Macromolecules **2000,** *33,* 3077−3083

Influence of Thermal Treatment on Doped Polyaniline Studied by Resonance Raman Spectroscopy

J. E. Pereira da Silva, D. L. A. de Faria, S. I. Córdoba de Torresi, and M. L. A. Temperini*

Departamento de Química Fundamental, Instituto de Química, Universidade de São Paulo, C. P. 26077, 05513-970 São Paulo (SP), Brazil

Received May 21, 1999; Revised Manuscript Received December 6, 1999

ABSTRACT: Resonance Raman, ESR, and UV−vis−NIR techniques were used to characterize the secondary doping process in polyaniline (PANI). Experimental results obtained with the first two techniques showed the transformation of diamagnetic quinoid segments into radical semiquinone units while UV−vis−NIR experiments showed the increase of free carriers concentration due to extended conformation. Thermal effects on primarily and secondarily doped polyaniline were also studied by TGA, Raman, ESR, and UV−vis−NIR techniques. The appearance of new Raman bands with temperature was assigned to the formation of "phenazine-like" structures provoked by cross-linking. ESR and UV−vis−NIR experiments showed the absence of formation of addition radicalar structures due to thermal treatment in contrast to that observed after treatment with *m*-cresol.

Introduction

The additional increase in polyaniline (PANI) conductivity due to the interaction of a functionalized organic acid dopant with an appropriate solvent was first shown by Cao et al.[1] The authors associated the conductivity increase with a conformation change of the polymeric chain from a coil structure to a more extended one. The same phenomenon was also studied by Mac Diarmid et al.,[2] who introduced the term "secondary doping" to characterize the effect of some solvents on PANI, "primarily doped" by a functionalized organic acid. The highest conductivity was found in the system formed by PANI, camphorsulfonic acid (CSA), and *m*-cresol[2] which was also investigated by Ikkala et al.,[3,4] who postulated a very particular architecture between PANI/CSA/*m*-cresol, evidencing the formation of a supramolecular complex. Recent results[5] show that resonance Raman spectroscopy is a very useful tool which allows us to identify that, during the secondary doping process, there was also a conversion of quinoid segments into semiquinone ones. These results were corroborated by electron spin resonance (ESR) measurements.

It is well-known that temperature is a very important parameter in the processability of PANI, and thus, it is important to understand the effect of thermal treatment on the oxidation state and structure of PANI films. Structural studies of polyanilines[6] have shown that heating from room temperature to ca. 100 °C produces mainly the loss of solvent molecules, leading to changes in chain packing and stacking.

The aim of this paper is to study, from a vibrational point of view, changes induced by thermal treatment on PANI/CSA films and to compare these results with those obtained for secondarily doped samples.

Experimental Section

Polyaniline films doped with CSA were electrochemically grown by potential sweeps between −0.2 and +0.75 V at 0.05 V s^{-1} sweep rate onto a platinum electrode in an aqueous 0.5 M aniline + 1 M CSA electrolytic solution. A platinum wire was used as a counter electrode, and all potentials were referred to the saturated calomel electrode (SCE). This polymer film was grated from the electrode after drying; then, the powder obtained was dissolved in *m*-cresol or in $CHCl_3$ (1.1 mg mL^{-1}). The mixtures were treated in an ultrasonic bath until a substantial solubility was achieved as checked by the color and viscosity of the polymer solution (typically from 4 to 10 h). The resulting solution was then filtered in order to obtain a limpid solution from which films were prepared by the "dip coating" technique onto platinum or glass substrates. Mechanically stirred samples were also prepared which presented the same characteristics when compared to the sonicated ones.

Resonance Raman spectra for the 632.8 nm exciting radiation (He−Ne laser, Spectra Physics, model 127) were recorded in a Renishaw Raman imaging microscope (system 3000) containing an Olympus metallurgical microscope and a CCD detector. The laser beam was focused on the sample in a ca. 1 μm spot by a ×80 lens. Laser power was always kept below 0.7 mW at the sample, aiming to avoid its degradation.

The Raman spectra as a function of temperature were obtained with a controlled temperature cell at a heating rate of 10 °C min^{-1} from room temperature to 150 °C. A TMS 92 (Linkam Scientific Instruments) temperature control module was used.

Thermogravimetric analysis were performed in a Hi-Res TGA 2950 (T. A. Inst.), using platinum crucibles with ca. 2 mg of the sample, under a nitrogen atmosphere and a heating rate of 20 °C min^{-1}.

ESR spectra were recorded from powders on a Bruker ER 200 spectrometer operating in the X-band (~9.5 GHz). Samples were extensively pumped prior to investigation in order to eliminate *m*-cresol (secondarily doped samples) and water (primarily doped samples).

UV−vis−NIR spectra were obtained in a Guided Wave (model 260) spectrophotometer using a tungsten−halogen lamp and a Si−Ge detector. Electronic spectra as a function of temperature were obtained using the same cell utilized in the Raman experiments.

