

# Deposition of Poly(diphenylamine-co-o-chloroaniline) by Pulse Potentiostatic Method: Growth Equation and Characterization

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**ABSTRACT:** Electrochemical copolymerization of diphenylamine (DPA) with o-chloroaniline (OCA) was performed in aqueous 4M sulfuric acid using the pulse potentiostatic method (PPSM). By employing the tunable parameters in PPSM, polymeric films were deposited under different conditions. Cyclic voltammetry was used for evaluating the characteristics of the deposited polymeric films. A suitable growth equation for the deposition of polymer, relating the charge associated for the film deposition and the pulse parameters in PPSM, was deduced. Various surface parameters are evaluated. The formation of copolymer during PPSM deposition was revealed through critical analysis of

the results. The characteristic differences between the individual homopolymers, poly(diphenylamine) and poly(o-chloroaniline) and the copolymer, poly(diphenylamine-co-o-chloroaniline), were brought out. The copolymer was also synthesized through a chemical method and characterized through infrared and ultraviolet-visible spectroscopic analysis. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 389–397, 2003

**Key words:** pulse potentiostatic; polymer film deposition; growth equation; surface parameters; characterization

## INTRODUCTION

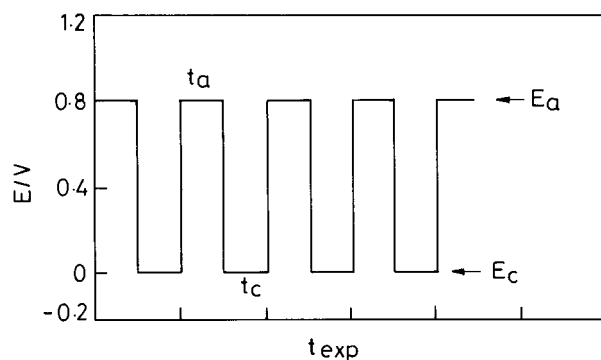
The widespread application of conducting polymers as newer materials in rechargeable batteries, electromagnetic interference shieldings, electrochromic display devices, sensors, and the possible extension to even molecular computing has necessitated extensive research.<sup>1–4</sup> Among the conducting polymers, polyaniline (PANI) has unique properties like ease of preparation in aqueous medium, good stability in air,<sup>5</sup> simplicity in the doping process,<sup>6</sup> much improved electronic properties,<sup>7</sup> electrochromic effects,<sup>8</sup> and moderately high conductivity in the doped form.<sup>9</sup> These aspects make PANI a suitable candidate of great technological promise. One of the major difficulties in this area is the limitation of processability of the formed polymers.

In the search for newer conducting polymers with improved mechanical strength and processability, copolymerization has been found to be effective in improving the mechanical properties of the already-known brittle polymers.<sup>10</sup> Several reports on copolymerization with aniline and substituted anilines are available.

Diaz et al.<sup>11</sup> have reported the synthesis and characterization of the copolymer, poly[aniline-co-N-(4-sulphophenyl)aniline]. Copolymers of aniline and metanilic acid were synthesized by Yue et al.<sup>12</sup> by the direct sulfonation of PANI. Simultaneous electropolymerization of aniline and metanilic acid has resulted in the formation of similar products.<sup>13</sup> Poly(aniline-co-aminobenzonitrile) film<sup>14</sup> was synthesized by electrochemical oxidative copolymerization in an aqueous acid medium. Cyclic voltammetry has been used recently for the copolymerization of aniline with 2-amino diphenyl amine,<sup>15</sup> 2,2'-dithiodianiline,<sup>16</sup> and 1-naphthyl amine.<sup>17</sup> For the preparation of conducting polymers, electrochemical methods are often preferred over chemical methods.

Electrochemical methods offer special advantages over other methods due to the possibility of simultaneous characterization. Several conducting polymers were synthesized by electrochemical oxidation of monomers either potentiostatically<sup>18</sup> or galvanostatically,<sup>19</sup> or by using the potential cycling technique.<sup>20</sup> Tsakova et al.<sup>21,22</sup> prepared polyaniline films by the pulse potentiostatic method (PPSM) consisting of periodic cathodic and anodic rectangular pulses. A number of operational parameters such as switching potential, pulse number ( $P_n$ ), pulse width ( $P_w$ ), etc., are available in this method that can influence the growth and electrochemical characteristics of the deposited polymeric materials.

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**Scheme 1** Schematic representation of the pulse program.

PPSM has not been adopted so far toward copolymerization of diphenylamine (DPA) with *o*-chloroaniline (OCA). The present work directs its attention to use PPSM for the polymerization of DPA with OCA and to follow the growth behavior of deposited films by cyclic voltammetry. Besides that, cyclic voltammetric method has been used here for the electrochemical characterization of deposited films for evaluating surface parameters. Further, the changes in growth behavior in contrast to their homopolymeric deposition are monitored by a critical comparison of the results. Chemical synthesis and consequent characterizations were also made on the homopolymer/copolymer.

## EXPERIMENTAL

### Chemicals

DPA (Qualigens, India) and OCA (Fluka, USA) were used as such. The other chemicals used were of purest quality available, mostly from BDH, India. AnalaR sulfuric acid was used for preparing background electrolyte and all other reagents were prepared from doubly distilled water.

### Electrochemical copolymerization

The electrochemical copolymerization was carried out in a BAS 100-A electrochemical analyzer using a three-electrode cell assembly employing the mixture of DPA and OCA of varying feed ratios of DPA (0.2, 0.4, 0.5, 0.6, and 0.8) and keeping the total molar concentration as 50 mM in 4M aqueous sulfuric acid solution using a platinum disk (0.0225 cm<sup>2</sup>) as working electrode, platinum wire as counter electrode, and Ag/AgCl as reference by applying specific cathodic ( $E_c$ ) and anodic ( $E_a$ ) potential pulses with cathodic time interval ( $t_c$ ) and anodic time interval ( $t_a$ ) for the total experimental time ( $t_{exp}$ ). (See Scheme 1.)

