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The Complex Micro-Nano-Structure of Polyaniline doped with Benzene Sulfonic Acid in the Presence of the Anionic Surfactant Sodium Dodecylbenzene (SDS)

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Abstract. The synthesis of polyaniline (PANI) doped with benzene sulfonic acid (BSA) was conducted in the presence of a micellar solution containing the anionic surfactant sodium dodecyl sulfate (SDS) as a soft template (PANI-BSA/SDS) *via* the chemical oxidation polymerization of the aniline. The formation of micelles depended on the reaction conditions and especially, the critical micelle temperature and the critical micelle concentration (CMC). By this synthesis way, it was expected that the coordination effect of both the micelles with inter-molecular interactions and the use of a sulfonated organic dopant (BSA) with low surface energy might result in molecular self-assembly giving ordered 3D- microstructures. The obtained samples were characterized by elemental analysis, Fourier transform infrared spectroscopy (FTIR), proton nuclear magnetic resonance (^{1}H NMR), X-ray diffraction, scanning electron microscopy, (SEM), electron paramagnetic resonance (EPR) and electrical characterization. The XRD measurements of the PANI-BSA/SDS revealed the simultaneous presence of both persisting crystals of SDS and a typical semi-crystalline doped PANI. When minimizing the presence of crystalline SDS, the resulting material consisted of a poorly semi-crystalline doped PANI. Moreover, the electrical measurements showed that the PANI-BSA exhibited an electrical conductivity of 400 S/m and the PANI-BSA/SDS with a conductivity value of 1 S/m.

Keywords: *polyaniline, benzene sulfonic acid (BSA), structural properties, soft template*

1. Introduction

Among several electrically conducting, conjugated polymers, polyaniline has been widely studied for electronic and photonic applications **[1]**. Polyaniline is of particular interest due to its inexpensive monomer, ease of synthesis, environmental stability and simple proton doping/ dedoping chemistry **[2]**. The processibility of the PANI can be readily improved by increasing its solubility in organic solvents by doping the PANI with organic protonic acids, such as camphor sulfonic acid (CSA) or dodecylbenzene sulfonic acid (DBSA) **[3]**. The emeraldine salt conductive form of PANI is then obtained with negatively charged sulfonated groups and positively charged backbones of the polymer in strong ionic interaction.

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DBSA is known to be a surfactant but can act simultaneously as an amphiphilic organic dopant. Surfactants are a class of molecules that form thermodynamically stable aggregates with inherently nano-scale dimensions both in solution and in an interface. The amphiphilic character of the surfactants is often used as a soft template in the formation of nanostructures of the PANI. An amphiphilic dopant consisting of a hydrophilic polar part and a hydrophobic alkyl chain is very promising for preparing regular nanostructures of the PANI **[4]** because it plays the role of both dopant and soft-template.

In this research, we used sodium dodecyl sulfate (SDS) having an aliphatic structure composed of 12 carbon atoms and a hydrophilic part composed of the sulfonate group. In the presence of the surfactant, spherical micelles were formed during the initial stage of PANI polymerization due to the low surface energy of SDS. These spherical micelles can be aggregated to form cylindrical bilayers depending on the reaction conditions **[5]**. In the literature we found many papers that included the use of some surfactants in the synthesis of PANI. For instance, the synthesis of PANI particles in micelle solutions composed of various molecular weights of hydrophobic end-capped poly(ethylene oxide)s (PEO) has been reported **[6]**. The polymerization of aniline occurred at the micelle-water interface and around the hydrophilic PEO chain loops in an aqueous system where the PEO chain acted as a steric stabilizer. The particles started to polymerize at the oil-water interface composed by the monomer molecules. The authors showed the PANI particles had a ringlike shape and the crystallinity and conductivity (around 10^{-1} S/cm) depended on the size of the micelles. As far as the SDS surfactant is concerned, Hassam et al. studied the effect of aniline hydrochloride on the size and shape of SDS micelles **[7]**, while Zhou et al. reported obtaining a tubular hierarchical structure of the PANI in dilute SDS/HCl solution **[8]**. The presence of the SDS in the synthesis of the PANI in two weak organic acids (polyacrylic acid and in 2-acrylamido-2-methyl-1-propanesulfonic acid) resulted in the production of conducting PANI nanofibers **[9]**. The SDS has also been used with graphene in the synthesis of PANI/graphene composites and resulted in a higher value of the conductivity than the PANI/graphene composite without SDS **[10]**.