Results and Discussion

In a previous paper the secondary doping process of polyaniline was studied using resonance Raman spectroscopy, and the obtained results led to the conclusion

---

* To whom correspondence should be addressed. E-mail mlatempe@quim.iq.usp.br.

10.1021/ma990801q CCC: $19.00

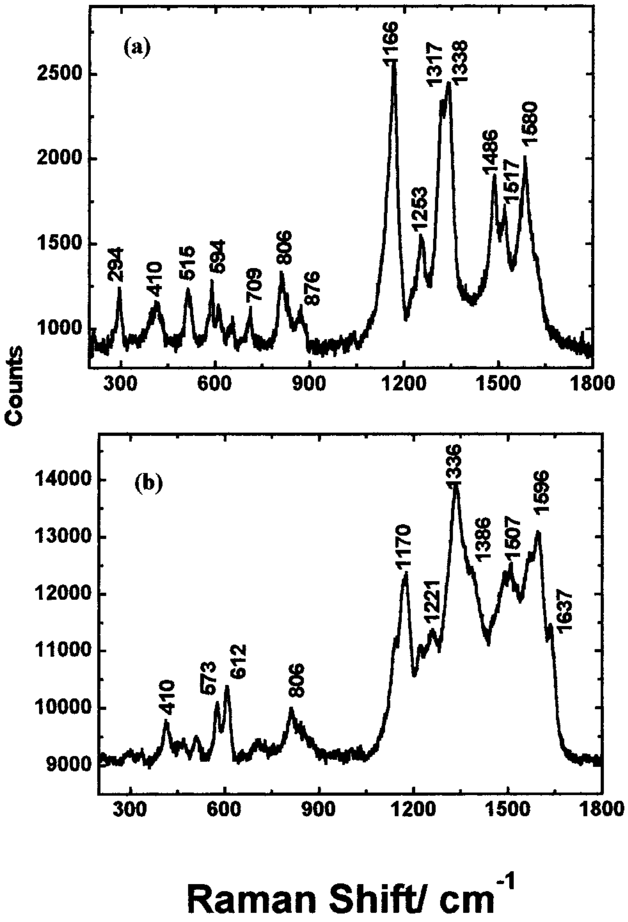

Figure 1. Resonance Raman spectra of polymer powders: (a) primarily doped PANI/CSA and (b) secondarily doped PANI/CSA/*m*-cresol. $\lambda_0 = 632.8$ nm. Baseline corrected.

that the secondary doping induces not only conformational change in the polymeric chains but also a transformation of quinoid units into semiquinone ones.[5]

Figure 1 shows the Raman spectra of PANI/CSA primarily and secondarily doped, obtained with the 632.8 nm excitation line. As can be observed, the relative intensity of the band at 1486 cm^{-1}, assigned to the C=N stretching of the quinoid diimine units, diminishes when the PANI/CSA sample is treated with *m*-cresol (Figure 1b). The same behavior is observed for the 1580 cm^{-1} band assigned to the C=C stretching of the quinoid ring. The bands at 1596 cm^{-1} (ν(C−C) benzenoid units) and 1221 cm^{-1} (ν(C−N) benzenediamine units) only appear in the spectrum of PANI/CSA treated with *m*-cresol (Figure 1b). Comparing parts a and b of Figure 1, it can be noticed a small shift of the 1166 cm^{-1} band to 1170 cm^{-1}, the former being assigned to the C−H bending of the quinoid rings while the latter is attributed to the same mode in the benzoid segments.[7] All these changes are consistent with the transformation of quinoid units into benzenoid ones.

Regarding the characteristic bands of the radical cation at 1317 and 1338 cm^{-1} (C−N$^{\bullet+}$ stretching) in the spectrum of primarily doped PANI/CSA (Figure 1a), they coalesce in a large band centered at 1336 cm^{-1} and a shoulder appears at 1386 cm^{-1}, after the treatment with *m*-cresol (Figure 1b). The latter band was already observed as one of the most intense bands in the resonance Raman spectrum excited with the 1047 nm line, which is close to the electronic absorption of free charge carriers in the metallic form of polyaniline and was assigned to extended polarons.[8] To confirm this assignment, the 1064 nm line of a Nd:YAG laser was used to excite the FT-Raman spectra of the sample (spectrum not shown), and despite the low signal/noise ratio, the intensity of the 1386 cm^{-1} band was the same for both primarily and secondarily doped samples. Laska et al. observed an intense band at 1376 cm^{-1} in the FT-Raman spectrum of nonprotonated polyemeraldine,[9] thus reinforcing our hypothesis that such a band cannot be associated with free charge carriers as stated before.[8] The assignment of the 1386 cm^{-1} peak will be discussed later.