### Characterization by cyclic voltammetry

The polymer-coated electrode was then placed in a monomer-free electrolyte and equilibrated by repeti-

tive cycling between 0.0 to +0.8 V vs Ag/AgCl until a constant cyclic voltammogram pattern without any appreciable change in peak potential and peak current values was obtained. Equilibration was achieved within a few cycles of potential scanning, which is indicative of the stable nature of the film. The cyclic voltammogram (CV) of the stabilized copolymer film was then recorded.

Electrochemical homopolymerization of DPA and OCA was also performed individually under different pulse conditions and the cyclic voltammogram of the homopolymer coated electrode was recorded as mentioned earlier.

### Chemical polymerization

The copolymer of DPA with OCA was prepared by the oxidation of the mixture of monomers in a fixed feed ratio (1:1) using potassium peroxodisulfate (PDS) as oxidant in aqueous acidic medium. The procedure for the preparation of poly(DPA-co-OCA) is outlined below: A mixture containing DPA and OCA was prepared by dissolving 0.825 g of DPA (25 mM) and 0.563 g of OCA (25 mM) in 200 mL of 4M sulfuric acid. It was cooled well below 273 K using a freezing mixture. A precooled solution of PDS (60 mM) containing 1.4 g in 80 mL of 4M sulfuric acid was then added dropwise to the mixture with stirring and was further stirred for about an hour in the freezing mixture.

The resulting green precipitate was filtered through a sintered-glass crucible and washed well with 4M sulfuric acid till the filtrate became colourless. The acid-doped copolymer was then dried under dynamic vacuum at room temperature.

### Other characterizations

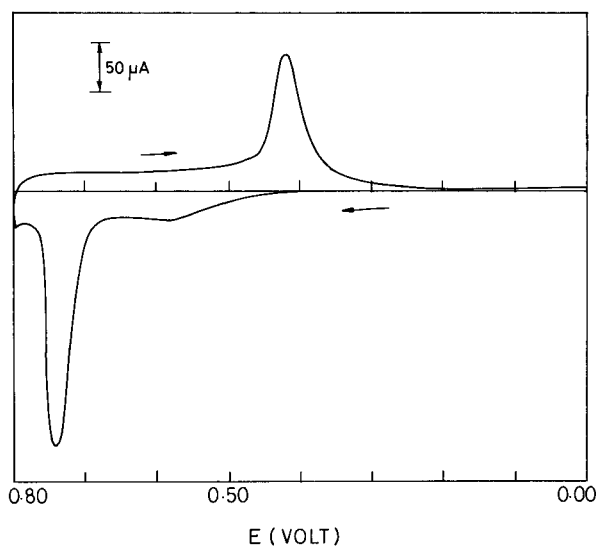
The conductivities of chemically synthesized copolymer sample of DPA and OCA was determined using the Four-probe resistivity setup (Concord Instruments, India).

The Fourier transform infrared (FTIR) spectrum of the chemically synthesized copolymer was recorded using a Bruker IFS 66v FT-IR spectrophotometer in the region 500–4000 cm<sup>-1</sup> using KBr pellets.

Ultraviolet (UV)-visible spectra of chemically prepared copolymer/homopolymers were recorded in dimethylformamide (DMF) solvent (solution concentration is 0.05 mg/mL) using a Shimadzu UV-Visible spectrophotometer-2401 PC model.

## RESULTS AND DISCUSSION

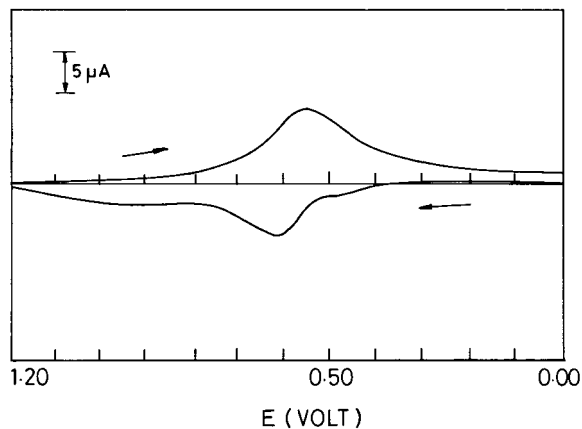
By employing PPSM, electrochemical polymerization of DPA by PPSM on a bare platinum electrode was performed in 4M sulfuric acid medium by keeping [DPA] = 50 mM,  $P_n$  = 1000, and  $P_w$  = 100 ms in the



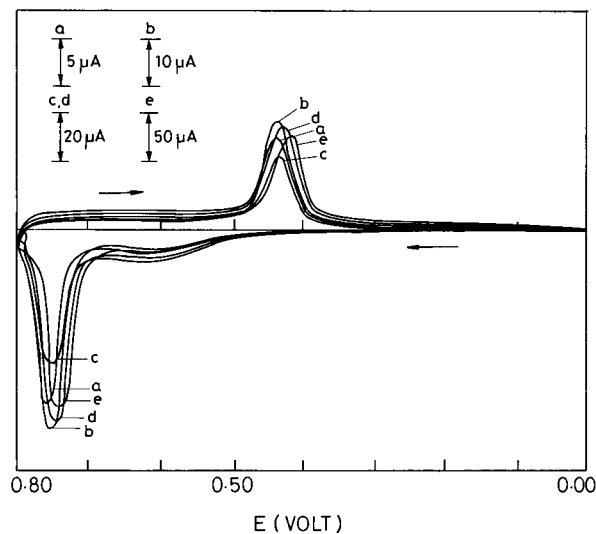
**Figure 1** Cyclic voltammogram of PDPA film deposited by PPSM. PPSM: [DPA] = 50 mM,  $P_n = 1000$ ,  $P_w = 100$  ms, and  $E_c/E_a = 0.0/0.8$  V. CV of film:  $E_c/E_a = 0.0/0.8$  V and scan rate = 100 mV/s.

switching potential of 0.0 and +0.8 V vs Ag/AgCl. The CV of the stabilized film is given in Figure 1. As seen from the figure, two anodic and one cathodic peak appears with  $E_p^a(\text{I})$  at 0.58 V,  $E_p^a(\text{II})$  at 0.73 V, and  $E_p^c(\text{I})$  at 0.42 V.

