Electrosynthesis and characterization of poly(1,4-phenylene) films with improved electroactivity

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Homogeneous undoped films of poly(1,4-phenylene) (PPP) can be deposited onto a solid cathode by electroreduction of 4,4'-dibromobiphenyl (DBB) activated by an unusual zero-valent nickel complex. The $Ni(O)D_2$, described as a non-reactive complex against aromatic halide, is obtained by electrochemical reduction of $NiCl_2D$ and D [D = 1,2-bis(diphenylphosphinoethane)] equimolar mixture. Electrodeposition was carried out from electroanalytical study of the above complex without and then with DBB.PPP thin layers exhibit an improved electroactivity; indeed, they can either be oxidized or unusually reduced in the presence of lithium salt as supporting electrolyte in acetonitrile.

(Keywords: electroactivity; poly(1,4-phenylene); films)

INTRODUCTION

The insolubility of poly(1,4-phenylene) (PPP) constitutes a hindrance to producing films by chemical techniques except when a soluble polymeric precursor such as a copolymer (styrene-*b*-phenylene)[1] can be synthesized. On the other hand, this insolubility is a propitious property to producing thin layers on conducting supports using electrochemical techniques[2–7]. Formation of PPP films by benzene or biphenyl anodic oxidation leads to doped materials[2–5]. Undoped films can be obtained, for example, by 4,4'-dibromobiphenyl (DBB) electrochemical reduction in the presence of zero-valent nickel as catalyst[7]. The reduction of the complex 1-1($NiCl_2D$) formed by reaction of nickel dichloride and 1,2-bis(diphenylphosphinoethane) (D) leads to the catalyst Ni(O) which undergoes an oxidative addition to DBB in order to form an aryl nickel(II) complex. Then, the reduction of this complex provides an active species which is condensed with the aryl nickel(II) complex leading to PPP by chain propagation[8]. The thin PPP layers were characterized by u.v.–visible and *FT*i.r. spectroscopies[7].

A detailed study[9] of the nucleation as well as growth of undoped PPP films obtained by the above method onto indium tin oxide (ITO) substrate has been reported.

One of the first electrochemical studies of PPP films exhibits either an oxidation or a reduction process in NBu_4ClO_4/acetonitrile medium[6]. However, it is surprising that all peaks are very sharp. Furthermore, film analysis reveals the presence of nickel.

We have recently shown[10] the possibility of covering the whole potential range from reduction to PPP oxidation in the same electrolyte (propylene carbonate or acetonitrile with a quarternary ammonium (NR_4^+) salt as electrolyte). In these conditions, prepeaks appear at the oxidation or reduction threshold of PPP. The potential difference of these two processes seems to be correlated with the energy of the optical absorption threshold found in such films (2.8–2.9 eV).

It should be pointed out that the oxidation or reduction have already been studied in various media by other workers[4,5,7]. Oxidation has only been observed in the acetonitrile/lithium salt system[4,7], or in dichloromethane with NR_4^+ salt as electrolyte[5]. Reduction has only been described in the presence of NR_4^+ salt as electrolyte in tetrahydrofuran[7], acetonitrile[4,6] or dichloromethane[5]. As far as we know, electrochemical reduction of undoped PPP film has never been described with a well defined voltammogram using a lithium salt as electrolyte in an organic solvent.

We have found that thin PPP layers can be formed from cathodic reduction of DBB with $NiCl_2D$ containing excess of 1D/$NiCl_2D$ as catalytic presursor. This result is surprising because $Ni(O)D_2$ is described as being non-reactive with most aromatic monohalides[11,12]. Furthermore, PPP powder cannot be obtained from electroreduction of DBB on a mercury pool[13] in the above conditions.

In this work, we describe the synthesis of PPP films, their characterization by optical spectroscopy and electrochemical behaviour, and finally their improved electroactivity revealed by reduction in lithium salt electrolyte.

EXPERIMENTAL

Reagents

DBB (Janssen Chimica) and acetonitrile (Carbo Erba, polarografia grade) were used as received

N,*N*-dimethylacetamide (DMA) was distilled twice over calcium dihydride prior to use for the electrosynthesis of PPP films.