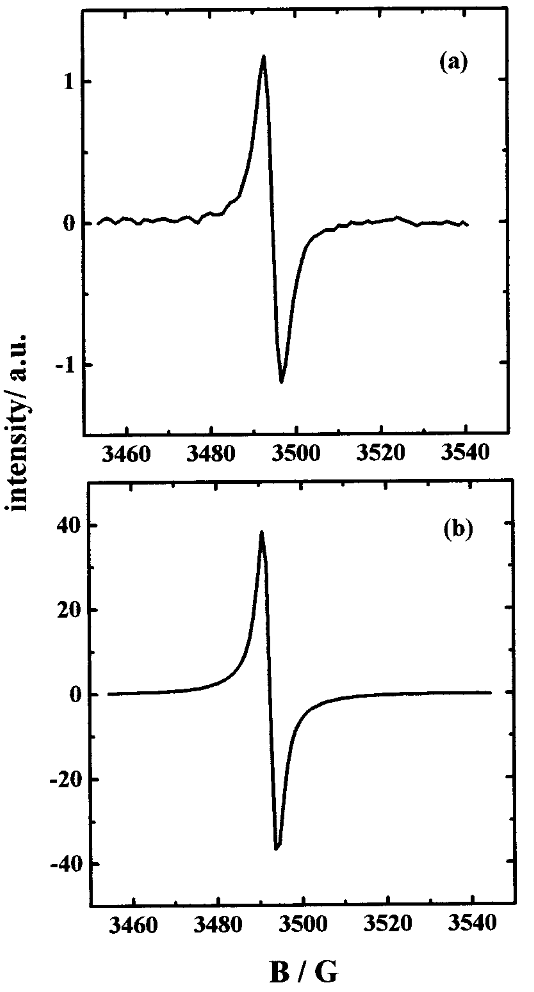

Figure 2. ESR spectra of polymer powders: (a) primarily doped PANI/CSA and (b) secondarily doped PANI/CSA/*m*-cresol.

Considering these Raman results, the samples were analyzed using the electron spin resonance (ESR) technique in order to confirm whether the concentration of free radicals increased with the *m*-cresol treatment.

Figure 2 shows the ESR spectra of PANI/CSA powders obtained after solvent evaporation from the solutions prepared in $CHCl_3$ (Figure 2a) and in *m*-cresol (Figure 2b). The integrated area in the primarily doped PANI/CSA spectrum is 25 times smaller than that corresponding to the secondarily doped sample, indicating an increase in the spin concentration after the treatment with *m*-cresol. These results are consistent with the resonance Raman data which show a conversion of quinoid segments to semiquinone radical cation units.

On the other hand, it was already reported in the literature[6] that thermal treatment of PANI-doped pow-

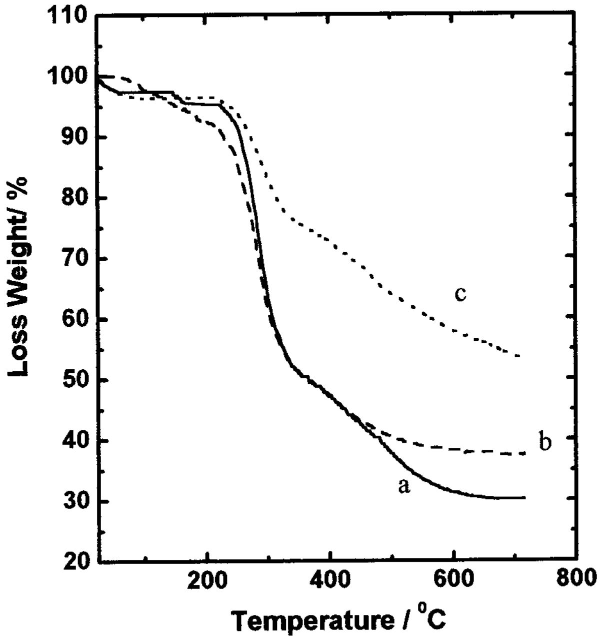

Figure 3. TGA curves of (a) primarily doped PANI/CSA, (b) secondarily doped PANI/CSA/*m*-cresol, and (c) primarily doped PANI/CSA preheated at 150 °C.

ders induces structural and conformational changes when low temperatures (ca. 100 °C) are used. These changes were attributed to the release of water molecules, and in this case, a change in the chain package of the polymer lattice would be expected which could affect the interaction between chain and counterions. With this idea in mind, Raman spectra at different temperatures were recorded for both PANI/CSA primarily and secondarily doped powders.

At this point, it is important to ensure that the samples are not affected by a temperature-induced dedoping process. In Figure 3 TGA curves of primarily and secondarily doped PANI and of preheated primarily doped PANI/CSA are shown. From room temperature to 50 °C there is no weight loss while in the 50−150 °C range the weight loss was only ca. 5%. This loss can be attributed to water release from the polymeric matrix, and since this value is low, it cannot be assigned to dedoping.[10] It can also be inferred that, until a temperature of ca. 200 °C, no polymer decomposition leading to a significant loss of mass was observed.

