

Article

The Spectroscopic Characterization of Polydiphenylamine and one of its Oligomeric Fractions

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Dedicated to Prof. Oswaldo Sala on the occasion of his 70th birthday,
and in recognition of his contribution to vibrational spectroscopy

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A polidifenilamina (PDPA) sintetizada eletroquimicamente pelo método potenciodinâmico foi caracterizada pelas espectroscopias Raman e de absorção no UV-vis e no infravermelho. Dependendo do potencial aplicado, são formados dois tipos de filmes poliméricos adsorvidos sobre o eletrodo. Uma fração oligomérica formada na solução eletrolítica foi também caracterizada. Os espectros Raman do filme polimérico, formado em valores mais positivos de potencial final, e da fração oligomérica apresentaram a predominância de estruturas difenosemiquinoniminas. Estes resultados foram complementados por dados de UV-vis e condutividade e mostraram que a energia do "gap" para o polímero condutor é dependente da presença de estruturas difenosemiquinonas na matriz polimérica. Os espectros no infravermelho apresentam frequências que indicam ligações de hidrogênio intercadeias.

Polydiphenylamine (PDPA), electrochemically synthesized by a potentiodynamic method, was characterized by UV-vis absorption, Raman, and infrared spectroscopies. Depending on the potential applied, two types of adsorbed polymeric films were obtained on the electrode. A soluble oligomeric fraction formed in the electrolyte solution was also characterized. The Raman spectra of the polymeric film formed at more positive final potential and of the oligomeric fraction show the predominance of the diphenosemiquinoneimine structure. These results, along with the UV-vis and conductivity data, show that the band gap energy of the conducting polymer is dependent on the diphenosemiquinoneimine structure present in the polymer backbone. The IR spectra show some features that indicate interchain hydrogen bonding.

Keywords: *conducting polymer, Raman, UV-vis, and infrared spectroscopies*

Introduction

Since the successful synthesis of polyacetylene by Shirakawa in 1974¹, and especially after the discovery of its dramatic enhancement of conductivity after doping², electronic conducting polymers have raised great interest because of their many possible applications.

One of these polymers, polyaniline (poly(4-aminophenyl)), has been the object of intense multi-disciplinary research due to its environmental stability, low cost, and high conductivity³. In order to increase the performance of polyaniline, incorporation of substituents along the poly-

mer backbone or modification of its chains as strategies that have been used⁴. One of the resulting polymers is polydiphenylamine (poly(4-aminodiphenyl)), which possess an intermediate structure between polyaniline and poly(p-phenylene).

In the polyaniline family the ground electronic state is non-degenerate, and the charged species created after doping are radical cations (polarons) or dications (bipolarons), which present electronic transitions in visible and near infrared regions. Recently, it was shown that these species are stabilized by interchain hydrogen bonding⁵.

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Vibrational spectroscopy, and Raman spectroscopy in particular, have been extremely useful in the structural characterization of polymers⁶. More recently, resonance Raman spectroscopy proved to be instrumental in the understanding of the nature of the bond and the relationship between structure and conductivity in conducting polymers^{7,8}.

In previous work, we have monitored the first stages of the electrochemical oxidation of diphenylamine, DPA, by using resonance Raman spectroscopy⁹. In this work the vibrational bands of the diphenylbenzidine radical cation, $DPB^{+\cdot}$ and of the dication, DBP^{2+} , were assigned and the experimental conditions for the interconversion between the $DPB^{+\cdot}$ and DPB^{2+} were determined.

In this report two types of polymeric films of PDPA and an oligomeric fraction are characterized by UV-vis absorption, Raman, and infrared spectroscopies, with the aim of identifying the species present in the polymers. In addition, a correlation between electrical conductive and spectroscopic features is investigated. The thermal behavior of the PDPA oligomeric fraction is monitored by IR spectroscopy in order to better understand the nature of interchain interactions.

Experimental

Diphenylamine, DPA, (Merck) was purified by double recrystallization from petroleum ether. Acetonitrile (Merck), sodium perchlorate (Merck), and tetraethylammonium tetrafluoroborate, Et_4NBF_4 (Aldrich), were used as received.