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$LiClO_4$ (used as the supporting salt in DMA or acetonitrile) and NBu_4BF_4 (supporting electrolyte in acetonitrile) were dried under vacuum overnight at 120°C.

$NiCl_2D$ was prepared following the procedure previously described[14].

Electrochemical processes

Electrochemical studies were carried out using a Radiometer-Tacussel apparatus (PJT 35-2 potentiostat, GSTP4 generator, IG5N coulometer). This system was connected to a one-compartment cell with three electrodes.

Preparation of electrodeposited PPP films

DMA (30 ml) together with 0.3 mol l^{-1} of dry $LiClO_4$, 0.1 mmol of $NiCl_2D$, 0.1 mmol of D and 0.4 mmol of DBB were introduced into the one-compartment cell. A potential of −1.6 V/saturated calomel electrode (SCE) was applied to the working cathode (glassy carbon, 7 mm^2 surface area, or ITO glass, 200 mm^2 surface area).

The counter-electrode was a platinum plate. Electrolysis was stopped when the integrated charge reached about 0.02 C for the glassy carbon cathode or 0.2–0.5 C for the ITO. The obtained film was rinsed with acetonitrile and dried at 60°C before its characterization using a Varian DM5 100 S spectrophotometer.

The electrochemical behaviour of the PPP film was studied in acetonitrile with NBu_4BF_4 or $LiClO_4$ as electrolyte. A silver wire containing $AgClO_4$ (0.1 mol l^{-1}) was used as reference electrode in this medium.

RESULTS AND DISCUSSION

Electroanalytical study of $NiCl_2$ D with excess 1 D/$NiCl_2D$

At a glassy carbon electrode, linear sweep voltammetry of 0.1 mmol of catalytic precursor $NiCl_2D$ in DMA (30 ml), including 10 mmol of $LiClO_4$ as supporting salt, exhibits two monoelectronic diffusion controlled reduction steps ($E_{red1} = -0.9$ V/SCE, $E_{red2} = -1.5$ V/SCE) (*Figure 1a*).

As previously explained[12], these two processes correspond to:

$$Ni(II)D^{2+} \xrightarrow{+e^-} Ni(I)D^{+} \xrightarrow{+e^-} Ni(O)D$$

Ni(O)D being unstable after electrolysis on a mercury pool. With an excess of D (0.1 mmol), we can only observe (*Figure 1b*) one reduction wave occurring at −0.9 V/SCE, the intensity of which is double that of each observed wave before addition of D. So, the disappearance of the second step in these conditions results in the bielectronic reduction of $Ni(II)D_2^{2+}$ to $Ni(O)D_2$. Furthermore, coulometry on a mercury pool in a $NiCl_2D$ solution with an excess of D (1D/$NiCl_2D$) shows that two electrons are consumed to achieve electrolysis. $Ni(O)D_2$ appears to be much more stable than Ni(O)D after electrolysis.

The linear voltammogram recorded after addition of 0.4 mmol of DBB is shown as curve c in *Figure 1*. The $Ni(II)D^{2+}$ bielectronic reduction to $Ni(O)D_2$ is almost unaltered. The addition of DBB mainly involves the presence of a new low cathodic wave, the half-wave potential of which is at −1.6 V, followed by a reduction barrier at −1.8 V. The intensity of the low cathodic signal is slightly increased with the added DBB. So, this wave could be attributed to the reduction of aryl nickel(II) complex obtained from DBB and $Ni(O)D_2$; however, as $Ni(O)D_2$ is very stable, the kinetics of $Ni(O)D_2$ insertion into C–Br linkage is very slow. Consequently, only a low complex amount is formed close to the working electrode and the corresponding cathodic wave is very small.

