Polymer 50 (2009) 6043–6048

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Structure of chemically prepared poly-(*para*-phenylenediamine) investigated by spectroscopic techniques

Ricardo H. Sestrem [a], Daniela C. Ferreira [a], Richard Landers [b,c], Marcia L.A. Temperini [a], Gustavo M. do Nascimento [a,*]

[a] *Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, CP 26.077, CEP 05513-970, São Paulo, SP, Brazil*
[b] *Departamento de Física Aplicada, Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, CP 6165, CEP 13083-970 Campinas, SP, Brazil*
[c] *Laboratório Nacional de Luz Síncrotron, CP 6192 13084-971, Campinas, SP, Brazil*

ARTICLE INFO

Article history:
Received 19 August 2009
Accepted 11 October 2009
Available online 30 October 2009

Keywords:
Diamines
Polyaniline
Raman

ABSTRACT

The structure of chemically prepared poly-*p*-phenylenediamine (PpPD) was investigated by Resonance Raman (RR), FTIR, UV–VIS–NIR, X-ray photoelectron (XPS), X-ray Absorption at Nitrogen K edge (N K XANES), and Electron paramagnetic Resonance (EPR) spectroscopies. XPS, EPR and N K XANES data reveal that polymeric structure is formed mainly by radical cations and dication nitrogens. It excludes the possibility that PpPD chains have azo or phenazinic nitrogens, as commonly is supposed in the literature. The RR spectrum of PpPD shows two characteristic bands at 1527 cm^{-1} and 1590 cm^{-1} that were assigned to $\nu C{=}N$ and $\nu C{=}C$ of dication units, respectively, similar to polyaniline in pernigraniline base form. The presence of radical cations was confirmed by Raman data owing to the presence of bands at 1325/1370 cm^{-1}, characteristic of $\nu C–N$ of polaronic segments. Thus, all results indicate that PpPD has a doped PANI-like structure, with semi-quinoid and quinoid rings, and has no phenazinic rings, as observed for poly-*o*-phenylenediamine.

1. Introduction

Polyaniline (PANI) and its derivatives are an important class of conducting polymers and have been attracted great attention since their discovery [1], owing to their peculiar electrical, optical and magnetical properties [2]. In more recent years, aromatic diamines have been employed in the synthesis of new conjugated polymers, with the aim to acquire materials which can exhibit better chemical functionality, mechanical and thermal properties than PANI [3]. There is a great variety of aromatic diamines suitable to the oxidative polymerization, nevertheless the phenylenediamines (PDs) have been more frequently used. FTIR, UV–VIS–NIR and ^1H NMR spectroscopies are commonly used in the study of the structure of polymers derived from aromatic diamines [3–9]. However, there is not a real conclusion about the structure of these polymers in the literature.

There are three main structural proposals for the chemical structure of poly-(*p*-phenylediamine) (PpPD). Cataldo [5] proposed a ladder structure with phenazine rings for PpPD (see Scheme 1) prepared in acidic aqueous media with ammonium persulfate as oxidant. In addition the author described that the electronic structure is more similar to that of PANI in its pernigraniline base form; Ichinohe et al. [8] proposed a linear structure with hydrazo bounds for chemical polymerization with hydrogen peroxide catalyzed by horseradish peroxidase. In a theoretical calculation work; Lakard et al. [9] concludes that PpPD polymerization mechanism takes it to a emeraldine salt form of polyaniline (PANI-ES).

Our group have been employed the resonance Raman (RR) scattering as main tool in the elucidation of polymeric structures derivate from aromatic amines [10]. Our interest is to carry out the vibrational and electronic characterization of conducting polymers, in order to give subsidies for the understanding of the structure–property relationships in these materials. In fact, by means of the resonance Raman (RR) effect it is possible to identify the bands of each chromophoric species in the polymeric chains, thus providing unique information about vibrational frequencies and electronic transitions. This chromophore selectivity endows the resonance Raman spectroscopy with the capacity to study different segments present in the complex structure of conducting polymers [11]. Recently, it was possible to determine the characteristic chromophoric segments of oligomers and polymers derivate from *ortho*-phenylenediamine by using Raman spectroscopy as main tool [12]. It was proposed that poly-*ortho*-phenylediamine is formed by phenazine-like rings having different protonation and oxidation

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* Corresponding author. Tel./fax: +55 11 5671 2419.
E-mail address: morari@yahoo.com (G.M. do Nascimento).