In this work, we studied the behavior of PANI in the presence of both an organic dopant with cyclic structure (BSA) and with both BSA and the anionic surfactant (SDS) with an aliphatic structure. The two syntheses were conducted under the same conditions. A sample of PANI-BSA was obtained in the presence of the BSA as a dopant and another sample of PANI-BSA/SDS was obtained in the presence of BSA and a small quantity of *SDS in order to preserve a very acidic* medium because many results cited in the literature have reported a relationship between crystallinity, acidity and the molecular weight of PANI **[11]**. For these reasons, in this work, we choose to proceed to the polymerization at low temperature (-10 °C) and low pH (around 1), two conditions expected to favor obtention of highly crystalline PANI. *As additional advantage*, that BSA and SDS are soluble in water. In order to study the effect of the surfactant in these chosen conditions, several methods of characterization were used (FTIR, ^{1}H NMR, TGA, 1D and 2D XRD, SEM, EPR and electrical conductivity). The electrical properties results showed that the PANI doped with BSA with cyclic structure and the SDS with an aliphatic structure and lipophilic zones, decreased from 400 S/m for PANI-BSA to 1 S/m for PANI-BSA/SDS.

2. Experimental

2.1.Reagents

Ammonium peroxydisulfate (APS) 99% was obtained from Panreac. Sulfonic benzene acid (BSA) 90%, Ethanol 99.8%, aniline 99% and sodium dodecyl sulfate (SDS) were obtained from Sigma Aldrich, all were used as received.

2.2.Preparation of the PANI-BSA

10 ml of aniline were introduced in a double wall reactor with 150 ml of distilled water. Subsequently, 28.47 g of BSA was added and the solution was left stirring at room temperature for 4 hours (obtaining a colloidal brown solution). The temperature then was decreased to -10 °C and 29.4 g of the oxidizing solution dissolved in 162 ml of distilled water was added dropwise; the reaction was exothermic and the pH of the solution was around 1. While stirring for 4 hours the color of the solution changed to blue with the formation of a colloidal suspension and finally a dark green precipitate. The product was recovered by filtration under vacuum and washed several times with distilled water, acetone and ethanol. Finally, the powder was dried for 3 days at 60 °C. The yield of the reaction was 98%.

2.3. Preparation of the PANI-BSA/SDS

In the same reactor 10 ml of aniline were introduced with 150 ml of H_2O, then 6.85 g of sodium dodecyl sulfate and 23.72 g of BSA were added. After four hours of stirring, a white colloidal suspension was obtained. The temperature was then decreased to -10 °C. Subsequently, an oxidizing solution (APS/H_2O) prepared under the same conditions as for the PANI-BSA was introduced dropwise to lower the pH value of the solution to 1.5 under exothermic reaction conditions. After 4 hours of stirring, a dark green precipitate was formed. The recovery of the product and the drying were done under the same conditions as those for the PANI-ABS. The yield of the reaction was 97%.

2.4 Characterization Techniques

FTIR measurements were performed on powdered samples diluted in KBr pellets (2 mg of each sample in 200 mg of dried KBr) using an FTIR 84005 Spectrometer Shimadzu in the 400 to 2000 cm^{-1} wave number range (1 cm^{-1} resolution). Proton NMR results were recorded with an Advance 400 spectrometer BRUKER operating at a frequency of 400.13 MHz. Samples were solubilized in DMSO-d_6 (10 mg in 500 μ L of solvent at 25 °C) and were filtered before use on a 0.45 μm porous membrane. 45% was removed from the sample PANI-BSA and 30% from the sample PANI-BSA/SDS. Proton NMR spectra were recorded with a 4.006 Hz spectral width, 32,768 data points, 4 s acquisition time, 0.1 s relaxation delays and up to 64 scans.

The thermal stability was studied by thermogravimetric analysis (TGA) under a N_2 atmosphere and the measurements were carried out on a Setaram-92 device.

X-ray powder diffraction measurements were carried out at room temperature in the Θ/2Θ reflection mode using X' PERT PW3040 diffractometer provided with a cobalt anticathode ($K_{\alpha1}$ radiation, λ= 1.789 Å). Another series of powder X-rays diffraction measurements were performed using a Philips PW 3830 diffractometer with the CuK_{α} radiation, λ=1.5418 Å at T= 25 °C. A two dimensional Fuji "flat images" was used having a high dynamic allowing a quantitative analysis of the diffracted intensities. The Fuji film plates were exposed for 1 hour under vacuum, then read by laser scanning using a BAS 1800 II phosphor imager. Diffraction diagrams were calibrated using calcite (*d* = 0.3035 nm).

SEM studies were carried out using a JEOL JSM 6100 microscope, provided with a tungsten filament and a secondary electron detector (resolution 15nm). The various samples were characterized as powder deposited on a carbonized tape. The samples were metalized by a sputtering method with a gold palladium (Au/Pd) deposit with a thickness of about 6 nm.

The electrical conductivity of the samples (in the form of lozenges of 0.2 mm thik) was measured at room temperature using a standard four probe method with a CMT-SR 2000N meter.

EPR spectra were recorded from powder using an EMX Bruker spectrometer operating at 9 GHz at room temperature. ΔB_{pp}. The obtained EPR signals give the density of radical species present in the samples. That could be fixed radicals or delocalized electronic spins linked to charge carriers. Thus the number of signals, their intensity, their shapes (in particular, the peak to peak width □H_{pp}) and their field position give information respectively on the densities of these species and the extent of their delocalization.