Electrodeposition of PPP films and characterization

Undoped PPP films of various thicknesses (0.1–2 μm following the passed charge) can be obtained by applying to the working cathode (ITO or glassy carbon) a potential

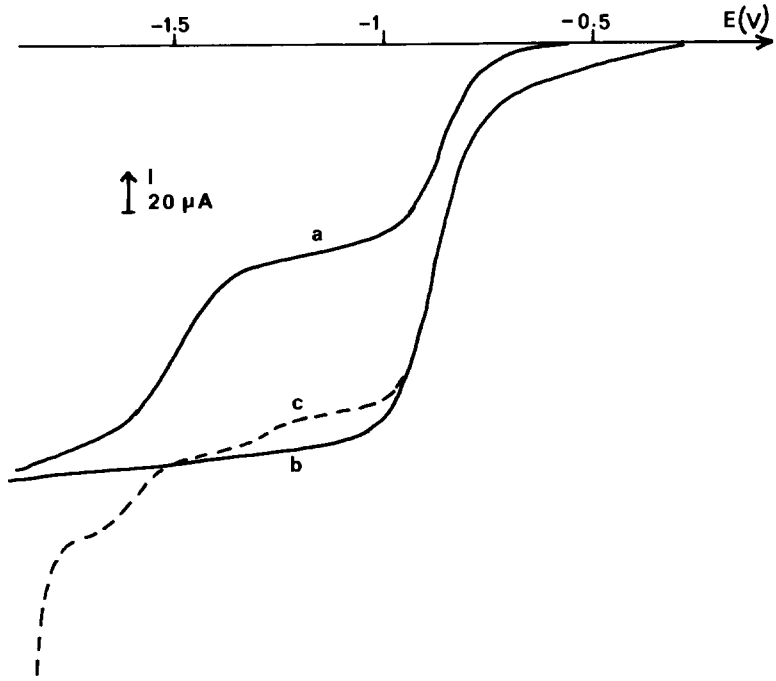

Figure 1 Voltammograms recorded with a glassy carbon electrode in a DMA solution with $LiClO_4$ as electrolyte in the presence of: (a) $NiCl_2D$ (0.1 mmol); (b) $NiCl_2D$ (0.1 mmol) + D (0.1 mmol); (c) b + 4,4′-dibromobiphenyl (0.4 mmol)

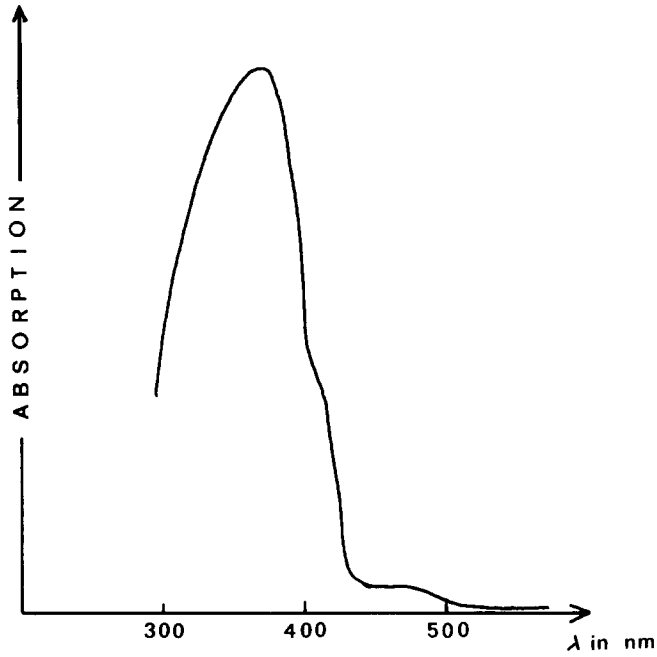

Figure 2 Optical spectrum of electrodeposited PPP film onto ITO glass from $NiCl_2D$ (0.1 mmol), D (0.1 mmol) and 4,4'-dibromobiphenyl (0.4 mmol) (applied potential, −1.6 V/SCE; charge passed, $Q = 0.3\,C$)

of −1.6 V/SCE from the above mixture. Indeed, a yellow, transparent and homogeneously dispersed film is deposited on the ITO substrate.