Electropolymerization was performed in a single compartment cell equipped with a 1.2 cm^2 Pt (99.99%) working electrode, a Pt sheet as the auxiliary, and a saturated calomel electrode (SCE) as the reference electrode. The electrochemical equipment was a potentiostat-galvanostat PAR 273 EG&G connected to a HP 7090A system. The electrolyte solution was $10^{-1}\text{ M DPA} + 10^{-1}\text{ M } Et_4NBF_4$ in deaerated acetonitrile. The polymerization of DPA was carried out by continuous cycling of the potential between 0.0 and 1.5 V until a charge of 25 C cm^{-2} was reached. The polymer adsorbed on the electrode surface was obtained in two forms: i) the PDPA(Ox) obtained by taking the working electrode at 1.0 V out of the electrolyte solution, and ii) the PDPA(Red) obtained by holding the electrode potential at 0.0 V for approximately 30 min, during which the reducing current was reduced to zero.

The oligomeric fraction of PDPA formed in the electrolyte solution ($3 \times 10^{-1}\text{ M DPA} + 1\text{ M NaClO}_4/\text{acetonitrile}$) under the above conditions was isolated by drying the solvent. The solid obtained was purified with water in a Soxhlet, for about one hour, to remove the excess $NaClO_4$. This material was extracted with acetonitrile in a Soxhlet and dried under vacuum for 12 h. The use of $NaClO_4$ instead of Et_4NBF_4 as the electrolyte salt was due to the higher yield of oligomeric fractions obtained when an electropolymerization was done in a $NaClO_4/\text{acetonitrile}$ solution.

The gel permeation chromatograms (GPC) of the oligomeric fraction and of the dimer (DPB) were obtained on a Shimadzu chromatograph. This equipment was coupled to a UV-vis spectrophotometer, and the detection was done at a fixed wavelength of 254 nm. The calibration of the system was made by using monodispersed polystyrene samples. The solvent used was tetrahydrofuran (THF).

The differential scanning calorimetry (DSC) curves were obtained with a DSC 25 cell from a Mettler system TA 4000 Series. We used aluminum crucibles with 2 mg of the sample, under nitrogen atmosphere (30 mL/min). The heating rate was $10\text{ }^\circ\text{C/min}$.

Electrical conductivity was measured by the two-probe technique for pressed film¹⁰.

The *in situ* reflectance spectra of a platinum electrode in $10^{-3}\text{ M} + 10^{-1}\text{ M } Et_4NBF_4/\text{acetonitrile}$ solution, and the *ex situ* spectra of PDPA (Ox) and (Red) adsorbed on ITO electrodes were obtained on a Guided Wave (model 260) spectrometer equipped with a silicon-germanium detector, coupled to a microcomputer. The background for the *in situ* spectra was a spectrum of the platinum electrode in the electrolyte solution, while that for the *ex situ* spectra was a spectrum of the bare ITO electrode. The spectroelectrochemical cell used for the *in situ* reflectance experiment has been described elsewhere¹¹.

The Raman spectra were obtained with a Spex Triplemate 1877 fitted with an OMA-III multichannel detection system. The exciting radiation was the 514.5 nm Ar^+ laser line with 30 mW at the sample (*ca.* 8 W cm^{-2}).

The IR spectra were obtained with an FT-Michelson Bomen using KBr pellets. A variable temperature Perkin-Elmer cell model 124 was employed to obtain the spectra of the oligomeric fraction at high temperatures.

The UV-vis spectra of the compounds in the KBr pellets were obtained with a Beckman DU 70.

Results and Discussion

Three kinds of polymers, PDPA (Ox), PDPA (Red), and a soluble fraction, were obtained by the electrochemical polymerization of DPA, using the potentiodynamic method described in the Experimental Section. The PDPA (Ox) and PDPA (Red) are formed on the surfaces of the platinum electrodes when the synthesis is finished, at potential values of +1.0V and 0.0V, respectively. Due to the low solubility of PDPA (Ox) and PDPA (Red) in THF, only the gel permeation chromatogram of the soluble fraction is presented in Fig. 1, together with the chromatogram of diphenylbenzidine (DPB). As can be seen, the oligomeric soluble fraction presents peaks corresponding to a trimer (at 26 min, ~15%) and to a dimer (at 27 min, ~10%), together with the peak from the electrolytic salt (at 29 min).

