X-Ray Photoelectron Spectroscopy and Electrical Conductivity of Polyaniline Doped With Dodecylbenzenesulfonic Acid as a Function of the Synthetic Method

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ABSTRACT: X-ray photoelectron spectroscopy (XPS) has been employed to investigate the protonation degree of polyaniline doped with dodecylbenzenesulfonic acid (Pani.DBSA) obtained by different synthetic methods. The protonation degree has been compared to electrical conductivity. Pani.DBSA prepared through the redoping process in an agate mortar displays conductivity values within the range of 1 S/cm. A protonation level of 48% with almost all imine groups being protonated. Pani.DBSA was also synthesized by oxidative polymerization of aniline in the presence of DBSA, which acts simultaneously as a surfactant and as protonating agent. This in situ doping polymerization was carried out in aqueous or toluene media. In both cases, protonation degrees higher than 50% have been achieved, indicating that a substantial portion of amine units have also been protonated. Higher doping degree has been achieved by aqueous dispersion polymerization of aniline. The C/N and S/N molar ratios obtained by XPS analysis indicate that the polyaniline chains obtained by in situ polymerization are protonated by both sulfonate and hydrogen sulfate anions. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 556–565, 2001

Key words: polyaniline; dodecylbenzenesulfonic acid (DBSA); in situ doping polymerization; X-ray photoelectron spectroscopy

INTRODUCTION

The increasing demand for electrical conducting polymeric materials with good processing proper-

ties has encouraged several research groups in developing systems constituted by conducting polymer particles dispersed in a thermoplastic matrix. Among several intrinsically conducting polymers, polyaniline is one of the most promising candidates because of its straightforward polymerization and good environmental and thermal stability, as well as its electrical properties, which can be reversibly controlled by changing the oxidation state and by protonation of the imine nitrogen groups.[1,2] In spite of these interesting characteristics, its use in polymer blends has

been hampered because of its intractable nature, especially in the doped form. Significant progress in this field has been possible, however, with the use of functionalized protonic acids as the doping agent for polyaniline.[3] According to Cao et al.,[3] polyaniline doped with dodecylbenzenesulfonic acid (DBSA) could be soluble in various organic solvents. The solubility is significant only in the presence of an excess of DBSA.[4] The functionalized counteranion acts as a surfactant and induce some compatibility with polymer matrices with similar molecular structures.

Pani.DBSA complex (Pani doped with DBSA) can be doped in several ways. The first and more studied method consists of redoping the Pani emeraldine base (undoped and nonconducting form of Pani) with DBSA. This process can be performed by suspending the Pani base as a fine powder in an appropriate acid solution under stirring,[5,6] or by mechanically blending both Pani powder and DBSA in an agate mortar.[7–9] Redoping by mechanical blending in the absence of solvents can also be carried out in an internal mixer at elevated temperature by a process known as thermal doping.[10,11] The doping level and conductivity increase with the temperature because the ability of DBSA to penetrate the Pani domains is increased as a consequence of the enhanced thermal mobility of DBSA.[5] This phenomenon also results in an increased orderliness of DBSA chains.

In addition to a redoping process, Pani.DBSA can also be prepared by a method known as in situ doping polymerization. In this process, aniline is polymerized directly in the presence of DBSA as the protonating agent. The polymerization can be carried out in aqueous medium, giving rise to a colloidal Pani dispersion[12] or in an emulsion medium consisting of a small amount of water and a nonpolar or weakly polar organic solvent.[13] In both systems, DBSA acts simultaneously as a surfactant and as a protonating agent for the resulting Pani. According to Ö and coworkers,[13] the molecular weight of the emulsion polymerized aniline is significantly higher than that of Pani polymerized in aqueous solution. The conductivity was found to be within the range of 0.1–5.0 S/cm, and a fibrillar morphology was achieved.

