C– link as a consequence of the linking of the NH_2 group of MA with the phenyl carbon atom of DPA.[11] The band around 1316 cm^{-1} is assigned to stretching vibration of C-N groups with partial double bond characteristics. The ratio of the intensity of the peak corresponding to C-N single bond (1236 cm^{-1}) to the intensity of the peak around 1316 cm^{-1} indicates that the copolymers have more imine units and hence are conductive.

The absorption peak around 807 cm^{-1} is assigned to the C-H stretching frequency of 1, 2, 4-trisubstituted aromatic ring. The variations in the ratio of intensity of peaks around 1170 cm^{-1} (due to the diphenoquinoneimine) and 807 cm^{-1} can be considered as due to the variations in DPA and MA units in the copolymer. The probable differences in the absorptivity at these peaks restricted us to quantitatively correlating with the ratio of the two monomers in the copolymer determined through elemental analysis. The relative intensity of the bands around 1114 cm^{-1} (C-H in plane deformation vibration) to 1596 cm^{-1} can be considered as the measure of

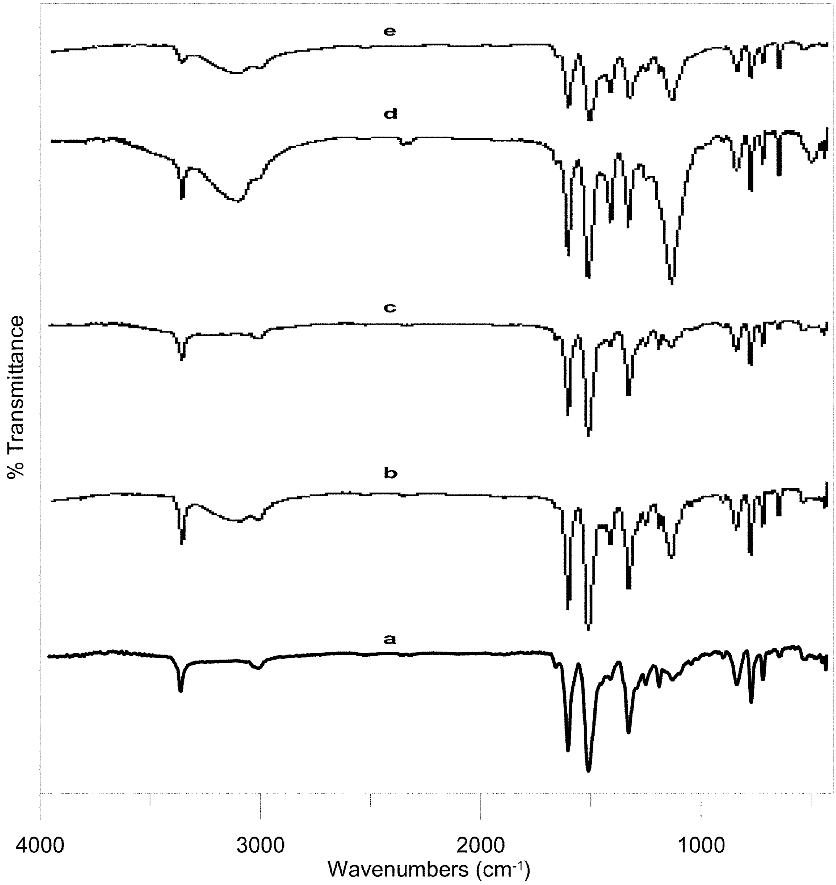


Figure 7. FT-IR spectra of poly(DPA-co-MA) prepared with different feed ratios of DPA: 0.25 (a), 0.38 (b), 0.50 (c), 0.63 (d), and 0.75 (e).

oxidative level in the copolymer. The ratio of intensities (I_{1114}/I_{1596}) increases with increasing composition of DPA units in the copolymer from 0.39 to 0.52 and thereafter decreases. This is consistent with the observed changes in copolymer composition beyond the molar feed ratio of DPA of 0.5 (Figure 7) and also the changes in electrochemical characteristics as seen in cyclic voltammetric studies (Figure 1).