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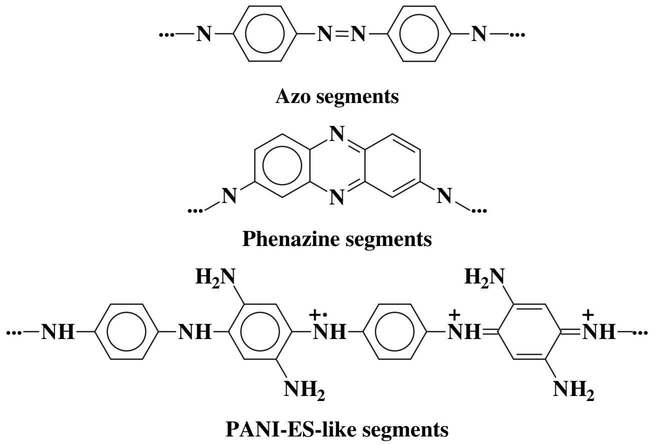
doi:10.1016/j.polymer.2009.10.028



Scheme 1. Schematic Representation of Probable Chromophoric Segments Present in PpPD chains.

levels, but the polymeric backbone also presents segments with structure similar to that of quinoid rings of PANI.

In this work the RR technique was used in the study of the characteristics segments of PpPD formed by chemical oxidative polymerization in acidic aqueous medium. In addition, the Electronic paramagnetic resonance (EPR), X-ray photoelectron (XPS) and X-ray absorption near nitrogen K edge (N K XANES) spectroscopies were used for the determination of kinds of nitrogen present in the polymeric matrix.

2. Experimental section

2.1. Materials

The used compounds were analytical grade and were used as received without any further purification. Phenazine (Merck), *para* and *ortho*-Phenylenediamine (Merck) was used after recrystallization with activated carbon.

2.2. Preparation of poly(p-phenylenediamine) (PpPD)

Oxidative polymerization of the monomer by ammonium persulfate in aqueous acid medium proceeded in the same conditions of the literature [6]. The bluish-black polymers obtained by this route were labeled PpPD. The MALDI data of PpPD shows a broad molecular ion band, it indicates that medium molar mass of the polymer is around 2248 Da, which represents roughly 21 monomeric units of *p*-phenylenediamine for each polymeric chain.

2.3. Preparation of poly(o-phenylenediamine) (PoPD)

The preparation of PoPD was described elsewhere [12]. *ortho*-Phenylenediamine (0.40 g) was dissolved in warm ($\approx 40\,^{\circ}$C) glacial acetic acid (30 mL) in a 100 mL round bottomed flask Ammonium persulfate (2.52 g), dissolved in 2 mL of distilled water, was added dropwise to the warm amine solution over a period of 10 min. The resultant solution was refluxed at 118 °C for 72 h. The black colored powder was filtered and vacuum dried. The resultant product was soxhlet extracted with tetrahydrofuran (THF). The MALDI data of PpPD shows a broad molecular ion band, it indicates that medium molar mass of the polymer is around 2950 Da, which represents roughly 27 monomeric units of o-phenylenediamine for each polymeric chain. The PoPD shows a weak EPR signal at 2.0006*g*.

2.4. Preparation of poly(aniline) forms

The emeraldine salt and base (PANI-ES and PANI-EB, respectively) forms of PANI were prepared according to the procedure described by Mac Diarmid [1]. The pernigraniline base form (PANI-PB) was prepared through oxidation of PANI-EB following procedure described in the literature [13].