Another interesting way to produce Pani.DBSA directly is by the chemical oxidative polymerization of dodecylbenzenesulfonic acid aniline salt.[14] In this procedure, the salt was isolated and submitted to a suspension polymerization in chloroform with a small amount of water. The resulted

Pani.DBSA presented conductivity values of ~1 S/cm.[14] The anilinium-DBSA salt has been also polymerized in aqueous medium giving rise to Pani.DBSA with conductivity value of 0.7 S/cm after 270 min of reaction at 0°C.[15]

Several reports concerning the synthesis of Pani.DBSA did not emphasize the differences in protonation degree achieved using different synthetic methods. In this article, we compare the protonation degree and electrical conductivity of Pani.DBSA as a function of the synthetic method. The doping degree was determined by X-ray photoelectron spectroscopy (XPS) technique, which is considered more reliable than other methods based on elemental or gravimetric analysis. Through XPS analysis, the various intrinsic redox states of Pani, as well the different neutral and positive nitrogen species, can be quantified. Thus, one can distinguish, for example, whether the acidic doping agent is present in the sample as molecular or ionic species. The present article also considers the changes in electrical conductivity and doping degree, using different precipitating and washing media to isolate and purify Pani. DBSA.

EXPERIMENTAL

Materials

Aniline (analytical grade, Merck) was distilled twice under vacuum and stored under nitrogen in a refrigerator. Ammonium peroxydisulfate (APS) (analytical grade, Merck), chloridric acid (analytical grade, Merck) and dodecylbenzenesulfonic acid (DBSA) (technical grade, Pro-Química do Brazil) were used without purification.

Synthesis of Pani.DBSA

Method I: Redoping of Emeraldine Base

Polyaniline doped with HCl (Pani.HCl) was prepared by chemical oxidative polymerization of aniline in aqueous acidic medium (1M HCl) with APS as an oxidant, according to the procedure reported by MacDiarmid et al.[16] The reaction was carried out at 0°C for 3 h. Deprotonation of Pani.HCl was performed by stirring the Pani salt as a powder in a 0.1M aqueous solution of ammonium hydroxide for 24 h at room temperature, thus obtaining the emeraldine base (EB), which was washed several times with water and dried under vacuum for 48 h at room temperature. The redop-

ing of EB with DBSA was performed by mixing EB powder with DBSA (EB/DBSA = 1:3 by weight) and then grinding in an agate mortar, according to procedure adapted from the literature.[7] The Pani.DBSA was obtained as a green pastelike material. In order to remove the excess of DBSA, this mixture was stirred in deionized water for 24 h, filtered, washed with water, and dried, to obtain a fine green powder. The polymer yield was determined by relating the amount of aniline monomer used in the preparation of the Pani.HCl with the amount of the emeraldine base obtained after treatment of Pani.HCl with ammonium hydroxide.

Method II: In Situ Aqueous Dispersion Polymerization of Aniline

The aqueous Pani.DBSA dispersion was prepared according to the Gospodinova's procedure,[12] by mixing 0.01 mol of aniline (Ani) in a solution of 0.01 mol of APS in 5 mL deionized water. Then, 100 mL of an aqueous solution $0.1M$ of DBSA was added into the stirred solution of Ani/APS. The polymerization was carried out at 10°C for 4 h. After the reaction, the dispersion was poured into acetone or methanol, and the dark green powder was washed with methanol and dried under vacuum for 48h at room temperature.

Method III: Emulsion Polymerization of Aniline

The emulsion polymerization of aniline was performed by adapting a procedure described in literature.[13] In a typical polymerization, 24.5 g (0.075 mol) of DBSA and 4.7 mL (0.051 mol) of aniline was dissolved in 250 mL of toluene under stirring. The medium was kept at 0°C, and an aqueous solution containing 4.68g (0.021 mol) of APS in 20 mL of water was added over a period of 10 min in order to avoid heating of the reaction mixture. The total polymerization time was 6 h. The polymerization was terminated by pouring the emulsion into methanol or acetone. The precipitate as a dark green powder was filtered, washed with acetone or methanol, and dried under vacuum at room temperature.

To determine the yield of Pani.DBSA prepared by the in situ polymerization (methods II and III), the samples were first submitted to a dedoping process with ammonium hydroxide. The amount of aniline monomer used in the preparation of these samples were related to the amount of the emeraldine base obtained after the dedoping process.

Characterization

Electrical conductivities of the Pani.DBSA samples were measured using a Keithley 614 electrometer and the usual four-probe method. Specimens of 0.5-mm thickness were obtained by compression molding the pastelike material or the powder at room temperature at a pressure of 1MPa.