To identify the species present in the polymers, the *ex situ* Raman spectra of the three samples are shown in Fig. 2. The spectra of PDPA (Ox) and of the oligomeric fraction

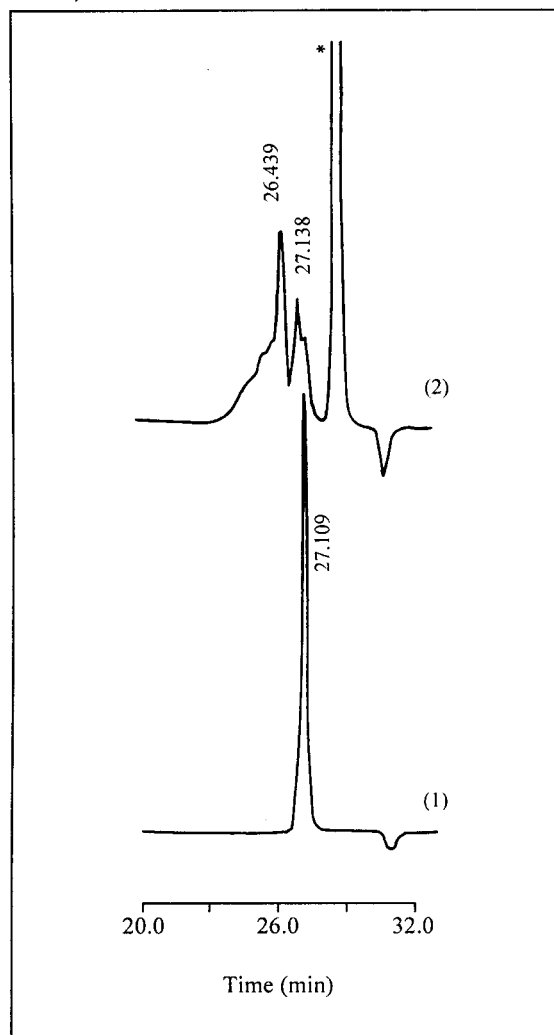


Figure 1. GPC Chromatogram of DPB (1) and of the oligomeric fraction (2). * electrolyte peak.

show the bands at 1609, 1584, 1531, 1320, 1202, 999, 888 and 820 cm^{-1} , which were assigned to the $\text{DPB}^{\cdot+}$.⁹ The similarity between these spectra may indicate a predominance of the radical dimer, $\text{DPB}^{\cdot+}$, in the PDPA (Ox) chain, or the non-dependence of the Raman frequencies on the chain length of the charge carriers. The features at 1390 and 1287 cm^{-1} observed in the spectrum of PDPA (Red) are characteristic of DPB^{2+} and $\text{DPB}^{\cdot+}$. Another indication that this polymer presents the diphenylamine and diphenyl diamine structures is the upwards shift of the band at 1618 cm^{-1} in the spectrum of PDPA (Red) in relation to the 1610 cm^{-1} observed in the dimer spectrum (not shown). This behavior has also been observed in the spectra of doped polyaniline by Furukawa *et al.*¹²

Figure 3 shows the *in situ* reflectance spectra of a platinum electrode in 10^{-1} M DPA + 10^{-1} M Et_4NBF_4 acetonitrile solution for different applied potentials. DPA is a colorless species, so during the first positive potential