Thermal Analysis

Figure 8 represents the thermogram of the copolymer samples with DPA content of 0.25, 0.50, 0.63, and 0.75. The copolymer showed major weight

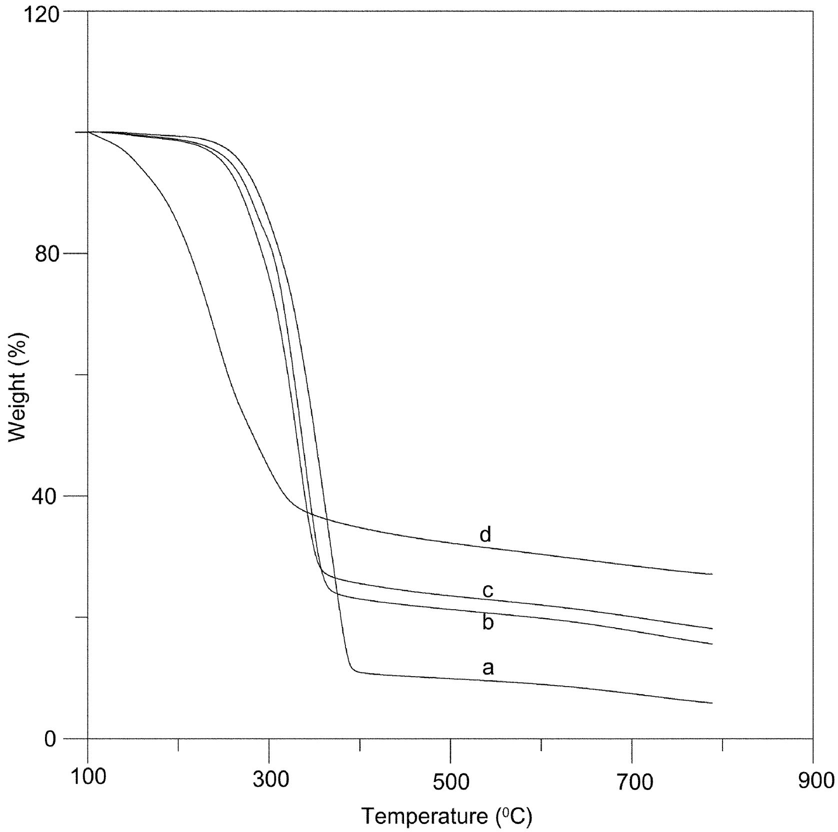


Figure 8. Thermogravimetric analysis of poly(DPA-co-MA) prepared with different feed ratios of DPA: 0.25 (a), 0.50 (b), 0.63 (c), and 0.75 (d).

changes in the temperature range 275–400°C. Removal of dopants and degradation of main chain units mainly occur at these temperature ranges.[42] The onset temperature of decomposition of the main chain and removal of dopants was found to be shifted to higher temperatures for the copolymers with higher proportion of DPA units.

CONCLUSIONS

The cyclic voltammograms representing the growth of copolymers during electrochemical copolymerization of DPA and MA on the electrode surface were found to show variations based on compositional changes of the two monomers in the copolymer. The values of reactivity ratios of DPA and MA as determined through the Fineman-Ross and Kelen-Tudos methods agree with each other. DPA and MA have reactivity ratios close to each other (0.241) and the presence of DPA and MA units in the copolymer in various proportions influences the redox characteristics of the copolymer. The copolymer composition goes through an azeotrope at ≈ 0.5. The presence of peaks at $1170\,\mathrm{cm}^{-1}$ (diphenoquinone imine units) and $807\,\mathrm{cm}^{-1}$ (1,2,4 trisubstituted aromatic amine units) as evident from FT-IR spectroscopy signifies the existence of DPA and MA units in the copolymer.

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