The morphology was studied on a Jeol JSM-5300 scanning electron microscope (SEM), using powder samples covered with a thin layer of gold. UV/vis spectra were recorded by using a Varian Cary-3E spectrometer. The spectra ranged from 300 to 900 nm. The samples were dissolved in chloroform. XPS analysis were performed on a Kratos Analytical Instrument XSAM-800 dual-chamber spectrometer equipped with a hemispherical electron energy analyzer and a quad-anode X-ray source. The analyzer was operated in a fixed retardation ratio (FRR) mode The energy scale calibration and the conditions of operation were previously described.[17] To compensate the surface charging effects, all binding energies were referenced to the C1s neutral carbon peak at 284.6eV. In peak synthesis, the linewidth of the gaussian peaks was maintained constant for all components in a particular spectrum.

RESULTS AND DISCUSSION

Electrical Conductivity

Table I summarizes the results of electrical conductivity and yield for Pani.DBSA prepared by a redoping process of EB. The difference in the APS/Ani ratio used during the synthesis of the Pani.HCl strongly influenced the yield. As expected, higher amount of the oxidant contributes to a higher conversion of aniline into polymeric materials. The conductivity of the Pani.DBSA samples presented a little decreasing after the washing process with water. This results indicate that the washing process used to eliminate the excess of DBSA also contribute to a dedoping process by eliminating some DBSA acting as a counteranion.

The electrical conductivity of Pani.DBSA obtained by in situ doping polymerization (colloidal dispersion and emulsion) are compared in Table II. In both cases, the products were isolated by pouring the reaction medium into acetone or methanol. After precipitation, the polyaniline salt was filtered and washed with the same precipi-

Table I   Electrical Conductivity of Pani.DBSA Produced by the Redoping Process (Method I)

Exp. No.	APS/Ani Molar Ratio	Conductivity (S/cm)		Yield (%)	Density (g/cm^3)
		a	b		
1	1:1	0.92 ± 0.21	0.67 ± 0.42	75	1.15
2	1:4	0.90 ± 0.31	0.72 ± 0.38	20	1.19

[a] Conductivity measured directly from the pastelike material.
[b] Conductivity measured from the powder obtained after washing the Pani.DBSA paste with water for 24 h.

tating medium (acetone or methanol). Pani.DBSA recovered from the methanolic medium was also washed with water in order to verify the effect of the purification process on the conductivity. The oxidant/aniline molar ratio exerts little influence on the conductivity of Pani.DBSA produced by both methods but strongly affects the polymer yield. Increasing the amount of the oxidant increases also the polymer yield. Similar results were obtained in the conventional polymerization of aniline in the presence of HCl as the protonating agent and were also reported by Österholm et al.[13] in their studies on emulsion polymerization of aniline.

With regard to the aqueous dispersion polymerization (method II), the conductivity reaches values within the range of 3–4 S/cm. Such values were higher than those found by using the redoping method in an agate mortar and were not affected by the nature of the precipitating medium (acetone or methanol) or by the washing process with water.

The method based on the emulsion polymerization (method III) also results in Pani.DBSA complexes with conductivity values around 4 S/cm when the polymer samples were isolated from methanolic medium. Contrary to the aqueous dispersion method, the conductivity of the Pani. DBSA obtained by the emulsion polymerization in toluene is significantly influenced by the methodology employed in the purification step. When the emulsion was poured into methanol, higher conductivity values were achieved. These values decrease when acetone was employed as the precipitating medium, indicating that acetone promotes some dedoping of Pani.DBSA.

The conductivity of the Pani.DBSA obtained by the two different in situ polymerization methods was differently influenced by the washing process with water. Whereas the conductivity of Pani. DBSA obtained by the colloidal dispersion process (method II) did not change with the treatment with water, the polyaniline prepared by the emulsion polymerization in toluene presents a considerable decrease in conductivity after washing with water (around one order of magnitude). The different behaviors observed by the two different methods may be related to the morphology developed during polymerization.