During the electrochemical polymerization of OCA by PPSM, a green color deposit was seen on the platinum electrode surface with redox characterization as seen in Figure 2. The CV of the film has an anodic peak  $E_p^a(\text{I})$  at 0.61 V and a cathodic peak  $E_p^c(\text{I})$  at 0.56 V. However, the peak current values are found to be very low. On increasing the value of  $P_n$  above 2000, the film deposition was not observed. Thus, a limited growth of insulating film of poly(o-chloroaniline) (POCA) was noticed.



**Figure 2** Cyclic voltammogram of POCA film deposited by PPSM. PPSM: [OCA] = 50 mM,  $P_n = 1000$ ,  $P_w = 100$  ms, and  $E_c/E_a = 0.0/1.2$  V. CV of film:  $E_c/E_a = 0.0/1.2$  V and scan rate = 100 mV/s.



**Figure 3** Cyclic voltammograms of polymeric films deposited by PPSM with different feed ratios of DPA. PPSM:  $P_n = 1000$ ,  $P_w = 100$  ms, and  $E_c/E_a = 0.0/0.8$  V. CV of film:  $E_c/E_a = 0.0/0.8$  V and scan rate = 100 mV/s. Feed ratio of DPA: (a) 0.2, (b) 0.4, (c) 0.5, (d) 0.6, and (e) 0.8.

A study on the electropolymerization of DPA in the presence of OCA was further made, and the results have been critically compared with the homopolymerization of DPA and OCA. PPSM was used for the electropolymerization of the mixture of monomers, DPA and OCA. The electropolymerization was done by keeping fixed pulse parameters such as  $P_n$  and  $P_w$  as 1000 and 100 ms, respectively, for various feed ratios of DPA and OCA. The following general observations were noted: (1) the color of the reaction medium did not change during the course of study, and (2) the visible appearance of green color was noticed on the electrode surface.

These observations indicated the absence of dissolution of oligomeric products and the deposition of good adherent polymeric material on the electrode surface. This is different from the one reported by Zotti et al.<sup>23</sup> for DPA polymerization in the mixture of 4M sulfuric acid and ethanol, where oligomeric products were found to dissolve out from the surface of working electrode. The reproducibility of the CV pattern of the deposited films within a few cycles during stabilization in this study is indicative of a stable polymeric film formation by PPSM.

Figure 3 shows the CVs recorded for the polymeric films deposited by PPSM with DPA and OCA for varying feed ratios of DPA (0.2, 0.4, 0.5, 0.6, and 0.8). Apparently, these CVs are similar to those recorded for polymerization of DPA as there are two anodic peaks and a cathodic peak. But a detailed analysis reveals significant differences with regard to peak potential, peak current values, and other growth characteristics.

TABLE I  
Electrochemical Behavior of Poly(DPA-co-OCA) Films Deposited by PPSM: Half Wave Potential, Peak Current, and FWHM Values for Various Feed Ratios of DPA

Feed Ratio of DPA	Half wave potential, $E_{1/2}$		Peak current, $i_p$			FWHM					
	$E_{1/2}^a$ (mV)		$E_{1/2}^c$ (mV)			$i_p^a$ ( $\mu$ A)		$i_p^c$ ( $\mu$ A)	Anodic (mV)		Cathodic (mV)
	I	II	I	I	II	I	I	II	I		
0.2	526	697	492	03	19	10	64	27	31		
0.4	523	695	489	06	43	24	65	28	32		
0.5	519	693	486	08	57	32	67	29	33		
0.6	517	691	483	11	84	46	69	31	34		
0.8	516	689	481	23	187	102	72	33	36		

PPSM:  $P_n = 1000$ ,  $P_w = 100$  ms,  $E_c/E_a = 0.0/0.8$  V. CV of film:  $E_c/E_a = 0.0/0.8$  V, scan rate = 100 m V/s.

### Dependence of peak potential and peak current on feed ratio of DPA

The CVs of the films have two anodic peaks in the ranges 0.58–0.59 and 0.73–0.75 V respectively. The close analysis of these two redox peaks with corresponding peaks for PDPA (0.57 and 0.73 V) clearly shows the differences between them. The CVs of the films are having more anodic peak potentials than PDPA. The characteristics of POCA with redox processes were not exactly reflected at all in these films. Hence the polymeric films deposited by the mixture of DPA and OCA are not the films corresponding to the codeposition of PDPA and POCA by simultaneous polymerization. The absence of such a combined CV pattern of PDPA and POCA clearly indicate the deposition of an entirely new polymeric material, possibly through copolymerization between DPA and OCA involving reactions between phenyl ended radical from DPA and OCA.

Further support to this view has been obtained from the analysis of other characteristics of these films in contrast to the PDPA and POCA films. The peak current values of the two anodic peak potentials,  $i_p^a$ (I) and  $i_p^a$ (II) were found to increase slightly with increase in feed ratio of DPA. It is interesting to note that  $i_p^a$ (I) and  $i_p^a$ (II) values of these polymeric films were found to be totally different from the values experimentally observed for PDPA deposition with the same concentration of DPA in the mixture.

For making such comparisons,  $i_p^a$ (I) and  $i_p^a$ (II) values calculated for the polymerization can be considered. For example, when [DPA] was 10 mM in the homopolymerization,  $i_p^a$ (I) was noted as 10  $\mu$ A. On the other hand, when the DPA was maintained as 10 mM (feed ratio of 0.2) in the polymerization with the mixture of monomers DPA and OCA,  $i_p^a$ (I) was only 3  $\mu$ A. Low  $i_p^a$  values were observed for the film deposited with the mixtures of monomers, DPA and OCA. The  $i_p^c$  values of the films were also observed to be different in comparative conditions of [DPA] in homopolymerization and copolymerization (Fig. 3) The differences observed on peak potential and peak current values in

contrast to PDPA indicate the deposition of new polymeric material in the present case. On increasing [DPA], the peak current values were found to increase.

