

Spectroscopic investigation on polymer films obtained by oxidation of *o*-phenylenediamine on platinum electrodes at different pHs

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An investigation on the structure of poly(*o*-phenylenediamine) (PPD) films, obtained by electropolymerization of *o*PD (1,2-diaminobenzene) on platinum at different pH values, was performed by X-ray Photoelectron Spectroscopy (XPS).

XPS could be used as a “bulk” technique for PPD films analysis, due to their extremely low thickness. The presence of different functionalities, like primary/secondary aminic, iminic and, as minor species, oxygenated groups (carbonyl, oximes) was suggested by curve fitting of carbon (C1s) and nitrogen (N1s) XP spectra. The use of chemical derivatization reactions (CD–XPS) confirmed the presence of primary aminic and hydroxy groups, showing that NH₂ groups are present in the PPD structure even at low pH values, though their amount increases on increasing the pH of polymerization.

Optical spectroscopy in the visible region was also performed on the electrolytic solutions at the end of polymerization, suggesting a higher conjugation of the *o*PD oligomers at low pH, which indirectly confirms XPS findings on the presence of NH₂ groups in the polymer.

Introduction

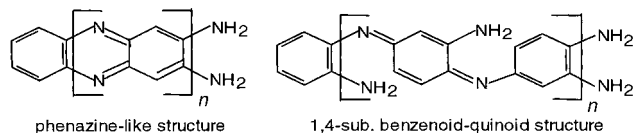
Since the first report¹ on the polymerization of *o*-phenylenediamine (*o*PD) on conducting substrates by electrochemical oxidation, a number of papers have appeared on the possible applications of the resulting polymer films.

In particular, poly(*o*-phenylenediamine), commonly abbreviated as PPD, has been extensively used, both in our laboratory^{2–8} and by other authors (see, for example, refs. 9–18), for the development of biosensors. In these devices its main role of enzyme entrapping membrane was coupled to its peculiar permeability,¹⁹ which enabled rejection of different species potentially acting either as fouling agents or as interferents on the biosensor response.

More recently,²⁰ we have explored a new possible application for PPD in the field of molecularly imprinted polymers (MIPs), using glucose as a molecular template during electropolymerization of *o*PD. The same approach has been successively adopted by other authors²¹ to prepare an electrosynthesised MIP.

The interactions between PPD and molecules like enzymes, in biosensors, or template compounds, in MIPs, raise questions about the polymer structure, which is probably involved also in the selective permeation of species through its matrix. Different analytical techniques have been then adopted to draw information on the PPD structure and make hypotheses on the polymerization mechanism.

Works^{22–31} based on infrared, Raman and UV–VIS spectroscopies, quartz crystal microbalance, radiometry and electrochemical techniques, have led to the hypothesis of a phenazine-like structure for PPD, although the presence of 1,4-substituted benzenoid–quinoid units along its backbone, involving free NH₂ groups, has been also proposed, either as the main repeating units³² or as defects in the phenazine-like structure.²²



It is worth noting that almost all these investigations deal

with PPD electrosynthesised in very acid solutions (sometimes with pH < 1), whereas no information is available on the material obtained by polymerization in slightly acid or neutral solutions, which are the conditions usually adopted for its synthesis, especially in enzyme-based biosensors development.

Due to our interest in PPD membranes used in these devices we have started an investigation on the polymer films electrosynthesised on platinum at different pH values, in order to understand whether the electrosynthesis pH could have a significant effect on the film structure. We have chosen X-ray Photoelectron Spectroscopy (XPS) for PPD analysis, since the extremely small thickness of the polymeric films obtained in our conditions (< 100 Å) allows application of XPS as a “bulk” technique. Furthermore XPS is able to provide not only qualitative but also, through careful curve fitting, quantitative information on the different chemical environments of carbon and nitrogen in the polymer structure. This could be fundamental to verify whether a fully condensed structure, like the phenazine-like one, having only one nitrogen type, could be assigned to PPD at any pH of polymerization.