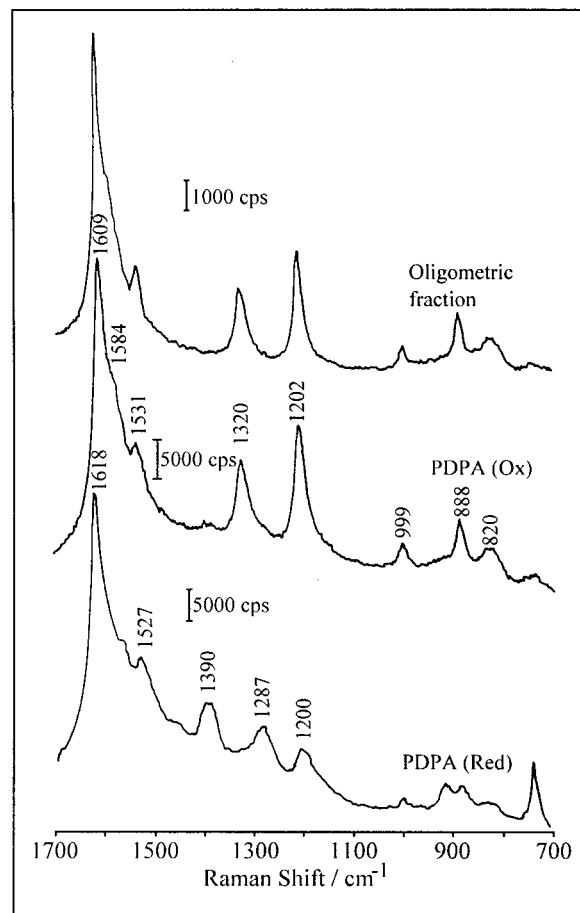


Figure 2. Raman Spectra of PDPA (Red), (Ox), and the oligomeric fraction.

sweep, only after the beginning of its oxidation near 0.85V, the absorption bands at 475, 588 and 1120 nm appear. The bands at 450-490 nm (2.75-2.53 eV) and 588 nm (2.11 eV) were assigned to the $\text{DPB}^{\cdot+}$ and DPB^{2+} , respectively.⁹ As can be seen in Fig. 3, the bands at 450-490 and at 1120 nm (1.10 eV) present the same behavior with the applied potential. Therefore, the 1120 nm band can be assigned to the $\text{DPB}^{\cdot+}$ species.

Figure 4 shows the *ex situ* reflectance spectra of PDPA (Ox) and PDPA (Red). The absorptions in the 1000-1400 nm (1.24-0.88 eV) region are characteristic of conducting polymers¹³. The strong increase of the background in this region in the spectrum of PDPA (Ox) in comparison with that of the PDPA (Red), is an indication of the higher conductivity of the former. The PDPA (Red) presents bands at 410 nm (3.02 eV), 490 nm (2.53 eV), and 660 nm (1.88 eV), while the bands at 430 nm (2.88 eV), 520 nm (2.38 eV), and 770 nm (1.61 eV) were observed in the PDPA (Ox) spectrum. Comparing the two spectra, it is possible to see that there is a systematic shift of the peaks in the PDPA (Ox) spectrum to higher wavelengths. This result suggests that the degree of doping of PDPA (Ox) is

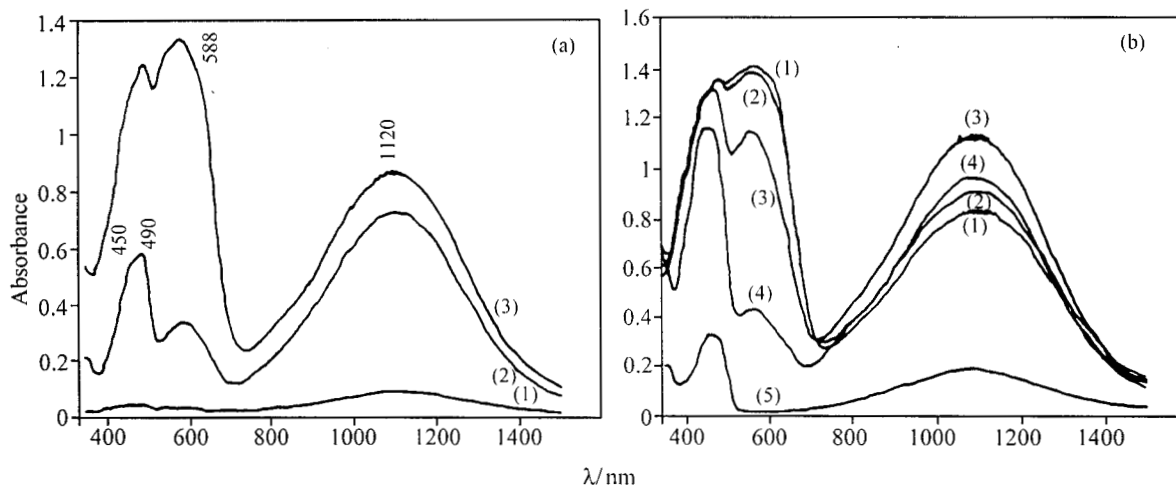


Figure 3. *In situ* reflectance spectra of a platinum electrode in DPA 10^{-1} M + 10^{-1} M Et₄NBF₄/acetonitrile during the process of: (a) oxidation, curves (1) 0.85 V, (2) 0.95 V and (3) 1.05 V, and (b) reduction, curves (1) 1.00 V, (2) 0.95 V, (3) 0.90 V, (4) 0.85 V, and (5) 0.00 V.