2.5. Equipments

Resonance Raman (RR) spectra of solid samples were obtained using the 632.8 nm exciting radiation (He–Ne laser, Spectra Physics, model 127) and the 514.5 nm exciting radiation (Ar^+ laser, Omnichrome model 543-AP) were recorded in a Renishaw Raman Imaging Microscope (system 3000) containing an Olympus metallurgical microscope and a CCD detector (cooled by a Peltier). The laser beam was focused on the sample in a ca. 1 μm spot by an ×80 lens. Laser power was always kept below 0.7 mW at the sample to avoid sample degradation. Fourier transform Raman (FT-Raman) spectra of solid samples were recorded in a RFS 100/S FT-Raman Bruker spectrometer with the 1064.0 nm laser line from an air-cooled diode-pumped Nd:YAG laser. The calibration of the equipment (wavenumbers and intensities of the peaks) was performed using a standard Nylon sample. Experiments were performed under room conditions with a backscattering geometry. The laser beam with approximately 1 mm spot (the largest spot available) was focused on the center of the aluminum disc (using the laser guided of the FT-Raman as reference) containing the sample at the front compartment using different laser powers.

FTIR spectra were obtained using a BOMEM MB-100 instrument and the samples dispersed in a KBr pellets. EPR spectra were recorded at room temperature from powders on a Bruker ER 200 spectrometer operating in the X-band ($\sim$9.5 GHz). UV–VIS–NIR spectra of the samples dissolved in DMF were obtained in a Shimadzu UVPC 3101 Scanning Spectrophotometer.

XANES spectra at N K-edge were obtained using the facilities of the National Synchrotron Light Laboratory (LNLS), Campinas, Brazil. The spherical grating monochromator beam line (the spectral resolution $E/\Delta E$ of spherical grating is better than 3.000) has a focused beam of roughly 0.5 mm^2 spot, and the spectra were recorded in total electron yield detection and with the sample compartment pressure at 10^{-8} mBar. Measurements were done with the sample surface normal to the beam. All energy values in the N K-edge spectra were calibrated using the resonant peak at 405.5 eV in the N K-edge XANES spectrum of potassium nitrate [14]. XPS measurements were done using characteristic K_α radiation from Al anode to excite samples and a 100 mm mean radius hemispherical analyzer operated with a constant pass energy of 44 eV, that resulted in 1.6 eV FWHM for Au 4f line. A small quantity of each sample was pressed between two stainless steel plates to form a thin conglomerate that was fixed to sample holder with double faced conducting tape. Analyses were done at base pressure of 5×10^{-9} mBar and charging effects were corrected by shifting spectra so that C 1s line was at 284.6 eV.

MALDI mass spectrometry was performed in an Amersham Biosciences Ettan MALDI-TOF mass spectrometer. The (α-Cyano-4-hydroxycinnamic acid) matrix was dissolved in an acetonitrile (49%)/ethanol (49%)/trifluoracetic acid (2%) solution while the samples were dissolved in ethanol. For sample preparation the dried-droplet method was used.

3. Results and discussion

The UV–VIS–NIR spectrum (see Fig. 1) of PpPD displays bands at ca. 355, 420 and 540 nm, which are similar to that obtained in

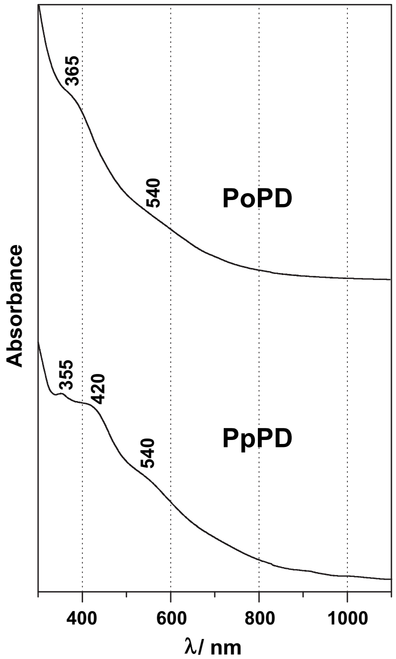


Fig. 1. UV–VIS–NIR of PpPD and PoPD samples dissolved in DMF.

Ref. [5]. It was observed that the UV–VIS–NIR spectrum of PpPD is like to that obtained for PANI in its pernigraniline form (PANI-PB) [5], and it was suggested that both polymers have similar structure. However, it can be seen that the spectrum of PpPD has similitude to that of the ladder PoPD polymer (see Fig. 1). Thus, it is not possible to determine conclusively the polymeric structure of PpPD only considering the UV–VIS–NIR data.