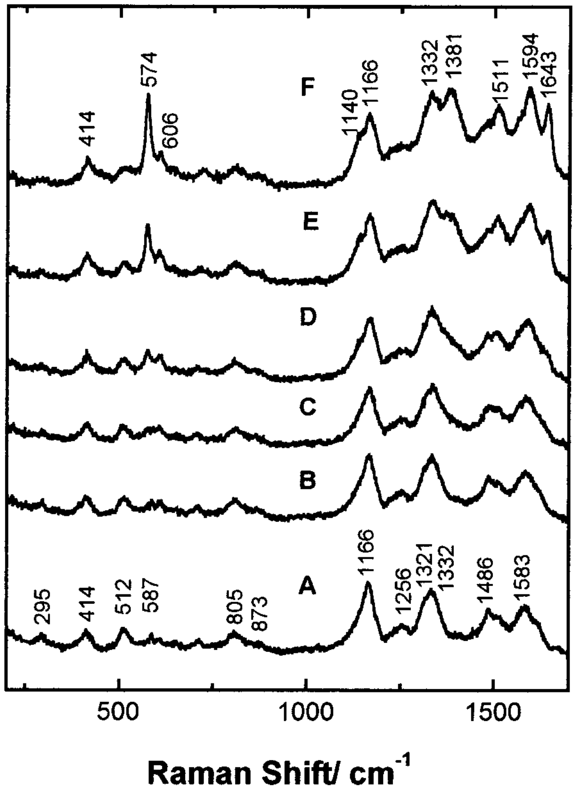

Figure 4. In situ resonance Raman spectra of primarily doped PANI/CSA as a function of temperature: (A) 25, (B) 50, (C) 75, (D) 100, (E) 125, and (F) 150 °C.

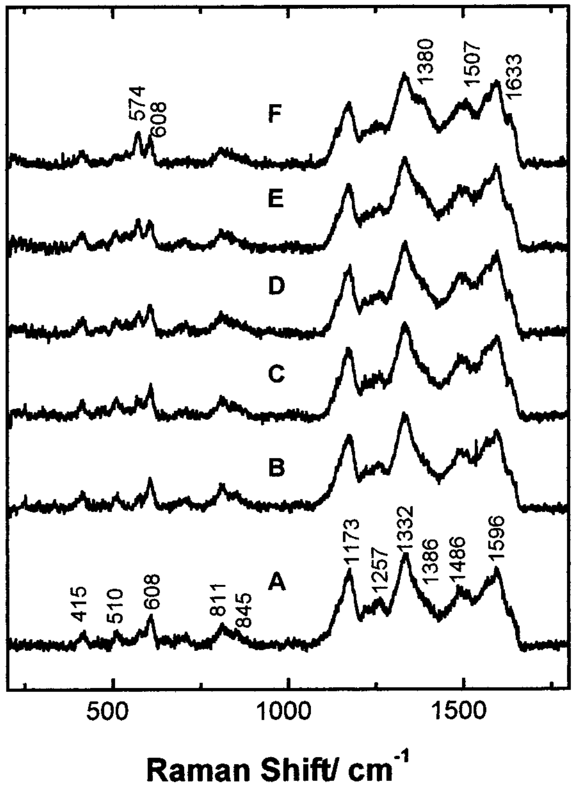

Figure 5. In situ resonance Raman spectra of secondarily doped PANI/CSA/*m*-cresol as a function of temperature: (A) 25, (B) 50, (C) 75, (D) 100, (E) 125, and (F) 150 °C.

Considering the thermogravimetric data, Raman spectra were obtained from room temperature to 150 °C. Figures 4 and 5 show the Raman spectra obtained from the primarily and secondarily doped polymers, respectively. Analysis of Figure 4 shows that the PANI/CSA powder suffers significant changes during heating. At room temperature the bands located at 574, 1381, and 1643 cm^{-1} are not observed, but they start to grow at 100 °C and become the most intense bands in the spectrum at 150 °C. Together with the appearance of these bands, it can be observed a decrease in the relative intensity of the band located at 1486 cm^{-1}. As already pointed out, this band is assigned to the C=N stretching of the quinoid units. Another evidence for a reduction in the concentration of the quinoid units with the temperature is the decrease in intensity of the 1583 cm^{-1} band (ν(C=C) of quinoid ring) and the enhancement of the 1594 cm^{-1} band (ν(C−C) benzenoid units). It is important to point out that bands at 574, 1381, and 1643 cm^{-1} were already observed with low intensities in the spectrum of secondarily doped PANI (Figure 1); the assignment of these bands will be discussed later.