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3. Results and discussion

3.1. Elemental analysis

PANI-BSA, even if dried for an extended period of time, always contains some molecules of water capable of forming hydrogen bonds with amine or imine groups of the polymer chains. The elemental analysis of the PANI-BSA sample could only be fitted assuming the presence of water:

Measured: %C = 58.76, %H = 4.75, %N = 9.15, %S = 6.18, %O = 20.64 and S/N = 0.74.

Calculated for $[C_6H_{4.5}N(C_6O_3H_6S)_{0.34}(H_2O)_{0.8}]_x$

%C =60.82, %H =5.13, %N = 8.83, %S = 6.86, %O = 18.35 and S/N = 0.78.

This result suggests that 12 monomers of aniline were decorated with 4 molecules of BSA and 10 molecules of water. Thus it can be concluded that in our preparation conditions the doping rate was only partial in nature giving one dopant molecule per 3 or 4 aniline monomers.

3.2. Infrared Spectroscopy

The FTIR characterization of the PANI-BSA sample revealed the main expected vibrations of the polyaniline around 1568, 1290 and 1129 cm^{-1} **[12]** (see Fig.1). while other bands centred at 1244 cm^{-1}, can be associated with the presence of sulfonate groups (SO^{-3}) [13]; another band located between 1000-1035 cm^{-1} can be assigned to the S=O vibration **[13, 14]**. Finally the band at about 709 cm^{-1} may correspond to the mono-substituted benzene of BSA.

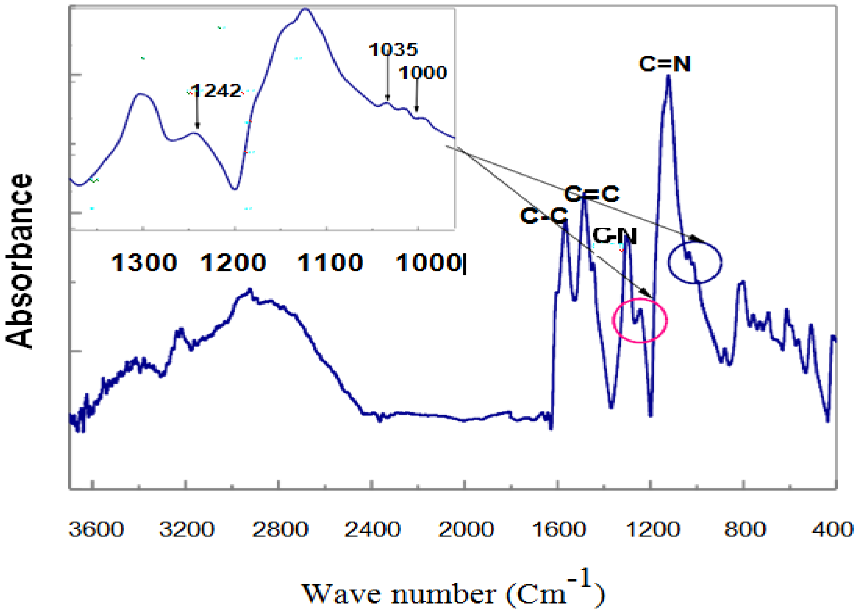


Figure.1. FTIR Spectrum of the PANI-BSA

The FTIR spectra of the PANI doped with BSA in the presence of sodium dodecyl sulfate (see Fig. 2) exhibited also the main bands of the PANI shifted to around 1568, 1470, 1400 and 1130 cm^{-1} **[15]**. We observed the appearance of the asymmetric and symmetric CH_2 stretching vibrational frequencies at 2920 and 2846 cm^{-1} [16] (2920 cm^{-1} (υ_{as} of CH of the group CH_3), 2846 cm^{-1}(υ_{as} of CH of the group CH_2)) and around 2380 cm^{-1}(υ_s of the CH_3 group) respectively. According to the works of R.P. Sperline **[17]**, the obtained vibration value at 2846 cm^{-1}, which was lower than 2852 cm^{-1} is a good indication of more order crystalline structure of the SDS. The presence of the vibration at 1470 cm^{-1} is a sign of an all trans $\upsilon(CH_2)$ confirmation. The asymmetric and symmetric vibrations of the SO_2 function appeared at 1259, 1096 and 1082 cm^{-1} respectively **[18]**. The vibrations at 1042 and 709 cm^{-1} related with the S=O vibration and to mono-substituted benzene of BSA. The vibrations situated at 3120 and 3425 cm^{-1} related to the aromatic function amine connected and free.