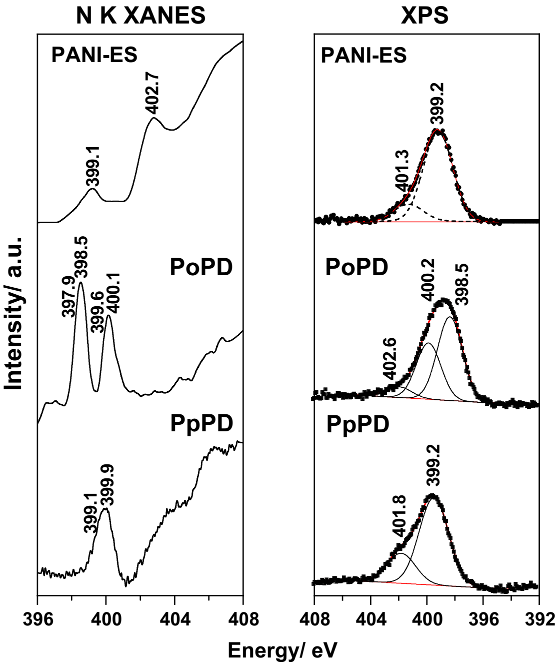


Fig. 2. N K XANES and XPS spectra of PANI-ES, PpPD and PoPD solid samples.

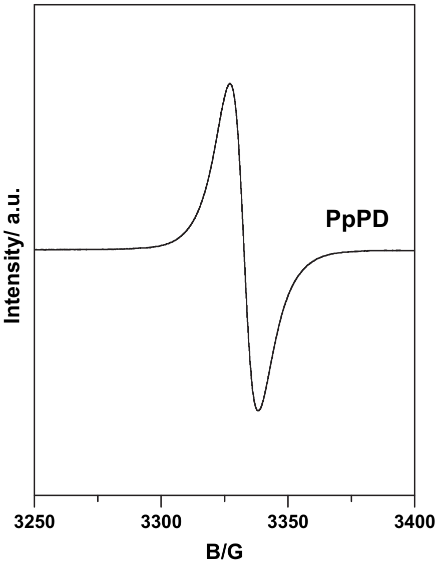


Fig. 3. EPR spectrum of PpPD sample.

In order to elucidate the oxidation and protonation states of nitrogens in the PpPD chains, EPR, N K XANES and XPS techniques were used. The N K XANES spectrum of PpPD was assigned using the data previously obtained for several nitrogenated molecules [10d,15,16]. The N K XANES spectrum of PpPD shows bands at 399.1 and 399.9 eV that can be assigned to radical ($-\overset{+}{N}=$) and protonated imine ($>\overset{+}{N}=$) nitrogens, respectively. Neither N K XANES bands related to phenazinic (at 398.5 eV, as observed in Fig. 2 for PoPD) nor azo nitrogens (at ca. 398.7 eV) were observed in the N K XANES spectrum of PpPD [10d,15]. The presence of radicals nitrogens was confirmed by a strong signal at 3200g ($g = 2.0004$) in EPR spectrum (see Fig. 3) of PpPD, corroborating the N K XANES data.

The XPS spectrum of PpPD sample (see Fig. 2) is very similar to that of PANI-ES. Thus, the bands at 399.2 and 401.8 eV can be assigned to amine nitrogens (-NH-) and charged nitrogens ($-\overset{+}{N}=$ and $>\overset{+}{N}=$), respectively [10d,15]. In addition, similar to that observed in XANES data, the XPS spectrum of PpPD is different to that of PoPD sample. Thus, considering the EPR, XANES and XPS data it is possible to conclude that the PpPD have amine (-NH-), radical ($-\overset{+}{N}=$) and dication ($-\overset{+}{N}=$) nitrogens.

Fig. 4 displays the spectra of PpPD and PoPD samples at three laser lines. At first view, it can be seen that the spectral profile and the resonance Raman behavior of PpPD and PoPD are very different, mainly when the spectra obtained at 514.5 nm are compared. This is an indication that the structures of the polymers are very different, on the contrary to that is suggested in the literature [3]. The bands at 1350–1402 cm^{-1}, that are correlated to phenazine rings, are not observed in the spectra of PpPD.