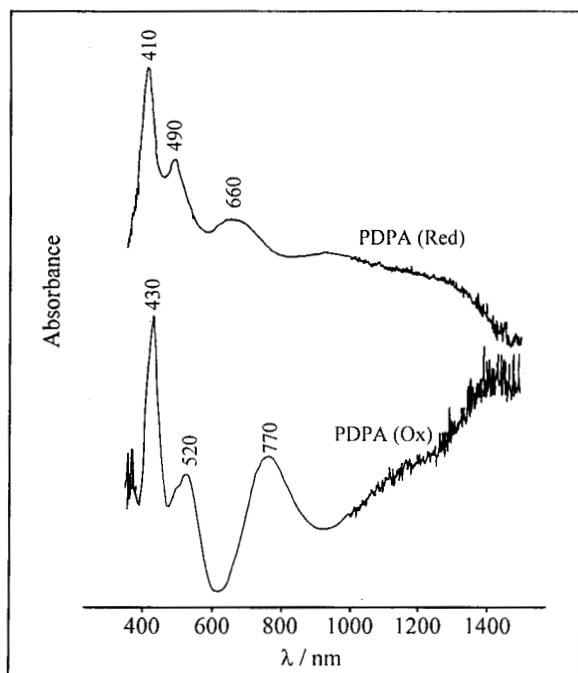


Figure 4. *Ex situ* reflectance spectra of PDPA (Ox) and (Red).

higher than that of PDPA (Red). As has been observed for polyaniline, the doping of emeraldine produces a shifting of the electronic bands to lower energy¹⁴. This is consistent with our results, therefore we can consider the structure PDPA-BF₄ the PDPA(Ox) similar to the emeraldine salt⁹. The measured conductivity of PDPA (Red) was *ca.* 10^{-6} Scm⁻¹, and that of PDPA (Ox) was in the order of 10^{-3} Scm⁻¹, which also confirms the higher conductivity nature of the latter.

Comparing the *in situ* reflectance spectrum at 1.05 V (Fig. 3a) with the *ex situ* spectrum of PDPA (Ox) (Fig. 4),

the well resolved absorption band at 1120 nm in the former collapsed to an absorption continuum in the latter, evidence of a higher degree of doping of PDPA (Ox) than of the film formed at 1.05 V.

Figure 5 shows the absorption spectra of the polymers and the dimer in the interband region. The band at 340 nm in the absorption spectrum of DPB shifts to 305 nm in the spectrum of the oligomeric fraction. This blue shift is smaller than that observed for PDPA (Ox) and (Red), which present peaks near 286 nm (4.33 eV). This shift is due to the presence of diphenosemiquinone and diphenoquinone rings in the backbone of the polymers¹⁵.

Figure 6 presents a simplified diagram of energy levels for PDPA (Ox) and PDPA (Red). They were built taking into account the transitions observed in the absorption (Fig. 5) and reflectance spectra (Fig. 4) of the polymers, together with their conductivity data. The presence of the unpaired electron and of a quantity of levels in the gap are necessary conditions for the conductivity in the polymer.

In order to prove the nature of the bonds in the oligomeric fraction, the FTIR spectra at different temperatures were obtained together with a DSC curve. The DSC curve of the oligomeric fraction in the temperature range of 20 to 120 °C, presented in Fig. 7, shows an endothermic peak at 52 °C, that is due to a thermal event without mass loss, as observed in the TG-DTG curves¹⁶. The infrared spectra obtained near this value, maintaining the temperature constant during spectrum acquisition, are shown in Fig. 8. The bands at 3400 and 3380 cm⁻¹ are assigned to νNH stretching. The difference in the frequencies of these bands are an indication that there are NH groups involved in hydrogen bonds of different strengths. This is based on the assignments of vibrational spectra of ¹⁵N-substituted and C-deuterated polyanilines¹². The band around 3386 cm⁻¹ in the reduced-alkali-treated polyaniline was assigned to the