In the emulsion polymerization (method III), the medium is toluene, which is a good solvent for the hydrophobic portion of DBSA. When the aque-

Table II   Electrical Conductivity of Pani.DBSA Obtained by *In Situ* Doping Polymerization

Exp. No.	Method	APS/Ani Molar Ratio	Conductivity, S/cm			Yield (%)	Dens. (g/cm^3)
			a	b	c		
3	II	1:1	3.3 ± 0.5	3.2 ± 0.4	3.6 ± 0.2	47	1.10
4	II	1:4	3.9 ± 0.4	3.8 ± 0.3	4.1 ± 0.3	30	1.13
5	III	1:1	4.0 ± 0.2	1.2 ± 0.7	0.34 ± 0.1	77	1.29
6	III	1:2	4.2 ± 0.4	1.1 ± 0.5	0.38 ± 0.2	32	1.32
7	III	1:4	3.9 ± 0.3	0.9 ± 0.8	0.50 ± 0.2	18	1.35

[a] Reaction medium poured into methanol.
[b] Reaction medium poured into acetone.
[c] Product isolated from methanol and washed with water for 24 h under stirring.

ous solution of the oxidant is added, the polymerization takes place inside the small aqueous micelles containing the oxidant and the aniline salt formed with the hydrophilic portion of DBSA. These micelles are surrounded by the hydrophobic portion of DBSA, together with some free DBSA. When the emulsion is broken by pouring into a precipitating medium, the DBSA located at the outside of the precipitated particles may be eliminated. The washing process with water promotes an additional removal of the DBSA resulting in a partial deprotonation of the Pani.DBSA, which leads to decreased conductivity.

In aqueous dispersion polymerization (method II), the hydrophobic portion of the DBSA is located inside the micelles with the sulfonic acid terminal groups at the outside. The aniline monomer reacts with these groups thus forming amine salts. The polymerization moves from the organic phase to the aqueous phase and forms very fine dispersed particles mainly constituted by polyaniline chains at the outside part and surrounded by the aqueous medium. This morphological situation avoid the withdrawn of the DBSA by washing with water, and the conductivity is not affected.

Morphology

Figure 1 shows the morphological aspect of the Pani.DBSA particles synthesized by the three different methods and employing an APS/Ani molar ratio of 1:1. These micrographs were taken from the polyaniline powder obtained after washing the product with water. Pani.DBSA samples obtained by the redoping process [Fig. 1(a)] and by in situ emulsion polymerization in toluene [Fig. 1(b)] constitute small particles, together with some aggregates. The morphological aspect of Pani.DBSA obtained by aqueous dispersion polymerization is quite different. The sample constitutes mainly large aggregates with the formation of some elongated and fibrillar structure [Fig. 1(c)]. During polymerization, a very fine colloidal dispersion of Pani.DBSA particles is obtained, which coalesces and forms aggregates with elongated structures with the precipitation. The formation of these large aggregates protects the DBSA counteranion against the elimination by the washing process with water and may explain why the conductivity of these samples is not affected by the purification. The SEM images of Pani.DBSA samples taken at higher magnification are illustrated in the right side of Figure 1.

Pani.DBSA samples prepared by the redoping process [Fig. 1(a′)] and by emulsion polymerization [Fig. 1(b′)] present a granular morphology whereas Pani.DBSA obtained from aqueous dispersion displays a more elongated structure, like flakes [Fig. 1(c′)].

UV-Vis Spectroscopy

UV-Vis spectra of Pani.DBSA samples obtained by using an APS/Ani molar ratio of 1:4 were measured in chloroform solution, as shown in Figure 2. As can be seen, the synthetic method does not affect the spectrum profiles. All Pani.DBSA samples present typical spectra of doped polyaniline, that is, two absorptions of medium intensity (350–450 nm), related to the $\pi-\pi^*$ transition on the polymer chain and a strong absorption around 750 nm, attributed to the polaron band, caused by protonation of the imine groups of the polyaniline chains.[18]

XPS Analysis

XPS analysis constitutes a powerful tool with which to characterize the doping degree of conducting polyaniline.[19] From the characteristic binding energies (BE) of the photoelectron, the elements involved can be identified and the peak intensity can be directly related to the atomic concentration in the sample surface. In addition, the various intrinsic redox states of Pani as well as the different neutral and positive nitrogen species can be quantified from the properly curve-fitted N1s core-level spectrum.