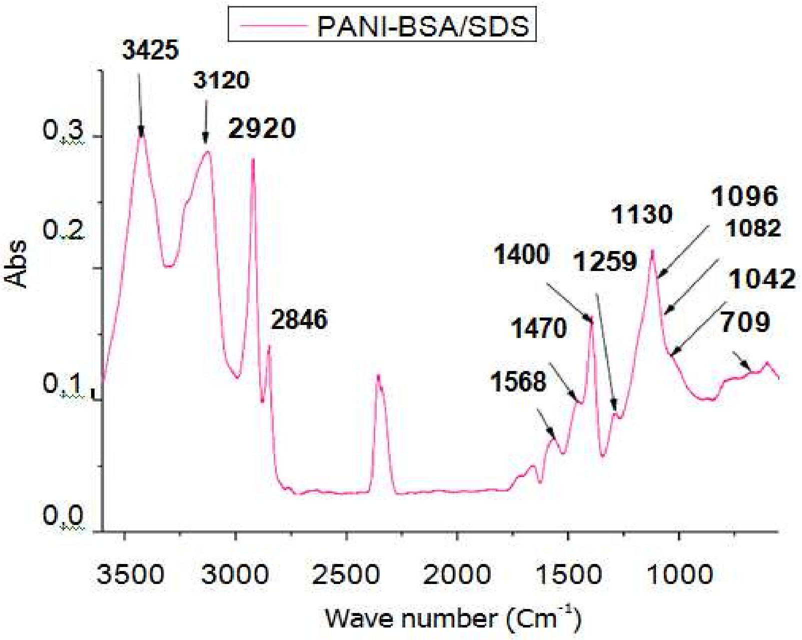


Figure. 2. Spectrum FTIR of the PANI- BSA/SDS

3.2.NMR measurements

Generally, the nucleus ^{14}N possesses a spin number I around 1 and according to the formula 2I+1, the proton which is attached to this nucleus, as well as the proton on an atom of neighboring carbon, should present three peaks of equal intensities. However two factors may complicate the spectrum in the case of the existence of the nitrogen atom in the structure; the speed of exchange of the proton connected to the atom of nitrogen and the quadupolar electric moment of the nucleus ^{14}N. Thus the characterization by liquid NMR is only made with the aim of confirming the chemical NMR displacements of the doped PANI and is very complex to confirm the chain constituents because of the delocalization of electrons pi (the Zeeman effect is not preserved. Indeed, the addition of charges on the chain of the polymer, results in a competition between the electrostatic energy which tends to push away the charged monomers from each other and the interfacial energy which reduces the unfavorable contacts between monomers and solvent).

PANI-BSA: the chemical shifts of the protons of the PANI (see Fig.3) were between 7.0 and 7.70 ppm **[12]** and the chemical shifts of the dopant used were as follows:

BSA$^-$: ^{9}H (δ7.97 ppm), this proton is considered the most unshielded proton ^{10}H and ^{11}H are located in the same proton zone of the PANI form (δ 7.0-7.75 ppm).