The u.v.-visible absorption spectrum of an as-grown PPP film on an ITO substrate is shown in *Figure 2*. This spectrum is quite similar to that observed for PPP film obtained without excess D[7]. The absorption maximum occurs at 380–390 nm. Moreover, the presence of a shoulder at 410 nm may arise from the contribution of the longest chains[7].

Electrochemical characterization of PPP films deposited onto glassy carbon electrode was investigated by cyclic voltammetry in acetonitrile with 0.1 mol l^{-1} of NBu_4BF_4 as electrolyte (*Figure 3*). Voltammograms in the oxidation range (0 to 1 V, *Figure 3a*), in the reduction domain (−2 to −3 V, *Figure 3b*) and finally in the whole potential domain (*Figure 3c*) were quite similar to those previously described[7,10]. However, all the redox processes observed are more precise than for PPP film obtained without excess D, particularly in the reduction. In the two limited ranges, oxidation and reduction of PPP reveal, respectively, p-type doping and n-type doping on the film. In the extended domain, PPP film exhibits two prepeaks appearing at the oxidation and reduction threshold. These prepeaks are explained[10] in terms of

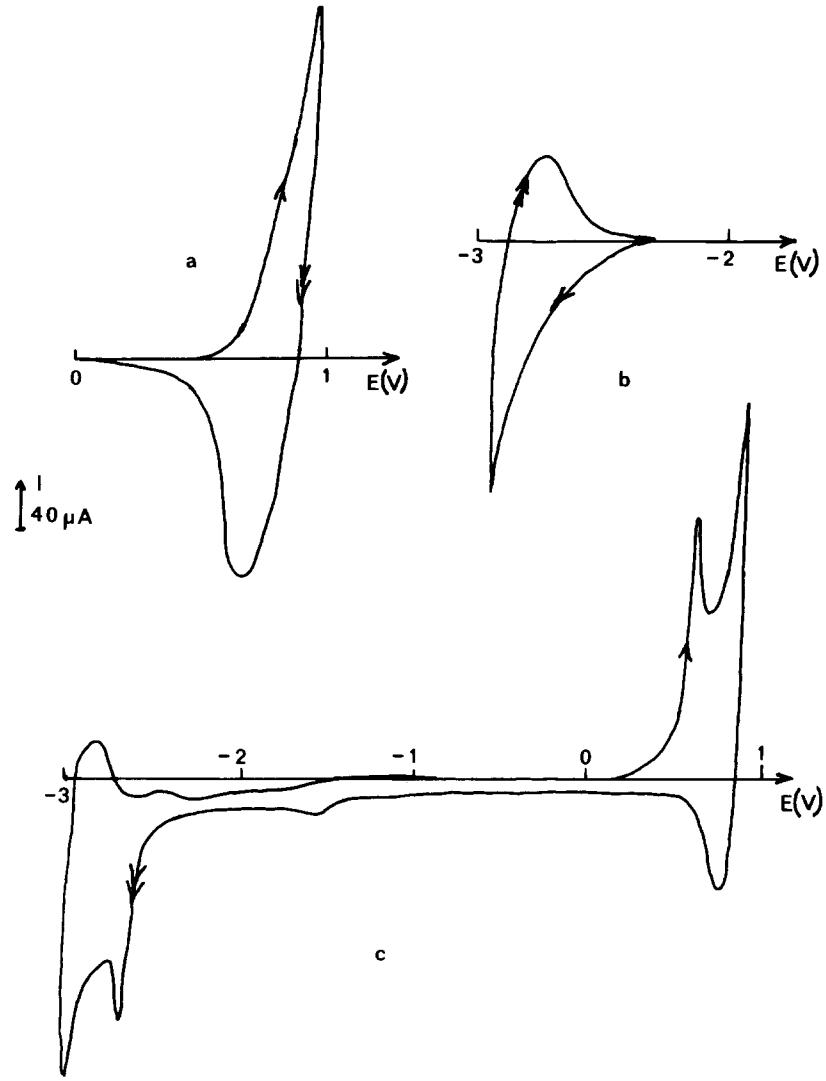

Figure 3 Cyclic voltammograms (scan rate 100 mV s^{-1}) of electrodeposited PPP film (with 1 D excess/$NiCl_2D$) on glassy carbon electrode in acetonitrile with NBu_4BF_4 as supporting salt: (a) oxidation range; (b) reduction range; (c) oxidation and reduction ranges