Table III presents the surface elemental analysis of Pani.DBSA samples as a function of the synthetic method. If one assumes that the samples are in the emeraldine oxidation state (amine/imine ratio 1:1) and only the imine groups are protonated by DBSA, the theoretical C/N and S/N molar ratios for Pani(DBSA)$_{0.5}$ complex should correspond to 15.0 and 0.5, respectively. As observed in Table III, these ratios are higher than the theoretical values in all samples, indicating that the amine nitrogens are also protonated and/or a considerable amount of molecular DBSA are present in the sample.

Pani.DBSA prepared by the redoping process (method I) displays the highest C/N molar ratio value because the analyzed sample has not been submitted to posttreatment with water and then, an excess of DBSA is present. To determine the amount of DBSA actually involved on the proto-
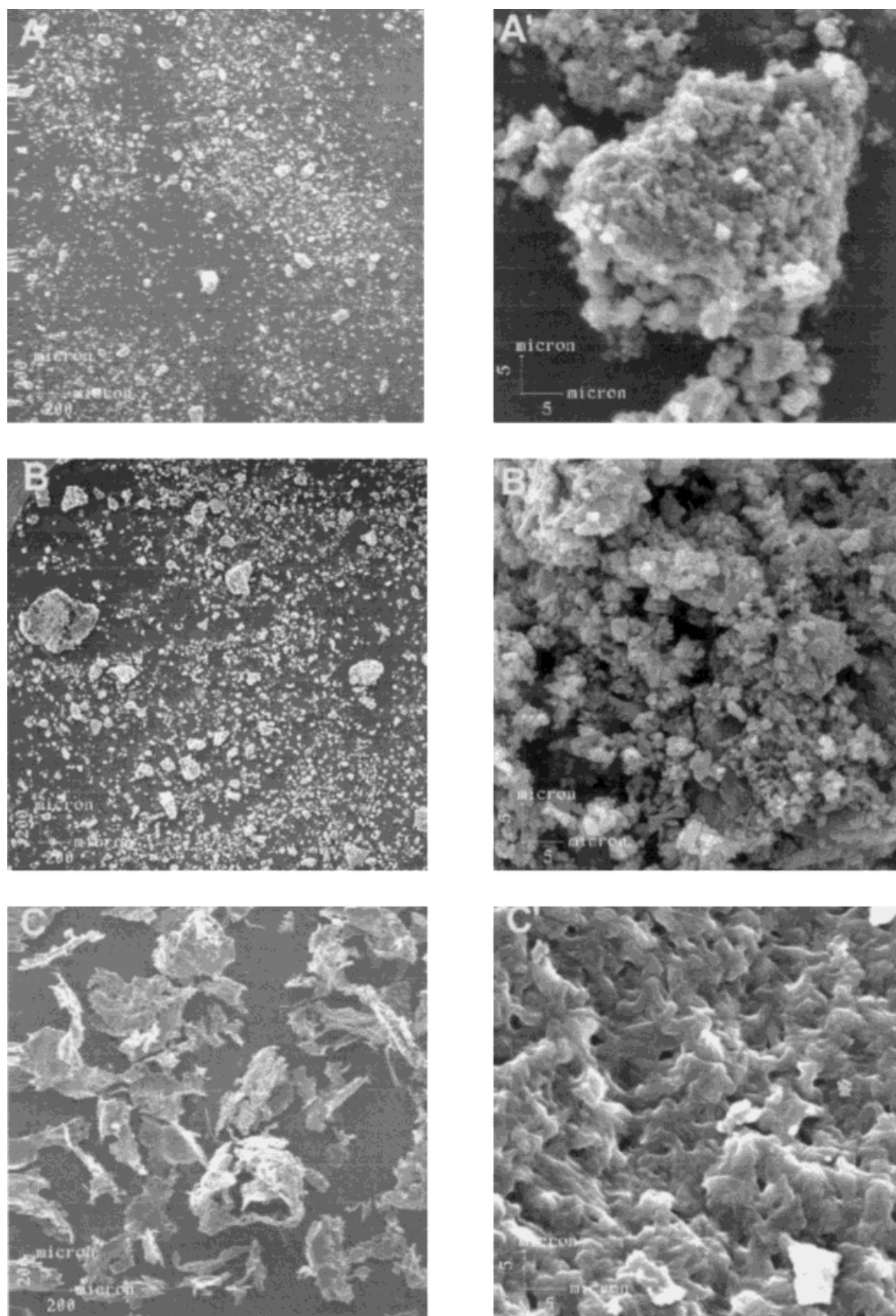
Figure 1 Scanning electron micrographs of Pani.DBSA obtained by (A) method I, (B) method III, and (C) method II and washed with water for 24 h with stirring. (Micrographs on the right, A′, B′, and C′, were taken at higher magnification (2000 ×) and micrographs on the left were taken at magnification = 35×.