Half-wave potential ( $E_{1/2}$ ) values of these polymeric films can now be compared with the PDPA and POCA films. The  $E_{1/2}$  values of PDPA are found to be  $E_{1/2}^a$ (I) = 0.51 V,  $E_{1/2}^a$ (II) = 0.67 V, and  $E_{1/2}^c$ (I) = 0.48 V (Fig. 1). The copolymeric films deposited in this study by PPSM are found to have the  $E_{1/2}^a$  values of 0.51–0.52, 0.69–0.70, and an  $E_{1/2}^c$  value of 0.48–0.49 V, respectively (Table I). The  $E_{1/2}$  values for the redox processes of POCA as  $E_{1/2}^a$ (I) = 0.52 V and  $E_{1/2}^c$ (I) = 0.74 V (Fig. 2) were also compared with these copolymeric films. The  $E_{1/2}$  values of copolymeric films were found to be in between the  $E_{1/2}$  values of PDPA and POCA films—similar to the observation noted in the copolymerization of ANI with OT by Wei et al.<sup>24</sup> through cyclic voltammetric studies favoring genuine copolymer formation in the present case.

Full-width at half maximum (FWHM) values of the CVs for poly(DPA-co-OCA) films deposited with various feed ratio of DPA are presented (Table I) and these values are used to evaluate the surface parameters of the deposited copolymeric films (Table II).

### Electrochemical characterization of poly(DPA-co-OCA) films deposited by PPSM using cyclic voltammetry

The charges associated with the anodic and cathodic portions of the CVs of the films deposited by PPSM (Fig. 1) were deduced by using the method of graphical integration with the potential limits between 0.0 and +0.8 V. The background charges were suitably subtracted while evaluating the charge values.

### Dependence of charge on feed ratio of DPA

The charges associated with the first and second anodic as well as the cathodic peaks were calculated. The total anodic charge,  $Q_a^*$ , and cathodic charge,  $Q_c$ , are

TABLE II  
Surface Parameters for Poly(DPA-co-OCA) Films Deposited by PPSM for Various Feed Ratios of DPA

Feed ratio of DPA	Charge, $Q_{ox}$ (mC)	$\Gamma_{ox} \times 10^{-7a}$ (mol cm <sup>-2</sup> )	$d$ ( $\mu$ m) <sup>b</sup>	$C_{ox}$ (M)	FWHM (V)		$C_{ox} \cdot r_a$		$r_a$ (M <sup>-1</sup> )	
					I	II	I	II	I	II
0.2	0.008	0.033	0.022	1.50	0.064	0.027	0.444	1.170	0.296	0.780
0.4	0.019	0.077	0.055	1.40	0.065	0.028	0.425	1.151	0.304	0.822
0.5	0.027	0.110	0.081	1.36	0.067	0.029	0.386	1.131	0.284	0.832
0.6	0.042	0.171	0.129	1.33	0.069	0.031	0.346	1.092	0.260	0.821
0.8	0.112	0.456	0.364	1.25	0.072	0.033	0.288	1.053	0.230	0.842

PPSM:  $P_n = 1000$ ,  $P_w = 100$  ms,  $E_c/E_a = 0.0/0.8$  V. CV of film:  $E_c/E_a = 0.0/0.8$  V, scan rate = 100 m V/s.

<sup>a</sup>  $Q_{ox}/nFA$ .

<sup>b</sup>  $Q_{ox}V/zrF$ .

<sup>c</sup>  $1.7 - (0.47 \Delta E_{p/2} nF/RT)$ .

taken to comparison with the charges associated with PDPA films during homopolymerization of DPA with the same [DPA] maintained in copolymerization.

The values of  $Q_a^*$  and  $Q_c$  were found to be much lower for the copolymeric films in comparison with the PDPA films deposited with the same [DPA],  $P_n$  and  $P_w$ . These differences noted in the charge values between the polymeric films deposited with the mixtures of two monomers and single monomer favours the copolymeric film deposition.  $Q_a^*$  and  $Q_c$  were found to increase with the increase in the feed ratio of DPA. Consequently, the total anodic and cathodic charges show a negative trend with increase in feed ratio of OCA.

For deducing growth equation, a general equation relating [DPA] and [OCA] at constant  $P_n$  and  $P_w$  can be written as

$$\begin{aligned} \text{Growth} &= \text{Charge, } Q_a^* \text{ (or) } Q_c \text{ (mC)} \\ &= k'[\text{DPA}]^x[\text{OCA}]^y P_n \cdot P_w \end{aligned}$$

The above equation may be given as

$$\begin{aligned} \text{Growth} &= \text{Charge, } Q_a^* \text{ (or) } Q_c \text{ (mC)} \\ &= k[\text{DPA}]^x[\text{OCA}]^y \quad (1) \end{aligned}$$

where  $k = k' P_n \cdot P_w$ .

Since both concentration terms are found to vary simultaneously while maintaining feed ratios for constant  $P_n$  and  $P_w$ , the following procedure is adopted to find growth dependence. By substituting any two experimentally determined anodic or cathodic charge values corresponding to two different feed ratios of monomer at constant  $P_n$  and  $P_w$ , several pairs of equations were set up that were used to arrive at a simultaneous equation consisting of  $x$  and  $y$  terms. Solving these pairs of simultaneous equations for  $x$  and  $y$ , the average values of  $x$  and  $y$  were arrived at nearly as 1.0 and  $-1.0$ , respectively. This assignment of the values of  $x$  and  $y$  was further verified graphically by suitable double logarithmic and direct plots.