Figure 5 shows the same set of Raman spectra for secondarily doped PANI/CSA powder. In this case, the

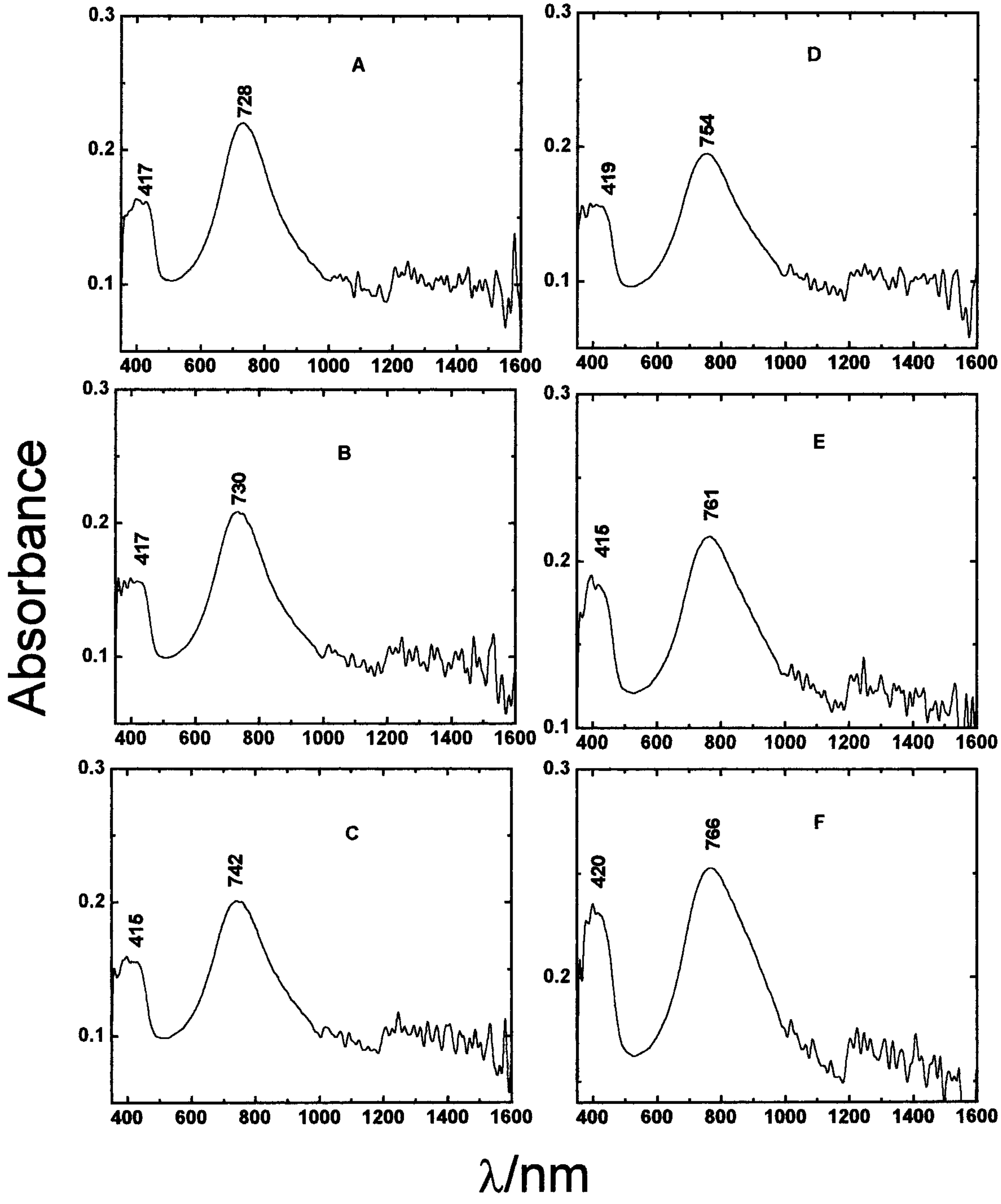

Figure 6. In situ UV−vis−NIR spectra of primarily doped PANI/CSA as a function of temperature: (A) 25, (B) 50, (C) 75, (D) 100, (E) 125, and (F) 150 °C.

effect of temperature on the Raman spectra is much smaller than for PANI primarily doped. The spectrum obtained at room temperature shows the characteristic features, already described, of secondarily doped PANI. When heated, this polymer presents neither the increase in relative intensity of the 1386 cm^{-1} band nor the change in relative intensity of the 1486 cm^{-1} band. Thus, these results show that the polymer treated with *m*-cresol presents a greater thermal stability than the primarily doped polymer.

At this point, it is important to discuss the origin of the bands at 574, 1381, and 1643 cm^{-1} which appear when the polymer is heated. To confirm whether the temperature causes a conformational change producing delocalized polarons, in situ UV−vis−NIR electronic spectra as a function of temperature were performed and are shown in Figures 6 and 7. As can be seen, in primarily doped PANI/CSA (Figure 6), thermal treatment does produce neither the increase in the absorption in the near-infrared region nor the disappearance of the band at ca. 750 nm (localized polarons) which only shifts slightly to lower energies with temperature, indicating that temperature is not inducing the formation of free charge carriers as demonstrated by the absence of an absorption tail in the NIR spectrum.