At 1064.0 nm laser line the spectrum of PpPD can be correlated to that of PANI-ES at same laser line (see Fig. 5). It was observed [17,18], that using 1064.0 nm, mainly bands due to the radical cations are in resonance in Raman spectrum of PANI-ES. The bands at 1171 and 1323/1352 cm^{-1} are assigned to $\beta_{C\text{-}H}$ and $\nu_{C\text{-}N}$ of radical cations segments, respectively. These bands can be correlated to the bands at 1178 and 1325/1370 cm^{-1} observed for PpPD sample at 1064.0 nm. For PoPD only a small band at 1353 cm^{-1} is clearly seen, indicating that radical cations are present in smaller amount than observed in PpPD. The bands at 1527 and 1590 cm^{-1} in the spectrum of PpPD could also be correlated to similar PANI-ES bands at 1064.0 nm. However, these bands have increased their Raman intensities, mainly at 632.8 and 514.5 nm, that are not observed in the PANI-ES spectra. This behavior suggests that at 632.8 and 514.5 nm laser lines another chromophoric unit is in resonance.

In fact, the Raman spectra of PpPD at 632.8 nm and 514.5 nm are like to the spectra observed for PANI-PB (see Fig. 5). The bands at 1170, 1527, and 1590 cm^{-1} in the spectrum of PpPD at 514.5 nm (see

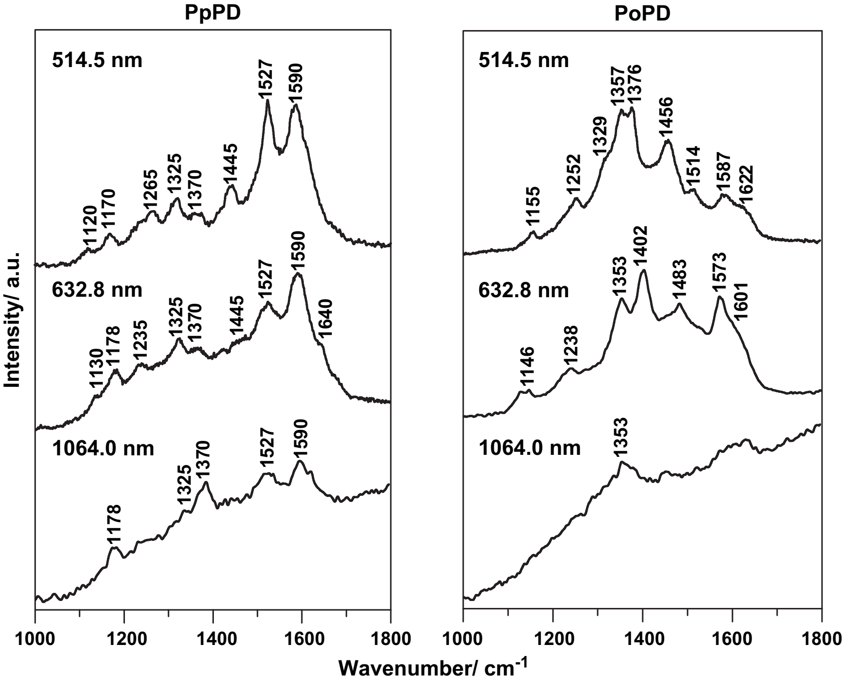


Fig. 4. Resonance Raman spectra of powdered samples of: PpPD and PoPD obtained at indicated laser lines.

Fig. 4) can be correlated to the PANI-PB bands at 1160, 1483, and 1575 cm^{-1}. These bands are assigned to $\beta_{C\text{–}H}$, $\nu_{C=N}$, and $\nu_{C=C}$ of quinoid diimine segments, respectively [19]. The mismatch between the bands at 1527 and 1483 cm^{-1} (related to $\nu_{C=N}$) observed for PpPD and PANI-PB, respectively, can be associated to differences in the conjugation length of the polymeric chains. It was demonstrated [20], that mainly $\nu_{C=N}$ band is sensible to changes in the conjugation length of the PANI chains. For PANI, the conjugation length is modulated by the torsion degree between the benzenoid and quinoid rings, being higher the torsion degree means higher the $\nu_{C=N}$ band values. Thus, the higher values of $\nu_{C=N}$ band of PpPD means that its chains have higher torsion degree. Another possibility is that in the PpPD chains the quinoid segments have certain protonation degree, shifting the $\nu_{C=N}$ band to higher values in comparison to pernigraniline base form of PANI (PANI-PB).