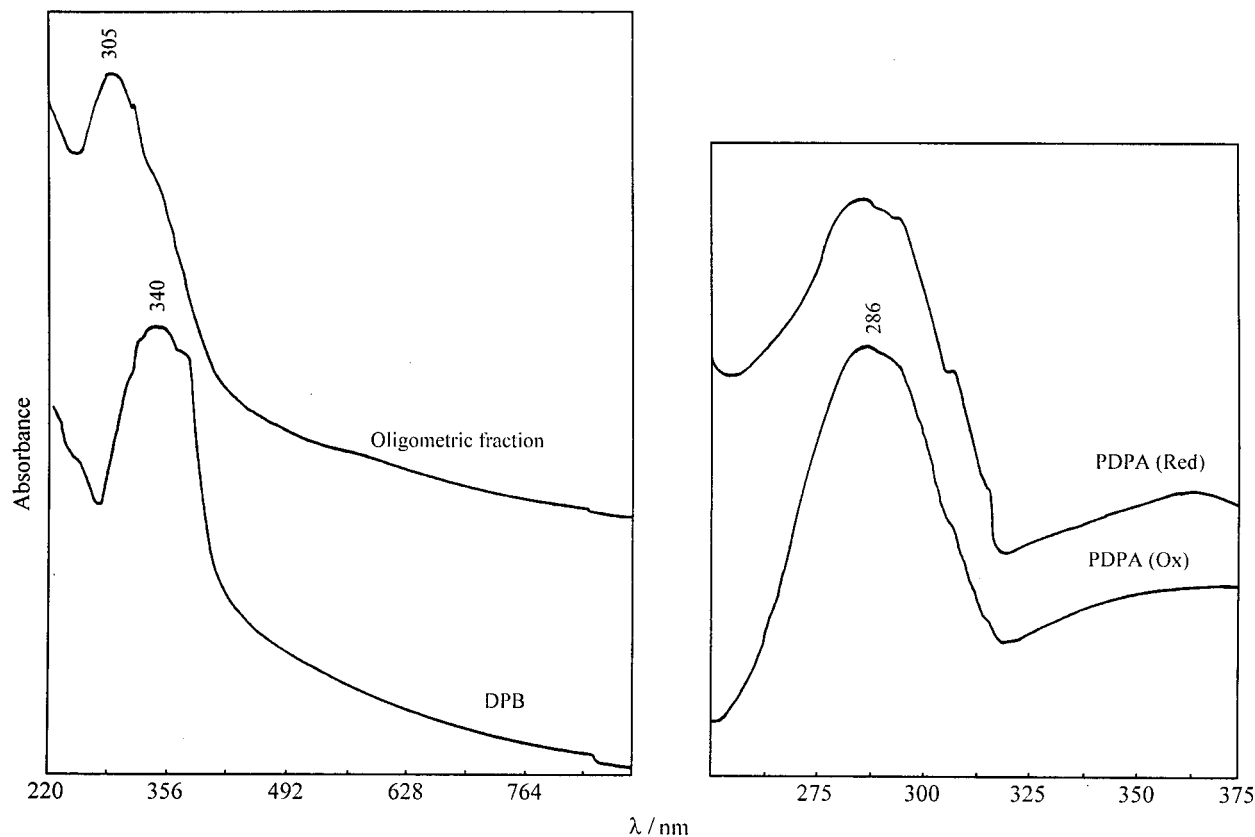


Figure 5. UV-vis absorption of DPB, the oligomeric fraction, PDPA (Ox) and (Red).

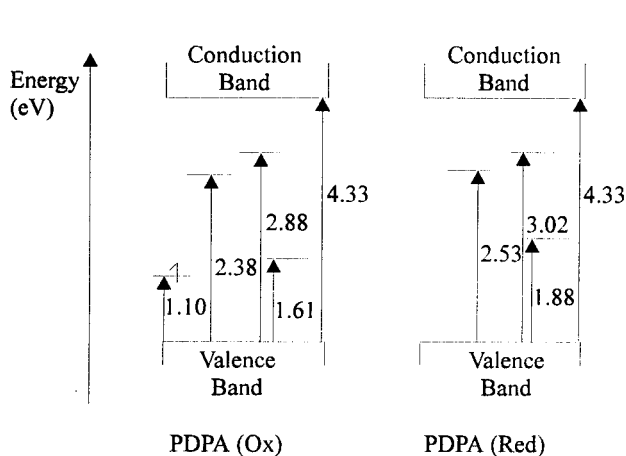


Figure 6. Diagrams of the energy levels of PDPA (Ox) and (Red).

