Preparation and Investigation on Structural, Spectral, Electrical and Magnetic Properties of Polyaniline doped by trifluroacetic acid in one step

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Abstract: The aim of the article is to give the electronic properties and delocalized charges as probed by the Electron Paramagnetic Resonance (EPR) spectroscopy of the Polyaniline (PANI) chemically synthesized in one step with the trifluoroacetic acid (TFAA). The amount of doping under these operating conditions was identified by elemental analysis. The structure is investigated by FTIR spectroscopy and the X-rays measurements. The polaronic nature of free carriers is further investigated by UV-visible- NIR and EPR analysis while a value of 12.0 S/m has been measured for the electrical conductivity. The thermal (TGA) and morphological methods were used to investigate the nature of the obtained TFAA-doped PANI.

Keywords: *Polyaniline, trifluoroacetic acid (TFAA), EPR, electrical properties*

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1. Introduction

Systematic studies on polymers exhibiting electrical properties of semiconductors or conductors have started at the end of the seventies of last century at the time of the highly conducting form discovery poly(acetylene) $(CH=CH-)_n$ by hoping either with an electron acceptor as AsF_5 for example or an electron donor as any alkali metal [1]. Concerning the polyaniline, the doping can be achieved by protonating the insulating emeraldine base form a protonic acid to obtain the conducting emeraldine salt form. Compared to other conjugated polymers, polyaniline has the advantage to have a conducting form which is very stable chemically and the temperature as well. This stability is comparable with that of the doped polyethylendioxythiophene (PEDOT) [2]. Moreover, the synthesis is can be controlled and certain properties can be modulated and to be used in several possibilities of applications [3]. In this paper, PANI is protoned by the trifluoroacetic acid. Other studies using this acid have been published [4-7] but none focused on the study of the structure-transport.

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The doped PANI is often a semicrystalline system in which coexist small crystalline parts (few nm in size) with more disordered parts. In the disordered parts, the electronic states are mostly localized; the transport is of diffusive type and is carried out by jumps activated in parts transport might be rather of metal type with a good delocalization of the charges, thus, from the electrical point view the material is heterogeneous presents the resultant of these two very different modes of conduction **[8, 9].** The aim in this proposed work is to compare the electrical conductivity and EPR results. In this way scale we aim to describe the transport properties both at macroscopic scale and the local nanoscopic .In addition to electrical conductivity and EPR spectroscopy, several methods of characterization of the structure, morphology and electronic structure are used (as X-rays-diffraction (XRD measurements, Fourier Transform Infrared spectroscopy, UV-Visible-NIR absorption spectroscopy, thermal gravimetric analysis (TGA) and Scanning Electronic Microscopy (SEM)).

2. Experimental and Methods

2.1. Reactants

Methanol 99.8%, Aniline 99%, trifluoroacetic acid (TFAA) 90% from FLUKA, ammonium persulfate 99% from PROLABO, dichloroacetic-acid ($C_2H_2Cl_2O_2$) 99% from [Acros Organics] were used in this study without purification.

2.2. Synthesis of PANI-TFAA

The synthesis of the PANI is synthesised in the presence of ammonium persulfate $\{(NH_4)_2 S_2O_8$ and an organic carboxylic acid the trifluoroacetic-acid (TFAA).

In a double wall glass reactor, solution of 10 ml of aniline in 150 ml of distilled water was mixed under mechanical stirring for 2 h. Then, 20.52 ml of TFAA were added to the solution (PH of solution = 2). The cooling was ensured by the circulation of methanol used as a cryogenic fluid. When the temperature was cooled down to -10 °C, we introduced one drop/second of the oxidizing solution of ammonium persulfate $((NH_4)_2S_2O_8)$ prepared in the concentration ratio [oxidant]/[aniline] equal to 1.15 under continuous mechanical stirring. After four hours of stirring, we noticed the appearance of a blue powder which was afterward transformed in a dark green powder. The product is recovered by simple filtration, washed several times with distilled water and with methanol. Finally, obtained powder is dried under vacuum during 48 hours at 60 °C.

2.3. Methods

The FTIR characterization carried out by using Shimadzu FTIR 84005 Spectrometer in range from 400 to 4000 cm^{-1} wave-number range with a spectral-resolution of 1 cm^{-1}. The UV-Vis-NIR absorption spectra were collected using a spectrometer Perkin-Elmer λ900 in a 300-2500 nm wavelength range. For these measurements 0.5g/L solutions of PANI compound in dichloroacetic-acid was used.

The thermogravimetry (TGA) measurement was done with a Setaram MTB apparatus with a "10^{-8}"sensitivity, under nitrogen purge (N_2) of 15 ml/min and the hating rate of 2 °C /min until from room temperature to 500 ^{0}C.