Fig. 6 shows the FTIR spectra of the PpPD and PoPD samples. For comparison purposes, the FTIR of some reference compounds are also shown. In the literature, different bands in the region of 600–900 cm^{-1} are used to characterize if the poly(phenylnediamines) are formed by phenazine units or by 1,4-substituted benzene rings [3]. However, this is a very imprecise approach, because both 1,4-substituted benzene rings and 1,2-substituted benzene rings present strong FTIR bands in this region (see Fig. 6, spectra of *para*-PD and *ortho*-PD).

In this work, the FTIR analysis was done considering the match of major number of bands between the spectra of the polymers (PpPD or PoPD) with the spectra of a standard molecule. For

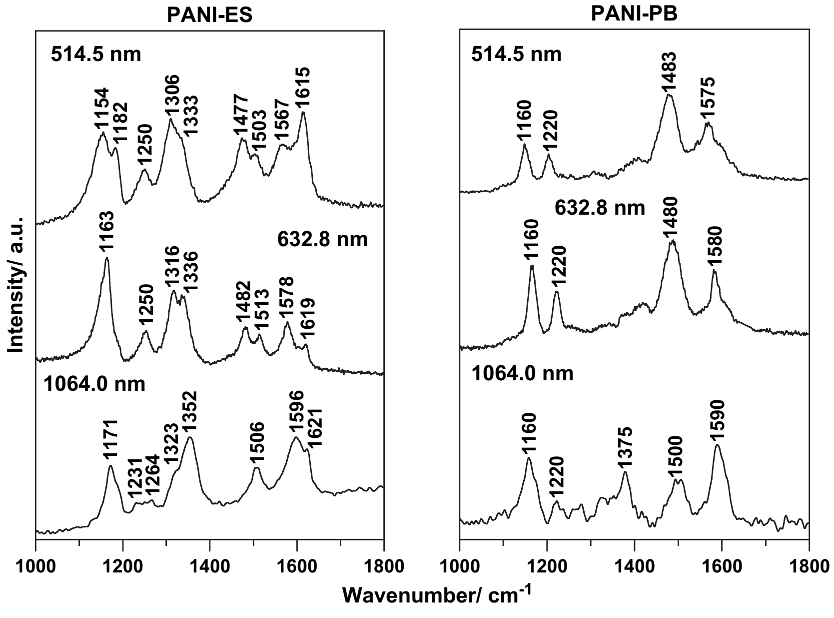


Fig. 5. Resonance Raman spectra of powdered samples of PANI-ES and PANI-PB obtained at the indicated laser lines.