In this work the results of the “conventional” XPS approach will be discussed together with a detailed presentation of data arising from chemical derivatization–XPS (CD–XPS) measurements. The latter were obtained using two different derivatization reactions, aimed at labeling selectively primary aminic and hydroxy groups, whose presence in the PPD structure had been suggested by preliminary XPS data¹⁹ and by the curve fitting of the nitrogen XP spectrum in the present work.

Spectra in the visible region relevant to the electrolytic solutions after PPD polymerization, containing soluble *o*PD oligomers, will be also presented, in order to make a correlation between the polymer structure and the properties of its soluble companions.

Experimental

Chemicals

o-Phenylenediamine (*o*PD) ca. 99% (Aldrich Chemical Co.) was sublimed under vacuum at 80 °C before use. The following

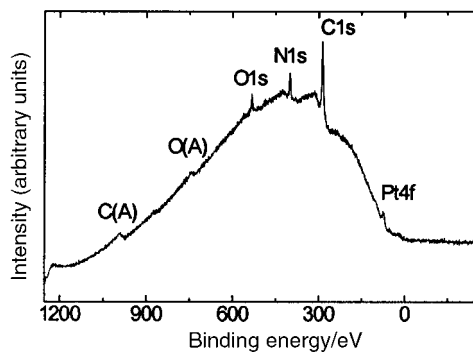


Fig. 2 XPS survey scan for a PPD film electropolymerised at pH 1.

cases no reduction peak is found in the reverse scans, thus suggesting that oxidised oPD is involved in further chemical processes leading to non-reducible species in the potential range adopted.

The CV peaks assignment is out of the scope of the present work; a more detailed electroanalytical investigation, also extended to different electrode substrates, is in progress and will be the subject of a future paper.

The progressive lowering of the oxidation current during the cycling clearly indicates that the deposited films passivate the electrode, covering exhaustively its surface and this phenomenon is faster the higher the pH value. This finding seems to suggest that only thin films can be grown by oxidation of oPD on platinum at these pH values and has been confirmed by XPS data.

XPS measurements

The XPS survey scan for a PPD sample grown on platinum at pH 1 is reported in Fig. 2; the presence of a signal due to the Pt 4f photoelectrons emitted by the film substrate is clearly evident. This finding (observed at all the pH values) suggests that the thickness of the PPD film is of the same order of magnitude of the Pt photoelectrons escape depth through the polymer, *i.e.* about 100 Å.

As to the major constituents of the polymer, carbon and nitrogen, the curve fitting of the relevant spectra (C1s and N1s)

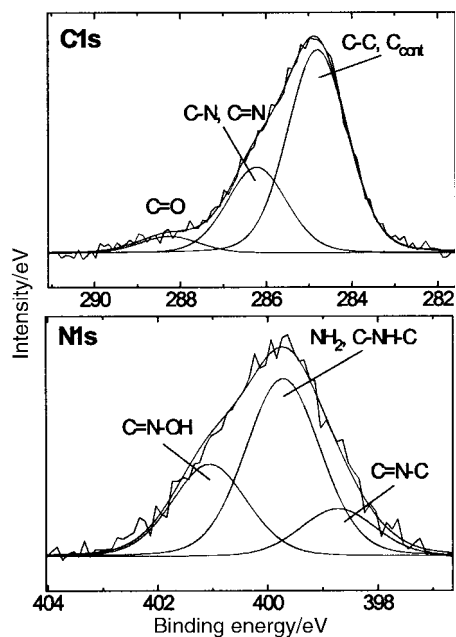


Fig. 3 Typical C1s and N1s spectra for PPD electrosynthesised at pH 1. The components and resultants obtained from curve fitting are also shown.