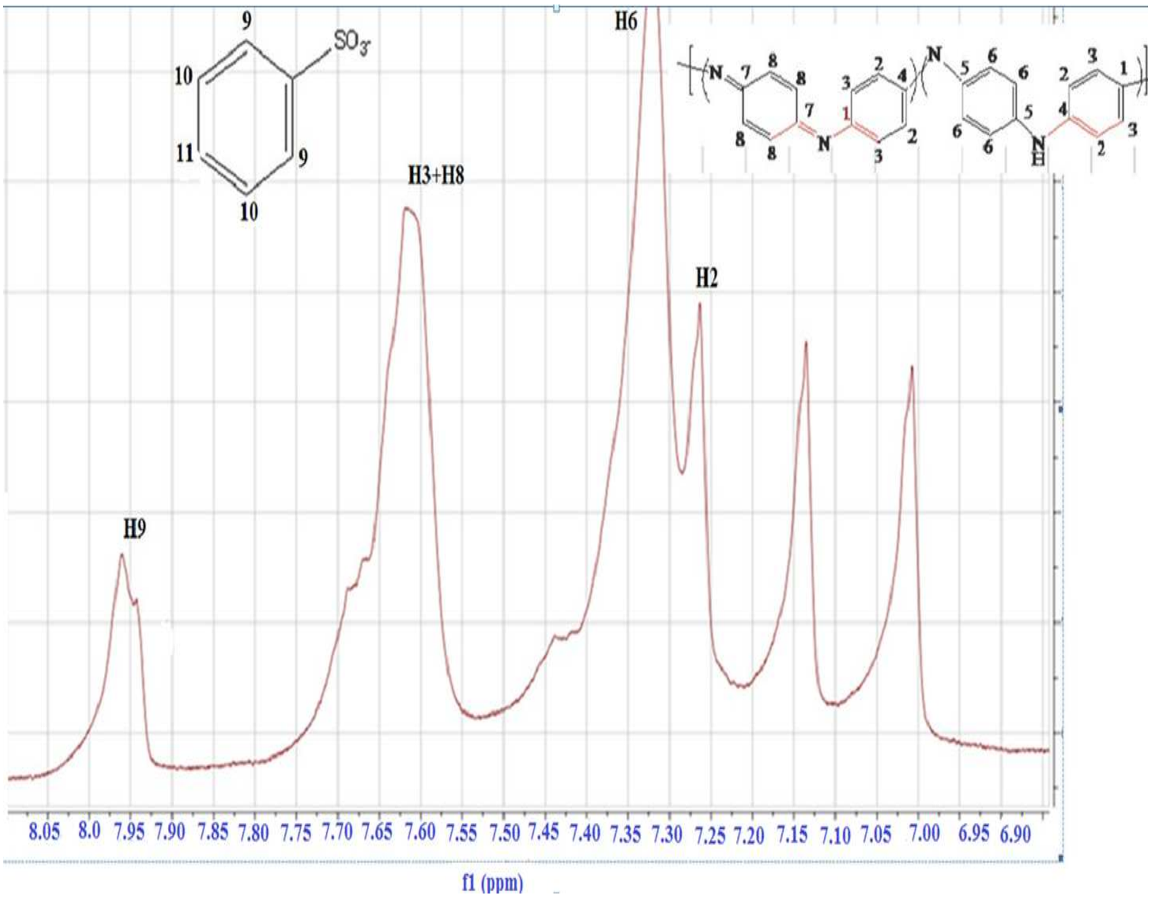


Figure. 3. ^{1}H NMR Spectrum of the PANI-BSA

PANI-BSA/SDS: a better solubility was observed for this sample, which confirms that the presence of a long-chain alkyl group can plasticize the polyaniline by increasing the inter- chain separation and thus facilitate the penetration of the molecules of the solvent into the polyaniline chains **[19]**. According to the intensities of the peaks obtained in the spectrum presented in fig. 4, BSA was not in majority in the soluble fraction. The chemical shifts from the spectrum were as follows:

- SDS: ^{4}H (δ1.25 ppm (3H)), ^{5,6,7} H (δ1.68-1.81-1.87 ppm (22H)), ^{8}H (δ3.76 ppm).