In the case of secondarily doped polymer (Figure 7), the NIR absorption tail is observed in all the temperature range despite a small decrease in its intensity, and a shoulder at 861 nm shifts to 943 nm. These results unambiguously show that the thermal treatment does not produce the same conformational changes as the treatment with *m*-cresol. Hence, the enhancement in the

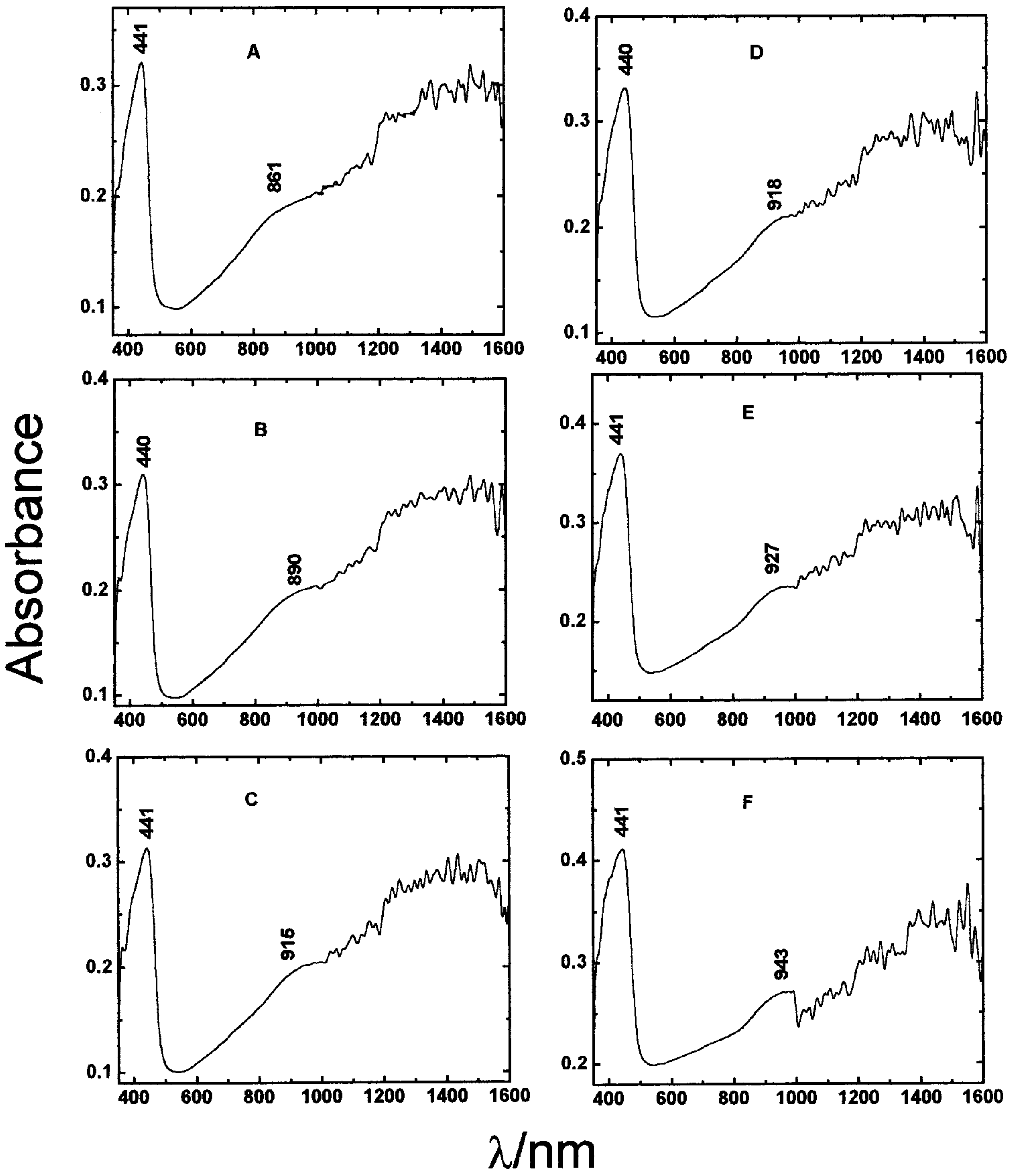

Figure 7. In situ UV–vis–NIR spectra of secondarily doped PANI/CSA/*m*-cresol as a function of temperature: (A) 25, (B) 50, (C) 75, (D) 100, (E) 125, and (F) 150 °C.

intensity of the vibrational bands observed with temperature is not due to the formation of delocalized polarons, and the band located at 1386 cm^{-1} cannot be assigned to these structures.

It was already reported by other authors[11–13] that temperature produces cross-linked polymers leading to the formation of other structures than radical ones, such as ternary cyclized nitrogen producing “phenazine-like” segments. Rodrigue et al.[13] have shown from XPS experiments that thermally treated protonated forms of PANI films originated cyclized nitrogen species especially detrimental to imine segments, with this cyclization reaching a maximum in the case of sulfonate-doped PANIs. This fact is consistent with our Raman results which show that there is a diminution in the relative intensity of bands corresponding to quinoid segments (1486 and 1583 cm^{-1}).