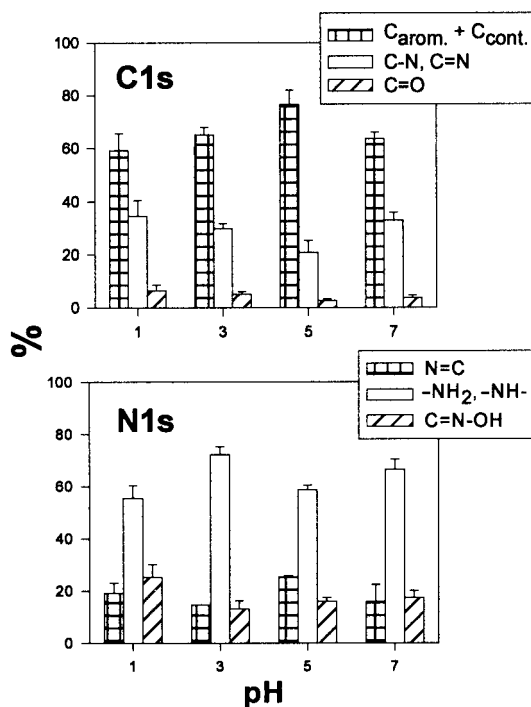


Fig. 4 Bar diagrams reporting the percentage distributions of components for C1s and N1s spectra obtained from PPD samples electrosynthesised at different pH.

leads to the identification of three components, as shown in Fig. 3, which is referred to a PPD sample grown at pH 1. The peak areas were used to quantify each component and their percentage distributions for PPD films synthesised at different pH are shown as bar diagrams in Fig. 4.

The assignment of each component to a particular chemical environment was made on the basis of a comparison of their binding energy (BE) values, shown in Table 1, with those reported in the literature on carbon and nitrogen functionalities.^{35–38} The major component of C1s is due both to PPD benzenic carbons not linked to nitrogen and to contamination carbon, and was used as an internal BE reference (at 284.8 eV).

Two other components are observed in the C1s spectrum of PPD. The first can be related to both benzenic carbon linked to nitrogen by a single bond (C–NH₂ or C–NHR) and to iminic carbon (C=N), as these two species do not show significantly different chemical shifts.^{37–38} The second carbon component, always minor in PPD films (and not present on the Pt substrate before polymerization), can be assigned to carbonyl groups, whose presence has been already suggested (in quinone imine units) for PPD electrosynthesised at acid pH.²²

As far as the N1s spectra are concerned, it is apparent that iminic (or phenazinic) nitrogen, though present, is not the only species, even in PPD synthesised at pH 1, thus suggesting that a perfectly phenazinic structure is not appropriate to describe the polymer. Indeed aminic nitrogen is the predominant type, although it is not possible to distinguish between primary and secondary aminic groups, due to their close chemical shifts.

Table 1 Binding energies/eV values for the components of C1s and N1s spectra (as obtained from curve fitting) relevant to PPD samples electrosynthesised at different pH (4 replicates for each pH)

	pH 1	pH 3	pH 5	pH 7
C1s	284.8 (ref.)	284.8 (ref.)	284.8 (ref.)	284.8 (ref.)
	286.16 ± 0.08	286.07 ± 0.03	286.20 ± 0.12	286.16 ± 0.06
	288.30 ± 0.14	288.23 ± 0.16	288.36 ± 0.10	288.14 ± 0.15
	289.73 ± 0.06	289.67 ± 0.08	289.51 ± 0.08	289.49 ± 0.11
N1s	398.70 ± 0.13	398.52 ± 0.14	398.44 ± 0.13	398.31 ± 0.16
	399.73 ± 0.06	399.67 ± 0.08	399.51 ± 0.08	399.49 ± 0.11
	401.09 ± 0.09	400.82 ± 0.16	400.75 ± 0.07	400.76 ± 0.09

The attribution of the third component in the N1s spectrum is more difficult. The BE values exhibited by this component correspond to those reported in the literature for some positively charged nitrogen species.^{36–38} It is likely that charged species like protonated NH₂ groups are formed during oPD polymerization, especially at low pH values. However, rinsing the samples with water after the polymer synthesis probably leads to almost complete deprotonation.