X-ray diffraction measurements were done at room temperature using a Philips X' PERT PW3040 diffractometer provided with a cobalt anticathode (K□1, □= 1.789 Å).

Scanning Electronic Microscopy was carried out by using a Jeol JSM 6100 microscope. Characterization is realized on powder. The sample was deposited on a carbon scotch Tape and metalized by sputtering of a 6 nm thick gold-palladium (Au/ Pd) layer.

The electrical conductivity at room temperature of PANI-TFAA was measured at 25°C by the standard four probe method using a CMT-SR 2000N meter.

EPR spectra were recorded from powder on an EMX Brucker spectrometer operating at 9 GHz at room temperature.

3. Results and Discussion

3.1. Elemental analysis

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

This analysis made possible to determine the co-protonation by the sulfuric acid [10, 11].

Calculated for $[C_6H_{4,5}N[(CF_3COOH)_{0,03}(H_2SO_4)_{0,15}](H_2O)_{1,5}]_x$

%C = 53.69, %H =5.77, %N = 10.33 and %O = 25.48.

Measured: %C = 53.90, %H = 4.56, %N = 10.46 and %O = 26.73.

The elemental analysis of this synthetic polymer; contain the monomer structure, the dopant, the co-dopant agent and the water. By checking calculation, an uncertainty of 0.3% in the percentage of the hydrogen and oxygen can be estimated. This result was already mentioned in the literature [12]. For the PANI-TFAA, it seems that the use of a doping agent containing carboxylic function in the synthesis supports the existence of the HSO_4-1 as co-dopant agent [13]. The rate of total doping (TFAA+H_2SO_4) is around 18% in which the rate doping of PANI by the H_2SO_4 is 15%.

3.2. Infrared Spectroscopy

The infrared spectrum of PANI-TFAA is shown in Fig.1. We notice bands at 1305 cm^{-1} and 1146 cm^{-1}; due to C-N stretching, particularly, benzoïd and quinoïd groups of the systems [14]. Another band at 1240 cm^{-1} corresponds to the C-N stretching. Doping by TFAA is confirmed by the presence broad

band around 1210 cm^{-1} which is characteristic of the delocalization of the e-π in the structure of the polymer [15]. Other bands around 1035 cm^{-1} and 1710 cm^{-1} are due to C-O ad C=O vibrations of the carboxylate function and the bands at 1054 and 577 cm^{-1} correspond to HSO_4^{-1} vibrations [16].
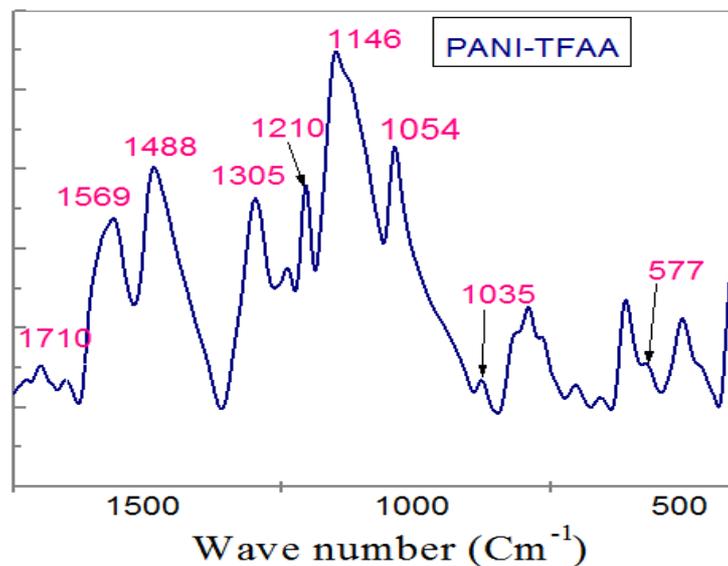
Figure.1. FTIR spectra of PANI-TFAA