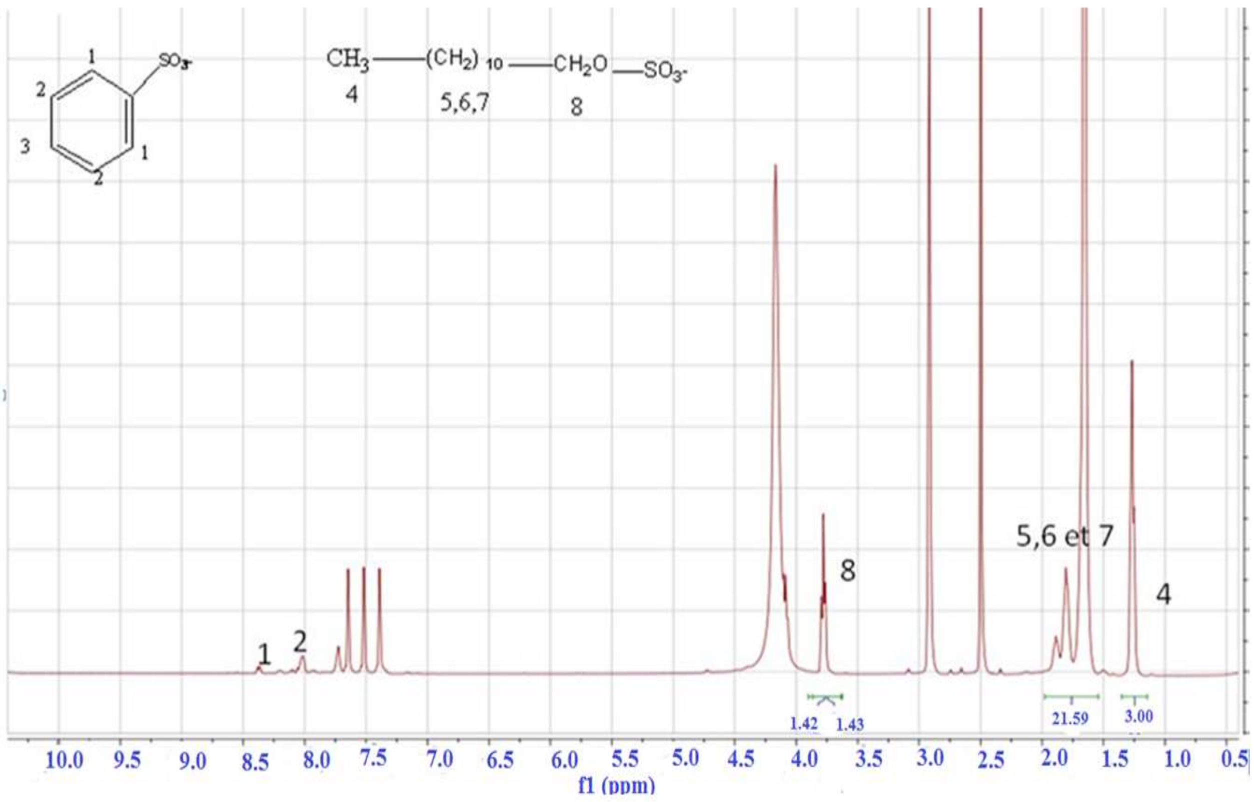


Figure. 4. ^{1}H NMR Spectrum of the PANI-BSA/SDS

According to the different thermograms obtained (see Fig. 5 and 6), the PANI-BSA sample showed two steps of loss of mass while the PANI-BSA/SDS presented three steps of loss of mass. The first small loss from 3 to 5% in the temperature range [22- 120 °C] cans be attributed to the departure of weakly bound water molecules. These water molecules interacted not only with the PANI chains themselves, but also with the anions from the dopant molecules, which can increase the percentage of the loss compared to that observed for the undoped form of PANI. Some authors **[20]** have estimated the first loss to be 5 to 10% for work carried out on PANI doped with organic sulfonic acids. In addition, the results also depend on the amount of relative humidity and the conditioning of the sample before the characterization. The second losses occurred in the 200-450 °C temperature range for the PANI-BSA and in between 180 and 245°C for PANI-BSA/SDS. Finally, a third loss also appeared in between 245 and 435 °C for the latter sample. These results are globally in good agreement with those already published in literature **[21]**. In general the observed steps of decomposition of doped PANI are interpreted first by the degradation of dopants followed by the degradation of the PANI chains. Taking into consideration this last point, concerning the results of PANI-BSA compound, after the reversible removal of some water, from 200°C the decomposition of BSA dopants starts resulting in a 29% loss of mass. This proves how strong the BSA/PANI interaction and breaking it required high energy is confirming the statement that organic sulfonic acids make PANI more stable **[22]**. Concerning the second compound containing SDS, it was found that the addition of SDS in a small quantity in the synthesis had a considerable influence on the thermal properties. Therefore, the second loss of mass of 26% in PANI-BSA/SDS in the 180-245 °C temperature range can similarly be attributed to the loss of BSA in the polymer matrix. The loss of SDS more probably occurred in the245-435 °C interval of temperature with amplitude of around 42%. The loss of mass is cited by Dallas et al. **[23]** regarding the doping of PANI by SDS alone and by Kim et al. for synthesis of the PANI doped by HCl in the presence of the SDS **[11]**.

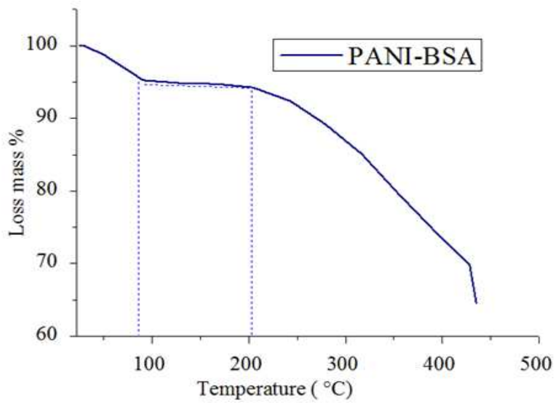


Figure. 5. TGA Analysis of the PANI-BSA

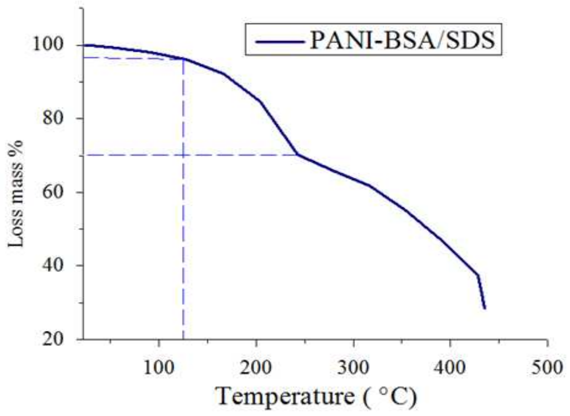
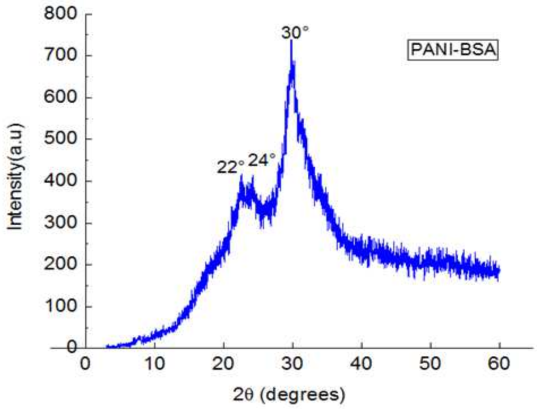