The appearance of the bands at 574, 1381, and 1643 cm^{-1} in the Raman spectra at high temperatures could thus be related to the vibrational modes of cyclized structures containing tertiary nitrogens formed by cross-linking. It is frequently observed a strong band at ~580 cm^{-1} in the Raman spectra of phenazine[14] and oxazine-type dyes.[15] In our case, another evidence for the formation of a cross-linked polymer comes from the TGA curves shown in Figure 3. As can be seen, the amount of residue obtained in the case of preheated PANI/CSA (curve c) is greater than for primarily and secondarily doped samples, showing that the polymer is more reticulated.[16]

To confirm the formation of cross-linking in the polymeric matrix during the thermal treatment, Fen-

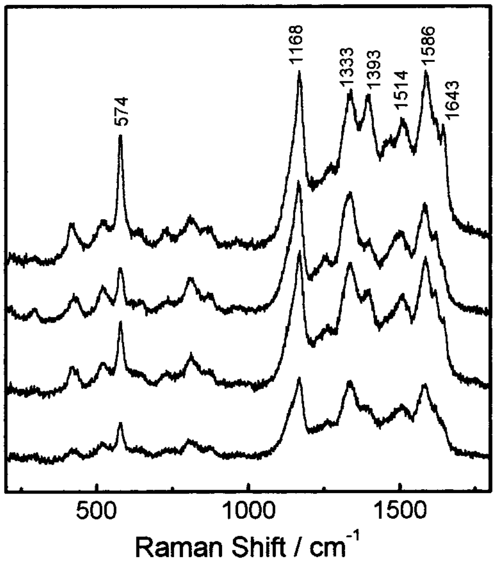

Figure 8. Resonance Raman spectra at different points of a primarily doped PANI/CSA sample treated with the Fenton's reagent.

ton's reagent[17] was used to provoke reticulation in the primarily doped PANI/CSA sample.[18] Figure 8 shows Raman spectra obtained at different points of a sample treated with Fenton's reagent. As can be seen, the spectra show the appearance of the same bands observed in thermally treated samples. It has to be pointed out that the relative intensities of these bands are different depending on the region of the sample. This fact shows that there are different degrees of reticulation in the polymer, and this experiment allows us to unambiguously assign these bands to the formation of cyclized "phenazine-like" structures.

Another aspect which has to be considered is that the increase in temperature may cause a redox process to occur due to reaction with oxygen. Li et al.[19] used XPS to investigate the effect of temperature on PANI with different oxidation states (leucoemeraldine, emeraldine, and nigraniline) and reported the respective [=N−]/[−NH−] ratios. The authors have found that for fully reduced leucoemeraldine this ratio increases almost linearly with temperature while the emeraldine (50% oxidized) polymer is more stable, and its [=N−]/[−NH−] ratio does not vary significantly with temperature. On the other hand, the [=N−]/[−NH−] ratio for nigraniline (75% oxidized) polymer decreases sharply with temperature, especially from room temperature to ca. 200 °C, unambiguously indicating a conversion of imine/amine segments. In the case of emeraldine base, they concluded that imine segments are proner to react with oxygen than the amine ones and, in fact, detected the formation of −OH and C=O groups with IR spectroscopy.

Figure 9 shows the ESR spectra performed with primarily doped PANI/CSA as a function of temperature (heating made ex situ). Integration of the ESR signal demonstrated that there is a decrease in the amount of spins with temperature, and since the thermal treatment was performed in air, oxygen could react with the paramagnetic centers in polyaniline. It is thus very likely that, besides cross-linking, a degradation of PANI is occurring as a consequence of heating, and preliminary results obtained from vibrational spectroscopy confirms such an assumption. At the moment, it is not possible to determine the relative contributions from reticulation and oxidation, but this point is currently under investigation.

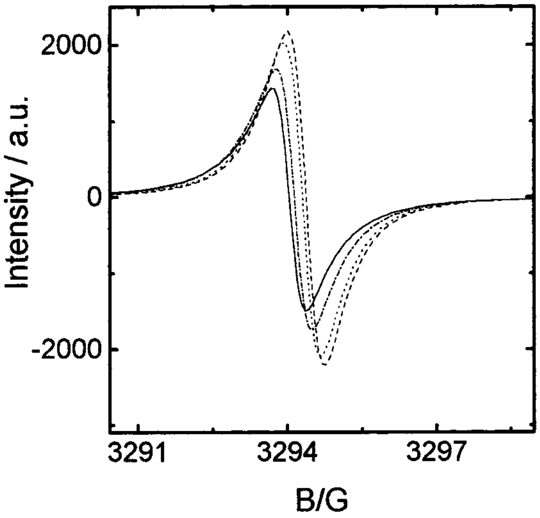

Figure 9. In situ ESR spectra as a function of temperature of primarily doped PANI/CSA powder: (- - -) 25, (· · ·) 50, (- · -) 75, and (—) 100 °C.