3.3. UV- Visible- NIR analysis

The spectrum absorption (see fig.2) exhibits a peak at 360 nm which corresponds to the π-π*.The intense peak centered at 870 nm corresponds to the localized polaronic excited state. The degree of the electronic localization depends on PANI/dopant/solvent associations [17, 18]. The peak at 440 nm corresponds to the polaron-π transition.
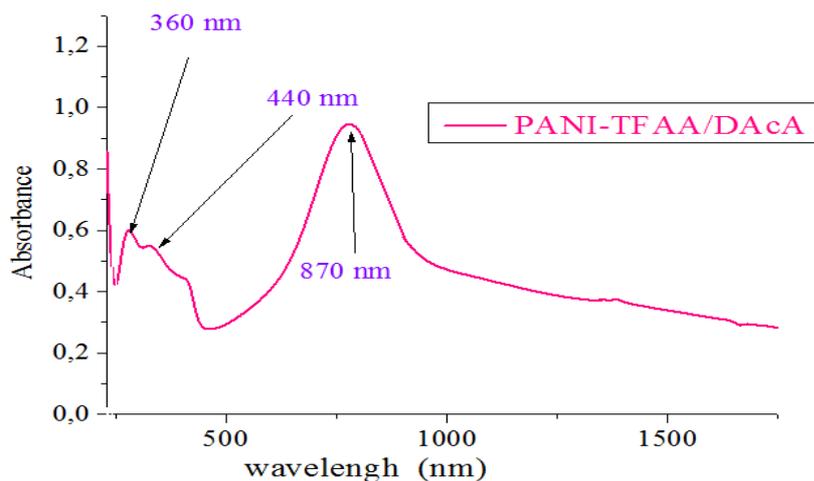
Figure 2. UV-Visible-NIR absorption spectra of PANI-TFAA

3.4. The thermal degradation analysis

According to the thermogram obtained (see. fig.3), two losses of mass are occur. A loss of 6.5% in a breach of temperature 22-120°C range of temperature. This latter is allotted to the departure of water molecules. This loss can be varying from one sample to another depending in which extent water interacts with both PANI chains and counter-ions [19]. Another loss of around 64.72 % occurs in a 130-450 °C temperature interval. This is related with the progressive degradation of the polymer. At least, two phenomena can be considered to occur during the thermal degradation [20]. First, the elimination of organic volatile species stayed in excess in material and second, the decomposition itself of the doping agent and the loss of mass will be related to the chemical nature of anion. Thus PANI-TFAA can be considered as stable up to the temperature at which this the second loss occurs. In this context, the PANI-TFAA presents the greatest loss (64.72%) and in the literature, it's mentioned that the existence of against majority inorganic anion makes the PANI structure less stable [20].
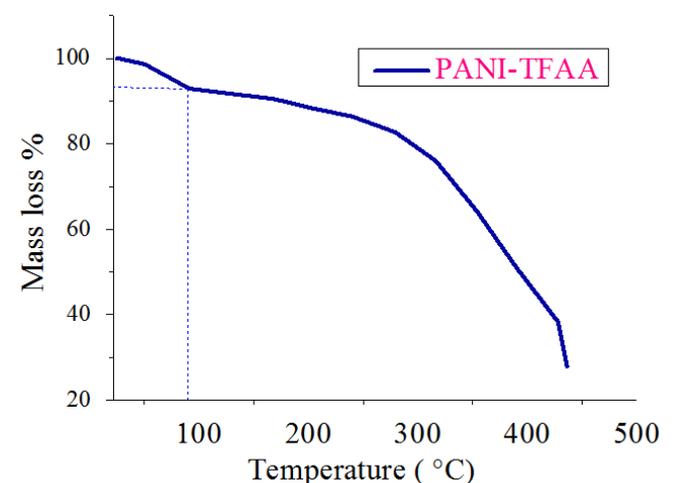
Figure 3. TGA thermogram of the PANI-TFAA

3.5. Structural Characterization

The X-ray powder profile of PANI-TFAA is shown in figure 4. The distances are calculated from the Bragg relation. The diffractogram showed an intense peak at the distance value of 3.45 Å. This peak is characteristic of π stacking of chains. Thus the presences of this peak suggest that the chains of a PANI could be regularly stacked in the crystalline parts [21].
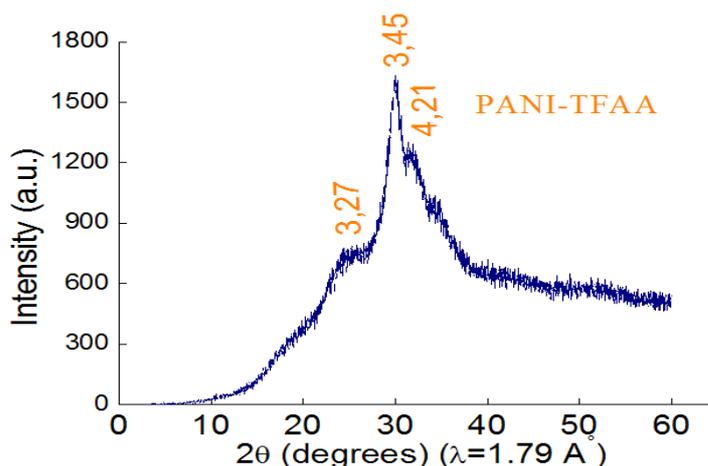
Figure 4. X-ray powder profile of PANI-TFAA