Figure. 6. TGA Analysis of the PANI-BSA/SDS

3.3.Structural Characterization

As shown in the Fig.7 and 8, the diffractograms were isomorphic with the presence of common peaks in 2Θ at 23 and 30° which correspond to the periodic distances of 4.49 and 3.46 Å respectively. The global aspect of the diffraction profile of the figure 7 is highly reminiscent of that published in **[24]** by Pouget et al for their model of the so-called ES-II type emeraldine salt for PANI doped with HCl. Considering that BSA dopant is clearly less globular in shape as camphor sulfonic acid, the resulting molecular stacking is more to be compared with PANI-HCl **[24]**. Then, when SDS was first added in the preparation we obtained the X-ray profile shown in the figure 8. This profile also exhibited two main peaks of the crystallized emeraldine salt at 24 and 30° revealing a similar structure as that obtained with BSA only. The additional peaks seen on this profile cannot be attributed to the macromolecular structure but to crystals of SDS itself because their width is too small to be considered as coming from the polymer. These peaks prove that in our protocol some SDS does not really participate to the doped polymer to form independent crystals.

We have then tried to eliminate these crystals to obtain a homogeneous material built on PANI-BSA and SDS. The best result is shown in figure 9 in which were shown the X-rays diffractograms of SDS alone and of the final product. First of all, some peaks of SDS alone can be recovered indeed in the figure 8 with the narrow peaks evoked before, especially for d spacings of 4.9 Å (2 at 21° in figure 8 and 18° in Fig.9) and 3.3 Å (2 Θ at 31° in Fig. 8 and 27° in Fig.9). Moreover in the 2D diffractogram of the material some Bragg spots from the crystalline SDS are still seen (encircled in blue in the corresponding inset of the figure 9) proving we did not succeed to eliminate all the SDS crystals. Finally considering the diffraction lines of the polymer with BSA and SDS we can see that peaks are even broader proving less crystallinity than in PANI-BSA. But interestingly enough the main peaks of the diffractogram shown in figure 9 reveals distances like 4.44 Å suggesting a similar interchain distance as found in PANI-BSA but also distances like 3.83 and 3.71 Å which could suggest a somewhat different mode of pi-stacking of chains when SDS is introduced in the structure.



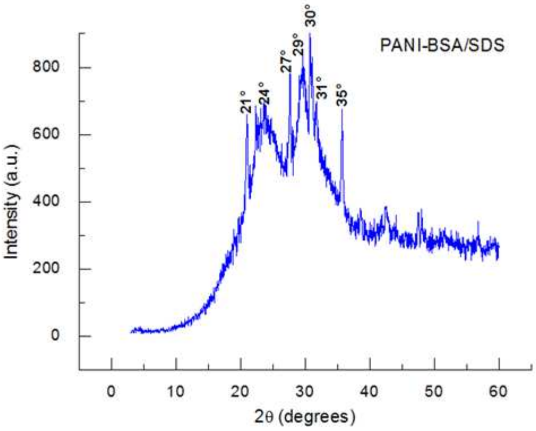


Figure.7. Diffractogram 1D of the PANI-BSA

Figure. 8. Diffractogram 1D of the PANI-BSA/SDS

2θ (degrees)

Figure. 9. Diffractogram 2D of SDS and PANI-ABS/SDS

3.5. Electrical measurements

The four-probe electrical measurements carried out at room temperature gave an electrical conductivity of 400 S/m for the PANI doped with BSA and only one 1 S/m for PANI-BSA/SDS. At this stage it is not possible to give definitive interpretation of this result but we can notice that the lower crystallinity of PANI-BSA/SDS sample may explain this difference. We can also remark that the adjunction of SDS at this stage does not help to obtain a molecular organization more favorable for the charge transport in the system.

3.6. Morphological results

Morphological results

The micrographs obtained with PANI-BSA powder (see Fig. 10) confirmed the microscopic more or less spherical granular morphology with a large distribution of sizes of grains in the material. For the PANI-BSA/SDS (see Fig. 11) the result is similar and in this case it had been also possible to visualize small needles which are likely SDS crystals confirming again our attempt to eliminate them was not 100% successful