Conclusions

In this work, it was shown that resonance Raman spectroscopy is a very useful tool to characterize the secondary doping process in polyaniline, indicating that, in addition to conformational changes of the polymeric chains, there is also a chemical modification such as the conversion of quinoid units into semiquinoids ones. These results were confirmed by ESR measurements which have shown that the amount of spins is 25 times greater in the secondarily doped sample than in the primarily doped one.

In the case of thermally treated polyanilines, Raman results show the appearance of new bands probably related to cyclized "phenazine-like" structures due to cross-linking. A higher degree of reticulation in preheated polyanilines was confirmed by TGA results which have shown a lower weight loss than the observed for primarily and secondarily doped samples. Nevertheless, reaction with oxygen during heating is also occurring, but its relative contribution to the observed spectral changes was not quantified.

Considering the Raman spectra at high temperatures for secondarily doped PANI/CSA samples, where the bands at 574, 1381, and 1643 cm^{-1} have low relative intensities, two explanations can be considered:on one hand, because of its more extended conformation, there are less imine groups in the polymer backbone to be converted in tertiary nitrogens, and on the other hand, the lubricating effect of the primary/secondary dopants pair shields each chain, avoiding the formation of cyclized structures.

Acknowledgment. Authors thank Brazilian Research Agencies CAPES, FAPESP, and CNPq for financial support.J.E.P.S. thanks CNPq for the scholarship granted. Authors are also indebted to Profs. O. Augusto, A. M. C. Ferreira, Y. Kawano, and H. Toma (IQ/USP) for ESR, TG, and UV−vis−NIR facilities.

References and Notes

(1) Cao, Y.; Smith, P.; Heeger, A. J. *Synth. Met.* **1992**, *48*, 91−97.

(2) MacDiarmid, A. G.; Epstein, A. J. *Synth. Met.* **1994**, *65*, 103−116.
(3) Ikkala, O. T.; Pietilä, L. O.; Ahjopalo, L.; Österholm, H.; Passiniemi, P. J. *J. Chem. Phys.* **1995**, *103*, 9855−9863.
(4) Ikkala, O. T.; Pietilä, L. O.; Passiniemi, P. J.; Vikki, T.; Österholm, H.; Ahjopaloc, L.; Österholm, J. E. *Synth. Met.* **1997**, *84*, 55−58.
(5) Pereira da Silva, J. E.; Temperini, M. L. A.; Córdoba de Torresi, S. I. *Electrochim. Acta* **1999**, *44*, 1887−1891.
(6) Boyle, A.; Penneau, J. F.; Geniès, E.; Riekel, C. *J. Polym. Sci. B* **1992**, *30*, 265−274.
(7) Louarn, G.; Lapskowski, M.; Quillard, S.; Pron, A.; Buisson, J. P.; Lefrant, S. *J. Phys. Chem.* **1996**, *100*, 6998−7006.
(8) Engert, C.; Umapathy, S.; Kiefer, W.; Hamaguchi, H. *Chem. Phys. Lett.* **1994**, *218*, 87−92.
(9) Laska, J.; Girault, R.; Quillard, S.; Louarn, G.; Pron, A.; Lefrant, S. *Synth. Met.* **1995**, *75*, 69−74.
(10) Rannou, P.; Nechtschein, M. *Synth. Met.* **1997**, *84*, 755−756.
(11) Geniés, E. M.; Lapkowski, M.; Penneau, J. F. *J. Electroanal. Chem.* **1989**, *249*, 97−107.
(12) Scherr, E. M.; MacDiarmid, A. G.; Manohar, S. K.; Masters, J. G.; Sun, Y.; Tang, X.; Druy, M. A.; Glatkowski, P. J.; Cajipe, V. B.; Fischer, J. E.; Cromack, K. R.; Jozefowicz, M. E.; Ginder, J. M.; McCall, R. P.; Epstein, A. J. *Synth. Met.* **1991**, *41−43*, 735−738.
(13) Rodrigue, D.; Riga, J.; Verbist, J. J. *J. Chim. Phys.* **1992**, *89*, 1209−1214.
(14) Takahashi, M.; Goto, M.; Ito, M. *J. Electroanal. Chem.* **1989**, *51*, 177−188.
(15) Widera, J.; Grochala, W.; Jackowska, K.; Bukowska, J. *Synth. Met.* **1997**, *89*, 29−37.
(16) Wang, X. H.; Geng, Y. H.; Wang, L. X.; Jing, X. B.; Wang, F. S. *Synth. Met.* **1995**, *69*, 263−264.
(17) Halliwell, B.; Gutteridge, J. M. C. In *Free Radicals in Biology and Medicine*, 2nd ed.; Oxford University Press: New York, 1989.
(18) Ravve, A. In *Principles of Polymer Chemistry*; Plenum Press: New York, 1995; p 438.
(19) Li, Z. F.; Kang, E. T.; Neoh, K. G.; Tan, K. L. *Synth. Met.* **1997**, *87*, 45−52.

MA990801Q