ν NH stretching of the $-C_6H_4NHC_6H_4-$ involved in hydrogen bonding, and the bands in the $3380-3160\text{ cm}^{-1}$ range in doped polyaniline were assigned to the NH stretchings from the NH groups with much stronger hydrogen bonds than those giving rise to 3386 cm^{-1} . To analyze the change in the relative intensities of the NH bands with temperature, the CH stretching bands around 3040 cm^{-1} were taken as standard. When the material is heated to $50\text{ }^\circ\text{C}$ no spectral

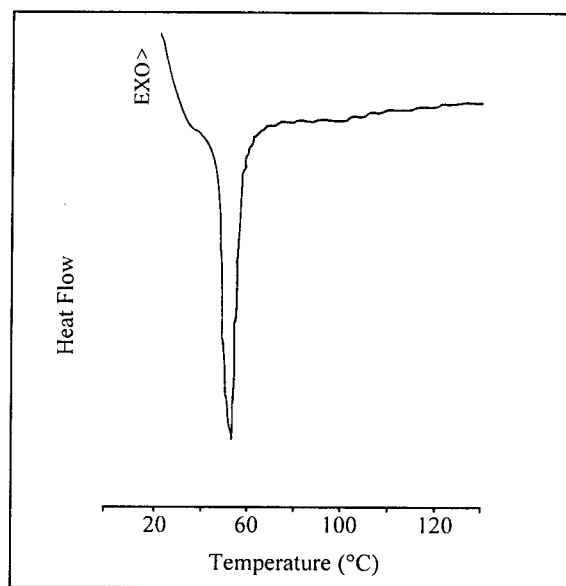


Figure 7. DSC curve of the oligomeric fraction.

change is observed. At $70\text{ }^\circ\text{C}$ the band at 3380 shifted to 3388 cm^{-1} , and the band at 1510 shifted to 1504 cm^{-1} . This last band can be assigned to the NH bending vibration¹⁷. The relative intensity, measured by the area under the bands, due to the NH stretching vibration decreases in the

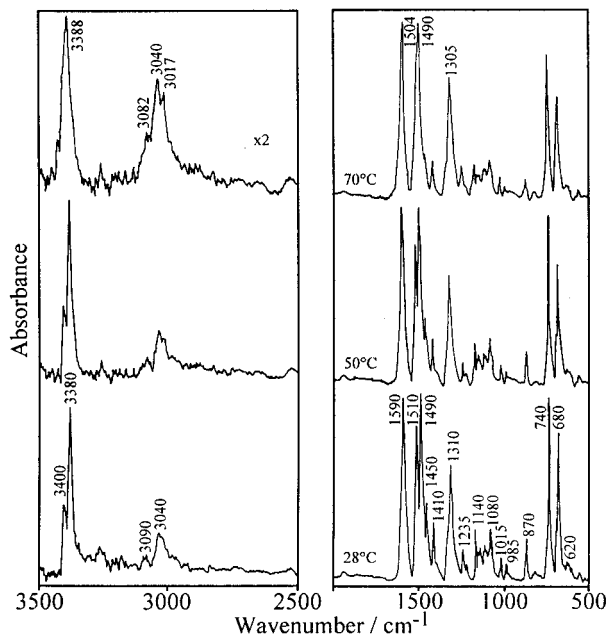


Figure 8. The FTIR spectra of the oligomeric fraction at different temperatures.

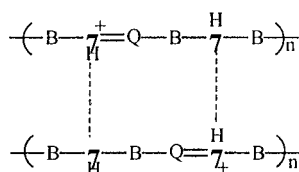


Figure 9. Model structure in the oligomeric fraction. B-Q are the diphenosemiquinone structures, and B indicates the phenyl rings.

spectrum at 70 °C. The shifts and the decrease in the intensities of the bands are consistent with the weakening of the hydrogen bond with the temperature. This behavior of the NH bands has been observed during the heating of nylon 66 by Garcia *et al.*¹⁸ These authors interpreted their data as resulting from the breaking of the interchain hydrogen bonds.

From our results it is possible to suggest a model to explain the interchain bonds in the oligomeric fraction, as shown in Fig. 9. The dependence of the frequencies on temperature corresponds to the NH stretching involved in the hydrogen bonds. Since the oligomeric fraction presents charged segments which play an important role in the property of conduction, it is possible that these charged species are stabilized by hydrogen bonding.

Acknowledgments

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