remnant charge intervention after dedoping. Data concerning the potential at which oxidation (E_{ox}), reduction (E_{red}) and prepeaks (E_{AN} and E_{CAT}) of PPP films occurs are presented in *Table 1*. All the values are very close to those reported with PPP film electrodeposited without excess D[10]. It should be noted that the potential difference between the foot of the anodic and cathodic prepeaks is also similar to that determined previously[10].

Table 1 Potential (V/Ag–Ag$^+$) of typical oxidation or reduction peak of PPP film on glassy carbon

Solvent/salt	Acetonitrile/ NBu_4BF_4	Acetonitrile/ $LiClO_4$
E_{ox} (maximum of the backward peak)	0.70	0.5
E_{AN} foot	0.35	0.45
maximum	0.6	0.7
E_{red} (maximum of the backward peak)	−2.85	−2.75
E_{CAT} foot	−2.5	−2.6
maximum	−2.65	−2.75
Difference foot potential (E_{AN}-E_{CAT})	2.80	3.05

The formation of PPP films with excess D suggests that a small amount of aryl nickel(II) species must be formed during electrolysis. That means that $Ni(O)D_2$ can react slowly with DBB leading to deposited film involving limited consumption of DBB. On the contrary, as PPP powder cannot be obtained on the mercury pool in these conditions[13], we can consider that this amount of formed aryl nickel(II) complex is not sufficient to realize exhaustive consumption of DBB. In the same way the dimerization of various aromatic monohalides is not possible from $Ni(O)D_2$[11,12]. So, it seems reasonable to conclude that $Ni(O)D_2$ does not react with most of the aromatic monohalides[11,12].

Electroactivity of PPP films with lithium salts

PPP films obtained from the DBB/$NiCl_2$ system[7] are only oxidizable in acetonitrile with $LiClO_4$ as supporting salt.

A well-defined process for the electrochemical reduction of PPP films has not been described yet[5,6]. On the