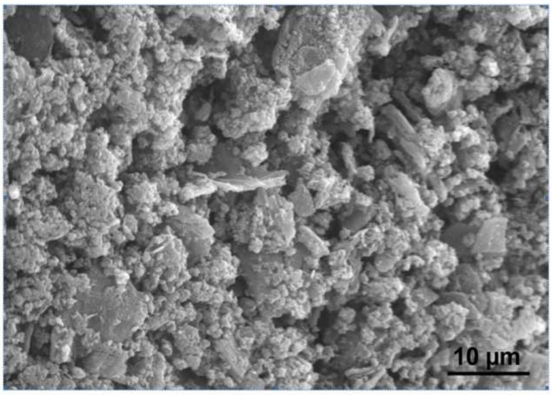


Figure. 10. Micrograph of the PANI-BSA

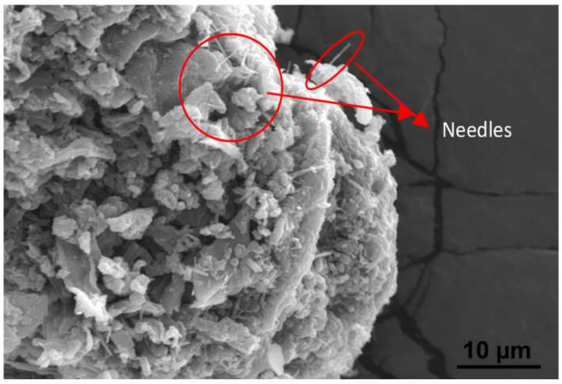


Figure. 11. Micrograph of the PANI-BSA/SDS

3.7. EPR spectroscopy

The PANI-BSA and the PANI-BSA/SDS EPR spectra were shown in the Fig. 12 and 13 respectively. In both cases we could de-convolute the global resonance signal in two lorentzian components, one broad (6.41 and 5.31G) and one narrow (1.3G and 2.8G) .The broad line revealed the presence of unpaired spins which were in strong dipolar interaction and accordingly it concerned mostly paramagnetic centers which were localized in the material

They may correspond to different electronic fixed defects. Besides, the narrow lines correspond more classically to more or less mobile polaronic species which were characteristic in this family of doped conjugated polymers **[25, 26]**. Interestingly enough the “narrow” component in PANI-BSA/SDS (2.8G) is broader than that of PANI-BSA (1.3G). This is a further indication that charge carriers were more mobile in PANI-BSA than in PANI-BSA/SDS, in agreement with the results we found with measurement of the macroscopic electrical conductivity.

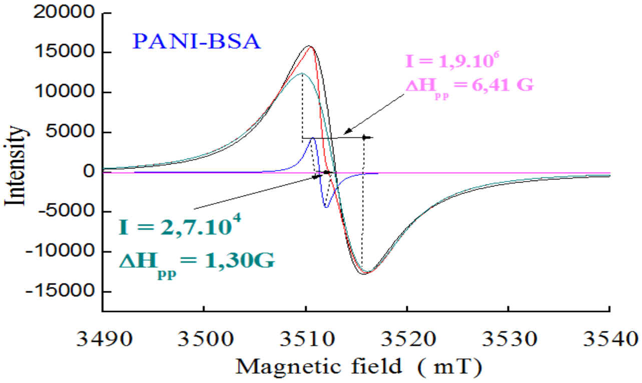


Figure. 12. The EPR decomposition spectrum of the PANI-BSA

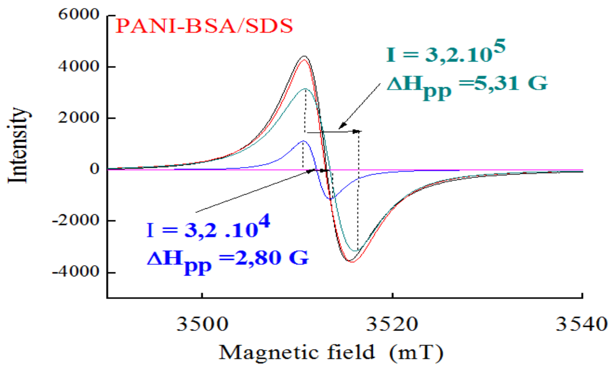


Figure.13.The EPR decomposition spectrum of the PANI-BSA/SDS

4. conclusion

In conclusion, PANI-BSA and PANI-BSA/SDS were successfully synthesized by the chemical polymerization with aniline at -10 °C and the reactions were exothermic. It is known that the micelles formed by SDS **[27, 28]** are affected by the temperature in aqueous solution and a poor micellar structure can be formed at low temperature. Thus, for our conditions, the majority of the SDS molecules were probably placed freely at the surface of the reaction solution and coalescing droplets can be formed in the solution with the dopant BSA (hydrophilic organic compound). As a consequence, the presence of BSA as a dopant in the PANI structure is less favorable in the case of PANI-BSA/SDS than the PANI-BSA synthesized under the same conditions. As a result it had been very difficult to incorporate SDS in PANI-BSA by preventing the formation of crystals of SDS as we could see by X-ray diffraction and electron microscopy. PANI-BSA had similar properties in terms of crystallinity and conductivity to a classical PANI-HCl and adding the SDS did not bring noticeable improvements for these two characteristics in these chosen conditions. It is clear that this route of preparation is still far from being optimize and in spite of encountered difficulties we still think this is a promising path to tailor desired structures and morphologies of cheap, stable and conducting compounds of polyaniline scale.

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