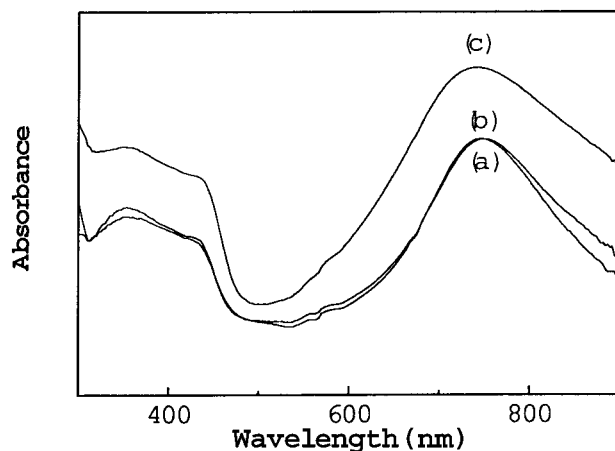**Figure 2** UV-visible absorption spectra of Pani.DBSA dissolved in chloroform and prepared by (a) method I; (b) method II and (c) method III.

Figure 3 XPS N1s core-level spectrum of Pani.DBSA obtained by a redoping method (method I) The proportion of each nitrogen component was found to be: =N— (0.06); NH (0.46); N^+ (0.48).

nation of the Pani chains, the nitrogen components in the N1s core-level spectrum were quantified. As shown in Figure 3, this Pani.DBSA sample exhibits five peaks related to the nitrogen components. The peaks with binding energies (BE) at about 398.2 eV and 399.4 eV are related to imine and amine groups, respectively. The three peaks with binding energies at 400.8, 402.0, and 403.5 eV are attributed to the positively charged nitrogens, according to the literature.[19] The proportion of these peaks was found to be 0.48, which corresponds to the protonation degree. The proportion of each nitrogen component indicates that the protonation of imine groups is almost complete, as expected for an emeraldine salt with good conducting property. The difference between the value of S/N molar ratio (1.0) and the positively charged nitrogen (0.48) corresponds to the amount of DBSA as molecular species. 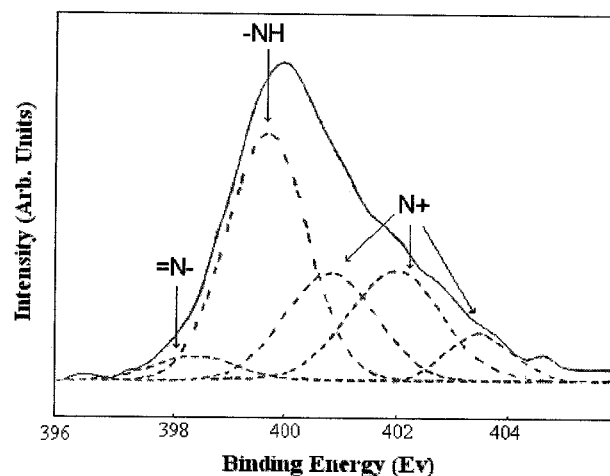This result is expected because the redoping process was performed through mechanical blending of Pani with DBSA in a proportion of 1:3 by weight. This proportion corresponds to an excess of DBSA within the range of 0.55 mol related to the imine groups and agrees with the difference found between the S/N molar ratio and the protonation degree.