Double logarithmic form of the proposed growth eq. (1) was used here for evaluating  $x$  and  $y$ .

$$\log Q_a^* \text{ (or) } \log Q_c = \log k + x \log [\text{DPA}] + y \log [\text{OCA}] \quad (2)$$

In order to determine the dependence of growth of [DPA], the tentatively assigned value of  $y = -1.0$  was incorporated and the double logarithmic plot of  $\log(Q_a^* [\text{OCA}])$  vs  $\log [\text{DPA}]$  (Fig. 4) was drawn for fixed values of  $P_n$  and  $P_w$ . The plot was found to be linear with slope value nearly 1.0, which is the same as obtained through solving equations. This suggests the first-order dependence of [DPA] on copolymer film growth.

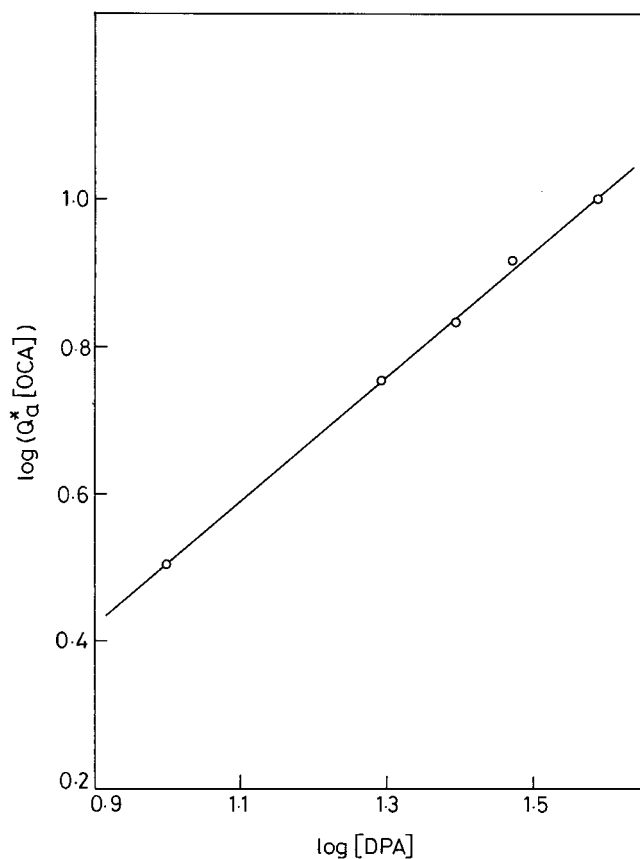
Similarly, the dependence of growth on [OCA] was evaluated by using the graphically derived value of 1.0 for  $x$ . The plot of  $\log(Q_a^* / [\text{DPA}])$  vs  $\log [\text{OCA}]$  (Fig. 5) was made for fixed values of  $P_n$  and  $P_w$ . The linear nature of the plot showing slope value of nearly  $-1.0$  confirms the inverse first-order dependence of [OCA] on copolymer film growth. Using the values of  $x$  and  $y$ , the growth equation was finally deduced as

$$\begin{aligned} \text{Growth} &= \text{Charge, } Q_a^* \text{ (or) } Q_c \text{ (mC)} \\ &= k[\text{DPA}] [\text{OCA}]^{-1} \quad (3) \end{aligned}$$

Making use of slope values of the plots  $\log(Q_a^* [\text{OCA}])$  vs  $\log [\text{DPA}]$  (Fig. 4) and  $\log(Q_a^* / [\text{DPA}])$  vs  $\log [\text{OCA}]$  (Fig. 5), the values of  $k$  were calculated and found to be  $2.85 \times 10^{-7} \text{mC(mM)}^{-1} (\text{ms})^{-1}$  and  $2.83 \times 10^{-7} \text{mC(mM)}^{-1} (\text{ms})^{-1}$ , respectively. The closeness of the values obtained through different approaches confirms the correctness of eq. (3) for the copolymer growth.

#### Determination of surface parameters

Owing to the equivalence of surface and thin layer electrochemical processes, data analysis methods have been developed to reversible thin layer and surface



**Figure 4** Effect of [DPA] on charge for poly(DPA-co-OCA) films deposited by PPSM. PPSM:  $P_n = 1000$ ,  $P_w = 100$  ms, and  $E_c/E_a = 0.0/0.8$  V. CV of film:  $E_c/E_a = 0.0/0.8$  V and scan rate = 100 mV/s.

electrode processes as well as polymer film deposits. These methods have been reviewed by Laviron<sup>25</sup> and Murray.<sup>26</sup> A special treatment of the theory by Brown and Anson<sup>27</sup> leads to an ingenious method to extract surface parameters from the shape of the peaks. Surface excess ( $\Gamma_{ox}$ ), film thickness ( $d$ ), thin film concentration ( $C_{ox}$ ) and interaction parameter ( $r_a$ ) are among these. This interesting approach has been adopted here in this study for the poly(DPA-co-OCA) films deposited by PPSM. Equations related to the peak current and charge associated with redox processes with these parameters are used here.

#### Determination of surface excess, $\Gamma_{ox}$

In the present study,  $\Gamma_{ox}$  values are calculated using the equation

$$Q_{ox} = nFA\Gamma_{ox} = nFAC_{ox}d \quad (4)$$

where  $Q_{ox}$  is the redox charge per unit area of the electrode surface,  $n$  is the number of electrons involved, and  $A$  is the electrode area and other terms have their usual significance.

The anodic charge,  $Q_{ox}$  associated with poly (DPA-co-OCA) films were calculated and used.

$\Gamma_{ox}$  was found to increase with increase in molar feed ratio of DPA (Table II). The values are ranging from  $0.033 \times 10^{-7}$  to  $0.456 \times 10^{-7}$  mol cm<sup>-2</sup> for the various copolymer films. Comparing these with  $\Gamma_{ox}$  obtained for PDPA films as  $0.31 \times 10^{-7}$  to  $1.8 \times 10^{-7}$  mol cm<sup>-2</sup>, it is inferred that the surface excess is low for poly(DPA-co-OCA) films.