This hypothesis is supported by the absence of any possible counterion (sulfate, citrate, acetate and phosphate, at pH 1, 3, 5 and 7 respectively) on the polymer surface, since no signal due to S, P and to COO⁻ groups was found in the PPD XP spectra.

For further confirmation, a PPD film, grown at pH 1 and washed with water as usual, was first analysed by XPS, then exposed to a basic solution (NaOH, pH 9) and finally re-analysed for comparison without a preliminary washing stage. No significant modification of the high binding energy N1s component was observed, whereas a considerable decrease would have been expected if that component corresponded to charged nitrogen. This finding indicates that even in PPD synthesised at the lowest pH the amount of charged nitrogen, after washing with water, is negligible.

The high binding energy N1s component was then tentatively assigned to oximic (C=N–OH) groups, which have similar chemical shifts³⁹ and could arise from PPD further oxidation. Moreover oximes and carbonyls could be responsible for the presence, observed at all the polymerization pHs, of the oxygen signal in the XPS survey scan of PPD (see Fig. 2).

Chemical derivatization–XPS results

In order to confirm the identification of the C=N–OH groups and verify the presence of the primary aminic ones, chemical derivatization–XPS, extensively and successfully applied in our laboratory also to electrosynthesised polypyrroles,^{40–43} has been exploited.

As far as NH₂ groups are concerned, PPD samples obtained at different pH were reacted with *p*-(trifluoromethyl)benzaldehyde (TFMBA), a reactant able to turn primary amines into imines containing three fluorine atoms for each reacted NH₂ group.

Indeed a signal due to F1s was observed, after reaction, on every PPD sample, even those synthesised at pH 1, suggesting the presence of NH₂ groups, which was confirmed both by the appearance (see Fig. 5) of a characteristic peak in the C1s spectrum, due to the CF₃ groups, and by the increase of the C=N component in the N1s spectrum (not shown) with respect to the non-derivatised sample. The latter finding leads to the exclusion of the possibility of a simple absorption of the TFMBA reactant on the samples, as confirmed by the O:N elemental ratio, which did not change significantly after the

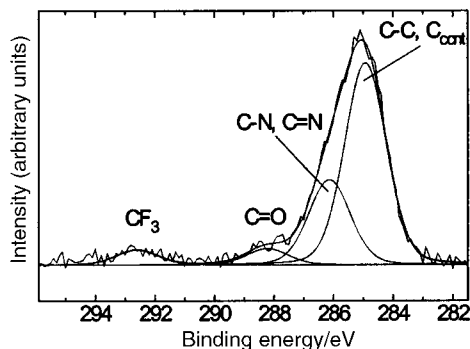


Fig. 5 C1s spectrum for a PPD film after derivatization with *p*-(trifluoromethyl)benzaldehyde (TFMBA). The components and the resultant obtained by curve fitting are also shown.

Table 2 Ratios between the number of different functionalities and total nitrogen obtained by chemical derivatization–XPS or conventional XPS for PPD samples synthesised at different pH. See text for the details of calculations

	PPD-TFMBA NH ₂ /N	PPD-TFAA (OH + NH ₂)/N	PPD-TFAA OH/N	Conv. XPS: N1s N _{HBE} /N ^a
pH 1	0.11	0.37	0.22	0.23
pH 3	0.10	0.26	0.15	0.16
pH 5	0.16	0.34	0.18	0.17
pH 7	0.28	0.39	0.12	0.13

^aN_{HBE} is the highest binding energy component obtained from curve fitting of N1s spectra.

reaction, whereas an increase (due to the aldehyde oxygen) would have been expected in case of absorption.

For a quantitative estimate of NH₂ amount, the F1s peak area, corrected by the relevant sensitivity factor, was used. In particular, one third of that area (three fluorine atoms correspond to a single reacted NH₂ group) was ratioed to the total N1s area, corrected by the relevant sensitivity factor, and the percentage of NH₂ over total nitrogen was calculated. The results are reported in Table 2. An increase is clearly observed when the PPD electrosynthesis pH is increased, suggesting that the polymer chains have more condensed rings (*i.e.* rings linked through both the nitrogen atoms of the monomer) at lower pH (1 and 3), though a primary aminic group is present every 5 monomer units (10 N atoms). On the contrary, at neutral pH the number of these groups is almost three times higher.