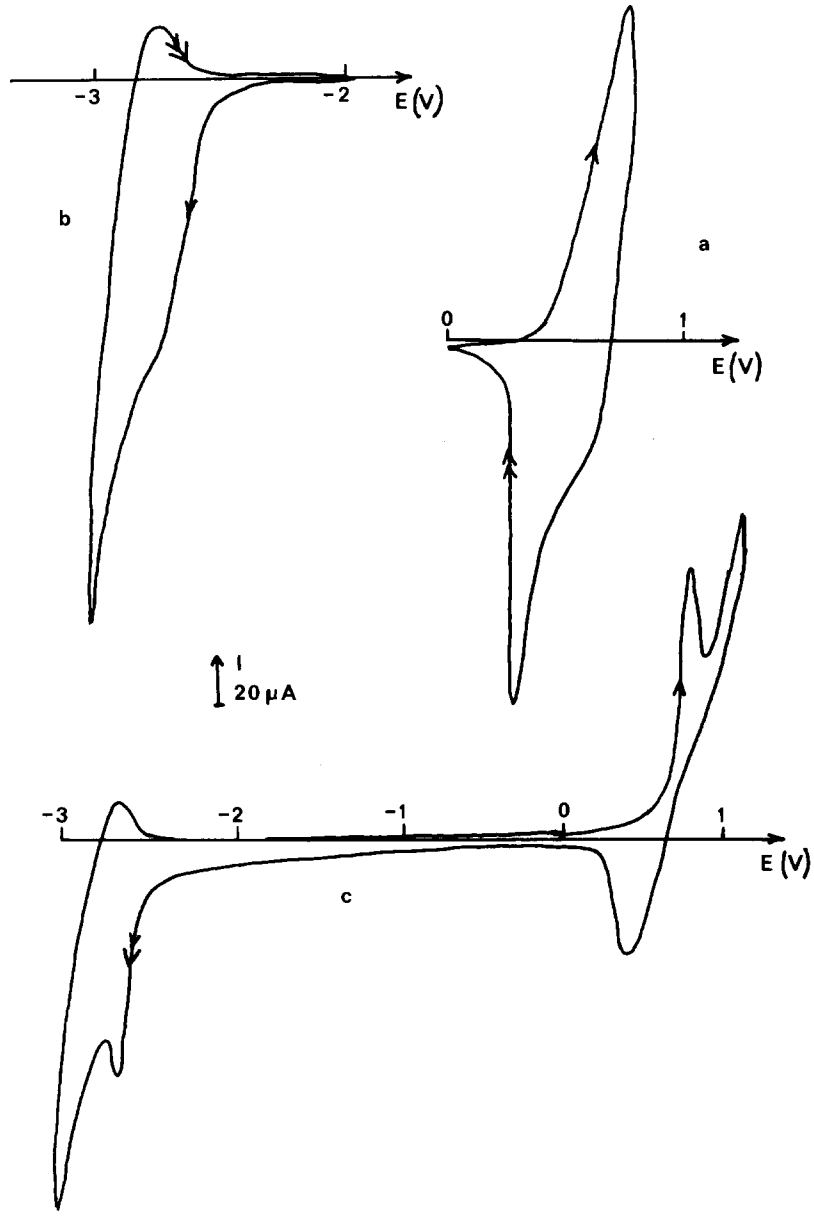

Figure 4 Cyclic voltammograms (scan rate 100 mV s^{-1}) of electrodeposited PPP film (with 1 D excess/$NiCl_2$D) on glassy carbon electrode in acetonitrile with $LiClO_4$ as electrolyte: (a) oxidation range; (b) reduction range; (c) oxidation and reduction ranges

contrary, the PPP films formed on glassy carbon electrode from our system ($DBB/NiCl_2D+D$) are both oxidizable and reducible in acetonitrile/$LiClO_4$ medium. The cyclic voltammograms of these films are recorded in *Figure 4*.

The anodic behaviour is quite similar to that observed by Meerholz and Heinze[5] in dichloromethane with NBu_4PF_6 as electrolyte. Indeed, an anodic peak occurs at 0.8 V/Ag–Ag^+, while a cathodic peak of oxidized PPP occurs at +0.4 V. However, the most unusual result is the presence of a well-defined oxidation peak of reduced PPP at −2.75 V/Ag–Ag^+ and associated with the electrochemical reduction process. It must be pointed out that this unusual phenomenon reveals a particular electroactivity of those thin layers deposited in such conditions. We have already noted that the electrochemical response is more sensitive in NR_4^+ electrolyte than for PPP films obtained by other methods. As the purification of the medium is no better than usual, we can suppose that this improved electroactivity arises from a better quality of film, probably due to adhesion and/or morphological effects.

On the cyclic voltammograms of the whole potential range, the two prepeaks located at the oxidation or reduction threshold exist as already mentioned in the acetonitrile/NBu_4BF_4 system. The peak potentials obtained with Li^+ salt are reported in *Table 1*. The main difference is the higher value (about 0.25 V) of $E_{AN}-E_{CAT}$ determined with $LiClO_4$ than with NBu_4BF_4. This difference seems to result from an anion effect during electrochemical p-doping as well as a cation effect when PPP is reduced. However, experiments to corroborate this viewpoint remain to be done.

Moreover, each peak current value is linearly dependent on the square-root of the sweep rate. This indicates a diffusion controlled process during the PPP electrochemical doping. Such an electrochemical behaviour has already been observed for undoped poly(*N*-alkylcarbazolylene)s film[15]. On the contrary, some doped conjugated polymers[16–18] exhibit a peak current linearly dependent on the scan rate.

Finally, the electrochromic properties of PPP films deposited on ITO glass are identical for both NR_4^+ and Li^+ salt media. The yellow undoped film becomes red when it is oxidized and purple when it is reduced.

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