Pani.DBSA samples obtained by the in situ doping polymerization (methods II and III) also present higher values of C/N and S/N ratios than the theoretical values, although these samples have been isolated from the reaction medium and washed several times with methanol to remove the DBSA in excess (Table III). Because DBSA may also be present as a molecular specie, the best way to determine the protonation degree is to quantify the various nitrogen species from the N1s core-level spectrum. Figure 4 illustrates these spectra corresponding to the Pani.DBSA

Table III   Elemental Analysis of Pani.DBSA Obtained by XPS Technique, as a Function of the Synthetic Method

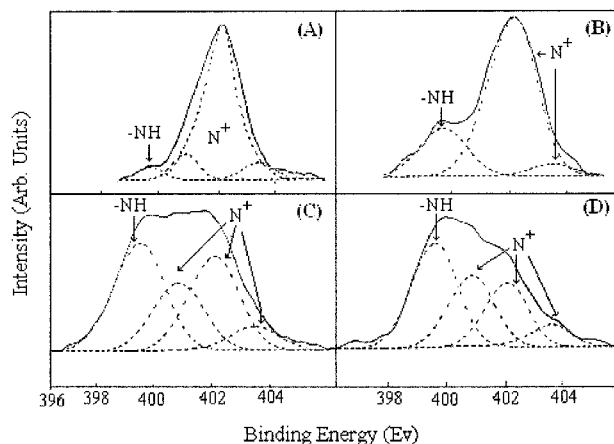| Exp. No.	Method	APS/Ani Molar Ratio	C (%)	N (%)	S (%)	O (%)	C/N Molar Ratio	S/N Molar Ratio
2	I	1:4	75.4	3.4	3.5	17.5	22.2	1.0
3	II	1:1	71.0	4.0	4.6	20.0	17.75	1.15
4	II	1:4	77.0	4.0	3.0	13.0	19.25	0.75
5	III	1:1	77.0	4.9	3.9	14.0	15.71	0.79
7	III	1:4	81.0	5.0	3.3	11.0	16.2	0.66

Figure 4 XPS N1s core-level spectra of Pani.DBSA obtained from the aqueous dispersion polymerization with an APS/Ani molar ratio of (A) 1:1 and (B) 1:4 and Pani.DBSA obtained from the emulsion polymerization in toluene with an APS/Ani molar ratio of (C) 1:1 and (D) 1:4.
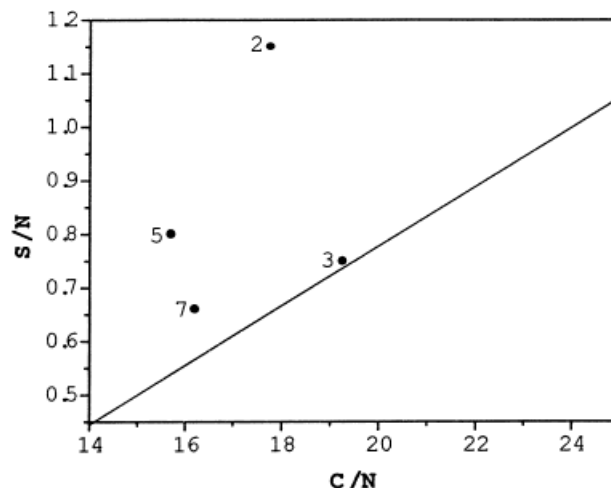

Figure 5 Theoretical relationship between C/N and S/N molar ratio in Pani.DBSA with different protonation degree and experimental values obtained from the XPS analysis (The number corresponds to the experimental number indicated in Table IV.)

samples obtained by methods II and III. These spectra reveal the presence of only the amine component at a BE of ~399.4 eV and a high BE tail corresponding to the positively charged nitrogens. All the imine groups have been protonated, as the peak at 398.2 eV has completely disappeared. Table IV summarizes the proportions of the various nitrogen species for the Pani.DBSA samples shown in Figure 4.

As observed in Table IV, the proportion of the amine nitrogens has decreased substantially below 0.5 and the proportion of positively charged nitrogen increased suggesting that the amine units have been also protonated. Similar results have been also reported by Kang et al.[20] in their studies concerning the protonation degree of Pani doped with H_2SO_4. The synthetic method based on the aqueous dispersion polymerization (method II) resulted in a higher protonation degree.

The amount of DBSA as a molecular species can be calculated from the difference between the S/N molar ratio and the proportion of the positively charged nitrogen (S/N—N^+), as indicated in Table IV.

An important result to be taken into account is related to the values obtained from the S/N and C/N molar ratios. The protonation with DBSA must produce an increased C/N molar ratio to a higher extent than the S/N molar ratio, as the DBSA molecule contains 18 carbon atoms per each sulfur atom. The theoretical relationship between these ratios is illustrated in Figure 5, together with the experimental value obtained for each sample.