As anticipated before, derivatization of OH groups was accomplished with trifluoroacetic anhydride (TFAA), thus using F again as a spectral marker.

It is worth noting that anhydrides are able to react also with the OH groups of oximes;⁴⁴ as a matter of fact a F1s signal was observed in the XPS survey scan of all the derivatised PPD samples. However, the reaction is known to occur, with comparable yield,⁴⁵ also on aminic groups, which are turned into amides by TFAA, as we checked using the reactant to derivatise polyallylamine, chosen as a standard polymer for NH₂ groups. A careful analysis of CD–XPS data, involving also the C1s and N1s spectra, was then necessary to separate the contributions due to OH and to NH₂ groups in PPD.

The C1s (a) and N1s (b) spectra for a PPD sample derivatised with TFAA are shown in Fig. 6, with the components and resultant obtained by curve fitting. The increase of the higher BE component in the N1s spectrum, with respect to non-derivatised PPD, is a clear indication that trifluoroacetic amide groups were formed, due to the presence of NH₂. On the other hand, the presence of components assigned to CF₃ and CF₃COO groups in the C1s spectrum confirmed that OH groups were also present on the sample. It is worth noting that the CF₃(CO)NH groups formed by the reaction of TFAA with NH₂ functionalities have a chemical shift (3.4 eV, measured in the C1s spectrum of TFAA-derivatised polyallylamine) too close to the one of carbonyls to be distinguished as another component (see Fig. 6).

The peak area of the trifluoroacetic ester (CF₃COO) component was then used for a quantitative estimate of the OH groups, whereas one third of the F1s area (as for TFMBA) was correlated to the total number of OH and NH₂ groups. The results for the different PPD samples, expressed as ratios between the functionalities and the total nitrogen, are shown in Table 2.

It can be seen from the third column that the number of OH groups increases on lowering the pH value, though the variation is not so evident as that observed for primary aminic groups. More important is the excellent agreement between the OH:N ratio obtained from TFAA derivatization

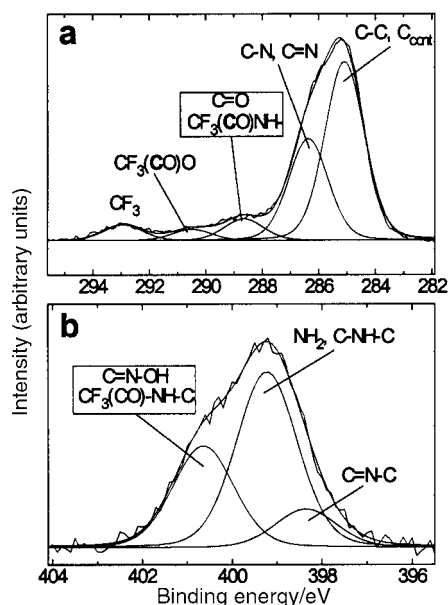


Fig. 6 C1s (a) and N1s (b) spectra for a PPD film after derivatization with trifluoroacetic anhydride (TFAA). The components and results obtained by curve fitting are also shown.

and the ratios between the areas of the highest BE component of nitrogen and the total N. This finding, though indirectly, confirms that this component is almost completely due to C=N–OH groups, whereas the presence of OH groups linked directly to benzenic carbons can be considered negligible.

Unlike carbonyls, which could arise from the hydrolysis of previously formed imine functionalities, the origin of oximes is not easy to explain.

It is noteworthy that an increase of the corresponding N1s component (compared to the as-synthesised polymer) has been observed by XPS in our laboratory¹⁹ when cycling a PPD film in the monomer-free electrolyte using an upper limit of 1.2 V (instead of 0.8 V) for the potential scan.