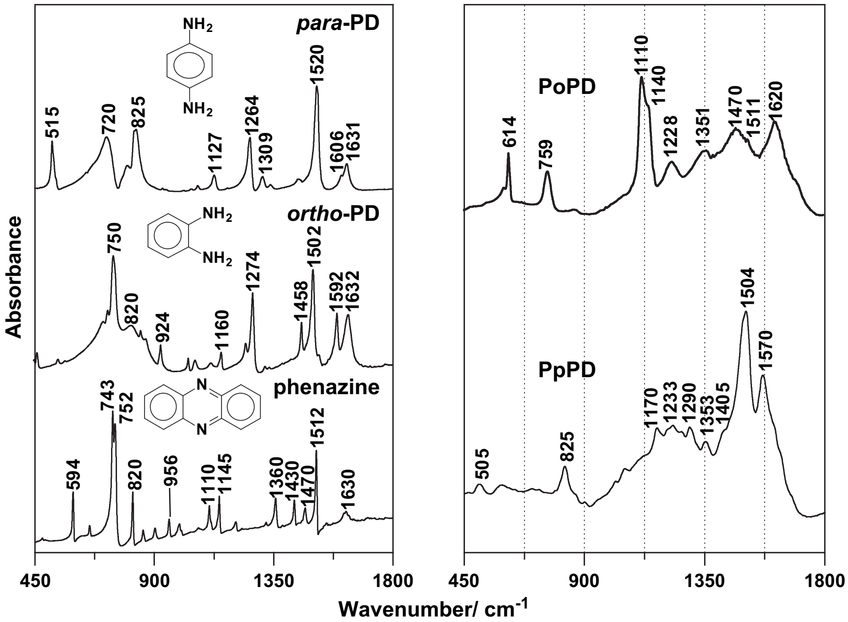


Fig. 6. FTIR spectra of the powdered samples of: *para*-PD, *ortho*-PD, phenazine, PpPD and PoPD dispersed in KBr discs.

Table 1
Band values, relative intensities, and tentative assignment of the Raman and FTIR bands of PpPD material.

FTIR	Raman 1064.0 nm	Raman 632.8 nm	Raman 514.5 nm	Tentative assignment
1170 *w*	–	–	1170 *w*[a] [1160]	β_{C-H} quinoid segments
–	1178 *w* (1171)[b]	1178 *w* (1163)	–	β_{C-H} radical cations
–	1325/1370 *w* (1323/1352)	1325/1370 *w* (1316/1336)	1325/137 *w* (1306/1333)	ν_{C-N} radical cations
1504 *s* {1502}[b]	1527 *w* [1500][b]	1527 *m* [1480]	1527 *s* [1483]	$\nu_{C=N}$ quinoid segments
1570 *m* {1592}	1590 *w* [1590]	1590 *s* [1580]	1590 *s* [1575]	$\nu_{C=C}$ quinoid segments

[a] *s* = strong, *m* = medium, *w* = weak.

[b] The numbers into (), [], and {} are the band values observed for PANI-ES, PANI-PB, and *ortho*-PD samples, respectively.

instance, the spectra of PoPD show many bands that can be correlated to the bands of phenazine molecule, being, the bands at 1620, 1511, 1470, 1140, 1110, and 759 cm^{-1} correlated to the bands at 1630, 1512, 1470, 1145, 1110, 752 cm^{-1}. The presence of phenazine units in the PoPD structure is in line with the Raman, XANES and XPS data. Differently to the PoPD, the spectrum of PpPD shows more similitude with the FTIR spectrum of *ortho*-PD molecule. The two strong bands at 1504 and 1570 cm^{-1} in the spectrum of PpPD can be correlated to the bands at 1502 and 1592 cm^{-1}, this is an indication that the structure of PpPD is constituted by 1,2-substituted benzene rings formed by polymerization of *para*-PD molecules. The tentative assignment of most representative FTIR and Raman bands at 1000–1800 cm^{-1} spectral region of PpPD are presented in the Table 1.

4. Conclusions

The set of spectroscopic results shows that the structure of chemically prepared PpPD and PoPD is different. The PpPD are formed by radical cations and dications nitrogens, neither azo nor phenazinic nitrogens were observed. The resonance Raman data show that PpPD chains are constituted for two kinds of chromophores, being the bands at 1527 cm^{-1} and 1590 cm^{-1} assigned to νC=N and νC=C of dication units, similar to polyaniline in pernigraniline base form, while the bands at 1325/1370 cm^{-1} show the presence of radical cations, similar to the PANI-ES. Thus, it is possible to suggest that the structure of PpPD is a doped PANI-like structure, with semi-quinoid and protonated quinoid rings, and has no phenazinic rings as observed for PoPD.

Acknowledgments

This work was supported by FAPESP (Brazilian agency). Fellowships from FAPESP (GM do Nascimento) and CNPq (RH Sestrem, DC Ferreira, R Landers and MLA Temperini). The authors would like to thank the National Synchrotron Light Laboratory (LNLS/Brazil) for XANES N K-edge (SGM 1026, 1427, 1432 and 2169) measurements. The authors are also grateful to Prof. A.M.C. Ferreira (IQ-USP) for the EPR data and Dr. Paolo di Mascio and Dr. Izaura N. Toma for MALDI data.

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