Pani.DBSA obtained by the aqueous dispersion polymerization (method II) displays a higher value of S/N ratio than the expected value, when

Table IV   Distribution of *N* Species on Surface of Pani.DBSA Samples Obtained by *In Situ* Polymerization

Exp. No.	Method	APS/Ani Molar Ratio	S/N Molar Ratio	C/N Molar Ratio	Proportion of			S/N — N^+
					=N—	—NH—	N^+	
2	II	1:1	1.15	17.75	0	0.10	0.90	0.25
3	II	1:4	0.75	19.25	0	0.22	0.78	≈0
5	III	1:1	0.79	15.71	0	0.38	0.62	0.17
7	III	1:4	0.66	16.20	0	0.40	0.60	0.06

Table V   Proportion of Nitrogen Species Obtained From XPS N1s Core-Level Spectra of Pani.DBSA Obtained by the Emulsion Polymerization in Toluene (Method III) and Submitted to Different Precipitation or Washing Process[a]

Precipitating Medium	Washing Medium	Proportion of Nitrogen		
		$=N-$	$-NH-$	N^+
Methanol	Methanol	0.00	0.38	0.62
Acetone	Acetone	0.00	0.43	0.57
Methanol	Water	0.11	0.47	0.42

[a] Pani.DBSA prepared with an APS/Ani molar ratio of 1:1.

prepared with a high proportion of APS (Exp. 2). This result may be attributed to the presence of HSO_4^- anions formed as a result of the oxidant reduction. By using a lower amount of oxidant (Exp. 3), the S/N ratio is similar to the theoretical S/N-versus-C/N relationship, indicating that the counteranions for Pani chains are supplied mainly by the DBSA, and not by HSO_4^-. A similar phenomenon has also been found with Pani.DBSA prepared by the in situ emulsion polymerization (method III).

As previously discussed, the conductivity values of Pani.DBSA prepared by the aqueous dispersion polymerization (method II) are not substantially affected by the washing process. Contrarily, Pani.DBSA obtained from the emulsion polymerization in toluene displays lower conductivity values when precipitated in acetone or washed with water. These behaviors may be associated with a dedoping process that can be confirmed by XPS analysis. Indeed, the proportion of the various nitrogen species obtained from the N1s core-level spectra of Pani.DBSA as a function of the precipitating medium and washing process agrees with the dedoping process. As observed in Table V, the amount of positively charged nitrogen decreases when Pani.DBSA is precipitated in acetone indicating a lower protonation degree. By washing with water, the protonation degree and the conductivity decrease even more. The results of conductivity and XPS analysis suggest that acetone and water are able to remove the DBSA from the sample surface.

CONCLUSIONS

Pani.DBSA prepared by the in situ polymerization of aniline in the presence of DBSA presents high conductivity values (within the range of 3–4 S/cm). XPS provides direct evidence that the amine units of the Pani chains are also susceptible to protonation when Pani.DBSA is synthesized by in situ polymerization, since the protonation degree in these samples was found to be higher than 50%. This phenomenon is more pronounced in aqueous dispersion polymerization. The higher protonation degree may be responsible for the higher solubilities of these samples in toluene and chloroform as compared with the solubility of the corresponding complexes obtained by mechanically mixing the emeraldine base form of polyaniline with the DBSA. In the latter situation, good solubility is only achieved when an excess of DBSA is present. The synthetic methods based on the in situ doping polymerization (methods II and III) resulted in Pani doped with both DBSA and hydrogen sulfate anion. The latter is supplied by the reduction of the oxidant (ammonium peroxydisulfate) during the polymerization. The presence of the hydrogen sulfate anion as the counteranion of Pani.DBSA is pronounced when the syntheses are carried out in the presence of a higher proportion of the ammonium peroxydisulfate. When aniline is polymerized in toluene medium, the conductivity and protonation degree of the resulting Pani.DBSA are influenced significantly by the precipitating medium and by the washing process. Both acetone and water are able to remove DBSA at the Pani particle surface in small extent giving rise to lower amount of positively charged nitrogen. This result is associated with a lower protonation degree.

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