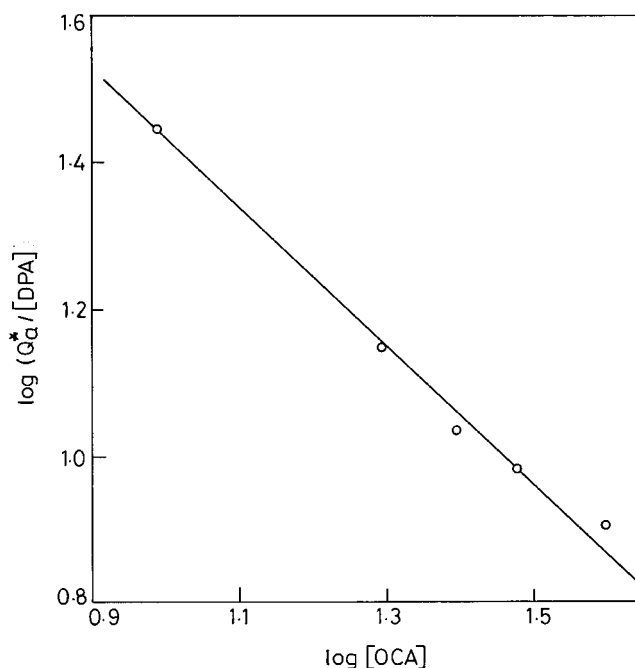
#### Determination of film thickness, $d$

Using the equation,  $d = Q_{ox}V/ZrF$ , where  $V$  is the molar volume,  $Z$  is the charge efficiency,  $r$  is the roughness factor of the working electrode, and  $F$  is the Faraday constant, the value of thickness of the film for all the copolymer films were calculated. The value of  $V$  was based on the molar feed concentrations and densities of the two monomers, DPA and OCA. The thickness of copolymer films varies from 0.02 to 0.36  $\mu$ m. These values can be compared with the much higher values of  $d$  ranging from 0.13 to 0.77  $\mu$ m obtained for PDPA films under identical conditions without OCA.

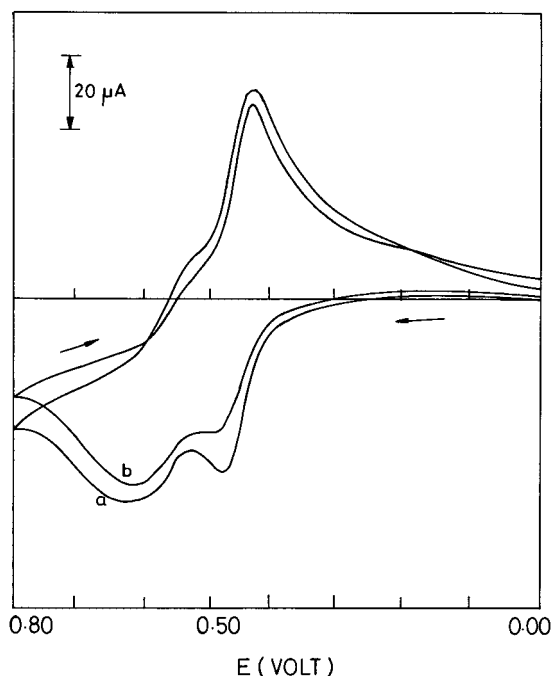
The thin film concentration,  $C_{ox}$ , was calculated for poly(DPA-co-OCA) films from the relation,

$$\Gamma_{ox} = C_{ox}d \quad (5)$$

and presented in Table II.



**Figure 5** Effect of [OCA] on charge for poly(DPA-co-OCA) films deposited by PPSM. PPSM:  $P_n = 1000$ ,  $P_w = 100$  ms, and  $E_c/E_a = 0.0/0.8$  V. CV of film:  $E_c/E_a = 0.0/0.8$  V and scan rate = 100 mV/s.



**Figure 6** Comparison of cyclic voltammograms of Pt/poly(DPA-co-OCA) modified electrodes: (a) chemically synthesized and (b) electrochemically deposited by PPSM.

#### Determination of interaction parameter, $r_a$

The  $r_a$  values were arrived from the value of FWHM<sup>24</sup> of the respective CVs (Fig. 3) of the films corresponding to their peaks. Substituting these values of FWHM and  $C_{ox}$  in the following equation—

$$C_{ox} r_a = 1.7 - (0.47 \times \text{FWHM} \cdot nF/RT) \quad (6)$$

the values of  $r_a$  was calculated and found to be positive for the first and second anodic peaks of the redox processes (Table II), suggesting attractive interaction between working electrode and the polymeric film. The values of  $\Gamma_{ox}$ ,  $d$ ,  $C_{ox}$ , and  $r_a$  determined for the poly (DPA-co-OCA) films are summarized in Table II.

#### Characterization of chemically/electrochemically synthesized poly(DPA-co-OCA)

Using the suspension of the copolymer in acetone, a film was cast onto the platinum electrode<sup>28</sup> and the copolymer film coated electrode was then placed in monomer free electrolyte (4M sulfuric acid) and pre-conditioned.

The CVs were recorded for the copolymer film coated electrodes in 4M sulfuric acid in the potential range of 0.0 to +0.8 V at a scan rate ( $\nu$ ) of 100 mV/s. The CVs obtained for the electrodes coated with the chemically synthesized poly(DPA-co-OCA) were compared with that recorded for the electrochemically deposited poly(DPA-co-OCA) films (Fig. 6). The re-

semblance observed among the CVs indicate that the samples of copolymers prepared through these two methods have similar electrochemical characteristics.