We have repeated the same experiment on two PPD films, using the curve fitting of the relevant N1s spectra to compare the N species distributions before and after potential cycling. Indeed, a remarkable increase of the C=N–OH component was observed and it was almost completely counterbalanced by the decrease of the C=N component.

This finding has led us to hypothesise that oximes could arise from the oxidation of previously formed imine functionalities when PPD is kept at high anodic potentials. It is then likely that, though at a lower extent, the same process occurs during the PPD polymerization itself, when the already deposited polymer is exposed to the anodic potentials of further polymerization cycles.

Visible spectroscopy

When oPD is electropolymerised on platinum, the electrolytic solution near the electrode surface becomes red–yellow coloured, even during the first cycle, at any pH. This phenomenon has been attributed to the formation of soluble oPD oligomers.¹ As the polymerization goes on, the color intensity increases and the diffusion of oligomers from the electrode environment towards the bulk of the solution can be easily visualized in the initially colourless solution.

Spectra have been then recorded in the visible region on the solutions obtained after polymerization of oPD at different pH, in order to draw information on the polymer structure starting from its oligomers. The spectra are shown in Fig. 7 and the values of the maxima wavelengths have been reported in the inset.

It is apparent that a red shift occurs in the maximum

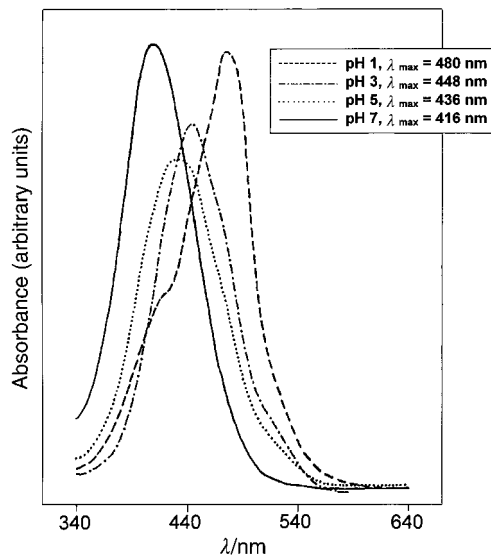


Fig. 7 Visible spectra of the electrolytic solutions after polymerization of oPD 5 mM at different pH.

absorption when going from neutral to acid pH, suggesting that the conjugation in the oligomers structure is extended when lowering the polymerization pH.

This finding seems to confirm the oPD tendency to form more condensed structures when polymerised at low pH.

A deeper investigation on the PPD oligomer structures has been then undertaken in our laboratory using Electrospray Ionization Ion Trap Mass Spectrometry, aiming for the identification of the different species. This study could also indicate if oxygenated groups are present also in the oligomers structure or if their formation occurs only on the deposited polymer. The results will be the object of a future work.

Conclusions

Thin polymer films obtained by electropolymerization of *o*-phenylenediamine (oPD) on platinum at different pH (1, 3, 5, 7) were characterised by XPS.

Different functional groups were identified and quantified both by careful curve fitting of carbon and nitrogen spectra and by using chemical derivatization (CD–XPS) reactions. The presence of carbonyl, primary/secondary aminic and oximic (C=N–OH) groups was observed in all the samples, together with iminic (phenazinic) nitrogen. In particular, the NH₂ groups were present even at pH 1 and their amount was found to increase with polymerization pH, thus indicating that the polymer structure is not completely conjugated, as previously suggested for PPD electrosynthesised in very acidic solutions. Indeed a 1,4-substituted benzenoid–quinoid structure seems to be more appropriate to describe the polymer structure, though a higher degree of conjugation was deduced for PPD electrosynthesised at low pH.

The latter finding was indirectly confirmed by visible spectroscopy on the electropolymerization solutions, coloured by the presence of PPD oligomers, since a red shift in the absorption maximum was observed when going from neutral to acidic polymerization solutions.

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