3.6. Morphological Characterization

The doped compounds of PANI can have different morphological forms. Each morphological structure depends on the reagent quantities, the synthesis mode and the doping agent **[10, 20]**. Your case, as shown in the fig.5 obtained a material with a homogenous granular morphological form.
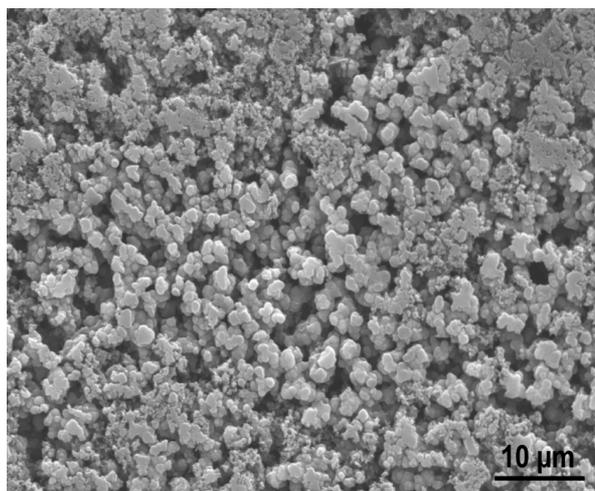
Figure 5. Micrograph of the PANI-TFAA

3.7. Magnetic properties

The motivation of these measurements is to detect the presence of eventual localised defects. The EPR spectra Electronic paramagnetic resonance is a hyper-frequency spectroscopic method (9 to 10 GHz) which makes possible to detect and to analyse the presence of paramagnetic species as free radical for example. The EPR analysis was carried out on a solid powder sample, for reasons of detection method (the signal is modulated). The EPR obtained signal in the measurements is in fact. Each resonant paramagnetic species is characterized by the parameter as the Moor G (which characterizes the EPR line field position for the fixed incident wave frequency), the double integral which is proportional to the EPR signal intensity the width of line peak-with-(ΔB_{pp}) peak,

it is possible that the obtained signal is more complex because the presence of several magnetic species.

 The PANI-TFAA spectrum (see fig.6) showed a broad and finer line. The decomposition of the obtained signal has leads to two broad lines and a centred finer line. For this system, the spectrum confirms the presence of a free centred defect localised. Obtaining this specific result certifies that the system is conducting. The microscopic UV-Visible-NIR spectroscopy result, confirmed the localised polarons. Nevertheless the width of lines PANI-TFAA is in agreement with the results found by Heeger and al. [25]. The reaction is made in a pH value around 2 and certain authors [26, 27] showed that electrons can be delocalized for syntheses of protonation made in pH value inferior at 2.5.
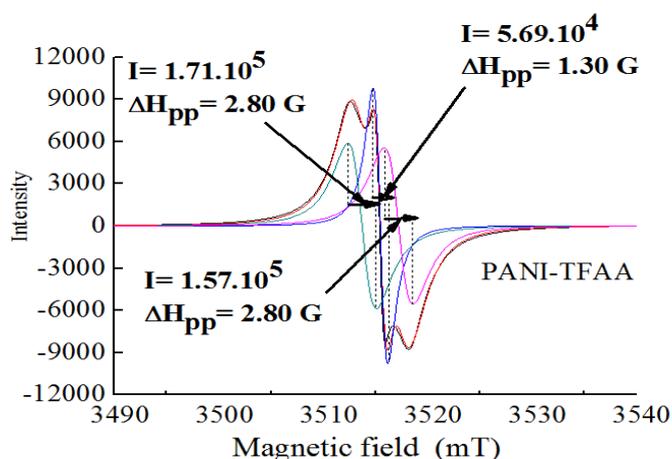
Figure 6. The EPR decomposition spectrum of the PANI-TFAA

4. Conclusion

In this work, the dopant played the role of solvent (very small quantities of TFAA as dopant confirmed by the elemental analysis) but proved an intrinsic delocalization of the load. The structural analysis confirmed the semi-crystalline character and the morphological analysis demonstrated the homogenous granular structure. The spectroscopic study (UV-Visible-NIR) showed the localization of the loads (polaron) carriers in the PANI. This latter depends on the PANI/dopant/solvent associations. The conductivity value of the synthesized system is of 12.01 S/m and this measurement is effectuated at macroscopic scale. The result obtained by the EPR confirmed the presence of a freer centred defect localised and the mobility of loads EPR obtained is a measurement which gives a data on the intrinsic conductivity of the studied system which can directly related to the order of the intra and intermolecular scale in the PANI structure at microscopic scale. Thus, we can conclude that the polyanilne doped in the presence of trifluoroacetic acid leads to obtaining the PANI doped with H_2SO_4.

5. References

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