#### Other characterizations of poly(DPA-co-OCA)

##### Conductivity measurements

The conductivities of chemically synthesized sample of poly(DPA-co-OCA) with feed of 1:1 monomer were determined using Four-probe technique. The conductivity,  $\sigma$  of the copolymer at room temperature was found to be  $1.13 \times 10^{-2} \text{ S cm}^{-1}$ , which is low when compared with the value reported for PDPA as  $2.59 \times 10^{-1} \text{ S cm}^{-1}$ . The incorporation of the electron-withdrawing chloro-group may produce such a pronounced influence on conductivity.

##### FTIR spectroscopy

FTIR spectrum was recorded for poly(DPA-co-OCA) in the range of 500–4000  $\text{cm}^{-1}$  (Fig. 7). The positions of the prominent peaks shown by the copolymer and their band assignment are made. The positions of the bands were found to have variations in positions and intensities in comparison with respective bands of PDPA.<sup>29</sup> This can be taken as the evidence for the copolymer formation. The absorption band at 3387  $\text{cm}^{-1}$  is caused by N—H stretching mode of secondary amine. The absorption peak at 1595  $\text{cm}^{-1}$  can be assigned to the different bending mode of aromatic secondary amine.<sup>30</sup> The strong absorption band at 1502  $\text{cm}^{-1}$  is characteristic of the C—C multiple bond stretching mode of benzene ring.<sup>31</sup> The C—N stretching mode of aromatic secondary amines causes the absorption band at 1316 and 1170  $\text{cm}^{-1}$ .<sup>31</sup> The weak band at 694  $\text{cm}^{-1}$  is due to the C—H out-of-plane in phase bending vibration of monosubstituted benzene rings at the ends of the polymer chains.<sup>30, 31</sup> The two bands at 1115 and 1019  $\text{cm}^{-1}$  are characteristic stretching modes in aromatics. Literature shows that the C—Cl absorption is at 1053  $\text{cm}^{-1}$  in the structure of 2-chloro-1,4-dihydrobenzoquinone.<sup>32</sup> For the copolymer under investigation these bands are observed.

##### UV-visible spectroscopy

The UV-visible spectrum was recorded for poly(DPA-co-OCA) using a solution of the copolymer in DMF (Fig. 8, curve a). This spectrum exhibits a peak at 280 nm and a broad band at 520 nm. These peaks may be assigned due to the  $\pi$ – $\pi^*$  transition of the benzenoid rings in the polymer backbone and polaronic excitation of benzenoid to quinonoid ring respectively. For comparison, the UV-visible spectra of PDPA (Fig. 8, curve b) and POCA (Fig. 8, curve c) were also recorded. The PDPA spectrum exhibits a peak at 330 nm

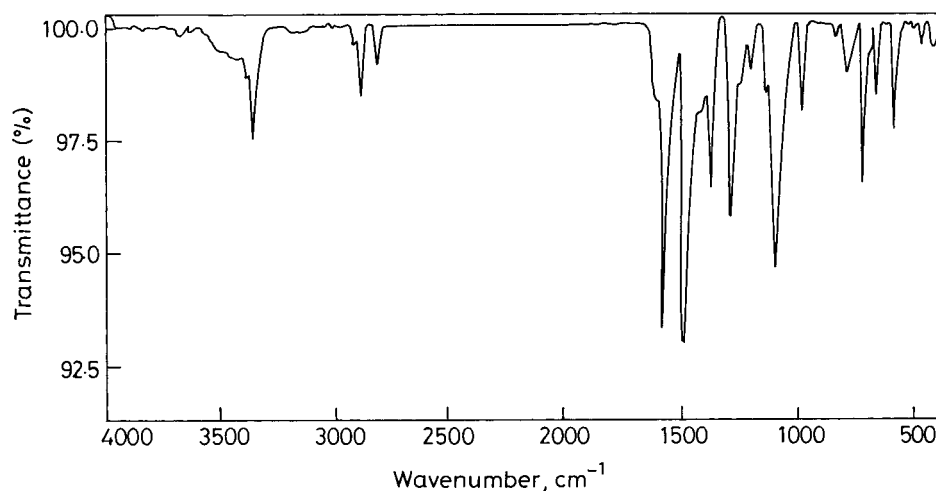


Figure 7 FTIR spectrum of poly(DPA-co-OCA).

and a broad band at 530 nm, and the POCA spectrum shows a peak at 310 nm and interestingly it exhibits no band in the visible region. The presence of peak at 280 nm indicates the incorporation of OCA moieties in the copolymer structure.

The slight hypsochromic shifts of the  $\pi-\pi^*$  peaks to 280 nm in the copolymer poly(DPA-co-OCA) perhaps reflects the decreasing order of conjugation due to steric effect and this decrease in conjugation can also be attributed to the presence of incorporated OCA moieties in the polymeric backbone.

## CONCLUSION

A pulse potentiostatic method has been employed for the deposition of copolymeric films involving diphenylamine and o-chloroaniline. Cyclic voltammetry was adopted to characterize those films. The cyclic voltammograms of the films showed differences in contrast to polydiphenylamine films. A growth equation relating the pulse parameters and the experimental conditions of polymerization was obtained. The closeness of the growth rate constant obtained

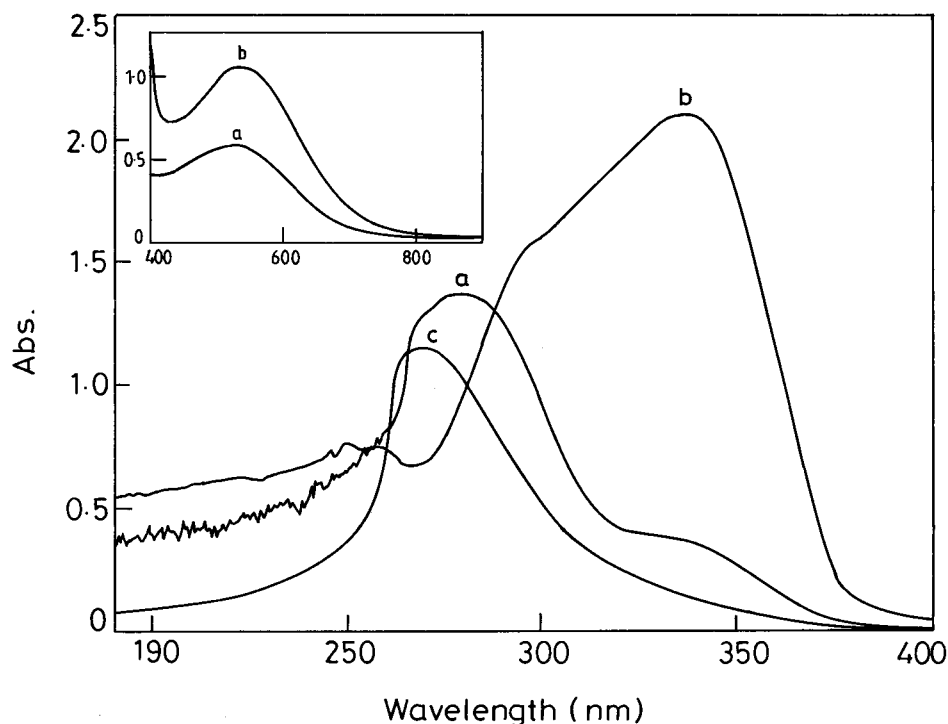


Figure 8 UV-Visible spectra of copolymer/homopolymer in DMF: (a) poly(DPA-co-OCA), (b) PDPA, and (c) POCA.



through different routes justifies the deduced equation. Chemical synthesis and subsequent characterization supports the poly(diphenylamine-co-o-chloroaniline) formation.

## References

1. Skotheim, T. A., Ed. Handbook of Conducting Polymers, Vols. I and II; Marcel Dekker: New York, 1986.
2. Patil, A. O.; Heeger, A. J.; Wudl, F. Chem Rev 1988, 88, 183.
3. Bredas, J. L.; Chance, R. R., Eds. Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics and Molecular Electronics; Kluwer Academic: Dordrecht, The Netherlands, and Boston, MA, 1990.
4. Skotheim, T. A., Ed. Electroresponsive Molecular and Polymeric Systems, Vol. II; Marcel Dekker: New York, 1992.
5. LaCroix, J. C.; Diaz, A. F. J Electrochem Soc 1988, 135, 1457.
6. Paul, E. W.; Ricco, A. J.; Wrighton, W. S. J Phys Chem 1985, 89, 1441.
7. Wei, Y.; Focke, W. W.; Wnek, G. E.; Ray, A.; MacDiarmid, A. G. J Phys Chem 1989, 93, 495.
8. Salamedi, W.; Lundstrom, I.; Huang, W. S.; MacDiarmid, A. G. Synth Met 1986, 13, 291.
9. De Surville, R.; Jozefowicz, M.; Yu, L. T.; Perichon, J.; Buret, R. Electrochim Acta 1968, 13, 1451.
10. Noshay, A.; McGrath, J. E. Block Copolymers; Academic Press: New York, 1977.
11. Nguyen, M. T.; Kasai, P.; Miller, J. L.; Diaz, A. F. Macromolecules 1994, 27, 3625.
12. Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G. J Am Chem Soc 1991, 113, 2665.
13. Lee, J. Y.; Cui, C. Q. J Electroanal Chem 1996, 403, 109.
14. Sato, M.; Yamanaka, S.; Nakaya, J.; Hyodo, K. Electrochim Acta 1994, 39, 2159.
15. Chen, W. C.; Wen, T. C.; Gopalan, A. J Electrochem Soc 2001, 11, 148.
16. Wen, T. C.; Huang, L. M.; Gopalan, A. J Electrochem Soc 2001, D14, 148.
17. Chung, L.; Wen, T. C.; Gopalan, A. Mater Chem Phys 2001, 71, 148.
18. Mohilner, D.; Adams, R.; Argersinger, W. J., Jr. J Am Chem Soc 1962, 84, 1618.
19. Kobayashi, T.; Yoneyama, A.; Tamura, H. J Electroanal Chem 1984, 161, 419.
20. Genies, E. M.; Tsintavis, C. J Electroanal Chem 1985, 195, 109.
21. Tsakova, V.; Milchev, A. Electrochim Acta 1991, 36, 1583.
22. Tsakova, V.; Milchev, A. J Electroanal Chem 1993, 85, 346.
23. Comisso, N.; Daolio, S.; Mengoli, G.; Salmaso, R.; Zecchin, S.; Zotti, G. J Electroanal Chem 1988, 255, 97.
24. Wei, Y.; Tang, X.; Sun, Y.; Focke, W. Polym Sci Polym Chem Ed 1989, 27, 2385.
25. Laviron, E. In Electroanalytical Chemistry; Bard, A. J., Ed.; Marcel Dekker: New York, 1982; Vol. 12.
26. Murray, R. W. In Electroanalytical Chemistry; Bard, A. J., Ed.; Marcel Dekker: New York, 1982; Vol. 12.
27. Brown, A. P.; Anson, F. C. Anal Chem 1977, 49, 1589.
28. MacDiarmid, A. G.; Chiang, J. C.; Richter, A. F.; Somasiri, N. L. D. In Conducting Polymers; Alacer, L., Ed.; Reidel: Dordrecht, Holland, 1987.
29. Rajendran, V.; Gopalan, A.; Vasudevan, T.; Wen, T.-C. Mater Chem Phys 2000, 65, 320.
30. Furukawa, Y.; Veda, F.; Hyodo, Y.; Harodo, I.; Nakajima, T.; Kawagoe, T. Macromolecules 1988, 21, 1297.
31. Pavia, D. L.; Lampman, G. M.; Kriz, G. S. Introduction to Spectroscopy; W. B. Saunders: London, 1979.
32. Grasselli, J. G.; Ritchey, W. M., Eds. Atlas of Spectral Data and Physical Constants of Organic Compounds; CRC Press: Cleveland, OH, 1975; Vol. 2.